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## STUDIES ON SORPTION OF MERCAPTANS VAPOURS ON ANION EXCHANGER RESINS

The efficiency of sorption of mercaptans vapours by the selected ion exchangers has been studied, and the results obtained presented. The laboratory studies allowed to state that of the selected, strongly alkaline anion exchangers the best effects can be obtained by applying anion resins of the Lewatit MP-500 and Wofatit SBW types. The pilot scale studies performed with Wofatit SBW (this resin being more available in Poland) have shown that in order to obtain a satisfactory from the atmosphere protection point of view level of deodorization of gases from digesters in the sulphate cellulose plants the layer of this resin bed must amount to at least 30 mm and should be sprinkled with 4% solution of NaOH, (about 8g NaOH/m<sup>2</sup>s). Under these conditions the efficiency of treatment may be kept over 90%, even if the flow velocity of the gases treated increases up to 0.3 m/s.

### 1. INTRODUCTION

Of the methods used for separation of mixtures ion exchangers are becoming more and more popular. Conventional use of ion exchangers is based on filtration of liquids through an ion exchanging bed, which results in ions transfer between the liquid and the bed. Taking into consideration a high efficiency of the process and a rather simple mechanism by which some ions are educed from solution to the ion exchanger media a tentative application of this process to purification of air containing odor-forming mercaptan vapours is presented.

### 2. LABORATORY STUDIES

Based on studies by WINTERS and KUNIN [6], KUNIN and MC GARVEY [3], LINDSAY and D'AMICO [4] and YORSTONE [7] it may be assumed that, slightly acidic in nature, mercaptan vapours would be best removed from air by strongly alkaline anionic exchangers, where the following exchange reaction will take place:



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where:

$R_1-A$  — partially dissociated multimolecular base (anion exchanger with an  $A^-$  anion)

$R_2-S^-$  — alkylsulphide anion undergoing exchange.

As for the present there are no commercially available ion exchangers, manufactured especially for the purpose of separation of the gas mixtures, the attempt has been made to base the investigations described in this paper on anion exchangers, manufactured for the separation of liquid mixtures.

The Zerolit S-1095 selected from the anion exchanging media manufactured by the Permutit Co. Ltd should, according to GOSTOMCZYK [1], evidence sufficiently high sorption efficiency for vapours of substances acidic in nature.

Beside those anion exchangers other media were also used for some comparative studies. These included anion exchanging resins manufactured by Farbenfabriken Bayer AG Leverkusen (GFR) under trade names Lewatit MP600; and a Wofatit SBW resin manufactured by Chemie Kombinat Bitterfeld (GDR).

Laboratory equipment used in this study is presented in Fig. 1.

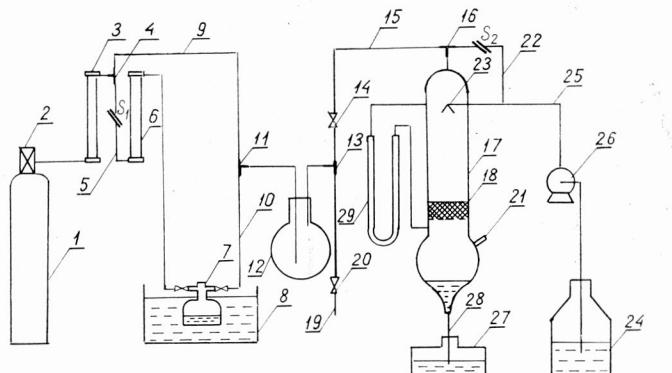


Fig. 1. Scheme of laboratory equipment for removal of mercaptan vapours through ion resins  
1 — compressed air cylinder; 2, 14, 20 — valves; 3, 6 — rotameters; 4, 11, 13, 16 — tees; 5, 9, 10, 15, 22, 25, 28 — connectors; 7 — mercaptan container; 8 — thermostat; 12 — mixer; 17 — ion exchange column; 18 — ion exchange bed; 19, 21 — sampling ports; 23 — sprinkling nozzle; 24, 27 — tanks; 26 — pump; 29 — manometer;  $S_1$ ,  $S_2$  — clamps

Rys. 1. Schemat aparatury laboratoryjnej do oczyszczania powietrza z par merkaptanów za pomocą wymieniaczy jonowych

1 — butla ze sprężonym powietrzem; 2, 14, 20 — zawory; 3, 6 — rotometry; 4, 11, 13, 16 — trójniki; 5, 9, 10, 15, 22, 25, 28 — przewody łączące; 7 — pluczka z badanymi merkaptanami; 8 — termostat; 12 — mieszalnik; 17 — kolumna jonowymienia; 18 — złożo anionitu; 19, 21 — króćce do poboru próbek; 23 — dysza zraszająca; 24, 27 — zbiorniki; 26 — pompa; 29 — manometr;  $S_1$ ,  $S_2$  — ścisakacze

Mercaptan content in the air samples was determined by means of „Picos” electrochemical analyser manufactured by Hartman-Braun A. G.

By changing the mass and type of anion exchange media in the column, as well as air flow rate and varying mercaptan vapours content, and using various methods of bed treatment (activating the anion exchanger with NaOH solution prior to the column input

without further spraying in the column, or similarly by initial activating but connected with further spraying of the bed with regeneration 0–10% solutions of NaOH) the author could determine the effects of these parameters on the direction of change of efficiency of sorption for the air polluting mercaptan vapours, and at the same time on the efficiency of deodorization of air.

The results of the studies are presented in Figures 2 and 3.

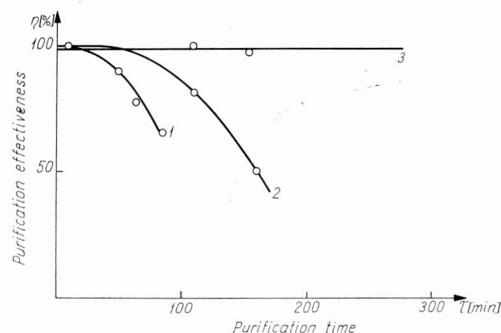


Fig. 2. Effectiveness of the ethyl mercaptan vapours removal ( $0.93 \cdot 10^{-4}$  g/s) as a function of both the time of the puryfication process (performed by using a 0.03 m thick (10g) S-1095 Zerolit layer) and of the kind of sprinkling (at a constant velocity of the supplied air 8.7 cm/s)

1 –  $\text{H}_2\text{O}$  spray  $0.75 \text{ dm}^3/\text{h}$ ; 2 – without spraying; 3 – 5% NaOH spray  $0.75 \text{ dm}^3/\text{h}$

Rys. 2. Zależność skuteczności oczyszczania powietrza z par merkaptanu etylowego ( $0.93 \cdot 10^{-4}$  g/s) od czasu trwania procesu oczyszczania na 0,03 m (10 g) warstwie Zerolitu S-1095 oraz od rodzaju zraszania przy stałej prędkości doprowadzanego powietrza 8,7 cm/s

