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High-temperature Oxidation of Fe-Cr Steels in Steam Condition – A Review

Tedi Kurniawan, Farah Alia Binti Fauzi, and Yuli Panca Asmara*

Faculty of Mechanical Engineering, University Malaysia Pahang, Pekan 26600, Pahang, Malaysia.
*Corresponding author: Email: tedikurniawan@ump.edu.my

ABSTRACT

The development of supercritical (SC) and ultra-supercritical (USC) power plants requires materials with better corrosion properties. Deep understanding on the oxidation mechanism in the boiler environment is one of the important factors to support this development. In this work, high temperature oxidation of Fe-Cr steels in steam condition is reviewed. Several mechanisms that explain the effect of water vapor in the oxidation behavior the steel were presented.

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1. INTRODUCTION

The International Energy Agency (IEA) reported in their World Energy Outlook 2015 (WOE2015) Factsheet: "Global Energy Trends to 2040" that energy demand in the world will increase for about one-third in between 2013 and 2040. This higher demand will cause the energy-related carbon dioxide emissions are to be 16% higher by 2040. In order to reduce greenhouse gas emission from this energy demand, IEA stressed on five energy sectors that need to be taken for further actions: improving energy efficiency in the industry, buildings and transport sectors; phasing out the use of the least-efficient coal-fired power plants; further boosting investment in renewables-based power generation technologies; gradually phasing out fossil fuel subsidies; and reducing methane emissions from oil and gas production. (Source: http://www.worldenergyoutlook.org) (Accessed: April 3, 16).

The IEA also reported on their South East Asia Energy Outlook 2015 that the energy demand in Asia will rose by 80% in 2040, following the regional economic growth that triple in size and also the rise of population by almost a quarter to 760 million. (Source: http://www.iea.org/publications/freepublications/publication/world-energy-outlook-special-report-on-southeast-asia-2015.html) (Accessed on April 3, 16). To meet the increase of energy demand, fossil fuels such as coal, natural gas, and oil are still the main sources for the primary energy demand.

Figure 1 shows the estimation of fuel share for energy demand in Southeast Asia from 1990 to 2040. The utilization of coal will be triple by 2040 or grow at 4.6% per year. By 2020, coal's share of primary energy demand will overtake natural gas, and by 2040 coal just surpasses oil to become the most consumed fuel. The utilization of fossil fuels has been a cause to the environmental problems since industrial revolution.

Figure 2 shows the carbon emission that estimated by the Carbon Dioxide Information Analysis Center (CDIAC) from 1750 until 2013. (Source: http://cdiac.ornl.gov/trends/emis/tre_glob_2013.html) (Accessed: April 3, 16). Since 1971, approximately 392 billion metric tonnes of carbon have been released to the atmosphere from the consumption of fossil fuels and cement production. It showed that, carbon emission started to grow by 1850 along with the beginning of manufacturing era.

Electricity power generation, industry and transportation are three primary sources of CO_2 emission. Based on the limitation of existing natural resources (fossil fuel) and also the needs of reduction on the effect of CO_2 emissions on global warming, has push forward the power industry to have a more efficient energy conversion processes and systems. Optimization on the combustion process, increasing the steam parameters, reducing the condenser pressure and improving the internal efficiency of the steam turbines are some of the well known levers for raising the overall plant efficiency. (Source: http://www.energy.siemens.com/us/pool/hq/power-generation/power-plants/steam-power-plant-solutions/coal-fired-power-plants/CGE09-ID34-Advanced-SPP-Cziesla-Final.pdf) The utilization of carbon capture storage (CCS) in the future power plant will also drastically reduce the greenhouse gas emission to the environment (i.e. atmosphere).

