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ON THE USE OF FREEZE-DRYING TO RECOVER FLOODED ARCHIVAL MATERIALS

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Abstract: This paper aims investigating the freeze-drying process to recover flooded archival materials. Good restauration results can be obtained through this process as water freezing, after soaking, allows stopping all undesired chemical and physical phenomena caused by liquid water, and, then, ice removal through sublimation, at low pressure, allows avoiding any further damage. An extensive experimental investigation was carried out in an industrial-scale freeze-dryer, aiming to prove the effectiveness of the process and to provide guidelines for carrying out the freeze-drying process. A simple mathematical model is proposed to evaluate the effect of some operating conditions on the drying time.

Keywords: freeze-drying, paper material, product quality, process design, mathematical modeling.

Introduction

Today there is a growing interest in finding an effective method for the recovery of soaked archival and librarian materials, aiming to get a high-quality product and to shorten the duration of the recovery process. Various damages are, in fact, caused by liquid water, namely swelling, cockling, adhesion of leaves, migration of inks and dyes, distortion, and also microbiological infections, depending on the type of paper and archival material and on the modality of flooding.

Despite manual recovery can result in a high-quality product, the high costs and the slow kinetics of the process motivated the investigation of different drying methods as vacuum drying, freeze-drying, microwave drying [1-5].

In this framework freeze-drying appears to be a particularly efficient and effective technology as, in this case, liquid water is immediately frozen after soaking, thus stopping all undesired chemical and physical phenomena, and then the ice is removed through sublimation, at low temperature and low pressure. The water removal from the liquid to the vapour phase allows avoiding further damages to the material being dried. Also, mechanical resistance of the dried material appears to be not affected by the freeze-drying process [6].

This paper deals with the freeze-drying of flooded archival materials aiming to show the effectiveness of the process for water removal, and the effect on the qualitative characteristics of the materials, through an extensive experimental investigation in an industrial-scale freeze-dryer. A simple mathematical model is proposed to evaluate the effect of some operating conditions on the drying time. Various guidelines are finally provided for the management of various stages of the archiving of paper/archival materials, and of the emergency due to flooding, as well as for carrying out the freeze-drying process.

Materials and Methods

Experimental investigation was carried out in an industrial-scale freeze-dryer (UEL 1100 Ing. Brizio Basi & C s.a.s., Milano, Italy), with 11 shelves and a total shelf area of about 15 m^2. The freeze-dryer has two condensers, each of them with a capacity of about 45 kg of ice: after a pre-set time interval, the connection between the drying chamber and the condenser in use is closed, and the valve connecting the chamber to the second condenser is opened; defrosting of the first condenser is then carried out. This operation is periodically carried out, and the condensers are alternatively connected to the drying chamber, in such a way that the accumulation of a too high amount of ice in the condenser is avoided.

Pressure in the drying chamber and in the condensers was measured through piezoresistive gauges (Siemens SITRANS P, Z series, Nurnberg, Germany). Product temperature was measured by means of PT100 thermoprobes.

Various tests were carried out for characterizing the equipment, considering that the dryer is slightly different from that generally used for food processing (and, obviously, for pharmaceuticals):

1. Evaluation of the minimum pressure achievable in the freeze-dryer: this test was simply carried out switching on the two condensers (and the two vacuum pumps connected to them) and evaluating the minimum value of pressure achieved in the (empty) drying chamber when both condensers are connected to it.
2. Leak test, to evaluate air leakage through chamber door, at the minimum pressure achieved in the freeze-dryer. This test was carried out in two steps: at first the minimum value of pressure was achieved in the (empty) drying chamber (through the same procedure previously presented), and, then, the chamber was isolated from the condensers and the pressure increase in the chamber, due to air leakage (as no product was inserted in the chamber), was measured. The test was repeated at different values of shelf temperature.
3. Evaluation of the uniformity of the heating conditions over each shelf and among the various shelves in the freeze-dryer. The test was carried out loading on all the shelves of the freeze-dryer some plastic bowls (5 bowls for each shelf): the area of the surface of contact of each bowl with the shelf was 0.0567 m^2, and each bowl was filled with about 1 kg of water. After freezing, ice sublimation was carried out at a certain pressure and temperature for 2 h and, then, water loss was measured. The test was repeated at different values of shelf temperature.

