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Workability and setting parameters evaluation of colloidal silica bonded refractory suspensions

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Abstract

The efficiency of colloidal silica as a binder agent for castable matrix suspension in the presence of different setting agents and curing temperatures was evaluated. The tests were carried out trough rheometric techniques according to a systemic approach specifically developed for ceramic systems (oscillatory and normal force tests). Colloidal silica performed well as a binder agent for refractory suspensions when a suitable additive was selected. Among the additives analyzed, magnesium oxide was the most suitable for the evaluated systems. MgO addition in the range of 0.3–0.6 wt% and curing temperature of 25 °C were the suggested parameters for alumina and microsilica systems.

Keywords: A. Suspensions; D. SiO_2; D. Al_2O_3; E. Refractories; Colloidal silica

1. Introduction

Calcium aluminate cement (CAC) is the most used hydraulic binder in refractory castables. However, the presence of CaO in the composition can be deleterious to the refractoriness of some ceramic systems, such as those containing microsilica. Moreover, CAC based castables impose some special requirements concerning their curing and drying condition that could extend the processing time [1]. In this context, colloidal silica has been pointed out as an alternative for a calcium-free binder agent for refractory castables [2,3].

Colloidal silica is a stable dispersion of nanosized particles of amorphous silica. The different production routes available can lead to sols with distinct solids concentration, particle size and shape, and pH [4]. Colloidal silica particles can be linked together using different setting mechanisms, such as gelling and coagulation, providing initial strength when applied to ceramic systems. Concerning gelling, the interaction of silica particles triggers the siloxane bonding (Si–O–Si) and the build-up of a three-dimensional network. Regarding the coagulation, an additive (usually electrolytes) bridges the particles causing close-packed clumps. Both setting mechanisms are influenced by the pH change, the particle size and its concentration, the presence of electrolytes and organic liquids, and the temperature [4]. Besides its binder effect, colloidal silica is also reported as a dispersant for ceramic powders [2,4,5].

Despite the advantages concerning refractory castable processing and properties present in the literature with the use of colloidal silica as a binder [6], further understanding of its consolidation mechanism and interaction with other ceramic systems is still required.

Alumina, microsilica and magnesia are the main raw materials used in the matrix of current refractory castable formulations. Each of them presents a distinct chemical behavior: amphoter, acid and basic, respectively.

Alumina is the most used synthetic oxide ceramic mainly because of its refractoriness, hardness and corrosion resistance [7]. It is the most important raw material for the refractory industry, including coarse aggregates and fine matrix products. Microsilica is a by-product of silicon or ferrosilicon alloys. It consists of very fine amorphous spherical particles of silicon dioxide with an average diameter close to 0.1 μm [8] and specific surface area close to 20 m^2/g [9]. In refractory castables, microsilica fills the voids initially occupied by water, improving the system packing. When alumina is present, it also induces a mullite formation, increasing the hot-strength and thermal shock properties [9]. Magnesia is another important raw material for the refractory industry due to its high

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refractoriness (melting point of 2800 °C), corrosion resistance and relatively low cost [10].

In the present work, the behavior of colloidal silica containing systems was evaluated in alumina, microsilica and magnesia suspensions. In order to better understand these interactions, a systemic rheological approach using oscillatory and normal force tests to evaluate the setting behavior and demolding conditions [11] was carried out. Oscillatory tests make it possible to differentiate the elastic and viscous responses, which are expressed by the storage modulus (G') and by the loss modulus (G''), respectfully. G' represents the elastic component and G'' the viscous one [12]. The normal force (N_f) measurements show the specimen response to an elastic deformation imposed uniaxially [12]. Both tests characterize the viscoelastic properties of materials, which can be related to the physical changes during colloidal silica particles' aggregation, as the sol changes from a low viscous liquid to an elastic solid. The evaluation of refractory suspensions using viscoelastic properties (G', G'' and N_f), unlike those traditionally performed directly in the castable can be carried out with less material consumption and time demand.

