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Criteria of Determination of Safe Grain Storage Time – A Review

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1. Introduction

Cereals, before being consumed as food, go through the process of cultivation, harvesting, drying, preparation and marketing (including storage) all under natural conditions, and therefore, often involve microbiological contamination and infection (Abdullah et al., 2000).

Therefore it can be stated that grain starts deteriorating from the time of harvest, due to interactions between the physical, chemical and biological variables within the environment (Mason et al., 1997). Cereal grains just after being harvested contain microbial contamination coming from several sources, such as dust, water, ill plants, insects, solid, fertilisers and animal feces. Bacteria found in grains mainly belong to the families *Pseudomonadaceae*, *Micrococcaceae*, *Lactobacillaceae* and *Bacillaceae*, and moulds are mostly *Alternaria*, *Fusarium*, *Helminthosorium* and *Cladosporium*, although other genus can also be present. The microbial composition of the cereals is of great importance for the storage of grains, since at high moisture levels the microorganisms could grow and alter the properties of product (Laca et al., 2006). Grain deterioration is also related to respiration of the grain itself and of the accompanying microorganisms. The evolution of carbon dioxide, water and heat is associated with this respiration or deterioration (Steele et al., 1969).

A 13 % moisture content is considered to be the maximum value for the storage of wheat, corn, barley and rice during short periods, though temperature and oxygen concentration also play an important role (Laca et al., 2006).

Harvesting high moisture grain such as wheat, corn or rice has become, however, common practice to protect the grain from wet weather conditions which can cause weathering and mould infection of grain in the field. High moisture grain is susceptible to deterioration by microorganisms and hence should be dried before unacceptable quality loss occurs. A

knowledge of deterioration rates of high moisture grain under various storage conditions would help farmers and grain managers to know how quickly to dry the grain or adjust the storage conditions to prevent further quality loss (Kakunakaran et al., 2001). It is generally accepted that 5-15 % of the total weight of all cereals, oilseeds, and pulses is lost after harvest (Padin et al., 2002). Improved storage conditions would allow a 10 – 20 % increase in the supply of food available to people (Christiansen and Kaufmann, 1969).

Grain quality is critical in today's grain trade because of more stringent food-safety demands and an increase in market competition, therefore to avoid spoilage of grain during storage it is necessary to determine the safe grain storage time.

Safe storage time is the period of exposure of a product at a particular moisture content to a particular relative humidity and temperature below which crop deterioration may occur and beyond which the crop may be impaired. To keep losses low, crops must be dried to the safe storage moisture content (i. e. moisture content required for long term storage) within the safe storage time (Ekechukwu, 1999). Determination of safe grain storage time is an answer to the following question: how long can grains of particular moisture content and temperature be stored without the risk of the quality deterioration (Ryniecki, 2006).

Known in the bibliography of the subject are tables and graphs of the storage times. Sometimes, however, mathematical formulas are more useful. They can be easily incorporated into the mathematical models of grain drying or aeration and expert systems which are aids for storage-grain management (Arinze et al., 1993; Courtois, 1995; Fleurat-Lessard, 2002; Kalleta, 1996). Such formulas known in the bibliography of the subject and own formulas developed by the authors of the chapter are presented in the paper.

To test the effect of grain parameters on the safe storage period, three criteria have been applied: carbon dioxide (CO₂) production and dry matter loss, appearance of visible moulds, and germination capacity.

2. Carbon dioxide production and dry matter loss

Grain deterioration is related to respiration of the grain itself and of the accompanying microorganisms. Respiration is the process of oxidizing (combusting) carbohydrates and yielding carbon dioxide, water vapour and energy. Therefore, respiration consumes dry matter.

The complete combustion (aerobic respiration) of a typical carbohydrate such as starch is represented by the following equation:

According to this equation during the breakdown of 1 g of dry matter by aerobic respiration using 1.07 g of oxygen, 1.47 g of carbon dioxide, 0.6 g of water, and 15.4 kJ of heat energy are released. It means that a 1 % loss in grain dry matter carbohydrate is accompanied by the

evolution of 14.7 g of carbon dioxide per kg of grain matter. Therefore respiration rate is closely related to grain dry matter loss and, consequently, global quality loss. Modelling CO₂ production can be used to simplify the prediction of rate of quality loss, assuming predominantly aerobic respiration.

Contamination of harvested grain by microorganisms is natural and permanent. In temperate climates with medium wet or moist grain at harvest, the genera *Fusarium*, *Alternaria* and *Helmintosporium* (called “field flora”) are predominant. During long term storage, xerophilic fungi of the genera *Aspergillus* and *Penicillium* (called “storage flora”) progressively replace the “field flora” over a period of several months of storage. At 15-19 % moisture content, most species of the field flora are inhibited or die whereas storage flora species slowly grow (Fleurat-Lessard, 2002; Frisvad, 1995; Pelhate, 1988). Since the respiratory processes of microorganisms or of hidden insect infestation are similar to those of the grain itself, the combustion of carbohydrates is a representation of grain, microorganisms and insect respiration (Fleurat-Lessard, 2002; Sinha et al., 1986; Steele et al., 1969).

The following mathematical formulas for predicting carbon dioxide production and dry matter loss can be found in the bibliography of the subject.

White et al. (1982) carried out numerous experiments on the carbon dioxide release rates of wheat and developed the following equation for general prediction of the instant rate of CO₂ release from grain:

$$X = a + bT + ct + dt^2 + eM_w \quad (2)$$

where X is the rate of CO₂ production in mg kg⁻¹d. m. per 24-h period, T is the grain temperature in °C, t is the time in h, M_w is the grain moisture content in % w. b., and a , b , c , d , and e are empirical constants.

