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CORROSION IN THERMAL ENERGY GENERATING PLANTS

Amabogha B.[1]

Research Scholar, Dept. of Chemical Engineering, Univ. of Benin P.M.B 1154, Benin City, Edo State, Nigeria
Author: Research Scholar, Univ. of Benin P.M.B 1154, Benin City, Edo State, Nigeria
Email: bamabogha@yahoo.com

ABSTRACT:

Most of the electricity produced throughout the world is from thermal energy generating plants such as fossil fuel, nuclear, hydroelectric, geothermal, solar etc.
Thermal energy generating plants may be shut down due to planned or unplanned maintenance or due to low seasonal power demand. During the shutdown, corrosion can take place on all or parts where the ambient air, which always contains certain quantity of water vapour, comes into contact with metal surfaces of the generating plant. This is due to ineffective corrosion awareness on the part of the engineer or designer. In this article, the location within plants most likely affected and an overview of protective materials most often used to withstand the aggressive environment in thermal energy generating plant such as Coal fired power plants, Gas Turbines of various researchers are reviewed.

Keywords: Corrosion; Thermal Energy; Coal Power plant; Gas Turbine; Temperature

1. Introduction

Corrosion is an electrochemical process which can take place on metal surfaces due to the simultaneous action of water and oxygen, where the oxygen is being dissolved in the water.

Thermal energy generating plant is a power station, also known as generating station, power plant or power house. Thermal energy generating plant is an industrial facility for the generation of electric power.

At the centre of nearly all power stations is a generator, a rotating machine that alters mechanical energy into electrical energy by making relative motion between a magnetic field and a conductor, and a modular synth from which all power comes. In thermal generating plants coal, oil, natural gas etc. are employed as primary source of energy.

Thermal energy generating plants can be divided into several types such as fossil fuel, nuclear, hydroelectric, cogeneration, geothermal, solar, wind etc. The majority of thermal energy generating plants is the fossil and nuclear steam supply system.

Thermal energy generating plant components are subject to corrosion when they are not in operation. A plant may be shut down due to intended or unplanned maintenance, or due to low seasonal power demand. During the shutdown corrosion can, therefore take place on all or part of thermal energy generating plants parts where the ambient air, which always contains a certain amount of water vapour, comes into contact with metal surfaces. The ability of the air to absorb water vapour depends on the temperature and pressure of the air. Because of the complex and often pressure environments in which thermal energy generating plants operates, corrosion has been a serious problem with a important influence on the operation of the plants. However, with the aging of several plants old problems persist and new ones appear. For example, corrosion remains to be a problem with electrical generators and turbine.

Environmental requirements and deregulation of the power industry often result in less attention being paid to corrosion and weakening of materials of contruction. If corrosion issues are not addressed in a timely way, these materials will disintegrate to the point that major repair and restoration will be required. The cost of corrosion will then increase significantly.

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Many thermal energy generating plants corrode due to either poor materials collection or due to ineffective corrosion consciousness on the part of the plant engineer or designer. Components are often replaced only to fail again within only a very short time. The plant can suffer considerable downtime during the period in which removal ordering and replacement are taken place. It is vital to comprehend the mechanism by which failure occurs and to take informed steps to guarantee an exchanged lifetime for the replacement component. This may need changes to the water treatment package component material or to the plant operating conditions or all three

The accomplishment of high temperatures has been imperative in the growth of civilization for many countries. Structural materials in many front-line high technology areas have to operate under extreme circumstances of temperature, pressure and corrosive environment. So, Materials degradation at high temperatures is a serious problem in several high technological industries. Gas turbines in aircraft, fossil fuel power plants, refineries, and petrochemical industries, and heating elements for high temperature furnaces are some examples where corrosion limits their use or decreases their life, considerably affecting the competence.

World-wide, the majority of electricity is generated in coal-fired thermal plants, in which the coal is burned to boil water: the steam so produced is expanded through a turbine, which turns a generator. The steam at the low pressure exit end of the turbine is condensed and returned to the boiler.

