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RHEOLOGICAL PROPERTIES AND HYDRAULIC PERFORMANCE OF HYDROXYAPATITE/GYPSUM/PLASTER BLENDS

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Abstract

A Permeable Reactive Barrier (PRB) is a passive technique using reactive materials placed in the ground to remediate contaminated groundwater. This study is focused on the evaluation of the main properties required for PRB materials such as permeability, stability and reactivity. In order to obtain a continuous material for PRB applications, different formulations based on calcium hydroxyapatite in gel/paste form (with Ca-HA as the reactive material), or on calcium sulfate wastes (using Gypsum ($d < 1\text{mm}$) and Plaster ($d < 0.25\text{mm}$) as support matter) were blended with water. The influence of calcium sulfates and water content on the rheological behavior of Ca-HA/(wastes) blends was studied through steady rheological tests. Blend stability was evaluated by zeta-potential measurement. Results showed that all blends and formulations exhibited shear-thinning behavior. Plaster hydration plays a major role in the stabilization of the Ca-HA structure, which maintains the gel-paste form. Gypsum particles (already hydrated) enhance Ca-HA dispersion. The fixation of sulfate ions on the Ca-HA surface leads to the modification of the surface charge of the particles, and plays an important role in the phase transition. The characterization performed revealed that Ca-HA is a silty-sand-like structure with a permeability of $5 \cdot 10^{-7} \text{m.s}^{-1}$. Permeability tests carried out on Ca-HA/gypsum ($d < 1\text{mm}$) (60/40%wt) showed an increase in the permeability value which can reach up to 10^{-6}m.s^{-1} .

1. INTRODUCTION

The calcium phosphate group is known for its high capacity to retain and sequester heavy metals and radionuclides in a thermodynamically stable crystalline lattice, characterized by a stoichiometric structure ($\text{Ca/P}=1.67$). In the literature, several application methods have been studied for calcium phosphate injection to stabilize contaminated soil and to prevent the infiltration of solutes toward groundwater [1-2]. In the last decades, the application as a PRB of calcium phosphate in apatite form (Apatite II, $[\text{Ca}_{10-x}\text{Na}(\text{PO}_4)_{6-x}(\text{CO}_3)_x(\text{OH})_2]$, where $x < 0$], derived from fish bones) have shown a high ability and capacity to treat contaminated groundwater [3].

Gypsum, a by-product of the phosphoric-acid production process, can be added to Portland cement for setting control, or to reactive material such as fly ash. It can also be used to enhance the mechanical properties of the soil and reduce the plasticity index, moisture and water content [4]. Studies reviewed by SINGH [5] have shown that the porosity of a gypsum binder is the major parameter determining the durability performance in terms of compressive strength and architectural structure. The hydration period and cure conditions also affect the mechanical properties. Relative humidity influences porosity, as observed in gypsum samples, where scanning electronic spectroscopy reveals the presence of cracks and the creation of pore voids at a constant relative humidity of 98% [6].

The main purpose of this work is to investigate the rheological behavior of water/gypsum, water/plaster, Ca-HA/gypsum and Ca-HA/plaster blends. This is a preliminary step in a project devoted to the formulation and characterization of a Ca-HA-based permeable reactive barrier. The evaluation of the rheological behavior of a mixture of *gypsum* and *plaster* on the Ca-HA_{Gel} aims to better understand the development of the matrix microstructure, and consequently to assess its workability. The porosity and permeability of materials and formulations containing hydroxyapatite gel (Ca-HA_{Gel}) and both hemihydrated and dihydrated calcium sulfate will be investigated.

2. MATERIALS AND METHODS

2.1. MATERIALS

In this work, calcium phosphate (Ca-HA_{Gel}) and calcium sulfates were used as reactive material and support material respectively. The gypsum (G, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and the plaster calcium sulfate (P_α , $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) used in this work are residues from the production of phosphoric acid (H_3PO_4). Both were provided by PRAYON[®] (Belgium). The plaster was used as received and the gypsum was sieved to under 1mm and the larger fraction discarded. The Ca-HA_{Gel} was obtained by reaction between the calcite (CaCO_3 , 98% pure, Fisher Scientific) and ammonium phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$, 99.4% pure, Fisher Scientific) at 25°C with a molar ratio of $\text{Ca/P}=1.67$, and an amount of demineralized water three times higher than that of the calcite.

