Features of Use of Limestone and Lime in Wet Desulphurisation Technology

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Abstract
Flue gas of coal boilers has required cleaning of sulphur dioxide with the efficiency of at least 96% to meet the requirements of Directive 2010/75/EU. Wet scrubbers with forced oxidation, which use limestone or lime as sorbent, are the most used desulphurisation plants at the world thermal power industry. They allow providing the efficiency of sulphur dioxide removal up to 98% and obtaining a gypsum as product. Lime is much more chemically active and expensive sorbent, than limestone, but it’s using requires a lot of time to dissolve the calcium sulphite scale. The use of particles of limestone, measuring up to 10 microns, at washing slurry wouldn’t only allow providing the high efficiency of desulphurization but also reducing the risk of scaling at the upper part of the scrubber.

Keywords: Flue gas, wet desulphurisation, lime, limestone, gypsum.

Introduction
The problem of reducing sulphur dioxide emission as a result of high-temperature oxidation of sulphur fuel was of great significance for developed countries in the 1960s. Millions of tons of sulphur dioxide, as well as hundreds of thousands of tons of nitrogen oxide were released into atmosphere after combusting the tens of millions of tons of coal and fuel oil at thermal power plants. That emission was the main cause of acid rains, which, in turn, has led to deterioration of human health, reduction of crop yields and reduction of pH level in water ponds, forest destruction and damage of architect monuments. That emission was the main cause of acid rains, which, in turn, has led to deterioration of human health, reduction of crop yields and reduction of pH level in water ponds, forest destruction and damage of architect monuments. This was a stimulus to develop technologies of flue gas desulphurisation which began to be introduced at the thermal power plants in Japan, U.S. and Western Europe already in the 1970s. Today, almost all the coal plants in the Western Europe and Japan are equipped by high-efficiency desulphurization plants.

In the developed countries at the legislative level, the strict limitations of allowable concentrations of exhaust gases pollutants were adopted to stimulate introducing the flue gas cleaning plants. Excess of emission limit values has led to either stopping the thermal power plant exploitation or paying a huge penalty. In the European Union, emission limit values of large combustion plants are regulated by Directive 88/609/EEC and Directive 2001/80/EC, and what's more, the new Directive has adopted the stricter requirements. Directive 2010/75/EU on industrial emissions has determined the new restrictions for emission limit values for sulphur dioxide. In cases of new large coal-fired boilers with a total rated thermal input exceeding 300 MW, emission limit value for sulphur dioxide is 150 mg/m³. Where that is impossible to comply with emission limit values for sulphur dioxide due to high sulphur content at local coal, it is permitted to use as a limit value the minimum rate of desulphurization which amounts to 96% for large boilers.

This requirement significantly limits the choice of technologies of flue gas desulphurisation at thermal power plants. Wet scrubbers are the most used desulphurization plants at the thermal power industry through the world. They use the effect of the dissolution of sulphur dioxide SO₂ in water, formation of sulphurous acid H₂SO₃ and its dissociation into the anions of hydrosulphite HSO₃⁻ and sulphite SO₃²⁻ and the protons H⁺. Since the concentration of sulphurous acid in the solution (mol/l) is proportional to the equilibrium pressure of sulphur dioxide at the boundary layer of the gas medium according to Henry equation, therefore the use of large water consumption allows considerable reducing the output concentration of sulphur dioxide. Rozenknop showed that it is necessary to supply water with the specific flow rate of 30 l/m³ in order to comply with sanitary norms of 1950s via water washing of flue gas containing 2000 ppm of sulphur dioxide at a temperature of 50 °C.

The main difficulty of flue gas water cleaning consists in forming a large amount of acid waste water that is not less dangerous to the environment than the emission of sulphur dioxide into the atmosphere. Furthermore, it is necessary to have a source of water and to use powerful pumps for pumping the washing water in the reaction volume. For a boiler with a steam capacity of 1000 t/h the estimated value of flow rate of washing water amounts to about 33,000 t/h. It is necessary to pump significant amounts of acidic water into the special treatment plant for waste water.

However, adding alkaline compounds into the flue gas washing liquid enhances its pH via binding of cations with anions of these substances and cause sulphite to hydrosulphite salts formation.
thus significantly reducing the fluid flow. Figure-1 shows the mole fraction of the sulphur compounds in solution versus pH\(^{11}\). It is obvious that for low output concentrations of sulphur dioxide it is necessary to maintain pH of the washing solution above 5, when the proportion of sulphurous acid is almost zero.

**Material and Methods**

In thermal power industry of the developed countries, the plants for the wet desulphurization most often use limestone or lime as a sorbent with gypsum obtaining. First wet lime desulfurization plants was used the lime as a chemically active substance. At the present time, are increasingly used as a sorbent limestone as a widespread mineral. The question arises about the features of using one or the other sorbent. For this purpose a cycle of experiments to study the process of absorption of sulphur dioxide in the slurry sorbents containing calcium, in a laboratory wet scrubbing bubble reactor schematically shown in figure-2\(^{14}\).

