WATER VAPOUR AND HEAT TRANSFERS IN GRAINS SILOS AND THEIR CONSEQUENCES ON STORAGE

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The preservation of grain quality during storage in aerated elevator and airtight or confined silos is chiefly depending on the temperature and the water content of the grains (Sinha, 1973). In experimental studies these parameters are generally kept constant (Pixton, Griffiths, 1971; Yaciuk and al., 1975). But even if this is possible in experimental conditions, it is not at all the case in practice. Very often some important gradients of temperature and water distribution occur in elevators, the consequence of which are moisture and heat transfers through bulk grains. Water content and temperature can increase in some particular points, inducing the development of molds and starting the alteration process.

In order to discuss these phenomena, it is previously necessary to describe the equilibrium state of water in grains. Then we will report the results of our studies on water and heat transfers in aerated conditions, discussing finally about some suggestions concerning airtight conditions.

1. THE EQUILIBRIUM STATE OF WATER IN GRAINS

1.1. Water adsorption in grains

Due to their high polarity, water molecules can easily form hydrogen bonds with polar groups of macromolecules like starch and proteins. The amount of water adsorbed is a function of the number and accessibility of these polar sites (Guilbot and al., 1961, 1979; Eagland, 1975).

When a thermodynamical equilibrium is reached it is common to define in the product the "Activity of Water" (A_W). This concept is closely correlated to the chemical potential of water (Morin, 1979), but it is easy to demonstrate that A_W is, in practice, with a very small error, equal to the relative humidity (R.H.) of intergranular air.

The affinity between cereal products and water (sometime called hygroscopicity) could be macroscopically depicted by sorption-desorption isotherms. Typical curves are shown in Figure 1, in which the A_W of the product (or the R.H. of air in equilibrium) is shown on the X-axis and the moisture content of the product is plotted on the Y-axis.



Fig. 1. Sorption (S) and desorption (D) isotherms curves of maize, for different temperatures.

One must emphazise that every point on these curves corresponds to a thermodynamical equilibrium state between product and surrounding atmosphere.

Sorption curves, the shape of which is generally sigmoidal for biological products, is mainly characterized by two properties :

- the desorption curve (obtained by a dehydration process of wet product) is higher than adsorption curve (humidification process of dry product); this fact generally called hysteresis, has no clear explanation;

- the curve, often called "isotherm", is depending of temperature : higher the temperature, lower is the moisture content for the same A_w .

Adsorption and desorption are respectively exo- and endothermic processes (corresponding to the energy of formation and rupture of hydrogen bonds).

1.2. Functionnal availability of water, and its role in storage technology

Very interesting for storage studies is the interpretation of sorption curves in terms of mobility and functionnal availability of water. The concept of "solvent water", has been established by Guilbot and Lindenberg (1960) and more recently by Duprat (1975). These authors have demonstrated that water fraction comprised between the sorption curve and its extrapolated linear part, shows marked solvent properties ; this water has a sufficient mobility to play the role of a diffusion medium for biochemical reactions. The fraction of water below the linear part, strongly bound, is un-available, and has no solvent pro- perties at all.

It has been shown that many reactions require a minimum quantity of "solvent water" to start and their speeds increase as a function of the amount of available "solvent water", e.g., enzymatic reactions (Loncin and al., 1968; Drapron, 1972), denaturation of proteins (Multon and Guilbot, 1975), carbohydrate gelification (Doublier and al., 1975), growth of microorganisms (Scott, 1957). Figure 2 shows the Aw threshold of the main types of alterations causes occuring in cereals.



Fig. 2. A_W threshold above or below which the biochemical reactions of alterations may occur in natural products.

Of course all the parameters characterizing the surrounding medium interact with A_W and it is advised to express faint differences in the principles shown on fig. 2 with respect to time, temperature and oxygen composition of atmosphere. For example, even if the grain is very wet, in lack of oxygen, fungi cannot grow, enzymatic oxydations (and particularly grains and bacterial respiration) cannot occur. This is the reason of the success of airtight storage.