1 – zraszanie  $\text{H}_2\text{O}$ ,  $0.75 \text{ dm}^3/\text{h}$ ; 2 – bez zraszania; 3 – zraszanie 5% NaOH,  $0.75 \text{ dm}^3/\text{h}$

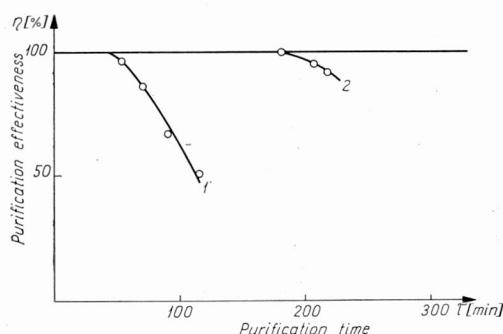


Fig. 3. Effectiveness of the ethyl mercaptan vapours removal ( $0.93 \cdot 10^{-4}$  g/s) as a function of both the time of the purification process (performed by using a 0.06 m thick (20 g) S-1095 Zerolit layer) and of the kind of sprinkling (at a constant velocity of the supplied air 8.7 cm/s)

1 –  $\text{H}_2\text{O}$  spray  $0.75 \text{ dm}^3/\text{h}$ ; 2 – without spraying; 3 – 5% NaOH spray  $0.75 \text{ dm}^3/\text{h}$

Rys. 3. Zależność skuteczności oczyszczania powietrza z par merkaptanu etylowego ( $0.93 \cdot 10^{-4}$  g/s) od czasu trwania procesu oczyszczania na 0,06 m (20 g) warstwie Zerolitu S-1095 oraz od rodzaju zraszania, przy stałej prędkości doprowadzanego powietrza 8,7 cm/s

1 – zraszanie  $\text{H}_2\text{O}$ ,  $0.75 \text{ dm}^3/\text{h}$ ; 2 – bez zraszania; 3 – zraszanie 5% NaOH,  $0.75 \text{ dm}^3/\text{h}$

It follows from these relations that the highest purification efficiencies were attained when the anion exchanging bed was sprinkled with an aqueous solution of NaOH. It must be admitted that though correspondingly high removal efficiencies were obtained in the samples without sprinkling — where the bed was activated only initially (transformed into the OH form before the initiation of the air treatment tests), nevertheless, this condition has occurred only in the initial, appropriately shorter stage of the treatment process. The air purification efficiencies during bed spraying with pure water were relatively the smallest ones, and decreased rapidly; this probably resulted due to negligible solubility of mercaptans in water.

The importance of ion exchange between mercaptan vapours and anion exchanging bed in the air treatment processes is evidenced by relationship in Fig. 4.

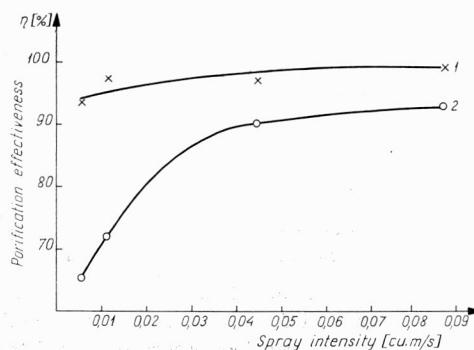


Fig. 4. Efficiencies of a S-1095 Zerolit layer (0.016 m thick), and of analogical layer of polystyrene beads (of the diameter of 2.3–3.4 mm) sprinkled with 5% NaOH solution, at a constant emission of ethyl mercaptan of  $8 \cdot 10^{-5}$  g/s and constant velocity of the supplied air of 8.7 cm/s

1 — Zerolit S-1095; 2 — polystyrene beads

Rys. 4. Porównanie skuteczności oczyszczania 0,016 m warstwy Zerolitu S-1095 zraszanego 5-procentowym roztworem NaOH ze skutecznością oczyszczania analogicznej warstwy perełek polistirenowych o średnicy 2,3–3,4 mm, przy stałej emisji par merkaptanu etylowego  $8 \cdot 10^{-5}$  g/s i stałej prędkości doprowadzanego powietrza 8,7 cm/s

1 — Zerolit S-1095; 2 — perełki polistirenowe

While comparing the change in the air purification efficiencies for methyl mercaptan vapours, depending on the spraying intensity on the Zerolite S-1095 layer and for the analogical layer made of polystyrene beads, it could be stated that the ion exchange — being the only distinguishing factor in the studied media — allowed to obtain much higher purification efficiencies with respect to the efficiency attained in the tests conducted without the use of ion exchangers.

While analyzing the relations presented in Fig. 5 it may be noticed that beside the sprinkling intensity, the thickness (mass of media) is another parameter significantly affecting the resulting treatment efficiency of the anion exchanging layer. For instance, in

order to obtain 99% removal efficiency by means of air purification on 5 g of Zerolite S-1095 the sprinkling intensity should amount to approx.  $0.09 \text{ cm}^3/\text{s}$ , while the doubling of the bed mass allows to reduce this parameter to approx.  $0.06 \text{ cm}^3/\text{s}$ . An increase of the media mass by a factor of four allows to decrease sprinkling intensity down to  $0.01 \text{ cm}^3/\text{s}$ .

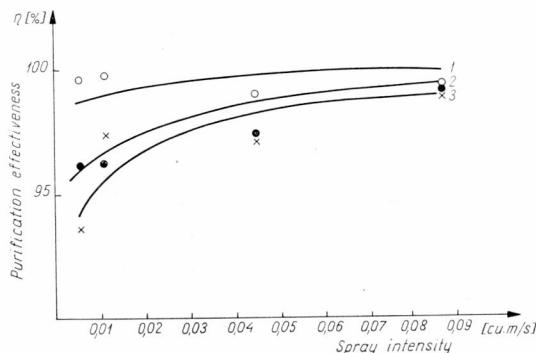


Fig. 5. Effect of the S-1095 Zerolit amount on the relative removal percentage at a constant emission of ethyl mercaptan ( $8 \cdot 10^{-5} \text{ g/s}$ ) and a constant velocity of gases  $8.7 \text{ cm/s}$

1 – 20 g; 2 – 10 g; 3 – 5 g

Rys. 5. Wpływ ilości Zerolitu S-1095 na skuteczność oczyszczania powietrza przy stałej emisji par merkaptanu etylowego  $8 \cdot 10^{-5} \text{ g/s}$  i stałej prędkości przepływu gazu  $8.7 \text{ cm/s}$

1 – 20 g Zerolitu S-1095; 2 – 10 g Zerolitu S-1095 3 – 5 g Zerolitu S-1095

As the purification efficiency is also conditioned by the parameters characterizing the air under purification, Figures 6 and 7 demonstrate the effects of quantity of mercaptans contained in air, and of air flow rate on the results obtained.

