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ОПРЕДЕЛЕНИЕ ОПТИМАЛЬНЫХ УСЛОВИЙ ЭФФЕКТИВНОГО ПОГЛОЩЕНИЯ ОКСИДОВ АЗОТА И СЕРЫ ЖЕЛЕЗОМАРГАНЦЕВЫМИ КОНКРЕЦИЯМИ

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Рассмотрена характеристика железомарганцевых конкреций (ЖМК), активным компонентом в которых выступает оксид марганца (IV) MnO_2, с точки зрения состава материала и его сорбционных свойств. Предложен способ использования суспензии ЖМК для улавливания таких промышленных выбросов, как оксид азота (II) NO и оксид серы (IV) SO_2. Данный способ включает реакции поглощения оксида азота (II) оксидом марганца (IV) MnO_2 в присутствии азотной кислоты HNO_3 с образованием нитрата марганца $Mn(NO_3)_2$; также реакции поглощения оксида серы (IV) SO_2 оксидом марганца (IV) MnO_2 с образованием сульфата марганца $MnSO_4$. Разработаны специальные установки для исследования и отработки процесса сорбции. Представлены результаты экспериментальных исследований процесса сорбции оксида азота (II) NO и оксида серы (IV) SO_2 суспензией на основе ЖМК. Установлена возможность поглощения оксида азота (II) NO из газовой смеси со степенью извлечения до 85%, оксида серы (IV) SO_2 из соответствующей газовой смеси до 99%. Указаны основные параметры влияния на процесс работы системы: время выхода на постоянный режим, температура рабочей суспензии, способ перемешивания. Приведены таблицы и рисунки с указанием опытных результатов процессов при различных факторах влияния. Экспериментальным путем определены наиболее оптимальные условия для максимально эффективного проведения процесса поглощения оксида азота NO и оксида серы SO_2 до 85% и 99% соответственно из модельных смесей, соответствующих отходящим газам. Проведен сравнительный анализ процессов поглощения NO и SO_2. Установлены различия в проведении данных процессов.

Ключевые слова: железомарганцевые конкреции, монооксид азота, оксид серы, отходящие газы, параметры поглощения газов, сорбционная очистка

DETERMINATION OF OPTIMAL CONDITIONS FOR EFFECTIVE ABSORPTION OF NITROGEN AND SULFUR OXIDES BY IRON-MANGANESE CONCRETIONS

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Iron-manganese concretions (IMC) absorption characteristic and composition of the material was studied. The active component in it is manganese (IV) oxide MnO_2. A method is proposed for using a suspension of iron-manganese concretions ore to capture industrial emissions: nitrogen oxide (II) NO and sulfur oxide (IV) SO_2. This method involves the reaction of the absorption of nitrogen oxide (II) NO by manganese (IV) oxide MnO_2 in the presence of nitric acid HNO_3. The formation of manganese nitrate $Mn(NO_3)_2$ occurs. Also, the reaction of the absorption of sulfur oxide (IV) SO_2 by manganese (IV) oxide MnO_2 with the formation of manganese sulfate $MnSO_4$ takes place. Special installations for research and development of the process of sorption were developed. The results of experimental studies of the sorption process of nitrogen oxide (II) NO and sulfur oxide (IV) SO_2 by a suspension based on IMC are presented. The main parameters of the influence on the process of the system operation are indicated: time for reaching a constant mode, temperature of the working suspension, method of mixing. Tables and figures are given showing the experimental results of the processes with various factors of influence. Optimal conditions for maximum efficient conduction of nitrogen oxide and sulfur dioxide absorption process were determined for adsorption of these gases to 85% and 99%, respectively, from the model mixtures that corresponds to the waste gases. Comparative analysis of sorption processes of NO and SO_2 was performed.

Key words: iron-manganese concretions, nitrogen monoxide, sulfur oxide, off-gases, gases sorption parameters, sorption purification

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INTRODUCTION

Nitrogen oxides are released in significant amount during operation of fossil fuel power stations, internal combustion engines and burning of fuels. Metallurgy, manufacture of explosives and a nitric acid are the sources of a nitrogen oxide emission into the atmosphere as well. High levels of a nitric acid in the atmosphere leads to the pollution of the environment and possess a treat to health and life of the living organisms [1-7].

Therefore, the activities for a search of ways to reduce the amount of NO and SO_2 in waste gases are deployed worldwide at the moment.

The existing methods of purification of the gaseous exhausts from sulfur dioxide and nitrogen are subdivided into the followings:

- absorptive – the sorbent is liquid;
- adsorptive – the sorbent is solid;
- catalytic methods.

The method of catalytic reduction of oxides and nitrogen oxides started to being applied relatively recently and is the most perfect among the methods for the time present [8-18]. However, this method shortcomings are the formation of new substances that are to be removed by the other methods (absorption, adsorption), as well as large capital costs of equipment fabrication and use of expensive catalyst, regeneration of which requires considerable expenses too.

