Humidity Mass Transfer Analysis in Packed Powder Detergents

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Abstract: Powder detergents containing sodium percarbonate and bleach activators undergo chemical decomposition when exposed to high relative humidity. In this paper we show how we leveraged COMSOL to model the complex mechanism of moisture migration and absorption in the outer package and powder matrix. The underlying physics is that of a mass transfer through diffusion and absorption, in presence of two phases: bound water in the powder with a non-linear absorption profile, and mobile water in vapor phase. We have used this model to design product and package properties to guarantee a sufficient moisture control throughout the whole supply chain.

Keywords: Water diffusion, powder detergents, product stability.

1. Introduction

Sodium Percarbonate (PC) and bleach activators are typical ingredients of powder detergents. The main function is to deliver hydrogen peroxide and peracids in the wash solution as bleaching species to enhance the cleaning performance of the detergent. The challenge, from a product stability point of view, is to avoid unwanted degradation of these species during the supply chain of the product, from the date of production until when the product gets used in consumers' home. There are a number of factors that can negatively impact product stability, in this paper we will focus on temperature and environmental moisture. It is well known in literature [1] that high temperature and relative humidity trigger the following decomposition reaction:

$$Na_2CO_3 \ 1.5H_2O_{2(s)} + H_2O_{(l)}$$
$$\xrightarrow[k_2]{} Na_2CO_3Na_2CO_3 * H_2O_{(s)}$$
$$+ 1.5H_2O_{2(l)}$$
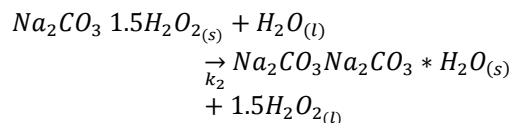
The rate of this reaction depends on the water activity rather than water concentration (see [3]). Here oxygen gas is released, as well as free water and heat (exothermic reaction); hence temperature and relative humidity are further increased; these are the basis for an autocatalytic reaction, and indeed powder products containing sodium percarbonate are subject to the risk of thermal runaway if not controlled properly [2]. Finished product is normally produced at very low moisture content, however over aging water is absorbed from external environment.

Controlling the moisture intake and the environmental temperature is therefore a critical need to avoid unwanted product degradation during the supply chain. While we have limited control over temperature, we can protect the products from environmental moisture uptake by proper design of outer package, or controlling water activity in the product, at parity moisture uptake, by introducing water binding materials which act as moisture sinks. However, at the same time, we also need to minimize the overall cost of the product/package combination. To find an optimal solution we have leveraged COMSOL multiphysics capability.

2. Theory and Governing Equations

In this paper we want to simulate the diffusion and accumulation of water in a packed powder detergent; the eventual goal is to predict water activity in the powder matrix, which is the driving factor behind chemical decomposition. Water is present in two phases: as vapor phase in the air space, and as bound water in the powder particles. We define the concentration of the first species c_v [mol/m^3] and of the second species c_b [mol/m^3] (Fig 1)
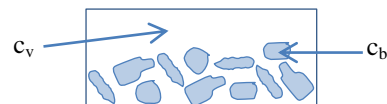

Fig 1 Water concentration in vapor phase and bound phase

The overall water concentration c_w in a given volume is represented by equation (1) :

$$c_w = (1 - \varepsilon)c_b + \varepsilon c_v \qquad (1)$$

where ε is the void fraction, i.e. the percentage of volume not filled by solid particles.

The powder particles interact with the environmental moisture by absorbing water, reaching eventually a dynamic equilibrium; the level of absorbed water is a non-linear function of the environmental moisture concentration c_v, and the process follows a kinetic which is dependent on the specific material. To this aim we have used two routes to describe the phenomenon: an approximated model where we assume the bound water is in constant equilibrium with the vapor phase (no absorption dynamic) and a full model which takes into account the absorption dynamics.

2.1 Constant equilibrium model (no dynamic)
In this approach we assume that the concentration of bound water is in constant equilibrium with the vapor phase, according to sorption isotherm (2)

$$c_b = f_{DVS}(c_v) \qquad (2)$$

This relationship is in general quite complex, and can be determined experimentally using dynamic vapor sorption technique (DVS). This isotherm is specific for each individual material; in our approach we have assumed that the overall sorption curve of the total mixture can be calculated as the weighted average of the individual sorption curves of the starting raw materials.

