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Modelling the kinetics of crab shell demineralization

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Abstract

Results are presented of an investigation of the effects of crab shell composition, mass, area, volume and thickness and exposure conditions of inorganic acid concentration and temperature on the rate and duration of alkaline earth carbonates dissolution in the context of a "shrinking core" kinetic model which is experimentally validated.

Shell thickness is shown to be the dominant determinant of the duration of the dissolution period which is otherwise independent of shell dimensions and varies inversely with the concentration of acid at low levels becoming progressively less influential as its concentration is raised. The impact of operating temperature and the merits of stepwise rather than single acid dosage are discussed.

Keywords: Demineralization, kinetic model, dimensional and temperature effects

Introduction

A proliferation of green crabs (*Carcinus maenas*), a small, destructive, invasive species in our local coastal seawaters, prompted this investigation of the kinetics of crab shell demineralization by a strong inorganic acid, preparatory to future studies of the relative merits of strong inorganic and weak organic acids as demineralizing agents and of the subsequent processing steps involved in converting the liberated chitin constituent into chitosan or glucosamine.

Effects of shell mass and thickness and exposure conditions of temperature and hydrochloric acid concentration and dosage profile on the rate and duration of dissolution of the shell content of alkaline earth carbonates are investigated.

Materials and Methods

The shells of these crabs that we received had been stored in air in a freezer for an unknown period and were usually placed under water for at least 24 hours to stabilize their moisture content before demineralization testing. In some instances, specimens were oven dried to constant weight at 50-60 °C, weighed and then re-moisturized to constant weight before demineralization testing.

Batch demineralization and stepwise acid addition tests were carried out in a five liter reactor equipped with a variable speed stirrer, temperature, conductivity and pH sensors monitored by the Vernier Logger Pro data collection and analysis system ^[1], and fitted with a surface screen to keep shells submerged. Individual shell tests were carried out in a similar smaller system. Acid working solutions were made up from a 5.00 M stock solution of hydrochloric acid.

The progress of demineralization was followed by periodically removing shell specimens from the acid solution at noted time intervals, removing surface moisture, weighing them and the returning them to the acid solution. Unless otherwise indicated, tests were carried out on shell carapaces.

In terms of size, these crabs ranged in carapace area from approximately 10 to 30 cm². Area measurements were made based on the weights of paper cut-outs of shell projected area outlines multiplied by a factor of 1.2 to allow for their curvature. Shell volumes were determined by an application of Archimedes Principle, as the difference between their weights suspended in air and in water.

Results and Discussion**Properties of the Shell Sample**

Relationships between volume, single surface area and moist carapace weight are shown in

Figure 1. The proportional relationship between volume V and moist carapace mass m_s over the observed size range corresponds to a constant density $\rho = m_s / V = 1.66 \text{ g ml}^{-1}$, which is indicative of a constant moist shell composition regardless of size and therefore of a constant mass fraction of alkaline earth carbonates x_o , largely consisting of the calcite polymorph of calcium carbonate according to Chen *et al.* [2].

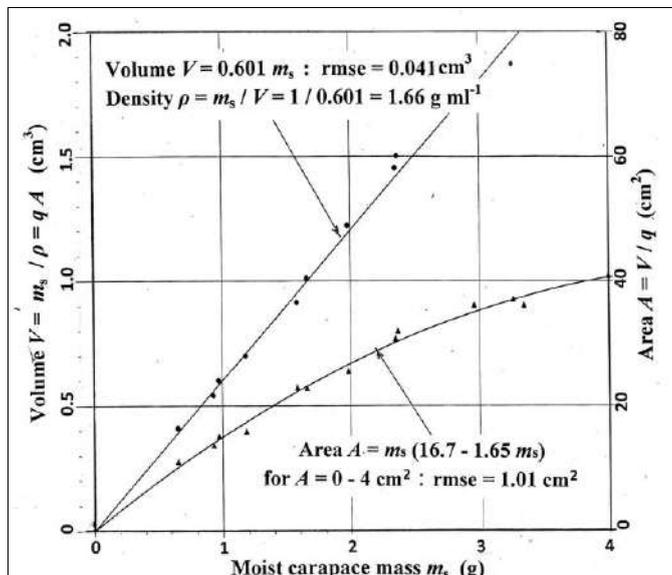


Fig 1: Carapace volume, area and mass relationships. (appended)

As shown, the relationship between the single surface area and moist carapace mass is well represented by a quadratic regression in which the constant term is set equal to zero, namely

$$A = m_s (16.7 - 1.65 m_s) = m_s / (q \rho) \quad (1)$$

from which the carapace thickness

$$q = 1 / [\rho (16.7 - 1.65 m_s)] = 1 / [1.66 (16.7 - 1.65 m_s)] \quad (2) \\ = 1 / (1.66 \cdot 16.7) = 0.0361 \text{ cm}$$

in the limit as m_s tends to zero, increasing to 0.0400 cm at $m_s = 1.0 \text{ g}$, and to 0.0513 cm at $m_s = 3.0 \text{ g}$, representing a change in thickness of 28% as the carapace mass increases threefold as crabs mature and moult.

Figure 2 shows a representative carapace drying and demineralization versus time profile obtained at ambient temperature (22 °C) and carried out in a large excess of a 2.00 M hydrochloric acid solution to maintain a near constant hydrogen ion concentration throughout the demineralization process.

