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Metal Emissions, NO₂ and HC Reduction from a Base Metal Catalysed DPF/FBC System

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ABSTRACT

Due to concerns over NO_2 emissions from platinum catalysts a base metal catalysed diesel particulate filter (DPF) has been developed and used in combination with fuel borne catalysts (FBC). Results are presented showing reductions in HC, NO_X , NO_2 , and PAH emissions along with an assessment of the emissions of metals used in the FBC and the catalysed DPF. This data is used to show the likely reduction in overall iron and other metal emissions as a result of using the catalysed DPF/FBC system. A similar system has also been assessed for durability for over 2000 hours when fitted to a bus in regular service in Switzerland.

INTRODUCTION

In a conventional diesel engine a readily ignitable fuel is injected into hot compressed gas towards the end of the compression stroke. This fuel then begins to vaporise and mix with the surrounding air. Unfortunately with conventional diesel fuels a flammable air/fuel mixture will be achieved before a sufficiently high air/fuel ratio has been achieved to ensure there is enough oxygen to combine with all the carbon present in the fuel. As a result some carbon is initially un-reacted and this is the familiar diesel soot. Most of the soot so produced will oxidise later in the combustion cycle as there is always excess oxygen present. The quantity and the quality of the soot emitted from the cylinder depend upon the engine design. The quantity and quality of soot that is finally emitted to the atmosphere depend upon the exhaust system and any aftertreatment device that is present.

Many years ago it was realised that the soot that was emitted was detrimental to both health and the environment. Measures have therefore been put in place to reduce diesel soot emissions. The most reliable method of quantifying the soot emissions was to filter the exhaust gas, thus collecting the soot on the filter material that could then be weighed to determine the mass of soot or particulate matter (PM) emitted. With this metric engine and fuel injection equipment (FIE) manufacturers have made significant advances, resulting in typically two orders of magnitude reduction in PM emissions. However these reductions in PM emissions have largely been achieved by the reduction of the larger soot particles. As the general level of emissions has diminished. the environmentalists and epidemiologists have looked in more detail at how the qualities of these particles influence their The consensus is currently that the smaller soot impact particles are more harmful to health (1-3). The changes in engine and FIE design have done little to reduce the number of finer particles.

The balance of opinion is thus moving in favour of exhaust gas filtration as a means to achieve the desired results. This view is bolstered as researchers have developed exhaust filtration systems that meet not only the efficiency needs of the environmentalist and epidemiologists but also the durability requirements demanded by the vehicle operator and increasingly by legislation. The tunnelling and mining industries and other industries that work in a closed environment have been at the forefront of this development (4-6). In these environments diesel particulate filters (DPFs) are now commonplace.

Two of the biggest challenges to be overcome are the robustness of the filter, in terms of both structure (7-14) and material (15-21), and how to remove the trapped soot and hence regenerate the DPF (22-32). Some of the methods for regenerating the DPF rely on a platinum catalyst (33). Without stringent controls and careful design, these systems run the risk of increasing the emissions of nitrogen dioxide (NO₂), which is a poisonous gas. Legislation has now been enacted to ensure that aftertreatment devices do not increase This can increase the challenge of NO_2 emissions (34). ensuring reliable regeneration. The use of an iron based fuel borne catalyst (FBC) has been shown both to produce reliable regeneration and a reduction in NO₂ emissions (35). Bv applying a catalytic coating to the DPF it is also possible to reduce the emissions of unburned hydrocarbons (HC) and By careful development of this carbon monoxide (CO).

catalytic coating it is also possible to significantly reduce the NO_2 emissions (36).

As with any aftertreatment device, care must also be taken to ensure that in reducing regulated emissions, one or more nonregulated pollutants are not produced or increased. To ensure that there is no increase in emissions, either regulated or nonregulated a protocol has been devised known as the VERT Secondary Emissions Test (VSET) (37). This procedure forms part of the VERT DPF verification process (38) which is designed to ensure that DPFs will provide the required filtration efficiency and durability with no adverse side effects. The combination of a base metal catalysed DPF and FBC were subjected to the VERT verification process. The major results of the testing are reported in the following sections.

TEST EQUIPMENT AND PROCEDURES

Engine testing was performed at the University of Applied Sciences, Biel-Bienne. The engine used for the laboratory testing was a Liebherr D914T, this is a 6.1 ltr, direct injection, turbocharged non-inter-cooled, in-line 4 cylinder engine. The engine was installed on the test bench coupled to an eddy current dynamometer. The engine was operated according to the ISO 8178 C1 procedure. This consists of eight steady state operating conditions, 100%, 75%, 50% and 10% load at the rated power speed, 100%, 75% and 50% at the rated torque speed, plus idle.

