EUROPEAN UNION
European Structural and Investment Funds
Operational Programme Research,
Development and Education

MINISTRY OF EDUCATION,
YOUTH AND SPORTS

Environmental friendly technologies

KEE/ENT

ESF IIproject of the University of West Bohemia
in Pilsen
reg. č. CZ.02.2.69/0.0/0.0/18_056/0013239

Study material III.

Reducing emissions from burning fossil fuels

Ing. Milan Bělík, Ph.D.

EUROPEAN UNION
European Structural and Investment Funds
Operational Programme Research,
Development and Education

MINISTRY OF EDUCATION,
YOUTH AND SPORTS

1. Reducing emissions from the combustion of fossil fuels

The rapid development of industry after World War II necessitated a considerable need for energy, which was covered by the burning of fossil fuels, especially coal. Coal deposits are accompanied to a greater or lesser extent by sulfur, which during the combustion of coal changes mostly to sulfur dioxide, partly to sulfur trioxide and to a lesser extent binds solid combustion residues, which are fly ash and cinder blocks. The proportion of sulphur bound to fly ash and cinder block depends primarily on the character of the ash in the coal, but also on the combustion technology. Coal with a high content of alkalis and especially calcium binds a greater proportion of sulfur dioxide to fly ash and cinder blocks, while coal containing mainly SiO_2 and low alkali content only negligible amounts. Combustion processes taking place at lower temperatures (e.g. fluidized bed boilers) usually bind more sulphur oxides to solid residues than boilers burning coal at higher temperatures (e.g. melting or granulation boilers).

Measurements carried out on granulation boilers burning Czech brown coals, which have ash mostly acidic (SiO2 content of about 50 % w/w), showed that 95% of the sulphur contained in the coal escapes into the flue gases and only a small amount of sulphur (about 5%) binds to solid residues.

Pathways to reduce sulphur oxide emissions

There are a number of options to limit sulphur oxide emissions from combustion processes. They are:

- **absolute reduction of fuel consumption.** This can be achieved either directly by burning them in installations with higher energy efficiency, or indirectly by appliances with lower energy intensity, or by reducing heat consumption, e.g. by improving the thermal insulation properties of buildings;
- **replacing sulphur-containing fuels with low-sulphur or non-sulphur fuels.** It is a substitute for burnt coal with a high sulphur content for low-sulphur coal, for low-sulphur liquid fuels or natural gas;
- **coal desulphurization.** The effective reduction of sulphur in coal by coal desulphurisation processes has not yet been satisfactorily managed industrially. Sulfur is usually contained in coal in several forms that behave differently to individual separation processes;
- **by flue gas desulphurisation.** Flue gas desulphurization by some processes can be considered industrially mastered and is applied to a wide range of power plants and heating plants. Decisive for each application are the level of emission reduction and the costs by which energy production becomes more expensive.

2. Coal desulphurization

The development of an efficient coal desulphurization process for the purpose of reducing SO_2 emissions is based on the different behavior of individual forms of sulfur contained in coal. Sulfur in coal can occur as pyritic, organic, sulfate, sulfide and elemental. Each of these forms behaves differently in terms of the possibility of applying the chemical and physical processes of its separation from the coal mass. The decisive factor is whether the desulphurization of coal will achieve the emission limits for sulphur oxides set by the legislation after its subsequent combustion.

2.1.1 Mechanical separation of pyritic sulphur

The easiest way to separate pyritic sulfur from coal is to separate pyrite from coal if pyrite is embedded in coal mass in the form of large grains. In this case, the different melithability of coal and pyrite is used, which is more durable and preserves the original grain size. This is followed by one of the separation processes to separate pyrite from the coal mass.

Most Czech coals contain pyrite embedded in the coal mass in the form of small particles that are difficult to separate from the coal mass.

Partially or completely sulfur can be separated from the coal mass by the following processes.

2.1.2 Myersův method

It consists in leaching pyritic sulfur with a solution of iron sulfate at a temperature of 90 - 130 oC and at increased pressure. The extraction mechanism is complex and can be affected by the following schematic reaction:

$$FeS_2 + Fe_2(SO_4)_3 + H_2O \rightarrow FeSO_4 + H_2SO_4 + S$$

Regeneration of the formed ferrous sulfate is carried out by air oxygen:

$$FeSO_4 + H_2SO_4 + O_2 \rightarrow Fe_2(SO_4)_3 + H_2O$$

In this way, pyrite can be separated effectively, but the organically bound sulfur is not changed by this process.

