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INVESTIGATIONS ON SORPTION OF ACID GASES ON ANION EXCHANGERS

Literature data referring to sorption of acid gases on anion exchangers have been analyzed. Results from investigations on sorption of sulphur dioxide, nitrogen oxides, hydrogen fluoride, hydrogen sulphide and carbon disulphide on anion exchangers have been presented. Basic parameters of sorption process have been developed. It has been stated that the anion exchangers with an increased granulation can be used in the technology of the purification of waste gases.

1. INTRODUCTION

Air pollution due to the emission of toxic substances contained in waste gases is one of basic problems the developing industry must cope with. This is due not only to different physicochemical properties and varying compositions of the separate gaseous substance, but also to different proportions of their contents, their frequently explosive and aggressive character, as well as to different volumes of the flow-rate of gases emitted to the atmosphere. The most important in this respect are highly toxic geseous compounds of fluorine, nitrogen oxides and sulphur compounds, such as sulphur dioxide, hydrogen sulphide and carbon disulphide, as well as the vapours of some organic compounds.

Of numerous methods intended to remove gaseous pollutants from waste gases the most important are sorption methods, among which — independently of traditional sorbents — the usage of ion exchangers is more frequently suggested. A relatively small difference between the properties of the ion exchangers produced, and the lack of ion exchangers with a well developed active surface were the factors limiting the application of ion exchangers to softening and demineralization of water and industrial wastewater treatment exclusively.

It was only due to the rapid progress in synthesis of anion exchangers with a well developed active surface and the studies on physicochemical properties of porous anion exchangers that a considerable increase in the possibilities of their usage in removal of acid gaseous pollutants from waste gases, was achieved.

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2. SORPTION OF ACID GASES ON ANION EXCHANGERS

The work on the application of anion exchangers to gas sorption has been directed toward the utilization of their sorption, chemisorption and catalytic properties.

Numerous papers published in the last decade have presented the results of preliminary laboratory tests concerning gas sorption on anion exchangers [1–14], [16–34]. These papers signal the possibility of the application of anion exchangers in the technology of gas purification but have a rather fragmentary form. Most of this work as carried out in the laboratory scale, being confined to determining and/or improving the sorption capacity of anion exchangers.

However none of these papers give the data on the resistance of gas flow through the layer of anion exchanger, and on the parameters of mass exchange between the gas and anion exchanger layer. On the other hand, from the review of literature data it follows that sorption capacity of anion exchangers depends on functional groups of anion exchanger and increases with the increasing moisture content in the sorption system. In numerous works on the sorption of acid gases on anion exchangers a boundary value of the moisture below which sorption capacity decreases rapidly, has been observed in gaseous mixture or anion exchanger. The influences of moisture content in a sorption system on the sorption process has been presented in detail by KREJCAR [6] VULIKH [23, 24], and ZAGORSKAYA [33] while interpreting results of experiments on sorption of sulphur dioxide, carbon dioxide, nitrogen oxides, and hydrogen halogens. From their investigations it follows that a decisive role in the sorption process is performed by an adequately high moisture content of anion exchangers and gases being purified.

From the comparison of adsorption and desorption properties of anion exchangers with those traditional sorbents such as silicic acid gel, activated carbon or molecular sieves it follows that the properties of anion exchangers are, very often much better [1].

From the analysis of literature data it follows, moreover, that the anion exchangers were used by most researchers in cycles consisting of sorption, regeneration and washing, thereby wasting the possibility of increasing anion exchanger sorption capacity. To implement this method the mechanism of acid gases sorption on anion exchangers must be widely studied, and a number of technological tests performed to determine optimal parameters of this process.

3. PARAMETERS OF THE PROCESS OF ACID GAS SORPTION ON ANION EXCHANGERS

These investigations were aimed at development of a modern method of neutralization and utilization of acid gases from industrial waste gases. The investigations conducted on the sorption of sulhur dioxide, nitrogen oxides, hydrogen fluoride, hydrogen sulphide and carbon disulphide on anion exchangers are justified both from the standpoint of economy (low investment and maintenance costs) and protection of natural environment.

