



Xiaoyang Gaus-Liu (Autor)

High-Temperature Chlorine Corrosion during Co-Utilisation of Coal with Biomass or Waste

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Germany

Telefon: +49 (0)551 54724-0, E-Mail: info@cuvillier.de, Website: <https://cuvillier.de>

1. Introduction

Material failures are the leading cause of outages and availability losses in power plant boilers. According to statistics, about 50% of tube failures are related with corrosion problems. The threatened areas by corrosion could be located both on the water/steam side and on the fireside of the furnace and along the flue gas pass /1/. Whereas the material problems on the water/steam side are well understood, which are related with water quality and material strength, the fireside corrosion, which is the result of complicated interactions among fuel, flue gas, ash deposits and alloy characteristics, still requires deeper understanding. Such interactions on fireside corrosion and corresponding topics will be engaged in this research work.

1.1 Fireside corrosion limits the efficiency of coal-fired power plants

Due to unforeseeable oil and gas prices, the base-load electricity generation in Germany is based on coal –fired power plants /2/. The classic concept of pulverized-fuel (PF) combustion is still widely used due to its competitive efficiency and well-proofed technology. It is estimated that pulverized fuel will be applied in about 80% of worldwide new coal-fired power plants /3/. At present the efficiency of bituminous coal PF plants is about 45%. A further improvement of efficiency requires the application of new boiler materials /4/, which can withstand high pressure and corrosion attack. The improvement of net efficiency of PF power plants by the application of advanced materials is shown in Fig. 1.1 /5/. At present, the live steam parameters of PF plants is about 600/620°C of superheater (SH)/ reheater (RH),

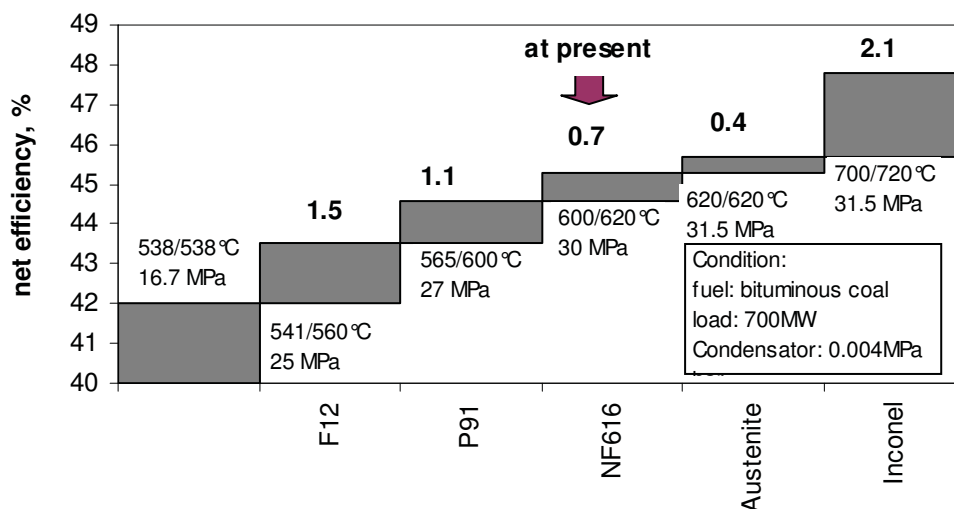


Fig. 1.1. The dependence of power plant efficiency on material development /5/

and 27MPa, corresponding to a net efficiency of 45% /6/. For such steam parameters, 9-12%Cr ferritic and martensitic steels are applied at the hottest part of superheater/reheater. For the next generation of ultra super critical (USC) plants with even higher steam temperature and pressure, austenitic and nickel-based alloys are required /7,8/.

In the last fifty years, experiences have shown that material problems are the main barrier for a further increase of steam temperature. Between 1957 and 1968, more than 30 supercritical units were put into operation in the USA /2/. Two power plants with the highest steam parameters were: Ohio Power Co. in Philo: 32Mpa, 621/565/538°C SH/RH1/RH2 and Eddystone Co.: 34.5MPa, 649/565/565°C (SH/RH1/RH2). However, such high steam parameters, especially high steam temperatures, could not be maintained due to material problems. After this period, high steam temperatures were not applied worldwide /9-11/. In the last ten years, supercritical steam parameters have gradually taken considerable share of new-built power plants. The improvement has been mainly achieved in increasing steam pressure. The increase of steam temperature, however, undergoes very cautiously. This can be shown by following examples: two 800MW units of Germany “Schwarze Pumpe” with 28.5MPa, 547/565°C SH/RH; Germany “Niederaußen” Unit K, 950MW, with 26.4MPa, 580/600°C SH/RH and China Shanghai “Waigaoqiao”, two 900MW units with 25.8MPa, 542/568°C SH/RH /12/.

