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Humic Acid as Dispersant of an Alumina Suspension and its Rheological Behaviour

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Humic acid was extracted and employed as a dispersant in an alumina suspension. The higher zeta potential for HA (-42 mV) was measured at pH 11 showing that an electrostatic repulsion might occur in the alumina/HA suspension. As a consequence of the long chain molecules of HA it was also expected a steric effect on deflocculation. The best dispersion conditions for the alumina suspension (28 vol%) were found with 0.016 wt% HA, close to the viscosity achieved with a commercial sodium polyacrylate. The rheological characterisation showed results beneficial for the slip casting process, such as slightly thixotropy and pseudoplastic behaviour. The excellent colloidal stability at pH 11 as evidenced through rheological and sedimentation tests was attributed to the polyelectrolyte nature of the HA. From deflocculated suspensions it was possible to obtain high density pieces by slip casting method.

Keywords: *humic acid, dispersant, alumina suspension, rheological behaviour, stability.*

1. Introduction

Alumina suspensions are widely used for component production in the ceramic industry. The properties of alumina such as high mechanical strength, resistance to thermal shock, resistance to wear, non-oxidizability and low thermal conductivity have motivated the studies in this area, including alumina composites with other metallic oxides in order to further improve some of these properties[1-3].

Due to the high solids content in a suspension and the generally submicrometric size of the alumina powder, the contact between suspended particles occurs frequently and the Van der Waals attractive forces determine the interaction and formation of agglomerates. The use of dispersants plays a key role in preventing agglomeration by increasing the interparticle repulsion while maintaining colloidal stability. In concentrated aqueous suspensions of alumina, the most commonly used dispersants belong to the class of the (poly) acrylic and methacrylic acid salts. The surface properties and size of the molecular chain determine that these polyelectrolytes act by the electrosteric dispersion mechanism[4]. The common feature of polyelectrolytes is the presence of more than one ionisable surface group[5].

The chemical nature of humic acid (HA) renders it a polyelectrolyte dispersant[6]. The surface properties of HA and its ability to complex metal ions make it attractive to a number of applications such as agriculture, remediation of pollution in soil and water, in the pharmaceutical and cosmetics industry, among others[7]. Like other more common polyelectrolytes, the high density of negative charges in HA occurs in alkaline medium, in which it acquires a fully extended molecular conformation maximising the steric effect. According to these properties, the HA molecules present great potential in the stabilisation of ceramic suspensions, probably acting through the electrosteric mechanism.

The interaction of the humic molecule with different metals and metal oxides, including alumina, has been studied by several authors[8-11]. Several interfacial processes in solution are common to polyacrylic and humic acids dissolved in aqueous solutions or adsorbed onto alumina particles[6]. It should be noted that none of these authors worked with concentrated ceramic suspensions.

The interaction of polyelectrolytes with alumina particles and factors such as pH, ionic strength of the medium and solids concentration interfere with the stability of the suspension[4,12-14]. For this reason, the investigation of the rheological behaviour of alumina suspensions is essential in colloidal processing since rheological parameters directly influence the casting rate and quality of the formed bodies. Stable suspensions with well dispersed particles and good packaging generate a high density structure in these pieces[15].

There is no ideal dispersant for all wet ceramic process[16]. Currently, dispersants derived from carboxylic acids dominate the market and citric acid has also been widely utilised. Recently, humic acid was utilised as dispersant and film forming agent to various materials by electrophoretic deposition (EPD)[11]. The utilisation of humic acid as single dispersant in concentrated ceramic suspensions as presented herein has not yet been reported in the current literature. The low cost to obtain the subbituminous coal (US$ 10/ton) and the good yield of HA from coal[17] represents a relative easy way of manufacture and excellent potential for use as a ceramic dispersant. The objective of this work was to study the use of HA as dispersant in a submicrometric alumina suspension. Alumina was selected as the most studied material with a large body of data available for comparison

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of results. Nonetheless, HA also has the potential to be a good dispersant for many ceramic powders. The rheological behaviour of the suspensions was analysed by characterising the viscosity curves and the stabilisation of the suspensions. This study provides new data in the literature on the behaviour of suspensions entirely dispersed by humic substances.