Into the bubbling reactor enters 100 ml of slurry containing 0.05 mol of sorbent. The particle size of limestone and lime particles does not exceed 10 microns. Sulphur dioxide flow rate was 2 l/min or 1.4 mmol/s. During the experiments, the gaseous mixture from the \(\text{N}_2 + \text{SO}_2\) balloon, containing 1400 ppm of sulphur dioxide, enters the bottom of bubbling reactor. For study of the effect of oxygen on the absorption process in the gas stream the latter was added in some experiments with the concentration of 6% vol. At the outlet, the sulphur dioxide concentration and pH were measured of the solution during the feed gas mixture at intervals of 1 min.

![Fraction of the sulphuric compounds versus pH of the solution](image1)

**Figure-1**

Fraction of the sulphuric compounds versus pH of the solution \([10]\)

![Scheme of wet gas cleaning facility](image2)

**Figure-2**

Scheme of wet gas cleaning facility
Results and Discussion

Figure 3 shows results of studies of the absorption of sulphur dioxide in the slurry of lime Ca(OH)$_2$ depending on the amount of feed to the reactor of sulphur dioxide for the two model gases – N$_2$ + SO$_2$ and N$_2$ + SO$_2$ + O$_2$, respectively. The presence of oxygen in the gas volume concentration of 6% and a pH in the curves passing sulphur dioxide SO$_2$ by absorption in the lime slurry occurs only in an acidic medium (figure 3).

The molar ratio of sulphur dioxide-to-sorbent m is below 1.0-1.2, pH value of the solution for both model gases corresponded to the value of a saturated solution of lime. In this case, formation of calcium sulphite occurred, which was precipitated. SO$_2$ output concentration equalled zero. For values of m from 1.2 to 1.5 in the reactor acidic environment was observed, which was dominated by the conversion of solid calcium sulphite into soluble calcium hydrosulphite with almost complete absorption with the sulphur dioxide. And only when m exceeded 1.5 and pH dropped to the point below 4 and output SO$_2$ concentration started to rise, there were differences between the curves of SO$_2$ values and pH for each model gas. Output concentration of sulphur dioxide in case of the second model gas (N$_2$+SO$_2$+O$_2$) exceeded the level of the inlet concentration. Furthermore, the presence of O$_2$ in the model gas causes to reduce the pH by almost the unit.

Figure 4 shows results of studies of the absorption of sulphur dioxide in the slurry of limestone depending on the amount of feed to the reactor of sulphur dioxide for the two model gases – N$_2$ + SO$_2$ and N$_2$ + SO$_2$ + O$_2$, respectively.
The outlet concentration of sulphur dioxide is equal to zero in
the m value range from 0 to 1.15. One can observe by the pH
curve the first drop for both model gases up to the value of the
molar ratio of SO\textsubscript{2}/sorbent less than 0.1. This is due to the
presence of very small amount of limestone dissolved in water.
In the range of molar ratio of SO\textsubscript{2}/sorbent from 0.1 to 1.0, the
pH curves are almost identical for both gases – the presence of
oxygen in the gas doesn’t show up. The pH values of solution
about 6 indicate a weak acidic medium, and the main sulphite
compound in the solution is hydrosulphite anion HSO\textsubscript{3}\textsuperscript{−}. If the
m value is above 1 and when a sorbent is almost fully spent, the
pH level drops. The presence of oxygen in the model gas is
shown in an acidic medium increased sulphur dioxide concentration values and low pH limestone is practically
insoluble substance. Its solubility is 0.00153 g per 100 g of
water, and is increasing slightly with growth.\footnote{Calcium sulphite is practically insoluble substance (solubility
product of CaSO\textsubscript{3} equals 3.2×10\textsuperscript{−}9) and is easily deposited\textsuperscript{9,16}. Reaction (3) will be prevailing as long as the slurry will contain
the undissolved lime particles, and the main sulphite product in
the solution shall remain SO\textsubscript{3}\textsuperscript{2−} anion (figure 1).}

Therefore, to prevent solid particles maintaining in the wet
scrubbers, it is advisable to use a counter-current scheme, when
the flow of the washing solution or suspension is directed
downwards, and the flue gas is moving from bottom to top.\footnote{In such a case, drops containing calcium sulphite particles,
when falling down, are coming in contact with the flue gas
containing sulphur dioxide. SO\textsubscript{2} dissolution in water with partial
 dissociation of sulphurous acid leads to increase of protons
concentration in the solution, i.e. thus increasing the acidity of
the solution.}

In the range of molar ratio of SO\textsubscript{2}/sorbent less than 0.1. This is due to the
presence of very small amount of limestone dissolved in water.
In the context of fast protolithic chemical reactions, mass
transfer coefficient k is determined by the rate of diffusion of
protons through the boundary layer near the liquid particles.
Specific surface area \(S_s\) is a characteristic of solid substance,
dissolution of which occurs in acidic medium. In this case a
calcium sulphite crystals or hydrate thereof.