2.2. FORMULATIONS

Rheological tests were carried out on pure Ca-HA_{Gel}, on binary water/gypsum (W/G) and on water/plaster (W/P). Binary blends were prepared by mixing the selected material with de-ionized water according to different mass ratios ranging from 0.4 to 1.4. Solid concentrations of binary blends (Γ_{BI}) and *water/gypsum* and *water/plaster* mass ratios were calculated following equations (1), (2) and (3) respectively:

$$\Gamma_{B1} = \frac{V_s}{V_s + V_w} \quad (1)$$

$$\frac{W}{G} = \frac{1 - \Gamma_B}{\rho_G \Gamma_B} \quad (2)$$

$$\frac{W}{P} = \frac{1 - \Gamma_B}{\rho_P \Gamma_B} \quad (3)$$

Where V_s is the volume of the solid phase, V_w is the volume of water and ρ_G and ρ_P are the densities of gypsum and plaster respectively. The Ca-HA_{Gel} content considered was from 0 to 50wt% Ca-HA_{Gel}. The solid concentration of binary blends (Γ_{B2}) containing either gypsum or plaster (calcium sulfate powder) with Ca-HA_{Gel} was calculated using equation (4):

$$\Gamma_{B2} = \frac{V_{ST}}{V_{ST} + V_{WT}} \quad \text{with:} \quad V_{ST} = V_{Ca-HA_{Powder}} + V_{CS_{Powder}} \quad ; \quad V_{WT} = V_{Ca-HA_{Water}} \quad (4)$$

Where V_{ST} is the total volume of solid material equal to the sum of Ca-HA_{Powder} volume ($V_{Ca-HA_{Powder}}$) and calcium sulfate powder volume ($V_{CS_{Powder}}$), and V_{WT} is the total water equal to Ca-HA water volume ($V_{Ca-HA_{Water}}$).

2.3. RHEOLOGICAL TRAILS

The rheological measurements were performed using a Rheostress (HAAKE RS 150 Rheometer). The rheological behavior and viscosity η (Pa.s) were evaluated for shear rates ranging from 0 to 500s⁻¹ at constant temperature (20±5°C). The samples were placed in a cylindrical vessel and the strain was applied by a double-helical ribbon impeller. Samples were homogenized before measuring the shear stress τ (Pa) and the viscosity versus the applied shear rate $\dot{\gamma}$ (s⁻¹).

2.4. PERMEABILITY

Permeability assessment of formulations was carried out using an experimental device illustrated in **Figure 1**. Valves (V.1 Air pressure valve; V.2 Water flow control and purge valve; V.3 Water flow control valve) were installed to control air pressure and water flow. The cell volume of 343.36cm³ was filled by the test sample and the applied pressure was a differential pressure assured by compressed air varying from 1.1 to 1.5bars relative pressure.

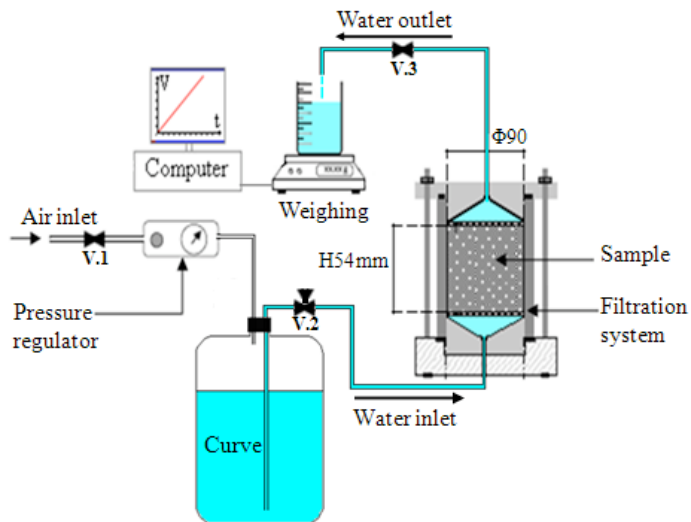


Figure 1 : Constant head permeability test

The flow rate was measured by the mass of filtered water for 1h of filtration (i.e. to achieve constant flow). The permeability value (intrinsic permeability, K) was calculated by using Darcy's relationship illustrated by equation (6): $K = \frac{Q}{A} \frac{H}{\Delta P} \rho g$