2. Experimental

Humic acid (HA) was obtained from a low-cost subbituminous coal by alkaline extraction. In this method, the coal was mixed with alkaline solution and stirred until the solubilisation of the humic acids. The supernatant was separated and acidified then allowing the obtaining of HA since they are insoluble in acidic medium. The precipitate containing the HA was purified, double-washed, dried and stocked to be used as a dispersant. The complete method of extraction can be found elsewhere[17]. The elemental analysis of HA showed the following contents: C: 68.79%, O: 23.64% and H: 5.29% (Elementar Vario Macro analyzer), which are in agreement with the presence of carboxylic and phenolic groups as determinated by FTIR analisys (Shimadzu IRAffinity-1). The essential properties of HA were investigated[17] and are summirised on Table 1.

A commercial submicrometric alumina was used (CT-3000 SG, Almatis, USA), with a purity of 99.78%; specific area of 10.66 $m^2\,g^{-1}$; D90% < 3.0 μm and density of 3.90 g cm^{-3}. The main phase present is α-alumina (JCPDS 00-042-1468).

The zeta potential measurement was performed for a diluted suspension (0.01 wt%) of pure alumina, and for an alumina suspension containing 0.1 wt% of HA (referred to as HA-suspension) (Zetasizer Nano Z, Malvern, UK). A KNO_3 10^{-3}M solution was used to maintain the ionic strength and from this starting solution the aliquots were acidified or alkalinised with HCl or NaOH, respectively.

The alumina suspension was prepared with 28 vol% (60 wt%) solids in 0.02 M NaOH solution under constant mechanical stirring. Adjustment to pH 11 was achieved with 1M NaOH solution. After mixing, the suspension was homogenised in a ball mill for one hour. The humic acid was used as a dispersant by dissolving it in a 0.005 M NaOH solution (3 g L^{-1}).

Table 1. Properties of humic acid molecule

Zeta potential (pH 11)	-42 mV
Configuration on SEM (pH 11)	extended molecule
Turbidity at pH 11	minimum (<250 NTU)
Loss on ignition	95%
Decomposition temperature	Between 300 and 600 °C
Functionality	primarily carboxylic and phenolic groups
Yield of HA extraction	1.2 % based on the initial organic matter

The apparent viscosity of the suspension was measured in a viscometer (RVDV-II +, Brookfield, USA) equipped with small volume adapter (Spindle SC4-18). Viscosity was measured as the HA was added, obtaining the deflocculation curve. Commercial sodium polyacrylate (Reoflux HS/B, Lamberti, IT) at the same concentration (3 g L^{-1}) was used for comparison. The rheological behaviour of the deflocculated suspension (density of 1.77 g cm^{-3}) was determined in a viscometer (HBDV-II +, Brookfield, USA) with cone-plate geometry (Spindle CP-40). The viscosity curve was obtained by accelerating the viscometer to 750 s^{-1}. The reading was performed after 60 s at each shear rate. Apparent viscosity dependence with shear time was recorded for 1800 s at a shear rate of 75 s^{-1}. The sedimentation tests at pH 3,5 e 11 showed the settling behaviour of the suspensions. Particles in a well-defloculated suspension settle relatively slowly[18] and the interface between the supernatant and the sediment can be difficult to distinguish[19]. The suspensions were packed in polyethylene bottles, sealed to prevent evaporation of the water and kept in a sheltered place for sedimentation by gravity. The rheology of the suspension was followed by 336 hours at a constant shear rate (75 s^{-1}).

Alumina samples were conformed on a plaster mould. The as-cast samples were dried in air for 24 h and at a stove at 50 ºC for 48 h. The green bodies were first fired at 1100 ºC for 1 hour at 2.5 ºC min^{-1}. Sintering was performed at 1600 ºC for 1 hour at 5 ºC min^{-1}. Technical characterisation of the sintered alumina bodies was performed by the Archimedes method and by electron micrograph using a JSM 6060 scanning electron microscope (Jeol Ltda. Tokyo, Japan).

