Rheological and Dispersion Behaviour of Calcined Aluminas with Deflocculants

E. Chabas, C. Ulrich, A. Lafaurie, E. Papin, D. Dumont

Several criteria are very significant in the formulation of refractory castables, the water demand should be minimal and the flowability of a castable maximised in the intended application (self-flowed, vibrated castable, etc.). A major component of this is the flowability of the alumina constituent in the cement matrix of castables. These criteria are almost always regarded by refractory customers as a first step. To assist this, one solution is to determine the flowability of alumina and the minimum water demand for its dispersion. The aim of this study is to understand, which mechanism could be at the origin of calcined alumina flowability, in order to enhance these properties. In this sense, this study is aiming to identify which physical (particle size, morphology of particles, pH, zeta potential, etc.) and/or chemical (impurities) parameters could explain the capacity of alumina to flow.

Introduction

In aqueous media, the origin of the surface charge of the metal oxides of the alumina is well known. In the case of alumina, the role of protons H^+ and OH^- hydroxides, as ions determining the potential, has been well established. The mechanism by which the charge appears is composed of two steps: the surface hydration followed by dissociation of hydroxides surface. The dissociation of the surface of the hydrated alumina can produce, in water, a positively or negatively charged surface (Fig. 1). According to the authors, the point of zero charge ranges from 8 to 9,5 for alpha alumina. This wide range of pH for the zero point charge has been attributed to the surface chemistry of the alpha alumina powder.

Several parameters can influence the dispersion of alumina, such as the surface chemistry of alumina, deflocculant, particle size or the morphology of alumina particles.

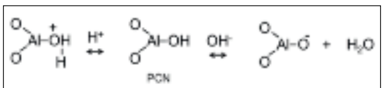

Fig. 1 **Amphoteric character of the surface of alumina in water**

Surface chemistry (impurities) can have a significant effect on aqueous suspension properties, and thus on the stability of the suspension. Some authors have observed that a difference in the surface chemistry of alumina could lead to a difference in the initial pH, initial mobility and even in the sign (zeta potential) of the particles [1].

Some authors show that grindability or impurities in alumina can change the surface energy of alumina and therefore the dispersion behaviour of alumina [2].

Deflocculants are used to ensure stability of suspensions and preserve the desired state of dispersion. Each deflocculant has an optimum effective concentration in water, and an excess of deflocculant has a negative effect on the sedimentation volume of suspension. Among the simple deflocculants (non-polymeric deflocculant), acids are also good candidates for alumina. Their ability to create complexes with Al^{3+}, brings a negative charge to the particles. Polyelectrolytes are widely used for the dispersion of alumina in water; there are carboxylates, sulfates, sulfonates, phosphates esters, etc. Among the most commonly used, there are polycarboxylates that strongly adsorb to the surfaces oxides. The adsorption of the deflocculant onto the alumina will depend on the charging characteristic of the deflocculant and the surface of the powder.

Some authors observe a decrease in minimum viscosity with increasing average particle size. Some others connect the rheology of the slurry to the concentration of dry matter or to the total surface of the particles in suspension [1].

Calcined aluminas have the particularity to have a crystalline morphology consisting essentially of plates. Some authors have shown a slight decrease in viscosity when the platelet content increases [2].

Experiment

Experiments were conducted on monomodal ground calcined aluminas from *Alteo* (4,3–5,4 µm). These aluminas were ground in industrial conditions. Physical and chemical parameters are presented on Tab. 1 and 2. Particle size distribution was measured by Sedigraph technology from *Micromeritics*. Several tests are realized on aluminas slurries first in view to integrate aluminas in LCC castable formulations.

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Tab. 1 Physical parameters of aluminas

	Physical Parameters			
	SSA		PSD	
	BET [m²/g]	d_{10} [µm]	d_{50} [µm]	d_{90} [µm]
A1	1,35	2,0	4,3	12,8
A2	0,97	2,2	4,8	15,7
A3	0,79	2,5	5,4	23,6

Tab. 2 Chemical parameters of aluminas

	Chemical Parameters [ppm]			
	Na_2O	SiO_2	CaO	Fe_2O_3
A1	2150	145	210	190
A2	2350	125	205	155
A3	2500	125	210	175

Flowability was measured by a cone test. The aim of this test is to fill a cone (height: 30 mm, lower diameter: 30 mm, upper diameter: 50 mm) with slurry, remove the cone, and measure the spread diameter (two opposed diameters) after one minute. The results are expressed in centimetre.

Zeta potential

A method for studying the surface properties of powders is the measurement of their surface electrical potential, called zeta potential, when the powders are dispersed in an aqueous or organic media. The dispersion is subjected to an electric field "E", which moves the charged particles. The speed of particles "v" was measured. From "v" the electrophoretic mobility "U" was calculated, and then aligned to the zeta potential, which is directly proportional to "U". The tests were performed on a *Malvern* device.

Viscosity

Tests were performed on a *Thermo Fischer* device.

