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# Statistical experimental design for studies of porosity and compressive strength in composite materials applied as biomaterials

H. Oudadesse[a], A.C. Derrien, and A. Lucas-Girot

Université de Rennes 1, Institut de Chimie, CNRS - UMR 6511, Campus Beaulieu, 263 avenue du Général Leclerc, 35042 Rennes, France

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**Abstract.** Composites studied in this work are the associations of aluminosilicates and 13% of calcium phosphates. These composites present great interest. They are destined to be applied in biomedical field, particularly in orthopedic or jawbone surgery. Calcium phosphates are composed of HA (hydroxyapatite) and TCP (tricalcic phosphate). The success of synthesised bony biomaterials depends on two determinant factors: the porosity (which facilitate the cells deposition and the vascularisation) and the compressive strength (which permits the support of body charge). In this way, a statistical experimental design was employed to quantify the influence of these two synthesis parameters. It concerns the effect of the $K_2O/SiO_2$ molecular ratio ($X_1$) and the effect of the calcium phosphate (HA/TCP) weight % ($X_2$). The $K_2O/SiO_2$ molecular ratio characterises the synthesis of the aluminosilicate. It varies between two limit levels: the stoichiometric ratio $K_2O/SiO_2 = 0.54$ corresponding to: $X_1 = -1$ and the ratio $K_2O/SiO_2 = 0.80$ corresponding to $X_1 = 1$. In bony biomaterials field, various calcium phosphates are commonly used as biomaterials. In our previous works, the influence of the commercial hydroxyapatite HA and tri-calcium phosphate TCP (13 wt%) addition was investigated. To study the effect of calcium phosphate composition, the weight percentage of mixing HA and TCP varied between two levels: the composite aluminosilicate with 13 wt% of HA ($X_2 = -1$) and the composite aluminosilicate with 13 wt% of TCP ($X_2 = 1$). Eight samples were studied. The statistical experimental design predicted answer surfaces for compressive strength and percentage of porosity. After the validation of models, it was possible to determine composite which presents best compromise between percentage of porosity and compressive strength. This composite will be evaluated by "in-vitro" and "in-vivo" studies to investigate its potential for forthcoming applied as biomaterial.

**PACS.** 81.05.Mh Cermets, ceramic and refractory composites – 68.55.Nq Composition and phase identification – 72.80.Tm Composite materials

## 1 Introduction

The aim of this work was to synthesise and to characterise a new type of composite materials (aluminosilicates/calcium phosphate) which are in the border between glass and porous phosphate. Ceramics materials such as $\beta$-TCP (Tri Calcic Phosphate), HA (Hydroxyapatite) and their association used as biomaterials [1,2] are well known for their good osteoconduction properties linked to their micro and macro porosity. On the other side, amorphous or vitroceramic systems based on silicium [3,4] are used for their good ability to create links between bone and biomaterials.

Aluminosilicates are characterized by an amorphous network made by the succession of $SiO_4$ and $AlO_4$ tetrahedra. The Si/Al ratio of about 21 belongs to the geopolymers family [5–7].

The association of this aluminosilicate with HA/TCP or both permit to obtain composites, made of an amorphous aluminosilicate of the matrix containing calcium phosphate [5]. The weight percentage of calcium phosphate at 13% was fixed in order to get good level of porosity.

The osteoconductivity of biomaterials is linked to their percentage of porosity and pore size [8,9]. The increasing of the percentage of porosity and pore size facilitates the cells colonisation and the vascularisation of the composite material. On the other hand, it induces the decrease of the compressive strength, which is an important parameter for biomaterials [10,11]. To remedy for this decrease, the $K_2O/SiO_2$ used for synthesis was studied. In this work, we focused on these two parameters in order to determine

[a] e-mail: hassane.oudadesse@univ-rennes1.fr

the most efficient synthesis parameters. The goal is to obtain composites which offer the best compromise between porosity and mechanical properties.

These two parameters varied simultaneously between to limit values, the statistical experimental design present the law of variation percentage of porosity and of mechanical properties as function of the $K_2O/SiO_2$ ratio and the HA/TCP association with aluminosilicate.

## 2 Materials and methods

### 2.1 Synthesis of composites

At first, KOH was added to a potassium silicate solution $K_2O$, $3SiO_2$, $21H_2O$. The quantity of KOH was fixed in the respect of the molecular ratio $K_2O/SiO_2$.

