# Study of loose bulk cargo storage conditions and water transportation

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**Abstract.** When transporting such cargos as mineral fertilizers by water, they absorb moisture, which stimulates cargo self-heating and ultimately leads to dangerous temperature limits. When transporting ANP fertilizer in holds, its equilibrium moisture content can change significantly, which can lead to the cargo damage. The article presents the findings on the processes of hydrothermal moistening of porous bodies on the example of ANP fertilizer associated with the phenomena of sorption and desorption. There is no analytical description of moistening processes of porous bodies associated with these phenomena in the scientific literature. The optimal conditions for storage and transportation of bulk materials have been determined on the example of ANP fertilizer transported through the Novorossiysk seaport. As a result of the study, the moisture content intervals associated with various types of absorption were established. Thus, in the range of φ from 0% to 16% moisture content, monomolecular adsorption prevails, which corresponds to the normal moisture content of ANP fertilizer. In the range of φ from 16% to 54%, polymolecular adsorption predominates, and at the value of φ greater than 87%, a smooth transition from predominantly polymolecular adsorption to capillary condensation occurs, which will negatively affect the process of humidification and cargo caking.

## 1 Introduction

When choosing the conditions for bulk cargo storage and water transportation, it is necessary to regard the physicochemical characteristics of the cargo. Bulk cargo transportation is significantly influenced by the temperature and humidity of the environment. During long-term storage, bulk materials can lose their flowability with varying degrees and even form a single monolith. This occurs as a result of an increase in the adhesion forces between the individual particles, which results in a strong three-dimensional structure. These processes arise spontaneously since their formation is accompanied by a decrease in the free energy of the system and a corresponding decrease in entropy. It is impossible to completely prevent this process. However, the choice of optimal storage and transportation conditions significantly slows down the caking process and the product in a stationary state does not lose flowability.

To select the optimal conditions for bulk materials storage and transportation, it is necessary to determine the factors strengthening the contact between the particles and the kinetics of the processes occurring on the particles surface. The surfaces of hydrophilic particles in contact with the atmosphere are always covered with an adsorption layer of water. Even if the product entered for storage was subjected to preliminary drying under production conditions, its moisture content was at least 0.02%, which corresponds to several adsorption monolayers of water. Particles of a substance entered for storage are always covered with an adsorption layer of water (or, more precisely, an aqueous solution of a given substance), and the thickness of the adsorption layer increases with an increase in air humidity.

The contact area functionally depends on the diffusion coefficients $D_r$ and $D_s$, and this dependence is expressed by the following equation: $D_r = D_0 exp\ (-E/RT)$, where E is the activation energy of the transition between neighboring equilibrium positions of molecules in the diffuse layer. The activation energy can change significantly even with small fluctuations in the layer thickness, which is determined by the air humidity while being poured into the bunker and during cargo storage.

The contact area stops expanding when the contact stresses are removed, and the gradient of the chemical potential being the driving force of diffusion decreases. The size of the contact zone becomes commensurate with the size of the particles.

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The particles at this stage remain separated by a layer of aqueous solution. The interaction of crystals is carried out by molecular or Van der Waals forces. According to the classification, this is a coagulation-type contact.

A further increase in the adhesion strength of the particles can occur during the transition from coagulation contacts to phase contacts. Such a transition can be carried out in two ways.

In the first case, there is a breakthrough of the liquid layer on a site with an area of several elementary structural cells of the crystal surface. A violation of the continuity of the interlayer can occur as a result of the fluctuation union of several vacancies in the adsorption layers. In this case, the germ of phase contact occurs. In the area of the breakthrough, forces that significantly exceed the molecular ones act, leading to the fusion of granules.

Then the breakthrough area spreads over the entire contact surface between the particles. Such a process is more likely with a small thickness of the adsorption layer. With a large layer thickness, phase contact can be carried out by the appearance of a crystalline embryo formed from dissolved powder molecules in the layer. Growing, this bridge fills the entire area of contact between the particles.

## 2 Problem setting

The water vapor adsorption on the surface of objects being in contact with air must be considered in production processes since this leads to a change in the properties of absorbing substances.

Adsorption occurs under the influence of the molecular forces of the adsorbent surface and is accompanied by a decrease in the free surface energy. According to the theory of P.A. Rebinder [1], this leads to an adsorptive decrease in the strength of solids and a significant decrease in their resistance to deformation and destruction. The adsorbate molecules approaching from the volume of a gas or solution to the interface are attracted from this surface. Thus, the surface of the adsorbent can be mono- or polymolecular.

During physical adsorption, which decreases with decreasing adsorbate concentration, the molecules of the latter retain their individuality. Physical adsorption is reversible (desorption process). Physical adsorption of vapors is often accompanied by capillary condensation of the substance in the pores of the adsorbent, which can cause sorption hysteresis, the phenomenon of incomplete reversibility of the adsorption process, and the retention of a larger amount of the adsorbed substance by porous bodies during desorption than during adsorption.

