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USING PLASMA CATALYSIS FOR OXIDATION OF SULPHUR DIOXIDE TO SULPHUR TRIOXIDE[*]

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Abstract

The paper researches the influence of the main properties of streamer discharge on the conversion of sulphur dioxide into sulphur trioxide and the effect of gas exposure to a streamer discharge for the oxidation of sulphur dioxide. It has been defined that the change of peak to peak voltage has the most impact on the efficiency of sulphur dioxide capture. It has been found out that delivery of voltage pulses with a period of 1ms allows having the conversion rate of sulphur dioxide at about 96.7%. It has been detected that with the pulse duration of 350 ns the conversion rate of sulphur dioxide is 98.6%.

Keywords: corona discharge, conversion rate, pulse duration, pulse period, streamer discharge, sulphur dioxide, voltage

1. Introduction

Sulphur dioxide is considered to be one of the most dangerous air pollutants. Its primary sources in the environment are the emission of chemical, oil refining, energy and metallurgy industries. (Cherchintsev and Savina, 2012). Sulphur dioxide irritates the mucous membranes of the eyes and respiratory tract. Prolonged inhaling of sulphur dioxide causes chronic bronchitis, laryngitis, pneumonia, and physical impairments in children. Moreover, the concentration of sulphur dioxide in the air at more than 1ppm increases the death rate. It should be mentioned that sulphur dioxide has adverse effects not only on people or animals but also on plants decreasing agricultural yield and causing deforestation. Sulphur dioxide emission also causes destruction of metal and building structures.

Nowadays, there are a lot of methods for the removal of sulphur dioxide from flue gases (Cherchintsev and Savina, 2012; Martins et al., 1999; Matukhno et al., 2019; Muzadi

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and Kotzé, 2013; Smotraev and Manidina, 2016). The theoretical analysis showed that the well-known methods have certain drawbacks as a result of which they cannot be widely used for flue-gas desulphurization: the need for preliminary dedusting of gases; sensitivity to gas components; cumbersome equipment; high energy consumption; low sorption capacity of absorbing solutions; high cost of reagents; high capital costs (Muzadi and Kotzé, 2013).

Thus, gas emissions with a low concentration of sulphur dioxide which cannot be turned into finished products like sulphuric acid or sulphur as it is economically unviable pose the biggest threat to the environment. Therefore, developing a method of purifying gas emissions with a low concentration of sulphur dioxide is an urgent matter.

Sulphur trioxide is known to have higher water solubility than sulphur dioxide. The paper by points to the relevance of using absorption methods at the preliminary conversion of sulphur dioxide into sulphur trioxide. Catalysis or physical fields can be used for such conversion. Based on the research of (Belokon et al., 2019; Cherchintsev and Savina, 2012), it is necessary to pre-dedust the gas and remove gas compounds that poison the catalyst before using catalysis as a method.

According to the data in the papers by (Pavlenko and Rumyantsev, 1995), plasma catalysis is the most effective method of gas treatment using electrical discharges. When plasma catalysis is used, gas passes through a gas discharge reactor where harmful substances are transformed exposed to low-temperature plasma. Exposed to plasma, molecules, atoms, and radicals are excited, which facilitates a further catalytic stage of purification where there is deep oxidation of products formed in the process of gas passing through the plasma-chemical reactor. It allows neutralizing toxic substances using a small amount of energy.

The generation of low-temperature plasma is based on corona or streamer discharges. The paper by (Pavlenko and Rumyantsev, 1995) states that to use a corona discharge, it is necessary to ensure the passage of the entire volume of gas treated near the electrode at a distance of not more than 10% of the interelectrode one. In other words, using corona discharge is not efficient for purifying large volumes of industrial waste gas emissions.

The work by (Pavlenko and Rumyantsev, 1995) specifies the main characteristics of streamer discharge:

1. Streamers that facilitate the creation of unstable particles occupy the entire interelectrode space. Thus, ionization and excitation of molecules take place in the entire interelectrode gap.
2. The current flowing during a streamer discharge is determined by a flow of electrons, in contrast to the mainly ionic currents during a corona discharge.
3. With the help of short pulses lasting about 200 ns, a streamer discharge forms a high-voltage current that is several times higher than the breakdown value. A corona discharge stably exists only in the pre-breakdown mode.

