survival theory (Lal et al., 1969) that for a given saturation, a nucleus has to have a size greater than the critical size to survive. Size dependent birth rate in the SSBCR analysis recognizes that secondary nucleation dominated by contact nucleation (Clontz and McCabe, 1971) may not necessarily generate nuclei of equal size.

The quantity $N(t, L)$ can be easily obtained by use of a Coulter counter so long as the smallest size it can measure is less than the critical size. It has been shown (Cise and Randolph, 1972) that a Coulter counter can be used to measure the size of small particles down to 1 μm range. However, the inability to measure the size of small particles could become the limiting factor. In such a case, Equation (2) should be integrated from L to $L = \infty$ to yield

$$\int_L^\infty n(t, \zeta)d\zeta - G(L)\int_0^t n(\tau, L)d\tau = t_r\int_L^\infty b_n(\zeta)d\zeta \tag{5}$$

since $n(t, \infty) = 0$. This is to say that for all practical purposes, the number of crystals with infinite size is zero in any experiment. Equation (5) can be rewritten in terms of the cumulative number of oversize crystals, and we have

$$\overline{N}(t, L) = G(L)x(t, L) + t_r\overline{B}(L) \tag{6}$$

Equation (6) is again a straight line with a slope of $G(L_s)$ and an intercept of $t_r\overline{B}(L_s)$ for a given size, L_s, when $\overline{N}$ is plotted against x. Therefore, either Equation (6) or Equation (4) can be used for the determination of growth rate and cumulative birth rate of secondary nuclei. Birth rate can be obtained by differentiating the cumulative birth rate with respect to size.

It has been tacitly assumed that the duration of an experiment is not long enough for the secondary crystals to become the source of secondary nuclei. In this regard, it is notable that an estimate of the threshold size above which the secondary crystals themselves become the source of secondary nuclei can be made by simply allowing the secondary nuclei to grow and then utilizing the results of Figure 3*a*. The size in Figure 3*b* at which the cumulative birth rate breaks away from a plateau it reached (L_t in Figure 3*b*) would then become the threshold size.

NOTATION

b = birth rate
b_n = net birth rate, $b - d$
$B(L)$ = cumulative birth rate, $\int_0^L b_n(\zeta)d\zeta$
$\overline{B}(L)$ = cumulative oversize birth rate, $\int_L^\infty b_n(\zeta)d\zeta$
d = death rate
$G(L)$ = linear growth rate, dL/dt
L = characteristic size of a crystal
L_c = critical size
L_t = threshold size
$n(t, L)$ = number of crystals with size L
$N(t, L)$ = cumulative number of crystals with size up to L, $\int_0^L n(t, \zeta)d\zeta$
$\overline{N}(t, L)$ = cumulative number of oversize crystals, $\int_0^\infty n(t, \zeta)d\zeta$
t = time
t_r = time at which a seed crystal is removed from a crystallizer
$x(t, L) = \int_0^t n(t, L)dt$

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The Effect of pH on Continuous High-Temperature/Short-Time Sterilization of Liquid Foods

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Thermal sterilization of liquid foods for preservation is an important operation in the food industries. High-temperature/short-time (HTST) processing is gaining increasing applications because of the improved product quality (Pfeifer and Vojnovich, 1952; Holdsworth, 1969). Furthermore, the continuous process permits greater control of the processing temperature and exposure time than is possible with the batch process. A major disadvantage of the

