

Analysis of Material Degradation in Chlorine Environment of Power Plants

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ABSTRACT

The chlorine containing deposits in the power plant environment is very harmful in terms of degrading the plant component materials. The cyclic reaction starts by the chlorine gas shorten the life of the plant components. In this study, this cyclic reaction is study in detail, which is required further to find the preventive methods for slow down the degradation of the plant components, especially in waste incinerators.

Keywords

Boiler Tubes, Incinerator, Chlorine, Active oxidation, Hot corrosion

1. INTRODUCTION

The degradation and hence failure of the boiler, superheater and other material components of the power plant industry is still a serious issue. The main reason this failure is the presence of corrosive elements in the flue gases generated during burning of the fuel in these plants. These flue gases elements are more aggressive in nature in the energy producing plants like waste incinerators, where alkali and heavy metals becomes highly corrosive in the presence of chlorine. The high-degradation of materials in the presence of chlorine still needs an acceptable solution, and thus extensive study and research is still required in this area. Another important point which should be considered during this study is that fuels and its elements could not be changed for power plants which are based primarily on waste management like incinerators [1-4].

2. HOT CORROSION

The material degradation at high temperature under the presence of thin layer of molten salts under suitable atmosphere is known from the year 1940. This phenomenon of corrosive failure under the presence of molten salts is known as hot corrosion. Hot corrosive failure of the components is more severe under the presence of chlorine containing molten deposits, and was first observed in the aircraft engine failures which mainly operated above the chlorine containing sea water [4-8]. During this phenomenon, the protective oxide layer usually formed on the metal/alloy surfaces is dissolved, and a non-protective layer is formed, thereby results in accelerating the surface degradation [5,6]. The corrosive attack in boilers materials of thermal power plants and waste incinerators is also due to hot corrosion phenomenon [9].

2. OXIDATION PRINCIPLE

It is a well known concept that metal and their alloys develop self healing layer of oxides of metal/alloy elements during reaction with the atmospheric oxygen. This surface layer acts as barrier to the corrosive and environment elements and prevent them from reacting with the metal/alloy elements. This results in safety of the metal/alloy surface below the

oxide layer. However, there are molten deposits of the flue gases corrosive elements on the material surface in the boiler environments. These deposits dissolve the surface oxide layers of the metals or alloys. Also the presence of these deposits breaks contact of the metal/alloys from the surrounding oxygen. The reducing atmosphere this formed prevents the further formation of protective oxide layer on the surface of the boiler materials [10] In incinerators and gas turbines, the presence of salt deposits on the materials reduces the local oxygen pressure and results in destroying protective oxide barriers on the surfaces of alloys [11,12]. As oxygen is a desirable component for the protective oxide layer, hence reducing atmosphere around the substrate is more corrosive in nature. The destruction or failure of the surface oxide layer is the first step towards the start of the hot corrosion phenomenon on the metal/alloy surface. The presence of molten deposits, temperature variations and erosion caused by flue gas elements are some of the reasons of the failure of the surface layers. The dissolution of the surface layer by molten deposits is known as fluxing, which can be acidic or basic fluxing depends upon the surrounding environment. It is observed that the acidic fluxing is more harmful over the basic one [5, 6, 13-16]. For low oxygen ion activity in the molten salts, it is observed that acidic fluxing takes place [16]. The study found that alloys having high amount of Mo, V and W faced acidic fluxing. For incinerators Hara et al. [17] reported the basic fluxing of surface oxide layer of Cr element, as:
$$\text{Cr}_2\text{O}_3 + 3\text{SO}_3 + 2\text{O}^{2-} = 2\text{CrO}_4^{2-} + 3\text{SO}_2 \quad (1)$$

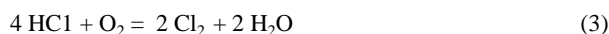
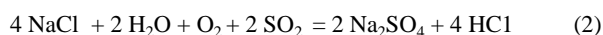
3. CHLORINE BASED FAILURE MECHANISM

The presence of chlorine element in the molten deposits on the surface of metal or alloys further increases the pace of the attack of corrosion elements. This attack is known as 'Active-Oxidation', in which combination of oxidation and chlorination reactions takes place on the material surface. During this mechanism chlorine gas is not consumed and just act as catalyst to speed up the oxidation of the material elements. This accelerated oxidation means formation of non-protective and porous surface oxide layer, and only 0.1 % presence of chlorine can be very harmful, since chlorine is not consumed [9, 18-24]. Thus it is important to study the failure of the power plant components by the chlorine containing environment. This mode of failure mechanism generally has following steps [10]:

a) First chlorine should be generated from the surrounding environment and present on the material surface, b) In next step chlorine goes inside the oxide layer to affect the metal/alloy elements, c) Further the chlorine reacts and forms chlorides, d) In next stage chlorides come in contact with surrounding environment, e) Formation of oxides from the chlorides by interaction with the available oxygen and chlorine again ready to start the cyclic reaction [9].

