Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

1. Details about ash deposition probe

Fig. 1 the temperature-controlled ash deposition probe

The sampling ring used for collecting deposits was made of 0.2 mm thick steel plate, as shown in Fig. 2. After deposits sampling, there was no need to take the deposits off the ring. A little piece of the ring would be cut off and analysed directly. SEM-EDS analysis was only conducted on the surface of each sample to get the information of intermediate state, rather than the whole deposits. Thus, more in-depth data and details about the dynamic deposition process could be found.

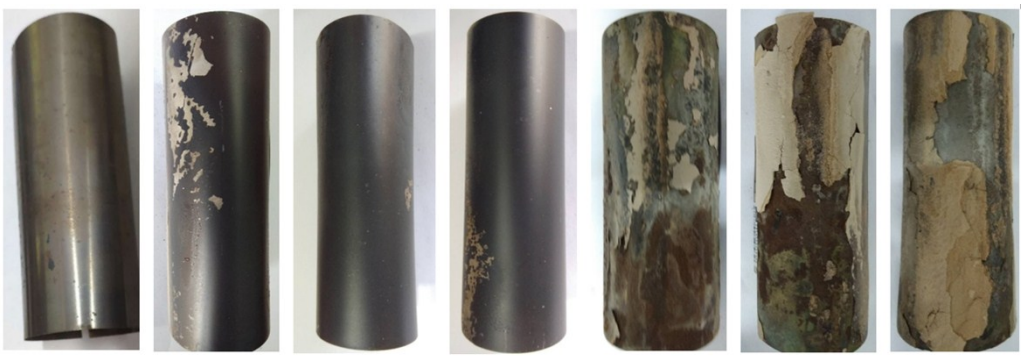


Fig. 2 the sampling ring with deposits

2. SEM image of corrosion caused by alkali metal

Corrosion was found on the surface of the sampling ring after stripping off the 2-day deposits, as shown in Fig. 3. Fe, Cr, Mn and Ni are the main ingredients of the sampling ring. High content of K indicates that corrosion was caused by KCl. A possible reaction mechanism of corrosion is:

$$2KCl(s,l)+Fe_2O_3(s)+(1/2)\ O_2(g) \rightarrow K_2Fe_2O_4(s,l)+Cl_2(g)$$

In the main article, we only discussed the deposition process. Corrosion caused by alkali metal needs further study.

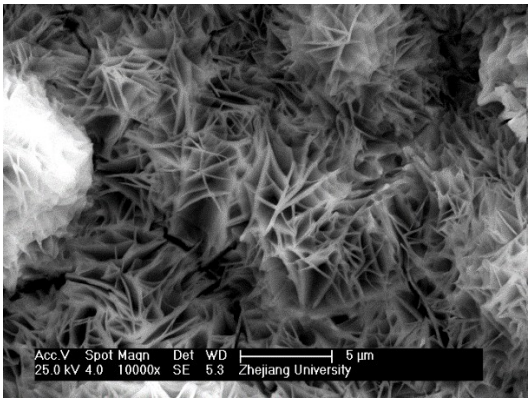


Fig. 3 corrosion on the surface of the sampling ring

Table 1 the elemental composition of the corrosion products

Element	O	Cl	K	Ca	Cr	Mn	Fe	Ni
Wt%	33.51	0.69	6.63	0.99	3.17	0.75	45.79	8.49

3. Mature deposits derived directly from high-temperature superheater

During boiler maintenance, the mature deposits were derived directly from the high-temperature superheater. As shown in Fig. 4, the surface of the deposits showed obvious signs of erosion. And the interior contained a large amount of white crystal salt [both in Fig. 4(a) and (b)], which was tested as KCl. After stripping the deposits from the superheater, in Fig. 4(b), obvious corrosion traces could be found on the surface of tubes, which were dark brown.

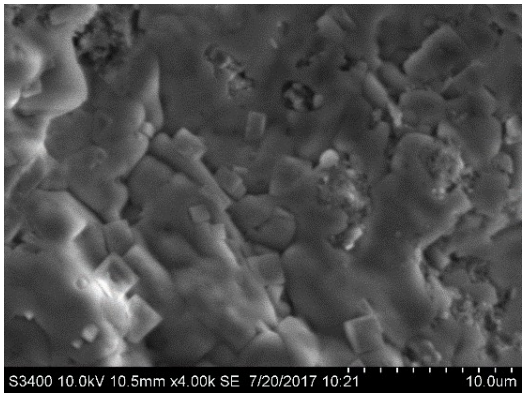
(a) deposits and white crystal salt (b) deposits and corrosion on the tube surface