Generalizing the relations presented one may find that both the increase of air rate and the increase in the quantity of mercaptan vapours in the air result in a non-linear decrease of purification efficiency.

As in the studied system: mercaptan-anion exchanger, the basic condition for the anion exchange to take place is the dissociation of the air polluting substance, it seems advisable to determine the most appropriate conditions for its transfer to the liquid electrolyte.

Analysis of the relationships in Fig. 8 evidences that an increase in the concentration of the NaOH solution above 5% has no practical effect on the quantity of removed mercaptans. Hence, the factory recommended 5% NaOH solution may also be regarded as a sufficiently effective liquid media in the air purification process consisting of mercaptans removal on the sprinkled Zerolite S-1095 media. It must be mentioned, however, that some increase of the solution concentration above the 5%, though it has no effect on purification efficiency it, however, may exert a significant effect on the utilization of the post-sorption solutions

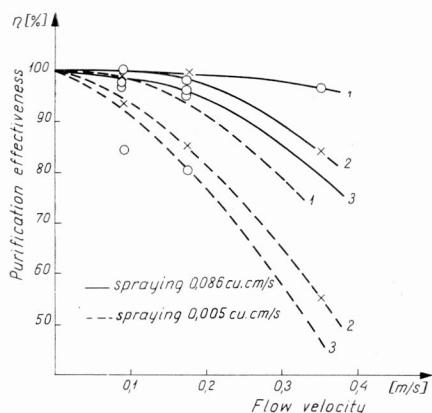


Fig. 6. Effect of linear gas velocity on the effectiveness of its purification for the S-1095 Zerolit layer of a thickness of 0.016 m at a constant emission of ethyl mercaptan ( $8 \cdot 10^{-5}$  g/s) and varying 5% NaOH sprinkling intensities

1 —  $0.086 \text{ cm}^3/\text{s}$ ; 2 —  $0.044 \text{ cm}^3/\text{s}$ ; 3 —  $0.011 \text{ cm}^3/\text{s}$   
4 —  $0.005 \text{ cm}^3/\text{s}$

Rys. 6. Wpływ prędkości liniowej gazu na skuteczność jego oczyszczania przez 0,016 m warstwę Zerolitu S-1095 przy stałej emisji par merkaptanu etylowego  $8 \cdot 10^{-5}$  g/s, dla różnych zroszeń 5-procentowym roztworem NaOH

1 — natężenie zraszania  $0,086 \text{ cm}^3/\text{s}$ ; 2 — natężenie zraszania  $0,044 \text{ cm}^3/\text{s}$ ; 3 — natężenie zraszania  $0,011 \text{ cm}^3/\text{s}$ ; 4 — natężenie zraszania  $0,005 \text{ cm}^3/\text{s}$

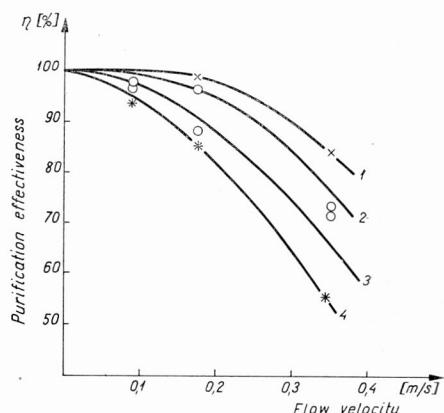


Fig. 7. Effect of varying emission rate of ethyl mercaptan on the effectiveness of gas purification for a 0.016 m thick (5g) S-1095 Zerolit layer sprinkled with 5% NaOH solution

1 —  $1.7 \cdot 10^{-5}$  g/s; 2 —  $8 \cdot 10^{-5}$  g/s; 3 —  $11 \cdot 10^{-5}$  g/s

Rys. 7. Wpływ emisji par merkaptanu etylowego na skuteczność oczyszczania gazu przez 0,016 m warstwę Zerolitu S-1095 zraszaną 5-procentowym roztworem NaOH

1 — emisja  $1,7 \cdot 10^{-5}$  g/s; 2 — emisja  $8 \cdot 10^{-5}$  g/s;  
3 — emisja  $11 \cdot 10^{-5}$  g/s

Taking into account the supplementary studies, illustrated in Figures 9 and 10, one must note that other strongly alkaline anion exchangers have proved to be applicable in the process of mercaptan vapours removal from the air.

From the figures presented above it may be inferred that the highest purification efficiency of air polluted with the ethyl mercaptan vapours has been stated for the Lewatit MP-500 and Wofatit SBW, and slightly lower for the Lewatit MP-600. The efficiency of Zerolit S-1095 was the lowest one but not considerably different from the remaining anion exchangers.

At the same time, it follows from Fig. 11 that the efficiency of air treatment through the layer of the most effective Lewatit MP-500 depends only slightly on the kind of collected mercaptans. It seems that such a small difference in removal efficiency of neighbouring homologues of the aliphatic mercaptan series may primarily result from the fact that at the constant emission of the mercaptans ( $8 \times 10^{-5}$  g/s) the respective quantities of the

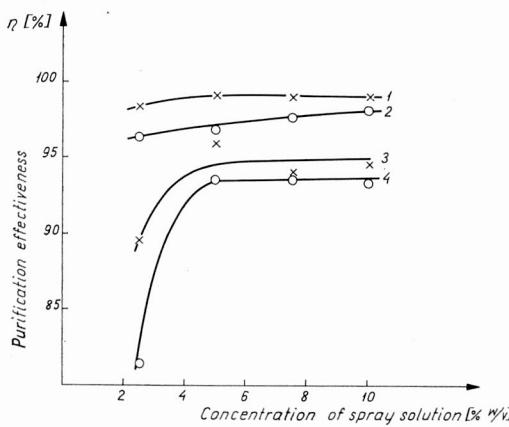


Fig. 8. Effect of NaOH concentration in spraying solution on the ethyl mercaptan vapours removal for a 0.0016 thick (5 g) S-1095 Zerolit layer at a constant emission of ethyl mercaptan ( $8 \cdot 10^{-5}$ ) and a constant velocity of gases (8.7 cm/s); NaOH spray expressed in  $\text{cm}^3$

1 — 0.086; 2 — 0.044; 3 — 0.011; 4 — 0.005

Rys. 8. Wpływ stężenia roztworu zraszającego na skuteczność oczyszczania powietrza z par merkaptanu etylowego przepuszczanego przez 0,016 m (5 g) warstwę Zerolitu S-1095 przy stałej emisji merkaptanu ( $8 \cdot 10^{-5}$  g/s) i prędkości przepływu 8,7 cm/s

