

# Drawbacks Treatment Associated with use of Conventional Corrosion Inhibitors Especially in Combustion of Vanadium-Contaminated Liquid Fuels using Nickel Compounds

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## Abstract

A new process where used for the treatment of drawbacks resulting from using conventional corrosion inhibitors in thermal equipment (such as Boilers, Diesels and Turbine engines) that burning vanadium-contaminated fuels. Nickelous compounds were used in this work as a base material for the manufacture of these corrosive inhibitors. Nickel hydroxide salt was used in this new work as a suspension in an aqueous solution or an organic solvent with respect to the treated fuel. The results show that this salt is a good choice used as anticorrosion agent in high temperatures equipment that use burning fuels contaminated with Vanadium. The new anticorrosion agent must contain (8 - 10) % by weight of Nickel metal and (Ni:V) active weight ratio is (2.25: 1).

**Keywords:** Drawbacks treatment, Vanadium-contaminated, inhibitor, high temperature corrosion, molten electrolytes

## 1-Introduction:

Ash fouling and flame-side corrosion of metal surface, together with heat transfer surface fouling are major problems in power generation stations when burning heavy oils. Vanadium occurs in the form of porphyrinic and non-porphyrinic in crude oils [1]. These compounds decompose in gas stream to give mainly vanadium pentoxide ( $V_2O_5$ ), which is considered to be the most damaging agent due to its low melting point ( $690^\circ C$ ) i.e. it is in liquid state at normal combustion temperature. Sodium in the oil is mainly present as (NaCl) and is readily vaporized during the combustion process [2]. The presence of a liquid phase on the surface of a metal is usually necessary for corrosion reactions to occur at high rates. The most likely liquid phases are based on vanadium pentoxide and sodium sulphate complexes depending upon the exact analysis of the fuel used [3]. A series of compounds are formed between ( $Na_2O$ ) and ( $V_2O_5$ ), some of which have melting points below the operating temperatures of boilers and turbines. The eutectic formed between ( $5Na_2O.V_2O_4.11V_2O_5$ ) and sodium metavanadate ( $Na_2O.V_2O_5$ ) melts at ( $527^\circ C$ ). However, under an atmosphere containing oxides of sulphur, other components can form e.g.  $Na_2SO_4$ ,  $Na_2S_2O_7$ ,  $V_2O_5.2SO_3$  and  $V_2O_5.1/2 SO_3$  [4].

Prevention of hot corrosion is impossible and a reduction can be effectively performed. In contaminated combustion atmospheres, there are three basic ways to reduce the hot ash corrosion problems [5]:

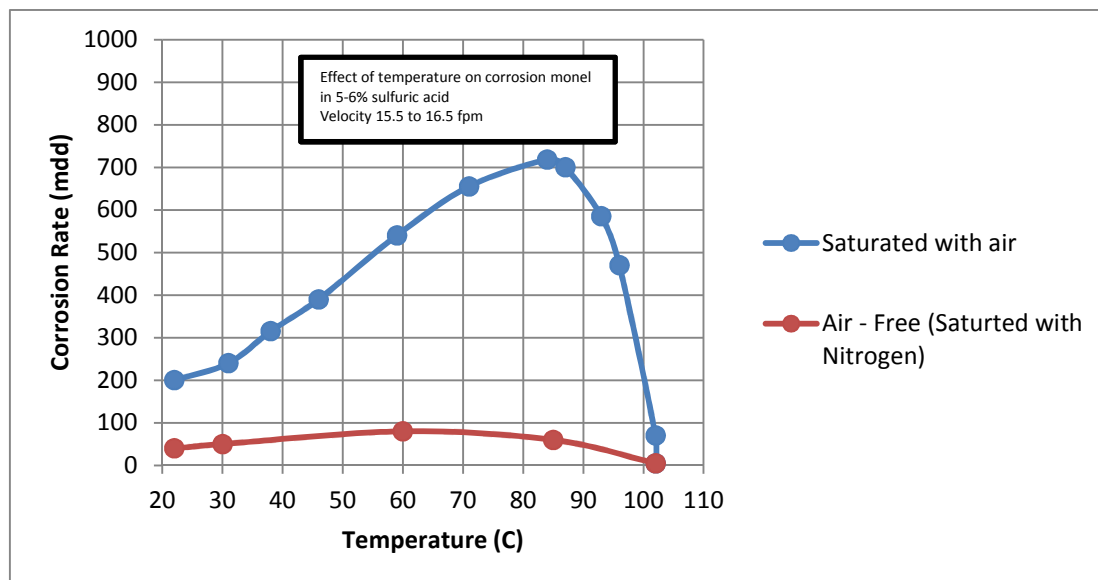
1-Removal of harmful impurities presents in environment.

