Comprehensive
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The Hydration of Grains: A Critical Review from Description of Phenomena to Process Improvements

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Abstract: Hydration is a crucial step during grain processing. It is performed prior to many other processes, such as germination, cooking, extraction, malting and fermentation. The number of publications on this topic studying the description of the mechanisms involved and recent technologies for processing enhancement has increased recently. However, due to the complexity of the hydration process, there are still many aspects that are little understood. For that reason, this review provides not only an overview of recent developments in this field, but also a critical discussion of publications from the last 2 decades, as well as suggestions for future innovative studies. This review discusses the importance of hydration in the grain industries, the pathway for water entry into the various grains, the mass transfer and fluid flow mechanisms in the process, the behavior of the hydration kinetics, the mathematical modelling, the technologies used to accelerate the process and other necessary requirements that must be performed to complement and complete our knowledge of this process.

Keywords: cereals, grains, hydration, legumes, steeping

Introduction

Grains are plant seeds that are produced for purposes other than that of plant reproduction. For example, they are used for animal and human consumption, as well as for the extraction of different components (oils, proteins, and more). The most widely-consumed grains are the cereals (from the *Poaceae* family) and legumes (from the *Fabaceae* family), even though there are grains from others, such as the *Cucurbitaceae* (gourd seeds) and *Amaranthaceae* families (Figure 1). Cereal grains, such as corn kernels, barley kernels, sorghum kernels, and wheat kernels, are important mainly for their starch content (more than 60%) (Koehler and Wieser 2013). On the other hand, legumes are important mainly for their protein content (20% to 40%), as well as for some minerals, such as iron and zinc. Common beans, peas, lentils, chickpeas, cowpeas, lupins, and soybeans are examples of legumes (Siddiq and others 2011). Gourd seeds are rich in lipids and proteins, and are consumed in some regions of the world, mainly in African countries and India (Patel and Rauf 2017). Grains from the *Amaranthaceae* family have high a protein content and are rich in lysine (Berghofer and Schoenlechner 2002). These are widely consumed in Africa and Latin America. In fact, grains are part of a "healthy" diet due to their nutritional composition, especially legumes as a protein source (FAO 2016)

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In general, grains are harvested dry, as dryness is a big advantage to extend shelf-life during storage. Therefore, before being consumed or processed, they need to be hydrated to increase the moisture content. For these reasons, the process of hydrating grains is a crucial step, one which has already been studied for decades (Table 1). Distinct aspects have been studied, such as characterizing different kinetics behavior, describing the process and looking for innovative technologies to accelerate it (Table 1). In addition, many mathematical models have been used to describe hydration kinetics and predict the moisture content as a function of the process time (Table 2). Despite that, there is still the necessity to conduct more studies to better understand and optimize the process. In fact, there has been a recent increase in the number of grain hydration studies, especially those using innovative technologies to improve the process and proposing new mathematical models to describe it. Therefore, a review which organizes the knowledge about this complex process is important to avoid future studies replicating work already done and to point out which areas need to be studied. In addition, the latest review related to hydration was published by Swanson and others (1985) and dealt only with legumes. Consequently, this comprehensive review presents a discussion of the results about the grain hydration process and gives information about aspects that still need to be explored.

Importance of the Hydration Process

The hydration of grains is a process that consists of soaking them in water in order to increase their moisture content. This is a crucial step in industrialized processing and provides several beneficial effects on their physicochemical and nutritional

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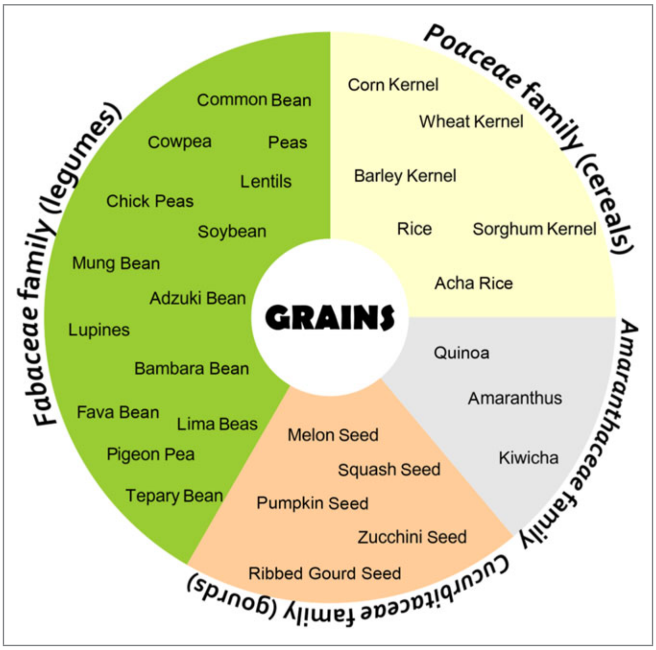

Figure 1–Example of different grains consumed in the world classified by their taxonomic family.

quality (Drumm and others 1990; Carmona-García and others 2007; Huma and others 2008; Yasmin and others 2008; Bordin and others 2010). Soaking is widely used in processing different grains for many reasons, as hydration is necessary for processes like cooking, extraction, fermentation, germination and malting.

The hydration of grains before cooking helps to soften the bean structure and so, reducing the cooking time (Silva and others 1981). This process promotes the activation of cell-wall enzymes, decreases the degree of polymerization of rhamnogalacturonan I and increases the solubility of polygalacturonan and galactan, which results in better polysaccharide solubility and shorter cooking time (Martínez-Manrique and others 2011). In addition, hydration enhances the homogeneous gelatinization of the starch and the homogeneous denaturation of proteins during cooking (Wood 2016). Therefore, a similar texture is obtained in the whole grain. Moreover, the heat transfer through the grain during cooking is enhanced by the absorbed water, thus improving the inactivation of anti-nutritional factors (Sefa-Dedeh and Stanley 1979) such as protease inhibitors, lectins, saponins, vicine, convicine, phytates, alkaloids, and indigestible oligosaccharides (Wang and others 2009)

Hydration also improves component extraction from grains, which in this case is sometimes called the steeping process. The most commonly-extracted component from grains is starch, especially from cereal grains, and is conducted by wet milling. Softening the grains by hydration improves their wet grinding and so facilitates starch purification (Singh and Eckhoff 1996). In addition, the hydration process is used to extract toxic components from beans. For instance, the Andean lupin (*Lupinus mutabilis* Sweet) has a high level of toxic alkaloids (lupanine), which needs to be extracted before being consumed. This extraction is performed in water; thus, the grains need to be hydrated (Carvajal-Larenas and others 2013). In addition, during the hydration process, some anti-nutritional compounds, such as phytic acid, tannins, phenols, α-amylase, and trypsin inhibitors, are extracted (Abd El-Hady and Habiba 2003).

Some grains are fermented before being consumed or to produce sauce products, which need elevated water activity for microbial development. For that reason, the hydration process is important. For example, soy sauce is a popular sauce in whose production the soybean is fermented after a hydration process (Luh 1995). In addition, fermentation has been demonstrated as an effective way to reduce antinutritional factors in common beans (*Phaseolus vulgaris*) (Barampama and Simard 1995; Granito and others 2002).

Germination is the natural process after the hydration of grains. This is mainly used for the development of new plants. The water uptake of the grains is important for the biochemical activation and the increase in breathing rate for embryo growth (Bewley and Black 1978). Besides the reproductive function, germination is important for sprout production and the malting process. Some pulses are germinated to produce sprouts that are consumed as food. The sprouts have the advantage of better nutritional properties than the nongerminated beans (breakdown of complex molecules and a lower level of antinutritional factors), for example in mung beans, lentils, kidney beans, and purple corn (Kylen and McCready 1975; Mbithi and others 2001; Paucar-Menacho and others 2017). Cereal grains are germinated for enzyme activation and the characteristic color, aroma, and flavor formation of malt to produce some alcoholic beverages (Barreiro and others 2003; Montanuci and others 2016), a process known as malting. This process is performed mainly with barley kernels and other grains, such as corn kernels and sorghum kernels.

Consequently, the hydration process is of significant importance in the industrialization of grains. However, this step is a batch process, which can take many hours and uses a substantial quantity of water. For that reason, its study, description and optimization are very desirable.

Description of Mechanisms and Mathematical Modeling

Seeds need to absorb water to activate their metabolism for germination. In fact, they naturally have a hydration kinetics with 3 stages (Figure 2) (Bewley and Black 1978). In stage I, the seeds absorb water mainly through physical mechanisms in order to reach an appropriate moisture content to activate their metabolism. Bewley and Black (1978) stated that this stage is independent of the seeds' metabolic activity, so this occurs equally well in live and dead seeds. However, sometimes, dead seeds can absorb more water than the living seeds as the turgor pressure in living seed counteracts hydration (Bewley and others 2013), and the effect of grain metabolism in this stage still needs investigation. In stage II, the seeds prepare for germination by breaking the reserve molecules into simple ones to be used by the embryo. In this stage, there is no significant gain of water. Germination starts in stage III. The cells start to reproduce and the tissues to grow, increasing the moisture content again. The present review is focused on stage I of hydration, since the development of the new plant is not our target, but rather the hydration of grains for food processing and consumption.

The grain hydration process is mainly a mass transfer unit operation, in which the water activity difference acts as the driving force. In other words, the water is transported from a substance with a high effective water concentration (soaking water) to a substance with a low effective water concentration (grain), a phenomenon called diffusion. In addition, the complex structure and different tissues and cells of the grains form channels of many

Table 1–Grains hydration works of grains with Downward concave shape behavior (DCS) and sigmoidal behavior performed from the last 2 decades.