1 — zraszanie NaOH 0,086  $\text{cm}^3/\text{s}$ ; 2 — zraszanie NaOH 0,044  $\text{cm}^3/\text{s}$ ; 3 — zraszanie NaOH 0,011  $\text{cm}^3/\text{s}$ ; 4 — zraszanie NaOH 0,005  $\text{cm}^3/\text{s}$

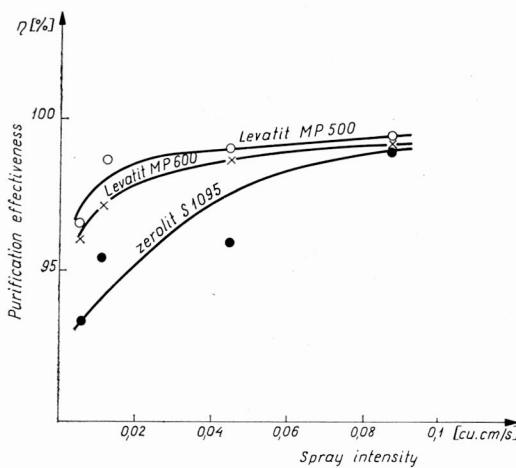


Fig. 9. Relation between the removal of ethyl mercaptan vapours and sprinkling with 5% NaOH solution for selected anion exchangers at a constant mercaptan emission  $8 \cdot 10^{-5}$  g/s and a constant gas velocity 8.7 cm/s

Rys. 9. Zależność skuteczności oczyszczania powietrza z par merkaptanu etylowego od natężenia zraszania 5% roztworem NaOH dla wybranych anionitów przy stałej emisji merkaptanu  $8 \cdot 10^{-5}$  g/s i stałej prędkości przepływu gazów 8,7 cm/s

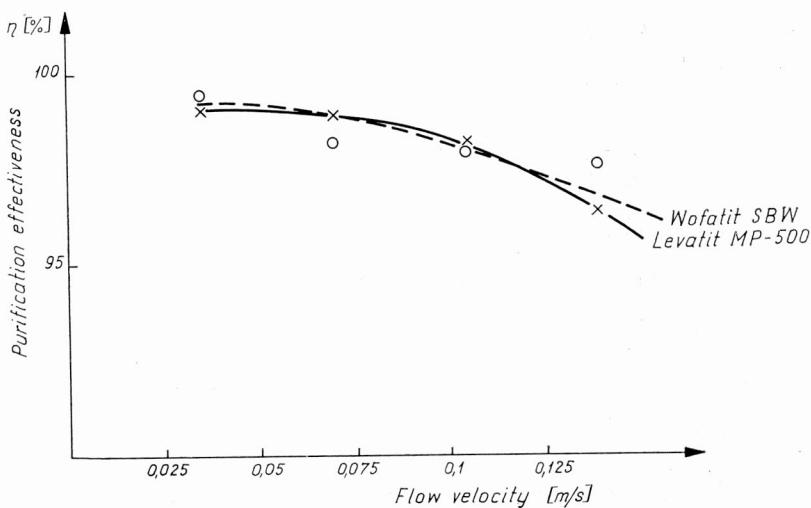


Fig. 10. Comparison of ethyl mercaptan removals on 0.035 m layer of Lewatit MP-500 and Wofatit SBW, as a function of linear gas velocity at constant emission  $= 1.7 \cdot 10^{-5}$  g/s and at 5% NaOH spray of 0.02  $\text{dm}^3/\text{h}$

Rys. 10. Porównanie skuteczności oczyszczania powietrza z par merkaptanu etylowego przez 0,035 m warstwę Lewatitu MP-500 i Wofatitu SBW w funkcji prędkości liniowej oczyszczonego gazu, przy stałej emisji merkaptanu  $1.7 \cdot 10^{-5}$  g/s i stałym natężeniu zraszania 5% roztworem NaOH  $- 0.02 \text{ dm}^3/\text{h}$

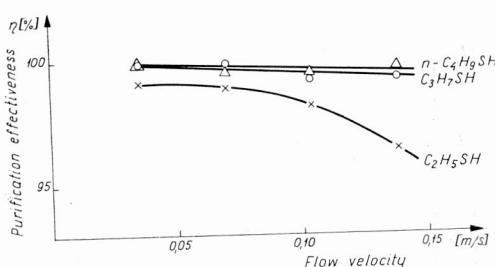


Fig. 11. Effect of types of mercaptan on the effectiveness of air purification on a 0.035 m layer of the MP-500 Lewatit sprinkled with 5% NaOH solution ( $0.02 \text{ dm}^3/\text{h}$ ) at a constant mercaptan emission equal to  $1.7 \cdot 10^{-5}$  g/s)

Rys. 11. Wpływ rodzaju merkaptanu na skuteczność oczyszczania powietrza przez 0,035 m warstwę Lewatitu MP-500 zraszaną 5% roztworem NaOH w ilości  $0.02 \text{ dm}^3/\text{h}$ , przy stałej emisji par merkaptanów  $1.7 \cdot 10^{-5}$  g/s

propyl mercaptan and butyl mercaptan moles flowing in the unit of time are only 0.82, and 0.78 of the quantity of introduced ethyl mercaptan moles.

Evaluating the results of the laboratory studies one may conclude that the ion exchange processes between the anion bed and dissociated mercaptans polluting the air may yield high purification efficiencies, close to 100% (which means a practically complete

deodorization of the atmosphere), provided, however, that the technical conditions, i.e. proper selection of the NaOH sprinkling intensity on the bed corresponding to the quantity of gas, are fulfilled.

### 3. PILOT SCALE STUDIES

From the literature data [2] it may be seen that, so far, there are no adequately precise equations which would describe the absorption processes accompanied with chemical reactions. Although some attempts have been made to generalize these problems theoretically, nevertheless, in design of a full-scale installation the results of laboratory tests are usually not applied directly, some additional tests being performed in pilot-scale plants. This procedure allows to increase the scale of the technological parameters of the process proposed, as well as of the constructional lay-out of the treatment equipment.

