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DESULFURIZATION OF FLUE GASES OF THERMAL POWER PLANTS WITH OBTAINING POTASSIUM-MAGNESIUM FERTILIZER (KALIMAGNESIA)

Olha Khatsevych[1,2], Sofiia Fedorchenko[1], Sergiy Kurta[1], Ihor Mykytyn[1], Olha Derzhko[2]

[1] Vasyl Stefanyk Precarpathian National University,
57, Shevchenko Str., Ivano-Frankivsk, 76018, Ukraine
[2] State Institution "State Scientific Research and Design Institute of Basic Chemistry",
5a, Fabrychna Str., Kalush, Ivano-Frankivsk Region, 77304, Ukraine
khatsevich.olga@meta.ua

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Abstract. A new method of flue gas desulfurization with the production of a valuable is proposed. The essence of the method is to pass flue gases through a scrubber (Venturi) filled with magnesium hydroxide suspension. At the same time, SO_2 of the flue gases will react with magnesium hydroxide according with the formation of magnesium sulfite. Crystals of magnesium sulfite are able to interact with new portions of SO_2 and turn into hydrosulfite. As a result of such "washing" of flue gases, a suspension of sparingly soluble salt $MgSO_3{\cdot}6H_2O$ in a 12–15 % solution of $MgSO_4$ is obtained. Magnesium hexahydrate will precipitate as large crystals and be separated in a hydrocyclone. Separated crystals of magnesium sulfite will be oxidized under the influence of air oxygen to magnesium sulfate.

Keywords: flue gases, sulfur(IV) oxide, desulfurization, sulfate-type potassium-magnesium fertilizer, magnesium hydroxide.

1. Introduction

At the time of accession to the EU, all European approaches, standards and principles should work in Ukraine. EU policy and legislation in the field of industrial pollution is one of the most complex and well-developed areas of the EU acquis. The key act in this area is Directive 2010/75/EC on industrial emissions. The implementation of these legislative acts requires significant financial and administrative resources and time. It is also closely related to relevant macroeconomic and other key national policies. The directive contains particularly strict requirements for the operation of large combustion plants (with a thermal capacity of more than 50 MW).

Since this directive is among the obligations under the Association Agreement and the Energy Community, certain work on the analysis of compliance and implementation has already been carried out in Ukraine, significant support for these processes is observed from international technical assistance projects. Provisions regarding large incineration plants were separately implemented, in particular through the adoption of a national emission reduction plan for them (Analytical Report, 2023).

During the burning of coal during the production of electricity, dangerous substances are released into the air, which harm human health and cause a large number of premature deaths: solid particles containing unburned carbon and oxides of heavy metals, carbon monoxide (CO) and toxic organic compounds, volatile ash, sulfur and nitrogen oxides, fluorine-containing compounds, as well as gaseous products of incomplete fuel combustion. Among the countries polluting air from coal power in Europe, Ukraine is among the top three. Ukraine (27 %), Turkey (24 %), Serbia (15 %) and Bosnia and Herzegovina (11 %) are the largest sources of emissions of sulfur (IV) oxide SO_2 from coal-fired power plants in Europe (EMBER, 2024). Since harmful aerosols can be carried over thousands of kilo-

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meters, the problems of individual countries become problems of the entire continent.

Sulfur (IV) oxide is one of the most toxic gaseous emissions of power plants, which makes up more than 90 % of emissions of sulfur-containing compounds with flue gases of boiler units (the rest is SO_3). As a result of photochemical reactions and oxidation in the air, SO_2 turns into SO_3, forming sulfuric acid in atmospheric air. The effect of these products on living organisms depends on the concen-tra-tion and many environmental factors (Kryzhanivs-kyi, Koshlak, 2016).

Over the previous 140 years, the global emission of sulfur into the atmosphere has increased 20 times. The rate of reduction of the emission of oxidized sulfur into the atmosphere should be the measure of economic development and ecological maturity of society.

Energy production is one of the main causes of air pollution in Ukraine. Most of the power units of the TPP are designed to burn hard coal of domestic production, it currently makes up 98 % of the fuel base of the TPP. TPPs of Ukraine consume more than 35 million tons of coal with an ash content of 23–25 % and a sulfur content of more than 2 %. Burning such quantities of low-quality fuel leads to significant emissions of pollutants into the atmosphere and the formation of a large amount of solid waste (ash and slag). In Ukraine, 34 % of the consumed electricity is provided by TPPs built before 1976, none of which are equipped with desulfurization equipment, with the exception of the 2nd power unit of the Trypil TPP, where a flue gas desulfurization system was installed as a pilot project. Most of our TPPs do not have high-quality dust-capturing filters, sulfur removal, so the concentration of SO_2 in the flue gases of Ukrainian TPPs is high and depends on the sulfur content in coal. And in some types of coal, the content of organic and pyritic sulfur can be up to 7 % (Ecodia, 2023).