This procedure is used to test engines for varying applications. Each operating point is weighted, with different weighting factors according to the intended application of the engine. For the work presented here the weighting factors applicable to construction site engines were used. Thus the idle condition plus the 100%, 75% and 50% load: at rated power speed received a weighting factor of 0.15 with the other four operating points having a weighting factor of 0.10. Considering the very low levels of some of the parameters being investigated it was not considered practical to try to evaluate these parameters at each of the eight operating points. Instead the engine was operated at each of the operating points in sequence with an operating time of 10 minutes or 15 minutes according to the weighting factor for that stage. This gave a total cycle time of 100 minutes; the cycle was then repeated to give a total operating time of 200 minutes.

At each of the eight operating points the regulated gaseous pollutants were measured using a Horiba exhaust gas analysis bench with non-dispersive infra-red (NDIR) analysers for CO and CO₂, and a chemiluminescent analyser for NO and NO_x. An Amluk flame ionisation detector (FID) was used for the HC determination. Particle number by scanning mobility particle sizer (SMPS), size specific particle mass by electrical low pressure impactor (ELPI), particle surface characteristics by NanoMet photoelectric aerosol sensor and diffusion charging sensor (PAS/DC) were also determined from a diluted exhaust gas sample but are not reported here. The samples accumulated from the 200 minutes of operation, on each of the 12 ELPI stages, were used to determine the size classified metal emissions.

An undiluted portion of the exhaust gas was used to collect samples for the determination of poly-aromatic hydrocarbon (PAH), nitro-PAH (NPAH) and poly-chlorinated di-benzodioxins and furans (PCDD/F) emissions. Here again a cumulative sample taken over the full 200 minutes of test operation was used. A more detailed description of the testing protocol can be found in references (37) and (38).

The testing procedure was conducted with three fuel/aftertreatment configurations. The engine was tested on an untreated ultra-low sulphur diesel (ULSD) fuel with no aftertreatment device fitted. The engine was then tested on a FBC treated sample of the same batch of ULSD, again with no aftertreatment fitted. The base metal catalysed DPF was then fitted to the exhaust system and the engine was again run on the FBC treated fuel. Details of the untreated ULSD are given in the appendix along with details of the lubricant used throughout the testing.

The FBC used for the testing was a commercially available product containing both iron (Fe) and strontium (Sr) as the active metals. The Fe and Sr are present in the FBC in the ratio of 4:1. In line with the VERT protocol the FBC was added to the untreated fuel at twice the maximum recommended treat rate. The FBC was therefore used at a level to give 50 mg/kg of metal in the treated fuel.

The DPF used for the work reported here was an Adastra LC15 unit. This is a 25.4 cm x 30.5 cm (10" x 12") Liqtech silicon carbide (SiC) DPF coated with a proprietary Haldor Topsøe A/S catalytic coating. The catalytic activity derives from a mix of three base metals.

SYSTEM PERFORMANCE

REGULATED EMISSIONS

The results of the emissions analysis for total hydrocarbons are presented in Figure 1 below. The chart shows the results for the test with untreated diesel fuel and the test with the DPF fitted and running with FBC treated fuel. It is clear from the chart that the DPF/FBC system significantly reduces the HC emissions at each of the eight test stages. When these individual results are converted to an emissions factor they show the overall reduction in HC emissions to be 72%.



Figure 1. Total HC emissions with and without DPF/FBC.

Figure 2 shows the corresponding results for CO. As can be seen from the chart the base metal catalyst on the DPF significantly reduces the CO emissions at all test stages with the exception of stage 4. Stage 4 is the high speed, 10% load stage and as is also evident in Figure 1 is characterised by poor combustion brought about by the short combustion time and the lower temperatures. These characteristics are also likely to make the engine more sensitive to changes of exhaust back pressure. It is postulated that an increase in exhaust back pressure as a result of fitting the DPF has resulted in increased engine out emissions of CO and due to the lower exhaust temperatures at this condition the catalytic coating on the DPF is less effective at reducing these emissions.



Figure 2. CO emissions with and without DPF/FBC.

The efficiency of the DPF at reducing the CO emissions is also relatively low at the idle stage, stage 8. Again this is thought to be due to the lower exhaust temperature. This test stage contributes only 10% to the overall emissions factor; consequently the reduction in the overall CO emissions level is still 65%.

Figure 3 shows the results of the NO_X measurements for the eight stages of the cycle. Consistent with previous work the fitting of the DPF tends to reduce the total NO_X emissions. It is thought that this also may be as a result of slightly increased exhaust back pressure as a result of fitting the DPF. The increased back pressure increases the amount of residuals left in the cylinder, effectively introducing internal exhaust gas recirculation (EGR). The use of EGR is a well known approach to reducing NO_X emissions.