2. Materials and methods

2.1. Raw materials and suspension mix

Alumina (A17NE–Almatis, USA) and colloidal silica (Bindzil 40 wt%—Nalco) suspensions containing 56.6 vol% of solids and 1.92 mg/m^2 of polyethyleneglycol based polymer, FS10 (SKW Polymers), as dispersants were used for the experiments. The FS10 was added to alumina suspensions not only due to its dispersing effect, but mainly to its benefit on viscoelastic properties, lowering G' and G'' values and improving workability. Alumina particles are better dispersed in colloidal silica than in water [5], but the addition of FS10 to the alumina–colloidal silica system further decreased the viscosity of this system [13].

The other analyzed systems were composed of: (a) microsilica (971 U—Elkem Materials South America) and colloidal silica suspensions with 53.0 vol% of solids and 0.46 mg/m^2 of polycarboxylate based polymer, FS20 (SKW Polymers), as a dispersant, and (b) magnesia sinter (M-30B—Magnesita S/A, Brazil) and colloidal silica suspensions with 30.0 vol% of solids. The volume percentage amounts used were the maximum solid content attained for each system. No additional water was added to these systems.

Magnesium oxide (MgO), magnesium hydroxide ($Mg(OH)_2$), magnesium chloride ($MgCl_2$), magnesium sulfate ($MgSO_4$), calcium oxide (CaO), calcium hydroxide ($Ca(OH)_2$), calcium chloride ($CaCl_2$) and calcium sulfate ($CaSO_4$), all PA grade (Synth, Brazil), were tested as setting agents. These inorganic compounds were selected due to their solubility range and basicity.

The suspensions were prepared in a laboratory mixer (Ética Scientific Equipments, Brazil) at 40 rpm for 5 min. Ultrasonic dispersion of this system triggered the colloidal silica gelling

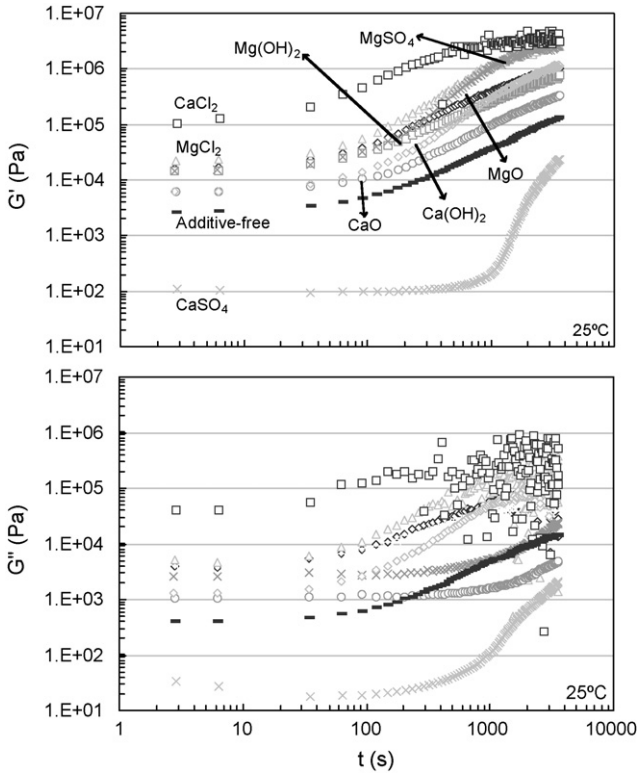

Fig. 1. Storage (G') and loss (G'') moduli as a function of time for alumina–colloidal silica suspensions with different inorganic compounds as setting agent at 25 °C.

