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SUMMARY

Shelf life estimation is a very important issue in the beverage industry. Depending on the packaging application, estimation of the carbon dioxide loss or of the oxygen ingress through the plastic bottle walls has always been desirable and challenging at the same time.

Up to now, most of this work is being carried out experimentally measuring the O_2 or the CO_2 transport through the package. In this work an FEM approach is presented, which is shown to be able to replace time consuming, expensive lab tests.

Gas permeability through the package is treated as a transient state diffusion problem in a 2D axisymmetric geometry.

As required inputs, the exact bottle drawing is needed with the estimated or the measured thicknesses along the various bottle sections. Cap geometry and initial fill level must also be input. Data of strain induced crystallinity as obtained by density for the main bottle areas (unoriented areas, shoulder, base and body) have to be fed into the software as well.

For each plastic material involved, data of gas (O_2 or CO_2) solubility and diffusivity are entered as a function of temperature and crystallinity of the material.

The model was able to fit the experimental measurements of CO_2 loss and O_2 ingress with an average error lower than 5%.

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Shelf life of pet bottles estimated via a finite elements method simulation of carbon dioxide and oxygen permeability

Key words: carbon dioxide, FEM, oxygen, permeability, PET bottles, shelf life

INTRODUCTION

Very often the shelf life of a packaged food is heavily dependent on the resistance that the polymeric container walls are able to offer to various compounds diffusing through them.

Examples of this condition are carbonated mineral waters, soft drinks and beer. The carbonation level in these products decreases with time as a result of permeation mechanisms through the bottle walls.

Moreover, their organoleptic properties are mostly determined by their gas content in such a way that a carbon dioxide reduction of only 15% is generally enough for the drink to taste flat. The beverage industry is therefore much involved in testing for CO_2 loss or O_2 ingress in order to check that each modification imparted to the packaging (bottle weight reduction, cap change, new bottle shape, etc.)

does not significantly decrease the required shelf life.

This is normally achieved through labour and especially time intensive experimental measurements, which require the containers to be filled and repeatedly measured over time up to several months.

A modelling tool able to reduce this stage to no more than a few hours would speed up the process and would rationally optimise many features of the packaging (especially the thickness, i.e. the final weight).

As a matter of fact, models very often tend to use oversimplified assumptions, like the reduction of the container to a mono-dimensional film (just radial diffusion is taken into account) and the disregard of local geometry variations in terms of thickness distribution of the bottle walls and of the local physical properties (density/crystallinity). This features

noticeable difficulties in properly defining what is the average effective diffusivity and solubility, when material properties do vary on a variable geometry itself.

In this work these restraints could be relaxed by using a 2D radial symmetric model, which therefore has all the characteristics of a 3D model, in which the real bottle geometry is used as the integration domain.

MATERIALS AND METHODS

Bottles

All the containers used for the experimental measurements of permeability were manufactured in PET (Poly(ethylene terephthalate)). PET from various suppliers was used, but it was always of "water grade" type (modified with about 2% isophthalic acid and solid stated to a final intrinsic viscosity of 0.74-0.80 dL/g).

The bottles were produced by a two stage technique consisting first of injecting the preforms on dedicated injection molding machines (Husky Injection Molding Systems Ltd., Bolton, Ontario, Canada) and then stretch blow molding these preforms on blowing machines (Sidel, Le Havre, France).

Closures

Bottles were closed with various caps, which were mainly of the one-piece type (high density polyethylene monomaterial) or of the two-piece type (polypropylene outer shell + ethylene vinyl acetate seal).

Chemical carbonation

All the carbon dioxide (CO₂) permeability measurements were done via chemically carbonating the bottles with sodium bicarbonate (VWR International) and hydrochloric acid (standard solution 6 mol/L from Riedel-de Haen).

Stoichiometric amounts of acid and base were added to deionised water to develop the desired initial CO₂ levels in the bottles.

Permeability

CO₂ levels were measured via pressure and temperature readings. Pressure in the bottles was measured using an aphrometer (similar to the Zahm&Nagel piercing devices) equipped with an MBS 3000 pressure transducer (Danfoss A/S, measuring range: 0-10 bar, accuracy: $\pm 0.5\%$ FS). Temperature readings were performed with a Checktemp digital thermometer, supplied by Hanna Instruments Inc. (accuracy: $\pm 0.3^\circ\text{C}$). Knowing pressure, temperature and volume of the headspace of the bottle (which can be easily measured), the ideal gas law can be applied to calculate the moles of CO₂ in the gas phase. By Henry's law and knowing the Henry's constant for the CO₂/water system, the concentration of CO₂ in water can then be determined.

