FUELOIL
AND   ITS
CORROSIVE   EFFECTS
IN THE INDUSTRIAL
COMBUSTION

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Optimización de la combustión = Ecología y Ahorro

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1. - INTRODUCTION

This study has been carried out to offer a global vision of the corrosion problems that exist when heavy fuel oil is used in power plants. It takes advantage of the experience acquired by **"rb bertomeu, S.L."** in different plants.

In it, the circumstances that surround the fuel oil and its combustion are exposed and a parallel is traced to extrapolate the experience to the gas turbines and steam generation boilers in order to show that the achievements in these power plants with engines can perfectly be accomplished in this other type of plants.

2. - CHARACTERISTICS OF THE FUELOIL

Fuel oil is a residual product of the distillation of oil that can come from a single distillation stage, or be a mixture of products of different stages, in order to adjust the characteristics of the different specifications to produce the desired type of fuel oil.

As a rule, fuel oil is a complex heterogeneous system made up of:

> a. - Liquid hydrocarbons whose number of carbon atoms is > 2O.
> b. - Solid hydrocarbons emulsified in the liquid phase.
> c. - Dissolved gaseous hydrocarbons or emulsified in the liquid phase.
> d. - Water emulsified in the liquid phase.
> e. - Metallic salts dissolved in the emulsified water.
> f. - Occluded metals.
> g. - Compound organic or inorganic metals forming part of the liquid phase or of the emulsified solids.
> h. - Sulphur components.

In this study, points d, e, f, g, and h are of great importance as they, together, constitute what is designated the fuel impurities, and give cause for different types of corrosion in the exhaust gas circuit when the fuel oil is used as fuel, as will be seen in the chapter 4.

Generally, the emulsified water is saturated with NaCl and also tends to contain small quantities of carbonates and calcium and magnesium sulphates.

The metals present, in atomic form, oxide form, or in the form of organic or inorganic acid salts, are very varied in addition to Na, Ca and Mg already mentioned. The most important, by their implication in the corrosion process, as well as by their quantity are:

Vanadium   (V)
Nickel   (Ni)
Iron   (Fe)
Aluminium (Al)
Zinc   (Zn)
Copper   (Cu)

Sulphur is present as much in its free state as combined in various forms. The most characteristic are:

Mercaptans (R - SH)
Sulphurs and Disulphurs (R-S-R, R-S-S-R)
Cyclical compounds (Thiophene, sulphur ethylene)
Sulphates (R_1 - SO_2 - R_2)
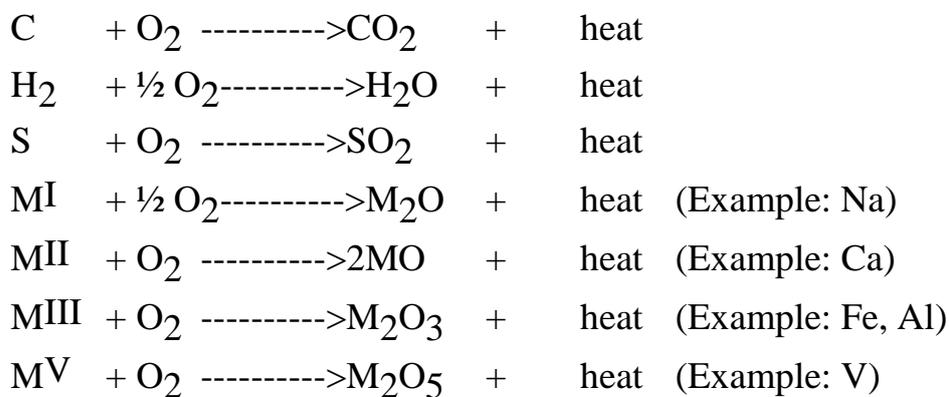Sulphides (R_1 - SO - R_2)
Sulphonic acids (R - SO_3H)

The total quantity of sulphur and the distribution of the type of compounds that form depend on the origin of the crude oil, although this detail is not so important as all the sulphur is oxidised to SO_2, independently of the form in which it is found, when the fuel is burnt.

