Ink-jet printability of aqueous ceramic inks for digital decoration of ceramic tiles

Gülşen L. Güngör[a,b,*], Alpagut Kara[a,b], Davide Gardini[c], Magda Blosi[c], Michele Dondi[c], Chiara Zanelli[c]

[a]SAM, Ceramic Research Center, Anadolu University, Yunusemre Campus, ETGB Anadolu Sciencepark, No: 107-103, 26470, Eskişehir, TURKEY

[b]Department of Materials Science and Engineering, Anadolu University, Iki Eylül Campus, Eskişehir, 26555, TURKEY

[3]CNR-ISTEC, Institute of Science and Technology for Ceramics, Via Granarolo, 64 - 48018 Faenza, ITALY

*Corresponding author. Tel.: +90 222 323 82 76; fax: +90 222 322 29 43

E-mail address:glgungor@anadolu.edu.tr (G. L. Güngör)

Abstract

Digital decoration of ceramic tiles has turned to be a prevalent and dynamic technology in the last decade. Current printers use drop-on-demand (DOD) ink-jet print heads (IJP) fed with solvent-based inks containing ceramic pigments as coloring agents. However, due to environmental constraints, water-based systems are envisaged as a green alternative for ceramic tiles decoration. Nevertheless, aqueous suspensions are difficult to be managed because physical properties of water are far away from the DOD-IJP operating window. Thus, the control on the stability, homogeneity and rheology of such water-based systems is an important factor to achieve better product performances. This study was aimed at exploring both the rheological behavior and stability of three inks based on micronized pigments dispersed in water and water-MEG solutions: $(V,Zr)SiO_4$ (turquoise zircon, TZ), $(Cr,Sb)TiO_2$ (orange rutile, OR) and $(Co,Mn)(Fe,Cr)_2O_4$ (black spinel, BS). The pigments were ground to submicronic size in water using a circulation type agitator mill and by changing the main parameters affecting the particle-size distribution (rotation speed, type and amount of dispersants). The stability of aqueous pigment suspensions was studied by measuring the zeta potential as function of pH and by sedimentation tests. The zeta potential was sufficiently strong (lower than −30 mV) to render the inks stable in the 7-10 pH range. Rheological measurements of the suspensions showed a Newtonian flow behavior for zircon and rutile inks and slightly pseudoplastic for the spinel one. An attempt was also made to evaluate the inks printability with the help of dimensionless numbers based on the relevant physical and rheological properties affecting the jetting, i.e. viscosity, surface tension and density. It was observed that the ground aqueous systems fall in the printable fluid region obtained with semi-empirical models.

Keywords: aqueous inks, ceramic pigments, digital decoration, ink stability

1. Introduction

Ink-jet printing is an emerging technology with many applications being explored [1]. The growth of digital decoration in ceramic tile production is proceeding at breakneck speed towards a saturation of manufacturing lines [2]. Ceramic tiles are printed by the drop-on-demand method, which is the most commonly used technique in modern industrial applications. It deposits precise quantities of functional inks (in the form of 6 to 80 pL droplets) on the green tile surface by applying a short pressure pulse through a nozzle which is typically 20-50 μm in diameter. Under suitable conditions, the fluid is ejected into a single droplet for high quality ink-jetting [1].

The ceramic inks are normally dispersed in non-aqueous media; however, the preparation of suspensions of ceramic powders in aqueous media represents a desirable advancement for handling, safety and the environment [3]. In addition, the legislation in many countries is forcing the ink-making industry to reduce the level of volatile organic solvents as well as solventborne additives used to adjust the chemical and physical properties of ceramic inks [4].

Both solvent and water-based inks have basically the same components: colorant (pigment for ceramic decoration), vehicles (the so called "solvent" and "co-solvent"), and additives. The difference between the two systems lies mainly in the pigment dispersion mechanism, as all these inks are designed to work in the DOD-IJP operating conditions. Solvent-based systems can show a wide range of physical properties (being shear viscosity and surface tension the most important) and dispersion mechanisms, which are easily reversible and controlled by vehicle blends and proper additives designed to achieve a steric stabilization of the colloidal system (using in particular block co-polymers) [5]. The ink formulations are set up for modulating the proper viscosity and surface tension as requested by DOD ink-jet printers. The dispersion mechanisms are quite different with water-based inks, whose colloidal stability is firstly pursued by an electrostatic approach (achieving a sufficiently high zeta potential acting on the pH and using proper additives) [6]. In addition, hybrid systems are also used in ceramic tile decoration: these inks contain water (usually from 5% to 60% of the total amount of carrier) together with water-soluble or easily miscible solvents (e.g., alcohols and glycols) [5].

