

## PRIMARY METHOD FOR REDUCTION OF SO<sub>2</sub> EMISSION IN PULVERIZED OIL SHALE-FIRED BOILERS AT NARVA POWER PLANTS: TEST 1 – WATER INJECTION AFTER SUPERHEATER

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**Abstract.** *A primary method if used in pulverized oil shale-fired boilers in operation enables one to achieve the target value of SO<sub>2</sub> specific emission – 400 mg/Nm<sup>3</sup>. It is also possible to meet the SO<sub>2</sub> specific emission limit value, 200 mg/Nm<sup>3</sup>, set by the European Union for the new-installed solid fuel boilers by further optimization of the technological parameters of pulverized oil shale firing on the basis of primary methods. The intermediate injection of water (one of the primary method measures) during the test (the offered solution is somewhat similar to the LIFAC method) after the superheater decreases the SO<sub>2</sub> emission from 2146 to 1760 mg/Nm<sup>3</sup>, i.e. by 17%. At the same time, the production of steam in the boiler decreases from 285 to 260 t/h, i.e. by 25 t/h. The performed tests proved to be technically ineffective and failed to give expected results.*

**Keywords:** *primary method, oil shale pulverized combustion, SO<sub>2</sub> reduction, sorbent activation, injection of technical water, flue gas humidification.*

### 1. Introduction

The role of oil shale (OS) is very important in Estonian economy, particularly in employment and regional development. The oil shale industry accounts for 4% of Estonia's gross domestic product. At the same time, it is responsible for generating the majority of wastes polluting air, water and soil [1]. The current state where the brent crude oil price has dropped significantly is a real challenge to oil shale industries and related research. There is a vast amount of research to do to find proper solutions and

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technologies for shale oil and OS power co-production to make this industry more efficient and environmentally friendlier to survive [2].

The primary method for the reduction of SO<sub>2</sub> emission is intended to increase the binding of SO<sub>2</sub> in pulverized shale-fired boilers (the SO<sub>2</sub> capture coefficient of a boiler at the Eesti Power Plant (EPP) is ca 75%, and the emission of SO<sub>2</sub> is approximately 2200 mg/Nm<sup>3</sup> [3]) with the sorbent components in OS. This problem does not occur in circulating fluidized bed boilers [4–6].

The pre-condition for binding is the big non-used potential (the quantity of the SO<sub>2</sub> capture sorbent components such as CaO, MgO, K<sub>2</sub>O, etc., in OS is large, the stoichiometric ratio Ca/S is about 10 [7, 8]) and the understanding of the use of the low-efficiency sorbent so far, which may serve as a basis for the optimisation of the processes.

The use of primary methods in shale-fired boilers is described in [8]. The article gives an overview of the principles of the primary methods and consolidates investments related to the application of the methods and the results of binding SO<sub>2</sub> but not the performance of certain experiments.

In continuation of [8], the first author decided to handle the performance of selected tests carried out in the OS fired boilers of EPP to decrease the SO<sub>2</sub> emission by applying primary methods during the years 2011–2012, for which arrangement he was responsible. The goal is to give a thorough overview of the planning and performance of certain tests and the analysis of the results.

This article discusses the injection of technical water after the steam superheater of the boiler, the aim of which is to activate the free calcium oxide in the core of the OS fly ash and to increase the efficiency of the desulphurisation of the flue gas by it.

The authors think that the description of the planning and performance of certain tests and the analysis of the results give additional value to the main article by providing base materials and argumentations to some statements and values used therein. The authors of the article hope that the published empirical results help to implement primary methods and plan other experiments.

## **2. Materials and methods**

### **2.1. Background**

The aim of the injection of technical water after the steam superheater of the boiler activates the free calcium oxide in the OS fly ash and the increase of the efficiency of the flue gas desulphurisation by it [8]. As the formation of fly ashes at the pulverized firing (PF) of Estonian OS takes place at temperatures higher than 1200 °C, a molten phase plays an important role in the formation of particle shape and surface properties – many particles are characterized by a regular round shape and smooth surface [9]. The amount of calcium oxide in the ash of OS varies within the range of 40–60% and the

content of the free calcium oxide (chemically unbound CaO free) in the OS ash within the range of 10–20% [7, 10–14].