Various approaches were tested to evaluate the ending point of the ice sublimation to verify their applicability to the actual equipment:

1. The measurement of product temperature: during ice sublimation, the temperature of the product rises from the value achieved in the freezing stage to a certain value that is a function of the heat supplied to the product (through the heating shelf above which the product is placed, but also through radiation from chamber walls and door) and of the heat removed through ice sublimation. In any case, when ice sublimation does not occur any more, the temperature reaches a steady-state value (that should be equal to the shelf value, in case radiation from chamber walls and door does not play a significant role in product heating).
2. The measurement of the pressure loss between the chamber and the condenser: such pressure loss is a function of the water vapor flow rate and reaches a value close to zero (in case air leakage is almost null, and no inert gas is introduced in the chamber for pressure control) when ice sublimation is no longer occurring.

3. The pressure rise test: during the drying process the chamber is isolated from the condensers and the pressure rise in the chamber is measured for a short time interval. This pressure rise is due to ice sublimation and to air leakage. As the value of air leakage was previously measured, from the curve of pressure rise it is possible to state if the ice sublimation is still taking place or not.

One of the most important issues arising when loading the freeze-dryer with the flooded material concerns the thickness of the material loaded onto each shelf. In case it is required to freeze-dry books with a thickness equal to L which is the optimal configuration between loading the shelves with one layer of books, or with two layers of books (thus with a thickness equal to $2L$)? in the second case the batch load is double, but it is necessary to assess if the drying time is more than doubled or not. To this purpose, a simple analysis is proposed in the following.

In order to obtain a general guideline for process design, the drying process is assumed to occur only in one direction, orthogonal to the heating shelf, and the heat to the product is assumed to be transferred only from the heating shelf, as depicted in Figure 1.

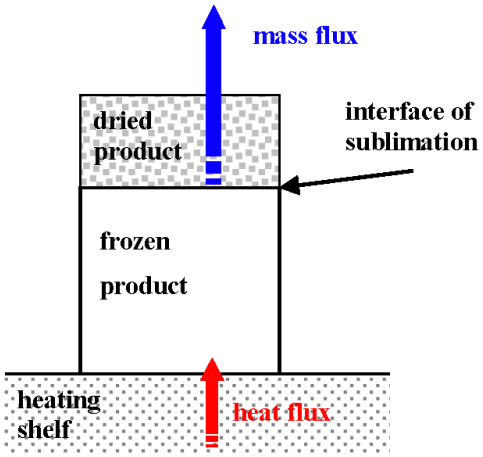

Fig. 1. Sketch of the freeze-drying process

At a certain time interval, the heat flow rate provided to the product is given by the following equation:

$$\frac{dQ}{dt} = UA\left(T_{shelf} - T_i\right) \tag{1}$$

where A is the contact area between the product and the shelf, U is the overall heat transfer coefficient, T_{shelf} and T_i are, respectively, the temperature of the heating shelf and of the interface of sublimation. Taking into account the heat transfer mechanisms from the shelf to the interface of sublimation, it is possible to write:

$$\frac{dQ}{dt} = \frac{1}{\frac{1}{K} + \frac{x}{\lambda_f}} A\left(T_{shelf} - T_i\right) \tag{2}$$

where K is the heat transfer coefficient between the shelf and the product, x is the thickness of the frozen product and λ_f is its thermal conductivity. The amount of heat dQ transferred to the

interface of sublimation in the tine interval *dt* is used for ice sublimation, thus causing a reduction of the ice volume that can be calculated through the following heat balance:

$$dQ = \Delta H_s \varepsilon A dx \rho_f \tag{3}$$

where ΔH_s is the heat of sublimation, ε is the ice fraction in the product, dx is the movement of the sublimation interface and ρ_f is the density of the frozen product. If equations (2) and (3) are equated it is possible to obtain the following equation:

$$\Delta H_s \varepsilon A dx \rho_f = \frac{1}{\frac{1}{K} + \frac{x}{\lambda_f}} A\left(T_{shelf} - T_i\right) dt \tag{4}$$

and, after some manipulations:

$$\Delta H_s \varepsilon \rho_f \left(\frac{1}{K} + \frac{x}{\lambda_f} \right) dx = \left(T_{shelf} - T_i\right) dt \tag{5}$$