3. Results

3.1 Zeta potential and rheological behaviour of the suspensions

Figure 1 shows the effect of humic acid dispersant (HA) on the zeta-potential of the alumina suspension over a wide range of pH values. The alumina Isoelectric Point (IEP) or the point in which surficial charges cancel each other was next to pH 6.5. Above pH 6.5 the increase of negative zeta potential of HA-suspension can be seen quite clearly, when compared to the alumina-suspension (without HA). The zeta-potential was higher than -25 mV, which is necessary for the deflocculation of a colloidal slip due to double layer repulsion effect[18]. The HA-suspension reached a value of ~ -40 mV at pH 9-11. This maximum value was achieved as a consequence of the negative surface charges in both HA and oxide particles above the IEP[20]. Such negative charges repel each other thus allowing the electrostatic stabilisation to occur[18]. In addition, the extended conformation of the HA molecules in alkaline medium[20] can assure the physical hindrance to interparticle attraction in short-range as expected by the steric mechanism[21]. In moderated to concentrated

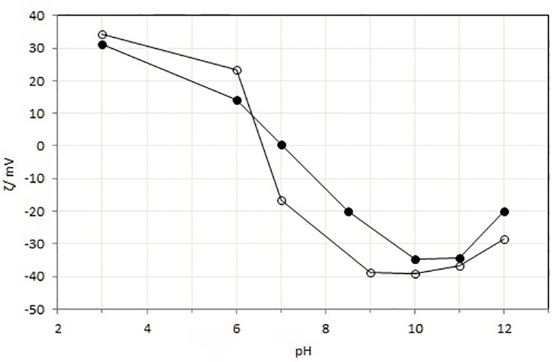

Figure 1. Zeta potential as a function of pH. Alumina-suspension (closed circles) and HA-suspension (open circles, 0.1 wt%). Each value corresponds to the average of three readings. The lines are just to guide the eyes.

systems, such as ceramic suspensions, especially those with high ionic strength, the steric effect is usually the most important to the deflocculation[9].

The high zeta potential of HA in alkaline medium as well as its extended conformation were the driving force to test HA as a dispersant in a colloidal alumina suspension. Using pH 11 as in this work, good dispersion stability can be expected since the specific adsorption is reduced[20] and the humic molecule has the potential to act by an electrosteric mechanism thus preventing the occurrence of agglomeration.

In fact, humic acid was effective to reduce the suspension viscosity as shown in the deflocculation curve (Figure 2). The addition of small amounts by weight of HA promoted a significant reduction in apparent viscosity in the suspension from 1680 mPa.s to ~ 600 mPa.s. The optimum amount of HA was 0.016 wt% relative to the dry weight of alumina, considering that a suspension is never deflocculated to the minimum in the viscosity curve[22]. In order to compare the results with a commercial deflocculant, a defloculation curve was performed with sodium polyacrylate under the same conditions. The apparent viscosity values achieved with sodium polyacrylate were lower than that found using humic acid as dispersant. Polyacrylate salts are a well-established and optimised electrosteric dispersants for alumina suspensions, with one carboxylic group per repetition unit in the structure[23]. Surfacial charges are the responsible for the great repulsion capability of the dispersant[16]. On the other hand HA has a complex and not totally understood structure. Previous characterisation showed carboxylic and phenolic groups in a heterogeneous matrix of aliphatic and aromatic portions[17]. Thus, this work shows the excellent performance of HA as dispersant achieving viscosities very close to that found using a well stablished dispersant (Figure 2). Furthermore, the drop in viscosity promoted by HA is desirable to slip casting process once one expects fluidity and high solids content to a good casting rate[12].

The use of HA as a dispersant in the alumina suspension promoted the reduction of shear stress in the range of applied shear rates studied, resulting in less resistance to flow when HA was present in the suspension, as showed in Figure 3. The breakage of weakly bound agglomerates with increasing shear rate results in an apparent viscosity reduction, which represents the pseudoplastic behaviour of the HA-suspension, as expected to ceramic suspensions [1,24]. The apparent viscosity changed from ~ 1000 mPa.s to ~ 300