Figure 3. NO_x emissions with and without DPF/FBC

The overall emissions of NO_X were reduced by 7% when running on FBC treated fuel with the base metal catalysed DPF fitted. However when the measured NO is removed from the total NO_X the results are significantly different. This is discussed in the following section regarding non-regulated emissions.

NON-REGULATED EMISSIONS

In this work it is assumed that the total NO_X consists only of NO and NO_2 . The results obtained by subtracting the measured NO from the total NO_X are therefore reported as NO_2 . When the engine was run on the FBC treated fuel with the catalysed DPF present, the first set of measurements in five out of the eight stages produced NO and NO_X values which were the same, indicating no NO_2 emissions. The second set of measurements indicated no NO_2 in all eight stages. The average of the two sets of NO_2 data are presented in Figure 4.



Figure 4. NO₂ emissions with and without DPF/FBC

It is not yet fully understood by what mechanism the reduction in NO₂ emissions is brought about. However it is well known that when the temperature exceeds about 250°C, NO₂ is a very good oxidising agent for trapped carbon. It has thus been postulated (35) that with an uncoated DPF there will be a reduction in NO₂ as some of the trapped soot is oxidised. If the catalytic coating of the DPF is well chosen, no additional NO₂ will be produced and the reaction between the NO₂ and trapped soot and hydrocarbons may be enhanced. The preand post-DPF temperatures for the eight test stages are given in the Appendix.

For the determination of PAH, NPAH and PCDD/F emissions a sample was obtained over the complete 200 minute test cycle. A regulated proportion of the raw exhaust gas was passed through a heat exchanger, a condensation separator and filter before being passed through a two-stage absorber. The samples were then analysed by gas chromatography (CG) and high resolution mass spectrometry (HR-MS). Analysis of PAH was restricted to 4 to 7 ring PAH.

The sum of the measured PAH, expressed as $\mu g/m^3$ with the DPF in place and the engine running on FBC treated fuel was only 1.3% of that measured on the untreated fuel with no DPF present. This is shown in the left hand columns of Figure 5. As most of the measured PAH are classed as carcinogenic,

both by the US EPA and by the International Agency for Research on Cancer (IARC) the results for the individual PAH have been weighted by the appropriate EPA and IARC weighting factors to arrive at a total emissions value for PAH. The results according to the two different weightings are also shown in Figure 5.

For the analysis of NPAH emissions the samples were subjected to electron impact ionisation prior to analysis by GC-MS. Again due to volatility considerations only 2 to 4 ring nitro and dinitro-PAH were analysed. Figure 5 shows the total NPAH emissions and the dinitro-PAH emissions values. These also showed a reduction of over 90% due to the use of the DPF/FBC system. Running on the treated fuel with the DPF present no dinitro-PAH were detected.



Figure 5. PAH and NPAH emissions factors

It has been suggested that if chlorinated compounds are burned in the combustion chamber, then due to the presence of the DPF the residence time of these gases in the exhaust is increased. This coupled with the high temperatures due to the thermal capacity of the DPF may promote the formation of PCDD/F within the DPF. The presence of a catalyst, either on the filter surface or combined with the trapped particulate, may exacerbate this situation. The level of PCDD and PCDF were measured for the untreated fuel without the DPF present and for the FBC treated fuel with the DPF present. In both these tests the chlorine originated in the lubricating oil, details of which are given in the appendix.

The measured PCDD and PCDF emissions were reduced by 54% and 55% respectively in the presence of the FBC and DPF. This is shown graphically in Figure 6.

Testing with the DPF/FBC was repeated with the fuel additionally treated to give 10 mg/kg of chlorine in the fuel. This test did result in higher emissions of PCDD than the test without chlorine in the fuel, but the PCDD emissions were still over 40% lower than for the base ULSD in the absence of the DPF.

From the above analysis it is concluded that the combination of the FBC for regeneration of the DPF, and the base metal catalytic coating for volatile emissions control, not only has a beneficial impact on regulated emissions but also significantly reduces the non regulated emissions.



Figure 6. PCDD/F emissions factors

METAL EMISSIONS

Due to the fact that a conventional diesel engine is constructed predominantly from metallic components, and there is metal to metal contact, there is inevitably wear of these metal components. Some of these particles of wear metals may pass directly into the exhaust stream whilst others will accumulate in the lubricating oil and may enter the combustion chamber with this oil, some of which will be burned thus allowing the metals to enter the exhaust system. Most lubricating oils also contain metal based additives which will again find their way into the exhaust system as a result of combustion of small quantities of lubricating oil. A previous study (39) showed zinc emissions from a school bus, a truck tractor and a transit bus to range from 0.31 mg/km to 0.58 mg/km (0.913 mg/mi to 0.363 mg/ml) on different diesel fuels. This was typically reduced to below the detection level of 1.6 μ g/km (1 μ g/ml), with the use of a DPF.