Where Q is the flow rate of filtered water (cm³.s⁻¹); A is the cross section of the test sample (cm²); H is the length of the test sample (cm); ΔP is the pressure difference ($P_2 - P_1$) (P_1 is the

applied pressure of inlet water (Pa) and P_2 is the pressure of outlet water equal to atmospheric pressure (1.013MPa)); ρ is the density of water and g is the gravity constant (9.81m.s^{-2}). This method was chosen to evaluate the permeability of $\text{Ca-HA}_{\text{Gel}}$ and $\text{Ca-HA}_{\text{Gel}}$ blended with gypsum, i.e. for materials presenting a high head loss.

3. RESULTS AND DISCUSSION

3.1. RHEOLOGICAL BEHAVIOR

Apatite gel is characterized by a specific texture caused by absorption of water and interaction between fine particles. The identification of the behavior and the structure $\text{Ca-HA}_{\text{Gel}}$ requires an understanding of the influence of parameters such as material deformation, strength and stability.

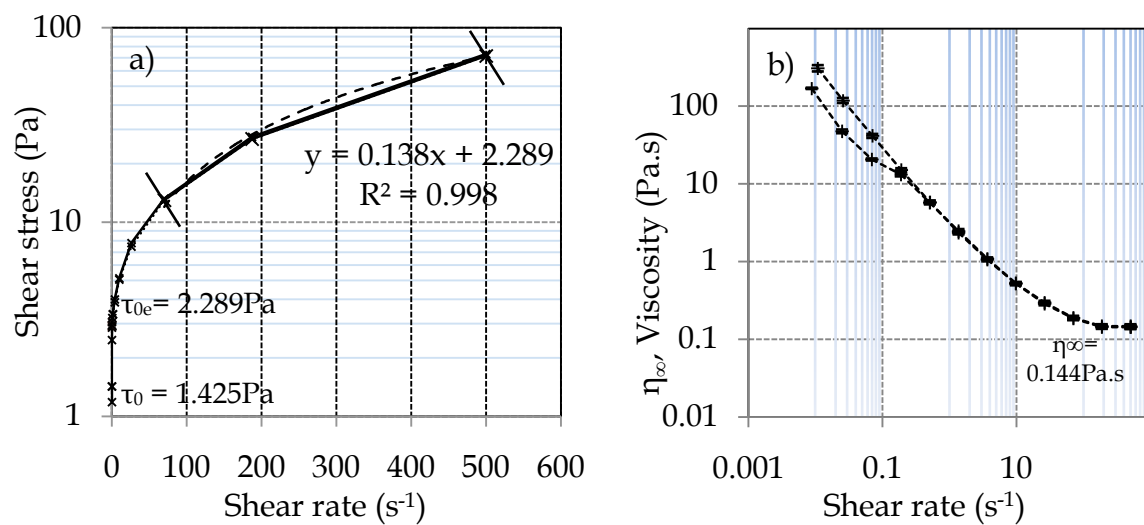


Figure 2: Rheological behavior and viscosity of $\text{Ca-HA}_{\text{Gel}}$ after 48h of synthesis, a) $\tau=f(\dot{\gamma})$; b) $\log(\tau)=f(\dot{\gamma})$ (—x—Shear stress (Pa), —+—Viscosity (Pa.s))

