CHAPTER II

THEORY

2.1 Gelatin

The basic animal tissue from which gelatin is made is called collagen. It is the white connective tissue of the animal and is found associated with other protein tissues such as keratin, mucin, elastin and chondrin. In addition there are present various non-protein organic materials and inorganic salts. Gelatin can form a film gel in an aqueous medium.

The first step in the manufacture of gelatin is the separation of the collagen as completely as possible from the other substances and with the least possible injury to the collagen itself. Properly conditioned collagen when heated with water slowly changes to gelatin, but unless this process is carried out carefully, the gelatin will be further hydrolyzed in the hot solution, as shown below :

$$\underset{\text{Collagen}}{C_{102}H_{149}N_{31}O_{38}} + \underset{\text{Water}}{H_2O} \quad = \quad \underset{\text{Gelatin}}{C_{102}H_{151}N_{31}O_{39}}$$

$$\underset{\text{Gelatin}}{C_{102}H_{151}N_{31}O_{39}} + \underset{\text{Water}}{2H_2O} \quad = \quad \underset{\text{Semiglutin}}{C_{55}H_{85}N_{17}O_{22}} + \underset{\text{Hemicollin}}{C_{47}H_{70}N_{14}O_{19}}$$

2.1.1 Chemical composition and Structure

Like the molecules of the other proteins, gelatin molecules are very large and complex. Values of the average molecular weight of gelatin range from 10,300 to 100,000(1), but the fractionation procedures have yielded material with molecular weights up to 250,000(1). The percentage composition of gelatin has given as : C, 50.5% ; H, 6.8% ; N, 17.5% ; and O, 25.2%.

Complete hydrolysis of gelatin yields a member of simple amino acids of known structure in the following properties(2):

- alanine	11.2 %
- arginine	8.5 %
- aspartic acid	9.6 %
- cystine	0.1 %
- glutamic acid	6.1 %
- glycine	26.5 %
- histidine	1.1 %
- 4-hydroxy proline	14.6 %
- isolucine	1.9 %
- leucine	4.1 %
- lysine	4.8 %
- methionine	0.9 %
- proline	17.2 %
- serine	3.7 %
- threonine	1.7 %
- valine	2.8 %

The nature and number of the amino acids and the manner in which they may be combined in gelatin molecules lead to an almost endless variety of possible structures. Fundamentally, the behavior of gelatin indicates an arrangement in which amino acid residues are joined through peptide linkage; $-CH_2-NH-CO-$. Due to the comparatively high percentages of proline, hydroxy proline, and arginine in gelatin hydrolyzates, two other possible linkages, through a nitrogen atom have been suggested:

(a) $-CH_2-NH-CH_2-$ a stable linkage found in proline and hydroxyproline

(b) $-CH_2-NH-C_1=NH$ found only in arginine

2.1.2 Physical and Chemical Properties

Pure, dry, commercial gelatin is a tasteless, orderless, hard, transparent, brittle, vitriform solid, very faint yellow to amber in color. At normal temperatures and humidities, it contains 9-12%(3) water and has a specific gravity of 1.3 - 1.4. The important properties of gelatin solutions are functions of pH, electrolyte, thermal history, aging, concentration, source and manufacturing procedure.

- Gelatin as a colloidal. The most characteristic property of gelatin is its ability to form a gel or the jelly in aqueous mediums at temperatures below 35-40 °C. The term jelly is often reserved for heat-reversible gels; and usually refers to a gel of high liquid constant which appears homogeneous and transparent.

- Bloom. The Bloom gelometer measures that ability to gel or the jelly strength. Better gelatin has a higher Bloom reading when its gel is formed under standard conditions of concentration, time and temperature. Bloom also determines the price of gelatin with the higher

Bloom strength demanding a higher price. Gelatin is available from 50 to 300 Bloom.

- Viscosity. Standard viscosity is the viscosity of a gelatin solution at the Bloom concentration ($6\frac{2}{3}\%$) using a modified Ostwald pipette at 140 $^{\circ}$F. Flow or coating properties of gelatin depend upon their particular usage. Viscosity varies from three to seven centipoises.

- Amphoteric Character. Gelatin is a typical protein in its ability to act as an acid or a base. This behavior, while influenced by the presence of dibasic and dicarboxylic amino acid residues, is best illustrated by glycine, NH_2CH_2COOH, the simplest and dominant amino acid in gelatin. It is generally believed that glycine exists in solution as the dipolar ion, $^{+}NH_3CH_2COO^{-}$, often referred to as a "zwitter ion". In acid medium, the positive ion $^{+}NH_3CH_2COOH$ is formed, while in alkaline medium, the negative ion $NH_2CH_2COO^{-}$ is formed, the degree of ionization depending on the pH of the solution. This ability of the dipolar ion to react with acid and bases is used to explain the amphoteric character of amino acids and proteins.