For this study, three solutions were prepared involving the following molecular ratio $K_2O/SiO_2 = 0.54$ (stoichiometric ratio); $K_2O/SiO_2 = 0.67$ (middle value ratio) and $K_2O/SiO_2 = 0.8$ [5].

Aluminosilicates (GPS) were synthesised by mixing the solution obtained previously with $SiO_2$ and $Al_2O_3$ [5]. After a good homogenisation, the GPS were soaked at least 24 hours at –15 °C, then, 13 weight % of calcium phosphate were added. After synthesis composites presented a basic character ($pH > 10$) due to synthesis conditions. It is a disadvantage for a potential application in contact with bony matrix. To reduce $pH$ values and to increase porosity [5], composites were heat treated at 250 °C and 500 °C respectively during 150 and 180 minutes.

### 2.2 Statistical Experimental Design (SED)

The optimization of mechanical properties linked to percentage of porosity should propose the best composites as possible for the in vitro and the in vivo investigations. We focused on two important parameters which were the molecular ratio $K_2O/SiO_2$ ($X_1$) and the added weight percentage of HA/TCP ($X_2$). The results were treated by statistical experimental design method [12]. It was possible to quantify the influence of each factor and their interactions with the compressive strength and the percentage of porosity. According to this method, factors were varied between two limit levels to realize all possible combinations of samples (Tab. 1). The model improvement was made by the comparison between calculated values (obtained by SED) and experimental values. The statistical model was an adaptation of Doehlert plan for 2 parameters ($X_1$: $K_2O/SiO_2$ ratio and $X_2$: wt% of HA in the calcium phosphate added). The base was square in order to optimize results in the border of the domain ($\sigma_{\text{calculated}} / \sigma_{\text{experimental}} < 1$).

### 2.3 Materials investigation

15 mg of fine grounded powder of materials were mixed with distilled water, the solution was stirred and $pH$ values were measured with $pH$-meter Orion 730. For each composite, 3 different samples were analysed.

**Table 1.** Matrix of experiment.

| | const | $X_1$ | $X_2$ | $X_{12}$ | $X_1^2$ | $X_2^2$ |
|---|---|---|---|---|---|---|
| y1 | 1 | –1 | –1 | 1 | 1 | 1 |
| y2 | 1 | 1 | –1 | –1 | 1 | 1 |
| y3 | 1 | –1 | 1 | –1 | 1 | 1 |
| y4 | 1 | 1 | 1 | 1 | 1 | 1 |
| y5 | 1 | 0 | –1 | 0 | 0 | 1 |
| y6 | 1 | 0 | 1 | 0 | 0 | 1 |
| y7 | 1 | –1 | –0.2 | 0 | 1 | 0 |
| y8 | 1 | 1 | –0.2 | 0 | 1 | 0 |

| | $X_1$ | $X_2$ |
|---|---|---|
| Level –1 | $K_2O/SiO_2 = 0.54$ | 100 wt. HA |
| Level –0.2 | – | 60 wt% HA; 40 wt% TCP |
| Level 0 | $K_2O/SiO_2 = 0.67$ | 50 wt% HA; 50 wt% TCP |
| Level 1 | $K_2O/SiO_2 = 0.8$ | 100 wt. TCP |

X-ray diffraction (XRD) study was realized on an INEL CPS120 diffractometer with a curred position sensitive detector (Cu $K_{\alpha 1}$ radiation). The diffractogram permitted to verify that samples present similar structures in the whole SED domain area.

The ratio between real density $d_{\text{real}}$ (measured on massive samples in an He pycnometer Accupic 1330, MICROMERETICS) and geometric density $d_{\text{geom}}$ (ratio of sample weight to sample volume) corresponds to the percentage of porosity:

$$\%\text{porosity} = 1 - d_{\text{geom}}/d_{\text{real}}. \quad (1)$$

The morphology of composites was ascertained with SEM (Scanning Electron Microscopy) technique using a JEOL 6301F. This method permitted to estimate the range of pore size and the eventual modifications induced by the different syntheses.

