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Mass Transfer in Cheese

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1. Introduction

1.1 Introduction to food preservation

Food transformation of raw items, preservation of food characteristics, and supplying of food products are the main goals for the food industry. The transformation and preservation of food materials involve a diversity of processes oriented to produce intermediate or final items, maintaining their nutritional, physical, and other desired properties. In order to transform foods and preserve their properties at the best conditions, the operational variables of the food processes should be correctly identified to get maximum benefits.

Among the many transformation processes used for foods making, there are some frequently applied in the milk industry, such as refrigeration, standardization, homogenization, centrifugation, pasteurization, evaporation, salting, and dehydration, among others, depending of the dairy product to be manufactured. Each one of them offers characteristics and advantages that may be combined to get a better dairy product.

Furthermore, the combination of preservation treatments has been and should be oriented to influence positively the properties of the final products. In general, the preservation processes may be divided in conventional and minimal, the first group produces foods that are shelf stable, they can be stored by several months at normal environmental. Whereas the minimally processed foods have a shorter shelf life, they retain their freshness, and nowadays, they are more acceptable by consumers. Most of the studies about the conventional, minimal, and combination of methods, also known as hurdle technology, have covered microbiological, chemical, and quality aspects, and only a minor quantity of works have focused on engineering and physical aspects. Therefore, more efforts and studies should be dedicated to cover the engineering approach, such is the case of mass transfer in food systems, cheeses among them.

1.2 System equilibrium

From the engineering point of view, a food item is a system strongly influenced by the surroundings (Figure 1), or it influences importantly the immediate environment. When the food material is not suffering any change, the system is balanced or in equilibrium, but if some of the food properties change due to a physicochemical driven force, the specific food will develop a transport phenomenon approaching to the equilibrium. Thus, a dairy product may be in chemical, mass, mechanical, phase and/or thermal equilibrium (Cengel and

Boles, 2006), depending of the particular conditions, otherwise the food system will present changes as a result of natural or artificial processes in which a physicochemical potential exists. The physical processes developed in a food system are normally an expression of one of the transport phenomena, momentum, heat or mass transport, even as a single or simultaneous change, in which the processes are also identifies as unit operations or food process operations.

Fig. 1.

When thermodynamic aspects are considered for the state of a food system, there is a Gibbs free energy that determines the equilibrium. A null free energy implies an equilibrium state, while a free energy different to zero is for food systems with a changing nature or exposing to a given process. Gibbs free energy includes enthalpy, temperature and entropy properties (Karel and Lund, 2003).

The lack of equilibrium of any food system requires specific considerations of the involved phases in the mass transfer phenomenon; thus, vapor (or gas)-liquid equilibrium is implied in dehydration and distillation, whereas the liquid-liquid equilibrium is involved in extraction, and solid-liquid equilibrium is considered in lixiviation. Further the gas-solid or vapor-solid equilibrium is too much transcendental in food systems transformations.

1.3 Transport phenomena

A transport phenomenon is the evolution of a system toward equilibrium; that is to say, it is a change of the food system, some or several of the food properties are modified due to the given change and those transformations are mathematically modeled by the so named equations of change, in which the quantity or volume of the dairy product will affect the rate of transport, whereas the geometry of the changing system will affect the direction. If a momentum gradient is present between the food system and the surroundings a transport of momentum will happen. When a difference of temperatures exists between them, a heat transfer will occur. And finally, if a chemical potential or a concentration driven force among the milk components is observed, then a mass transfer will be experienced (Vélez-Ruiz, 2009).

Any change developed within process equipment, also identified as food process operation may be analyzed from a basic principle in which one, two or three transport phenomena are taking place. As examples of food process operations in the milk industry, in which a transport of momentum is present, are: milk pumping and transportation through pipes, homogenization of fat globules in milk, and separation of fat from skim milk by centrifugation. Cooling, heating, pasteurization, and evaporation are unit operations in which thermal treatments or heat transfer are mainly involved; whereas salting, drying, and volatiles loss/gain or cheese components migration through of packaging films, are processes involving mass transfer, just to mention a few.

The work of many food engineers or scientists in the industrial or manufacturing role involves the development or selection of processes, the design or evaluation of the required equipments, and the successful operation of food plants, that are based on their fundamental concepts.

