Ceramics International 31 (2005) 647–653

CERAMICS
INTERNATIONAL

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The effect of deflocculants on the self-flow characteristics of ultra low-cement castables in Al_2O_3–SiC–C system

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Received 12 January 2004; received in revised form 2 February 2004; accepted 29 June 2004
Available online 7 March 2005

Abstract

The influence of several deflocculants on the self-flow characteristics of an ultra low-cement high-alumina castable in the Al_2O_3–SiC–C system has been studied. The behavior of various deflocculants in high-alumina castables was evaluated in terms of apparent viscosity and pH of the matrix and self-flow value of the castable.

Our study shows that the best self-flow characteristics in the Al_2O_3–SiC–C system is obtained using sodium polyacrylate and the optimum content is considered to be 0.06 wt.%.

Keywords: Castable; Self-flow; Ultra low-cement; Deflocculants; Al_2O_3–SiC–C; Rheology

1. Introduction

The development of low and ultra low-cement castables (LCC & ULCC) started in the late 1970s by replacing part of the cement with fine (1–100 μm) and ultra fine (<1 μm) particles such as fume silica and reactive alumina [1,2]. Successful performance of these castables during the installation and their high-temperature properties have been attributed to the ability of fine and ultra fine particles to fill in the voids between aggregates (>100 μm), resulting in the higher packing density [3,4].

Due to reduced cement content and higher packing density, the water demand in high-alumina castables is decreased remarkably. Therefore, both LCC and ULCC exhibit better physical properties than the traditional medium-cement castables [1–5]. Furthermore, it is easily recognized that the particle size distribution (PSD) of the castables is an important factor in improving the flowability of the mix. The fine and ultra fine particles can increase the separation distance between aggregates and improve flowability. The idea of self-flow and pumpable castables has, indeed, been developed from this improved flowability [1–3].

Self-flow castables are characterized by their consistency after mixing, which allows them to flow and de-air without the application of external energy (i.e., vibration) [6,7]. In addition to the PSD of the castable and nature of the raw materials, the choice of a proper deflocculant is the key factor in modern self-flowing refractory castables [5,8].

The refractory castables used in blast furnace (BF) trough linings have to withstand high temperatures and exhibit high thermal shock resistance. They should also have good corrosion and erosion resistance. Castables in the Al_2O_3–SiC–C system have been developed by different workers for such applications [9–11].

The main raw materials are fumed silica, reactive alumina, calcium aluminate cement (CAC), silicon carbide and carbon (graphite or pitch).

Silicon carbide is commonly used to increase the thermal conductivity and decrease the thermal expansion coefficient of high-alumina castables so as to enhance their resistance to

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doi:10.1016/j.ceramint.2004.06.023

Table 1
Raw materials and composition of the Al_2O_3–SiC–C ultra low-cement castable studied

Raw materials		wt.%
Tabular alumina	Alcoa Chemicals, T-60	63.5
Silicon carbide	Chinese Origin	15
Pitch	Palayesh Gatran-Iran	3
Fume silica	Elkem, 971U	4.5
Reactive alumina	Alcoa Chemicals, CTC 20	12.5
Calcium aluminate cement	Lafarge, Secar 71	1.5

thermal shock. Carbon has a similar effect on these properties and inhibits metal and slag corrosion because of its non-wetting nature. Incorporation of these raw materials into the refractory composition is expected to increase the complexity of the matrix particles. This is mainly caused by the non-oxide nature of silicon carbide and the decreased wetting ability of carbon [11].

The dispersion of high-alumina zero-cement castables containing silicon carbide and graphite has been investigated in many articles [11]. However, less attention has been paid to the ultra low-cement castables in the same systems.

In this paper, the effects of deflocculants on the properties of ultra low-cement self-flowing Al_2O_3–SiC–C castable is studied. The effect of four industrial deflocculants; namely, sodium polyacrylate acid (Na-PAA), citric acid (CA), sodium tripolyphosphate (TPP) and sodium hexametaphosphate (HMP) on the apparent viscosity and pH of the matrix and the self-flow value of the castable is evaluated.