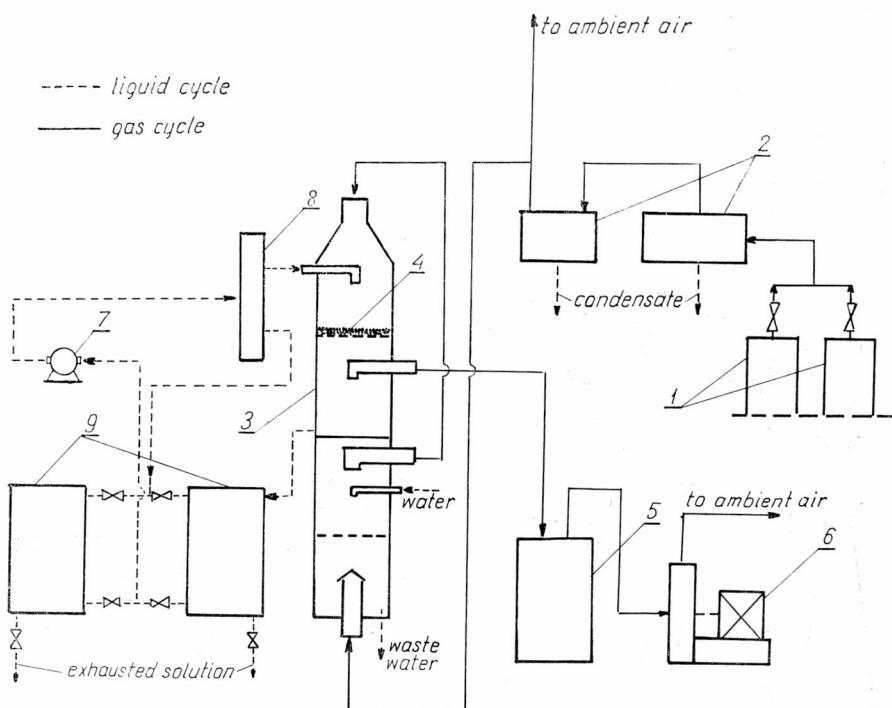


Fig. 12. Pilot plant layout

1 — digesters; 2 — condensers; 3 — sorption column; 4 — anion exchanger bed; 5 — drop separator; 6 — fan; 7 — pump; 8 — valves; 9 — tanks

Rys. 12. Schemat doświadczalnej instalacji ułamkowo-technicznej

1 — warniki; 2 — skraplacze; 3 — kolumna sorpcyjna; 4 — złożo anionitu; 5 — odkraplacz; 6 — wentylator; 7 — pompa; 8 — bateria zaworów; 9 — zbiorniki

Taking into account the above remarks this paper presents the studies on treatment of effluent gases from the „Chemitex-Celwiskoza”, Kraft Pulp Mill at Jelenia Góra. The manufacturing process has been studied earlier [5], and because of the sulphate method applied, this plant is considered as a typical emission source of mercaptan vapours and their derivatives.

As follows from the lay-out presented in Fig. 12, treated gases collected from the cellulose digesters (1), after passing through the cooling units (2) are directed to the lower part of column (3), where due to the counter-current water irrigation the gases are partly washed-out of soluble compounds. Subsequently the gases containing primarily the vapours of mercaptans poorly soluble in water are directed to the upper part of column (3), where the basic ion exchange process takes place on the fixed bed (4) of the Wofatit SBW anion exchanger, sprinkled with an aqueous NaOH solution. In order to attain a better stability of bed, and thus the improvement of the column working conditions, the treated effluent

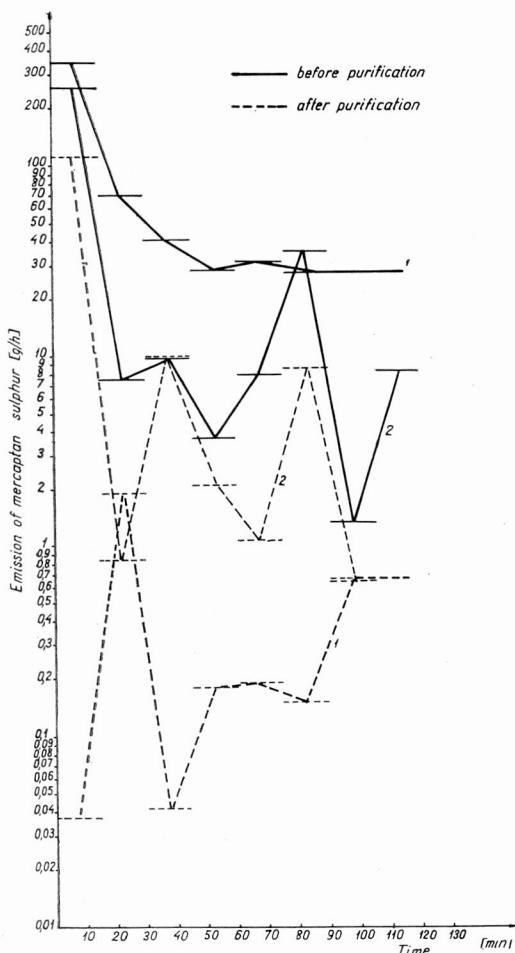


Fig. 13. Comparison of mercaptan sulphur content in gases (from pressure reduction cycles in digesters) before and after being let through 30 mm Wofatit SBW bed, sprayed with 6% NaOH solution at  $1.55 \cdot 10^{-4} \text{ m}^3/\text{m}^2\text{s}$  for  
1 — normal pressure reduction process; 2 — perturbed process

Rys. 13. Porównanie ilości siarki merkaptanowej zawartej w gazach odprowadzonych z warunków podczas redukcji ciśnienia przed i po przepuszczeniu ich z prędkością  $0.26 \text{ m/s}$  przez 30 mm złożenie Wofatitu SBW zraszane 6% roztworem NaOH w ilości  $1.55 \cdot 10^{-4} \text{ m}^3/\text{m}^2\text{s}$  dla

1 — normalnego przebiegu procesu redukcji ciśnienia;  
2 — przebiegu zakłóconego

gases and the irrigation solution are introduced co-currently. The treated gases, after passing through the anion layer, were directed to the drop separator (5) — where, after passing through the MWW-14 type fan (6) connected at the suction side, are discharged to atmosphere.

An S-14b special pump (7) was used to pump the liquid trickling over the anion exchanging bed. A set of multi-channel valves (8) made it possible to change the amounts of spraying liquid introduced to the column, and a simultaneous partial recirculation of the liquid to the tanks (9), the latter being also fed with the effluent from the upper part of the column.

Quantitative determination of mercaptan vapours concentrations in gas samples, collected in 15 min. periods before and after the anion exchanging bed, were made with the automatic mercaptometer OH-403/1 manufactured by Electrochemical Instruments "Radelkis" — Budapest, Hungary.

Taking into account the fact that the analyzer is designed for measuring the mercaptan concentrations in the petroleum fractions, it was necessary to transfer the sulphur compounds from the tested gases into the selected petroleum solvents. In this case pure n-hexane was used, since it proved to be non-reactive with respect to the absorbed mercaptan vapours which were selected previously.

Basic difficulties accompanying the studies were connected with instability of the emission source of investigated gases.