- Isoelectric Point. Since gelatin particles are charged in acid or alkali solutions, they will migrate in an electric field. The pH at which no migration occurs is called the isoelectric point. At this pH there is a maximum concentration of uncharged gelatin molecules. The isoelectric point of gelatin is sometimes referred to as the point of minimum physical properties, or as the pH of maximum turbidity in the gel state. It will also correspond to the point of minimum combining capacity with acid and bases.

- Stability. Pure, dry gelatin at room temperature, stored in tight containers, will retain its properties for years with minor variations, but it changes when heated above 65 °C. Aqueous solutions of pure gelatin stored under cool, sterile conditions are stable for long periods.

- Corrosiveness. Gelatin in solution, even at neutral pH, readily attacks metals, Iron, one of gelatins favorite targets, soon becomes pitted. Little brownish-black buttons will form on exposed iron. They break off and leave pits that eventually can cause mechanical failure of the metal. Aluminium has been used as a material of construction, but stainless steel appears to be better. Glass, Teflon, and fiber glass-reinforced polyesters have also been found to be excellent construction materials.

2.1.3 Manufacturing Processes

The aim in gelatin production is the convert of material containing collagen of different degree of insolubility into a maximum quantity of soluble of highly purified gelatin with good properties.

Process used in gelatin production depends on type of raw materials and finished product but it is based on three stages(4,5):

(a) Preparation of raw material, i.e., the elimination of non-collageneous component (fat, mineral salts for examples) from the stock material with or without the reduction of crosslinkages between collagen components.

(b) The conversion of the purified collagen into gelatin.

(c) Refinement and recovery of gelatin in dried form.

The prefered raw materials are bone; hide and pigskin. Raw materials is to swell the fibrous collagen particles in acid or alkali and weaken the linkages by topochemical hydrolysis and steam, the final linkage rupture take place without complete distintegration, thus preserving gelatin with high average molecular weight.

The manufacturing process is shown in Figure 2.1, which is based upon known average practices in industry. The points where the flow lines meet refer to similarity of process.

2.1.4 Uses.

The industry recognized four different kinds of gelatin

- Edible
- Technical
- Pharmaceutical
- Photographic

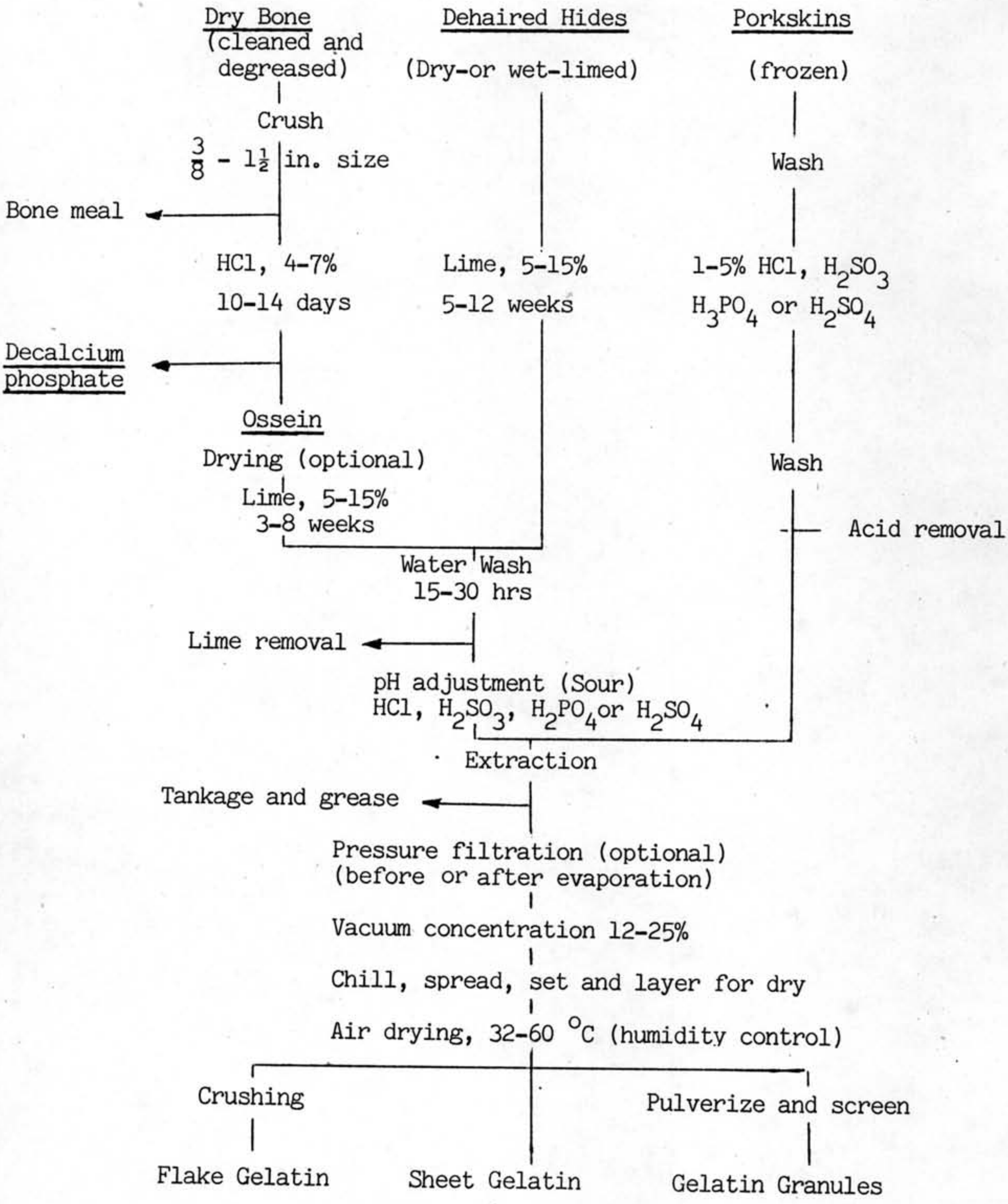
Gelatin is used extensively in food formular as a gelling agent; as a whipping agent in foams; as a clearing agent in fruit juices, wines, and beer; to increase viscosity; and to prevent ice-crystal growth in frozen desserts.

