



Oxidation studies on 209 T1 and 213 T11 alloys with Inhibition Corrosion By Using MgO

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Abstract

Hot ash corrosion of high temperature combustion equipment from burning petroleum fuels containing Na, S and V, and recommendations for preventing or controlling fuel oil may result in severe damage to metal surfaces. The use of MgO as a fuel additive to combat vanadic corrosion is widely accepted practice for boilers operating on residual or low grade fuels. MgO has the ability to form high melting stable vanadate but the presence of Na₂SO₄ can react with the magnesium and reduce its effectiveness. This paper aims to quantify the effectiveness of MgO as an inhibitor in the presence of increasing amounts of Na₂SO₄. A method of determining permissible levels of Na₂SO₄ to satisfy predict remind corrosion rates or additive efficiencies is described. Examples of the loss of additive efficiency with weight of Na₂SO₄ at temperature of 750 and 850°C are given for both 209 T1 and 213 T11 alloys.

Key-words : Furnace, MgO, Na₂SO₄, V₂O₅, balance

Introduction

The relatively high content of vanadium, sodium and sulfur of heavy fuel oils leads to the formation of a mineral ash composed of sodium sulfate and vanadium pentoxide during ignition-Boilers burning low-grade or residual fuel oils suffer high temperature corrosion problems which can be directly attributed to the presence of fuel impurity combustion products [1,2]. The principal impurities associated with residual fuel oils are based on vanadium, sodium and sulphur and give rise to combustion products which may be present in their molten form on the outer surfaces of pipes boilers or in the atmosphere around them, this induced hot corrosion [3].

Hot corrosion occurs when metals are heated in the temperature range (700-800 c) in the presence of deposits for med as a result reaction between sodium chloride and sulphur compounds in the gas phase surrounding the metals [4]. Hot corrosion is basically attack by fuel and /or ash compounds of Na ,v , s and C / that are present in the coal or in fuel oil (heavy fuel oil) used for combustion , in the mentioned application [5,6]

Various means were employed to prevent such corrosion, which is known as the hot ash corrosion. These include the use of highly resistant alloys [7] and the use of corrosion preventive additives to fuel oil. The first method needs high investment, whereas fuel additives receive much greater attention among engineers and scientists. Magnesium is the most important constituent of these additives [8]. Magnesium inhibits the formation of the low melting sodium vanadyl vanadate sulfate by forming magnesium vanadates melting at temperature higher than 1000°C [9]. Magnesium oxide is an excellent candidate to perform this job, but it is an insoluble and rather non-miscible solid with the fuel oil. The miscibility requires extremely fine particles to ensure even dispersion and hence better reaction with fuel mineral constituents [8,10].

The corrosion of boilers pipes alloys can be markedly reduced by using MgO in such that a molecular ratio of 3 MgO: 1 V₂O₅ is maintained in the deposit on the alloy surface. When the ratio MgO: V₂O₅ was less than 3 : 1 the reaction products contained Mg₃V₂O₈ and excess V₂O₅, whilst when the ratio exceeded 3:1, excess MgO was formed in the reaction products. However, the MgO-V₂O₅ system is also affected by the presence of Na₂SO₄ from sulphur and sodium contamination in the fuel [10,11].

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The aim of the present work is to study the preparation of several magnesium containing additives and their application with synthetic mineral ash on steel pieces of the same type used in the pipes and structures of the Power Generation Stations.

Control of High Temperature Corrosion

There are three basic ways in which the environmental conditions can be modified to reduce high temperature problems and these are:

I. Fuel Treatment

Washed crude oils and residual-grade fuel oils containing, vanadium, lead, nickel, sodium, potassium etc. . In these applications the fuel has been purified through a centrifugal or electrostatic treatment plant to reduce water-soluble sodium and potassium contaminants to an acceptably low level (typically 0.5 or 1.0 ppm Na + K max.). [12].