The purpose of the experiments conducted was to determine some parameters essential for the technological processes. Anion exchangers used in the experiments were of polymeric type with a different degree of cross-linkage, obtained from copolymere of styrene with divinyl-benzene (Ambertite, Dowex, Wofatit, Zerolit and others), and of a polycondensate one (FFD) synthetized from formaldehyde and metaphenylediamine [15].

The experiments were performed in laboratory scale on gases artificially prepared, employing the technology developed at this Institute [3]. According to this technology anion exchanger layer was continuously regenerated with sodium hydroxide during sorption. This procedure allowed to multiply sorption capacity of the anion exchanger. In the experiment conducted several, or sometimes more measurements, constituted one series. Within one series the thickness of anion exchanger layer, gas concentration, sodium hydroxide concentration in sprinkling solution and sprinkling rate were the constant parameters, linear velocity of gas being the variable parameter.

3.1. SORPTION OF SULPHUR DIOXIDE

At first the experiments were conducted on a 0.3 m layer of the anion exchanger SBW, its granulation ranging within $(0.2–2.0) \times 10^{-3}$ m, by applying at all times an excess of sodium hydroxide in sprinkling solution with respect to the concentration of SO_2 in gas. Since during several day tests SO_2 was not detected in gas, then it has been assumed that the efficiency of sorption is 100%. Sorption capacity of the column under experimental conditions was practically unlimited, and dependent only on the concentration of SO_2 in the gas. At the gas flow rate in column ranging within 0.3 m/s resistances were very high $(7 \times 10^4$ N/m^2). In further experiments on the reduction of flow resistance 90% of anion exchanger was removed leaving the layer 0.03 m thick. It has been stated that the layer, 0.03 m thick, sprinkled continuously with the solution of sodium hydroxide ensures total removal of SO_2 from the treated gas. At the same time the gas flow resistance diminished from 7×10^4 N/m^2 to 1.5×10^4 N/m^2, the remaining parameters being unchanged.

The reduction of gas flow resistances to the 3×10^3 N/m^2 assumed as the cost effective economical in industrial systems can be achieved without detriment to the process, by increasing the diameter of the exchanger grains. Considering the fact that an arbitrary amount of anion exchanger FFD with a different granulation can be easily synthetized under laboratory conditions, it has been decided to use it for further investigations on sorption of acid gases.

From the comparative experiments it follows that in dynamic conditions the properties of anion exchanger are similar to those of Wofatit SBW, whereas the resistances of gas flow through the layer of the anion exchanger FFD are much lower. Experiments aiming to determine the dependence of gas flow resistance on the layer thickness, sprinkling intensity and gas velocity allowed to eliminate such experiments in which the resistances

of the anion exchanger FFD layer could exceed 3×10^3 N/m². This condition is satisfied if the velocity of gas flow through the anion exchanger is lower than

0.47 m/s for the layer 0.1 m,
0.80 m/s for the layer 0.07 m,
1.1 m/s for the layer 0.05 m,
1.2 m/s for the layer 0.03 m.

Basic condition enabling the usage of the said method in the technology of gas treatment is the reduction of contact time between gas and anion exchanger. That is why further experiments were to determine the relation between gas-anion exchanger time and efficiency of SO_2 sorption. Sprinkling intensity, thickness of anion layer, concentration of NaOH in sprinkling solution and SO_2 concentration in gas were treated as essential parameters determining the above relation.

The experiments were conducted under process parameter range specified in table 1.

Table 1

Range of parameters studied and optimized parameters for sorption of geseous pollutants on anion exchangers