Sedimentation test

Both compacting rate and sediment nature are significant to measure sedimentation characteristics.
The compacting rate is calculated by the ratio of the volume percentage of the powder and the volume percentage of the sediment. A good dispersion is characterized by a high compacting rate. Respectively, if the supernatant is cloudy or clear, the suspension will be deflocculated or not.

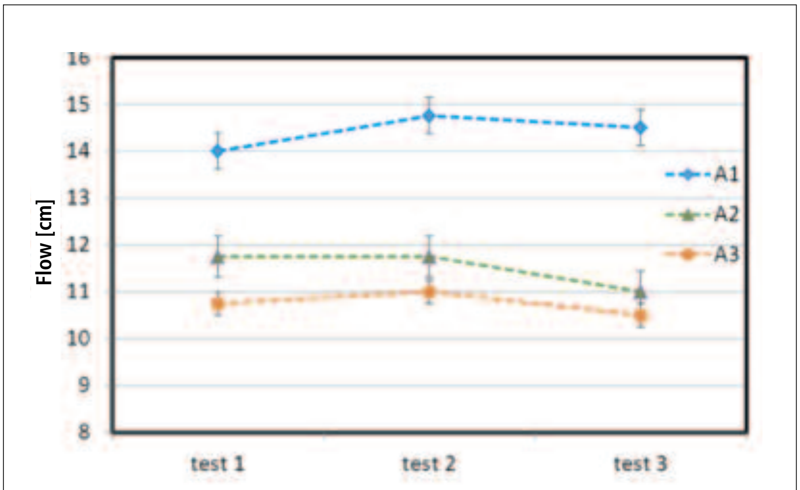

Fig. 2 Flowability of aluminas A1, A1 and A3

Results and discussion

Impact of particle size distribution

Flowability with the cone test described in the previous part, is measured on three slurries (water addition is around 30 mass-% of dry matter) composed of alumina A1, A2, and A3. The results are presented in Fig. 2. This graph presents an average value of several spread diameters. Tests are reproduced three times. It is observed that the flowability of alumina A1 is better than the two others ones. Then, flowability follows the logical order of particle size distribution of aluminas. It is shown there is an influence of particle size distribution on the flowability of aluminas.
However, grinding these aluminas modifies the impurity content on the surface of aluminas. Indeed, the chemical species contained within agglomerates prior to grinding, will be released progressively during the grinding and increase the impurity content of fine particles. In the next paragraph, we try to explain the impact of impurities of flowability.

Impact of impurities of aluminas

After grinding, the impurity content can be changed on the surface of aluminas. In this case, the soda level can be modified during grinding and the isoelectrical point is slightly changed. Some authors [2] show that the silica content can shift the isoelectrical point to acid pH. In this study, the difference between the impurity contents in aluminas is too low to identify the influence of chemistry on these properties. The isoelectrical point for all these aluminas was measured between 8,1 and 8,3.

Impact of deflocculants

Deflocculants are used to ensure the stability of suspensions and preserve the desired state of dispersion. In this part, different deflocculants on alumina A2 were tested with different water percentage (30, 40, 50 mass-%). Deflocculants used are CX (0,05 and 0,075 mass-%), FS20 and FS40 from BASF (0,05 mass-%), and TPP (tripolyphosphate) with 0,02 mass-%. Deflocculant rates were optimized in previous studies. Fig. 3 presents results of the flowability of slurries A2 including deflocculants, and the values of pH.

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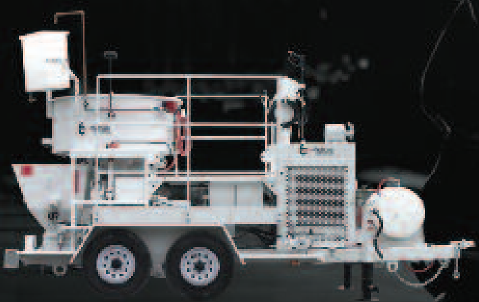

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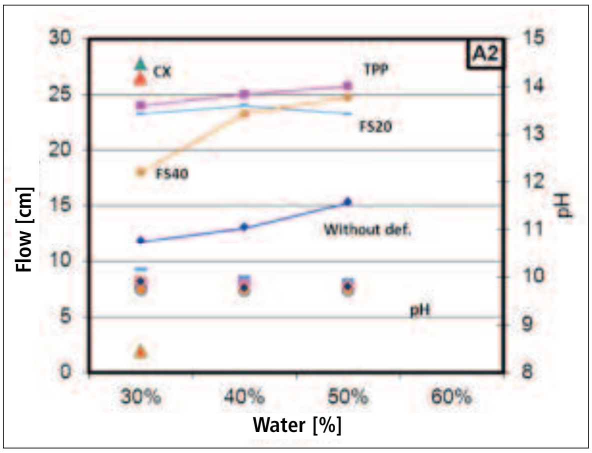