By measuring the CO₂ amount repeatedly at various storage times a carbonation loss curve can be built. Five bottles for each storage time were measured. Bottles were stored at $22 \pm 1^\circ\text{C}$ or at $40 \pm 1^\circ\text{C}$.

Dissolved oxygen (O₂) measurements were carried out by means of a YSI 550 dissolved oxygen meter (YSI Inc.)

For O₂ ingress measurements, deionised water was previously deaerated by Nitrogen bubbling through the water under vacuum; Argon flushing of the headspace ended the procedure before capping the bottle. In this manner reproducible values of dissolved O₂ could be attained (around 0.2 mg/L).

The bottles were then stored for various times at $22 \pm 1^\circ\text{C}$ and analysed for dissolved O₂ in water. Five bottles for each time batch were used. In this way an O₂ ingress curve over time can be generated.

Bottle thickness

A Gawis OD9500 device from AGR-

TopWave LLC was used for automatic thickness measurement of the bottle walls along various heights.

Density

Various bottle parts were measured for density using an AG 204 DeltaRange balance from Mettler Toledo International Inc., equipped with the density determination kit for determining the density of solids.

Percent crystallinity values (X) were computed from density measurements using the following formula:

$$X = \frac{\rho - 1.335}{1.455 - 1.335} \quad (1)$$

where ρ is the density of the sample. The density of completely crystalline PET is assumed to be 1.455 g/cm³ while that of completely amorphous PET is 1.335 g/cm³.

Software

AutoCAD 2006 from Autodesk Inc. was used to work on the bottle technical drawings before importing them into FEMLAB 3.1 (COMSOL Inc.), which was used to run the FEM simulations.

PERMEABILITY MODELING

The process of mass transport through a package is complex, very often not allowing an analytical mathematical solution, so that use of numerical methods is required.

In fact, the solutions are further complicated by practical problems, such as migration with media partitioning, dependence of diffusion coefficient D on sorbed penetrant concentration C, such that $D = D(C)$, deviations from Fickian behaviour in diffusion, which are related to different penetrant sorption modes (Comyn J., 1985) (see for instance dual mode sorption in glassy

polymers) and the case of binary gas mixtures, in which the effects of competition between both components must be taken into account (Chern R.T. *et al.*, 1983). In such cases, analytical solutions are rarely available, if not feasible at all.

Actual geometries (thicknesses) and physical properties (density) of the bottles are also varying locally from zone to zone, following complex features, whose approximation by the regular plane sheet concept (Crank J., 1975) is rather questionable in the real case. Therefore, the finite element method was selected in this work to approach some of these complicated problems in a simpler and more efficient way.

The basic assumptions used to carry out the modelling work have been (depending on the case of CO₂ exit or O₂ ingress through the package):

- Initially, the migrant is distributed uniformly in the packaging matrix and/or in the food.
- Migration occurs from one side of the packaging to a liquid food or vice versa.
- The liquid food is well mixed so that there is no migrant concentration gradient in the food.
- The surface mass transfer coefficient is much larger than the diffusion coefficient, implying the migration is controlled by Fickian diffusion in the packaging and the effect of mixing is negligible.
- Diffusion coefficient and partition coefficient are constant during migration and depend only on temperature.
- Equilibrium exists all the time during migration at the interface of packaging and food.
- No significant swelling of the polymer is assumed to occur when a gas permeates through the polymer itself.
- When modelling CO₂ or O₂ mass transfer, the effects of competition on the sorption of the pure components studied and other possible components (e.g. N₂) are neglected.

All these assumptions lead to a Fickian

diffusion of the gases through the PET bottle walls, in which the transfer amount and rate are controlled by the diffusion coefficient and the partition factor.

Generally PET, being a glassy polymer below 70°C, fits poorly into a pure Fickian diffusion mechanism.

Other models are therefore preferred to predict the mass transfer through PET, like the dual-mode sorption model (Barrer R.M. *et al.*, 1958) and the gas-polymer matrix model (Raucher D. and Sefcik M.D., 1983). The latter seems to be slightly favoured in the PET case (Brolly J.B. *et al.*, 1996).

