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(54) **USE OF NICKEL COMPOUNDS AS VANADIUM CORROSION INHIBITORS**

(76) Inventors: **Michel Moliere**, Vetrigne (FR); **Emmanuel Rocca**, Villers les Nancy (FR); **Pierre Steinmetz**, Vandoeuvre les Nancy (FR)

Correspondence Address:
YOUNG & THOMPSON
745 SOUTH 23RD STREET 2ND FLOOR
ARLINGTON, VA 22202

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(57) **ABSTRACT**

The invention concerns inhibition of vanadium corrosion of thermal equipment materials burning vanadium-contaminated liquid fuels using nickel compounds. The invention is applicable in particular to liquid fuel combustion in gas turbines.

USE OF NICKEL COMPOUNDS AS VANADIUM CORROSION INHIBITORS

[0001] The present invention relates in general to the vanadium corrosion inhibition of materials used in thermal plant burning vanadium-contaminated liquid fuels.

[0002] It proves to be economically beneficial to be able to exploit medium-quality oil-bearing extracts such as, for example, products variously contaminated with impurities.

[0003] The presence of organic vanadium compounds in liquid fuels burnt in different types of thermal plant, such as boilers, diesel engines, gas turbines, etc. is liable to cause high-temperature corrosion of the metallic materials in contact with the combustion gases. This corrosion, called vanadium corrosion, can be severe to a greater or lesser extent, depending on the type of metal or alloy of the thermal plant, the actual type of this thermal plant, the service temperature range and the operating life and conditions.

[0004] This corrosion is caused by the formation in the combustion gases of low-melting-point vanadium derivatives, such as vanadium pentoxide (V_2O_5) (pure vanadium corrosion) and V_2O_5—Na_2SO_4 eutectic mixtures (vanadium-sodium corrosion), which are liable to induce, under the temperature conditions prevailing at the surface of the metal components in question, electrochemical etching which develops in a molten electrolyte environment and in the presence of oxidants, especially the oxygen contained in the smoke and the sulfate ions formed from the sulfur in the fuel. Since potassium has a similar corrosive effect to sodium, the term "sodium" will mean in the rest of the description "sodium or potassium".

[0005] The metallic materials are subjected to two main corrosion mechanisms:

[0006] type I corrosion, or high-temperature corrosion, which typically occurs at temperatures from 800 to 900° C.;

[0007] type II corrosion, or low-temperature corrosion, which typically occurs at temperatures from 550 to 750° C.

[0008] Type I corrosion is the etching in a hot oxidizing medium of the metallic materials by molten electrolytes, such as those rich in vanadium pentoxide. Type II corrosion is generally associated with the formation of eutectics comprising Na_2SO_4 and another metal (for example vanadium or cobalt). In most thermal plant, both types of corrosion risk exist. It should be noted that sodium sulfate is generally present in the form of traces in the thermal plant. This sodium sulfate results from the reaction between the sodium contained in the combustion air and the sulfur derivatives present in fuel oils. Thus, in a gas turbine comprising several successive stages, the first stage of the turbine is in contact with the combustion gases at high temperature and is exposed to type I corrosion, whereas the last stage sees the flow of cooler combustion gases and is exposed to type II corrosion. Thus, to combat vanadium corrosion in gas turbines, it is essential to control both corrosion mechanisms.

[0009] The corrosivity of these vanadium compounds can be inhibited by chemically "trapping" V_2O_5 within refractory compounds. Thus, the corrosive molten electrolyte medium is eliminated. Conventional vanadium inhibitors are represented by alkaline-earth metal salts, such as calcium salts and magnesium salts, the latter being most commonly used. Under certain temperature and inhibitor dosage conditions, the vanadium forms with the inhibitor of the refractory alkaline-earth metal orthovanadates of the $M_3V_2O_8$ type, where M represents an alkaline-earth metal.

[0010] The dosage of the inhibitor must be sufficient both to allow all the vanadium present in the fuel to be trapped and to prevent the formation of substoichiometric vanadates, such as pyrovanadates ($M_2V_2O_7$) or metavanadates (MV_2O_6), which are insufficiently refractory to provide the intended inhibition.

