

Application of High Steam Temperature Countermeasures in High Sulfur Coal- Fired Boilers

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ABSTRACT

Achieving higher plant efficiency in thermal power plants is one of the major global challenges from the viewpoint of reducing carbon dioxide emission levels, particularly in coal-fired boilers, irrespective of the type of coal being burned. There are a number of ways to improve plant efficiency. Upgrading the turbine plant cycle by utilizing higher steam temperatures and pressures or by using a double reheat configuration are two effective and widely used methods. The double reheat configuration was used in supercritical units when they were first introduced. However, the single reheat with a high steam temperature is preferable rather than double reheat configuration because of the capital cost benefit. Furthermore, utilizing water attemperation to simultaneously control the 1st and 2nd stage reheat steam temperature should be avoided even if a fluctuation in heat absorption occurs due to slagging phenomena and /or change in the coal properties. In recent times, it has been possible to increase the steam temperature in coal fired supercritical plants without too much of a cost impact. The temperature has already been increased to 1112°F for main steam and 1130°F for reheat steam. However, this application is only for fuels having a sulfur content of less than 1.2%. For high sulfur coal, special provisions have to be made for high temperature corrosion on heating surfaces located in the high temperature zone as well as for sulfidation on the furnace water wall.

It has been proved that material containing high chromium has a beneficial effect on controlling high temperature corrosion. A high strength 25Cr-20Ni austenitic steel has been specially developed for such high temperature steam applications. Utilizing this material provides a cost effective solution to the demands of burning high sulfur coal in

supercritical boilers using high steam temperatures, and ensures good life cycle capability.

In this presentation we would like to provide our design considerations and the measures we apply for supercritical plants with steam temperatures up to 1100°F, burning coal with a sulfur content in excess of 4%.

1. Introduction

Reducing carbon dioxide (CO₂) emissions, especially for coal-fired units, is the key issue for environmental protection on a global basis. To achieve this, a high plant efficiency is essential for any grade of coal. A high steam temperature is the single most cost effective way to realize efficiency benefits among several methods in turbine and boiler. Until the 1980's, oil had been the primary fuel for thermal power plants. However, after two oil crises in 1973 and 1978 in Japan, fuel has shifted to coal and gas. Since around the mid-1990's, Babcock-Hitachi K. K. (BHK) has followed a steady program of steam condition upgrades for coal-fired units in Japan and now the maximum condition has reached 3600psig/1112°F/1130°F. The quality of imported coals to Japan, the maximum sulfur content of which has been and will be around 1.2% at the highest. Thanks to this, while it causes a relatively high running cost, superheater and reheater tubes are almost free from high temperature corrosion under the severe steam condition. However, as far as coals would be the primary fuel for future boilers, the ever lasting request to cut the electricity generating cost will naturally promote the utilization of coals which can be supplied locally or are lower in price than low sulfur coal. Aiming at a steam condition at 1100°F for coal-fired boiler projects in the United States, we are now focusing on high sulfur coal as promising fuel for the improvement of total plant performance, because our extensive material study and experiences of high sulfur fuels other than coals have confirmed that corrosion problems associated with high sulfur coal and the advanced steam condition can be well controlled by selecting appropriate high strength materials, utilizing an advanced burner design/combustion technology, and applying an additional corrosion protection if necessary. This paper describes the features necessary for reliable boiler design of 1100°F class supercritical pressure units.

2. Upgrading Steam Parameter

In 1967, Anegasaki unit 1 of Tokyo Electric Power Co., a 600MW oil fired boiler with 3500psig/ 1000°F/ 1050°F, became the first supercritical pressure boiler with single reheat, to go into commercial operation in Japan. Since then, almost all of the large capacity utility boilers have been supercritical pressure units. In those days, double reheat type supercritical units were also introduced. However, because of their higher capital cost and rather complicated reheat temperature control, the single reheat type boiler configuration has been preferred.

A history of the upgrading of steam conditions of domestic supercritical boilers supplied by BHK is shown in Figure 1^[1]. Over the last two decades, we have developed a number of advanced boiler technologies for high efficiency coal-fired plants, including in-flame NOx reduction technology, and the use of advanced steam parameters. As the results of this ongoing development work to reduce fuel costs and control CO₂ emissions without significant cost impact, we have introduced a 1,050 MW coal-fired sliding pressure BHK-type Benson boiler with advanced steam conditions of 3600psig/1112°F/1130°F for the Tachibana-wan Unit No. 2 of Electric Power Development Company Ltd. These steam temperature increases were achieved based on the development of high strength materials and the appropriate manufacturing technologies such as forming and welding, as well as highly sophisticated boiler design. As mentioned above, the sulfur content of coals used in Japan is not high. However, recently developed materials for high steam temperature applications can have excellent corrosion resistance against high sulfur coal firing, as is described in the next section. We are able to utilize our experience with difficult residual oil and oil cokes, which can contain sulfur as high as 8%.

