American Journal of Engineering Research (AJER)
e-ISSN: 2320-0847 p-ISSN : 2320-0936
Volume-5, Issue-12, pp-266-270
www.ajer.org
Research Paper Open Access

Effect of Chlorine and Sulphur on Stainless Steel (AISI 310) Due To High Temperature Corrosion.

Onaivi Daniel Azamata[1], Titus Yusuf Jibatswen[2], Odinize C. Michael[3]
[1]*Department of Chemical Engineering, Federal University Wukari, Taraba State*
[2]*Department of Mechanical Engineering, Federal University Wukari, Taraba State*
[3]*Department of Chemical Engineering, Federal University of Technology, Minna*

ABSTRACT: *In a power station boiler, there are temperature of regimes of corrosion which occurs mainly in the economizer, boiler steam generation tubes, super-heater tubes and air tubes. The specific gas temperatures in degrees centigrade for the following include: 150 – 370^{o}C for the economizer, 1000 – 1650^{o}C for the boiler steam generation tubes, 650 – 1000^{o}C for super-heater tubes and 1000 – 1200^{o}C for air tubes. For power station boilers that burn coal as the source of fuel it is recommended that a coal with low Chlorine and low Sulphur content is utilized to avoid the high rate of corrosion on the mentioned parts of the power station boiler. The major type of corrosion experienced by such power station boilers is called high temperature corrosion. For high temperature corrosion due to Sulphur, research has revealed that it can be reduced by ensuring that there is an oxidizing atmosphere and eluding flame impingement on the furnace walls that use "air belting" in the furnace basket. For high temperature corrosion due to chlorine, research has shown that chlorine attack starts at 204^{o}C while hydrogen chloride attack will occur until a temperature of about 426^{o}C. A suitable material that is suggested to be used in power station boilers, that has a high resistance corrosion rate is Stainless steel (AISI 310); substantial research has shown that it can be utilized in super-heater tubes.*

Keywords: *Chlorine, Sulphur, Stainless steel (AISI 310), High temperature corrosion, Power station (Boilers)*

I. INTRODUCTION

Global energy consumption has almost doubled over the past three decades of the last century. 77.8% of the primary energy consumption was gotten from fossil fuels in 2004. (32.4% oil, 21.2% natural gas and 24.1% coal), 5.4% from nuclear fuels and renewable resources consists of 16.5% [1].

From previous research, it has been indicated that the rate of corrosion which occur in fireside of a plant can be affected by change which comes from the combustion medium composition. Henceforth any rise in the quantity of oxygen can maximize the risk of boiler corrosion. Fireside metal losses in boilers can happen either by deposit induced liquid phase or gas phase oxidation corrosion and this can be reduced by utilizing substances which are resistant to oxidation at the required temperature levels. While deposit induced corrosion of substances is a fast means of attack, which is affected by condensation and vaporization of little quantity of impurities which include potassium, sodium, chlorine, sulphur and vanadium these are contained within the feedstock that is coal. As indicated in Fig 1.0 the gas temperature Increase from 150 to 370°C is for region of the economizer formation of phosphorus pentoxide rich slags exists and from 1000 to 1650°C is the region of boiler steam generation tubes where sodium/potassium pryosulfates exist. From 650 to 1000°C where alkali iron trisulfates exist is the superheater tubes section of the boiler. 1000 to 1200°C is the slag alkali sulfates exists in the air tubes[7]. Hence this shows that as temperature increases the rate of corrosion also increases in the different· parts of the boiler. Fig 1.0 represents the temperature regimes that corrosion occurs.

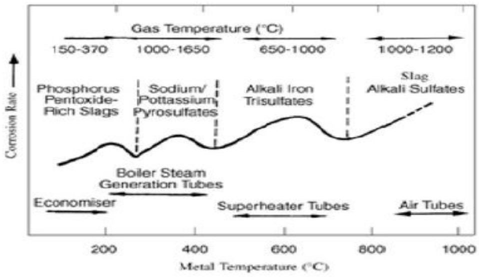

Fig 1.0 Temperature of regimes of corrosion[14]

II. HIGH TEMPERATURE CORROSION DUE TO SULPHUR

There was a rise in demand for electricity in the 1940's and 1950's which lead to an increase in thermal efficiency from 27% in 1948 to 38% in 1963, with a project rise of up to 40% in 1965. To attain higher efficiencies, steam temperature was raised from about *454°C* in 1948 to 565°C in 1963[9].

