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Assessment of Corrosivity Associated with Exhaust Gas Recirculation in a Heavy-Duty Diesel Engine

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ABSTRACT

A high-resolution corrosion probe was placed within the airhorn section of the exhaust gas recirculation (EGR) loop of a heavy-duty diesel engine. The corrosion rate of the mild-steel probe elements was evaluated as a function of fuel sulfur level, EGR fraction, dewpoint margin, and humidity. No significant corrosion was observed while running the engine using a No. 2 grade, < 15ppm sulfur diesel fuel; however, high corrosion rates were observed on the probe elements when operating the engine using a standard grade No. 2 diesel fuel (~350 ppm sulfur) while condensing water in the EGR loop. The rate of corrosion on the mild steel elements was found to increase with increasing levels of sulfate in the condensate. However, the engine conditions influencing the sulfate level were not clearly identified in this study.

INTRODUCTION

BACKGROUND

Exhaust gas recirculation (EGR) is being used as a means of lowering NOx emissions from heavy duty diesel engines. During this process, a portion of the exhaust is recirculated back to the cylinder (via the intake manifold) where the exhaust gas acts as a diluent. This lowers combustion temperature which reduces the formation of nitrogen oxides (NOx). EGR is currently used to meet on-highway NOx emissions for Tier 3 emission levels for heavy-duty diesel engines. Very high levels of EGR have been shown to push combustion to low temperature regimes where both NOx and PM levels are low. This is currently an area of intense study.

During the combustion of diesel fuel, corrosive gases containing sulfur and nitrogen are produced. With EGR these corrosive gases are returned to the intake manifold where ambient conditions (such as temperature and humidity) and coolant conditions are believed to play a critical role in the formation of highly corrosive acidic compounds, especially sulfuric acid (1,2). Development of an in-situ measurement system would significantly advance the understanding of the corrosion potential associated with EGR, thereby enabling engine manufacturers to establish boundary conditions on engine operation to avoid high levels of corrosion.

SULFURIC ACID FORMATION

During the combustion of sulfur-bearing fuel with excess air, most of the sulfur is converted into gaseous SO_2 or absorbed into the particulate matter (PM) emissions. A small fraction is also converted into gaseous SO_3 (1-4).

Sulfuric acid is primarily formed in diesel exhaust by a two-step process. In the first step gaseous SO_2 reacts with oxygen in the exhaust to form SO_3 which is described as follows:

$$2SO_2 + O_2 \rightarrow 2SO_3$$

The SO_3 subsequently reacts with moisture in the exhaust to form sulfuric acid according to the following reaction:

$$2SO_3 + H_2O \rightarrow H_2SO_4$$

Under typical exhaust conditions sulfuric acid will condense near temperatures approaching 150^{o}C while water condensation will occur at temperatures close to 25-30^{o}C (1-4).

PROBE DESCRIPTION

The corrosion probe used in this study is an electrical resistance (ER) based probe manufactured by Cormon Ltd. The probe uses their proprietary CEION technology to enable high resolution measurement (< 1micron) at relatively high sample rates (up to 0.25 Hz). A photograph showing the probe tip is shown in Fig. 1. The overall diameter of the probe is 2.54 cm and contains two, essentially identical spiral elements; one (which is the shiny element in Fig. 1) contains the actual exposed corroding surface, while the other (dark element in Fig. 1) is protectively coated to inhibit corrosion. This second element simultaneously measures the gas temperature and provides for temperature compensation (since temperature had a pronounced effect on electrical resistance). The signal processing unit has up to 4 channel capability. This system was originally developed to monitor oil pipeline wear and for subsea applications (6). We believe this paper represents the first published report describing the application of this technology to monitor corrosion within engine exhaust.

