# Experimental and Mathematical Investigations of Dicalcium Phosphate: Moisture Sorption Isotherms

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**Abstract**

The aim of this work was to determine desorption isotherms of Tunisian dicalcium phosphate. The equilibrium moisture contents of dicalcium phosphate were measured using the gravimetric method at four temperatures (50, 60, 70 and 80°C) and in wide range water activity (0.021-0.989). Desorption data of dicalcium phosphate were best fitted by the Guggenhein, Anderson and de Boer model at four temperatures.

**Keywords**: Dicalcium phosphate; Moisture; Sorption isotherms

## Introduction

The parameters necessary for dryers design and for carrying out the process of drying under optimum conditions can be found in both experimental and theoretical ways. The latter seems to be more convenient and economical in the present state of computational techniques.

A theoretical treatment, however, needs the knowledge of the mechanism of moisture transfer in a dried body together with an appropriate mathematical description that appears to be still a problem requiring solution.

Lewis [1] first published the paper dealing with moisture transfer during drying of solid materials and proposing also a simple mathematical description. Since then hundreds of various papers have been issued bringing a great number of different, very often partly contradictory views and opinions. The authors rarely give comprehensive, critical review of state of the art thereby making full understanding of the problem more difficult. Dicalcium phosphate, yet named monoacid precipitate [2], is known in the anhydrous state $CaHPO_4$ (monétite) and dihydrate state $CaHPO_4$, $2H_2O$ (brushite). This compound exists in superphosphate and complex fertilizers with nitrogen, phosphorus and potassium (NPK) basis. In the pure state, dicalcium phosphate is used in the preparation of food for livestock and toothpastes.

Brushite $CaHPO_4, 2H_2O$, the only well-established hydrate of calcium hydrogen phosphate, has applications in the fertilizer and animal-food industries [3] in water decontamination [4].

Monetite is the anhydrous form of brushite and can be obtained via heat treatment of brushite or by the modification of the precipitation conditions [5].

A sound knowledge of sorption isotherms is essential for drying processes. The final moisture content of dried product and the energy required for drying can be estimated from sorption isotherms. Due to the complexity of the product, there is no one model that fits all the cases well. As a consequence, many models have been proposed in the literature, and it is interesting to check how well some of them fit to experimental data [6].

Dicalcium phosphate, which is composed from 40 to 45% of $P_2O_5$ and 20 to 25% calcium, is characterized by a ratio of Ca/P=1.3, is made in the chemical group of Gabes at a rate of 4.8 t/h and a mass composition of 41.7%.

We were interested in determining the desorption isotherms of water vapor on dicalcium and modeling these isotherms which allows us a better understanding and a good characterization of the industrial product and therefore to optimize the phosphate operating parameters of the industrial drier.

## Smoothing Sorption Isotherms

Given the complex multi-component product structure, sorption isotherms are only representative of the tested material [7]. Given the complexity of the phenomena occurring during the desorption of water (mass transfer and heat), various simplified mathematical models have been proposed for predicting the dependence of the equilibrium water content ($X_{eq}$) and water activity (aw) (and typically (T)). These isotherm models can be theoretical, semi theoretical or empirical. The choice of suitable model depends on a number of factors. We focus on those that describe mathematically the best experimental sorption curves for practical drying applications dicalcium phosphate.

## Modelling of Sorption Isotherms

The dry basis moisture contents were used for the modelling. The experimental sorption isotherms data were fitted using ...mathematical models as shown in Table 1. To evaluate the ability of each model to fit the experimental data, the standard error (ES) and the coefficient of correlation (r) between the experimental and the predicted data were determined using the following equations:

$$ES = \sqrt{\sum_{j=1}^{N} \frac{\left( X_{jcal} - X_{jexp} \right)^2}{N - np}}$$

$$R = \sqrt{1 - \frac{\sum_{j=1}^{N} \left( X_{jcal} - X_{jexp} \right)^2}{\sum_{j=1}^{N} \left( X_m - X_{jexp} \right)^2}}$$