3. - COMBUSTION REACTIONS OF THE FUELOIL

The combustion of the fuel oil (or any other fuel) is defined as the rapid oxidation of each and every of its constituent elements.

Therefore, to burn a fuel it is necessary to have oxygen, which is provided in the form of combustion air which, as is known, contains basically 21% of O_2 and 79% of N_2.

In essence, the principal reactions that happen in combustion can be synthesised as:

$$C \quad + O_2 \text{ ---------->} CO_2 \quad + \quad \text{heat}$$
$$H_2 \quad + \tfrac{1}{2} O_2 \text{----------->} H_2O \quad + \quad \text{heat}$$
$$S \quad + O_2 \text{ ---------->} SO_2 \quad + \quad \text{heat}$$
$$M^I \quad + \tfrac{1}{2} O_2 \text{----------->} M_2O \quad + \quad \text{heat} \quad \text{(Example: Na)}$$
$$M^{II} \quad + O_2 \text{ ---------->} 2MO \quad + \quad \text{heat} \quad \text{(Example: Ca)}$$
$$M^{III} \quad + O_2 \text{ ---------->} M_2O_3 \quad + \quad \text{heat} \quad \text{(Example: Fe, Al)}$$
$$M^V \quad + O_2 \text{ ---------->} M_2O_5 \quad + \quad \text{heat} \quad \text{(Example: V)}$$
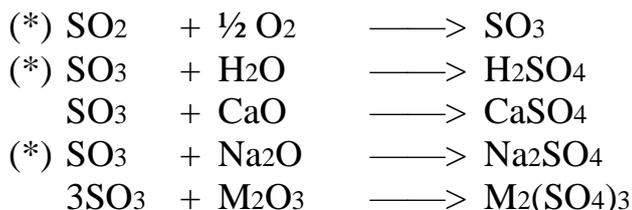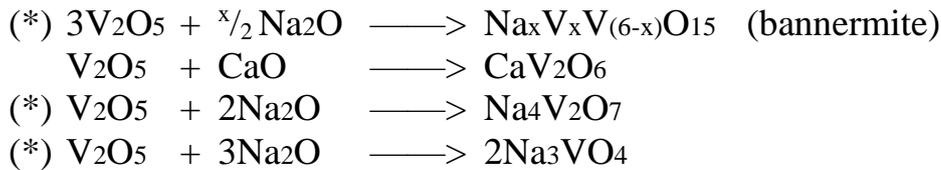
M means valence metal I to V.

The most important, concerning energy efficient use of the fuel, are the first three, the oxidation of the C, H_2 and S, in this order.

Once these reactions are completed, or at the same time, other minor reactions take place related to the impurities of the fuel oil (Sulphur and metals), that in some instances are related to the corrosion processes that happen in the exhaust gas circuit.

Among them we can cite the following:

$$(*) \; SO_2 \quad + \tfrac{1}{2} O_2 \quad \longrightarrow SO_3$$
$$(*) \; SO_3 \quad + H_2O \quad \longrightarrow H_2SO_4$$
$$SO_3 \quad + CaO \quad \longrightarrow CaSO_4$$
$$(*) \; SO_3 \quad + Na_2O \quad \longrightarrow Na_2SO_4$$
$$3SO_3 \quad + M_2O_3 \quad \longrightarrow M_2(SO_4)_3$$

$$(*) \quad 3V_2O_5 + {}^{x}/_{2}Na_2O \longrightarrow Na_xV_xV_{(6-x)}O_{15} \quad \text{(bannermite)}$$
$$V_2O_5 + CaO \longrightarrow CaV_2O_6$$
$$(*) \quad V_2O_5 + 2Na_2O \longrightarrow Na_4V_2O_7$$
$$(*) \quad V_2O_5 + 3Na_2O \longrightarrow 2Na_3VO_4$$

The list is not exhaustive, but shows the important reactions and those which are directly bound with corrosion, marked with (*).