Mechanical tests were performed on cylinders of 6 mm diameter and 12 mm length in a compressive mode, on a Lloyd Instrument LR 50K machine, using 0.2 mm/min as speed displacement for the piston. The compressive strength $\sigma$ (MPa) is:

$$\sigma(\text{MPa}) = F/S \quad (2)$$

$F$: maximal load value (N)
$S$: surface ($mm^2$).

## 3 Results

### 3.1 Physicochemical characterisation

The $pH$ parameter is an important factor for forthcoming evaluation as potential biomaterials; it permits to define the temperature of thermal treatment of composites. According to Figure 1, $pH$ values decreased with the increase of the temperature of thermal treatment. After thermal treatment at 500 °C, all composites presented $pH$ values

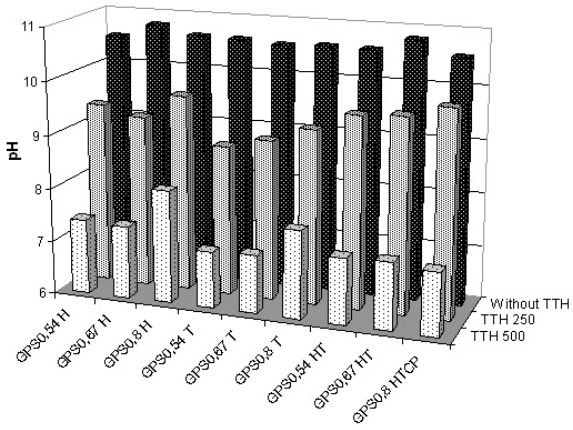


**Fig. 1.** Histograms of $pH$ values versus a thermal treatment of all composites.

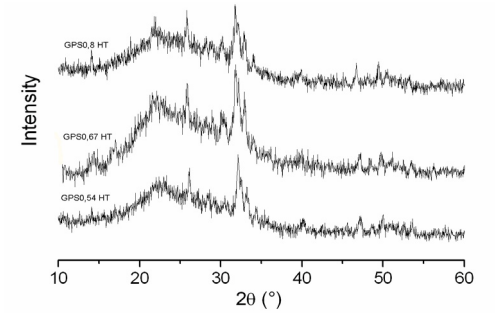


**Fig. 2.** XRD of composites GPS/(HA-TCP) versus $K_2O/SiO_2$ after a thermal treatment at 500 °C.

of about 7. The incertitude of $pH$ measures is less than 0.25 $pH$ units.

X-ray diffraction was used to control structure of composites. After the thermal treatment at 500 °C, composites presented the same type of structure: an aluminosilicate amorphous matrix characterized by a diffuse halo between 16° and 38° $2\theta$ and the weak $SiO_2$ impurity reflection (JCPDS 82-1561) and peaks which characterize the calcium phosphates associated (Fig. 2). Composites crystalline structures were not influenced by any factor that would be studied (wt% of HA and $K_2O/SiO_2$ ratio).

The SEM pictures of composites were characterised by equivalent range of pore sizes from a few micrometers to a few hundred micrometers for micro and macroporosity (Fig. 3). The observations made for composites on this figure were the same for the other composites which were not presented in this work.

As the variation of $K_2O/SiO_2$ ratio ($X_1$) and wt% of HA ($X_2$) did not influence the structure and the general morphology of composites. It has been acceptable to apply the SED method to determine composite which presents the best arrangement between % of porosity and compressive strength.

### 3.2 Statistical method investigation

One of the most adapted models for the two parameters study has been proposed by D. Doelhert [13]. This model was calculated with 7 experimental points which were uniformly disposed in the domain of experiment. It gave a second order polynomial equation, which could describe a non linear phenomenon. The hexagonal shape of Doelhert model's imposed high values for $d(\hat{y}_p)$ (Eq. (3)) on border of the square domain of investigation. It was detrimental for our study because corner areas could not be neglected.

In order to reduce the values of in most of the experiment domain, eight experimental points were used and listed in experiment matrix (Tab. 1). They correspond to the equal error curves in Figure 4. These curves represent the ratio between the standard deviation of remainders and the experimental standard deviation (Eq. (3)).

$$d(\hat{y}_p) = \sigma_{y\,\text{calculated}}/\sigma_{y\,\text{experimental}} \tag{3}$$

$\hat{y}_p$ corresponds to the point $p$ of the domain where we calculate the value $y$ (% of porosity or compressive strength).