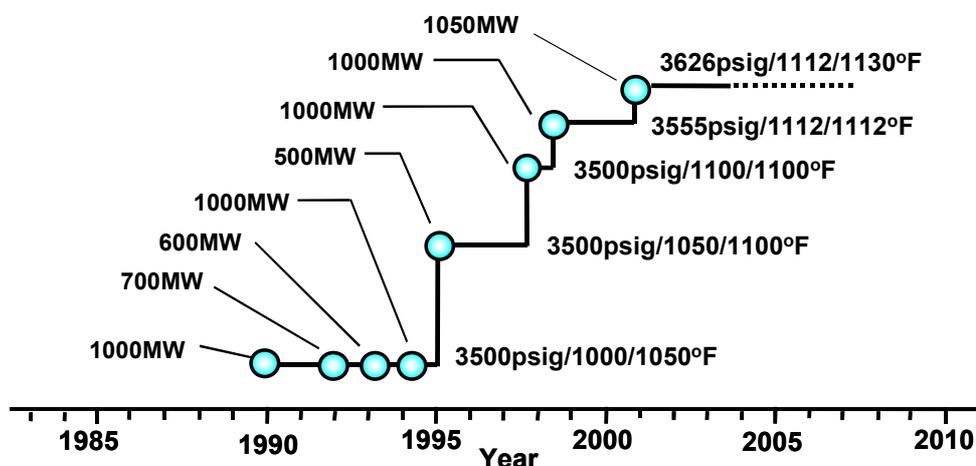


Figure 1. Improvement of Steam Conditions for coal fired plant in Japan

3. Material Development for Advanced Steam Condition

3.1 Austenitic Stainless Material for Superheater Tubing

The main reason that such severe steam conditions can be achieved is due to the ongoing development work on high strength materials at a competitive price. Performance of those materials is shown in Figure 2. Comparing the conventional austenitic stainless steels such as A213TP321H, the advanced 18Cr-8Ni grade such as A213UNS S30432 (18Cr-9Ni-3Cu-Cb-N), or higher chromium austenitic stainless steels such as NF709 (20Cr-25Ni-1.5Mo), or A213TP310HCbN (25Cr-20Ni-Cb-V), show allowable stresses at a metal temperature of 1200°F, almost twice that of the conventional grades. As is described later, for high sulfur coal firing, high chromium austenitic stainless steels are the favored materials.

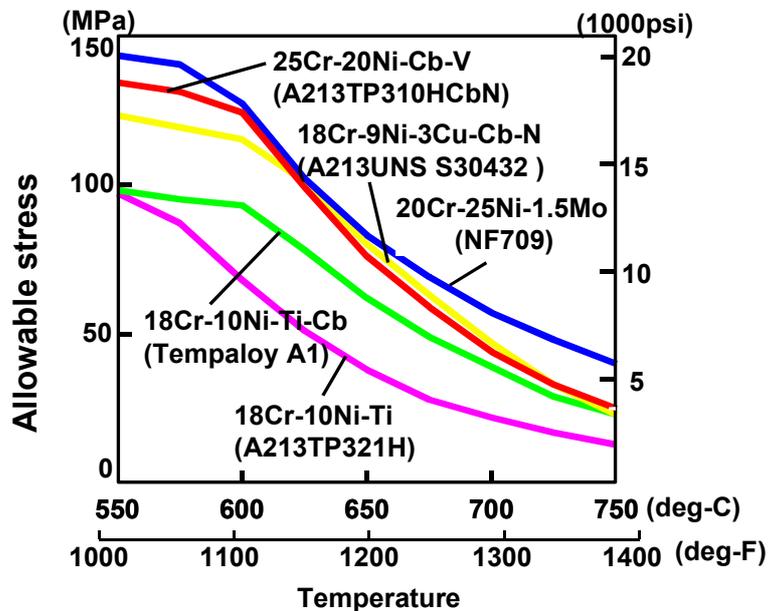


Figure 2. Comparison of Allowable Stresses between Conventional and Advanced Stainless Steel Tubes

3.2 Ferritic Material for Header Section Component

The Modified 9Cr1Mo steel (P91) was developed by Oak Ridge National Laboratory in the USA as the first innovative high strength ferritic steel. P91 has been widely used in Japan since the late 1980's for main steam temperatures of 1000°F through 1112°F. There has been a significant effort in Japan to produce higher strength ferritic materials than P91, and tungsten bearing high strength ferritic steels, such as P92 (NF616) and

P122 (HCM12A) have been developed. These new steels have already been used in some recently constructed boilers and will be used much more on forthcoming projects.