In chapter 4 the corrosion mechanisms cited are studied in greater detail.

Finally, it is worth noting that if the fuel oil was a fuel free of Sulphur and metals, it would not generate, during its combustion, compounds harmful to the metal parts of the waste gas circuits.

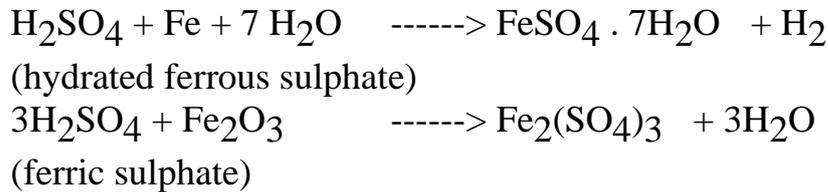## 4. - BASIS OF CORROSION IN THE WASTE GAS CIRCUITS

A) CORROSION LINKED TO SULPHUR COMPOUNDS

The oxidation reaction of SO_2 to SO_3, and the combination of this with the vapour of the H_2O in the gases to form H_2SO_4 has already been described.

Note that the reaction $SO_2 \longrightarrow SO_3$ is catalysed by the presence of metallic oxides, and especially by the vanadium pentoxide (V_2O_5) . Therefore, the more vanadium the fueloil contains, the later it transforms the V_2O_5 into a less catalytically active form (alkaline-earth vanadates), the quantity of SO_3 formed will be greater and, because of this, there will be more probability that sulphuric acid is formed, H_2SO_4.

The equilibrium point of reaction $SO_3 + H_2O \longrightarrow H_2SO_4$ is between 200º and 500º C. Below 200º C, H_2SO_4 has the form of semi-corrosive vapour, while above 500º C the H_2SO_4 is very unstable and is separated in SO_3 and H_2O. Between both temperatures, the H_2SO_4 vapour coexists with the SO_3 and H_2O.

H_2SO_4 vapour begins to condense below 150º C, approximately when it is converted into a highly corrosive compound which attacks the metal surface following these reactions:

$$H_2SO_4 + Fe + 7\,H_2O \quad ------> FeSO_4 . 7H_2O \; + H_2$$
(hydrated ferrous sulphate)
$$3H_2SO_4 + Fe_2O_3 \quad ------> Fe_2(SO_4)_3 \; + 3H_2O$$
(ferric sulphate)

It is obvious that this type of corrosion will only happen in the waste gases circuit, at points where the temperature is below 200º C, and especially if it is below 150º C. That is to say, at the end of the combustion process (waste gas purifiers, chimneys, etc.).

The SO_3 formed can merge with the metallic oxides present to form sulphates (see section 3).

Of all the metallic sulphates that can be formed, sodium sulphate (Na_2SO_4) is the main one which is accountable for the corrosion of the metal surfaces. All the sodium salts are barely corrosive at ambient temperatures, but at increased temperatures the corrosion speed is increased rapidly when the fusion point of the salt is reached. In the case of $Na_2\,SO_4$, it is 888º C, when it comes into contact with metal surfaces iron corrosion is produced, probably by the formation of double sulphates of Fe and Na. The real mechanism is not very well-known, though from what has been said before, the corrosive effect of sodium sulphate at high temperature is fully acknowledged.

This type of corrosion will happen, therefore, in high-temperature areas of the circuit, near the area of combustion and before the diluting effect of the air decreases the temperature lower than 850º C.

B) CORROSION LINKED TO VANADIUM COMPOUNDS

Vanadium form several oxides such as V_2O_2, V_2O_3, V_2O_4 and V_2O_5. The acid nature raises the degree of oxidation, V_2O_5 (pentoxide) has the most acidic nature and is therefore the most corrosive. On the other hand, under combustion conditions where large amounts of O_2 and high temperatures exist, any form of vanadium present in the fuel oil will have a tendency to be oxidised into V_2O_5, therefore, its presence will be certain in the combustion gases and in a liquid state (established at 690º C) where two very harmful effects originate:

- Catalysis of the oxidation of SO_2 to SO_3.
- Corrosion of the metal surfaces to form ferric meta-vanadates ($Fe(VO_3)_3$).