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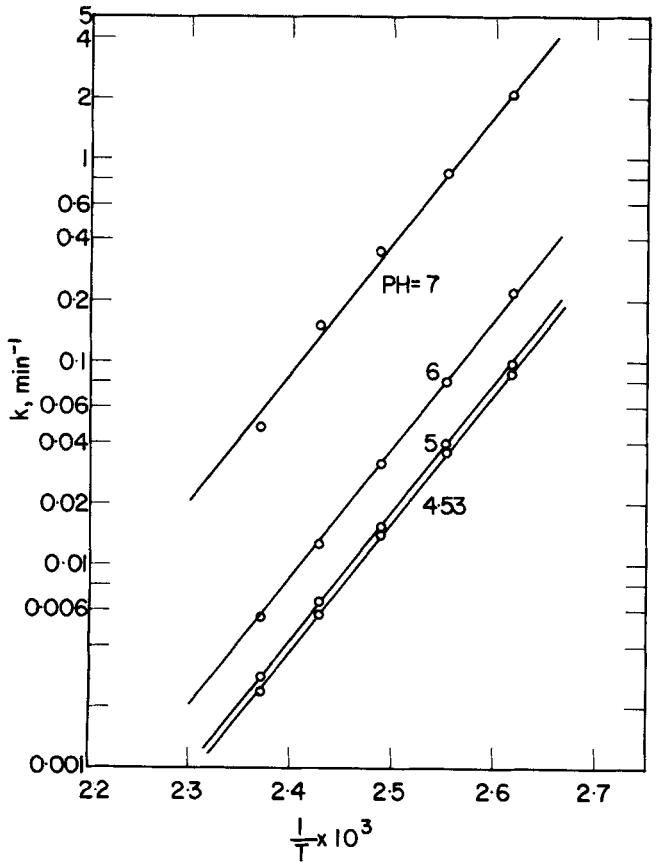

Fig. 1. Plot of the rate coefficient for thiamine denaturation against $1/T$ for different pHs.

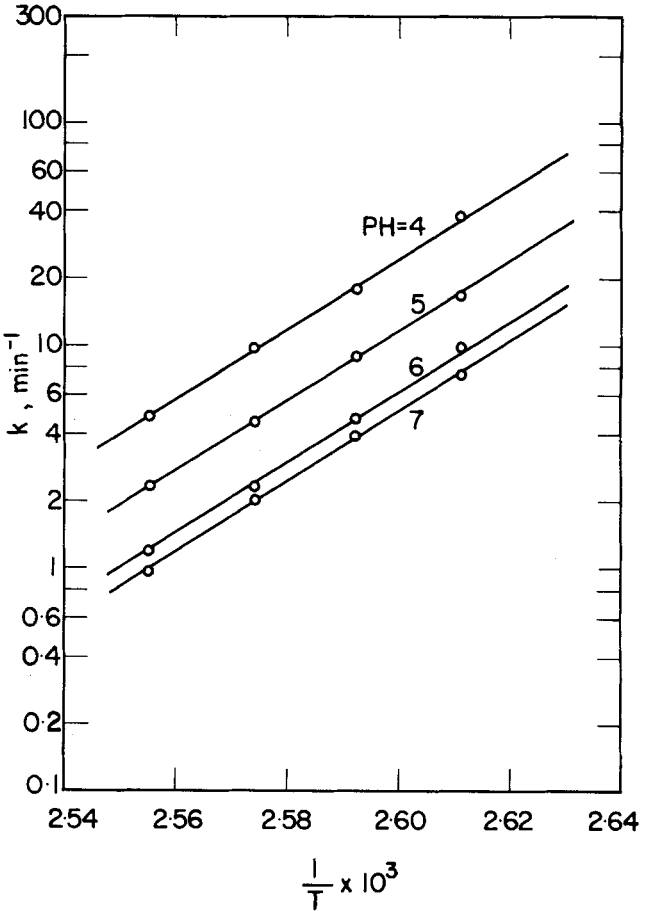

Fig. 2. Plot of the rate coefficient for Cl. botulinum inactivation in spaghetti, tomato sauce, and cheese against $1/T$ for different pHs.