The method of the injection of technical water after the steam superheater somewhat resembles the LIFAC method, pursuant to which the activation of the fly ash with the injection of technical water and the desulphurisation of the flue gas take place in the reactor, which is located after the air preheater [15, 16].

The hardened crust of the OS fly ashes, which consist of glazed ( $\text{CaSO}_4$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{Ca}_2\text{SiO}_4$ , etc.) minerals, blocks the sulphating of the free calcium oxide (CaOfree in Fig. 1) and the desulphurisation of the flue gas.

Activation, or to be more precise, the fission of the OS ash particle, takes place due to thermal shock, which occurs thanks to the collision of the water drops or water vapour and the ash particles. Activation liberates the free calcium oxide contained in the nucleus of the OS fly ash. The sulphating of the released calcium oxide and the desulphurisation of the flue gas take place (Fig. 1).

The equipment selected for testing the activation of the OS fly ash is the boiler TP-101 of EPP (Fig. 2, which is based on the layout from [7]). TP-101 is a high-pressure boiler with the steam output of 320 t/h, with the double steam superheating at a steam pressure of 13.8/2.2 MPa, and temperature of 520/525 °C and supply water temperature of 230 °C. The place of activation is the flue (10), in which the flue gas is at a temperature up to 800 °C between the steam superheater (6, 7) and the economizer (8). The flue gas is desulphurised in the flue of the economizer (8) and the air preheater (9), whose temperature range is 200–700 °C.

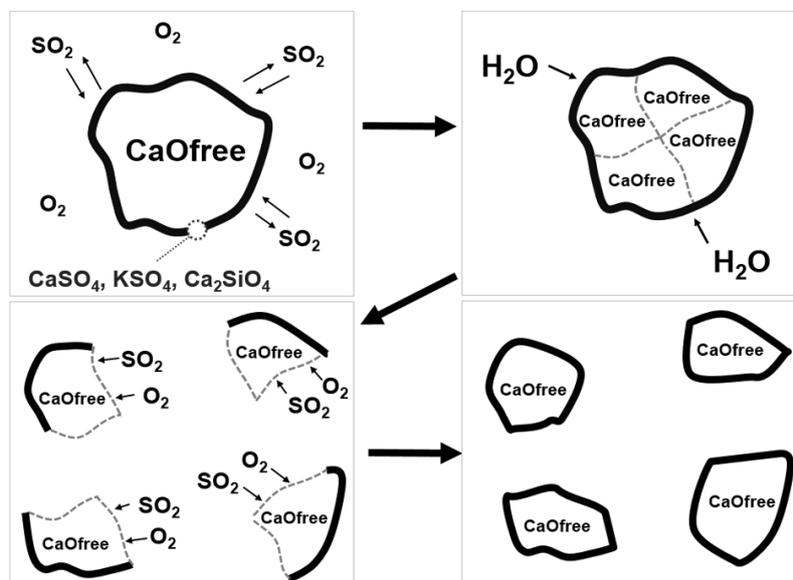


Fig. 1. The conceptual scheme of the activation of the fly ash and the desulphurisation of the flue gas.