In Figure 4, the main part of the domain presents values below 1. The middle point of the domain presents $d(\hat{y}_p) > 1$ so the model validity would be tested by comparing calculated values and experimental values on this point. Values of the wt% of HA ($X_2$) were non-centred on zero: we worked with a special composition of 40 wt% of HA and 60 wt% of TCP, which presents advantages in the medical, field [14,15]. The comparison between equal error curve of our model and an equal error curve obtained with centred points did not show major differences, so our model has been used.

The statistical model was calculated using 8 experimental values for mechanical properties and percentage of porosity. The experimental results are presented in Table 2, incertitudes are given by 95% Student statistical method.

Samples named $y_1$ to $y_8$ were used to calculate the mathematical model and samples named $y_9$ permitted the validation of the model.

Minus square coefficients of the model (Matrix $\hat{a}$) were obtained by the relation below:

$$\hat{a} = (X^t X)^{-1} X^t y \tag{4}$$

$X$: the experiment matrix (Tab. 1),
$X^t$: the transpose of $X$,
$y$: the matrix of the experimental results ($y_1$ to $y_9$).
Thus matrix of calculated values ($\hat{y}$) for the all domain is given by equation (5)

$$\hat{y} = X\hat{a}. \tag{5}$$

For each coefficient, the standard deviation by the relation (Eq. (6)) was calculated:

$$\sigma(\hat{a}) = \sigma_r(\text{Diag}(X^t X)^{-1})^{1/2} \tag{6}$$

$\sigma_r$: the variance of the remainders and the lack of fit of the model.
The model gave the matrix of coefficients $\hat{a}$ with $\hat{a}^t = [a_0 a_1 a_2 a_{12} a_{11} a_{22}]$ and $\sigma(\hat{a})$.

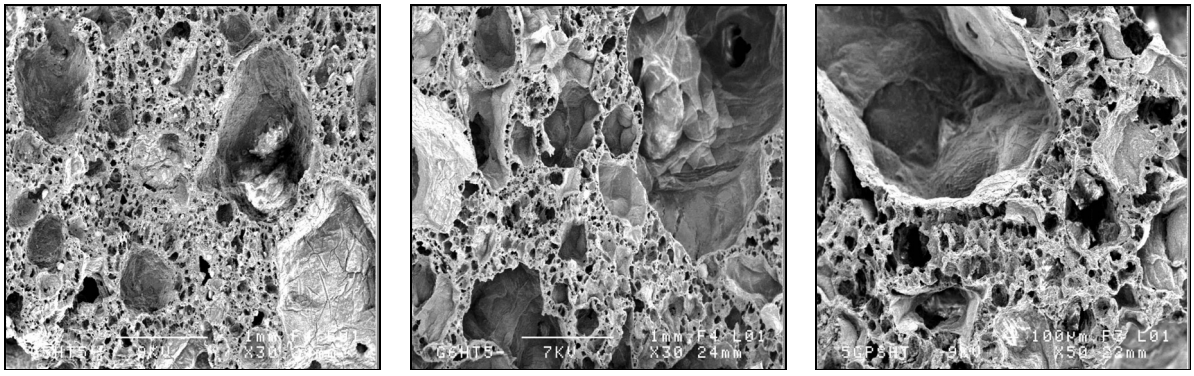

**Fig. 3.** Morphology of composites GPS with 60 wt% HA and 40 wt% TCP after the thermal treatment at 500 °C (from left to right: GPS0.54 HT (×30), GPS0.67 HT (×30), GPS0.80 HT (×50)).