Ceramic pigments are currently micronized down to a mean particle diameter around 0.3 μm in order to prevent clogging of print heads [13-14]. However, micronization causes a strong increase in the specific surface area of pigments, with the drawback of a high tendency of particles to agglomerate. Therefore, the main concern is to ensure the colloidal stability of inks after grinding. For this purpose, the pigment dispersion is stabilized by proper additives, besides micronized pigment particles, once dispersed in the vehicle, are in continuous random movement due to collisions with the solvent molecules in thermal agitation (Brownian motion). As the particles collide or come very close, attractive forces pull the particles closer together. These intermolecular forces come from attractive dipole-dipole interactions known as van der Waals forces, or, in particular, London forces [7]. This is very often the cause of flocculation. In order to overcome the flocculation, the steric hindrance effect by polymer adsorption to the pigment has been usually studied [8].

The knowledge of the rheological behavior of suspensions is important to control their flow and to increase the solid volume content, keeping the desired fluidity, avoiding sedimentation and agglomeration phenomena [9]. The DOD-IJP technology imposes many constraints on the inks, which must fulfill requirements about viscosity and surface tension (to ensure the printability), suspension stability and pigment particle size (to avoid sedimentation and nozzle clogging), and solid load (to achieve the desired color strength) [10-11]. The requirements are 4-40 mPa.s for viscosity (best 4-10 mPa.s) and 20-45 mN/m for surface tension (best 25-35 mN/m). The pH has to be in the 5-10 range to prevent nozzle corrosion and the pigment solubility should be very low [11]. However, the physical characteristics of water (especially shear viscosity ~1 mPa.s and surface tension ~73 mN/m at room temperature) are far away from the above-mentioned DOD-IJP operating window [12].

The objective of this study is to explore the ink-jet printability and stability (colloidal and over time) of water-based ceramic inks containing different types of micronized pigments. The inks performance was assessed by measuring their physical and rheological properties (particle size, viscosity and surface tension) and testing their zeta potential and sedimentation rate in order to answer to the main questions about the potential use of water-based ceramic inks in place of solvent-based commercial counterparts.

2. Experimental

The pathway followed in the development of pigmented aqueous systems was firstly to micronize conventional pigments dispersed in water and secondly to assess the physical and rheological properties of aqueous suspensions (pigment particle size, density, surface tension and viscosity). Three industrial ceramic pigments were selected: turquoise zircon (TZ, V-doped $ZrSiO_4$), orange rutile (OR, Cr,Sb-doped TiO_2), and black spinel (BS, a Co-Cr-Fe-Mn oxide).

The pigment micronization process was carried out by a circulation type agitator bead mill (Labstar LS1, Netzsch, Germany) with a 30 wt.% solid loading of pigments in water and 0.3 mm bead size. The milling conditions were varied between 1000 and 3000 rpm for the rotation speed and between 30 and 120 min for the grinding time, in order to reach the target of around 0.3 µm in terms of median particle size (d_{50}). Two types of dispersants, added in the same amount (0.5 wt %), were used: Darvan C-N (DC), an ammonium salt of polymethacrylic acid (Vanderbilt, USA), and Dolapix G10 (DX) a sodium salt of a polycarboxylic acid (Zschimmer and Schwarz, Germany). Particle size distribution was determined by laser diffraction (Mastersizer 2000, Malvern, UK).

Rheological properties were measured at 25°C with a rotational rheometer (Gemini 2000, Malvern Bohlin, UK), the surface tension was measured with a tensiometer (K100, Krüss, Germany), and the density with a liquid picnometer. Suspension stability over time was studied by measuring the zeta potential dependence on pH, by observing the sedimentation behavior for different grinding times (15, 30, 60, 90, and 120 min) and by evaluating the effect of different dispersants on such behaviour. Zeta potential was measured with Zetasizer Nano ZS (Malvern, UK).

In order to increase the viscosity of inks, with the aim to improve the ink performances, 10 wt.% and 20 wt.% of monoethylene glycol (MEG) were added to the water-pigment systems and the viscosity and zeta potentials were measured.