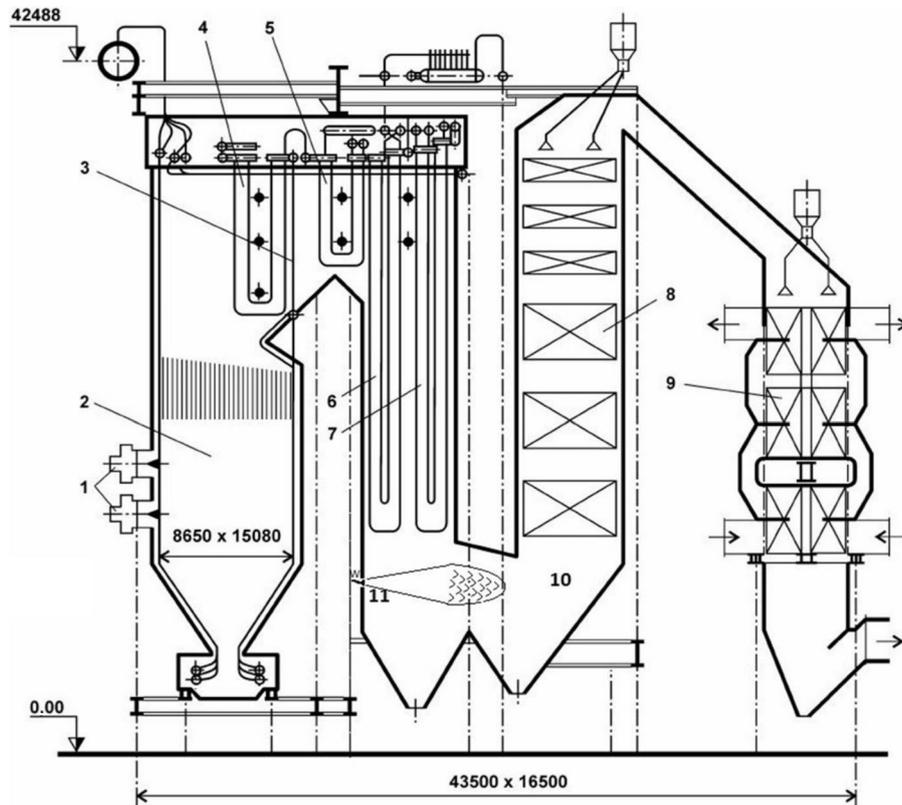


Fig. 2. The conceptual scheme of the injection of technical water by vapour sprayers into the flue after the steam superheater of the boiler TP-101: 1 – burners; 2 – furnace; 3 – outlet screen; 4 – furnace platen superheater; 5 – intermediate platen superheater; 6 – hanging platens of primary superheater; 7 – hanging platens of reheater; 8 – economizer; 9 – air preheater; 10 – flue; 11 – vapour sprayers of technical water.

According to the plan activation is performed by injecting technical water via vapour sprayers (11) into the flue located after the steam superheater (10).

Tests methodology was worked out including the following stages:

- pre-setting of vapour sprayers outside the boiler;
- setting of vapour sprayers in the standing boiler;
- testing of vapour sprayers in the operating boiler.

## 2.2. Pre-setting of vapour sprayers outside the boiler

The goal of the pre-setting of vapour sprayers outside the boiler is:

- to establish the spraying distance of the vapour sprayers and the opening angle of the spray pattern;
- to pre-set the vapour sprayers before installing them on the boiler.

It is planned to pre-set the vapour sprayers pursuant to the program on a corresponding setting display. The chosen vapour sprayers are the product of Schlik (model Mod. 0/5 S-24, D5.903; Austria). The nominal water consumption rate of the vapour sprayers is 3.5 t/h, pressure 3.7 bar, air consumption 900 Nm<sup>3</sup>/h, pressure 5.8 bar, the opening angle of the fan 10–40°, the length of the fan 15–40 m, the diameter of water drops 90–100 µm [17].

During the pre-setting it is planned to measure:

- the pressure of technical water and the pressurised air;
- the spraying distance of the vapour sprayer and the diameter of the spray pattern at the distance of 3 and 5 m.

### 2.3. Setting of vapour sprayers in the standing boiler

The goal of setting the vapour sprayers in the standing boiler is:

- to install the vapour sprayers on the boiler at prescribed installation angles;
- to check-up the pre-setting of vapour sprayers to avoid water drops on the brickwork;
- to fix (photograph) the initial condition of the metal on heated surfaces (before testing in the operating boiler).

During the setting it is planned to measure:

- the pressure of technical water and the pressurised air;
- the temperature of the flues;
- the consumption of the pressurised air and pressure rates of the compressor unit.

### 2.4. Tests in the operating boiler

The main goal of the tests of the vapour sprayers in the operating boiler is:

- to establish the efficiency of the desulphurisation of the flue gas by spraying the vapour of technical water and the deputed water of the ash field ponds after the superheater at the maximum (ca 290 t/h), optimal (ca 225 t/h) and minimal (ca 130 t/h) loads of the boiler.

The sub-goals of the tests are:

- to establish the efficiency of capturing the fly ash in the electrostatic precipitator (ESP) at the maximum load of the boiler by spraying the vapour of technical water and the deputed water of the ash field ponds after the steam superheater;
- to assess on the basis of the obtained results the economic efficiency of the desulphurisation by vapour spraying the flue gas in the rotary chamber after the steam superheater between the superheater and the economizer.

