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FORMALDEHYDE REMOVAL FROM AIR BY SUSPENSION OF CALCIUM CARBONATE IN AQUEOUS SOLUTION OF AMMONIUM NITRATE

Problem of air pollution has been characterized, a special attention being given to emission of formaldehyde from chip- and flax-board manufacturing plants. Experimental results have indicated that the suspension of calcium carbonate in aqueous solution of ammonium nitrate is an affective sorption medium for formaldehyde. The optimum conditions yielding the highest removals of this pollutant have been determined.

Air pollution has recently become a serious problem throughout the world. From the reports of the air pollution control staff in many countries it is noted that the quantity of waste products released into the atmosphere continues to increase rapidly. The concentrations of many air pollutants approach the allowable levels but in some instances this level has already been exceeded even by several times.

Formaldehyde, a toxic odour-forming substance, is amongst those air pollutants that have been neglected so far because of its almost unnoticeable presence in the natural environment [11]. Chip and flax-board manufacturing plants are typical examples of industrial formaldehyde emission sources in which formaldehyde is released from urea-formaldehyde resins used as binding agents. To prevent the staff from poisoning with formaldehyde, polluted ambient air is sucked off through fume extractors installed at various points within the plant. It is anticipated that the formaldehyde emitted in this way accounts for about 0.5% of the quantity of resins being used [14] or 0.33 kg of formaldehyde per 1 m^3 of chip- or flax-board produced.

Having these in mind (and considering the fact that the yearly volume of chipboards manufactured in Poland amounts to about 10^6 m^3 to give an annual formaldehyde emission of over 300 Mg), attempts have been made to develop a treatment method that would permit a complete separation of this pollutant before it enters the atmosphere.

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The conventional methods used for separation of formaldehyde are given in a number of references [2, 5–9]. These methods have one feature in common — they remove formaldehyde by sorption in the aqueous solutions of ammonia, ammonium carbonate or ammonium bicarbonate to yield hexamine which is practically harmless [10]. The methods in question, though highly efficient, have some shortcomings due to ammonia losses leading to recontamination of the atmosphere.

The investigations reported in this paper aimed at selecting such a sorbent that would enable a high removal efficiency and, at the same time, prevent recontamination from ammonia emissions. Considerations were focussed on the reaction described by Walker [13], in which hexamine is produced from formaldehyde and ammonium salts of strong acids (NH_4X). The first step yields methylamine according to the following equation:

$$NH_4X + CH_2O = NH_2CH_2OH \cdot HX = NH{=}CH_2(HX) + H_2O. \tag{1}$$

Methylamine is an intermediate product which leads to the formation of small amounts of hexamine, but the reaction itself is inhibited because the reaction medium is acidified. However, after addition of sodium hydroxide or even ammonia the reaction proceeds as follows:

$$6NH{=}CH_2(HX) + 4NaOH = C_6H_{12}N_4 + 2NH_4X + 4NaX + 4H_2O, \tag{2}$$

$$6NH{=}CH_2(HX) + 4NH_4OH = C_6H_{12}N_4 + 6NH_4X + 4H_2O. \tag{3}$$
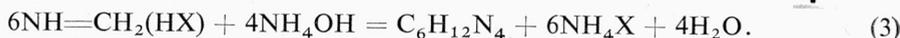
A German patent [3] indicates that these reactions can be used for the purification of flue gases. The method, however, has disadvantageous effects, i.e. a considerable escape of ammonia or decrease the sorption efficiency depending whether overdose or underdose of the neutralizing agent is used.

Some preliminary results obtained by the authors of this report [12] show that the neutralization process described by equations (1) and (2) may involve calcium carbonate instead of alkalies. Equation (4) illustrates this method of neutralization:

$$6NH{=}CH_2HX + 2CaCO_3 = C_6H_{12}N_4 + 2CaX_2 + 2CO_2 + 2NH_4X + 2H_2O. \tag{4}$$
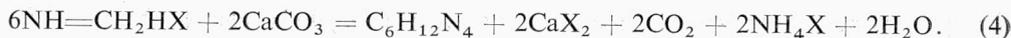
The sorption of formaldehyde in aqueous solutions of ammonium salts of strong acids neutralized with calcium carbonate is possible when the latter is suspended in the aqueous solution of the given ammonium salt. Formaldehyde will react with the ammonium salt according to (1), but, owing to the neutralizing action of calcium carbonate, no acidification occurs. It follows that the conversion of formaldehyde into hexamine will no longer be inhibited on the methylamine stage. Calcium carbonate, as a soft neutralizing agent, does not decompose the ammonium salts of strong acids to give free ammonia. A double substitution of ammonium salt with a small amount of dissolved calcium carbonate may yield ammonium carbonate:

$$CaCO_3 + 2NH_4X = CaX_2 + (NH_4)_2CO_3. \tag{5}$$

This small amount of ammonium carbonate will react with the formaldehyde sorbed to give hexamine:

$$2(NH_4)_2CO_3 + 6CH_2O = C_6H_{12}N_4 + 2CO_2 + 8H_2O. \tag{6}$$
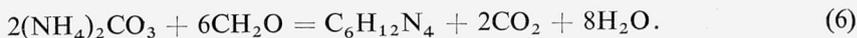
Irrespective of the reactions (1) and (4), as well as (5) and (6) occurring successively, the transformation of formaldehyde to hexamine can be described as follows:

$$6CH_2O + 4NH_4X + 2CaCO_3 = C_6H_{12}N_4 + 2CaX_2 + 2CO_2 + 8H_2O. \tag{7}$$

As can be seen from foregoing, the calcium carbonate suspension in the aqueous solution of strong acid ammonium salts (which is a novel sorbent of formaldehyde) seems very promising from the practical point of view due to its ability to control the course of the formaldehyde-to-hexamine conversion. Owing to this ability, the sorbent is not so intensively acidified as before, and the efficiency of formaldehyde sorption does not de-
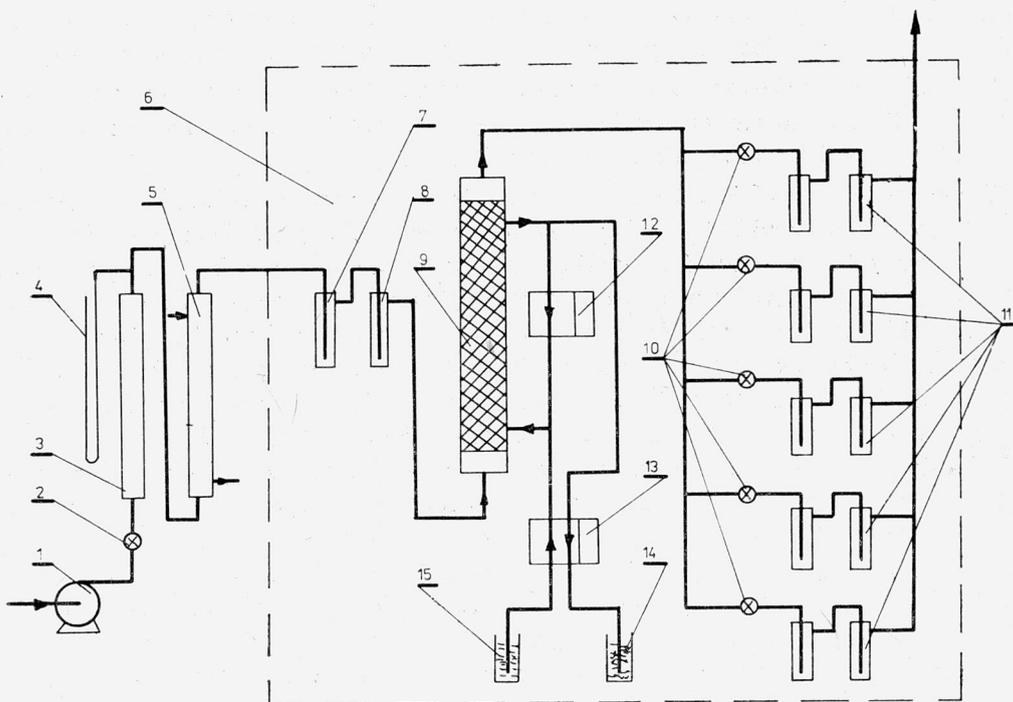