2.1.3 Gravimelt method

It consists in the extraction of ashes from coal mass by melted NaOH at temperatures of 320 - 415 °C. Ashes contained in coal are transformed in an alkaline medium into silicates, ferrites and sodium aluminates, which are separated from the insoluble coal mass.

The coal is first ground and then added together with the molten NaOH to the rotary furnace. The melt is transferred to an aqueous solution, the coal mass is separated and then washed with water. The alkalinity of the coal mass is neutralized in an appropriate way with acids. This almost completely separates the ashes from the coal mass. Desulphurised coal is obtained in the form of a coal suspension with an ash content of about 1 %.

The extract containing the dissolved ashes is neutralized, iron hydroxides are excreted, which are separated and which can be processed in the metallurgical industry into individual metals.

This process was developed in the USA in the late 80s for the separation of sulfur from black coal. It is not known to have been industrially implemented.

2.1.4 Biological removal of sulphur from coal

Biological removal of sulphur from coal

$2\ FeS_2 + H_2O + 7{,}5\ O_2 \rightarrow Fe_2(SO_4)_3 + H_2SO_4$

$FeS_2 + Fe_2(SO_4)_3 \rightarrow 3\ FeSO_4 + 2\ S$

$2\ S + 6\ Fe_2(SO_4)_3 + 8\ H_2O \rightarrow 12\ FeSO_4 + 8\ H_2SO_4$

Kyselé vody z biologického loužení obsahují H_2SO_4 a musí se neutralizovat CaO nebo $CaCO_3$.

Bakteriologický pochod je pomalý, závisí na teplotě. Při 16 °C se prakticky zastaví. Průmyslová aplikace přímo v ložisku ve středoevropských klimatických podmínkách prakticky nepřichází v úvahu. Realizace u tepelných centrál by vyžadovala otápěné loužící reaktory značných rozměrů. Relativně nízká je účinnost procesu, při kterém se nedochází k extrakci organické síry z uhlí, stěží může splňovat stávající nebo připravované emisní limity.

2.1.5 Summary

The application of coal desulphurization processes in power or heating practice encounters low coal desulphurization efficiency and thus the possibility of reaching the set values of emission

limits. Research and development to date has shown that they are economically unable to compete with flue gas desulphurisation processes.

Nevertheless, many power engineers expect that in the future they will be able to develop such a process of coal desulphurization that will make it possible to replace the current generation of flue gas desulphurization equipment and thus get rid of the operation of these complex end-of-pipe plants and energy-distant chemical plants.

2.2 *Flue gas desulphurisation*

-Unlike coal desulphurization, flue gas desulphurization is an industrially established process.

Flue gas desulphurization technology can be characterized by:

- significant volumes of flue gases to be purified;
- low concentrations of pollutants in the flue gas; which are SO_2, SO_3, Cl^- and F^-;
- huge mass flows of these substances.

The production of flue gases also depends on the type of fuel burned and on the excess of combustion air. The normal values for electricity generation at 200 MW calculated on standard terms are for:

- brown coal approx. 1.0 – 1.2 million m 3.h-1;
- black coal approx. 0.7 million m 3.h-1;
- liquid fuels approx. 0.5 – 0.6 million m 3.h-1.

Larger volumes of purified flue gases are disadvantageous in terms of costs because they require larger apparatuses. The higher the sulphur content of coal, the higher the sulphur oxide emissions that need to be separated from the flue gases. Large quantities of desulphurization products are difficult to recover.

The measure of emission of oxides during the combustion of fuels is considered to be the specific sulphurity of the fuel. This is defined as the mass sulphur content of coal per unit of fuel calorific value:

$$S_m = S^r_h * (Q^r)^{-1},$$

where S_m is the specific sulphurity of the fuel, S^r_h is the sulphur content in 1 kg of fuel in its original state

and Q^r the calorific value of the fuel in its original state. For example, for coal with a sulphur content of 2 % w/w in its original state. and the calorific value of the original fuel of 15 MJ. $^{kg-1}$ is the specific sulphurity:

$$S_m = 20 * 15^{-1} = 1,33 \text{ g S*MJ}^{-1},$$

Czech brown coals have a low calorific value and a relatively high sulphur content related to the calorific value. Compared to coal, energy coal, imported into Western Europe from China or South Africa, these coals have higher emissions because they also have a high specific sulphurity, as the following example shows.

