Abstract

At last! A cost effective, high performance solution for many of the marine industry’s problems associated with heavy fuel oil.
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Introduction

DFT Petrol offers a wide range of effective products developed and manufactured using state of the art technologies and methodologies. These products are currently in use to address devastating environmental hazards throughout the world. One area of environmental concern is fuel efficiency and pollutants on seagoing merchant and commercial passenger vessels that use Heavy Fuel Oils (HFO).

FCC-V has been developed to address these concerns.
Background

The world would not be the same without the marine transport and shipping industries that make up a significant portion of the world’s ocean maritime traffic. The world is a lot “smaller” than it used to be, and that means businesses around the world now export and ship more goods to their global neighbours in other countries than at any point in history.

Heavy fuel oil and marine fuel oil are the dominant fuels of choice for these essential business sectors. These fuels are less expensive than lighter #2 diesel fuel oil but they also have higher levels of harmful inorganic components like sulphur and vanadium.

Heavy Fuel Oil Properties – Problems

1. High viscosity
2. High specific gravity
3. High carbon residue
4. High sulphur content
5. High ash content
6. High vanadium content
7. Sodium (salt water)
8. Incompatibility
9. Low flash point
10. High Aluminium / Silica (catalyst fines) causes rapid and excessive wear on piston rings & ring grooves, cylinder liners, fuel injection pumps and injectors.
For further information on vanadium, please see Appendix B.

Where there are high levels of sulphur and vanadium in the fuel, there are often concerns with corrosion damage of the engines and its associated parts. The sulphur will oxidise during combustion in the engine, with the vanadium contributing in a catalytic role, and the resulting SO2 and SO3 emissions gases will combine with water vapour already present after combustion, with sulphuric acid as the result. This is bad news for expensive ship engines, fuel systems and exhaust emissions equipment. For further information about Vanadium in fuel, please see Appendix B.
Maintenance Costs

All the above-mentioned problems increase maintenance cost, decrease efficiency and increase toxic environmental emissions. The cost of labour for cleaning and downtime of expensive equipment must be calculated in fuel expense costs making the treatment of the fuel even more important.

The Treatment

In today’s competitive and cutthroat world of business, marine fuel oil users need all the help they can get. It is cost-effective for ships burning these kinds of fuels in heavy, slow-screw diesel engines, to implement a consistent additive program for their fuel oil, often with a fuel treatment to remediate these problems. But what kind of treatment is best to use?

DFT Petrol has found that the best maritime fuel oil treatments should contain most or all of the following elements:

• Organometallic corrosion inhibitors and neutralisers – to prevent costly and damaging corrosion
• Combustion improvers
• Surfactants – to remove accumulation of heavy end fallout from the fuel oil and to keep fuel delivery and injection systems clear and functioning at optimal performance.

FCC-V (Fuel Conditioner Concentrate - Vanadium)

DFT Petrol offers a formulated product to address these needs - FCC-V (Fuel Conditioner Concentrate - Vanadium)
FCC-V is formulated to provide needed corrosion relief and combustion improvement for large diesel engines that burn heavy fuel oils with higher levels of sulphur and vanadium. It is a well-balanced mixture of components specifically designed for heavy petroleum fuels.

Engines that use FCC-V experience better combustion, performance and fuel usage rates, cleaner MFO delivery and injection systems, and reductions in costly long-term corrosion damage to expensive parts of the engine system.

With the use of FCC-V, fuel use is stabilized and entire fuel-power systems are maintained cleaner thereby reducing downtime, reducing corrosion, reducing residual deposits, increasing lubrication for moving components and significantly decreasing toxic emissions.

Operational performance, fuel storage stability, corrosive inhibition, optimization for water control in fuels and reliability is greatly enhanced.

The effect of FCC-V on the decrease in hot corrosion (vanadium related), cold corrosion, and a decrease in carbon, sulphur, metals, and sediments enhances operational efficiency.