By this model, it is assumed that D increases with C and S decreases with C and thus the permeability $P = D \cdot S$ can turn out to be practically unaffected by C , as can be verified in the case of the data provided by Brolly J.B. *et al.* (1996). So, the approach of this work has been to try keeping the simpler Fickian model and test it against the experimental observations of gas permeability through actual PET bottles. This Fickian approach has also been followed by others (Del Nobile M.A. *et al.*, 2003).

The simulations were run on a 2D axisymmetric domain, exploiting radial symmetry. The advantage over other models, which try to predict the prod-

uct shelf life in plastic bottles (Del Nobile M.A. *et al.*, 1997), is that the domain is not approximated to a plane sheet, having the surface of the real bottle and a thickness equal to the average thickness of the bottle itself; rather, the actual 2D drawing was used with the further advantage of using the actual thickness and crystallinity distribution (see details in **fig. 1**), the latter not being usually modelled (Del Nobile M.A. *et al.*, 2003). The partial differential equation to solve for was:

$$\frac{\partial C}{\partial t} = \nabla(D\nabla C) \quad (2)$$

to be solved in non-steady state conditions, where C is the concentration of the gas and D the diffusion coefficient.

The boundary conditions were:

Constant gas concentration on all the outer boundaries (CO₂=0; O₂=external concentration in the environment). Flux continuity at each domain boundary between different phases (e.g. headspace-water, etc.), but different concentrations from domain to domain due to partitioning.

The initial conditions were:

CO₂ concentration = 0 in all domains

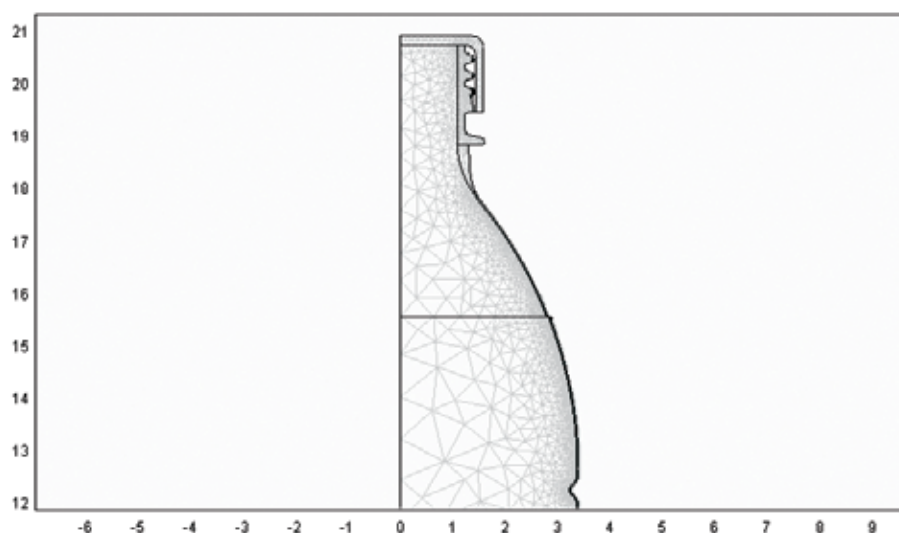


Fig. 1 - Bottle drawing representing the level of details.

except in the water domain, in which it was set at the concentration obtained by the chemical carbonation; O_2 concentration = initial known concentration in the water and in the headspace.

Diffusion coefficient for CO_2 and O_2 in the polymer was considered a function of temperature, T , and of crystallinity, X , being introduced into the model in the following form:

$$D_{eff} = \alpha e^{\frac{b+cX}{T}} \quad (3)$$

where D_{eff} stands for the “effective” Fickian diffusion coefficient α is a pre-exponential factor, b and c are positive constants, X is the percent crystallinity, T is the temperature in K. Solubility was similarly expressed as per the following form:

$$S = a(b - cX)e^{\frac{d}{T}} \quad (4)$$

in which a , b , c and d are positive constants.



Fig. 2 - Non-oriented or amorphous areas of the bottle as assumed in the model (coloured areas).



Fig. 3 - Partially oriented areas of the bottle as assumed in the model (coloured areas).

