# Influence of Liquid Hydroxide Based Additives on Suppression of Slag Formation in Granulation Furnaces

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## Abstrakt

*The article deals with the possibility of limiting slag formation in specific heating plant boilers by adding an additive to the batch. The possibilities of reducing slag formation in energy boilers have already been investigated in laboratory conditions where the addition of the NALCO 8270 additive has not led to demonstrable results [13]. X-ray diffraction and X-ray fluorescence of slag samples collected from granulation boilers were performed within the experiment. Furthermore, calculations of the efficiency of the boilers operated in the heat plant were performed using the indirect method. The efficiency was calculated for boilers without dosing and with additive dosing. The results show that using the additive increases the efficiency of the boiler by about 1%.*

*Keywords: slag, slagging, fouling, granulation furnace, ash fusion temperature, boiler efficiency*

**Introduction**

In addition to flammable substance, coal contains ash and water. Minerals contained in coal in the natural state are referred to as ash matter. Burning coal with ash matter generates ash. If the combustion temperature is higher than the melting point of ash matter, slag formation occurs. Ash, unlike slag, is a mixture of minerals, while slag is their melt [1], [2]. Slags forming on the walls of boilers and the granulation grate lead to many negative effects. Fouling of flue gas pathways may occur, which may reduce boiler output, reduce heat transfer, or cause mechanical stress on the pipes. Corrosion of the boiler may also occur under the slag formed. In addition to the composition of ash matter and the thermoplastic properties of ash, the iron content also has the decisive influence on the formation of slag. The temperature of plastic deformation decreases with greater iron content, and it is therefore more susceptible to slag formation1. The problem of the dependence of the thermoplastic properties of ash on its chemical composition has been dealt with theoretically by a number of studies [3], [4], [5], [6], [7]. Although the principles of slag formation on boiler heating surfaces are known, this phenomenon cannot be simply avoided in practice. For example, in standard practice, suitable coal for the particular boiler type, homogeneity, the same thermoplastic properties of ash cannot be ensured permanently. At present, there is a significant amount of additives on the market to reduce the formation of sediment in boilers. The purpose of these additives is to increase the ash melting point, to reduce the strength of the resulting sediments for their subsequent removal, or to reduce the corrosive effects of fly ash. The additives used include magnesium oxide ($MgO$), calcium oxide ($CaO$), silicon dioxide ($SiO_2$), limestone ($CaCO_3$), magnesite ($MgCO_3$), dolomite ($CaMg(CO_3)_2$), brucite ($Mg(OH)_2$), kaolinite ($Al_2Si_2O_5(OH)_4$) and vermiculite ($(Mg,Fe^{2+},Al)_3(Al,Si)_4O_{10}(OH)_2.4H_2O$) [8], [9], [10], [11]. In connection with the development of scientific knowledge and the commercial manufacture of chemical products, a theoretical and practical possibility of reducing slag was investigated using a chemical preparation referred to as NALCO 8270. This product mainly consists of magnesium hydroxide. By dispensing this liquid MgO-based additive, metal oxides in the ash structure are replaced to produce a high temperature reaction $MgO$-$Al_2O_3$-$SiO_2$, thereby increasing the softening temperature of the slag-forming components. It increases the porosity of slag, which then has less adhesive strength and it is easily released from surfaces. This product also keeps ash in the form of non-sticking powder, suppresses sticking of fly ash inside the boiler tubes and neutralizes acidic $SO_3$ [12]. This product is sprayed in a simple way onto a conveyor belt.

**X-ray diffraction and slag fluorescence**

Slags were collected from the boilers without and with the use of an additive and biomass (Tab. 1).

Slag 1 was collected from the K3 boiler, which combusted coal with biomass. The combusted biomass/coal ratio was 1:10. The resulting slag was dark in colour, sharp on the edges, and shiny. The slag from the heat exchange surface could not be simply removed. The X-ray diffraction shows (Table 7) that this slag contains a 100% amorphous fraction. This value could be explained by the insufficient temperature required to melt ash matter and its transition to an amorphous state. Figure 1 shows the slag collected.