Coal is a complex and relatively dirty fuel that contains varying quantity of sulfur and a substantial fraction of non-combustible mineral constituents, commonly called ash. The vast technical literature available is evidence that corrosion and deposits on the fireside of boiler surfaces or in gas turbines epitomize important difficulties. Metals and alloys may experience accelerated oxidation when their surfaces are coated by a thin film of fused salt in an oxidizing gas. This mode of attack is called hot corrosion, and the most dominant salt involved is Na_2SO_4. High temperature degradation is one of the main failure modes of hot-section components in the gas turbines, so an understanding of this high temperature oxidation is very necessary.
Erosive, high temperature wear of heat exchanger tubes and other structural materials in coal-fired boilers are recognized as being the main cause of downtime at power-generating plants, which could account for 50-75% of their total arrest time. Repairs costs for replacing broken tubes in the same installations are also very high, and can be estimated at up to 54% of the total production costs.

High temperature oxidation and erosion by the impact of fly ashes and unburned carbon particles are the main problems to be solved in these applications. Therefore, the expansion of wear and high temperature oxidation protection systems in industrial boilers is a very important topic for engineering.
Just about every utility facility that makes power or involves in some form of incineration must deal with corrosion issues.

Since the acceptance of the Clean Air Act of 1990, gas-scrubbing technologies have amplified the importance of preserving the assets of power plants and other incineration infrastructure. These demands will increase further with the arrival of new mercury removal requirements to be phased in during the near future.

This paper recognizes common corrosive processes, the locations within plants most likely affected, and an overview of protective materials most often used to withstand the aggressive environment in thermal energy generating plant.

2. COAL FIRED POWER PLANTS

To fully comprehend the solutions to power plant corrosion, let's first review the basic operating conditions and components of a typical coal-fired power facility.

The accessibility of electrical power and the progress of million of devices that use it have made electricity the energy of choice in contemporary industrial societies. In any event, the fossil fuel power plant is and will continue to be the mainstay of electric power production.

The fossil fuel working in a steam turbine plant can be pulverized coal (PC), oil, or natural gas. Of these, coal is the most abundant and hence the most commonly used fuel for steam turbine plants, while gas turbine plants generally employ oil and natural gas. Figure 1 shows the arrangement of the various elements of a PC fossil plant. Here, water is first preheated to a relatively low temperature in feed water heaters and pumped into tubes contained in a boiler. The water is heated to steam by the heat of

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combustion of pulverized coal in the boiler and then superheated. Superheated and pressurized steam is then allowed to expand in a high-pressure (HP) steam turbine and causes rotation of the turbine shaft. The outlet steam from the HP turbine may once again be reheated and made to expand through an intermediate pressure (IP) turbine and then through a low-pressure (LP) turbine. The turbine shafts are all connected to one or more generator shafts which in turn rotate and convert the mechanical energy of rotation into electrical energy in the generator. The exit steam from the LP turbine is condensed in the condenser and is once again fed back to the boiler through the feed water heater and pumps. A closed loop of the water and steam is thus maintained.