The following equation was developed by Srour (1988):

$$X = \exp(aM_w + bT + c) \quad (3)$$

where X is the rate of CO₂ production in mg (100 gd. m.)⁻¹ per 24-h period, M_w is the grain moisture content in % w. b., T is the grain temperature in °C, and a , b , and c are empirical constants.

Karunakaran et al. (2001) determined the deterioration rate of wheat stored at 25°C by measuring the respiration rate of grain and microorganisms. The measured rates of CO₂ production during storage at 17, 18, and 19 % m.c. wet basis were combined and fitted to the following equation:

$$\ln X = -15.56 + 0.21t - 0.004t^2 + 1.08M_w \quad (4)$$

where X is the rate of CO_2 production in $\text{mg d}^{-1} \text{ kg}^{-1} \text{ d. m.}$, t is the storage time in d, and M_w is the moisture content in % w. b.

There are however some problems in using equations (2) - (4) to describe quality changes. They are based on the measurement of CO_2 release rate, either from a grain sample or directly in a grain bin. Such measurements can be done using sophisticated equipment and in laboratory conditions. Additionally, when grain moisture is below 14 % (w. b.) the release rate is very low and therefore it is very difficult to measure it. However, the above formulas are not useful in prediction the storage life.

Another option for the prediction of safe storage life is the calculation of dry matter loss (DML) as a function of grain temperature, grain moisture content, and storage time.

Seib et al. (1980) stated that the amount of dry matter loss from respiration is an indication of grain quality. They also stated that rough rice stored at 15 % and 18 % w. b. moisture content fell below U. S. Grade Nos. 1 and 2 if DML exceed 0.75 %. Some authors assumed that an acceptable level of dry matter loss is 0.5 %. In high moisture maize (corn, 25 % m.c.) a loss of 0.5 % dry matter can occur in 7 days, sometime without any visible moulding. However, this way found to be sufficient to render maize grain unfit for use, and also to produce aflatoxins (Marin et al., 1999). Kreyger (1972) considered grain to be fit for animal feed with DML of up to <2 %. However, Hall and Dean (1978) suggested 1 % DML was acceptable in grain for food use and that this could be applied to both wheat and maize. White et al. (1982) stated that 0.1 % was unacceptable for wheat of premium grade and proposed the absolute limit of DML at 0.04 %. Therefore the problem of what is the limit for an acceptable level of dry matter loss is still controversial.

Seib et al. (1980) developed the following expression to determine DML of long-grain rough rice as a function of grain temperature, grain moisture content, and storage time:

$$\text{DML} = 1 - \exp\left\{-At^C \exp\left[D(1.8T - 28)\right] \exp\left[E(M_w - 0.14)\right]\right\} \quad (5)$$

where DML is the dry matter loss in decimal form, t is the storage time in $\text{h } 10^{-3}$, T is the grain temperature in $^{\circ}\text{C}$, M_w is the grain moisture content in decimal w. b., and A , C , D , and E are empirical constants.

Equation (5) was developed for rice with constant airflow being forced through the grain and for the average grain temperature and the average grain moisture content over the storage time in question. The aerobic conditions were moreover assumed. When rice is stored in airtight units a shortage of O_2 would decrease the respiration rate as well as decrease the rate of DML. Therefore, for bunker conditions, equation (5) would be expected to overestimate the actual DML since it was based on the premise of having adequate O_2 to be used by the respiration process (Freer et al., 1990; Hu et al., 2003).

Weinberg et al. (2008) examined the effect of various moisture contents on the quality of maize (corn) grains in self-regulated modified atmospheres during hermetic storage. The ex-

periments were conducted *in vitro*. Maize at 14, 16, 18, 20 and 22 % m.c. was initially conditioned for 28 days in tightly wrapped plastic bags and then stored in sealed containers at 30°C for up to 75 days. Carbon dioxide produced within the containers replaced the oxygen. As the moisture content increased the time for O₂ depletion shortened, from 600 h at 14 % m.c. to 12 h at 22 %. The maize at 20 and 22 % m.c. exhibited the highest DML (0.59 % and 0.74 % respectively after 75 days) and the maize at 14 and 16 % m.c. the lowest (0.02 % and 0.15 %). Adhikarinayake et al. (2006) found out that during airtight storage of 14 % m.c. paddy in a ferro-cement bin, oxygen concentration dropped to 2.7 % within 30 days and carbon dioxide rose to 9.1 %. After 6 months storage, DML was 0.4 %. Varnova et al. (1995) noted that a sealed bulk of barley declined to 4 % O₂ after 50 days.

When grain temperature and moisture content cannot be assumed constant for the entire storage time used, the method of rates was used to calculate DML (Freer et al., 1990):

$$d(\text{DML})/dt = ACt^{(C-1)}e^ye^ze^{-xe^ye^z} \quad (6)$$

where $x=At^C$, $y=D(1.8T-28)$, $z=E(M_w-0.14)$

The values of the constants for long-grain rough rice used in the equations (5) and (6) were found to be (Seib et al., 1980): $A=0.001889$, $C=0.7101$, $D=0.02740$, $E=31.63$.

