

CONTROL OF FORMULATION AND OPTIMIZATION OF SELF-FLOW CASTABLES BASED ON PURE CALCIUM ALUMINATES

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ABSTRACT

The main aspects that determine properties of self-flow castables, as represented in a triangle of interactions, are analyzed. From the point of view of particle size distribution, different models of distribution are compared in order to define which one corresponds to the best solution for self-flow castables. The roles of the additives are reviewed and different combinations are proposed for the best deflocculation of the system. The characteristics of the fine fillers like alumina and silica fume are discussed in the context of the main parameters that need to be controlled along with the optimum additions as constituents of the matrix. Finally, pure calcium aluminate cement and its interaction with the whole system is considered as a key parameter in achieving the best properties of the self-flow castables.

1. INTRODUCTION

From the initial growth of low cement castables during the 70's, refractory castables have evolved in terms of performance and complexity up to the gunning of low cement castables. Initially concretes were formed from only cement and aggregates. This was followed by the addition of deflocculants and fine fillers, evolving into systems of deflocculants with other additives. The objective was to optimize the control of properties such as workability as a function of time after mixing with water and less susceptibility to ageing.

The reduction of cement content was achieved in parallel with the use of fillers such as alumina and fume silica. This has allowed, together with additives, the reduction of the amount of water necessary for flow. This is accompanied by increases in

density and higher mechanical strengths. The calcium aluminate cement of these deflocculated systems is of basic importance. Their purity and control of mineralogical phases are key elements in determining castable behaviour. The aggregates which can be considered as chemically inert, form together with the additives, fillers and the calcium aluminate, a particle-size distribution whose influence on the rheological behavior is decisive.

The graphical representation of these complex systems and their interactions is shown using a Triangle of Interactions as in Figure 1.

2. FREE FLOW CASTABLES

The low- and ultra-low cement castables presented, just as the conventional castables, have a need for vibration, sometimes more intense, due to poor flow with reduced water content. The filling of all spaces without defect creation in complex forms and of difficult access has been a limitation. New developments have created

the possibility to produce castables which eliminate the need for vibration during placing. These castables, known as free flow or self flow castables can be placed without external vibration. Additional benefits include fewer mold defects and reduced installation costs. The control of the capacity of castables to flow freely with time, after mixing with water, is of utmost importance for high quality placing.

Following the definition of ASTM C71 - free flow is the capacity to flow readily under its own weight without segregation or splitting. Normally, it is considered a minimum of 50% of flow for a given amount of water for a free flow castable.

2.1. Consistency Determination of Free Flow Castables

Consistency is defined as the degree of flow of a refractory concrete under a specific method of application. In the case of free flow castables, it is the degree of flow under its own weight with a predetermined amount of water, measured in intervals of

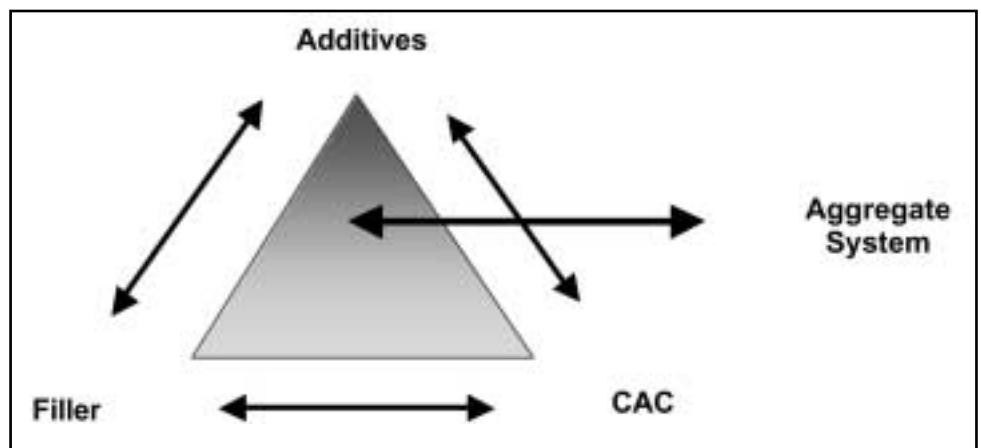


Figure 1: Triangle of interactions showing the main components for the properties of castables in deflocculated systems