With continuous use of Illinois basin coals which were considered to be enriched with sulphur, chlorine and sodium resulted to the diminution of furnace walls, diminishing superheater tubes and also fouling of the depleting superheater at the entry to the heat recovery zone, Hence corrosion by alkali trisulfates grew fast and became an issue[9].

The existence of alkali pyrosulfates in furnace wall deposits was discovered in 1945, Corey et al. Alkali iron trisulfates was also discovered on the verge of the final superheater tube surface as mostly the cause for tube depletion[5], Moreover in these two cases the deposit was constituted of hard white enamel like substance and corrosion depended on the presence of the molten phase.

A report made by Corey et al, (1945) Nelson and Cain presented that the alkali iron trisulfates desired about 250ppm S03 to form. Therefore, the alkali iron trisulfates are molten at 894°C and decompose above 525°C[5].

Further research on alkali trisulfates have revealed that high temperature corrosion of furnace wall and superheater surface can be evaded by ensuring that there is an oxidizing atmosphere and eluding flame impingement on furnace walls that use "air belting" in the furnace basket and also keeping steam temperature to approximately 537°C, using shielding to rise the unprotected parts to the temperatures going above the melting temperature of the alkali trisulfates and stopping the sulphur (that is iron level) and alkali level (that is K_20 and Na_20) of high bituminous coals[9].

III. HIGH TEMPERATURE CORROSION DUE TO CHLORINE

One problem that furnace walls and superheaters face while firing pulverized coal is chlorine. Around the late 1950's in the United Kingdom, chlorine content rose as high as 0.8% with an average of about 0.25%[9].

Hence from past experience, the operators learnt they could maintain a corrosion free process if they did not let the chlorine concentration in the coal to be above 0.3% on a dry coal basis. Although, most of the coals in North America have less than 0.3% of chlorine on a dry basis. Moreover, there are still some quantities of reserves in this area that have high levels of chlorine greater than 0.3% on a dry coal basis. Such reserves are situated in the deep mines limited to the Illinois basin[3].

Not until recent times have the availability of high sulphur/low chlorine coals have given an economic alternative to the use of coal with a corrosion potential. However, the availability of high chlorine fuel is limited, the rise in constrictions on the use of high sulphur coal has designed an incentive that is growing for exploiting these reserves[8].

The mode that the chlorine occurs is essential as they determine the mineral transformation during combustion, which generally affects the fireside behaviour of the species. The character in which chlorine ensues also defines their potential for deduction during the fuel preparation as a corrective measure for fireside complications. It was discovered that three major methods of occurrence of chlorine in coal have been recommended. They include: Inoganic chlorides, Organo-chlorine compounds and chloride ions in brines and other water associated with coal[4].

In the past, it was believed that chlorine existed as a chloride of sodium, potassium and calcium as a result of the intrusion of saline water a position which was firstly supported by Gluskoter of Illinois geological survey with regard to central Illinois coals. Some aqueous leaching test primarily revealed time correlation amongst the chloride and alkali ions which they were connected as an organic alkali compound. Although, new aqueous leaching experiments carried out by Gluskoter et al and Chen et al have further made the investigations to go contrary to the original thinking about chlorine in North American coals from chlorine found predominantly as inorganic alkali chlorides to a combination of both soluble chlorides and unspecified "organic" chlorides. After conducting an Electron probe analysis of an upper Freeport bituminous coal discovered that chlorine is homogeneously disseminated throughout a given maceral. Hence, no correlation was found with any other inorganic species presented[13].

Huggins and Huffman carried an X-ray Absorption fire structure spectroscopy (XAFS) on various grades of coals that have chlorine of about 0.04 and 0.84% which disclosed the chlorine in most of the coals examined was discovered as chloride anion in the moisture together with the micro cracks and openings in the coal. Secondly another Conn of occurrence was exemplified as crystalline NaCI which apparently precipitated from the chloride rich solution as the coal dried. In Illinois geological survey, Chou presented the same results donating that chlorine occurring predominantly as anions of moisture in acceptable cracks and pores [11].

