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IMPROVING OPERATION OF WET GAS CLEANING EQUIPMENT BY DILUTION OF CIRCULATING WASH SOLUTION TO AVOID GYPSUM DEPOSITS

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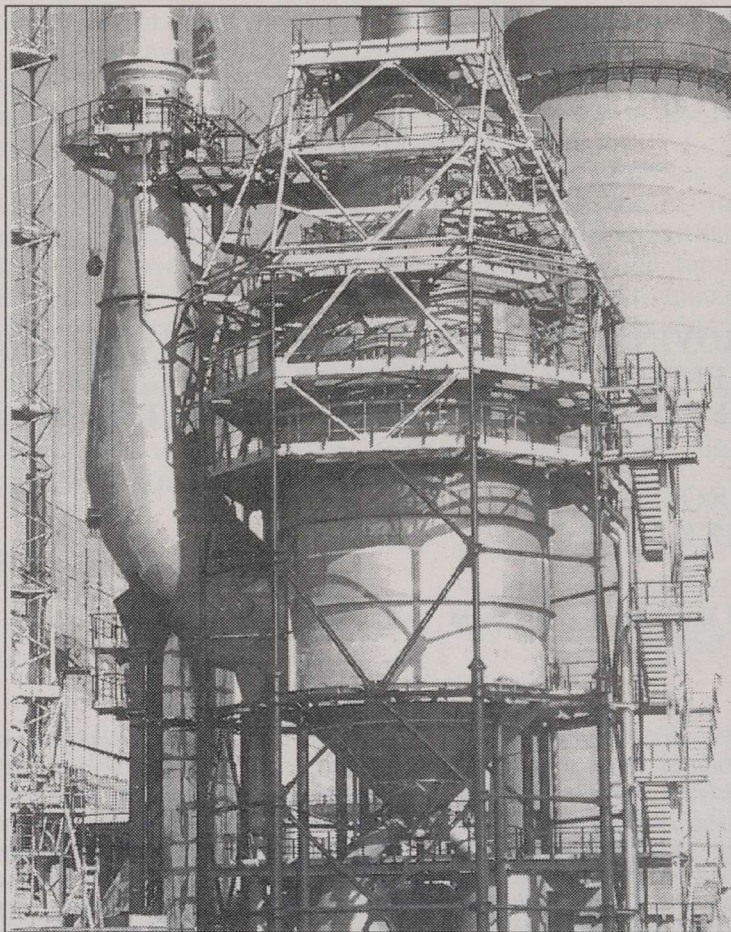
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Wet gas cleaning equipment of AHLSTROM, that uses clarified water from sediment traps, was started at the Baltic Power Plant in Narva in 1993. It was induced from the feasibility to lower expenses of neutralizing sulphurous acid at SO₂ catching by using clarified alkaline water, circulating in hydraulic ash removal system. Preparation of reactants (mainly of CaCO₃ suspension) usually used for this purpose is very expensive. However, quite soon the exploitation experience showed that intensive growth of hard bound gypsum deposits on equipment surfaces became the main problem at its operation. Analyses showed that Ca²⁺ and SO₄²⁻ content in these deposits were 60-80 % or even more indicating quite clearly their origin.

The possibility to avoid gypsum deposits disturbing the operation of the wet gas cleaning equipment in the Baltic Power Plant by dilution of circulating wash solution has been studied in the paper.

Attempts to solve the problem by constructional changes did not give the decisive effect because the main conditions for the deposition of CaSO₄ · 2H₂O were not eliminated.

Absorption of SO₂ by circulating wash solution in a scrubber takes place in an acidic medium. (In alkaline medium the intensive deposition of carbonate deposits by binding CO₂ from gases sufficiently rich in latter will take place.) Absorbed SO₂ reacts with water and forms sulphurous acid that further is bound into a sulphurous acid salt. This process is needed for decreasing the partial pressure (equilibrium pressure) of SO₂ above the droplets of wash solution to intensify absorption process. Sulphurous acid as a divalent acid may dissociate in two stages. In acidic medium of the gas cleaning equipment it reacts with the cations present in wash solution giving bisulphites like Ca(HSO₃)₂, KHSO₃, etc.



Wet gas cleaner of Ahlstrom in the Baltic Power Plant

These salts react with oxygen of flue gas and may quite easily be converted into sulphates. The formation of sulphites, according to literature, takes place at pH values above 5 when, for instance, very sparingly soluble $\text{CaSO}_3 \cdot 0.5\text{H}_2\text{O}$ is formed. This determines the upper limit of pH in wash solution. At pH values higher than seven formation of also very sparingly soluble CaCO_3 starts, as it was already mentioned above.