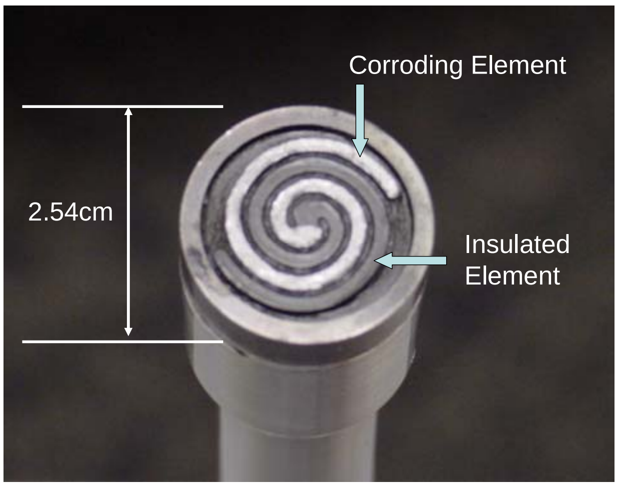

Fig. 1. Photograph of the corrosion probe tip showing the location and geometry of the corroding and insulated elements

The standard method for elucidating the corrosion behavior within engine exhaust systems is to place specialized coupons in an exhaust stream and expose them for long time periods. Accurate measurement of corrosion rate normally necessitates running an engine in excess of 100 hours for a given test condition, which is time consuming and costly. These coupons must be replaced before each test condition and also require careful preparation prior to analysis. A quicker, less-intrusive technique is to utilize a highly sensitive ER corrosion probe. This method enables corrosion rate determination within 1 hour and does not require removal between each set point. Prior evaluations using the Cormon probe have shown that an accurate measurement could be made within 30 minutes for each operating setpoint and the measured corrosion rates were determined to be highly repeatable (typically within 5%).

The purpose of this investigation was to evaluate the performance of the Cormon probe and to assess the relative corrosivity associated with exhaust gas recirculation in a heavy-duty diesel engine. In particular, we were interested in evaluating the corrosion behavior as a function of condensation (sulfuric acid and moisture) and fuel sulfur level.

The subject of corrosion induced by EGR has proven to be a sensitive topic for engine companies. Therefore, we have not included any engine related specifics in this paper. The EGR system used in this study is not used in a commercial configuration, and the engine model is several years old. We do not believe that the results we present are specific to any particular make, model or class of engine. It is also important to note that condensing and/or corrosive conditions in engines with EGR may be relatively uncommon for many applications, and could be minimized through engine control, especially in cold weather. The reader should also bear in mind that the all corrosion-related data pertains to mild steel only. It is well understood that the corrosion behavior is a direct function of the material being corroded and, as such, corrosion rate results obtained on mild steel cannot be predicted or extrapolated to another material type. This is especially true for diesel engines, which do not typically contain mild steel components. However, the corrosion results obtained using the mild steel probe elements can be used to evaluate the relative corrosivity between operating conditions and the corrosion potential of the exhaust gas environment.

EXPERIMENTAL

ENGINE SETUP

A heavy-duty diesel engine was equipped with a high-pressure EGR system containing an EGR valve that enabled manual control. The engine was coupled to a General Electric direct current motoring dynamometer capable of absorbing 224 kW (300 hp). A schematic showing a top-view engine layout is shown in Fig. 2. The recirculated exhaust gas fraction was injected downstream of the intercooler as depicted. The probe was mounted vertically on top of the airhorn as shown and the probe elements protruded approximately 1 to 2 cm into the intake gas stream. The length of recirculated exhaust and inlet air mixing was approximately 1.2 meters from the inlet air/recirculated exhaust junction to the intake manifold. This was a modification to ensure the exhaust and fresh compressed air charge were completely mixed in the intake. In addition a water injection system was installed to add moisture to the (after-turbo, compressed) supply air if necessary.

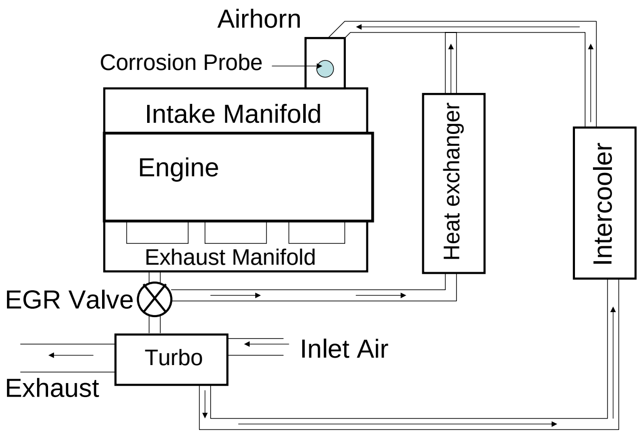

Fig. 2. Schematic of engine layout including EGR loop.