2. Experimental procedure

2.1. Raw materials and composition

The raw materials and composition used for the ultra low-cement self-flowing castable in Al_2O_3–SiC–C system are listed in Table 1 [10].

Particles, with a small mean diameter (<100 μm) and a large specific surface area (>1 m^2/g) play a major role in the dispersion of the castable. These particles constitute the castable matrix [5,11]. The purity and physical characteristics of the raw materials in the matrix are shown in Table 2. The four deflocculants used in our study and their sources are listed in Table 3. It was necessary to add small amounts of a wetting agent to the refractory composition to compensate for the low wetting ability of pitch. The wetting agent employed is the non-ionic polymer polyoxyethylene cetyl ether [$C_{16}H_{33}(OCH_2CH_2)\cdot 20OH$, 1120 g/mol, Sigma–Aldrich]. Separate tests were done to determine the exact amount of the wetting agent needed and an optimum content of 0.02 wt.% was obtained.

2.2. Particle size distribution

The PSD of the castable was adjusted to a theoretical self-flow continuous curve based on the Andreasen model as follows:

$$\mathrm{CPFT} = 100\left(\frac{d}{D}\right)^q$$

where CPFT, d, D, and q indicate the cumulative percentage finer than, particle size, the largest particle size (5000 μm) and the distribution modulus, respectively. In order to achieve self-flow, the q values should be in the range 0.21–0.26 [4]. For the present study, q is chosen to be 0.24, and the particle size distribution of the castable with this value of q is represented in Fig. 1.

2.3. Viscosity measurements

Due to the presence of coarse particles up to 5000 μm, it is very difficult to measure the viscosity of the castables directly. It is the rheology of matrix (the finer fraction of the raw materials (<100 μm), additives, and water form the matrix of refractory castable), which determines the flow behavior of the castable. In the absence of coarse particles, the viscosity of the matrix can be measured using a coaxial cylinder viscometer, which offers a wider range and a higher precision in measurements [12]. Therefore, a Brookfield digital rheometer (model LVD-III) was used for viscosity measurements. Steady-shear rheological tests have been carried out on the suspensions by applying a shear rate from 2.5 to 50 s^{-1}. Apparent viscosity at a shear rate of 50 s^{-1} was used in the matrix rheological analysis because of its good correlation with castable flowability [5,13]. The contents of raw materials and solids loading used to prepare the matrix representative suspensions are shown in Table 4. Because of the viscosity variation with time in the castables containing calcium aluminate cement, apparent viscosity was measured

Table 2
Purity and physical characteristics of matrix particles

Raw materials	Characteristics			
	Purity (wt.%)	Specific surface area (m^2/g)	Density (g/cm^3)	Particle size D_{50} (μm)
Tabular alumina	>99	0.83	3.83	7.70
Silicon carbide	>94	0.54	3.22	36.73
Pitch	>67	0.52	1.46	53.43
Fumed silica	>97.1	17.12	2.27	0.25
Reactive alumina	>99.7	2.10	3.91	1.90
Cement	(Al_2O_3)>70	1.00	2.93	3.03

Table 3
Deflocculants and their sources

Type	Source	MW (g/mol)
Sodium polyacrylate (Na-PAA)	Vanderbilt	2500
Sodium tripolyphosphate (TPP)	Kimia mavad	305.91
Sodium hexametaphosphate (HMP)	Kimia mavad	469.90
Citric acid (CA)	Kimia mavad	192.13

10 min after water addition. This 10-min interval exactly equals the time lapse in self-flow evaluations.

2.4. pH measurements

The pH values of the matrix suspensions were measured using a WTW 521 pH-meter. These measurements were also taken 10 min after water addition. In fact, viscosity and pH measurements were taken simultaneously.