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| Modèle | Equation du modèle | References |
|---|---|---|
| BET | $X_{eq} = \dfrac{A\,Xm\,aw}{(1-aw)(1+(A-1)aw)}$ | (Brunauer, 1938) |
| BET modifié (1996) | $X_{eq} = \dfrac{A}{1-B.aw}$ | (Brunauer, 1938) |
| Smith | $X_{eq} = A - B.\ln(1-a_w)$ | (Smith, 1947) |
| Iglesias et chirife | $X_{eq} = A + B.\dfrac{aw}{1-aw}$ | (Iglesias, 1981) |
| White et Eiring | $X_{eq} = \dfrac{1}{A+B.aw}$ | (Castillo, 2003) |
| Peleg | $X_{eq} = A.(aw)^B + C.(aw)^D$ | (Peleg, 1993) |
| Guggenhein, Anderson and Boer | $X_{eq} = \dfrac{X_m.A.B.aw}{(1-B.aw)(1-B.aw+A.B.aw)}$ | (Van Der Berg, 1981) |
| Oswin | $X_{eq} = A.\left(\dfrac{aw}{1-aw}\right)^B$ | (Oswin, 1946) |
| Adam | $X_{eq} = A + B.aw + C.aw^2 + D.aw^3$ | (Chirife, 1978) |
| Caurie | $X_{eq} = \exp(A + B.a_w)$ | (Castillo, 2003) |
| Freundlich | $X_{eq} = A.a_w{}^B$ | (Freundlich, 1909) |
| Halsey | $X_{eq} = \left(-\dfrac{A}{\ln(aw)}\right)^{(1/B)}$ | (Halsey, 1948) |
| Langmuir | $X_{eq} = X_m\dfrac{A.aw}{(1+C.aw)}$ | (Langmuir, 1916) |

**Table 1:** The mathematical models used for smoothing curves sorption of dicalcium phosphate.

$$X_m = \frac{\sum_{j=1}^{N} X_j \exp}{N}$$

Where $X_{jcal}$ and $X_{jexp}$ are respectively the calculate and the experimental values of X (X is the moisture content). The models were compared according to their standard error (SE) and the coefficient of correlation (r) for the studied temperatures.

Xmoy: the arithmetic average value of the experimental values of the water contents in the case of reduced kinetic drying and water content at equilibrium in the case of the sorption isotherms.

N: the number of experimental points.

np: the number of model constants.

The models are compared using the standard error (SE) and the correlation coefficient (r) to the different heating powers and temperatures studied taking into account the graphs. In what follows, we include the different models used for smoothing of the experimental results.

## Experimental Study

The amount of adsorbed molecules is taken either by direct methods or by indirect methods. Gravimetric and volumetric methods are direct methods. In a volumetric method, the adsorbed amount is expressed as the volume per unit area or per unit mass of the sample powder. Furthermore, IR and UV spectroscopy in most other instrumental

methods are indirect methods. It is noted that in general, a direct method is indirect method accuracy.

During the work we opted for the gravimetric method.

### Device experimental

The assembly diagram is shown in Figure 1.

It consists essential of:

• An air compressor; Two silica gel columns to dehumidify the air (2);

• Two Bubblers (3) which provides air saturated with water vapor at the temperature set by the thermostat balance;

• Five thermostated bath (4);

• A main tube (5) dipping into a water bath (6) to keep moist air at a constant temperature; drift tube by four tubes each opening into a desorption stage (7) having a fixed temperature;

Using this experimental device was able to conduct further experiments in parallel desorption temperatures: 50, 60, 70 and 80°C. The risk of condensation was avoided by using the heaters of each head surrounding the sorption column.

The amount of desorbed water vapour is measured from the change in mass of different samples using a Sartorius balance with an accuracy of 10-4.