Thompson (1972) took into account negative influence of mechanical damages on dry matter loss and obtained the following expression to determine the DML (in %) of shelled corn:

$$\text{DML} = 0.0883(\exp 0.006t_r - 1) + 0.00102t_r \quad (7)$$

where:

$$t_r = \frac{t}{M_M \cdot M_T \cdot M_D} \quad (8)$$

$$M_M = 0.103 \left\{ \exp \left[455(100M)^{-1.53} \right] - 0.845M + 1.558 \right\} \text{ for } 0.149 \leq M \leq 0.538 \text{ kg H}_2\text{O} \cdot \text{kg}^{-1} \text{ d.m.} \quad (9)$$

$$M_T = 32.3 \exp \left[-3.48(0.03T + 0.53) \right] \text{ for } T \leq 15.6^\circ\text{C or } M_w \leq 19\% \quad (10)$$

$$M_T = 32.3 \exp \left[-3.48(0.03T + 0.53) \right] + 0.01(M_w - 19) \exp \left[0.61(0.03T - 0.47) \right] \quad (11)$$

for $T > 15.6^\circ\text{C}$ and $19 < M_w \leq 28\%$

$$M_T = 32.3 \exp[-3.48(0.03T + 0.53)] + 0.09 \exp[0.61(0.03T - 0.47)] \quad (12)$$

for $T > 15.6^\circ\text{C}$ and $M_w > 28\%$

$$M_D = 0.001(\text{MD})^2 - 0.1101(\text{MD}) + 3.426 \text{ for } 2\% \leq \text{MD} \leq 40\% \quad (13)$$

(equation (13) is developed by authors of the chapter on the basis of Steele et al. (1969) data)

where T is the grain temperature in $^\circ\text{C}$, M_w is the grain moisture content in % w. b., t is the storage time in h, M_M is the moisture multiplier, M_T is the temperature multiplier, M_D is the mechanical damage multiplier, and MD is the mechanical damage in %.

Scherer et al. (1980) investigated the dry matter loss of corn. Based on their data we developed the following relationship between monthly DML, grain temperature and grain moisture content:

$$\text{DML} = 6.479 - 0.339T - 0.498M_w + 0.002T^2 + 0.015TM_w + 0.009M_w^2 \quad (R^2 = 0.9530) \quad (14)$$

where DML is the monthly dry matter loss in %, T is the grain temperature in $^\circ\text{C}$, M_w is the grain moisture content in % w. b., and $5^\circ\text{C} \leq T \leq 20^\circ\text{C}$, $14\% \text{ w. b.} \leq M_w \leq 35\% \text{ w. b.}$

From equation (5) and from Scherer (1980) data increase in the dry matter loss with the increase of both grain temperature and moisture content can be observed. In such conditions the respiration of grains is more intensive. DML increase with the duration of the grain storage.

Scherer's et al. (1980) investigations on damaged grain confirmed the negative influence of mechanical damages on dry matter loss shown by Thompson (1972). Scherer et al. (1980) stated that increase in amount of damaged corn caused the decrease in safe storage time. They accepted the limit of DML at 0.5 % and observed that 1 % of damaged grain together with 1 % of chaff and fines reduced the safe storage time in almost 6 %, however 20 % of damaged grain and 5 % of chaff and fines reduced the time in almost 38 %. They explained obtained results by more intensive respiration of chaff and fines, and damaged grain comparing with undamaged grain.

Brooker et al. (1974) assumed for stored corn the limit of DML at 1 %. Based on their data the following relationship between safe storage time, grain temperature and grain moisture content can be presented:

$$t = 3774.98 - 88.12T - 252.55M_w + 0.587T^2 + 2.686TM_w + 4.223M_w^2 \quad (R^2 = 0.861) \quad (15)$$

where t is the storage time in d, T is the grain temperature in °C, M_w is the grain moisture content in % w. b., and $1^\circ\text{C} \leq T \leq 24^\circ\text{C}$, $15\% \text{ w. b.} \leq M_w \leq 30\% \text{ w. b.}$

Al-Yahya (2001) examined the conditions of safe storage of wheat. Based on these data the following relationship between storage time, grain temperature, grain moisture content and DML can be presented:

$$t = \exp(6.490336 - 0.024165T - 0.163337M_w + 1.292568(\text{DML})) \quad (R^2 = 0.9393) \quad (16)$$

where t is the storage time in d, T is the grain temperature in °C, M_w is the grain moisture content in % w. b., DML is the dry matter loss in %, and $4^\circ\text{C} \leq T \leq 40^\circ\text{C}$, $15\% \text{ w. b.} \leq M_w \leq 24\% \text{ w. b.}$, $0.25\% \leq \text{DML} \leq 1\%$.

From Brooker et al. (1974) data and from Al-Yahya's (2001) data increase in the safe storage time of grains with the decrease of both grain temperature and moisture content can be observed. In such conditions the respiration of grains is less intensive.

According to equation (1) heat energy is released during the respiratory process of grain, microorganisms and insects. The heat produced within the pockets of wet grain is especially harmful. It is not dissipated rapidly because of the low thermal conductivity of the grain (Kaleta, 1999; Kaleta and Górnicki, 2011) and the slow free convection currents in the granular bulk. The elevated grain temperature and moisture content of the pocked provide a favourable environment for further growth of microorganisms, thereby making the heating process self-accelerating. Heat production in stored grain ecosystems was investigated by e. g. Cofie-Agblor et al. (1997), Karunakaran et al. (2001), Scherer et al. (1980), and Zhang et al. (1992). Wilson (1999) proposed a mathematical model for predicting mould growth and subsequent heat generation in bulk stored grain. Unlike previous models, it was intended to be applicable in conditions that change with time. Starting from a model for mould growth in varying conditions the work of a number of authors was combined to produce a model to predict the heat production at all parts in a grain bulk. The effect of temperature and relative humidity on the mould growth rate was decoupled, so that the resulting equation for mould growth was a product of one-parameter terms. The heat generation rate was then written as a specific function of the mould population and mould grow rate. The model's current predictions for very wet grains was good, but for dried grain model performs less well.

3. Appearance of visible moulds

Spoilage of grains is the result of microorganisms (bacteria, yeast, fungi, and moulds) utilizing the nutrients present in the grain for growth and reproductive processes, spoilage may result in a loss of nutrients from the grain since microorganisms use these nutrients in much the same way as livestock. Also, microorganisms produce heat and moisture during growth which can cause a temperature rise in stored grain. Heating initiated by microbial growth

can cause “heat damage” and can sometimes render grain unfit for feed. Such conditions have been known to cause fires and dust explosions in storage structures (Ross et al., 1979).