The obstacle to limit steam temperature exceeding 600°C comes from fireside corrosion. There is a peak value of corrosion rate between 600°C and 700°C of austenitic steels, as shown in Fig. 1.2 /13/. In this temperature range, due to interactions between flue gas and ash deposits, low-melting-point salts build up on heat transfer surfaces. During formation or decomposition of such salt melts, the product of the reaction, which can be SO₃ in oxidizing atmosphere, or SO₂/S₂ in reducing atmosphere, are transported to the scale/metal interface and

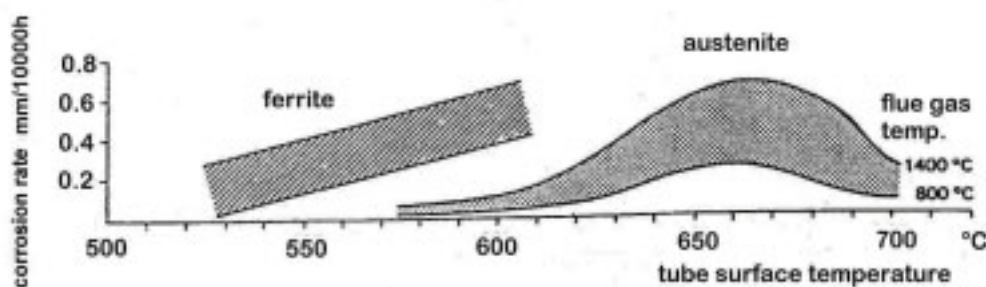


Fig. 1.2. Fireside corrosion rate as a function of material temperature /13/

lead to high corrosion rate. This kind of corrosion is so called “hot corrosion”. Over this temperature range, the salt melts are not stable, as consequence, hot corrosion is alleviated.

It is always an issue for boiler designers to balance thermal efficiency, material cost and the risk of material failures. In order to get a substantial improvement of the boiler efficiency, developing and testing new boiler tube materials are urgently required. The new materials should not only show high mechanical properties, but also show superior resistance against fireside corrosion. Moreover, a further understanding of interactions between flue gas, deposit ash and material degradation, especially for new materials, are of the same importance.

1.2 Fireside corrosion in biomass and waste combustion systems

Interests in firing biomass and waste

Biomass and waste are drawing increasing interest as renewable energy resources for power and heat supply. Firing biomass and waste is foreseeable market-near technology to reduce CO₂ emission and at the same time, to protect environment and to save valuable primary energy resources /14/. Since a gradually transition from fossil fuels to renewable energies is unavoidable on the way to reduce CO₂ emission, the European Commission demands actions to enhance the use of renewable energy that would take 12% of electrical production by year 2010. To meet this demand, the application of renewable energy should be at least doubled till the year 2010.

Germany is one of the countries which makes great efforts to encourage biomass utilization: a new renewable energy ordinance (EEG) is in power which obliges electricity distributors to buy electricity from renewable energy sources at an increased reimbursement /15/. Contaminated old wood is regarded as biomass in this ordinance. The ordinance shall make firing biomass profitable, so that the large potential of available biomass can actually be explored.

There is another reason for enhanced use of biomass in European countries: there is a great surplus of agriculture production due to intensive plantation technique. Industrial utilization of raw agriculture materials provides a new way for continuous development of agriculture, without changing land structures and cutting farming jobs.

Waste incineration becomes also an important topic of environmental protection policy. German Federal Department of Environment has made a new ordinance with high

environmental protection measures in August 1999. The ordinance ensures there will be an end of the landfill of inadequately pretreated wastes no later than 2005. Domestic waste should be either directly thermal disposed or thermal disposed after mechanical-biological pretreatments. The thermal disposal plants should meet the emission limits set by the 17th federal pollution protection ordinance (the 17th BimSchV) /16-17/.

The motivation behind the waste incineration is to reduce negative environmental impacts of waste landfill. Through thermal treatment of waste, following benefits can be achieved:

- destroying harmful or dangerous substances in wastes
- reducing amount and volume of wastes
- utilization of waste residues after thermal treatment or making it capable for deposit
- using the energy from wastes as far as possible.