Type of gaseous pollutant	Unit —	Sulphur Dioxide — SO_2 —		Nitrogen oxides Range studied $NO_{2/3}$	Hydrogen fluoride Range studied HF	Hydrogen sulphide and carbon disulphide Range studied H_2S ; CS_2
		Range studied	selected optimum			
Linear velocity of gas	m/s	0.2–3.0	0.6	0.2–3.0	0.2–3.0	0.1–1.1
Sprinkling intensity	m³/s	$(2.8–56) \times 10^{-7}$	8.4×10^{-7}	$(2.8–56) \times 10^{-7}$	$(2.8–56) \times 10^{-7}$	$(0.45–11.2) \times 10^{-7}$
Gas flow resistances	N/m²	$< 3 \times 10^3$	1.28×10^3	—	—	—
Thickness of anion exchanger layer	m	0.3	0.03	0.03	0.03	0.03–0.10
Contact time	s	$(1–15) \times 10^{-2}$	5×10^{-2}	$(1–15) \times 10^{-2}$	—	0.03–03
Sorption efficiency	%	—	99	—	—	—
Concentration of NaOH in sprinkling solution	% (wt)	10	0.19	10	10	5
Concentration of the pollutant in gas	kg/m³	5×10^{-3} (SO_2)	5×10^{-3} (SO_2)	3×10^{-3} ($NO_{3/2}$)	1.5×10^{-3} (HF)	0.04–0.40(H_2S)·10^{-3} 0.08–1.15 $CS_2 \times 10^{-3}$
Excess of NaOH in sprinkling solution	%(wt)	—	20	—	10	—

Results of these experiments are presented in fig. 1. From the above relations it follows that the effectivenees of SO_2 sorption depends to a great extent on the sprinkling intensity and contact time. Sorption efficiency of the order of 99% can be achieved at sprinkling intensity $2.8 \times 10^{-7} m^3/s$ as well as at $28 \times 10^{-7} m^3/s$, but at different contact times amounting
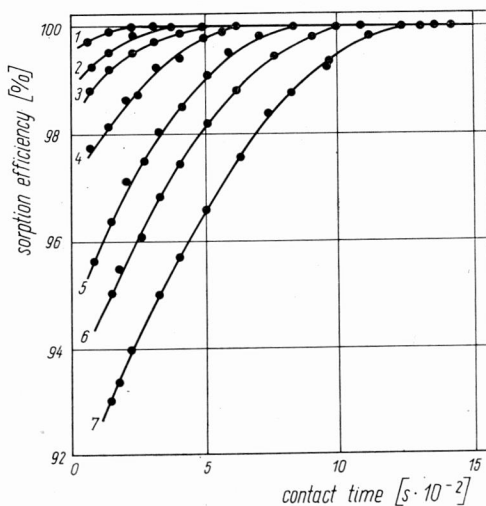

Fig. 1. Effectiveness of SO_2 sorption vs. contact time and sprinkling intensity

Rys. 1. Efektywność sorpcji SO_2 w zależności od czasu kontaktu i intensywności zraszania

$1 - q = 56.0 \times 10^{-7}$ m³/s, $2 - q = 28.0 \times 10^{-7}$ m³/s, $3 - q = 14.0 \times 10^{-7}$ m³/s, $4 - q \times 11.0 \times 10^{-7}$ m³/s, $5 - q = 8.4 \times 10^{-7}$ m³/s, $6 - q = 5.6 \times 10^{-7}$ m³/s, $7 - q = 2.8 \times 10^{-7}$ m³/s.

to $8.7 \times 10^{-2}s$ and $0.2 \times 10^{-2}s$, respectively. Obviously both flow resistances and SiO_2 concentrations in the post sorption solution will be also different.

The performed laboratory tests allowed to specify optimum parameters of this experimental series, which are presented in table 1.

From technological viewpoint only sorption efficiency and contact time are satisfactory parameters. All the remaining ones, except for concentration of sprinkling solution, are acceptable while the concentration of sprinkling solution is too low and does not allow a further utilization of sulphite solutions.

The investigations performed constituted the basis for the design of the system pilot scale. They were aimed to check the possibility of a considerable improvement of essential parameters of SO_2 sorption of anion exchangers.

3.2. SORPTION OF NITROGEN OXIDES

Further investigations were intended to state whether the sorption parameters will be changed if the kind of gas flowing through the experimental set up is changed. The experiment was conducted at the parameters presented in table 1.