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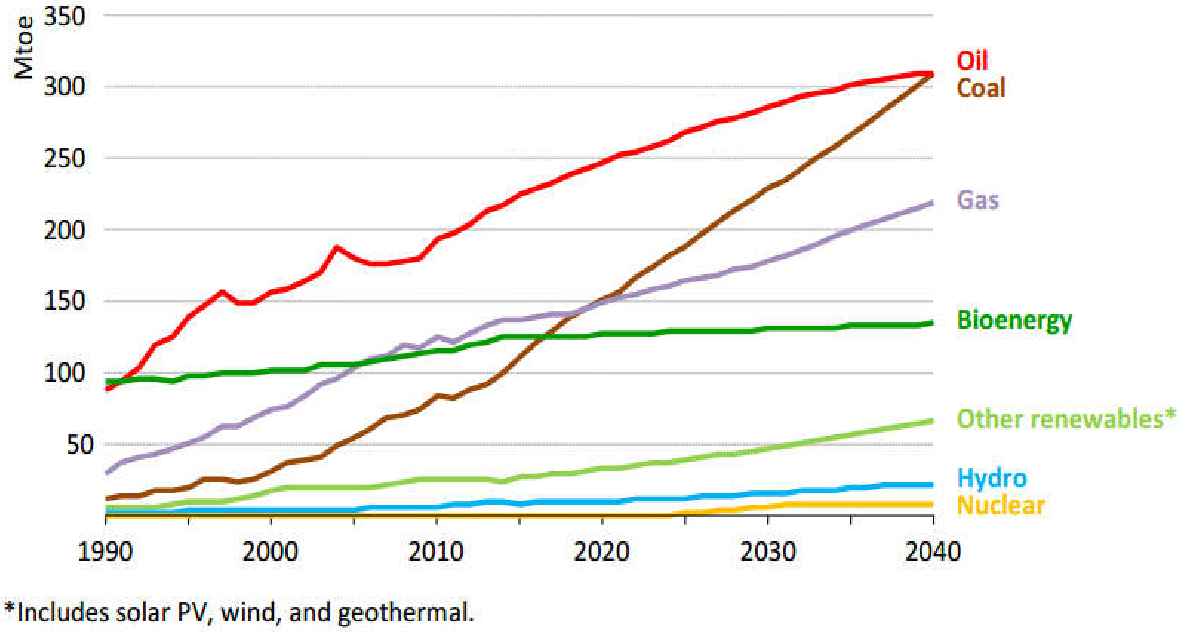

Figure 1. Primary energy demand in Southeast Asia, 1990-2040. (Source: http://www.iea.org/publications/freepublications/publication/world-energy-outlook-special-report-on-southeast-asia-2015.html)

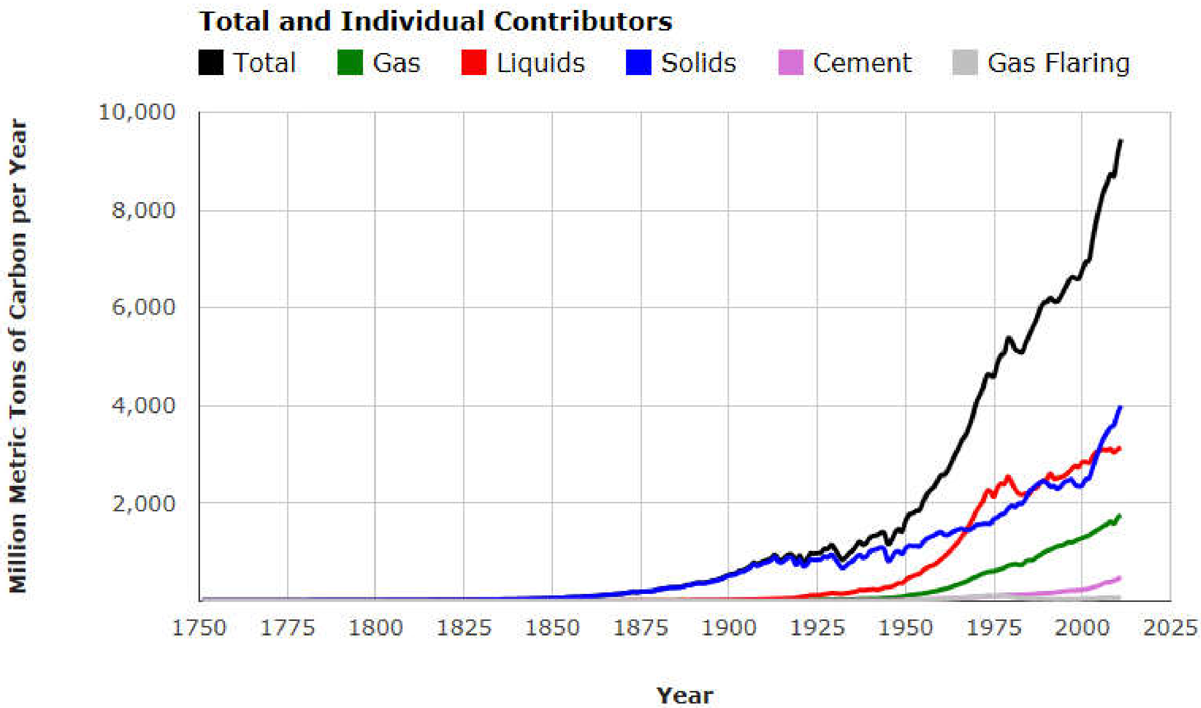

Figure 2. Estimation of global carbon emission from the consumption of fossil fuel and cement production in the world from 1970 to 2013 (Source: http://cdiac.ornl.gov/trends/emis/tre_glob_2013.html)

