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EFFECT OF THE OIL ADDITIVES ON THE THERMAL POWER STATIONS AND THEIR AIR POLLUTANT EMISSION

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Abstract

On the basis of the facts summarized above, the application of the additives is rational, when the technology of supplement can be supervised. And the recovery of dust content from the flue gas has been elucidated, otherwise the disadvantageous offset the benefits expected.

Keywords: power stations, oil additives; NO_x emission, SO_2 emission.

Introduction

The boilers in the hydrocarbon fuelled power stations operate in wide range of their capacity, which increases the corrosion on the flue gas side, extremely at the case of fuel oils. The corrosion is increased by disadvantageous change in the composition of the fuel (higher sulfur, vanadium, and asphalt content, lower calorific value) [1]. To decrease the undesirable effects mentioned above, we have tested different oil additives in Danube Power Station Co. for several years.

1. Advantage and Composition of the Additives

The additives must comply with the following advantages (as producers promote these products):

- increase pH value of the fly ash above 4,
- decrease in the $FeSO_4$ content of the fly ash significantly (at least by 50 %) (declining of the low-temperature corrosion),
- decrease in the high-temperature vanadium corrosion substantially (at least by 50%),
- reduction in the temperature of the flue gas significantly (at least by 20 °C) at stable pH value,, 4.5–5.5 (higher efficiency),
- more perfect combustion, less soot emission.

First of all, the producers want to achieve the effects above mentioned, using MgO type additives which are modified by different metallic oxides. The additives contain magnesium-oxide in suspension form (density ~ 1.7g/cm^3, MgO content ~ 1200 g/l, carrier - light fuel oil).

Table 1 shows the composition and size distribution of the three different additives (A, B and C).

Table 1
Properties of the additives

Components	A	B	C
MgO%	92.1	92.7	81.8
CaO%	0.71	1.67	3.64
SiO_2%	0.52	0.88	4.39
Fe_2O_3	0.78	0.28	1.95
Al_2O_3	0.27	0.27	0.59
Diameter			
Average	1 μm	7 μm	5μm
below 20 μm	100%	92%	–
below 10 μm	100%	66%	71%
below 5 μm	98%	43%	–
below 1 μm	55%	25%	28%

This table shows that all additives contain MgO, as agent, at least 80% (together with CaO 85%). The size of particle is decisively below 10 μm, even below 1 μm, that means very small particle diameters. The small size MgO particles are expected to take part completely in reaction with SO_3.

2. Results

2.1. Analysis of Advantages Expected

Our first test was carried out with additive B during more than three months (between February 24 and June 9). At the beginning, the additives were mixed directly into the fuel (till March 17), later they were separately led into the upper part of the fire zone.

As effect of additive, we gained the following experience:

1. pH values started from 2 and achieved 3.5 while additives were directly mixed into the fuel oil (till March 17). After feeding modification, the pH values increased quickly, but after contamination of overheating

system (TH_4) dropped under 4. In the second step, after washing and cleaning, pH values increased rapidly and became steady between 4 and 5.

2. By reduction of the iron-sulphate, the iron loss in the Ljungström preheater, and the low-temperature corrosion can be controlled indirectly.

On the basis of the tests [2], the fly ash iron content declined from 16% to 1.5–4.5%, and stabilized, which means 85% reduction.

The weight comparison of test cassettes located on the cold side of Ljungström preheater confirms significant reduction in iron loss. According to this weight comparison, the iron loss decreased by 62.5% as effect of using additives.

3. Decrease of the high-temperature corrosion was analyzed indirectly [2]. Melting point of deposits collected (mechanically) from overheater tubes (TH_4) was observed. According to these measurements, softening point of the middle layer, which was the heaviest, increased by 200–300 °C, insuring substantial decrease in corrosion.

4. Dew point declined from 150–155 °C (at 215 MW) to about 140 °C in the first term of testing. Although it gradually increased with growth of the deposition in the heating surfaces to 145 °C. In the second term, after cleaning, dew point fell to 130 °C, indicating the lack of catalysis initialized by the sediment formed on the overheater.

Acidic dew points were measured both before and after the Ljungström preheater. Typically the latter was lower by 1–2 °C.