Results of experiments are presented in fig. 2. Comparison of sorption efficiency curves for SO_2 (fig. 1) and NO_3 (fig. 2) obtained from the experiments conducted under identical conditions, have shown that SO_2 is sorbed much easier than $NO^3/_2$. If the $NO^3/_2$ sorption of the order of 98.5% is achieved at flow-rate equal to 0.5 m/s and sprinkling in-

tensity 56×10^{-7} m^3/s, then for the same efficiency for SO$_2$ may be obtained at flow-rate of 3 m/s and sprinkling intensity equal to 14×10^{-7} m^3/s. Nevertheless, the results of experiments performed in this scale were so promising that it has been decided to check whether the anion exchanger can be used as sorbent of nitrogen oxides in a pilot scale.
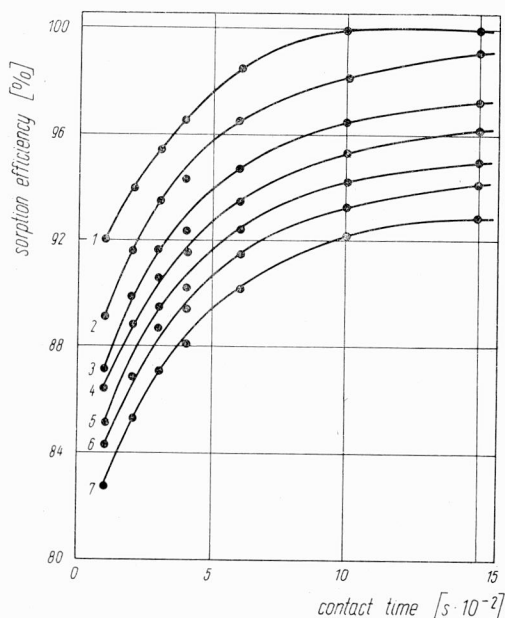

Fig. 2. Effectiveness of NO$_{3/2}$ sorption vs. contact time and sprinkling intensity

Rys. 2. Efektywność sorpcji NO$_{3/2}$ w zależności od czasu kontaktu i intensywności zraszania

$1 - q = 56.0 \times 10^{-7}$ m^3/s $2 - q = 28.0 \times 10^{-7}$ m^3/s, $3 - q = 14 \times 10^{-7}$ m^3/s $4 - q = 11.2 \times 10^{-7}$ m^3/s, $5 - q = 8.4 \times 10^{-7}$m^3/s, $6 - q = 5.4 \times 10^{-7}$m^3/s, $7 - q = 2.8 \times 10^{-7}$m^3/s

3.3. SORPTION OF HYDROGEN FLUORIDE

For these investigations laboratory apparatus had to be made from suitable materials, i. e. from polyethylene and teflon. An appropriate mixture of hydrogen fluoride and air has been achieved by passing the air through the cylinder containing a 90% hydrofluoric acid. The range of parameters assumed for the experiment is presented in table 1.
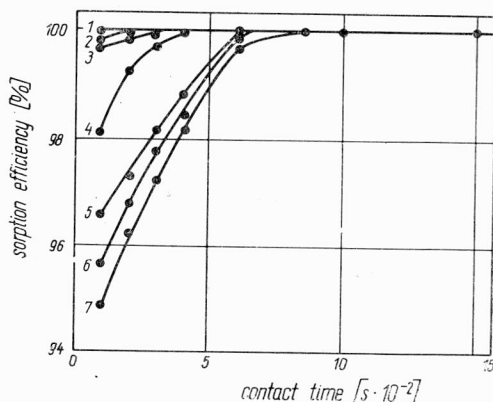

Fig. 3. Effectiveness of HF sorption vs. contact time and sprinkling intensity

Rys. 3. Efektywność sorpcji HF w zależności od czasu kontaktu i intensywności zraszania

$1 - q = 56.0 \times 10^{-7}$ m^3/s, $2 - q = 28.0 \times 10^{-7}$ m^3/s, $3 - q = 14.0 \times 10^{-7}$ m^3/s, $4 - q = 11.2 \times 10^{-7}$ m^3/s, $5 - q = 8.4 \times 10^{-7}$ m^3/s, $6 - q = 5.6 \times 10^{-7}$ m^3/s, $7 - q = 2.8 \times 10^{-7}$ m^3/s

The comparison of plots shown in figs 1, 2, 3 obtained under identical experimental conditions for the anion exchanger FFD allows to state the best sorption of HF, somewhat worse of SO_2 and the worst one in case of nitrogen oxides. Results of sorption of HF on this anion exchanger were checked in experimental system station while treating waste gases emitted by the plant producing hydrofluoric acid.