3. Results and Discussion

3.1. Grinding effect

The particle size distribution of micronized pigments varies according to both intrinsic properties of each pigment and milling conditions. Figure 1 shows the particle size distribution assessed for the inks obtained grinding at 3000 rpm for 2 h in presence of 0.5 wt. % of DC dispersant. The grinding process gave rise to a monomodal particle size distribution for TZ and OR inks and bimodal particle size distribution with a coarser tail for BS ink in the case of more intensive milling conditions. Bimodal distribution is probably due to agglomeration phenomena. The new surface area created by comminution increases linearly with milling time, but different trends in the increase in specific surface area were seen as a function of median particle size, indicative of complex changes in particle size and shape as confirmed by the pigments' microstructure, that were illustrated in the first two parts of this study [13,14]. The particle size data for the three pigments achieved in different experimental conditions are reported in Table 1. Grinding process affected each pigment in a different manner. When comparing particle sizes before grinding and grinding under 2000 rpm, a significant change was observed for TZ pigment while BS pigment could not be ground effectively. After using a dispersant, particle sizes of all three pigments were decreased due to having more stabilized surfaces. But DX did not change particle size of BS pigment as significant as the others. Increase of rotation speed with using 0.5 wt.% DC caused coarsening of d99 value due to agglomeration and creation of new surfaces. It would be helpful to study the amount of the dispersant in detail.

3.2. Rheological behavior

The rheological properties of colloidal suspensions depend on the microstructure that is determined by interparticle interactions, Brownian motion, and viscous forces acting on the suspension. [15]. Flow curves of TZ, OR and BS suspensions are shown in Figure 2. The rheological behavior of the TZ and OR suspensions is Newtonian with viscosities of about 24 and 6 mPa s, respectively, while the BS ink exhibits a slight pseudoplastic flow with viscosities ranging from about 110 to 80 mPa s when the shear rate passes from about 60 to 100 s^{-1} indicating the possible formation of agglomerates. Although the viscosities for TZ and OR inks are inside the range indicated as optimal for ink-jet printing (4-40 mPa s) higher viscosities could avoid secondary phenomenon like sedimentation and dripping from the nozzles. Therefore it was investigated also the effect of the addition to the three inks grinded at 3000 rpm for 2 hours of 10 and 20 wt. % of monoethylene glycol (MEG) used as rheological modifier. The replacement of part of water with a more viscous medium should increase the viscosity of the final system.

However, the viscosity of the TZ suspension decreased with the MEG addition (more with the 10 wt. % addition than with the 20 wt. %), turning into a more

Newtonian flow behavior that may be convenient in the printing process (Fig. 3). This effect could be explained supposing that the expected increase of viscosity imposed by the addition of 10 wt. % of MEG is overcome by the viscosity decrease arising from the destruction of the weak microstructure presents in the TZ ink The further MEG addition to the system with the microstructure completely breakdown increases the viscosity simply because to the higher viscosity of MEG (about 16 mPa s at 25°C).

Unlike TZ ink, the the OR suspension, initially without any microstructure, shows a progressive increase of viscosity (from about 6 to 18 mPa s) with the concentration of MEG added and the formation of a weak microstructure (Fig. 4).

The addition of 10 wt. % of MEG to the BS suspension, however, seems to provoke a gelation with an increase of viscosity of about 20 mPa s. On the other hand, the addition of 20 wt. % of MEG bring back the viscosity to values comparable with the BS ink without MEG as if the excess of MEG would induce a partial rupture of the structure.

3.3. Ink Jettability

It is crucial to tailor the ink properties (surface tension, viscosity, and density) to the specific demand of the DOD-IJP system in order to obtain a proper jettability, which affects the image quality and to some extent the color strength too. However, the final quality of the image will also depend on other basic issues: the firing process (which is able to change the color coordinates) and the ink addressability, which is function of several variables (jetting frequency, drop volume, ink solid load, native printing resolution, and velocity of tiles along the decoration line).

For the three water-based inks prepared by micronizing the pigments at 30 wt. % solid loading, at 3000 rpm for 2 hours and 0.5 wt. % of dispersant DC, surface tension, viscosity and density were measured (Table 2). Surface tension values fit the DOD-IJP requirement (20-45 mN/m) except for the BS ink, that presents a slightly lower value (about 14 mN/m).