$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ deposition from wash water, circulating in the wet gas cleaning equipment, is caused by an increase in the content of Ca^{2+} and SO_4^{2-} in wash water during the process. This, in turn, depends on the character of the SO_2 absorption process, where SO_2 bound in wash solution is oxidized into SO_4^{2-} , as well as by calcium and sulphate compounds added with flue gas ash and alkaline water of sediment traps used for SO_2 neutralization. Consequently, the sources of Ca^{2+} addition are the following:

- Ca^{2+} ions present in the clarified water of ash fields used in scrubber;

- dissolution in water of Ca compounds from ash particles given into the scrubber with flue gases.

The sources of SO_4^{2-} addition are the following:

- SO_2 absorbed in the scrubber formed from which bisulphites and sulphites are oxidized into sulphates;
- SO_4^{2-} ions given into the scrubber with clarified water of ash fields;
- dissolution in water of sulphates from ash particles present in flue gases.

Attention must be paid to quite a great quantity of calcium and sulphates entering the gas cleaning equipment with flue gas ash particles and with clarified ash field water. For instance, every cubic meter of flue gas contains up to 0.14 g of potentially soluble calcium (taking into account free CaO present in ash particles) and up to 0.25 g of sulphur in the form of sulphate (calculated as SO_4^{2-}). In ash field water the content of dissolved Ca^{2+} is 700-1000 g/m³ and the content of SO_4^{2-} is in most cases 2000-3000 g/m³ or more. Accordingly, if the amount of flue gas entering the scrubber is 250,000 m³/h and the amount of ash field water is 130 m³/h, the amounts of entered Ca^{2+} and SO_4^{2-} will be up to ~160 kg/h and ~450 kg/h, respectively.

Precipitation of relatively low-soluble CaSO_4 from solution is determined by the solubility product, in general case expressed by the following equation

$$K_{\text{CaSO}_4} = a_{\text{Ca}^{2+}} \cdot a_{\text{SO}_4^{2-}} = [\text{Ca}^{2+}] \cdot [\text{SO}_4^{2-}] \cdot f^2,$$

where

$$a_i = C_i \cdot f_i.$$

Here a_i is the ionic activity;
 C_i is the ion content of solution, g-ion/l;
 f_i is the ionic activity coefficient;
 $[\text{Ca}^{2+}]$ and $[\text{SO}_4^{2-}]$ is the content of calcium and sulphate ions, respectively, g-ion/l.

The value of the activity coefficient f depends on the ionic strength μ of solution

$$\mu = 0.5 \left(C_1 z_1^2 + C_2 z_2^2 + \dots + C_n z_n^2 \right) = 0.5 \sum_{i=1}^n C_i z_i^2$$

and may be estimated from the Debye-Hückel Equation

$$\log f_i = -0.5 z_i^2 \frac{\sqrt{\mu}}{1 + \sqrt{\mu}}$$

where z_i is the valence (charge number) of ion.

Therefore, the value of solubility product of a low-soluble salt depends on valence and concentration of ions present in solution. Solubility of the same salt differs in different solutions.

If the product of $[Ca^{2+}]$ and $[SO_4^{2-}]$ in circulating solution at some point of wet gas cleaning equipment exceeds the value of solubility product at given temperature, the solution becomes supersaturated and $CaSO_4$ starts to crystallize out from the solution. In case of wet gas cleaning equipment placed after oil shale boilers, the liquid phase contains plenty of solid particles caught from flue gas, which represent good centres for crystallization. Therefore, the deposition of $CaSO_4$ may take place onto equipment's surfaces as well as onto ash particles present in water. It is essential to mention that crystallization occurs only at conditions of supersaturated solution. Therefore the main mean enabling to avoid the deposition of $CaSO_4$ from a circulating wash solution is its dilution to the degree, where the product of $[Ca^{2+}]$ and $[SO_4^{2-}]$ in given conditions will not exceed the value of solubility product.

The principal recommendation for dilution of water circulating in scrubber was given by the Thermal Engineering Department of Tallinn Technical University (TED TTU). Provisionally only the questions how to make the dilution and how large water amounts are needed were left open. In principle there exist two possibilities:

- adding technological water to the circulating wash-solution;
- dilution with the water from the second ash field.

The Baltic Power Plant has two ash fields. Now the first one is used for ash storing and its clarified water was foreseen to be used in the wet gas cleaning equipment. The second field is lying idle. Waters of these ash fields have changed noticeably differently in the course of time. Comparable data on total alkalinity and Ca^{2+} and SO_4^{2-} content in waters of both ash fields, received from the Chemical Laboratory of the Baltic Power Plant (average data for the year 1994), are presented in the Table.