As other metals are also present in the fuel oil (see sections 2 and 3), part of the V_2O_5 has a tendency, by its reactivity, to form salts (vanadates) with the alkaline metals and alkaline-earth.

The alkaline-earth vanadates have a high fusion point, 1000º - 1200º C, therefore as a rule, after combustion it is found in a solid state, in the form of a powder which is carried by the gases. In this type of salt we find the calcium vanadates and magnesium vanadates:

$(Mg/Ca)_1 \ V_2O_6$

$(Mg/Ca)_2 \ V_2O_7$

$(Mg/Ca)_3 \ V_2O_8$
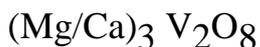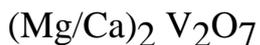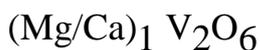
The alkaline vanadates, mainly the distinct sodium vanadates have a much lower fusion point (350º to 650º C), and are therefore found in a wide zone of the waste gases circuit in liquid state. These vanadates are very reactive with the iron and iron oxides, dissolving them to form vanadates or double sulphovanadates, above all in the presence of sodium sulphate.

The fusion temperature of the different sodium vanadates that can be formed comes from data of the molecular weight relation V_2O_2/Na_2O, according to the following table:

Rel. V_2O_5/Na_2O	Fusion Temp. ºC
0	400
1	550
2	450
3	350
4	530
6	580
8	620
10	640
∞	690

We see therefore, that in the waste gases circuit, there exists a great probability of finding sodium vanadate in a liquid state, corrosive, above all when the molar relation V_2O_5/Na_2O is 3. Nevertheless, though such relation will be higher or lower in a combustion installation of the engine, gas turbine or boiler type, there are many important areas of metal parts subjected to greater temperatures greater than 690º C, therefore the corrosive effects of the alkaline vanadates are practically guaranteed.

At this point, the question is: if the fuel oil contains impurities of S, V and Na, is the formation of corrosive sodium sulphate and sodium vanadate unavoidable? Certainly, unless correction factors are introduced into the process. These factors should meet two requirements to avoid or minimize these kinds of corrosion.

a) As N is basically found dissolved in the water of the fuel oil, this must be separated at the bottom by decantation, centrifuge, etc. so that the N sent to the combustion will be much less.

b) Since Vanadium is found in the fuel oil in soluble form and it is not possible to separate it by decantation or centrifugation, the rapid formation of alkaline-earth vanadates (Ca, Mg) is favourable in the combustion for two purposes:

b-1) to avoid the catalytic action of the V_2O_5 on the reaction of

$$SO_2 + ½ O_2 ----------->SO_3$$

b-2) to raise the fusion temperature of the vanadates so that they will be carried in the form of powder.

C) THE SOLUBLE MAGNESIUM (MOLECULES) NEUTRALIZES THE CORROSION PRODUCED BY VANADIUM AND SODIUM COMPOUNDS

In order to avoid Vanadium and Sodium corrosion in ENGINES and GAS TURBINES by using additives containing magnesium and **not making any damage by scratching or hitting the metallic parts** in pumps, fuel injection nozzles, blades, rotors and turbines, it is only possible when Magnesium is in form of Fatty acid Organic Salt SOLUBLE in HYDROCARBONS, as in the **"rb bertomeu"** additives where the Magnesium is in form of molecules.

Depending on the specific needs and requirements, the **"rb bertomeu"** additives are supplied with up to 30% wt/wt of Magnesium and varying percentages of other components.