During the testing period, the composition of the fuel oil was more or less stable. Sulfur content was between 2.76–3.18%, vanadium 130–150 mg/kg, sodium content varied from 2.5 to 3.0 mg/kg.

5. Ratio of unburned particles was 20–30 m/m% in the fly ash at the beginning. Its value did not change considerably after using additives. Even if we realized a small degree deterioration taking into account the excess volume of the fly ash.

2.2. Analysis of Air Pollutants [4]

During the representative measurements, we analyzed the air pollutant content of the flue gases. The air pollutants analyzed are:

- sulfur dioxide (SO_2),
- carbon monoxide (CO),
- nitrous oxide (NO_x) and
- particles (dust).

To measure gas emissions, we used devices worked on the principle of infra red, and chemiluminescent detecting. Monitoring points located after the air preheater (Ljungström), and before the ECO (economizer).

The change resulted by the supplement is shown on *Figs. 1* and *2*, as function of time. The NO_x emission (*Fig. 1*) depends on the power and beyond that the amount of the oil additive. The additives do not effect on the CO emission, that is why it cannot be seen on the figures.

At the beginning, the NO_x emission increased significantly (*Fig. 1*) on the basis of using oil additive. Mainly this can be explained by the high additive-fule ratio (1:1000). The additive was deposited on the surfaces in the fire space. This deposit restricted the heat transfer, which led to higher flue gas temperature and formed more thermal nitrogen oxide. When the additive ratio decreased (1:2000 and 1:2500) and the boiler was cleaned, the NO_x emission declined, whereas it remained above the initial value.

Table 2 shows the change of relative SO_2 emission (SO_2 eff/SO_2 max) as the effect of the supplement.

Table 2

Relative SO_2 change during measurement

Date	24/02	02/03	17/03	07/04	09/06
$\frac{SO_2 \text{ eff}}{SO_2 \text{ max}}$	0.90	0.91	0.87	0.86	0.86
	0.90	0.91	0.87	0.86	0.86

Before starting the use of additives (February 24 and March 2) all the sulfur content of the fuel was not able to form SO_2, the difference was about 9–10% found as SO_3. After supplement this range became higher (13–14%), but the flue gas contained only 2% SO_3, the remnant (11–12%) presumably was in the fly ash.

The solid material – was not measured directly, however, some calculations can be made knowing the composition of the additives. 1000 ml additive – according to the producers brochure – contains 1200 g MgO. If the ratio is 1: 2000 (1 liter additive to 2000 kg fuel oil), 1 kg fuel oil contains 0.6 g MgO. Burning 1 kg fuel oil gives approximately 10 m^3 dry flue gas (lambda=1). 1 m^3 from such gas includes 60 mg MgO. If the magnesium oxide is entirely transformed into $MgSO_4$ (molecule weight ratio – 40:120) the flue gas holds 180 mg/m^3 $MgSO_4$. If O_2 content of the flue gas is 3%, it becomes 154 mg/m^3. The additional solid material (dust particles) increases the dust emission substantially (by 100%).