1.4 Water activity

The adsorption and desorption of water vapor by foods, is highly related to their stability and perishability. And although the water content is a control factor, several food items with the same moisture concentration exhibit different stability or perishability; thus the term of water activity (A_w) expressing the water associated to nonaqueous constituents, has became the physicochemical or thermodynamic concept more related to microbial, biochemical and physical stability. Water activity as an objective concept, that has been defined from the activity or fugacity relationship between the solvent and the pure solvent; it is expressed by the equation 1, a practical expression of it, in which the assumptions of solution ideality and the existence of thermodynamic equilibrium are been considered (Saravacos, 1986; Fennema, 1996; Vélez Ruiz, 2001; Toledo, 2007):

$$A_w = \frac{p_w}{p_w^0} = \frac{\%RH}{100} = \frac{\%ERH}{100} \tag{1}$$

Where: A_w is the water activity (dimensionless), p_w is the partial pressure of water in the food (Pa or mm Hg), $p_w{}^0$ is the partial pressure of pure water (Pa or mm Hg), $\%RH$ is the percentage of relative humidity, and $\%ERH$ is the percent of equilibrium relative humidity.

As it is known and expected, water activity (0 – 1.0) has been associated with stability problems and several reactions developed during the storage, such as microbiological growth, kinetics of nutrients loss, browning reactions, and also with physical changes, like dehydration or rehydration and textural modifications. Particularly, the A_w is different for each cheese type, due to variability in composition and moisture gradients, as well as salt content. For this reason, several authors have proposed to evaluate the A_w for cheeses, by utilizing the chemical composition through of empirical relationships (Saurel et al., 2004). Some examples of cheeses in which empirical equations have been obtained for water activity evaluation, are the following: European varieties (Marcos et al., 1981), Emmental (Saurel et al., 2004), and Manchego type (Illescas-Chávez and Vélez-Ruiz, 2009). A couple of examples for evaluation of A_w are presented next:

i. Saurel et al. (2004) obtained a practical relationship for French Emmental cheese as a function of three variables, water, salt and free NH_2 concentrations ($R^2 = 0.92$):

$$A_w = 1.07 - 0.19X_{water} - 3.49X_{NaCl} - 0.33X_{NH_2} + 6.51X_{water}X_{NaCl} + 0.57X_{water}X_{NH_2} \tag{2}$$

X is the component content (mass fraction) of water, salt and free NH_2.

ii. Illescas-Chávez and Vélez-Ruiz (2009) used an empirical correlation between salt content and water activity (R^2 = 0.996) for Manchego type cheese, showed by a quadratic expression:

$$264A_w - 175.9A_w^2 = 89.77 + X_{NaCl} \tag{3}$$

A_w is the water activity in cheese, and X_{NaCl} is the salt concentration (g/100g).

2. Cheese as a system

Cheese as a biological system and as a dairy product, is one of the first, most popular and universal elaborated food item. Cheese represents a product in which the milk components are preserved. This food item, is known as cheese (in English), "fromaggio" (in Italian), "fromage" (in French), "kase" (in German), and "queso" (in Spanish). Thus, a cheese is a food system in which due to many components, it is exposed to many changes, either biochemical and/or physical. Thus, a cheese is a dairy product made to preserve most of the milk components, including fat, protein and minor constituents from the milk, eliminating water and/or serum and adding salt and other ingredients, with a special flavor and with a solid or semisolid consistency (Vélez-Ruiz, 2010).

2.1 Cheese manufacturing

Though there are a lot of cheese types, the elaboration process involves common stages in which the variations in some of the steps contribute to generate a diversity of cheese products. These treatments, food process operations or unit operations may be summarized in a number of six, in which some specific equipments and process conditions may vary (Vélez-Ruiz, 2010).

i. Milk recollection. Milk is recollected, clarified and cooled down, to ensure a hygienic raw material.

ii. Milk preparation. Basic processes such as, standardization, mixing, homogenization, heating and/or addition of microorganisms may be carried out in this part. The fat-protein ratio is frequently standardized, $CaCl_2$ is normally added, and pH is sometimes controlled to a needed value. On the other hand, pasteurization destroys pathogenic microorganisms and most of enzymes.

iii. Milk coagulation. Addition of rennet, coagulant or acid is completed in order to transform milk into a coagulum. The enzyme acts on a specific amino acid of the casein, whereas the acid generates precipitation of proteins.

iv. Whey elimination. The formed coagulum contracts and expel part of the entrapped serum, constituting the syneresis phenomenon. Whey elimination from the cheese is favored by cutting, scalding, and/or stirring, and lately by salting.

v. Curd brining/salting. Salt is added to the curd, as a solid material or as a solution to favor elimination of whey, to develop desired flavor, and to preserve cheese.

vi. Final treatments. Agitation, milling, heating, pressing, casing, turning, packing, waxing, wrapping, ripening and/or other treatments, are some of the final operations than may be utilized as part of the cheese making, to reach those specific characteristics of each type. Of all these possible treatments, ripening is the most important due to the biochemical, microbial and physical modifications occurring during this period.