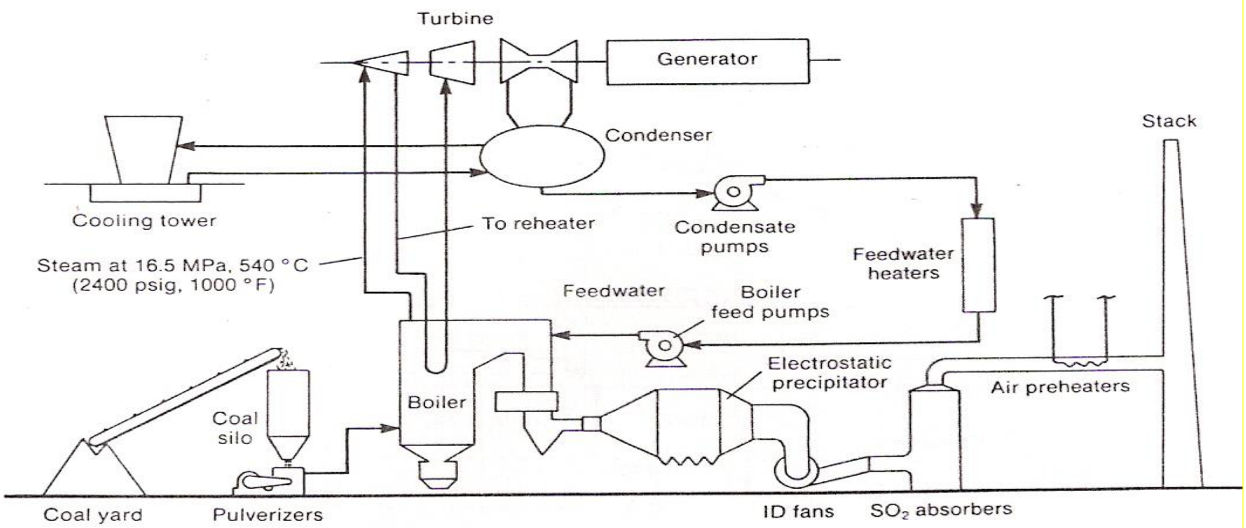

Figure 1: Schematic diagram of a coal-fired steam power plant

The corrosive nature of the gaseous environments, which contain oxygen, sulfur, and carbon, may cause rapid material degradation and result in the premature failure of components.

Combustion of coal produces very corrosive media mainly near the superheater tubes of the boilers. In the boiler tubes suffering severe fireside corrosion, sulphate salts concentrate at the deposit/scale interface and become partially fused since these salts contain alkali metals of sodium and potassium. In the combustion systems, much of the sodium and potassium is volatized from the mineral matters in the flame to form Na_2O and K_2O vapours. The sulphur released from the coal, forms SO_2 with a minor amount of SO_3 and reacts with the volatilized alkalis to form Na_2SO_4 vapours, which then condense together with fly ash on the pendant superheater and reheater tubes in the boiler.

The vast technical literature available is evidence that corrosion and deposits on the fireside of boiler surfaces or in gas turbines represent important problems. When a comparison is made between the amount of ash collected in a boiler or a gas turbine, in the form of deposits, and the total amount of ash released during combustion, the conclusion is clear that most of the ash passes through the unit. For particles to collect on boiler surfaces or blade surfaces, they must first be brought close to the surface itself and be of the proper size. This can be attributed to physical phenomenon including the reaction of particles to the forces to which they are subjected within the stream of gases passing near the surfaces.

A particle may hit and then rebound from the surface. If it hits or rubs the surface with sufficient force, erosion will result. On the other hand, if the particle is captured physically or chemically by the surface, a deposit is initiated whose growth appears aerodynamically unavoidable. Because of high temperatures, reactions can then take place between the various particles deposited, and also with the gases passing nearby, particularly SO_3 and SO_2. The resulting compounds may then react, by diffusion, with the metal structure on which they are attached and cause accelerated corrosion.

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3. AREAS IN NEED OF CORROSION PROTECTION IN THERMAL ENERGY GENERATING PLANT

The following are specific areas typical of power generating facilities that are most vulnerable and in need of protection:

- Flue Gas Inlet Ducts: A network of ductwork directs flue gas from the boiler to various parts of the flue gas system or directly to the stack via a bypass duct in the event of an upset or bypass condition. In addition to high temperatures at the beginning of the process, the gases also contain acids and fly-ash which can attack the duct both chemically and physically.
- Scrubber Outlet Ducts: This structure carries the scrubbed flue gas from the scrubber to the stack. The gas temperature in the outlet duct is much lower (<200ºF) than that in the inlet duct, and relatively free of abrasive fly-ash.
- Bypass Ducts: The duct has the same conditions as the inlet duct: high temperature, acidic and abrasive flue gas.
- Stacks: Flue gas is formed during fuel combustion and industrial chimneys carry away the gases formed by burning coal, oil, gas and refuse. Industrial stacks usually consist of a windshield, an annulus area and an independent liner or multiple liners. Some stacks are free standing and do not have windshields. Because of the potentially high temperatures and acidic environments found in flue gas applications, unprotected liners quickly suffer chemical attack as well as thermal shock.
- Steel Liners: Historically, carbon steel-lined stacks used traditional refractory linings-calcium aluminate bonded cements, such as luminite-haydite and sodium silicate linings. In time, potassium silicates demonstrated upgraded properties. While this technology enabled longevity of the stack, it also permitted potential environmental hazards by allowing the escape of heated, unscrubbed gasses likely to initiate acid rain. This directly contributed to the passage of the aforementioned Clean Air Act of 1990.
- Brick Liners: These continue to be among the most durable methods of constructing new liners.