This type of corrosion initiates from the Vanadium in the fuel which forms a low melt glaze during combustion with other metals in the fuel like sodium, aluminium, iron, as well as sulphur and oxygen. These low melt glass-like compounds not only corrode equipment but prevent heat transfer to water in tubes. Additionally these low-melt compounds form a hard glaze when they cool that make cleaning very difficult.

These corrosive vanadium compounds reduce efficiency in heat transfer, resulting in lost BTU's and a more costly power output.

For further information on Vanadium, please see Appendix B.

Testing results using FCC-V has proven that at the correct dosage and specifications, this corrosion can be prevented. FCC-V creates a Vanadium compound during combustion that has a higher melting point and is noncorrosive, giving a more complete combustion. This eliminates
black smoke exiting the stacks and thereby leads to less toxic environmental emissions and more effective and efficient fuel and plant operations.

When added to fuel systems using HFO in the proper concentrations (4000-1), FCC-V has been shown to greatly improve performance and reliability and is directly responsible for fuel savings and dramatic improvements in fuel exhaust toxic emissions.

FCC-V is a proven, tested and effective additive concentrate for use in HFOs.

**Key features of FCC-V**

- FCC-V is a carefully balanced blend of additives, magnesium and surfactants specially formulated to be used in power plants, electrical generating, desalination plants or seagoing merchant and commercial passenger vessels.

- FCC-V improves fuel stability, cleans and maintains the entire fuel system and its component parts, controls corrosion and deposits and provides lubrication for moving parts with the operating fuel systems, while demonstrably and dramatically decreasing toxic emissions.
FCC-V greatly reduces unburned hydrocarbons, carbon monoxide, sulphur dioxide, opacity and particulate matter resulting in enhanced efficiency in fuel systems, functioning under optimum conditions and emitting fewer toxins into the atmosphere - all resulting in efficient fuel operating systems proven to benefit from significantly less downtime and associated maintenance costs.

Use of FCC-V provides a reduction in un-burnt fuel and a reduction in emissions. As a result the use of FCC-V results in the reduction of fuel consumption.

Use of FCC-V reduces and protects against fouling and corrosion components, resulting in improved operational efficiency and the lowering of environmental impact with safer exhaust gases.

Other Applications

FCC-V was designed and tested for use in systems that utilise HFOs, as well as in the marine industry, these HFO systems include power plant operations such as oil refineries, desalination plants and electrical power plants which can all create hazardous pollutants.
Appendix A - Fuel Storage Stability

Fuel storage stability is crucial in the utilization of fuels. The basis to efficient fuel use is stability in storage.

Rust and Corrosion

FCC-V contains effective rust and corrosive inhibitors to prevent and control corrosion in storage tanks and fuel systems.

Deposit Formation

FCC-V contains various special concentrations of inhibitors to improve oxidation and colour stability, thus preventing the formation of deposits in the fuel and in the storage system. By minimizing fuel deposits, the life of fuel filters in the system is extended and operations remain efficient, economic and without increased toxic emissions.

Dispersion

FCC-V contains an extremely tried, tested, proven and effective dispersant system (FCC). FCC-V will clean and control deposits in storage tanks and distribution systems and eliminate problems associated with fuel incompatibility. Insoluble residues that precipitate and cause filter clogging will be eliminated.

Bacterial Growth

One way in which FCC-V addresses fuel operations is by addressing the fact that the growth of bacteria can lead to fuel problems. This occurs as a result of water and condensation accumulating in the fuel, which provides an ideal environment for bacterial growth. FCC-V disperses the water into the fuel slowly, causing the water to be burned off and when this is accomplished, bacteria cannot live let alone reproduce thus bacterial problems are eliminated.
Water Controls

FCC-V has been carefully formulated using the knowledge accumulated over the last 20 years with FCC. FCC is tested and proven to provide optimum control of water in fuels. Actual testing has demonstrated that FCC-V will solubilise water in the fuel and emulsifies water into the fuel.