4. Subjects for the Application of High Sulfur Coal

The major corrosion phenomena of high sulfur coal-fired boilers are caused by sulfur compounds as combustion products. For boilers with advanced steam conditions, especially in the superheater and reheater, external hot corrosion and internal steam oxidation are the most significant. Also, water-wall corrosion is another issue for high sulfur coal-fired boilers. Levels of corrosion damage, which would be accelerated by using high sulfur coals, are summarized in Table 1.

Table 1. Corrosion Damage and Countermeasures in High Sulfur Coal Fired-Boiler

Location	Corrosion Type	Phenomenon	Countermeasures
SH RH	External: High Temp. Corrosion Internal: Steam Oxidation	Corrosion by low molten Coal: Alkali Iron Sulfate Oxidation caused by steam	a. Thermal spray b. High chromium material c. Composite tube d. Additives
Furnace Water Wall	Sulfidation Corrosion	Corrosion loss caused by hydrogen sulfide in reducing atmosphere combustion gas, and iron sulfide in deposit ash	a. Improvement of combustion condition b. Thermal spray c. Clad welding
Burner	Oxidation/ Sulfidation	Oxidation or sulfidation at high temperature (>1800°F)	a. Heat resistance material
Air Heater	Low Temperature Corrosion	Sulfuric acid dew point corrosion	a. High cold end metal temperature b. Corrosion Resistant material

For high temperature corrosion of superheater and reheater tubes, the metal temperature, the sulfur content in coal and the chromium content of material to be used are the most important factors that must be considered seriously in supercritical boiler designs. The high temperature corrosion of superheater and reheater tubes in coal-fired boilers is normally caused or accelerated by molten salts consisting of sodium-potassium-iron tri-sulfates $(Na,K)_3Fe(SO_4)_3$ in deposit ash. Figure 3 shows a schematic illustration of the progress of such high temperature corrosion during operation.

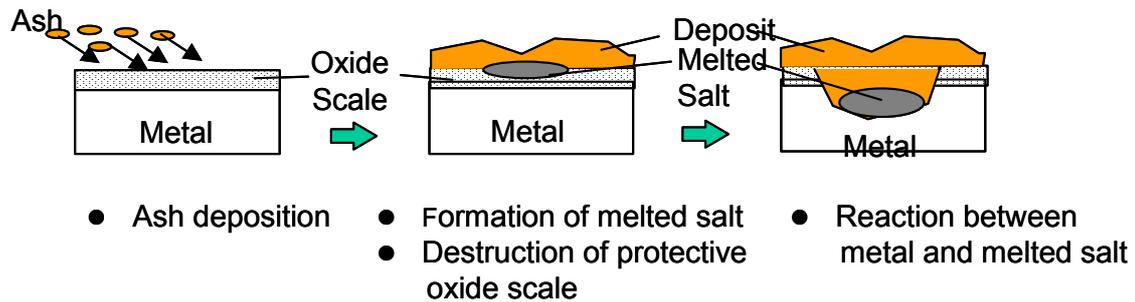


Figure 3. Illustrating Mechanism of High Temperature Corrosion

For furnace or water-wall corrosion, the key factors are the hydrogen sulfide (H_2S) concentration near the wall, the metal temperature, the sulfur content in coal and the stoichiometric ratio at the burner zone. Depending on the atmosphere and operation condition, various types of scales and deposits can form on the furnace wall as shown in Figure 4. They often consist of pure iron oxide, or a mixture of iron oxide and iron sulfide or nearly pure iron sulfide^[2]. Although the basic corrosion mechanism is the sulfidation of iron, it is further influenced not only by the structure and composition of scale and deposit, but also by the surrounding gas compositions.