2.5. Self-flow measurements

Self-flow tests were carried out, based on the ASTM C-1446-99 standard, to provide an index of castable flowability [14]. The same mass ratio (water)/(solids loading), used to prepare the matrix representative suspensions was also used for the mix preparation, which resulted in a fixed water content of 6 wt.% based on dried solids. After dry mixing the batch for 30 s in a planetary mixer (Hobart), all the water (distilled and deionised) was added within 10 s while the mixer was running. The wet mixing was conducted for 5 min at a slow speed (Hobart, speed 1).

After the mixing, the castable was transferred to a sealed container and care was taken to keep the moisture constant. Ten minutes after water addition, the mixed castable was poured into a standard cone with a base diameter of 100 mm (ASTM C-230). The cone was then elevated to allow the mix to flow, and after 60 s the patty diameter was measured.

Table 4
Content of raw materials and solids loading used to prepare the matrix representative suspensions

Raw materials	wt.%
Tabular alumina	16.41
Silicon carbide	24.97
Pitch	6.27
Fume silica	12.55
Reactive alumina	35.30
Cement	4.21
Solid content	83.27

The percentage increase in spreading diameter after 60 s is taken as the self-flow value according to the following formula:

$$\text{Self-flow}\,(\%) = (D_\text{f} - D_\text{i})\frac{100}{D_\text{i}}$$

where D_f is the final average diameter after removal of mould and D_i is the initial diameter (100 mm).

The castable is considered self-flowable when the above value lies within the range of 80–110% of the base diameter [6,7]. During the self-flow evaluation, the ambient temperature was controlled to be in the 20–24 °C range.

3. Results and discussion

The effect of various deflocculants on the apparent viscosity of Al_2O_3–SiC–C suspensions is shown in Fig. 2. It can be seen that suspensions containing different deflocculants show similar behavior with increasing deflocculant content. It is further evident that the use of sodium polyacrylate (Na-PAA) gives the lowest values of apparent viscosity.

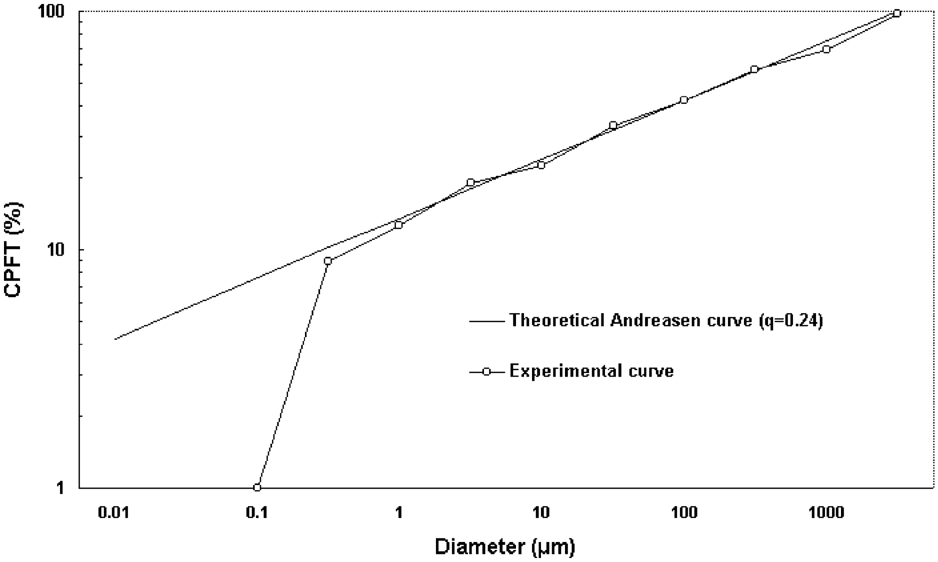

Fig. 1. Theoretical and experimental particle size distribution of self-flowing castable.