The condensation sampling line was located in the bottom of the airhorn almost directly underneath the probe as shown in Fig. 3. This location allowed condensate to accumulate via gravity in the sampling line during a test run. The sampling line had valves at both ends to facilitate condensate collection and removal without having to stop the engine.

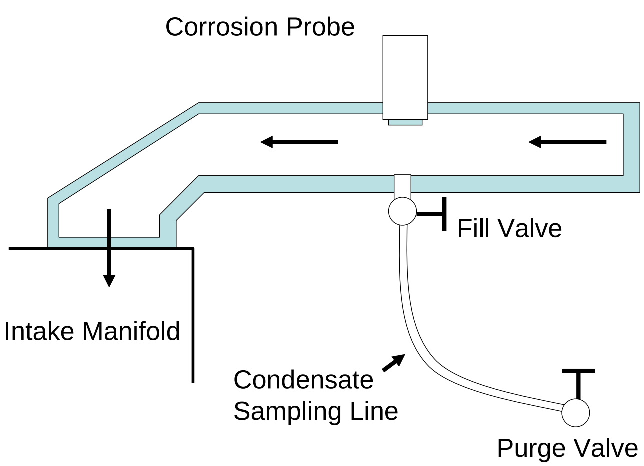

Fig. 3. Side view schematic of modified airhorn showing the locations of the corrosion probe and the condensate sampling line.

TEST PROTOCOL

An important part of this study was to confirm that fuel sulfur concentration is, in fact, the major contributor to the corrosivity associated with recirculated exhaust. In this study two fuel types were evaluated; an ultra-low sulfur-bearing fuel containing less than 15 ppm S (BP-15) and standard No. 2 diesel fuel containing approximately 350 ppm sulfur. (Note that the No. 2 diesel fuel meets the current EPA guidelines, while the BP-15 meets the 2007 on-highway diesel requirements.) The engine was run at speeds between 1200 and 1550 rpm and torque settings ranging from 454 to 542 Nm (80-95% of full load). The exhaust pressure at these conditions was high enough to overcome the boost pressure, thereby introducing significant levels of exhaust into the intake. The level of exhaust to be recirculated was manually controlled using a prototype EGR valve (included in Fig. 2) and control system. By manipulating the valve position, we were able to set and maintain the EGR fraction for a given test condition. During this investigation the EGR level was set at values which ranged from 5 to ~16 %, depending on the test condition. A standard analytical bench was used to measure the NOx, CO, CO_2, HC and oxygen concentrations in the exhaust and in the intake manifold. The humidity, and therefore dewpoint temperature, was maintained by a conditioned combustion air handing system. A water injection system was also installed on the air supply line to provide additional humidity to the EGR loop, if needed.

Prior experience using the corrosion probe to measure exhaust gas corrosion indicated that a minimum sampling time of 30 minutes was necessary to obtain reliable corrosion rate values; therefore, corrosion monitoring times in this study were typically longer than 45 minutes. During the course of the investigation, the airhorn as measured by the probe For each test condition where condensation was observed to occur, the condensate sampling line was thoroughly purged prior to condensate collection by opening the fill and purge valves (see Fig. 3). When the sample line contained appreciable levels of condensate, the condensate was emptied into a Teflon vial by first closing the fill valve and opening the purge valve to release the condensate into the vial. These condensate samples were subsequently analyzed for acetate, formate, sulfate, nitrate, and nitrite content via ion chromatography.

RESULTS AND DISCUSSION

During this investigation the supply air humidity and temperature were maintained near 56 percent and $24^{o}C$, respectively. The water dewpoint temperature inside the airhorn was estimated according to the following general scheme:

1) The flowrate, temperature and relative humidity of intake air are measured values in the plenum leading to the engine. Water partial pressure in the air was estimated by programming standard atmospheric psychometric data (atmospheric pressure is a good approximation at the measurement point) into the data acquisition system as fitted polynomial equations.

2) The flowrate of diesel fuel is measured and the composition is approximated as $CH_{1.85}$, (1.85 H atoms for every carbon atom). All hydrogen is assumed to be burned to form water.

