ного газа для полного использования его химического потенциала. Введено и рассмотрено такое понятие, как коэффициент использования водорода. Установлено, что реализация рециркуляции водорода возможна только на газоплотном агрегате. Разработаны порошковые затворы для уплотнения торцов конвейерных печей восстановления и отжига металлических порошков. Предложено и реализовано энергоэффективную схему восстановления железа с рециркуляцией и регенерацией водорода. Данный способ дает возможность приблизить расходы газа до стехиометрических показателей. *Библ. 15, рис. 4, табл. 2.*

Ключевые слова: восстановление, водород, железный порошок, рециркуляция, регенерация.

Охорона навколишнього середовища

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Peculiarities of Absorption of Sulfur Dioxide and Nitrogen Oxide in Suspensions and Solutions of Manganese Compounds

It is proposed to use manganese compounds to reduce emissions of sulfur and nitrogen oxides, large deposits of which are in Ukraine. The results of experimental studies of the binding of sulfur dioxide and potassium permanganate of nitric oxide in water by manganese oxide are presented. In the experiments, the model gas in the form of small bubbles was passed through the reactor with liquid. Heat and mass transfer processes between the gas and liquid phases occurred on the bubble surface. The gas-liquid contact time is the bubble rise time. The absorption reactions take place in the liquid phase. Complete absorption of sulfur dioxide takes place in an acidic environment, provided that the molar ratio MnO_2/SO_2 is not less than 2. The reaction product is manganese sulfate, which is a useful product. The maximum absorption of nitrogen oxide is achieved at a molar ratio of KMnO_4/NO not less than 5. The reaction forms a precipitate of manganese oxide, which can later be used in the desulfurization process. *Bibl. 12, Fig. 6, Tab. 3.*

Key words: flue gas, gas purification, sulfur dioxide, nitric oxide, manganese.

The problem of reducing emissions of pollutants generated by fuel combustion in boilers of thermal power plants, heating plants and boilers is becoming increasingly important. Ukraine's implementation of the Energy Community Treaty [1] provides for the incorporation of EU envi-

ronmental directives into Ukrainian environmental legislation, in particular Directive 2010/75/EU on industrial emissions [2] and Directive 2015/2193 / EU on the limitation of emissions of certain pollutants from medium incinerators [3]. To comply with their require-

ments, it is necessary to reduce many times the concentrations of pollutants such as sulfur dioxide SO_2 and oxides of nitrogen NO_x .

Among the methods of reducing sulfur dioxide emissions in the heat industry are flue gas desulfurization (FGD) technologies, in which the absorption of sulfur dioxide occurs due to contact of flue gases with alkaline or alkaline earth sorbents or sorbents with a large specific surface area. These include: limestone, lime, sodium bicarbonate, sodium hydroxide, activated carbon, ammonia, hydrogen peroxide, seawater, sodium sulfite, dolomite lime and more [4].

Existing technologies for reducing emissions of nitrogen oxides in the heat industry provide for the integrated application of primary regime-technological measures and the use of nitrogen treatment technologies. Selective catalytic reduction (SLE) and selective non-catalytic reduction (SLE) technologies are most commonly used in thermal power plants, when the reaction with ammonia NH_3 or urea results in the conversion of nitrogen oxide NO and nitrogen dioxide NO_2 to molecular nitrogen N_2 [4].

An alternative to the reduction of nitrogen oxides can be the oxidation of nitric oxide to higher oxides with the subsequent formation of industrial nitrogen compounds. The classical technology of obtaining nitric acid from ammonia includes the stage of its catalytic oxidation to nitric oxide and subsequent oxidation of the latter to nitrogen dioxide [5].

Ukraine has large deposits of manganese ores [6]. Significant amounts of manganese dioxide MnO_2 [7] and potassium permanganate KMnO_4 can be obtained from their enrichment wastes, and as a result of their chemical interaction with sulfur dioxide SO_2 and nitric oxide NO useful substances will be formed [8].

The reactions of chemical interaction of sulfur dioxide and manganese oxide are as follows [9]:

Dissolution of sulfur dioxide and dissociation of sulfuric acid:

The reaction of the surface of solid particles of manganese dioxide in an acidic environment with the formation of the cation of manganese methahydroxide:

Reaction of manganese methahydroxide cation with hydrosulfite anion to form manganese sulfate:

At $\text{pH} < 3$, manganese dithionate MnS_2O_6 is formed:

decomposing into manganese sulphate and sulfur dioxide:

That is, the preferred product of the coupling reaction is manganese sulfate, which has a high cost and wide industrial application. The binding efficiency of sulfur dioxide to the MnO_2 suspension primarily depends on the total surface area of the manganese oxide particles in the suspension, as there is a reaction on the surface of the particles.