Considerations of time, cost and seismological zones combine to make new brick liners somewhat rare today.

- Fuel Handling Areas: Coal, one of the primary fuels used in power generation, is extremely abrasive. In addition to its abrasiveness, coal can also leech sulfurous acid when wet. Regardless of whether coal is stored horizontally, as in a bunker, or vertically, such as silos and hoppers, environmental laws prevent it from being stored on unlined areas where the acid might ultimately combine with rainwater and leach out or run off.
- Scrubber Module (Quencher, Absorber): Scrubbers are the heart of the flue gas cleaning system. In addition to removing the acids, scrubbers reduce the heat of the gas and help strip it of abrasive fly-ash. Because of the many complex factors involved in the scrubbing process, some of the acid gets through, so the scrubber needs protection from this chemical and physical abuse.
- Demineralized Water Areas: Water used in the boiler must be demineralized and free of contaminants. This is accomplished by ion exchange cartridges which are, in turn, cleaned with sodium hydroxide and treated with sulfuric acid. Because of this aggressive process, the concrete and steel of these structures are subject to corrosion. Demineralized water is also very aggressive to concrete.
- Collection Sumps/Neutralization Basis: These structures are exposed to the chemical effluent of the water demineralization process. These environments can be both acidic and caustic. The method of protection used will depend on environmental conditions including temperature, substrate and chemical exposure.

4. CORROSION IN GAS TURBINES

Gas turbine materials in FBC (Fluidized Bed Combustion) cogeneration systems that use air as the working fluid are exposed predominantly to heated air, with supplemental heat from burning of clean fuel such as natural gas. Corrosion of materials has been observed over a much wider temperature range (600 – 950°C) in the FBC effluent than in conventional gas turbines (800 – 950°C). Corrosion test data obtained from the effluent of a pressurized FBC system showed that both nickel- and cobalt-based alloys were equally susceptible to accelerated Type II hot corrosion. This form of corrosion, also known as low-temperature hot corrosion, involves eutectics of base metal sulfates and sodium sulfate, and, therefore, occurs predominantly at lower temperatures, especially in the effluent of the FBC environment. For example, the eutectic temperature for sodium sulfate-cobalt sulfate is 565°C. In this case, the transient oxides of cobalt or nickel (which nucleate in the early stage of oxidation in chromium- and aluminum-containing super alloys) react with

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sodium sulfate to form eutectic salts that prevent formation of protective chromia or alumina. The corrosion process is strongly dependent on the partial pressure of sulfur trioxide at the melt/scale interface, but the process occurs at much lower temperatures than the melting point of sodium sulfate. This susceptibility to accelerated corrosion at lower temperatures was attributed to the presence of potassium in the FBC effluent.

5. TYPES OF CORROSION THAT AFFECTS THERMAL ENERGY GENERATING PLANT

5.1. HOT CORROSION

Oxidation is a type of corrosion involving the reaction between a metal and air or oxygen at high temperature in the absence of water or an aqueous phase. It is also called dry-corrosion. The rate of oxidation of a metal at high temperature depends on the nature of the oxide layer that forms on the surface of metal. Metals and alloys may experience accelerated oxidation when their surfaces are coated by a thin film of fused salt in an oxidizing gas. This mode of attack is called hot corrosion.

