Investigation on control in oxide scale formation and prevention of peeling off in ultra-supercritical unit

Tianyu Zhang¹, *, Xin Zhang¹, Xiufeng Shi², Zhenning Zhao¹

¹North China Electric Power Research Institute, Beijing 100032, China
²Henan Jingneng Huazhou Thermal Power Co., Ltd., Huaxian 456400, China

*Corresponding author: zzzttttyy456@126.com

Abstract. It is a common problem that oxide scale of boiler tube peels off in supercritical unit. In recent years, many boiler tube burst accidents have been caused by oxide scale peeling off and blocking. Therefore, the analysis and research of oxide scale is of great significance. In order to control the occurrence of such accidents and reduce the economic losses of thermal power plants, this paper mainly analyzes the factors influencing the oxide scale growth rate, peeling off condition and puts forward corresponding prevention and treatment measures.

1. Influencing factors of oxide scale growth rate

1.1. Type of steel
As investigated in other literature, oxide scale of ferrite and austenitic steel shows different formation and contracture. More than 20 kinds of ferrite steel, austenitic and nickel-based alloys have been placed in flowing steam at 650 °C for 4000 hours in the relevant literature [1]. The experimental results show that the oxidation resistance of ferrite is far less than that of chromium containing alloy steel, while the oxidation resistance of austenitic steel and nickel-based alloy steel is superior. The field operation data show that the thickness of oxide scale formed by ferrite steel is about 60 ~ 106um, while that of austenite is about 20 ~ 25um after 10149 hours of operation at 545 ~ 565 °C.

![Fig 1. Comparison of oxide scale formation growth rate in different type of steel [2].](image-url)
For austenitic steel, the higher the Cr contents, the stronger the oxidation resistance. On one hand, the stroke of spinel inner layer with higher Cr content will reduce the diffusion rate of metal ions; on the other hand, the higher Cr content is easy to form protective Cr$_2$O$_3$ film at the interface between oxide film and matrix. The content of Cr in HR3C was the highest and its antioxidant activity was the highest.

1.2. Temperature
Temperature has an important effect on the growth rate of oxide film. With the increase of temperature, the oxidation weight gain of austenitic steel Super304H increases. In the test environment [3], the oxidation weight gain at 600 °C is about twice that at 550 °C.

1.3. Time
Through the detection and statistics of oxide scale during boiler operation, it can be seen from the curve of oxide skin formation thickness and operation time of austenitic steel that the formation rate is fast in the early stage, showing a linear relationship (linear oxidation stage), and the growth rate gradually decreases in the later stage, showing a slow growth rate, showing a parabolic relationship (parabolic oxidation relationship).

1.4. Application of feedwater
According to EPRI of the United States, the generation of oxide scale in superheater pipe has nothing to do with water condition. However, from the investigation of superheater tube burst in China, the dissolved oxygen content has a significant impact on the production and violence of superheater oxide scale. It is found that the oxide scale without oxygen stripping problem is less, and it is easy to burst after adding oxygen. During maintenance, it is found that the oxide scale accumulated in the pipe generation is relatively thick, such as Huaneng Qinbei and Guohua Taicang. In addition, there are some power plants due to improper oxygen addition, resulting in high temperature heating surface oxide peel accident, such as Jingneng Ningdong, etc. According to the corresponding calculation, the proportion of oxygen decomposed from water is very small compared with the added oxygen, so the way of water supply plays a decisive role in the oxygen content in water. The important point of monitoring the oxidation rate of heating surface is to monitor the hydrogen content in the water quality report. When the value exceeds 10ug / L, it indicates that there is a strong steam oxidation reaction.

2. Mechanics of oxide scale peeling off
The properties of oxide scale include thermal expansion coefficient, elastic modulus and so on. Therefore, in the process of temperature change, the oxide scale will be subjected to tensile and compressive stress due to the existence of constraints, which will lead to peeling.

Fig 2. Thermal expansion coefficient of metal and oxide scale.
In fact, the corresponding mathematical model of oxide scale peeling (or failure) caused by tensile stress and compressive stress is different. For example, the oxide skin peeling caused by tensile stress is mainly reflected in the oxide skin through cracking, and the tensile strain is mainly evaluated by the surface fracture energy of oxide skin; while the failure under compressive stress is reflected in the shear energy of oxide skin surface area. Therefore, the failure and peeling of oxide scale is the comprehensive effect of the stress of oxide scale matrix system and the influence of environment (steam flow rate, pressure, pipeline material) and other factors. It can be seen from the figure below that the oxide scale is about thick, and the stress level required for peeling is smaller. For stainless steel, the critical peeling thickness is 100 ~ 150μm; for chromium molybdenum steel, it is 200 ~ 500μm.