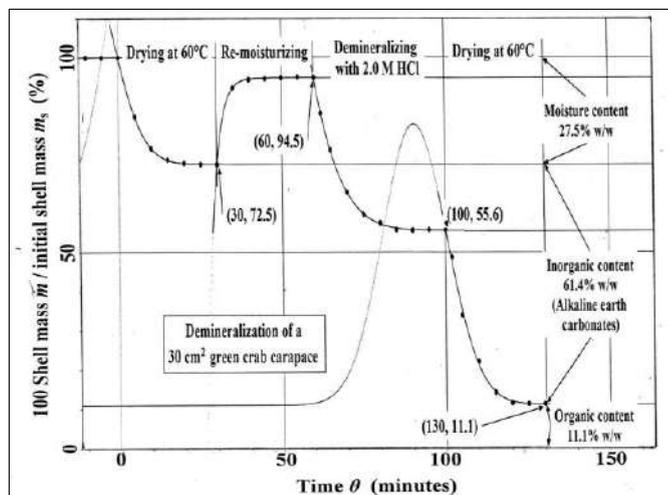


Fig 2: Carapace demineralization and drying profile.

From these test data, the composition of this carapace sample was determined to be 61.4% w/w acid soluble constituents, assumed to be calcium carbonate (calcite), 27.5% w/w water and 11.1% w/w organic constituents. Assuming specific gravity values for these constituents of 2.7, 1.0 and 1.3 respectively, this composition corresponds to a density of $((0.614 / 2.7 + 0.275 / 1.0 + 0.111 / 1.3)^{-1} = 0.588^{-1} =) 1.70 \text{ g ml}^{-1}$ which is intermediate between a density value measured after drying and re-moisturizing (after the second step in Figure 2) of 1.75 g ml^{-1} and the value of 1.66 g ml^{-1} obtained from the data set in Figure 1.

We have frequently observed a small increase in density following drying and re-moistening, possibly due to slight shrinkage during drying and accounting for this higher density value of 1.75 g ml^{-1} . The sample only re-moistened to 94.5% of its original moist weight, indicating that 0.945 g of moist shell mass occupied a volume of $(0.945 / 1.75 =) 0.540 \text{ ml}$, suggesting that the density without the 5.5% contraction would have been $((0.945 + 0.055) / (0.540 + 0.055) =) 1.68 \text{ g ml}^{-1}$.

The moisture content of 0.275 g per g of moist shell mass of density 1.68 g ml^{-1} , equivalent to $(0.275 \cdot 1.68 =) 0.462 \text{ g}$ of water per ml of shell volume, corresponds to a voidage of $(100 \cdot 0.462 \text{ g ml}^{-1} / 1.00 \text{ g ml}^{-1} =) 46.2\% \text{ v/v}$ indicating that the carapace was highly porous.

Relationship of Crab Shell Structure to Demineralization Behavior

Crab shells do not disintegrate when fully demineralized and essentially retain their original dimensions, indicating that their organic constituents form a continuous framework within which their mineral constituents are embedded.

Chen *et al.* [2] describe the structure of a crab shell as "highly anisotropic" and state that in the direction normal to

its surface "... there are well-developed, high density, pore canals containing long, flexible tubules penetrating through the exoskeleton. These tubules play an important role in the transport of ions and nutrition during the formation of the new exoskeleton during molting," and they likely also play an important role in facilitating acid access to the alkaline earth, largely calcium, carbonate content embedded within the organic constituent matrix of the shell.

These aspects of exoskeleton structure suggest that its calcium carbonate content may be more accessible to acid attack from the surfaces than from the edges of shell fragments. In this event, the common commercial practice of pre-drying and crushing shells, which adds considerably to processing costs and makes subsequent processing steps more difficult to carry out, should be only marginally beneficial for increasing the rate of demineralization. While Khan *et al.* [3] contend that crushing to about 1 mm is necessary to enhance demineralization, Oh *et al.* [4] observed only "a very slight effect" of crab shell fragment size on demineralization rate over sizes ranging from less than 1 mm to greater than 30.0 mm and noted that larger fragments facilitate processing and subsequent product recovery. (For a shell thickness of 0.50 mm, crushing a 30.0 mm square fragment into 900 1.0 mm squares would approximately double the total exposed surface area from $(2 \cdot 30.0^2 + 4 \cdot 30.0 \cdot 0.50) = 1860 \text{ mm}^2$ to $(2 \cdot 30.0^2 + 4 \cdot 1.0 \cdot 900 \cdot 0.50) = 3600 \text{ mm}^2$).

Because of thickness variation within a shell, it is difficult to ascertain accurately the effect of shell fragment size on dissolution rates. However any such effect does appear to be small. For shell fragments with moist weights of 0.928, 0.881, 0.281, 0.161 and 0.082 g, we observed weight losses during a twenty minute demineralization period of 16.6, 19.7, 22.3, 23.8 and 23.1%.