From the observations it follows, that in case of a proper performance of the technological units in the digester department, the gradual decrease of amount of mercaptans evolving during the average 120 minutes period of pressure reduction in digesters is a na-

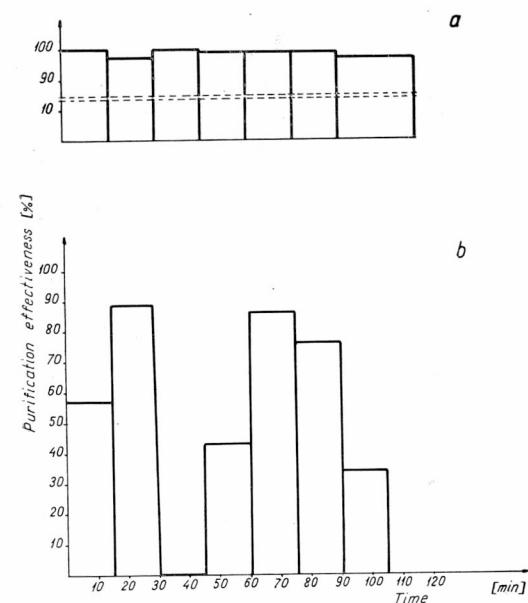


Fig. 14. Effectiveness of mercaptan vapours removal from discharge gases (formed during pressure reduction cycles in digesters) after being let through 30 mm Wofatit SBW bed (velocity of flow 0.26 m/s) sprayed with 6% NaOH solution at  $1.55 \cdot 10^{-4} \text{ m}^3/\text{m}^2\text{s}$ , for a) normal pressure reduction process, b) perturbed process

Rys. 14. Skuteczność oczyszczania z par merkaptanów gazów odprowadzanych z warników podczas redukcji ciśnienia przy przepuszczaniu ich z prędkością 0,26 m/s przez 30 mm warstwę Wofatitu SBW, zraszaną 6% roztworem NaOH w ilości  $1,55 \cdot 10^{-4} \text{ m}^3/\text{m}^2\text{s}$  dla a) normalnie przebiegającego odprowadzenia gazów, b) odprowadzania gazów przebiegającego z zakłóceniami

tural phenomenon. As follows from Figures 13 and 14, in determining the variability of attained purification efficiencies of mercaptans collected on the Wofatit SBW media sprinkled with an aqueous solution of NaOH, this phenomenon is much weaker than in situation, where — due to the improper work of some of the technological units (condensers, heat exchangers, etc.) — the treated effluent gases contain terpine and resin soap vapours, poisoning rapidly the ion exchanger.

Taking account of these comments, further studies were conducted in the period of

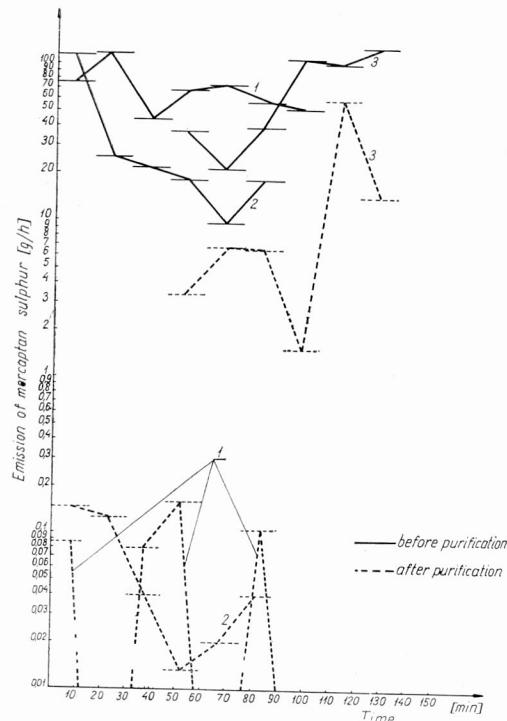


Fig. 15. Comparison of mercaptan sulphur content in gases from pressure reduction cycles in digesters, before and after being let through Wofatit SBW bed (velocity of flow 0.17 m/s), sprinkled with 6% NaOH solution at  $1.55 \cdot 10^{-4}$  m<sup>3</sup>/m<sup>2</sup>s, for the bed thickness

1 — 60 mm; 2 — 30 mm; 3 — 18 mm

Rys. 15. Porównanie ilości siarki merkaptanowej zawartej w gazach odprowadzanych z warników podczas redukcji ciśnienia przed i po przepuszczeniu ich z prędkością 0,17 m/s przez złożo Wofatitu SBW, zraszane 6% roztworem NaOH w ilości  $1.55 \cdot 10^{-4}$  m<sup>3</sup>/m<sup>2</sup>s, o grubości

1 — 60 mm; 2 — 30 mm; 3 — 18 mm

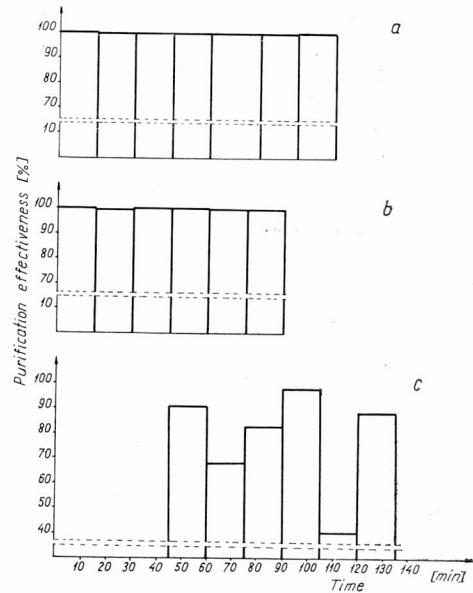


Fig. 16. Skuteczność oczyszczania z par merkaptanów gazów odprowadzanych z warników podczas redukcji ciśnienia przy przepuszczeniu ich z prędkością 0,26 m/s przez złożo Wofatitu SBW, zraszane 6% roztworem NaOH w ilości  $1.55 \cdot 10^{-4}$  m<sup>3</sup>/m<sup>2</sup>s, o grubości

a) 60 mm; b) 30 mm; c) 18 mm

Rys. 16. Skuteczność oczyszczania z par merkaptanów gazów odprowadzanych z warników podczas redukcji ciśnienia przy przepuszczeniu ich z prędkością 0,26 m/s przez złożo Wofatitu SBW, zraszane 6% roztworem NaOH w ilości  $1.55 \cdot 10^{-4}$  m<sup>3</sup>/m<sup>2</sup>s, o grubości

a) 60 mm; b) 30 mm; c) 18 mm

a proper performance of all technological units through which effluent gases have passed; results are presented in Figures 15–20.