[0011] The vanadates resulting from this inhibition process produce ash suspended in the combustion gases, some of the ash being deposited on the walls of the combustion chambers and of the components of the combustion apparatus which are located downstream of the combustion chambers. This causes the combustion apparatus to become gradually fouled in operation and results in a corresponding and gradual reduction in its energy performance.

[0012] In addition, to ensure suitable operation of the equipment treated with these vanadium inhibitors, it is absolutely essential that these deposits (1) form in minimal amounts and (2) be able to be removed, as completely as possible, without burdening the economics of the operation. Thus, the cost of the cleaning operation and the time during which the equipment is out of commission have to be minimal.

[0013] Two cleaning methods are commonly used, especially in the case of gas turbines, namely dry cleaning and water washing.

[0014] Dry cleaning consists in introducing, into the equipment while continuing to run, a slightly abrasive material containing no corrosive compounds and no ash.

[0015] In water washing, hot water is made to flow through the turbine, the flames being extinguished but with the rotor rotating at a reduced speed in order to ensure air flow over the surfaces to be cleaned. Dissolving the sulfate phase results in mechanical destabilization of all the insoluble solid phases which are associated with it in the deposit, particularly the alkaline-earth metal vanadates. The washing water entrains the deposit, partly in dissolved form and partly in suspension in the water.

[0016] In the following, magnesium will be taken as an example of a conventional inhibitor since, its sulfate being very soluble, it is more widely used on a industrial scale than, for example, calcium, whose sulfate is not very soluble.

[0017] The formation of magnesium sulfate at the same time as that of the orthovanadate requires, in order to "trap" all of the vanadium, magnesium be supplied greatly in excess compared with the stoichiometry of the reaction with, in practice, a magnesium/vanadium mass ratio of greater than or equal to 3.

[0018] This excess inhibitor consumption incurs an additional direct operating cost.

[0019] In addition, magnesium orthovanadate is not very stable in the presence of sodium with which it reacts to form low-melting-point salts. This means that in the presence of sodium the magnesium dosage must be increased. Thus, a magnesium/vanadium mass ratio of 10 is required when the sodium contamination represents 20% by weight of the vanadium contamination.

[0020] Moreover, more rapid fouling of the combustion equipment is observed, resulting in an accelerated degradation of the performance and the need for more frequent defouling, especially using water, in order to ensure suitable operation.

[0021] Another drawback associated with the use of conventional inhibitors based on alkaline-earth metals, and especially magnesium, relates to the "derating" of the thermal plant used. The term "derating" is understood to mean that the flame temperature of the gas turbines subjected to such an inhibition treatment must be reduced from the nominal value of the gas turbine model in question. The flame temperature is defined as the temperature of the hot gases at the inlet of the first stage of moving blades of the turbine and constitutes one of the parameters essentially determining the energy performance of the turbine.

[0022] The reason for this "derating" stems from the fact that desulfation of the magnesium is observed at high temperature. Knowing that, on the one hand, the rate of desulfation and, on the other hand, the rate of desulfation at the equilibrium of the reaction increase with temperature and that the magnesium oxide, produced by the desulfation, is moreover insoluble in water, it turns out that, above a certain flame temperature value and a certain period of continuous operation, the proportion of sulfate remaining in the deposit becomes insufficient to ensure correct removal of the deposit by water washing.

[0023] At the present time, the combustion of vanadium-contaminated fuels using magnesium as inhibitor in gas turbines results in the flame temperature being limited to around 1100° C.

[0024] The need to limit the flame temperature precludes, for economic reasons, the use of gas turbines of the latest technology. These have nominal flame temperature levels greater than 1100° C. and higher efficiencies. However, the purchase cost per kW electric of such turbines is higher than that of turbines whose flame temperature is of the order of 1100° C. (so-called class "E" machines), so that their operation with a reduced flame temperature is not economic.

[0025] Moreover, when the flame temperature is set in the region of this limiting value of 1100° C., rather than at a lower level, specifically for the purpose of maximizing the energy performance of the gas turbine, the more rapid desulfation of the magnesium requires more frequent washing, thereby reducing the availability of the equipment.

[0026] Thus, in the light of the drawbacks observed with conventional inhibitors, it would seem to be desirable to have vanadium corrosion inhibitors, in particular those which inhibit type I corrosion and type II corrosion, which can be used especially during the combustion of vanadium-contaminated liquid fuels, in particular in the presence of sodium, causing reduced fouling of the thermal plant used and therefore increasing its availability, especially in the case of gas turbines.