On the other hand a lot of physical properties of grains and their components are also functions of the quantity of available water, and of A_W . Particularly important are : rheological behavior of wheat grains ; thermal characteristics, heat capacity and heat transfer coefficient, heat of hydration.

After this short recall on state of water in equilibrium with grains, let us now discuss on the consequences of non equilibrium conditions.

2. WATER AND HEAT TRANSFER IN GRAINS

Two different non equilibrium conditions can occur separately or simultaneously in bulk grains : water activity gradient, and or temperature gradient. The resulting phenomena - water and heat transfer - are very complicated and associate all together convection and conduction, desorption and condensation with corresponding heat exchanges.

As it has been recently shown by Troude (1979) in a general review, most authors have tried to modellize these phenomenon, and to describe them with appropriate equations. But these mathematical representations are unable to explain the mechanisms themselves. Following a different way, we have studied separately water and heat transfer in bulk grains, trying to explain them with regard to sorption properties.

2.1. Water activity gradients between maize grains

Generally speaking when a lot of grains is homogeneous and stabilized, the distribution of the moisture content of individual kernels is gaussian, with a variation coefficient comprised between 2 and 5 %; the mean value of the distribution is equal to the moisture content measured by ordinary oven methods (Beullier and Multon, 1976).

If two parcels of grains, the moisture contents of which are different, are mixed at the same temperature, there is between the grains a "water activity" gradient, associated to a difference of water vapour pressure in atmosphere in close contact with the grains ; it induces a water molecules transfer which go on, until "Activity of Water" would be the same in all grains (at that time, the moisture content of grains will be the same, in the limit of hysteresis effect).

We have studied these transfers in a confined and airtight atmosphere by measuring the change, as a function of time, of the distribution of moisture content among individual kernels (Beullier and Multon, 1976).

The figure 3 shows that in case of wet and dry grains just mixed (time zero), the two populations are well separated on the frequency histogramm ; after 1 to 3 days, the distribution is yet bimodal, and after 5 to 6 days, there is only one homogeneous gaussian population, where it is not possible to distinguish the original population from the mixture.

Therefore, 5 or 6 days are necessary to equilibrate the A_W between grains and a mechanical shaking of the grains does not quicken the process.

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Fig. 3. Change, as a function of time, of frequency distribution of moisture content of individual kernels in a mixture of wet and dry grains.

Similarly, in case of addition of liquid water into bulk grains, a minimum of 5 days is required in order to homogenize the sample.

Thus transfers of water vapour in grains, without temperature gradients, are very slow; when equilibrium is reached, a small dispersion of moisture content remains always and indefinitely between grains, due to hysteresis effect.

2.2. Temperature gradient

More often, cereals in bulk are subjected to a temperature gradient, for example :

one part of a silo is heated by sun, the other part is ir the shade;
in hot countries, at night, the grain in peripheric part of the silo is cooler than grain in the middle of the cell; it is the opposite during the day;
in a boat, grains in contact with the side and bottom of the hull are cooler than in the center.

In bulk grains, a gradient of temperature generates several phenomena :a heat transfer starts from hotter part towards cooler part

- a water transfer (mass transfer) takes place from hotter grains towards cooler grains, according to sorption equilibrium curves.

Therefore in certain places, temperature and or moisture content of grain can increase. If the availability of water becomes sufficient, bacteria and molds can multiply : their respiration (or fermentation at a lesser degree) produces water and heat, increasing again the availability of water. With such exploding process, alteration of grains can develop very quickly.

In order to have a better view of these phenomena, we have set up a pilot elevator in which a constant heat gradient was created; heat and water transfers were followed with appropriate sensors, as a function of time, during 80 days (Multon and al., 1980).

The cylindric metal elevator under a non heated shed, diameter 3.28 m, height 5 m, and capacity 35 metric tons, was equipped with 48 thermocouples and 6 hygrometric probes, connected with recorders. The elevator was filled with maize.

A spherical electric radiator, 22.25 cm diameter, located at the geometric center of the elevator was maintained at 60° C to simulate the effects of a localized heating in the grain. The gradient temperature was about 48° C between the surface of the radiator (60° C) and the walls of the elevator (12° C).