Previous equations can be integrated in time considering that the thickness of the frozen product moves from L to zero, and the time from zero to t_d, the drying time, thus obtaining the following equation:

$$\Delta H_s \varepsilon \rho_f \left(\frac{L}{K} + \frac{L^2}{2\lambda_f} \right) = \int_0^{t_d} \left(T_{shelf} - T_i\right) dt \tag{6}$$

In case both the temperature of the heating shelf and of the interface of sublimation do not change significantly during the drying process, the drying time can be calculated through the following equation:

$$t_d = \frac{\Delta H_s \varepsilon \rho_f}{T_{shelf} - T_i} \left(\frac{L}{K} + \frac{L^2}{2\lambda_f} \right) \tag{7}$$

This equation is very similar to that proposed by Oetjen and Haseley [7]. In case T_{shelf} and T_i change during the drying process, the integral appearing in equation (6) can be replaced by the (integral) mean of the difference (T_{shelf} - T_i). If we thus compare the drying time required for similar products, having the same values of ρ_f, λ_f and ε, processed in the same operating conditions (and, thus, with the same T_{shelf} and roughly the same T_{shelf} - T_i), but with different product thickness (namely L_1 and L_2), the ratio between the drying times (t_{d1} and t_{d2} respectively) is given by the following equation:

$$\frac{t_{d2}}{t_{d1}} = \frac{L_2}{L_1} \left(\frac{K L_2 + 2\lambda_f}{K L_1 + 2\lambda_f} \right) \tag{8}$$

Considering equation (8) it appears that if L_1 and L_2 are significantly smaller than $2\lambda_f/K$ then the ratio between the drying time is exactly corresponding to the ratio between the two

thickness values and, thus, when loading the dryer with a double thickness product the drying time is exactly doubled. Figure 2 shows the trend of the ratio of the drying time as a function of the ratio of product thicknesses. The curves are calculated for a certain couple of values of λ_f and K (λ_f = 2.5 W m^{-1}K^{-1} and K = 20 W m^{-2}K^{-1}), that can be considered representative of the case study under investigation, but, in any case, the trend does not change if the curves are calculated considering different couples of values.

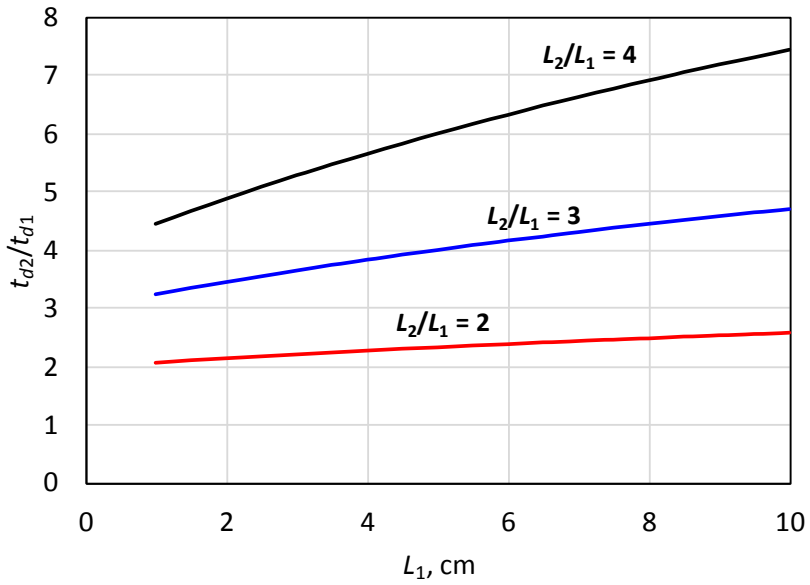

Fig. 2. Values of the ratio t_{d2}/t_{d1} calculated for different L_2/L_1 as a function of L_1.