Each operation contributes to the milk/curd/cheese transformation in which the biochemical (enzymatic, acidification, hydrolysis, lipolysis, proteolysis, etc), microbial (bacteria or molds) and physical changes (homogenization, shearing, mixing, gelation, syneresis, curd fusion, solids diffusion, etc) are important parts of this food system. In summary, through the manufacturing process, there are three stages affecting most importantly the cheese characteristics a) the milk formulation, with a huge number of ingredients such as calcium chloride, cream, lactoperoxidase, ropy microorganisms, milk powder, just to mention a few; b) the used operational variables, rennet, salt, forces or stresses (centrifuge, pressure, shear), temperatures of cooling and heating, treatment times, and shear rates, among others; and c) the biochemical and/or physicochemical transformations developed during the elaboration and maturing stages.

2.2 Classification of cheeses

Grouping of cheese types is extremely complicated due to the enormous variety of them, in addition to the aforementioned factors, there are variants due to size, shape, as well as culture of the region of manufacture. A number of efforts have been realized to classify cheese, taking different points of view in order to meaningfully group them. Some classifications are based on the cheese origin (animal, country), involved coagulation process, applied manufacturing operations, presence of microorganism, rheological parameters, moisture content, or other considerations.

A simple and practical classification of cheeses, that may be very useful, is based on the existence of a ripening process stage, grouping them in fresh and ripened cheeses. This classification ignore if cheese ripening is completed by bacteria or molds, neither includes size and external appearance.

Fresh cheeses have a shorter shelf life, they are high in moisture content; and if a package is used, a null or insignificant mass transfer through the film may be considered, being the salting the main treatment in which a mass transfer phenomenon is developed. In contrary, a ripened cheese will have a larger shelf life, normally they are more dried and packaged with different types of films; and in these cheeses three mass transport changes can occur: salting in the manufacturing process, drying during maturation in the cave of ripening, and migration of volatiles and components through the package.

2.3 Mechanisms of mass transfer

A good number of food process operations are based on the mass transfer phenomenon involving changes in concentrations of foods and cheese components, depending of the phases and particular components in the food or cheese item, considered as a multi-component mixture, or as a binary one to simplified the physical analysis.

Mass transfer is the result of a concentration difference or driven force of a specific component, the component moves out from a portion of the food item or cheese with a portion or phase of high concentration to one of low, without to forget the influence of the surroundings.

Mass transfer is analogous to heat transfer and depends upon the dynamics of the food systems in which it occurs. It is known that there are two mechanisms of mass transfer, the diffusion and convection phenomena; in the first one, the mass may be transferred by a random molecular movement in quiescent food fluids or static solid items; and in the second one, the mass is transferred from the food surface to a moving fluid. And such it happens in many food processes, both mechanisms are developed simultaneously. Mass diffusion and convection may be more or less important depending of the specific operation. In salting and constituents migration of cheese, the diffusion is by far the most important; whereas in dehydration of cheese by exposing to a dry atmosphere, both mechanisms are very important.

Diffusion

The basic relation for molecular diffusion for a food system defines the molar flux related to the component concentration, for steady processes it is modeled by the Fick´s first law (Bird et al., 1960; Welty et al., 1976; Crank, 1983; Welti-Chanes et al., 2003; Vélez-Ruiz, 2009):

$$J_{iz} = -D_{im} \frac{dC_i}{dz} \tag{4}$$

Where: J_{iz} is the molar or mass flux of the i component in the z direction (mol/m^{2}s or mg/m^{2}s), D_{im} is the mass diffusivity or diffusion constant (m^2/s), being specific for the i component in a given medium, dC_i/dz is the concentration gradient of the i component in the z direction (mol/m^4 or mg/m^4), dC_i is the concentration difference or driven force (mol/m^3 or mg/ m^3), and dz is the interface separation or separation distance between two points or portions with different concentration of the i component (m).

The molar flux of the involved component, in equation 4, may be converted to mass units of kilogram by considering the molar weight. Some diffusion constants have been evaluated for particular systems, few data are included in Table 1 (Welty et al., 1976; Okos et al., 1992). As it may be observed, gas diffusion is easier than liquid and solid diffusion, as well as liquid diffusion is easier than solid diffusion.