On the basis of semi-empirical models related with the occurrence of the main phenomena involved in ink-jet printing (drop formation, possible presence of satellite drops and drop splashing during impact) a printable fluid region of reference was individuated in the literature. Such a region can be visualized in a diagram in the space of the two most representative dimensionless numbers for such phenomenon, like Reynolds and Ohnesorge [12]. The Reynolds (*Re*) number is the ratio of inertial to the viscous forces:

$$Re = \frac{\rho v d}{\eta} ,$$

while the Ohnesorge number (*Oh*) compares the viscous forces with the capillary and inertial ones:

$$Oh = \frac{\eta}{\sqrt{\rho \gamma d}} ,$$

where ρ, η, γ, d and v are the density, viscosity, surface tension, nozzle diameter and droplet velocity, respectively. Calculating the values of such dimensionless numbers for the three pigmented aqueous inks under investigation and assuming common values for the nozzle diameter (25 µm) and droplet velocity (6 m/s) in ink-jet ceramic digital printers, it was observed that the inks fall inside the region of printable fluid with DOD-IJP technology (Fig. 6).

3.4. Ink stability over time

3.4.1.. Effect of grinding time on ink stability. The magnitude of the zeta potential gives an indication of the colloidal stability of the ink. If the particles in suspension have a large negative or positive zeta potential, they will tend to repel each other contrasting the tendency of particles to agglomerate and leaving them well-dispersed. Commonly a suspension is considered stable if the particles have zeta potentials higher than +30 mV or lower than -30 mV [16]. In Figure 7, the change of zeta potential was illustrated for TZ, OR and BS inks ground under different conditions (except grinding time). Firstly, grinding without additives was performed to get the zeta potential blank values. Further trials were carried out on the inks ground in presence of the two different dispersants, or increasing the rotation speed or adding MEG as co-solvent. As a general trend, the zeta potential decreased with increasing rotation speed . This is thought to be due to the creation of new particles with an increase of the total surface area; such a circumstance implies the need of more dispersant. The MEG-bearing inks, including also DC, probably due to the chelant effect of the glycol, exhibit an enhanced colloidal stability, and the zeta potential value sharply increased to nearly -110 mV.

3.4.2. Effect of pH on ink stability. In aqueous media, the pH is one of the most important factors affecting the zeta potential. Typically, passing from acid to basic conditions a pH value at which the zeta potential becomes zero is found (so-called isoelectric point) and where the colloidal system is less stable [16]. Therefore, in order to obtain stable suspensions, it is necessary to work in regions far from the isoelectric point.

In aqueous systems, there are many cases in which the electrical double layer is more predominant than the polymer adsorption layer, because of its high dielectric constant. The use of proper dispersants is the effective procedure for dispersing the pigment, and is currently being studied in detail [17].

For the three inks ground under 3000 rpm rotation speed for two hours without additives, the zeta potential changes with pH are shown in Fig. 8. The TZ and OR inks have a slightly basic natural pH (about 8.2 and 7.2, respectively), while the BS ink is basic (pH 10). In these conditions, all the inks have zeta potentials lower than -30 mV (ranging from about -34 to -41 mV). By decreasing the pH, the stability of the systems is deteriorated (especially for the BS ink), but the zeta potential remains in the stability range until pH 6 (for BS ink becomes -24 mV). Therefore, the range of pH 6-10 can be considered a working window for the inks, taking also into account that it is comprised within the known interval to prevent the corrosion of nozzles [18].

3.4.3. Effect of dispersants on ink stability. Two different dispersants were used: Darvan C-N (DC), which is a type of ammonium polymetacrylate, and Dolapix G10 (DX), which is a sodium salt of a polycarboxylic acid. The zeta potential values of the three inks ground at 2000 rpm for 1 h were given in Table 3. No significant change was observed with the dispersant type, although it was expected an increasing of zeta potential and therefore of the stability of the system. In any case, this observation is consistent with previous studies [19] where the effect of polyacrylate on zeta potential of $ZrSiO_4$ with the change of pH was investigated. As expected, the addition of negative charged dispersants in a certain amount, increase the already negative zeta potential , so improving the stability of the suspension.