The chemical synthesis process by "rb bertomeu" produces the before-mentioned Magnesium Fatty acids Organic salts completely soluble in hydrocarbons where the Magnesium particles are Mg^{2+} ions, with a radius of 72 picometers (1 picometer is 1,000 times smaller than a nanometer).

The surface reactivity of these magnesium ions over conventional materials (oxides and hydroxides of magnesium) is about 10 times higher if the particles are nanometric and 100 times higher if the particles are micrometric.

The "rb bertomeu" additives with soluble Magnesium are the most reactive agents known to neutralize corrosion by Vanadium pentoxide and Sodium vanadates and cannot make any damage by hitting or corroding the gas turbine's blades because the Magnesium particles are molecules. Being the additive in molecular form, it provides an active area (~ 1,800 m^2 / g Mg) between 10 and 100 times higher than the one in nanometer-sized and micrometer-sized particles, and thereby increasing by a proportional factor the chemical reactivity.

During the combustion, the SOLUBLE Magnesium of the additives manufactured by **"rb bertomeu"** react with the Vanadium oxide and forms Magnesium Vanadate of high melting point (more than 1,200ºC), which is solid and non-corrosive at the internal temperature.

The action of fixing heavy metals (Vanadium), is also translated into a decrease in the oxidation of SO_2 to SO_3 (formed from the fuel oil's Sulphur) by minimizing its catalytic action on the reaction; as a consequence, the formation of Sodium sulfate is reduced (Na_2SO_2) that melts at 888 ºC and also diminishes the appearance of Sulfuric acid condensation when the combustion gases cool down and, along with it, cold corrosion.

The Magnesium (Mg) molecule becomes integrated in the Vanadate molecule along with the rest of solid residues formed in the combustion (for example, MgV_2O_6 or $Mg_3V_2O_8$). The rest of the organic components of the "rb bertomeu" additives, including the organic anion which has supported the atom of Magnesium in soluble form, are burned during the combustion, generating residual gases as CO_2 and H_2O, like the fuel oil itself, and not generating solid residues.

Magnesium salts formed during the combustion are inert (non-corrosive), unlike the Calcium salts also formed from Calcium contained in the fuel and from Calcium contained in the engine oil burned by the engine.

The theoretical damage[1] that the in-suspension Magnesium oxide or hydroxide nanometric particles could make in the combustion chamber by hitting or corroding it (as it might happen in some additives), cannot be given in the case of the additive "rb bertomeu "beco Mg Concentrated, because there is no Magnesium oxide or hydroxide present, neither solid nor liquid and neither before nor after combustion. In the additive "rb bertomeu" beco Mg Concentrated, Magnesium is in form of Fatty Acid Organic Salt (molecules) SOLUBLE in HYDROCARBONS.

5. - COMBUSTION TEMPERATURES OF THE FUELOIL

It is widely known and easy to calculate the volume of stoichiometric air necessary to achieve combustion per Kg. of fuel oil according to the reactions described in chapter 3.

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[1] The Magnesium Oxide and the Magnesium Hydroxide particles, which are solid minerals, can damage the fuel injection system. The injection pumps in engines fed with fuel oil have the piston adjusted approximately to 1 micron and work under a pressure of 400-500 bars.
The Magnesium Oxide and the Magnesium Hydroxide solid particles would cause the breakdown of the injection system.

Supposing that the form of standard fuel oil has an calorific value of less than 9,500 Kcal/Kg., and it is burnt with air at 20º C and 60% HR, the temperature of the combustion gases, in relation to the total air provided (excess combustion air plus dilution air), would be approximately the following (excluding heat loss by dissipation):

Total air in excess over stoichiometric	Gas temp.
0 %	2,060º C
5 %	1,985º C
10 %	1,920º C
20 %	1,800º C
50 %	1,500º C
100 %	1,200º C
150 %	990º C
200 %	850º C
250 %	740º C
300 %	660º C

The real temperatures will depend on the heat loss due to conduction, convection and radiation of the equipment, but, as a rule they can be assumed to be between 5% or 10% below the theoretical temperatures without any appreciable error.