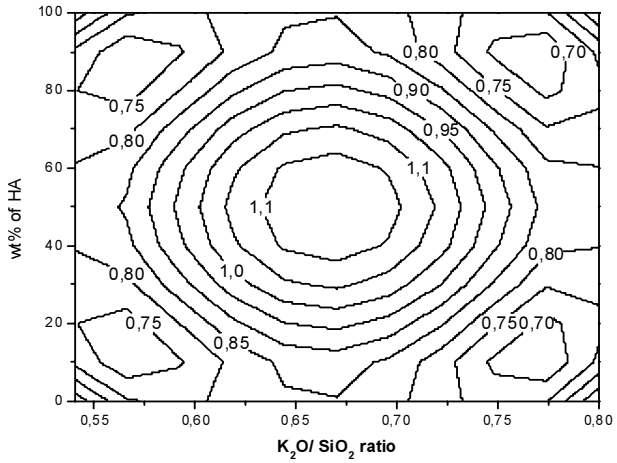


**Fig. 4.** Curve of equal error obtained in the case of the shown plan.

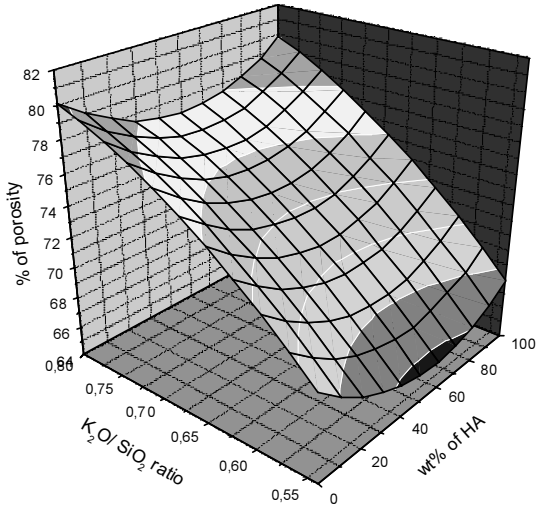


**Fig. 5.** Answer surface of the percentage of porosity versus $K_2O/SiO_2$ ratio ($X_1$) and wt% of HA ($X_2$).

## 3.3 Model setting

### 3.3.1 Percentage of porosity

Results of % of porosity $y_1$ to $y_8$ presented in Table 2 permit to obtain different calculated coefficients $a_{ij}$. Thus the following equation was established:

$$\%\text{porosity} = 72.72 + 5.63X_1 + 0.52X_2 - 0.36X_{12} - 1.31X_1^2 + 2.98X_2^2 \quad (7)$$

$X_1$: the $K_2O/SiO_2$ molecular ratio, $X_1 = ((K_2O/SiO_2) - 0.67)/0.13$
$X_2$: the wt% of HA, $X_2 = (50 - (\text{wt\% HA}))/50$.
Where 0.67 corresponds to the middle value of $K_2O/SiO_2$ ratio; 0.13 corresponds to the weight of HA/TCP associated.

The most influent factor is the $K_2O/SiO_2$ ratio, its decrease induces the decrease of percentage of porosity. The influence of the percentage of HA was not neglected as shown in answer surface curve (Fig. 5).

### 3.3.2 Compressive strength

In the same way, we evaluated and listed in Table 2 the compressive strength of samples in order to calculate the model. The comparison between a linear and an exponential model permits to choose the exponential model and to describe the variation of compressive strength values versus $K_2O/SiO_2$ ratio and wt% of HA. The determination of the coefficients was proceeded in the same way as for the percentage of porosity, the only difference consisted in using the values ln ($\sigma_{\exp}$(MPa)) instead of $\sigma_{\exp}$(MPa) of our 8 samples [16,17]. The different coefficients were calculated and then, the following relation was established:

$$\sigma_{\text{cal}} = 3.298 \exp\big(-0.440X_1 - 0.058X_2 - 0.060X_{12} - 0.029X_1^2 - 0.217X_2^2\big) \quad (8)$$

$\sigma_{\text{cal}}$: calculated compressive strength (MPa).

The $K_2O/SiO_2$ molecular ratio variation induced the major variation on compressive strength, the percentage of HA was not neglected as shown in the answer surface curve (Fig. 6).