Of course, there are many other sources of air pollution, such as transport, waste disposal, but installing quality filters at large industrial stationary sources should be the first action to improve air quality. The regulatory framework for such sources is already well established in the EU and provides stable results, and if properly implemented in Ukraine, it can significantly improve air quality by addressing emis-sions at the source. However, there are significant obstacles to solving this problem: the modernization of outdated coal-fired thermal power plants requires the investment of significant funds.

In Ukraine, the “National plan for reducing emissions from large incineration plants” was adopted, according to which all incineration plants included in the national modernization plan must have modern dust filters and sulfur purification by the end of 2028. And by December 31, 2033, all of them must also install nitrogen purification and fully comply with European emission standards (Order Cabinet of Ministers of Ukraine 2021; Order of the Cabinet of Ministers of Ukraine 2019).

To achieve the goals of the National Emission Reduction Plan, the following technical measures are envisaged:

● modernization of existing combustion plants in order to improve the efficiency of fuel energy use;

● joint burning of biomass with solid fuel (coal);

● replacement of existing dust collectors with new devices for dust cleaning of flue gases (electro-filters, fabric filters);

● construction of flue gas desulfurization installations for installations with a nominal thermal capacity:

from 50 to 500 MW, it is expedient to use coal with a low sulfur content and to build semi-dry or wet flue gas desulfurization units;

for P > 500 MW, it is advisable to use wet flue gas desulfurization installations;

● primary measures: improvement of fuel combustion processes in order to reduce NO_x emis-sions (regime-technological measures – staged supply of air and fuel, low-emission burners, flue gas recir-culation and their combination);

● secondary measures: construction of flue gas purification plants from NOx – technologies of selective catalytic reduction and selective non-cata-lytic reduction, depending on individual conditions.

2. Materials and Methods

Classification and characteristics of methods for cleaning flue gases from SO_2. Wet methods are based on absorption, hot exhaust gases are washed with absorbent solutions, due to which, along with the extraction of SO_2, the gas is cooled to the dew point. Wet processes are used in cases where high concentrations of inorganic pollutants are emitted at the same time, for example, with a high SO_2 content of more than 2500 mg/m^3.

Dry methods are based on adsorption, and gas purification occurs with solid sorbents without a significant decrease in temperature.

In recent years, a new direction has appeared to reduce the SO_2 content in the flue gases of thermal power plants by burning fuel with additives (lime) that bind sulfur in a fluidized state.

The large number of methods is caused, on the one hand, by the fact that one universal method has not yet been found that would satisfy all the requirements for further purification of gases from SO_2, and on the other hand, a decisive number of methods arose and were patented in developed countries with a market economy, the core of which is competition. In this regard, each gas purification company tried to offer its own method, which often differs slightly from the other, but has a different name.

The most common are cleaning technologies with the addition of absorbents. The essence of cleaning is to add an absorbent in dry or wet form (semi-dry gas cleaning) to flue gases to remove SO_x emissions. To achieve highly efficient absorption, it is very important to ensure sufficient gas residence time between the injection point and the dust collector. Reactive grades of MgO can be used as effective SO_2 absorbents for the magnesia industry, in the cement industry, and for cleaning flue gases of TPPs. Despite its low efficiency compared to other absorbents, the use of reactive grades of MgO for the magnesia industry has several advantages.

When choosing flue gas cleaning methods, it is very important to consider the quality of the energy source.

3. Results and Discussion

A new method of flue gas desulfurization with the production of a valuable sulfate-type potassium-magnesium fertilizer is proposed. The essence of the method is to pass flue gases through a scrubber (venturi) filled with magnesium hydroxide suspension. At the same time, SO_2 of the flue gases will react with magnesium hydroxide according to reaction (2) with the formation of magnesium sulfite. Crystals of magnesium sulfite are able to interact with new portions of SO_2 and turn into hydrosulfite. As a result of such “washing” of flue gases, a suspension of sparingly soluble salt $MgSO_3{\cdot}6H_2O$ in a 12–15 % solution of $MgSO_4$ is obtained. Magnesium hexahydrate will precipitate as large crystals and be separated in a hydrocyclone. Separated crystals of magnesium sulfite will be oxidized under the influence of air oxygen to magnesium sulfate according to reaction (3). Magnesium sulfate is converted into shenite by adding potassium chloride, the process proceeds according to reaction (4). The waste product of shenite conversion is magnesium chloride solution, which is returned to the beginning of the process to obtain magnesium hydroxide according to reaction 1.

$$MgCl_2 + CaO + H_2O = Mg(OH)_2 + CaCl_2\,, \quad (1)$$

$$Mg(OH)_2 + SO_2 + 6H_2O = MgSO_3{\cdot}6H_2O\downarrow\,, \quad (2)$$

$$MgSO_3{\cdot}6H_2O\downarrow + 1/2O_2 = MgSO_4 + 6H_2O\,, \quad (3)$$

$$2MgSO_4 + 2\,KCl + 6\,H_2O =$$

$$= K_2SO_4{\cdot}MgSO_4{\cdot}6\,H_2O + MgCl_2 \text{ (to reaction 1).} \quad (4)$$

Experimental studies have confirmed that the magnesium method makes it possible to extract 97–98 % of SO_2 from flue gases at a concentration of 0.3–0.4 % by volume.