Analysing the dilution variants given above, it may be noted that the addition of the required amount of technological water to circulating one is connected with serious problems. First of them is the intense water balance of the ash fields, moreover, the great additional water consumption. Adding of the water previously used in the power plant (for instance, wash water from the chemical purification is sent to ash fields in any case) does not give an essential effect because of its small amount. Adding previously unused water to circulating one, in conditions where about 1-1.5 million cubic meters of water will be added to ash fields of the Baltic Power Plant every year, is out of question.

Indicator	Water of the first ash field	Water of the second ash field
Total alkalinity, mg-equiv./l	72.5	33.5
Ca^{2+} content*, mg/l	723.4	7.2
SO_4^{2-} content, mg/l	1959.5	876.9

* The Ca^{2+} is calculated from the total hardness of water.

Tests on the scrubber fulfilled by the plant's staff, as well as calculations made by using methods elaborated in TED TTU showed that it is quite possible to fight against gypsum deposits. The procedure can be successfully realized using the clarified water of the second ash field as an alkaline reagent for binding absorbed SO_2 in the scrubber. Moreover, by using the water of the second ash field, the content of Ca^{2+} and SO_4^{2-} ions in circulating wash solution will remain significantly below the saturation limit. Even the dissolution of gypsum deposits previously formed in the equipment will occur instead of the deposition of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

In that case the circumstance that general alkalinity of clarified water from the second ash field is significantly lower than that from the first one can be the problem. Due to that the required for the neutralization of caught SO_2 amount of water from the second ash field is ~2-3 times higher than that from the first one. The water used in the gas cleaning equipment will finally be sent to the first ash field. Such significant increase in the water amount may cause problems in the water balance, especially if more than one gas cleaning equipment will be required in the future. Another question is how much water from the second ash field will be in use. Calculations and tests showed that in case of existing wet gas cleaning equipment, working with water from the second ash field, the water consumption is 300-370 m^3/h . It makes 1.5 million m^3 per year if the equipment is in operation for 5000 hours. In case of larger water amounts, the equalization of chemical composition of these two ash field waters will not be excluded. Therefore the optimal ratio between these water amounts, warranting deposit-free regime at the minimal total water consumption, should be found. There are principally two solutions for solving the problem:

- continuous use of waters from both ash fields with their optimal ratio;
- operation of the scrubber with the water from the first ash field until fouling followed by its cleaning with water from the second ash field and so on, i.e. working at varying mode of operation.

To find the optimal ratio between the waters of the first and the second ash fields, in the Thermal Engineering Department of TTU a special computer program has been worked out. The program allows to estimate, proceeding from the given data, whether circulating water becomes saturated by CaSO_4 under given conditions. Computations showed very clearly that at using water only from the first ash field the formation of gypsum deposits was inevitable. In case of using water from the second ash field the dissolution of gypsum deposits in circulating water should take place. Evidently the optimal ratio is the operation mode, during which a little more than half of required alkalinity is covered by the water from the first ash field and the rest by the water from the second one.

Tests should show which mode of operation will finally prove to be the best. The worked-out computer program allows to find theoretically optimal water ratio for the first variant (continuous mode of operation). In practice, it must be taken into consideration that, due to the partial

deposition of CaSO_4 onto solid particles in circulating water, fouling free operation may be obtained also by a little worse than the optimal ratio. Proceeding from the water consumption there is the possibility that the optimal may be the operation with slow growing of deposits but that must be controlled by tests. Also in the case of varying mode of operation the total amount of water must be estimated. For this one has to know the water consumption both at the deposition mode of operation (water of the first ash field) and at the cleaning mode (water of the second ash field), i.e. at all the cycles.

Finally, on the base of the present work it may be declared that fouling of a wet gas cleaning equipment with gypsum deposits, when the clarified water of oil shale ash field is used, may be avoided by dilution of the wash solution. The water of the second ash field, if used in large amounts, is capable to dissolve formed gypsum deposits and so it represents a suitable dilution agent for the given case.

The water from the second ash field, more exactly, its usable amount (taking into account the seasonally changing conditions of the year) proves to be the key question at solving the problem. Therefore the main attention should be paid to the preparation of water with low content of Ca^{2+} and SO_4^{2-} from the water of the first ash field, and, besides it, to finding the optimal ratio of two ash field waters. It is particularly essential considering the further perspective. From the standpoint of enlarging the wet gas cleaning, it is very essential how much water with the properties of the water from the second ash field may be prepared during a certain amount of time (a year, a month) in the ash field system. That is what determines the number and productivity of devices using water from the second ash field, and it should inevitably be known before equipping a power plant with new gas cleaning devices.

Summary

The possibility to avoid gypsum deposits disturbing the operation of the wet gas cleaning equipment in the Baltic Power Plant by dilution of circulating wash-solution has been studied. Possibility of that has been shown. It was found that the best dilution agent is the water from the second ash field of the power plant. The problem is how to get the required amount of this water, and water balance of the first ash field has to be made.

Presented by I. Öpik

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