**Table 2.** Values of $\sigma$(MPa) and % of porosity obtained by the statistical model design.

| No. | Name | Compressive strength | | Percentage of porosity | |
|---|---|---|---|---|---|
| | | $\sigma$exp (MPa) | $\sigma$cal (MPa) | porosity exp (%) | porosity cal (%) |
| y1 | GPS0.54 H | 3.62 (±1.10) | 4.00 (±0.24) | 69.04 (±4.15) | 67.88 (±1.00) |
| y2 | GPS0.8 H | 1.88 (±0.30) | 1.87 (±0.24) | 79.11 (±0.79) | 79.86 (±1.00) |
| y3 | GPS0.54 T | 4.06 (±0.82) | 4.01 (±0.25) | 70.08 (±2.63) | 69.64 (±1.00) |
| y4 | GPS0.8 T | 1.60 (±0.23) | 1.47 (±0.25) | 79.35 (±0.62) | 80.19 (±1.00) |
| y5 | GPS0.67 H | 3.09 (±0.88) | 2.81 (±0.22) | 74.79 (±1.14) | 75.19 (±0.88) |
| y6 | GPS0.67 T | 2.28 (±0.57) | 2.50 (±0.22) | 76.63 (±0.82) | 76.23 (±0.88) |
| y7 | GPS0.54 H60T40 | 5.38 (±2.88) | 4.93 (±0.22) | 64.13 (±3.32) | 65.72 (±0.89) |
| y8 | GPS0.8 H60T40 | 1.92 (±0.20) | 2.09 (±0.22) | 78.72 (±0.57) | 77.13 (±0.89) |
| y9 | GPS0.67 H60T40 | 2.91 (±0.61) | 3.30 (±0.30) | 74.79 (±0.78) | 72.74 (±1.21) |

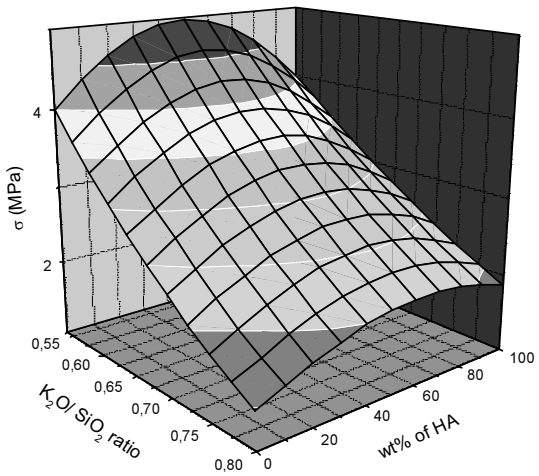


**Fig. 6.** Answer surface of the percentage of the compressive strength $\sigma$(MPa) versus $K_2O/SiO_2$ ratio ($X_1$) and wt% of HA ($X_2$).

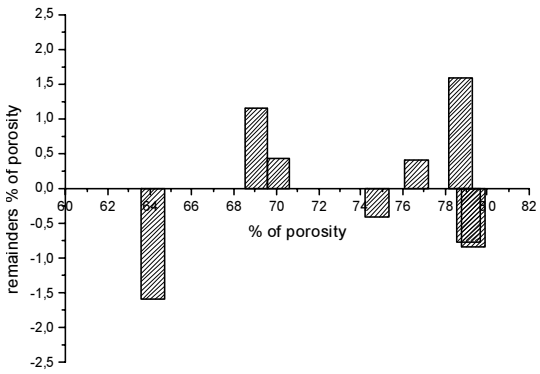


**Fig. 7.** Remainders values (the difference between the experiments and the calculated values of percentage of porosity).

## 3.4 Model validation

For both percentages of porosity and compressive strength, experimental points were used to establish a potential model to describe the whole experimental domain. The evaluation of the postulated model was made by the calculus of 3 statistical parameters:

- the Fisher test ($F$, ratio of the variance of the calculated model by the variance of experimental results),
- the $R^2$ (degree of model explication to experimental values, which varied between 0 and 1),
- the remainders (considered difference between experimental and calculated values as a function of experiment values).

If those three parameters allowed improving the model, we could validate it by synthesis of samples in the domain and comparison between experimental and calculated results. This improvement was the determinant character to confirm the model and determinate its validity. According to Figure 4, the validation of the middle area of the domain where $d(\hat{y}_p) > 1$ was needed. Seven samples with the following characteristics were synthesized: $K_2O/SiO_2 = 0.67$ (corresponded to $X_1 = 0$) and 60 wt% of HA and 40 wt% of TCP ($X_2 = -0.2$). HA and TCP biomaterials offer a good resorption properties [18].