As a shell is demineralized, the new voids created immediately fill with water. Consequently the observed decrease in the mass of the shell sample will be less than the mass of calcium carbonate dissolved. The example illustrated in Figure 2, shows a decrease in the mass of 100 g of moist shells to 94.5 g when re-moisturized after drying. The mass decrease of $(94.5 - 55.6) = 38.9 \text{ g}$ observed during the demineralization step represents the difference between the mass of calcium carbonate dissolved and the mass of water that filled the vacated voids. The mass of water filling these voids will be equal to that removed during the second drying step minus the amount of water already present in the re-moisturized shell mass, that is $(55.6 - 11.1) - (94.5 - 72.5) = 22.5 \text{ g}$ indicating an original calcium carbonate content equal to this mass of water plus the mass loss observed during demineralization, that is $22.5 + (94.5 - 55.6) = 61.4 \text{ g}$.

The original moist mass composition of the shell carapace sample before the first drying was therefore 61.4% calcium carbonate, 11.1% organic constituents and $(100 - 61.4 - 11.1) = 27.5\%$ water, corresponding to a dry mass composition of $(61.4 / (1 - 0.275)) = 84.7\%$ calcium carbonate and $(100 - 84.7) = 15.3\%$ organic constituents.

If a mass y of calcite of density 2.71 is dissolved and replaced by water of density 1.00, the observed mass decrease should be $y - (1.00 / 2.71) y = (1.71 / 2.71) y$ from which it follows that the amount of calcium carbonate dissolved may be estimated by multiplying the observed moist sample mass change by $2.71 / 1.71$. For the above example of a mass decrease of 38.9% during

demineralization, the estimated value of the calcium carbonate content would be $38.9 \cdot 2.71 / 1.71 = 61.6\%$ which is in close agreement with the observed value of 61.4%.

If the mass fraction of calcium carbonate in a shell of initial moist mass m_s decreases from x_0 to x over a time period θ , during which its observed mass decreases from m_s to m , the mass of calcium carbonate dissolved in this period may be estimated from the relationship

$$m_s (x_0 - x) = (m_s - m) 2.71 / 1.71 \quad (3)$$

Development of the "Shrinking Core" Demineralization Process Model

Given that, as noted previously, the mineral content is embedded in a continuous organic constituent framework which appears not to change significantly in thickness during the demineralization process, hydrogen ions must traverse increasingly deep passages in this structure to reach the retreating surface of the remaining calcium carbonate content, resulting in a progressively decreasing rate of reaction over time. Assuming equal rates of dissolution at the outer and inner surfaces of the shell, this pore depth will increase from zero to half the shell thickness as the reaction proceeds.

A general kinetic model of this shrinking core type of reaction system has been proposed by Yagi and Kunii [5] for spherical particles, including a diffusion controlled case in which the reacting species is immediately consumed upon its arrival at the core surface with the result that its concentration at this surface is always essentially zero.

Ameh *et al.* [6] applied the diffusion controlled version of this spherical particle model to their data obtained from the demineralization of shrimp shells with 0.40 M lactic acid and achieved a moderate fit to their data represented by an r^2 value of 0.93. (The coefficient of determination r^2 is an insensitive measure of goodness of fit).

A geometrically more realistic shrinking core, diffusion controlled model for crab shell demineralization would be one based on a flat plate rather than a sphere which may be developed as follows. The diffusion controlled shrinking core model is based on a premise that the reaction rate is proportional to the reactant concentration gradient across the reaction path and that the reactant concentration is constant at its entrance and zero at the reaction surface, in effect that the reactant is immediately consumed upon its arrival at that surface.

Applied to the crab shell demineralization process at a pore depth d , this gradient will be equal to $[H^+] / d$ at time θ , in which $[H^+]$ is the assumed constant hydrogen ion concentration in the surrounding acid solution phase. Also at time θ , if x is the residual mass fraction of calcium carbonate present in a shell of initial moist mass m_s , the rate of dissolution at that time may be expressed as $-m_s dx / d\theta$ and to be proportional to the hydrogen ion concentration gradient. Assuming a Fick's Law diffusional process, the dissolution rate

$$-m_s dx / d\theta = D(t) 2A ([H^+] / d) \quad (4)$$

in which $D(t)$ represents the diffusivity of the acid medium at temperature t , m_s the initial moist mass of the shell sample, A its single surface area and x the mass fraction of calcium carbonate undissolved at time θ . If the mean shell thickness is q , the depth to the reaction surface d will

increase from 0 to $q/2$ as the reaction proceeds on each side of the shell and therefore

$$d = (q/2)(x - x_0) / x_0 = (q/2)(1 - x/x_0) \quad (5)$$

and thus, eliminating the variable depth d , the rate equation becomes

$$-m_s dx / d\theta = D(t) 2A [H^+] / ((q/2)(1 - x/x_0)) \quad (6)$$

Rearranging

$$-(1 - x/x_0) dx = D(t) 2A [H^+] / (m_s q/2) d\theta \\ = x_0(1 - x/x_0) d(1 - x/x_0) = (x_0/2) d(1 - x/x_0)^2 \quad (7)$$

from which

$$d(1 - x/x_0)^2 = 8 D(t) A [H^+] / (m_s x_0) d\theta \quad (8)$$

Integrating between $\theta = 0$ and θ for a given shell at a given acid concentration and temperature, that is for the values of $D(t)$, A , $[H^+]$, m_s , x_0 and q all constant,