The constants were directly taken or fitted to permeability, diffusivity and solubility values found in the literature

for the CO_2 /PET and O_2 /PET systems (Brolly J.B. *et al.*, 1996, McGonigle E.A. *et al.*, 2001, Lewis E.L.V. *et al.*, 2003, Lin J. *et al.*, 2001, Koros W.J. and Paul D.R., 1978, Michaels A.S. *et al.*, 1963, Natsu A.A. *et al.*, 2005).

By filling in the right value for X , each main zone of the bottle could be properly taken into account without extreme approximations, as shown in the following figures (fig. 2 and 3).

Fig. 2 shows the practically “pure” amorphous areas of the bottle, while fig. 3 depicts the partially oriented zones in the neck and in the base. All the remaining sectors (body and shoulder) are fully oriented and described by an average strain induced crystallinity value. All the crystallinity values were experimentally measured via density, as described in the previous section.

Solubility and diffusivity values for CO_2/O_2 in the cap were also introduced using expressions of the same type as n. 3 and 4, with the proper constants.

Solubility and diffusivity values for CO_2/O_2 in water were calculated re-

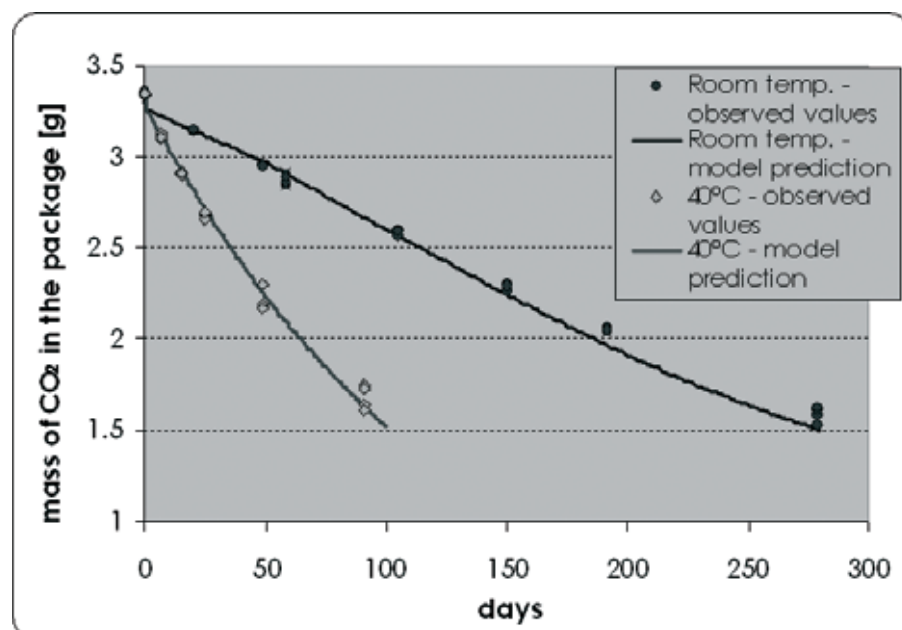


Fig. 4 - CO_2 loss for a 0.5 L bottle – 26 g – room temperature vs 40°C. Initial product carbonation: 3.3 CO_2 vol (STP).