If a catalysed exhaust aftertreatment device is fitted then there is a possibility that some of the catalyst metal can be shed from the device and emitted with the exhaust gas. If a catalyst is added directly to the fuel then inevitably, more metal will be introduced to the exhaust stream. However if the aftertreatment device is a particulate filter, some of these metal particles will be trapped in the filter.

FBC metal emissions

For the purpose of the VSET testing the FBC was added at twice maximum recommended treat rate. Thus Fe was added to the fuel at a total of 40 mg/kg. The diesel particulate was size classified using the ELPI. To perform metals analysis the ELPI was loaded with polycarbonate collection filters. These filters, along with the accumulated particulate matter, were digested in acid and then diluted in ultra-pure water. The resultant sample was then analysed by HR-ICP-MS. A series of three unused polycarbonate filters were stored and handled in the same manner as the test filters. These filters were also digested to determine the average background metal content of the filter media. The reagent was also analysed in order to determine a detection level for each metal.

Figure 7 shows the results of the analysis for Fe of the blanks, when the engine was run on the untreated fuel, and when run with the treated fuel and the DPF fitted. The results are

plotted as μ g of metal per ELPI stage. It is clear from the chart that there is no clear pattern as to how the total Fe emissions are distributed in terms of particle size range, either with or without the DPF/FBC system. The detection level for Fe was 18 ng and the average for the blank filters was 28 ng. The readings for all of the test run samples were well above this level giving good discrimination between the blank and test filters.

It is also clear from Figure 7 that although 40 mg of Fe is added to each kg of fuel used, the total Fe emissions are not consistently higher when the FBC is used in combination with the DPF. The total Fe emissions when running on the untreated fuel were $3.29 \ \mu g$. The total Fe emissions when running on the treated fuel with the DPF present were $3.30 \ \mu g$.



Figure 7. Fe emissions with and without DPF/FBC system

The difference between the total Fe emissions when running on the reference fuel and the total Fe emissions when the FBC is added and the catalysed DPF is fitted was thus below the detection limit for Fe.

Figure 8 shows the results of the tests on the untreated fuel, the treated fuel without the DPF and the treated fuel with the DPF.



Figure 8. Fe emissions with and without FBC and with and without DPF/FBC system

In each case the average Fe mass for the blanks has been subtracted from the measured mass for the test sample. It should be noted that no results were obtained for stage 7 for the test with the treated fuel without the DPF. From Figure 8 it is clear that by adding 40 mg of Fe to each kg of fuel significantly increases the Fe emissions. It is also clear that the Fe produced from the FBC tends to be found in the smaller particles. From the results of the tests with FBC treated fuel, both with and without the DPF, the apparent filtration efficiency can be determined for the catalysed DPF. This is shown in Figure 9. Again note that no data was available for stage 7.

Whilst it is very encouraging to see that the filtration efficiency is so high for the first three stages, which are the smaller more harmful particles, it is a little disappointing and somewhat puzzling as to why the apparent filtration efficiency is so low for the higher stages. However as noted above the FBC did also contain Sr at 10 mg/kg. If the results for the analysis for Sr are used to determine the apparent filtration efficiency it is found that only stage 11 has an apparent filtration efficiency below 95% and then it is still over 90%.



Figure 9. DPF filtration efficiency for Fe particles

These results would suggest that the Fe and Sr are not associated with one another in the soot particles and that the catalysed DPF preferentially filters smaller particles containing Fe whilst at the same time being nondiscriminatory for particles containing Sr. Another explanation which the authors are more inclined to believe is that some Fe present in the system downstream of the DPF has been entrained and collected with the test sample during the test with the DPF present.

If the Fe emissions from the test with the untreated fuel are subtracted from those of the test when the fuel is treated with the FBC in the absence of the DPF, this indicates the quantity of Fe emanating from the FBC. If the same process is repeated for the Sr measurements this shows the amount of Sr emanating from the FBC. As the two metals are added to the fuel in the ratio of 4:1 it would be expected that they would contribute to the emissions in the same proportions. The ratio of Fe to Sr is shown in Figure 10.

From Figure 10 it can be seen that for stages 1 to 6 the calculated Fe to Sr ratio is fairly consistent and close to 4, however beyond stage 7 there is more variability in the calculated ratio. As the absolute levels of metal in these stages is very low, as can be seen in Figure 8, any calculation is therefore far more sensitive to rounding errors in the original measurement.