It is observed that in an industrial combustion installation, of the engine or gas turbine type, where the provided total air oscillates between 150% and 300% of the stoichiometric necessary for combustion, there will be metal areas submitted to temperatures between 600º C and 1,000º C. Logically this corresponds to areas near to the combustion area, when cooling has already been produced by dilution with air of the gases generated in the aforesaid combustion.

Examples:

A) In the gas turbines and power engines and, that work with an excess of air of 200% to 300%, the initial temperature of the combustion will begin at

approximately 2,000º C, but it will quickly drop to 700º - 800º C in the engine exhaust valves and to 1,000-1,300ºC in the gas turbine inlet. Thereafter, due to the high heat loss of the circuit, it will be about 500-600 ºC in the engine's turbos and around 400-650º C at the gas turbine exhaust and afterwards, 200º - 250º C at the exit of the steam boilers of the power plant.

B)   In steam boilers (with burners) it will be about 1,200º - 1,500º C in the central area and 800º - 900º C in the contact zone of the gases with the reheater pipes.

6.- EXPERIENCE OF "rb bertomeu, S.L." IN POWER   PLANTS

For years, **"rb bertomeu, S.L."** has been studying the corrosion problems that exist in power plants that use fuel oil as fuel. From this study we have come to the following conclusions:

a) the fuel oil always contains impurities, though in variable proportions according to its origin.
b) partial and total corrosions are produced in the exhaust valves of the engines, more corrosion occurs when the quantity of vanadium and sodium in present the fuel oil is higher. The temperature in this point is about 800º C.
c) solid residual deposits are produced in the exhaust valves of the engines, gas collectors and turbos, these are directly proportional to the vanadium content of the fuel oil and of the calcium (TBN) in the engine oil.
d) corrosions are not produced in points of the circuit whose temperature is understood to be between 350º and 200º C.

Taking these conclusions into account, and the reasoning shown in chapter 4, we have developed a treatment which avoids or minimises the corrosion problems of the exhaust valves of the engines, which, we recall, is the point where the temperature is most critical in relation to the melted salts present.

This achievement comes endorsed by the users of our **"rb bertomeu"** additives who have been able to compare present results with those of prior situations when they were not using the current treatment.

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Parallel to the elimination of corrosion we have also been able to reduce, by 70% - 80%, the deposits of hard solid residues on the stems of the exhaust valves, collectors and turbos.

All this has been translated into an increase in the useful life of the valves, in better operation of the engines by obstruction-free maintenance of the exhaust gases circuit, and in a greater capability of production by a decrease in the maintenance necessary between programmed inspections.

Recalling what was said in chapter 4, the treatment designed **"rb bertomeu, S.L."** consists of the application of an additive whose components develop the following effects in relation to corrosion:

A. - To aid the decantation of the water, contained in the fuel oil in the storage tank, so that the quantity of sodium salts will be reduced. In this way sodium sulphate and vanadate formation is minimised. The water decanted should be eliminated periodically from the tank by bleeding or centrifugation in the fuel oil purifiers.

B. - To achieve a perfect pulverisation of the fuel oil in order to eliminate residual carbons which could act as base of adhesion for residual saline.

C. - To neutralize the V_2O_5 (vanadium pentoxide) obtaining alkaline-earth vanadates of high fusion point, at the same moment of combustion, which achieves:
   - eliminate corrosion by V_2O_5.
   - eliminate the appearance of sodium vanadates below fusion point.
   - obtain vanadates of high fusion point (> 1,200º C) which are carried by the flow of combustion gases without being deposited in the circuit.

D. - To neutralize the formation of Sulphur trioxide (SO_3), blocking the formation of Sulphuric acid (H_2SO_4) and Sodium Sulphate (Na_2SO_4).