Another discovery was made by Gibb as he recently showed that extremely fast de-chlorination of coal happens in the early stages of de-volatilization thus giving of chlorine as hydrogen chloride or chlorine and he identified this phenomenon as the activity to the presence of chlorine which exists as weakly bonded ions in the coal matter[9].

Engdahl et al and Krause et al (1979) disclosed that chlorine has not been established in the incinerating steam generating flue gases, henceforth substantiates equilibria predictions when applied to incinerators. Equilibria for hydrogen chloride and chlorine is most desired when the creation of HCI at low temperature oxidizing conditions to which furnace wall deposits are normally exposed[6].

English and North American coals that are rich in chlorides also have high levels of sulphur. Cutler et al, Boll and Patel, Wibberley and Wall, Halstead and Hart and Wall carried out experiments to examine the thermodynamic equilibria of chlorides and sulfates which happen at levels that are frequently seen in high chlorine coals together with alkali partitioning under reducing conditions, this was in an attempt to have a clear knowledge of the formation of the alkali chlorides or sulphates on tube surfaces. Chlorine is known to have a secondary effect on potassium naturally revealed in coal as a steady silicate such as feldspar or illite. This potassium may be isolated by sodium or chlorine at high temperatures creating a chloride or sulphate and henceforth making a second alkali capable of engaging in the fireside corrosion issue[4]. Culter et al and Rausk suggested the following reactions:

$$\begin{aligned} &\mathrm{m}K_2\mathrm{O.XSiO_2\ .Y}AL_2\,\mathrm{O_3(Condesed)} + \mathrm{2NaCl(gas)} \\ &\qquad \rightleftharpoons (\mathrm{m}-1)\ K_2\mathrm{O}.K_2\mathrm{O.}Na_2\mathrm{OXSiO_2\ XY}AL_2\,\mathrm{O_3(Condesed)} \\ &\qquad + \mathrm{2KCl(gas)} \qquad (2.1) \end{aligned}$$

$$\mathrm{2KCl} + \mathrm{SO_3} + \mathrm{O_2} \rightleftharpoons K_2SO_4\mathrm{(gas)} + \mathrm{HCl} \qquad (2.2)$$

From research it has shown that illite exhibits a characteristic of being sticky down to temperatures that are as low as 950 to 1000°C and thus this generates the mechanism for moving potassium from the flue gas to the leading edge of corrective bank lubes where they are collected as a semi molten deposit making a source for K2S04 or KCI [9].

Brown et al and Battelle carried out investigations which revealed that chlorine attack starts at 204°C while hydrogen chloride attack will not occur until a temperature of about 426°C [8]. As represented in fig 1.1 below.

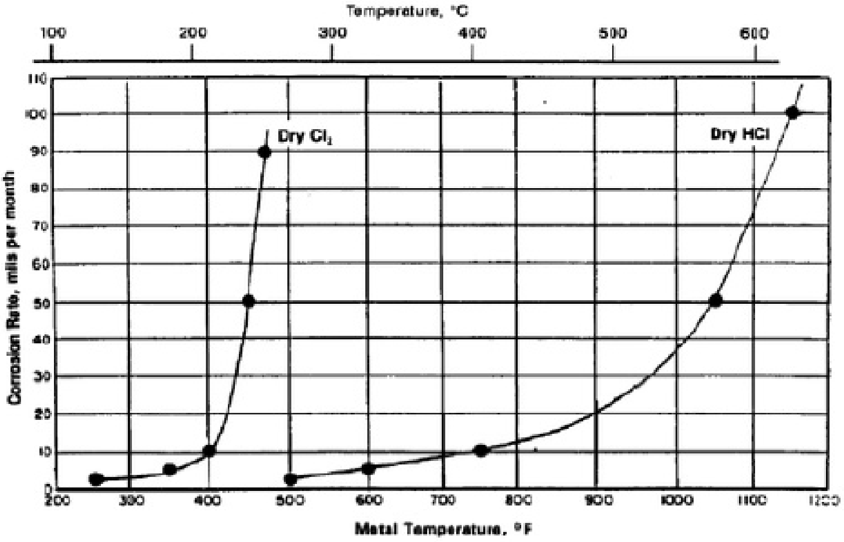

Fig 1.1 The rate of corrosion of carbon steel in HCl and Chlorine as a function of temperature. Source[9]

Equilibria does not favour the formation of Cl_2 that appears in the flue gas at the furnace walls under oxidizing conditions, thus attacks by Cl_2 mainly occurs beneath the deposit[9].