Thus, due to its characteristics, the streamer discharge transmits more energy to the molecule than the corona discharge, ensuring more efficient neutralisation of toxic substances.

The objective of this work is to define how the streamer discharge effects the efficiency of the conversion of sulphur dioxide into sulphur trioxide.

2. Materials and methods

The sulphur-containing gas was prepared by decomposing sodium sulphite in a reaction with concentrated sulphuric acid. The concentration of sulphur dioxide ranged between 0.2 and 10.0 g/m^3. The content of sulphur oxide in the gas before and after the gas discharge reactor was determined by the photocolorimetric method based on the oxidation of sulphur dioxide by hydrogen peroxide to sulphuric acid and the reaction of the latter with barium chloride to form a suspension. The method for the determination of ozone is based on its reaction with potassium iodide and colorimetric analysis of the formed iodine by pink discoloration of the product of the interaction of iodine with dimethyl-p-phenylenediamine. The temperature of the sulphur-containing gas was between 22°C and 100°C. The gas residence time in the discharge zone started from 3.5 s.

The streamer discharge was produced using a nanosecond pulse generator developed on the basis of an inductor and a semiconductor circuit breaker (SOS-diode) (Lytvynenko et al., 2012). The initial characteristics of the streamer discharge: pulse duration 100 - 350 ns; pulse voltage 15 - 100 kV.

3. Results and discussion

The exposure of gas-containing sulphur dioxide to a streamer discharge can trigger the following reactions:

$$SO_2+1/2O_2 \rightarrow SO_3 \quad (1)$$

$$SO_2+1/3O_3 \rightarrow SO_3 \quad (2)$$

$$O_2+1/2O_2 \rightarrow O_3 \quad (3)$$

$$O_2 \rightarrow O\bullet + O\bullet \quad (4)$$

$$O_2+O\bullet \rightarrow O_3 \quad (5)$$

$$SO_2 + O\bullet \rightarrow SO_3 \quad (6)$$

$$N_2 \rightarrow N\bullet + N\bullet \quad (7)$$

$$H_2O \rightarrow OH\bullet + H\bullet \quad (8)$$

The analysis of the thermodynamic properties of the above reactions over the temperature range from 0 to 100 °C carried out in the paper by (Lytvynenko et al., 2012; Smotraev and Manidina, 2016) showed that the degree of sulphur dioxide oxidation using ozone is more complete than using oxygen. The reaction of ozone formation (3) is unlikely over the analyzed range of temperatures, so it is necessary to use some activation processes. It was also found out that if the gas was pre-exposed to streamers with particular properties, there was almost no energy loss on nitrogen decomposition. The streamer's general properties are its voltage, pulse period and duration.

The empirical evidence (Fig. 1) showed that the change of peak to peak voltage has the most impact on the efficiency of sulphur dioxide capture. The increase of the applied voltage to more than 100 kV causes breakdowns in the interelectrode space.

The highest conversion rate of sulphur dioxide is achieved at its lowest concentrations (0.2 g/m^3) and is about 99 %. The decrease of the conversion rate at a higher sulphur dioxide concentration is explained by the need to chemically bond more toxic substance with the same amount of active particles. To increase the sulphur dioxide conversion rate it is necessary to increase the residence time of the gas mixture in the gas discharge reactor.

The analysis of the thermodynamic properties of the reactions that are likely to occur when sulphur-containing gas is exposed to a streamer discharge showed that sulphur dioxide oxidation by ozone is the most feasible method (Lytvynenko et al., 2012) To determine the effect of discharge voltage on the amount of ozone produced in the streamer discharge, the ozone concentration over the range of voltage from 0 to 45 kV was measured. The research results (Fig. 2) showed that at the voltage below 20 kV, there is almost no ozone in the gas mixture. With the voltage increase to over 40 kV, the ozone concentration increases too.