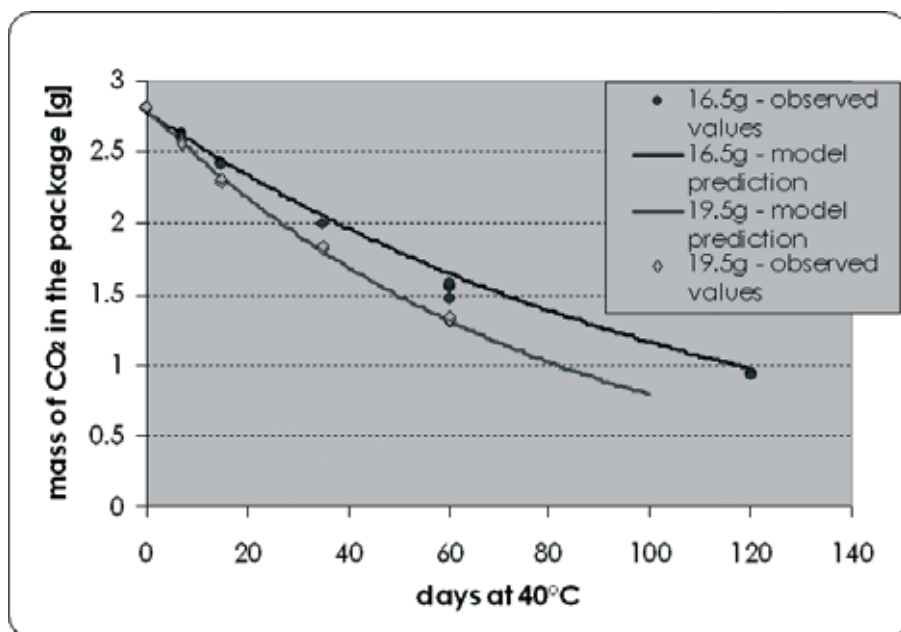


Fig. 5 - CO₂ loss for a 0.5 L bottle – 40°C – 19.5 g vs 16.5 g.
Initial product carbonation: 2.8 CO₂ vol (STP).

spectively by using Henry's law and experimental data available in the literature.

Temperature could be treated as a constant or a variable, with the possibility of studying different thermal cycles.

RESULTS

The main purpose of this work was to run various models implying different bottle geometries, different storage conditions, etc. and assessing their predictive ability by comparing the theoretical results with the experimental measurements.

The following graphs show how the predicted permeability curves (solid lines in the figures) matched with the respective experimental observations (points in the figures). Permeability is graphed in terms of CO₂ mass loss from the container or O₂ concentration increase in water.

Fig. 4 compares room temperature versus 40°C storage for a half litre

bottle, all other things being equal.

Fig. 5 shows how 3 grams difference in the bottle weight affects the permeability in a half litre bottle stored at 40°C.

Fig. 6 illustrates the same comparison

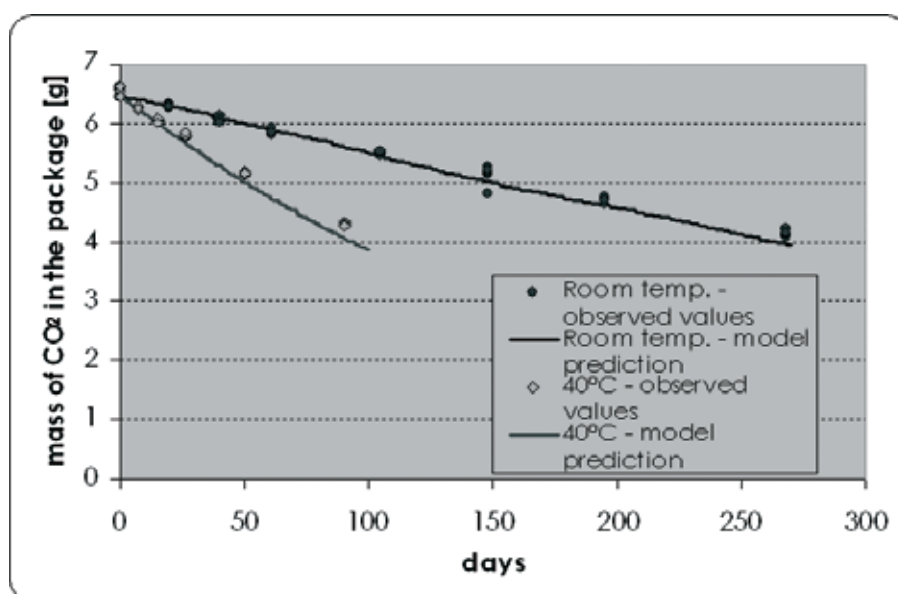


Fig. 6 - CO₂ loss for a 1 L bottle – 44 g – room temperature vs 40°C.
Initial product carbonation: 3.3 CO₂ vol (STP).

as fig. 4 but for a 1 litre bottle.

Fig. 7 highlights how, for a complex temperature variation pattern (white curve) actually input into the model, the model itself is able to capture the real permeability trend (black curve); if the average temperature were used instead, then the model would predict less reliably as per the grey curve.

Fig. 8 illustrates the O₂ ingress curves for a half litre bottle comparing two different weights (19.5 g vs. 16.5 g). The single highest deviations observed between experimental points and theoretical curves were in the range of $\pm 10\%$, being on average below $\pm 5\%$.

