

# Selective Removal of Naphthalene by Means of Anionic Clays Different Composition

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## Introduction

Methods for obtaining selective sorbents of naphthalene and its derivatives have been created. The technology of naphthalene removal from gas emissions has been developed. The technological parameters of the reactors are calculated. The final concentration of naphthalene in  $12 \text{ mg/m}^3$  was obtained that is lower than the maximum allowable concentration.

Naphthalene is one of the products of "INCORE" Company. The process of its manufacturing is accompanied with emission of gaseous naphthalene into the premises' air and then into the atmosphere, thus polluting it.

This work is based on the order for designing an installation for removal of naphthalene from ventilation emissions at enterprise, belonging to "INCORE" Company, which is a subsidiary of "Metinvest Holding". The main requirement for the installation was the final concentration of naphthalene below  $20 \text{ mg/m}^3$  (Table 1).

Naphthalene is one of the most important products of coal-tar resin refinement. It is a valuable raw material for chemical industry. Maximal extraction of naphthalene from coal-tar resin and its rational use is a task of a paramount importance [1].

The main initial raw material for obtaining naphthalene is naphthalene fraction, obtained at resin fractioning and containing up to 80-85% of naphthalene, it being 92-93% of its total content in resin.

Naphthalene fraction contains methyl-naphthalenes - up to 6%, thionaphthene - up to 3.8%, phenols - up to 2.3%, unsaturated compounds - up to 0.4%, indole - 0.3%. The main admixtures, making the process of obtaining pure naphthalene difficult are thionaphthene among sulphur containing admixtures and indene and coumarone among unsaturated compounds [2].

At present various methods of entrapping and neutralization of gaseous and vaporous compounds from air are used. In industry the following methods of gas purification are used: absorption, adsorption, catalytic, thermal and others [3]. The methods of apparatuses design are based on regularities of mass and heat transfer.

Naphthalene is poisonous. The lethal dose is 10 g for adults, and 2 g - for children. Poisoning can happen at inhaling of vapour or dust, at penetration through skin or admitting into stomach. Naphthalene dust in the air is explosive at 1.7-8.2%.

According to the order for design of an installation for naphthalene removal from ventilation emissions at the department of pressed naphthalene the outgoing gas flow consists of air, water and naphthalene. According to the data, obtained by chromatographic analysis, which is listed below, the emissions also contain  $\alpha$ -methyl-naphthalene.

Moreover, the data, regarding naphthalene concentration in gaseous phase at the specified temperature contained in the specification testify the absence of airborne naphthalene particles, despite their obvious presence.

The most important parameter for naphthalene removal from the gaseous phase is the dependence of the partial pressure upon the temperature, evaluated here and shown in [4] (Figure 1).

Concentration of  $20 \text{ mg/m}^3$  corresponds to  $0.000156 \text{ mmol/l}$ , it corresponding to  $0.00088 \text{ kPa}$ , which corresponds to temperature  $264.75 \text{ K}$ , it corresponding to temperature  $-8 \text{ }^\circ\text{C}$ .

A well-known method of naphthalene absorption is its entrapment by organic solvents, mostly by absorption oil. Efficient final concentration, reached by this method is  $0.8\text{-}0.4 \text{ g/m}^3$ .

Also known are the following methods of naphthalene removal: adsorption on activated carbon, polymeric carriers, metals, zeolites et al.

A method of gas cleaning from naphthalene by washing it with water and introducing any naphthalene solvent, light resin, for instance for into the flushing water is well known.

When all these conventional methods are applied, as well as many others the degree of naphthalene removal is not big enough, so their application will not allow reaching the established maximum permissible concentrations.

Nowadays, there exists a variety of methods of removal of naphthalene and its derivatives from gaseous phases, including physical, chemical, rectifying, absorption, adsorption and others.

Still, there is not a single method of naphthalene removal from the gaseous phase, capable of reaching the required ecologic parameters -  $20 \text{ mg/m}^3$ .