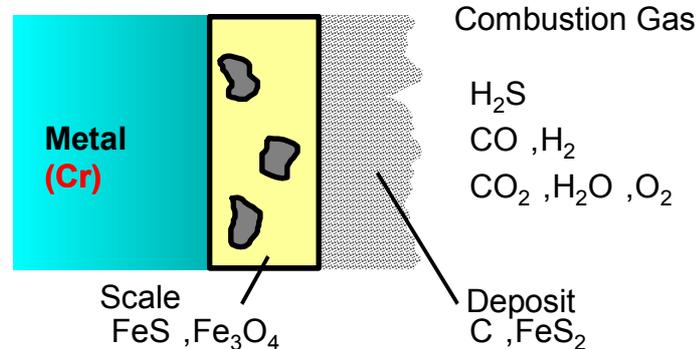


Figure 4. Illustration of Hydrogen Sulfide Scale & Deposit

5. High Sulfur Coal-Fired with 1100deg-F Steam Temperature Boiler Design

5.1 Countermeasure for High Temperature Corrosion of SH/ RH

As one of the key factors in high temperature coal ash corrosion, we studied extensively the effect of the sulfur dioxide (SO_2) content in combustion gas. The SO_2 content in the combustion gas is almost proportional to the sulfur content of the fuel. Thus, the effect of sulfur in coal can be compared to the effect of SO_2 content in the combustion gas. Figure 5 is a typical equi-corrosion loss map for 18Cr8Ni austenitic stainless steel as a function of SO_2 content and temperature. This data was obtained in

a laboratory test using the standard corrosion mixture (SCM: 1.5molNa₂SO₄-1.5molK₂SO₄-1.0molFe₂O₃) under the atmosphere containing various amounts of SO₂. The corrosion rate (mm/10y) shown in Figure 5 was deduced from weight loss data (mg/cm²) of 18Cr8Ni stainless steel, assuming a linear rate law. The corrosion rate is affected by SO₂ content above 0.15% at around 1200°F for 18Cr8Ni stainless steel. The corresponding sulfur content (indicated at the top line of Figure 5) to this SO₂ content in the gas is around 2%.

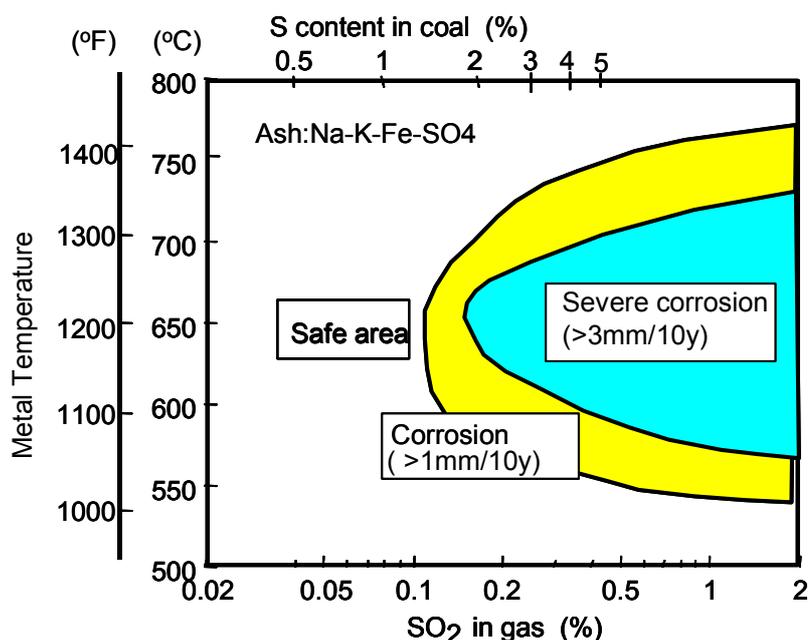


Figure 5. Corrosion Map of 18Cr8Ni Stainless Steel after 10 years

Figure 6 shows the relationship between the chromium content of various boiler tube materials and corrosion loss in an accelerated corrosion test using SCM with 1% SO₂ in gas. While the effect of chromium content on corrosion loss is not much at low metal temperature condition, dependency of the chromium content at high temperature region is significant. It is clear that the materials containing higher chromium has an excellent resistance against high temperature corrosion. Especially the material with chromium content of 25% and over is promising to restrain the corrosion rate in a reasonable level. The high strength 25Cr-20Ni stainless steel, A213TP310HCbN (25Cr-20Ni-Cb-V), newly developed for high steam parameter application, has been used over ten years in superheater and reheater for power boilers as well as industrial or refuse-fired boilers. Utilizing this type of material enables high steam temperature supercritical boilers to operate effectively using high sulfur coal without penalties in component life,

or in having a prohibitively high capital cost.