Tab. 2. Chemical composition of Slag 1

Tab. 2. Skład chemiczny próbki żużla 1

| analyte | weight [%] |
|---|---|
| $Na_2O$ | 0.14 |
| MgO | 3.08 |
| $Al_2O_3$ | 18.90 |
| $SiO_2$ | 60.40 |
| $P_2O_5$ | 0.07 |
| $SO_3$ | 0.04 |
| $K_2O$ | 2.93 |
| CaO | 4.47 |
| $TiO_2$ | 1.04 |
| MnO | 0.18 |
| $Fe_2O_3$ | 8.45 |
| FeO | 0.38 |

Tab. 3. Chemical composition of Slag 2

Tab. 3. Skład chemiczny żużla 2

| analyte | weight [%] |
|---|---|
| $Na_2O$ | 0.02 |
| MgO | 2,49 |
| $Al_2O_3$ | 16.40 |
| $SiO_2$ | 64.50 |
| $P_2O_5$ | 0.06 |
| $SO_3$ | 0,01 |
| $K_2O$ | 2,80 |
| CaO | 3,69 |
| $TiO_2$ | 0.81 |
| MnO | 0.19 |
| $Fe_2O_3$ | 8.54 |
| FeO | 0.38 |

Tab. 4. Chemical composition of Slag 3

Tab. 4. Skład chemiczny Żużla 3

| analyte | weight [%] |
|---|---|
| $Na_2O$ | 0.18 |
| MgO | 2.04 |
| $Al_2O_3$ | 21.10 |
| $SiO_2$ | 61.20 |
| $P_2O_5$ | 0.07 |
| $SO_3$ | 0.02 |
| $K_2O$ | 3.87 |
| CaO | 2.25 |
| $TiO_2$ | 1.03 |
| MnO | 0.14 |
| $Fe_2O_3$ | 6.64 |
| FeO | 0.30 |

Tab. 5. Chemical composition of Slag 4

Tab. 5. Skład chemiczny żużla 4

| analyte | weight [%] |
|---|---|
| $Na_2O$ | 0.15 |
| MgO | 2.10 |
| $Al_2O_3$ | 21.40 |
| $SiO_2$ | 60.90 |
| $P_2O_5$ | 0.07 |
| $SO_3$ | 0.02 |
| $K_2O$ | 3.93 |
| CaO | 3.15 |
| $TiO_2$ | 1.07 |
| MnO | 0.13 |
| $Fe_2O_3$ | 6.50 |
| FeO | 0.29 |

Tab. 1. Distribution of input material for the formation of slag
Tab.1. Dodatek materiału dodatkowego do wsadu

| slag | fuel | additive |
|---|---|---|
| 1 | intermediate layer + biomass | - |
| 2 | intermediate layer | - |
| 3 | intermediate layer | - |
| 4 | intermediate layer | 5 kg/100 t |
| 5 | intermediate layer | 10 kg/100 t |

Fig. 1. Slag 1 [photo by the author]
Fig. 1. Żużel próbka 1

Fig. 2. Slag 2 [photo by the author]
Rys. 2. Żużel 2

Fig. 3. Slag 3 [photo by the author]
Rys. 3. Żużel 3

Fig. 4. Slag 4 [photo by the author]
Rys. 4. Żużel 4

Fig. 5. Slag 5 [photo by the author]
Rys. 5. Żużel 5

Slag 2 (Fig. 2) was collected from the K3 boiler, where only the Ostrava intermediate layer was combusted. The resulting slag is dark in colour, and it is very hard. Removal of the resulting slag from the heat exchange surfaces of the boiler is very difficult due to its hardness. The X-ray diffraction shows (Tab. 7) that the slag contains the biggest proportion of amorphous fraction. It also contains more cordierite and cristobalite. In smaller quantities, it contains quartz, magnetite and albite. In comparison with other samples, the lowest amount of quartz and albite is found in this slag.