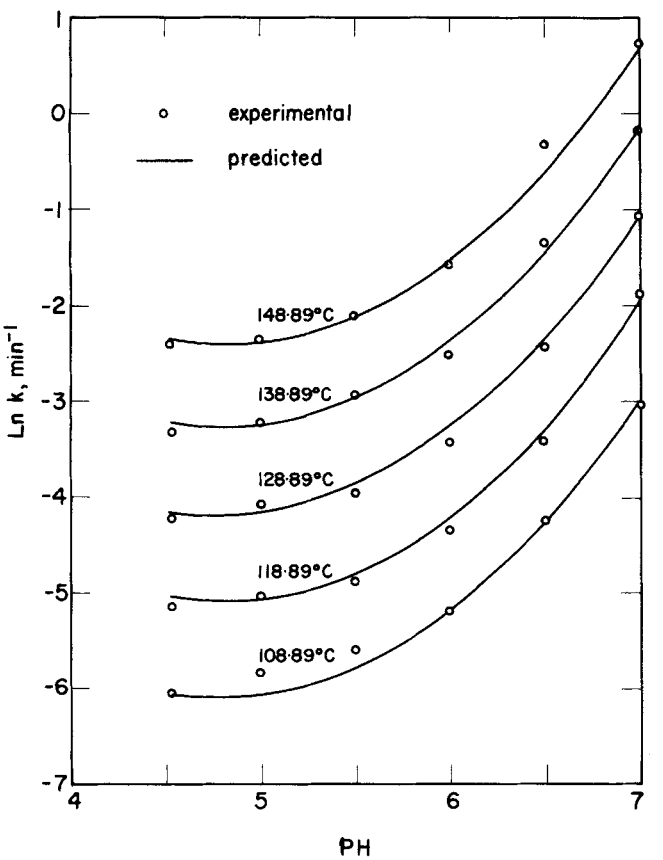

Fig. 3. Plot of the rate coefficient for thiamine denaturation against pH for different temperatures.

batch process is the time involved in the heating and cooling periods, where up to half of the sterilization can occur (Richards, 1965).

It has been recognized for a number of years that the pH of foods significantly influences the heat resistance of microorganisms and nutrients (Holdsworth, 1969; Charm, 1971). However, no attempt to correlate the rate coefficient with both pH and temperature has been made previously. Failure to allow for pH variation may lead to an incorrect sterilizer length determination. This paper presents a comparison of two sets of experimental data, where the pH

Table 1. Rate Coefficient for Cl. Botulinum Inactivation and Thiamine Denaturation

$$\ln k = -\frac{\Delta E}{1.987\,T} + a\,(p\mathrm{H})^2 - b\,(p\mathrm{H}) + c$$

	ΔE, Kcal/g mole	a	b	c
Cl. botulinum in				
Spaghetti, tomato sauce, and cheese	74.29	0.1634	2.3248	105.06
Macaroni creole	72.50	0.1878	2.6147	104.38
Spanish rice	74.71	0.2032	2.7949	107.81
Thiamine in				
Phosphate buffer	29.39	0.6530	6.2861	47.767

K in minute^{-1}.

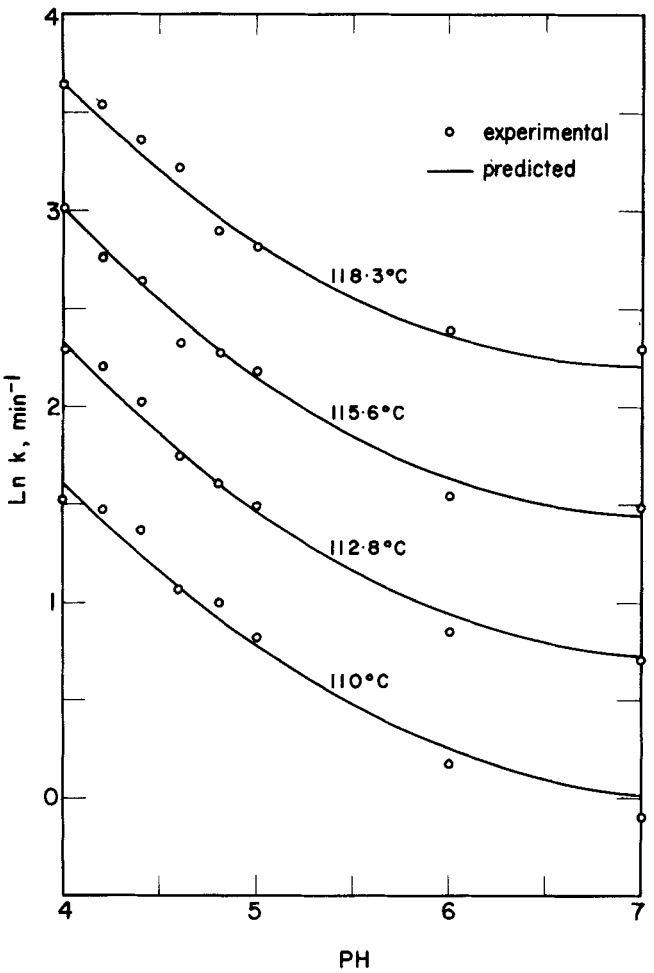

Fig. 4. Plot of the rate coefficient for Cl. botulinum inactivation in spaghetti, tomato sauce, and cheese against pH for different temperatures.