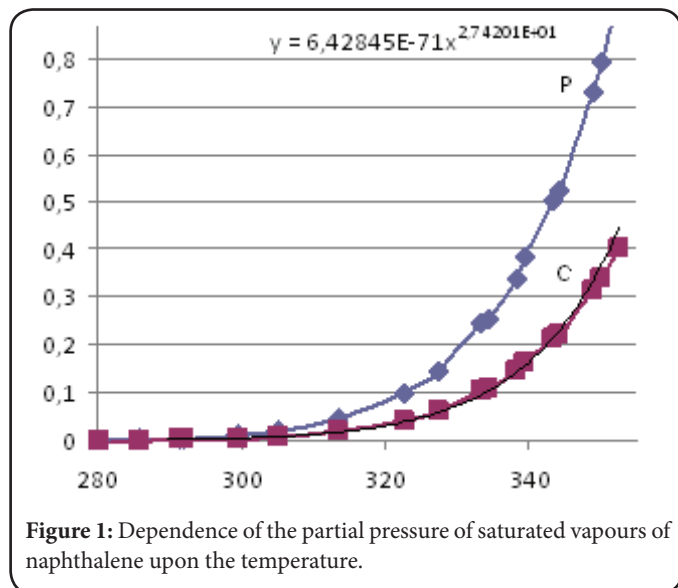
Reaching such parameters requires developing of a special technological process of naphthalene removal from gaseous phase.

The methods that could be laid into the foundations of the developed technology may include: absorption method; method of catalytic destruction; method of thermal neutralization; condensation method; adsorption method.

Absorption removal of naphthalene is possible even with water. Aromatic hydrocarbon vapours are absorbed in the system air-water. The wet process of adsorption through formation of fog with subsequent enlargement of drops is used. For efficient absorption and removal of naphthalene vapours with subsequent formation of water drops formation of fog particles from 14 to 200 microns in size is required. At particles seize smaller than 50 microns absorption of naphthalene

**Table 1:** Main requirements for the technology of naphthalene deleting.

Initial naphthalene concentration	1,000 mg/m <sup>3</sup>
Temperature of emission	50 °C
Volume flow rate	300 m <sup>3</sup> /h
Humidity	50 %



**Figure 1:** Dependence of the partial pressure of saturated vapours of naphthalene upon the temperature.

vapour is higher than follows from their phase equilibrium gas-liquid, in other words surface adsorption takes place. Introduction of a surface active substance has a positive effect on absorption of naphthalene vapors by water drops.

Adsorption, also, finds application in cases when a selective removal of certain gaseous components from the mixture is required, besides, adsorption is the best method of reaching trace concentrations.

Adsorption is the most universal means of purification of emissions from gaseous contaminants. It is possible in principle to remove any contaminant from emissions in a wide range of concentrations by means of adsorption. However, it is more convenient to undergo highly concentrated contaminants (supposedly, with concentrations exceeding 10<sup>-3</sup> kg/m<sup>3</sup>) a preliminary treatment (condensation, absorption) to reduce their concentrations.

Sorption experiments were conducted for investigation of naphthalene and β-naphthole on layered double hydroxides. Comparison with β-naphthole was chosen for the research, because sorption of β-naphthole and naphthalene occurs in accordance with different mechanisms. After completion of the process of sorption the specific surface was determined and inter-plane distances were measured. Changes in the dimensions of the internal space were made with the help of phase X-ray analysis [5]. The results of the experiments are summarized in (Figure 2).

Three X-ray curves, pictured in are very similar, this showing very little alternation of the structure (Figure 2). It can be seen in the detached insertion that intenseness drops and the peak 11.8 degrees is shifted towards the area of smaller angles. This shift to the left means an increase in inter-plane distance; it verifies penetration of the organic into the lattice it is also confirmed by the fact that at angles' values of 43, 61 and 62 degrees there are also similar shifts. A change in the structure is observed, there are shifts of some peaks, there appear some new they grow in intensity, the position and intensity of others remain

unchanged. The changes in the structure grow in the row: original, with naphthalene and with β-naphthole.