The variation of water mass in the elemental volume can be obtained by differentiating (1) and substituting (2) thus obtaining:

$$\frac{\partial c_w}{\partial t} = \frac{\partial c_v}{\partial t}\left[(1-\varepsilon)\frac{\partial f_{DVS}(c_v)}{\partial c_v} + \varepsilon\right] \qquad (3)$$

In the term within brackets, the derivative of the sorption isotherm appears. Note that with this approach there is only one independent variable.

The driving force for moisture diffusion is the water vapor concentration, and that diffusion follows a fickian process; we adopt the assumption that the bound water in the powder particle has a very low mobility, i.e. particle to particle diffusion is very slow compared to vapor phase diffusion. The overall model describing moisture accumulation and diffusion is therefore expressed by equation (4)

$$\frac{\partial c_v}{\partial t}\left[(1-\varepsilon)\frac{\partial f_{DVS}(c_v)}{\partial c_v} + \varepsilon\right] - D\nabla^2 c_v = 0 \qquad (4)$$

where D is an apparent diffusion coefficient that can be measured experimentally.

2.2 Dynamic absorption model
In this approach the absorption of water in the powder particles is modeled as a reaction of the type

$$c_v \rightleftharpoons c_b \quad K_{eq} = \frac{c_b}{c_v} = \frac{k_d}{k_i} \qquad (5)$$

Where the equilibrium constant is a non-linear function of c_v and can be obtained from the sorption isotherm curves (eq (2)). We further postulate that this reaction follows a first order mechanism, and the rate coefficient can also be determined experimentally using the full DVS curve information, as shown in Fig 2; note that also the time constant is a function of c_v.

The full model can be obtained with similar assumptions using in the previous section, but now we have two species, each with its own governing equation, coupled by a reaction dynamic:

$$\begin{cases} \dfrac{\partial c_v}{\partial t} - D(c_b)\nabla^2 c_V = -R(c_v, c_b) \\ \dfrac{\partial c_b}{\partial t} = +R(c_v, c_b) \end{cases} \qquad (6)$$

In this model we assume that the diffusion coefficient can be also a function of water concentration in the bounded phase. The physics here is that above a certain threshold concentration carbonate decahydrate is formed, reducing the void fraction and forming on the surface an encrustation which hinders further diffusion of moisture in the powder core.

2.3 Model comparison and choice
The equilibrium model can be used whenever moisture rate of change in the product is slow, giving time to the two phases to reach an equilibrium. In our experimental conditions we have found that the bottleneck for moisture diffusion is offered by the package barrier; therefore the diffusive time of vapor within the powder and the absorption time constant are orders of magnitude faster than the diffusive time through the package barrier. For this reason, to

model product in a package we can use the equilibrium model. On the contrary, if we want to model usage conditions (open pack, moisture environment, etc.) at a consumer home, we need to use the dynamic model.

2.4 Outer package model – boundary conditions
Both models described above need to be coupled with an outer package model, which gives the boundary conditions for the problem. These are the equations that describe how the detergent package limits the moisture pick-up from the surrounding environment. Moisture protection is provided by various plastic lining materials embedded in the package, with a thickness dependent on the grade of protection desired. Normally the level of moisture protection is measured via a standard test that yields the MVTR (moisture vapor transmission rate), where a desiccant material is placed inside the closed package, and the whole assembly is placed in a climatic chamber to keep the driving force constant. MVTR is proportional to the mass gain during one day (water absorption), and can be expressed as an absolute number (per single pack) or normalized by the pack surface.

Once the MVTR is known, the moisture flux through the package barrier can be modeled as a simple diffusive flux (7) where the partial pressure differential across the plastic film is the driving force. Vapor partial pressure is proportional to c_v.

$$-D\nabla c_v \cdot \vec{n} = D_{MVTR}(p(c_v) - p_v^{ext}) \qquad (7)$$

This gives the boundary conditions needed to solve eq 3 and 6

3. Parameters Characterization
A powder detergent is made up of various particles mixed together; we have obtained the full DVS curve of the final mixture by measuring the individual DVS for each ingredient alone, and then assembling the total DVS using a weighted average. Fig 2 shows a sample DVS curve on a single raw material. Here we can see the absorption dynamic taking place.
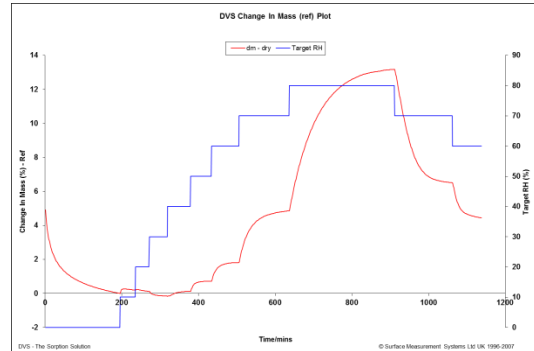