Fossil fuel power plant burns coal, natural gas, or petroleum to produce electricity. (McKendry, 2002) **Figure 3** shows the schematic illustration of fossil fuel power plant with coal as its fuel source. The heat from fossil fuel burning increases the temperature and the pressure of the steam that flow inside boiler tubes. This high pressure and high temperature steam spins the turbine that connected with generator to produce electricity. The steam condensed back into water, and pumped to the boiler to start the same process.

According to the Carnot cycle, the most effective ways for increasing the efficiency of power plant is by raising the maximum steam temperature. Therefore, the development of advance power plant, such as supercritical (SC) and ultra-supercritical (USC) power plants has been a main subject in many countries (Viswanathan *et al.*, 2005). This development is targeted to achieve higher efficiency of the power plant, so that the CO_2 emission can be reduced.

The steam pressure and temperature rose sharply since 1950 in order to achieve higher plant efficiency (Source: https://www.mhi.co.jp/technology/review/pdf/e401/e401012.pdf). One of the main reasons for this improvement was due to rapid developments of heat resisting materials, such as Fe-Cr ferritic and austenitic steels (Vishwanathan *et al.*, 2001). Currently, the maximum steam condition of the thermal power plant is about 650^oC. In the future, the steam condition is expected to be raised to 700^oC or higher (Viswanathan *et al.*, 2005).

Figure 4 shows the example of power plant improvement that is done by Mitsubishi Heavy Industry in Japan starting from 1910. This improvement was gained due to the advancement in boiler and turbine technology.

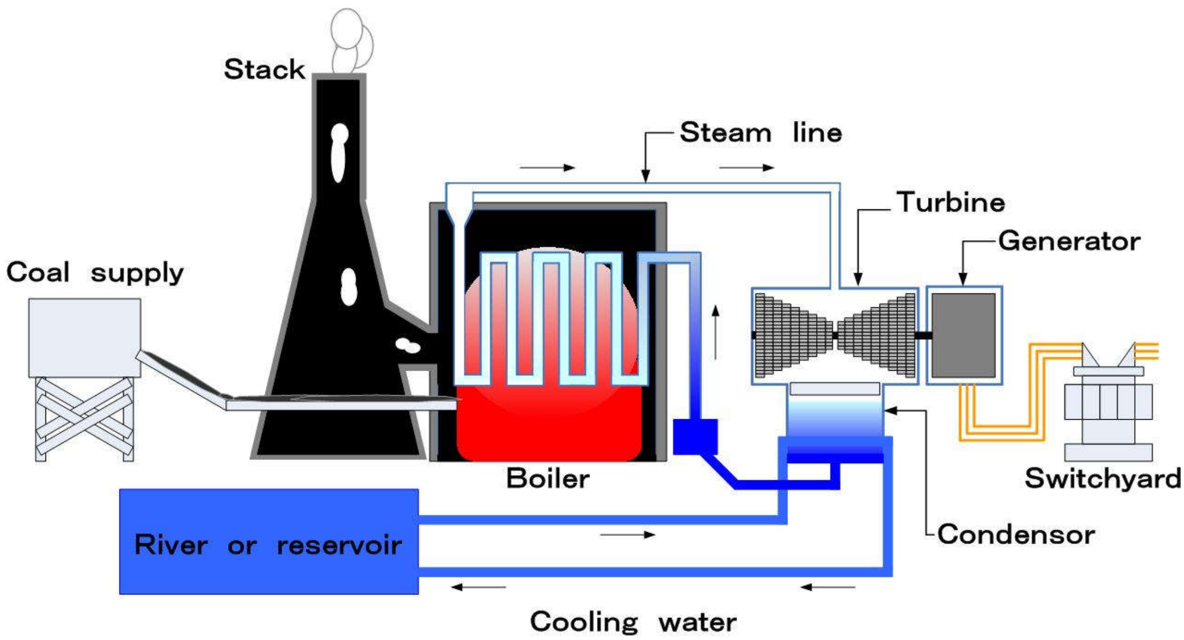

Figure 3. Schematic illustration of fossil fuel power plant. Adopted from reference (Kurniawan, 2013a)