The addition of FCC-V doesn’t interfere with the action of on board water separators that only separate free water.

Appendix B – Chemical Information

Vanadium
No economical process exists for removing vanadium from either crude oil or residual fuel. Vanadium is a metal present in all crude oils in an oil-soluble form of porphyrine complexes. The actual level is also related to the concentrating effect of the refinery processes used in the production of the residual.

Vanadium deposits can be very hard and may cause extensive damage to the turbocharger nozzle ring and turbine wheel. The only way to remove vanadium deposits is to disassemble the components and erase the deposits mechanically. Vanadium, in combustion with sodium, may lead to exhaust valve corrosion and turbocharger deposits. This can occur especially in the weight ratio of sodium to vanadium exceeds 1:3, and especially in the case of a high vanadium content.

Most residual fuels have vanadium levels of less than 150 mg/kg. Some fuels however, have a vanadium level greater than 400 mg/kg.

In general, fuel when delivered contains a small amount of sodium, which is typically below 50 mg/kg. The presence of seawater increases this value by approximately 100 mg/kg for each per cent of seawater. If
not removed in the fuel treatment process, a high level of sodium will give rise to post-combustion deposits in the turbocharger.

These complexes get concentrated on the higher-boiling fractions, which are the base of heavy residual fuel oils. Residues of sodium, primarily from sodium chloride and spent oil treatment chemicals, are also present. More than 100 ppm of sodium and vanadium will yield ash capable of causing **fuel ash corrosion**.

Most fuels contain small traces of vanadium. The vanadium is oxidized to different vanadates. Molten vanadate present as deposits on metal can flux oxide scales and passivation layers. Furthermore, the presence of vanadium accelerates the diffusion of oxygen through the fused salt layer to the metal substrate; vanadates can be present in semiconducting or ionic form, where the semiconducting form has a significantly higher corrosive rate, as the oxygen is transported via oxygen vacancies. Ionic form in contrast transports oxygen by diffusion of the vanadate, which is significantly slower. The semiconducting form is rich on vanadium pent oxide.

At high temperatures or lower availability of oxygen, refractory oxides - vanadium dioxide and vanadium trioxide - form. These do not promote corrosion. However, at conditions most common for burning, vanadium pent oxide gets formed. Together with sodium oxide, vanadates of various composition ratios are formed. Vanadates of composition approximating $\text{Na}_2\text{O}.6\ \text{V}_2\text{O}_5$ have the highest corrosion rates at the temperatures between 593°C and 816°C; at lower temperatures the vanadate is in solid state, at higher temperatures vanadates, with higher proportion of vanadium, provide higher corrosion rates.

The solubility of the passivation layer oxides in the molten vanadate depends on the composition of the oxide layer. Iron (III) oxide is readily soluble in vanadates between $\text{Na}_2\text{O}.6\ \text{V}_2\text{O}_5$ and $6\ \text{Na}_2\text{O}.\text{V}_2\text{O}_5$, at temperatures below 705 °C in amounts up to and equal to the mass of the vanadate. This composition range is common for ashes, which
aggravates the problem. Chromium (III) oxide, nickel (II) oxide, and cobalt (II) oxide are less soluble in vanadates; they convert the vanadate to less corrosive ionic form and their vanadate are tightly adherent, refractory, and acting as oxygen barriers.

The corrosion rate by vanadates can be lowered by lowering the amount of excess air for combustion - thus forming preferentially the refractory oxides, refractory coatings of the exposed surfaces, or use of high-chromium alloys, e.g. 50% Ni/50% Cr or 40% Ni/60% Cr.

The presence of sodium in a ratio of 1:3 gives the lowest melting point and must be avoided. This melting point of 535°C can cause problems on the hot spots of the engine like piston crowns, valve seats, and turbochargers.