As shown in **Figure 2**, the shear stress increased with the shear rate when the stress exceeded a threshold value τ_0 (1.425Pa), indicating that $\text{Ca-HA}_{\text{Gel}}$ exhibits a shear-thinning behavior. Viscosity reached an apparent value of ($\eta_{\infty}=0.144\text{Pa.s}$) above $\dot{\gamma}=200\text{s}^{-1}$. The critical shear rate corresponding to the Ca-HA dispersion was characterized by an extrapolated maximum yield stress τ_{0e} (2.289Pa) and minimum yield stress τ_0 (1.425Pa), related to the response of the gel to the deformation. The increase in the shear stress led to the disruption of the gel structure, and when the shear stress stopped, the suspension tended to recover its original structure (i.e. the flow was reversible). Beyond the shear stress threshold, with an increasing shear rate, the flow was enhanced by the gradual dispersion of particles, promoting the separation effect which caused the decrease in viscosity. Once the apparent viscosity stabilized at high shear rates, no further modification was observed for the structure of $\text{Ca-HA}_{\text{Gel}}$.

3.2. RHEOLOGICAL BEHAVIOR OF BINARY BLENDS

The viscosity of the binary matrix was measured and plotted versus the concentration of added powder, as illustrated in **Figure 3** and **Figure 4**. W/G and W/P blends exhibited shear-thinning behavior. **Figure 3** shows that the viscosity of W/G blends decreased with a decreasing gypsum concentration until achieving an almost constant apparent viscosity for

W/G ratios above 0.6. The viscosity plateau revealed no influence of water on the particle surface of the gypsum and showed that the grains underwent the action of gravity and buoyancy (characterized by an apparent density of 1.25g.cm^{-3} in the cylindrical vessel).