[0027] Moreover, it would also seem to be desirable to be able to use, without prior "derating", or with minimal derating, turbines of the latest technology, which operate with a high flame temperature for the purpose of better energy efficiency.

[0028] From another standpoint, it would also seem to be desirable to make the use of vanadium-contaminated fuels more efficient and economically more profitable.

[0029] Finally, it would seem to be particularly desirable to remedy the drawbacks associated with the use of conventional inhibitors, especially in the combustion of vanadium-contaminated liquid fuels.

[0030] The applicant has now discovered that it is possible and particularly advantageous to use nickel-based compounds, the mass ratio of nickel to contaminating vanadium being greater than or equal to 1.74, in order to inhibit the vanadium corrosion of metallic materials, especially thermal plant burning vanadium-contaminated liquid fuels, even at high temperature. The subject of the present invention is therefore the use of nickel-based compounds to inhibit the vanadium corrosion of metallic materials, characterized in that the mass ratio of nickel to contaminating vanadium is greater than or equal to 1.74.

[0031] The metallic materials whose corrosion may thus be inhibited are of any type and especially ferrous metals (non-alloy steels, low-alloy to high-alloy steels and stainless steels) or superalloys (based on chromium and/or nickel and/or cobalt). This application to any type of metallic material stems from the nature of the inhibition in which the vanadium, trapped by the nickel, is extracted from the medium as a corrosive agent.

[0032] The term "thermal plant" is understood to mean any type of combustion apparatus, such as diesel engines, boilers, gas turbines, etc.

[0033] According to a preferred use of the invention, the metallic materials of gas turbines are protected from vanadium corrosion.

[0034] These nickel-based inhibitors may substitute for those based on alkaline-earth metals in any application in which these can be used, whatever the type of combustion apparatus and the type of vanadium-containing fuel, while overcoming the drawbacks associated with the use of these inhibitors based on alkaline-earth metals.

[0035] The applicant has in fact established that certain chemical compounds of nickel combine with the vanadium contained in the fuels to form, under appropriate temperature and stoichiometry conditions, nickel orthovanadate ($Ni_3V_2O_8$). Nickel orthovanadate is a refractory and non-corrosive compound capable of inhibiting the high-temperature vanadium corrosion of metallic materials.

[0036] Within the temperature range prevailing at the surface of the materials of thermal plant to be protected, nickel, unlike magnesium, does not form a sulfate. This obviates the need for inhibitor overdosing owing to the formation of this salt.

[0037] The vanadium corrosion protection afforded by these nickel-based inhibitors is very effective because not only is nickel orthovanadate thermally stable, but it is also chemically inert within the temperature range prevailing at the surface of the components of the equipment to be protected, even in the presence of sodium sulfate.

[0038] Under the same conditions, a substantial fraction of the magnesium, when this is used as inhibitor, combines with sodium sulfate to form $MgSO_4$—Na_2SO_4 eutectics which have a low melting point and are therefore potentially corrosive. The vanadium corrosion protection provided by the nickel-based inhibitors is therefore better than that provided by the magnesium inhibitors, especially in the presence of sodium which is liable to be introduced into the thermal plant, either via the fuel circuit or via the combustion air. This is due to the fact that nickel orthovanadate is very stable in the presence of sodium and does not form low-melting-point salts. The use of nickel is therefore particularly well suited for inhibiting vanadium corrosion of metallic materials by a vanadium-contaminated liquid fuel in the presence of sodium. The sodium may be provided by the fuel and/or by the combustion air. Thus, an Ni/V mass ratio of 2.25 affords effective protection against compositions containing sodium and vanadium, with a sodium concentration of less than or equal to 0.1 ppm in the combustion gas, equivalent to 5 ppm in the fuel oil.

[0039] The use of nickel-based compounds as inhibitors also has the additional advantage of reducing the soot particles within the thermal plant owing to the action of atomic nickel in the hydrocarbon flames.