Fig. 4 mature deposits on the high-temperature superheater

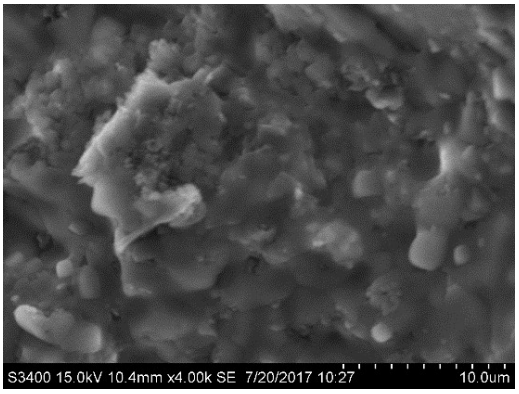
The mature deposits were stratified into the inner layer (tube side), cross section and the outer layer (flue gas side), and were tested by SEM-EDS respectively. The elemental composition is given in Table 2, and the SEM images are in Fig. 5.

The micromorphology of the tube side deposits was similar to that of the 5 h probe deposits in the manuscript. The result of elemental composition shows that KCl accounted for up to 90%. It is consistent with the conclusion reported in the previous research that the tube side of the deposits is mainly composed of alkali metals. The initial thermophilic deposition layer of submicron particles on 1 h probe deposits could not be found in the tube side of the mature deposits. It is because that this initial layer is so thin that it cannot be observed in mature deposits.

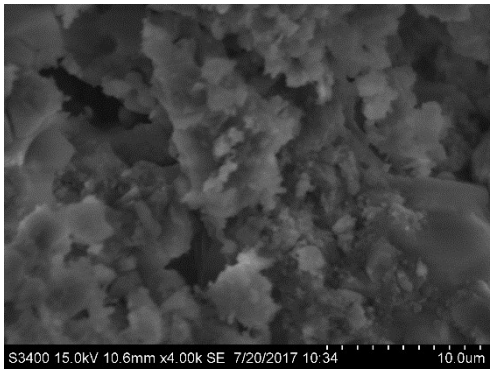
Different from the tube side and the cross section of deposits, granular or flocculent particles could be obviously found in flue gas side of the mature deposits in Fig. 5(c), which was the fly ash particles captured by the viscous KCl. In general, with growing of deposition, the element composition of the deposits began to show a trend of decrease in content of KCl and increase in content of Ca salt and SiO_2, which was consistent with the conclusion in the ash deposition probe experiment.



(a) Tube side of deposits



(b） Cross section of deposits



(c) Flue gas side of deposits

Fig. 5 SEM pictures of the mature deposits

Table 2 Major elements in the deposits

Element	Na	Mg	Al	Si	P	S	Cl	K	Ca
Tube side	4.13	0.75	1.11	1.36	0.44	1.30	45.07	41.30	4.54
Cross section	2.87	3.59	3.00	4.27	1.89	4.84	30.89	33.15	15.50
Flue gas side	0.20	8.47	6.53	12.19	4.41	9.63	8.11	8.67	41.79

XRD analysis of mature deposits is in Fig. 6. The main components of deposits include KCl, $CaCO_3$, $CaSO_4$, SiO_2 and NaCl. $CaCO_3$ and SiO_2 are the main components of fly ash, which were captured by sticky KCl. The main source of $CaSO_4$ was likely to be generated by the sulfate salinization reaction of $CaCO_3$ during the long-term deposition process.

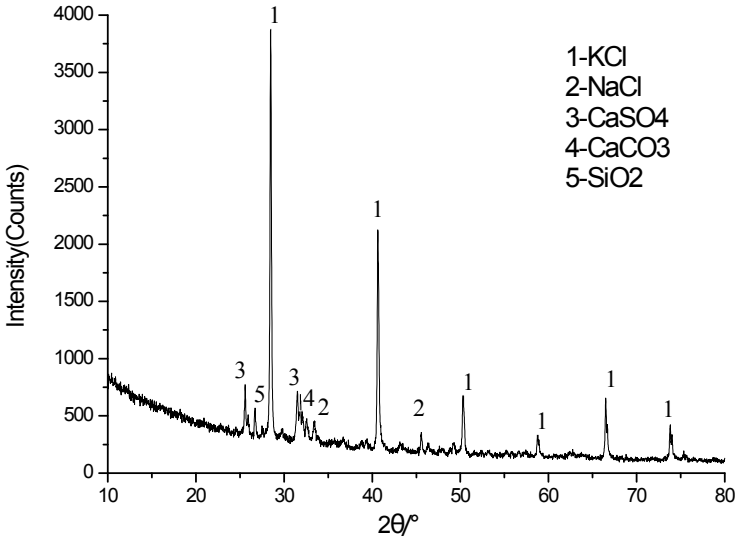


Fig. 6 XRD diagram of the mature deposits