time specified after the water addition. The ASTM C-1446-99 method indicates the procedure for measuring the consistency of free flow castables. The results indicate the increase of the diameter of the sample initially formed as a truncated cone of base 100 mm (ASTM C-230). Figure 2 illustrates the main stages of the test, where D1 is equal to 100 mm and D2 the final diameter after flow.

2.2. Determination of Workability Time

ASTM C-1446-99 also guides the determination of the Workability Time since the first measurement is made sixty seconds after the withdrawal of the cone. An interpolation should be made between the first value and the last one above 25%, assuming a linear behavior. The time obtained by

interpolation after the water addition and the value above 25% is considered the Workability Time of the free flow castable. The main stages, schematically, during the application of free flow castables are shown in Figure 3.

- Workability Time is the time after mixing where vibration is needed for installation.
- Gel Formation is the period between loss of characteristic flow and the total loss of workability. It can be seen as a false cementing.
- Setting Time is the time after mixing, where mechanical resistance is developed to allow demolding.
- Hardening is the period of mechanical resistance development after gel formation and setting.

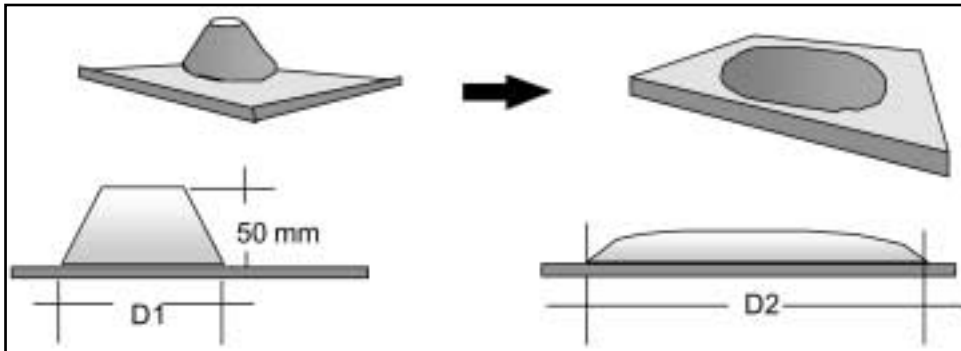


Figure 2: Method of measurement and calculation of the consistency of free flow castables

