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Feature article

# Selected sugar acids as highly effective deflocculants for concentrated nanoalumina suspensions

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ABSTRACT

The possibility to fabricate nanoceramic materials by techniques based on colloidal processing requires the use of effectively working deflocculants (dispersing agents) which are able to stabilize and decrease the viscosity of aqueous nanopowders suspensions. Galacturonic and lactobionic acids have been used in the research as deffloculants for nanoalumina; they allowed to obtain ceramic suspensions of high solid loading (50 vol%) and relatively low viscosity (ca. 4 Pa s at a shear rate 10 $s^{-1}$). High solid loading could be achieved through combining three factors: the application of sugar acids as deflocculants, water leaching of the nanopowders from the surface impurities and precise defoaming of the slurries. Density of sintered bodies equalled 98% TD.



## 1. Introduction

The way to make use of the potential of the ceramic nanopowders is to provide such moulding and sintering methods which lead to obtain dense and uniformly packed material of nanometric grains. Ceramic nanopowders are still of high interest, beginning from the development of new methods of their synthesis, through optimization of shaping techniques up to research on advanced sintering methods. Ceramic nanopowders can be synthesized by a large number of methods, such as co-precipitation [1,2], flame spray synthesis [3,4], combustion synthesis [5,6] and microwave-assisted auto-combustion synthesis [7], Pechini method [8], self-propagating high-temperature synthesis (SHS) [9,10], sol-gel and microwave hydrothermal methods [11], etc. The next technological step, after synthesis, is shaping of nanopowders into desired geometry. Colloidal processing which recently attach much attention allows to obtain homogenous ceramic components of different geometries without using high-pressure apparatus. Nanopowders can be formed by slip casting [12,13], tape casting [14], gelcasting [15,16], direct coagulation casting [17], roller casting [18] or robotic deposition [19]. Finally, sintering of nanometric sized particles is also very challenging [20]. In the wide range of sintering methods it is worth to mention SPS – spark plasma sintering [21–24], flash sintering [25] or two-step sintering [26,27].

The starting point for the colloidal shaping of nanopowders is to obtain stable and well dispersed suspensions of nanoparticles in water [28,29]. It is particularly important to find effective methods of nanopowders deffloculation and deagglomeration which is a real challenge in comparison to powders of higher particles size [30,31]. Generally, the suspension viscosity increases with decreasing particle size, therefore nanopowder suspensions exhibit very high viscosities. According to the literature data, one of the possible explanations is the fact that the separation distances between particles are much shorter in nanopowder systems resulting in excessive agglomeration. During Brownian movement, there is a high probability of aggregation, because the attractive van der Waals forces are more effective at small separations. Unless an electrostatic or steric barrier is built on the surface, aggregation is inevitable [32]. Moreover, the interactions within a ceramic particle suspension are complex; there are solvent-particle, particle-particle, solvent-dispersant, and dispersant-particle interactions [33]. This phenomenon has not been fully explained, however there exists models regarding viscosity of nanofluids [34,35].

There are known research in which saccharides and L-ascorbic acid as well as monosaccharides and their methyl and acryloyl derivatives have been used as dispersing agents for selected ceramic nanopowders [32,33,36,37]. However, the maximal solid loading of nanoalumina achieved with the use of mentioned compounds was still lover than in case of $Al_2O_3$ of submicrometer or micrometer particles size.

The aim of the study was to examine the influence of galacturonic and lactobionic acid on the rheological properties of

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nanoalumina suspensions of high solid loading, equalling 40, 45 and 50 vol%. Galacturonic acid is an oxidized form of D-galactose. It is non-toxic to human skin, exhibits bacteriostatic properties and is often used in cosmetics. Lactobionic acid is a disaccharide composed of D-galactose and gluconic acid which is an oxidized form of D-glucose. It can be also synthesized by oxidation of D-lactose. Lactobionic acid is also used in cosmetics as an antioxidant and in food industry as a preservative. Alumina nanopowder has been pre-treated by water leaching in order to purify its surface. Finally, the obtained slurries have been deaerated what allowed to remove the air form the suspensions and thus reduce the viscosity.

## 2. Experimental

### 2.1. Materials

The research has been carried out for $Al_2O_3$ NanoTek® (Nanophase Technologies Corporation, USA) of an average particle size 47 nm. The powder was a mixture 70:30 of $\delta$-$Al_2O_3$ and $\gamma$-$Al_2O_3$ phases with a density 3.53 g/cm$^3$ (measured on helium pycnometer AccuPyc II 1340, Micromeritics) and a specific surface area 36 m$^2$/g (measured on ASAP 2020 V3. 01, Micromeritics).

Two dispersing agents have been used in the research: D-galacturonic acid monohydrate (≥97%, Sigma-Aldrich) and lactobionic acid (97%, Aldrich). In the experiments deionized MilliQ water was used.