Fig 2 Sample DVS Curve. Blue line is the imposed eRH while the red line is the recorded weight gain

For the coefficient of diffusion D used in (4) and (6) we have fitted experimental data obtained in a mono-dimensional diffusive system, i.e. a stainless steel tube, open on one side only, equipped with relative humidity (RH) sensors at 3 different positions. The tube has been filled with the sample powder, with a known initial eRH (equilibrium RH). RH is proportional to the water vapor concentration c_v through the saturated water vapor pressure relationship; hence measuring RH at a given temperature is equivalent to measuring c_v.
The experimental setup described above has been exposed to an environment with a constant RH and the profile of the internal probes has been recorded.

The void fraction ε has been calculated by dividing the bulk density of the powder mix by the weighted average of crystal densities of the single raw materials. For our test product we obtained a value of 0.45

4. Use of COMSOL Multiphysics
The equilibrium model has been implemented using the Mathematics module→Classical PDEs→Convection-Diffusion Equation; with this system we can easily express the non-linear term indicated in (4).
The kinetic model has been implemented using the chemical species transport module, with two separate chemical species, linked via a reaction implemented in the reaction engineering module.

The sorption isotherm characteristics (2) of the mixture is calculated directly in COMSOL starting from the individual sorption isotherms of the raw materials; this enables us to play with the formulation in order to screen different product design options as well as packaging barriers.

As initial condition for the water content of our powder products we have used typical values obtained from production data. Boundary conditions have been set as fixed temperature and relative humidity when we wanted to mimic experimental tests run in our climatic chambers, and by downloading environmental log data when we wanted to predict the stability profile during our supply chain.

5. Validation tests
Before using the model for design purposes we have run a series of validation tests, to understand the level of confidence in the results.

5.1 Inert powder in climatic chamber test
As a first verification of the model we have compared the simulation results with experimental data generated with an "inert" sample powder stored in a test package in a climatic chamber. By "inert" we mean a test product without those chemically active species which react with environmental moisture; this was done to avoid any chemical effect that could introduce noise in the system. In Fig 3 we show the model prediction (dotted line) vs the experimental data obtained with a 3 weeks test (solid line).
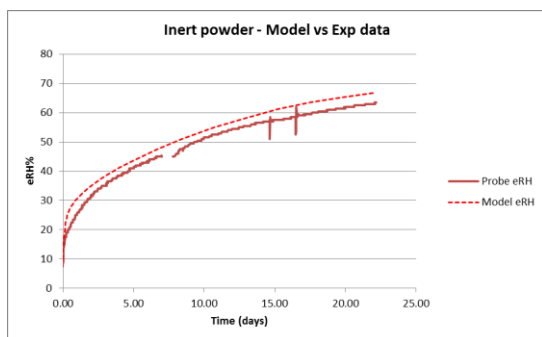

Fig 3 Inert powder experimental data

The model prediction is sufficiently close to what we observe, and most of the error appears when humidity is low, which is where DVS data are most noisy (water weight gain is low compared to the accuracy of the instrument scale). Overall we were satisfied with this result

5.2 Powder detergent in climatic chamber test
As next step we have compared the simulation results with experimental aging data obtained on a sample product containing sodium

percarbonate, kept in a climatic chamber for up to 10 weeks as shown in Fig 4. Here again, the solid line represents experimental data while the dotted line is the model prediction.
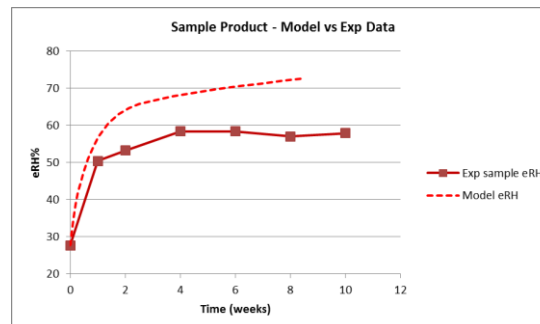

Fig 4 Sample product experimental data

Here we see a discrepancy of results when the RH value goes above 50%. We believe that beyond this point sodium percarbonate decomposes very fast generating carbonate deca-hydrate, thus absorbing significant amount of moisture without increasing water activity. This is not captured by this model.