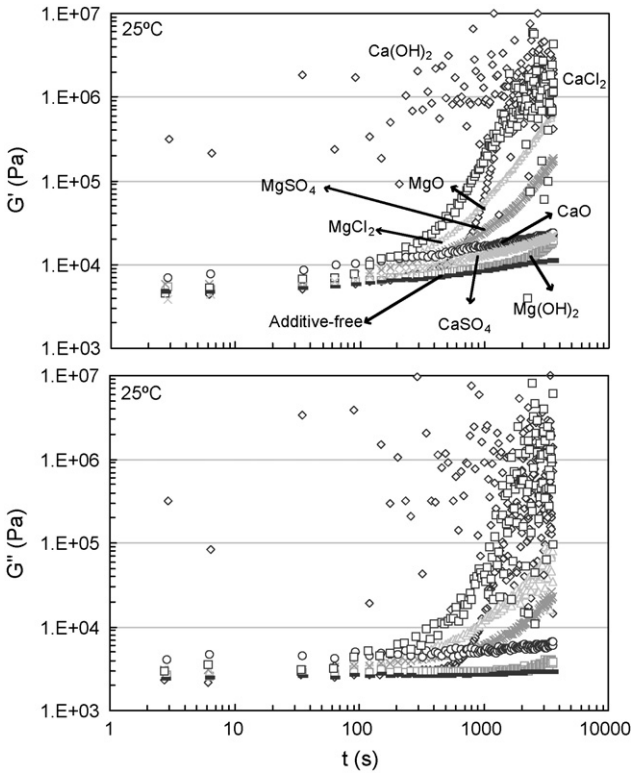

Fig. 2. Storage (G') and loss (G'') moduli as a function of time for microsilica–colloidal silica suspensions with different inorganic compounds as setting agent at 25 °C.

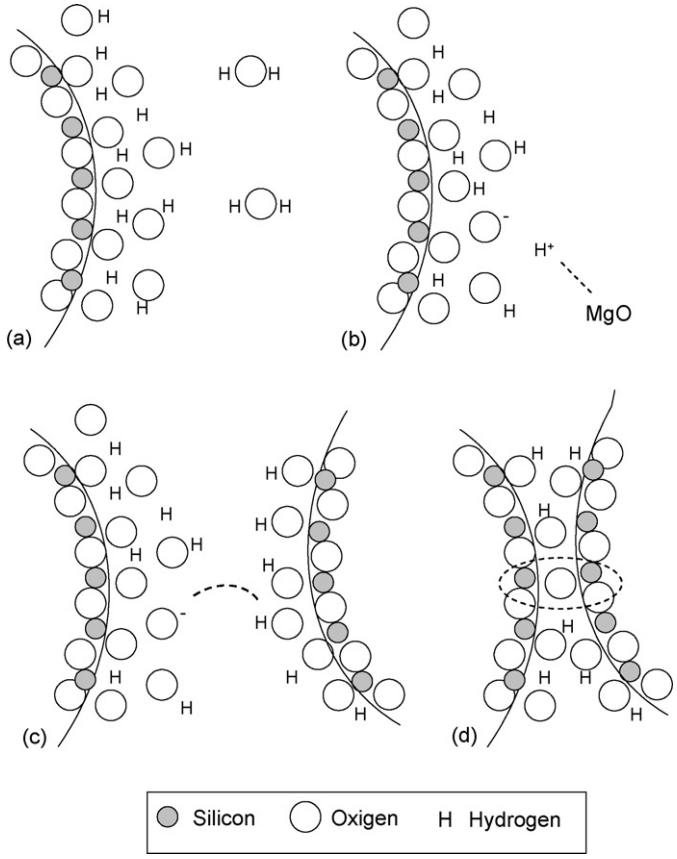

Fig. 3. Schematic representation of colloidal silica consolidation through the gelling mechanism: (a) colloidal silica particle surface, (b) MgO addition, (c) siloxane bonds formation and (d) siloxane bonding (–Si–O–Si–) (adapted from Ref. [4]).

reaction and was not carried out. Additionally, ball mill mixing presented the same results as stirring the colloidal silica ceramics suspension. The rheological characterizations of the suspension were carried out in a rotative rheometer RS300 (Thermo Haake, Germany) with temperature control.