Technical gelatin is quite an arbitrary name applied to small amounts used for miscellaneous purposes such as for sizing paper, textiles and straw hats.

Gelatin is used by pharmaceutical houses for making capsules and as an emulsifier.

Gelatin has played an important part in the rapid development of the motion-picture and photographic industries. It is coated on the film base, constituting the sensitized emulsion of the light-sensitive silver salts.

Figure 2.1 Flow diagram for Gelatin Manufacture(2)



2.2 Drying

In general, drying a solid means the removal of relatively small amounts of water or other liquid from the solid material, to reduce the content of residual liquid to an acceptably low value. Water or other liquids may be removed from solids mechanically by presses or centifuges or thermally by vaporation.

The moisture content of a dried substance varies from product to product. Occasionally the product contains no water, and is called "bone-dry". More commonly, the product does contain some water. Dried table salt, for example, contains about 0.5 per cent water, dried coal about 4 percent, and dried casein about 8 percent. Drying is a relative form and means merely that there is a reduction in moisture content from an initial value to a final one.

For convenient reference, certain terms used to describe the moisture content of substances are summarized below(6)

Moisture content (wet basis) The moisture content of a solid or solution is usually described in terms of weight percent moisture, and unless otherwise qualified this is ordinarily understood to be expressed on the wet basis, i.s., as (lb moisture/lb wet solid) 100 = $\left[\text{lb moisture}/(\text{lb drysolid} + \text{lb moisture})\right] 100 = 100\,X / (1+X)$

Moisture content (dry basis) This is expressed as lb moisture/lb dry solid = X.

Percentage moisture, dry basis = 100 X

Equilibrium moisture X* This is the moisture content of a substance when at equilibrium with a given partial pressure of the vapor.

Bound moisture This refers to the moisture contained by a substance with exerts an equilibrium vapor pressure less than that of the pure liquid at the same temperature.

Unbound moisture This refers to the moisture contained by a substance which exerts an equilibrium vapor pressure equal to that of the pure liquid at the same temperature.

Free moisture Free moisture is that moisture contained by a substance in excess of the equilibrium moisture : $X - X^*$. Only free moisture can be evaporated, and the free moisture content of a solid depends upon the vapor concentration in the gas.

This relations are shown in Figure 2.2 for a solid of moisture content X exposed to a gas of relative humidity A