II. Fuel Additives

The remaining ash-causing are in organic forms, principally vanadium, nickel, zinc and other trace metals. The corrosive effect of these elements can be neutralized by chemical additives. Fuel additives are organo metallic compounds containing Mg, Al, Si, Cr elements in the form of sulphonate or carboxylate. The concentration of active ingredient is 2-15% w/w. Fuel treatment is the removal of at least the water soluble species by washing the fuel. [7,13].

The function of magnesium is to form magnesium vanadate compounds of melting point higher than 1100°C during combustion, instead of the low melting point, sodium vanadate. The dose of magnesium is determined by the level of vanadium with respect to sodium in the oil. For example in case of Na/ V ratio of 0.1, Mg/V ratio is 3/1 [8,10].

III Protective Coatings

Requirements for superalloys for boilers have been stated as follows:-

- I. resist thermal cyclic oxidation.
- II. resist hot corrosion.
- III. resist thermal fatigue cracking, and
- IV. resist particulate erosion.

All current coatings are based on the use of aluminum as the primary constituent. The processes used are:

- A. Pack cementation.
- B. Hot dipping.
- C. Plasma spraying.
- D. Cladding , and
- E. Physical vapour deposition (PVD).[3].

Experimental Methods

To demonstrate the effects under investigation, two typical alloys were chosen. 209T1 and 213T11 , table (1, 2), were taken from South Baghdad Power Station (boilers pipes). Specimens were cut from this pipes in to rectangular pieces (5 * 15 * 25 mm) (thickness * width * length). The surfaces of each sample were polished flat to 1000µm finish using SiC. Each specimens was then coated with V₂O₅+ Na₂SO₄ or V₂O₅ +



$\text{Na}_2\text{SO}_4 + 3\text{MgO}$, using the following method: a suspension of $\text{V}_2\text{O}_5 + \text{Na}_2\text{SO}_4$ or $\text{V}_2\text{O}_5 + \text{Na}_2\text{SO}_4 + 3\text{MgO}$ in acetone was sprayed onto preheated (80-90°C) alloy specimens. At this temperature the acetone evaporated, leaving of the desired contaminant on the alloy surface.

Exposure tests were carried out in the tube furnace, samples, either coated or uncoated, were positioned in the hot zone of a furnace preheated to the required test temperature and exposed for 16 hours duration to the required test environment. The samples were exposed in air environment at a flow rate $10\text{cm}^3 \text{min}^{-1}$ for the test duration.

Table (1): Chemical Analysis of (209T1) Alloy

Component	C	Mn	P	S	Si	Mo	Cr	Fe
Wt.%	0.15	0.5	0.025	0.035	0.25	0.35	0.080	Rem.

Table (1): Chemical Analysis of (213T1) Alloy

Component	C	Mn	P	S	Si	Mo	Cr	Fe
Wt.%	0.1	0.4	0.025	0.025	0.7	0.55	1.5	Rem.

Results and Discussion

A. Effect of contaminants and Inhibitor

The effects of various levels of V_2O_5 and $\text{V}_2\text{O}_5 + 3\text{MgO}$ upon the high temperature oxidation of 209T1 and 213 T11 in the absence and presence of Na_2SO_4 contamination, are shown graphically in Figs. (1-6) as plots of corrosion loss (g cm^{-2}) at (16h) vs. the amount of surface V_2O_5 (mg cm^{-2}) in various environments.

From the results in Figs. (1-6) the following points are evident;

- (i) The presence of V_2O_5 on the surface of both 209 T1 and 213 T11 at 750°C and 850°C has resulted in enhanced high temperature oxidation which increases with both temperature and the amount of V_2O_5 .
- (ii) 209 T1 appears to be less resistance than 213 T11 towards V_2O_5 accelerated high temperature oxidation,
- (iii) The addition of MgO to the V_2O_5 deposit (molecular ratio $3\text{MgO}:1\text{V}_2\text{O}_5$) on both 209 T1 and 213T11 at 750°C and 850°C has resulted in a marked reduction in measured corrosion over the (16h) test period. This behaviour is evident for all tested levels of V_2O_5 when a molecular ratio of $3\text{MgO}:1\text{V}_2\text{O}_5$ is maintained on the alloy surface,
- (iv) The presence of Na_2SO_4 contamination in the test atmosphere above the system [Alloy + $\text{V}_2\text{O}_5 + 3\text{MgO}$ (209 T1 and 213 T11)] results in a marked reduction in the effectiveness with which MgO inhibits V_2O_5 corrosion and hence an increase in the measured corrosion,
- (v) The measured corrosion rises with increasing Na_2SO_4 contamination. In fact, at the highest concentration Na_2SO_4 the corrosion is worse on the system Alloy+MgO + $\text{V}_2\text{O}_5 + \text{Na}_2\text{SO}_4$ than if no MgO or Na_2SO_4 is present, i.e. Alloy+ V_2O_5 +air,