Figure 10. Fe/Sr ratio derived from metal emissions

Because the FBC was used at twice the maximum recommended treat rate this tends to exaggerate the overall Fe emissions. If the Fe emissions from the test with the untreated fuel are subtracted from those when the fuel is treated with the FBC in the absence of the DPF to indicate the quantity of Fe emaating from the FBC, and this value is then reduced by 60% to represent the contribution from the recommended treat rate of 16 mg/kg of Fe and 4 mg/kg of Sr, the result can then be added to the result from the untreated diesel to calculate the overall Fe emissions which could be expelled with the normal FBC treat rate.

The results of these calculations are presented in Figure 11 along with the results from the untreated fuel.



Figure 11. Fe emissions with and without DPF/FBC system

Although there appears to be an increase in Fe emissions on three of the stages, the overall result is a reduction of Fe emissions of over 50%. As no data was available for stage 7 for the test with the treated fuel and no DPF present only the eleven remaining stages were used to determine the overall result for both sets of data.

If the same approach is taken with the Sr emissions the results are as shown in Figure 12. In this case the overall effect is to leave the level of Sr emissions unchanged from the untreated fuel, no DPF situation.



Figure 12. Sr emissions with and without DPF/FBC system

It was thus concluded that despite adding metal to the fuel in the form of an FBC, the presence of the coated DPF ensured that the overall emissions of these metals would not significantly increase and by assumption the overall emissions of other metals would be significantly decreased.

DPF catalyst metal emissions

In addition to the two metals that are deliberately added to the aftertreatment system as FBC, a further three metals are deliberately added as catalysts in the catalytic coating on the DPF. An analysis was also performed for these metals using the samples taken from the ELPI. The formulation of the catalytic coating is proprietary and the three metals are referred to as A, B and C.

Figure 13 shows the results for catalyst metal A. The detection level for this metal was 0.04 ng. The chart shows the results from both the base, untreated ULSD without DPF and the case for the FBC treated fuel and the catalysed DPF fitted. The result from the average of three blank collecting filters is also included.



Figure 13. Catalyst metal A emissions with and without DPF.

The average for the blank collecting filters was 1 ng. The average for the base ULSD test and the test with the FBC and catalysed DPF were 0.7 ng and 1.2 ng respectively if it is assumed that the result below the detection level is zero. If this result below the detection level is assumed to be the detection level the latter value becomes 1.1 ng. As can be seen from the chart all but four of the emissions results are

below the level of the blank filters. It is thus considered that there are no measurable emissions of metal A with or without the catalysed DPF, and that what is being measured is emanating from the ELPI filter material.

For catalyst metal B the blank collecting filters were analysed and all registered below the detection level of 10 ng. It is obviously not known how far below the detection level these blanks were. For the ELPI filters collected from the test with untreated ULSD and no DPF present the results ranged from below the detection level to 20 ng. It is therefore assumed that these 12 values are in fact an indication of the variability in the metal B levels in the blank ELPI filters. The results from the test with the FBC and catalysed filter were also in the same range with the exception of ELPI stage 3 which gave a result of 40 ng. These results are shown in Figure 14.



Figure 14. Catalyst metal B emissions with and without DPF.

In the above chart the value for catalyst metal B in the blank filter has been illustrated as being at the detection level.

For catalyst metal C the detection level was 0.4 ng and the average value for the three blank filters was 1.5 ng. The range of results for the test with the untreated ULSD with no DPF present was from 0.9 ng to 2.1 ng. Again there is no reason why this metal should be present in the exhaust gas from this test and it is assumed that this is in effect further information on the levels of this metal in the blank ELPI filters.

The results from the test with the FBC treated fuel and with the catalysed DPF present ranged from 0.7 ng to 2.1 ng. This is a similar range to that of the baseline case and suggests that what is being measured is in fact the blank filter. There is however a pattern of increasing metal concentration over the first four ELPI stages that follows that for catalyst metal A. This is shown in Figure 15. If these readings are taken to be an indication of true metal emissions then subtracting the blank filter value for each reading and calculating the ratio of metal A to metal C yields values ranging from 2.5 to 4 for these four stages. This calculation is meaningless for all the other stages where the measured value is below the blank filter concentration. Over the first four ELPI stages the variability of the Fe/Sr ratio was much smaller and in agreement with the ratio added to the fuel. However, the variability in the A/C ratio is much wider and not in agreement with the ratio in which the metals A and C are included in the catalytic coating; it is most likely therefore that there are no significant metal emissions emanating from the catalytic coating of the DPF, and what is being measured is the variability of these metals present within the filter blanks.