3.4.4. Effect of grinding speed on ink stability. In order to see the effect of grinding speed by changing the rotation cycle, current inks were ground for one hour and with no additives under two different rotation speeds i.e. 2000 rpm and 3000 rpm (Table 4). The rotation speed increment affects the particle size distribution, in fact the increment of the rotation speed decreased the zeta potential for OR inks which means a deterioration of colloidal stabilityThis effect, similarly to the effect of grinding time, can be due to the new surface creation and the need of further dispersant, dissolution of the ions or the phase changes during grinding due to plastic deformation on the particles. On the other hand, different trends were observed for the TZ and BS inks. Change of zeta potential range was wider for the TZ suspensions which may be an indicator of finer particle size population and higher free surface area with more uniform adsorption of dispersant to the surface. For the BS ink, zeta potential did not change.

3.5. Effect of grinding time by sedimentation tests

The sedimentation behavior after one month for the TZ ink ground at 3000 rpm for 15 min in presence of 0.5 wt. % of DC (vial 1) shows dense sediment at the bottom of the vial and a turbid and not clear supernatant on the top (Fig. 9). In Figs. 9-11, on the right of each vial a sketch illustrating the heights of the different interfaces are reported for clarity. By increasing the grinding time up to 2 hours, the height of the sediment increases (vials 4 and 5). This can be explained by the fact that a longer grinding makes the particles finer enhancing the flocculation phenomena. A short grinding (vial 1) gave compact sediment, but with respect to the other samples more particles were kept in suspension, as the turbid and not clear supernatant shown. A close packed sediment together with a colored supernatant means that the dispersant screens well both the large and the small particles, and the latter, due to their small sizes, remain suspended improving the stability over time. In order to match the requirements to have sufficient stability over time, a compromise between a good colloidal stability preventing large agglomerates and easy redispersibility of the sediment has to be found [20]. The TZ ink ground for 15 min possibly represents a good choice since, although its colloidal stability is lower than the others, it allows to keep the particles in suspension for a longer time and to easily redisperse the sediment.

The same sedimentation tests were made for the OR ink (Fig. 10) and similar considerations can be done, but the sediment height was higher than that of the TZ suspension due to a finer particle fraction (Table 1).

Instead BS ink shows an irregular sedimentation behavior, connected with its higher viscosity and bimodal particle size distribution, that may lead to incipient gelation (Fig. 11).

A cluster of particles, having a larger radius, will have a faster sedimentation in a given applied field when compared to that of a single particle. However, if the clustering process is reversible a cluster may disagglomerate to form smaller clusters or particles. Diffusion of particles and clusters is also important during the sedimentation process. As sedimentation proceeds, the solids concentration in the lower region of a sedimentation column is higher than that in the top. There is, in analogy with the better-known diffusion process involving solutes, a driving force for particles and clusters to move against the concentration gradient (i.e, upward the sedimentation column). As a result, there is an impetus for particles or clusters to resist sedimentation [21].

4. Conclusions

The requirements of aqueous inks for digital decoration of ceramic tiles were appraised in terms of rheological and physical properties. It was possible to obtain inks having properties within the jettability range and proper colloidal stability (zeta potential below -30 mV with basic pH) for all the micronized pigment systems (zircon, rutile and spinel). The pigment loading (30 wt%) and the correction by a second vehicle (MEG) made the ink viscosity one order of magnitude higher than water (for TZ and OR) and, at the same time, dropped the surface tension in different maounts for each ink systems.. However, a different rheological behavior was found for zircon and rutile inks on one side and for the spinel ink on the other side. The former two behave as Newtonian fluids, while the latter exhibits a pseudoplastic behavior, being also affected by higher viscosity with clue of incipient gelation phenomena.

The colloidal stability was deteriorated in acid pH and for prolonged milling, since in both cases the zeta potential increased. An increase of the dispersant amount was beneficial to keep zeta potential below –30 mV during milling. The use of a dispersant increased the suspension stability, while changing the dispersant type had no significant difference in terms of zeta potential.

5. Acknowledgement

We would like to thank the National Research Council of Italy (CNR) and the Scientific and Technological Research Council of Turkey (TUBİTAK), on behalf of the joint cooperation program, under the contract number 111M773 and title “Water based inks for ceramic tile decoration by inkjet printing”, between the Department of Materials Science and Engineering of Anadolu University and the Institute of Science and Technology for Ceramics (CNR-ISTEC). Authors are also grateful to Ceramic Research Centre (SAM) for the financial and technical support.