From Figs. (1-6) it is evident that the additions of MgO to a V_2O_5 deposit, using a molecular ratio of $3\text{MgO}:1\text{V}_2\text{O}_5$, provides a viable method of reducing vanadic corrosion. It can be seen from the above that corrosion control in low grade or residual fuel oils depends upon the formation of solid vanadium containing compounds and the formation of these compounds is modified by the presence of Na_2SO_4 . The presence of V_2O_5 on both alloys which affords little protection to the underlying metal. The attack front is approximately uniform with scale are porous. The addition of 3MgO to the V_2O_5 gives slightly porous but coherent protective

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surface oxide which is thicker than that obtained in air with no V_2O_5 contamination. However, when Na_2SO_4 is also present (i.e. the system $V_2O_5 + MgO + Na_2SO_4 + Air$) the corrosive attack does give internal attack down grain boundaries and the outer scale is a typical vanadic corrosion scale.

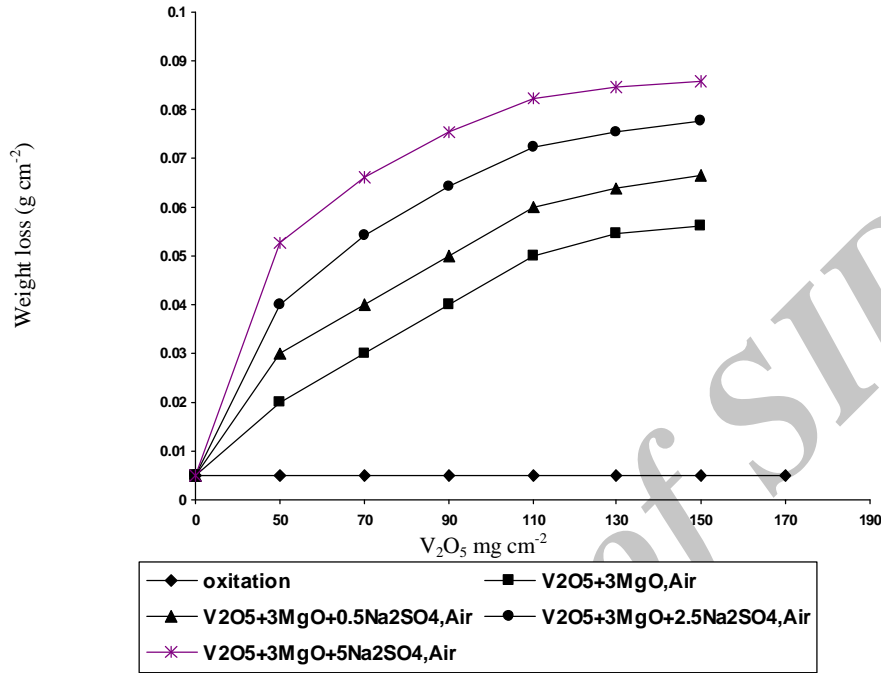


Fig.(1): Effect of contaminates and inhibitor on the high temperature corrosion of 209 T1 at 750 °C (16h).