The dependence analysis (Fig. 1) and (Fig. 2) showed that there is more sulphur dioxide converted than ozone produced. Sulphur dioxide is probably oxidized by atomic oxygen according to the reaction (6).

Laboratory studies of the dependence of the conversion rate of sulphur dioxide in the streamer discharge on the applied voltage pulse period showed that the efficiency increases with a shorter pulse period (Fig. 3). The empirical evidence proved that the pulse period of 1ms ensures the conversion rate of sulphur dioxide at about 96.7% (with the initial concentration of sulphur dioxide 0.61 g/m^3, voltage 45 kV).

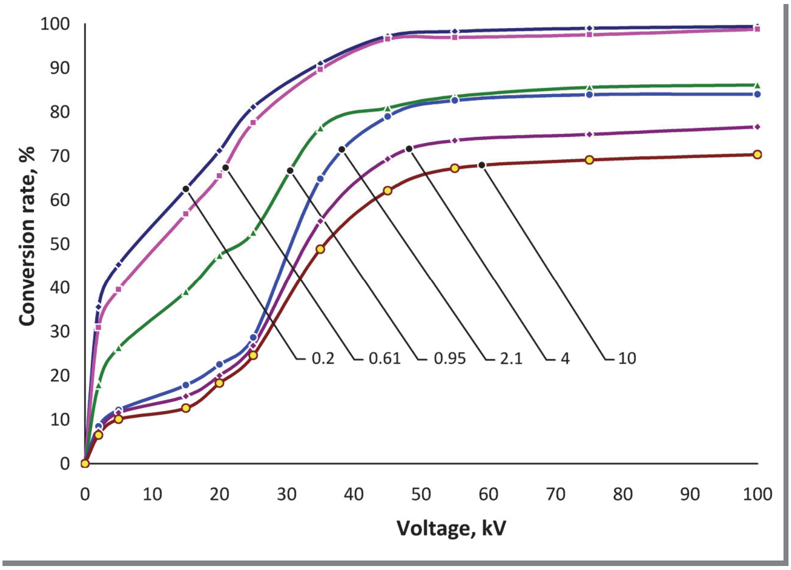

Fig.1 Dependence of the conversion rate of sulphur dioxide on the voltage of the streamer discharge at different initial concentrations of sulphur dioxide: pulse period 1 ms; pulse duration 200 ns.

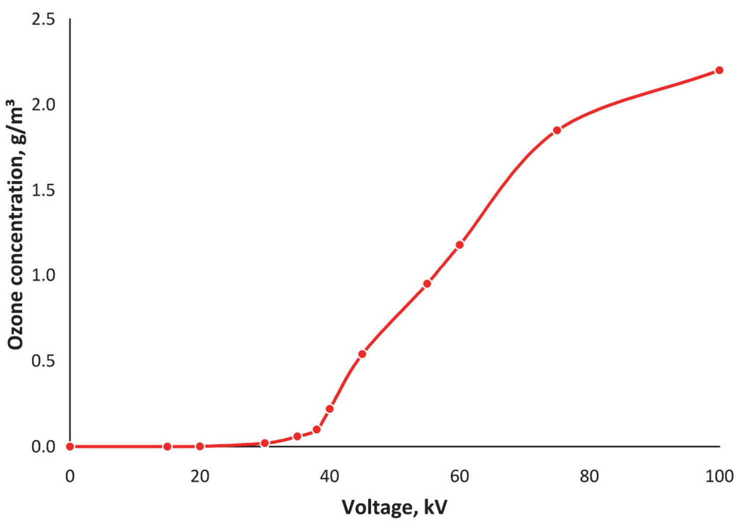

Fig. 2 Dependence of ozone concentration on the voltage of streamer discharge: pulse period - 1 ms, pulse duration - 200 ns