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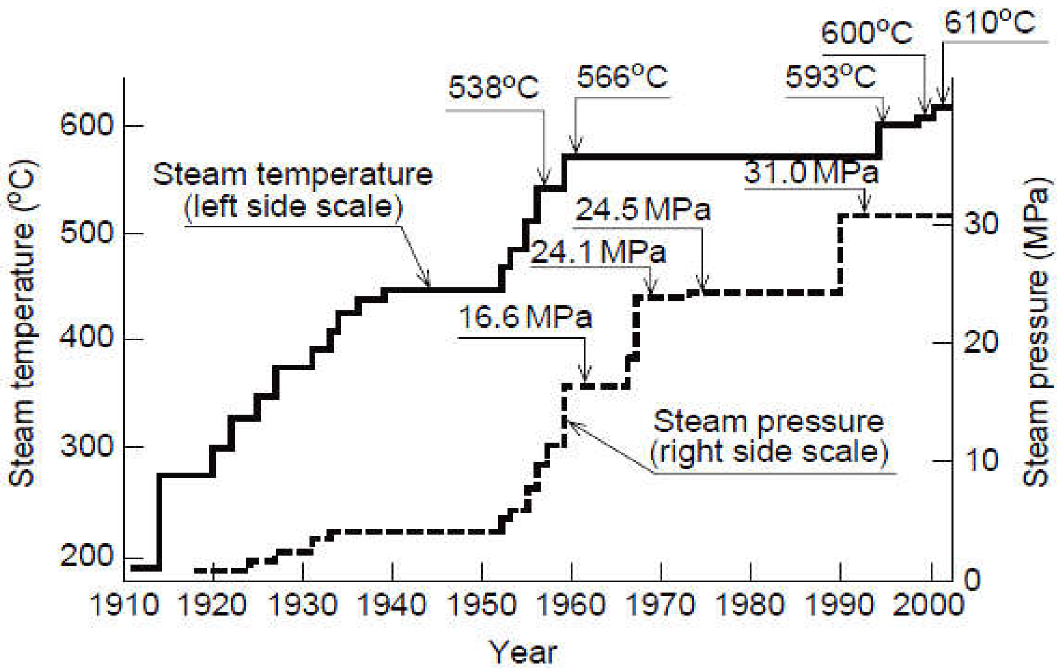

Figure 4. Improvement of stem condition of fossil fuel power plant in Japan (Source: https://www.mhi.co.jp/technology/review/pdf/e401/e401012.pdf)

2. OXIDATION BEHAVIOR OF IRON-CHROMIUM STEEL IN STEAM CONDITION.

Up to date, Fe-Cr ferritic and austenitic steels have been widely used as materials for superheaters and reheaters in fossil fuel power plants. Inside of boiler tube (either in the superheaters or reheaters) is exposed to produce high pressure steam (steam side), and the outer side is exposed to combustion gases (fire side). Many researches have reported that the morphology of the scale from the steam oxidation depends on the oxidation condition. In the steam condition, protective chromium oxide (Cr_2O_3) that is expected to be formed on the surface of the tube is retarded by the growth of non-protective oxide (Lepingle *et al.*, 2008 ; Żurek *et al.*, 2004). Ueda and Maruyama investigated a superheater tube (JIS STBA27) that had been exposed at 550-575°C for about 70,000 hour in power plant. (Ueda & Maruyama, 2005) Their results showed that the exposed tube consist of two layers of oxide scales, i.e. outer and inner scales. The outer scales consist of Fe_3O_4 and Fe_2O_3, and the inner scale consist of $(Fe, Cr)_3O_4$. Intermediate layer with a lot of voids was formed in between the inner and the outer scale, and this is possibly enhance the exfoliation of the outer scale (Kurniawan *et al.* 2013b; Ueda & Maruyama, 2005).

The formation of the non-protected oxides scale becomes a big concern in the power plants industry. There are three failures that are known, which are due to the steam oxidation (Ennis & Quadakker, 2007; Huang *et al.*, 2013):

(1) The thickness loss due to oxidation can increase stress in the tube wall, leading to premature creep failures.

(2) Lower thermal conductivity of oxide scale can reduce heat transfer across the tube wall, causing the increase of steel temperature and accelerate creep and corrosion processes.

(3) The exfoliated oxide scale can be accumulated inside tube bends, causing blockage of tubes. If the oxide particles enter the steam turbine, erosion in turbine blades and nozzles can happen.

As the operating temperature of power plant is expected to be increased, materials of boiler tubes will face more severe oxidations than that in the current condition. In order to achieve the target, deep understanding on the oxidation behavior of Fe-Cr steel is important. Its mechanisms also must be well-understood. This is because this information will provide valuable information, especially for the development of Fe-Cr steel. Thus, it can be applied at the temperature of above 700^{o}C.