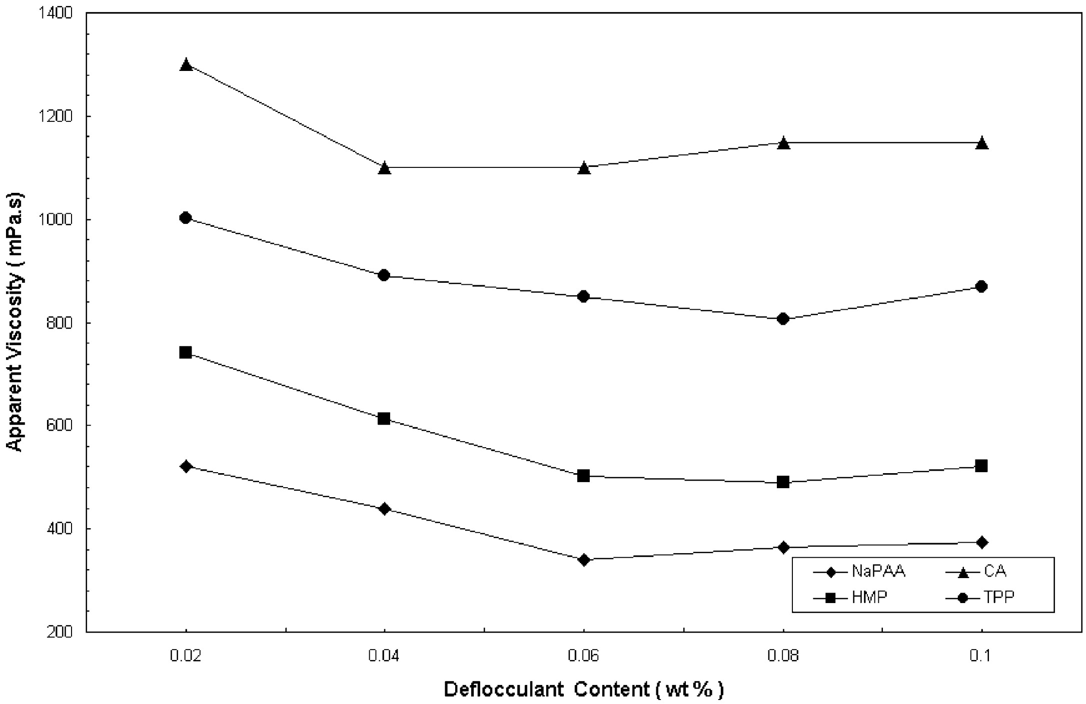

Fig. 2. The effect of various deflocculants on the apparent viscosity of the castable matrix vs. deflocculant content (16.73 wt.% water was added to the matrix).

Fig. 3 shows the variation of self-flow values of the same castables with increasing deflocculant content for various kinds of deflocculants. It is clearly seen that the best flow values are obtained with Na-PAA. Moreover, the optimum deflocculant content for minimum viscosity and maximum self-flow is seen to be 0.06 wt.% for Na-PAA. From Fig. 3, one can see that the self-flow values of the Al_2O_3–SiC–C castable with Na-PAA is about 85%, in agreement with the definition of self-flow castables in Section 2.5.

According to the DLVO theory on the stability of colloidal systems, the viscosity of a suspension is a function of attractive and repulsive forces between its particles. Attraction forces lead to flocculation and low flowability, whereas; the repulsion forces tend to increase the total