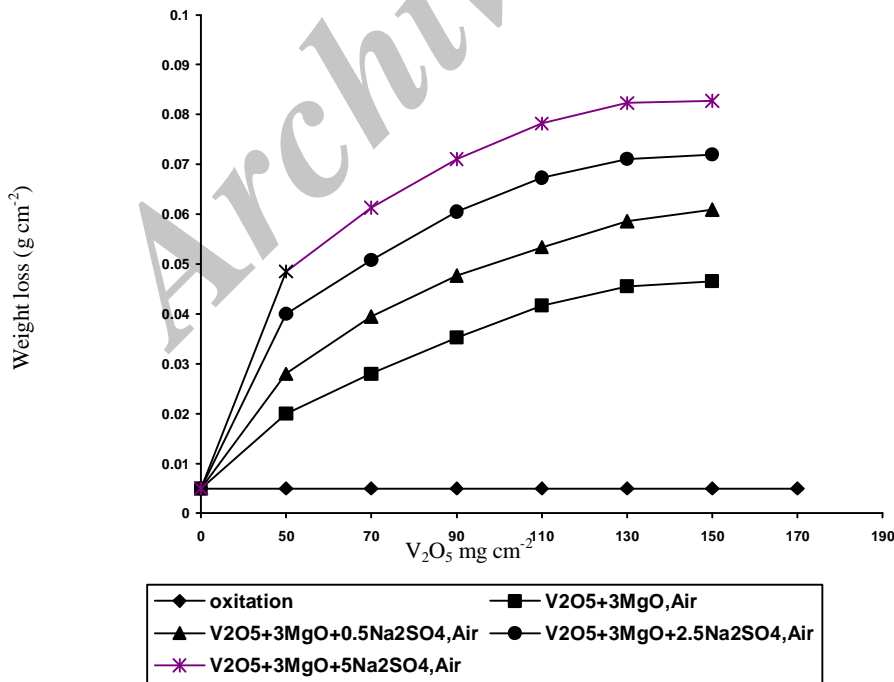


Fig.(2): Effect of contaminates and inhibitor on the high temperature corrosion of 209 T1 at 850 °C (16h).

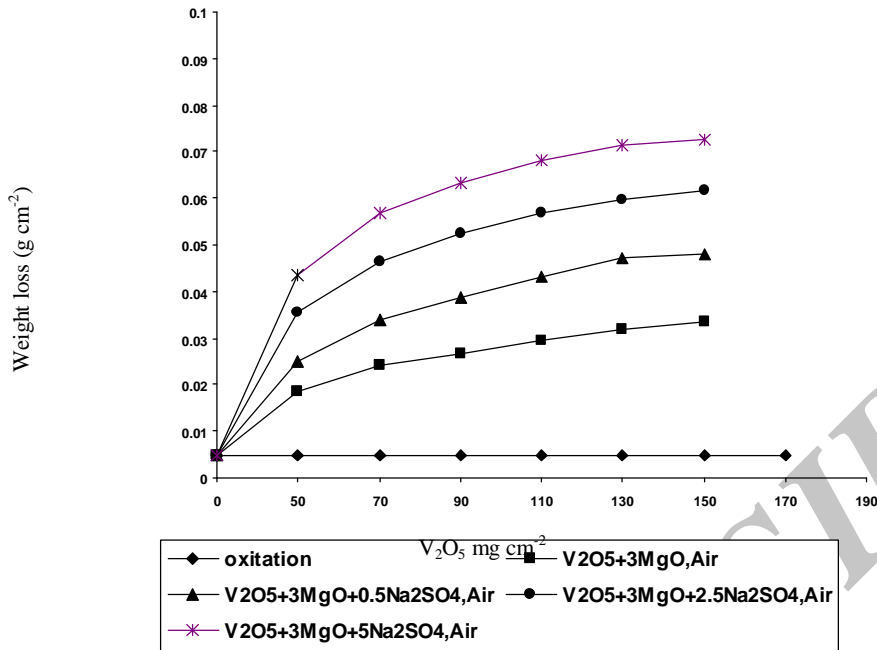


Fig.(3): Effect of contaminates and inhibitor on the high temperature corrosion of 213 T11 at 750 °C (16h).