Grain common name	Grain scientific name	Family	Hydration behavior	Model	Studied effect	Reference
Acha rice	*Digitaria exilis*	*Poaceae*	DCS	Peleg	Temperature	Tunde-Akintunde Toyosi (2010)
Adzuki beans	*Vigna angularis*	*Fabaceae*	Sigmoidal	Kaptso et al.	Temperature	Oliveira and others (2013)
Adzuki beans	*Vigna angularis*	*Fabaceae*	Sigmoidal	Kaptso et al.	Initial moisture content	Miano and Augusto (2015)
Adzuki beans	*Vigna angularis*	*Fabaceae*	Sigmoidal	Weibull	High hydrostatic Pressure	Ueno and others (2015)
Amaranth grain	*Amaranthus cruentus*	*Amaranthaceae*	DCS	Fick	Temperature	Resio and others (2006)
Andean lupins	*Lupinus mutabilis*	*Fabaceae*	Sigmoidal	Kaptso et al.	Temperature	Miano and others (2015b)
Bambara beans	*Vigna subterranea*	*Fabaceae*	DCS	Peleg	Temperature	Jideani and Mpotokwana (2009)
Barley kernels	*Hordeum vulgare*	*Poaceae*	DCS	Peleg, Fick, 1st order, Weibull	Temperature	Montanuci and others (2015)
Barley kernels	*Hordeum vulgare*	*Poaceae*	DCS	Peleg	Any evaluated	Miano and others (2017c)
Black Bambara groundnuts	*Voandzeia subterranea*	*Fabaceae*	Sigmoidal	Kaptso et al.	Temperature	Kaptso and others (2008)
Black kidney beans	*Phaseolus vulgaris*	*Fabaceae*	DCS	Peleg	Any evaluated	Miano and others (2017c)
Caballero beans	*Phaseolus vulgaris*	*Fabaceae*	Sigmoidal	Kaptso et al.	Nothing	Miano and others (2017c)
Calabash seeds	*Lagenaria siceraria*	*Cucurbitaceae*	DCS	Peleg, Kaptso et al.	Temperature	Edith and others (2016)
Chickpeas	*Cicer arietinum* L.	*Fabaceae*	DCS	Ibarz et al.	High hydrostatic Pressure	Ibarz and others (2004)
Chickpeas	*Cicer arietinum* L.	*Fabaceae*	DCS	Peleg	Temperature	Gowen and others (2007)
Chickpeas	*Cicer arietinum* L.	*Fabaceae*	DCS	Peleg	Ultrasound	Yildirim and others (2010)
Chickpeas	*Cicer arietinum* L.	*Fabaceae*	DCS	Peleg	Ultrasound	Ranjbari and others (2013)
Chickpeas	*Cicer arietinum* L.	*Fabaceae*	DCS	Peleg	Nothing	Miano and others (2017c)
Chickpeas	*Cicer arietinum* L.	*Fabaceae*	DCS	Peleg, Khazaei	Nothing	Shafaei and Masoumi (2014)
Chickpeas (Split)	*Cicer arietinum* L.	*Fabaceae*	DCS	Peleg	Temperature	Johnny and others (2015)
Chickpeas (Split)	*Cicer arietinum*	*Fabaceae*	DCS	Peleg, Fick, Exponential	Temperature	Prasad and others (2010)
Canary beans	*Phaseolus vulgaris*	*Fabaceae*	Sigmoidal	Kaptso et al.	Any evaluated	Miano and others (2017c)
Carioca kidney beans	*Phaseolus vulgaris*	*Fabaceae*	Sigmoidal	Kaptso et al.	Any evaluated	Miano and others (2017c)
Common beans	*Phaseolus vulgaris*	*Fabaceae*	Sigmoidal	Peleg, 1st order, Kaptso et al.	Ultrasound Probe Pretreatment	Ulloa and others (2015)
Common beans	*Phaseolus vulgaris*	*Fabaceae*	Sigmoidal	Peleg, 1st order, Kaptso et al., Weibull	Ultrasound Probe Pretreatment	Ulloa and others (2015)
Common beans	*Phaseolus vulgaris*	*Fabaceae*	Sigmoidal	Peleg	Temperature	Piergiovanni (2011)
Common beans	*Phaseolus vulgaris*	*Fabaceae*	DCS	Peleg, Kumar	Temperature	Pramiu and others (2017)
Common beans	*Phaseolus vulgaris*	*Fabaceae*	DCS	Peleg, Kumar	High hydrostatic Pressure	Pramiu and others (2017)
Common beans	*Phaseolus vulgaris*	*Fabaceae*	Sigmoidal	Peleg, 1st order, Kaptso et al., Weibull	Ultrasound Probe Pretreatment	López López and others (2017)
Common beans	*Phaseolus vulgaris*	*Fabaceae*	Sigmoidal	Peleg	High hydrostatic Pressure	Belmiro (2016)
Corn kernels	*Zea mays*	*Poaceae*	DCS	Becker	Temperature	Verma and Prasad (1999)
Corn kernels	*Zea mays*	*Poaceae*	DCS	Peleg, 1st order, Page, Ibarz et al., Two-terms	Ultrasound	Miano and others (2017a)
Corn kernels	*Zea mays*	*Poaceae*	DCS	Nicolin-Jorge	Temperature	Nicolin and others (2017)
Cowpeas	*Vigna unguiculata*	*Fabaceae*	DCS	Fick	Nothing	Sopade and Obekpa (1990)
Cowpeas	*Vigna unguiculata*	*Fabaceae*	DCS	Peleg	Nothing	Miano and others (2017c)
Cucumber seeds	*Cucumis sativus*	*Cucurbitaceae*	DCS	Peleg, Kaptso et al.	Temperature	Edith and others (2016)
Dark red kidney beans	*Phaseolus vulgaris*	*Fabaceae*	Sigmoidal	Kaptso et al.	Any evaluated	Miano and others (2017c)
Egyptian kidney beans	*Lablab purpureus*	*Fabaceae*	Sigmoidal	Kaptso et al.	Any evaluated	Miano and others (2017c)
Fava beans	*Vicia faba*	*Fabaceae*	DCS	1st order	Temperature	Haladjian and others (2003)
Fava beans	*Vicia faba*	*Fabaceae*	DCS	1st order	pH	Haladjian and others (2003)
Fava beans	*Vicia faba*	*Fabaceae*	Sigmoidal	Kaptso et al.	Nothing	Miano and others (2017c)
Garoua cowpeas	*Vigna unguiculata*	*Fabaceae*	Sigmoidal	Kaptso et al.	Temperature	Kaptso and others (2008)
Lentils	*Lens culinaris*	*Fabaceae*	DCS	Peleg, Kaptso et al. et al., Weibull, 1st order	Temperature	Oroian (2017)
Lentils	*Lens culinaris*	*Fabaceae*	DCS	Peleg	Nothing	Miano and others (2017c)

(*Continued*)

Table 1–Continued.

Grain common name	Grain scientific name	Family	Hydration behavior	Model	Studied effect	Reference
Lentils (Green)	*Lens culinaris*	*Fabaceae*	Sigmoidal	Kaptso et al.	Nothing	Miano and others (2017c)
Lima beans	*Phaseolus lunatus*	*Fabaceae*	Sigmoidal	Not modeled	Growing season	Piergiovanni and others (2012)
Mung beans	*Vigna radiata*	*Fabaceae*	DCS	Peleg, Fick	Temperature	Sharanagat and others (2016)
Mung beans	*Vigna radiata*	*Fabaceae*	Sigmoidal	Kaptso et al.	Ultrasound	Miano and others (2016b)
Navy beans	*Phaseolus vulgaris*	*Fabaceae*	DCS	Peleg	Ultrasound	Ghafoor and others (2014)
Navy beans	*Phaseolus vulgaris*	*Fabaceae*	DCS	Peleg	Temperature	Ramaswamy and others (2005)
Navy beans	*Phaseolus vulgaris*	*Fabaceae*	DCS	Peleg	Radiation (pretreated)	Ramaswamy and others (2005).
Navy beans	*Phaseolus vulgaris*	*Fabaceae*	DCS	Peleg	High hydrostatic Pressure	Ramaswamy and others (2005)
Ñuña beans	*Phaseolus vulgaris*	*Fabaceae*	DCS	Peleg	Nothing	Miano and others (2017c)
Panamito beans	*Phaseolus vulgaris*	*Fabaceae*	DCS	Peleg	Nothing	Miano and others (2017c)
Peanuts	*Arachis hypogaea*	*Fabaceae*	DCS	Fick	Nothing	Sopade and Obekpa (1990)
Pink kidney beans	*Phaseolus vulgaris*	*Fabaceae*	DCS	Peleg	Nothing	Miano and others (2017c)
Pinto beans	*Phaseolus vulgaris*	*Fabaceae*	Sigmoidal	Peleg	Pressure gradients	Zanella-Díaz and others (2014)
Pinto beans	*Phaseolus vulgaris*	*Fabaceae*	Sigmoidal	Not modeled	Nothing	Kinyanjui and others (2015)
Quinoa var. Blanca de Juli	*Chenopodium quinoa Willd*	*Amaranthaceae*	DCS	Peleg, Fick	Temperature	Ramos and others (2016)
Quinoa var. Kancolla	*Chenopodium quinoa Willd*	*Amaranthaceae*	DCS	Peleg, Fick	Temperature	Ramos and others (2016)
Quinoa var. Pasankalla	*Chenopodium quinoa Willd*	*Amaranthaceae*	DCS	Peleg, Fick	Temperature	Ramos and others (2016)
Quinoa var. Salcedo Inia	*Chenopodium quinoa Willd*	*Amaranthaceae*	DCS	Peleg, Fick	Temperature	Ramos and others (2016)
Red Kidney Beans	*Phaseolus vulgaris* L.	*Fabaceae*	DCS	Peleg	Temperature	Abu-Ghannam (1998)
Rice kernels	*Oryza sativa*	*Poaceae*	DCS	Fick	Temperature	Bello and others (2004)
Rice kernels	*Oryza sativa*	*Poaceae*	DCS	Nicolin-Jorge	Temperature	Nicolin and others (2017)
Rice kernels (parboiled)	*Oryza sativa*	*Poaceae*	DCS	Nicolin-Jorge	Temperature	Balbitoni and others (2018)
Rose coco beans	*Phaseolus vulgaris*	*Fabaceae*	Sigmoidal	Not modeled	Nothing	Kinyanjui and others (2015)
Sesame seeds	*Sesamum indicum* L.	*Pedaliaceae*	DCS	Peleg, Weibull, 1st order, Khazaei	Temperature	Khazaei and Mohammadi (2009)
Sorghum kernels	*Sorghum* spp.	*Poaceae*	DCS	Peleg	Temperature	Kashiri and others (2010)
Sorghum kernels	*Sorghum* spp.	*Poaceae*	DCS	Peleg	Ultrasound	Patero and Augusto (2015)
Sorghum kernels	*Sorghum* spp.	*Poaceae*	DCS	Peleg	Nothing	Miano and others (2017c)
Soybeans	*Glycine max*	*Fabaceae*	DCS	Fick	Nothing	Sopade and Obekpa (1990)
Soybeans	*Glycine max*	*Fabaceae*	DCS	Hsu	Temperature	Coutinho and others (2010)
Soybeans	*Glycine max*	*Fabaceae*	DCS	Hsu	Temperature	Nicolin and others (2012)
Soybeans	*Glycine max*	*Fabaceae*	DCS	Peleg	Temperature	Fracasso and others (2015)
Soybeans	*Glycine max*	*Fabaceae*	DCS	Peleg, Nicolin Jorge	Temperature	Borges and others (2017)
Squash seeds	*Cucurbita maxima*	*Cucurbitaceae*	DCS	Peleg, Kaptso et al.	Temperature	Edith and others (2016)
Squash seeds	*Cucurbita moschata*	*Cucurbitaceae*	DCS	Peleg, Kaptso et al.	Temperature	Edith and others (2016)
Tepary beans	*Phaseolus acutifolius A. Gray*	*Fabaceae*	DCS	Peleg	Pressure gradients	Zanella-Díaz and others (2014)
West cowpeas	*Vigna unguiculata*	*Fabaceae*	Sigmoidal	Kaptso et al.	Temperature	Kaptso and others (2008)
Wheat kernels	*Triticum* spp.	*Poaceae*	DCS	Peleg	Temperature	Maskan (2001)
Wheat kernels	*Triticum* spp.	*Poaceae*	DCS	Fick	Nothing	Igathinathane and Chattopadhyay (1997)
Wheat kernels	*Triticum* spp.	*Poaceae*	DCS	Peleg	Nothing	Miano and others (2017c)
White Bambara groundnuts	*Voandzeia subterranea*	*Fabaceae*	Sigmoidal	Kaptso et al.	Temperature	Kaptso and others (2008)
White kidney beans	*Phaseolus vulgaris*	*Fabaceae*	DCS	Fick	High pressure	Naviglio and others (2013)
White kidney beans	*Phaseolus vulgaris*	*Fabaceae*	Sigmoidal	Kaptso et al.	Nothing	Miano and others (2017c)
White lupins	*Lupinus albus*	*Fabaceae*	DCS	Peleg	Nothing	Miano and others (2017c)
White lupins (roasted)	*Lupinus albus*	*Fabaceae*	Sigmoidal	Peleg	Temperature	Solomon (2009)
White-seed melons	*Cucumeropsis mannii*	*Cucurbitaceae*	DCS	Peleg, Kaptso et al.	Temperature	Edith and others (2016)
Yellow peas	*Pisum sativum*	*Fabaceae*	DCS	Peleg, Fick, Kaptso et al.	Temperature	Mercier and others (2015)

Table 2–Mathematical models used to describe the grains hydration process.