$$(1 - x/x_0)^2 = 8 D(t) A [H^+] / (m_s x_0 q) \theta \quad (9)$$

from which the time period required to complete dissolution at which $x = 0$

$$\theta_{x=0} = m_s x_0 q / (8 D(t) A [H^+]) \quad (10)$$

Therefore

$$(1 - x/x_0)^2 = \theta / \theta_{x=0} \quad (11)$$

which is the proposed shrinking core model relationship. This relationship is consistent with that listed by Levenspiel^[7] for a diffusion controlled, flat plate shrinking core system and indicates, for example, that the first 10% of the mineral content should be dissolved in only $(100(1 - 0.9)^2 = 1\%)$ of the total dissolution time ($\theta_{x=0}$), that 90% should be dissolved in $(100(1 - 0.1)^2 = 81\%)$ of the total dissolution time, and therefore that it should take 19 times as long to dissolve the last 10% as the first. (The ease with which the near surface layer of calcium carbonate is dissolved suggests the interesting possibility of pre-processing a fresh batch of shell solids by using it to neutralize the necessarily somewhat acidic effluent from the preceding batch before its discharge).

Approximate support for this shrinking core relationship is provided by the experimental data set in Figure 3, in which this ratio showed a somewhat lower value of $((445 - 259) / 12 = 16)$, possibly because prevailing hydrogen ion concentration levels were somewhat higher towards the end than at the beginning of the dissolution process.

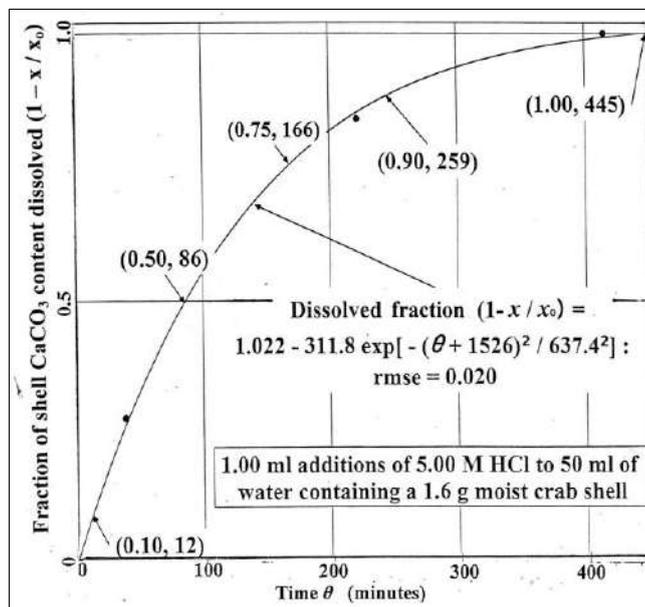


Fig 3: Slowing rate of carbonates dissolution.

The shell mass per unit area $m_s / A = \rho q$ and therefore the dissolution period

$$\theta_{x=0} = m_s x_0 q / (8 D(t) A [H^+]) = \rho x_0 q^2 / (8 D(t) [H^+]) \quad (12)$$

Given that the value of ρ is a constant independent of shell mass (as shown in Figure 1) suggesting that the fractional calcium carbonate content x_0 is also a constant, the model indicates that the duration of the dissolution period should be proportional to the square of shell thickness, inversely proportional to acid concentration and affected by temperature through its influence on the diffusivity coefficient. The shell mass and area do not appear in the second expression of this relationship because their influences on the process are subsumed in the determining parameter, the shell thickness $q = m_s / (\rho A)$.

As noted previously, the progress of the dissolution process may be monitored by removing the shell sample from the acid solution at timed intervals, removing surface moisture, weighing the shell and then returning it to the acid solution. The data reported in Figures 1 through 8 were all obtained by this procedure.

Validating the Shrinking Core Kinetic Demineralization Model

The validity of this model for representing the separate effects of shell mass, acid concentration and temperature on the kinetics of the carbonate dissolution process will be considered subsequently. Applying the model to a given shell at a given acid concentration and temperature

$$(1 - x/x_0) = \sqrt{\theta / \theta_{x=0}} \quad (13)$$

in which (from eqn. 12) the value of

$$\theta_{x=0} = \rho x_0 q^2 / 8 D(t) [H^+] \tag{14}$$

If m is the mass of the moist shell sample at time θ , it was previously shown (in eqn. 3) that the mass of calcium carbonate dissolved in the time period 0 to θ may be estimated as

$$m_s (x_0 - x) = (m_s - m) 2.71 / 1.71 \tag{12}$$

making the correction for water infiltration into the vacated shell voids. Re-arranging,

$$(1 - x / x_0) = (1 - m / m_s) (2.71 / 1.71) / x_0 \tag{13}$$

Therefore, the shrinking core model

$$(1 - x / x_0) = \text{sqrt}(\theta / \theta_{x=0})$$

will be valid if

$$(1 - m / m_s) (2.71 / 1.71) / x_0 = \text{sqrt}(\theta / \theta_{x=0}) \tag{14}$$

or, re-arranging, if

$$\text{sqrt}(\theta) = \alpha - (\alpha / m_s) m \tag{15}$$

in which

$$\alpha = (2.71 / (1.71 x_0)) \text{sqrt}(\theta_{x=0}) \tag{16}$$

is a constant under the assumed conditions of a given shell, acid concentration and temperature.