The main stages of the new method of magnesium purification of flue gases with the production of kalimagnesia:

1. The flue gases are passed through the $MgSO_4$ solution, which evaporates in the scrubber to a concentration of 30 % due to the heat of the flue gases (t = 150–200 °C).

2. After the evaporative scrubber, the gases are washed with an aqueous suspension of $Mg(OH)_2$ to obtain a 12 % $MgSO_4$ solution during subsequent oxidation.

3. The $MgSO_3{\cdot}6H_2O$ suspension obtained during SO_2 absorption in the $MgSO_4$ solution is blown with air to convert sulfite into magnesium sulfate. After purging, the resulting solution of magnesium sulfate is fed to the evaporative scrubber for evaporation.

4. The 30 % $MgSO_4$ solution obtained in the evaporative scrubber is mixed with sulfate (shenite) solution and potassium chloride. The resulting suspension is evaporated and then cooled. During the cooling process, a double salt crystallizes – shenite $K_2SO_4{\cdot}MgSO_4{\cdot}6\,H_2O$, which is separated from the solution (mother liquor) and dried to kalimagnesia.

5. The mother liquor (after crystallization of shenite) is mixed with $CaCl_2$ solution. As a result, gypsum is deposited according to the reaction:

$$CaCl_2 + MgSO_4 + 2\,H_2O \rightarrow CaSO_4{\cdot}2H_2O + MgCl_2.$$

The desulfated solution is separated from the gypsum and treated with milk of lime to precipitate magnesium hydroxide. The magnesium hydroxide obtained (1) is settled, washed countercurrently and sent to the absorbing scrubber in the form of an aqueous suspension. The resulting $CaCl_2$ is a production waste. Below (Fig. 1) is a basic block diagram of the flue gas desulfurization process with the production of valuable potassium-magnesium fertilizer.

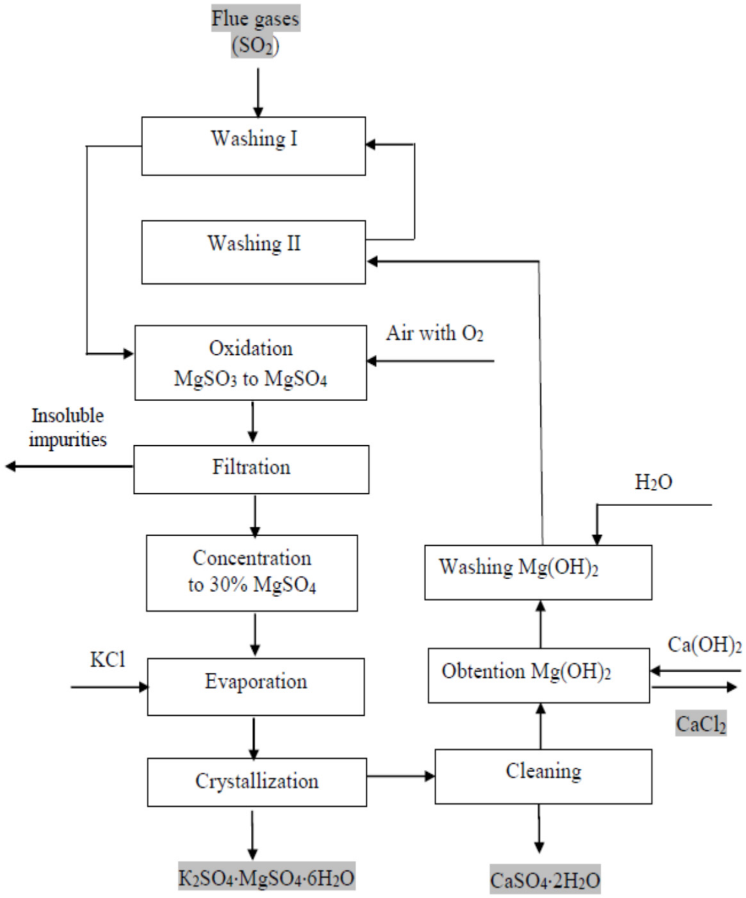

Fig. 1. Basic block diagram of flue gas desulfurization technology with the production of potassium-magnesium fertilizer.

4. Conclusion

In order to protect human health and the environment from air pollution in Ukraine, urgent actions at various levels are necessary. In particular, to ensure the fulfillment of the goals and tasks established by the Law of Ukraine "On the Basic Principles (Strategy) of the State Environmental Policy of Ukraine for the Period Until 2030" regarding the development of strategic, programmatic and planning documents for all branches of the Ukrainian economy, which include tasks and measures for their greening through technical re-equipment, introduction of energy-efficient and resource-saving technologies, low-waste, zero-waste and environmentally safe technological processes; to promote scientific research, research and development and applied works on the creation of environmentally friendly technologies and processing (recycling) of industrial waste, implementation of pilot projects/programs in the field of waste management (Resolution, 2023). Such industrial waste processing technologies include flue gas desulfurization technology with the production of potassium-magnesium fertilizer.

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