

Modeling the Chemical Decomposition of Sodium Carbonate Peroxyhydrate

M. Brundu*, V. Guida
Procter & Gamble Italia

*Corresponding author: brundu.m.1@pg.com

Abstract: Sodium Carbonate Peroxyhydrate (SPC - $\text{Na}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}_2$) undergoes chemical decomposition and physical degradation during the shelf life.

We used the Chemical Engineering Module of COMSOL Multiphysics to develop a lumped kinetic model of the chemical decomposition of SPC that involves five different species, three solid state and two homogeneous reactions. Our innovative approach for the description of complex solid phase reactions consists in the introduction of the appropriate solid state kinetic models in the modeling tool. These describe the variation of the reaction rate with conversion and allow the introduction of complex phenomena such as reagent and product diffusion, particle shrinkage, crystal granulation and growth.

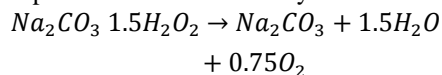
We complemented the work with experimental studies for the estimation of the kinetic parameters. The model is able to reproduce the decomposition of SPC over the shelf life and simulate the switch between the different mechanisms. The results are in good agreement with the experimental data.

Keywords: Percarbonate, Decomposition, Kinetics, Chemical engineering.

1. Introduction

The challenge with the use of Sodium Carbonate Peroxyhydrate ($\text{Na}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}_2$ - SPC) as a bleach source in dry detergent formulations, is its lower stability in comparison with other materials, and the risk of quality losses of the product over the shelf life. The issue can be solved with the understanding and modeling of the decomposition mechanism of the powder.

The global process driving the decomposition of SPC is usually summarized by:



In this reaction SPC releases hydrogen peroxide that easily decomposes to give water and oxygen.

The decomposition is apparently very simple, but the mechanism hasn't been understood yet. One important limitation to its investigation is that water is a product of reaction but may also interact with unconverted SPC and sodium carbonate; it is demonstrated that the decomposition is faster when the material is exposed to high relative humidity (RH). Furthermore, the study is particularly difficult at the conditions of interest for dry laundry detergents. Indeed, between 30°C and 40°C the equilibrium of the system water-Sodium Carbonate shows a region where different hydrates may exist and small variations of the experimental conditions lead to phase transformations, water pick up/release and consequent hydration/dehydration of the solid [3]. Furthermore, water is produced during the decomposition but it may also arrive to the system from the environment. Therefore, it is very difficult to interpret the experimental data and make predictions on the behavior of the system.

The literature shows mainly experimental studies of the system, but modeling exercises are scarce. Galway [1] investigated the decomposition of SPC and fitted the kinetic data with existing solid state kinetic models. Lunghi et al [5] fitted the kinetic data produced with calorimetric experiments to get the activation energy of the whole process. Comprehensive models that fully characterize the decomposition have not been developed yet.

The case study presented in this work deals with the chemical decomposition of pure SPC, and is a part of a wider analysis aiming at the simulation of the decomposition of a dry laundry detergent inside a pack. The full model, still under development, involves the moisture diffusion through the pack [4], moisture adsorption in the product and the chemical decomposition.

2. Experimental investigation

The experimental investigation consisted in the characterization of SPC by isothermal calorimetric measurements (TAM Air – TA instruments), iodometric titration and the equilibrium relative humidity of the sample. Further analyses were carried out to complement the results and support the calorimetric data.

The thermostat of the TAM unit was set to 60°C; the sample size was 12g; the material used was Oxyper S-142, a commercial sodium percarbonate provided by Solvay. Sample weight and oxygen content were measured before and after the experiment. Different experiments had different durations in order to correlate the heat flow of the sample to conversion; in particular, duration ranged between few and 55 days.

The decomposition causes high gas release with consequent pressure increase in closed systems. In order to prevent the phenomenon we used a needle to punch the cap of the ampoules. For comparison we also run some experiment without punching the cap.

We developed a correlation between heat developed and activity loss of the material and, by means of the total heat developed from start of reaction to total decomposition, we translated the heat flow curve Vs time in Conversion Vs time. In the below are reported examples of the conversion profile at 60°C for two different replicates of the same material.

