FUTURE DEVELOPMENT OF SCIENCE OF DRYING OF CAPILLARY-POROUS COLLOIDAL MATERIALS*

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The science of drying of moist materials (colloidal capillary-porous substances) includes the thermodynamics of the moist gas and material, heat- and mass-transfer theory, the theory of forms of bound moisture, physicochemical mechanics, and some areas of special technological knowledge.

Prediction of development in such scientific fields is very difficult and, hence, only a rough outline of the future development of drying science can be given. Some predictions were made in a review "Achievements in the science of heat and mass transfer," published in Inzhenerno-Fizicheskii Zhurnal, 13, No. 5 (1967).

1. This review pointed out that the first fundamental contribution to the development of drying theory was L. K. Ramzin's I–d diagram, which provided a scientific basis for the calculation and design of driers. In this area of drying theory Soviet scientists can claim priority not only in the development of the thermodynamics of a moist gas, but also in the technique of heat-engineering calculations for driers, which is superior to the technique used in the West.

The development of drying theory in the Soviet Union began with the work of the Drying Laboratory in the F. É. Dzerzhinskii All-Union Heat-Engineering Institute, which was set up in 1923 on the initiative of V. I. Lenin.

The literature of the last 10 years contains papers which represent a further development of the method of calculation of driers with the aid of I–d diagrams for moist air. They relate to work carried out in the Soviet Union and in France. Work in this direction will obviously continue in the future. The main idea of such studies is to link the statics and kinetics of the drying process on the basis of the desorption isotherms of moist materials. Such a concept is a first approximation, of course, and is valid in principle for infinitely slow drying. Nevertheless, it is a step forward in drier calculation technique.

A complete solution of this important practical problem will not be obtained until the thermodynamics of a moist gas has been further developed and improved and, in addition, the thermodynamics of moist material has been sufficiently well developed. It is quite conceivable that the use of desorption diagrams is an extremely inefficient technique. This raises the problem of creation of a common scale of moisture transfer potential and a reliable experimental method of determining this potential. As recent work in the hygroscopic region has shown, the chemical potential can be taken as the moisture transfer potential. A great deal of work on calculation of the specific mass capacity and temperature coefficient of moisture has been done, and tables for a large number of diverse materials have been published. These accumulated data must now be used to devise a method of calculating driers by means of the I–d diagrams of moist air. This will be a better method than the French one and will obviously be devised within the next 5-10 years.

2. The development of a method of determination of the moisture transfer potential scale is a very urgent problem not only for the correlation of the statics and kinetics of drying. It is essential also for the wide adoption of methods of drying thermolabile materials with the aid of satellite capillary-porous substances. The presence of the satellite greatly accelerates the drying process due to contact moisture

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transfer between the material and the satellite. It should be noted, in general, that the development of thermodynamics of a moist material is one of the most important problems in drying theory. In fact, the thermodynamic characteristics or properties of moist materials determine the energy and form of binding of moisture with colloidal capillary-porous substances and enable us to class materials to be dried in particular groups, which, having related properties, will dry at approximately the same rate and in the same way. This will lead to a considerable reduction of the time required for experimental tests to select optimum drying conditions. This work will obviously be completed within the next 10 years and thermodynamic properties, such as moisture capacity, temperature coefficient of moisture transfer, and moisture transfer potential, will be used instead of the sorption and desorption isotherms for each material at different temperatures.

3. Great progress has been made in the last five years in the field of drying kinetics. Despite the numerous investigations connected with the solution of the differential moisture transfer equations and, hence, the large number of proposed formulas for calculation of the drying process, the most reliable method is still the approximate method involving the relative drying coefficient. The wide adoption of this method has been assisted by the fact that calculation of the drying rate in the second period requires only two additional constants; the relative drying coefficient and the equilibrium moisture content. For an exploratory calculation the relative drying coefficient can be determined from the initial moisture content of the material.

Further improvements in calculation of the drying rate will obviously proceed along the same lines and, in particular, by the two-region method, i.e., division of the falling drying rate period into two regions with their own drying coefficients. This is due to the fact that the so-called Dalton formula for calculation of the evaporation rate is unsuitable for the falling rate period, since the evaporation coefficient (moisture transfer coefficient) is an unknown function of the heat content of the material. The magnitude of this change in the moisture transfer coefficient is an order or more. It is quite obvious that such a relationship is unsuitable for calculations.