System	T (°C)	Dim (m^2/s) at 1 atm	Reference
Air in Water	25	6.37×10^{-2}	Welty et al., 1976
Carbon dioxide in water	25	5.90×10^{-2}	"
Hydrogen in water	20	3.06×10^{-1}	"
Sodium chloride in water	18	4.36×10^{-6} at 0.2 kg mole/m^3	"
Sodium chloride in water	18	4.46×10^{-6} at 1.0 kg mole/m^3	"
Sodium chloride in water	18	4.90×10^{-6} at 3.0 kg mole/m^3	"
Acetic acid in water	12.5	3.28×10^{-6} at 0.10 kg mole/m^3	"
Acetic acid in water	12.5	3.46×10^{-6} at 1.0 kg mole/m^3	"
Water in whole milk foam	35	8.50×10^{-10}	Okos et al., 1992
Water in whole milk foam	40	1.40×10^{-9}	"
Water in whole milk foam	50	2.00×10^{-10}	"
Water in nonfat milk	25	2.13×10^{-11}	"

Table 1. Diffusion Constants or Effective Diffusion of Some Particular Systems

Convection

Convective mass transport occurs in fluids as a result from the bulk flow, natural and forced motion is involved. It is very similar to heat convection, therefore the properties of the two interacting phases, in which any of them may be a cheese or food item are very important. The supplying medium and the flowing phase, as well as some physical parameters of the system, are also involved through of dimensionless groups for the evaluation of the convective mass transfer coefficient.

The molar flux of a given component may be computed from the equation 5 (Bird et al., 1960; Welty et al., 1976; Welti-Chanes et al., 2003; Vélez-Ruiz, 2009), and as in the case of diffusion, it occurs in the decreasing concentration direction:

$$N_i = k_m \Delta C_i = k_m \left(C_{is} - C_{if} \right) \tag{5}$$

Where: N_i is the molar or mass flux of the i component in the flow stream direction (mol/m^{2}s or mg/m^{2}s), k_m is the convective mass transfer coefficient (m/s), ΔC_i is the concentration difference or driving force (mol/m^3 or mg/m^3), involving a concentration difference between the boundary surface concentration (C_{is}) and the average concentration of the fluid stream (C_{if}).

Mass transfer coefficients are expected to vary as a function of the dynamic conditions, geometrical aspects of the involved system, and physical properties of the fluid and solid phases. Although there are a good number of equations for the evaluation of the convective mass transfer coefficient, food systems and processes particularities are demanding for more specific correlations.

2.4 Salting, drying and migration through packege

Three are three mass transfer phenomena related to cheese manufacturing and storing, that are briefly commented next.

Cheese salting

Salting process during cheese manufacturing favors the development of well accepted quality attributes, both organoleptic and textural, it also suppresses unwanted microorganisms, affects acceptability favorably, causes volume reduction, and determines ripening in some degree. And although salt concentration and distribution play an important role on the aforementioned aspects, there is a limited knowledge about engineering principles of the salting phenomena in cheese, related with the mass transfer.

Cheese drying

Cheese dehydration as a mass transfer phenomenon involves the removal of moisture from the food material, the dehydration or drying process in a cheese reduces its moisture content. This process is not intentionally favored in cheese manufacturing, except during the coagulation part by mechanical means. It is developed as a consequence of the moisture difference between the cheese type and the surroundings (atmosphere, refrigerator, and maturation cave, for instance). Thus the control of relative humidity of the surroundings is needed to avoid undesirable and excessive dehydration; as an udesired phenomenon it is identified as weight loss.

A model of the mass loss of Camembert type cheese was established experimentally during ripening by Hélias et al. (2009), in which the O_2 and CO_2 mass concentrations, A_w, vapor pressure, and convective coefficients for mass transport phenomena were considered (weight loss as the most important).

Migration through a package

Migration of cheese components through a package may become other mass transfer phenomenon, commonly found in these dairy systems. Of those cheese components (volatiles and water vapor), moisture loss or gain is the most important that influences the shelf life of cheese. A cheese system has a micro-climate within a package, determined by the vapor/gas pressure of cheese moisture at the temperature of storage and the permeability of the specific package; in the case of cheeses with appreciable quantity of fat or other oxygen-sensitive components, the uptake of oxygen is also important. Therefore the control of vapor and gases exchange is needed to avoid undesirable spoilage, dehydration, condensing, texture changes, and oxidation, among others. Oxygen and off-odors scavengers may be utilized when the correspondent damages are serious problems. Some interchange of gases is also involved in modified atmospheres in order to preserve cheese characteristics.

Most of the studies of mass transfer in cheese have been focused on salting to favor it, and properly, the other two mass transfer phenomena (drying and migration through a package, without consideration of modified atmospheres as preservation method) are undesirable for most of cheese varieties.