In conjunction to the available methods row of serious shortcomings, the development of the methods for wastes purification from oxides of nitrogen and sulfur, providing the highest purification degree at the minimum capital costs and the simplicity of a technological scheme, presents an interest. The authors propose to carry out sorption process of NO and SO_2 on the accessible sorbent on the basis of manganese – iron-manganese concretions (IMC) from the bottom of the Baltic Sea [19].

Its active component is manganese dioxide, which, as it would be expected, will suppress the secondary emission of nitrogen oxides during purification of gases from these oxides and will allow to exclude slow process of nitrogen oxide transformation to dioxide oxidation [20]. Thus, there are all the reasons to suppose that IMC, having the great natural catalytic and sorption properties, could serve as an effective sorbent of unhealthy components of industrial gaseous emissions. This method is simple in its apparatus realization and it have been demonstrated by high purification degree from NO and SO_2.

The aim of the current article is the determination of optimal conditions for the effective use the of iron-manganese concretions suspension for the sorption purification of industrial off-gases from nitrogen oxide and sulfur dioxide.

EXPERIMENTAL METHOD

During the process of off-gases purification from the nitrogen oxide (II), by the means of manganese derivatives, the correspondent nitrates are formed from a nitric acid due to the aqueous sorption of NO_2 according to the reactions:

$$2NO + 4HNO_3 + 3MnO_2 \rightarrow 3Mn(NO_3)_2 + 2H_2O \quad (1)$$

$$NO_2 + H_2O \rightarrow HNO_3 + HNO_2 \quad (2)$$

Special installation was made for the chemisorption purification of the off-gases from NO by the method developed.

The experiments for NO sorption were conducted at the temperatures 25, 55 and 70 °C. The concentration of NO in the flow of gas-air mixture was 130 mg/m^3.

The concentration of the initial gas was measured by gas analyzer "MONOLITH" that is a multifunctional device equipped with the systems of the samples preparation and acquisition. After the measurement was done, the gas flow was directed to the bubbler, where the sorption of NO_2 by water with the consequent nitric acid HNO_3 generation occurred. At the final stage nitrogen oxides content after the adsorption was controlled.

For the off-gases purification from SO_2 by chemisorption method the special installation was made as well.

The experiments for SO_2 sorption were conducted at the temperatures 25 and 55 °C, the volumetric flow of gas-air mixture V = 97.2 dm^3/h and the concentration of SO_2 in it was 12500 mg/m^3. The pH of the suspension was 8. The measurements were conducted by the pH-meter/ion-meter Mul'titest IPL-201.

For SO_2 concentration measurement gas-analyzer MONOLITH was used. The gaseous mixture was withdrawn to the analysis by the three-way cocks. Sulphur dioxide suspension sorption by IMC was conditioned by the reactions:

$$2MnO + 2SO_2 + O_2 = 2MnSO_4 \quad (3)$$

$$MnO_2 + SO_2 = MnSO_4 \quad (4)$$

From the development of the sulphur dioxide and nitrogen monoxide sorption process and its industrial realization estimation of perspectives points of view, the important question is the possibility of the spent suspension regeneration and the extraction of valuable components from the suspensions. The method of the suspension purification from iron by the means of the initial iron-manganese concretions was tested as applied to the sulphur dioxide sorption process. At that pyrolusite that is contained in the concretions, being the strong oxidizer in the acid environment, could replace air, and sulphur acid being emitted during iron hydrolysis process will dissolve nonferrous metals, becoming neutral by this way.

After that the deposition by the mean of ammonia water (25% mass) in presence of oxygen at 50 °C temperature was performed. The received suspension was filtered and solid phase content was determined by X-ray fluorescence analysis. As a result, quite pure product was received – the manganese sulphate, application of which for the further needs is actual today, while sulphates of the other metals that are generated during the reactions with IMC do not represent the interest of such kind.

Applicably to the nitrogen monoxide sorption process the sorbent regeneration is possible, which consist of the two stages: thermal decomposition of manganese nitrate to MnO_2 and NO_2 with the return of manganese dioxide to the sorption process and the capture of nitrogen dioxide by water or alkali for nitrogen acid generation.

RESULTS AND DISSCUSSION

The analysis of the system working parameters that affects the nitrogen oxide NO by the aqueous suspension of IMC sorption process was conducted. Such parameters are turned out to be: the sorbing suspension temperature, mixing intensity and the residence time.

The experimental data that are given in the Table 1 demonstrates suspension temperature influence on the sorption degree. Significant increase in the sorption ability of the IMC suspension with respect to nitrogen monoxide occurs as the temperature rises to 55 °C.

Table 1

Degree of NO sorption at different suspension temperatures

***Таблица 1.* Степень сорбции NO при различных температурах суспензии**

IMC suspension's temperature, °C	Absorbed NO amount, %	Absorbed NO_2 amount, %
25	21.5	65
55	83	66
70	51	55

The dependence of the sorption ability on the temperature has the extremum since the further growth of the temperature in the consequence of exothermicity of the process and partial change of phase composition of the system leads to NO sorption decrease.

During the experiments it was noticed that at the additional suspension mixing by the magnetic mixer the extraction degree increased significantly as the solid phase distributed more homogeneously in the absorber volume (Table 2).