3) The exhaust mass flowrate is known from the air and fuel flowrates into the engine. The amount of water in the exhaust is known from steps 1 and 2.

4) The intake manifold gas is composed of air and a fraction of exhaust. This fractional amount of EGR is calculated by measuring NOx levels in the exhaust stream and in the intake manifold air/exhaust mixture.

5) From proper accounting in the previous steps, the mole fraction of water in the intake manifold is known. The manifold pressure is measured, allowing the partial pressure of water to be calculated and from that value, the dew point. A thermocouple near the corrosion probe provides the temperature value to compare with the dew- point, giving the dew-point margin.

Condensation of moisture could be clearly observed in the condensate sample line (Fig 3). The onset of moisture condensation was observed to correlate very well when the manifold temperature dropped below the calculated dewpoint value. During this investigation, the temperature in the airhorn section fluctuated between 29°C and 35°C depending on the test condition. This temperature fluctuation corresponded to the rise and fall of the supply water temperature to the intercooler. Typically, during conditions of condensation, the temperature inside the airhorn could be maintained between 1 and 2 degrees Celsius lower than the dewpoint value. However, because the intercooler water temperature oscillated 5 degrees it was difficult to stabilize the temperature inside the airhorn for long time periods.

CORROSION PROBE RESULTS

Influence of Condensation

The measured effect of condensation and EGR fraction on the corrosion rate for 15 ppm fuel sulfur and 350 ppm fuel sulfur is plotted in Figs. 4 and 5 respectively. The results obtained while operating the engine using ultra-low sulfur (15 ppm) fuel are shown in Fig. 4. Here the corrosion rate was less than 1 mmpY. Except for the highest and lowest data points, the remainder of the data resided near a value of 0.4 mmpY. As shown by the spread of the data points, there was no observable difference between the values representing the condensing and noncondensing conditions. In addition the EGR fraction does not appear to have any discernable effect on the corrosion rate. The median value of 0.4 mmpY is considered to be a measurable but relatively insignificant corrosion rate.

In contrast the corrosion rate determined for the 350 ppm fuel sulfur level was greatly affected by the onset of condensation as shown in Fig. 5. The rates of corrosion obtained during condensation for this fuel type were all greater than 4 mmpY, which is considered significant, while the data point representing the noncondensing condition was 0. This point is significant because a number of investigations have demonstrated that the onset of condensation for sulfuric acid can be expected to occur near temperatures approaching 150°C for combustion exhaust systems (1,2). The temperature inside the intake manifold during this investigation ranged from 25 to 34°C, which is considerably below the sulfuric acid dewpoint temperature; however, no observable corrosion was measured for this condition. These results indicate that enhanced corrosion occurs not with the onset of sulfuric acid condensate but with the onset of moisture condensation.

The data in Fig 5 also do not show any clear relationship between the rate of corrosion and the fraction of EGR for the fuel containing 350 ppm sulfur. However, a more elaborate investigation with better humidity and temperature control is needed to determine whether this is true or not. A direct comparison of the 15 ppm and 350 ppm sulfur fuel types is shown in Fig. 6 which more clearly shows that in spite of the large scatter, the corrosion rate is substantially higher when running the engine on 350 ppm fuel sulfur versus operating the engine using ultra-low sulfur fuel (BP-15). This result indicates that potential corrosion within a heavy-duty diesel intake manifold, due to EGR, can be mitigated by running the engine on a low sulfur fuel.

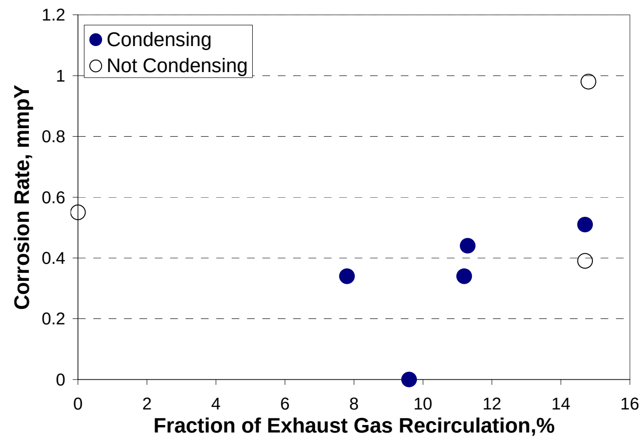

Fig. 4. Corrosion rate within the airhorn as a function of EGR fraction and condensation for low sulfur (15 ppm) fuel.