The setting agent source was the first variable analyzed for each system using oscillatory, mechanical strength and porosity tests. Afterwards, the effects of the best setting agent content and curing temperature were evaluated by oscillatory and normal force tests.

Table 1
Inorganic compounds solubility in aqueous solution at 20 °C [15]

Compounds	Solubility (g/100 g_{water})
$CaSO_4$	0.21
$MgSO_4$	33.00
$MgCl_2$	54.20
$CaCl_2$	74.50

2.2. Oscillatory tests

The oscillatory tests were carried out at stress control mode with frequencies and stresses preliminary determined within the linear viscoelastic regime: 1 Hz and 1 Pa for alumina suspensions or 0.5 Hz and 1 Pa, for the microsilica ones. G' and G'' moduli were measured with the time using a vane sensor. The suspension surface was covered with an oil layer in order to avoid drying [11]. Setting of colloidal silica's particles was detected by G' and G'' increase indicating the material's transition from a viscous liquid to an elastic solid [12].

2.3. Mechanical strength and porosity tests

The mechanical strength of the ceramic systems was determined through compressive measurements [14] in a universal testing machine (MTS 810—USA) under a constant loading rate (11 N/s). The apparent porosity was evaluated according to the immersion test [15], using kerosene as the immersion liquid. For these purposes, the suspensions were cast in cylindrical molds (20 mm high and 20 mm in diameter) and kept in an acclimatized chamber at 25 °C (humidity ∼5%) for 48 h for curing (aggregation of colloidal silica particles) and at 50 °C for 24 h for drying.

2.4. Normal force tests

The normal force tests were carried out with a blade-shaped sensor at a deformation rate of 1 mm/s for the alumina system

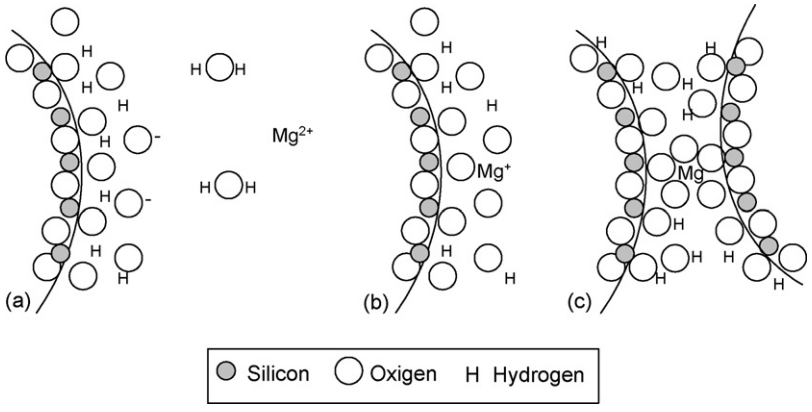

Fig. 4. Schematic representation of colloidal silica consolidation through the coagulating mechanism: (a) colloidal silica particle and magnesium soluble salt addition, (b) reaction between the cation and silica surface and (c) Mg^{2+} acting as a bridge by reacting with two particles (adapted from Ref. [4]).

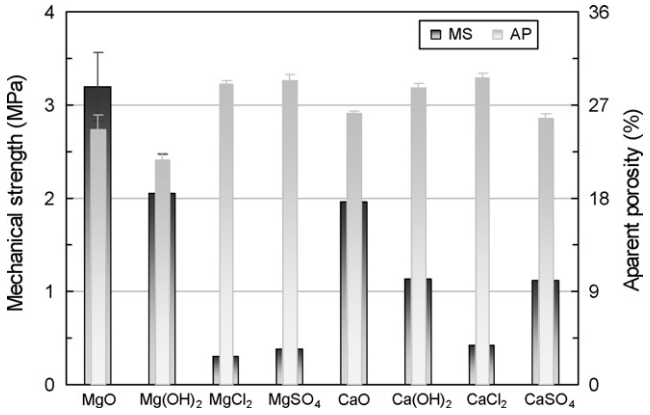

Fig. 5. Compressive mechanical strength (MS) and apparent porosity (AP) for alumina–colloidal silica specimens with different inorganic compounds as setting agent.

and 0.5 mm/s for the microsilica one. These values were previously determined in order to avoid the sample's damage. The samples prepared for a given suspension were kept in an acclimatized chamber (Vösth, model 20-20) with a surface covered with oil. Each sample was tested at a regular time interval after the mix suspension. The total testing time was 3 h. Samples reached their maximum deformation resistance when normal force rate became nearly constant [11].

