Water activity and equilibrium relative humidity

What are they and why are they important to safe grain storage?

Len Caddick, CSIRO Stored Grain Research Laboratory

Water in grain
Equilibrium relative humidity
Water activity
Moisture isotherms
Cereals versus oilseeds
Safe storage limits

Water in stored grain has an important influence on quality changes that occur during storage. Bio-deterioration due to insect and mould activity and the rate that chemical and enzymatic processes take place within the grain are strongly related to water present inside and outside the grain.

Moisture content is a well recognised index of safe storage. Storage handlers are aware of management issues associated with bulk grain stored at a range of moisture contents. For example, cereals stored at 14 percent (%) moisture content without active cooling are at risk of quality loss. In this instance 14% of the total grain wet weight comprises water. Grain moisture content is the best indicator of drying costs and is the parameter used to market grain. Storage handlers however will often come across references in published information to water activity, relative humidity and equilibrium relative humidity. How do these terms relate to grain moisture content and to each other?

Water in grain

Water is present in grain in different states. Strongly bound water forms a chemical union with components of the grain complex and is difficult to remove, even under high temperature. In cereals, this form of bound water approximates 5 to 6% of the total moisture content. Water bound by molecular attraction is less tightly held and can be removed using high temperatures. Loosely bound water held by capillary action accounts for water present in cereal grains above 13 to 14% moisture content.

Water in a grain bulk is in a continually state of flux. Water which is not tightly bound to the grain substrate moves between grain and surrounding air. At some stage the continual movement of water from grain to the air, and air to the grain, will reach a state of equilibrium. Evening-out water within and between grains in bulk storage is a passive, slow process. When equilibrium is reached the amount of water bound or held to the grain substrate will not change as long as conditions - relative humidity and temperature - remain the same.

Forced movement of air through a bulk during drying or cooling processes rapidly change grain conditions. Cooling using aeration can be used to rapidly even-out both moisture and temperature in grain bulks.

Equilibrium relative humidity

The amount of water in the air, present as vapour, is described by the term relative humidity and is expressed as a percentage. The capacity of air to hold water is dependant on temperature, where warm air has a greater capacity to hold water than cold air. Air reaches saturation at 100% at which the vapour condenses to form water droplets. Relative humidity is the ratio between the amount of water the air is carrying and the amount it could carry at the same temperature when fully saturated. Equilibrium relative humidity (ERH) describes the amount of water in the air surrounding the grain when in equilibrium with water in the grain.

If air in contact with grain has a relative humidity lower than the equilibrium value, water is removed from the grain by air, reducing the grain moisture content and increasing the relative humidity of the air. Conversely, if the air in contact with grain has a relative humidity higher than the equilibrium value, the grain moisture content will be increased by the transfer of water from the air to grain.

Temperature also influences the behaviour of water in bulk grain. As temperature decreases, water is more tightly held to the grain substrate. For example, in cool grain, an ERH equal to 70% occurs at higher grain moisture contents, compared to warm grain. This characteristic can be used to advantage, particularly when storing grain at high moisture contents. Cooling grain using aeration enables wetter grain to be safely stored within limits.

Water activity

Water is present on the grain surface and present as water vapour in the interstitial spaces between grains influences the growth of moulds, insects and mites. The absolute water content of grain is less important to the majority of biological agents, except where development occurs within the grain substrate (endosperm or embryo tissue). The availability of water to insects and moulds present on stored grain is therefore better indicated by equilibrium relative humidity (ERH) or water activity (aw). ERH and aw are numerically the same, except ERH is expressed as a percentage and aw is given as a fraction of one, or percentage of saturation over pure water, aw = % relative humidity/100. For example, an ERH = 70% is equivalent to aw = 0.70.

Knowledge of the relationship between grain moisture content and ERH or water activity at different temperatures is important to understanding the limits of safe storage of grain. Moulds cannot develop when relative humidity is below 68%. For cereals, an ERH of 65% is considered a safe level for long-term storage. A lower ERH of 60% is recommended for oilseeds due to the risk of overheating during storage and susceptibility of the oil to quality loss.