The experimental $\text{sqrt}(\theta)$ versus m data set in Figure 4, obtained from a single crab shell in 500 ml of 1.00 M HCl, do show the requisite linear relationship between these variables, namely

$$\text{sqrt}(\theta) = 14.74 - 7.73 m \tag{17}$$

with a coefficient of determination (r^2) of - 0.999 and a root means square error (rmse) of 0.10 minutes^{1/2}.

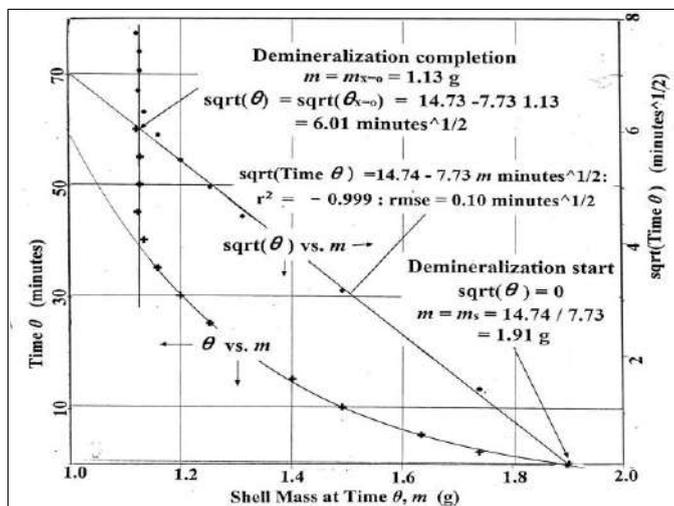


Fig 4: Kinetic model validation.

From the parameters of this relationship

$$\alpha / m_s = 14.74 / m_s = 7.73 \tag{18}$$

The initial moist mass of the shell is therefore indicated to be indicated to be $m_s = 14.74 / 7.73 = 1.91$ g, which is in close agreement with the observed value of 1.90 g. Corresponding to the observed moist sample mass at the completion of dissolution of 1.13 g, this relationship indicates a value of

$$\text{sqrt}(\theta_{x=0}) = 14.74 - 7.73 m_{x=0} = 14.74 - 7.73 * 1.13 = 6.01 \text{ minutes}^{1/2} \tag{19}$$

and therefore a dissolution time of $(6.01^2) = 36$ minutes. Corresponding to this value of $\text{sqrt}(\theta_{x=0})$, the eqn. 16 relationship suggests an initial mass fraction concentration of calcium carbonate of

$$x_0 = (2.71 / 1.71) \text{sqrt}(\theta_{x=0}) / \alpha = (2.71 / 1.71) * 6.01 / 14.74 = 0.646 \tag{20}$$

fort his whole shell sample which is somewhat higher than the value of 0.614 previously observed for a shell carapace. The effects of individual parameters on the duration of the dissolution period will be examined next.

Effect of Sample Mass (m_s) on the Dissolution Period Duration ($\theta_{x=0}$)

According to the model relationship, the duration of the demineralization process

$$\theta_{x=0} = (m_s x_0 q / 2) / (2 D(t) A [H^+]) = (x_0 \rho q^2 / 2) / (2 D(t) [H^+]) \tag{21}$$

since the carapace density $\rho = m_s / (q A)$.

The data set in Figure 1 show a constant density of 1.66 g ml⁻¹ over the observed shell carapace mass range of 0 to 3 g, indicative of constant composition and therefore a constant calcite mass fraction x_0 . Therefore, according to the model, at a given temperature and with a large acid excess such that the hydrogen ion content does not change significantly during demineralization process, the duration of the dissolution process should be proportional to the square of shell thickness and is affected by the carapace mass only through its relationship to thickness, previously exemplified in eqn.2 as

$$q = m_s / (\rho A) = 1 / [\rho (16.7 - 1.65 m_s)] = 1 / [1.66 (16.3 - 1.65 m_s)] \text{ cm} \tag{22}$$

The small available range of carapace sizes did not permit of a substantial experimental assessment of the effect of shell thickness on the duration of the carbonates dissolution process. However, an indication of the validity of the assumption that the dissolution time is proportional to the square of the thickness of the shell, and therefore that the square root of the dissolution period is proportional to its thickness, may be obtained as follows from the experimental data set shown in Figure 5 for carapace samples with moist masses ranging from 0.613 to 3.25 g in 5 liters of 0.500 M HCl.

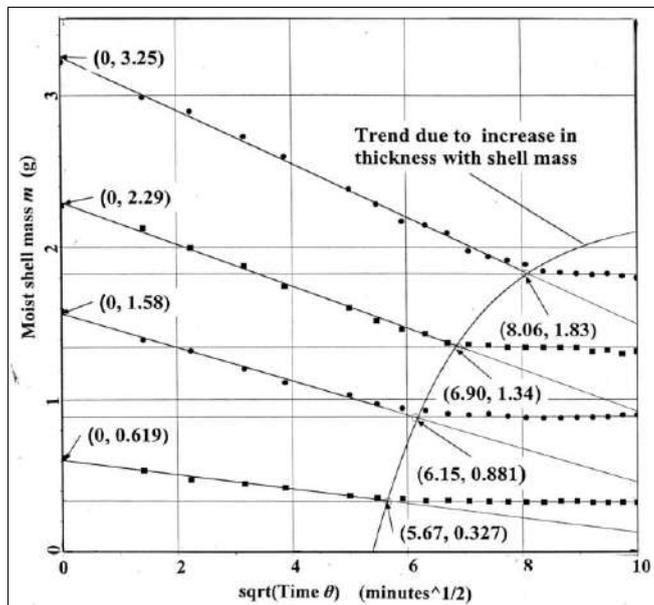


Fig 5: Shell mass effect on the dissolution period duration.