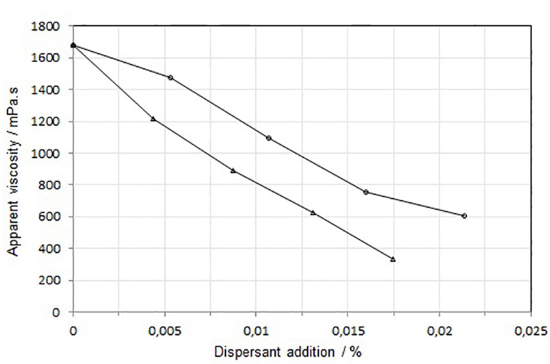

Figure 2. Apparent viscosity of alumina suspension (solid loading of 28 vol%, pH 11) as a function of HA (circles) or sodium polyacrylate (triangles) addition (solutions of 3 g L^{-1} each). Constant shear rate of 13.2 s^{-1}.

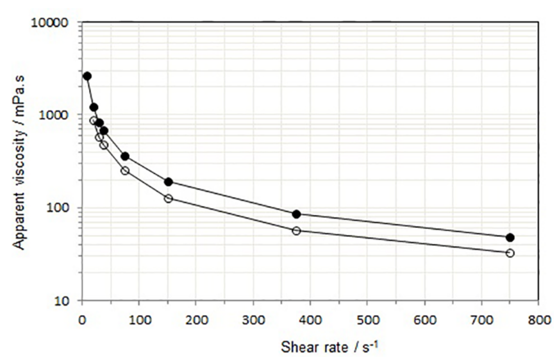

Figure 3. Apparent viscosity (in log scale) as a function of shear rate to an alumina-suspension (closed circles) and HA-suspension (open circles) with 0.016 wt% of HA.

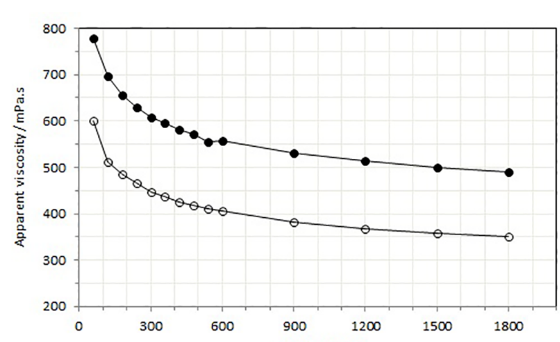

Figure 4. Apparent viscosity variation as a function of time to an alumina-suspension (closed circles) and HA-suspension (open circles) with 0.016 wt% of HA. Constant shear rate of 75 s^{-1} to a suspension after 48 hours of rest. pH 11.

mPa.s at low rates (<100 s^{-1}). Subsequently, it reached ~ 30 mPa.s at high shear rates (Figure 3).

The apparent viscosity variation with shear time represents the time dependency of the suspension, and was analysed at low shear rate (Figure 4) for a suspension that was allowed to stand for 48 h, the usual condition in the ceramic industry. Figure 4 shows a lower thixotropy for the HA-suspension. Suspensions with low thixotropy present small hysteresis in flow curves[24]. This character can be attributed to the weak flocculation force between oxide particles and the polyelectrolite molecules, which can be easily broken by the application of shear[21]. Such interaction is responsible for the presence of a yield point in the deflocculated suspension. A slight thixotropy, as shown here, is desired in the ceramic production, since it prevents rapid body formation during the casting process[23].

The behaviour of the deflocculated suspension with HA showed excellent properties for the slip casting process. Low viscosity at high shear rates is required for the pumping step during ceramic processing, while low thixotropy at low rates and low pseudoplastic behaviour are important to avoid the rapid sedimentation of the particles, thus benefiting the casting process[24].

The HA-suspension reached a viscosity 200 mPa.s lower than the alumina-suspension throughout the curve. Less than 600 seconds were required for the apparent viscosity values to decrease from ~ 600 mPa.s to ~ 400 mPa.s. After this time, the apparent viscosity hardly changed at a constant shear rate probably indicating that a gel structure was broken and the system reached equilibrium (Figure 4). The stabilisation of the suspension was also verified in the rheological behaviour after rest, confirming the effectiveness of deflocculation using HA (Figure 5). Apparent viscosity was low to HA-suspension even at 336 hours of rest. After 168 hours (one week) at rest the apparent viscosity was <600 mPa.s.