Fig. 1. Scheme of laboratory equipment for formaldehyde removal from air

1 — pump, *2* — valve, *3* — rotameter, *4* — U-tube, *5* — heat exchanger, *6* — thermostatic chamber, *7, 8, 11* — washers, *9* — washer-reactor, *10* — system of plug valves, *12, 13* — system of pumps, *14, 15* — tanks

Rys. 1. Schemat aparatury laboratoryjnej do usuwania formaldehydu z powietrza

1 — pompa, *2* — zawór, *3* — rotametr, *4* — U-rurka, *5* — wymiennik ciepła, *6* — komora termostatyczna, *7, 8, 11* — płuczki, *9* — płuczka-reaktor, *10* — układ zaworów zatyczkowych, *12, 13* — system pomp, *14, 15* — zbiorniki

crease. Considering the fact that calcium carbonate is a weak neutralizing agent, ammonia losses will also be very small. Thus, the chief shortcoming of the former methods has been eliminated.

From among the ammonium salts which are widely used in engineering practice: NH_4NO_3, NH_4Cl, and $(NH_4)_2SO_4$, we have selected NH_4NO_3. Ammonium chloride may bring about an unfavourable side-reaction yielding dichlorodimethylether, which is a carcinogenic factor. Ammonium sulphate leads to the formation of calcium sulphate which, by blocking the surface of calcium carbonate, may cause a deactivation of calcium carbonate, thus deactivating the suspension as a sorbent.

The chemisorption of formaldehyde in the calcium carbonate suspension in the aqueous solution of ammonium nitrate proceeds in two steps. The first step consists of a fast physical sorption process which is manifested in the diminishing diffusion resistance on the side of the liquid phase, as reported by Hobler [4]. In this process, formaldehyde is sorbed in water, i.e. in the medium in which the suspension is formed. In the second step, formaldehyde is subject to chemical reaction to give hexamine according to equation (7). This step of the chemisorption process is responsible for the removal efficiency degree.

The objective of the experiments reported here was to determine the optimum composition of the sorbing suspension, i.e. such that would meet the requirements mentioned earlier. The experimental apparatus is shown in fig. 1.

The procedure is as follows. Pure air is pumped by a pump 1 and being controlled by valve 2, rotameter 3 and U-tube 4 is passed to the heat exchanger 5. From there it is sent into two washers 7 and 8. The former (7) contains water where the passing air is humidified. The second one (8) contains an aqueous solution of formaldehyde and the air is saturated with formaldehyde vapours until the concentration required is achieved. The air-formaldehyde mixture obtained via the above route is sent to the washer-reactor 9 which is packed with Raschig rings ($7 \times 7 \times 1.5$ mm). The maximum height of the packing was 0.45 m to allow a working capacity of the sorbent of 0.2 dm³. There, both the sorption process and the chemical bounding of formaldehyde in the reaction suspension take place. In some instances, when higher concentrations were needed, formaldehyde in a liquid form was sent to the washer-reactor 9 through a system of pumps 12, 13 and tanks 14, 15. The air leaving the washer-reactor 9 is saturated with formaldehyde in an equimolar ratio to its free form in which formaldehyde occurs in the suspension. From the washer-reactor the mixture is passed through a system of plug valves 10 to reach the washers 11 in which samples are prepared for analyses. Formaldehyde content was determined with the titration method described by Walker [13]. Formaldehyde concentration in the air was measured colorimetrically with the use of chromotropic acid (Polish standard PN-71/C-04593). Ammonia escaping from the washer-reactor was measured colorimetrically using Nessler's reagent [1].

The quantity of calcium carbonate (applied in a orioirtion of 100 kg $CaCO_3$ per 1 m³ of suspension) was kept constant throughout the experiments. The concentration of the remaining constituents of the suspension, its volume and the process temperature were

anticipated for each individual run and also kept at the constant levels. The process temperature was automatically controlled by a thermostatic chamber 6.