Serious fireside corrosion by firing biomass and waste materials

High concentration of chlorine in biomass and waste leads to severe fireside corrosion. This becomes a new problematic for both combustion engineering and material engineering /19/. Due to the rapid material degradation, most waste incineration plants must limit their live steam temperature below 400°C /20/. In spite of this, frequent tube failures and outages can not be prevented.

High corrosion rate usually occurs when the heat transfer surface is covered with chlorine-rich deposits. In the case of biomass, the deposit is enriched in alkali chlorides; in the case of waste materials, the deposit is enriched in sodium chlorides and chlorides of some heavy metals, such as $ZnCl_2$ /21/. During oxidation of such chlorides, chlorine gas (Cl_2) is formed, which is a directly attack medium to the underlying material. Since the melting temperature of chlorine-containing ashes is usually low, fouling, slagging and sintering of the deposit occur, which in return facilitate chemical reactions among ash particles.

Another character of chlorine-induced corrosion is the structure of material degradation. Not only rapid material loss by forming a corrosion scale is reported, but also internal corrosion under the corrosion scale is detected, which results in material ability loss. Some advanced materials, such as some austenitic steels, which have good corrosion resistance against sulphate corrosion in coal-firing system, have shown deep internal corrosion zone under chlorine attack /22/.

Co-combustion of biomass with coal

The interest in co-combustion of biomass with coal in large scale plants is growing due to a number of considerations, e.g. low investment cost, well established power plant nets and existing flue gas cleaning facilities /23/.

Considered as energy resources, biomass includes a variety of low-grade fuels, characterised by high volatiles, high chlorine and high alkali content /24/. The problematic features of biomass imply a range of difficulties in operation, such as gas cleaning and residue utilization during co-combustion and fireside corrosion /25-28/. Fireside corrosion is one of the most complicated difficulties, which is strongly influenced by the selection of primary fuel (coal) and secondary fuel (biomass or waste) and operational parameters /19, 29, 30/.

1.3 Fireside corrosion on waterwall

Waterwall corrosion often appears when waterwall tube surface is impinged by particle-loaded flame or located in an oxygen-depleted zone. This kind of corrosion is usually a result of flame maladjustment or the application of low-NO_x technologies /31/. The oxide scale, which is otherwise stable in oxidizing environment, is not compact and not adherent in reducing environment. Such scale is subjected to the attack of chlorine and sulphur. Moreover, the corrosion rate in an alternative oxidizing-reducing condition is greater than only in a stable reducing atmosphere /20/.

1.4 Objectives and research methods in this study

In this study, emphases have been given on the corrosion related issues during biomass and waste combustion. Following open questions in corrosion mechanisms, deposition behaviour of chlorine compounds and fuel selection to minimize chlorine deposition were studied:

a) Corrosion mechanisms

- Morphologies and mechanisms of chlorine corrosion in reducing and oxidizing atmospheres
- Corrosion kinetics of chlorine-induced corrosion
- Combined influences of flue gas composition and ash deposits on corrosion rate
- Corrosion resistance of ferritic, ferritic/martensitic and austenitic steels under deposits from coal and biomass combustion.

The investigations of corrosion mechanisms were carried out experimentally in a laboratory furnace with well-defined gas and deposit test conditions.

b) Deposition behavior in combustion process and its influence on fireside corrosion

Since the deposition of chlorine-rich ashes on tube surface accelerates corrosion rate enormously, deposition behaviour of chlorine compounds during combustion process was the main concern in the combustion tests. The combustion tests were carried out in a well-defined test rig, in which cooled deposit probes were inserted. The influences of fuel characteristics, material temperature and flue gas temperature on the chlorine deposition were studied. Furthermore, elemental distributions in the heterogeneous deposit around a tube surface were systematically investigated.

c) Searching of suitable fuel blends to minimize chlorine corrosion

Which kind of coal is suitable to be co-fired with chlorine-enriched waste fuels, and which is the suitable share of such waste fuels? With the help of thermodynamic calculation program FACTSage, the cases of co-firing straw with bituminous coal and co-firing straw with lignite were studied. The fuel characteristics to minimize the deposition of chlorides were discussed, and the suitable mix rates of straw were predicted. The calculation results have been examined by corresponding experimental tests.

Finally, the limitation of the research work and suggestions for future research have been discussed.