From the relationship between carapace thickness and mass in eqn. 22, $q = 0.0394$ cm for $m_s = 0.613$ g and 0.0551 cm for $m_s = 3.25$ g for a ratio value of $0.0551 / 0.0394 = 1.40$. If the assumed effect of shell thickness is valid, the square root of the ratio of the dissolution periods for carapaces of these thicknesses should be 1.40. Referring to Figure 5, the observed value of this ratio was $8.06 / 5.67 = 1.42$.

Effect of Acid Concentration ($[H^+]$) on Dissolution Period Duration ($\theta_{x=0}$)

Recapitulating, *i*) shell density and therefore presumably composition does not appear to change significantly with shell size and therefore with crustacean age, *ii*) shell mass affects the duration of carbonates dissolution ($\theta_{x=0}$) only indirectly through its relationship to the mean thickness of the shell (q), that is by its volume per unit surface area ($m_s / (\rho A)$), in which ρ is assumed to be constant, *iii*) shell thickness increases less than proportionally with shell mass and varies somewhat between shells of the same mass, *iv*) the duration of the dissolution period varies as the square of the shell thickness, and *v*) for a given shell sample at a specified temperature the model suggests that the duration of the dissolution period should vary inversely with the acid concentration which is assumed to remain constant in large excess during the dissolution process.

Investigation of the effect of acid concentration on the dissolution process necessarily involves the treatment of a number of different shells. For this purpose, shell carapaces of approximately the same mass were selected to minimize the dominant effect of thickness variation. Density measurements suggest that the mass fraction of calcium carbonate initially present (x_0) may also be assumed to be the same in each of the shells. Under these conditions, from eqn. 3, the mass of calcium carbonate dissolved at time θ $m_s (x_0 - x) = (m_s - m) 2.71 / 1.71$ in which m is the measured moist shell mass at time θ and from which

$$1 - m / m_s = (x_0 - x) 1.71 / 2.71 \tag{23}$$

The value of x_0 was previously found to be 0.614. At the end of the dissolution period $x = 0$, $\theta = \theta_{x=0}$ and

$$1 - m_{x=0} / m_s = x_0 1.71 / 2.71 = 0.614 1.71 / 2.7 \approx 0.39 \tag{24}$$

Thus the duration of the dissolution period ($\theta_{x=0}$) may be taken to be the time at which the fractional moist shell weight loss reaches a value of 0.39. The dissolution data plotted in Figure 6 were obtained from shell carapaces of approximately the same mass exposed to acid concentrations ranging from 0.10 to 5.00 M and show modest scatter above and below this weight loss factor of 0.39. At this value, the data suggest that the model assumption that the duration of the dissolution period is inversely proportional to the acid concentration is realised as this concentration tends to zero and applies closely at low concentrations. Doubling the acid concentration between 0.100 M and 0.200 M halved the dissolution time from 135 to 67 minutes, but the acid was found to be less effective at higher concentrations. Increasing the acid concentration from 0.200 M to 0.500 M reduced the dissolution time from 67 only to 39 minutes versus the model prediction of $(67 \cdot 0.200 / 0.500) = 27$ minutes.

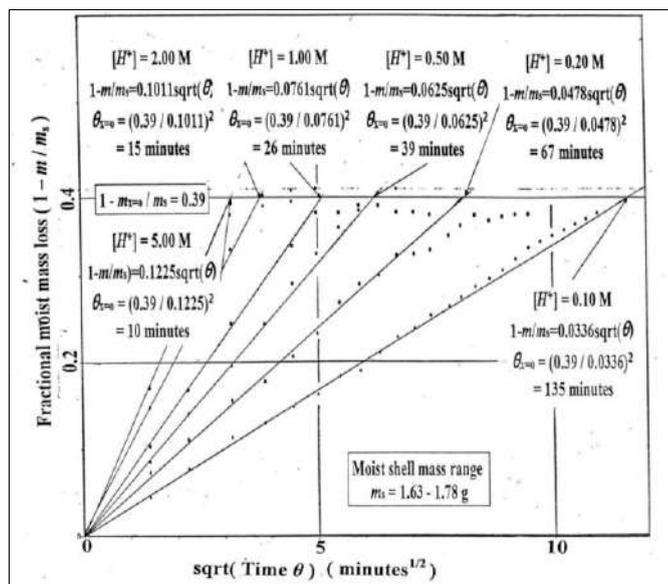


Fig 6: Acid concentration effect on dissolution period duration.

Increasing positive deviation of the observed value from the predicted value of the dissolution time as the hydrogen ion concentration is raised is presumably due to rising viscosity of the acid solution and the fact that these hydrogen ions must flow through the shell channels to the reaction surface against larger counter-flows of carbon dioxide gas and positively charged calcium ions.

