Dynamic Simulation Test of Chemical Cleaning of Superheater

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Abstract. The dissolution of superheater oxide skin by compound cleaning agent was studied in a dynamic simulation test device. The corrosion rate of compound cleaning agent on various materials was studied by weight loss method. The results show that the compound cleaning agent can remove the oxide skin formed on the surface of various materials and the austenitic steel was cleaned without intergranular corrosion.

1. Introduction
With the increase of the parameters of coal-fired units, the growth of oxide skin on the inner wall of superheater and reheater tube is inevitable. Under the superimposed interference of multiple factors, such as unit start and stop, load fluctuation and oxygen fluctuation, the oxide skin is easy to peel off, causing the superheater and reheater to burst the tube[1,2]. How to remove oxide skin safely and effectively is a problem to be solved. The oxide skin on the surface of austenitic steel such as tp347hfg, super304h and hr3c can be divided into the surface oxide skin and the bottom chromium-rich layer[3]. The surface oxide skins are loose and easy to peel off, while the chromium-rich layer is not easy to peel off and has a protective effect on the surface.

Chemical cleaning of the superheater and reheater can remove the oxide skin. The cleaning solubility of the cleaning agent to the oxide skin and the corrosion of various metal materials in the superheater and reheater need to be tested before cleaning.

The dissolution of composite cleaning agent on oxide skins of 12crlmov, tp347hfg, super304h and hr3c was studied in dynamic simulation test device. The state of the inner surface of the sample was characterized by microscope[4,5], and the corrosion rate of the cleaning agent on various materials was studied by weight loss method.

2. Experiments
Oxide skin dissolution test. The tube sections with inner surface covered with oxide skin were processed into experimental tube samples. The serial numbers and materials are e001 ~ 12crlmov, e002 ~ 12crlmov, e003 ~ tp347hfg, e004 ~ super304h, e005 ~ tp347hfg, e006 ~ hr3c. The quality of each sample was weighed by analytical balance, and the thickness of oxide skin was measured by digital metallographic microscope (model xjp-6a).

Fig 1 shows the chemical cleaning dynamic simulation test device, which is composed of cleaning pump, flowmeter, temperature control device, tube sample and test piece loading device. The test tube was placed on the dynamic simulation test-bed for the scale dissolution test. The cleaning medium was 6% citric acid + 1% edta + 0.2% reducing agent + 0.5% inhibitor, the temperature was 90 ± 2 ℃, the body surface ratio was 2.5ml: 1cm², the flow rate was 0.7-1.2m/s, and the cleaning time was 48h. Dry
the sample after cleaning and measure the quality of the sample. The thickness of residual oxide skin on the inner surface of the tube was measured by digital metallographic microscope.

![Diagram](image.png)

1- cleaning box, 2- valve, 3- filter, 4- cleaning pump, 5- heater, 6- temperature controller, 7- flow meter, 8- device for placing samples

Fig 1. chemical cleaning dynamic simulation test equipment

**Corrosion test.** After cleaning, the tube samples e003, e004 and e006 were eroded with a mixture of 10mL nitric acid and 30mL hydrochloric acid (aqua regia) for 2 minutes. Then, the state of the surface and inner wall of the sample was characterized by the research level inverted universal material microscope (model axio observer a3).

The experimental tube samples were processed into corrosion test pieces. The sample numbers and materials were (c001, c002) ~ 12crlmov, (c003, c004) ~ tp347hfg, (c005, c006) ~ super304h, (c007, c008) ~ hr3c. The original mass of the specimen was measured by an analytical balance. The sample was placed on the dynamic simulation test device for corrosion test. The cleaning medium was 7% citric acid +1%edta+0.2% reducing agent +0.5% corrosion inhibitor. The temperature was 95±2℃, the flow rate was 1.2 ~ 1.7m/s, and the cleaning time was 24h. After the test, clean the test pieces with anhydrous ethanol and dry them in the oven. The mass of the sample was measured again by analytical balance and the corrosion rate was calculated by weight loss method.

3. Results and discussion

**Thickness of oxide skin on the inner surface of tube samples with different materials.** Fig 2 shows the macro photos and inner wall section photos of the low temperature superheater tube. The thickest part of the oxide skin in the e001 sample was 37.62μm, and the thinnest part was 8.90μm. There was no local peeling of the oxide skin. The thickness of the oxide skin in the e002 sample reached 145.81μm on average, and the oxide skin was partially detached.
Fig 2-1 macroscopical and inner wall section morphology of low temperature superheater (12crlmov) e001

Fig 2-2 macroscopical and inner wall section morphology of low temperature superheater (12crlmov) e002

Fig 3 shows the macro photos and inner wall section photos of the screen superheater tube. The thickness of the oxide skin in the tube sample is 13.47μm ~ 47.02μm. Macroscopically, the oxide peel is relatively dense without local peeling.

Fig 3 macroscopical and inner wall section morphology of screen superheater tube (tp347hfg) e003

Fig 4 -1 shows the section photo of the inner wall of the screen superheater tube numbered e004, and the thickness of oxide skin in the tube sample is 13.67μm ~ 30.58μm. Fig 4 -2 shows the cross section of the inner wall of the high temperature superheater tube numbered e005. The thickness of the oxide skin in the tube sample is 24.65μm ~ 64.05μm.
Fig 5 shows the macro photos and inner wall section photos of the high temperature superheater tube (hr3c) numbered e006. The thickness of the oxide skin in the tube sample is 0.77µm ~ 3.04µm. Macroskopically, the oxide peel is relatively dense without local peeling.