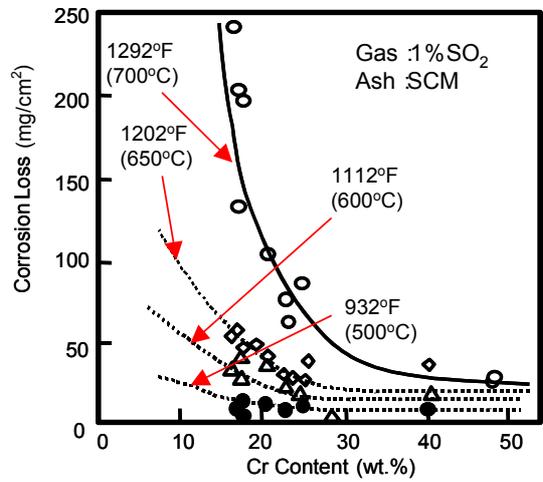


Figure 6. Relationship between Cr and Corrosion Loss

Based on the test results shown above, we have established guidelines for material selection and tube metal temperatures for burning fuels with a sulfur content of 4% or more (not only coal but also oil or residues) as shown in Figure 7.

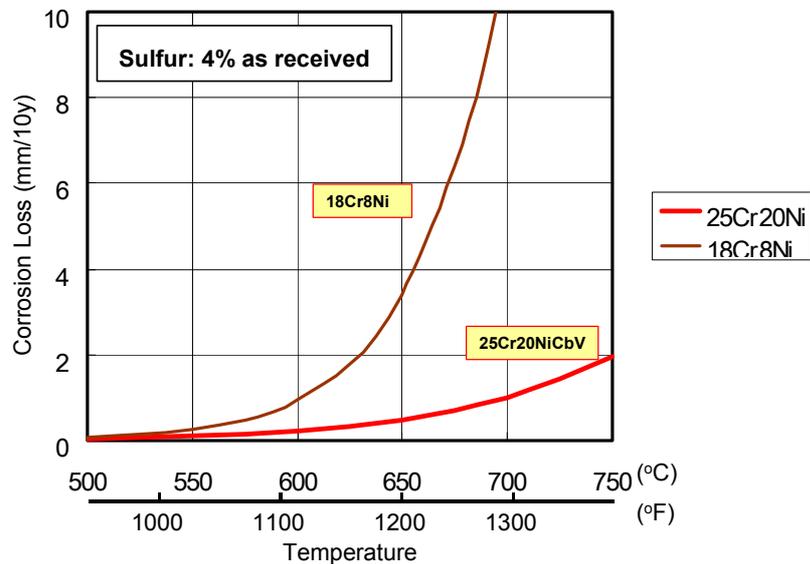


Figure 7. Expected Corrosion Loss in Thickness vs. Metal Temperature

Using this data, we can predict the loss in thickness versus plant life as shown in Figure 8. In our predictions, the losses were assumed to follow a linear law, which would result in an overestimated but ultimately safe life expectancy. As is seen, the developed 25Cr-20Ni is considered to be practically applicable to steam temperatures up to 1100°F with a reasonable corrosion allowance.