3. Results and discussion

For the magnesia sinter–colloidal silica system the reaction was so fast that it was not possible to prepare a homogenous suspension. During mixing, silica particles immediately gelled around the magnesia ones, forming an impermeable external layer, which hindered the powder dispersion. The formed agglomerates settled on the rheometer's cup. Therefore, no further measurements were taken in this system.

The consolidation behavior of alumina–colloidal silica and microsilica–colloidal silica suspensions in the presence of different inorganic compounds as setting agents was evaluated using oscillatory tests. The compounds tested were oxides (MgO and CaO), hydroxides ($Mg(OH)_2$ and $Ca(OH)_2$) and salts ($MgCl_2$, $MgSO_4$, $CaCl_2$ and $CaSO_4$). They were added in equivalent amounts according to cation's mol content (7×10^{-5} $mol_{cation}/g_{colloidal\ silica}$) in order to compare the data (Figs. 1 and 2) more effectively. The time at which the moduli started to increase indicated the beginning of the setting reaction, whereas where G' and G'' values become nearly constant pointed out its end [11].

All setting agents speeded up the colloidal silica consolidation in alumina and microsilica suspensions, except $CaSO_4$ in the alumina–colloidal silica system (Fig. 1). In general, the reaction rate imposed on the colloidal silica by calcium and magnesium salts was greater than that promoted by the oxides and hydroxides, for both systems. It is highly likely that the basicity and the solubility of the added compounds play an important role in the reaction.

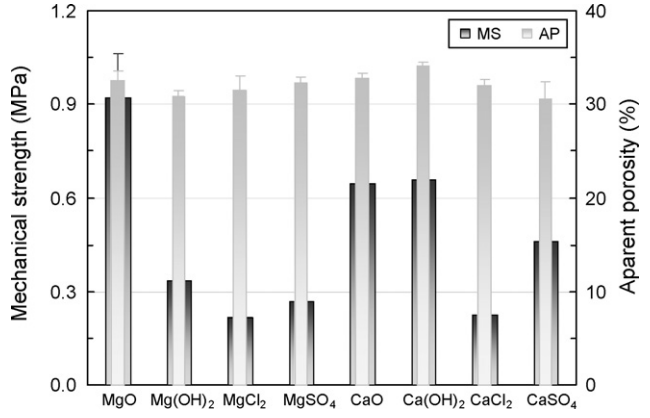

Fig. 6. Compressive mechanical strength (MS) and apparent porosity (AP) for microsilica–colloidal silica specimens with different inorganic compounds as setting agent.