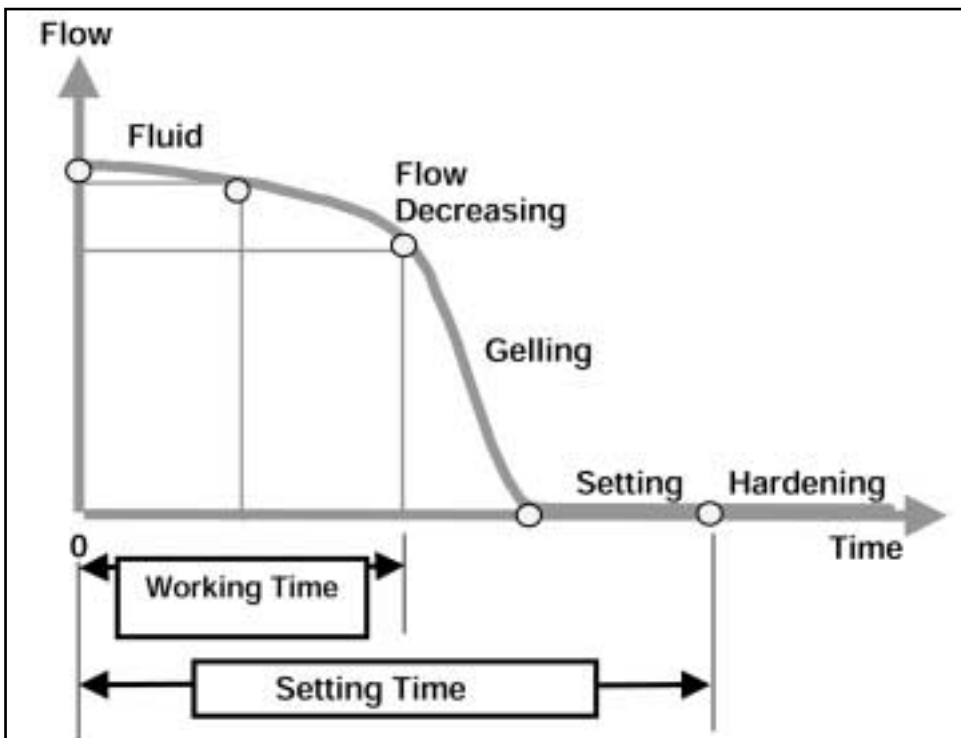


Figure 3: Main stages in the application of free flow castables

2.3. Factors that influence the results during the test

The main factors that are considered as influential regarding consistency and workability of free flow castables are:

- Amount of liquid for mixing
- Temperature
- Time between addition of water and deformation of the cone
- Level of the mold filling
- Time after removing the mold
- Lubrication of the mold before filling
- Return of tested concrete to container for next measurement
- Storage of concrete in bucket of the mixer
- Surface of the table for flow test

It is also important to prevent evaporation during the intervals of measurements. The volume of the mixer bucket must not be greater than double that of the stored concrete.

3. AGGREGATES SYSTEM

The system of aggregates together with the matrix of fillers and calcium aluminate cement determines the particle size distribution of the concrete. Figure 4 represents the size bands for aggregates and the components of the matrix.

The volume and size of particles of the matrix is of fundamental importance since they allow the movement of grains (flow), without loss of refractory properties. The dissolution of the cement is the first step in the hydration sequence and normally occurs soon after mixing and generally after the solubilisation of the additives. However, the amount entering solution is relatively small and therefore the contribution of the cement to the overall particle size distribution of the cement needs to be considered.

Essentially, the granulometric distribution allows more or less contact between particles as well as contributing to the water demand. The particle packing affects the viscosity and the fluidity directly. Figure 5 represents this physical interaction.

Two paths can be followed for adjusting the granulometric distributions of free flow castables: modification of the relation between coarse and fines with an increase in the matrix volume or creation of discontinuities in the distribution. The mathematical models commonly used to develop a

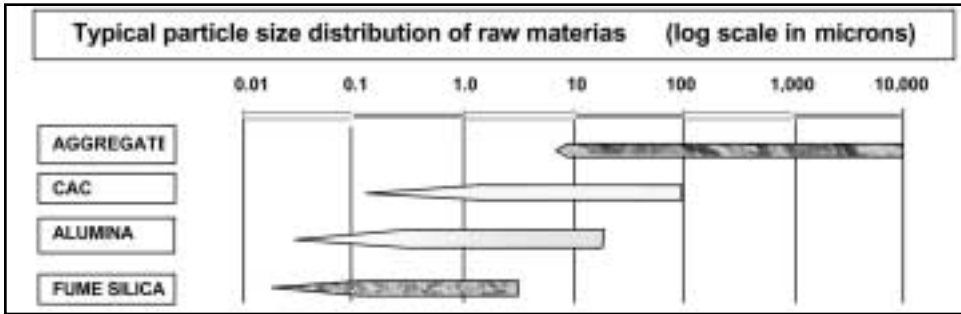


Figure 4. Particle size distribution of aggregates and concrete components of the matrix for free flow refractory castables