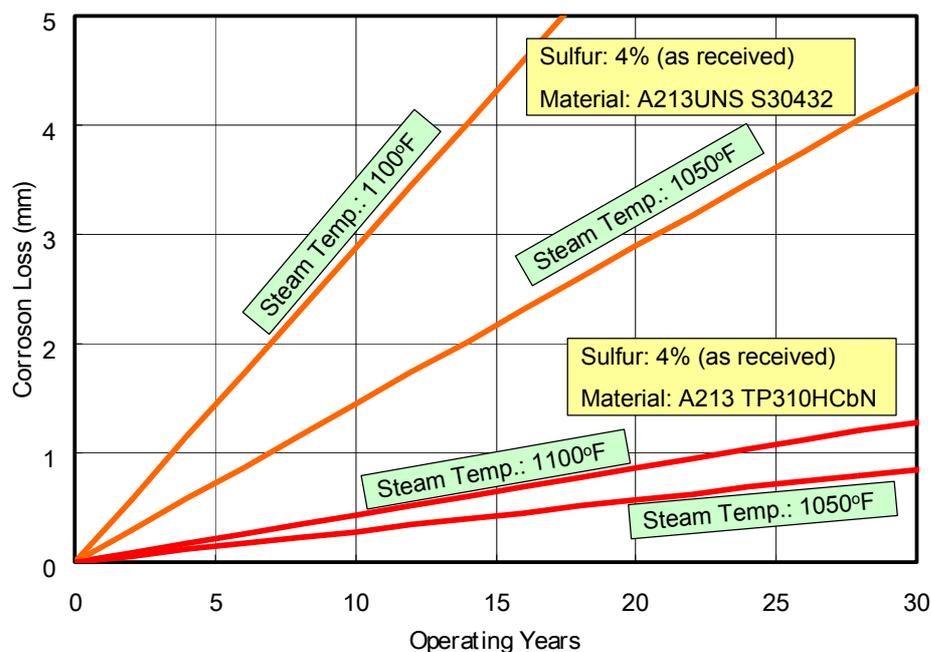


Figure 8. Expected Corrosion Loss in Thickness vs. Steam Temperature

5.2 Steam-side oxidation

Another material issue for high temperature applications is steam-side oxidation of tubes. When the thickness of the steam oxidation scale grows significantly, it causes the hindrance of heat transfer. This situation results in many difficulties, i.e. a serious increase in outside tube metal temperature, the clogging or blockage of tubes and erosion damage to turbine blades by exfoliated oxide scale. The application of fine grained materials and/or high chromium materials is not satisfactory for preventing the growth of oxide scale as shown in Figure 9. However, the internally shot blasted material produces only a fairly thin oxide scale (several micron meters) up to 1300°F. Our experience with shot blasted SH and RH tubes in domestic boilers have been successful over 25 years, and their performance will last longer according to our periodic inspections. Thus we are confident that this shot-blasting can minimize the problems caused by steam oxide scale even for advanced steam conditions.

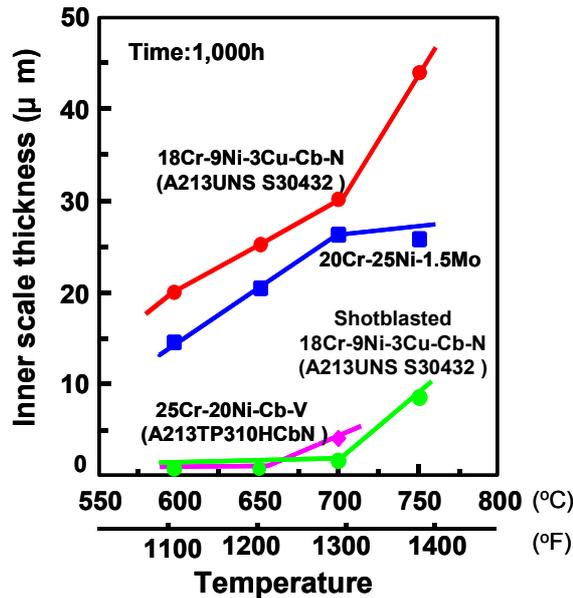


Figure 9. Behavior of Oxide Scale

5.3 Prevention of Water Wall Corrosion

Water wall corrosion is caused by H_2S under a reducing atmosphere at the burner zone in the furnace. To prevent it, we have developed several countermeasures. Those are moderate two-stage combustion, side stream airport system and thermal spraying of corrosion resistant material on the tube surface.

(1) Moderate Two Stage Combustion

It is well known that two-stage combustion is capable of reducing NO_x generated at the burner zone. This could result in a reducing atmosphere around the burner, and consequently the generation of H_2S will become significant. The H_2S concentration depends on the stoichiometric ratio at the burner zone. We studied the influence of the stoichiometric ratio under the two-stage combustion on the generation of H_2S in our own test furnace. Test results using 4% sulfur coal are shown in Figure 10, and demonstrate that H_2S concentration drastically increases when the stoichiometric ratio is below 0.9. This increase in H_2S concentration can cause acceleration of water wall corrosion. Therefore, there will be an appropriate value of stoichiometric ratio in terms of suppression of H_2S and NO_x generation, depending on the design parameters such as water wall tube life or adoption of aftertreatment of combustion gases, such as selective catalytic reduction (SCR) of NO_x . Our philosophy, which is well supported by our experience on supercritical boilers, is that the value of stoichiometric ratio should be kept above 0.9. We call this Moderate Two Stage Combustion.

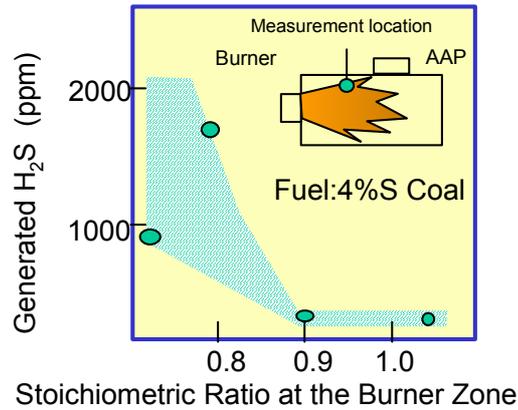


Figure 10. Influence of Stoichiometric Ratio against H₂S Generation

(2) Side Stream Air Port (SSAP)

H₂S generation is greatly affected by a complicated stream of gases around the burner area. Reducing atmosphere is easily formed in the burner zone of a boiler furnace and thus, this region is quite susceptible to H₂S corrosion. However, this type of corrosion damage is not only limited to the area around the burner zone, but also expands to a wider area. This latter corrosion damage is often caused by the impingement of reducing flames on sidewalls. To prevent the impingement of flame on the side-walls, we developed a novel side stream air injection system (SSAP) in which high velocity air is supplied from SSAP to furnace along the sidewalls as shown in Figure 11. This can make the atmospheric pressure along the sidewall positive relative to the center of the furnace.