3. Salting of cheeses

Cheese is a matrix of protein, fat and aqueous phase (with salt and minerals), that is subjected to salting as a very important stage. From the engineering viewpoint, salting as a mass transfer process involving salt uptake and water loss at the same time, that are the main studied mass transport phenomena.

3.1 Mass transfer characteristics

In cheese mass transfer, generally it has been recognized that the weight of salt taken up is smaller than the quantity of water expelled from the cheese, giving a loss of weight as consequence of the difference in mass balance. Salt travels from the external medium to the center of a piece within the liquid phase of the cheese, whereas in a contrary direction and mayor flow, there is a movement of water out from the cheese interior into the salt solution or to the atmosphere.

Some factors involved in the mass transfer through of cheese salting are cited next. These factors and their effects have been studied by different researchers, porosity (in Gouda cheese by Payne and Morison, 1999; in Manchego type by González-Martínez et al., 2002; Illescas-Chavez and Vélez-Ruiz, 2009; in Ragusano cheese by Mellili et al., 2005) and tortuosity (in experimental Gouda by Geurts et al., 1974) within the structure of the cheese, geometry and shape of cheese samples (in spherical geometry of experimental Gouda cheese with different weights by Geurts et al., 1974, 1980; in wheel shaped Romano type by Guinee and Fox, 1983; in finite slabs of Cuartirolo cheese by Luna and Bressan, 1986, 1987; in small cubes of Cuartirolo cheese by De Piante el al., 1989; in cylinders of Fynbo cheese by Zorrilla and Rubiolo, 1991, 1994; in cylinders and parallelepipeds of fresh cheese by Sánchez et al., 1999; in blocks of Ragusano cheese by Mellili et al., 2003a; in rectangular samples of white cheese by Izady et al., 2009), relation in which water is bound in cheese, viscosity of the free water portion, volume ratios of brine and solid (in Fynbo cheese by Zorrilla and Rubiolo, 1991), as well as the interaction of salt with protein matrix as the main; presalting and brine concentration (in experimental Gouda by Geurts et al., 1974, 1980; in white cheese by Turhan and Kaletunc, 1992; in Cheddar cheese by Wiles and Baldwin, 1996a, b; in Gouda cheese by Payne and Morison, 1999; in Emmental cheese by Pajonk et al., 2003; in Ragusano cheese by Mellili et al., 2003a; in Pategras cheese by Gerla and Rubiolo., 2003), brine temperature (in experimental Gouda by Geurts et al., 1974; in white cheese by Turhan and Kaletunc, 1992; in Ragusano cheese by Mellili et al., 2003b; in Emmental cheese by Pajonk et al., 2003; in white cheese by Izady et al., 2009). Internal pressure (in Manchego type by González-Martínez et al., 2002; Illescas-Chavez and Vélez-Ruiz, 2009), and ultrasound (in fresh cheese by Sánchez et al., 1999) have been also considered.

The water loss of cheese causes some shrinkage of the structure and decrease in porosity, limiting both mass transfer phenomena, moisture flow out of the item and salt movement into the cheese matrix. In general terms, water diffusivity has been related with temperature and moisture contents, it increases as a function of temperature and salt content in cheese aqueous phase.

3.2 Modeling of the salting process

Diffusion phenomenon is pretty much the main approach used to fit the mass transfer of components through a cheese system. Diffusion rates are expressed using effective coefficients of solutes in the solid; solutes such as sodium chloride, potassium chloride, and lactic acid have been modeled, as well as the water diffusion. The unstable equation or second Fick´s law (Eqn. 6) has been used for modeling of this diffusion process, in which different mathematical solutions have been applied depending of the particular cheese characteristics and process conditions. With the same meaning for the included variables (diffusivity of salt in water) and taking just one dimension for the mass transport, taking the external mass transfer as negligible.

$$\frac{\partial C}{\partial t} = D_{NaCl/water}\left(\frac{\partial^2 C}{\partial x^2}\right) \tag{6}$$

When more than one direction is considered in the mass transfer phenomenon, the corresponding dimensions should be incorporated (y, z, and r for radial effects). Most of the applied mathematical solutions have been based on Crank (1983) considerations. Table 2, includes reported data for mass diffusivity, obtained for salting of different types of cheese in a variety of process conditions.

If more than one component is considered in the diffusion process, the following relation (Eqn. 7), as a variation of equation 4, expresses the mass flux of n-1 solutes and the solvent, in a solid in contact with a homogeneous solution, without chemical reaction and insignificant convective mass transfer (Gerka and Rubiolo, 2003):

$$J_i = \sum_{j=1}^{n-1} D_{ij} \nabla x_j \tag{7}$$

Where: J_{iz} is the mass flux of the i solute or component (g/cm^{2}s), D_{ij} is the diffusion coefficient (cm^2/s), of the i component in a multicomponent system, ∇ is the gradient operator, and x is the local concentration of the j component (g/cm^3). Other mathematical approaches include empirical fittings, analytical solutions different to Fick´s law, such as the Boltzmann equation, hydrodynamic mechanisms and numerical solutions, among others.