Figure 15. Catalyst metal C emissions with and without DPF.

The overall conclusion is thus that the additional metals introduced by the aftertreatment system should not increase tail-pipe emissions of these metals, and that the aftertreatment system should significantly decrease the emissions of other metals. These conclusions are confirmed in the VSET report.

DURABILITY

Over the last two years a significant number of the base metal catalysed DPFs discussed above have been installed on older, pre-1997 specification vehicles in the UK. The results of these activities have been reported elsewhere (36, 40-42). An un-catalysed DPF of the same design as discussed above was also tested as part of the VERT verification process. This DPF was run on a Euro III specification bus in Switzerland.

From data logging of this bus the distribution of pre-DPF temperature was determined and is shown in Figure 16.



Figure 16. Pre-DPF temperature distribution over 2000 hours

Fro this chart is is clear that this is a fairly mixed duty cycle with 5.3% of the time spent with a pre-DPF temperature of below 150°C but with 5.7% of the time with the temperature above 350°C. The majority, 63.9% of the time was spent in the range 200°C to 300°C.

The distribution of pre-DPF pressure was also determined. This is shown in Figure 17.



Figure 17. Pre-DPF pressure distribution over 2000 hours

For 97.5% of the operating time the pre-DPF pressure was below the 20 kPa limit set by VERT. The remainder of the time that the pressure was above 20 kPa, consisted of short pressure "spikes". These pressure "spikes" are associated with hard accelerations with probably high soot loadings within the DPF and will usually be associated with the start of a DPF regeneration event. These short high pressure episodes are not thought to have any significant affect on engine durability. In a durability trial using SiC honeycomb DPFs and FBC, pre-DPF pressures reaching 100 kPa were observed. An engine strip-down after a ¹/₄ million km showed no adverse affects on the engine (43).

As would be expected with any DPF system, ash will accumulate in the DPF causing the back pressure to rise. It would therefore be expected that the exhaust back pressure would be correlated with operating time. However a far greater influence on the exhaust back pressure is likely to be the vehicle operating condition which will determine the volumetric gas flow through the DPF. To reduce the amount of data to be handled the mean exhaust back pressure and mean pre-DPF temperature were determined on a daily basis throughout the test. Multiple linear regression analysis was then performed on the pre-DPF pressure and the square of the pre-DPF temperature. The predicted and measured mean pressures are shown in Figure 18.



Figure 18. Evolution of pressure over 2000 hours

From this analysis the underlying increase in exhaust back pressure was 6.17 kPa per 1000 hours of operation. This data was used to support the inclusion of this type of DPF substrate in combination with the FBC on the VERT Filter List. The DPF with the base metal catalytic coating is currently undergoing a similar durability assessment.

CONCLUSION

A catalytic coating has been formulated to control HC and CO emissions whilst avoiding any increase in NO_2 emissions. This coating has been applied to a SiC honeycomb DPF which relies on a Fe and Sr based FBC to ensure regeneration. This catalysed DPF/FBC system has been tested according to the rigorous VERT secondary emissions test protocol. From the results of that testing the following conclusions have been drawn:

- The base metal catalytic coating was very effective at controlling HC and CO emissions; reductions of 72% and 65% respectively were observed.
- There was a reduction in total NO_X emissions of 7%.
- The NO₂ emissions were almost totally eliminated.
- Emissions of PAH and nitro-PAH compounds were also significantly reduced, both in terms of mass and toxicology.
- Dioxin and furan emissions were also reduced by over 50% under standard conditions, and by over 40% if the fuel was doped with chlorine.
- When the FBC was used at twice the maximum recommended treat rate, there was a slight increase in the emissions of the metals contained in the FBC, however it is calculated that at the recommended treat rate the overall metal emissions reduction due to the DPF would far outweigh any increase due to the presence of the FBC.
- There were no significant emissions of the metals used in the catalytic coating of the DPF.

Service application of this type of catalysed DPF/FBC combination, on vehicles from pre-Euro to Euro III specification has failed to show any durability issues.