As shown in **Figure 1** we observed that the decomposition of pure SPC coming from the same material and lot shows different pathways

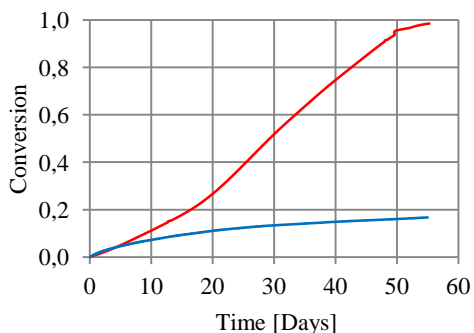


Figure 1. Examples of solid conversion profiles of samples showing the catalytic (Red) and non catalytic (Blue) behavior.

that we called catalytic and non catalytic. Catalysis enhances the decomposition originating stability issues; indeed, the material fully decomposes in 55 days while conversion is 20% for non catalytic systems. Experimental evidence showed that the product of reaction was Sodium Carbonate Monohydrated either for the catalytic, or the non catalytic process.

At the end of the experiment non catalytic samples were very dry, still a free flowing powder. On the contrary, samples showing the catalytic behavior appeared wet; the powder was packed and caked. Starting from this consideration, and complementing the analysis with data regarding the initial content of free water of the different samples, we are able to conclude that the difference between the two mechanisms is in the content of free water, whether produced, exchanged with external or initially present in the system.

From the experimental result we could postulate the reaction mechanism to be used to model the decomposition.

3. Use of COMSOL Multiphysics

The innovative application of COMSOL Multiphysics in this context is the use of the chemical reaction engineering module to develop a lumped kinetic model of the decomposition of a bed of particles. Indeed, we developed a time dependent study of the constant volume batch reactor involving five different species: Sodium Carbonate Peroxyhydrate (SPC), Anhydrous (CSA) and Monohydrate (CSM) Sodium Carbonate, Water (W) and Hydrogen peroxide (HP); and involving three solid state and two homogeneous reactions. Modeling this kind of systems is usually complicated because of the changes at particle scale and the phenomena occurring in the solid state. Nevertheless, we approached the description of such complexity trying to avoid the development of a complicated 3D model. The versatility of COMSOL allowed the introduction of the appropriate solid state reaction kinetic models able to describe the variation of the reaction rate with conversion. Thus, the tool helped us to keep the computational simplicity, and at the same time introduce complex phenomena such as reagent and product diffusion, particle shrinkage, crystal granulation and growth.

Model equations for this module are very simple and can be summarized as:

$$\frac{dC_i}{dt} = R_i$$

$$i = SPC, CSA, \dots$$

Where:

C_i Density of component i
 $R_i = \sum_1^{nr} \nu_j^i r_j$ Reaction rate for component i
 r_j Reaction rate for reaction j

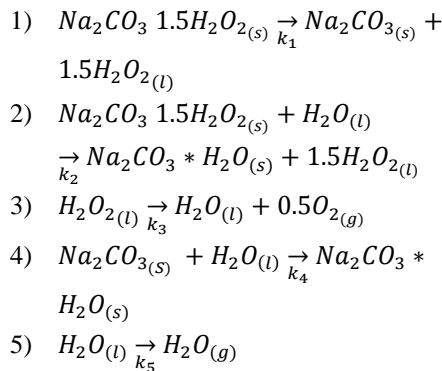
3.1 Model assumptions

The model for the isothermal system assumes concentrated parameters, constant volume, and negligible vaporization of hydrogen peroxide. Furthermore, we assume the homogeneousness of the system.

The system we consider is open and the relative humidity (RH) of the air surrounding the solid should be time dependent; nevertheless, we use RH as an operating parameter and its influence is verified in a sensitivity analysis.

3.2 Reaction kinetics model

The model assumes that Sodium Percarbonate decomposes to give water, oxygen and sodium carbonate according to the set of consecutive and competitive reactions listed below:



Experimentally we found good agreement between the Jander's model for a 3D diffusion limited process and the kinetic data referred to dry systems, for this reason we decided to use the equation to calculate the dependence of the dry SPC decomposition on conversion for reaction 1.