[0040] Thus, according to a first aspect of the invention, at least one nickel-based compound, with a mass ratio of nickel to contaminating vanadium of greater than or equal to 1.74, is used to inhibit the vanadium corrosion of metallic materials, especially materials for thermal plant, and more particularly superalloys for industrial gas turbines burning vanadium-contaminated liquid fuels.

[0041] According to the invention, the fuel may be any type of vanadium-contaminated liquid fuel, and especially a fuel which is lightly contaminated with vanadium, such as a gas condensate or a heavy distillate of petroleum, or a fuel which is very highly contaminated with vanadium. In both cases, the use of magnesium as inhibitor results in significant fouling of the active hot components to the detriment of the proper operation of the thermal machine.

[0042] The combustion according to the invention may take place at high temperature, especially above 1100° C. and more particularly from 1100° C. to 1300° C.

[0043] This is because the melting point and decomposition temperature of the nickel orthovanadate ($Ni_3V_2O_8$) which forms are 1310° C. and about 2000° C., respectively.

[0044] These characteristics give the nickel-based inhibitor a range of applications which is potentially more extensive than that of inhibitors based on magnesium, whose orthovanadate melts at 1200° C. In particular, these characteristics help substantially to increase the flame temperature of gas turbines burning vanadium-contaminated fuels and make the combustion of such fuels possible in the higher-performance gas turbine models of the latest technology.

[0045] The mass ratio of nickel to contaminating vanadium is preferably from 1.9 to 2.5 (a ratio of 2.25 is even more particularly preferred). On the one hand, in order to provide an acceptable safety margin for industrial applications [lacuna]. On the other hand, excess nickel results in the formation of refractory and noncorrosive nickel oxide which is slightly abrasive and acts as a self-cleaning agent for the thermal plant, this being favorable to maintaining the energy performance of said equipment. Adjustment of the nickel/vanadium ratio makes it possible to adjust this self-cleaning power of the inhibitor.

[0046] Furthermore, within this range, it has been found that the amount of ash formed by the nickel-based compound is less than the amount of ash formed by a magnesium-based compound by a factor of at least 2.

[0047] This may be explained by two facts:

[0048] the nonadherent nature of the nickel-based ash under temperature and speed conditions prevailing within the combustion gases near the surfaces to be protected;

[0049] the slightly abrasive nature of these particles, particularly nickel oxide particles, which tend to erode any deposit being formed on the surface of the fixed and moving components of the thermal plant.

[0050] Thus, the frequency with which the cleaning operations are carried out on the thermal plant is greatly reduced and the availability of the equipment increased.

[0051] Furthermore, the applicant has found that the nickel-based deposits, composed of nickel oxide and orthovanadate, are both extremely friable and of porous structure.

[0052] As a consequence, there are three beneficial effects in the nickel-based ash ablation operations:

[0053] a) the particularly high effectiveness of the dry cleaning operations, thanks to the friability of the deposits;

[0054] b) the effectiveness of water washing operations, despite the insolubility of the nickel ash; this is because, during a washing operation with hot water, the water penetrates the porous structure of the deposit which, because of its low mechanical strength, disintegrates under the combined effect of the capillary forces and the hydrodynamic forces caused by the circulation of the washing water (the circulating effect is particularly great in the case of a gas turbine because of the rotation of the blades). The wettability of the deposit may be further increased by the addition of a wetting agent which contains no sodium in order to prevent the corrosive effect of this metal, such as a cationic or nonionic surfactant;

[0055] c) the increased reactivity compared with a possible chemical reactant.

[0056] The invention also relates to the use of nickel-based compounds, in the proportions described above, in order to inhibit type I corrosion of metallic materials and to inhibit type II corrosion of metallic materials.

[0057] According to another aspect of the invention, the nickel-based compounds are used to inhibit the vanadium corrosion of metallic materials by a vanadium-contaminated liquid fuel in the presence of sodium.

[0058] The expression "in the presence of sodium" is understood to mean that the sodium is present in the liquid fuel and/or in the combustion air.

[0059] The nickel-based compounds can also be used to inhibit the vanadium corrosion of metallic materials during combustion of a vanadium-contaminated liquid at temperatures above 1100° C. Preferably, the combustion temperature is from 1100° C. to 1300° C.