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The resulting from reactions (4) and (5) calcium hydrosulphite
in presence of oxygen in solution reacts to calcium sulphate:\footnote{Another product of the reaction (7) is a sulphurous acid H\textsubscript{2}SO\textsubscript{3},
whose presence in the solution shows up in the growth of the
output concentration of a sulphur dioxide (figure-3 and figure-
4).}

Use of forced oxidation for wet desulphurisation plants allowed
to obtain useful by-product – gypsum bihydrate CaSO\textsubscript{4}·2H\textsubscript{2}O.\footnote{Use of forced oxidation for wet desulphurisation plants allowed
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When feeding lime slurry into the scrubber, calcium sulphite
CaSO\textsubscript{3} is formed at the first stage via the following reaction
Ca\textsuperscript{2+} + SO\textsubscript{3}\textsuperscript{2−} ↔ CaSO\textsubscript{4}↓.
molar concentration of calcium sulphate in the lower part of the scrubber above 5.0×10^{-3} mol/l precipitation occurs in the form of large crystals of the bihydrate of calcium sulphate CaSO_4·2H_2O.

The air for oxidation must be supplied to the bottom of the scrubber, wherein the rinse solution has a lower pH value. Formation of sulphate anion SO_4^{2-} or sulphate salts occurs through the formation of the anion sulphite HSO_3^{-}.

Use of limestone slurry in a wet desulphurization sorbent is based on its dissolution in an acidic medium to form calcium cation Ca^{2+} and evolution of carbon dioxide: 10,18
\[
CaCO_3 (\text{solid}) + H^+ \rightarrow Ca^{2+} + HCO_3^- (8)
\]
\[
HCO_3^- + H^+ \rightarrow H_2O + CO_2 \uparrow (9)
\]

Limestone dissolution rate is described by the equation (6). It could be increased by the increase of specific surface area S of the sorbent when it is ground. Another option to enhance limestone dissolution is to increase concentration of protons in the volume of washing solution by adding in a weak organic acid. 3,10,20 These acids generate a proton upon dissociation of H^+, and at the step of limestone slurry preparation when fed into a scrubber, calcium cation is form. However, a disadvantage of this method is the complexity of the wastewater treatment.

The total absorption of sulphur dioxide, which observed in Figure-4, in the suspension of finely ground limestone with a large value of specific surface area S of the sorbent when it is ground. Another option to enhance limestone dissolution is to increase concentration of protons in the volume of washing solution by adding in a weak organic acid. 3,10,20 These acids generate a proton upon dissociation of H^+, and at the step of limestone slurry preparation when fed into a scrubber, calcium cation is form. However, a disadvantage of this method is the complexity of the wastewater treatment.

In the zone of low pH, the presence of oxygen in water results in formation of the calcium sulphate as well as giving off the sulphur dioxide into the gaseous medium from the solution according to reaction (7). The zone with increased pH value is necessary for SO2 absorption. That is why, the counter-current flow scheme of the gas stream and washing liquid is needed for the wet limestone desulphurization.

Conclusions

At the world power industry, the most used desulphurization plants are wet scrubbers with the efficiency of up to 98%. Wet desulphurization plants are able to ensure a compliance with the requirements of European Directive 2010/75/EU on industrial emissions. Limestone and slaked lime are used as the main sorbents for wet desulphurization technology because of their availability and prices, and the end product is the gypsum.

Wet desulphurization plants, based on calcium sorbents, should apply a counter-current flow scheme for input of flue gas and washing slurry to prevent the calcium sulphite scaling at the upper part of the scrubber.

The use of particles of limestone, measuring smaller than 10 microns, at washing slurry allows absorbing the sulphur dioxide with the efficiency not less than by using of slaked lime.

Obtaining the calcium sulphate as a product occurs only via the stage of formation of calcium hydrosulphite in acidic solution and its subsequent oxidation.

To use a lime as sorbent needs to increase the size of the scrubber due to much time that required for the dissolution of the calcium sulphite deposition formed through input of lime slurry into the scrubber.

When using fine particles of limestone as sorbent, water-soluble calcium hydrosulphite is the main sulphite compound in the solution, which, by reacting in liquid with oxygen, is rapidly oxidised to calcium sulphate. Therefore, for the wet desulphurization technology, finely ground limestone has advantages over lime both on the economical part and on technological part.

References

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