2-Addition of a compound to counteract the harmful impurities.

3-Changing combustion conditions (fuel treatment and control of burning) to minimize attack.

In general, corrosion increases with temperature. A passive metal may become "active" at a higher temperature, blistering or hydrogen embrittlement increases with temperature. The change in corrosion rate of monel metal in sulfuric acid with change in temperature is shown in Figure.1 below [6].

Fuel oils primarily consist of residues from distillation of crude oil in petroleum refinery. Sulfur content in residual fuel oils can vary from a fraction of a percent for lighter oils to (3-5) for some residual oils.. Two other corrosive constituents in fuel oils are vanadium and sodium, vanadium exists in crude oils as an oil-soluble co



**Figure (1): The effect of temperature on corrosion of monel in (5-6) % Sulfuric Acid**

Fuel oils primarily consist of residues from distillation of crude oil in petroleum refinery. Sulfur content in residual fuel oils can vary from a fraction of a percent for lighter oils to (3-5) for some residual oils.. Two other corrosive constituents in fuel oils are vanadium and sodium, vanadium exists in crude oils as an oil-soluble complex. Middle Eastern crudes contain high levels of vanadium with up to several hundred part per million (ppm). Sodium can originate from crudes, the neutralizer used in crude distillation during the refining process, and contamination with sea water in transportation and storage.

During combustion, compounds formed by these three constituents make up a major part of the ash that deposit on metallic components such as, superheater and preheater tubes in boilers, gas turbine and petrochemical furnaces. When the metal temperature of component reaches (540)°C or higher, compounds in the ash may become molten and corrosion attack can become severe [7]. During combustion of fuel oils that contain vanadium, sulfur and sodium, low melting compounds are mixtures of V<sub>2</sub>O<sub>5</sub>, Na<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>O. Table (1) below lists a number of oil-ash constituents and their melting points.

**Table-1 Melting Points of some Ash Constituents.**

Compound	Melting Point , °C
Nickel Oxide	2090
Nickel Sulfate	1545 to NiO
Sodium Sulfate	880
Vanadium Pentoxide	675
Sodium Metavanadate	630
Nickel Orthovanadate	> 900
Sodium Vanadic Vanadate	625

It is clear from table (1) that the melting point of ash salt deposit can vary widely, depending on composition [8]. The combustion of contaminated fuels using magnesium as inhibitor in gas turbines results in the flame temperature being limited to around (1100) °C. The metallic materials of most thermal power plants are subjected to the following two main types of corrosion mechanisms:

Type1 corrosion, which is high temperature corrosion typically occurs at temperatures between(800° and 900)°C. Type 2 corrosion, or low temperature corrosion, which typically occurs at temperatures between (550°and750) °C.

In most thermal plants, both types of corrosion risk exist, type 1 corrosion is the etching in a hot oxidizing medium of the metal by molten electrolytes, such as those rich in vanadium pentoxide, where type 2 corrosion is associated. with the formation of eutectics comprising sodium sulphate and another metal ( for example vanadium or cobalt) Sodium sulphate results from the reaction between sodium contained in combustion air and the sulphure derivatives present in fuel oil, so to resist vanadium corrosion in thermal plant it is essential to control both corrosion mechanisms [9].

Corrosion is described as a hot corrosion in a sulfidation processes, hot corrosion is an accelerated oxidation of alloys caused by the deposition of Na<sub>2</sub>SO<sub>4</sub>. Oxidation results from the ingestion of salts in the engine and sulfur from the combustion of fuel. Sulfidation corrosion is considered as the form of hot corrosion in

which the residue that contains alkaline sulfates.

Corrosion causes deterioration of blade materials and reduces component life. Hot corrosion is a rapid form of attack that is generally associated with alkali metal contaminants, such as sodium and potassium, reacting with sulfur in the fuel to form molten sulfates. The presence of only a few parts per million (ppm) of such contaminants in the fuel, or the equivalent in the air, is sufficient to cause this corrosion. Sodium can be introduced in a number of ways, such as salt water in liquid fuel, through the turbine air inlet at sites near salt water or other contaminated areas, or as contaminants in water/steam injections. Besides the alkali metals such as sodium and potassium, other chemical elements can influence or cause corrosion on bucketing. Notable in this connection is vanadium, primarily found in crude and residual oils.