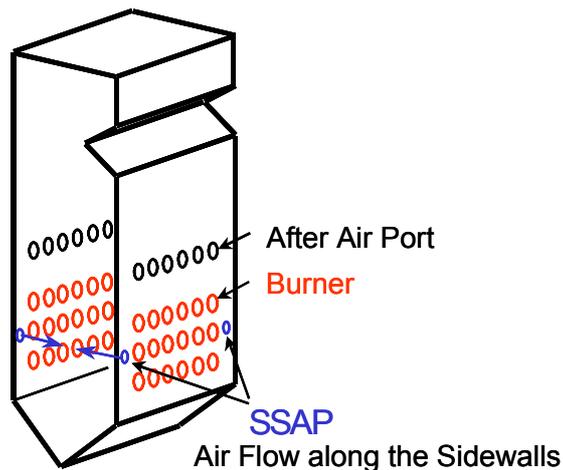


Figure 11. Location of SSAP

The effect of the SSAP on the H₂S generation inside the furnace was analyzed by a powerful computer code developed by Hitachi Ltd. A simulation result with and without the SSAP for a 1000MW coal fired boiler is shown in Figure 12. As can be seen, the SSAP system drastically reduces the H₂S generation along the side-walls. This invention will contribute to the reduction of corrosion damage and related maintenance work on the water-wall. Furthermore, the SSAP is expected to reduce carbon monoxide and unburned carbon in fly ash.

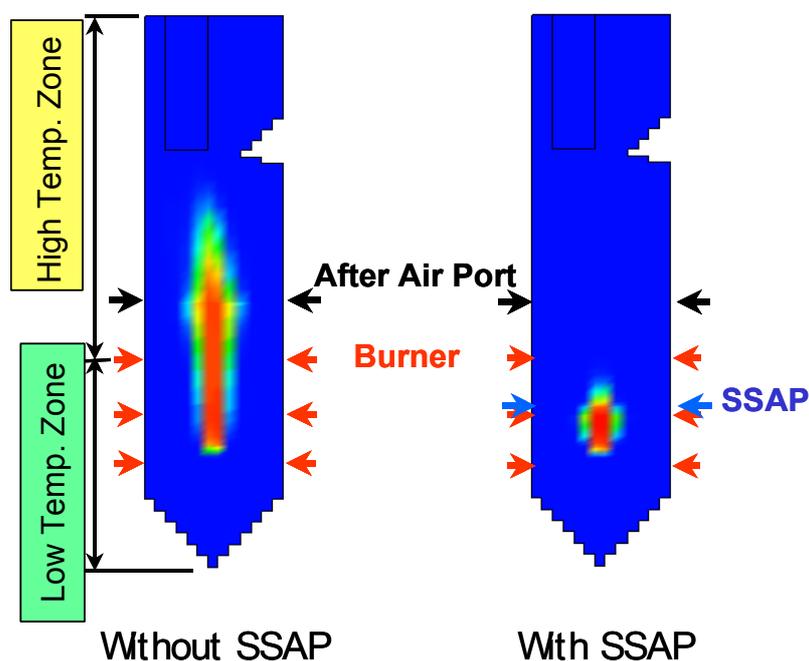


Figure 12. Concentration of H₂S near Side Wall

(3) Thermal Spraying of Corrosion Resistant Material

When possible severe corrosion damage on the water-wall (tubes and membranes) is expected, it is desirable to apply a corrosion protection on the water-wall. The current methods for typical corrosion protection are an overlay welding of a corrosion resistant material, a use of composite tubes (austenitic stainless steel outside/ ferritic steel inside) or a thermal spraying of appropriate materials. Of these, we studied primarily an HVOF (High Velocity Oxy-Fuel) thermal spray^[3] method using various materials, which included not only metallic materials but also ceramic-metal composites of our own specification. Figure 13 shows a typical corrosion test result of 50Cr50Ni thermal

spraying produced by the HVOF in an actual boiler environment where corrosion by H₂S was considered severe enough for testing. The effectiveness of the thermal spraying was confirmed. The key feature of this method is that very low porosity coatings with high bond strength to the substrate can be produced in our manufacturing facilities or on site, with the appropriate surface preparation. The coating materials can be selected from several grades, depending on operating conditions.