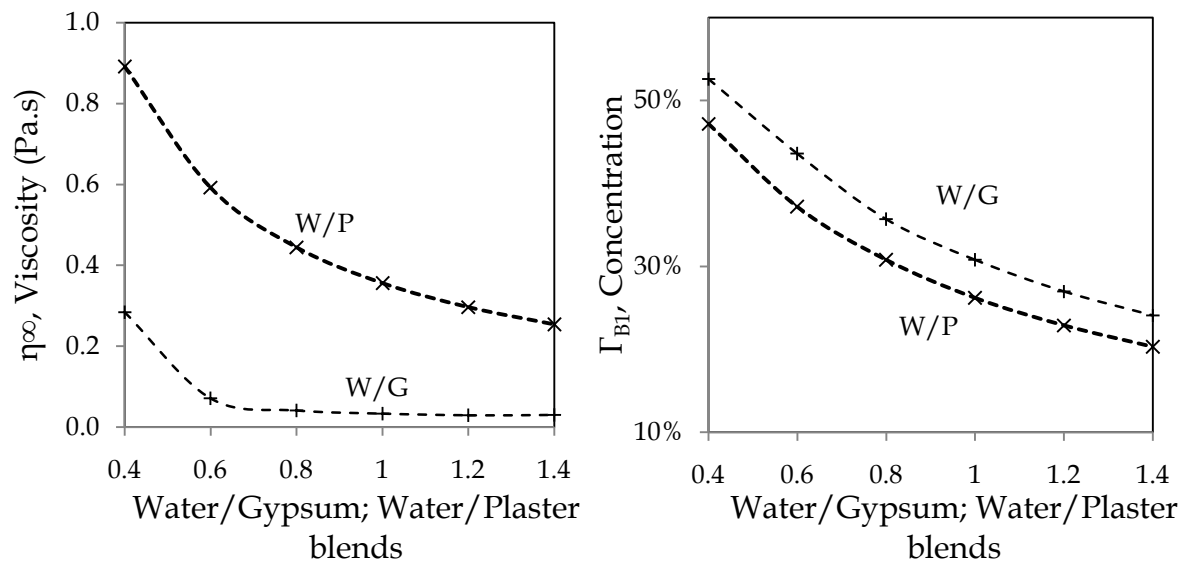


Figure 3: Viscosity of W/G and W/P blends at different mass ratios

Hydrated gypsum particles presented similar double-electric layers of a common charge (negatively charged), which generates *electrostatic repulsion* between particles (due to the overlap of the electrical double-layers). Gypsum grains are mainly negatively charged and surrounded by a diffuse layer of positive average charge. This positive charge layer stabilizes the dispersion through particle repulsion, avoiding particle aggregation. At rest, particles tend to precipitate. If a stress is applied, the suspension is dispersed, leading to a decrease in viscosity. The gypsum concentration controls the dispersed state; the repulsive forces tend to stabilize the suspension, because the particles are negatively charged. The apparent viscosity is obtained at a high shear rate where gravity forces are negligible. It can be seen that above a 0.6 W/G ratio, inter-particle distance is large enough to make apparent viscosity independent of gypsum content. As regards the plaster blends (W/P), the viscosity decreased with decreasing plaster concentration. The hydration of hemihydrate particles requiring 1.5 water molecules, led to crystallization. In general, the contact of plaster particles with water triggers dissolution, which induces the saturation or supersaturation of the solution in Ca^{2+} and SO_4^{2-} , leading to the formation of gypsum nuclei [7]. The high specific-surface area of *plaster* particles plays a major role in the multiplication of inter-granular links. Interaction between plaster particles occurs by *electrostatic forces* and attractive forces (*Van der Waals*) responsible for *adhesion*. Furthermore, adhesion is described as the formation of two $\text{Ca}^{2+}/\text{SO}_4^{2-}$ layers bound together by ionic interaction, constructing a growth slice [7]. The predominance of reactive sites on the grains attracts cations which form a rigid network that surrounds the layer of adsorbed water molecules. It is also known that the attraction of plaster particles requires cohesion between atoms to form the contiguous flakes. The development of this agglomerated structure depends on the amount of hydration water. According to the stoichiometry, the α -hemihydrates require a W/P ratio higher than 0.186 to be transformed into gypsum. To improve the consistency of the blends, the hydration rate was chosen from a range of 0.4 to 1.4. The apparent viscosities of W/G blends are lower than those of W/P blends. This can be explained by hydration and surface interaction. The difference observed in specific-surface area may provide an explanation.