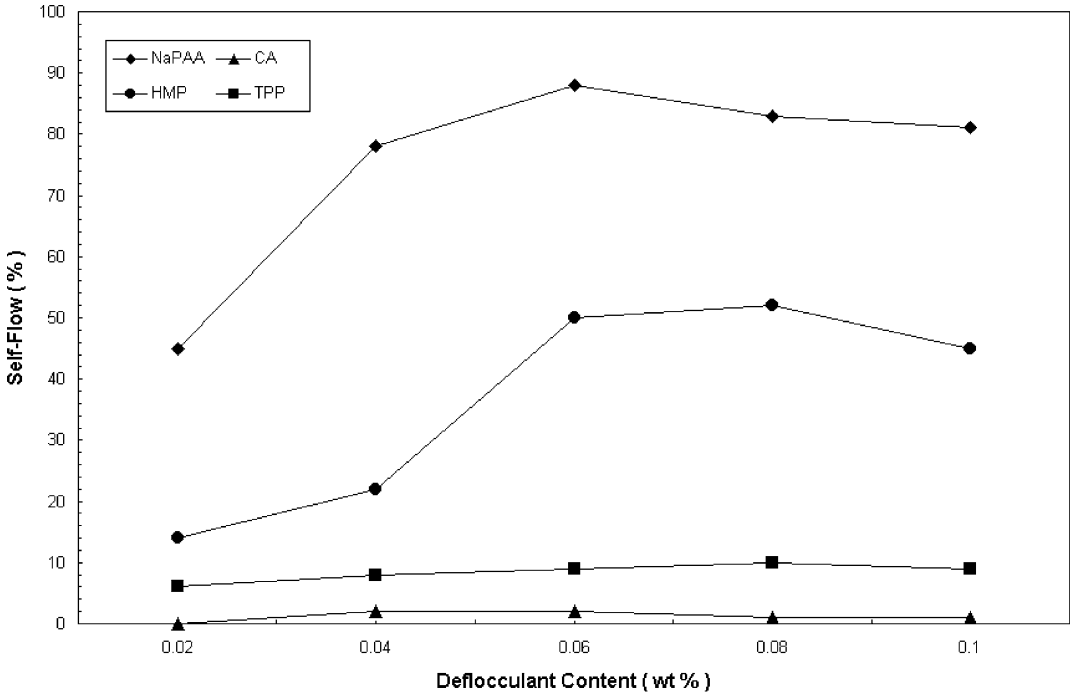

Fig. 3. The effect of various deflocculants on the castable self-flow vs. deflocculant content (6 wt.% water was added to the castable).

potential of the system; hence, reducing the viscosity and increasing the flowability [5]. It is, therefore, desirable to investigate the surface charges on the particles of the constituent materials, which, in this study, are presented in Table 4.

The zeta-potential of fume silica is normally around −20 to −30 mV in aqueous systems. The zero point of charge (zpc) occurs at a pH range of 2–3 [4]. The surface of silicon carbide particles is most likely oxidized during the synthesis, resulting in a significant concentration of silanol groups (Si–OH) on the particle surface. Such groups tend to be predominantly deprotonated by OH^- ions. Therefore, the silicon carbide particles show high negative values of zeta-potential over the entire pH range. The surface of pitch particles can also be oxidized to form a wide range of functional groups (e.g., C=O and COOH) that are readily deprotonated in the presence of OH^- ions. Therefore, the pitch particles also show a negative zeta-potential within a wide range of pH [11]. On the contrary, the cement and alumina particles may show a slightly positive charge depending on the pH value of castable. Hence, a slurry mix of these particles will not be stable, but prone to coagulation. The calcium ions, originating from the cement are absorbed on the fume silica and silicon carbide surface, causing coagulation. The result is a castable that, at best, can be a fairly vibratable or a ramming mix unless a significant amount of water is added.

In order to prevent the coagulation, one has to reduce the absorption of the calcium ions on the fume silica and silicon carbide powder surfaces. Therefore, a proper amount of suitable deflocculant should be added to the mix to achieve this end [4].

The deflocculant, absorbed on the powder surfaces, not only impedes the absorption of the calcium ions but also creates negative charges on the particle surfaces of the matrix suspension, resulting in repulsive forces. Hence, a better dispersion of the particles is achieved. Having broken up the agglomerations, the enclosed water is released making the castable more flowable requiring less water [15].