CONCLUSIONS

A computer model, which accurately reflects the physics of the permeability process of a gas through a plastic bottle, was developed using the finite element method. The accuracy of the model in predicting permeability was successfully demonstrated by comparing the simulation results to experimental data, both for CO₂ and O₂

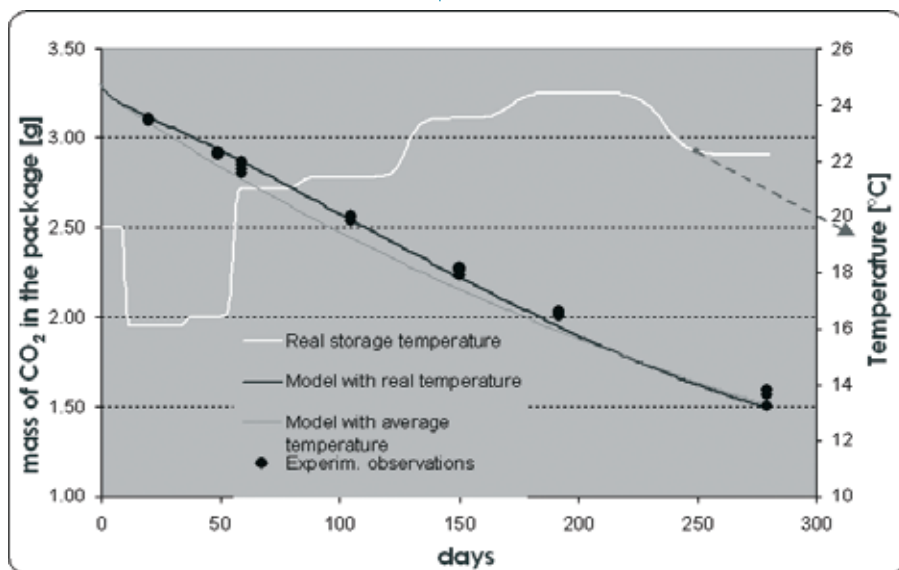


Fig. 7 - CO₂ loss for a 0.5 L bottle – 26 g – effect of random temperature cycling. Initial product carbonation: 3.3 CO₂ vol (STP).

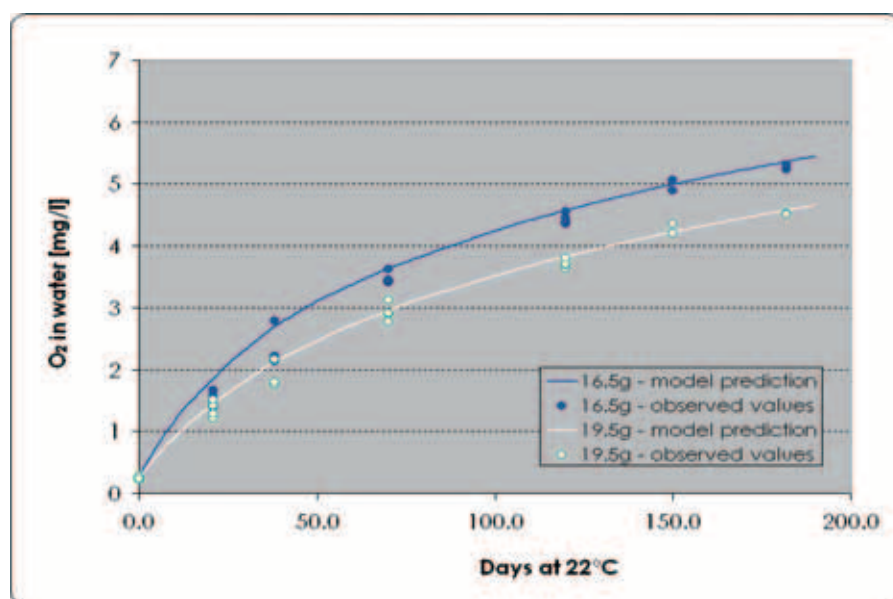


Fig. 8 - O₂ ingress for a 0.5 L bottle – room temperature – 19.5 vs 16.5 g. Initial oxygen concentration in water: 0.25 ppm.

permeation. Maximum differences between predicted and observed values were below $\pm 10\%$, while average differences were below $\pm 5\%$.

Although a simpler Fickian diffusion assumption was used, very good fitting to the experimental measurements was achieved. Therefore, no further theoretical refinement of the model,

especially to include D and S dependence on the penetrant concentration, was deemed necessary.

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