3.4. SORPTION OF HYDROGEN SULPHIDE AND CARBON DISULPHIDE

This series of experiments was intended to check the possibility of utilization of sorption properties of the anion exchanger FFD to remove hydrogen sulphide and carbon sulphide from gases emitted by the plant producing man-made fibres by viscose method.

The experiments was conducted within a broad range of variable parameters, as presented in table 1.

Under experimental conditions H_2S was fully removed from the gas treated. The influence of linear gas velocity on the efficiency of CS_2 sorption on the anion exchanger FFD is shown in fig. 4. From the relations presented it may be seen that the efficiency decrea-

Fig. 4. The effect of linear velocity of gas on the effectiveness sorption of CS_2 through 0.04 m layer of anion exchanger FFD at constant concentration of CS_2 in gas $c_0 = 0.19$ g/m^3 for various intensities sprinkling with a 5% solution of NaOH

Rys. 4. Wpływ prędkości liniowej gazu na efektywność sorpcji CS_2 przez 0.03 m warstwę anionitu FFD przy stałym stężeniu CS_2 w gazie ($c_0 = 0,19$ g/m^3) dla różnych intensywności zraszania 5% roztworem NOH

$1 - q_1 = 5.65 \times 10^{-7}$ m^3/s, $\quad 2 - q_2 = 4.24 \times 10^{-7}$ m^3/s, $3 - q_3 = 2.60 \times 10^{-7}$ m^3/s, $\quad 4 - q = 1.30 \times 10^{-7}$ m^3/s, $5 - q = 0.89 \times 10^{-7}$ m^3/s, $\quad 6 - q = 0.45 \times 10^{-7}$ m^3/s
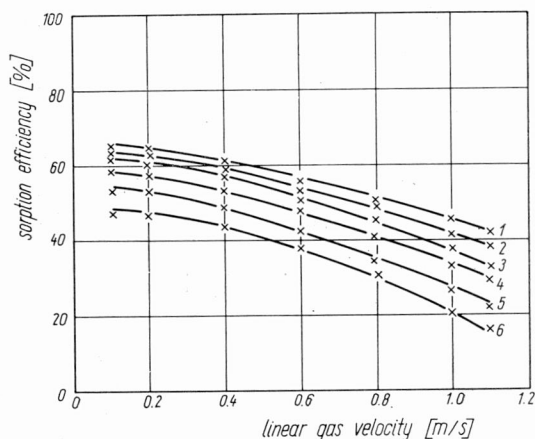
ses distinctly with the increasing linear velocity of gas. Starting with 0.4 m/s it has been observed that for lower sprinkling intensities this drop is greater. The shortening of gas contact time below 0.15 s distinctly decreases sorption capacity of the anion exchanger. From the comparison of results obtained in laboratory and pilot scales it follows that the increase of the scale does not cause the deterioration of basic process parameters.

4. UTILIZATION OF POST-SORPTION SOLUTIONS

Utilization of post-sorption solution should be investigated separately. Solution obtained from sorption (Na_2SO_3, $NaHSO_3$, $NaNO_2$, $NaNO_3$, NaF, Na_2S, $NaHS$ etc.) is utilized differently, depending on the solution regenerating the anion exchanger ($NaOH$, NH_4OH, KOH, Na_2CO_3).

Post-sorption solutions obtained from the sorption of sulphur dioxide on anion exchangers may be utilized in different ways:

a) by thermal decomposition with the recovery of SO_2 and NaOH. SO_2 is given back to the production of sulphuric acid and NaOH is used again in the sorption process,

b) by electrodialyse, according to the reaction

$$Na_2SO_3 \xrightarrow{H_2O} 2NaOH + SO_2 (25-50\% \text{ of volume})$$

SO_2 is given back to the production of sulphuric acid, and NaOH is used again in the sorption process,

c) by oxidation of sodium sulphite to sodium sulphate, and then by reaction with Ca $(OH)_2$ — according to reaction

$$Na_2SO_3 \xrightarrow{O_2} Na_2SO_4 \xrightarrow{Ca(OH)_2} CaSO_4 + 2NaOH$$
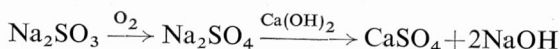
d) by using it as absorption solution in first stage of SO_2 removal from waste gases.