According to the model developed by Jander:

$$\frac{d\alpha}{dt} = k_1 \frac{3(1-\alpha)^{2/3}}{2(1-(1-\alpha)^{1/3})}$$

Where:

$$\alpha = \frac{C_{SPC}^{MAX} - C_{SPC}}{C_{SPC}^{MAX}} = 1 - \frac{C_{SPC}}{C_{SPC}^{MAX}}$$

Thus we assume that:

$$r_1 = -k_1 C_{SPC}^{MAX} \frac{3\left(\frac{C_{SPC}}{C_{SPC}^{MAX}}\right)^{2/3}}{2\left(1 - \left(\frac{C_{SPC}}{C_{SPC}^{MAX}}\right)^{1/3}\right)}$$

Experimentally we found good agreement between the Avrami-Evrofe'ev model for nucleation and growth limitation in solid state reactions and the kinetic data referred to the wet system. We decided to use the same equation to calculate the dependence of the wet SPC decomposition on conversion for reaction 2. Nevertheless, this would not be enough to simulate the switch between the dry and wet mechanism. For this reason we provided the expression of the reaction rate with an exponential term on the concentration of water in the solid.

Thus, we assume:

$$r_2 = -k_2 e^{-\left(\frac{C_w^*}{C_w}\right)^n} 3C_{PC}^{MAX} \left(\frac{C_{SPC}}{C_{SPC}^{MAX}}\right) \left[-\ln\left(\frac{C_{SPC}}{C_{SPC}^{MAX}}\right)\right]^{\frac{2}{3}}$$

Hydrogen peroxide decomposition has been extensively studied in the past. For the affinity to the system under investigation, we refer to a kinetic study carried out by Galway [1-2]. In his work he modeled the decomposition of H_2O_2 in a saturated solution of sodium carbonate with a 1st order reaction rate. Thus, we assume:

$$r_3 = k_3 C_{H_2O_2}$$

We also assume:

$$r_4 = k_4 C_{H_2O} C_{CSA}$$

Water evaporation is one of the key steps in our process. We calculate the evaporative flux as:

$$r_5 = k_5 (eRH - RH)$$

Where:

$$eRH = f(C_w)$$

$$k_5 = ak' \frac{P_{H_2O}^{sat}(T)}{RT} PM_{H_2O}$$

The Water Vapor Sorption isotherm of the sample was used to establish a correlation between eRH and the water content of the solid and introduced in the software.

3.3 Numerical method

The time dependent study was solved with MUMPS, one of the direct methods provided by the software. The stop condition on the content of SPC in the powder was required to avoid computational errors. We run the program in a Hp PROBOOK 6460b machine, with an Intel® Core™i5 processor running at 2.50GHz and 4GB RAM

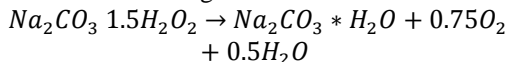
Solution of the equations is fast, calculation time is about 3 seconds for a simulation of 55 days of reaction.

4. Results and discussion

The model was used to reproduce the behavior observed during the experimental investigation and understand the influence of the balance of water in the decomposition.

To estimate the initial conditions we considered that the solid has an initial diffusive layer constituted by Boron Silicate (coating) and Sodium Carbonate (coming from SPC already converted). The main importance of coating is to form a diffusive layer surrounding the particle. Its presence can be considered in the model by the introduction of an initial conversion different from zero.

Thus, we assumed that the solid is initially constituted by Sodium Percarbonate, Sodium carbonate monohydrated and Water. We calculated the initial conversion and the initial concentration of SPC from stoichiometric calculations on the global reaction:



We measured the initial water content typical for our system and assumed the initial concentration of CSM as

$$C_{CSM}^0 = C_s^0 - C_W^0 - C_{SPC}^0$$

The initial concentration of the other components was set to zero.

In a first step the kinetic parameters were estimated separately for each reaction, some of them measured directly, some retrieved in the Literature as explained in the previous paragraph.