Hard coal burned in Western Europe	**Brown North Bohemian Energy Coal**
Calorific value approx. 25 $^{MJ.kg-1}$	Calorific value approx. 9 – 12 $^{MJ.kg-1}$
Sulphur content 0,5 – 0,8 % w/w.	Sulphur content 1,3 %
Specific sulphurity 0,2 – 0,3 g S*$^{MJ-1}$	Specific sulphurity 1,1 – 1,5 g S*$^{MJ-1}$

The above example shows that per unit of energy produced (e.g. MWh) emissions of sulphur oxides in the Czech Republic are about five times higher than in Western Europe. To produce 1 MWh of electricity, about 11 GJ in fuel is required. The hourly emission of SO_2 (E_h^{SO2}) of the 200 MW lignite power plant unit at full use of the installed capacity and with a sulphur content of 1,3 % in the original fuel and a calorific value of 12 MJ*$^{kg-1}$ shall be:

$$E_h^{SO2} = 200 * 11/12 * 0,013 * 2 * 0,95 = 4,53 \text{ t*h}^{-1}$$

where a value of 0,95 characterises that 95 % of the sulphur contained in the coal passes into the flue gas.

With **an annual use of the installed capacity**[1] **of** the boiler of 5000 hours, the annual emission (E_r^{SO2}) is 200 MW of the unit:

$E_r^{SO2} = 5000 * 4,53 = 22650\ t * r^{-1}$

and a power plant with 4 units with a nominal output of 200 MW then

$E_r^{SO2} = 4* 22600 = 90600\ t\ SO_2 *r^{-1}$

3. Classification of flue gas desulphurization processes

There are a number of approaches to the separation of sulphur dioxide from flue gases, only some of which have become widespread in the practice of power plants and heating plants. A wide range of potential flue gas desulphurisation options can be classified according to various criteria.

A frequently used criterion is sorting according to the processing of the reagent that was used to dispose of SO_2. Accordingly, we distinguish between **flow and regeneration** processes.

Flow processes consist in the fact that the reagent used to capture SO_2 binds it and with it exits the process in the form of a product. An example of a flow process can be the binding of SO_2 with limestone as calcium sulfate dihydrate:

$$2\ CaCO_3 + 2\ SO_2 + O_2 + 4\ H_2O = 2\ CaSO_4.2H_2O + 2CO_2$$

Regenerative processes, compared to flow-through agents, regenerate the reagent used and return it back to absorption. An example is the sodium sulphite process, in which the input agent is Na_2SO_3 arising from NaOH or Na_2CO_3 depending on the reaction:

$$2NaOH\ + SO_2\ = Na_2SO_3 + H_2O$$

$$Na_2SO_3\ + SO_2 + H_2O = 2\ NaHSO_3,$$

which is regenerated by heating:

$$2\ NaHSO_3 = Na_2SO_3 + H_2O + SO_2,$$

and the sulphur dioxide released is further processed as necessary to S, H_2SO_4 or liquid SO_2

Another way of classifying desulphurization processes is the division into **dry and wet**. Initially, processes in which sorption took place at temperatures higher than the dew point H_2SO_4 in the flue gas were considered **to be wet, dry** desulphurization methods operating above the dew point H_2SO_4. This original formulation has changed over time to such an extent that the washing of SO_2 with aqueous solutions of most often alkaline reacting substances can be considered wet processes, while sorption and catalytic processes, taking place on solid sorbents or catalysers at temperatures above 100 °C, can be considered dry. An example of a wet process can also be the already mentioned wet limestone method, where sorption of SO_2 takes place at about 60 ° C in a water suspension of limestone, for dry e.g. catalysis of sulphur dioxide to SO_3 on a catalyst (V_2O_5 to Al_2O_3) followed by the formation of sulphuric acid:

$$2\ SO_2 + O_2 + 2\ H_2O = H_2SO_4.$$

The last criterion is the **physical or chemical nature of the process,** according to which desulphurization methods can be divided into:

- **absorption**, e.g. the wet limestone method or the sodium sulphite process;
- **adsorption,** e.g. adsorption of SO_2 on silica gel and
- **catalytic processes,** see above.

In the next explanation of the individual methods, we will keep the division into flow and regenerative processes.