During the tests it is planned:

- to measure the pressure of technical water, the deputed water of the ash field ponds and the pressurised air in the vapour sprayers;

- to measure the contents of flue gases (SO<sub>2</sub>, NO<sub>x</sub>, CO, CO<sub>2</sub>, O<sub>2</sub>) after the IDfan of the boiler;
- to measure the temperatures and pressures of the boiler steam, supply water, combustion air and the flue gas;
- to measure the self-consumption of the induced draft fans, ventilators and compressors;
- to measure the fly ash flow by the ProMo meter and the voltage and power of the supply mechanisms of ESP electric filters;
- to establish the concentration of the fly ash in the flue gas after ESP;
- to establish the contents of organic carbon in the taken samples.

The sub-goals serve as a basis for evaluation of the economic and technical feasibility of the desulphurisation.

Tests are planned to carry out at different steam loads of the boiler, with vapour sprayers, the consumption of technical water and pressurised air, (pressure of technical water up to 10 bar and pressurised air up to 6 bar) according to the program of tests agreed on previously.

### 3. Results

#### 3.1. Pre-setting of vapour sprayers outside the boiler

The pre-setting of vapour sprayers was carried out according to the above-mentioned program.

The vapour sprayers were connected to the hoses of the pressurised air and water (Fig. 3a) and pre-setting tests were carried out at different cone angles of water streams from the vapour sprayers, pressures of water and air (Fig. 3b).



Fig. 3. (a) Connection of the vapour sprayers with pressurised air and water hoses; (b) one of the regimes of the pre-settings of the vapour sprayers (water pressure 4 bar, air pressure 2 bar, the position of the thread regulating the cone of the water spray is minimal).

The pre-setting of the vapour sprayers enabled us to set the opening angles of the fan, which would avoid the water drops on the brickwork, used as the basis of the scheme developed for the installation of the vapour sprayers in the boiler.

### 3.2. Setting of vapour sprayers in the standing boiler

Vapour sprayers were installed according to the corresponding project prepared in harmony with the results of pre-setting. The main data of the project of the installation of the vapour sprayers are as follows:

- 6 pneumatic water vapour sprayers are installed in the frontal wall of the down-going flue after the steam superheater at a height of 10.5 m.
- The vapour sprayers are installed at an angle of about  $10^\circ$  in regard to the horizontal axis and the angle of the cone of the water spray is  $30^\circ$ . The step of the installation of vapour sprayers is 2.5 m. The burners at the edges are installed farther (approximately 3.25 m) from the axis of the columns bearing the housing of the boiler.

After taking photos during the check-up of the vapour sprayers (a couple of photos made of the injection of technical water during the cold test in the standing boiler are presented in Figure 4), the review of the video material and as the result of the visual observation the following conclusions were made:

- The vapour sprayers are installed in conformity with the installation angles provided in the project.
- The installation of vapour sprayers avoids water drops on the brickwork of the boiler.

During cold tests the initial condition of the metal on the boiler device is fixed (before the tests in the operating boiler).

During cold tests the following parameters were measured:

- the pressure of technical water and the pressurised air;
- the temperature of flues;
- the consumption and pressure of the pressurised air in the compressor unit.



Fig. 4. Photos of the injection of technical water during cold tests in the boiler.

The obtained measurement results were in conformity with the expectations or, in other words, the installation of the vapour sprayers, and the parameters of the water and pressurised air were suitable for carrying out the tests.

### 3.3. Tests in the operating boiler

19 different trials were performed during hot testing in the operating boiler.

The hot testing of vapour sprayers was performed:

- at different loads of the boiler (the maximum load of the boiler 290 t/h, the optimal load 230 t/h and the minimal load 170 t/h);
- with different combinations of operating vapour sprayers (2, 4 and 6 sprayers);
- with the pressure of technical water within the range of 2–10 bar;
- at air pressure 2–5 bar;
- with the injection of technical water and the depurated water of the ash field ponds.