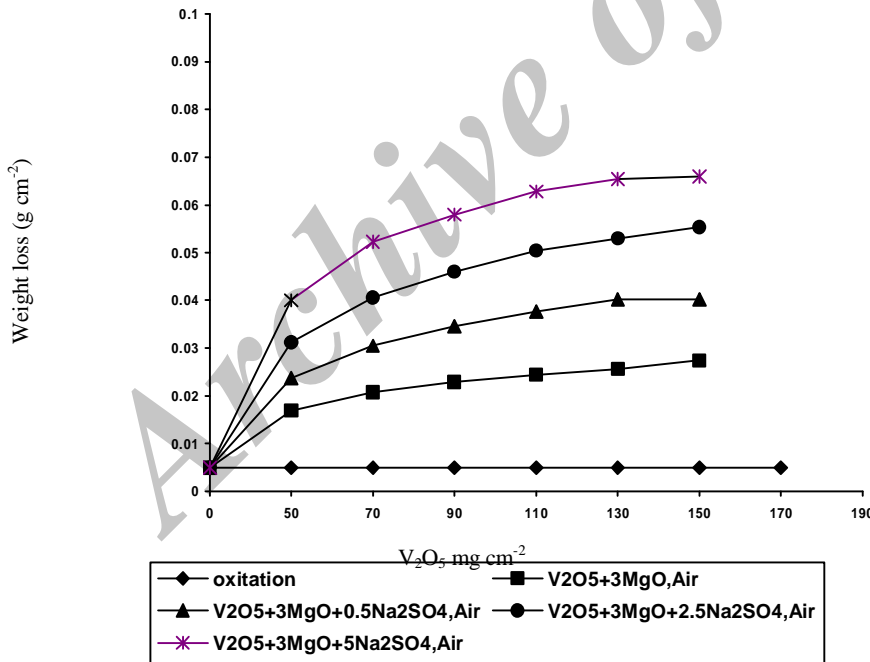


Fig.(4): Effect of contaminates and inhibitor on the high temperature corrosion of 213 T11 at 850 °C (16h).

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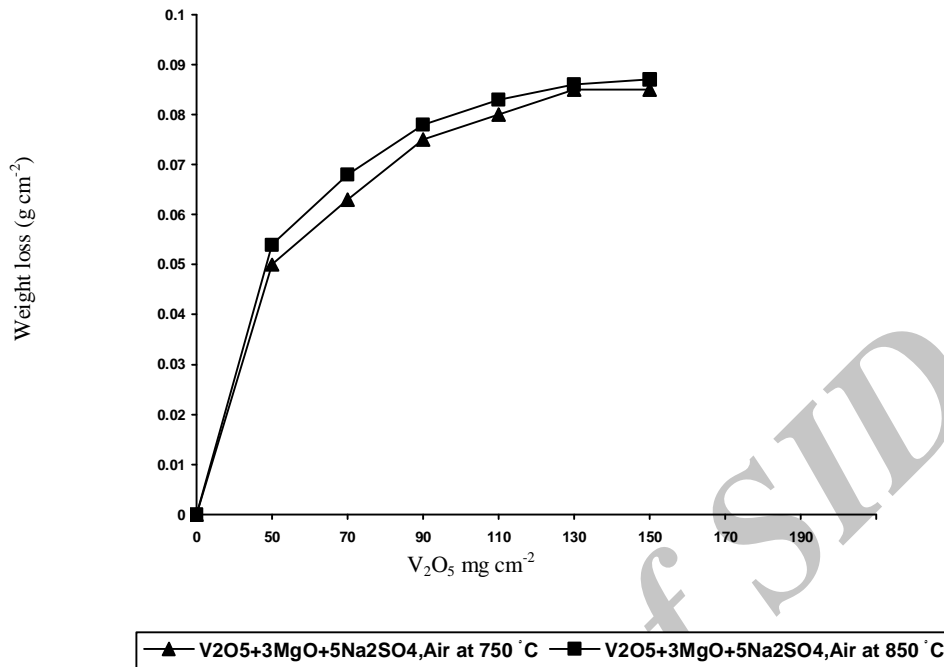


Fig.(5): Effect of contaminates and inhibitor on the high temperature corrosion of 209 T1 at 750 and 850 °C (16h).