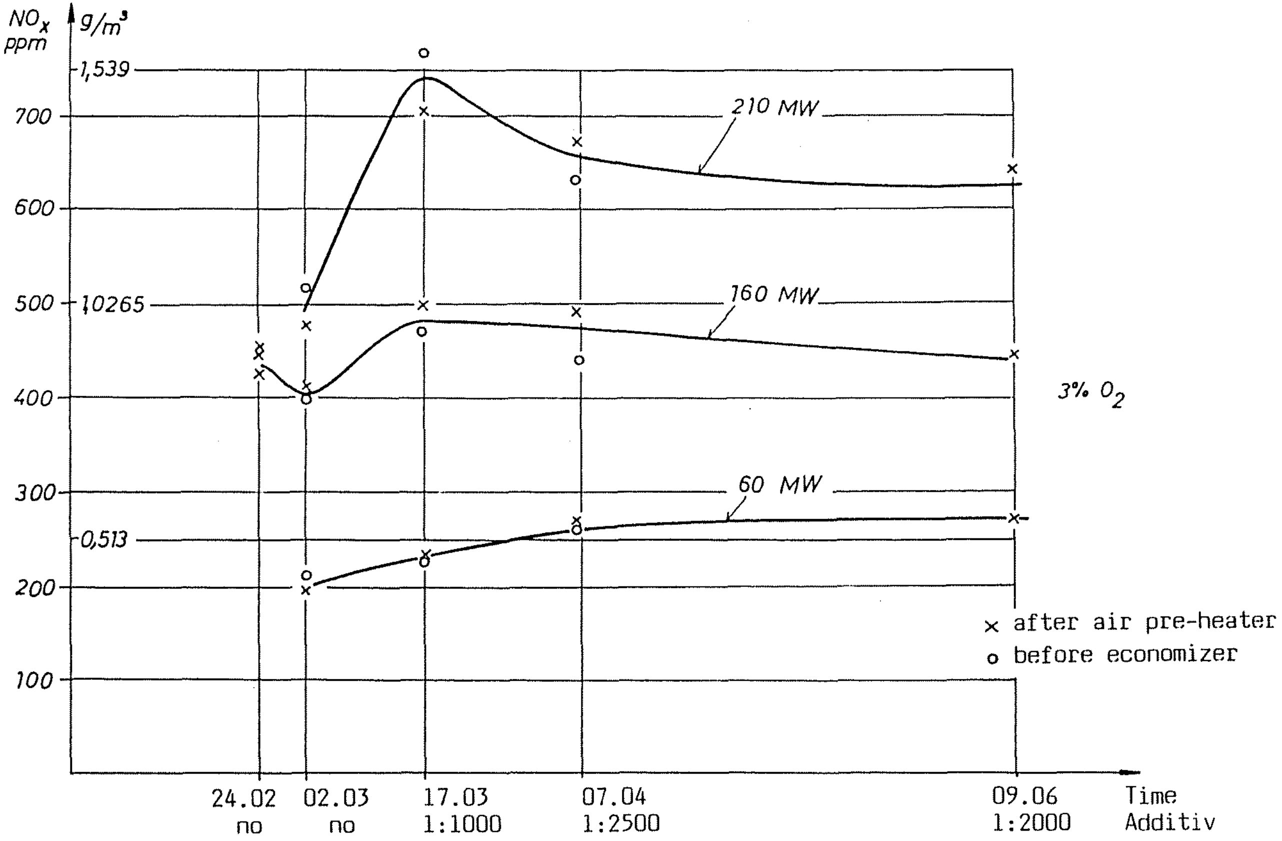

Fig. 1. NO_x emission as function of time and power

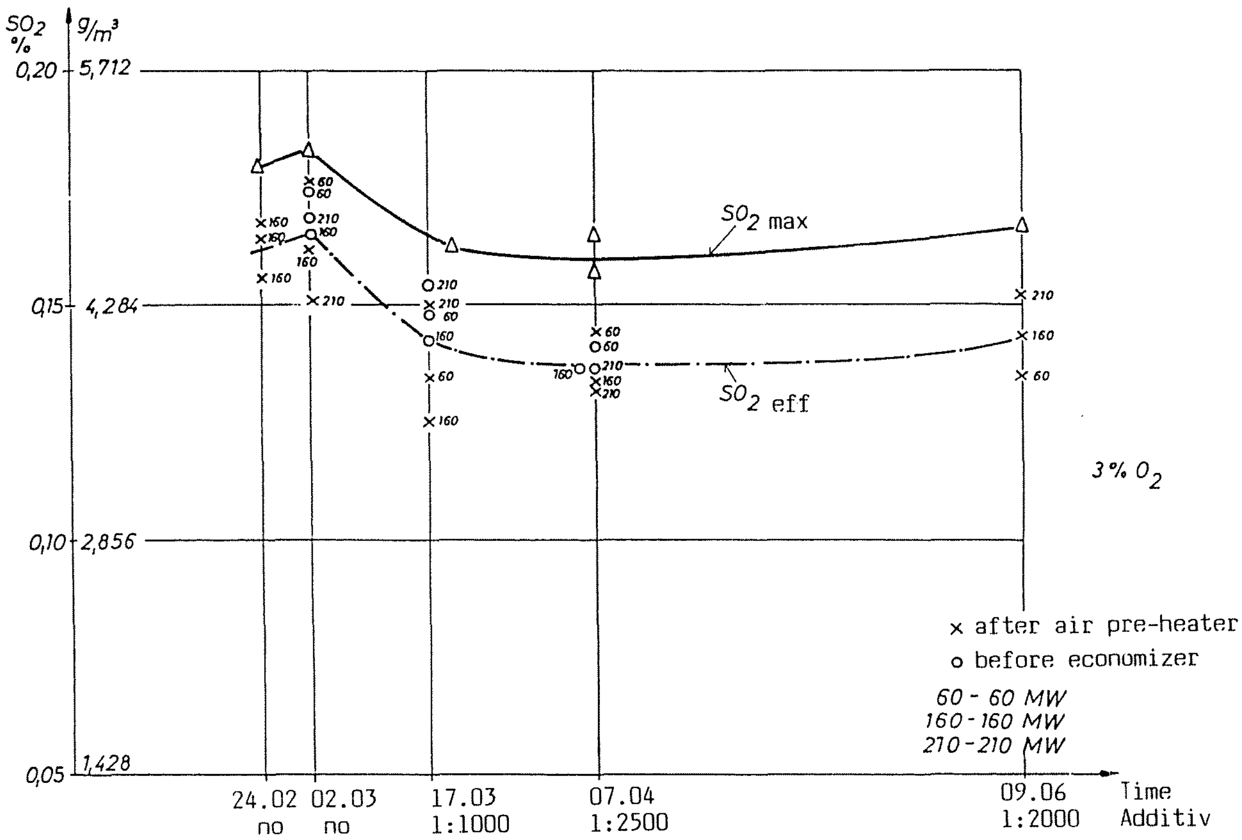

Fig. 2. **SO_2 emission as function of time**

2.3. Analysis of Other Effects

2.3.1. Role of supplement site

Unfortunately, there are undesirable side effects during the supplement. Direct supplement and big doses result fast modification of the heat transfer on the heating surface in the boiler. At the beginning, additional and fast deposition was observed on the previously contaminated surface in TH_4. Parallel, when the ratio was 1:1000, a part of MgO additive was deposited on the surface of the fire space coloring it white and reduced the heat radiation. Two effects together resulted the overheating of the large surface reheater getting too much high temperature combustion products, which could not be balanced by injection. Naturally, the above mentioned effect could be observed in the further stages. The flue gas temperature before the ECO went up from 460 °C to $\sim$ 570 °C, causing dangerous impact on the steel construction of the dilatation, and the flue channels. Similarly, the flue gas temperature rose nearly 100 °C after the ECO.

Because the flue gas temperature increased dangerously, principle of the supplement had to be changed.

After 12 day work of the boiler, we stopped the unit and had the injectors installed. In the new system, we could control the ratio depending on the outlet. On the basis of experience, we can announce that the supplement into the fire space is more beneficial than mixing into the fuel. In that case the pH improvement is faster and there is no temperature shift. However, the injection into the fire space is technically more complicated.