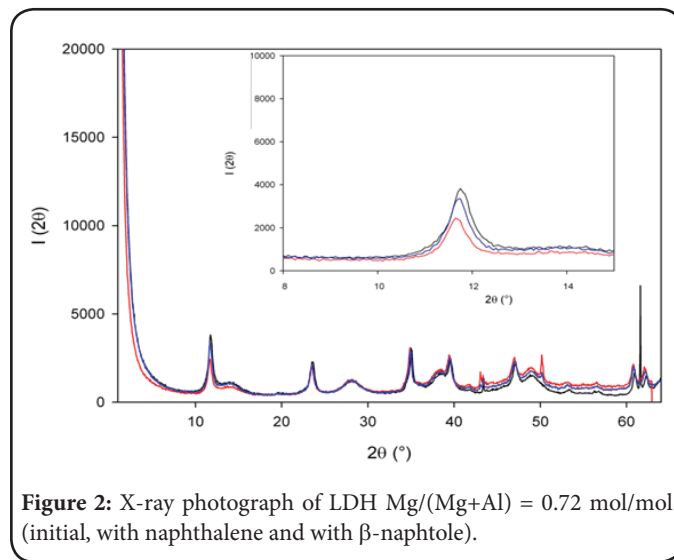
It can be seen on the X-ray photographs that the highest deviations are observed at sorption of with β-naphthole. The possible reason is that aromatic rings of the adsorbed naphthalene are arranged parallel to inorganic layers, irrespective of concentration of the active centres. Interaction of π-electrons of the aromatic rings with the matrix layers lead to an alternation of the inter-plane distance.

Specific surface of the sorbents with adsorbed organic compounds was determined by BET method. The results are summarized in the (Table 2).

It can be seen from the data, represented in the Table 2 that at low values of the relation Mg/(Al+Mg) sorption of naphthalene and β-naphthole has practically no influence upon the values of the specific, while at high values of Mg/(Al+Mg) relation the changes are much bigger.

Naphthalene sorption is the process of physical sorption, β-naphthol is a relatively strong acid and the process of sorption goes on much faster than for alcohols. The aromatic rings of the adsorbed naphthalene are arranged parallel to inorganic layers, irrespective of the concentration of the active sites. The inter-plane distance is about 7 Å. This value is comparable to the “thickness” of the aromatic ring, which is equal to ~3,5 Å, while the diameter of a molecule of benzene is 7.1 Å. And for β-naphthol plane-parallel arrangement is observed only at the initial stage of ionic exchange [6] (Figure 3).

Efficient area for β-naphthol is 9.89 Å<sup>2</sup>. Later on an equilibrium is set, accompanied with an increase in the inter-plane distance and growth of the number of active sites, available for the following molecules of β-naphthole. This process is accompanied with an enlargement of the specific surface of layered double hydroxides.



**Figure 2:** X-ray photograph of LDH Mg/(Mg+Al) = 0.72 mol/mol (initial, with naphthalene and with β-naphthole).

**Table 2:** The value of specific surface m<sup>2</sup>/g, for the specimens of layered double hydroxides.

(Mg/(Al+Mg), mol/mol)	Initial	β-naphthole	Naphthalene
0,52	162,4	155,7	156
0,72	14,4	14,4	14,4
0,81	9,2	12	19,59
0,86	22	28	34,7

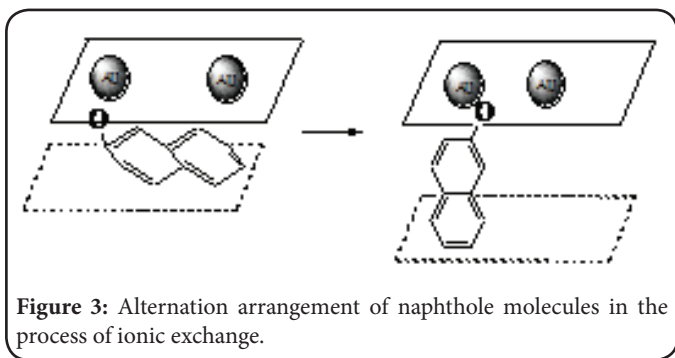


Figure 3: Alternation arrangement of naphthole molecules in the process of ionic exchange.