Cheese type	Experimental conditions	Dx10^6 (m^2/h)	Comments	Author(s)
Experimental Gouda	Pseudo diffusion of salt at 12.6, 18 and 20.1°C at different days	0.73 – 1.17	Brine concentrations of 19.6-20.0 g NaCl/ 100g H_2O	Geurts et al., 1974
Romano	Apparent salt diffusion at 20°C	0.96	Cylinders of 8 cm height and 20-21 cm diameter	Guinee and Fox, 1983
Cheddar	Salt diffusion in 20 kg blocks	0.63	Periods of 24 and 48 h	Morris et al., 1985
White	Salt diffusion at 4, 12.5 and 20°C with 15 and 20% w/w	0.76 - 1.40	As a function of temperature and salt concentration	Turhan and Kaletunc, 1992
Fynbo	KCl and Na Cl diffusion at 12°C	1.41 & 1.49	Cylinders of 6 cm height and 12 cm diameter	Zorrilla and Rubiolo, 1994
Cheddar	Salt diffusivity in 20 kg blocks	4.17	Stored at 10°C	Wiles and Baldwin, 1996a
Fresco	Water diffusivity at two temperatures Na Cl diffusivity at two temperatures	1.73 & 4.68 2.84 & 4.32	Acoustic brining at 5 & 20°C Acoustic brining at 5 & 20°C	Sánchez et al., 1999
Manchego	Na Cl pseudodiffusion Na Cl pseudodiffusion Na Cl average pseudodiffusion	1.58 & 1.87 2.20 & 3.02 2.54 & 3.60	Upper & lower parts, brine immersion Upper & lower parts, pulse vacuum impregnation Upper & lower parts, vacuum impregnation	González et al., 2002
Pategrass	NaCl and lactic acid diffusion by two approaches and lactic acid by two approaches	1.15 or 1.26 0.34 or 0.36	Series or short solution/ternary Series or short solution/ternary	Gerka and Rubiolo, 2003
Emmental	Na Cl effective diffusion as a function of temperature and time	0.22 & 0.27 0.44 0.35 & 0.68 0.80	At 4°C, 24 and 48 h At 8°C and 48 h At 13°C, 24 and 48 h At 18°C and 48 h	Pajonk et al., 2003
Camembert	NaCl and KCl diffusion. Agitation Numerical solution to Fick´s eqn.	1.01 (NaCl) 1.06 (KCl)	Reduction in NaCl Finite element method	Bona et al., 2007

Table 2. Effective Diffusivity Coefficients for Cheese Salting

3.3 Integral approach

An average velocity factor (AVF) was proposed as an integral mathematical relationship, that considers the cumulative mass transfer of salt in cheese through a selected period of time. It is obtained from those kinetic parameters evaluated from the Peleg´s equation (Illescas-Chavez and Vélez-Ruiz, 2009), and is defined as:

$$\frac{dNaCl_t}{dt}=\frac{1}{k_1+k_2t}-k_2\frac{t}{\left(k_1+k_2t\right)^2}$$
$$AVF=\frac{\int_0^{t_p}\frac{dNaCl_t}{dt}}{24} \tag{8}$$

Where: *dNaCl/dt* is the sodium chloride flux or mass transfer (= J_{NaCl}, g/h); k_1 (h/g) and k_2 (1/g) are constants of the Peleg´s model, $NaCl_t$ is the sodium chloride concentration at any time *t* (g), and *AVF* is the thus defined, average velocity factor (g/h) as an integral value for a given process time (t_p in h).

Peleg´s (1988) equation has been applied to many sorption/desorption processes as an empirical non-exponential model with the two aforementioned parameters, in which the $NaCl_0$ is the sodium chloride concentration at the beginning of the process:

$$\frac{t}{NaCl_t-NaCl_0}=k_1+k_2t \tag{9}$$

The averaged velocity factor pretend to be a most representative value of the overall salting process, in which certainly the computed values are based on Peleg´s constants. Therefore, if this approach is selected, the two constants of the Peleg model should be previously evaluated. Illescas-Chavez and Vélez-Ruiz (2009), applied this AVF approach to three different salting treatments of Manchego type cheese. The sample cheese was divided in twelve zones, 3 vertical, of 1.1 cm each (1 for the upside, 2 for the center portion, and 3 for the down part), and 4 radial divisions, of 2.6 cm each (A for the center, D for the external ring, B and C for the intermediate rings). For the correspondent calculations (differential and integral equations), a proper software was utilized (Maple V, Maplesoft, Ontario, Canada), some results are commented next. Table 3 shows the corresponding Peleg´s constants for the three salting processes (conventional by immersion, pulsed vacuum with immersion, and vacuum with immersion) applied in Manchego cheese manufacturing, after manipulation of salt concentrations determinations.