2.3.2. Deposits

Before testing the inlet part of the overheater, the black deposit thickness was 2–4 mm, and its removal was difficult. The supplement resulted higher thickness (4–8 mm), but it was much more easily to be dislocated.

Before testing, the ECO was covered by 2–3 mm thick, dusty, very fine, and easily removable deposit of thickness which increased to 3–4 mm before cleaning, but remained easily removable.

Generally, the physical properties of all deposits changed in every surfaces. They became more loose, porous and easily removable (by hand).

3. Summary, Conclusions

We have gained the experience written above, using additive type 'B'. But the results are similar applying additive type 'A' [5]. It is understandable, because the additives contain decisively MgO, as agent. The effect of the additive:

1. low temperature corrosion decreased,
2. high temperature corrosion decreased,
3. acidic dew point of flue gas decreased,
4. combustion of fuel did not change,
5. gaseous pollutant emission (CO, NO_x, SO_2) did not change, if the supplement was made in the suitable amount, and location,
6. solid particle emission (dust) increased by the solid material content of the additive,
7. amount of deposits increased, but it became more easily removable.

On the basis of the facts summarized above, the application of the additives is rational, when the technology of supplement can be supervised. And the recovery of dust content from the flue gas has been elucidated, otherwise the disadvantageous offset the benefits expected.

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