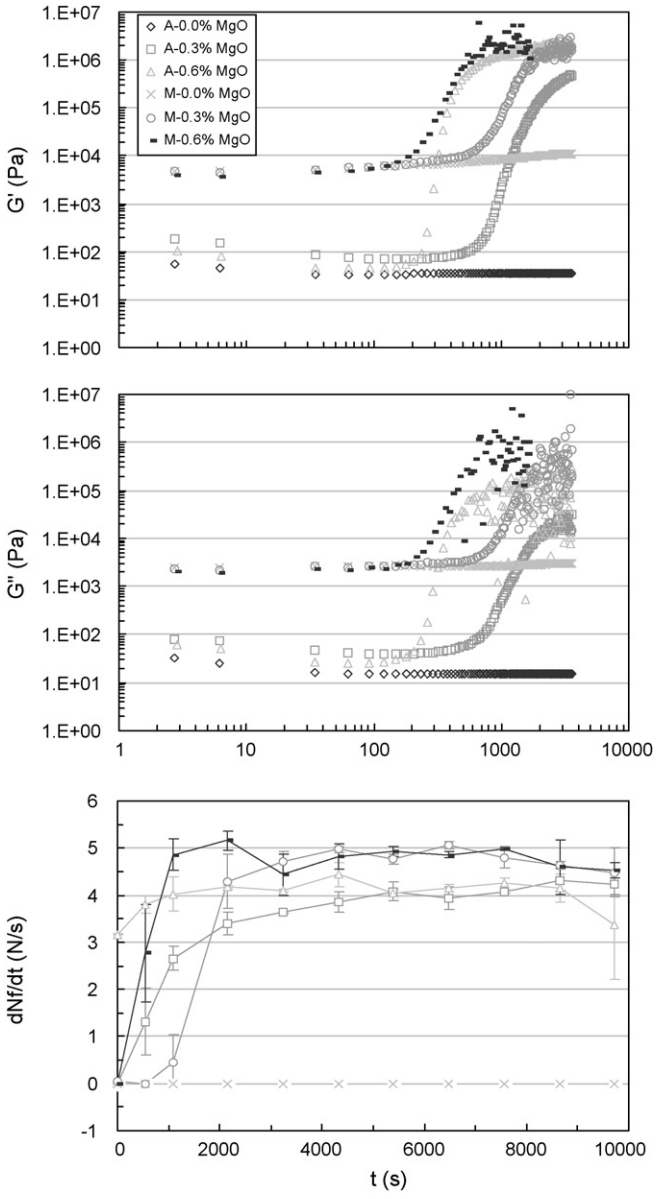

Fig. 7. Storage modulus (G'), loss modulus (G'') and normal force rate (dN_f/dt) as a function of time for alumina–colloidal silica (A) and microsilica–colloidal silica (M) suspensions with different MgO contents at 25 °C.

Basic oxides favor anionic reaction mechanisms on their surfaces [16]. They could withdraw hydrogen ions out of the Si–OH groups on the surface of silica particles increasing the siloxane bond formation (Si–O–Si) and, thus, the gelling rate, according to Fig. 3. Therefore, due to their basicity and insolubility, the tested oxides would favor the colloidal silica consolidation through the gelling mechanism [17]. CaO is a stronger basic oxide than MgO, but the latter one is less soluble in water, which explains its greater efficiency in promoting gelling.

Nevertheless, soluble compounds, such as salts (Table 1), when added to the suspension release ions that could act as coagulating agents, as schematically shown in Fig. 4. The higher the salt solubility, the higher the cation release and its efficiency as a coagulating agent. Calcium sulfate presented a small effect on the increase of coagulation rate, most likely because it is almost insoluble in water (Table 1). Nevertheless, it had a retarding effect on the coagulation rate when added to the alumina–colloidal silica system. It is possible that $CaSO_4$ reacted with water to form gipsite ($CaSO_4{\cdot}2H_2O$), but further investigation is required in this matter.

For the tested hydroxides, the OH^- released in the medium catalyzes the siloxane bonds [4], accelerating the gelling. $Ca(OH)_2$ resulted in a higher gelling rate as its basicity is higher than the $Mg(OH)_2$ one: the solubility product (K_{ps}), which denotes the dissociation grade of a compound in solution, is 6.5×10^{-6} for $Ca(OH)_2$ and 7.1×10^{-12} for $Mg(OH)_2$ [18]. The significant effect of $Ca(OH)_2$ on the microsilica–colloidal silica system when compared to the alumina–colloidal silica one, is most likely due to the stronger acidity nature of the former. Based on the common ion effect [18], it is reasonable to assume that the minor OH^- concentration on microsilica suspension favors the $Ca(OH)_2$ dissociation.

The results showed that the salt addition (except $CaSO_4$) led to a shorter reaction end in comparison to the oxides and hydroxides additions. The results point out that the salts could be more eligible for refractory applications. Nevertheless, the higher the interaction between the agent and silica particles, the faster the setting process, which could lead to the generation of more loosely packed agglomerates [19]. In order to verify these effects, mechanical strength and porosity tests were carried out (Figs. 5 and 6).