Certain microorganisms, when allowed to grow under the proper environmental conditions, can produce toxins or other products which, if consumed by either livestock or humans, can cause serious illness and even death. A number of these toxins and the microorganisms which produce them have been identified.

Toxigenic fungi infect agricultural crops both in the field and in storage. Converse et al. (1973) found the following variety of fungi in the corn at harvest and after 28 days of aeration in bins: *Fusarium*, *Cephalosporium*, *Alternaria*, *Cladosporium*, *Mucor*, *Nigrospora*, *Penicillium*, *Aspergillus flavus*, *A. glaucus*, *A. niger*, and *A. ochraceus*. Pronyk et al. (2006) noted that initial fungal counts showed that canola seeds were infected with high levels of pre-harvest fungi *Alternaria alternata*(Fr.) Keissl. and *Cladosporium* spp. and low levels of storage fungi *Eurotium* spp., *Aspergillus candidus* Link, and *Penicillium* spp.

Fungal infections can be discolour grain, change its chemical and nutritional characteristics, reduce germination and, most importantly, contaminate it with mycotoxins, the poisonous metabolites produced by certain fungal genera.

Ergot is a disease of cereal crops caused by the fungus *Claviceps purpurea*. It causes reduced yield and quality of grain. The effect of the ergot’s alkaloid toxins on man and animals is, however, of much greater significance (Moreda and Ruiz-Altisent, 2011).

Aflatoxins are secondary metabolites produced by *Aspergillus flavus* Link and *A. parasiticus* Speare. These compounds are only few of over 120 mycotoxins produced by fungi. The aflatoxin’s dietary effect upon poultry can result in poor growth, increased mortality, poor feed conversion, and increased condemnations. A number of other animal species are also subject to aflatoxicosis. Aflatoxin has been known to act as a potent toxin, a carcinogen, a teratogen, and a mutagen (Brekke et al., 1977; Liu et al., 2006; Wieman et al., 1986).

The fumonisins are secondary metabolites produced by *Fusarium moniliforme* Sheldon and *F. proliferatum* (Matsushima) Nirenberg. They show a worldwide distribution and can be isolated from maize and maize-based food and foodstuffs naturally contaminated with *Fusarium*. The fumonisins have been associated with leukoencephalomalacia (ELEM) in equines, porcine pulmonary edema (PPE), diarrhea and reduced body weight in broiler chicks, carcinogenicity in rats and leukoencephalomalacia and hemorrhage in the brain of rabbits. In addition, epidemiological evidence suggest a correlation between the consumption of *F. moniliforme* contaminated maize and a high incidence of human esophageal carcinoma (Marin et al., 1999; Orsi et al., 2000).

Mites also infect stored cereals. These arthropods contaminate grains and are a matter of great concern in the medical and veterinary fields, since they may act as carriers of bacteria and toxigenic fungi. Grains contaminated by mites may cause acute enteritis when ingested, and severe dermatitis and allergy in cereal handlers. Furthermore, mites can feed on the germ of kernels, thereby reducing the content of iron and vitamins of the B complex and germination ability. Stored – product mites can survive and multiply by feeding on several

species of seed – borne fungi. Fungal spores and mycelia contain small amounts of essential nutrients (e. g. vitamins of the B complex and steroids), and moisture levels adequate for the metabolic demands of mites. The constant migration of mite populations within a granary ecosystem efficiently contributes to the dispersal of viable fungal spores of several species, including *Aspergillus* spp. and *Penicillium* spp., carried on the vector's body surface or deposited with its feces (Franzolin et al., 1999).

Conditions favouring the development of mycotoxins in cereals before and after harvest are important to grain – exporting countries concerned with marketing high – quality products. In post-harvest situation, crop spoilage, fungal growth, and mycotoxin formulation result from the interaction of several factors in the storage environment. These factors include: moisture, temperature, time, insect vectors, damage to the seed, oxygen levels, composition of substrate, fungal infection level, prevalence of toxigenic strains of fungi, and microbiological interactions. An understanding of the interactions involved would facilitate prediction and prevention of mycotoxin development in grains (Abramson et al., 2005).

Investigations of conditions favouring the development of mycotoxins in grains before and after harvest were carried out by many researches for the following grains: barley (Abramson et al., 1999; Gawrysiak-Witulska et al., 2008), canola (Pronyk et al., 2006), maize (corn) (Franzolin et al., 1999; Liu et al., 2006; Marin et al., 1999; Orsi et al., 2000; Reed et al., 2007; Wicklow et al., 1998), rice (Liu et al., 2006; Abdullah et al., 2000), wheat (Abramson et al., 2005; Padin et al., 2002).

Abramson et al. (1999) stated that ochratoxin A, citrinin and sterigmatocystin reached mean levels of 24.38 and 411 ppb by 20 weeks in the 19 % moisture content barley, but were absent in the 15 % m.c. barley, and no other mycotoxins were detected. *Penicillium* species and *Aspergillus versicolor* (Vuill.) Tiraboschi comprised the predominant microflora. The effect of storage time was apparent at both 15 and 19 % moisture content for grain temperature, *Alternaria alternata* (Fr.) Keissler, *Penicillium* species and *Aspergillus versicolor*. At 19 % moisture content, storage time also affected moisture content, CO₂ level, ergosterol content, seed germination, and mycotoxin production. At 19 % m.c., elevated ergosterol levels at weeks 4 and 8 appears to offer early warning of the appearance of sterigmatocystin at week 12, and of ochratoxin A and citrinin at week 20.