Model	Equation	Reference
Downward concave shape behavior		
Fick's Second law	$\frac{\partial C_A}{\partial t} = D_{AB} \cdot \nabla^2 C_A$	Fick (1855)
Solutions for Fick's Second law	Rectangular coordinates: $\frac{M_t - M_\infty}{M_0 - M_\infty} = \sum_{i=1}^{\infty} \frac{2Bi}{\beta_i^2 + Bi^2 + Bi} \frac{\cos(\beta_i n)}{\cos(\beta_i)} \exp(-\beta_i^2 Fo)$ Cylindrical coordinates: $\frac{M_t - M_\infty}{M_0 - M_\infty} = \sum_{i=1}^{\infty} \frac{2Bi}{\beta_i^2 + Bi^2} \frac{J_0(\beta_i n)}{J_0(\beta_i)} \exp(-\beta_i^2 Fo)$ Spherical coordinates: $\frac{M_t - M_\infty}{M_0 - M_\infty} = \sum_{i=1}^{\infty} \frac{2Bi}{\beta_i^2 + Bi^2 + Bi} \frac{\sin(\beta_i n)}{\sin(\beta_i)} \exp(-\beta_i^2 Fo)$	Crank (1979)
First order	$\frac{M_t - M_\infty}{M_0 - M_\infty} = exp(-k_L \cdot t)$	Bera, Sahu, Mukherjee, Bargale and Sharma (1990)
Peleg	$M_t = M_o + \frac{t}{k_1 + k_2 \cdot t}$	Peleg (1988)
Modified Peleg	$M_t = \frac{t}{k_{1.1} + k_{2.1} \cdot t} + \frac{t}{k_{1.2} + k_{2.2} \cdot t}$	Paquet-Durand and others (2015)
Page	$\frac{M_t - M_\infty}{M_0 - M_\infty} = exp(-k_p \cdot t^n)$	Page (1949)
Ibarz et al.	$M_t = (\frac{k_{I1}}{k_{I2}}) - (\frac{k_{I1}}{k_{I2}} - M_0) \cdot \exp(-k_{I2} \cdot t)$	Ibarz, González and Barbosa-Cánovas (2004)
Two-steps hydration	$\frac{M_t - M_\infty}{M_0 - M_\infty} = p \cdot (1 - \exp(-k_{M1} \cdot t)) + (1 - p) \cdot (1 - \exp(-k_{M2} \cdot t))$	Miano, Ibarz and Augusto (2017a)
Weibull	$\frac{M_t}{M_\infty} = 1 - exp[-(\frac{t}{\beta})^\alpha]$	Hahn and Samuel (1967), Machado and others (1998)
Nicolin-Jorge	$\frac{d\rho_A}{dt} = \frac{A}{V} \cdot k_s \cdot (\rho_{eq} - \rho_A)$	Nicolin and others (2015)
Becker	$\frac{M_t - M_\infty}{M_0 - M_\infty} = \frac{2}{\sqrt{\pi}} \cdot \frac{A}{V} \cdot \sqrt{D \cdot t}$	Becker (1959)
Khazaei	$M_t = M_0 + M_{rel} \cdot (1 - \exp(-\frac{t}{t_{rel}})) + k_{rel} \cdot t$	Khazaei and Mohammadi (2009)
Hsu	$\frac{\partial M}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r}(r^2 \cdot D \cdot \frac{\partial M}{\partial r})$	Hsu (1983)
Sigmoidal shape behavior		
Kaptso et al.	$M_t = \frac{M_\infty}{1 + exp[-k_k.(t - \tau)]}$	Kaptso, Njintang, Komnek, Hounhouigan, Scher and Mbofung (2008)
Ibarz and Augusto	$M_t = \frac{M_\infty}{1 + \frac{M_\infty - M_0}{M_0} exp[-k_{IA}.M_\infty.t]}$ $t_{(lag\ phase)} = \frac{1}{k_{IA} \cdot M_\infty} ln(\frac{M_\infty + M_0}{M_0})$	(Ibarz and Augusto 2015)

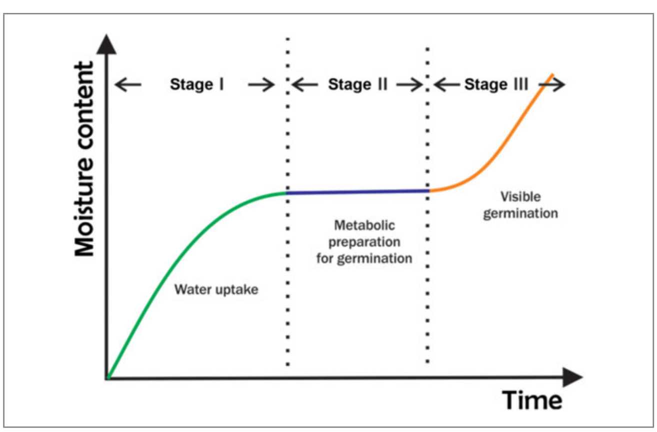

Figure 2–Seed water imbibition during the hydration – germination process. Adapted from Bewley and Black (1978). Stage I can have 2 different patterns, as described in Figure 6 and Section "Water uptake pathways and hydration behavior."

sizes, structure, composition, zones with varied permeability through which the water can flow. Therefore, the water does not only enter the grains by diffusion, but also by capillary flow. Thus, the hydration process is not as simple as it seems and involves not only mass transfer mechanisms, but also those of fluid flow.

Grain structure

Figure 3 and 4 show the structure of the most-widely consumed grains: cereals and legumes, respectively. The structures of cereal and legume grains are very different as a result of which they have different hydration behavior.

In fact, cereal grains, such as corn kernels, sorghum kernels, wheat kernels, and rice kernels are caryopses (that is, a small one-seeded dry indehiscent fruit, without pulp), whose pericarp is fused with the seed coat forming part of the bran (Bewley and Black 1978). The bran is the most external layer of cereal grains and is made up of many layers of different tissues (Figure 3). This structure is permeable to water (Syarief and others 1987) and so lets the water enter the grain by diffusion. The largest volume of cereal grains is occupied by the endosperm, in which the reserve components are stored. There are 2 kinds of endosperm: floury endosperm, which is more disorganized and easy to disintegrate during milling, and glassy or vitreous endosperm, which is more compact, organized and difficult to disintegrate (Kikuchi and others 1982). In addition, cereal grains have the germ, which is the main structure of germination. Some cereal grains, like corn kernels, have an external porous structure called tip cap, which contributes to the entry of water by capillarity (Ramos and others 2004; Miano and others 2017a).

Regarding structure of legume grains, the seed coat is the most external structure. In contrast to cereal grains, the seed coat

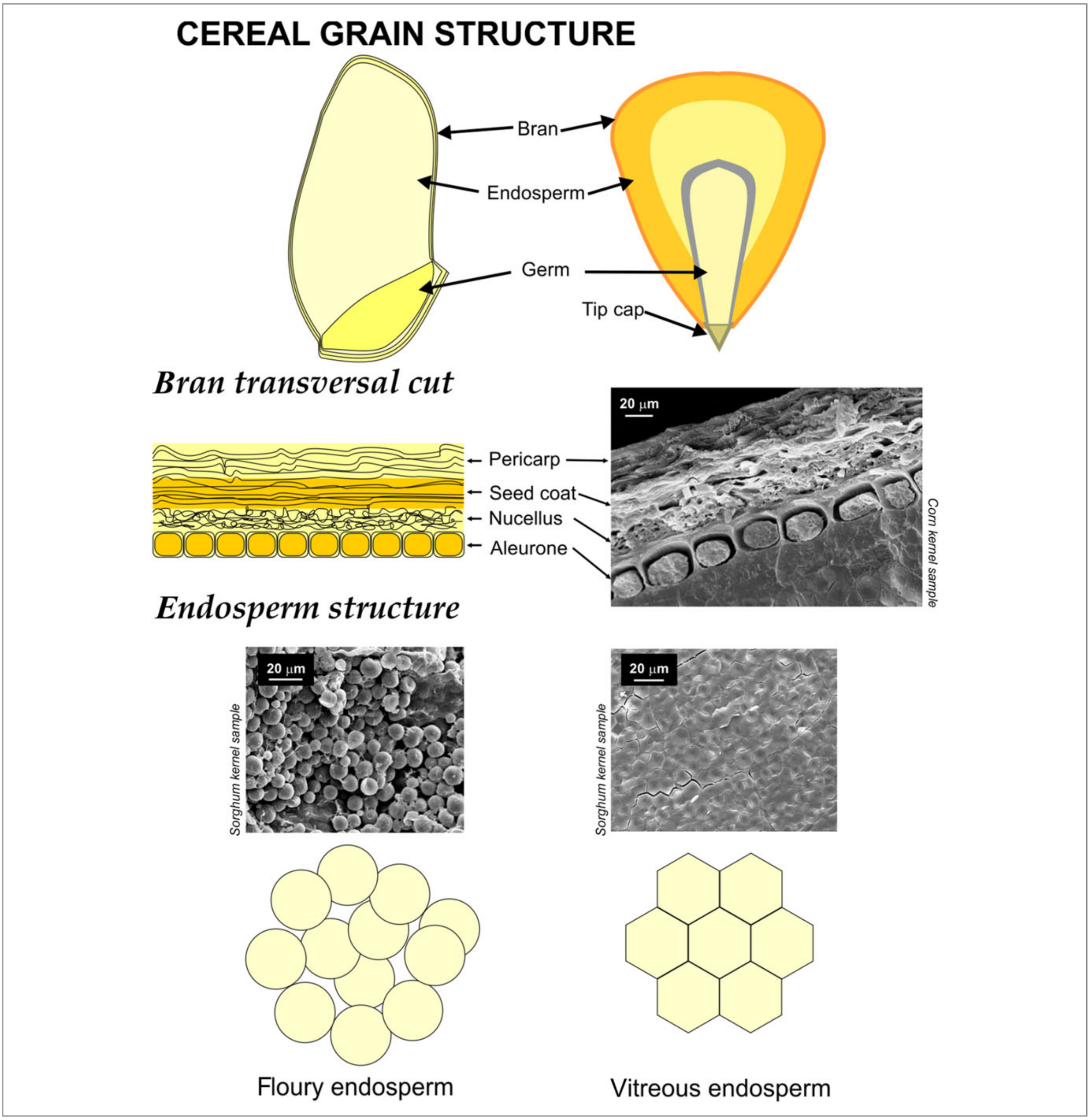

Figure 3–General structure of cereal grains. The figure is an adaptation of several schematizations and micrographs from Bewley and Black (1978), Evers and Millar (2002), Miano and others (2017a).

structure is more complex in legume grains. Firstly, this structure can be completely or partially impermeable to water, depending on its composition and structure. Figure 4 shows the general structure of the seed coat. There is an external layer of wax that makes the seed impermeable (Graven and others 1997). Then, there are 3 layers of tissues. The first layer is macrosclereid cells that form the palisade tissue. This tissue is very compact and has many hydrophobic components (Castillo and Guenni 2001). Consequently, it is a barrier to the entry of water. The second layer is formed of osteosclereid cells (bones-like cells), which have large intercellular spaces where water can flow by capillarity (Miano and others 2015b). The third layer of the legume grain seed coat is the sclerified parenchyma, made up of flat dead cells, which can be easily hydrated (Miano and others 2015b).