This result shows the limit of validity of the model described in this paper: the prediction is accurate only below the eRH threshold of 50%. Below this limit the chemical degradation reactions are very slow (good for our products!), hence their impact on eRH/water content is limited. The key conclusion is that we can safely use the model to predict when we reach the conditions for product instability, which is exactly our ultimate goal, i.e. to design formula and package for a safe transit in our supply chain. In a separate work (see [3]) we are working to develop a full chemical model that predicts the full set of reactions taking place in the product, leveraging the COMSOL reaction engineering module, and later on will be integrated with the water mass transfer system described in this paper to mimic the full system.

6. Case Study: optimization of package and product design for powder products
In this example we show how we have used the model to design the package and the formulation moisture buffer for one of our powder products.

The geometry of the system in this case is quite simple, we have a carton box with a parallelepipedal shape for the product package,

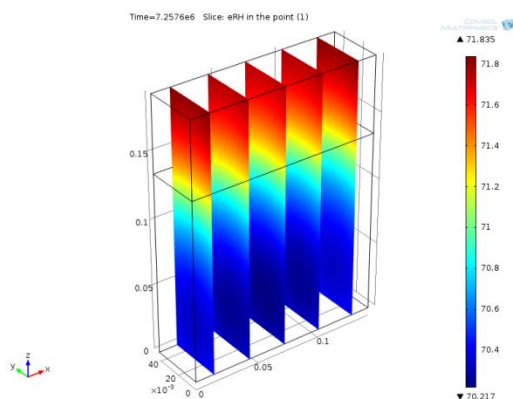filled with sample powder for roughly 70% of its volume, as shown in Fig 5.

Fig 5 3D model of powder detergent box, showing eRH profile inside the powder and in the headspace above it

This model contains approx. 5000 degrees of freedom and was solved on a standard laptop in few minutes.

We have used COMSOL to simulate the product internal moisture evolution over time using different packaging options (different MVTR) and different levels of a moisture stabilizer mixed in the powder product. Fig 6 shows the result obtained with different packaging options; the various eRH evolution graphs are compared with our success criteria of not going above eRH=50%. In the figure we can clearly see that the first two options do not offer enough moisture protection and should be discarded, while both opt3 and opt4 are good candidates.

Fig 7 shows the results we obtained by varying the level of a moisture control ingredient mixed in the powder product. As we can see the positive effect is limited compared to what we obtain from the different packaging options. From these simulations we could select the most cost-efficient way to obtain the level of protection we required
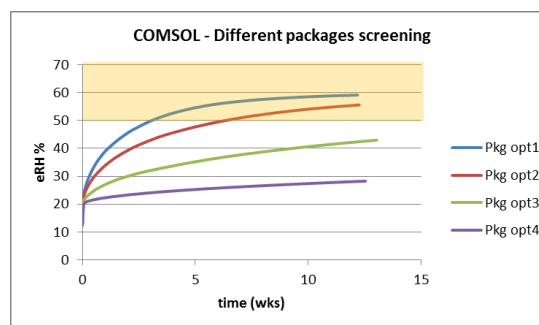

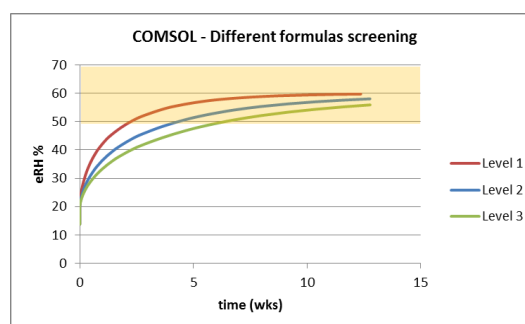**Fig 6 Screening of different packages through COMSOL simulations**

Fig 7 Screening of different levels of a formula stabilizer ingredient (moisture buffer) in the powder product

7. Conclusions and Next Steps

We have leveraged COMSOL multiphysics to successfully predict the conditions that trigger product instability in packed powder detergents and we have used this approach to predict the package and product protection during our supply chain.

Our next development step is to couple this model with a separate work happening in our group (see [3]) to be able to fully model the chemical stability profile

8. References

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