By comparing Figs. 2 and 3, one can immediately see the correlation between self-flow value and the apparent viscosity for the different deflocculants. Therefore, the variation of the self-flow values can directly be represented as a function of the apparent viscosity of the castable matrix. This, indeed, has been represented in Fig. 4, for different amounts of Na-PAA. It is evident that the apparent viscosity must be less than 375 mPa s for our system to be self-flowable.

Fig. 5 shows the variation of the matrix pH as a function of the deflocculant content for the different types of deflocculants used. The rheology of the castable matrix is strongly dependent on the zeta-potential of particles, which, in turn, depends on the ionic strength of the suspension and its pH value for fine particles ($<100\ \mu m$) [13]. We, therefore, conclude that the variation in the pH of the suspension will change the flowability. According to Fig. 5, the addition of citric acid has decreased the pH of the suspension to values as low as 6.5 due to its acidic nature.

Other deflocculants, on the other hand, have not produced such a dramatic change and pH values have relatively stabilized.

From Figs. 2 and 5, we conclude that the introduction of Na-PAA in the Al_2O_3–SiC–C system increases the zeta-

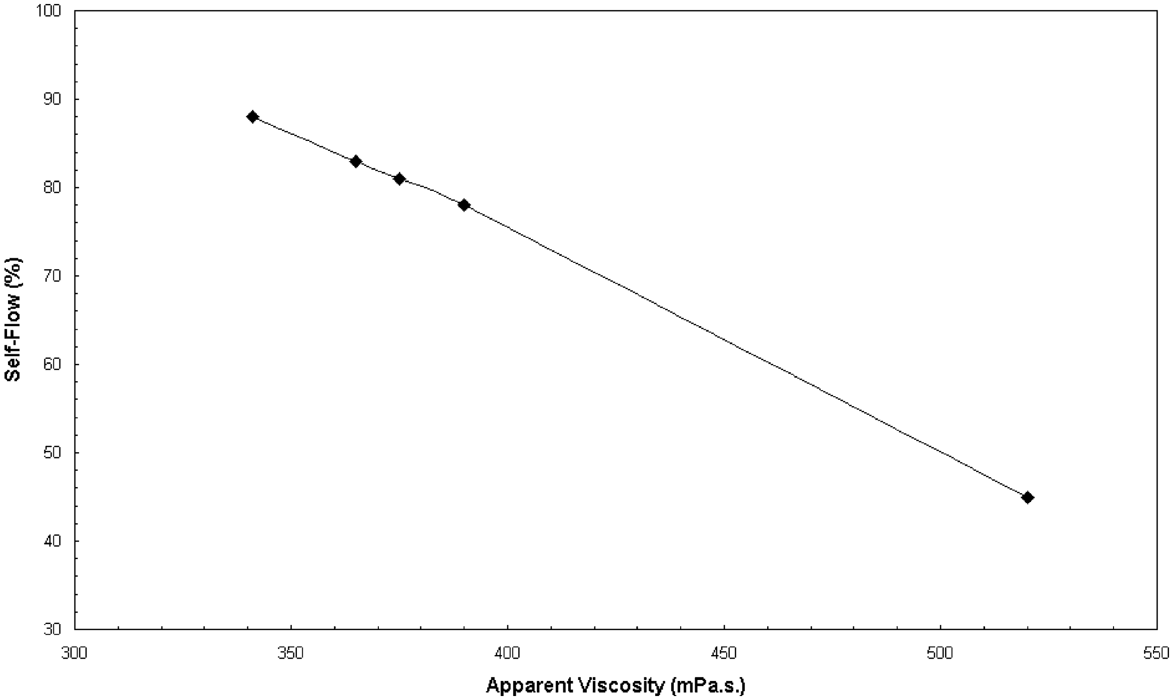

Fig. 4. Self-flow values of castable vs. apparent viscosity of the castable matrix containing 0.06 wt.% Na-PAA and 6 wt.% water.