[0060] The methods of injecting this nickel-based inhibitor are similar to those for conventional inhibitors. It may be injected in the form of an oil-soluble additive mixed directly with the liquid fuel in the storage tanks or mixed in line before the fuel is injected into the combustion chamber. It may also be used in the form of a water-soluble additive, emulsified in line in the liquid fuels before injection into the combustion chamber, or else injected separately into the thermal plant.

[0061] Depending on the method of addition of the nickel-based compound into the liquid fuel, it may be in an oil-soluble or water-soluble form, in the form of a water-in-oil or oil-in-water emulsion or microemulsion, or in the form of a suspension.

[0062] When it is in an oil-soluble form, the nickel-based compound is chosen especially from organometallics, such as nickel sulfonates, carboxylates or alkanoates having a variable hydrocarbon chain containing from 2 to 12 carbon atoms, and preferably 6 or 7 carbon atoms, dissolved in an organic solvent compatible with the liquid fuel.

[0063] When it is used in a water-soluble form, the nickel-based compound especially consists of an aqueous solution of an organic or inorganic nickel salt such as, for example, a nitrate or sulfate.

[0064] When the nickel-based compound is used in the form of a water-in-oil emulsion or microemulsion, it is then an aqueous solution of at least one organic or inorganic nickel salt, such as a nitrate or a sulfate, emulsified in a solvent compatible with the fuel to be treated, by means of an emulsifier having a suitable hydrophilic/lipophilic balance, such as, for example, a polyethoxylated nonylphenol of generic formula CH_3—$(CH_2)_8$—(C_6H_4)—O—$(CH_2CH_2O)_nH$, and introduced in an appropriate concentration. The compound of generic formula CH_3—$(CH_2)_8$—(C_6H_4)—O—$(CH_2CH_2O)_nH$ may represent up to 10% by weight of the solution. The long-term stability of the emulsion, essential for industrial applications, can be increased by the addition of a cosolvent, such as oleic acid, introduced in a small proportion.

[0065] When it is used in the form of an oil-in-water emulsion or microemulsion, it is an organic solution of a nickel sulfonate, carboxylate or alkanoate emulsified in an aqueous solution by means of an emulsifier having a suitable lipophilic/hydrophilic balance of the same type as described above and introduced in an appropriate concentration. A cosolvent may also be added thereto.

[0066] When the nickel-based compound is used in the form of a suspension, it is a solid compound such as a nickel oxide, partially hydrated oxide, hydroxide or superbase, in particulate form, or in suspension in an aqueous solution or in an organic solvent compatible with the fuel to be treated.

[0067] Nickel compounds in oil-soluble form, which are easily miscible with the fuel to be treated, and can be used directly, are often preferred.

[0068] The very high reactivity of nickel with respect to vanadium makes it possible, according to one application of the invention, to use it in combination, in the form of a mixture in any proportion, with one or more other metals. Thus, it is conceivable to combine it with at least one or more metals having other corrosion-inhibiting functions, chosen especially from chromium, silicon, aluminum, zinc and magnesium. It is also conceivable to combine it with at least one or more metals which act as a combustion catalyst, chosen especially from iron, manganese and cerium.

[0069] According to another method of implementing the. invention, the vanadium-contaminated fuel also contains nickel as an appreciable metallic contaminant.

[0070] The use of nickel-based inhibitors allows particularly economic combustion of these naturally nickel-containing fuels. This is because the amount of inhibitor nickel to be added is then equal to the difference between the concentration corresponding to the intended nickel/vanadium ratio and the natural concentration of nickel in the fuel. By way of examples of this type of fuel, mention may be made of crude oils and residuals coming from the distillation of certain oils, such as crude oils from China and Indonesia, "Low Sulfur Waxy Residuals" from the South-East Asian oil market.

[0071] Another aspect of the invention relates to a method of combustion of a vanadium-contaminated liquid fuel, which, apart from the known conventional steps accompanying the combustion, includes a step of introducing at least one nickel-based compound into the thermal plant, separately or as a mixture with the contaminated liquid fuel.

[0072] The nickel is added in proportions such that the mass ratio of nickel to contaminating vanadium is greater than or equal to 1.74 and preferably from 1.9 to 2.5. A mass ratio of 2.25 is particularly preferred.