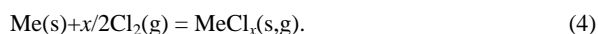
3.1 First Step of chlorine produced on the surface

The presence of chloride containing salts at temperature higher than their fusion range like in boilers and incinerators is the first to start the degrading reaction. There are many different reactions through which chlorine is produced in the form of gas in the region close to the metal/alloy surface. It is not only chloride compounds, but the presence of alkali and sulfur compounds contained in waste incinerators also activates the reaction. The sulfur compounds play a contributory role in promoting corrosion through its chlorine liberating action as shown in the following reaction:



3.2 Second step of generation of chlorides

After the generation of chlorine in the form of gas, it is able to enter into the surface oxide layer of the materials and starts interacting with the base material elements. The entrance path for the chlorine is expected to be cracks and pores in the surface layer. At lower surface the partial pressure of oxygen is less and that of chlorine is high due to the presence of chloride deposits in the incinerator conditions. This pressure of 10^{-10} - 10^{-13} bar is enough for the formation of chlorides of metal/alloy elements, and for these reactions it is found that Gibbs free energy has high value towards negative side. Thus, the thermodynamics is in favor for the formation of chlorides, in gaseous or volatile solid form. The general reaction for this interaction of elements with chlorine is:



As the high negativity of the Gibbs free energy, the chloride of chromium has high preference of formation in comparison of iron and nickel. The growth of chlorides between oxide and metal surface will weaken the bonding of the oxide layer with metal and thus decreases the protective ability of the oxide layer [9-12, 19].

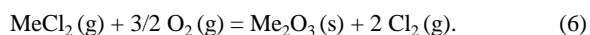
3.3 Third Step of chloride vaporization

In next step after the formation of chlorides, these become vaporized because of enough required vapor pressure as:



3.4 Last step of reaction of gaseous chlorides

The gaseous chlorides, formed in third step, come out through the passages in the oxide layer and interact with the surrounding environment. Now the atmosphere outside the oxide scale is oxidizing and thus has high partial pressure of oxygen. Due to this high value of oxygen pressure the chlorides come out in gaseous form interacts with oxygen as:



It is noticed that oxides of metal/alloy elements formed and chlorine which was consumed in second step is again released in the atmosphere. This chlorine is again ready to interact with the metal elements and cycle of reactions starts.

Also the oxide formed in this cycle of four steps and is not through direct interaction between metal/alloy elements and oxygen. This type of oxide formed on the surface is noticed to be porous and loosely bonded with surface. Thus, this oxide layer is not able to provide blockage to the corrosive and damaging environment elements.

For alloy containing different elements, depending upon the vapor pressure of chlorides and partial pressure of oxide formation, the oxide layer consists of a layered structure. The chromium oxide formed at low oxygen pressure in comparison to iron and nickel. Thus the region of layer close to surface is rich in oxide of chromium and upper region noticed to be rich in nickel oxide, and in-between mixture of oxide of chromium, iron and nickel is observed. Thus, if during study this type of layered oxide structure is noticed on the boiler or other components, then it can be concluded that 'Active oxidation' the possible phenomenon in that environment conditions [11, 12, 19].

Thus, the ways should be found out to stop or hinder that phenomenon by various available techniques. The study of these techniques is not in the scope of this study.

4. CONCLUSION

The presence of chloride deposits, such as NaCl, accelerates the corrosion in waste incinerators and marine based gas turbines. The NaCl plays as a catalyst accelerating the corrosion reaction. The mechanism of chlorine based active oxidation especially under NaCl deposits is the oxy-chloridation, chloridation and re-oxidation process. This mechanism is cyclic in nature and is harmful for the degradation of the materials used in these plants. Thus, still a detailed study is required to gain in-depth view of this mechanism. Also research should be focused develop easy and reliable methods to protect the precious materials from degradation at low cost.

5. REFERENCES

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