As shown in Figure 7, the dissolution time may be related to the acid concentration over the complete test range of 0.100 to 5.00 M as follows:

$$\log (\theta_{x=0}) = 1.414 - 0.658 \log ([H^+]): \text{rmse} = 0.050; r^2 = -0.994 \tag{25}$$

from which

$$\theta_{x=0} = 25.9 [H^+]^{-0.658} \text{ minutes} \tag{26}$$

indicating values of 120 minutes at 0.100 M and 26 minutes at 1.00 M. (It is a matter for future study to determine whether a 26 minute exposure to a 1.00 M acid

concentration causes more or less hydrolytic damage to the chitin shell constituent than 120 minutes in an 0.100 M solution. Similarly concerns arise in regard to lengthy exposure to a weak organic acid, for example lactic acid, compared with a short dip into a strong mineral acid at the same analytical concentration level but a much higher hydrogen ion concentration. Should the rate of hydrolytic attack prove to be proportional to the acid concentration, the extent of hydrolytic damage by an 0.100 M strong acid solution should be proportional to the rate – time product of (0.100 M x 120 minutes =) 12.0. Corresponding values of this product for acid concentrations of 0.200 M, 0.500 M, 1.00 M, 2.00 M and 5.00 M are 13.4 19.5, 26.0, 30.0 and 50.0 respectively).

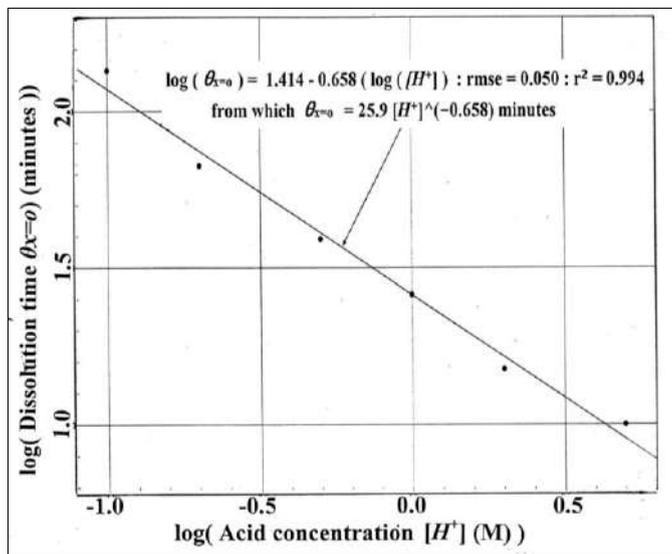


Fig 7: Acid concentration effect on dissolution period duration.

Effect of Temperature (t) on the Dissolution Period Duration ($\theta_{x=0}$)

Using the $1 - m_{x=0} / m_s = 0.39$ procedure, $\theta_{x=0}$ dissolution period values for 0.5 to 3.5 g shell carapace samples were determined in a large excess of 0.500 M hydrochloric acid at temperatures of 1, 23 and 51°C.

As shown in Figure 8 for the case of the 2.0 g carapace size, the dissolution period duration approximately doubled, corresponding to halving of the value of the diffusion coefficient $D(t)$, increasing from 39 to 86 minutes upon cooling from room temperature (23 °C) to near the freezing point (1°C), and may be approximately halved by heating from room temperature to 51°C, reducing the exposure period from 39 to 18 minutes. (Temperature adds another dimension to the effects of hydrogen ion concentration and length of exposure on the extent of hydrolytic damage to

chitin during the demineralization stage of processing).

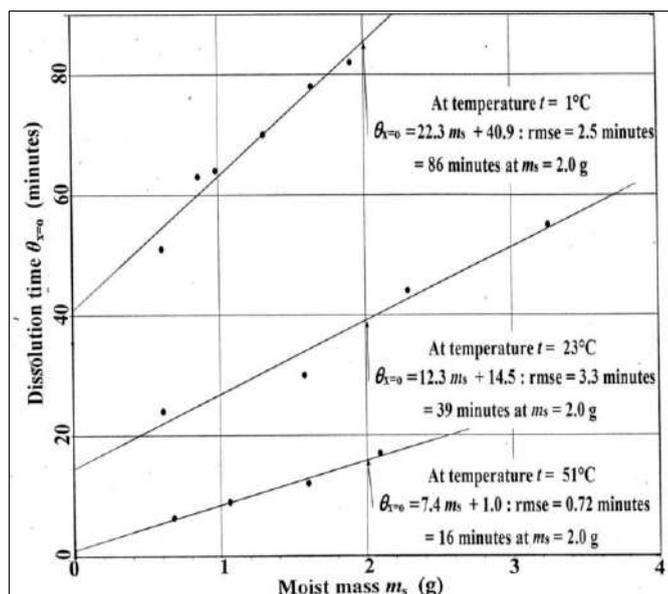


Fig 8: Temperature effect on dissolution period duration

A Stepwise Acid Dosage Procedure

The above tests were carried with large excesses of acid, sufficient to ensure that its concentration fell by considerably less than 5% during these procedures. In typical commercial crustacean demineralization procedures, the stoichiometrically required acid dosage plus some excess is introduced at the start of the demineralization process, which means that its concentration is highest when it is least needed because the calcium carbonate content is then most accessible. However the availability of mineral acids at concentrations much higher than that operationally or chemically desirable for the demineralization process permits of a more flexible approach to dosage profiling, for example introducing the same total dosage in a series of small amounts of the concentrated acid in equal or larger and larger increments as demineralization proceeds: hydrochloric acid is commercially available at concentrations up to 11.6 M and demineralization is generally carried out at initial levels below 2 M. Stepwise acid addition has been proposed elsewhere by Percot *et al.* [8] and by Rhazi *et al.* [9].