**High temperature corrosion** and fouling can be attributed to vanadium and sodium in the fuel.

During combustion, these elements oxidise and form semi-liquid and low melting salts that adhere to exhaust valves and turbochargers.

It is essential to ensure exhaust valve temperatures are maintained below the temperatures at which liquid sodium and vanadium complexes are formed and for this reason valve face and seat temperatures are usually limited to below 450°C.

Magnesium has the effect of increasing the fusion temperature of vanadium / sodium from about 500°C to about 2500°C and providing the cooling system is functioning correctly, this critical temperature will not be reached thus most, if not all, of this type of damage will be eliminated.

High-temperature corrosion is a mechanism of corrosion that takes place in gas turbines, diesel engines, furnaces or other machinery coming in contact with hot gas containing certain contaminants. Fuel
sometimes contains vanadium compounds or sulphates, which can form compounds during combustion having a low melting point. These liquid melted salts are strongly corrosive for stainless steel and other alloys normally inert against the corrosion and high temperatures. Other high-temperature corrosions include high-temperature oxidation, sulfation and carbonization.

Sulphates
Two types of sulphate-induced hot corrosion are generally distinguished: Type I takes place above the melting point of sodium sulphate and Type II occurs below the melting point of sodium sulphate but in the presence of small amounts of SO.

In Type I the protective oxide scale is dissolved by the molten salt. Sulphur is released from the salt and diffuses into the metal substrate forming discrete grey/blue coloured aluminium or chromium sulphides so that, after the salt layer has been removed, the steel cannot rebuild a new protective oxide layer. Alkali sulphates are formed from sulphur trioxide and sodium-containing compounds. As the formation of vanadate is preferred, sulphates are formed only if the amount of alkali metals is higher than the corresponding amount of vanadium.

The same kind of attack has been observed for potassium and magnesium sulphate.

Sodium
Sodium is normally present in the fuel as a salt-water contamination and may, as such, be removed by centrifuging. Sodium can also reach the engine in the form of airborne seawater mist.
Magnesium
Magnesium, either present in the fuel, in saltwater contamination or introduced via additives can, to some extent, increase the melting point of the vanadium, thus preventing the formation of deposits. Vanadium is bound in chemical complexes in the fuel and, consequently, cannot be removed.

Lead
Lead can form a low melting slag capable of fluxing protective oxide scales.

Appendix C – Dose Rates

The mix ratio will depend on the vanadium in the fuel.

Dose rates for FCC - V are based on a recommended 3:1 ratio of Mg vs. V to prevent vanadium hot corrosion in the turbine hot gas path, although higher rates of up to 5:1 have been used for fuels that have higher than normal sodium-to-vanadium ratios. The best treat rates will provide the most magnesium for the neutralizing of corrosion while minimizing overtreatment of the boiler and the possible boiler fouling that may result.

Appendix D – Catalyst fines.

The drive towards low sulfur fuels is causing fuel-refining processes to change, some of which result in below standard HFO being delivered to ships.
A higher presence of tiny (5 – 30 microns) but very abrasive particles called catalyst fines is precipitating very costly engine damage. Comprising aluminum and silicon oxides, are carried over from the catalyst during the refining process and find their way into the fuel. As these particles are harder than the engine surfaces, it’s the engine that wears - not the particles.

Cat fines have always been present in bunker oils and standard ISO 8217 (2005) permits up to 80 ppm, but the problem is that more than 15 – 20 ppm already causes damage to engine parts.

Appendix E - SGS Test results.

Test carried out by SGS Testing & Control Services Singapore Pte Ltd
OGC Jurong Laboratory, 1 Seraya Avenue, Jurong Island, 628208, Singapore.

SGS is the world’s leading inspection, verification, testing and certification company. They are recognized as the global benchmark for quality and integrity. With more than 80,000 employees, they operate a network of more than 1,650 offices and laboratories around the world.
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Appendix F – Contact Information

Please don’t hesitate to contact us with any queries or for further information:

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