Pronyk et al. (2006) found that total ergosterol (fungal – specific membrane lipid used as an indicator of fungal infection in grain) levels in stored canola increased with storage time, temperature, and seed moisture content.

Liu et al. (2006) noted that no significant linear relationship existed in whole grain rice and brown rice between the amount of aflatoxins and the length of storage. The amount of aflatoxins in whole grain rice samples from 1 to 10 yr ranged from 2.79 to 2.93 µg kg⁻¹ and peaked in the samples that were storage for 7-8 yr (6.23 µg kg⁻¹). With increasing storage length, the aflatoxin content in brown rice was consistently low ranging from 0.74 to 1.19 µg kg⁻¹. However, in maize samples, the amount of aflatoxins significantly increased with storage length. The average amount of aflatoxins in 1-yr maize was only 0.84 µg kg⁻¹, while in 2-

yr maize it was as high as $1.17 \mu\text{g kg}^{-1}$. Practically, no maize grains were kept in storage for more than 3 yr.

Franzolin et al. (1999) examined the ability of mites of the species *Tyrophagus putrescentiae* to spread the toxigenic fungus *Aspergillus flavus* from contaminated maize to sterile grains under controlled conditions. The obtained results confirms that *T. putrescentiae* is a means of dispersal for toxigenic fungi in stored grain kept under warm and moist conditions. The levels of aflatoxin contamination recorded after 90 days of incubation exceeded the safe limits established by Brazilian legislation.

Abdullah et al. (2000) examined the average numbers of days before visible fungal development at 25°C on, among others, ordinary rice and glutinous rice. They found that ordinary rice at 13.0 % moisture content (d. b.) and glutinous rice at 12.9 % m.c. (d. b.) would be safe for about 2 months (57 ± 2 days and 73 ± 1 days respectively). However, ordinary rice at 14.1 % m.c. and glutinous rice at 14.2 % m.c. may spoil in about 20 days. Hence, an error in the moisture content of 1.1 % for rice and 1.3 % for glutinous rice is disastrous. At 21.9 % m.c. ordinary rice and 25.6 % m.c. glutinous rice the data indicated a shelf-life of about 7 days.

Abramson et al. (2005) stated that ochratoxin A and citrinin reached mean levels of 6.5 and 11.6 mg kg^{-1} , respectively, by 20 weeks at 20 % m.c., but were absent at 16 % m.c., and no other mycotoxins were found. *Penicillium* species were the predominant microflora. Ergosterol levels remained between 3.9 and 8.4 mg kg^{-1} at 16 % m.c., but increased from 3.9 to 55.5 mg kg^{-1} at 20 % m.c. during 20-week trial period.

There is, however, lack of simple equations predicting the length of safe storage period by a combination of, at least, moisture content of grain and storage temperature.

Bailey and Smith (1982) (cited after Bowden et al. (1983)) developed the following empirical formula predicting the duration of a safe barley storage period without occurrence of visible mould under the good aeration conditions:

$$t = 67 + \exp \left\{ 5.124 + (39.6 - 0.8107T) \left[(M_w - 12)^{-1} - 0.0315 \exp 0.0579T \right] \right\} \quad (17)$$

where t is the storage time in h, T is the grain temperature in $^{\circ}\text{C}$, M_w is the grain moisture content in % w. b., and $5^{\circ}\text{C} \leq T \leq 25^{\circ}\text{C}$, $16 \% \text{ w. b.} \leq M_w \leq 26 \% \text{ w. b.}$

Kreyger (1972) investigated the safe storage times of several grains. He assumed that the best criterion for safe storage times is the one that is based on the time to the appearance of visible moulds. Based on Kreyger's (1972) data, we developed the following formula:

$$t = \exp(A + BT + CM_w) \quad (18)$$

where t is the storage time in weeks, T is the grain temperature in $^{\circ}\text{C}$, M_w is the grain moisture content in % w. b., A , B , C are empirical constants given in Table 1, and $10^{\circ}\text{C} \leq T \leq 25^{\circ}\text{C}$.

Grain	Coefficients			R^2	Range of application
	A	B	C		
wheat	50.66928	-0.272909	-2.52755	0.9707	16.1 %w.b. $\leq M_w \leq 23.0$ %w.b.
barley	27.04320	-0.174362	-1.17856	0.9727	15.6. %w.b. $\leq M_w \leq 22.7$ %w.b.
oats	31.60300	-0.201594	-1.55997	0.9728	14.8 %w.b. $\leq M_w \leq 22.0$ %w.b.
rye	34.58371	-0.283607	-1.58288	0.9779	15.4 %w.b. $\leq M_w \leq 24.4$ %w.b.

Table 1. Values of coefficients in equation (18) and range of application

Equation (17) and (18) confirm that the duration of the safe storage time increases with the decrease of both grain temperature and grain moisture content. Such conditions are not favourable for the mould development.

There are, however, controversies about the criterion of appearance of visible moulds. Several researches (Ryniecki and Nellist, 1991; Nellist, 1998), followed Kreyger (1972), took it as the best criterion for safe storage time. Some of them (Armitage, 1986; Fleurat-Lessard, 2002) mentioned, however, several drawbacks of this criterion. The main drawback of this kind of prediction of safe storage life of stored grain is the subjective determination of visible mould on the kernel. Another drawback is the lack of progressiveness in the prediction. Before the onset of visible spoilage, grain is theoretically sound and its quality is not altered. The day after spoilage is seen, the grain is deteriorated and should be downgraded.