2.1. Peeling process of oxide scale
For ferritic steels, a double-layer oxide scale is initially produced on the substrate surface under high-temperature steam environment. With the running time going on, the double layer structure changes into multilayer structure, and the oxide skin in the initial outer layer is easy to appear through cracks. The multilayer whole oxide skin completely peels off at the interface between the substrate and oxide skin, and the oxide scale peeling fragments also show multi-layer structure. The peeling of T91 oxide scale is different, and multi-layer oxide skin will not be formed.
For austenitic steel, the oxide scale structure is generally double-layer, just like ferrite steel. The outer layer is rich in Fe, and the inner layer is composed of Cr Fe spinel, which can play a good anti-oxidation protection, but the local thickness is thin and uneven (except for high Cr content steel). With the increase of time, the interface of the inner oxide skin is empty, and the content of Fe$_2$O$_3$ in the outer oxide skin increases. During the cooling process of the heating surface, the outer oxide skin is subjected to compressive stress, and the development of the cavity chain between the inner and outer layers will cause the outer oxide scale to peel off in large area, and the inner layer will not fall off.

**Fig 5.** Actual SEM figure of oxide scale peeling [5].

### 2.2. Determination of peeling degree of oxide scale

The degree of oxide skin peeling off of superheater tube is generally evaluated by the area of oxide skin stripping in the whole heating surface area (unit:%) or the peeling quality per unit tube length (unit: g / M). The latter has more convenient application in engineering. It can be divided into mild, light, medium, severe and very serious, and the corresponding values are < 3, 3 ~ 30, 30 ~ 60, 60 ~ 125 and > 125g / m, respectively.

### 3. Key elements of preventing oxide scale

#### 3.1. Temperature control

In addition to controlling the over temperature, preventing the rapid formation of oxide scale and avoiding the sudden change of temperature are the conventional factors that lead to oxide scale problems. In addition to the above factors, different wall temperature changes on oxide scale shedding research experiments show that for the high temperature heating surface with TP347H and T91, under the condition of conventional oxide skin thickness, the critical temperature of oxide skin shedding is 450 ~ 480 °C (corresponding to the stage with large difference in thermal expansion coefficient), so it is necessary to avoid repeated or long-term stay in this temperature section during the start-up and shutdown of the unit. At the same time, steam soot blowing is also a cooling effect for the heating surface pipe wall in an instant, so the drain temperature of soot blowing can be appropriately increased (e.g. to 300 °C). In the initial stage of start-up, the temperature change rate should be controlled reasonably and the secondary desuperheating water should be avoided as far as possible.

#### 3.2. Chemical cleaning

At present, the main methods to control the oxide scale are by-pass purging and pipe cutting purging, but in fact, chemical cleaning is an effective method to completely remove the oxide layer on the inner wall of the pipe. Of course, compared with water wall, pickling of superheater and reheater is not very common. Firstly, there are no mandatory regulations on Pickling of superheater and reheater system in China. Secondly, the heating surface of π - type furnace has U-shaped bend due to the hanging of heating
surface. Conventional pickling solution will remain at the bottom, resulting in intergranular corrosion of stainless steel. However, it is very inconvenient and dangerous to use HF which does not produce intergranular corrosion.

3.3. Optimize start and stop plan
According to the model of oxide scale growth and peeling, more frequent start-up and stop can make smaller scale peeling and reduce the risk of blockage. Less start and stop frequency and longer continuous operation time lead to thicker oxide scale. If the shutdown interval is long, there is a high risk of blockage caused by a large-scale peeling. At the same time, with the passage of time, the tendency of oxide scale accumulation in each shutdown is reduced, which is the reason why the protective layer gradually forms. Therefore, it can guide the unit to gradually extend the start-up and shutdown interval from the start-up of high-frequency start-up and shutdown, so as to control the risk of blockage and tube burst caused by oxide skin peeling.

4. Conclusion
The mechanism of oxide scale growth, peeling and flow, problem analysis and related accident prevention and control are interdisciplinary, difficult to reproduce and online evaluate the experimental conditions, and even there is no consensus on some issues (such as oxygenation of water supply). In this paper, the growth rate, peeling mechanism and process of oxide scale are briefly introduced. The description of the problem is inevitably not rigorous, even inconsistent with the objective facts. Therefore, this paper is just a small background to introduce a large-scale problem of oxide scale, and provide ideas for readers' further research and problem analysis.

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