The absorption of NO by potassium permanganate occurs by the oxidation reaction in the liquid phase to NO_3^- , and the formation of MnO_2 [8]:

This reaction in a weak alkaline or neutral solution can be expressed as follows [10]:

To study the processes of interaction of sulfur dioxide with a suspension of manganese dioxide and nitric oxide with a solution of potassium permanganate, a series of experimental studies was carried out on a wet gas cleaning unit (Fig. 1) [6, 11]. The basis of the wet scrubber is a bubble reactor 7 in which the absorption of sulfur dioxide from the model gas and a chemical reaction with a suspension or solution of the sorbent (MnO_2 or KMnO_4). The model gas supplied to the bubbler reactor from cylinder 1 is a mixture of nitrogen with the addition of SO_2 (1978 ppm) or NO (1008 ppm). The consumption of model gas of the cylinder is regulated by a gas reducer 2 and is controlled by a manometer 3. The consumption of model gas is measured by rheometer 4, it was 1.2 l/min. for all experiments.

Fig. 1. Scheme of installation of wet gas cleaning: 1 – cylinder with gas mixture; 2 – cylinder reducer; 3 – manometer; 4 – the crane regulator; 5 – rheometer; 6 – crane; 7 – bubbler reactor; 8 – pH meter electrode; 9 – ionomer sensor.

After the control and measuring devices, the model gas is fed to the lower part of the bubbler reactor through a porous glass filter (for spraying gas into small bubbles) and enters the sorbent solution or suspension. The suspension of manganese dioxide in the reactor consisted of 120 ml of distilled water with the addition of a certain portion of MnO_2 with a purity of 92 %. The potassium permanganate solution was made by adding a certain amount of KMnO_4 solution with a concentration of 12 g/l to 120 ml of distilled water. After passing the reactor, the gas is fed to the gas analyzer, and the excess is discharged to the hood. The ionomer sensor 9 allows you to record in time the pH and temperature of the solution. All experiments were performed at a temperature of 15–25 °C.

The scheme of the absorption process in all methods of contact of the reagents can be represented as follows: there are flows of gas and liquid,

there is a phase boundary, the components are transferred through the interface. The reaction proceeds in the liquid phase. There is no fundamental difference between the methods of contact of the «gas – liquid» phases: whether there is bubbling (dispersed gas in the form of bubbles rises in the liquid layer) or irrigation (dispersed liquid in the form of droplets moves in a gaseous medium). The laboratory model in the gas phase is a model of an ideal displacement reactor, and in the liquid phase – a model of a perfect mixing reactor. The «gas – liquid» contact time is the rise time of the bubble.

To study the uptake of sulfur dioxide by manganese oxide, three experiments with different concentrations of MnO_2 were performed. The main parameters of the experiments are shown in Table 1.

Table 1. Parameters of experiments with sulfur dioxide Model gas A mixture of N_2 and SO_2 (1978 ppm)

Parameter	Experiment		
	1	2	3
Mass of sorbent, g	0.07	0.35	0.7
Concentration of MnO_2 in the reactor, g/l	0.588	2.92	5.88

The results of experimental studies are changes in the concentration of sulfur dioxide at the reactor outlet and the pH of the suspension of manganese dioxide in the reactor. As can be seen in the graph of the dependence of the initial concentration of SO_2 (Fig. 2) in all experiments the maximum efficiency of binding of sulfur dioxide to manganese oxide is more than 97 %. The reaction takes place in an acidic environment (pH 2–3). data from the graph of changes in time of the pH indicator (Fig. 3).

Fig. 2. Time change of sulfur dioxide concentration at the reactor outlet.

Fig. 3. Change in time of pH of manganese dioxide suspension in the reactor.

At these pH values in an acidic environment, the surface reaction of solid dioxide particles occurs. The increase in the initial concentration of sulfur dioxide occurs when the molar ratio of SO_2/MnO_2 is more than 0.5 (Fig. 4).

The rate of binding of sulfur dioxide to MnO_2 suspension is low, so the amount of bound sulfur dioxide is determined by the concentration of manganese dioxide in the solution [6].

Fig. 4. Dependence of the initial SO_2 concentration on the SO_2/MnO_2 ratio.

Effective binding of sulfur dioxide occurs in the presence of 2 moles of MnO_2 per 1 mole of SO_2 . This feature is probably due to the fact that the reaction process of sulfur dioxide and manganese dioxide occurs in several stages: surface reactions on MnO_2 particles, the formation of intermediates and reactions of manganese sulfate MnSO_4 and manganese dithionate MnS_2O_6 .

An experimental study of the absorption of nitric oxide by a solution of potassium permanganate was performed as follows: a prepared solution of potassium permanganate with a con-

centration of 12 g/l was added to 120 ml of distilled water in the reactor. The study consisted of four series of experiments, the parameters of which are shown in Table 2. The variable parameter of the experiments was the concentration of KMnO_4 , the change of which was achieved by introducing different volumes of prepared potassium permanganate solution with a concentration of 12 g/l. The results of experimental studies are time measurements of the concentration of sulfur dioxide at the outlet of the reactor and the pH of the solution of potassium permanganate in the reactor (Fig. 5 and Fig. 6).