Other important structures of the legume grains are the raphe, hilum and micropyle. As the seed coat can be completely impermeable to water, many works have attributed these structures as the main entry path for water. For instance, Sefa-Dedeh and Stanley (1979), stated that the hilum is the main water entrance in cowpeas; Korban and others (1981), stated that the hilum, raphe and micropyle were the main water entrances in carioca and black beans; Varriano-Marston and Jackson (1981) and Miano and

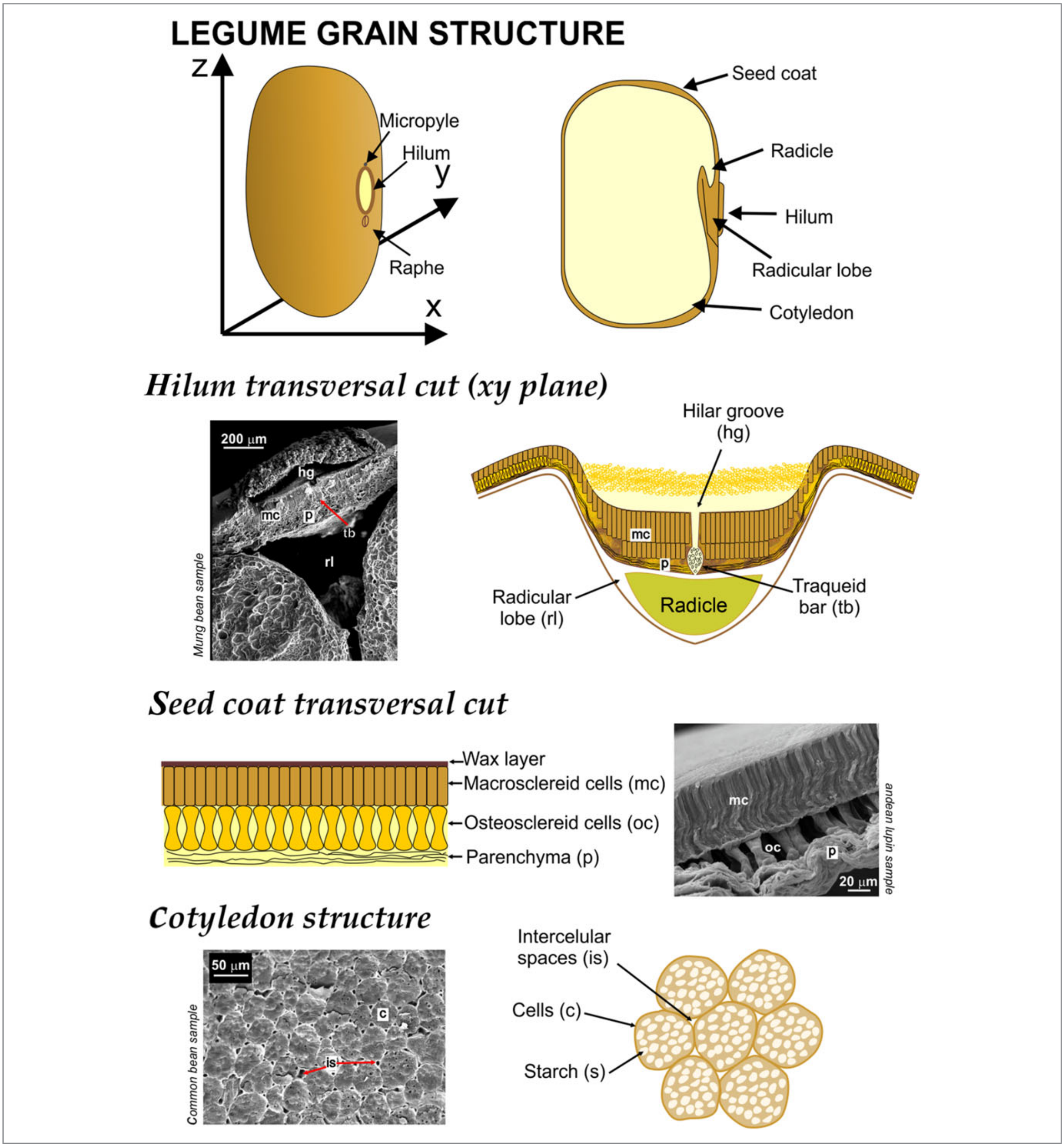

Figure 4–General structure of (a) cereal grains and (b) legume grains. The figure is an adaptation of several schematizations and micrographs from (Hyde 1954), Bewley and Black (1978), Lush and Evans (1980), Lersten (1982), Berrios and others (1998), Perissé and Planchuelo (2004), (Miano and others 2015b), Miano and others (2016b).

others (2015b) claimed that only the hilum is the main water entrance in black beans and Andean lupins. Most of the works attributed the main water entry to the hilum in legume grains. In fact, the hilum is considered as a valve, which controls the entry and exit of water (Hyde 1954). In a transversal cut of the hilum (Figure 4), it is observed that there is an aperture called the hilar groove, which is directly connected to a porous tissue called the traqueid bar (Lersten 1982). The traqueid bar facilitates gas exchange (Lersten 1982) and also water vapor exchange. Furthermore, the hilum area is larger than the micropyle and raphe. Therefore, the hilum is the best candidate for water entrance in grains from the *Fabaceae* family.

The cotyledon of legume grains is formed of the storage parenchyma tissue, whose structure is more homogeneous. It is made up of regular cells with small intercellular spaces (Figure 4), where water can cross. The main storage molecules by legume

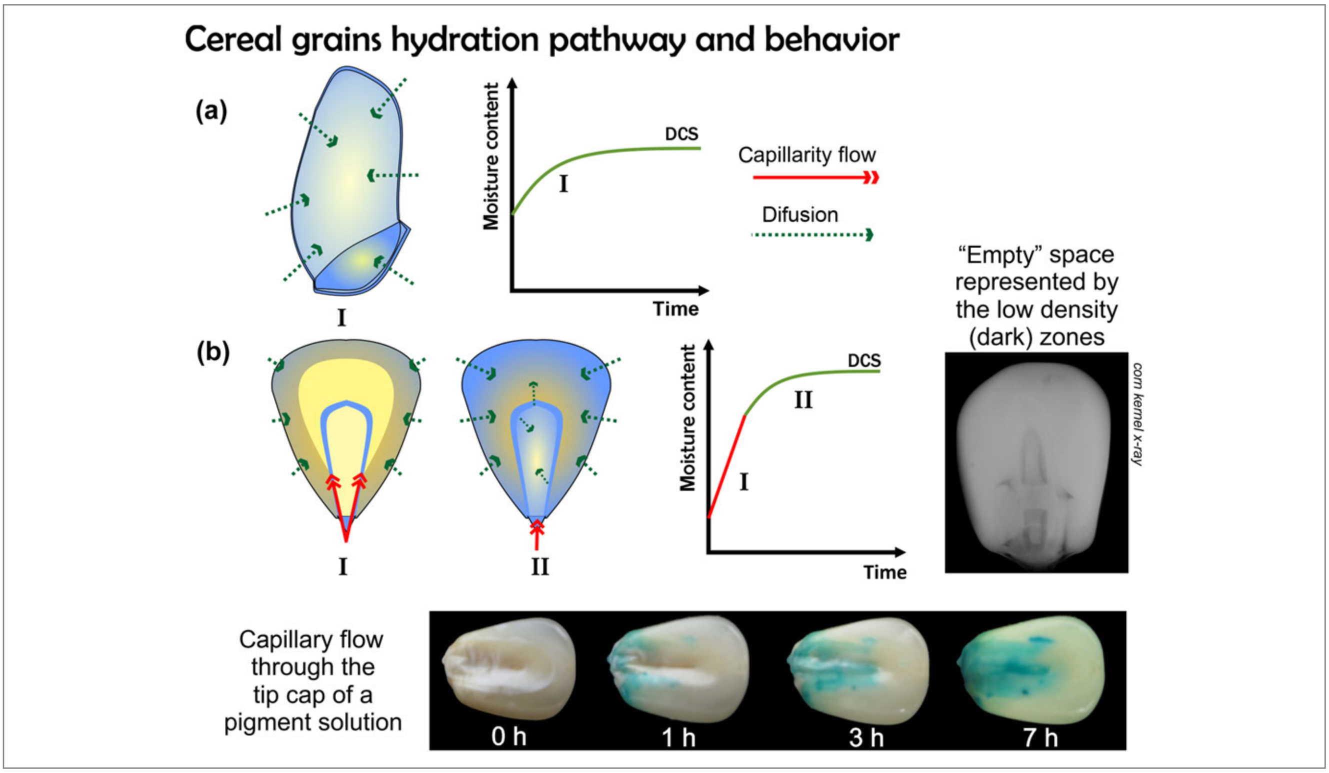

Figure 5–Water uptake pathway and hydration kinetics behavior of cereal grains. The arrows represent the direction and way water may enter: by diffusion or by capillary flow. (a) Downward concave shape behavior with 1 step – wheat kernel as an example. (b) Downward concave shape behavior with 2 steps – corn kernel as an example.

grains are starch, proteins, and lipids (Siddiq and others 2011), and depending on their relative quantities, water could enter more easily.

Water uptake pathways and hydration behavior

As stated, the hydration of grains is not a simple diffusional process. It means that water is not merely transported into the grain homogeneously. The water follows specific pathways to hydrate the grains, causing different hydration kinetics behavior, depending on the grain structure and composition.

One issue to be studied first is to determine where is the first entry of water into the grain. The seed coat in legume grains and the bran in cereal grains are the first structures that water were in contact with. Therefore, depending on the permeability of the seed coat, water can easily cross it or not. Therefore, water can flow through other grain structures. In fact, to determine the structure the water enters through, some structures can be waterproofed by using, for example, nail polish or contact glue (Ramos and others 2004; Miano and Augusto 2015; Miano and others 2017a) and then verify if the grain hydrates or if the hydration rate is reduced. By studying the internal structure of the grain (looking for "empty" spaces between the tissues) and the composition, the water uptake pathway and the hydration kinetics behavior can be determined. Another interesting way to follow the water entry pathway is by using Magnetic Resonance Microscopy (Mikac and others 2015). However, this technique is expensive and results in low-resolution images.

Cereal grain hydration kinetics. In cereal grains, as the bran is permeable to water, the water crosses all the surface area of the grains (Syarief and others 1987; Fast Seefeldt and others 2007). Therefore, the water is transferred by diffusion into the grain, making the water activity difference as the driving force. As starch is the main reserve component and the structure of the endosperm is usually compact, the total hydration process can take excessively long. In this case, the hydration kinetics behavior has a downward concave shape (DCS) (Figure 5). This behavior is characterized by a reduction in the hydration rate from a maximum value to zero when the grain absorbs the maximum water that it can hold (equilibrium moisture content). In other works, the driving force of mass transfer is reduced until the equilibrium is reached.

Some cereals can present "empty" spaces inside the grains and porous structures causing the water to be transferred by capillarity. For instance, corn kernels have a porous structure called tip cap and a space between the germ and the endosperm (Miano and others 2017a). Figure 5 shows that by immersing corn kernels in a pigment solution, the pigment follows a preferred pathway: the pigment enters by the tip cap and fills the space between the germ and the endosperm. In other words, the pigment solution enters by capillarity through the porous structures of corn. On the other hand, the endosperm is hydrated from the beginning of the process, suggesting that the water, besides entering by the tip cap, can cross the bran by diffusion without the pigment molecules (this probably because they are bigger molecules). This is one way to demonstrate that the grain hydration process can take place by diffusion and capillarity flow.