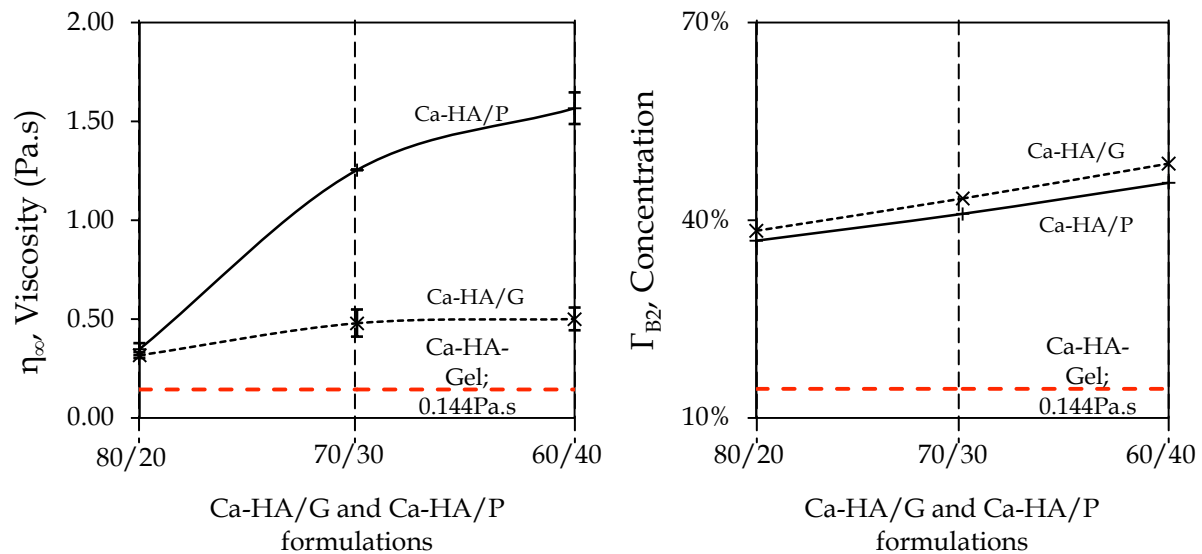


Figure 4: Viscosity of Ca-HA/G and Ca-HA/P formulations

Figure 4 shows that the viscosity increases when the solids concentration (Γ_{B2}) increases, the latter being calculated relative to the water (by wt%) present in the $\text{Ca-HA}_{\text{Gel}}$. The water content in Ca-HA is enough to hydrate plaster particles. Replacing 20% of $\text{Ca-HA}_{\text{Gel}}$ by gypsum or plaster produced little influence on viscosity. As regards the already-hydrated gypsum particles, increasing the gypsum concentration in the blend up to 40% produced a slight increase in viscosity. The addition of plaster to Ca-HA requires a high stress to cause the flow. Plaster particles in contact with Ca-HA water cause plaster hydration, creating strong bonds that encompass the Ca-HA particles and make the flow of the blend difficult. Hydrated plaster strongly increases the viscosity of $\text{Ca-HA}_{\text{Gel}}$ by its own weight. Blends containing more than 40% of gypsum are almost solids.

3.3. INTERACTION BETWEEN PARTICLES

Figure 5 shows that the Ca-HA particles are characterized by a negative ζ -potential, indicating that these particles are positively charged ($\approx -20\text{mV}$) [8], while the gypsum particles are negatively charged ($\approx 20\text{mV}$) [9]. The Ca-HA ζ -potential value indicates the instability of the gelled particles. Adding gypsum to Ca-HA leads to charge modification. High ζ -potential values prevent the presence of repulsive forces and indicate colloidal dispersion. However, sulfate adsorption changed the charge distribution, generating the change from positive to negative charge. The adsorbed amount of anionic sulfate on Ca-HA particles is equal to the Ca-HA electrically charged sites, and the coating of gypsum sulfate Ca-HA particles is the main reason for the modification of ζ -potential. The surfaces of the plaster particles are characterized by a positive charge, and hydration changes the surface charge to negative. The formation of a plaster solid body is explained by the cohesion between particles and is illustrated by a low ζ -potential value.

With the increase in the amount of plaster, the ζ -potential remains constant (with similar values to the plaster at the beginning of the hydration process), while the surface charge of Ca-HA changes. The nucleation process of hemihydrated particles starts by the formation of $\text{Ca}^{2+}/\text{SO}_4^{2-}$ bound double layers, and the concentration of sulfate decreases, indicating that it is consumed during the hydration. However, the fixation of the remaining sulfate in solution on the Ca-HA surface leads to the change in the charge.

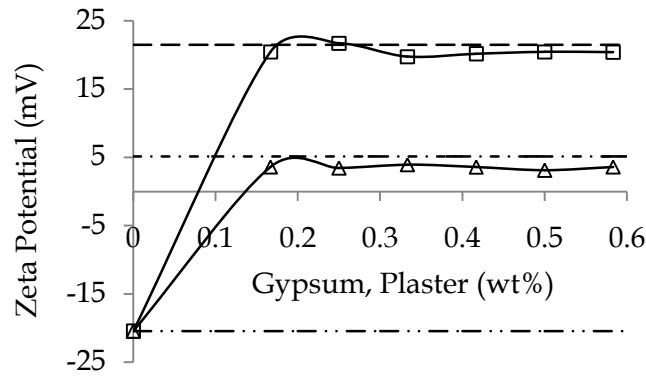


Figure 5: Zeta potential of Ca-HA/(G) and Ca-HA/(P) formulations without added water (— ζ -potential of gypsum (≈ 20 mv), -.- ζ -potential of plaster (≈ 5 mv), ζ -potential of Ca-HA (≈ -20 mv), —□— ζ -potential of Ca-HA /G formulations, —Δ— ζ -potential of Ca-HA /P formulations)

3.4. HYDRAULIC PERFORMANCE

3.4.1. POROSITY AND PERMEABILITY

The porosity was calculated by evaluating the compactness of formulations. The compactness Φ relationship is as follows:

$$\Phi = \frac{1}{1 + \rho_B \frac{W}{S}} \text{ with } \emptyset = 1 - \Phi \quad (7)$$