The AVF calculations for three zones with different salting method are presented as examples of this approach:

i. zone C1 (third ring, upside) by conventional immersion (CI):

$$NaCl_{C1}=0.131+\frac{t}{1.489+0.188t}$$
$$\frac{dNaCl_t}{dt}=\frac{1}{1.489+0.188t}-0.188\frac{t}{\left(1.489+0.188t\right)^2}$$
$$\int_0^{24}\left(\frac{dNaCl}{dt}\right)=3.984,\quad AVF_{CI}=\frac{3.984g}{24h}=0.166\,{}^{g}\!/\!_{h}$$

Process	Zone	k_1 (h/g)	k_2 (g^{-1})	R^2
Conventional Immersion (CI)	A1	1.41	0.22	0.99
	B1	1.33	0.20	0.99
	C1	1.49	0.19	0.99
	D1	1.10	0.12	0.99
	A2	23.8	0.42	0.62
	B2	14.5	0.56	0.97
	C2	13.5	0.62	0.86
	D2	1.67	0.16	0.97
	A3	2.05	0.17	0.99
	B3	1.54	0.20	0.99
	C3	1.61	0.18	0.98
	D3	1.02	0.13	0.99
Pulsed Vacuum Immersion (PI)	A1	1.61	0.19	0.99
	B1	1.70	0.19	0.99
	C1	1.84	0.18	0.96
	D1	0.87	0.14	0.99
	A2	12.7	1.12	0.98
	B2	14.6	0.99	0.88
	C2	16.7	0.55	0.92
	D2	1.82	0.15	0.95
	A3	1.83	0.19	0.98
	B3	1.63	0.19	0.99
	C3	1.85	0.17	0.99
	D3	0.90	0.14	0.99
Vacuum Immersion (VI)	A1	1.82	0.18	0.94
	B1	1.37	0.19	0.93
	C1	0.96	0.20	0.99
	D1	0.86	0.13	0.99
	A2	47.1	0.48	0.99
	B2	45.5	0.49	0.83
	C2	17.1	0.09	0.98
	D2	1.81	0.15	0.95
	A3	2.27	0.17	0.92
	B3	1.02	0.26	0.97
	C3	1.66	0.17	0.92
	D3	0.60	0.14	0.99

Table 3. Peleg´s Kinetics Contants (k_1 and k_2) for Salting of Manchego Cheese

ii. zone B2 (second ring, center) by pulsed vacuum immersion (PI):

$$NaCl_{B2} = 0.131 + \frac{t}{14.610 + 0.992t}$$

$$\frac{dNaCl_t}{dt} = \frac{1}{14.610 + 0.992t} - 0.992\frac{t}{(14.610 + 0.992t)^2}$$

$$\int_0^{24}\left(\frac{dNaCl}{dt}\right) = 0.624, \quad AVF_{PI} = \frac{0.624g}{24h} = 0.026\, {}^{g}\!/\!_{h}$$

iii. zone D3 (external ring, down zone) by pulsed vacuum immersion (VI):

$$NaCl_{D3} = 0.131 + \frac{t}{0.601 + 0.142t}$$

$$\frac{dNaCl_t}{dt} = \frac{1}{0.601 + 0.142t} - 0.142\frac{t}{(0.601 + 0.142t)^2}$$

$$\int_0^{24}\left(\frac{dNaCl}{dt}\right) = 5.976, \quad AVF_{VI} = \frac{5.976g}{24h} = 0.249\, {}^{g}\!/\!_{h}$$

In according with the AVF values, lower salt rates were developed in cheese zones A2, B2 and C2; similar rates (with a mean of 0.163 g/h) were obtained for A1, B1, C1, A3, B3, C3, and even the D2 zone with a small increasing (0.184 g/h vs. 0.163 g/h). Whereas D1 and D3 exhibited the highest salting velocities (with a mean of 0.246 g/h), for the three salting treatments.