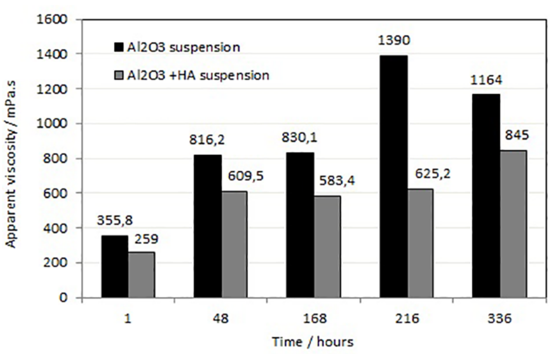

Figure 5. Apparent viscosity variation as a function of rest time. Constant shear rate of 75 s^{-1}. pH 11.

3.2 Sedimentation behaviour of the HA-Suspension with pH

Sedimentation tests were performed on different HA-suspensions with the optimum amount of dispersant at pH 11 and pH 3.5, the two extremes of the zeta potential curve (Figure 1). Figure 6 shows the behaviour of the suspensions upon standing. Humic acid promoted the deflocculation of the alumina suspension at pH 11, maintaining a higher dispersion volume even after one week at rest. On the other hand, the suspension at pH 3.5 rapidly initiated sedimentation, leaving a clear supernatant and reducing the dispersion volume (Figure 6). The instability of this suspension can be attributed to the rapid agglomeration of the particles, thus resulting in a lower dispersion volume[14].

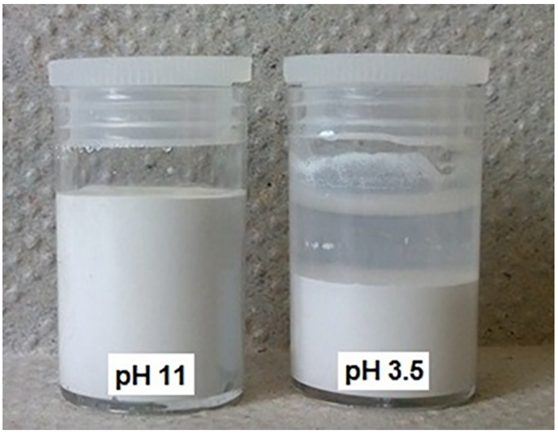

Figure 6. Sedimentation tests of alumina suspension defloculated with HA in alkaline (left) and acidic medium (right). One week at rest.

3.3 Technical characterisation of the formed bodies

Concerning the study of rheological behaviour of the alumina suspension deflocculated with humic acid and its stability, it was possible to process ceramic bodies by slip casting method in a plaster mold (Figure 7). Figure 8 shows a homogeneous packing of the sintered body and a dense grain compacts formation with grain sizes ranging from small (~1 µm) to large (>3 µm). Technical properties of the casted using HA as dispersant are showed on Table 2.

Figure 7. Conformed body after sintering up to 1600 ºC.

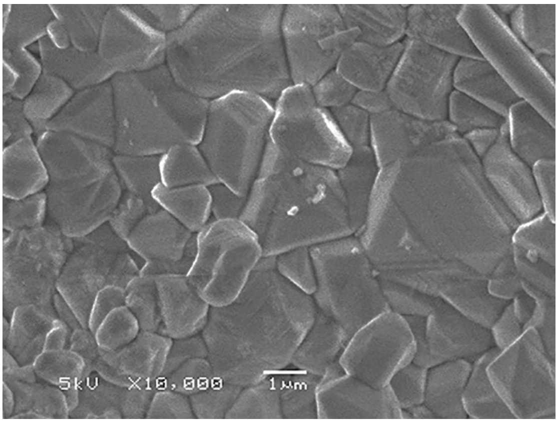

Figure 8. Scanning electron micrograph of sintered body.

Table 2. Technical properties of the casted bodies.

	Weight loss (%)
Stove dried at 50 °C	22
Fired at 1100 °C	0.5
Sintered at 1600 °C	0.25
Total	22.75
Properties of sintered body	
WA[1](%)	0.27
AP[2](%)	1.05
D[3](% of theoretical)	98.7
Wall thikness[4](mm)	~3.5
Linear retraction (%)	~18.5

1Water absorption;

2Apparent porosity;

3Density;

4Wall thickness measured after a casting time of 4 minutes.