The samples containing oxides and hydroxides setting agents presented a higher mechanical strength than those with salts for both systems, whereas the porosity results did not show any significant differences. It shows that the three-dimensional particle's gelling network is more homogeneous and resistant than the coagulated one. During gelling, the particles arrange themselves in chains, which branch out as a network. On the other hand, during coagulation, the particles are closely packed, but not linked to the others, generating a weaker structure. Despite the higher consolidation rate presented by the salt containing suspensions, the addition of agents that promote gelling is recommended due to the better mechanical strength attained. Therefore, MgO presented the best result related to reaction time and mechanical properties, confirming its efficiency as a setting agent for refractory systems [3].

Because MgO was the most suitable additive for both systems, the effect of its content (0, 0.3 and 0.6 wt%—based on colloidal silica weight) and the curing temperature (8, 25 and 50 °C) on the consolidation of colloidal silica containing systems was evaluated using oscillatory and normal force tests. The results obtained for alumina and microsilica–colloidal silica systems are presented in Figs. 7 and 8.

G' and G'' moduli profiles indicate the beginning and kinetics of gelling reaction and are useful to define the molding working time, whereas the normal force test better describes the mechanical strength evolution and can be used to evaluate the demolding time [11]. Based on these data, the obtained parameters are presented in Table 2. G'_o is the initial storage modulus value and should be as small as possible to favor suspension workability; t_0 and t_f are, respectively, the starting and final time of the gelling. t_0 must be long enough

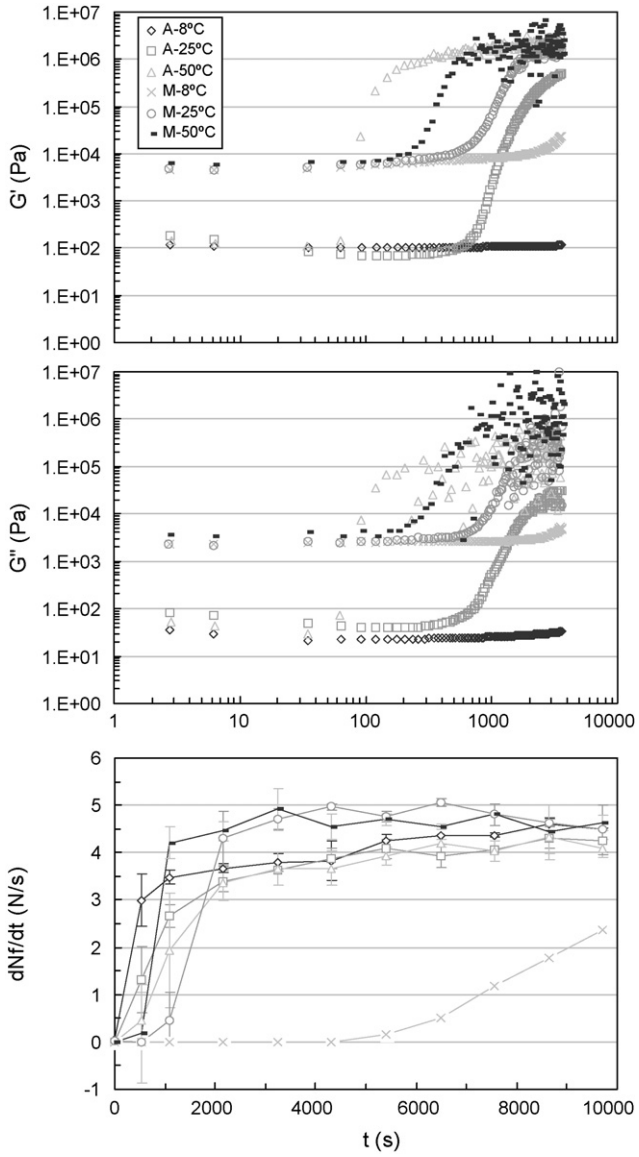

Fig. 8. Storage modulus (G'), loss modulus (G'') and normal force rate (dN_f/dt) as a function of time for alumina–colloidal silica (A) and microsilica–colloidal silica (M) suspensions with 0.3 wt% of MgO at different temperatures.