[0073] According to a variant of the method of the invention, the nickel-based compounds are used to inhibit the vanadium corrosion of metallic materials by a vanadium-contaminated liquid fuel, the combustion taking place in the presence of sodium.

[0074] The expression "in the presence of sodium" is understood to mean that the sodium is present in the liquid fuel and/or in the combustion air. Because of this presence, the combustion gases contain sodium.

[0075] More particularly, according to a preferred method of implementing the invention, this method is applied to combustion in gas turbines. This is because, in a gas turbine, the performance is closely linked to the state of cleanliness of the components of the expansion turbine. In addition, the applicant has found that nickel oxide, which is stable above 650° C., under the SO_3 partial pressure conditions in the combustion gases, is essentially available as a self-cleaning agent in the hottest regions, that is to say precisely at the points where the deposits are the most difficult to remove. These regions are the flame tubes, the transition components and the first expansion stages (essentially the first and second stages).

[0076] Three advantages of the nickel-based inhibitors help substantially to increase the flame temperature of the gas turbines burning vanadium-contaminated liquid fuels. These are:

[0077] the refractory and nonadherent nature of the nickel-based ash particles;

[0078] the low rate of fouling of the turbine components which results therefrom; and

[0079] obviation of the need to form water-soluble sulfate ash.

[0080] As a result, it is possible to apply the process, advantageously, to higher-performance gas turbines of the latest technology, the flame temperatures of which are above 1100° C. and especially from 1100° C. to 1300° C.

[0081] The nickel-based compound may be in the forms defined above, which depend especially on its manner of addition. This takes place using conventional methods described above.

[0082] The liquid fuel may be any type of vanadium-contaminated liquid fuel, and especially those described above.

[0083] According to one particular way of implementing the method of the invention, the method of combustion of vanadium-contaminated liquid fuels also includes a step of leaching the nickel-based ash using an organic reducing acid.

[0084] The chemical leaching of the ash instead of simply washing it with water allows the state of cleanliness of the hot components of the turbine at the end of cleaning to be optimized and thereby the energy performance of the latter during the next operating cycle to be improved.

[0085] In accordance with this embodiment, any nickel-based deposits that might accumulate in the thermal plant, and especially the turbine, for example over long periods of operation without stopping, are removed by means of a solution based on an organic reducing acid.

[0086] The Applicant has established that a particularly suitable organic reducing acid is oxalic acid. Remarkably, this acid dissolves the $Ni_3V_2O_8$, NiO and $CaSO_4$ solids and their mixtures. The dissolution reactions are the following:

$$Ni_3V_2O_8+4H_2C_2O_4+4H^+\rightarrow 3NiC_2O_4\downarrow+2CO_2+2VO^{2+}+6H_2O \quad (1)$$

$$NiO+H_2C_2O_4\rightarrow NiC_2O_4\downarrow+H_2O \quad (2)$$

$$CaSO_4+H_2C_2O_4\rightarrow CaC_2O_4\downarrow+2H^++SO_4^{2-} \quad (3)$$

[0087] Reaction (1) is essential as the orthovanadate constitutes the main phase and requires both the reduction of the vanadium from oxidation state V to oxidation state IV under acid conditions and the formation of an insoluble nickel salt so as to displace the reaction from the left to the right. Oxalic acid combines these properties and also has the advantages of being only slightly corrosive, very soluble in water and of moderate cost.

[0088] Thus, a 0.5M aqueous oxalic acid solution at 80° C., obtained from commercial $H_2C_2O_4.2H_2O$, provides a degree of dissolution of 90% after leaching for three hours.

[0089] The oxalic acid may be used with an additive consisting of an inhibitor for the acid corrosion of carbon steels and cast irons, such as thiourea, benzotriazole or tolyltriazole, so as to protect the ferrous alloys present in the mechanical structures of the turbine.

[0090] A wetting agent, such as a cationic or nonionic surfactant, may also be added to the oxalic acid so as to increase the rate of diffusion of the oxalic acid into the pores of the deposit and the rate of dissolution of the latter.

[0091] Finally, the ability of oxalic acid also to dissolve calcium sulfate is useful when the fuel is contaminated with calcium: petroleum-based fuels may contain calcium in water-soluble form (mineral salts contained in residual water droplets emulsified in the fuel oil) or in oil-soluble form (organic calcium salts dissolved in the fuel oil phase). This is because the combustion of calcium-contaminated fuel oils forms calcium sulfate, which is very insoluble in water, adheres strongly to the hot components of the turbine and is liable to trap therein the other phases of the ash, including those rich in nickel.