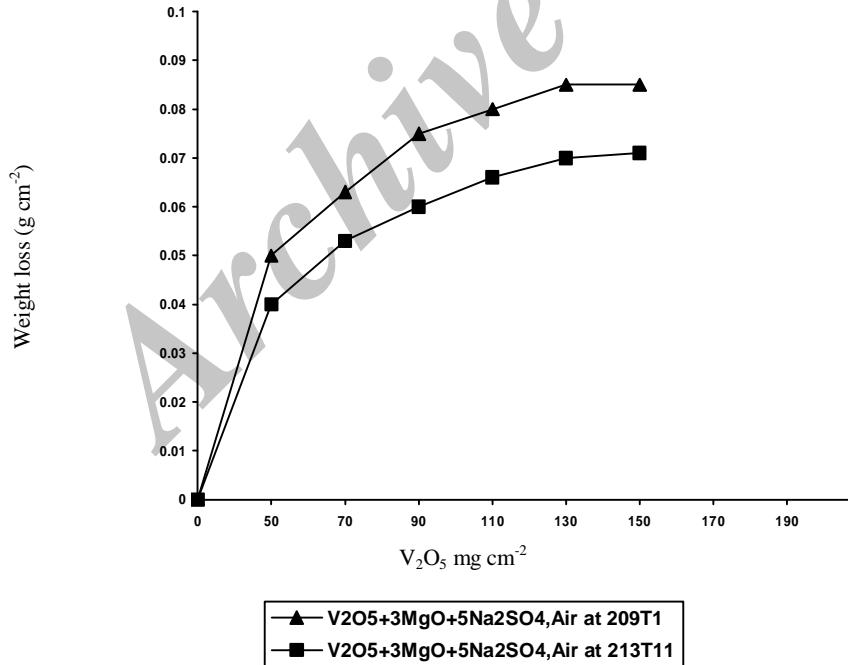


Fig.(6): Effect of contaminates and inhibitor on the high temperature corrosion of 209T1 and 213T11 at 750°C (16h).

B. The Inhibition Efficiency

To express the effectiveness with which MgO inhibits vanadic corrosion a term "inhibitor efficiency" may be evaluated as follows:



$$\text{Inhibition Efficiency [I]} = \frac{w_1 - w_2}{w_1} \times 100$$

Where: w_1 = weight loss in the system Alloy+V₂O₅, Air.

w_2 = weight loss in the system Alloy+V₂O₅+3MgO, Air.

From Figs.(7-10) it is evident that for both 209T1 and 213T11 at 750 and 850°C the measured corrosion in MgO treated system is higher than that obtained for air oxidation and so the inhibitor is not 100% efficient.

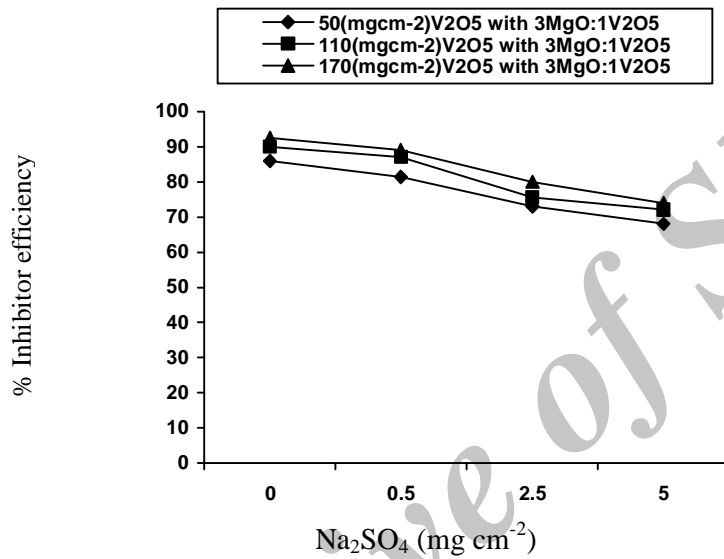


Fig. (7): Inhibitor efficiency Vs. Na₂SO₄ for the system 209 T1 (MgO+V₂O₅+Na₂SO₄, Air) at 750°C