The initial step of high temperature corrosion starts with the formation of a protective film on the tube surface. Secondly, the Cl_2 that is released by coal produced from the decomposition of hydrogen chloride under reducing conditions passes through the oxide scale and reacts with the elemental iron to form $FeCl_2$ which generally separates the protective coating and corrosion product from the tube surface[9].

$$\mathrm{Cl_2} + \mathrm{Fe} \rightleftharpoons \mathrm{FeCl_2} \qquad (2.3)$$

$FeCl_2$ vapour diffuses through an outward path which passes through an oxide scale and gets oxidized on its way to FC304 and Fe203 releasing new Cl_2 for attack of the base metal[9]. This process is cyclic. Reduced conditions are basic to giving off the initial Cl_2: while conditions which oxidize are needed for the corrosion to continue. Consequently, oxidizing conditions which revolve in a cyclic pattern that are stimulated by flame impingement develop the worst conditions. Hydrogen chloride may react with the protective coating of $Fe_2 0_3$, to produce $FeCl_3$, and this happens at low temperature surfaces[2], hence:

$$1/3Fe_2 0_2 + 2HCl \rightleftharpoons 2/3FeCl_2 + H_2 0 \qquad (2.4)$$

Further experiments conducted by Mayer and Marulesco showed that 0.2 volume percent can make $Fe_2 0_3$ layer porous while 0.8 volume percent can utterly disintegrate it. Hence $FeCl_3$ is highly volatile and will not stay on tube surfaces in most steam generators[10].

IV. CORROSION IN BOILERS (POWER STATIONS)

Corrosion attack which causes failure in boiler rubes is a regular phenomenon in power plants which tend to result to unpredicted plant shut down. this leads to great losses in industrial production and disruption to civil amenities.

The ways in which the future of boiler tubes shows is in forms of bulging, bending, wearing or rupture, cracking, causing of leakage of tubes. Hence the failure of boilers can come about by certain modes such as overheating, stress corrosion cracking (SCC), Creep, hydrogen embrittlement, flame impingement, sulphide attack, weld attack and dew point corrosion.

Fig 1.2 shows the different parts of a power station boiler which include the burners, air heaters primary super-heater, secondary super-heater, tertiary super-heater, steam drum, re-heater and an economizer. Recent type of high capacity boilers vary in various sizes, designs and configuration to suit a large range of applications and they have capacities of about 1000 to 10,000,000Ib/h (0.13 to 1260kg/s) with pressures ranging from l atm to above critical pressure[2].

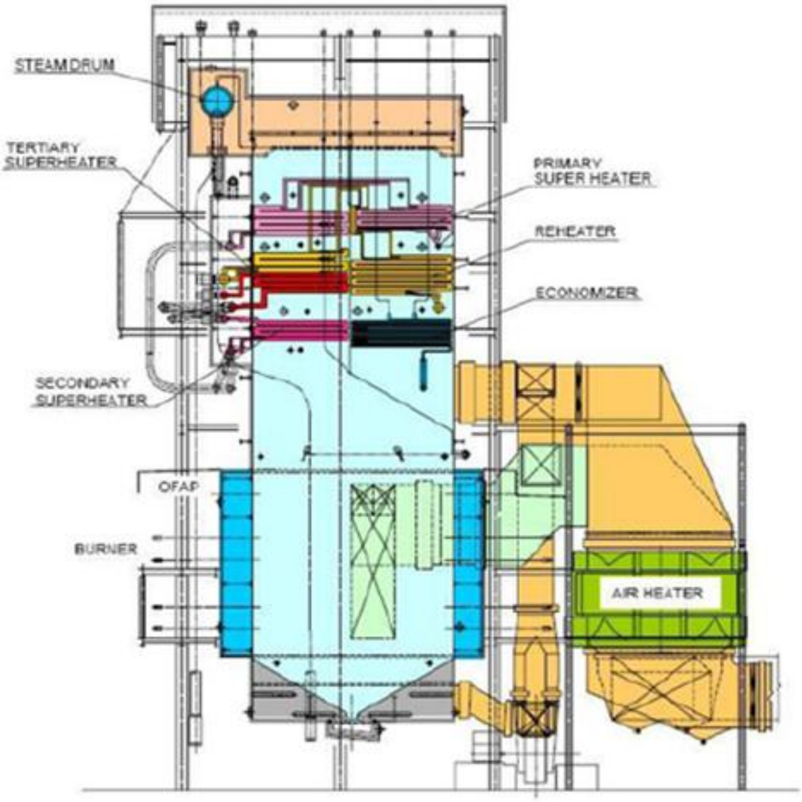

Fig 1.2 Power station boiler[15]