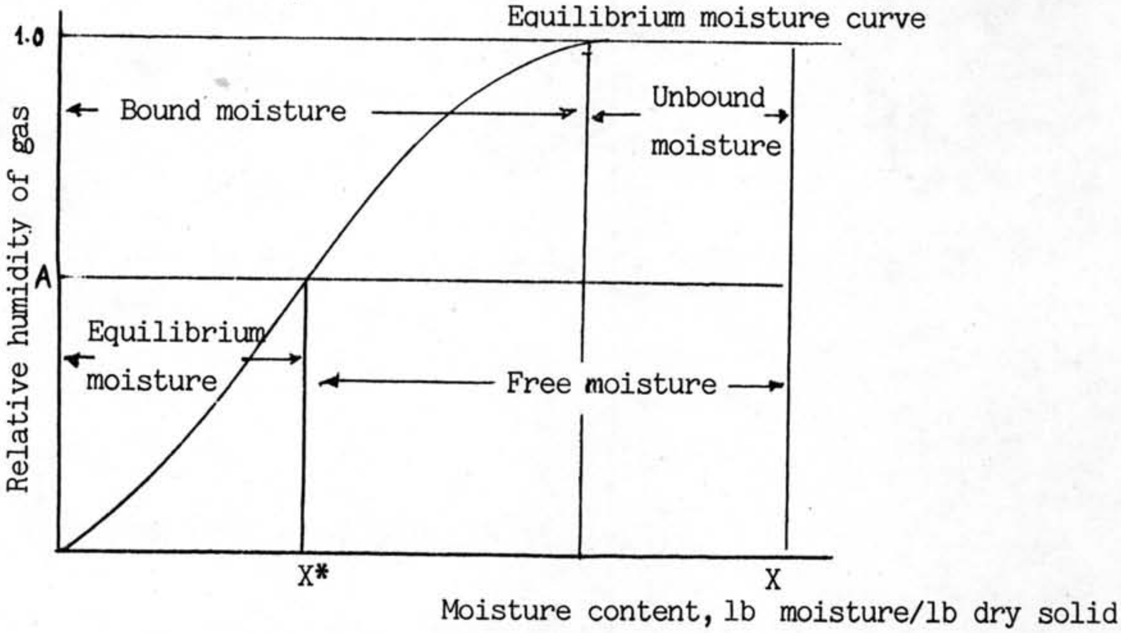


Fig 2.2 Types of moisture

2.2.1 Equilibria

Equilibrium relationships in drying are those between a solid and moist air a typical relationship is illustrated in Figure 2.3. In this figure moisture content is expressed in molal units

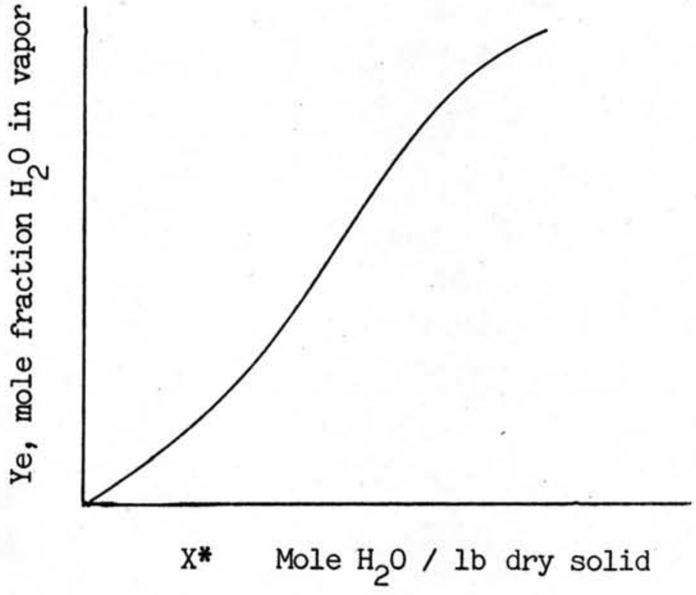


Figure 2.3 Equilibrium curve

When a wet solid is brought into contact with air of lower humidity than that corresponding to the moisture content of the solid as shown by the humidity-equilibrium curve in Figure 2.4, the solid tends to loose moisture and dry to equilibrium with the air. When the air is more humid than the solid in equilibrium with it, the solid absorbs moisture from the air until equilibrium is attained.

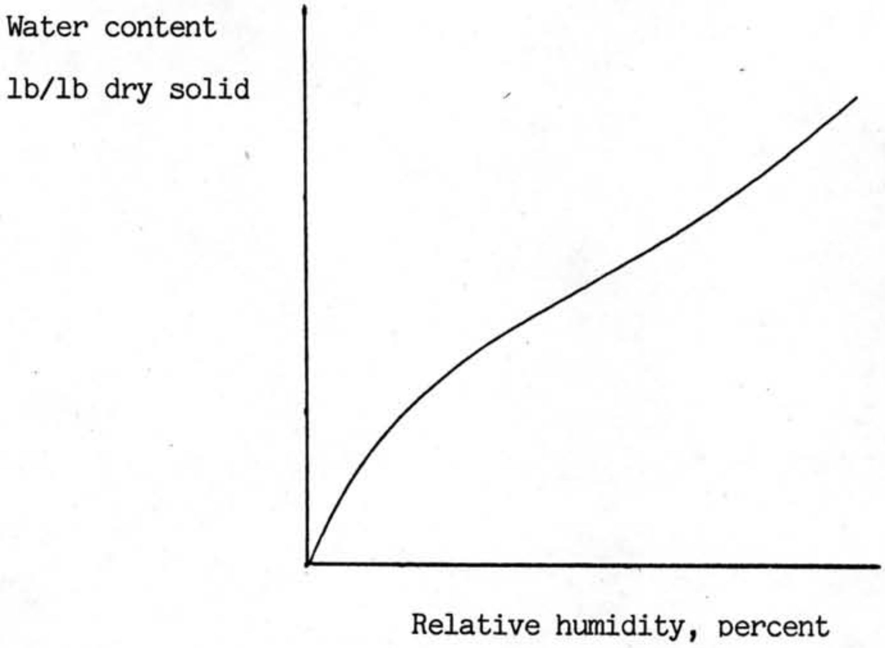


Figure 2.4 Equilibrium - moisture curve

The moisture-content-versus-time plot (Figure 2.5) is the form in which drying test data might be obtained Figure 2.6, the rate-of-drying-versus-moisture-content plot, is much more descriptive of the drying process. However, it is obtained by differentiating data in the form of Figure 2.5 and thus is subject to considerable scattering of data and resulting uncertainty.