4. Germination capacity

Various factors can reduce the storage life of some premium grade quality cereals. Moisture content of the harvested grains and storage temperature can encourage mould and insect pest damage. The best studied quality parameter is germination capacity, which is only of direct importance for grains. Nevertheless, this is probably the best surrogate measure of cereal grain soundness (Pomeranz, 1982). Cereals retaining a high level of viability in storage are also likely to retain the other main parameters of commercial or technological quality (Fleurat-Lessard, 2002).

Germination is defined as the appearance of the first signs of growth, i. e. the visible protrusion of the radical (Black, 1970). Germination can be affected by many factors such as grain temperature, grain moisture content, grain damages, fungus and insect infection. Much research has been conducted to determine the effect of various factors on germination.

McNeal (1966) found that soybean can be kept for 12 months without an expressive decline in germination if the temperature is kept below 16°C and the moisture content is not higher than 16.2 %, dry basis. Mayeux et al. (1972) noted that the germination of soybean seed is influenced by the percentage of split beans in stored seed, and storage temperature and moisture play an important role in maintaining the soybean seed quality. Kreyger (1972)

used percentage germination as an indicator of grain deterioration. He studied the effect of many levels of grain moisture content and grain temperature on the percentage germination. His findings will be discussed below.

Parde et al. (2002) studied the storage behaviour of soybean seed and the loss in quality due to free-fall from different heights (0.5-2 m) on to different surfaces (cement and galvanized iron) were studied. They found that soybean seed is susceptible to mechanical damage. The severity of damage varies with moisture content of seed because the dryer seed is harder. The height of fall produces significant effects on germination. An average germination loss of 10 % and 31 % was noticed when the seed fell from a height of 1 and 2 m, respectively, on to the cement floor. This drop in germination was 7.5 % and 22 % when dropped from the same heights on to galvanized floor. The seed lots held at 12 % moisture content, dry basis, suffered less damage during free-fall from different heights than the lots held at 10 % and 11 % m.c. Soybean seed lots at 12 % m.c. retained germination ability for a longer period than the seed lots at lower m.c.

Pronyk et al. (2006) stated that germination decreased with storage time, temperature, and moisture content. After 56 days, germination of canola stored at 12 % m.c., wet basis and at 25-30°C dropped till 73 %. The same value of germination stored: at 12 % m.c. and at 30-35°C showed after approximately 27 days, at 14 % m.c. and at 25-30°C showed after 29 days, at 14 % m.c. and at 30-35°C showed after 12 days.

Weinberg et al. (2008) examined the germination percentage of the maize (corn) stored in the self-regulated atmospheres in the sealed containers. They noticed that the germination percentage decreased during the storage period, and decreased as the moisture content increased. With 18 % m.c. and above the germination percentage decreased to zero after 35 days of storage.

Genkawa et al. (2008) tested airtight storage of brown rice with a low moisture content. They stated that the germination rate of brown rice with 16.2 % m.c., wet basis, at 25°C declined from 97 % to 27 % but for rice with less than 12.8 % m.c. at 25°C germination was above 90 %.

There is, however, lack of simple equations predicting the length of safe storage period by combination of, at least, moisture content of grain and storage temperature.

Fraser and Muir (1981) developed a set of two regression equations for predicting allowable storage times for wheat before the germination capacity drops by 5 %:

$$\begin{aligned} \log t &= 6.234 - 0.2118 M_w - 0.0527 T, \text{ for } 12 \% \text{ w.b.} \leq M_w < 19 \% \text{ w.b.} \quad (a) \\ \log t &= 4.129 - 0.0997 M_w - 0.0576 T, \text{ for } 19 \% \text{ w.b.} \leq M_w \leq 24 \% \text{ w.b.} \quad (b) \end{aligned} \quad (19)$$

where t is the storage time in d, M_w is the grain moisture content in % w. b., T is the grain temperature in °C, and $10^\circ\text{C} \leq T \leq 40^\circ\text{C}$.

Kaletka (1996) used equation (19) in her computer program developed to simulate wheat drying in silos with radial (horizontal) and vertical airflow, predict grain spoilage under the si-

ulated conditions, and determine the most advantageous conditions of conducting the process of wheat drying in silos.

Muir and Sinha (1986) developed a set of two regression equations for predicting allowable storage times for canola before the germination capacity drops by 5 %.

$$\begin{aligned}\log t &= 6.224 - 0.302 M_w - 0.069 T, \text{ for } M_w < 11 \% \text{ w.b. (a)} \\ \log t &= 5.278 - 0.206 M_w - 0.063 T, \text{ for } M_w \geq 11 \% \text{ w.b. (b)}\end{aligned}\quad (20)$$

where t is the storage time in d, M_w is the grain moisture content in % w. b., T is the grain temperature in °C, and $10^\circ\text{C} \leq T \leq 40^\circ\text{C}$.

Arinze et al. (1993) used equation (20) in their computer program developed to simulate in-bin drying of canola grain, predict grain spoilage under the simulated conditions, and obtain an economic analysis of various drying schemes for canola for use as a management tool in the selection of the appropriate drying system. Equation (20) predicts the allowable storage times when canola is stored at constant temperatures and moisture contents. During a drying process, however, both temperature and moisture content vary with time. To predict grain spoilage or deterioration under dynamic or changing conditions, Arinze et al. (1993) used spoilage index (SI). A value of t was computed at each interval Δt from equation (20), and the calculated ratios of $\Delta t/t$ were calculated. Theoretically, grain loses 5 % of its germination when the sum of the computed $\Delta t/t$ values for each layer over the simulated drying period equals unity:

$$\text{SI} = \sum_{i=1}^n \left(\frac{\Delta t}{t} \right)_i = 1 \quad (21)$$

where n is the number of simulated time steps. SI is a spoilage or storage index and its instantaneous value represents the progress of grain spoilage. A spoilage index of 1 or greater indicates that the allowable storage time has elapsed and the 5 % loss in germination has occurred to the canola.