3. MECHANISMS OF OXIDATION IN STEAM CONDITION

Steam oxidation provides the higher rate of oxide growth and more severe exfoliation (if we compare to dry oxidation). Therefore, understanding on the mechanisms on how the effect of water vapor on the oxidation of steel is very crucial for further developments of power plant.

Asteman *et al.* investigated the effect of water vapor concentration, temperature and flow rate on the oxidation behavior of 304L steel in O_2/H_2O environment (Asteman *et al.*, 2000; Asteman *et al.*, 2002). They found that the oxidation of 304L steel was strongly affected by chromium evaporation in a form of $CrO_2(OH)_2$. The loss of Cr element promotes the conversion of protective chromium oxide into a non-protective iron oxide. Higher concentration of water vapor (as well as higher flow rate and temperature) has a consequence to an early breakdown of the protective chromium oxide.

Ehlers *et al.* investigated the influence of water vapor on the oxidation of P91 steel at 650^{o}C (Ehlers *et al.*, 2006). They reported that the presence of water vapor promoted the formation of large amounts of porous Fe_3O_4, and developed a continuous gap in the scale leading to breakaway oxidation of P91. Water molecule (H_2O) enter into the scale interior and create hole/porosity by vaporizing the $Fe(OH)_2$ species.

Essuman *et al.* investigated the effect of water vapor on the oxidation of Fe-Cr alloys at 900^{o}C (Essuman *et al.*, 2007; E. Essuman *et al.*, 2008). They proposed that water vapor could allow Cr element to be internally oxidized in Fe–Cr alloys by affecting the solubility and/or the diffusivity of oxygen into the alloy itself. Indeed, this accelerated the internal oxidation has a profound effect on the phenomenon of "breakaway oxidation" in Fe-Cr alloys. In addition to the above information, they proposed that the way how to protect alloy. In order to form protective chromia layer, higher chromium content is required, in which this must be higher than the alloy used in dry oxidation. The proposed mechanism by Essuman was also supported by the work done by several researchers (Setiawan *et al.*, 2010; Ani *et al.*, 2009). They had measured quantitatively the oxygen permeability in dry and humid condition during internal oxidation of Fe-Cr alloys at 700^{o}C and 800^{o}C. They found that the oxygen permeability in steam condition increased by a factor 1.2-1.4 as compared to dry condition.

Nakagawa *et al.* reported that water vapor in steam side can affect the oxidation rate of the dry side (Nakagawa *et al.*, 2001; Nakagawa *et al.*, 2003). This was due to hydrogen permeation from the steam side to the dry side. Their result was in a good correlation to the work done by several research groups (Nakai *et al.* (Nakai *et al.*, 2005; Ueda & Maruyama, 2005). This phenomenon strongly indicated that hydrogen from water vapor dissolved through the boiler wall and induced the oxidation behavior in the outer side of the

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tube. The boiler wall consisted of steel as boiler material, and also oxide layer which grow on the inner and outer sides of the tube. The hydrogen permeability in steels and iron oxides can play a decisive role in the phenomenon. Kurniawan measured the hydrogen permeability through a single phase FeO and also single phase Fe_3O_4 under a constant oxygen partial pressure condition (Kurniawan, 2013a). He found that the hydrogen permeability in each oxide just only on order magnitude lower than that hydrogen permeability in iron (Kurniawan, 2013). He indicated that permeation of hydrogen through boiler tube with the co-existence of magnetite or wüstite scale can be determined by the hydrogen permeation of the steel, since the thickness of boiler wall will be more than one order of magnitude thicker than the thickness of the scale. In addition to the above study, Kurniawan also investigated the possibility of the oxidation phenomenon in the alloys consisting of various elements, such as combination of iron and palladium. (Kurniawan *et al.*, 2013b)

4. CONCLUSION

We reviewed high temperature oxidation of Fe-Cr steels in steam condition. This review is important since understanding on the mechanisms on how the effect of water vapor on the oxidation of steel is very crucial for further developments of power plant. Based on the literature reviews, we conclude that the oxidation rate of Fe-Cr steel in steam condition is higher that that of steel in the dry atmosphere. The formation of protective chromium oxide scale is retarded due to the formation non-protective oxide scale. Water vapor has a great impact on the oxidation behavior of Fe-Cr steel during high temperature oxidation in steam environment.

5. AUTHOR'S NOTES

The author(s) declare(s) that there is no conflict of interest regarding the publication of this article. Authors confirmed that the data and the paper are free of plagiarism.

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