3.1 *Flow-through processes of flue gas desulphurization*

3.1.1 Wet limestone method — process chemistry

It consists in washing out sulphur dioxide with a watery suspension of lime or limestone, preferably at a temperature of about 60 °C according to the reaction:

$$2\ CaCO_3 + 2\ SO_2 + O_2 + 4\ H_2O = 2\ CaSO_4.2H_2O + 2CO_2$$

The control mechanism of the process is resistance to diffusion in the liquid phase, that is, the rate of dissolution of limestone. This process can be accelerated:

- reducing the particle size and increasing the limestone surface (finer grinding, typical graining is 90–100% < 40 μm);

- by increasing the stoichiometric ratio of $CaCO_3$: SO_2. However, this can lead to the formation of incrustations in washing machines and drop separators, which are undesirable. In practice, stoichiometry $CaCO_3$: SO_2 is 1.02 – 1.07 : 1 depending on the efficiency of the washing machine;
- by increasing the sprinkling ratio L : G [l . $^{m-3}$](ratio of the volume of suspension to the volume of flue gases under standard conditions)
- addition of additives (organic acids, Mg^{2+})
- greater retention of the suspension in the absorber sump
- by maintaining the pH in the more acidic region (the disadvantage is that at pH <5, Al^{3+} is leached from the unseparated residual fly ash trapped in the absorber and thus the formation of a complex AlF_6^{3-} ion, which causes the formation of deposits and deposits in absorbers and droplet separators).

Formation of deposits and deposits in the process of the wet limestone method

Deposits and deposits in absorbers and their circulation circuits are among the most serious problems of the wet desulphurisation limestone method. In absorbers, they form on the walls, built-ins and separators of drops, and their removal is difficult and laborious. It is often realized by spraying with pressurized water, but also by manual chipping. Therefore, it is necessary to limit their creation as much as possible. Their occurrence was an integral part of the operation of the first desulphurization units, when the causes of formation were not fully clarified.

There may be several causes of deposits and deposits. These may be structural defects, which are quite easy to eliminate. Another cause may be an incorrect technological regime, in which the necessary measures to master the crystallization chemistry of $CaSO_4$ are not observed. 2 H_2O. Also the cause is the so-called "limestone blinding", which is caused by the formation of a fluoro-aluminium complex formed in washing machines by leaching Al from fly ash in acidic areas of pH values (ca. pH<5).

Design flaws

Design flaws include, among other things, insufficient washing of the surfaces of absorbers or their pre-coolers. In this case, the flue gases that come from the heat exchanger with a temperature of 110 - 140 °C must be further cooled to the absorption temperature of SO_2, which is within the limits of 55 - 60 °C. This is done by adiabatic evaporation of water, either alone or from the incoming suspension. With an insufficiently sprinkled surface, water evaporates from the suspension on the surface of the apparatus and is overgrown with deposits consisting mainly of calcium sulfate dihydrate or residual fly ash not separated from the flue gases in the electro-separator.

These deficiencies can be eliminated by additional installation of wall sprays, or by directing the flue gas flow so that it is uniform over the entire surface of the apparatus.

Crystallization caso$_4$. 2 H_2O.

If the principles of a certain supersaturation of the Suspension CaSO 4 are not observed. 2 H_2O, crystal formation occurs inside the absorbers. Degree of supersaturation with calcium sulfate dihydrate is expressed as follows:

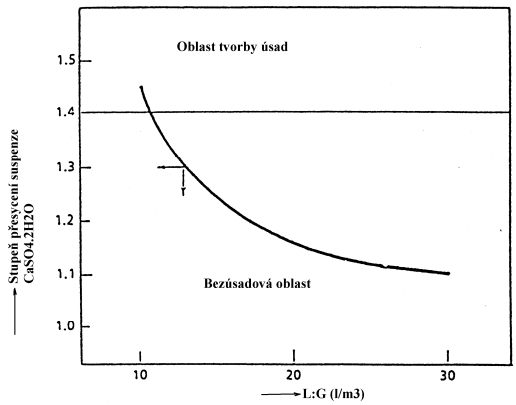
$$\alpha = \frac{[Ca^{2+}][SO_4^{2-}]}{K_{CaSO_4}},$$

where [Ca^{2+}] is the concentration of the Ca^{2+} ion in the liquid phase [mol . $^{l-1}$],

where [Ca^{2+}] is the concentration of the Ca^{2+} ion in the liquid phase [mol . $^{l-1}$],

where [Ca^{2+}] is the concentration of the Ca^{2+} ion in the liquid phase [mol . $^{l-1}$],