Karunakaran et al. (2001) defined the safe storage time of wheat as the storage time for the germination to decrease to 90 % and developed the following correlation equation for 19 % m.c., wet basis, wheat at 10-35°C:

$$\log t = 2.057 - 0.049 T \quad (22)$$

where t is the storage time in d, and T is the grain temperature in °C. They stated also, that the safe storage times of 17 % m.c. wheat were 5, 7, and 15 d at 35, 30, and 25°C, respectively.

The germination capacity of wheat at 17-19 % m.c., wet basis, stored at 25°C can be predicted from the measured respiration rate and moisture content by the equation (Karunakaran et al., 2001):

$$Y = 100 - 0.1X + 0.093M_w \quad (23)$$

where Y is the germination capacity of grain in %, X is the rate of CO_2 production in $\text{mg d}^{-1} \text{kg}^{-1} \text{d. m.}$, and M_w is the grain moisture content in % w. b.

Equation (23) is useful to determine the condition of the grains coming to grain-handling facilities, for which the storage conditions (time and temperature) are not known but the moisture content and respiration rate of the grain can be determined in 2 h rather than the 7 d required for germination. For wheat stored for a known length of time at 25°C and moisture levels of 17-19 %, the germination capacity can be predicted from the storage time, moisture content of the stored grain, and CO_2 production (Karunakaran et al., 2001):

$$Y = 54.56 - 1.213t + 2.823M_w - 0.076X \quad (24)$$

where Y is the germination capacity of grain in %, t is storage time in d, M_w is the grain moisture content in % w. b., and X is the rate of CO_2 production in $\text{mg d}^{-1} \text{kg}^{-1} \text{d. m.}$

Based on the germination data of Kreyger (1972), we developed the following formulas for predicting allowable storage times:

$$t = \exp(A + BT + CM_w) \quad (25)$$

where t is storage time in weeks, T is the grain temperature in °C, M_w is the grain moisture content in % w. b., A , B , C are empirical constants given in Table 2, and $10^\circ\text{C} \leq T \leq 20^\circ\text{C}$.

Al-Yahya (2001) explored some of the factors and conditions, such as grain moisture, grain temperature, and mechanical grain damage, that influence the germination of grain at various levels of dry matter loss during wheat storage. The objective was to determine the changes in percentage germination of stored wheat at different levels of DML under different storage conditions, i. e. different grain moisture contents, temperatures and levels of mechanical damage (MD). Based on Al-Yahya's (2001) data, we developed the following formulas:

the first one

$$Y = A + BM_w + C(\text{MD}) + DM_w^2 + EM_w(\text{MD}) + F(\text{MD})^2 \quad (26)$$

were Y is the germination capacity of grain in %, M_w is the grain moisture content in % w. b., MD is the mechanical damage in %, A , B , C , D , E , and F are empirical constants given in Table 3, and $15\% \text{w. b.} \leq M_w \leq 24\% \text{w. b.}$, $0 \leq \text{MD} \leq 30\%$.

Grain	Coefficients			R^2	Range of application
	A	B	C		
wheat	12.28039	-0.128973	-0.473026	0.9929	$12.0\% \text{w. b.} \leq M_w \leq 23.0\% \text{w. b.}$
barley	13.12305	-0.174000	-0.452103	0.9965	$11.0\% \text{w. b.} \leq M_w \leq 23.0\% \text{w. b.}$
oats	13.96125	-0.148378	-0.604968	0.9940	$11.0\% \text{w. b.} \leq M_w \leq 22.0\% \text{w. b.}$
rye	10.13185	-0.087999	-0.426973	0.9931	$11.5\% \text{w. b.} \leq M_w \leq 24.0\% \text{w. b.}$

Table 2. Values of coefficients in equation (25) and range of application

$T, ^\circ\text{C}$	DML, %	A	B	C	D	E	F	R^2
4	0.25	-113.667	22.569	0.032	-0.594	-0.022	0.004	0.940542
	0.5	-45.074	15.904	0.184	-0.475	-0.069	0.023	0.836703
	1	246.235	-19.763	-0.074	0.507	-0.062	0.017	0.729865
15	0.25	-83.9483	19.1422	-1.207	-0.5037	-0.03733	0.048	0.72055
	0.5	-204.267	31.578	-0.412	-0.852	-0.024	0.008	0.928671
	1	-80.551	15.347	-0.29	-0.42	-0.046	0.012	0.875763
25	0.25	-34.73	12.798	0.914	-0.323	-0.091	0.012	0.869765
	0.5	-37.747	13.559	-0.473	-0.381	-0.037	0.02	0.905906
	1	207.167	-17.628	-0.06	0.481	-0.063	0.016	0.734423
40	0.25	-4.483	9.097	0.606	-0.214	-0.067	0.004	0.448631
	0.5	-303.503	37.932	-2.536	-0.926	0.049	0.031	0.732198
	1	5.479	-2.086	-1.064	0.207	-0.03	0.026	0.917996

Table 3. Values of coefficients in equation (26)

and the second one

$$Y = A + BT + C(\text{MD}) + DT^2 + ET(\text{MD}) + F(\text{MD})^2 \quad (27)$$

where Y is the germination capacity of grain in %, T is the grain temperature in $^\circ\text{C}$, MD is the mechanical damage in %, A , B , C , D , E , and F are empirical constants given in Table 4, and $4^\circ\text{C} \leq T \leq 40^\circ\text{C}$, $0 \leq \text{MD} \leq 30\%$.

Equations presented in this section confirm that the changes in germination capacity of stored grain are lower with lower following parameters: grain temperature, grain moisture content, mechanical damage and storage time. In general, the conclusions are the same as in previous section: longer storage times are possible with lower both grain moisture contents and temperatures and with lower levels of mechanical grain damages.

