Studies on a Binder Matrix of Refractory Castables – Influence of Dispersants on Flow Characteristics

H. Hommer, K. Wutz

Abstract
For a successful installation of castables an appropriate flow behaviour is required. In order to acquire a more fundamental knowledge of the flow characteristics of microsilica containing refractories, the complex binder matrix (cement, alumina and microsilica) is studied in the presence of new polycarboxylate-based superplastiziers. Special focus is placed on different types of calcium aluminate cements and reactive aluminas. The results are verified in a bauxite-based castable. It is shown that the flow characteristics of castables with low or high range calcium aluminate cements strongly depend on the dispersant.

Zusammenfassung

1 Introduction
The development of low-cement castables started in the late 1970s by replacing part of the cement with ultrafine materials such as microsilica [1]. Due to a lower water demand, this approach led to castables with significantly improved physical properties compared to traditional ones [1–3]. Furthermore, it was readily recognized that the particle size distribution of the raw materials – particularly of fine material – was very important in order to improve the flowability of the castable. This was the beginning of the development of self-flowing and pumpable castables. All these improvements led to an ongoing replacement of shaped products with low cement monoliths.

One main parameter for improved physical properties is the fact that the water demand, which is necessary for an appropriate workability, can be reduced. Therefore, suitable additives such as dispersants are required. Dispersants help to improve the flow of such castables substantially. They are able to break up the agglomerates of the cement and microsilica particles which are formed due to their opposite surface charges. It is a generally accepted mechanism that the negatively charged dispersant molecules dock onto the positively charged surface of the cement grains. Thus, the surface of the cement grains becomes negatively charged and they repel each other as well as the negatively charged microsilica.

In the past, higher quality requirements of castables demanded further research in order to develop more effective dispersants [4]. The new types of dispersants developed in the past years belong to the group of polycarboxylatethers (Fig. 1), which combine electrostatic and steric stabilisation of the dispersed fine particles [5]. This new mode of action of these tailor-made polymers provide the best possible plasticisation and rheology of the castable. In order to get a more basic insight into the mode of action of this new polymer generation, the complex binder matrix of a microsilica (MS) containing castable as shown schematically in Fig. 2 was investigated. Special focus was put on different calcium aluminate cements (CAC) and types of reactive alumina (RA). Moreover, the obtained results are verified in a bauxite castable.

2 Experimental Work
2.1 Materials
Two different types of calcium aluminate cements were used. As a representative low range Calcium Alumi-
nate Cement (CAC). Ciment Lafarge Fondu was chosen and as high range CAC, Secar 71, respectively. The general composition of the CACs is shown in Table 1.

The types CTC 20 and CL 370 C were used as reactive aluminas, which were both from Alcoa Industrial Chemicals Europe (Germany) and had with a specified alumina content >99.7%, CTC 20 is a monomodal alumina with a BET surface of 2.1 m²/g and an average particle size (D₅₀, Cilas) of 1.9 µm and D₅₀ = 11.0 µm. CL 370 C is a bimodal alumina with a BET surface of 3.4 m²/g and an average particle size (D₅₀, Cilas) of 2.5 µm and D₅₀ = 12.0 µm [6]. The standard microsilica type 971 U from Elkem was used for all experiments.

The dispersants were as follows: Castament® FS 20 and the newly developed Castament® FS 40 for the evaluation of the binder matrix and the bauxite castable. Furthermore, Castament® FW 10 was used in combination with Castament® FS 40 to adjust the setting time of the castable. All dispersants are commercially available from SKW Polymers GmbH (Germany).

For all experiments the dry material (pure cement, pure reactive alumina or the mixture of cement and reactive alumina or the cement-microsilica-alumina mix) including dispersant was placed in a plastic container which was filled with the appropriate amount of water. The mixture was stirred for 2 min with a hand mixer and subsequently filled into a so-called Vicat ring with a 75 mm bottom diameter, a 65 mm top diameter and a height of 40 mm which was placed on a glass plate. The cone was lifted immediately after filling was completed. When the mixture stopped flowing, its spread was determined and measured two perpendicular diameters on average.

For the evaluation of the bauxite castable all ingredients were dry mixed in a Hobart mixer for 1 min. After water addition, mixing was continued for another 4 min. Immediately after mixing, the prepared castable was placed in a stainless steel cone with a bottom diameter of 100 mm, a top diameter of 70 mm and a height of 50 mm. The cone was lifted 10 min, 30 min, 60 min and 90 min after water addition. The test sample was vibrated for 20 s (amplitude 50 %, frequency 50 Hz). Two perpendicular diameter measurements d₁ and d₂ were taken. The average diameter, d, was used to calculate the flow value FV as a percentage, according to the following equation:

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FV/\% = \frac{d[mm] - 100mm}{100mm} \times 100
\]

### 3 Results and Discussion

#### 3.1 Basic Research on Reactive Components

First of all, the dispersing effect of Castament® FS 20 and FS 40 in the different types of CAC was evaluated with Ciment Lafarge Fondu and Secar 71. As shown in Figs. 3a and 3b, Castament® FS 40 is the most suitable dispersant for both types of CAC although Castament® FS 20 is a very powerful dispersant in bauxite and andalusite castables with a high range CAC [4].