V. CONCLUSION

The main methods to reduce high temperature corrosion include:

- Use of low sulphur and low chlorine content coals
- By applying good combustion control to avoid reducing conditions at the furnace wall.
- Flue gas desulfurization in the recycled gases at lower the concentration of SO_2 and Cl species inside the furnace.
- Finally, the use of corrosion resistant tube materials (stabilized) or of coatings.

ACKNOWLEDGEMENT

I wish to acknowledge my project supervisor who inspired my urge conduct this research. Many thanks to my colleagues in Federal University, Wukari for their assistance in developing this research paper.

REFERENCES

[1]. **Beretta.G.P.** World Energy Consumption and Resource: An Outlook For the Rest of the Century. *www.exergoecology.com.* [Online] 07 11, 2012. [Cited: 07 11, 2013.] www.exergoecology.com/members/gianpaoloberetta/BerettIJETM.pdf.

[2]. *Corrosion of Superheaters and Reheaters of Pulverized Coal Fired Boilers II.* **Cain, C.A.N.** s.l. : Sciencedirect, TransASME J Engng for Power , 1961. 468-474.

[3]. *Distribution of Sodium, Chlorine and Sulfur in illinois Coals Removal by Cleaning and their Behaviour during Combustion* . **C.L.C.** s.l. : Sciencedirect, Centre for research on sulfur in Coal, 1986.

[4]. *The Role of Chloride in the Corrosion Caused by the Gases and Their Deposits* . **Culter, A.J.B.H.W.D., Laxton W.D, Stevens C.G.** s.l. : Sciencedirect, ASME Winter Annual Meeting Paper, 1970.

[5]. *External Corrosion of Furnace Wall Tubes: Part II Significance of Sulfate Deposit and Sulfur Trioxide in Corrosion Mechanism* . **Corey, R.C.C., B.J, Reid, W.T.** s.l. : Sciencedirect, 1945. 67, 289-302.

[6]. *European Refuse Fired Energy Systems Evaluation of Design Particles.* . **Engdahl, B.B.D.J.A.B.P.** 17, s.l. : Sciencedirect, US Department of Commerce , 1979.

[7]. *Deposit Corrsion During Oxy-Fuel Combustion* . **Gosia Stein Brzozowska, R.N., P.Vuklurd, J.Maire, G.Sheffknecht.** s.l. : Sciencedirect, 2010.

[8]. *The Case for Stoichiometric Combustion* . **T.D.B.** 1966, Sciencedirect.

[9]. *Fireside Slagging, Fouling and High Temperature Corrosion of Heat Transfer Surface Due to Impurities in Steam Raising Fuels.* **W.Bryers, R.** 1995, Sciencedirect.

[10]. *The Case For Stoichiometric Combustion.* **Manulesco.A.V.M.P.A.** 1966, Sciencedirect.

[11]. *An XAFS Investigation of the Form of Occurence of Chlorine in US Coals Proceedings of CRSCEPRI first International Conference on Coal.* **G.P, H.F.F.A.H.** 1991, Sciencedirect, pp. 23-61.

[12]. *Oxyy-Fuel Combustion of Pulverized Coal: Characterization Fundamentals Stabilization and CFD Modelling.* **Lei Chen, S.Z.Y., Ahmed F.Ghoniem.** 2012, Sciencedirect.

[13]. *Chlorine in illionis Coal* . **Gluskoter, H.J.A.R., O.M.** 1964, Illinois Geological Survey, p. 372.

[14]. *Fireside and Steamside Corrosion of Alloys for USC Plants.* **K.Natesan, J.H.P.** 2007, Sciencedirect.

[15]. **Hamza, K.** Power Station Technology. [Online] 2011. [Cited: 04 15, 2013.] blogspot.co.uk/2011/01/boiler-steamgenerator.html.