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REFERENCES

- Peters, A., Wichmann, H. E., Tuch, T., Heinrich, J. and Heyder, J., 1997. "Respiratory Effects are Associated with the Number of Ultrafine Particles." American Journal of Respiratory Critical Care Medicine, 155, 1376-1383
- Kunzli N., Kaiser R., Medina S., Studnicka M. oberfeld G. and Horak F. "Air Pollution Attributable Cases-Technical Report on Epediiomology" Third WHO Miniserial Conference of Environment and Health. London 1999
- Bagley S. T., Baumgard K. J., Gratz L. D., Johnson J. H. and Leddy D. G. "Characterisation of fuel and aftertreatment device effects on diesel emissions" Health Effects Institute. Research Report No 76. Sept. 1996
- "Compliance with Diesel particulate Matter Standard in Underground Coal Mines" Mine Safety and Health Administration, Program Information Bulletin No P02-7, July 16, 2002
- Mayer A., Matter U., Scheidegger G., Czerwinski J., Wyser M., Kieser D. and Weidhofer J. "Particulate Traps for Retro-Fitting Construction Site Engines VERT: Final Measurements and Implications" SAE 1990-01-0116
- 6. Luftreinhalteverordnung, Ziffer SR-Nr. 814.318.142.1 February 3, 1998
- Pattas K. N., Lee S. H., Cho K. R., Papadopoulos S. G. and Kyriakis N. A. "Ceramic Trap System for Passenger Cars" SAE 940454
- Kiyota Y., Tsuji K., Kume S. and Nakayama O. "Development of Diesel Trap Oxidizer System" SAE 860294
- 9. Bloom R. "The Development of Fiber Wound Diesel Particulate Filter Cartridges" SAE 950152
- Mayer A., Emig G., Gmehling B., Popovska N., Hölemann K. and Buck A. "Passive Regeneration of Catalyst Coated Knitted Fiber Diesel Particulate Traps" SAE 960138
- Stobbe P., Petersen H. G., Sorenson S. C. and Høj J. W. "A New Closing Method for Wall Flow Diesel Particulate Filters" SAE 960129
- Matsunuma K., Ihara T., Hanamoto Y., Nakajima S. and Okamoto S. "Development of Diesel Particulate Filter Made of Porous Metal" SAE 960132 (porous metal DPF)
- 13. Pace L., Konieczny R. and Presti M. "Metal Supported Particulate Matter-Cat, a Low Impact and Cost Effective Solution for the Fiat 1.3 JTD Euro IV Engine" SAE 2005-01-0471
- Brillant S. and Zikoridse G. "Metal Fibre Diesel Particulate Filter: Function and Technology" SAE 2005-01-0580
- 15. Miyakawa N., Maeno H. and Takahashi H. "Characteristics and Evaluation of Porous Si_3N_4 DPF" SAE 2003-01-0386
- Ichikawa S., Uchida Y., Kaneda A and Hamanaka T. "Durability Study on Si-SiC Material for DPF (2)" SAE 2004-01-0951

- Ichikawa S., Harada M., Otsuka A., Hattori M. and Hashimoto S. "Durability Study on Si-SiC Material for DPF (3)" SAE 2005-01-0582
- Ohno K., Yamayose K., Sato H. and Ogyu K. "Further Durability Enhancement of Re-Crystalized SiC-DPF" SAE 2004-01-0954
- Swartzmiller S. B., Li C. G., Wallin S. A., Ziebarth R. R. and Mao F. "Properties and Performance of Diesel Particulate Filters of an Advanced Ceramic Material" SAE 2004-01-0955
- Ogunwumi S. B., Tepesch P. D., Chapman T. R., Warren C. J., Melscoet-Chauvel I. M. and Tennent D. "Aluminum Titanate Compositions for Diesel Particulate Filters" SAE 2005-01-0583
- Oya T., Yamayose K., Ogyu K., Hayashi M. and Ohno K. "Performance Evaluation of SiC-DPF Sintered with Sintering Additive" SAE 2005-01-0579
- Shirk R., Bloom R., Kitahara Y. and Shizawa M. "Fiber Wound Electrically Regenerable Diesel Particulate Filter Cartridge for Small Diesel Engines" SAE 950153
- 23. Okazoe H., Shimizu K., Watanabe Y., Santiago E., Kugland P. and Ruth W. "Development of a Full-Flow Burner Regeneration Type Diesel Particulate Filter Using SiC Honeycomb" SAE 960130
- Mayer A., Emig G., Gmehling B., Popovska N., Hölemann K. and Buck A. "Passive Regeneration of Catalyst Coated Knitted Fiber Diesel Particulate Traps" SAE 960138
- Ohno K., Taoka T., Ninomiya T., Sungtae H., Kojima M. and Komori T. "SiC Diesel Particulate Filter Application to Electric Heater System" SAE 1999-01-0464
- 26. Zikoridse G., Velji A., Heidrich E., Seguelong T., Naschke W. and Kaiser F. W. "Particulate Trap Technology for Light Duty Vehicles with a New Regeneration Strategy" SAE 2000-01-1924
- Zhi N., Xinyun Z. and He Y. "Radio-Frequency (RF) Technology for Filter Microwave Regeneration System" SAE 2000-01-2845
- Nixdorf R. D., Green J. B. Story J. M. and Wagner M. "Microwave-Regenerated Diesel Exhaust Particulate Filter" SAE 2001-01-0903
- 29. Zelenka P., Telford C., Pye D. and Birkby N. "Development of a Full-Flow Burner DPF System for Heavy- Duty Diesel Engines" SAE 2002-01-2787
- Mayer A. C. "Engine Intake Throttling for Active Regeneration of Diesel Particle Filters" SAE 2003-01-0381
- 31. Mayer A. C. R., Kany S., Noethiger P., Richards P., Andreassen L., Andreoni T. and Sem T. R. "Retrofitting TRU-Diesel Engines with DPF-Systems Using FBC and Intake Throttling for Active Regeneration" SAE 2005-01-0662
- Fayard J-C., Joubert E. and Seguelong T. "A New Active DPF System for "Stop & Go" Duty Cycle Vehicles: Durability and Improvements" SAE 2005-01-1754
- Cooper B. J., Radnor H. J., Jung W. and Thoss J. E. "Treatment of Diesel exhaust gases" US Patent 4,902,487 (1990)
- 34. "Potential Health Hazard Caused by Platinum Based Catalyzed Diesel Particulate Matter Exhaust Filters" Mine