Fig. 3 Flowability with deflocculant

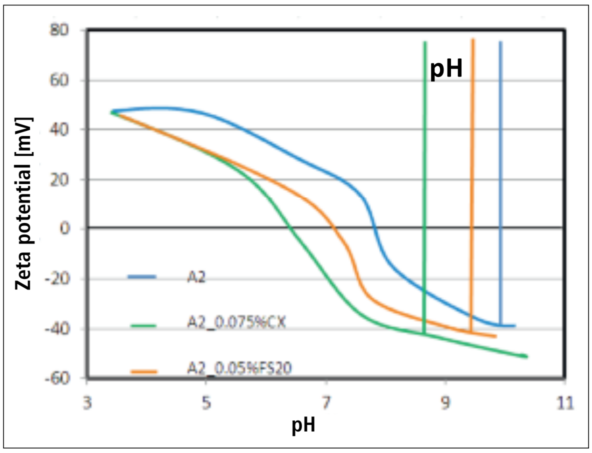

Fig. 4 Zeta potential of A2

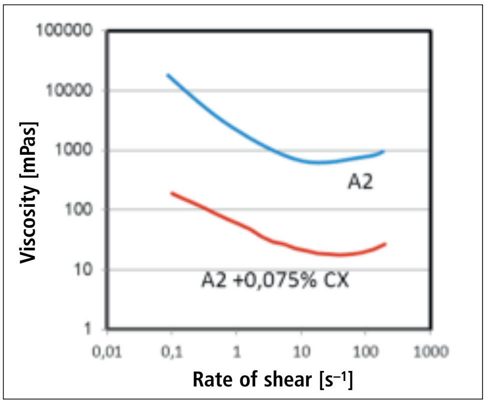

Fig. 5 Viscosity of A2

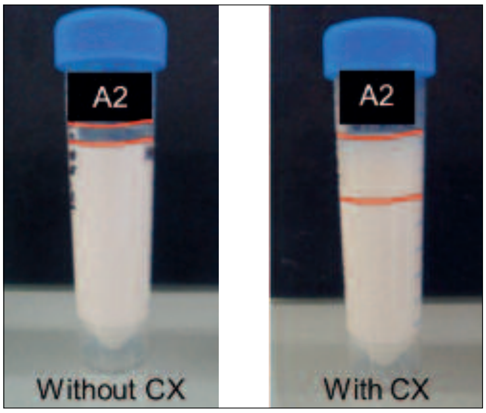

Fig. 6 Sedimentation test

The presence of deflocculants improves considerably the flowability of alumina, irrespective of the water content of slurry. Respectively, CX, TPP and FS20 present the best flowability of slurry. pH-values of slurries are quite similar (~9,5), except for CX presenting pH-values around 8,5.

By measuring the zeta potential, the difference in flowability from different types of deflocculant could be evaluated. The dispersion of divided solids in a liquid medium and stabilization of suspensions is mainly explained by two phenomena. In aqueous media, there is formation of a double superficial electric layer, for example by adsorption of surface active ions, which causes the repulsion of particles with the same electrical charge. In organic medium, the stabilization is primarily due to a steric phenomenon.

Layers prevent dispersing particles from getting close enough to obtain an agglomeration state. Fig. 4 presents zeta potential as a function of pH values for alumina A2, in presence of CX (0,075 mass-%) and FS20 (0,05 mass-%).

With these two deflocculants, the isolectrical point is shifted to acid pH. The delta of potential is amplified in the presence of deflocculants, which can explain the improvement of dispersion.

Viscosity

The viscosity of suspensions was also measured. Fig. 5 presents the viscosity measurements of alumina A2 with 0,075 mass-% of CX, as a function of the rate of shear.

Viscosity decreases with the presence of CX. A dilatancy effect is observed also with CX, but with a higher rate of shear. The addition of deflocculant improves rheological properties of alumina slurries (flowability and viscosity). Sedimentation is another significant parameter, which must be taken into account.

Sedimentation test

Fig. 6 presents pictures of sedimentation tests realized on alumina A2 with and without CX. This characterization is explained in the experiment section. Respectively on the left and right pictures, the test tube without and with CX is shown.

In the case without CX, the supernatant is clear and the compacting rate is calculated at 1,18.

For the example with CX, the supernatant is cloudy and the compacting rate is measured around 1,38. It can be concluded that the suspension free of CX is agglomerated while the slurry with CX presents a deflocculated state.

Conclusion

This study provides a better understanding of the origin of the flowability of aluminas – a criterion, which is very significant for refractory applications. Particle size distribution is the first parameter to take into account in the explanation. It was also stated that chemical parameters can modify properties, particularly the change of impurity content during grinding. But in this case, variations of chemical species contents are too low to modify the zeta potential and by consequence flowability.

Deflocculants, such as CX or FS20–FS40, enhance considerably rheological properties (viscosity and flowability) without causing too high sedimentation rates. The next steps are to introduce this type of alumina into castable formulations and to persue their industrialisation.

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