effect is clearly seen, together with an empirical correlation which enables the effect of pH to be incorporated in a design equation. The performance equation of Lin (1976) is used for this purpose.

THE EFFECT OF pH ON THE RATE COEFFICIENTS

The temperature-dependent rate coefficient for microorganism inactivation and nutrient denaturation can be represented by the Arrhenius equation (Garrett, 1956; Levine, 1956)

$$k = A \exp\left(-\frac{\Delta E}{R_g T}\right) \tag{1}$$

At a particular temperature, k is a function of A and ΔE, and if k is also a function of pH, it will be through A, ΔE, or both.

The experimental data of Feliciotti and Esselen (1957) for thiamine (vitamin B_{12}) denaturation and Xezones and Hutchings (1965) for Cl. botulinum spore inactivation are replotted in Figures 1 and 2. The influence of pH on k is clearly seen, and because the lines for different pHs are almost parallel on the semilog graph, the ΔE variation due to pH is very slight.

From Equation (1)

$$\ln k = -\frac{\Delta E}{R_g T} + \ln A \tag{2}$$

Assuming that only A is affected by pH, the following equation is obtained by least-squares fit of the data from Figures 1 and 2:

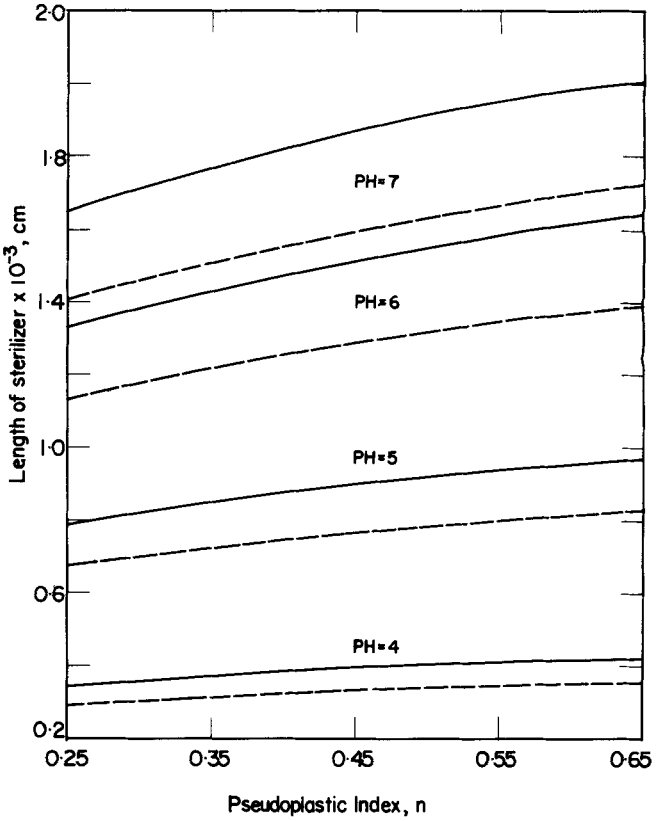

Fig. 5. Effects of pH and sterility requirement on the sterilizer length at an operating temperature of 121°C.
———— for sterility requirement of 10^{-14}.
- - - - - - - for sterility requirement of 10^{-12}.

$$\ln A = a\,(p\mathrm{H})^2 + b\,(p\mathrm{H}) + c \tag{3}$$

Table 1 illustrates the values of a, b, and c for the two systems. Figures 3 and 4, respectively, show the comparison of the predicted and observed rate coefficients for Cl. botulinum inactivation and thiamine denaturation. It is apparent that the agreement between them is rather good.