The amount of gas or dissolved matter adsorbed by a certain amount of a given adsorbent depends not only on the type of gas or solution but also on the process conditions such as gas pressure, concentration of the solute, and temperature. All other conditions being the same, the effect of pressure or gas concentration on the adsorbed matter can be depicted by adsorption isotherms. Sorption and desorption isotherms are usually determined empirically for each specific material. It is very difficult to determine the equations of these characteristics analytically since materials contain moisture with various bonding [1-6].

The task was to study the process of hydrothermal moistening of bulk cargo using the example of ANP fertilizer transported through the Novorossiysk commercial sea port.

## 3 Research methods

The scientific literature provides no analytical description of the processes of porous bodies moistening associated with the phenomena of sorption and desorption. An experimental study of the dependence of the specific moisture content of ANP fertilizer on the relative humidity of the ambient air was carried out using the tensometric method. The method principle is that a strictly defined and constant partial pressure of water vapor is established in a closed volume above the surface of a sulfuric acid solution of a given concentration. If a solution of sulfuric acid of a known concentration is placed in a desiccator, and bottles with weighed portions of the test substance are placed above its surface, then after a certain time interval the substance will acquire a strictly defined moisture content corresponding to the equilibrium moisture content. The experiment conducted in four desiccators with maintained relative air humidity from 0.2% to 95% aimed to determine the maximum range of exposure to humid air on the ANP fertilizer.

8 weighed portions of 5 grams of ANP fertilizer were placed in the weighing bottles and dried in thermostats HS31A and HS61A at a temperature of 120°C for 30 minutes, and then at a temperature of 80°C for 30 hours. The weighing bottles were weighed on an analytical balance with an accuracy of $1 \cdot 10^{-7}$ kg. After drying, the samples were placed in desiccators (two bottles in each). Periodic weighing was used to determine the moment of reaching a constant mass of the samples, which meant the onset of an equilibrium state of ANP fertilizer with moist air in desiccators. Then the

weighing bottles were moved until a constant mass was assumed.

The experimental data are shown in Table 1.

**Table1.**Results of exposure to humid air on ANP fertilizer

| Desiccatorno. | Sulfuricacid solution | | Water vapor over solution | | Relative humidity $P/P_0 \cdot 100 \%$ |
|---|---|---|---|---|---|
| | Density $\rho$, g/cm$^3$ | Concentration,% | Partial pressure P, Pa | Partial pressure at saturation P$^o$, Pa | |
| 1 | 1.730 | 80 | 15.42 | 220.8 | 7 |
| 2 | 1.495 | 60 | 376 | 2,350 | 16 |
| 3 | 1.305 | 40 | 1,265 | 2,342 | 54 |
| 4 | 1.140 | 20 | 2,023 | 2,325 | 87 |

The specific equilibrium moisture content of ANP fertilizer U $_i$ , kg/kg, is calculated using formula 1:

$$U_i = U_0 + \left(\frac{M_i}{M_0} - 1\right) \qquad (1)$$

Where U $_0$ is initial moisture, kg/kg; U $_0$ = 5·10$^{-2}$ kg/kg;

$M_i$ is mass upon reaching equilibrium moisture content, kg;

$M_0$ is initial weight, kg; $M_0$ = 0,005 kg.

The data for the calculation are given in table 2.

**Table 2**.Equilibrium moisture content for the processes of U $_i$ (I) sorption and U $_i$ (II) desorption of ANP fertilizer

| Measuring point no. | $\frac{M_i}{M_0}$ (I) | $\frac{M_i}{M_0}$ (II) | U $_i$ , kg/kg(I) | U $_i$ , kg/kg(II) | Initial moisture U $_0$ , kg/kg |
|---|---|---|---|---|---|
| 1 | 1.068 | 1.098 | 0.118 | 0.148 | 7 |
| 2 | 1.150 | 1.200 | 0.200 | 0.250 | 16 |
| 3 | 1.230 | 1.270 | 0.270 | 0.320 | 54 |
| 4 | 1.310 | 1.310 | 0.360 | 0.360 | 87 |

## 4 Results and discussion

The obtained specific equilibrium moisture content of ANP fertilizer at a specific relative air humidity during humidification and drying (Table 2) is approximated by two smooth curves: isotherms of sorption (I) and desorption (II), which coincide at two extreme points: ɷ = 0% and (87 %) (Fig. 1).

Over the entire range of changes ɷ ( P/ Po ·100%), sorption hysteresis is observed, which is characteristic of capillary-porous bodies. A gentle hysteresis loop leads to the conclusion that the structures of ANP fertilizer have so-called "bottle-shaped" pores with a wide range of sizes. They hold water molecules in the skeleton of a substance and cause capillary condensation in vapors.

The shape of the sorption isotherm of ANP fertilizer was compared with the main types of adsorption isotherms of gases and vapors, which showed that the S-shaped curve corresponds to the isotherm of the second type observed during physical multilayer adsorption characterized by the stages of polymolecular adsorption and capillary condensation.