It follows from the presented relations that within the range studied, even for the lowest value of effluent gases flow rate ( $w = 0.174 \text{ m/s}$ ) corresponding to the longest

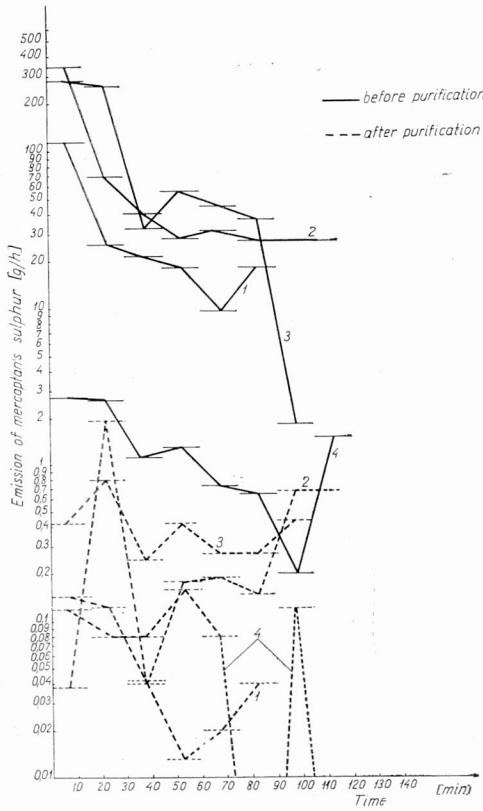


Fig. 17. Comparision of mercaptan sulphur content in gases from pressure reduction cycles in digesters, before and after being let through 30 mm Wofatit SBW bed, sprinkled with 6% NaOH solution at  $1.55 \cdot 10^{-4} \text{ m}^3/\text{m}^2\text{s}$ , for the following flow velocity of gases

1 —  $0.174 \text{ m/s}$ ; 2 —  $0.26 \text{ m/s}$ ; 3 —  $0.305 \text{ m/s}$ ; 4 —  $0.35 \text{ m/s}$

Rys. 17. Porównanie ilości siarki merkaptanowej zawartej w gazach odprowadzanych z warników podczas redukcji ciśnienia przed przepuszczeniem i po przepuszczeniu ich przez 30 mm warstwę Wofatitu SBW zraszaną 6% roztworem NaOH w ilości  $1.55 \cdot 10^{-4} \text{ m}^3/\text{m}^2\text{s}$  dla założonych prędkości przepływu gazów

1 —  $0.174 \text{ m/s}$ ; 2 —  $0.26 \text{ m/s}$ ; 3 —  $0.305 \text{ m/s}$ ; 4 —  $0.35 \text{ m/s}$

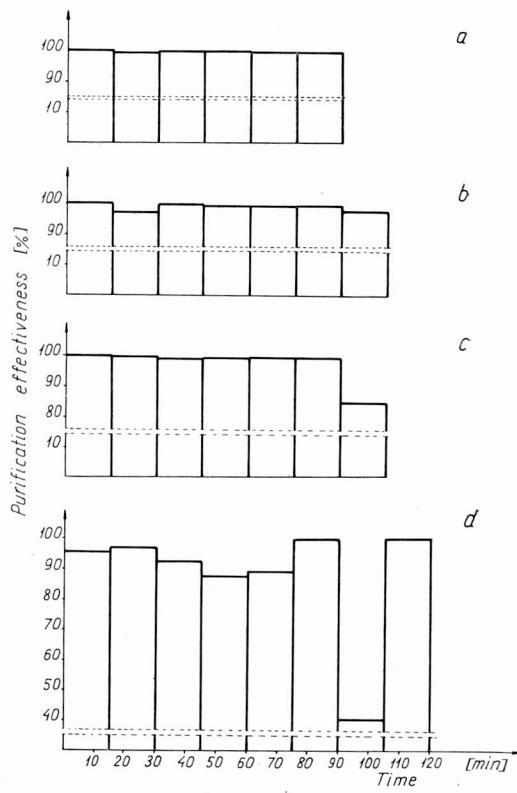


Fig. 18. Effectiveness of mercaptan vapours removal from discharge gases formed during pressure reduction cycles in digesters, after being let through 30 mm Wofatit SBW bed, sprinkled with 6% NaOH solution at  $1.55 \cdot 10^{-4} \text{ m}^3/\text{m}^2\text{s}$ , for the following flow velocity of gases

a)  $0.174 \text{ m/s}$ ; b)  $0.26 \text{ m/s}$ ; c)  $0.305 \text{ m/s}$ ; d)  $0.35 \text{ m/s}$

Rys. 18. Skuteczność oczyszczania z par merkaptanów gazów odprowadzanych z warników podczas redukcji ciśnienia po przepuszczeniu ich przez 30 mm warstwę Wofatitu SBW zraszaną 6% roztworem NaOH w ilości  $1.55 \cdot 10^{-4} \text{ m}^3/\text{m}^2\text{s}$  dla założonych prędkości przepływu gazów

a)  $0.174 \text{ m/s}$ ; b)  $0.26 \text{ m/s}$ ; c)  $0.305 \text{ m/s}$ ; d)  $0.35 \text{ m/s}$

contact time of mercaptan molecules with the Wofatit SBW bed, a decrease of the bed depth below 30 mm reduces significantly the purification efficiencies attained. The use, however, of bed with the depth of at least 30 mm, and similar sprinkling conditions allow to obtain purification efficiencies above 89% during the whole pressure reduction cycle in the digesters.

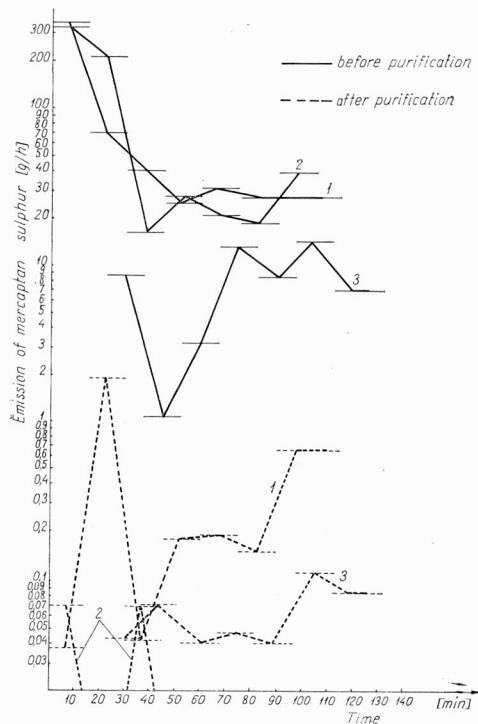


Fig. 19. Comparison of mercaptan sulphur content in gases from pressure reduction cycles in digesters, before and after being let through 30 mm Wofatit SBW bed (velocity of flow 0.26 m/s), sprinkled with NaOH solution (at the constant pure NaOH mass flowing to the bed — 1000 g/h) for the following concentrations

1 — 6%; 2 — 4%; 3 — 2%:

Rys. 19. Porównanie ilości siarki merkaptanowej zawartej w gazach odprowadzanych z warników podczas redukcji ciśnienia przed przepuszczeniem i po przepuszczeniu ich z prędkością 0,26 m/s przez 30 mm warstwę Wofatitu SBW zraszaną roztworem NaOH, przy zachowaniu stałej ilości czystego NaOH dopływającego do złożą, wynoszącej 1000 g/h, o następujących natężeniach

1 — 6%; 2 — 4%; 3 — 2%:

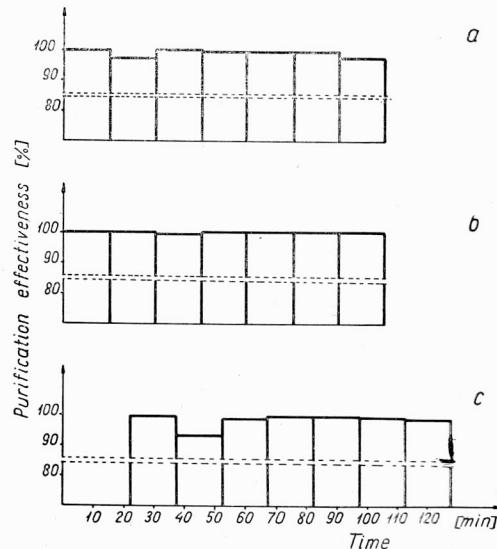


Fig. 20. Effectiveness of mercaptan vapours removal discharge gases formed during pressure reduction cycles in digesters after being let through 30 mm Wofatit SBW bed (velocity of flow 0.26 m/s) sprinkled with solution (at constant pure NaOH mass rate flowing to the bed 1000 g/h) for the following concentrations

a) 6%; b) 4%; c) 2%

Rys. 20. Zależność skuteczności oczyszczania z par merkaptanów gazów odprowadzanych z warników podczas redukcji ciśnienia, przepuszczanych z prędkością 0,26 m/s przez 30 mm warstwę Wofatitu CBW, od stężenia roztworu NaOH zraszającego anionit, przy zachowaniu stałej ilości czystego NaOH dopływającego do złożą, wynoszącej 1000 g/h

a) roztwór 6% NaOH; b) roztwór 4% NaOH; c) roztwór 2% NaOH

Moreover, at this seemingly lowest bed thickness of Wofatit SBW, still maintaining sufficient sorption of mercaptan vapours, it is possible to increase the velocity of flow of treated gases up to approx. 0.3 m/s, without risking the decrease of treatment efficiency below 90%.

A much characteristic of this method is the observed effect of NaOH concentration in the irrigation water on the attained treatment efficiency. Different NaOH concentrations in the water sprayed over the Wofatit SBW bed yielded different purification efficiencies, even in case of keeping constant the ratio of pure NaOH supplied to the unit bed area in unit of time. It was shown in these studies that for the assumed flow velocity (0.26 m/s) and the concentration (8.2 g NaOH/m<sup>2</sup>s) the lowest variations in the purification efficiencies were attained in the experiments with approx. 4% solution of NaOH in the sprinkling water.

## CONCLUSIONS

The studies on the treatment of effluent gases containing mercaptan vapours are aimed at the selection of more efficient sorption media.

The conducted laboratory studies have proved that among the selected strongly alkaline anion exchangers the best effects for sorption of mercaptan vapours were attained with the anion resins of Lewatit MP-500 and Wofatit SBW types.

The pilot-scale studies on Wofatit SBW, (which is more available in Poland) proved that in order to obtain a satisfactory level of deodorization of gases from digesters in the kraft pulp mills it is necessary to maintain the operating conditions, which were partially defined in this paper.

## BADANIA PROCESU SORPCJI PAR MERKAPTANÓW NA ANIONITACH

W pracy przedstawiono wyniki badań efektywności sorpcji par merkaptanów przez wybrane wymieniane jonowe. Na podstawie badań laboratoryjnych stwierdzono, że spośród wybranych silnie alkalicznych anionitów najbardziej przydatne do usuwania z powietrza odorotwórczych par merkaptanów są Lewatit MP-500 oraz Wofatit SBW. Badania ułamkowo-techniczne łatwiej dostępnego w Polsce Wofatitu SBW wykazały, że aby uzyskać zadowalający, z punktu widzenia ochrony atmosfery, stopień dezodoryzacji gazów odprowadzanych z warników celulozowni siarczanowych potrzeba co najmniej 30 milimetrowej warstwy złożą tego anionitu zraszanego 4% roztworem NaOH w ilości ok. 8 g (NaOH/m<sup>2</sup>s, przy czym istnieje możliwość utrzymywania skuteczności oczyszczania powyżej 90%, nawet przy wzroście prędkości przepływu oczyszczanych gazów do 0,3m/s.

## SORPTION VON MERKAPTANDÄMPFEN MITTELS ANIONENAUSTAUSCHERN

Im vorliegenden Bericht werden die Ergebnisse der Sorption von Merkaptandämpfen an ausgewählten Ionenaustauschern beschrieben. Laborteste liessen festzustellen, daß von verschiedenen, stark alkalischen Anionenaustauschern, die beste Abtrennwirkung von Merkaptan aus Luft-Merkaptan-Gemischen, Lewatit

MP-500 und Wofatit SBW hatten. Versuche im Pilot-Maßstab mit Wofatit SBW und Abluft aus Sulfatzellstoff-Kocher zeigten, daß zur Reinigung und Desodorisierung dieser Abgase, eine Mindestschicht von 30 mm der Ionenaustauschmasse notwendig ist. Die Sorptionsschicht wird im Gleichstrom mit 4% ger NaOH Lösung und einer Intensität von 8 g NaOH/m<sup>2</sup>s ständig regeneriert was sogar bei einer Gasgeschwindigkeit von 0,3 m/s einen Reinigungsgrad von mehr als 90% bewirkt.

#### ИССЛЕДОВАНИЕ ПРОЦЕССА СОРБЦИИ ПАРОВ МЕРКАПТАНОВ НА АНИОНИТАХ

В работе изложены результаты изучения эффективности сорбции паров меркаптанов избранными ионообменниками. На основе лабораторных исследований обнаружено, что среди избранных сильно щелочных анионитов самыми пригодными для удаления из воздуха запахообразовательных паров меркаптанов являются Леватит MP-500 и Вофатит SBW. Исследования легче в Польше доступного Вофатита SBW показали, что для получения удовлетворительной, с точки зрения очистки воздуха, степени дезодоризации газов, отводимых из котлов для крафт—целлюлозы, необходимо по крайней мере 30 мм слоя этого анионита, смачиваемого 4% раствором NaOH в количестве около 8 г NaOH/m<sup>2</sup>s, причем имеется возможность сохранения эффективности очистки более 90%, даже при повышении скорости течения очищаемых газов до 0,3 м/с.

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