Table 2

Sorption degree at different mixing methods

***Таблица 2.* Степень сорбции при различных методах перемешивания**

Mixing method	Amount of NO absorbed, %
By gas-air mixture	45
By gas-air mixture and magnetic mixer	87

The time of the process to reach the stationary state at the initial NO concentration of 130 mg/m^3 was about 180 min (Fig. 1).

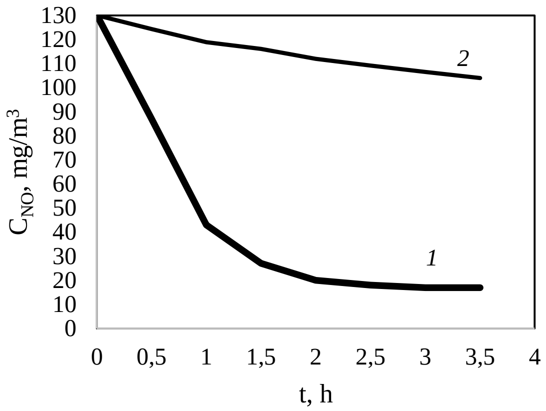

Fig. 1. The dependence of NO concentration on the time at the outlet of the absorber 1 – change in NO concentration at suspension temperature of 55 °C. 2 – change in NO concentration at suspension temperature of 25 °C

Рис. 1. Зависимость концентрации NO от времени на выходе абсорбера1- изменения концентрации NO при температуре суспензии 55 °C. 2- изменения концентрации NO при температуре суспензии 25 °C

Fig. 2 illustrates the results of the experiments of sorption purification of gases from sulfur dioxide. At that the experimental uncertainty did not exceed 12%. As it can be seen from the provided plot, during a long time interval almost full (up to ~99%) extraction of SO_2 from the gas flow occurs. Taking into account the gaseous mixture flow and sulphur oxide concentration in it, it is not hard to estimate IMC sorption capacity with respect to SO_2. At the end of the experiment a concretion sample mass of 100 g absorbs near 18 g of sulfur dioxide. Fig. 2 allows to understand the temperature influence on the chemisorption process as well. Increase in the suspension temperature to 55 °C shortens the saturation time by a factor of two that is connected, presumably, with the acceleration of the formation of sulfur and sulfuric acids under reactions with the IMC components. Besides, as the temperature rises the solubility of SO_2 in water become lower that makes skip of it through the suspension layer easier.

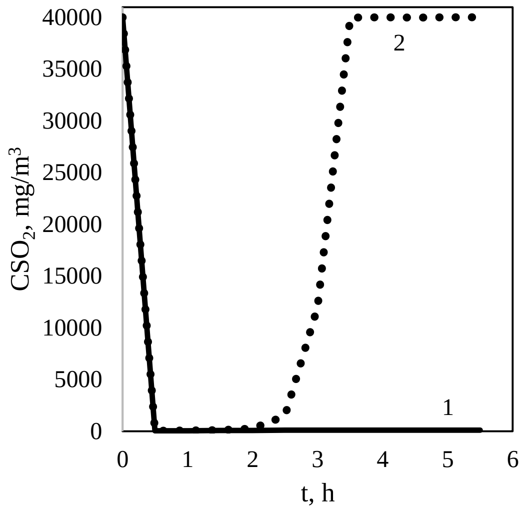

Fig. 2. Dependence of SO_2 concentration on time and temperature at the outlet of the absorber. 1 – change in SO_2 concentration at suspension temperature of 25 °C. 2 – change in SO_2 concentration at suspension temperature of 55 °C

Рис. 2. Зависимость концентрации SO_2 от времени на выходе абсорбера 1- изменения концентрации SO_2 при температуре суспензии 25 °C. 2- изменения концентрации SO_2 при температуре суспензии 55 °C

Experimentally chosen optimal conditions that provides the best sulfur and nitrogen oxides sorption are given in Table 3. The comparative analysis of the optimal sorption conditions shows essential difference of the system working parameters at sorption process conduction. This fact proves unreasonableness of the gas emissions from sulfur and nitrogen oxides purification processes joint conduction that has significance for those industries at which exhaust gases contains both oxides species.

Table 3

Optimal conditions for the sorption of nitrogen monoxide by IMC

***Таблица 3.* Оптимальные условия для сорбции монооксида азота железо-марганцевыми конкрециями**

Oxide sorbed, %	The most effective operation parameters of the system			
	T suspension, °C	Suspension mixing method	Contact t, min	Linear velocity of gas feed, m/s
NO, 83–85	55	Bubbling by gas-air mixture and magnetic mixing	180	2.17
SO_2, ~99	25	Bubbling by gas-air mixture and magnetic mixing	180	2.17

CONCLUSION

The conditions were determined experimentally that allows to perform deep purification up to 99% from sulfur dioxide SO_2 and up to 85% from nitrogen monoxide NO of the corresponding gaseous mixtures using the effective sorbent – suspension on the basis of the iron-manganese concretions. These iron-manganese concretions have a low price, easy to regenerate and they are chemically active. These factors convince in the reasonableness of the given sorbent industrial use.

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