As to improve the fitting with experimental results we carried out a large sweep on the most important parameters; the final set was chosen from the solution that that best fitted with real data.

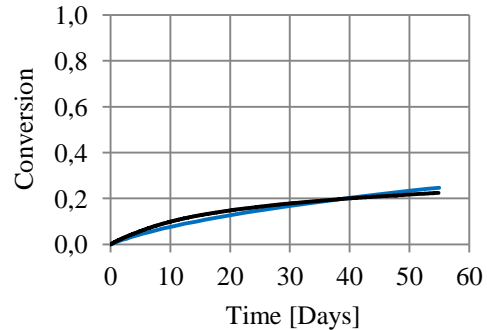


Figure 2. Comparison between conversion calculated by the model (**black**) and the experimental result (**blue**) for the non catalytic system

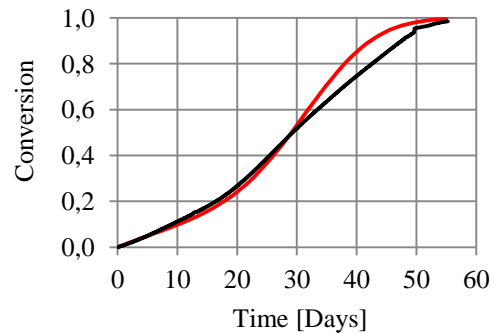


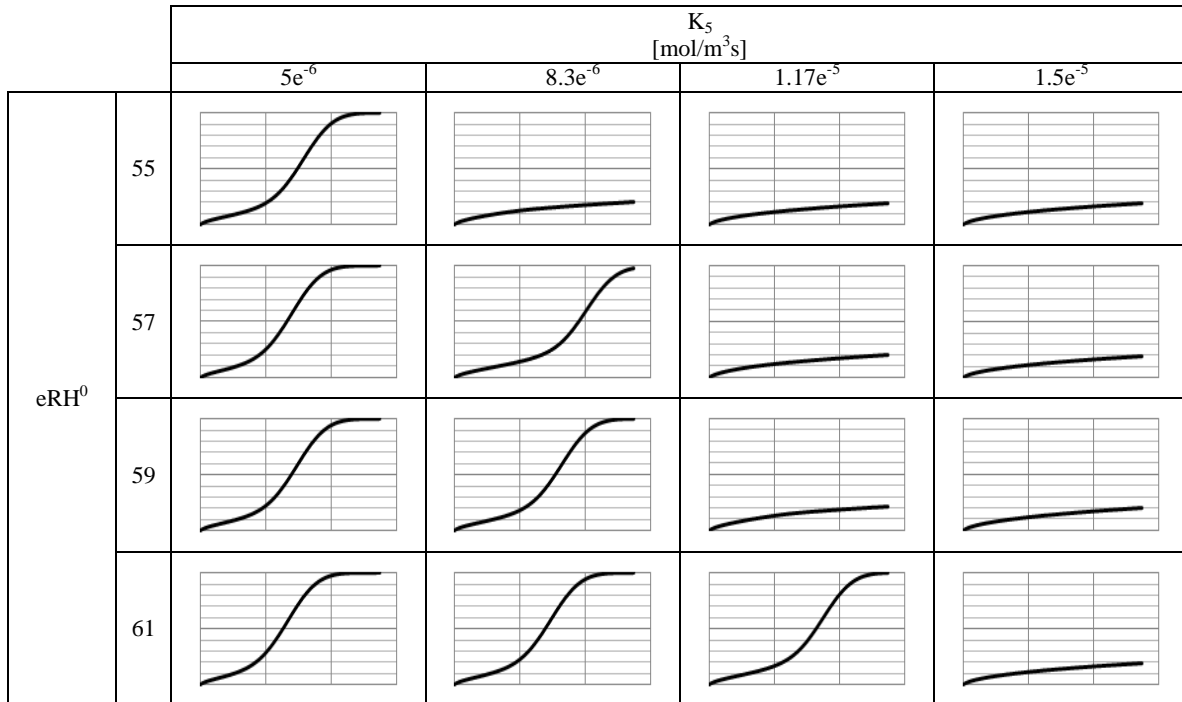
Figure 3. Comparison between conversion calculated by the model (**black**) and the experimental result (**red**) for the catalytic system

Default plots are the concentration profiles of each species involved in the process, that, together with the reaction rate have been very useful to understand the contribution of the single reaction to the global decomposition. Nevertheless, we used conversion for calibration purposes.