These typical drying curves are related to the mechanism by which drying occurs. The drying period represented by segment AB of the curves of Figure 2.5 and Figure 2.6 is the unsteady-state period during which the solid temperature reachs its steady-state value.

2.2.2 General Drying Behavior

In drying a wet solid with a gas of fixed temperature and humidity, one general pattern of behavior always appears. Immediately after contact between the sample and the drying medium, the solid temperature adjusts until it reaches a steady state. The solid temperature and the rate of drying may increase or decrease to reach the steady-state condition. At steady state, a temperature probe would find the temperature of the wet-solid surface to be the wet-bulb temperature of the drying medium. Temperatures within the drying solid would also tend to equal the wet-bulb temperature of the gas, but here agreement would be imperfect because of lag in movement of mass and heat. Once these stock temperatures reach the wet-bulb temperature of the gas, they are found to be quite stable, and the drying rate also remains constant. This is so called constant-rate drying period. The period ends when the solid reaches the critical moisture content. Beyond this point, the surface temperature rises, and the drying rate falls off rapidly. The falling-rate period may take a far longer time than the constant-rate period even though the moisture removal may be much less. The drying rate approaches zero at some equilibrium moisture content which is the lowest moisture content obtainable with this solid under the drying conditions used. Figures 2.5 and 2.6 show typical drying curves, one on a moisture-content-versus-time basis and the other on a rate-of-drying-versus moisture content basis.

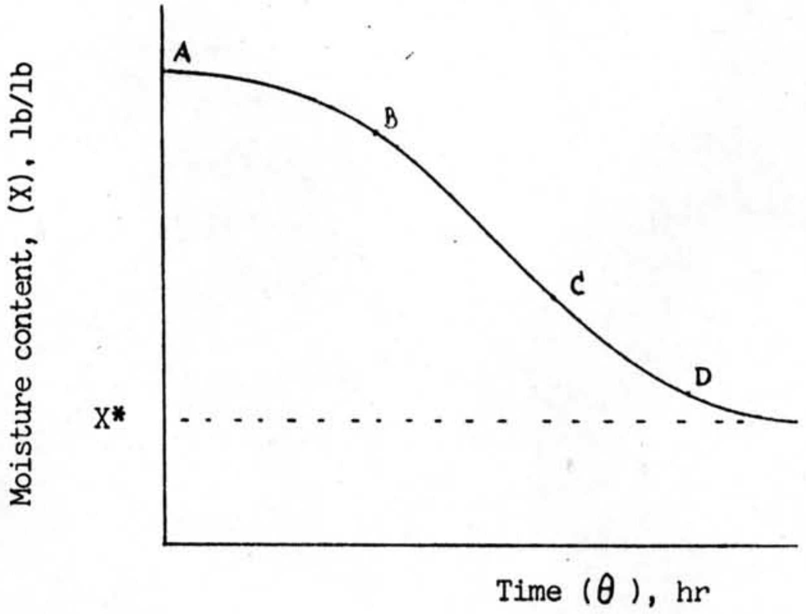


Fig 2.5 Typical drying curve for constant drying condition, moisture content as a function of time