From the AVF, the salt uptake ranged from 0.029 to 0.245 g/h (with a mean value of 0.145 for the twelve zones) for conventional immersion, 0.025 to 0.241 (with a mean value of 0.143 for the twelve portions) for pulsed vacuum immersion, and 0.018 to 0.256 g/h (with a mean value of 0.148 for all the zones) for vacuum immersion. The comparison of mean value for the three salting processes, did not show a significant difference ($p > 0.05$) utilizing this approach, that was attributed to the influence of cheese porosity, therefore additional studies are recommended.

A graphic expression of the AVF values is presented by Figure 2, showing a similar trend of the three salting treatments.

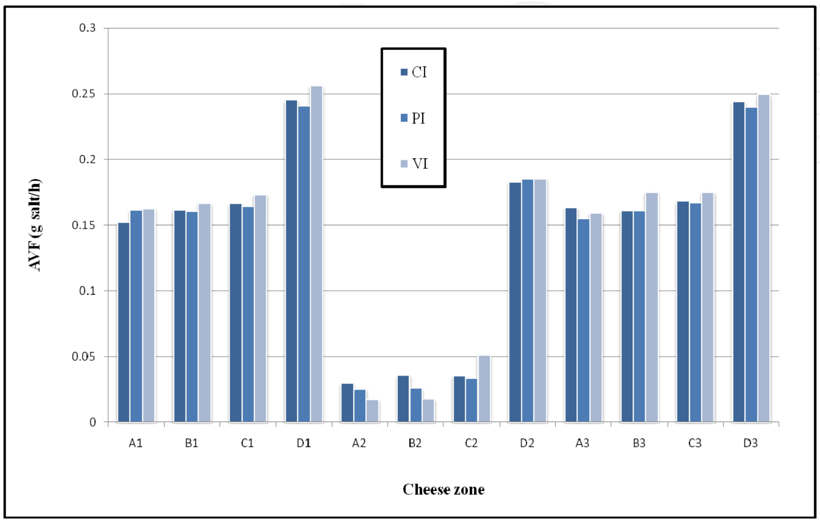

Fig. 2.

Thus, to model the salt or other component diffusion, there are several mathematical approaches, that imply limitations, advantages and disadvantages as well. To select the proper modeling will be function of the focus of the particular study.

4. Final remarks

The mass transfer phenomenon is very important through food transformation, manufacturing and preservation. Cheese as a biological system is characterized by a complex matrix in which all its components are exposed to mass transfer, either by diffusion as the most common or by convection. Although there are works related to mass transfer in cheese, mainly covering diffusion aspects, still there is a necessity of additional studies in order to achieve a more complete knowledge.

Salting as the most transcendental and analyzed mass transport process of cheese manufacturing has been satisfactory characterized, being the Fick´s mathematical approach the most utilized. Diffusion coefficients for various solutes involved in the brining or salting stage, have exhibited values in a range of 0.22 – 4.17 x 10^{-6} m^2/s for NaCl, obtained for different cheese types in an enormous variety of process and experimental conditions; other solute diffusivities have been scarcely quantified.

Furthermore to the diffusion approach, other mathematical solutions have been applied, such the average velocity factor, finite element, hydrodynamic mechanism and numerical approaches, offering advantages and limitations to each salt transport in cheese. The average velocity factor as an integral approach used to model the salting process, imply disadvantages as the rest of the analytical alternatives. More experimental studies are recommended in order to complete a clear scope and to model accurately this outstanding mass transport process of cheese salting.

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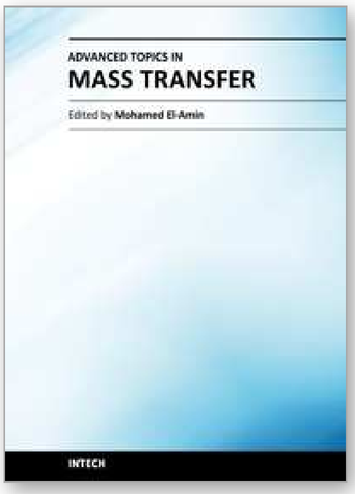

Advanced Topics in Mass Transfer
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This book introduces a number of selected advanced topics in mass transfer phenomenon and covers its theoretical, numerical, modeling and experimental aspects. The 26 chapters of this book are divided into five parts. The first is devoted to the study of some problems of mass transfer in microchannels, turbulence, waves and plasma, while chapters regarding mass transfer with hydro-, magnetohydro- and electro- dynamics are collected in the second part. The third part deals with mass transfer in food, such as rice, cheese, fruits and vegetables, and the fourth focuses on mass transfer in some large-scale applications such as geomorphologic studies. The last part introduces several issues of combined heat and mass transfer phenomena. The book can be considered as a rich reference for researchers and engineers working in the field of mass transfer and its related topics.

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