To determine the boundaries of the predominance of individual forms of moisture-ANP fertilizer connection, the theory of P.A. Rebinder [1], according to which the binding energy of the adsorbed substance with the adsorbent is proportional to the degree of dryness (U) of the sorbent and is expressed by the chemical potential of mass transfer μ, J/(kmol) was used:

$$\mu = R \cdot T \cdot In\, P/P_0 \qquad (2)$$

Where R is universal gas constant, J/mol;
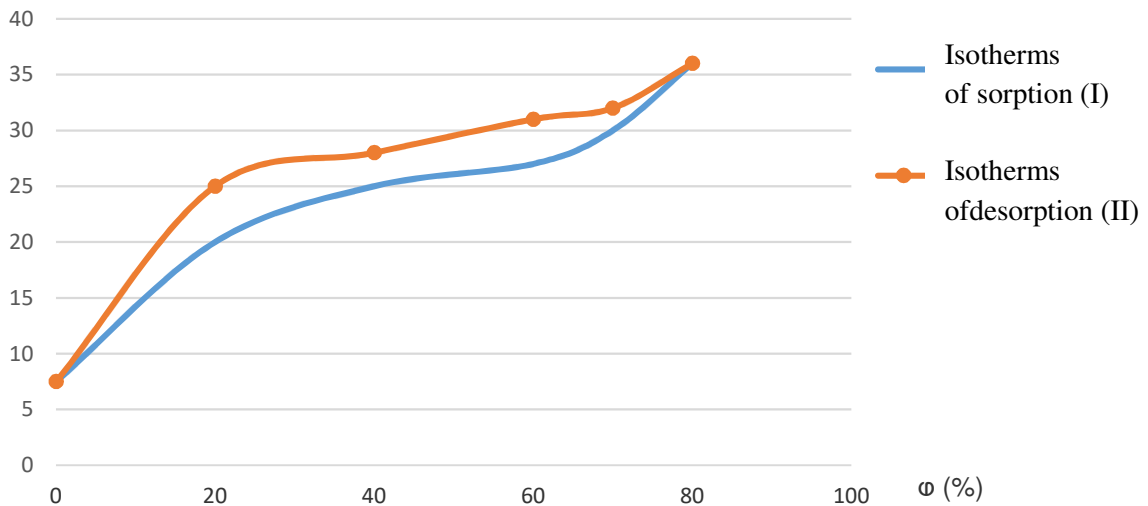T is temperature, K;
P/P$_o$ is relative air humidity, Pa/Pa.

**Figure 1**.Isotherms of sorption (I) and desorption (II) of moisture by ANP fertilizer

**Table 3.**Values of mass transfer chemical potential

| № | ϕ, % | $-\mu \cdot 10^5$, J/(kmol) | $U^{-1}$, kg/kg |
|---|------|----------------------------|------------------|
| 1 | 16 | 44.95 | 5.0 |
| 2 | 54 | 15,11 | 3.571 |
| 3 | 87 | 3.42 | 2.7 |

Table 3 shows the data for constructing the sorption isotherm of ANP fertilizer in the coordinates μ, $U^{-1}$ at T = 295 K calculated according to this equation.

The construction of the sorption isotherm of ANP fertilizer in the coordinates μ, $U^{-1}$ (Fig. 2) have revealed three singular points 1, 2, 3 at ϕ = 16%, 54%, 87%, respectively, which characterize the boundaries of the predominance of individual forms of bond with ANP fertilizer and confirm that the process of ANP fertilizer wetting is a physical adsorption.
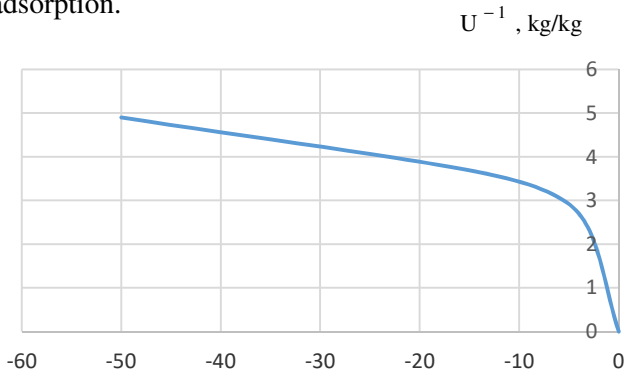


**Figure 2**.Moisture sorption isotherm

## 5 Conclusion

Thus, it was found that in the range of ϕ from 0% to 16% of the moisture content, monomolecular adsorption prevails, which corresponds to the normal moisture content of ANP fertilizer. In the range of ϕ from 16% to 54%, polymolecular adsorption prevails, and when ϕ is more than 87%, a smooth transition from predominantly polymolecular adsorption to capillary condensation occurs, which will negatively affect the process of moistening and caking of this cargo. Therefore, during the transportation of ANP fertilizer by water transport, there is the risk of a significant change in its equilibrium moisture content, which can lead to the cargo damage. To ensure the cargo safety, it is necessary to provide the cargo with a certain humidity condition, which during the sea transportation at least would not exceed the permissible parameters (over 16%) in order to preserve its bulk properties.

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