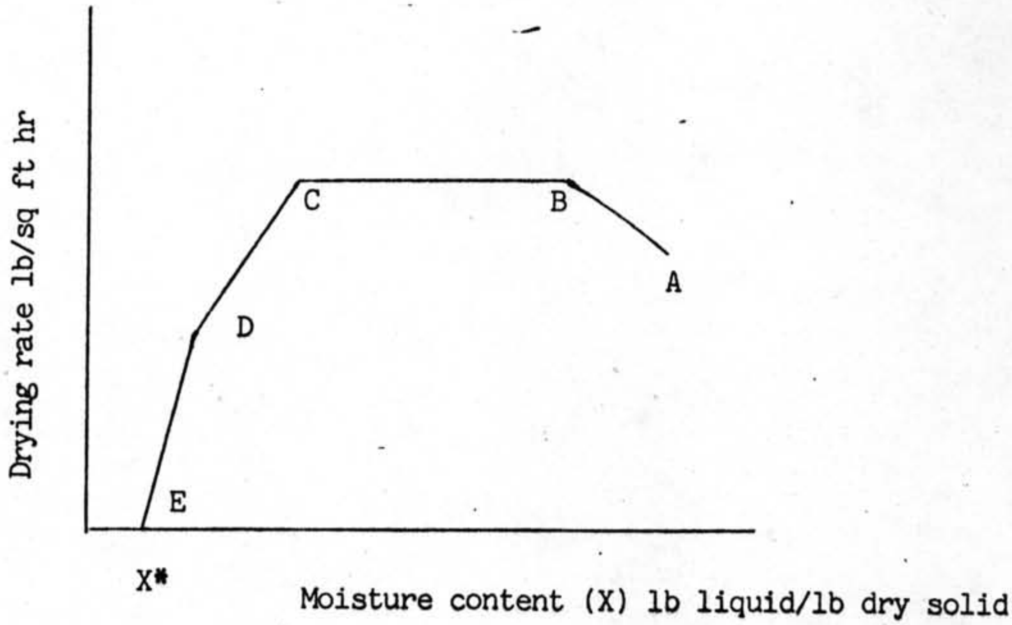


Fig 2.6 Typical drying rate curve for constant drying conditions, drying rate as a function of moisture content.

Although the shape shown is typical, almost any shape is possible, and AB may occur at decreasing rate as well as the increasing rate shown. During the constant-rate period (segment BC of the drying curves of Figures 2.5 and 2.6), the entire exposed surface is saturated with water. Drying proceeds as from a pool of liquid with the solid not directly influencing the drying rate. It is possible that the roughness of the solid surface over which the liquid film extends may increase mass-and heat-transfer coefficients, but this effect has not been firmly established. The surface temperature reaches the wet-bulb temperature as would be expected. The constant-rate-drying regime continues with the mass that is transferred from the surface continuously replaced by movement of liquid from the interior of the stock. The mechanism of liquid movement and consequently the rate of this movement vary markedly with the structure of the solid itself. With solids having relatively large open void spaces, the movement is likely to be controlled by surface tension and gravity forces within the solid. With solids of fibrous or amorphous structures, liquid movement is by diffusion through the solid. Since the diffusion rates are much slower than the flow by gravity and capillary, solids in which diffusion controls the liquid movement are likely to have short constant-rate period. At point C, the moisture content of the solid is barely adequate to supply the entire surface.

During the drying period between points C and D of Figure 2.6, called the "first falling-rate period," the surface becomes more and more depleted in liquid because the rate of liquid movement to the surface is slower than the rate of mass transfer from the surface, until at point D there is no significant area of liquid-saturated surface. The part of the surface that is saturated dries by convective transfer of heat from and of mass to the drying gas stream vapor from lower levels in the sample diffuses to the part of the surface that is not saturated and then continues its diffusion into the gas stream. This mechanism is very slow compared to the convective transfer from saturated surface.

At moisture contents lower than that at point D of Figure 2.6 all evaporation occurs from the interior of the solid. As the moisture content continues to fall, the path for diffusion of heat and mass grows longer, and eventually the concentration potential decreases until at X^*, the equilibrium moisture content, there is no further drying. The equilibrium moisture content is reached when the vapor pressure over the solid is equal to the partial pressure of vapor in the incoming drying gas. This period is called the "second falling-rate period."

2.2.3 Class of Material according to Drying Behavior

Materials may be divided into two major classes(7) on basis of their drying behavior.

The first class are granular or crystalline solids which hold moisture in the interstices between particles or in shallow. In these materials, moisture movement occurs as a result of the interplay of gravitation and surface tension or capillary forces. Examples of this class of material would be zinc sulphate monohydrate, sodium phosphate and catalysts.

The second class are most organic solids. These materials hold moisture as an integral part of the solid structure or trapped within fibers or fine interior pores. In these materials, moisture movement is slow and probably occurs by the diffusion of liquid through the solid structure. Examples of these material are either amorphous, fibrous or gel-like.

Gelatin is in the second class and therefore its drying rate is controlled by the rate of diffusion of liquid through the solid.

2.2.4 Diffusion Mechanism

Diffusion is characteristic of slow-drying materials such as fibrous organics, gel-like substances. The resistance to mass transfer of water vapor from the solid surface to the air is usually negligible, and diffusion in the solid controls the over-all drying rate. The velocity of the air has little or no effect, and the humidity of the air influences the process primarily through its effect on the equilibrium-moisture content. Since diffusivity increases with temperature, the rate of drying increases with the temperature of the solid.