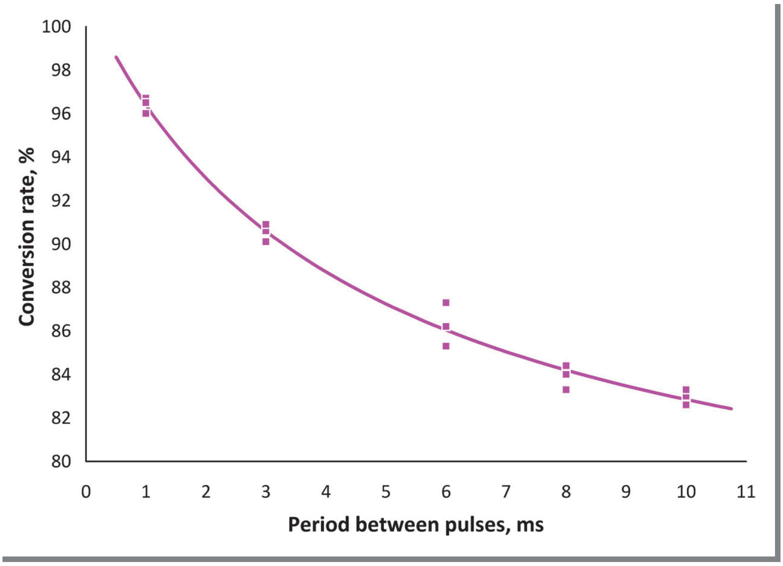

Fig. 3 Dependence of the conversion rate of sulphur dioxide on the applied voltage pulse period: the initial concentration of sulphur dioxide 0.61 g/m^3, voltage 45 kV

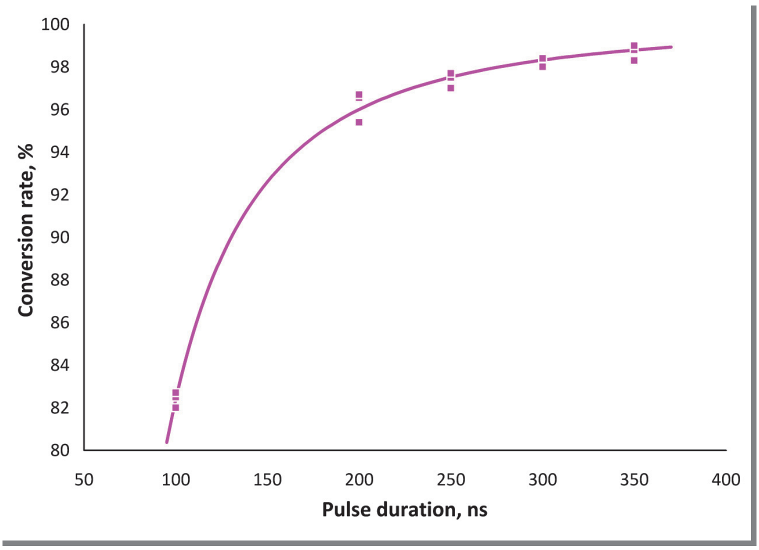

Fig. 4 Dependence of the conversion rate of sulphur dioxide on the pulse duration: voltage 45 kV; pulse period 1ms; initial concentration of sulphur dioxide 0.61 g/m^3

The change of the conversion rate of sulphur dioxide in the streamer discharge at a longer pulse period is caused by the ability to activate more gas molecules during the pulse (Fig. 4). It is determined that with the pulse duration of 350 ns, the conversion rate of sulphur dioxide is 98.6% (with the initial concentration of sulphur dioxide 0.61 g/m^3, voltage 45 kV), and with the minimum pulse duration of 100 ns (under the same conditions), it is 82.5%. Further increase in the pulse duration can cause a breakdown of the gas gap.

When using a streamer discharge for converting sulphur dioxide contained in industrial exhaust gases, the effect of the temperature of the gas mixture and dust presence must be considered. A temperature increase is known to reduce the lifetime of ozone and cause its decomposition (Lunin et al., 1998; Tatarchenko, 2013), which can lead to a lower conversion rate of sulphur dioxide due to its oxidation by ozone according to the reaction (2). Ozone is more likely to decompose to form atomic oxygen, which is known to be a more active oxidant than ozone (Lunin et al., 1998), which will have a positive effect on the conversion rate of sulphur dioxide into sulphur trioxide. The thermodynamic analysis of the reactions occurring when a sulphur-containing gas is exposed to a streamer discharge given in the paper by (Lytvynenko et al., 2012) showed that a temperature increase would have little effect on the oxidation of sulphur dioxide by atomic oxygen and ozone.