In Figure 2 and Figure 3 is shown the comparison between the output of the model and the experimental results observed during the long term analysis on a real SPC system. Modeling results for the catalytic and non catalytic process are obtained with the same initial conditions and the same set of parameters, but with a different evaporation rate.

Results are in qualitative agreement. Quantitatively, final conversion is slightly over estimated for the non catalytic system. In catalytic systems the model is able to capture the

Table 1. Influence of the mass transfer coefficient and the initial eRH of the material on the decomposition behavior of the sample.



first part of the experiment but time to total conversion is underestimated.

The qualitative agreement of the results indicates that our kinetic model is able to describe SPC decomposition.

In order to have a more complete picture of the influence of the content of free water, either initial or accumulated, we run a sensitivity analysis on the initial eRH and the rate of evaporation on a wide range. In this paper we present the selection of the results that are relevant for discussion. Figures below report the conversion of the system over time for a variation of the eRH⁰ in the range 55-61 and k_5 in the range: $5e^{-6}$ - $1.5e^{-5}$ mol/m³s.

We see both, either the catalytic, or the non catalytic path depending on a combination of the initial eRH and the sealing of the system to moisture exchange. The variation of the initial eRH from 55% to 57%, and from 57% to 59% fosters the catalytic pathway when k_5 is respectively $8.3e^{-6}$ and $1.17e^{-5}$ mol/m³s.

Results confirm that the combination of the initial content of free water and the ability of the system to consume water produced affects the

decomposition, and drives reaction to follow one mechanism or the other. Given the external conditions, small variations of the initial eRH may originate stability issues.

5. Conclusions

This work deals with the chemical decomposition of Sodium Carbonate Peroxyhydrate. In particular, we investigated the system by means of calorimetric and analytical methods and complemented the study with the development of a mathematical model of the process in COMSOL Multiphysics. During the experimental investigation we identified two overall decomposition paths of SPC decomposition depending on the balance of water generation and water consumption.

Furthermore, we proposed a reaction network for the decomposition and developed a mathematical model by means of the chemical reaction engineering module of COMSOL multiphysics that is valid at 60°C.

Based on the model above, we are able to quantitatively predict SPC decomposition

behavior and, based on slight variability of the initial water content, and on the goodness of moisture sealing of the system, we can simulate the switch between the two mechanisms observed experimentally.

6. References

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7. Nomenclature

avO^0	Initial activity	$\left[\frac{gO_2}{g_s} \right]$
C_i	Density of component i	$\left[\frac{Kg_i}{m_s^3} \right]$
C_s^0	Initial solid density	$\left[\frac{Kg_s}{m_s^3} \right]$
R_i	Reaction rate	$\left[\frac{Kg_i}{m_s^3 s} \right]$
PM_i	Molecular weight	$\left[\frac{Mol_i}{g_i} \right]$
eRH^0	Initial water activity	
k_j	Constant of reaction	
r_j	Reaction rate	$\left[\frac{Kg_i}{m_s^3 s} \right]$
ns	Number of species	
ΔH_j	Heat of reaction j	$\left[\frac{J}{g_i} \right]$

Greek letters

v_j^i	Stoichiometric coefficient
α	Conversion as $\alpha = \frac{C_{SPC}^{MAX} - C_{SPC}}{C_{SPC}^{MAX}}$

Superscripts

0	Initial
e	Equilibrium
MAX	Maximum value derived from stoichiometry

Subscripts

HP	Hydrogen peroxide
W	Water
CSA	Sodium Carbonate anhydrous
CSM	Sodium Carbonate mono Hydrated
SPC	Sodium percarbonate
s	Solid phase
g	Gas phase
l	Liquid phase