Slag 3 (Fig. 3) was collected from the K2 boiler. This slag was formed during the combustion of the Ostrava intermediate layer without dosing of an additive. The X-ray shows (Tab. 4) that this slag contains the biggest proportion of amorphous fraction. It also contains quartz and mullite. As in slag sample 2, albite and magnetite were detected here.

Slag 4 (Fig. 4) was collected from the K4 boiler. The NALCO 8270 additive was dosed into the boiler, 5 kg per 100 tons. In this slag (Tab. 7), the highest proportion of amorphous fraction was present. Mullite was also represented here, there was quartz in smaller quantities, as well.

The total content of basic elements recalculated to the oxidic form is given in Table 5.

Slag 5 (Fig. 5) was collected from the K4 boiler. Additive amounting to 10 kg per 100 tons was dosed into the boiler. In this slag (Tab. 7), the highest proportion of amorphous fraction was present again, and there were also labradorite and quartz. Only labradorite and spinel were found in this slag sample.

The total content of basic elements recalculated to the oxidic form is shown in Table 6. The X-ray diffraction results are shown in Table 7 and 8.

**Calculation of the boiler efficiency**

The efficiency calculation was performed by indirect method according to ČSN (Czech National Standard) EN 12952-15 Water-tube Boilers and Auxiliary Equipment – Part 15: Acceptance Tests. Two boilers were selected to calculate the efficiency of boilers, namely boilers K1 and K2. The efficiency was calculated for the boilers at the time when additive was not dosed, the so-called "fouled boiler", and at the time additive was dosed, the so called "clean boiler". To calculate the efficiency, input data had to be obtained from the operator.

Tab. 6. Chemical composition of Slag 5
Tab. 6. Skład chemiczny żużla 5

| analyte | weight [%] |
|---|---|
| $Na_2O$ | 0.07 |
| MgO | 2.18 |
| $Al_2O_3$ | 19.70 |
| $SiO_2$ | 62.40 |
| $P_2O_5$ | 0.06 |
| $SO_3$ | 0.06 |
| $K_2O$ | 3.74 |
| CaO | 3.53 |
| $TiO_2$ | 1.05 |
| MnO | 0.15 |
| $Fe_2O_3$ | 6.64 |
| FeO | 0.30 |

Tab. 7. X-ray diffraction of slag, fly ash and intermediate layer
Tab. 7. Analiza rentgenowska żużla, popiołu i warstw żużla

| | slag 1 [%] | slag 2 [%] | slag 3 [%] | slag 4 [%] | slag 5 [%] |
|---|---|---|---|---|---|
| amorphous fraction | 100.00 | 65.72 | 61.98 | 78.66 | 38.60 |
| quartz ($SiO_2$) | - | 4.16 | 19.11 | 5.29 | 15.30 |
| cordierite $(MgFe)_2Al_3(AlSi_5O_{18})$ | - | 13.26 | - | - | 6.20 |
| magnetite ($Fe_3O_4$) | - | 3.09 | 1.64 | - | - |
| albite ($Na(AlSi_3O_8)$) | - | 1.96 | 5.83 | - | - |
| quartz low temperature modification ($SiO_2$) cristobalite | - | 11.81 | - | - | 5.87 |
| mullite ($3Al_2O_3 \cdot 2SiO_2$) | - | - | 11.44 | 16.05 | 8.03 |
| labradorite ($(Na,Ca)(Si,Al)_4O_8$) | - | - | - | - | 17.66 |
| spinel ($MgAl_2O_4$) | - | - | - | - | 8.29 |
| hematite ($Fe_2O_3$) | - | - | - | - | - |
| sanidine ($KAlSi_3O_8$) | - | - | - | - | - |
| anhydride ($CaSO_4$) | - | - | - | - | - |
| muscovite $KAl_2(AlSi_3O_{10})(OH)_2$ | - | - | - | - | - |
| chlorite IIb $(Mg,Fe)_6(Si,Al)_4O_{10}(OH)_8$ | - | - | - | - | - |
| ankerite ($CaFe(CO_3)_2$) | - | - | - | - | - |