[0092] To illustrate the invention, three methods of implementation will be described below:

[0093] First Embodiment

[0094] A heavy fuel oil highly contaminated with vanadium was burnt in a conventional gas turbine called a "second generation" or class "E" gas turbine. Class "E" gas turbine is understood to mean a gas turbine which has a nominal flame temperature of from 1100° C. to 1150° C. The heavy fuel oil used, having a composition typical of those from the South-East Asian market, was a residual from the atmospheric distillation of petroleum, containing 50 ppm vanadium and 30 ppm nickel.

[0095] According to the invention, added to the liquid fuel, so as to inhibit vanadium corrosion, was an aqueous nickel nitrate solution emulsified using a metal-free surfactant and in an amount of 10 wt % nickel, in an organic solvent consisting of a kerosene-type middle distillate of petroleum, miscible with the petroleum-based fuel to be burnt. The nickel nitrate emulsion was injected using a metering pump into the low-pressure part of the liquid fuel circuit, and more specifically upstream of the high-pressure filters. The amount of nickel nitrate emulsion injected was such that the nickel/vanadium ratio was equal to 2.25. This amounted to injecting $(2.25\times50-30)=82.5$ mg of nickel per kg of fuel oil, whereas $3\times50=150$ mg of magnesium had been required using the conventional methods. Abrasive agents, such as coconut shells, were injected periodically into the circuit for the purpose of performing dry-cleaning operations, these being particularly effective with nickel-based ash.

[0096] It was found that the use of nickel as inhibitor according to the invention, applied to the combustion of a heavy fuel oil highly contaminated with vanadium in a class "E" gas turbine, reduced the rate of deposition of ash by a factor of 2.5 compared with the use of magnesium as inhibitor. This represents an increase in mean electrical power of around 6% for the same fuel consumption. In numerical terms, this increase represents about 300,000 dollars (i.e. 2.1 Million FFR in May 2001) for an annual production of 5 Million dollars (i.e. 35 Million FFR in May 2001)—a considerable increase.

[0097] The use of a step for chemically leaching the nickel-based ash optimized the state of cleanliness of the hot components of the turbine at the end of cleaning and, as a result, improved the energy performance of the latter during the next operating cycle.

[0098] Moreover, the thermal plant was made available for a longer time since the period of continuous operation of the turbine between two consecutive washing operations was increased by a factor of more than 2.5. In this way, a cumulative stoppage time of 60 hours over a period of 1000 hours was eliminated, which represents a more than 6% increase in availability.

[0099] Second Embodiment

[0100] A "gas condensate" very slightly contaminated with vanadium was burnt in a gas turbine called a "third generation" or class "F" gas turbine installed, for example, in a maritime region in which the air is contaminated with sodium. The class "F" gas turbine forms part of these new-generation gas turbines mentioned above in the description, these having a flame temperature of 1300° C. or higher. The fuel used corresponds to the fraction, condensable at ambient temperature and pressure, of the production from a natural gas well, after possible stabilization treatments (to lower the vapor pressure by flash distillation) and softening treatments (to remove H_2S). These gas condensates may typically contain from 0.2 to 1.5 ppm vanadium. The sodium concentration is about 2.5 ppm, corresponding to a 0.05 ppm concentration in the air.

[0101] A nickel compound in oil-soluble form, for example nickel carboxylate, containing 8% by weight nickel, was used with the same method of introduction into the turbine as in the previous method of application.

[0102] The Ni dosage/V ratio was 2.25 and the flame temperature of the gas turbine was, for example, 1280° C.