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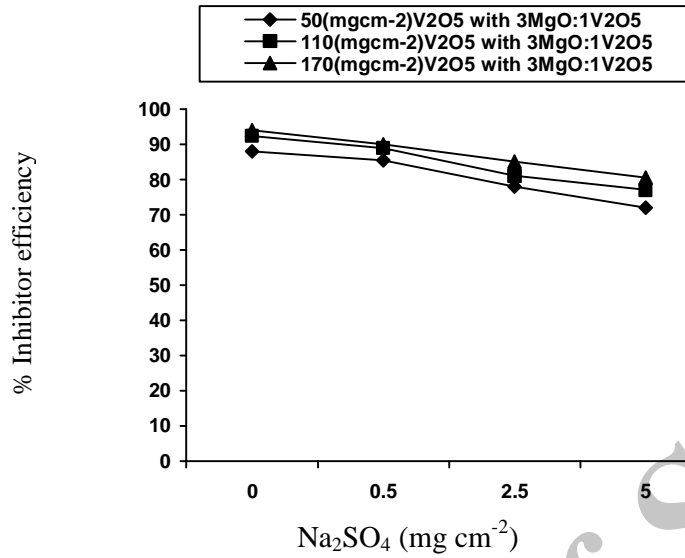


Fig. (8): Inhibitor efficiency Vs. Na₂SO₄ for the system 209 T1 (MgO+V₂O₅+Na₂SO₄, Air) at 850°C

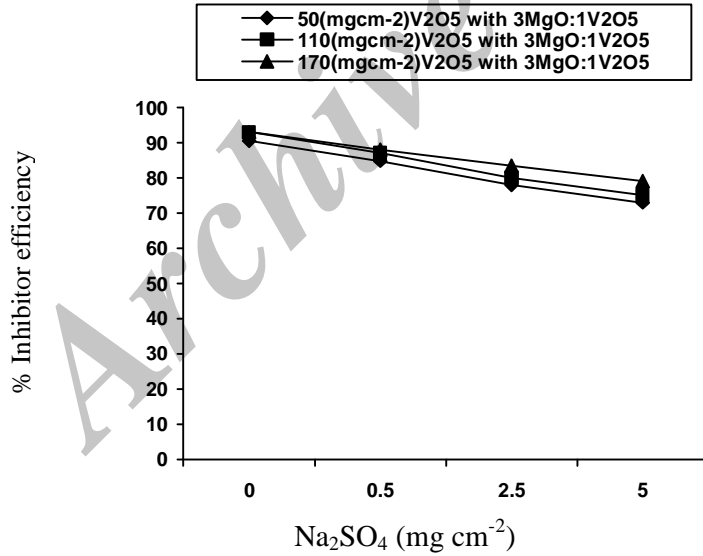


Fig. (9): Inhibitor efficiency Vs. Na₂SO₄ for the system 213T11 (MgO+V₂O₅+Na₂SO₄, Air) at 750°C.

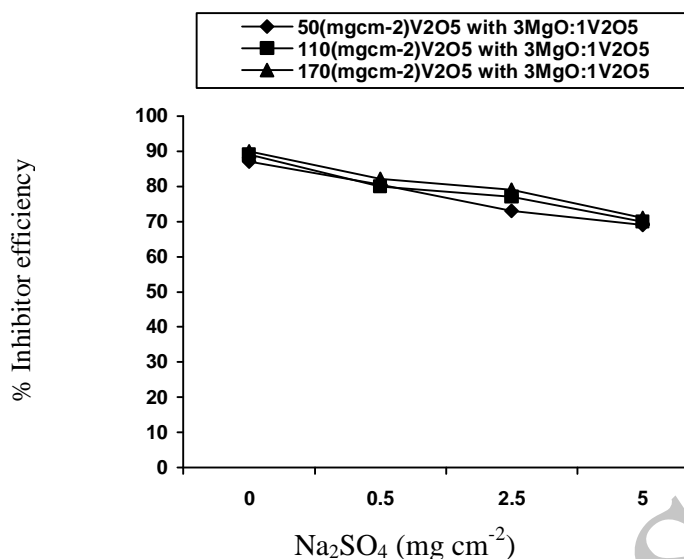


Fig. (10): Inhibitor efficiency Vs. Na₂SO₄ for the system
213T11 (MgO+V₂O₅+Na₂SO₄, Air) at 850°C