Hot corrosion was first recognized as a serious problem in the 1940s in connection with the degradation of fireside boiler tubes in coal-fired steam generating plant. Since then the problem has been detected in boilers, internal combustion engines, gas turbines, fluidized bed combustion and industrial waste incinerators. But, hot corrosion became a topic of important and popular interest in the late 60s as gas turbine engines of military aircraft suffered severe corrosion during Viet Nam conflict during operation over sea water. Metallographic inspection of failed parts often showed sulfides of nickel and chromium, so the mechanism was initially called “sulfidation”. However, studies by Goebel and Pettit and by Bornstein and DeCrescente showed that sulfide formation indeed resulted from the reaction of the metallic substrate with a thin film of fused salt of sodium sulfate base; the phenomenon has been renamed “hot corrosion”.
Thus, hot corrosion may be defined as accelerated corrosion, resulting from the presence of salt contaminants such as Na_2SO_4, NaCl, and V_2O_5 that combine to form molten deposits, which damage the protective surface oxides.

5.1.1. MECHANISM OF HOT CORROSION

Several mechanisms have been suggested to explain the process of hot corrosion. The hot corrosion degradation process of the super alloys usually consists of two stages:
1. An initiation stage during which the alloys behave much as they would have behaved in the absence of the deposits and
2. A propagation stage where the deposits cause the protective properties of the oxide scales to become significantly different than those that they would have been had no deposit been present.
Khana et al., in their review of degradation of materials under hot corrosion conditions, stated that corrosion-resistant alloys depend on selective oxidation to form the dense, compact protective scales of Cr_2O_3 and Al_2O_3 for their resistance. During hot corrosion a degradation sequence consisting of the eventual displacement of a more protective reaction product barrier by a less protective product is usually followed. The hot corrosion degradation sequence is not clearly evident, and the time for which the protective scales are stable beneath the salt layer is influenced by a number of factors, which affects the initiation of hot corrosion. The propagation stage of the hot corrosion sequence is the stage for which the superalloy must be removed from service since this stage always has much larger corrosion rates than for the same super alloy in the initiation stage.

5.2. EROSION

Erosion corrosion is the result of a combination of an aggressive chemical environment and high fluid surface velocities. Erosion corrosion is often the result of the wearing away of a protective scale or coating on the metal surface. Erosion corrosion may be enhanced by particles (solids or gas bubbles).
Solid particle erosion (SPE) is the progressive loss of original material from a solid surface due to mechanical interaction between that surface and solid particles. Erosion is a serious problem in many engineering systems, including steam and jet turbines, pipelines and valves used in slurry transportation of matter, and fluidized bed combustion systems. Erosive, high temperature wear of heat exchanger tubes and other structural materials in coal-fired boilers are recognized as being the main cause of downtime at power generating plants, which could account for 50-75% of their total arrest time. Maintenance costs for replacing broken tubes in the same installations are also very high, and can be estimated up to 54% of the total production cost.

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High temperature oxidation and erosion by the impact of fly ashes and unburned carbon particles are the main problems to be solved in these applications, especially in those regions where component surface temperature is above 600°C. Therefore, the development of wear and high temperature oxidation protection systems in industrial boilers is a very important topic for engineering. Erosion-corrosion at high temperature is a field within high temperature corrosion that is growing in importance. Degradation of materials is a function of many parameters. These are normally classified in terms of properties of the particle (size, shape, velocity, impact angle, and hardness), target (hardness, ductility, corrosion resistance) and the environment (temperature, partial pressure of the gaseous environments). A few different types of erosion-corrosion behavior are frequently observed. The model by Kang et al., describes four regimes, which were assigned "erosion of oxide only", "erosion enhanced oxidation", "oxidation affected erosion", and "erosion of metal only". The order follows that of increasing erosion and decreasing oxidation rate.