### 3.4.1 Percentage of porosity

The model obtained before consisted in a second degree polynomial model (Eq. (7)). For this model we obtain $F = 0.337$, $R^2 = 0.999$.
$R^2$ indicates a good accord between calculated and experimental values for points which were used to calculate the model. $F$ was calculated with all values obtained for each sample. We got an important number of samples for each composite because of our porous materials. In this case $F$ incorporated the distribution of results so the value was acceptable. The analyse of the remainders diagram (Fig. 7) showed a random distribution with small standard deviations. These three factors did not underline any major failure of the proposed model, the validation was possible. Calculated value of percentage (and incertitude) of porosity for middle point of the domain ($X_1 = 0$, $X_2 = -0.2$) was included in the range of answer of our 7 samples (GPS 0.67 HT) (Tab. 2). The statistical model described the variation of the percentage of porosity in the investigated domain.

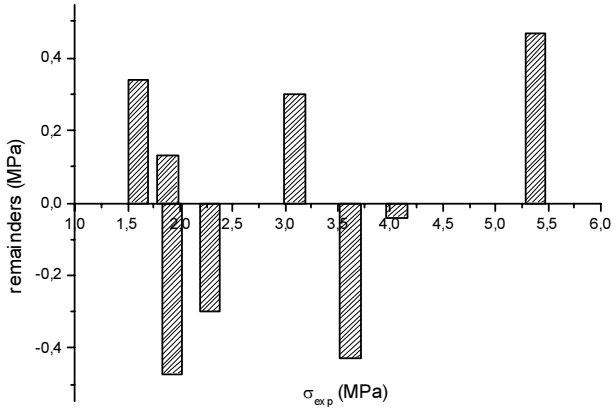


**Fig. 8.** Remainders values (the difference between the experiments and the calculated values of compressive strength $\sigma$(MPa)).

#### 3.4.2 Compressive strength

The model obtained before consisted in an exponential model (Eq. (8)). For this model we obtain $F = 1.078$, $R^2 = 0.994$. As for percentage of porosity, $R^2$ indicates a good accord between calculated and experimental values for points which were used to calculate the model. $F$ was calculated with all values obtained for each sample, this value could be considered correct as regard to the relative dispersion of compressive strength. Analyse of the remainder diagram (Fig. 8) showed a random distribution; its values increased with the increase of compressive strength experimental value. These three factors did not underline any major failure of the proposed model. The model validation was realised by the comparison between calculated and experimental values in the middle point of the domain. We tested compressive strength of 7 samples GPS 0.67 with 60 wt% HA and 40 wt% of TCP. Compressive strength and incertitude calculated with $X_1 = 0$, $X_2 = -0.2$ ($K_2O/SiO_2 = 0.67$ and 60 wt% of HA) was included in the range of answer of our 7 samples (Tab. 2). The statistical model described the variation of the percentage of compressive strength in the investigated domain.

### 3.5 Statistical experimental design and physicochemical properties

The SED method permitted to evaluate percentage of porosity and compressive strength in a whole study area, using only eight samples experiment. The choice of the mathematical model was confirmed by statistical criteria as $F$, $R^2$ and remainders curves. Goods results obtained by comparing experimental values and calculated values for samples of validation allowed the use of the model to describe compressive strength and percentage of porosity variation as function of $K_2O/SiO_2$ ratio and wt% of HA.

#### 3.5.1 Percentage of porosity

According to equation (7) and Figure 5, the variation of the ratio ($X_1$) between 0.54 ($X_1 = -1$) and 0.8 ($X_2 = 1$) was positive at the first degree and negative on the second degree, so the general influence of the augmentation of the ratio $K_2O/SiO_2$ contributed to the increase of the percentage of porosity ($a_1 = 5.63$), this augmentation varied in $-x^2$ ($a_{11} = -1.31$). The influence of wt% of HA in calcium phosphate ($X_2$) was not as much important as for $X_1$ ($a_2 = 0.52$) so the percentage of porosity was little influenced by the choice of calcium phosphate but the variation was non zero and percentage of porosity varied as $x^2$ between 0 wt% HA and 100 wt% HA with the inflection point (minimum of percentage of porosity) for 60 wt% of HA. The interaction between $X_1$ and $X_2$ could be neglected because the interaction coefficient $a_{12}$ was smaller than $\Delta(a_{12})$.