Post-sorption solution obtained as a result of sorption of nitrogen oxides on anion exchangers can be directly utilized as liquid fertilizer, e. g. $NH_4NO_2 + NH_4NO_3$ or utilized by means of electrodialysis. Decomposition of 10% of sodium nitrate yields nitrogen oxides ($NO_2 + NO$) and NaOH. This process, while conducted on full-scale, would enable the circulation of NaOH and introduction of nitrogen oxides, 25–30 of volume to the production system. The application of such a system would decrease the consumption of nitric acid from 18 kg per 1000 kg of H_2SO_4 to a maximum of 5.6 kg per 1000 kg of H_2SO_4.

Utilization of the post-sorption solutions obtained due to sorption of HF from waste gases in conducted according to the reaction

$$2NaF + Ca(OH)_2 \rightarrow CaF_2\downarrow + 2NaOH.$$
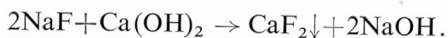
In this way one obtains the valuable artificial fluorite (70–90% of CaF_2) which finds various applications in the industry, and NaOH which is given back to sorption process. On the other hand, post-sorption solutions obtained due to sorption of H_2S and CS_2 from waste gases can be utilized in the technology of viscose fibers production. The ways in which post-sorption solutions obtained in the sorption process of acid gases on anion exchangers are to be utilized depend primarily on technological and economical considerations.

CONCLUSIONS

The investigations of acid gases sorption on anion exchangers lead to the development of the technology of the waste gases purification. The technology allows to conduct the treatment of waste gases in identical equipment, which differ only in overall dimensions. The temperature of gas treatment should not exceed 333 K and the gases should be preliminary dedusted. The concentrations and kinds of hydroxides in the sprinkling solution

may be arbitrarily changed, and the solutions of carbonates may be also used for sprinkling. Thus, the application of anion exchangers to industrial technology of waste gases purification consists, among others, in simplicity and economic efficiency of the process, and first of all in versatility of the method expressed by a high tolerance to the concentrations of acid impurities in the purified gas.

BADANIA NAD SORPCJĄ GAZÓW KWAŚNYCH NA ANIONITACH

W pracy dokonano analizy danych literaturowych dotyczących sorpcji gazów kwaśnych na anionitach. Przedstawiono wyniki badań nad sorpcją dwutlenku siarki, tlenków azotu, fluorowodoru, siarkowodoru i dwusiarczku węgla na anionitach. Opracowano podstawowe parametry procesu sorpcji. Stwierdzono· że istnieje możliwość zastosowania anionitów o zwiększonej granulacji w technice oczyszczania gazów odlotowych.

ZUR SORPTION SAURER ABGASE MIT HILFE VON ANIONENAUSTAUSCHERN

Die Verfasser legen ein Literaturstudium über Sorption von sauren Abgasen mittels Anionenaustauschern vor. Anschließend werden Sorptionsergebnisse von Schwefeldioxyd, Stickoxyde, Fluorwasserstoff und von Kohlenstoffdisulfid dargelegt. Versuche bestätigten die Annahme, daß eine Reinigung solcher Abgase mittels grobkörnigen Anionenaustauschern technisch durchaus möglich ist.

ИССЛЕДОВАНИЕ СОРБЦИИ КИСЛЫХ ГАЗОВ НА АНИОНИТАХ

В работе проведен анализ последних литературных данных по сорбции куслых газов на анионитах. Представлены результаты исследования сорбции двуокиси серы, окислов азота, фтороводорода, сероводорода и сероуглерода на анионитах. Определёны основные параметры процесса сорбции. Показана возможность применения анионитов повышенной грануляции в технологии очистки отходных газов.

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