The situation is similar in the case of heat transfer in the drying process. The Newton formula, according to which the specific heat flux is proportional to the temperature head, is also unsuitable for the falling rate period, since the heat-transfer coefficient, or the Nusselt number, is a function of the moisture content of the material being dried. Thus, calculation of the heat transfer by the classical heat-transfer formulas leads to large errors. This was the position before the publication of work on the interrelation of heat and moisture transfer. The introduction of the Rebinder number has made it possible to reduce the heat-transfer calculation to a moisture transfer calculation and thus to fill in a large gap in the study of drying kinetics. Work on the temperature curves during drying was published as far back as the thirties, but it was only in recent years that this research was brought to its logical conclusion. There is no doubt that the introduction of the Rebinder number is a very effective calculation technique. It allows the calculation of the composite heat transfer in convective – and conductive – radiant drying. In addition, the use of the Rebinder number makes it relatively easy to calculate the bulk temperature of material in the drying process, which is very important for drying technology and, in particular, for the selection of optimum drying conditions. An analysis of the development of research in this area of drying theory suggests that in the very near future a relationship will be established between the Rebinder number and the transport properties of moist material (heat and moisture diffusion coefficients, thermal diffusion coefficient, and phase transition number). The establishment of this relationship will require the use of analytical solutions of the system of differential equations of heat and mass transfer in capillary-porous substances with appropriate boundary conditions and, in particular, with integral boundary conditions. This will provide a means of calculating the Rebinder number from the transport and thermodynamic properties of the moist material. The Rebinder number at present is determined from experimental drying temperature curves.

The method of calculating heat and moisture transfer in the falling rate period can be improved by extending the two-region method of drying-rate calculations to heat-transfer calculations. A relationship can then be established between the relative drying coefficients, the equilibrium moisture content of the material, and the Rebinder number. Thus, in the very near future a direct connection will be established between analytical calculations of the system of differential heat- and mass-transfer equations and the engineering method of calculating the kinetics of the drying process with the aid of the drying coefficient and the Rebinder number. This is a very important and topical problem in drying theory.

4. Studies of the kinetics of the drying process usually involve an investigation of the distribution of moisture content and temperature within the drying material. The determination of the local values of temperature and moisture content entails the solution of the differential moisture- and heat-transfer equations. In this area of drying theory Soviet scientists lead the world. Scientists in the USSR were not only the first to derive a system of interrelated differential equations for energy and mass transfer in capillary-porous substances, but they have also obtained numerous solutions of these equations with the most diverse boundary conditions. It is not just by chance that one of the founders of the thermodynamics of irreversible processes, Professor de Groot, declared that in the Soviet Union "the analytical theory of the thermodynamics of irreversible processes was born as a result of studies of the dehydration of capillary-porous substances." It is only now that similar work is appearing in the West and this work is, in fact, a repetition of the work done in our country 10-15 years ago.

It should be noted, however, that the realization of the obtained solutions encounters considerable difficulties. One of the main reasons for this is the lack of experimental values for the transport coefficients. It is true that a number of papers published in recent years give quite reliable formulas for calculation of the moisture diffusion coefficient of a large number of moist materials. This work, on one hand, has brought the analytical solutions closer to the practical calculations but, on the other hand, has created certain difficulties. The fact is that the transport properties depend greatly on the moisture content and, hence, it follows that the system of differential transport equations becomes significantly nonlinear. This gives rise to an important task, which will take several years to accomplish – the solution of the system of transport equations by computer. Some work has been done on the solution of the system of transport equations by machine mathematics with due regard to the variation of the transport properties of the moist material, but the completion of this work will require several years more.

It is generally known that the above-mentioned system of transport equations is based on the classical laws of heat diffusion (Fourier law) and mass diffusion (Fick law) with the inclusion of the superimposed phenomenon of thermodiffusive moisture transfer. It follows from this that the hypothesis of infinite velocity of propagation of heat and mass is tacitly assumed. This hypothesis, however, is inconsistent with the physics of the transport phenomenon. While such a hypothesis does not introduce an appreciable error in the case of heat transfer (the period of relaxation of the heat stress in solids is of the order of 10^{-9}-10^{-11} sec, and the velocity of heat propagation is more than 1000 m/sec), the assumption of infinite mass-transfer velocity in the case of moisture transfer introduces a definite error. It is true that this error is excluded from the calculations by the experimental determination of the diffusion coefficients for each material. This, however, is one of the reasons for the pronounced nonlinearity of the transport equation and, hence, the difficulty of its analytical solution. A similar approach is adopted by investigators of the American school, in whose work the diffusion coefficient of capillary-porous substances (or the dispersion coefficient, as it is called in these investigations) is a function of the averaged intrapore velocity of motion of liquid moisture.