Because of the drying rate is controlled by the rate of diffusion of liquid through the solid, then the rate of moisture movement is expressed by Fick's Law

$$\frac{\partial x}{\partial t} = D_v' \frac{\partial^2 x}{\partial Z^2} \qquad .....(2.1)$$

2.2.5 Calculation of Drying Time

In calculations of drying time, the drying rate curve must be considered. The drying rate is defined as

$$R = \frac{-W_1 dX}{A\, dt} \qquad .....(2.2)$$

where R = drying rate, kg of liquid evaporated per hr and m^2 of solid surface

W_1 = Weight of drying solid, Kg

X = average moisture content, Kg moisture /Kg of dry solid

A = surface area of solid, m^2

Equation 2.2 can be rearranged and integrated to obtain the drying time

$$\int_0^t dt = -\frac{W_1}{A}\int_{X_1}^{X_2}\frac{dX}{R} \qquad \text{.....(2.3)}$$

where X_1 = average moisture content at time 0

X_2 = average moisture constant at time t

2.2.5.1 The constant Rate Period

For constant rate period R will be constant at Rc. Equation 2.3 may be integrated to obtain

$$t_c = \frac{-W_1}{A\,R_c}(X_{cr} - X_1) \qquad \text{.....(2.4)}$$

where X_{cr} = average moisture content at the end of the constant rate period, Kg moisture /Kg of dry solid

X_1 = moisture content at start of drying process

t_c = time of constant-rate drying, hr

2.2.5.2 Falling Rate Period

Assume that curve during the falling rate period is a straight line from critical moisture content to origin. Then,

$$\frac{R}{X} = \frac{R_c}{X_c} \qquad \text{.....(2.5)}$$

Substitute R in Equation (2.3)

$$\int_{t_c}^{t} d\,t = \frac{-\,W_1}{A}\int_{X_c}^{X} \frac{d\,X}{\frac{R_c}{X_c}\,.\,X} \qquad .....(2.6)$$

and integrating,

$$(t - t_c) = \frac{-\,W_1 X_c}{A\,R_c}\,\ln \frac{X}{X_c} \qquad .....(2.7)$$

Then time for falling rate period can be calculated

2.2.6 Drying of Gelatin

For most practical purposes, dry gelatin is obtained from concentrated sols by cooling to the solid gelatin gel and drying the gel.

The conditions of the step-by-step elimination of water are represented in the curve showing isothermal dehydration (Fig. 2.7)(8). This curve makes evident two separate regions. The main quantity of the water (A to B) can be eliminated by only a minor reduction of water vapour pressure, the drying air being able to have a relatively high moisture content. This continues until the gel has a dry matter content of about 60-70%. The elimination of the remaining quantity of water (B to C) calls for a substantial practice, such reduction of vapour pressure of the drying air is not possible in the normal driers, so a, water content of 10% is the minimum to be aimed at.

Saner and Veitinger(9) using a sheet of gel 2 mm thick, with 10% solids content, determined the course of weight reduction during drying in an air current at constant temperature. The air velocity was 1.5

litre/cm^2/minute and temperature was kept constant at 24 °C. Fig. 2.8 is a diagram showing the rate of water removal. This clearly shows the initial constant rate period during which the water loss is linear with time and the transition to the falling rate period.

The size and thickness of the gel layers is critical in deciding the drying rate. In order to study the influence of layer thickness on drying speeds Sauer and Veitinger (9) performed a series of drying experiments with gel sheets of increasing thicknesses (From 4-16 mm) from a gelatin solution with 10% solids content. The tests were done with air at 18 °C and a low air velocity, so that very long drying times were required. Under these conditions, which bear no relation to commercial drying, the drying rate is the same for all layer thicknesses, as shown by the parallel course of the curves.

Drying plant (10)

A number of systems have been applied in drying gelatin, but two types have dominated the market. In recent times a third type has been added, which also has prospects of being sucessfully applied for drying gelatin. These three types of driers differ in mode of operation and the manner in which they handle the gelatin. They are the

- batch drier
- band drier
- fluidized bed driers

Batch drier

Batch drier is best suited for small and medium production capacities.

The batch drier operates with hot air on the transverse flow principle, in a rotating drum with a cylindrical jacket that is permeable to air. The standard production line which built by the Wciss-Trocknungs-Anlogen is composed of three sections: the chilling drum (1), the patented square chip cutter (2), the drier (3).

The concentrated gelatin liquors gel on the surface of the chilling drum to a gel film that is cut to gelatin chips, 6X4X2.5 mm thick. A screw conveyor transports the chips to a container. The drying temperatures rise from the initial drying zone (38-40 °C) to 70 °C in the last drying zone. This is followed by sterilizing the dried material at 80-90 °C and then cooled. The rotation of the drum keeps the material in constant motion. Discharge is by dropping the dry gelatin into a collection trough from which it is pneumatically transported to storage.

Advantage of batch drier are

(i) automatic operation

(ii) good steam consumption figures, i.e. 2-3 Kg of steam per Kg of evaporated water.(10)

Band drier

The band drier is made up of several drying sections. The bottom of the drying sections is made from material through which air can freely pass. The band travels through a tunnel. It is arranged in such a manner that it passes through the initial drying zone at a slower speed than the later drying zones. The drying of gelatin gels in this drying system is best done using conditioned air, for which the Kathabar system has proved suitable.

The conditioning of the drying air for the band drier is of the prime requisites for drying gelatin gels: This also makes it possible to keep the drying time under 4 hours, depending on the quality and concentration of the material. Drying in the successive stages involves increases in air temperatures. In each stage the temperature and humidity of the drying air are fully regulated.