Fig. 13 Overconcentration dependeing on the flow L : G



As shown in Fig. 13, the formation of deposits depends on the degree of supersaturation . If the value is lower than 1.4, deposits are not formed in principle. Therefore, the degree of supersaturation must be kept below this value. Value can be controlled by the degree of sprinkling, the ratio of L:G and the concentration of $CaSO_4$. 2 H_2O in absorbent suspension. Figure 13 shows that

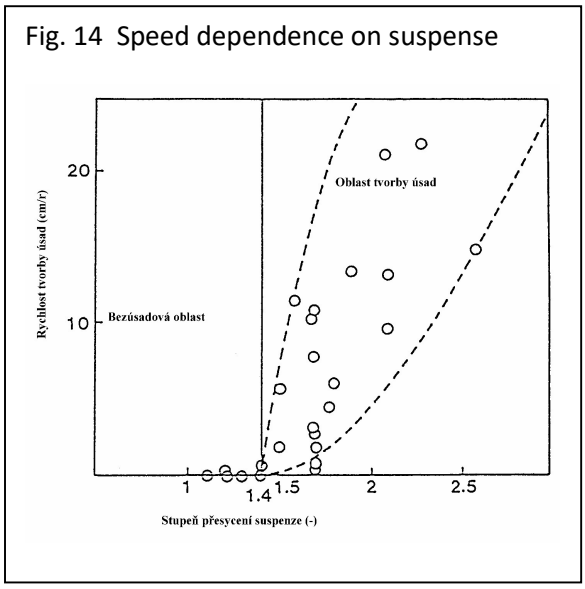
<1.4 the settle-free area lies within the limits of the content of $CaSO_4$. 2 H_2O between 20 - 30 %. The optimal values of the degree of sprinkling L:G in the non-additive suspension lie between 10 - 30 $l.m_{n-3}$.

Fig. 14 shows the dependence of the rate of deposit formation on the degree of supersaturation . Part of the image to the left of the value can be considered as a no-settled zone, on the right with increasing the layer of deposit grows rapidly, and the faster the value is higher.

Action of additives

The use of additives in the process of the wet limestone method is not new. Their use is common in the USA, where when tightening emission limits under the amendment to the Air Act, they serve to increase the efficiency of the desulphurization process. Even earlier, they were used in a wide range of installations to reduce deposits and deposits in washing machines. Currently, they are used in order to improve the quality of the produced energy gypsum and increase the effect of oxidation of the sulphite ion to the sulfate ion. Additives according to the mechanism of action can be divided into inorganic and organic.

Fig. 14 Speed dependence on suspense



As inorganic additives, mainly magnesium salts are used, although sodium salts have the same effect. Organic additives are considered to be mainly organic acids, whose dissociation constants lie between carbonic and sulfuric acids. However, the use of stronger acids or their salts is also not uncommon, such as formic acid or its potassium salts. Their common feature is that they form soluble calcium salts.

The term "additive" arose from the fact that in the USA the desulphurization of flue gases on a number of units was intensified only subsequently; it was therefore not part of the original project documentation. Today, they are used in new installations as a tool to direct the chemistry of the process, which saves investment costs and allows you to operate the equipment with lower costs, reliability and greater flexibility.9

Mechanism of action of additives

Anorganic additives

When magnesium sulphate is added to a limestone suspension, it causes a substantial increase in the alkalinity of the system due to an increased proportion of^{SO3-2}. SO_2 absorbed in suspension is significantly faster converted to SO_3^{2-} without the immediate need to bind to dissolved Ca^{2+}, as is the case with the non-additive process.

The increased effect of the additive on the absorption of SO_2 is explained by the formation of an ion pair $MgSO_3^o$. Since SO_3^{2-} is more alkaline than dissolved SO_2, then as the concentration of SO_3^{2-} increases, so does the solution's dissolving capacity. When using limestone with the addition of $MgSO_4$, the initial phase of the reaction is the same as in a non-additive system, i.e. there is a hydration of SO_2 to H_2SO_3, but it then reacts with the $MgSO_3^o$ ion pair to form the HSO_3 ion$^-$:

$$H_2SO_3 + MgSO_3^o \rightarrow Mg^{+2} + 2\ HSO_3^- \quad (1)$$

$$CaCO_3 + Mg^{2+} + 2\ HSO_3 \rightarrow MgSO_3^o + Ca^{2+} + SO_3^{2-} + CO_2 + H_2O \quad (2)$$