An example of our use of stepwise acid addition of 5.00 M hydrochloric acid, shown in Figure 9, clearly illustrates the greatly increasing difficulty of dissolving successive increments of the calcium carbonate content of the shells as predicted by the shrinking core model: the initial addition of 60 mls of acid reacted completely within 30 minutes while it took 338 minutes to deal with the last 28 ml addition.

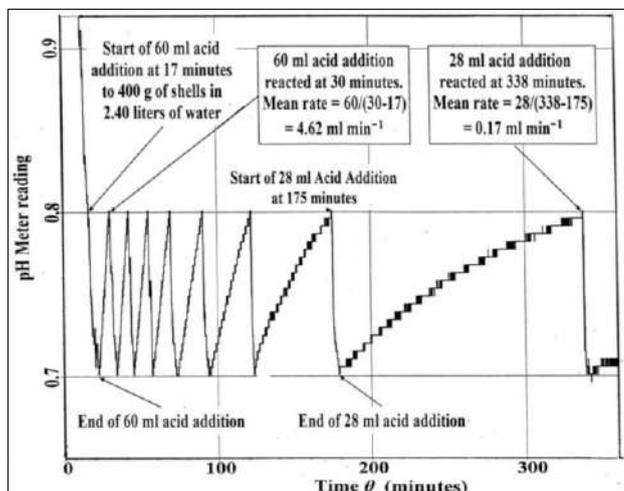


Fig 9: Demineralization by stepwise acid addition.

pH measurements were obtained from a pH electrode standardized against 4.0 and 7.0 pH buffer solutions and then calibrated against a series of standard hydrochloric acid solutions which delivered an activity coefficient value of 0.80 at the mid-range pH meter reading of 0.70 indicating that the demineralization process was carried out at a mean hydrogen ion concentration of $(10^{-0.70} / 0.80) = 0.25$ M.

Compared with a single dosage, introduction of the same total quantity of acid in a series of smaller additions as the demineralization process proceeds reduces the maximum hydrogen ion concentration to which the shells are exposed but extends the exposure period necessary to complete demineralization.

A more subtle advantage of stepwise strong acid addition is that it permits a reduction of the volume of the process effluent. For crab shells of a given calcium carbonate content and administration of the acid reagent as a single dosage at the start of the demineralization procedure, the analytical concentration of the acid will determine the maximum loading of shell solids that can be completely demineralized and hence the minimum effluent volume per unit mass of shell solids treated. For example, the stoichiometric requirement of a monoprotic acid to dissolve a 60% w/w content of calcium carbonate is $(0.60 \text{ g CaCO}_3 / \text{g shells}) / (100 \text{ g} / \text{mol CaCO}_3) (2 \text{ H}^+ \text{ ions} / \text{molecule CaCO}_3) = 0.012 \text{ mol of acid} / \text{g shells}$ which would for example be present in 12 ml of a 1.0 M acid reagent or 24 ml of an 0.5 M solution corresponding to a shell solids loading of 1: 12 or 24 g ml^{-1} and therefore a minimum effluent volume of 12 or 24: 1 ml g^{-1} of shell solids processed. In the example of stepwise addition shown in Figure 9, the initial solids loading was as high as 1: 6 g ml^{-1} , decreasing somewhat as successive additions of 5 M HCl were made.

Conclusions

A shrinking core kinetic model is presented which relates operational parameters to the duration of the demineralization process.

This shrinking core model envisages that the duration of the shell demineralization period will be proportional to the square of the thickness, for which limited corroborative evidence is presented, and to be only indirectly affected by shell mass through its weak relationship to shell thickness: shells of different mass but the same thickness should show the same dissolution period duration since the area over

which dissolution occurs will increase linearly with mass under this condition.

As evidenced by the constancy of density measurement values, shell composition does not vary detectably with shell size and therefore presumably with the age of the crustacean.

The model assumption of an inverse relationship between acid concentration and dissolution period duration is obeyed only at low acid concentrations and the effectiveness of the acid in this respect decreases progressively as its concentration is raised.

The temperature of the acid solution significantly affects the duration of the dissolution process, approximately halving it between 22 and 1°C and approximately doubling it between 22 and 51°C.

Nomenclature

A	single surface shell area (cm^2)
$D(t)$	diffusivity ($\text{g cm}^{-1}\text{minute}^{-1} \text{M}^{-1}$)
$[H^+]$	hydrogen ion concentration (M)
d	pore depth at time θ (cm)
m	moist shell mass at time θ (g)
m_s	moist shell mass at time $\theta = 0$ (g)
q	shell thickness (cm)
t	temperature (°C)
x	carbonates mass fraction at time θ (—)
x_0	carbonates mass fraction at time $\theta = 0$ (—)
θ	time (minutes)
$\theta_{x=0}$	carbonates dissolution time (minutes)
ρ	mean shell material density (g cm^{-3})

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