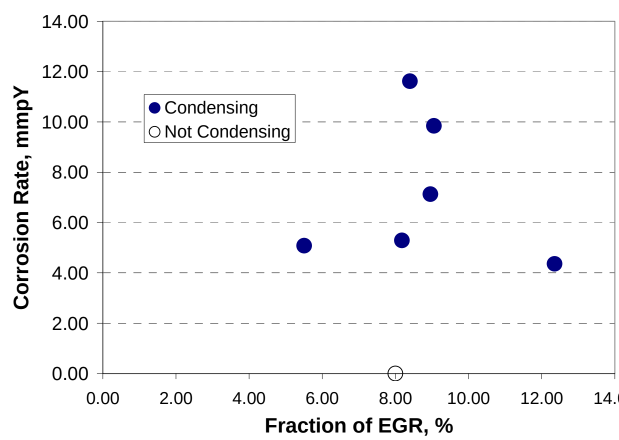

Fig. 5. Corrosion rate within the airhorn as a function of EGR fraction and condensation for high sulfur (`350 ppm) fuel.

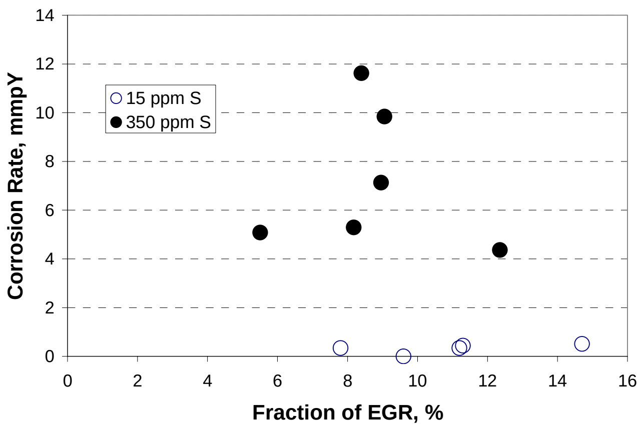

Fig 6. Corrosion rate determined as a function of fuel sulfur level during conditions of water condensation.

In summary the two factors that most influence the corrosion rate appear to be the fuel sulfur level and the onset of water condensation.

Influence of Humidity and Dewpoint Margin

Since significant corrosion rate values were obtained when operating the engine using 350 ppm sulfur-bearing fuel, the influence of humidity and dewpoint margin were examined for this condition. The humidity was controlled by manipulating the supply air handling system and by injecting a water spray into the supply air downstream of the compressor. The range of relative humidity varied between 53 to 58 % as shown in Fig. 7. The resulting data do not appear to show any correlation of the rate of corrosion with humidity while operating the engine using 350 ppm sulfur fuel in a condensing situation.

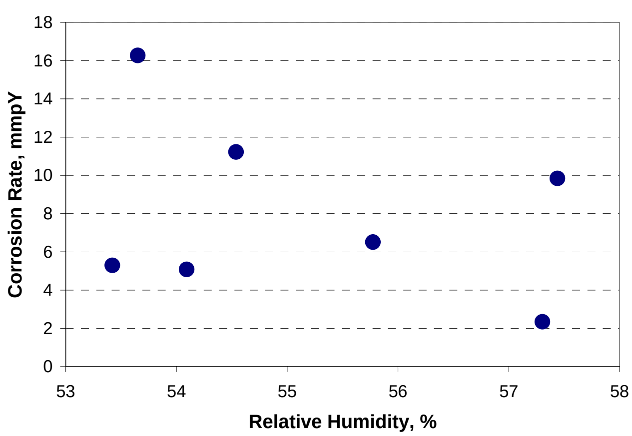

Fig 7. Measured corrosion rate as a function of humidity while operating using 350 ppm sulfur fuel and undergoing condensation.