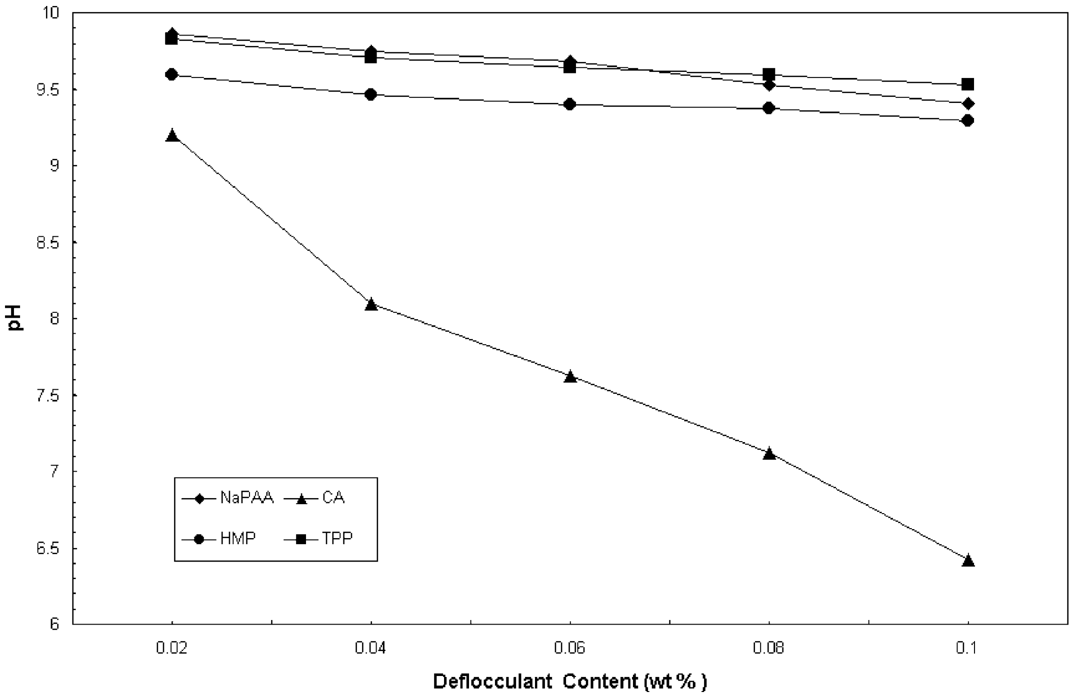

Fig. 5. Matrix pH as a function of the deflocculants content for the different types of deflocculants.

potential in the pH range of 9–10. The higher zeta-potential obtained using Na-PAA, would be expected to result in a suspension with lower apparent viscosity and higher self-flowability. The dispersion mechanism of these additives is via electrostatic stabilization. The molecules in stretched conformations such as sodium polyacrylate can also provide highly repulsive barriers due to electrosteric stabilization, which favors low apparent viscosity [11,13].

According to recent studies [11], fine alumina particles are the most important raw materials in the dispersion of zero-cement high-alumina castables containing silica, silicon carbide and carbon. Since alumina particles have a