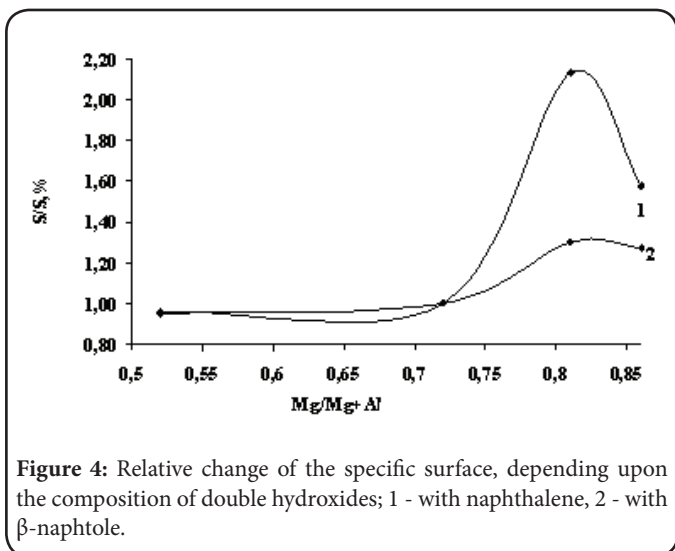


Figure 4: Relative change of the specific surface, depending upon the composition of double hydroxides; 1 - with naphthalene, 2 - with  $\beta$ -naphthole.

The dependence of the change of specific surface after sorption of naphthalene and  $\beta$ -naphthole, depending upon the content of layered double hydroxides is shown in (Figure 4). It is seen that with an increase in the degree of isomorphous substitution, sorption of organic compounds lead to big changes in the specific surface [7].

To simulate the industrial process of naphthalene sorption the following scheme was chosen (Figure 5). Naphthalene was placed on the bottom of a vessel, air was blown over naphthalene, then it passed through a tube and entered the reactor, filled with sorbent. The air was preliminarily dehumidified by passing it through the trap, equipped with the drier. The inlet and outlet temperatures were controlled. The required time for reaching a stationary mode was about half an hour. The gas flow passed through cryoscopic trap, naphthalene was dissolved in diethyl ether and then it underwent chromatography.

The rate of the gas flow was 0.05 m/sec, initial naphthalene concentration 0.23 g/m<sup>3</sup>, the final 0.0012 g/m<sup>3</sup>.

It was discovered during the investigation for neutralization of emissions of coke-oven production that at the contact of air and vapour mixture of naphthalene with adsorbent an intense desublimation occurs on its surface. Solid particles of naphthalene skipping through the layer of adsorbent it increases its concentration in the air after the adsorber.

When air and vapour mixture of naphthalene touches the surface of fresh adsorbent two processes occur simultaneously - adsorption and desublimation. As these processes are of a competing character, it may be supposed that desublimation will go more intensely on the adsorbent, already saturated with naphthalene.