### 2.2. Methods

$Al_2O_3$ nanopowder has been used in two states: "as received" and "water leached". Water leached powder has been prepared on the basis of the procedure described by Danelska et al. [38]. It has been evidenced that water leaching allows to remove the impurities from the powders surface [39,40]. The alumina nanopowder was dispersed in deionized water with mass ratio of 1:4. The suspension was stirred on a magnetic stirrer for 60 min with a speed of 500 rpm, and then kept at room temperature for 24 h to approach ionic equilibrium. Then the suspension was stirred again for 10 min and centrifuged at 15000 rpm for 30 min on MPW-350R, High Speed Brushless Centrifuge, MPW Med. Instruments. The centrifuged nanopowder was dried at 105 °C for 24 h. The procedure has been repeated twice.

Sugar acids have been dissolved in deionized water and then nanoalumina powder (as received or water leached) was added. Slurries were mixed in alumina containers in a planetary ball mill PM200 (Retsch) for 60 min with a speed of 300 rpm. Then the slurries have been mixed and degassed in a THINKY ARE-250 Mixing and Degassing Machine for 2 × 4 min with a speed of 800 rpm (mixing) and 1800 rpm (degassing). The equipment allows to remove bubbles >1 μm. The scheme of the slurries preparation is shown in Fig. 1.

The rheological properties of slurries with different amounts of sugar acids were measured using Kinexus Pro rheometer (Malvern Instruments) in a plate–plate geometry. The gap between plates was 0.5 mm. The viscosities of the slurries as a function of the shear rate were measured in a sequence that the shear rate was raised from 0.1 to 100 s$^{-1}$ and then decreased to 0.1 s$^{-1}$. The measurement time was 20 min. Zeta potential measurements in a function of pH were carried out on Zetasizer Nano ZS (Malvern Instruments, UK). The concentration of powder in water equaled 500 ppm. Samples were kept for 24 h at room temperature to approach the state of ionic equilibrium and ultrasonicated for 5 min prior to measurements. Solutions of 0.01 M and 0.1 M HCl as well as 0.01 M and 0.1 M NaOH were used as titrating agents. No electrolyte was added to samples. The pH of slurries was measured on LAB 850 Schott pH-meter.

Differential scanning calorimetry (DSC) has been used to estimate water melting effects. Measurements have been done on DSC Q200 V24.2 Build 107 (TA Instruments, USA) for the nanoalumina suspension based on water leached powders. In case of samples

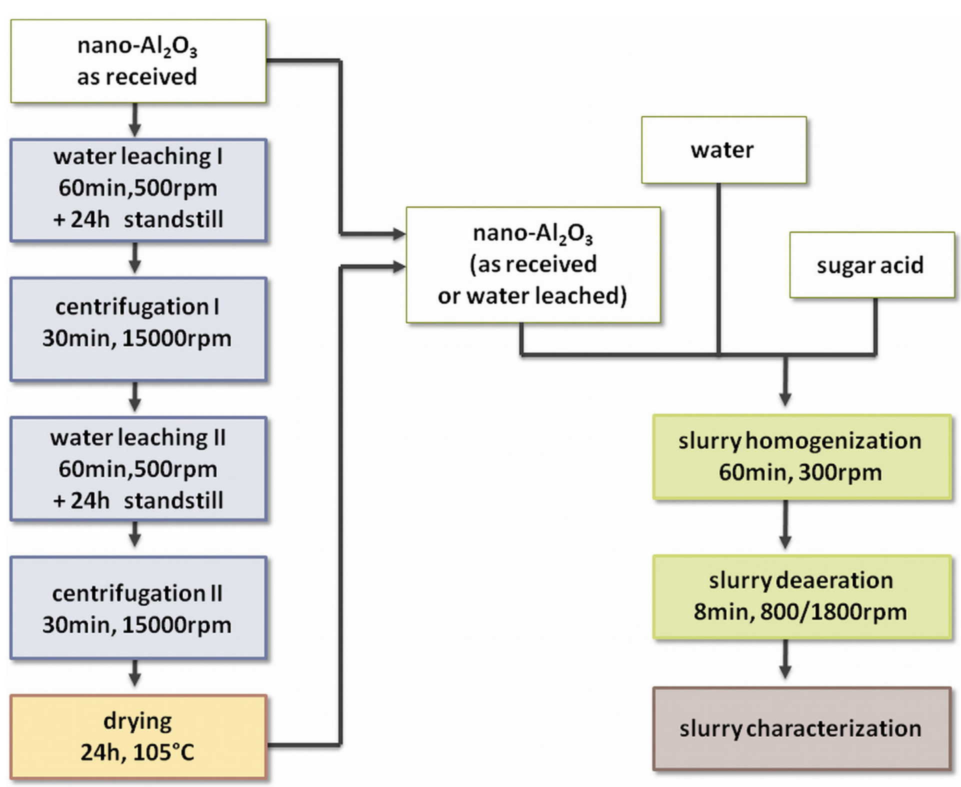


**Fig. 1.** Scheme of the preparation of nanoalumina slurries.