The next step involves the dispersing effect of Castament® FS 20 and FS 40 in various aqueous reactive alumina slurries. It can be seen from Figs. 4a
alumina as a function of the water content. In this case the use of a monomodal or a bimodal alumina is of minor importance. In both cases the flow values of the corresponding cement/alumina paste is nearly the same. Furthermore, in both examples only Castament® FS 40 contributes to an improved flow of the paste at lower water/solid ratios. Hence, it can be concluded that the dispersing effect on the cement is the dominant one, taking into account that Castament® FS 40 is a very effective dispersant for CACs (Fig. 3a and 3b).

Surprisingly, when the more complex system of CAC-microsilica-reactive alumina (ratio 1:1:1) with Ciment Lafarge Fondu was investigated, a strong dispersing effect (regarding the reference sample) was only found when the bimodal alumina CL 370 C was used in combination with Castament® FS 40. Only a moderate identical dispersing effect could be observed for the monomodal alumina CTC 20 with either Castament® FS 20 or FS 40 (Figs. 6a and 6b). Furthermore, comparing the flow characteristics of the reference sample in this three-component system, the flow of the mixture with CTC 20 was achieved with a lower water content than the amount added to the mixture with CL 370 C. Taking the particle size distribution of the raw materials [7] into account, it can be concluded that the overall particle size distribution of the binder matrix is more optimized when the monomodal alumina CTC 20 is used. But it is interesting to mention that nearly the same flow characteristics can be obtained when the bimodal alumina CL 370 C is used in combination with Castament® FS 40.

Analogous flow chart characteristics of both three-component systems were observed when using the high range alumina cement Secar 71. However, in this case, Castament® FS 20 is the better dispersant (Fig. 7a and 7b).

Finally, it can be concluded that Castament® FS 20 should disperse a microsilica containing castable with a high range calcium aluminate cement best, while Castament® FS 40 should be the most suitable for castables with a low range calcium aluminate cement.

3.2 Test with a Bauxite Castable

After finishing the basic research, the obtained results were proven by a low cement bauxite-based castable. The test composition is shown in Table 2.
The vibration flow of the castable, as a function of time, is shown in Figs. 7 and 8. When a low range CAC is used (Figs. 8a and 8b) in this test mixture, Castament® FS 40 is the outperforming dispersant as it is also in the 1:1:1 mixture of CAC, microsilica and alumina. Higher flow values with the bimodal alumina CL 370 C lead to the assumption that CL 370 C provides a superior particle size distribution in this case, which contributes to a better ball bearing effect. If Castament® FS 20 is applied as dispersant it is surprising that changing the type of alumina can either lead to a slightly delayed plasticification effect or to a slight flow decrease.

When changing from a CAC with low alumina content (Lafarge Fondu) to a high calcium aluminate cement, like Secar 71, Castament® FS 40 shows a very constant dispersing activity, yielding a vibratory flow value of the castable of about 100 % independent from the alumina type. However, Castament® FS 20 shows a more powerful initial dispersing effect than Castament® FS 40, but it decreases over time. It is necessary to mention that only slight modifications of the castable’s composition can lead to a vibration flow of more than 220 % over a period of at least 90 min, as shown in a previous publication [4].

### 3.3 Green Strength Development and its Acceleration

A very important characteristic is the green strength development of a castable. It is created by the formation of hydrates of the clinker phases. Thus, it can be determined by recording the heat of hydration – or the temperature – of the fresh castable over the elapsed period of time.

It is well known that the formation of the hydrate phases can be influenced by admixtures. Since SKW Polymers GmbH provides such an accelerated version of a dispersant (Castament® FW 10) it was interesting to research its compatibility with Castament® FS 40. The goal is to demonstrate the possibility of adjusting the hardening of the castable according to the needs, especially in winter time. Therefore, only a small amount of the dispersant Castament® FS 40 was substituted by Castament® FW 10 in the test composition. Four sets of data with different amounts of Castament® FW 10 were recorded at 20 °C. In Fig. 9, the time of the maximum hydration is plotted vs. the dosage of Castament® FW 10. Analyzing the data, a straight line can be drawn (regression coefficient R² = 0.97) demon-
Fig. 8  The flow of a bauxite-based castable with different CAC's

Fig. 9  Effect of Castament FW 10 on the setting time

Flow of castable with different CAC's

Flow of castable with Secar 71

Influence of Castament FW 10 on the Setting Time

4 Conclusion

Based on test results of a binder matrix with equal proportions, a detailed prediction of the flow characteristics of a real castable is impossible. This is most likely due to the fact that proportions and particle size compositions are completely different in both systems. It is clearly demonstrated that the flow characteristics and final physical properties of a castable are strongly dependent on the dispersant used. Therefore, the suitability of a specific dispersant has to be proven for each castable system. In general, however, Castament® FS 40 is recommended for low range CACs and Castament® FS 20 for high range CACs. For a fundamental understanding of the dispersant’s mode of action on a molecular basis, further studies are required and are in progress.

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References


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Dr. Herbert Hommer and Dr. Konrad Wutz
SKW Polymers GmbH, Dr. Albert-Frank-Strasse 32, D-83308 Trastberg, Germany
E-mail: skwpolymers@degussa.com