Both e001 and e002 are low temperature superheater tubes, but the thickness of oxide skin is quite different. The main reason is that the operating temperature of the two tubes is different [6]. The oxidation resistance temperature of 12cr1mov is 580 °C, and the operating temperature of e002 tube exceeds 580 °C, while the operating temperature of e001 tube is below 580 °C.

The ability of the cleaning agent to dissolve the oxidized skin of each material. Fig 6 shows the residual oxide skin on the inner surface of tube sample e002 ~ e006 after dynamic cleaning. After cleaning, the oxide skin on the inner wall of e002 tube sample has been completely cleaned. The oxide skin on the surface of e003 ~ e006 pipe sample has been completely removed, and the chrome-rich layer has been kept intact (the tube samples of e003 ~ e006 have been nickel-plated for the convenience of cross section observation). Table 1 shows the thickness of oxide skin before and after cleaning.

| Tube sample | Material          | Location                  | Thickness of oxide skin before cleaning [µm] | Thickness of oxide skin after cleaning [µm] |
|-------------|-------------------|---------------------------|--------------------------------------------|-------------------------------------------|
| e002        | 12cr1mov          | low temperature superheater | 145.81                                     | ≈0                                        |
| e003        | tp347hfg          | screen superheater        | 13.47 ~ 47.02                              | 15.19 ~ 20.05                             |
| e004        | super304h         | screen superheater        | 13.67 ~ 30.58                              | 5.58 ~ 17.42                              |
| e005        | tp347hfg          | high temperature superheater | 24.65 ~ 64.05                             | 9.62 ~ 28.35                             |
| e006        | hr3c              | high temperature superheater | 0.77 ~ 3.04                               | 1.85                                      |
When 6% citric acid +1%edta+0.2% reducing agent +0.5% corrosion inhibitor was used, the temperature was 90±2℃, the body surface ratio was 2.5ml :1cm², the flow rate was 0.7-1.2m /s, and the cleaning time was 48h, the oxide skins in the 12crlnmov tube samples could be completely cleaned, and the surface oxide skins in the tp347h, super304h and hr3c tube samples could also be completely removed, leaving the chrome-rich layer intact. This cleaning process is feasible to remove and dissolve oxidized skin.
Intergranular corrosion of austenitic steel in cleaning agent. Fig 7 shows the surface morphology of the chemically cleaned test tube after being eroded by a mixture of 10 ml nitric acid and 30 ml hydrochloric acid (aqua regia) for 2 minutes. There is no intergranular corrosion on the surface and inner wall of e003, e004 and e006, which shows that the dynamic cycle cleaning of austenitic steel in cleaning agent is safe.

Fig 7-1 surface and inner wall sections eroded by aqua regia (tp347hfg) e003

Fig 7-2 surface and inner wall sections eroded by aqua regia (super304h) e004

Fig 7-3 surface and inner wall sections eroded by aqua regia (hr3c) e006

Corrosion rate of each material in cleaning agent. When using 7% citric acid + 1% edta + 0.2% reducing agent + 0.5% inhibitor, the temperature is 95 ± 2 °C, the flow rate is 1.7m/s, and the time is 24h, the corrosion rate of 12cr1mov, tp347hfg, super304h and hr3csamples is less than 0.5g / (m²·h), and the corrosion rate is low[7]. Table 2 shows the corrosion rate of c001–c008 in dynamic simulation environment.
### Table 2 corrosion rates of various materials in dynamic tests

| specimen material | serial number | surface area [cm²] | weight loss [g] | corrosion rate [g/(m²·h)] | average corrosion rate [g/(m²·h)] |
|-------------------|---------------|-------------------|-----------------|---------------------------|----------------------------------|
| 12crlmov          | c001          | 17.25             | 0.0132          | 0.32                      | 0.33                             |
|                   | c002          | 17.21             | 0.0141          | 0.34                      |                                  |
| tp347hfg          | c003          | 18.42             | 0.0004          | 0.0090                    | 0.0079                           |
|                   | c004          | 18.34             | 0.0003          | 0.0068                    |                                  |
| super304h         | c005          | 18.23             | 0.0003          | 0.0069                    | 0.0080                           |
|                   | c006          | 18.37             | 0.0004          | 0.0090                    |                                  |
| hr3c              | c007          | 18.52             | 0.0005          | 0.011                     | 0.0090                           |
|                   | c008          | 18.19             | 0.0003          | 0.0069                    |                                  |

#### 4. Conclusions

6-7% citric acid + 1% edta + 0.2% reducing agent + 0.5% corrosion inhibitor, temperature 90-95 °C, body surface ratio 2.5ml: 1cm², flow rate 0.7-1.7m/s, 48 hours of dynamic cycle cleaning process can completely clean the oxide skin on the surface of 12crlmov material, and can completely remove the oxide skin on the surface of tp347hfg, super304h, hr3c material, and the chrome-rich layer can retain intact. The dynamic corrosion rate of the above materials by this cleaning process is less than 0.5g/(m²·h), and it will not cause intergranular corrosion of austenitic steel. This cleaning process can be used for reference in the cleaning of superheater and reheater.

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