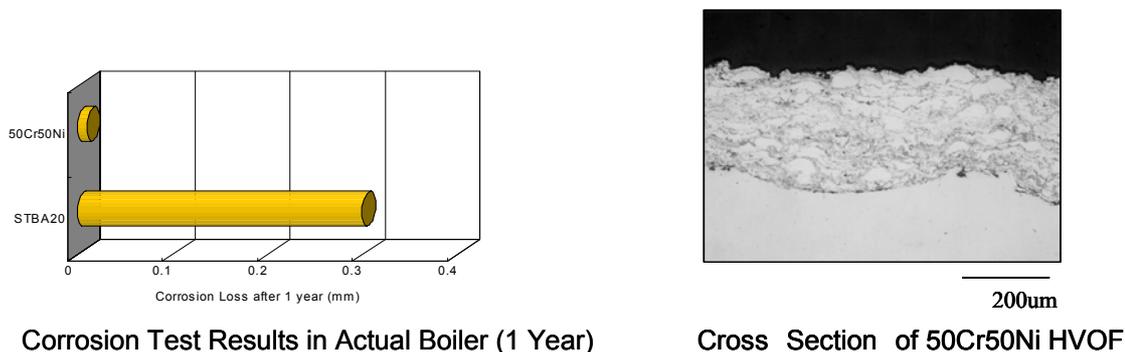


Figure 13. Performance of HVOF 50Cr50Ni on Actual Plant

5.4 Application of Supercritical Pressure Boiler for High Sulfur Coal

One of the frequently asked questions is; are there any difficulties in the application of high sulfur coal for super-critical boiler? To answer this question, a comparison of fluid temperature from economizer inlet to superheater outlet on both super- and sub-critical pressure units is shown in Figure 14. As can be seen, the fluid temperature of a sub-critical pressure unit is lower than that of a supercritical pressure unit except in the burner zone, which is one of the critical areas for a high sulfur coal-fired boiler design. While the burner zone metal temperature is the issue for both supercritical and sub-critical pressure units, there is essentially no difference between the two, and we don't see any problems in the supercritical design. However, as mentioned above, for further safety, we can apply either SSAP or thermal spraying of a high chromium material at the burner zones in a furnace, or both. In the critical temperature zones of superheater and reheater outlet, we can use the advanced 25Cr-20Ni stainless steel up to 1100°F steam conditions where there are potential corrosion areas. Corrosion possibilities of other pressure parts can be lowered by the appropriate selection of materials based on our considerable experience. Therefore, we have no concern about the adoption of 3500psig/ 1100°F/ 1100°F steam condition for Eastern coals containing 4% sulfur.

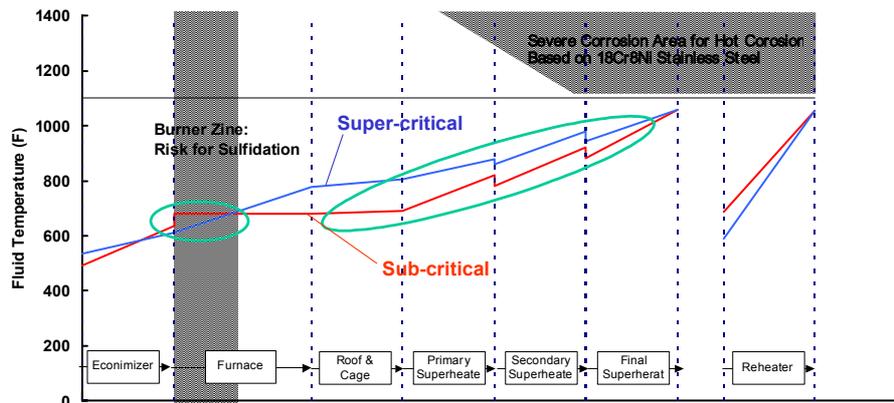


Figure 14. Temperature Distribution in Boiler System (as Fluid Temperature)

5. Conclusion

Babcock-Hitachi K. K. has significant experience at steam conditions as high as 3500psig/ 1100deg-F/ 1100deg-F by applying newly developed high strength austenitic and ferritic steels. For furnace corrosion, we have developed the Side Stream Airport system from the structural and operational point of view, and the thermal spraying of corrosion resistant materials at shop and on site against possible accelerated corrosion. Our ongoing use of these technologies has given us considerable experience in plants burning high sulfur fuels, such as oil residue, oil cokes or high sulfur heavy oil, we are achieving excellent reliability which bears out our design calculations, and we continue to collect additional operational data.

We are now ready to design and supply a plant with which can utilize locally deliverable high sulfur coal. A supercritical pressure plant using these coals is practically applicable and is probably the only way to achieve high plant efficiency without a significant cost impact.

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