Another variable that may be important is the dewpoint margin which is defined as the difference between the actual temperature and the dewpoint temperature during condensation. If the sulfate flux in the exhaust is constant for a given condition, then the concentration of sulfuric acid dissolved in the condensing water should be inversely proportional to the condensed water being formed. The data shown in Fig. 8 support the supposition of increasing corrosivity with decreasing dewpoint margin for those points where the dewpoint margin was greater than 1.5°C. However, the two corrosion rate values corresponding to the two lowest margin settings do not. This is another variable that warrants further investigation.

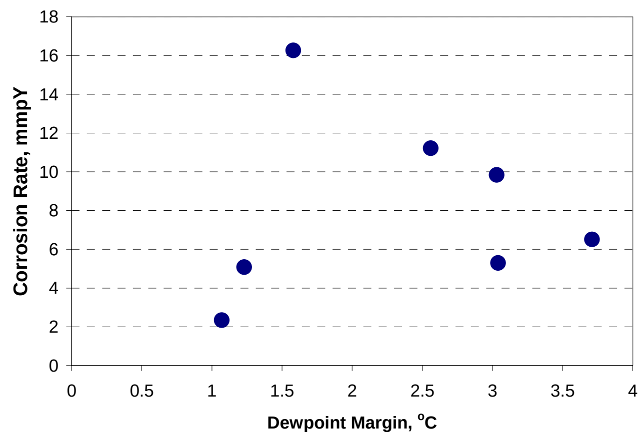

Fig. 8. Measured corrosion rates for different dewpoint margins while operating using 350 ppm sulfur-bearing fuel (No. 2 diesel).

Ion Chromatography Results

Ion chromatography was performed on the condensate specimens to measure the dissolved levels of acetate, formate, nitrite, nitrate and sulfate. Analysis of the data revealed that negligible amounts of acetate, formate, and nitrate were measured in the condensate samples. However, appreciable levels of nitrate and sulfate were detected in the collected condensate samples. The nitrate and sulfate concentrations found in the condensate samples taken from all of the operating conditions using 15 ppm fuel sulfur are shown 9. The results show that even though the fuel sulfur level was low, measurable amounts (5 to 110 mg/L) of sulfate and nitrate were detected. Note that it is very likely that a portion of this sulfate originated in the lubricant. The data also show that the concentrations of the nitrates and sulfates are on the same order and similar for several samples. These low concentrations of nitrate and sulfate in the condensate apparently do not create conditions of high corrosivity within the condensate.

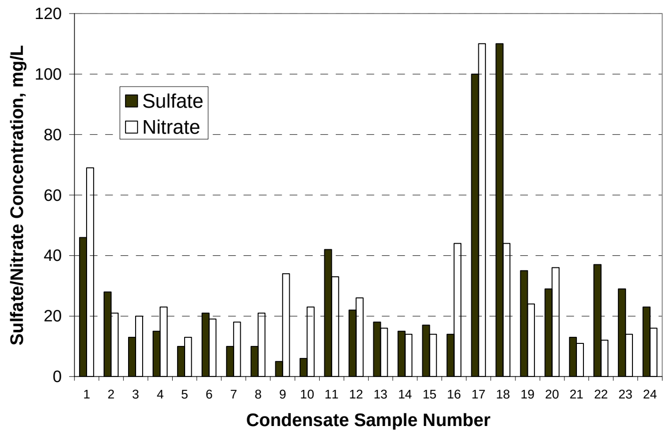

Fig. 9. Ion chromatography results for the 15 ppm fuel sulfur operating conditions.

The ion chromatography results for the operating conditions using 350 ppm fuel sulfur are shown in Fig. 10. For this fuel type the sulfuric acid concentration ranges from 100 to 1300 mg/L, which is dramatically higher than for the 15 ppm fuel sulfur, which varied from 10 to 100 mg/L. The nitrate levels, however, were very similar to the levels received from the 15 ppm sulfur-bearing fuel. This indicates that the fuel types studied in this investigation have no effect on the nitrate concentration in the condensate.