In this way favourable conditions were established for determining the amount of converted formaldehyde (m_{CH_2O}) from the difference of formaldehyde concentrations in the air measured analytically at the inlet to, and the outlet from, the washer-reactor 9.
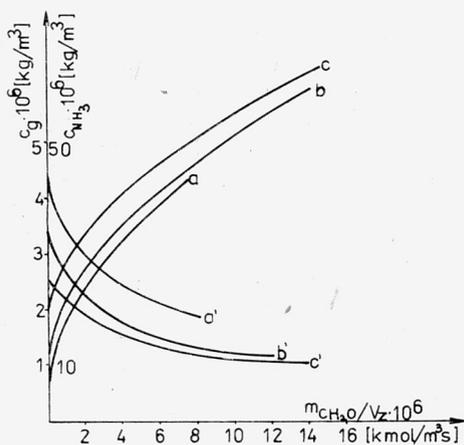

Fig. 2. Changes in formaldehyde c_g and ammonia c_{NH_3} concentrations in the air at the outlet of the washer-reactor as a function of the m_{CH_2}/V_z ratio and hexamine concentration

Temperature — 303 K, ammonium nitrate concentration in the chemisorbent — 1 kmol/m³
Hexamine concentrations in the chemisorbent: curves a, a' — 0.167 kmol/m³, curves b, b' — 0.278 kmol/m³, curves c, c' — 0.444 kmol/m³

Rys. 2. Zmiany w stężeniach formaldehydu c_g i amoniaku c_{NH_3} w powietrzu przy wylocie płuczki-reaktora w zależności od stosunku m_{CH_2O}/V_z i stężenia sześciometylenoczteroaminy

Temperatura — 303 K, stężenie azotanu amonowego w chemisorbencie — 1 kmol/m³
Stężenie sześciometylenoczteroaminy w chemisorbencie: krzywe a, a' — 0,167 kmol/m³, krzywe b, b' — 0.278 kmol/m³, krzywe c, c' — 0,444 kmol/m³

Fig. 3. Changes in formaldehyde c_g and ammonia c_{NH_3} concentrations in the air at the outlet of the washer-reactor as a function of the m_{CH_2O}/V_z ratio and ammonium nitrate concentration

Temparature — 298 K, hexamine concentration in the chemisorbent — 0.278 kmol/m³
Ammonium nitrate concentrations in the chemisorbent: curves d, d' — 0.6 kmol/m³, curves e, e' — 1.0 kmol/m³, curves f, f' — 2.0 kmol/m³

Rys. 3. Zmiany stężenia formaldehydu c_g i amoniaku c_{NH_3} w powietrzu przy wylocie płuczki-reaktora w zależności od stosunku m_{CH_2O}/V_z i stężenia azotanu amonowego

Temperatura — 298 K, stężenie sześciometylenoczteroaminy w chemisorbencie 0,278 kmol/m³

Stężenie azotanu amonowego w chemisorbencie; krzywe d, d' — 0,6 kmol m³, krzywe e, e' — 1,0 kmol/m³, krzywe f, f' — 2,0 kmol/m³
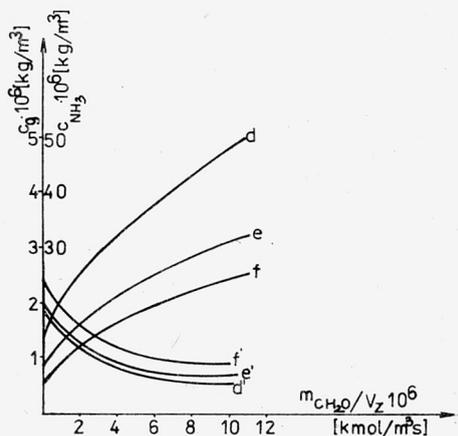
Figures 2–4 show changes in formaldehyde and ammonia concentrations in the air at the outlet of the washer-reactor as a function of the m_{CH_2O}/V_z ratio (V_z denotes the volume of the chemisorbent in m^3). The curves $a, b...g, h, j$ for formaldehyde show an increasing tendency, while those for ammonia ($a', b',... g'$) are decreasing.
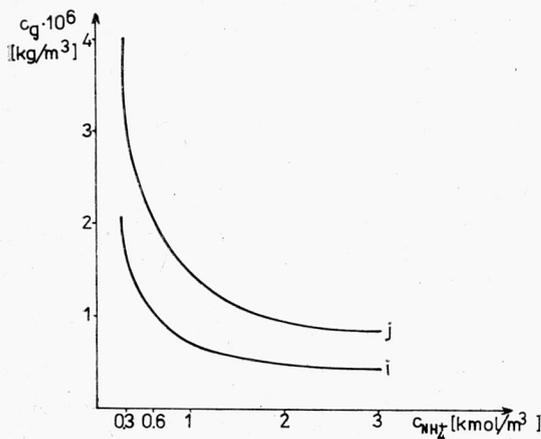
Fig. 4. Relation between formaldehyde concentration c_g in the air at the outlet of washer-reactor and ammonium nitrate concentration $c_{NH_4^+}$ in the chemisorbent