Therefore, depending on the structure, the DCS behavior can have a very high hydration rate at the initial part of the process due to the contribution of capillarity flow. Once the "empty" spaces of the grain are filled with water, the water hydrates the grain's other structures by diffusion. Consequently, the hydration kinetics have a DCS behavior with 2 steps (Figure 5): the first step with a high hydration rate due to capillarity is predominant; and the

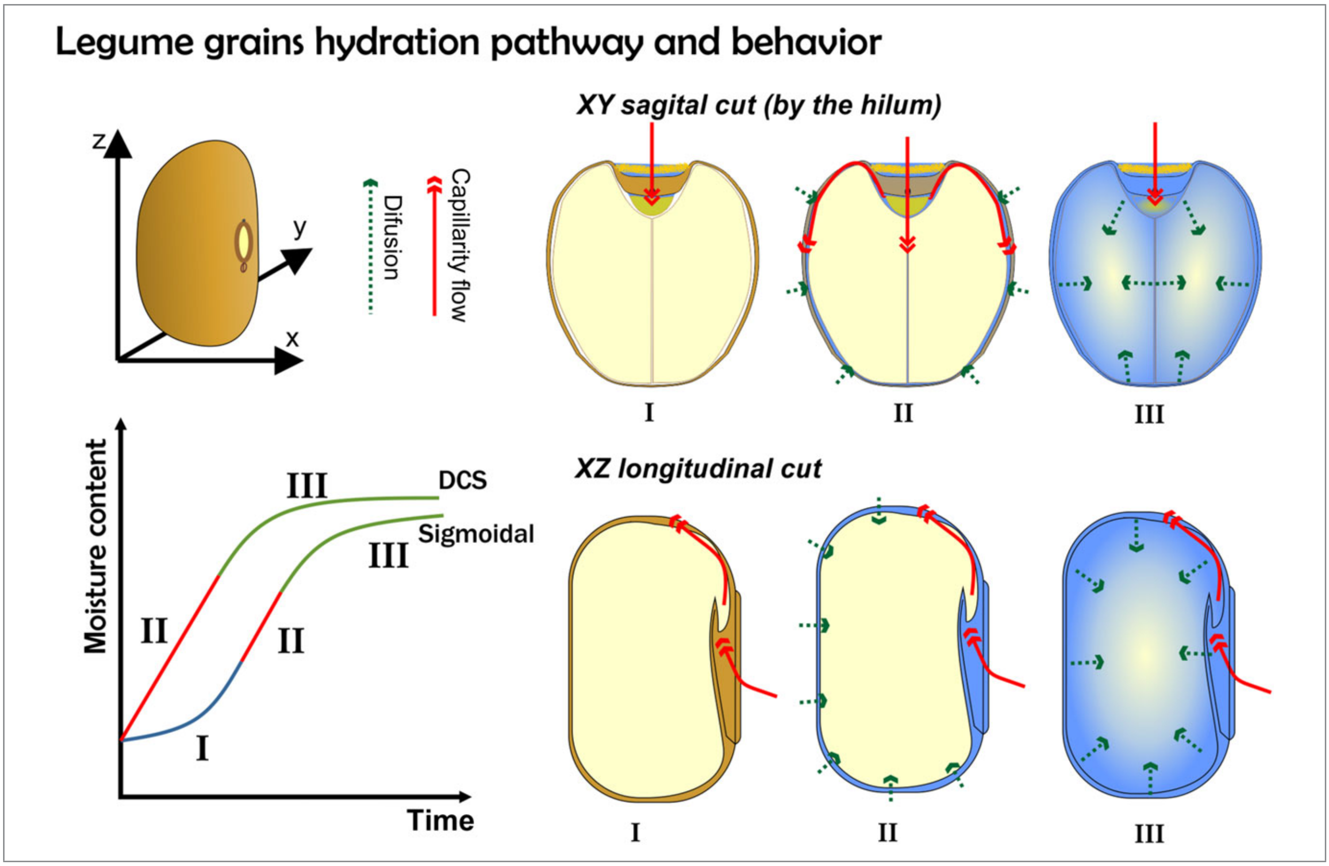

Figure 6–Water uptake pathway and hydration kinetics behavior of legume grains. The arrows represent the water pathway. The arrows represent the direction and way how water may enter: by diffusion or by capillary flow.

second, with a low hydration rated due to diffusion is predominant. This behavior is the main reason why some mathematical models, which consider hydration as only a diffusional process, do not fit or describe the hydration data well.

Legume grain hydration kinetics. Legume grains are more complex in structure than cereal grains. Therefore, besides the DCS behavior, the hydration kinetics behavior of legume grains can have a sigmoidal shape. This behavior has been little studied, especially regarding the search for suitable mathematical models to describe and predict it. As stated above, the seed coat of legume grains can be completely impermeable to water; therefore, water could only enter through the hilum. Figure 6 shows the water entrance pathway in legume grains and the possible hydration behavior divided into 3 stages. First (I): the water enters through the hilum, due to the impermeability of the seed coat, crossing the hilar groove and traqueid bar tissue to reach the radicle lob. Then, the water is distributed to the space between the internal face of the seed coat and the cotyledon. Second (II): once the seed coat is hydrated from inside, it becomes permeable to water (see section 2.3); thus, water starts to enter not only through the hilum but also crossing the seed coat by diffusion. Third (III): the cotyledon is hydrated by diffusion and capillarity depending on the structure and composition until reaching the equilibrium moisture. This water pathway causes a lag phase in the hydration kinetics, due to the impermeability of the seed coat, which limits the hydration process (Sayar and others 2001), giving this particular behavior (Miano and Augusto 2015). The legume grains with permeable seed coats have a DCS behavior of hydration kinetics, since the water pathway would start from the second (II) stage (Figure 6) skipping the lag phase. Table 1 shows different works describing legume grains with sigmoidal and DCS behavior. It is interesting to note that, despite the sigmoidal behavior, some works used mathematical models for DCS behavior, ignoring the actual sigmoidal behavior.

Effect of the Initial moisture content

The grain initial moisture content is an important condition that must be controlled to compare hydration kinetics among different samples. In fact, hydration behavior is affected by the initial moisture content, especially in legume grains (Tang and others 1994; Miano and Augusto 2015). Figure 7 shows how the initial grain moisture content influences its hydration behavior. Regarding grains with DCS behavior, the overall behavior is not changed, but the hydration rate is changed since the driving force of mass transfer is reduced (Figure 7a). However, in grains with sigmoidal behavior of the hydration kinetics, this turns into DCS as the initial moisture content increases. The explanation for this phenomenon is that the permeability to water of the seed coat increases with the increase in the water activity/moisture (Miano and Augusto 2015). This phenomenon can be explained with the glassy state theory (Ross and others 2013; Miano and Augusto 2015), which states that there is a condition (temperature or moisture content/water activity) when the seed coat components change from the glassy to rubbery state. Figure 8(a) is a general glass transition diagram, which shows that components change from the glassy state to the rubbery state by increasing their moisture content ($A \rightarrow B$) or their temperature ($A \rightarrow C$). When the components change from the glassy to the rubbery state, their properties (Fontana Jr and

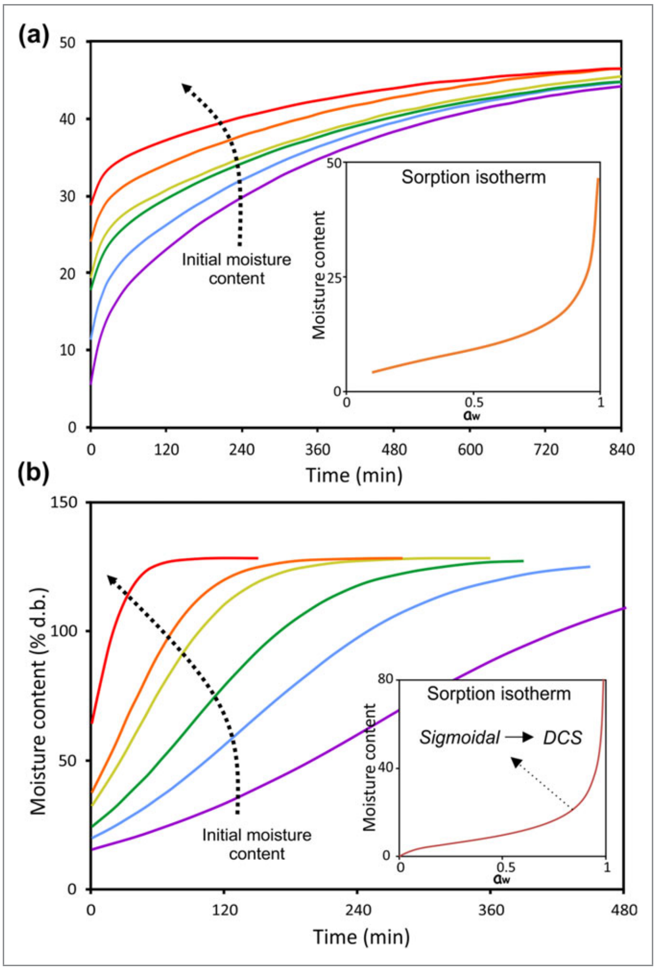

Figure 7–Effect of the initial grain moisture content with (a) Downward concave shape and (b) Sigmoidal behavior. Note the change from sigmoidal behavior to DCS at a certain initial moisture content.

others 2008), such as the permeability to water, are drastically modified. This also would be one of the causes why the hydration process is accelerated when performed at high temperatures. Ross and others (2008), state that the glassy transition temperature of the seed coat can be determined by Differential Scanning Calorimetry, measuring this property for the seed coat of different grains. However, as the seed coat is a multicomponent material, its exact determination is difficult as each component has a different glassy transition temperature.

In fact, there is a water activity/moisture content when the seed coat components change their state and become permeable to water. This moisture content could be estimated by the sorption isotherm of the grain (relation between moisture content and water activity).

The sorption isotherm (Figure 8b) has 3 characteristic zones in which the properties of water associated with each zone differ significantly (Reid and Fennema 2008). The moisture content where the sorption isotherm passes from zone II to zone III is attributed to the glassy state transition (Reid and Fennema 2008). In addition, this moisture content matches the initial moisture content when the hydration kinetics behavior changes from sigmoidal to DCS. Therefore, this "critical" moisture content can be estimated. It should be mentioned that this is 1 reason why the hydration kinetics behavior of the same grain is different in reported works.

Mathematical modeling

The hydration kinetics data can be fitted to a suitable mathematical model to predict the moisture content as a function of time and/or to study the process characteristics: the hydration rate, equilibrium moisture content and lag phase time (in sigmoidal behavior). Depending on the hydration kinetics behavior, there are many mathematical models available. Some of them are empirical and others are derivations from physical laws. The most widely-used models consider hydration as a purely diffusional process. However, as Sam Saguy and others (2005) stated, hydration and rehydration are governed by several mechanisms of imbibition in porous media. Furthermore, as described above, grains are not isotropic materials, being heterogeneous in both structure and composition.

Table 1 shows the different mathematical models used for many kinds of grains according to their hydration kinetics behavior. Note that there are many works in which, despite the grains having sigmoidal behavior, the authors used concave equations to fit the data (for example, see the discussion in Augusto and Miano (2017)). Next, some of the models most commonly used to describe the hydration kinetics of grains are presented.