At the end of the chapter it is worth to mention shortly the other grain quality criteria which can be important to consumer and food manufacturer.

Colour of white rice is an important criterion for judging quality and price. The white colour becomes yellow after a period of storage. Dry matter loss of grain and heat liberated from its respiration and biological activities may accelerate rice yellowing. Parameters affecting the rice yellowing are temperature and relative humidity (water activity) (Soponronnarit et al., 1998; Tirawanichakul et al., 2004).

M_w , % w.b.	DML, %	A	B	C	D	E	F	R^2
15	0.25	96.676	-0.72	-0.623	0.008	0.003	0.009	0.874369
	0.5	87.017	0.262	-0.572	-0.027	-0.015	0.008	0.90452
	1	67.972	0.178	-1.315	-0.033	-0.002	0.022	0.963953
18	0.25	100.072	-0.627	-0.144	0.014	-0.004	-0.001	0.8498037
	0.5	82.486	0.004	-0.352	$1.166 \cdot 10^{-4}$	$-7.455 \cdot 10^{-4}$	$5 \cdot 10^{-4}$	0.92672
	1	46.691	0.168	-0.955	-0.018	0.008	0.007	0.8205147
21	0.25	102.912	-1.133	-0.719	0.019	-0.024	0.022	0.95634
	0.5	78.891	0.084	-1.352	-0.002	-0.019	0.039	0.837519
	1	60.816	-0.15	-0.737	0.006	-0.027	0.006	0.963041
24	0.25	95.373	-0.941	-1.736	0.024	-0.005	0.037	0.75977
	0.5	69.078	-0.288	-2.259	0.012	0.021	0.034	0.971917
	1	70.357	-1.923	-2.238	0.049	0.016	0.03	0.895284

Table 4. Values of coefficients in equation (27)

Corn quality can mean wet-milling quality. It corresponds to the amount of survival thermo-sensitive proteins inside the grains and is very well correlated with the thermal history of the grains (Courtois, 1995).

The rate of quality changing can be represented with a simple zero- or first-order reaction (Labuza, 1980):

$$\pm \frac{dA}{dt} = k_0 \exp\left(-\frac{E_A}{RT}\right) A^n \quad (28)$$

where A is amount of a quality factor, $\pm dA/dt$ is the rate loss of a quality factor or production of undesirable effects, k_0 is the pre-exponential factor, E_A is the activation energy in J mol⁻¹, R is the gas constant in J mol⁻¹ K⁻¹, T is the temperature in K, and n is the reaction order (1 for first-order, 0 for zero-order).

Somponronnarit et al. (1998) stated that the yellowing rate of paddy can be explained by temperature and water activity and developed the following empirical equations to predict the change in the yellow colour:

$$\frac{db}{dt} = k \quad (29)$$

and

$$\ln k = 71.87 - 25.32(RH) - \frac{25919.13}{T} + \frac{10712.78(RH)}{T} \quad (30)$$

where b is yellowness of rice in Hunter b unit, t is the time in d, k is the constant value for the yellowing rate in Hunter b unit d⁻¹, RH is the relative humidity in decimal, T is the temperature in K, and 308 K ≤ T ≤ 338 K, 0.80 ≤ RH ≤ 0.95.

Courtois (1995) developed the following empirical equation to predict the change in the wet-milling quality of corn:

$$\frac{dQ}{dt} = -k_0 \exp\left(-\frac{E_A}{RT}\right) Q^2 \quad (31)$$

and

$$k_0 = -1.9561 \cdot 10^{16} + 5.4287 \cdot 10^{17} M + 6.8210 \cdot 10^{17} M^2 \quad (32)$$

where Q is the wet-milling quality, t is the time in s, k_0 is the pre-exponential factor in s⁻¹, T is the temperature in K, M is the grain moisture content in decimal d. b., and R is the gas constant in J mol⁻¹ K⁻¹, E_A = -133200 J mol⁻¹.

5. Conclusion

Nowadays grain is harvested with a combine harvester. Therefore it is possible to delay the process and to harvest ripe and dry grain, without any bigger losses caused by ridging of grain, yet in certain parts polluted with green parts of plants, straws and seeds of weeds or with unripe caryopses, moisture content can even exceed 30% w. b., and temperature is often above 30°C. This state can cause self-heating processes even when the grain itself is considered as dry. In such grain and even in grain considered as dry, vital functions connected with metabolism still exist, namely grain respiration, growth of moulds and other microorganisms as well as growth of insects. These processes lead to a decline in the quality of grain and even to its entire damage. The intensity of these processes depends mainly on the moisture content of grain and its temperature. For the purpose of safe grain storage one ought to limit its vital functions as soon as possible through lowering moisture content and temperature reduction. It can be realized by drying, and then cooling the grain. Due to economy in thermal energy consumption, grain is often dried with the atmospheric air or slightly heated air, but such a process runs very slowly, and grain has to stay in the drying chamber for quite a long time. During harvest, when granaries accept large quantities of harvested grain, it is not always possible to immediately clean, dry and cool the grain due to the limited capacity of devices. Therefore there is a necessity of periodic storage of the fresh grain mass, so there is a risk that undesirable processes will occur, which can lead to a decline in quality, and even entire damage of grain. It is therefore necessary to determine the time of safe grain storage, i. e. the time in which the growth of undesirable processes does not cause any essential changes in the quality of grain. The basic criteria of determination the length of this period are: CO₂ production and connected with it loss of the dry matter of grain, appearance of visible moulds, and germination capacity.

The dependencies for determining the time of safe grain storage were discussed. The general conclusions for all discussed criteria are the same: longer storage times are possible with lower both grain moisture contents and temperatures and with lower levels of mechanical grain damages.

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