Temperature — 298 K, hexamine concentration in chemisorbent — 0.278 kmol/m³
m_{CH_2O}/V_z: curve i — 0 kmol/m³s, curve j — 1.39 kmol/m³s

Rys. 4. Zależność stężenia formaldehydu c_g w powietrzu przy wylocie płuczki-reaktora od stężenia azotanu amonowego $c_{NH_4^+}$ w chemisorbencie

Temperatura — 298 K, stężenie sześciometylenoczteroaminy w chemisorbencie — 0,278 kmol/m³
m_{CH_2O}/V_z: krzywa i—0 kmol/m³s, krzywa j—1,39 kmol/m³s

The curves given in fig. 2 illustrate the variations of formaldehyde and ammonia concentrations in the air as a function of m_{CH_2O}/V_z for the chemisorbent tested at three selected concentrations of hexamine. The remaining parameters: temperature (303 K), ammonium nitrate concentration in the chemisorbent (1 kmol/m³) were constant. The difference in the plots a and b (illustrating the variation of formaldehyde concentration in the air for chemisorbents with hexamine concentrations of 0.167 kmol/m³ and 0.278 kmol/m³, respectively) is insignificant. Curve c (for hexamine concentration of 0.444 kmol/m³) follows a different behavioral pattern. Ammonia concentrations curves (a', b', c') behave in a quite different manner. The lowest ammonia concentrations in the air were obtained for the hexamine concentration of 0.444 kmol/m³, for the concentration of 0.278 kmol/m³ being only slightly higher, increasing evidently for the concentration of 0.167 kmol/m³.

Thus, the following generalization can be made: the most advantageous hexamine concentration in the chemisorbent is that approaching 0.278 kmol/m³, as it gives low concentrations of both formaldehyde and the escaping ammonia in the outlet air.

The curves in fig. 3 illustrate formaldehyde and ammonia concentrations as functions of m_{CH_2O}/V_z for three ammonium nitrate concentrations in the chemisorbent: 0.6 kmol/m³, 1.0 kmol/m³, and 2.0 kmol/m³, respectively. The remaining process parameters were kept at a constant level: temperature — 298 K and hexamine concentration in the chemisorb-

ent $- 0.278$ kmol/m^3. From curves f, e, and d it may be seen that with the increasing form-aldehyde concentration in the air, the concentration of ammonium nitrate in the chemi-sorbent decreases.

The position of curves e and d show that even a relatively small decrease of ammonium nitrate concentration in the chemisorbent deteriorates markedly the efficiency of the che-misorption process, especially for higher values of m_{CH_2O}/V_z ratio. The relationship between ammonia concentration in the air and ammonium nitrate concentration in the chemisorbent is shown by curves f', e' and d'. From these curves it is evident that at high concentration of ammonium nitrate in the chemisorbent (equal to the highest one employed in our experiments), the quantity of ammonia escaping into the air increases.

Figure 4 shows the relationship between formaldehyde concentration in the air and ammonium nitrate concentration in the chemisorbent. As can be seen from this figure, the decrease of ammonium nitrate below 0.6 kmol/m^3 increases the concentration of form-aldehyde in the air, thus contributing to a deterioration of the treatment efficiency. Ammonium nitrate concentrations exceeding 2.0 kmol/m^3 do not improve the removal efficiency.
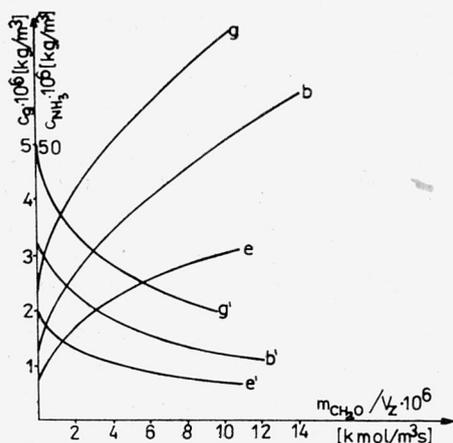