In turn, when dust particles enter the gas discharge zone, due to the adsorption of ions they become charged. The charged dust particles are larger in diameter than other chemically active particles. Therefore, the probability of ion contact on the dust particle increases, which accelerates the chemical reactions of the conversion of sulphur dioxide into sulphur trioxide.

4. Conclusions

The results of the theoretical and empirical research show that sulphur-containing gas treatment by plasma catalysis using a streamer discharge will ensure efficient conversion of sulphur dioxide into sulphur trioxide.

The study proves that the highest conversion rate of sulphur dioxide is achieved at its lowest concentrations (0.2 g/m^3) and is about 99 %. To increase the conversion rate of sulphur dioxide for more concentrated gases, it is necessary to increase the residence time of the gas mixture in the gas discharge reactor.

The study results indicate that at the voltage below 20 kV the conversion of sulphur dioxide occurs due to oxidation by atomic oxygen produced in the streamer discharge. When the voltage is increased to over 40 kV, the conversion of sulphur oxide occurs due to oxidation by atomic oxygen and ozone.

Laboratory studies of the conversion rate of sulphur dioxide in the streamer discharge showed that the efficiency of the conversion of sulphur dioxide increases at a shorter pulse period and longer pulse duration.

It has been defined that the change of peak to peak voltage has the most effect on the efficiency of the conversion of sulphur dioxide. When the voltage is increased to 100 kV, the conversion rate of sulphur dioxide reaches 99%.

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References

Belokon K.V., Manidina Ye.A., Fedchenok A., Matukhno E.V., (2019), Development of a method for catalytic purification of carbon-containing components of gas emissions from industrial enterprises, *Procedia Environmental Science, Engineering and Management*, **6**, 545-552.

Cherchintsev V.D., Savina Y., (2012), Improvement of absorption processes for capturing series dioxide from gas sinter production, (in Russian), *Vestnik of Nosov Magnitogorsk State Technical University*, 21-23.

Lunin V.V., Popovich M.P., Tkachenko S.N., (1998), *Physical chemistry of ozone*, (in Russian), *Fizicheskaya khimiya ozona*, Moscow State University, Moscow.

Lytvynenko T.M., Manidina Ye.A., Smotraev R.V., Budahova A.A., (2012), Effect of treatment of sulfur-containing gas by streamer discharge on oxidation of sulfur dioxide, (in Russian), *Issues of Chemistry and Chemical Technology*, 153-156.

Martins C.R., Neto C.A.C., Alwes J.J.F., Andrade J.B., (1999), Oxidation of sulfur (IV) by oxygen in aqueous solution: role of some metal ions, *Journal of the Brazilian Chemicsl Society*, **10**, 453-458.

Matukhno E.V., Belokon K.V., Shatokha V.I., Baranova T., (2019), Ecological aspects of sustainable development of metallurgical complex in Ukraine, *Procedia Environmental Science, Engineering and Management*, **6**, 671-679.

Muzadi P., Kotzé M., (2013), A new development in the oxidative precipitation of Fe and Mn by SO2/air, In *Proceedings of Base Metals Conference 2013*, Southern African Institute of Mining and Metallurgy, Johannesburg, 223-233, On line at: https://www.saimm.co.za/Conferences/BM2013/223-Muzadi.pdf.

Pavlenko Yu.P., Rumyantsev V.R., (1995), Evaluation of various types of electrical discharges for the decomposition of harmful gaseous components of industrial emissions, (in Russian), *Izvestiya. Ferrous Metallurgy*, 60-63.

Smotraev R.V., Manidina Ye.A., (2016), Kinetics of absorption of sulfur oxide(IV) by solutions of iron(II) and iron(III) salts, (in Russian), *Issues of Chemistry and Chemical Technology*, 44-50.

Tatarchenko H.O., (2013), Temperature dependence of the ozone recovery kinetics on the platinum surface, (in Russian), *Physicochemical Mechanics of Materials*, 126-130.