Safety and Health Administration, Program Information Bulletin No P02-4, May 31, 2002

- 35. Richards P., Terry B. and Pye D. "Experience of fitting London Black Cabs with Fuel Borne Catalyst assisted Diesel Particulate Filters - Part 2 Non-regulated emissions measurements" SAE 2002-01-2785
- Richards P., Terry B., Chadderton J. and Vincent M. W. "Retrofitting Urban Buses to Reduce PM and NO₂" SAE 2004-01-1939
- 37. Mayer A., Heeb N., Czerwinski J. and Wyser M. "Secondary Emissions from Catalytic Active Particulate Filter Systems" SAE 2003-01-0291
- 38. Mayer A., Czerwinski J., Legerer F. and Wyser M. "VERT Particulate Trap Verification" SAE 2002-01-0435
- Kev-On M., LeTavec C., Uihlein J., Alleman T. L., Lawson D. R., Vertin K., Thompson G. J., Gautam M., Wayne S., Zielinska B. and Sagebiel J. "Chemical Speciation of Exhaust Emissions from Trucks and Buses Fueled on Ultra-Low Sulfur Diesel and CNG" SAE 2002-01-0432
- 40. Richards P.: Vincent M. W. and Kalischewski W. "FBC: The Strategy for Successful Regeneration of DPFs in Low Temperature Duty Cycles" 2. FAD-Konferenz, November 2004
- Richards P. and Chadderton J. "Significant reduction in NO₂ and PM emissions through the careful design of DPF system" 9th Mining Diesel Emissions Conference (MDEC), November 2003
- 42. Richards P. and Chadderton J. "DPF Systems to Reduce Both PM and NO₂" 8th International ETH-Conference on Combustion Generated Particles, August 2004
- 43. Richards P. and Kalischewski W. "Results from a ¹/₄ million km, heavy-duty truck trail, using FBC regenerated DPFs" SAE 2004-01-0074

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APPENDIX

FUEL ANALYSIS

Property	unit	value	
Density, @ 15°C	kg/litre	0.8243	
Kinematic viscosity, @40°C	cSt	2.14	
Flash point	°C	67.0	
Cloud point	°C	-20	
CFPP	°C	-26	
Carbon residue	%	0.01	
Sulphur content	mg/kg	16	
Distillation			
IBP	°C	176	
10% vol.	°C	207	
50% vol.	°C	248	
90% vol.	°C	301	
95% vol.	°C	327	
polyaromatics	% vol.	3.0	
Cetane number		56.0	
Cetane index		52.4	

LUBRICANT ANALYSIS

Property	unit	value	
Density, @ 15°C	kg/litre	0.885	
Kinematic viscosity, @ 40°C	cSt	108.9	
Kinematic viscosity, @ 100°C	cSt	13.4	
Viscosity index		135	
Pour point	°C	-27	
Flame point	°C	227	
Total base number	mg KOH/g	11	
Elemental analysis			
Sulphur	mg/kg	7300	
Molybdenum	mg/kg	116	
Magnesium	mg/kg	422	
Zinc	mg/kg	1572	
Calcium	mg/kg	3655	
Phosphorous	mg/kg	1433	
Chlorine	mg/kg	123	

PRE- AND POST-DPF TEMPERATURES

Test stage	1	2	3	4	5	6	7	8
Pre-DPF (°C)	476-470	410-404	337-330	212-205	474-466	413-410	325-320	110-93
Post-DPF (°C)	410-406	354-351	298-290	216-203	371-357	347-344	286-278	169-108