Fig. 5. Changes in formaldehyde c_g and ammonia c_{NH_3} concentrations in the air at the outlet of the washer-reactor as a function of the m_{CH_2O}/V_z ratio and temperature

Hexamine and ammonium nitrate concentrations in the chemi-sorbent 0.278 kmol/m^3 and 1 kmol/m^3, respectively
Temperature: curves e, e' — 298 K, curves b, b' — 303 K, curves g, g' — 308 K

Rys. 5. Zmiany w stężeniach formaldehydu c_g i amoniaku c_{NH_3} w powietrzu przy wylocie płuczki--reaktora w zależności od stosunku m_{CH_2O}/V_z i temperatury

Stężenia sześciometylenoczteroaminy i azotanu amonowego w chemisorbencie — 0,278 kmol/m^3 i 1 kmol/m^3
Temperatura: krzywe e, e' — 298 K, krzywe b, b' — 303 K, krzywe g, g' — 308 K

In figure 5 formaldehyde and ammonia concentration are plotted against m_{CH_2O}/V_z for 298 K, 303 K, and 308 K. The experiments were run at the most favourable concen-trations of ammonium nitrate and hexamine in the chemisorbent (1 kmol/m^3 and 0.278 kmol/m^3, respectively). As shown by these curves, the increase of the process tem-perature brings about an undesirable increment in formaldehyde concentration.

Based on the experimental results the following conclusions can be drawn:

1. The optimum ammonium nitrate and hexamine concentrations in the chemisor-bent yielding the highest formaldehyde removals from the air are those approaching

1.0 kmol/m³ and 0.278 kmol/m³, respectively. They may be employed in the purification of industrial outlet gases emitted by flax- and chip-board manufacturing plants.

2. The temperature of the treatment process must be the lowest possible, e.g. similar to that of the water used for cooling down the outlet gases to be treated.

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USUWANIE FORMALDEHYDU Z POWIETRZA ZA POMOCĄ ZAWIESINY WĘGLANU WAPNIA W WODNYCH ROZTWORACH AZOTANU AMONU

Scharakteryzowano problem zanieczyszczenia powietrza atmosferycznego ze szczególnym uwzględnieniem emisji formaldehydu z wytwórni płyt wiórowych i paździerzowych. Stwierdzono przydatność zawiesiny węglanu wapnia w wodnym roztworze azotanu amonu do efektywnej sorpcji formaldehydu. Podano optymalne warunki uzyskania najwyższego stopnia usuwania formaldehydu z powietrza.

FORMALDEHYDBESEITIGUNG AUS DER ABLUFT DURCH KALZIUMKARBONATSUSPENSIONEN IN AMMONIUMNITRATLÖSUNGEN

Charakterisiert wird die Luftverunreinigung mit spezieller Betrachtung der Emissionen aus der Holzspäne- und Schäbeplattenherstellung. Aufgrund der Versuche konnte festgestellt werden, daß die Kalziumkarbonatsuspension in wässrigen Lösungen von Ammoniumnitrat sich zur Formaldehydsorption sehr gut eignet. Angeführt werden optimale Faktoren dieses Verfahrens.

УДАЛЕНИЕ ФОРМАЛЬДЕГИДА ИЗ ВОЗДУХА ПОСРЕДСТВОМ КАРБОНАТА КАЛЬЦИЯ В ВОДНЫХ РАСТВОРАХ НИТРИТА АММОНИЯ

Охарактеризована проблема загрязнения атмосферного воздуха с особым учётом его эмисси из завода фибролитовых плит из стружек и костры. На основе проведенных исследований отмечена пригодность суспензии карбоната кальция в водном растворе нитрата аммония для эффективной сорбции формальдегида. Приведены оптимальные условия получения наивысшей степени удаления формальдегида из воздуха.