Mathematical models for downward concave shape (DCS) hydration behavior. There are many different mathematical models

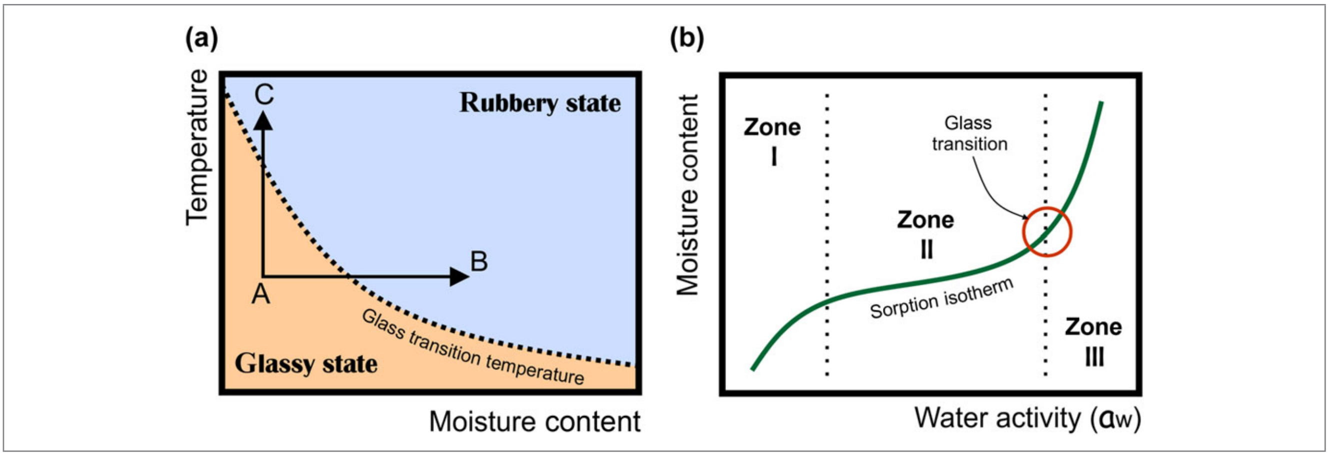

Figure 8–(a) General glass transition phase diagram: the component change from glassy stat to rubbery by increasing its moisture content or by increasing its temperature. Adapted from Bell and Labuza (2000). (b) General sorption isotherm diagram.

used to fit the data for the DCS hydration kinetics, the most used being Fick's Second law, the Peleg model and the first order kinetics equation. However, there are other mathematical models that are more specific for certain conditions that need to be better explored.

Fick's second law. Fick's Second law (Table 2) is used to describe the hydration process as an unsteady state purely diffusion process, being based on the diffusional works of Fick (Fick 1855). This equation has many solutions for regular geometries, such as infinite plates, infinite cylinders and spheres (Crank 1979), in the form of series with different terms. The main advantage of this equation is that only 1 parameter is estimated: the diffusivity (D_{AB}), which represents the diffusion of a component under isothermal and isobaric conditions (Laurindo 2016). Generally, it is described as an effective diffusivity (D_{eff}), a general diffusional coefficient considering all kinds of water transfer phenomena. The limitation of this equation is that some considerations must be assumed: (i) The geometry of the grain should be approximated to a regular geometry (plate, cylinder or sphere); (ii) The grain is an isotropic material, with homogenous composition and structure; (iii) The changes in volume and characteristic length during processing must be negligible; (iv) The water transfer only takes place by diffusion; (v) the diffusivity (D_{AB}), or effective diffusivity (D_{eff}), is a constant property of the grain (at each condition of temperature, for example), which does not change during processing and is the same in each part of the grain; (vi) Depending on the shape and process conditions, the solution of Fick's Second law becomes a sum of infinite terms, and a significant number of them have to be selected to estimate the diffusivity.

First-order model. This equation (Table 2) considers that the hydration of grains follows a first-order kinetics reaction (Abu-Ghannam and McKenna 1997a). In fact, the hydration rate is directly related to the difference between the equilibrium moisture content and the moisture reached at each process time (Bera and others 1990). This equation fits most of the grain hydration kinetics data with DCS behavior well. However, the structure of the grains must be very homogeneous to reach a suitable fitting, since this equation considers that the hydration kinetics is conducted mainly by diffusion. It means that it is assumed that all the tissues are hydrated at the same time and at the same hydration rate. In addition, this equation enabled us to estimate the equilibrium moisture content (M_∞) and the hydration rate (k_L).

Peleg model. This is the most commonly used equation for hydration and rehydration of different food products (Table 1). Although it is a semi-empirical equation (it was not derived from any physical law or diffusion theory), it fits the hydration of different products very well, using only 2 parameters (Peleg 1988) (Table 2). The advantage of this model is that both parameters have physical explanations for hydration process. The inverse of the value of k_1 is equivalent to the hydration rate and the sum of the initial moisture content plus the inverse of the value of k_2 is the equilibrium moisture content. Furthermore, during the data fitting, the initial moisture content can be set. Therefore, the predicted curve will always pass through the initial experimental moisture content. On the other hand, if the structure of the grain is too complex, this equation could not fit the experimental data well - as for corn kernels (Miano and others 2017a). Furthermore, new studies are enhancing the interpretation of the Peleg Model, such as by Kumar and others (2011), who stated that this equation can be defined according to a pseudo-second order kinetics expression.

Other models. There are many other models used to fit the hydration data of DCS grains (Table 2), some of them only used in certain conditions. For example, the model in Hsu (Hsu 1983) was developed considering the following assumptions: (i) spherical seeds, (ii) diffusion takes place only in a radial direction and (iii) the volume variation during hydration is negligible. Consequently, under these conditions, this equation can fit well for spherical grains like soybean, but this model is not suitable for other such grains as wheat kernel, rice kernels or beans.

Becker's model (Becker 1959) is an equation obtained by mathematical analysis of Fick's second law for arbitrary shapes. This equation was used for the drying and hydration of cereal grain like corn kernels and wheat kernels.

The Nicolin–Jorge model has demonstrated a suitable adjustment for grains including soybean, corn kernels and rice kernels. It was obtained from mass balance (Nicolin and others 2015). For fitting the hydration kinetics data, the grains should be considered to be regular geometry bodies, such as spheres, cylinders or parallelepiped.

Further, there are some models composed of 2 terms, which can be related to 2 mechanisms of hydration or 2 main structures. For example, the model proposed by Miano and others (2017a) to describe the hydration kinetics of corn kernels considers hydration as a 2-step process: the first where capillarity flow is predominant and the second where diffusion is the predominant water transfer phenomenon (Figure 5). In addition, the model proposed by (Paquet-Durand and others 2015) consists of a modified Peleg model with 2 terms. This equation was used to describe barley kernel hydration kinetics, where 1 term of the equation described the hydration of the bran, and the second the hydration of the endosperm.

The Page model (Page 1949) is widely used for drying processes, but it can be also used for hydration since it fits downward concave shape curves. This equation (Table 2) was empirically obtained, adding 1 more parameter (shape parameter) to the first order kinetics equation in order to adjust the data better. Even so, recently, Simpson and others (2017) stated that the Page equation parameters could have physical meaning, which can be interpreted using the fractional calculus approach: k_p would be related to the diffusion coefficient and the sample geometry and n would be related to the diffusion type and food microstructure.

In addition, Khazaei and Mohammadi (2009) proposed applying the same equation (Table 2) used to describe the creep of viscoelastic products (Rao and Steffe 1992) due to its similar curve shape. This model considers the hydration kinetics divided into 2 steps: the first with rapid water absorption, probably due to capillary mechanisms, and the second with a slow rate. It is interesting to note that this is the observed behavior for some grains, such as corn (Miano and others 2017a). However, this model considers that the grains do not reach an equilibrium moisture content and they absorb water linearly to infinite, which would be inadequate. Further, this model has 3 parameters: M_{rel} represents the quantity of water absorbed in the first part of the process, t_{rel} is the time needed to absorb 63% of the total water absorbed by the grain and k_{rel} is related to the water absorption rate in the relaxation phase. In fact, this model was used only in chickpeas and sesame seeds (Table 1).

Finally, another model used to fit the hydration kinetics is the Weibull distribution type equation (Machado and others 1998). This model has 2 parameters: ⟨ whose reciprocal is related to the process rate (it represents the time needed to reach 63% of the process) and β, known as a shape parameter (Marabi and others 2003).

Mathematical models for sigmoidal hydration behavior. Contrary to the DCS behavior, only 2 models are reported in the literature to describe the hydration of grains with sigmoidal behavior, probably due to this behavior being little studied and only found in certain legume grains. Consequently, there is still the need for more studies to find new mathematical models for describing the sigmoidal behavior of hydration, especially considering physical laws to deduce phenomenological models, but also considering empirical models with better adjustment, interpretation and/or convenience.

Kaptso et al. model. The first equation for sigmoidal behavior of hydration kinetics was proposed by Kaptso and others (2008). This semi-empirical equation has 3 interesting parameters that describe the sigmoidal behavior (Table 2). Parameter k_k is related to the hydration rate (curve slope), parameter τ is related to the lag phase time (inflexion point of the curve) and parameter M_∞ is the predicted equilibrium moisture. This equation successfully fitted the hydration kinetics data of many legume grains (Table 1).

Ibarz-Augusto model. This equation (Equation 5) was developed considering the hydration process as a second-order autocatalytic kinetics (Ibarz and Augusto 2015). In contrast to Kaptso et al. model, this equation is simpler since it has only 2 parameters: k_{IA},, which is related to a combination between the hydration rate and the lag phase time, and M_∞, which is the predicted equilibrium moisture content. However, with only 2 parameters, fitting the data could be challenging. Another drawback to this equation is that the lag phase time is not directly given by the equation. However, it can be calculated using another equation (Table 2).

Hydration Process Improvement

As the hydration process of grains is a batch and time-consuming process, its enhancement is very desirable. There are many technologies that have been used to accelerate grain hydration, such as the use of soaking water at elevated temperatures, high-power ultrasound and high hydrostatic pressure. Table 1 shows the technologies used for enhancing the hydration process of diverse kinds of grains and are described below.

Hydration at hot temperatures

This is the most frequently-used technology over the years for enhancing the hydration process. The use of soaking with hot water has effects not only on the hydration rate, but also on the equilibrium moisture content and the lag phase time. The main effects of this technology in each hydration characteristics are presented below.

All works (Table 1) have stated that the higher the temperature of the soaking water, the higher the hydration rate will be. This increase behaves exponentially; thus, the Arrhenius equation can be used to describe it and calculate the activation energy. The causes this improvement is attributed to are: (i) the increase in the reaction velocities; (ii) the reduction in water viscosity, which improves the capillary flow (Oliveira and others 2013); (iii) the dilatation of the tissues and pores (Oliveira and others 2013); (iv) the partial solution of some component, which increases the pore size.

In grains with sigmoidal behavior, the use of high temperatures reduced the lag phase time (Kaptso and others 2008; Piergiovanni 2011; Oliveira and others 2013; Miano and others 2015b). As the lag phase is related to the grain seed coat, the use of high temperatures reduces the lag phase time by: (i) accelerating the hydration of the seed coat by the mechanisms explained for the increase in the hydration rate (Oliveira and others 2013); (ii) reducing the minimum moisture content to change its component state (from glassy to rubbery), increasing its permeability to water (Figure 8a) (Ross and others 2013; Miano and Augusto 2015).