Table 2
Workability parameters for alumina and microsilica containing systems

	Alumina (25 °C)			Microsilica (25 °C)		
	Without MgO	0.3 wt% MgO	0.6 wt% MgO	Without MgO	0.3 wt% MgO	0.6 wt% MgO
G'_o (Pa)	53.8	183.0	101.0	46.7	4725.0	3950.0
t_0 (min)	–	8.3	3.3	0.05	8.2	1.8
t_f (min)	–	120.0	13.0	–	30.0	8.7
t_d (min)	–	90.0	36.0	–	72.0	36.0

	Alumina (0.3 wt% MgO)			Microsilica (0.3 wt% MgO)		
	8 °C	25 °C	50 °C	8 °C	25 °C	50 °C
G'_o (Pa)	116.7	183.0	141.2	4465.0	4725.0	6104.0
t_0 (min)	–	8.3	0.9	33.0	8.2	2.8
t_f (min)	–	120.0	4.8	120.0	30.0	8.7
t_d (min)	90.0	90.0	90.0	–	72.0	54.0

for the molding operation whereas, t_f must be as short as possible after the reaction begins. Additionally, t_d is the time that the normal force rate becomes nearly constant, indicating the demolding time and subsequent handling without shape deformation.

The gelling reaction was highly influenced by the MgO addition and the curing temperature. In general, the greater the MgO content and the temperature, the faster the gelling (minor t_0) and the shorter the demolding time (t_d) for both systems. The exception was the demolding time for alumina–colloidal silica system, which was not influenced by the temperature increase. A previous study reports that under some conditions, coagulation and gelling are greatly retarded or prevented permanently by heating the sol–80–100 °C before the reaction begins [4]. It is possible that this effect has influenced the alumina system: the silica aggregation started after the suspension preparation, which was detected by the G' increase, but was retarded during the measurement according to the temperature increase, leading to equivalent demolding times at 8, 25 and 50 °C.

In general, workability and demolding time decreased with MgO content and temperature increase. The exception was the alumina system at different temperatures: the demolding time (t_d) remained constant with a temperature increase, unlike t_0 and t_f. Because the various shaping processes require different time intervals to mold and demold, the additive content must be adjusted to promote the consolidation in this framework. MgO additions in the range of 0.3–0.6 wt% seem to be sufficient to adjust the setting time to reasonable values for alumina and microsilica systems. MgO contents higher than 0.6 wt% are not recommended for these systems, as t_0 is greatly reduced, making the molding process difficult. Concerning the microsilica suspensions, the temperature increase promotes t_0, t_f and t_d decrease, and a simultaneous G'_o increase, which is deleterious to the molding operation. In this context, 25 °C was the most suitable curing temperature for both systems.

Microsilica containing system presented smaller t_f values than the alumina one, which is a consequence of the higher gelling rate. It can be related to the fact that the microsilica system presented a pH value around 4–6, which is closer to the pH where the colloidal silica gelling rate is maximum (around pH 5) [4].

4. Conclusions

The results showed that colloidal silica is suitable as a calcium-free binder for alumina and microsilica ceramic systems. Nevertheless, additives are necessary to control its consolidation mechanism. Setting agents that promote consolidation via gelling mechanism are preferable than the coagulating ones due to the better green mechanical strength presented. Among the additives analyzed, magnesium oxide was the most suitable for the evaluated systems. In this work, workability and demolding time were obtained using oscillatory and normal force tests, which determined the gelling agent content and the cure temperature according to the conformation process used. MgO addition in the range of 0.3–0.6 wt% and curing temperature of 25 °C were the suggested parameters for alumina and microsilica systems.

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