4. Discussion

The study of the rheology of alumina suspensions showed that the humic acid dispersant provides excellent results from a technological point of view. These are shown in the curves studied:

Zeta potential (Figure 1): -40 mV at pH 11.

Viscosity as a function of wt% HA (Figure 2): minimum viscosity ~ 600 mPa.s. at 0.016 wt% HA. Furthermore, HA can easily compete with sodium polyacrylate since the viscosity values from both were very similar.

Viscosity as a function of shear rate (Figure 3): pseudoplastic behaviour and low resistance to flow;

Apparent viscosity variation as a function of time at constant shear rate (Figure 4): low thixotropy, equilibrium reached after 600 seconds in low shear rate;

Apparent viscosity variation as a function of rest time (Figure 5) and sedimentation tests of HA-suspension (Figure 6): low apparent viscosity after one week at rest (< 600 mPa.s), suspension stability and high dispersion volume at pH 11.

At pH 11, zeta potential of HA-suspension (Figure 1) is high due to the presence of negative surficial charges in both alumina particles and HA that repels each other. The coupling of the electrostatic mechanism with the extended conformation assumed by the HA molecule (maximum steric effect) makes it suitable for the stabilisation of the alumina suspension, with great resistance to sedimentation in the studied rest time (Figure 6). Such high dispersion volume in the suspension may be a result of a complete adsorption layer around the oxide[25]. Besides, at this pH the high affinity adsorption is reduced, so that there are only weakly bound agglomerates, as shown by the low thixotropy. The bridging effect appears not to occur as would be expected for high molecular weight polyelectrolytes[4]. Furthermore, the rheology of the suspension after long standing time showed little variation in apparent viscosity even after two weeks of rest (Figure 5). The pH is essential to obtain a stable alumina suspension, since it is decisive for the interaction between the polyelectrolytes and the oxide surface, along with other factors, as shown in the literature[9,13].

The addition of NaOH to reach pH 11 increases the ionic strength of the suspension and consequently reduces the Debye length. However, at this pH the HA molecules are in an extended conformation[16] in which steric repulsion can operate. The efficiency of the electrosteric mechanism in an alumina suspension with polyelectrolytes was postulated by Tari et al.[12]. According to the authors, the reduction of the average distance between the suspended particles acts until the steric forces become active thus preventing the contact between them, keeping the system at the secondary minimum of energy and providing a stable physical barrier to coagulation.

The rheological behaviour showed that the suspension was properly deflocculated with HA without evidence of tangling or bridging effect between the HA molecules. In concentrated systems, the bridging effect can occur due to polyelectrolyte concentration and ionic strength of the medium, by hydrogen bonding and electrostatic interactions between the positive sites on the particle and the anionic ones in the polyelectrolyte chain[4,13]. This fact renders the use of HA as dispersant very interesting, although further studies are still needed to elucidate this topic. Even with a structure that is not fully understood the lignocellulosic origin of HA and the presence of large aromatic portions in the structural network showed to be promising in the dispersion of alumina particles. Unlike the deflocculants commonly used, such as the polyacrylic acid salts, these large aromatic portions in HA bind hydrophobically to the particles while the charged portions designed for the solution promote another physical approach barrier, preventing contact between them [7].

The low concentration of HA required to obtain the best rheological properties draws attention to the obtained result. For example, in Gutiérrez and Moreno[21]it was necessary ~ 0.8 wt% of an ammonium salt of a polyacrylic acid to reach the best rheological properties for an alumina suspension. The HA was used as dispersant in an alkaline solution (3 g L^{-1}). According to our results, small amounts of HA solution were required to deflocculate large volumes of an alumina suspension, resulting in a great dispersant yield. For each kilogram of coal used as raw material, sufficient HA was extracted to act as dispersant for approximately 30 L of alumina suspension, according to Figure 2 (0.016 wt% HA, near to the minimum viscosity). The values obtained here are attractive when considering the cost to produce HA on a laboratory scale, estimated at ~ US$ 2 per gram of dry HA. This estimative considers the raw material and the reagents used in the extraction process[17]. Furthermore, we have proved the possibility to produce dense alumina bodies using HA as dispersant, which has not yet been shown in the literature (Figure 7).