6. References

[1] D. Jang, D. Kim, J. Moon, “Influence of fluid physical properties on inkjet printability” Langmuir, 2009, 25, 2629-2635

[2] G. P. Crasta, “Boom in digital technology” Ceramic World Review No:92 (2012), pp.64
[3] S. Obata, H. Yokoyama, T. Oishi, M. Usui, “Preparation of aqueous pigment slurry for decorating whiteware by ink jet printing” Journal of Materials Science 39 (2004) 2581 – 2584
[4] H.J.W. van den Haak, L.L.M. Krutzer, “Design of pigment dispersants for high-solids paint systems” Progress in Organic Coatings 43 (2001) 56–63
[5] S. Utschig, “Question:Why can the transition from alcohol to water based inks be so difficult?” Converting Magazine, Sept. 1998, 16, 9, pg.40
[6] D. Gardini, M. Dondi, A.L. Costa, F. Matteucci, M. Blosi, C. Galassi, G. Baldi, E. Cinotti, Nano-sized ceramic inks for drop-on-demand ink-jet printing in quadricromy. Journal of Nanoscience and Nanotechnology, 8 [4] (2008) 1979-1988
[7] L. W. McKeen, “Pigments, fillers and extenders” Fluorinated Coatings and Finishes Handbook, (2006), Pages 59-76
[8] T. Fujitani, “Stability of pigment and resin dispersions in waterborne paint” Progress in Organic Coatings 29 (1996) 97-105
[9] Z. Zhou, P. J. Scales, D. V. Boger, “Chemical and physical control of the rheology of concentrated metal oxide suspensions” Chemical Engineering Science 56 (2001) 2901-2920
[10] F. Matteucci, G. Baldi, D. Gardini, M. Blosi, E. Cinotti, M. Dondi, A.L. Costa, C. Galassi, “New nano-sized ceramic inks can provide good reproducibility and high color saturation on ceramic tile” Ceramic Industry, Oct. 2006, 156, 10, pp.20-21
[11] M. Dondi, M. Blosi, D. Gardini, C. Zanelli, “Ceramic Pigments For Digital Decoration Inks: An Overview”, Qualicer 2012
[12] Gardini D., Blosi M., Zanelli C., Dondi M., Ceramic Ink-Jet Printing for Digital Decoration: Physical Constraints for Ink Design. Journal of Nanoscience and Nanotechnology, 15 (2015) 3552-3561.
[13] G. L. Güngör, A. Kara, M. Blosi, D. Gardini, G. Guarini, C. Zanelli, M. Dondi, "Micronizing ceramic pigments for inkjet printing:Part 1.Grindability and particle size distribution" Ceramics International, Vol. 41, Issue 5, Part A, June 2015, pp. 6498-6506
[14] C. Zanelli, G. L. Güngör, A. Kara, M. Blosi, D. Gardini, G. Guarini, M. Dondi, "Micronizing ceramic pigments for inkjet printing:Part 2.Effect on phase composition and colour" Ceramics International, Vol. 41, Issue 5, Part A, June 2015, pp.6507-6517
[15] L. Bergström, “Shear thinning and shear thickening of concentrated ceramic Suspensions” Colloids and Surfaces A: Physichochemical and Engineering Aspects 133 (1998) 151-155
[16] Zeta potential. An introduction in 30 minutes, Malvern Instruments (http://www3.nd.edu/~rroeder/ame60647/slides/zeta.pdf)
[17] M. Roessner, R. Escámez, “Stabilisation of pigments in digital inkjet printing inks by wetting and dispersing additives based on new polymerisation technologies”. Proceedings of the 14th World Congress on Ceramic Tile Quality, QUALICER 2014, Castellón (Spain)
[18] R. Greenwood, “Review of the measurement of zeta potentials in concentrated aqueous suspensions using electroacoustics” Advances in Colloid and Interface Science 106 (2003) 55–81

[19] M. Dondi, M. Blosi, D. Gardini, C. Zanelli, P. Zannini, “Ink technology for digital decoration of ceramic tiles: an overview”, Proceedings of the 14th World Congress on Ceramic Tile Quality, QUALICER 2014, Castellón (Spain).
[20] L. B. Garrido, E. F. Aglietti, “Zircon based ceramics by colloidal processing” Ceramics International 27 (2001) 491-499
[21] J. S. Abel, G. C. Stangle, “Sedimentation in flocculating colloidal suspensions” J. Mater. Res., Vol. 9, No. 2, Feb 1994, 451-461