Equilibrium is reached when there is almost no variation of the mass (1%).
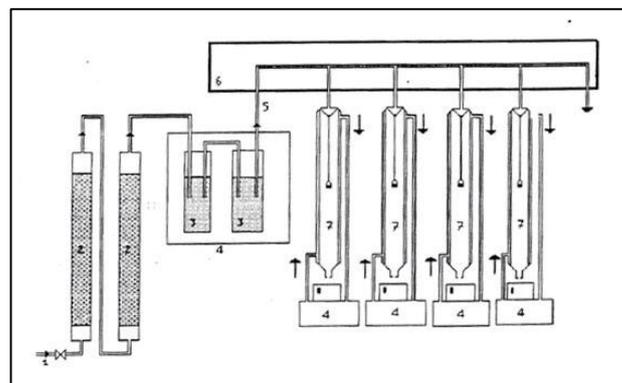


**Figure 1:** The Schema of the installation.
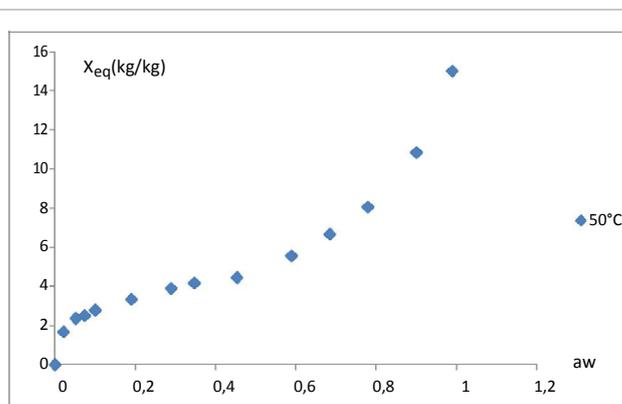


**Figure 2:** Desorption isotherme T=50°C.

**Figure 3:** Desorption isotherm T=60°C.



**Figure 4:** Desorption isotherm T=70°C.



**Figure 5:** Desorption isotherm T=80°C.
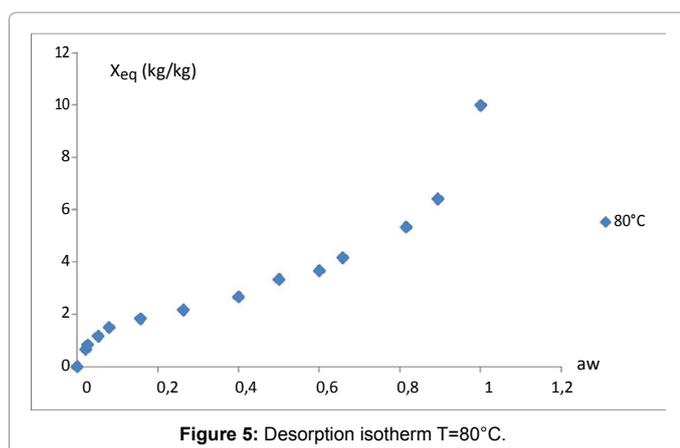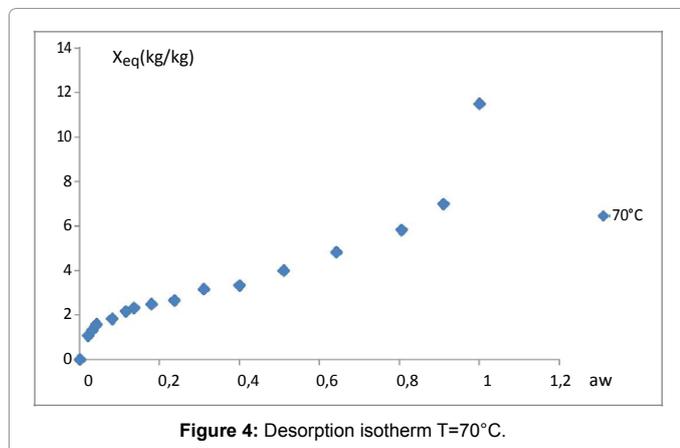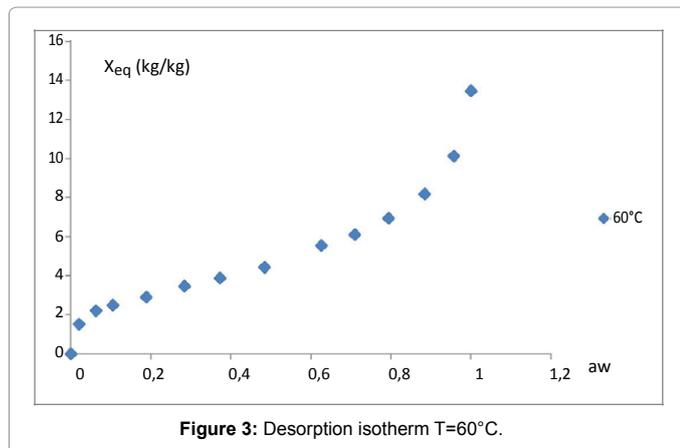
## Modelling Results