The bodies obtained by slip casting method appeared to be free of any visible defects after sintering at 1600 ºC, probably a result of good stabilisation of the suspension using HA. Besides, the casting time of 4 minutes was sufficient to achieve a good packed wall with ~3.5 mm size after sintering. The water remaining in wall thickness was mainly lost during drying in which the shrinkage occurred.

The decomposition temperature of humic acid was between 300 ºC and 600 ºC (Table 1). It will not interfere on the firing of the bodies due to the low quantity used and low decomposition temperature, which is approximated to kaolinite decomposition. Up to the maximum tested temperature the residual water and humic acid molecules were lost (Table 2) gradually resulting in a proper removal of the additive and avoiding pore formation. At high firing temperature such as 1600 ºC alumina undergo sinterisation and its grains coalesce and eliminate porosity thus increasing density. This feature was confirmed by the SEM image that showed a homogeneous microstructure and dense grain compacts on the sintered bodies. In addition, the microstructure of sintered bodies is a result of the excellent rheological properties of the alumina suspension when AH is used as the dispersant. Due to the rheological properties, it was possible to obtain density of green composites leading to dense bodies after sintering. As is well known, the structure of a consolidated body has a significant influence on the quality of the fired microstructure[26]. The high sintered density is an indicator of a good packaging of particles in the compact, since the stable suspensions of submicron particles consolidate in a dense packaging structure, thus reducing the porosity[26]. The density achieved was 98.7% of theoretical value which are in agreement with the micrograph of sintered body (Figure 8) and low porosity by Arquimedes method (Table 2). This density is higher than that obtained by Tsetsekou[23] with 80 wt% solids loading alumina suspension sintered at 1600 ºC with different dispersants. These features can indicate HA-alumina bodies with good mechanical properties[23,27] although it was not the focus of this work and further experiments are necessary to prove it.

Therefore, the humic acid was effective to promote a good stabilisation and well-dispersed colloidal alumina suspensions with homogeneous wall packing. Stabilisation was achieved probably due to HA action by both mechanisms electrostatic and steric, the former promoting electrostatic repulsion on the particle double-layers and the last acting as a hindrance to agglomeration on a short range separation distance.

5. Conclusions

Humic acid was extracted from a subbituminous coal in a relatively simply manner at laboratory scale with basic infrastructure. The polyelectrolyte nature of HA and its surface properties in alkaline medium make it suitable to act as a dispersant in ceramic suspensions. HA was effective as a dispersant of an alumina suspension at 28 vol% at pH 11 and the optimum amount of HA was found to be 0.016 wt% relative to the dry mass of alumina. The results are very close to that found with sodium polyacrylate as dispersant, therefore HA can be a good substitute to commonly used deflocculants. An HA deflocculated suspension was obtained with low thixotropy and pseudoplastic behaviour. The stability of the alumina suspension with HA was confirmed through the rheological behaviour by measurements in constant shear rate and after long resting time. Good stability was also obtained in the sedimentation test at pH 11. The results obtained via zeta potential demonstrate that HA presents a significant surface charge density at alkaline pH. Under such conditions it displays an extended conformation of its molecules so that it is more readily dissolved. However, at acidic pH the molecules are enveloped, making it impossible to dissolve and, therefore, to act as a dispersant under the conditions herein evaluated. The extended conformation of HA provides a steric effect to deflocculation, so that HA acts probably via the electroesteric mechanism. The good dispersion and stability generates solid bodies by slip casting process without flaws after sintering and with high density (98.7% of the theoretical density) as showed by dense and homogeneous microstructure on SEM. According to the yield extraction of HA from coal, the low quantity used in deflocculation and the diluted solution utilised (3 g L^{-1}) it can be estimated that 1 kg of coal can yield sufficient material to act as dispersant to approximately 30 L of alumina suspension. Although more studies on the subject are needed, the results found in this work suggest that HA works as dispersant and can be a good alternative to those commonly used in ceramic processing.

6. Acknowledgements

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