Fig. 4. Zones of thermal changes in artificial heating with radiator.

Changes of intergranular air temperature and relative humidity are very slow and were observed only in a zone (fig. 4) located above the radiator, never below.

This zone showed a curious shape of an inverted amphora, the bottom of which is the radiator; the top is the upper board of the elevator.

The grain layers within a few centimeters of the inner surfaces (zone B on fig.4) reflected the variations of outside temperature. But, in sectors other than A, B and a very limited adventitious point C, no variation in the grain temperature was noted.

At first temperature changes take place only above the radiator. Therefore, the heat transfer is induced, not by conduction or radiation, but by natural convection of intergranular air.

Considering the temperature sensors located vertically with regard to the radiator, we observe on fig. 5 that the increase of temperature starts much earlier near the radiator, but unexpectedly, nearer is the radiator and lower are the rate of increase and the maximum temperature reached (40°C for the nearest sensor, 53°C for the farthest one).



Fig. 5. Temperature changes as a function of time in artificial heating trial. (The place of sensor in the elevator, corresponding to each curve, is shown at right).

The connected changes in air relative humidity are shown on fig. 6. The three probes located horizontally show no change, except at the point in contact with the wall, which reflected the variations of the outside temperature.



Fig. 6. Intergranular relative humidity changes as a function of time in artificial heating trial. (The place of sensor in the elevator, corresponding to each curve, is shown at right).

Comparison between the simultaneous changes of temperature and R.H. shows that the arrival of the wave front of water vapour (R.H. increase) occurs about 10 days before the arrival of temperature front.

Samples taken during unloading of the elevator showed an increase of the moisture content of grains on the upper part, and indicated a high fungi growth, chiefly A. fumigatus, flavus, and Mucors.

In order to explain these complicated phenomena, both physical and biological, we may suggest the following hypothesis :

- When the radiator started to heat, the temperature of surrounding grains increases, inducing a water vapour desorption from grains ; then a convective phenomena takes place, the wet and hot air going up through kernels.

- Higher, in contact with colder layers of grains, the temperature of air decreases and its R.H. increases, as shown by probes (fig. 6) : then these grains adsorb water vapour and their moisture contents increase.

- Consecutively and gradualy, the slight amount of heat liberated by adsorption and the flow of heat coming from the radiator increase the intergranular air temperature, as shown by temperature probes (fig.5); A_W in grains is increased. - Wet and warm conditions being thus created, respiration of grains and microorganisms increases quickly, producing a high peak of temperature.

- The elevation of temperature induces a desorption, and again water vapour and heat go up ; vital phenomena are stopped ; temperature and R.H. decrease : the temperature tends to stabilize near 35° C, probably as a result of equilibrium

between heat flow coming from radiator and heat loss due to the convection.

These phenomenon, described on a point, spreads step by step, with an increasing intensity, from the radiator up to the top of the silo, where water vapour gathers : then moisture content of upper layers of grains increases (15 to 17 %).

Moisture increase and oxygenation near to the surface explain the development of molds, causing a great damage into grains.

Some other experiments were made with a "pocket" of very wet grains, instead of radiator, in order to simulate a natural heating. The behavior was quite different, even if there was also a convective migration toward the top of elevator.

CONCLUSION

Water and heat transfers described in aerated conditions are, of course, much more complicated when there are simultaneous gradients of water activity and temperature. In airtight conditions of storage, phenomenon are certainly quite different.

Concerning water vapour transfer, anaerobic storage changes probably nothing : according to Dalton's law, in a mixture of gas, each of them acts like if he was alone ; under vacuum, diffusion of water vapour would be accelerated. Concerning heat transfer, on the opposite, one can think that convection flow and heat exchanges could be decreased by vacuum.

After these first experimental approaches, a lot of work remains to do, concerning horizontal gradients, alternative gradients and airtight conditions. We are right now starting a new experiment with a more sophisticated device, with which we hope to improve our knowledge of these transfers.

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