6. PREVENTIVE MEASURES AGAINST HOT CORROSION AND EROSION IN THERMAL ENERGY GENERATING PLANT

A case study reported by Prakash et. al., pertaining to a coal fired boiler of a power plant where out of 89 failures occurring in one year duration, 50 failures were found to be due to hot corrosion and erosion by ash. Material losses due to erosion and corrosion are the major problems in many industries. Corrosion and its associated losses cannot be eliminated completely. However, 25 to 30% of annual corrosion related costs could be saved with the use of optimum corrosion preventive and control strategies. These facts emphasize the need to develop more and more corrosion resistant materials for such applications.
The option to use low grade fuel limits the improvement in hot corrosion and erosion environment. In that case hot corrosion preventive methods to the existing environment are (a) change of metal i.e. use of super alloy (b) use of inhibitors and (c) use of coatings. Regarding change of metal or use of super alloy, alloying elements which can improve the hot corrosion resistance of materials such as Cr, Al, etc., often have a negative effect on the mechanical properties in high temperature environments and are expensive.

Single materials are at their upper performance limits in all fields and coatings offer a way to extend these limits. One possible way to cope with these problems is by using thin wear and oxidation resistant coatings with good thermal conductivities.

6.1. HOT CORROSION & EROSION RESISTANT COATINGS

The coating can be defined as a layer of material, formed naturally or unnaturally or deposited artificially on the surface of an object made of another material, with the aim of gaining required technical or decorative properties. Coating technology is one of the more rapidly growing technologies in the field of materials. A combination of the development of materials specifically designed for erosion and corrosion resistance and the appropriate technique for the application of these materials, as a coating would be the optimum solution.

Recent studies show that 80% of the total costs for the protection of metals are related to coating applications. Organic coatings cover a large part of this percentage, but also metallic ones have a relatively big market. In fact, metallic coatings possesses together with good corrosion resistance, good aesthetics, brightness, and interesting mechanical properties such as hardness and wear resistance. In general, coating systems can be classified as either diffusion or overlay type, which are distinguished principally by the method of deposition and the structure of the resulting coating-substrate bond.

From a production point of view, three methods are in current use to deposit coatings, these being chemical vapour deposition (CVD), physical vapour deposition (PVD) and Plasma spraying. The CVD process comes under the category of Diffusion coatings, in which the coating material forms a chemical bond with the substrate. Whereas the PVD and Thermal spraying processes comes under the category of Overlay coatings, in which the desired material is placed over the substrate material

6.2. THERMAL SPRAYING

Thermal spraying is one of the most versatile hard facing techniques available for the application of coating materials used to protect components from abrasive wear, adhesive wear, erosive wear or surface fatigue and corrosion (such as that caused by oxidation or seawater) . Generally, any material

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which does not decompose, vaporize, sublimate, or dissociate on heating, can be thermally sprayed.

The technique of thermal spraying has developed at a fast pace due to progress in the advancement of materials and modern coating technology. Plasma-sprayed ceramic coatings are used to protect metallic structural components from corrosion, wear and erosion, and to provide lubrication and thermal insulation. In particular, coatings made of Al_2O_3 containing 13 wt% TiO_2 (Al_2O_3-13 wt% TiO_2) are commonly used to improve the wear-corrosion and erosion resistance of steel. In conventional plasma-spray processing of Al_2O_3-13 wt% TiO_2 coatings, powder particles are injected into a plasma jet, causing them to melt into droplets that are propelled towards the substrate. Solidification of the droplets stream onto the substrate as "splats" results into the buildup of the coating, typically 100-300μm thick. In order to obtain chemical homogeneity in the coating, the processing is performed at "hot" plasma conditions which ensure complete melting of the powder particles. Plasma sprayed zirconia coatings as thermal barrier coatings have been applied to hot section components of gas engines to increase temperature capability Ni-base super alloys.

7. CONCLUSION

The development of modern coal fired power generation systems and gas turbines with higher thermal efficiency requires the use of construction materials of higher strength and with improved resistance to the aggressive service atmospheres. These requirements can be fulfilled by protective coatings. For some years now a significant shift has occurred in the operation of power generation facilities, along with changes in attitudes towards the environment, resulting into problem emanating from these facilities due to corrosion. Just as these facilities have evolved and innovated, so too have the products and methodologies used to protect them, to not only ensure the life of the structure itself, but to add to the long-term benefits of its maintained existence.

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