Table 2. Parameters of experiments with nitric oxide Model gas A mixture of N_2 and NO (1008 ppm)

Parameter	Experiment			
	1	2	3	4
Volume of solution $KMnO_4$, introduced into the reactor, ml	1	5	10	25
Concentration of $KMnO_4$ in the reactor, g/l	0.10	0.48	0.92	2.07

From the analysis of graphs in Fig.5 and Fig.6 we can see that when the values of NO concentration approach the level of input concentration, the pH value of the solution increases due to full use of potassium permanganate in solution, resulting in the generation of new NO_3^- ions. After the experiments, solid MnO_2 particles were present in the reactor, which are the product of the reaction between potassium permanganate and nitric oxide [6].

Fig. 5. Time change of nitric oxide concentration at the reactor outlet. **Fig. 6.** Time change of pH of potassium permanganate solution.

Because the binding efficiency changed over time during the experiments due to the consumption of $KMnO_4$, Table 3 shows the maximum removal efficiency of nitric oxide at a certain concentration.

In all experiments, the maximum binding efficiency of nitric oxide corresponds to the value of the ratio $NO/KMnO_4 < 0.2$. That is, at least 5 moles of potassium permanganate are required per 1 mole of nitric oxide to achieve maximum binding efficiency under these conditions.

Table 3. The dependence of the maximum binding efficiency of nitric oxide on the concentration of $KMnO_4$ solution

Parameter	Experiment			
	1	2	3	4
Concentration of $KMnO_4$ in the reactor, g/l	0.10	0.48	0.92	2.07
Maximum value of the binding efficiency of nitric oxide NO, %	15.7	29.0	39.8	58.6

Given that the initial pH of the potassium permanganate solution is in the neutral pH range of 6–7, this nitric oxide binding mechanism will be appropriate using alkaline compounds such as sodium hydroxide, ammonia, urea, in addition to potassium permanganate. [8, 10, 12].

The resulting MnO_2 manganese precipitate can be used to efficiently bind sulfur dioxide, as evidenced by the results obtained above.

Conclusions

Manganese compounds, such as manganese oxide and potassium permanganate, can be used for the treatment of gas-like external streams such as sulfur dioxide and nitrogen oxide.

The reaction of sulfur dioxide with MnO_2 is added to the surface of the particles of the sorbent, and the result of the reaction is manganese sulphate, which can be used for the most part, and also dityonate manganese, which is deposited on the sulphate manganese. Outside of the reaction to sulfur dioxide, it occurs when the molar ratio MnO_2/SO_2 is greater than 2.

NO is bound by the reaction of oxidation of nitric oxide with potassium permanganate in the liquid phase to the anion NO_3^- to form a precipitate of MnO_2 particles, which can be used to absorb sulfur dioxide. The maximum binding efficiency of nitric oxide corresponds to a molar ratio of NO/KMnO_4 of not more than 0.2.

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Особливості поглинання діоксиду сірки та оксиду азоту в суспензіях та розчинах сполук мангану

Запропоновано використовувати для зниження викидів оксидів сірки та азоту сполуки мангану, значні поклади якого є в Україні. Представлено результати експериментальних досліджень зв'язування у воді оксидом мангану діоксиду сірки та перманганатом калію оксиду азоту. В експериментах модельний газ у вигляді дрібних бульбашок пропускався через реактор з рідиною. Тепло- і масообмінні процеси між газоподібною та рідкою фазами відбувалися на поверхні бульбашки. Час контакту «газ – рідина» є часом підйому бульбашки. Реакції абсорбції протікають у рідкій фазі. Повна абсорбція діоксиду сірки оксидом мангану має місце в кислому середовищі при дотриманні мольного відношення MnO_2/SO_2 не менш 2. Продуктом реакції буде сульфат мангану, який є корисним продуктом. Максимальне поглинання оксиду азоту перманганатом калію досягається при мольному відношенні KMnO_4/NO не менш 5. В реакції утворюється осад оксиду мангану, який надалі може бути використаний в процесі сіркоочищення. *Бібл. 12, рис. 6, табл. 3.*

Ключові слова: димові гази, газоочищення, діоксид сірки, оксид азоту, манган.

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Особенности поглощения диоксида серы и оксида азота в суспензиях и растворах соединений марганца

Предлагается использовать для снижения выбросов оксидов серы и азота соединения марганца, большие залежи которого есть в Украине. Представлены результаты экспериментальных исследований связывания в воде оксидом марганца диоксида серы и перманганатом калия оксида азота. В экспериментах модельный газ в виде мелких пузырьков пропускался через реактор с жидкостью. Тепло- и массообменные процессы между газовой и жидкой фазами происходили на поверхности пузырька. Время контакта «газ – жидкость» является временем подъема пузырька. Реакции абсорбции проходят в жидкой фазе. Полная абсорбция диоксида серы имеет место в кислой среде при соблюдении мольного соотношения MnO_2/SO_2 не менее 2. Продуктом реакции будет сульфат марганца, являющийся полезным продуктом. Максимальное поглощение оксида азота достигается при мольном соотношении KMnO_4/NO не менее 5. В реакции образуется осадок оксида марганца, который в дальнейшем может быть использован в процессе сероочистки. *Библ. 12, рис. 6, табл. 3.*

Ключевые слова: дымовые газы, газоочистка, диоксид серы, оксид азота, марганец.