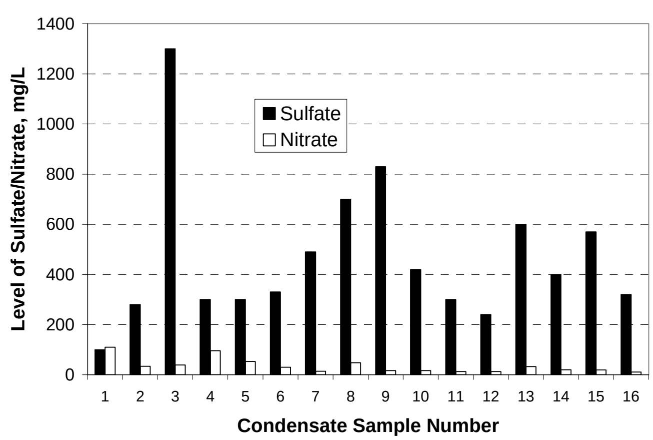

Fig. 10. Ion chromatography results for the 350 ppm fuel sulfur operating conditions.

Within this range measured values, the corrosion rate of mild steel can be expected to increase in a nearly linear fashion with increasing sulfuric acid concentration. As expected the high sulfate content was observed to have a noticeable effect on the corrosivity as revealed in Fig. 11.

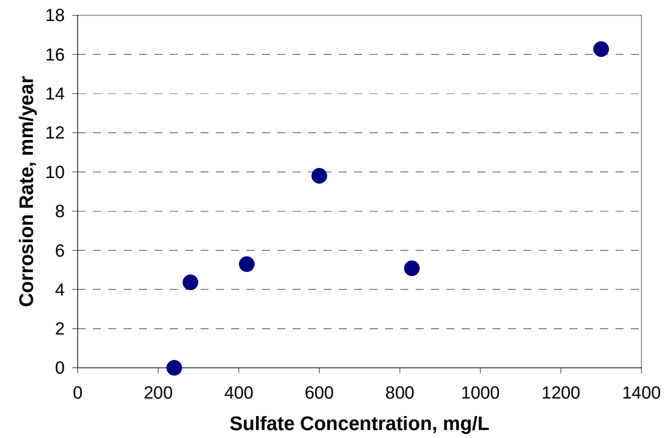

Fig. 11. Correlation of corrosion rate with condensate sulfate concentration for engine conditions using 350 ppm fuel sulfur.

The results in Fig. 11 show an observable increase in corrosion rate accompanying an increase in sulfate concentration of the condensate, which is expected over the range of concentrations measured. This correlation further confirms that the corrosion rate of the probe elements is influenced primarily by the sulfuric acid concentration in the condensate. Further analysis of the data did not show any correlation of the sulfate concentration in the condensate with the dewpoint margin and EGR fraction. This is an area that also warrants further investigation.

CONCLUSIONS

A key outcome was the successful demonstration and application of a corrosion probe for use in a diesel engine EGR loop. Specifically, we were able to demonstrate in-situ, near-real time measurement in engine exhaust.

The results of this investigation have shown that (for mild steel) for engines conditions using ultra-low sulfur diesel fuel, the corrosion rate is very low. However, for fuel sulfur levels approaching 350 ppm, the corrosion rate is enhanced with the onset of condensation. None of the variables investigated in this paper only appeared to influence the corrosivity with the possible exception of the dewpoint margin. Clearly further investigation is necessary to resolve the influence of temperature, EGR fraction, humidity, on the formation of sulfuric acid within a section of EGR. The major implication of this effort is that the data strongly suggest that corrosivity can be lowered significantly by switching to a very low sulfur-bearing fuel. Also conditions within the EGR section may need to be controlled to not enable the condensation of water. Further investigations need to be performed to better elucidate the influences of humidity, EGR fraction, and dewpoint margin on the corrosion rate for a given material and engine condition.

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DEFINITIONS, ACRONYMS, ABBREVIATIONS

ACRONYMS AND ABBREVIATIONS

EGR Exhaust Gas Recirculation

ER Electrical Resistance

EPA Environmental Protection Agency

HC Hydrocarbon

mmpY millimeters per year

NO_x Oxides of Nitrogen

NTRC National Transportation Research Center

ORNL Oak Ridge National Laboratory

PM Particulate Matter

DEFINITIONS

Dewpoint Margin: The difference between the dewpoint temperature and the actual temperature during condensation.