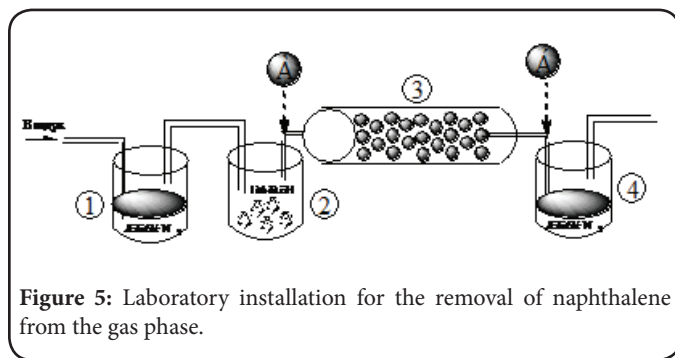


Figure 5: Laboratory installation for the removal of naphthalene from the gas phase.

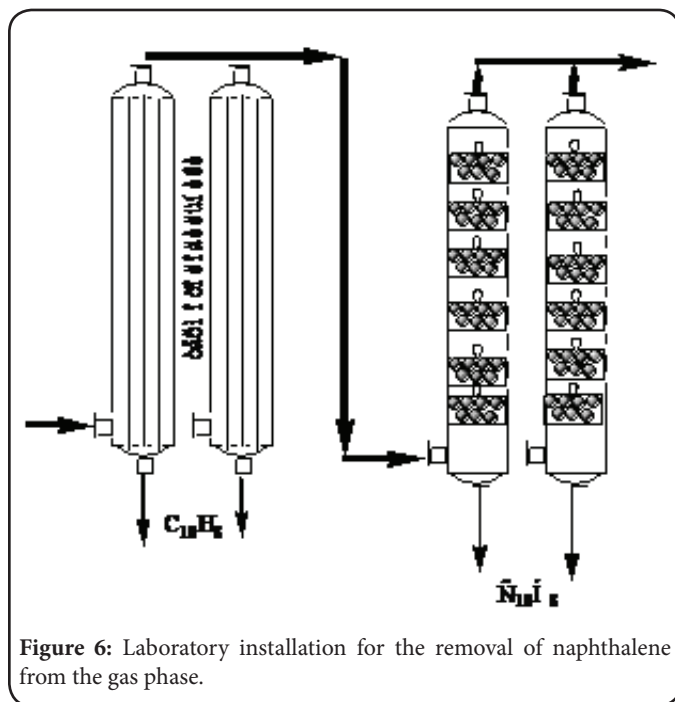


Figure 6: Laboratory installation for the removal of naphthalene from the gas phase.

The process of desublimation was investigated on LDH. For this naphthalene mixture was delivered from the metering device to the filter for removal of airborne particles and then it was passed to sorbent. The diameter of the device - 40 mm, the air flow rate - 0.03 m/sec, the height of the layer of sorbent - 45 cm. Samples were taken before and after sorbent, naphthalene concentration was determined by means of photocolorimetry with alloxantin. The initial naphthalene concentration was 20-30 mg/m<sup>3</sup>.

An efficient method of increasing dynamic capacity of sorbent is additional introduction of substances suppressing desublimation. Investigations showed that introduction of benzol vapors in relation to naphthalene 1:10 increased the exchange capacity by 25-30% and similar introduction of  $\alpha$ -methyl naphthalene - by 15-20%. Suppression of desublimation can be explained by deceleration of the chain reaction of sublimate formation.

At super-low naphthalene concentrations desorption and sublimation were not observed. The results obtained were the basis for a design of a sorption apparatus for bringing naphthalene emissions to the requirements of maximum permissible concentrations. (Figure 6) shows the principal diagram of removal of naphthalene from the gas flow by LDHs.

**Conclusion**

1. Naphthalene is a pollutant of the 4th hazard class, which has a negative impact on human health and the environment.
2. Existing methods of removing of naphthalene from the gas phase do not allow to purify industrial emissions to the maximum allowable concentrations (20 mg/m<sup>3</sup>).
3. Purification of gas emissions from naphthalene to values close to the maximum allowable concentration can be achieved by means of a complex of measures involving deep cooling.
4. Purification to the maximum allowable concentration and below can be carried out using layered double hydroxides with the size of interplanar distances corresponding to the size of the molecules of naphthalene.
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