For more information see Actions and benefits of "rb bertomeu" additives for heavy fuel oil

7. - TRANSFERRING THE EXPERIENCE IN ENGINE COGENERATION PLANTS TO STEAM BOILERS WITH BURNERS

Essentially, the process is the same in a diesel engine with fuel oil as in a steam boiler which burns fuel oil. The only difference is the excess of circulating air in respect to the theoretical stoichiometry, depending on of the type of installation used. Because of this, the temperature distribution can vary, but, inevitably, in a steam boiler, the flow of available hot gases at the centre will be 600º - 900º C in the air-water heat exchange area (heat exchange pipes or reheaters).

Concerning corrosion effects, this point (reheaters) would be the equivalent to the exhaust valves of an engine using fuel oil. For this reason, if corrosions and solid residual deposits are produced, it is logical to think that the same effects are also found in the heat exchange pipes of the boiler, which should produce two negative situations:

- A decrease in the useful life of the pipes of the boilers.
- Formation of encrustations in the pipes, that reduce the rate of heat transmission, and, therefore, their energetic efficiency.

The second effect is obvious and it does not need demonstrating if we take into account the principles of thermodynamics applied to heat transmission through a given surface.

The first effect, corrosion of the pipes, is a measurable parameter, above all the installation has statistics of the thickness measurement of the pipes over several years.

The system of checking the process of corrosion of the outer wall of the pipes (the part in contact with the gases) should be the following:

- annual measurement of the outer diameter of the pipes when they have been scraped to eliminate the solid residual encrustations.
- annual measurement of the thickness of the wall of the pipes, to verify whether or not there is corrosion on the internal wall (the part in contact with the water - steam).

This should provide sufficient data to follow the condition of the most critical part of the boiler, and to evaluate the possible life of the boiler. Equally, the economic value of the use of the **"rb bertomeu"** additives can be determined, which, as has been

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reported throughout this study, is the way to avoid corrosion and to notably lengthen the useful life of the equipment.

8.- TRANSFERRING THE EXPERIENCE IN LARGE ENGINES AT POWER PLANTS TO GAS TURBINES THAT RUN ON HEAVY FUEL OIL OR CRUDE OIL

Essentially, the process is the same in a diesel engine as in a gas turbine if both of them burn fuel oil.

The temperatures in both combustion chambers are approximately of 2,000 ºC. The temperature at the engines exhaust valves is of 700-800ºC and the one at the engine's turbo-compressor inlet is between 500 and 600 ºC.

The temperature at the gas turbine inlet is 1,000-1,300 ºC and the exit temperature is between 450 and 600ºC.

In regard of the corrosion / corrosion neutralization, the gas turbine blades would be the equivalent to the exhaust valves of an engine using fuel oil since both of them are within the temperature range where the Vanadium or Sodium corrosive reactions take place.

During the combustion, the SOLUBLE Magnesium of the additives produced by **"rb bertomeu"** reacts with the Vanadium oxide and forms Magnesium Vanadate of high melting point (more than 1,200ºC), which is solid and non-corrosive at the internal temperature of the engine or gas turbine exhaust.

a) The V_2O_5 is neutralized (vanadium pentoxide) obtaining alkaline-earth vanadates of high fusion point, at the same moment of combustion, which achieves:
   - eliminates corrosion due to V_2O_5.
   - eliminates the appearance of sodium vanadates below fusion point.
   - obtains vanadates of high fusion point (> 1,200º C) which are carried by the flow of combustion gases without being deposited in the circuit.
   - neutralizes the formation of Sulphur trioxide (SO_3), blocking the formation of Sulfuric acid (H_2SO_4) and Sodium Sulphate (Na_2SO_4).

b) It enhances the decantation of the water contained in the fuel oil in the storage tank, so that the quantity of sodium salts will be reduced. In this way sodium

sulphate and vanadate formation is minimised. The water decanted should be eliminated periodically from the tank by bleeding.

c) Helps achieving a perfect pulverisation of the fuel oil in order to eliminate residual carbons which could act as base of adhesion for residual saline.

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