From the results shown in Figure 2 it appears than doubling the thickness of the layer of product does not penalize the drying time (i.e. it increases of about two times) only when the thickness of the product is not very large, e.g. 1-2 cm, otherwise the increase of drying time is more than doubled. For larger thickness the influence of increasing resistance to mas transfer during drying of the already dried layer can become significant, affecting the (T_{shelf} - T_i) difference and, thus, making more unfavourable the processing when L increases. This effect is much more pronounced when considering higher values of the ratio L_2/L_1.

Beside the drying time, it is necessary to account also for the freezing time. As shown in [7] the freezing time t_f can be calculated using an equation similar to equation (7), namely:

$$t_f = \frac{\Delta H_f \varepsilon \rho_f}{T_{shelf} - T_f}\left(\frac{L}{K} + \frac{L^2}{2\lambda_f}\right) \tag{9}$$

where ΔH_f is the heat of freezing and T_f if the freezing temperature (at atmospheric pressure, as the freezing is not carried out under vacuum). Thus, when increasing the thickness of the product the freezing time increases in a way similar to that presented for the drying time, e.g. doubling the thickness of the layer of product does not penalize the freezing time (i.e. it increases of about two times) only when the thickness of the product is not very large, e.g. 1-2 cm, otherwise the increase of freezing time is more than doubled, and the effect is much more pronounced when considering higher values of the ratio L_2/L_1.

Results and discussion

Preliminary investigation was required for equipment characterization. Using the procedure described in the previous section it was possible to evidence that the minimum pressure achieved in the freeze-dryer is about 1 mbar and that the leak rate, at this pressure, is negligible. In fact, in well designed freeze-dryers the leak rate should be lower than $2 \cdot 10^{-2}$ mbar L s^{-1} and, thus, the pressure rise due to air leakage in the industrial equipment used for the experimental investigation (whose volume is about 2.5 m^3) should be equal to $8 \cdot 10^{-6}$ mbar s^{-1} (i.e. less than 0.03 mbar h^{-1}), and the measured value during the leak test is significantly lower than this value.

With respect to the test carried out to investigate the homogeneity of heating conditions over the shelves results appear to be satisfactory. For the test carried out at -20°C, considering a certain shelf, e.g. the 5th from the top, the mean value of the sublimation rate (calculated dividing the weight loss in the 5 bowls by the sublimation time) is equal to 0.21 kg $h^{-1}m^{-2}$, with a standard deviation equal to 10.9%, while at 0°C, for the same shelf, the mean sublimation rate is 0.55 kg $h^{-1}m^{-2}$, with a standard deviation equal to 8.9%. Similar figures were obtained for the other shelves of the freeze-dryer, as shown in Table 1.

Table 1. Results of the gravimetric test carried out for equipment characterization.

	Temperature -20°C		**Temperature: 0°C**	
shelf number	*(mean) sublimation flux, kg/h m^2*	*standard deviation*	*(mean) sublimation flux, kg/h m^2*	*standard deviation*
11	0.22	16.8%	0.48	20.7%
10	0.22	18.1%	0.57	14.4%
8	0.22	14.9%	0.55	9.8%
5	0.21	10.9%	0.55	8.9%
4	0.17	12.1%	0.59	7.7%

With respect to the identification of the drying time, various tests were carried out processing flooded archival materials. The temperature measurement and the pressure rise test were selected as the only suitable methods to identify when the ice sublimation is completed. In fact, considering the high minimum pressure reached in the freeze-dryer and the poor accuracy of the available sensors for pressure measurement it was not possible to get useful measurements from the pressure drop between chamber and condenser.