Desorption isotherms of water vapour at the temperatures 50, 60, 70 and 80°C on dicalcium phosphate are brought in Figures 2, 3, 4 and 5.

According to their shape, these isotherms are Type II on BET classification indicating that dicalcium phosphate is macro-porous (pore diameter>200 A°). Further interaction adsorbate-adsorbent is larger than the interaction adsorbate-adsorbate.

| Modèle | T=50 | T=60 | T=70 | T=80 |
|---|---|---|---|---|
| Halsey $X_{eq} = \left(-\dfrac{A}{\ln(aw)}\right)^{(1/B)}$ | | | | |
| A | 186.705 | 57.728 | 17.572 | 6.793 |
| B | 3.5039 | 3.006 | 2.582 | 2.131 |
| r | 0.959 | 0.977 | 0.97 | 0.974 |
| SE | 1.133 | 0.586 | 0.435 | 0.385 |
| White and Eiring: $X_{eq} = \dfrac{1}{A+Baw}$ | | | | |
| A | 0.363 | 0.389 | 0.4863 | 0.626 |
| B | -0.301 | -0.304 | -0.384 | -0.533 |
| r | 0.9937 | 0.985 | 0.957 | 0.961 |
| SE | 0.449 | 0.461 | 0.521 | 0.526 |
| BET $X_{eq} = \dfrac{A\,Xm\,aw}{(1-aw)(1+(A-1)aw)}$ | | | | |
| A | 64.489 | 61.529 | 35.038 | 36.144 |
| Xm | 2.839 | 2.563 | 2.303 | 1.747 |
| R | 0.997 | 0.998 | 0.989 | 0.991 |
| SE | 0.053 | 0.039 | 0.073 | 0. 069 |
| BET modifié $X_{eq} = \dfrac{A}{1-B\,.aw}$ | | | | |
| A | 2.748 | 2.57 | 2.055 | 1.597 |
| B | 0.827 | 0.783 | 0.791 | 0.852 |
| r | 0.993 | 0.985 | 0.957 | 0.961 |
| SE | 0.449 | 0.461 | 0.521 | 0.526 |
| Smith $X_{eq} = A - B.\left(\ln(1-aw)\right)$ | | | | |
| A | 2.68 | 2.386 | 1.821 | 1.196 |
| B | 2.984 | 2.669 | 2.397 | 2.492 |
| r | 0.983 | 0.985 | 0.969 | 0.984 |
| SE | 0.723 | 0.467 | 0.445 | 0.334 |
| Iglesias et chirife $X_{eq} = A + B.\dfrac{aw}{1-aw}$ | | | | |
| A | 4.4389 | 3.663 | 2.368 | 1.797 |
| B | 0.125 | 0.347 | 0.548 | 0.652 |
| r | 0.801 | 0.839 | 0.862 | 0.897 |
| SE | 2.403 | 1.495 | 0.9200 | 0.842 |
| Caurie $X_{eq} = \exp(A + B.\,a_w)$ | | | | |
| A | 0.607 | 0.681 | 0.541 | 0.166 |
| B | 2.035 | 1.651 | 1.557 | 1.892 |
| r | 0.985 | 0.992 | 0.984 | 0.989 |
| SE | 0.683 | 0.801 | 0.315 | 0.278 |
| Freundlich $X_{eq} = A.a_w^{\;B}$ | | | | |
| A | 12.168 | 8.714 | 6.493 | 6.022 |
| B | 1.012 | 0.703 | 0.547 | 0.708 |
| r | 0.916 | 0.949 | 0.974 | 0.969 |
| SE | 1.609 | 0.861 | 0.409 | 0.469 |
| Langmuir $X_{eq} = X_m \dfrac{A.\,aw}{(1+C.\,aw)}$ | | | | |
| Xm | 3.686 | 3.194 | 2.94 | 2.485 |
| A | 34.533 | 40.093 | 26.143 | 18.194 |
| r | 0.980 | 0.987 | 0.988 | 0.997 |
| SE | 0.138 | 0.110 | 0.089 | 0.039 |
| Oswin $X_{eq} = A.\left(\dfrac{aw}{1-aw}\right)^{B}$ | | | | |
| A | 5.266 | 4.625 | 3.825 | 3.19 |
| B | 0.244 | 0.265 | 0.277 | 0.338 |
| r | 0.982 | 0.996 | 0.995 | 0.997 |