The finite velocity of motion of liquid, however, may be taken into account directly. In this case, as a fairly rigid thermodynamic calculation shows, the differential moisture diffusion equation is converted to a hyperbolic diffusion equation, into which the period of relaxation of the diffusion stress or velocity of mass propagation is introduced as an additional transport property. Such investigations were first carried out several years ago in the Soviet Union. A system of hyperbolic transport equations was obtained and it was solved for one-dimensional problems with different boundary conditions. These solutions were checked by direct experiments, and experimental data for the diffusion stress relaxation period were obtained. It is obvious that such investigations, both analytical and experimental, will continue. A new physical basis for the system of hyperbolic transport equations has recently been proposed. In this case the velocity of heat and mass motion acquires the sense of the velocity of movement of the Monge surface, which is the evaporation surface. We must, however, critically assess these trends of development in phenomenological transport theory and select the most rational for use in drying theory. Which is the better representation of the distributions of moisture content and temperature – the solution of a system of parabolic transport equations or a system of hyperbolic differential equations – must be decided by experiment. Both systems may have to be used, depending on the specific situation. This will be one of the important problems of drying theory in the forthcoming years.

5. The local values of the temperature and moisture content of the material during drying are very important for drying technology. The migration of vaporous and liquid moisture, and the transport of water-soluble substances within the drying material, depend on the gradients of moisture content, temperature,

and total pressure, and ultimately determine the technological properties of the dried material. This accounts for the importance of research on the mechanism of moisture transport in capillary-porous substances. The lull in this line of research in the early sixties was followed by a period of rapid development. Radioactive tracer techniques, γ-scopy, paramagnetic resonance, and other physical techniques for the investigation of transport mechanisms are now being widely used. In some studies investigations of moisture transport have been combined with an investigation of the energy of binding of the moisture with the moist material, with the energetics of evaporation, and so on. These investigations on the physics and chemistry of surface effects and disperse systems are essential for the further development of drying technology and such research must be encouraged and developed in every possible way. One must, however, criticize some of the trends in this field of research. The fact is that studies of the mechanism of transport in capillary-porous substances are based on the vapor diffusion law, including the Stefan flux, the law of capillary and film-type motion of a liquid, and the Darcy law for transport of a vapor–air mixture in capillaries and pores. A common model of a capillary-porous substance is an assembly of cylindrical capillary tubes and a porous medium is often modeled by spherical grains packed in a particular way. In the best case differential curves of volume and surface distribution of pores as regards capillary or pore radius are used. Attempts have been made on the basis of such a scheme to explain even the mechanism of drying and, in particular, the presence of critical points on the drying rate curves.

Unfortunately, the matter is not so simple. Firstly, as recent work has shown, a considerable contribution to the transfer of vaporous moisture in nonisothermal conditions (and drying processes in most cases involve a change of temperature in time and according to the coordinates of the material) is made by heat slip in the capillaries and pores. The magnitude of this molar transport is comparable with the Stefan flux. Recent work has shown the presence of a new form of molar transport – diffusion slip. The rate of this kind of transfer is directly proportional to the concentration gradient. The presence of heat and diffusion slip introduces an appreciable correction to the rate of migration of vaporous moisture. In addition, diffusion slip is one of the main reasons for the migration of a dissolved substance in the liquid moisture in a porous material. This opens up a new area of study of the transfer of water-soluble substances in drying, which is of great importance for the technological properties of the material being dried. But the matter does not end there. The structure of a capillary-porous substance creates a very complex type of moisture distribution in the presence of a total pressure gradient and the capillary potential gradient. It should be noted that until recently studies of the structure of capillary-porous substances and transport phenomena in them constituted a rather avant-garde area of drying theory. However, owing to the development of space technology, in which capillary-porous substances are widely used for the transport of liquid and energy (heat tubes) in weightless conditions, investigations on transport phenomena in capillary–porous substances have become main-line research, and it is essential that the results obtained should be assimilated into, and used as soon as possible in, studies of the kinetics and technology of drying.

It can be noted, in particular, that the mechanism of mass transfer in a capillary-porous substance involves not only the factors mentioned above, but also the following facts: 1) mixing due to barriers in the structure; 2) presence of autocorrelation in the flux; 3) recirculation due to regions of reduced pressure resulting from contractions and expansions; 4) dispersion of the flux due to the presence of blind pores; 5) hydrodynamic dispersion due to the velocity profile of the liquid in the capillary; and 6) dispersion due to second-order imperfections of structure. Second-order imperfections are all those structural properties which are not included in the concept of nonuniformity, heterogeneity (homogeneity), or anisotropy. The porous structure is determined by the permeability probability function, which depends on five independent variables (the position by three Cartesian coordinates and the orientation by two angular coordinates). The dispersion coefficient, or the diffusion coefficient, is a fourth-rank tensor in the general case. This short list of transport characteristics indicates the level of scientific research on mass transfer in capillary-porous substances in space-rocket technology. This research is of particular importance for the study of mass transfer in moist porous materials being dried in vacuum.