When high temperatures are used during the hydration process, the equilibrium moisture content can be increased, reduced or maintained without variation. This depends on the grain thermosensitivity and the evaluated temperature (temperatures higher than 60°C can drastically change the properties of such grain components as starch and proteins). In addition, the effect of the temperature on the parameter can be different depending on the temperature range evaluated. In other words, the parameter values can increase, reduce or stay constant depending on the temperature range studied. In most cases, the equilibrium moisture content increases (Verma and Prasad 1999; Maskan 2001; Bello and others 2004; Resio and others 2006; Khazaei and Mohammadi 2009; Kashiri and others 2010; Fracasso and others 2015; Miano and others 2015b; Montanuci and others 2015; Edith and others 2016; Ramos and others 2016) due to some mechanisms: (i) the pores and spaces inside the grains expand, enabling more water to be held; (ii) the solubility of the components increases, opening the pores. On the other hand, and in few cases, the use of high temperatures reduced the equilibrium moisture content (Abu-Ghannam and McKenna 1997b; Gowen and others 2007; Prasad and others 2010; Oliveira and others 2013; Johnny and others 2015). This can possibly be due to some mechanisms: (i) a high quantity of water-soluble components, which are lixiviated (Abu-Ghannam and McKenna 1997b); (ii) damage to cell membranes and walls (Oliveira and others 2013); (iii) the rapid saturation of the external layer of the grains with water, decreasing the driving force of mass transfer (Oliveira and others 2013). Finally, some grains are more stable at high temperatures and their equilibrium moisture content is not significantly changed using elevated water soaking temperatures (Kaptso and others 2008; Coutinho and others 2010). In fact, these results could be only considered as true in the temperature range studied. Perhaps in this range the equilibrium moisture content of the grain is not affected. Therefore, to give conclusive statements, wider ranges of temperature need to be studied.

Nevertheless, although the use of elevated temperatures enhances the hydration rate, it has the following disadvantages: (i) it can cause nutritional changes; (ii) component changes like starch gelatinization and protein denaturation; (iii) additional costs of heating the whole mass of grain and water, as well as the thermal isolation. Accordingly, other technologies for improving the hydration process of grains were also studied. Only isothermal hydration kinetics were evaluated, thereby, the hydration kinetics under non isothermal conditions need to be studied, for instance, using higher temperatures at the beginning of the process and lower ones at the end to avoid damage to thermosensitive grains.

Ultrasound technology

The ultrasound technology was recently used to improve the grain hydration process with successful results (Table 1). Ultrasound is acoustic waves with frequencies higher than 20 kHz, which can cause physicochemical changes in food, depending on the power used (Mason and others 1996). This technology was applied directly to the hydration (ultrasound assisted hydration process) using ultrasonic water baths (Yildirim and others 2010; Ranjbari and others 2013; Ghafoor and others 2014; Patero and

Augusto 2015; Miano and others 2016b; Miano and others 2017a) or as a pre-treatment using an ultrasonic probe (Ulloa and others 2015; López López and others 2017).

Some mechanisms of mass transfer enhancement have been attributed to ultrasound technology (Miano and others 2017b). Those reduced the internal resistance to mass transfer, once the external resistance (from the bulk water to the external grain layer) is negligible. Ultrasound can enhance the water flow through the grains by direct or indirect effects (Miano and others 2016a). The direct effects are related to the acoustic wave passing through the grains. This provokes alternative compression and expansion of the medium (tissues, air, water) causing pressure differences (Floros and Liang 1994; Miano and others 2016a) and an increase in the capillary flow thus enhancing the hydration. This is also called the "sponge effect" and "inertial flow". The main indirect effect of ultrasound is the structural changes due to acoustic cavitation, which consists of the implosion of micro water bubbles inside the tissues causing cell and tissue disruption and the formation of micro cavities (Mason and Peters 2004). These cavities can enhance water transfer in the grains. However, acoustic cavitation has more effect in foods with high water activity (Miano and others 2016a). Therefore, this mechanism is intensified as the grains are hydrated (water activity increase), which could explain why ultrasound has more effect in the last part of the hydration process.

In fact, ultrasound technology accelerates the hydration process by increasing the hydration rate and reducing the lag phase time due to its direct and indirect effects. In addition, the higher the ultrasonic power, the better the improvement in hydration is (Yildirim and others 2010; López López and others 2017). Regarding the equilibrium moisture content, some studies have reported that this characteristic is increased (Ghafoor and others 2014; Patero and Augusto 2015; López López and others 2017; Miano and others 2017a), and others that it is not changed (Ulloa and others 2015; Miano and others 2016b). The increase in the equilibrium moisture content is attributed to the pores opening and the micro cavities and channels forming by ultrasound, which allow the grain to hold more water.

Besides increasing the hydration rate by direct and indirect effects, ultrasound also reduces the lag phase time in grains with sigmoidal behavior. Among the direct effects, ultrasound pumps water from the hilum to the empty space between the cotyledon and the seed coat, causing faster hydration of the latter. The permeability of the seed coat to water is increased thus reducing the lag phase time (Miano and others 2016b).

Moreover, it is interesting to mention that the use of ultrasound in grain processing did not alter its starch (one of the main components) (Miano and others 2016b; Miano and others 2017a), increased its germination speed (Miano and others 2015a; Miano and others 2016b) and reduced cooking time (Yildirim and others 2013; Ulloa and others 2015). Therefore, the use of ultrasound technology has different advantages, being a promising technology for improving grain hydration.

High hydrostatic pressure (HHP)

High hydrostatic pressure is an emerging technology used for enhancing many processes. The effect of this technology on grain hydration has been studied in few works (Table 1). Consequently, the possible enhancement of the hydration process by high hydrostatic pressures is still uncertain. There are 6 works that have used this technology to date (Sangronis and others 2002; Ibarz and others 2004; Ramaswamy and others 2005; Ueno and others 2015; Belmiro 2016), all applied high pressures as a pre-treatment for chickpeas, adzuki beans, navy beans, carioca beans and black kidney beans. All these works used pressures from 33 MPa to 700 MPa and reported that this technology improved the hydration process by increasing the hydration rate. Furthermore, Ibarz and others (2004) stated that by using HHP above 550 MPa, the equilibrium moisture content of the grains was reduced due to the compactness of the structure. These works attributed this improvement to structural changes.

However, due to the experimental design, this improvement may not be only associated to HHP, as the HHP pretreatment caused the initial moisture content of the grains to increase in those studies. Therefore, the hydration process was affected by this initial moisture difference (See section 2.3). As this effect was not evaluated, it is difficult to identify the real contribution of HHP. The initial moisture content effect must be isolated to study better the HHP and further studies are called for to give conclusive results.

Other technologies

Irradiation is another technology studied in the hydration kinetics. To date, there has only been 1 work using this technology (Ramaswamy and others 2005). This work irradiated navy beans at 2 and 5 kGy using a ^{60}Co γ-ray source, and concluded that irradiation improved the hydration process when it is used for more than 60 min. In addition, irradiation caused the equilibrium moisture to increase, perhaps due to the breaking of starch molecules. However, no further information or description was given about using irradiation on the hydration of grains.

Furthermore, the work by Naviglio and others (2013) stated that the hydration process is enhanced by using cyclical pressure changes. It should be made clear that this technology is different from the High Hydrostatic Pressure, since cyclical pressure changes (not necessarily high) are applied throughout the process. The improvement in hydration with this technology makes sense since the water is better transferred inside the grain by improving the capillary flow (similarly to the ultrasound technology, which causes alternating changes in pressure). Therefore, this cyclical application causes pressure differences inside the grains, and so improved the capillary flow. Similarly to this work, Zanella-Díaz and others (2014) applied gradient pressures during the hydration process with low and high pressures. They stated that with this application, the gases trapped inside the grains are driven out, causing water to enter by bulk flow.

In addition, microwave output power has been used in the hydration of cowpeas. The hydration kinetics accelerated as the microwave output power increased (Demirhan and Belma 2015). The mechanisms were not explained. However, as in the drying process, microwaves might help to improve the hydration process by transferring energy to the water molecules, facilitating their movement.

As can be seen, more research is needed to assess the role of microwaves, irradiation, and cyclical application of pressure in grain hydration.

Final Remarks: Research and Industrial Needs and Future Trends

Description of grain hydration

The hydration of grains is a complex process, which depends on the structure and composition of the grains and the technology used. It has yet to be fully described. The role of each grain structure and component in the hydration is still unknown (for example, the seed coat impermeability for the sigmoidal behavior of hydration kinetics), as is the correlation between the grain components and the structure and hydration characteristics (hydration rate, equilibrium moisture content and lag phase time). These studies are very important since there are many mistaken ideas about hydration kinetics that need to be clarified and revised. For instance, Miano and others (2017c) demonstrated that the following statements are not always fulfilled: grains with dark colored seed coats hydrate slower than light colored ones; grains with sigmoidal behavior of the hydration kinetics hydrate slower than the ones with DCS behavior; bigger grains have a slower hydration kinetics compared to smaller ones. Therefore, the hydration of grains is a complex process where such physical characteristics as color, size, hardness and porosity, and chemical composition including the starch, protein and fat contents, and phenolics. cannot be individually attributed to a specific characteristic of the hydration process. All those intrinsic characteristics interact during hydration, giving the particular behavior to the grain. Consequently, evaluating the causes of the characteristics of the hydration behavior (lag phase, hydration rate and the equilibrium moisture content) is still a challenge.

Another study that needs to be carried out to complement the description of hydration is into whether the grain metabolism has an influence on the hydration kinetics. During the hydration of grains, their enzymes are activated and their respiration rate is increased (Bewley and others 2013). Perhaps these can enhance or hinder the hydration rate. As living cells are capable of controlling osmotic pressure, they could also control hydration. Therefore, the hydration of "dead" grains should be studied to verify whether the metabolism makes any contribution to the hydration kinetics.

Modelling hydration kinetics

Due to the complexity of the process, the hydration of grains must not be considered merely as a diffusional process, since capillary flow has a significant contribution for water transport. Almost all the mathematical models used to explain this process consider diffusion as the main phenomenon. Therefore, it is necessary to conduct more studies to describe the mechanisms involved and find new equations that consider diffusion, capillary flow, volumetric expansion, exit of trapped gases, glassy transition and structure relaxation.

Furthermore, Sam Saguy and others (2005) recommended including the porous media theory to improve the modelling of hydration. The drawback to use this approach is to determine some grain physical properties, such as the porosity, hydraulic conductivity, permeability and fluidity, as well as considering the whole grain being isotropic. For example, the porosity of the grain is not homogeneous due to it having different tissues with varying porosities (size, tortuosity). However, by using techniques like scanning electronic microscopy (SEM), X-ray, X-ray microtomography and others, the porosity and its tortuosity can be studied. The other physical properties could be determined using soil science techniques. However, these require long hydration processes, which can cause microbial spoilage, swelling and physical destruction of the food (Troygot and others 2011). In fact, there are some works on food rehydration using this approach, including Weerts and others (2003) with tealeaves and van der Sman and others (2014) with freeze dried carrots, in both cases, products had a relatively homogeneous structure. However, there are no works on the hydration kinetics of grains. Therefore, the possibility of using the porous media and capillarity approach with grains is still open.

Another approach that can be considered in grain hydration modelling studies is the use of the hydric potential theory. This approach is used for studying the water transfer from the soil to the plant (Bewley and others 2013). The hydric potential is considered the driving force for water transfer and considers many physical mechanisms besides diffusion. The total hydric potential is divided into 4 potentials: pressure potential, osmotic potential, matrix potential and gravitational potential (Laurindo 2016). The pressure potential is related to the absolute pressure that water is submitted to and the turgidity of the cells; the osmotic potential is related to the osmotic pressure due to the dissolved solutes in the cell water; the matrix potential is related to the food porosity and depends on the sorption forces and surface tension (capillarity flow); and the gravitational potential is related to the pressure generated by a fluid due to the height difference over a reference level. There is only 1 work on the water potential theory approach in salting processing of chicken breast (Schmidt and others 2008), but no work using it for grain hydration. Consequently, it would be interesting to study it for modelling.