The experiments carried out in the boiler 4K-B of EPP and the tests of activating the fly ash by the injection of water via vapour sprayers after the steam superheater showed the following:

- The high temperature of the flue gas after the steam superheater (700–800 °C) enhances the fast evaporation of water drops. The length of the fan injected via vapour sprayers decreases from 6 meters in the standing boiler to 2 meters in the operating boiler. This decreases the volume of the humidified flue gas (the quantity of the activated fly ash) and the efficiency of the desulphurisation of the flue gas.
- The fast evaporation of water drops avoids their occurrence on the brickwork and the metal of the heated surfaces, which helps to prevent damage to the brickwork and the metal of the heated surfaces.
- The spraying of technical water neither decreases the temperature of the flue gas before ESP nor increases the efficiency of capturing the fly ash in it.
- The efficiency of the desulphurisation of the flue gas upon spraying technical water or the depurated water of the ash field ponds depends on the amount of the humidified flue gas and is approximately 150 mg/nm<sup>3</sup> per each 10% of the flue gas (maximum humidification achieved is ca 20% of the amount of the flue gas).
- At the maximum load of the boiler, 290 t/h, the injection of technical water to the amount of 32 t/h decreases the concentration of sulphur dioxide by 359 mg/Nm<sup>3</sup> (Fig. 5).
- At the optimal load of the boiler, 230 t/h, the injection of technical water to the amount of 30 t/h decreases the concentration of sulphur dioxide by 106 mg/Nm<sup>3</sup> (from the average 1449 mg/Nm<sup>3</sup> to 1343 mg/Nm<sup>3</sup>), and at the minimal boiler load, 170 t/h, the injection of technical water to the amount of 20 t/h decreases this concentration by 229 mg/nm<sup>3</sup>, from the average 1261 mg/Nm<sup>3</sup> to 1032 mg/Nm<sup>3</sup>.

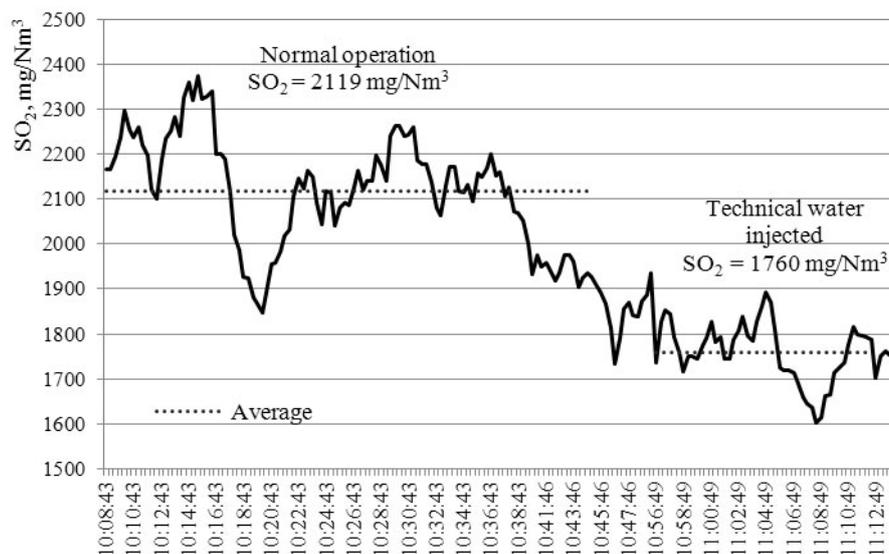


Fig. 5. Concentration of sulphur dioxide upon the injection of technical water in the boiler and outside (the load of the boiler 290 t/h, the quantity of injected water 32 t/h).

- The spraying of the depurated water of the ash field ponds does not increase the efficiency of the desulphurisation of the flue gas in comparison with the spraying of the vapourised technical water. The reason is the small molar ratio of chemically unbound (Ca, K<sub>2</sub>, Na<sub>2</sub>)/S in the depurated water, which is approximately 0.05. It may be caused by the fact that the temperature of the flue gas is too low for the sorbents containing Ca and Mg, and high for the sorbents containing Na and K. The addition of the limewash Ca(OH)<sub>2</sub> suspension or Ca(OH)<sub>2</sub> powder to the flue gas at temperatures up to 800 °C is ineffective as the optimal temperature for adding Ca(OH)<sub>2</sub> to the flue gas is about 1200 °C [18]. The activation of the fly ash by the injection of technical water and the depurated water of the ash field ponds after the steam superheater is technically possible but ineffective. It should be mentioned that economic viability was not fundamentally evaluated due to the ineffectiveness of SO<sub>2</sub> binding. In general, water injection after the superheater can be assessed as not economically viable because the steam production of the boiler decreases at maximum load from 32 to 25 t/h (8.6% of the steam production of the boiler before the injection), at optimal load from 30 to 40 t/h (17.4% of the steam production of the boiler before the injection) and at minimal load from 20 to 25 t/h (18.5% of the steam production of the boiler before the injection).