[0103] It should be noted that gas condensates frequently contain small amounts of vanadium which either exceed the permitted specification (for example, 0.5 ppm) for operation of the turbine without having to use a corrosion inhibitor or, if they do not exceed this permitted specification, reduce the lifetime of the active hot components of the machine when an inhibitor is not added. Because of the fact that conventional, especially magnesium-based inhibitors form very hard deposits, not removable by washing, when the turbine is operated with a high flame temperature, which is one of the specific features of class "F" gas turbines, the operation of such a machine would result in irreversible fouling of the blade assemblies. Such fouling would in fact require the machine to be dismantled in order for it to be cleaned manually. In addition, the magnesium orthovanadate starts to melt at 1100° C. and corrosion protection would therefore be thrown into doubt. These major drawbacks are eliminated when, according to the invention, a nickel-based inhibitor is used which also protects gas turbines from the deleterious effects of possible incursions of sodium present in the air. The flame temperature can be adjusted to a value of less than or equal to 1300° C.

[0104] Third Embodiment

[0105] A similar result is obtained if a heavy petroleum distillate is used as fuel. This type of fuel, which is slightly contaminated, also typically contains from 1 to 1.5 ppm vanadium. Moreover, such fuel oils contain appreciable amounts of sodium salts dissolved in water droplets present in the fuel oil. The sodium concentration is typically from 1 to 1.5 ppm in such heavy petroleum distillates.

[0106] The use of nickel as inhibitor thus makes it possible for class "F" gas turbines using a heavy distillate to be effectively protected against vanadium corrosion, the use of which fuel would hitherto have been regarded as risky in class "F" turbines.

1. Use of nickel-based compounds to inhibit the vanadium corrosion of metallic materials, characterized in that the mass ratio of nickel to contaminating vanadium is greater than or equal to 1.74.

2. Use according to claim 1, characterized in that the mass ratio of nickel to contaminating vanadium is from 1.9 to 2.5.

3. Use according to claim 1 or **2**, characterized in that the mass ratio of nickel to contaminating vanadium is equal to 2.25.

4. Use according to any one of claims 1 to 3, in order to inhibit type I corrosion of metallic materials.

5. Use according to any one of claims 1 to 3, in order to inhibit type II corrosion of metallic materials.

6. Use according to any one of claims 1 to 3, in order to inhibit the vanadium corrosion of metallic materials during combustion at temperatures above 1100° C.

7. Use according to claim 6, characterized in that the combustion temperature is from 1100° C. to 1300° C.

8. Use according to any one of claims 1 to 7, in order to inhibit the vanadium corrosion of metallic materials by a vanadium-contaminated liquid fuel in the presence of sodium.

9. Use according to any one of claims 1 to 8, characterized in that the nickel-based compound is in an oil-soluble or water-soluble form, in the form of a water-in-oil or oil-in-water emulsion or microemulsion, or in the form of an aqueous or organic suspension.

10. Use according to any one of claims 1 to 9, characterized in that the nickel-based compound is combined, in the form of a mixture in any proportion, with at least one other metal chosen preferably from chromium, silicon, aluminum, magnesium, iron, manganese, zinc and cerium.

11. Use according to any one of claims 1 to 10, characterized in that the liquid fuel is a fuel containing nickel as an appreciable metallic contaminant.

12. Method of combustion of a vanadium-contaminated liquid fuel, characterized in that it comprises a step of introducing at least one nickel-based compound, the mass ratio of nickel to contaminating vanadium being greater than or equal to 1.74.

13. Method of combustion of a vanadium-contaminated liquid fuel according to claim 12, characterized in that the mass ratio of nickel to contaminating vanadium is from 1.9 to 2.5.

14. Method of combustion of a vanadium-contaminated liquid fuel according to claim 12 or **13**, characterized in that the mass ratio of nickel to contaminating vanadium is equal to 2.25.

15. Method of combustion of a vanadium-contaminated liquid fuel according to any one of claims 12 to 14, characterized in that the combustion takes place in the presence of sodium.

16. Method of combustion of a vanadium-contaminated liquid fuel according to any one of claims 12 to 15, characterized in that the thermal plant is a gas turbine, and preferably a gas turbine having a flame temperature above 1100° C.

17. Method of combustion of a vanadium-contaminated liquid fuel according to claim 16, characterized in that the flame temperature is from 1100° C. to 1300° C.

18. Method of combustion of a vanadium-contaminated liquid fuel according to any one of claims 12 to 17, characterized in that it comprises a step of leaching the nickel-based ash using an organic reducing acid.

19. Method of combustion of a vanadium-contaminated liquid fuel according to claim 18, characterized in that it includes a step of leaching the nickel-based ash using oxalic acid.

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