There are now two distinct forms of hot corrosion recognized by the industry, although the end result is the same. These two types are high-temperature (Type 1) and low-temperature (Type 2) hot corrosion. High-temperature hot corrosion has been known since the 1950s. It is an extremely rapid form of oxidation that takes place at temperatures between 1500 °F/816 °C and 1700 °F/927 °C in the presence of sodium sulfate ( $\text{Na}_2\text{SO}_4$ ). Sodium sulfate is generated in combustion processes as a result of the reaction between sodium, sulfur, and oxygen. Sulfur is present as a natural contaminant in the fuel. Low-temperature hot corrosion was recognized as a separate mechanism of corrosion attack in the mid-1970s. This attack can be very aggressive if the conditions are right. It takes place at temperatures from 1100 °F (593 °C) to 1400 °F (760 °C) and requires a significant partial pressure of  $\text{SO}_2$ . It is caused by low melting eutectic compounds resulting from combination of sodium sulfate and some of the alloy constituents such as nickel and cobalt. It is, in fact, somewhat analogous to the type of corrosion called Fireside Corrosion in coal-fired boilers. The two types of hot corrosion cause different types of attack. High temperature corrosion features inter granular attack, sulfide particles, and a denuded zone of base metal. Metal oxidation occurs when oxygen atoms combine with metal atoms to form oxide scales. The higher the temperature, the more rapidly this process takes place, creating the potential for failure of the component if too much of the substrate material is consumed in the formation of these oxides. Low-temperature corrosion characteristically shows no denuded zone; no inter granular attack, and a layered type of corrosion scale. The lines of defense against both types of corrosion are similar. First, reduce the contaminants. Second, use materials that are as corrosion-resistant as possible. Third, apply coatings to improve the corrosion resistance of the bucket alloy [10].

## 2-Experimental Work:

The Nickel-based compounds in this new process used to inhibit the vanadium corrosion of metallic materials during to combustion of a vanadium-contaminated liquid fuel at temperatures above 1100° C, preferably, the combustion temperature is from 1100° to 1300° C. The aim of this new process is therefore is 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 1.25. According to a preferred use of the process, the metallic materials of gas turbines are protected from vanadium corrosion. The applicant has in fact established that certain chemical compounds of nickel combine and stoichiometry conditions, nickel orthovanadate with the vanadium contained in the fuels to form, under appropriate temperature. Nickel orthovanadate is a refractory and non-corrosive compound which is capable of inhibiting the high temperature vanadium corrosion of metallic materials. The vanadium corrosion protection afforded by these nickel-based inhibitors is very effective because not only nickel orthovanadate thermally stable, but it is also chemically inert within temperature range prevailing at the surface of the components of the equipment to be protected, even in the presence of sodium sulfate.

The vanadium corrosion protection given by the nickel-based inhibitors is therefore better than that given 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, a Ni/V mass ratio of 2.25:1 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. 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, 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 modern technology. On the other hand, excess nickel results in the formation of refractory and noncorrosive nickel oxide which acts as a self-cleaning agent for the thermal plant. 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.

The Nickel salt used in this process was Nickel Nitrate from ( Riedel-de Haen Company) have specifications as mentioned in Table (2) below :

**Table- 2 Specifications of Nickel salt used in the process.**

Property Description	Specifications	Units
Nickel Nitrate Hexahydrate, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	97	%
Co	0.01	%
Cu	0.002	%
Fe	0.005	%
Cl	0.003	%
$\text{SO}_4$	0.01	%
Pb	0.001	%
Zn	0.05	%

Potassium hydroxide used in this process from (Riedel-de Haen Company) has specifications as mentioned in Table (3)below:

**Table-3 Specifications of Potassium Hydroxide used in the process.**

Property Description	Specifications	Units
Potassium Hydroxide (KOH)	85	%
$\text{K}_2\text{CO}_3$	2	%
Al	0.001	%
Fe	0.001	%
As	0.0004	%
Na	0.5	%
Ca	0.002	%
heavy metals ( as Pb )	0.0005	%
Chloride ( Cl )	0.001	%
Phosphate ( $\text{PO}_4$ )	0.001	%
Sulfate ( $\text{SO}_4$ )	0.002	%
Silicate ( $\text{SiO}_2$ )	0.01	%
Total N	0.0005	%

The nickel compound is used in this process as a suspension in an aqueous solution or an organic solvent compatible with the fuel to be treated.