The investigation of heat and mass transfer in sublimation drying is of great interest. Despite systematic research in this field, the mechanism of energy and mass transfer is very obscure. Besides the detachment of solid particles from the surface of the body by sublimation, rarefaction waves and certain other specific effects are observed in certain regimes. Despite the complexity of the transport mechanism, however, one thing is clear – a full description of the evaporation process will involve not only the transport equations, but also the kinetics of the phase transition. Using the terminology of combustion theory, we must consider the evaporation process not only in the diffusion region, as is done at present, but also in the kinetic region and in the transitional diffusion-kinetic region.

Before concluding this critical review of research on drying technology mention must be made of the volume-stressed state of moist bodies and the reasons for the local and total destruction of the structure. Most of the work in this direction consists of phenomenological investigations, and very little work has been done on the mechanism of destruction due to molecular interaction of the moisture and material. This area of study is a part of modern physicochemical mechanics and rheophysics. While a fair amount of research on physicochemical mechanics is being carried out in the Soviet Union, little of it applies to drying. Hence, an important task in the forthcoming years is the study of the mechanism of destruction of moist substances during drying on the basis of modern physicochemical mechanics and rheophysics. These investigations will have to be closely linked with methods of selecting the optimum regime, since the ultimate aim of such investigations is to find the best method and conditions of drying.

We can surmise that in the next 10-15 years a sufficiently reliable method of selecting optimum regimes will be devised and this will obviate the need for the numerous investigations required for the selection of optimum drying regimes by purely empirical methods.

6. In speaking of the mechanism of moisture transfer up till now we have had in mind the effect of temperature, concentration, and pressure gradients on moisture transfer. Moisture transfer can be effected, however, by inhomogeneous acoustic, electric, and magnetic fields, and also by an alternating electromagnetic field. The investigation of the diffusion of moisture under the influence of these fields is an important problem for the immediate future.

It should be noted that a combined analysis of the variation of the thermophysical, hygrometric, and electrophysical characteristics with the moisture content of the material is now being used to determine the forms of binding of the moisture and material. To this complex of characteristics we will obviously have to add the magnetic properties of moist substances. The accumulation of experimental data on the complex physical characteristics and electromagnetic diffusion of moisture will lead to the application of new drying techniques involving the use of acoustic and electromagnetic fields. This is an urgent problem. At present we have driers which operate in randomly selected regimes. A decision regarding the advisability of extensive adoption of such driers and their economic profitability will require the expansion of all these lines of research on mass transfer in capillary-porous materials.

7. Studies of heat and mass transfer between the surface of a moist body and the surroundings, which is often called external heat and mass transfer, is of particular interest. We have already mentioned that the Newton convective heat-transfer law cannot be applied to drying in the falling rate period. A correct formulation of the problem reduces to solution of the so-called conjugate problem, where heat transfer between the surface of the body and the surroundings is treated as a problem of heat transfer in a boundary layer of liquid and in a solid with boundary conditions of the fourth kind.

A method of solving conjugate problems has now been devised, and several problems of convective heat transfer have been solved. It is important to note that the idea of solving convective heat-transfer problems as conjugate problems originated in the Soviet Union. It is of great importance not only for drying technology, but also for modern technology as a whole. It is not without reason that this method was used immediately by American scientists to solve some very complex problems of atomic energy and was introduced into the science of heat transfer.

The task of Soviet scientists is to develop this method in every way and to secure its wide application in drying theory. This is all the more important in that the physical formulation of the conjugate problem best reflects the actual process of energy and mass transfer between the surface of a body and the surroundings during drying. It is to be hoped that investigations on conjugate problems in drying will ultimately establish a qualitative and quantitative correlation between the Nusselt number and the moisture content of the body.

This important problem relates not only to drying theory, but also to the general theory of heat and mass transfer, and it will undoubtedly be resolved in the next 10-15 years.

A few other important trends in the field of external heat and mass transfer might have been mentioned, but they have several specific features and will not be discussed.

We should mention, however, that heat- and mass-transfer investigations should be conducted with varying external conditions, i.e., when the temperature, relative humidity, and velocity of the air vary continuously in the direction of the air flow. Such investigations will enable us to establish the laws of heat and mass transfer in varying drying conditions, which is extremely important. The fact is that most investigations on the kinetics and dynamics of the drying process are conducted in constant conditions, whereas in operating driers the parameters of the moist air vary continuously as the moisture evaporates from the material. The result is that the kinetic relationships obtained for drying on laboratory driers provide only a first approximation to conditions in industrial drying. This has led to a gap between the theory and practice of drying. This gap must be filled completely in the next 10-15 years in two ways. On one hand, investigations relating to drying theory will be conducted in varying conditions with analytical solutions of the corresponding conjugate problem and, on the other hand, engineers and operators will have to familiarize themselves more with drying theory and apply its achievement in their everyday work.

This account of future development, although brief and incomplete, gives some idea of the development of the science of drying of moist materials within the next few years.