#### 3.5.2 Compressive strength

According to equation (8) and Figure 6, the variation of the ratio ($X_1$) between 0.54 ($X_1 = -1$) and 0.8 ($X_2 = 1$) was negative at the first degree and negative on the second degree, so the general influence of the augmentation of the ratio contributed to the decrease of compressive strength ($a_1 = -0.44$), this augmentation varied in $-x^2$ ($a_{11} = -0.029$). The influence of wt% of HA in calcium phosphate ($X_2$) was not as much important as for $X_1$ ($a_2 = -0.058$) but the mixing of two calcium increased compressive strength values (whereas the influence on porosity was not significant). The compressive strength varied as $-x^2$ between 0 wt% HA and 100 wt% HA with the inflection point (maximum of $\sigma$ (MPa)) for 60 wt% of HA. The interaction between $X_1$ and $X_2$ could not be neglected because the interaction coefficient $a_{12}$ was taller than $\Delta(a_{12})$. The best compressive strength value of 5.38 MPa were obtained for samples, which presented both calcium phosphates (GPS0.54 H60 T40) with quasi-equal weight percentage.

#### 3.5.3 Physicochemical properties

Figures 5 and 6, which represent respectively the answer surface of the percentage of porosity versus $K_2O/SiO_2$ ratio ($X_1$) and wt% of HA ($X_2$) and the answer surface of the percentage of the compressive strength $\sigma$(MPa) versus $K_2O/SiO_2$ ratio ($X_1$) and wt% of HA ($X_2$), permit to determine the best compromise between these three determinant chemical properties for applications of this material as potential biomaterial.

The decrease of the molecular ratio $K_2O/SiO_2$ contributed to the increase of compressive strength, best composites were obtained with $K_2O/SiO_2 = 0.54$ ($X_1 = -1$) and 60 wt% of HA in calcium phosphate ($X_2 = -0.2$).

Statistical experimental design shows that the middle value of percentage of porosity was about 73 percent, with

bigger values at 80% of porosity and at least 69% of porosity. These percentages were large enough to enable a potential vascularisation so the choice of the best composite would be determined by mechanical properties studied in this work with the same method SED and in the same conditions. The decrease of $K_2O/SiO_2$ ratio played an important role in the first step of the synthesis. In fact, the reduction of the quantity of $K_2O$ added to the silicate solution corresponded to the non complete depolymerization of the silicate. Thus, there was less $SiO_2$ ($Q_0$) and the quantity of OH leaving from the structure of the GPS decreased. As the porosity was due to the start of OH groups, the percentage of porosity diminished with the decrease of $K_2O/SiO_2$ ratio.

The percentage of porosity was acceptable in the whole study area, the most interesting association resulting from this Statistical Method Investigation was a composite based on aluminosilicate with the molecular ratio $K_2O/SiO_2 = 0.54$ and 13 wt% of two calcium phosphate (60 wt% HA and 40 wt% TCP). These chemical properties are strongly linked. In this work, the SED permitted to evaluate clearly this relation on the whole domain area and serve as support for the choice of the geopolymer material with appropriate chemical properties and characteristics (porosity, compressive strength, and quantification of the added calcium phosphate material) for the applications as potential biomaterial.

In this way, composites with 64% of porosity and 5.38 MPa of compressive strength were experimented by the in vitro studies. They were immersed in the SBF (Simulated Body Fluid) versus time, from 2 hours to 30 days. Results obtained show the good chemical stability of these compounds. No exchanges of ions or atomic elements between the physiological liquid and the compounds were detected. The Al atomic element was particularly followed. This element is not released from compounds to liquid. It is an important result because of the toxic character of Al in the organism. This result traduces the good chemical stability of these composites, characterised by an amorphous network made by the succession of $SiO_4$ and $AlO_4$ tetrahedra.

## 4 Conclusion

This study made possible the quantification of the influence of synthesis parameters on the percentage of porosity and compressive strength with few samples. The association between aluminosilicate and calcium phosphate gave composites with an important percentage of porosity in the whole domain studied (from 70% to 80%). These composites characterised as an amorphous matrix included calcium phosphate. They all present high percentage of porosity and large range of pore size. For forthcoming in vitro and in vivo evaluations the aluminosilicate would be synthesize by mixing KOH with a potassium silicate solution $K_2O$, $3SiO_2$, $21H_2O$ using the molecular ratio $K_2O/SiO_2 = 0.54$. Composites will be obtained by addition of 13 wt% of calcium phosphate (60 wt% of HA and 40 wt% of TCP) to the aluminosilicate.

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