Finally, another tool for modelling grain hydration is the use of fractional calculus, a powerful tool that was recently used to explain Page's model (Simpson and others 2017) and also to describe the viscoelastic properties of food (Guo and Campanella 2017), among other applications in food processing. According to Simpson and others (2013), the application of this tool can provide many applications for modelling mass and heat transfer. As the food mass transfer does not take place only by diffusion due to the complex structure of food, these authors proposed the use of fractional calculus to solve Fick's Law. The fractional order (α) explains how diffusional the process is, this being related to the heterogeneous structure of food. When $\alpha = 1$, the equation becomes a simple exponential equation which would represent purely diffusional processes. However, when the fractional order is different, the equation obtained shows that diffusion is not the only mechanism during mass transfer. In fact, if $0 < \alpha < 1$, the mass transfer is considered a sub-diffusional process. It means that the diffusant (the component that is diffusing) takes more time to travel than the diffusional theory predicts. On the other hand, if $1 < \alpha < 2$, the mass transfer is considered a super-diffusional process. It means that the diffusant travels faster than the diffusional theory predicts. Our interpretation is that when $\alpha \neq 1$, other mechanisms than diffusion are important. For example, the "super-diffusional process" ($1 < \alpha < 2$) may indicate the importance of capillarity.

As can be seen, there are many approaches that can be used for modelling grain hydration kinetics. Consequently, new phenomenological models should be deduced to describe the process.

Technologies exploration and scaling up

Some technologies used to enhance the hydration process need to be studied better. For instance, High Hydrostatic Pressure and Irradiation. The few works that used HHP as a pre-treatment in the hydration process have shown no conclusive results. It is difficult to conclude whether HHP as a pre-treatment enhanced the hydration process, since, during pre-treatment, the initial moisture content is increased and this also affects the hydration kinetics. Therefore, future works keeping the initial moisture content constant during HHP pre-treatment need to be performed. Furthermore, more works with the use of irradiation to improve the hydration process must be also conducted to determine which hydration characteristic is affected.

Other technologies may be explored for the grain hydration process. For example, the application of pulsed electric fields (PEF) and moderated electric fields (MEF). These technologies cause reversible permeabilization of the cell membranes, improving the mass transfer, as in drying, osmotic dehydration (Barba and others 2015) and extraction (Sensoy and Sastry 2004). In addition, the use of alternating increases and reductions of pressure may be a promising technology to improve grain hydration, as in the work by Naviglio and others (2013). However, more studies are necessary. Furthermore, the use of plasma can be a good technology to enhance the hydration process as it can affect the food components (Knorr and others 2011). For example, it can be applied only to the seed coat to change its composition, and thus its permeability to water. Finally, as ozone is used for microbial decontamination of grains (Tiwari and others 2010), its effect on the hydration kinetics should be studied.

Although hydration is accelerated by many technologies, the process still takes too long. However, this drawback can be turned into an advantage, for example, by using the hydration time to incorporate some component into the grains. There is 1 published work where grains were soaked in mineral solutions (iron and zinc) in order to fortify the grains and evaluate the effect on cooking and germination (Oghbaei and Prakash 2017). This work demonstrated that by soaking the grains in mineral solutions, they can be fortified. However, the effect of these solutions on the hydration kinetics has not yet been studied. In fact, this issue is being studied by our research group, considering both dissolved and microencapsulated nutrients.

Furthermore, it is important to state that the optimal use of these technologies must be determined. Therefore, optimization studies are required, for example: determining if it is necessary to apply a technology throughout the whole hydration process or only to a specific part; determining the optimum conditions (temperature, ultrasound power, pressure); and optimizing the equipment design. After performing these studies, scaling up would be the next step.

Regarding comparing all the novel technologies for enhancing the hydration process, we can conclude that ultrasound technology is the most widely studied and most promising. Therefore, the way to scale this up must be studied. As grain hydration is a batch process, it is performed in tanks with large quantities of grains. One way to use ultrasound would be setting the ultrasonic transducers on all the tank surfaces. Zhai and others (2017), demonstrated that by setting ultrasonic transducers in each of the tanks, the energy distribution was better than only placing them on the bottom as in most of the equipment. Therefore, this would be one way to begin the scaling up process. In addition, according to Patist and Bates (2008), there are some aspects that have to be considered and studied for the commercial scale: (i) High-power ultrasound equipment with a suitable wave distribution for large commercial operations; (ii) Energy-efficient equipment; (iii) systems that are easy to install and/or retrofit; (iv) Competitive energy cost in comparison with conventional technologies; (v) Low maintenance cost.

The future studies

Since space exploration is moving fast and manned voyages to other planets are being planned, the future of food supply and processing needs to be explored. For example, although current space food is based in pre-processed meals, when going further and longer, the system must be changed to the production of foods – which is the reality in the planning of expeditions to Mars (Perchonok and others 2012). In this case, grain hydration kinetics could be different in extra-terrestrial condition since many terrestrial considerations will be discarded or different. For example, the most important effect would be gravity. The gravitational pull on Mars is lower than on Earth. Therefore, this would change how capillarity takes places, maybe increasing the water uptake in grains. In addition, the atmospheric pressure is different, affecting the volume changes of the components. Evidently, considerably more works about the hydration of grains will need to be conducted.

Conclusion

The hydration of grains is an important process for their industrialization and direct consumption. Over time, the research works have demonstrated that there are 2 kinds of behavior in hydration kinetics: the downward concave shape and the sigmoidal shape behavior, the second being exclusively for legume grains. These behaviors depend on the grain structure and composition. This process is a mass transfer unit operation in which not only diffusion, but also capillary flow take place and many mathematical models have been used to successfully describe the hydration kinetics. However, to date, not all the water transfer mechanisms have been considered in the deduction of the model. Furthermore, many works have verified that grain hydration can be accelerated by many conventional (hot water soaking temperatures) and nonconventional technologies (ultrasound, high hydrostatic pressure, irradiation, and so on). Finally, more studies are recommended to complement the knowledge about this important process, such as to understand the relation between the grain structure/composition and the hydration behavior, looking for more technologies to improve the process, deducing better mathematical models and optimizing the process, as well as studies on scaling it up.

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Author Contributions

AC Miano and PED Augusto conceived and designed this critical revision, studying and evaluating the available information and redacting the manuscript.

Hydration kinetics determination

The hydration kinetics data of grains is easy to obtain in laboratory. The moisture in the grains during hydration can be obtained by taking samples every certain time and measuring their moisture content using the oven method. However, this is a destructive method. A higher number of samples would be needed and the sample/water relation should be controlled. In fact, it is assumed that the mass gained (weight) by the grain is only due to the absorbed water. Many works have demonstrated that the mass loss caused by leaching of water-soluble components is negligible. Consequently, the grain moisture over the processing time can be obtained by mass balance.

Therefore, a recommended way to obtain the hydration kinetics data is as follow:

- ☐ Determine the initial moisture content of the grain. This can be determined by the oven method or by using an infrared moisture analyzer.
- ☐ Weigh a certain quantity of grains (for example 10 g) and put them into a net bag. The net bag helps to remove the grains easily from soaking water.
- ☐ Hydrate the grains, and remove them to be weighed at certain times. It is recommended to record more data at the beginning of the process to avoid losing information if the grain has sigmoidal behavior.
- ☐ Determine the moisture content of the grains by mass balance each time. Ensure that the solid leaching from the grains is negligible.
- ☐ Perform the experiment until the mass increase is negligible (for example, <2% of difference).
- ☐ Plot the moisture content (on a dry basis) against time and use the most suitable model to fit the data.

The main advantage of this method is that it is not a destructive analysis. Therefore, the samples can be used for further analysis, such as for cooking or germination. In addition, this method reduces the error of each replicate as the same grains are always analyzed.

There are some special experiments that can help to describe the hydration kinetics and determine the water entry pathway of the grains.

- ☐ Determine the hydration kinetics by sealing some structures: the hilum, seed coat, micropyle, pericarp, tip cap, etc. This will enable the contribution of each structure to water entry to be established (Ramos and others 2004; Miano and others 2015b; Miano and others 2016b; Miano and others 2017a). Some examples of materials adequate for this are wax, nail polish or contact glue. Ensure that the material used is not lost in the water or by the expansion of the grain.
- ☐ Use some analyses to determine the grain structure. These include scanning electronic microscopy (SEM), X-ray, X-ray microtomography, etc. These analyses will help to determine if there is some "empty" space into the grains and the porosity of each structure (Friis and others 2007; Miano and others 2015a; Miano and others 2015b; Miano and others 2017a). These techniques require the samples to be dried. Other techniques, such as nuclear magnetic resonance (NMR), can be also used to follow the water entry pathway.
- ☐ Determine the hydration kinetics of the grain at different initial moisture contents. This allows us to know how the hydration behavior is affected by the initial moisture content, as well as the initial moisture content at which the seed coat becomes more permeable to water (Miano and Augusto 2015). In addition, the sorption isotherm of the grains would be useful for determining the approximate moisture content when the seed coat passes from the glass transition state to rubbery state.

Nomenclature

A	Area (Table 2) [m^2]
Bi	Biot number (Table 2) [dimensionless]
C_A	Component concentration (Table 2) [mol/m^3]
D	Diffusivity or diffusion coefficient (Table 2) [m^2/s]
D_{AB}	Diffusivity (Table 2) [m^2/s]
Fo	Fourier number (Table 2) [dimensionless]
J_i	Bessel functions of i order
k_1	Peleg model parameter related to the hydration rate (Table 2) [s]
$k_{1.1}$, $k_{1.2}$, $k_{2.1}$, $k_{2.2}$	Modified Peleg model parameters. Same meaning as Peleg model (Table 2) [different units]
k_2	Peleg model parameter related to the equilibrium moisture content (Table 2) [100kg d.b./kg]
k_{I1}, k_{I2}	Ibarz et al. Model parameters (Table 2) [different units]
k_{IA}	Hydration rate (Table 2) [1/s]
k_k	Hydration rate (Table 2) [1/s]
k_L	Hydration rate (Table 2) [1/s]
k_{M1}, k_{M2}	Two-steps hydration model parameters related to the hydration rate of each step (Table 2) [1/s]
k_p	Hydration rate of Page's model (Table 2) [1/s]
k_{rel}	Rate of absorption in the relaxation phase (Table 2) [kg/100kg d.b. · s]
k_s	Overall mass transfer coefficient (Table 2) [m^2/s]
M	Moisture content (Table 2) [kg/100kg d.b.]
M_0	Initial moisture content (Table 2) [kg/100kg d.b.]
M_{rel}	Moisture content reached in the first part of the absorption (Table 2) [kg/100kg d.b.]
M_t	Moisture content as a function of time (Table 2) [kg/100kg d.b.]
M_∞	Equilibrium moisture content (Table 2) [kg/100kg d.b.]
n	Page fitting parameter (Table 2) [dimensionless]
p	Percentage of hydration contribution of each hydration step (Table 2) [dimensionless]
t	Hydration time (Table 2) [s]
t_{rel}	Time to hydrate 63% of the total absorbed water (Table 2) [s]
V	Volume (Table 2) [m^3]
α	Shape parameter (Table 2) [dimensionless]
β	Rate parameter (Table 2) [s]
β_i	are the roots of the equation: $\beta_i \cdot tan\ \beta_i = Bi$ for rectangular coordinates; $\beta_i \cdot J_1(\beta_i)/J_0(\beta_i) = Bi$ for cylindrical coordinates; $\beta_i / tan\ \beta_i = 1 - Bi$ for spherical coordinates; (Table 2) [dimensionless]
∇	Nabla operator
ρ_A	Volumetric moisture content (Table 2) [kg/m^3]
ρ_{eq}	Volumetric equilibrium moisture content (Table 2) [kg/m^3]
τ	Lag phase time (Table 2) [min]

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