Figures (7-10) show plots of inhibitor efficiency (I), VS. Na₂SO₄ (mg cm⁻²) for different amount of V₂O₅+3MgO. From the figures the following points are evident:

- for 209 T₁ and 213T₁₁ at both test temperature the inhibitor efficiency falls with rising weight Na₂SO₄,
- the beneficial effects of MgO additions occurs at (50-170 mg cm⁻²) Na₂SO₄ for 209 T₁ and 213 T₁₁ at both 750 and 850 °C.
- It would be expected that the specimen with the small amount of MgO: V₂O₅ deposits would be more susceptible to the influence of Na₂SO₄ present and this is demonstrated clearly by Figs.(7-10). This shows that deposition processes and rates will be of vital importance when trying to determine inhibitor efficiencies in oil fired boiler.

Conclusions

- The vanadic corrosion of 209 T₁ and 213 T₁₁ has been shown to depend upon both the test temperature and amount of V₂O₅.
- The effectiveness of MgO as an inhibitor of vanadic corrosion depends upon the amount of Na₂SO₄ present.
- Plots I Vs. Na₂SO₄ (mg cm⁻²) can be used to find permissible levels of Na₂SO₄ to satisfy a preselected tolerable corrosion rate or inhibitor efficiency in a V₂O₅+MgO+Na₂SO₄+Air containment system.

References

- O.M. Johnson, D. P. Whittle and J. Stringer "Mechanisms of Na₂SO₄-Induced Accelerated Oxidation" Corrosion Science, Vol.15, PP. (721-739), 1975.

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2. R.T. LeCren, "Advanced Combustion System for low-Grade Fuels", Turbomachinery Technology Seminar, Caterpillar Solar Turbines, 1992.
3. S. Shawki, S. Hanna, "Corrosion Control in Gas Turbines" Central chemical laboratories , Egyptian Electricity Authority, 1985.
4. T-S. Sidhu , S- Prakash and R-D . Agrawal "Hot Corrosion and Performance of Nickel – Based Coating , Current Science Vol . 9 , No.1 , January 2006 .
5. H. Singh , D. Puri and S. Prakash , "An Overview of Na₂ SO₄ and / or V₂O₅ Induced Hot Corrosion of Fe – and Ni –Based Superalloys" . Rev . Adv . Mater. Sci. 16 (2007) 27-50 .
6. I . Andijani , and A-V . Mali, "Sulfur and Vanadium Induced Hot Corrosion of Boiler Tubes " , Conference, King Sand University , Riyadh , on 11 to 15 Dec . , 2004 .
7. C.S. Giggins and F. S. Pettit, Hot Corrosion Degradation of Metals and Alloys: A unified theory, Pratt and Whitney Report, FR-11545, 1979.
8. M.M. Barbooti, "Corrosion Inhibition–Magnesium compounds Additives to Heavy Fuel Oil", Chem. Arab, Beirut, 10-14 January, 2001.
9. S. S. Dreyman and R. T. Henk, "Simplified System for Processing and Treating Ash-Forming Fuels", General Electric company Report GER-3132, 1981.
10. K. F. Al-Sultani, " A Pilot System for Evaluation of Hot Ash Corrosion Inhibition in Power Generation Boilers," Ph.D thesis, The Technology University, 2003.
11. I. L. Rozenfeld, "Corrosion Inhibitor ", McGraw-Hill, New York, 1981.
12. R.A. Newby and R. I. Bannister, " A Direct Coal-Fired Combustion Turbine Power System Based on Slagging Gasification with in-situ gas Cleaning", Trans ASME, 120, 450, 1998.
13. Child, H. G., "The Effect of Composition of Gas Turbine Alloys on Resistance of Scalling and Vanadium Pentoxide", J. I. S. I., 1985.

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