$$Ca^{2+} + SO_3^{2-} + 0{,}5\ H_2O \rightarrow CaSO_3.0{,}5\ H_2O \quad (3)$$

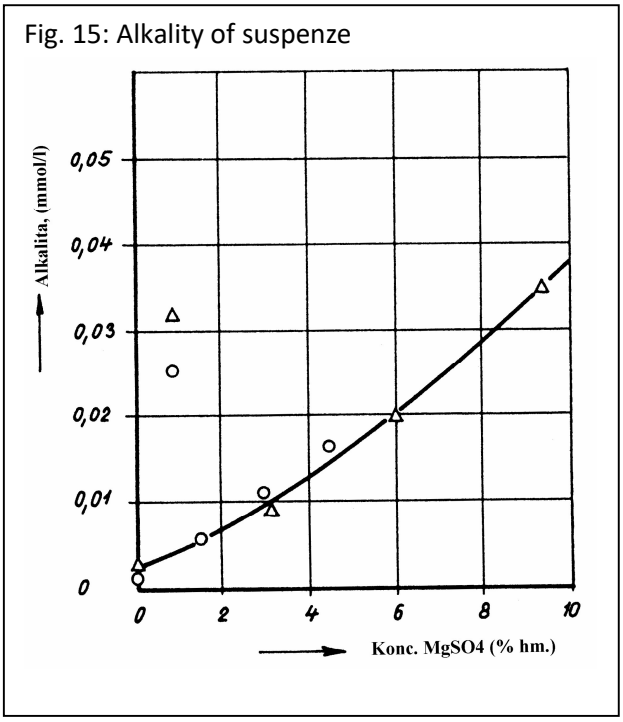
Reaction (1) is the neutralization of SO_2, the reaction (2) the regeneration of $MgSO_3^{by}$ taking place in the absorber well, and (3) the precipitation of the desulphurization product.

The action of $MgSO_4$ is explained by the fact that in response:

$$MgSO_4 + CaSO_3.O{,}5\ H_2O \rightarrow CaSO_4.2\ H_2O + MgSO_3^o \quad (4)$$

shifts the balance of reaction in favor of $CaSO_4 . 2 H_2O$, regenerating $MgSO_3^o$.

Fig. 15: Alkality of suspenze



The beneficial effect of $MgSO_4$ on the alkalinity of the suspension (i.e. ∑ (SO^{3-2}, $MgSO_3^o$, and HCO_3^- in $mol.l^{-1}$) is shown in Figure 15. On the axis of the sequences, the concentration of $MgSO_4$ is indicated up to 10 % w/w. However, higher concentrations can also be used. For a certain flue gas desulphurization efficiency, the concentration of $MgSO_4$ in suspension is selected, taking into account the content of SO_2 in the flue gas.

The disadvantage of using Mg^{2+} as an additive is its sensitivity to Cl^- and F^- in flue gases. Therefore, before the actual absorption, it is necessary to include the pre-washing of flue gases with water in an absorber with a separate washing circuit of the liquid.

Organic additives

The low concentration of Ca^{2+} in the washing suspension can be increased by the addition of organic acids, which, in terms of the value of the dissociation constant, usually lie between sulfuric and carbonic acid. These are acids that form soluble salts Ca^{+2}, which increase the soluble alkalinity of the suspension and act with their damping capacity. The mechanism can be described by equations:

$2\ HR + CaCO_3 \rightarrow CaR_2 + CO_2 + H_2O$ (5)

$CaR_2 \rightarrow Ca^{+2} + 2\ R^-$ (6)

$SO_2 + H_2O \rightarrow H_2SO_3$ (7)

$H_2SO_3 \rightarrow H^+ + HSO_3^-$ (8)

$HSO_3^- \rightarrow H^+ + SO_3^{-2}$ (9)

$Ca^{2+} + SO_3^{2-} \rightarrow CaSO_3$ (10)

$2\ H^+ + 2\ R^- \rightarrow 2\ HR$ (11)

According to equation (11), the added acid regenerates and reacts again to $CaCO_3$. Of the range of organic acids, especially those that suit the low price, low vapour tension, low molecular weight and stability in the washing solution are considered. The impact of their use on wastewater and solid waste must also be taken into account.

A distinctive feature of the use of organic acids in the process of the wet limestone method is their standby properties. These allow the maintenance of lower pH values in the absorber and its circulation circuit, which favorably affects the use of limestone.

An excellent feature of the use of organic acids is the fact that they are not sensitive to the content of chlorine and fluorine in the flue gases. This makes it possible to operate the process of absorption and cooling of flue gases in a single apparatus with a single circulation circuit, which is positively reflected in the acquisition costs.