- Despite all expectations for the injection of technical water by vapour sprayers after the steam superheater, the condensation of the flue gas does not increase the efficiency of the capture of the fly ash in ESP.

#### 4. Discussion

The methodology of the activation of the fly ash by spraying the vapour of technical water and the depurated water of the ash field ponds after the steam superheater according to the corresponding methodology proved to be technically ineffective and economically not viable.

To trigger the fly ash activation, tests have to be carried out in order to increase the efficiency of the desulphurisation according to the quantity of the humidified flue gas.

For that purpose it is reasonable to carry out tests not in a fully operated boiler but on a test board built by the boiler, where it is possible to achieve better conditions by simpler measures for the humidification of the flue gas.

If tests prove to be positive and the results obtained (efficiency of desulphurisation is about 150 mg/nm<sup>3</sup> per each 10% of the flue gas) valid also in case of humidifying bigger quantities of the flue gas, it will be reasonable to think about technical solutions (points of humidification, shape of the jet, size of the drops, etc.), implementation of which would enable us to increase the efficiency of the humidification of the flue gas in boilers.

#### 5. Conclusions

This article discusses the injection of technical water after the steam superheater and its impact on the desulphurisation of the flue gas, as well as the efficiency of the capture of the fly ash in the electrostatic precipitator by activating it. (This means the fission of the hardened crust of the oil shale fly ash by the impact of water drops or vapour due to thermal shock and by this increase the release of free calcium oxide contained in the nucleus of the oil shale fly ash).

Technical water, sprayed by vapour sprayers in the flue gas after the steam superheater, was used for activation of the fly ash. This method of injecting technical water after the steam superheater resembles somewhat the LIFAC method, according to which the activation of the fly ash by spraying technical water and the desulphurisation take place in the reactor located after the air preheater.

Tests were carried out in conformity with the developed methodology, which comprises preparatory stages (the pre-setting of vapour sprayers outside the boiler and the setting of vapour sprayers in the standing boiler) and the testing of vapour sprayers in the operating boiler (hot test).

During preparatory stages the opening angles of the fans of vapour sprayers and the position of installation of the vapour sprayers to avoid water drops on the brickwork, as well as the technical parameters of technical water and the pressurised air required for the verified hot tests were established.

Tests in the operating boiler showed that the activation of the fly ash by the re-injection of technical water via vapour sprayers after the steam superheater unfortunately did not provide expected results as it turned out to be technically ineffective.

The efficiency of the desulphurisation of the flue gas with technical water depends on the amount of the humidified flue gas and is approximately 150 mg/nm<sup>3</sup> per each 10% of the humidified flue gas.

At the maximum load of the boiler, 290 t/h, the injection of technical water to the amount of 32 t/h decreased the concentration of sulphur dioxide by 359 mg/Nm<sup>3</sup> on average (from the average 2119 mg/Nm<sup>3</sup> to 1760 mg/Nm<sup>3</sup>). The production of steam decreased to 25 t/h (8.6% of the load before the injection).

At the optimal boiler load of 230 t/h the injection of technical water to the amount of 30 t/h decreased the concentration of sulphur dioxide by 106 mg/nm<sup>3</sup> on average (from 1449 to 1343 mg/Nm<sup>3</sup>). The steam production decreased by 40 t/h (17.4% of the load before the injection).

At the minimal load of the boiler, 170 t/h, the injection of technical water to the amount of 20 t/h decreased the concentration of sulphur dioxide by 229 mg/nm<sup>3</sup> on average (from the average 1261 mg/Nm<sup>3</sup> to 1032 mg/Nm<sup>3</sup>). The production of steam decreased to 25 t/h (18.5% of the load of the boiler before the injection).

Despite expectations for the injection of technical water by vapour sprayers after the steam superheater to condensate the flue gas, the efficiency of the capture of the fly ash in the electrostatic precipitator failed to increase.

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