### 2.1- Preparation of Nickel compound inhibitor:

About 145 grams of nickel nitrate hexahydrate (Figure.2) were dissolved in 100 milliliters of freshly boiled distilled water. This solution was added dropwise with vigorous stirring to a solution containing about 100 grams of potassium hydroxide (Figure.3) in 100 milliliters of distilled water. The precipitate produced by chemical reaction was separated from most of the liquid by centrifuging, then dried at  $60^\circ\text{C}$ , the prepared product is the nickel compound inhibitor .



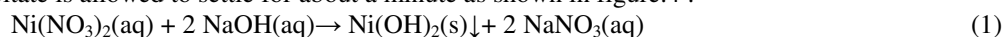
**Fig.2: Nickel Nitrate Hexahydrate,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$**



**Fig.3 Potassium Hydroxide, ( KOH )**

### 2.2- Mechanism of Chemical reactions:

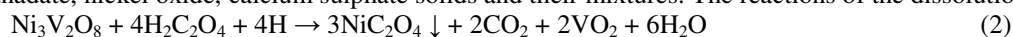
Adding colorless sodium hydroxide to green nickel(II) nitrate produces a light green precipitate. Approximately 2 ml of (0.5M) sodium hydroxide (colorless) solution is added to (0.2M)nickel (II) nitrate (green) with a dropping pipette. The mixture is then stirred with a glass stirring rod and the(light green) precipitate is allowed to settle for about a minute as shown in figure.4 :

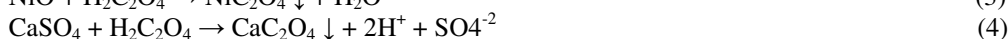


**Fig.4: Nickelous Hydroxide, Ni (OH)<sub>2</sub>**

The use of nickel compound inhibitors allows particularly economic combustion of these naturally nickel-containing fuels. This is because the amount of nickel inhibitor to be added is then equal to difference between the concentration corresponding to intended nickel/vanadium ratio and natural concentration of nickel in the fuel .The chemical leaching of the deposits 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.

According to this inclusion, any deposits that might accumulate in the thermal plant, over long periods of operation without stopping, are removed by a solution of ethanedioic acid (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>). This acid dissolves the nickel vanadate, nickel oxide, calcium sulphate solids and their mixtures. The reactions of the dissolution are:





### 3- Results and Discussion:

#### 3.1- Effect of Vanadium Slag:

The vanadium slag highly accelerated oxidation/hot corrosion of the alloys and most of the weight gain occurred within the high temperature regions many sodium-vanadium bronzes such as  $\text{NaVO}_3$ ,  $\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_5$ ,  $\text{Na}_2\text{O} \cdot 3\text{V}_2\text{O}_5$ ,  $\text{Na}_2\text{O} \cdot 6\text{V}_2\text{O}_5$  and  $\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_4 \cdot 5\text{V}_2\text{O}_5$  are formed. These compounds catastrophically oxidize the alloy components acting as oxygen carriers, metal oxide distorts, or dissolving agents of the protective oxide layer. The scale formed after the thermal treatment is sticky. This is the most important aggressive species in the (Na-V-O) system which became appreciable after the melting of the eutectic mixture ( $\text{Na}_2\text{SO}_4 - \text{V}_2\text{O}_5$ ) and increase with temperature. Therefore ( $\text{Na}_2\text{SO}_4$ ), which has no individual aggressive behavior towards the metal, facilitates the low temperature melting of the ash and initiates the formation of sodium vanadate, which attacks the metal surfaces.

#### 3.2- Effect of Nickelous Hydroxide Addition:

The mass ratio (2.25: 1) was very effective against high temperature corrosion due to the vanadium slag. These results show that the Nickelous Hydroxide was sufficiently effective against high temperature corrosion. According to the new process it was found the use of nickel compound as inhibitor in an amount of 8 to 10 wt. % Nickel as metal content. 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. Moreover, the thermal plant was made available for a longer time since the period of continuous operation of the turbine between two sequent washing operations was increased by a factor of more than 2.5.

### 4- Conclusion

Nickelous hydroxide is used in this new work as a suspension in an aqueous solution or an organic solvent compatible with the fuel to be treated. This salt is proved to be a good suggestion as a hot corrosion inhibitor for Boilers and Gas turbines in power generation stations. The Nickel compound is produced from the reaction mixture of Nickel salt and water soluble alkali metal hydroxide. The inhibitor is used in an amount of (8 to 10) wt. % Nickel. The mass ratio of Nickel to Vanadium (2.25: 1) was very effective against high temperature corrosion.

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