| ES | 0.741 | 0.244 | 0.169 | 0.129 |
|---|---|---|---|---|
| Adam $X_{eq} = A + B.aw + C.aw^2 + D.aw^3$ | | | | |
| A | 1.447 | 1.399 | 1.084 | 0.657 |
| B | 16.292 | 16.759 | 9.84 | 8.985 |
| C | -36.095 | -19.568 | -13.736 | -13.93 |
| D | 33.551 | 17.436 | 11.072 | 12.36 |
| r | 0.998 | 0.998 | 0.997 | 0.997 |
| ES | 0.230 | 0.177 | 0.13 | 0.14 |
| Guggenhein $X_{eq} = \dfrac{X_m.A.B.aw}{(1-B.aw)(1-B.aw+A.B.aw)}$ | | | | |
| Xm | 2.990 | 2.905 | 2.644 | 2.087 |
| A | 69.545 | 57.791 | 40.283 | 28.761 |
| B | 0.809 | 0.744 | 0.692 | 0.79 |
| R | 0.999 | 0.998 | 0.998 | 0.998 |
| ES | 0.105 | 0.137 | 0.113 | 0.092 |
| Peleg $X_{eq} = A.\left(aw\right)^B + C.\left(aw\right)^D$ | | | | |
| A | 9.649 | 5.69 | 3.499 | 3.87 |
| B | 5.223 | 4.42 | 3.197 | 0.414 |
| C | 5.782 | 5.371 | 4.519 | 4.09 |
| D | 0.319 | 0.335 | 0.349 | 3.817 |
| r | 0.999 | 0.998 | 0.998 | 0.998 |
| ES | 0.161 | 0.162 | 0.092 | 0.109 |

**Table 2:** Estimated parameters and fitting criteria of the models applied to experimental.

Furthermore, for the same relative humidity, the amount of desorbed water vapour increases with decreasing temperature which is consistent with the exothermic nature of the desorption.

## Smoothing Experimental Desorption Curves

The choice of the mathematical model is based on statistical parameters for the comparison of different models. Indeed, the greatest value of the correlation coefficient (r) and the lowest values of the standard error (SE) are the criteria that justify the choice of the most appropriate model for smoothing the experimental sorption curves. The Table 2 include constants and statistical parameters thirteen models used to smooth the desorption isotherms dicalcium phosphate. The results show that the model gives the best smoothing Guggenhein, Anderson and de Boer isotherms desorption temperature in the range of 50-80°C.

## Conclusion

The desorption isotherms of dicalcium phosphate were determined at four temperatures (50, 60, 70 and 80°C) using the gravimetric method. The desorption isotherms of calcium phosphate have a sigmoid form and display the type II on BET classification.

Guggenhein, Anderson and de Boer data of desorption isotherms in the range of investigated temperatures (from 50 to 80°C) and water activities (from 0.021 to 0.989).

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