A Votator is preferably set up in front of the band drier to produce the gel. The noodles extruded by Votator are brought onto the drying zones of the 1st drying band by means of a small reciprocating conveyor. The 1st drier band carries the gelatin gel through the initial drying zone and the noodles then drop onto the 2nd drying band. From this 2nd band the material is passed; fully dry, directly to a hammer mill where the gelatin noodles are broken down. This type of band drier is also used for the production of thin film gelatins.

The band drier of this type with the smallest capacity has an output of around 250 Kg per hour of dry gelatin. This shows that such a drying plant is only suitable for large production capacities.

Fluidized bed drier

No technical results are yet available to show the influence of the fluidized bed on the drying of gelatin gels. It is, however, known that the drying rate can be increased by fluidization, because the air flow simultaneously agitates the bed and increases the heat and mass transfer coefficients. Air circulates from bottom to top. With this form of circulation, either the drying capacity can be increased or the drying rate. The drying time required in Haag fluidized bed drier(10) can be about 2 hours which is short compared with other systems. The small gel chips are delivered to the 1st agitating zone by an impeller wheel. There they are distributed by an extra agitator and stimulated to fluidization. Over an overflow barrier the dry material is conveyed to the two drying zones. The drying temperature increases from zone to zone. The dried gelatin is delivered over an impeller wheel where finished.

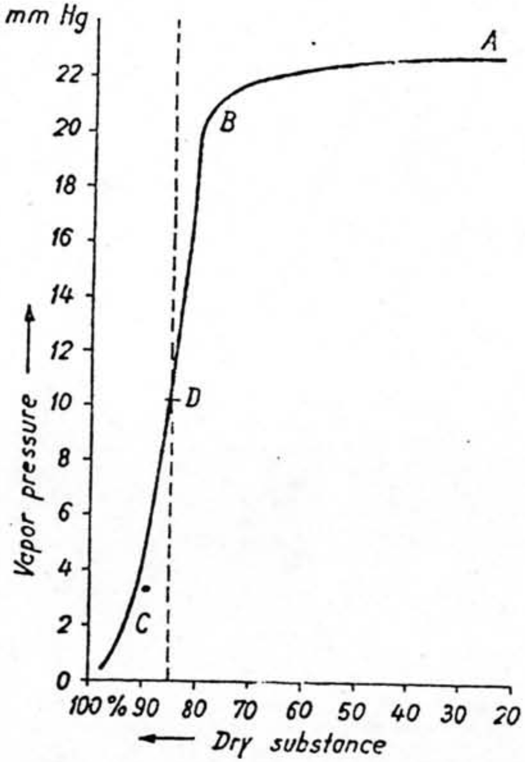


Figure 2.7 Progress of water elimina-tion of the gelatin gel.

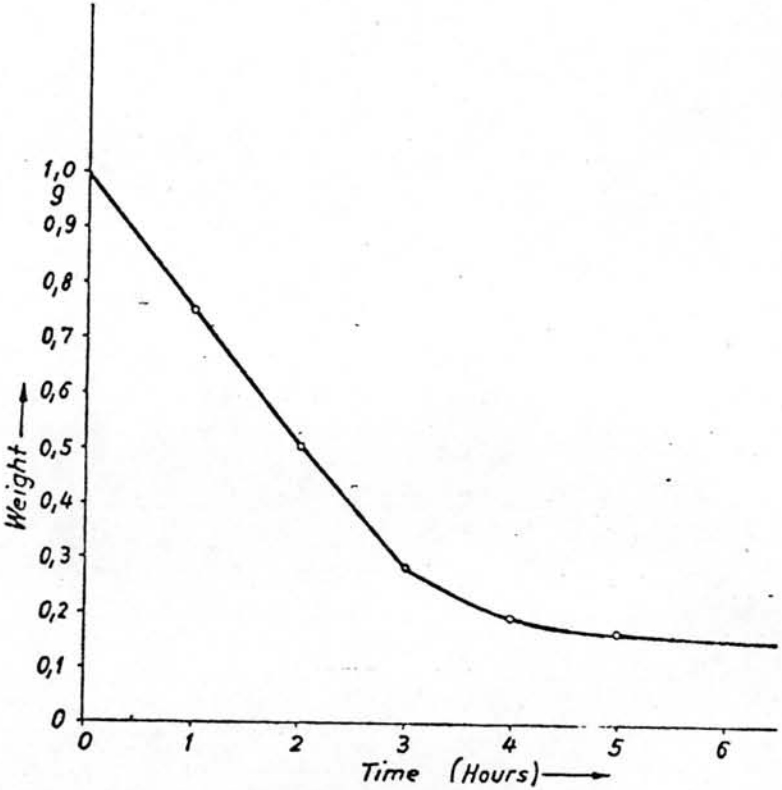


Figure 2.8 Progress of the water elimination of a gelatin jelly in an air current of constant temperature.