Tab. 8. X-ray diffraction of fly ash and intermediate layer
Tab. 8. Analiza rentgenowska popiołu lotnego i warstw żużla

| | fly ash [%] | intermediate layer [%] | melting temperature [°C] |
|---|---|---|---|
| amorphous fraction | 60.05 | 80.48 | - |
| quartz ($SiO_2$) | 20.27 | 7.33 | 1800 |
| cordierite $(MgFe)_2Al_3(AlSi_5O_{18})$ | - | - | 1435 |
| magnetite ($Fe_3O_4$) | - | - | 1592 |
| albite ($Na(AlSi_3O_8)$) | - | - | 1120 |
| quartz low temperature modification ($SiO_2$) cristobalite | - | - | 1695 |
| mullite ($3Al_2O_3 \cdot 2SiO_2$) | 8.94 | - | 1058 |
| labradorite ($(Na,Ca)(Si,Al)_4O_8$) | - | - | 1230 |
| spinel ($MgAl_2O_4$) | - | - | 2135 |
| hematite ($Fe_2O_3$) | 1.62 | - | 1567 |
| sanidine ($KAlSi_3O_8$) | 2.05 | - | 1200 |
| anhydride ($CaSO_4$) | 0.99 | - | 1450 |
| muscovite $KAl_2(AlSi_3O_{10})(OH)_2$ | 6.10 | 5.85 | 1400 |
| chlorite IIb $(Mg,Fe)_6(Si,Al)_4O_{10}(OH)_8$ | - | 4.94 | - |
| ankerite ($CaFe(CO_3)_2$) | - | 1.39 | 725 |

The results of the efficiency calculations clearly show that the boiler efficiency increased with the additive use. In the case of the K1 boiler, an increase in the efficiency was 0.84%. In the case of the K2 boiler, the efficiency increased by 1.04%.

## Conclusions

The aim of the experiment was to verify the possibility of suppressing slag formation in granulation boilers, which are particularly prone to slag formation, by adding an additive to the batch. The effect of the NALCO 8270 additive is clearly evident from the results of the efficiency calculations. In the case of the K1 boiler, an increase in the efficiency was 0.84%. In the case of the K2 boiler, the efficiency increased by 1.04%. In particular, increasing the boiler efficiency leads to saving fuel consumption and, last but not least, to reducing emissions. If we consider increasing the efficiency by 1%, it will reduce the consumption of the intermediate layer by 400 tonnes per year. In fuel costs, this saving amounts to about CZK 400,000. This saving is higher than the cost of the additive. Therefore, the experiments show that even though the laboratory experiments did not lead to clear results confirming the suitability of this method, this method can be recommended to suppress slag formation in the granulation boilers after the performed working tests.

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## *Wpływ dodatków na bazie ciekłego wodorotlenku na tworzenie żużla w piecach granulacyjnych*

*W artykule przedstawiono możliwość ograniczenia tworzenia się żużla podczas spalania w kotłach grzewczych poprzez dodatki do wsadu.*
*Możliwości ograniczenia powstawania żużla w kotłach energetycznych zostały już zbadane w warunkach laboratoryjnych, w których dodanie dodatku NALCO 8270 nie doprowadziło do pozytywnych wyników [13]. W ramach eksperymentu przeprowadzono dyfrakcję rentgenowską i fluorescencję rentgenowską próbek żużla pobranych z kotłów. Ponadto obliczenia wydajności kotłów pracujących w ciepłowni przeprowadzono metodą pośrednią. Wydajność obliczono dla kotłów bez dozowania i z dozowaniem dodatków. Wyniki pokazują, że dodatek zwiększa wydajność kotła o około 1%.*

*Słowa kluczowe: żużel, żużel, obrastanie, piec do granulacji, temperatura topnienia popiołu, wydajność kotła*