DETERMINATION OF STERILIZER LENGTH

Lin's laminar flow model (1976) is

$$\frac{\langle C\rangle}{C_0} = 2\int_0^1 \exp\left(-\frac{kL}{u}\right)\frac{u}{\langle u\rangle}\,R\,dR \tag{4}$$

$$\frac{u}{\langle u\rangle} = \frac{3n+1}{n+1}\left[1 - R^{(n+1)/n}\right] \tag{5}$$

in which $\langle C\rangle/C_0$ is the fraction of spore surviving after sterilizer length L. If we use Equations (4) and (5) with k evaluated from Equations (2) and (3), the dependence of sterilizer length on pH can be determined for different sterility requirements. This is illustrated in Figure 5 for Cl. botulinum inactivation in spaghetti, tomato sauce, and cheese. A significant effect is observed, the sterilizer length being almost doubled with a pH change from 5 to 7. Owing to the nonlinear variation of rate coefficient with pH, the magnitude of the effect on the sterilizer length is increased with a rise of pH.

CONCLUSIONS

For thiamine denaturation and Cl. botulinum inactivation, the sterilizer length and hence the residence time is strongly dependent upon pH, the extent of dependence being increased with increasing pH. An empirical correla-

tion is proposed which when used in association with a theoretical laminar flow model enables the required sterilizer length to be determined.

NOTATION

a = constant parameter in Equation (3)
A = frequency factor
b = constant parameter in Equation (3)
c = constant parameter in Equation (3)
C_0 = inlet spore or nutrient concentration
$<C>$ = bulk spore or nutrient concentration
ΔE = activation energy
k = rate coefficient for spore inactivation or nutrient denaturation
L = sterilizer length
n = pseudoplastic index
R = dimensionless radial coordinate
R_g = gas constant
T = temperature
u = local velocity
$<u>$ = bulk velocity, 10 cm/s

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The Prediction of Desorption Times for Fixed-Bed Adsorbers

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The problem of designing fixed-bed adsorption processes reduces, in effect, to the prediction of the breakthrough and regeneration curves for a packed adsorption column. In most practical systems, the adsorption step is carried out under conditions such that the equilibrium isotherm is highly favorable (type I of the Brunauer classification). For such nonlinear systems, exact mathematical analysis of the column response is difficult and time consuming (see, for example, Zwiebel, Gariepy, and Schnitzer, 1972; Garg and Ruthven, 1973, 1974*b*). For the adsorption cycle, however, constant pattern behavior is almost always achieved under practical operating conditions, and a sufficiently accurate prediction of the breakthrough curve may therefore be obtained simply from the equilibrium capacity and the constant pattern profile. Theoretical calculation of the constant pattern profile is straightforward, since this only requires the integration of the appropriate kinetic rate equation, subject to the boundary condition imposed by the equilibrium isotherm (see, for example, Hall, Eagleton, Acrivos, and Vermeulen, 1966; Fleck, Kirwan, and Hall, 1973). Alternatively, the spread of the constant pattern profile may be determined directly by experiment, and the dynamic adsorption capacity may then be estimated from the equilibrium capacity and the length of the mass transfer zone (length of unused bed), as outlined by Hersh (1961).

No such simple approximation is available for the desorption or regeneration cycle since, if the equilibrium relationship is favorable for adsorption, it will always be unfavorable for desorption. This is true even if the temperature is raised during the desorption cycle. At sufficiently high temperatures, the isotherm will approach linearity, but the curvature will not normally be reversed. The limiting form of the desorption profile will therefore be of the proportionate pattern type. Since desorption is generally the rate limiting step in a cyclic operation (Chi and Lee, 1969), the development of a simple method for predicting the desorption time is of considerable practical importance.

For most design purposes, it is not necessary to know the entire form of the desorption curve. Rather, the design engineer needs only to be able to predict the time, or the volume of the desorbing fluid, required to reduce the effluent concentration of the adsorbate to some arbitrarily chosen value close to zero. The slope of a type I isotherm increases continuously as the concentration decreases. The

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