After this preliminary investigation for equipment characterization, the following tests were carried out considering soaked books, processed at 1 mbar and 0°C. For the first time, the efficacy of the freeze-drying was demonstrated processing flooded bound books. We freeze-dried volumes from the XVII to the XIX century, characterized by different materials and assemblage techniques. The material selected includes books with bindings in leather covered cardboard, bindings in hard and soft parchment, editorial bindings in cardboard covered by paper with decorations. According to its age, the paper type can be variable from pure cellulose, pasted with gelatin, to industrial paper whitened and glued with additives. To facilitate a homogeneous drying, volumes were banded with a non-woven fabric (Figure 3). In this way, we prevented an excessive stress tension of the leather, and parchment of the back, as well as possible irreversible deformations.

In a first test one layer of books, with a mean thickness of 2 cm, was placed in the freeze-dryer and drying was completed after about 80 h. A second test was carried out considering thicker books, 3.5 cm, and using the same operating conditions. In this case, drying time appeared to be equal to 144 h. Considering both tests, the ratio between the drying times appeared to be very close to the ratio between the book thicknesses, as it was forecast by the theoretical investigation proposed in the previous section.

Fig. 3. Arrangement of the books in the freeze-dryer.

The best results were obtained from parchment bounded volumes (Figure 4), and mainly from the ones with soft bindings. In many cases the volumes can be considered 100% recovered and they are ready for consultation. The results were good for the volumes with the leather covers (Figure 5), even if the freeze-drying process could not cancel the damage caused by the water or by years of neglect. Besides, size change was almost negligible in all the books processed, and these volumes can be surely considered chemically and biologically stable, and should be object of other restorations in order to be easily consulted.

We consider our work on the bindings as a great success. Apart from deformation, which can still be corrected at a second stage by placing volumes under pressure, we managed to keep all the components, these latter representing an important historical testimony. The large amount of adhesives of different origins and the presence of washable inks make these volumes particularly vulnerable to water damage, and only sudden freezing can stop their degradation. The bindings of these volumes will be probably remade, using the restored original ones as a model.

Conclusions

The theoretical investigation of the books freeze-drying process evidenced that the drying time increases in a non-linear way when the product thickness increases. This means, for example, that if the thickness of the product on the shelf is doubled, then the drying time is more than twice, in particular when the thickness of the product is high. The result of this analysis suggests that it is better to archive documents avoiding too thick folders (1-2 cm can be considered an adequate size) in such a way that, in case they have to be frozen and freeze-dried after soaking, the drying time can be short and the high thickness does not impair the overall duration of the process, as well as the final product quality, as it has been verified

through experiments in an industrial-scale freeze-drier, considering the restoration of flooded bound books, characterized by different materials and assemblage techniques.

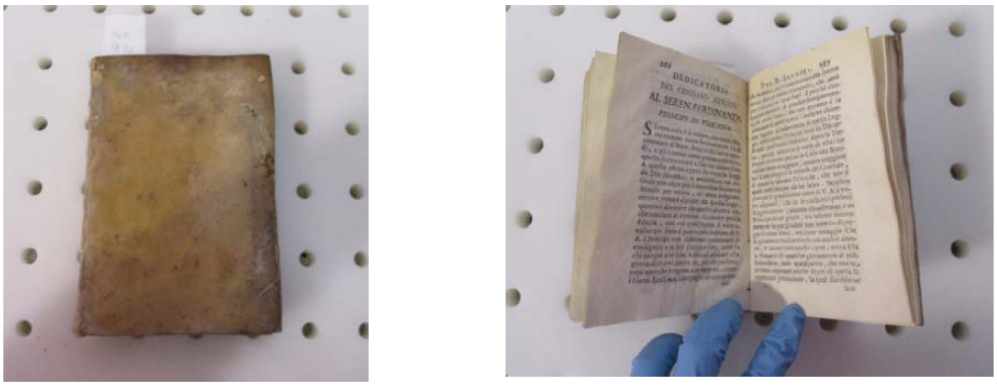

Fig. 4. Example of a recovered parchment bounded volume.

Fig. 5. Example of a book with a leather cover at the end of the freeze-drying process.

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