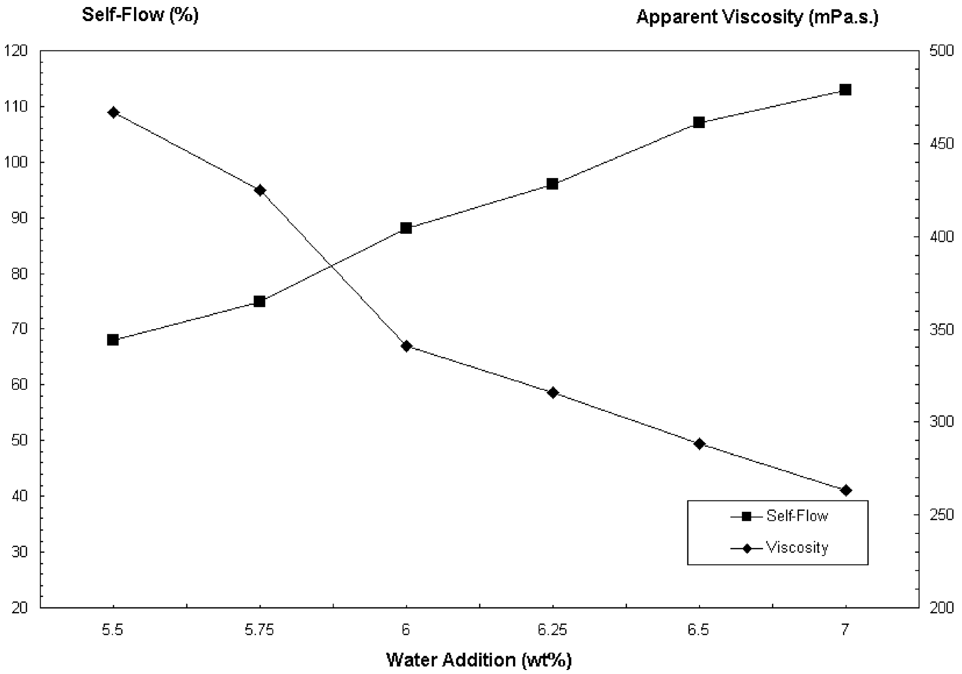

Fig. 6. Apparent viscosity of the matrix and self-flow values of the castable vs. total water consumption for 0.06 wt.% Na-PAA.

zpc corresponding to the usual pH range (8–10) of the castable, it is necessary to add anionic molecules such as; citric acid and polyacrylate, to appropriately disperse these high-alumina castables. The adsorption of polyacrylate or citrate molecules on the particle surface causes a significant change in the alumina surface potential. This is attributed to the presence of COO^- ions of the adsorbed citrate and polyacrylate molecules that increase the number of negative sites at the interface, shifting the alumina zpc to lower pH and increasing the absolute zeta-potential at the pH range (8–10) of the castable. The zeta-potential values of silicon carbide particles do not significantly change as a function of pH in the presence of COO^- ions. Pitch particles also display the same behavior because of the low affinity between COO^- ions and highly negative particle surfaces. However, in the castables containing cement such as LCC and ULCC, the fine cement particles have the higher density of positive sites on the surface and, therefore, are the most important raw materials in the dispersion of castables containing cement and other constituents.

The high zeta-potential of cement particles, which is possibly caused by released calcium cations, turns negative with the addition of the deflocculant. Acids such as citric acid are very effective in suppressing the dissolution of calcium aluminate cement, and this is the mechanism, which provides the castable with sufficient working time. It is believed that the delay in dissolution is due to a reaction on the cement grain surface that results in the formation of calcium citrate and calcium phosphate precipitates, which tend to block calcium aluminate cement dissolution [15,16]. Thus, as the citrate and phosphate ions are consumed, their dispersing effect decreases and, as a result, the flowability is reduced. Therefore, unlike zero-cement systems, deflocculants such as CA, HMP and TPP, do not produce the desired effect in systems containing cement.

Fig. 6 shows the apparent viscosity and self-flow values versus water consumption (different solids loading) for a fixed amount of Na-PAA (0.06 wt.%). It can be seen that the optimum content of the added water is about 6–7 wt.%. The aggregates and matrix will segregate if more water is used.

4. Conclusion

The effect of four different dispersing agents on the flow behavior of ultra low-cement Al_2O_3–SiC–C castables has been investigated.

It has been found that the apparent viscosity of the castable matrix should be lowered to values <375 mPa s in order to achieve self-flowability. Sodium polyacrylate has proved to be the most effective additive in reducing the viscosity of the castable matrix. The best results are obtained with 0.06 wt.% Na-PAA. The electrosteric mechanism of sodium polyacrylate appears to promote higher flowability in this system in comparison with the electrostatic mechanism of other dispersing agents such as phosphates.

Acknowledgements

The first authors would like to thank the management and the staff at the R&D Center of Azar Refractory Company for the support extended to him in this study.

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