Where \emptyset is the porosity, ρ_B is the bulk density of the solid ($\text{g} \cdot \text{cm}^{-3}$), W is the Ca-HA_{Gel} water (g) and S is the total amount of solid (g). For binary blends, ρ_B is the weighted average of solid densities with $Y_{\text{Ca-HA}}$, Y_P and Y_G are the proportions of Ca-HA_{Powder}, plaster and gypsum in the blends respectively ($\rho_B = Y_{\text{Ca-HA}} \cdot \rho_{\text{Ca-HA}} + Y_P \cdot \rho_P$ or $\rho_B = Y_{\text{Ca-HA}} \cdot \rho_{\text{Ca-HA}} + Y_P \cdot \rho_G$ with $Y_{\text{Ca-HA}} + Y_P = 1$ and $Y_{\text{Ca-HA}} + Y_G = 1$). **Figure 6** shows the porosity values of Ca-HA/P and Ca-HA/G formulations.

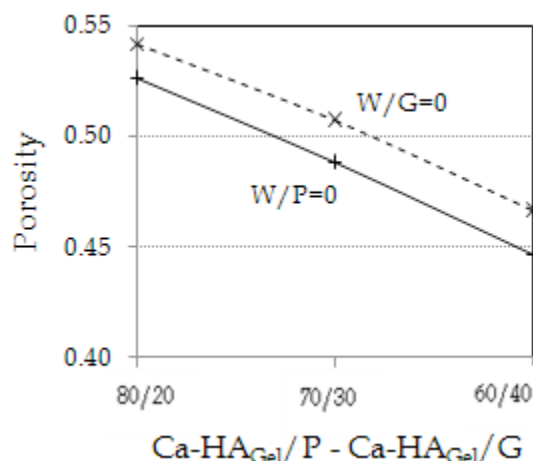


Table 3: Permeability values

| Sample | K ($\text{m} \cdot \text{s}^{-1}$) |
|-------------------------|--------------------------------------|
| Cell-calib | $4.00 \cdot 10^{-6}$ |
| G (<1mm) | $2.18 \cdot 10^{-6}$ |
| Plaster (cal.) | $1.00 \cdot 10^{-6}$ |
| Ca-HA _{Gel} | $5.00 \cdot 10^{-7}$ |
| Ca-HA _{Powder} | $7.00 \cdot 10^{-7}$ |
| 80%Ca-HA/20%G(<1mm) | $9.00 \cdot 10^{-7}$ |
| 70%Ca-HA/30%G(<1mm) | $3.00 \cdot 10^{-7}$ |
| 60%Ca-HA/40%G(<1mm) | $4.28 \cdot 10^{-6}$ |

Figure 6: Porosity of formulations containing Ca-HA_{Gel}, gypsum and plaster

Calculated porosity of formulations decreases by decreasing the amount of Ca-HA_{Gel}. The porosity of formulations containing Ca-HA_{Gel} and gypsum is higher than the porosity of Ca-

HA_{Gel}/P formulations. The dispersion effect plays a major role in the creation of porosity in the Ca-HA/G paste. The permeability of the gypsum particle ($d < 1\text{mm}$) bed allows good drainage, but the Ca-HA_{Gel} is impermeable (**Table 3**). There is no influence of gypsum on the permeability of Ca-HA_{Gel}. The permeability value increases by increasing the amount of gypsum in the Ca-HA_{Gel}/G formulations.

4. CONCLUSIONS

The negatively-charged gypsum particles cause the repulsion of particles (repulsive forces) and the viscosity of W/G (0.2–1.4) blends remains constant. Plaster is characterized by attractive forces and the particles are positively charged. The hydration of plaster leads to cohesion between particles, which explains the increase in viscosity of W/P blends compared to W/G blends. The ζ -potential of Ca-HA is negative and the dissolution of calcium-sulfate particles saturates the solution in sulfate ions (SO_4^{2-}); the charge of particles becomes positive, due to the fixation of SO_4^{2-} on the Ca-HA surface. The adsorption of sulfate on the Ca-HA particle surfaces influences the structure of the formulations and explains why the viscosity is independent of Ca-HA_{Gel} content. Plaster hydration plays a major role in the Ca-HA_{Gel} stabilization structure and gypsum particles enhance hydraulic performance.

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