The majority of stored grain insects are able to breed and develop at relative humidity levels below 60%. The only exception is psocids or booklice (Psocoptera). Mite (Acarina) pests of stored products also require relative humidity above 60% to successfully complete their development.

Moisture isotherms

A moisture isotherm describes the relationship between grain moisture content and ERH at a given temperature over a range of moisture levels. Data points obtained under controlled laboratory conditions are plotted onto a two-dimensional graph - grain moisture content versus ERH or water activity. The isotherm curve is calculated using regression analysis
to determine the least sum difference between data points and a "line of best fit". The "line of best fit" passes through the data points to form the isotherm curve. Figure 1 shows data plotted for Australian barley varieties. Data was determined under controlled conditions at 20 and 30°C.

Figure 1. Data plotted for Australian barley varieties at 20 and 30°C
Moisture content is often presented in isotherm graphs as percentage dry basis and needs to be converted to wet basis for practical storage management.

Cereals versus oilseeds
The moisture isotherm relationship is relatively straightforward for cereals, pulses and other seed types that contain low amounts of oil. Cereals, for example, contain about 2% oil. An example is shown in Figure 2 for Australian barley varieties at 20 and 30°C. Barley moisture content is shown as percentage wet basis and the values are plotted against ERH. The influence of temperature is also demonstrated. In this example, the safe moisture content recommended for barley stored at 20°C is approximately 1.2% higher than for 30°C. The difference is due to water being more tightly bound to the grain substrate at lower seed temperatures.

Figure 2. Moisture isotherm for Australian barley varieties at 20 and 30°C
The moisture isotherm relationship for oilseeds is more complicated since the amount of oil in the seed influences the behaviour of water in a bulk. The oil content in oilseeds can vary from 17% in soybeans, up to 50% in some new varieties of canola. Minimal amounts of water are absorbed by the oil fraction and the greater the oil content, the lower the total seed moisture level required to reach an ERH that can cause heating and loss of oil quality. A diagrammatic representation of the influence of oil content on the storage potential of canola is shown in Figure 3.
Figure 3. Three bins of canola produce the same ERH at a given temperature, even though moisture and oil contents differ.

Moisture content for oilseeds is often presented in isotherm graphs as percentage oil-free, dry basis (OFDB). To determine safe storage limits at specific oil and moisture contents, the moisture and oil values will need to be converted to wet basis. Where oilseed moisture content on an isotherm graph is not presented as OFDB, then the data has been derived from a single batch of seed, or batches of seed with the same oil content. Such data has limited value where oilseeds are received into bulk storage with varying oil contents. Australian canola varieties, for example, can vary in oil content (wet basis) from 35 to 50%.

**Safe storage limits**

The limit of safe long-term storage for cereals and oilseeds (ERH = 65% and ERH = 60% respectively) can be derived from a moisture isotherm curve. Conditions in a grain bulk typically vary during storage. In Australian temperate climatic zones, grain temperature is likely to range from 15 to 40°C during storage. The moisture content of freshly-harvested grain will also vary, and gradually equilibrates (evens-out) during storage. It is important that grain conditions do not exceed the threshold limit for mould development of ERH = 68%. Oilseeds stored in bulk are particularly susceptible to localised damage. The presence of temperature gradients, or differences in oil content, will result in different levels of water activity for oilseeds at the same moisture content. Therefore parts of an oilseed bulk can be at higher risk of heating and quality loss. Storage operators need to be aware that oilseeds are quite unique in this regard.

Safe storage limits for Australian canola varieties at 60% ERH and 25°C are given in Figure 4. Canola is at risk of quality loss when stored at conditions above the red line. For example canola with oil content of 35% can be safely stored at 8.5% moisture content. As oil content increases, the recommended safe moisture level decreases. Where canola with oil content of 50% is stored, the safe moisture level is 6.5%. At higher storage temperatures, the red line shown in Figure 4 will move downwards with canola becoming less storable. At lower storage temperatures, the red line will move upwards.

**Potential unsafe storage limits for Australian canola varieties at 60% ERH and 25°C**

Refer to Commodity Information for further details on the safe storage of cereals, pulses and oilseeds.