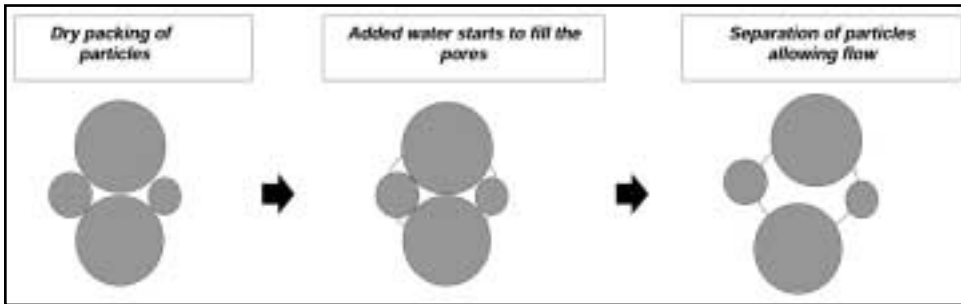


Figure 5. Relation between particle size distribution and particle packing

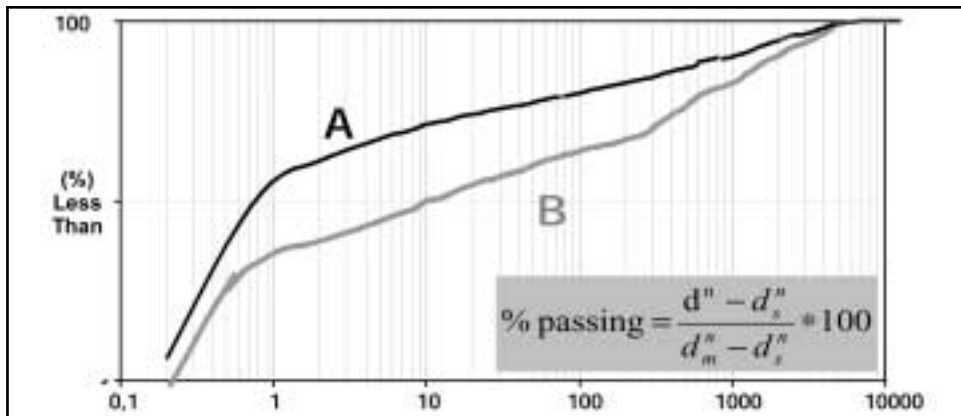


Figure 6. Particle size distributions for two free flow castables. Compositions A and B present the following matrix values for free flow, 90 and 30%, respectively and are shown in Table 1.

Table 1. Components in Figure 6		
	A	B
Fume Silica	6	3
Reactive Alumina	10	0
CAC	5	7
Volume of fines	38	20

granulometric distribution that favors free flow are the models of Andreasen, Dinger & Funk, Furnas and Fuller. Figure 6 shows two examples of the granulometric distribution for free flow castables.

4.0 ROLE OF ADDITIVES

The additives interact with the hydraulic agents during the hydration phase influencing properties such as workability, setting time and initial mechanical resistance. Figure 7 shows some details of this performance. In the case of the aluminite cement, after contact with water, the cement grains start to dissolve liberating ions Ca^{++} and $[Al(OH)_4]^-$, until the solution is saturated. It is followed by an incubation period during which nuclei are formed. After the formation of these of crystallization nuclei, a massive precipitation occurs. Macroscopically, this hydrate precipitation of calcium aluminates corresponds to the setting and hardening stages.

Plasticizer agents or water reducing agents are absorbed on the surface of the cement grains, increasing the zeta potential and promoting good dispersion due to the repulsion between charged positively grains. The mechanism of absorption on the surfaces of the cement occurs for retarding and plasticizer agents, which explains the similar effect in both. Citric acid, a good retarding agent also presents a flowing effect and water reduction, increasing the setting time.

Accelerators normally act in later stages during hydration. They influence the incubation period forming crystallization nuclei and reducing the necessary time for formation of homogeneous nuclei. In the case of lithium carbonate, the precipitation of lithium aluminates forms the nuclei. During the intense precipitation of hydrates, macroscopically seen as the setting, the additives do not modify the formed hydrates. Figure 8 shows an example of the action of an additives on a calcium aluminate cement of 70% of alumina.

With the incorporation of additives it is possible to increase the fluidity for a mortar with Secar 71 and sand under the standard

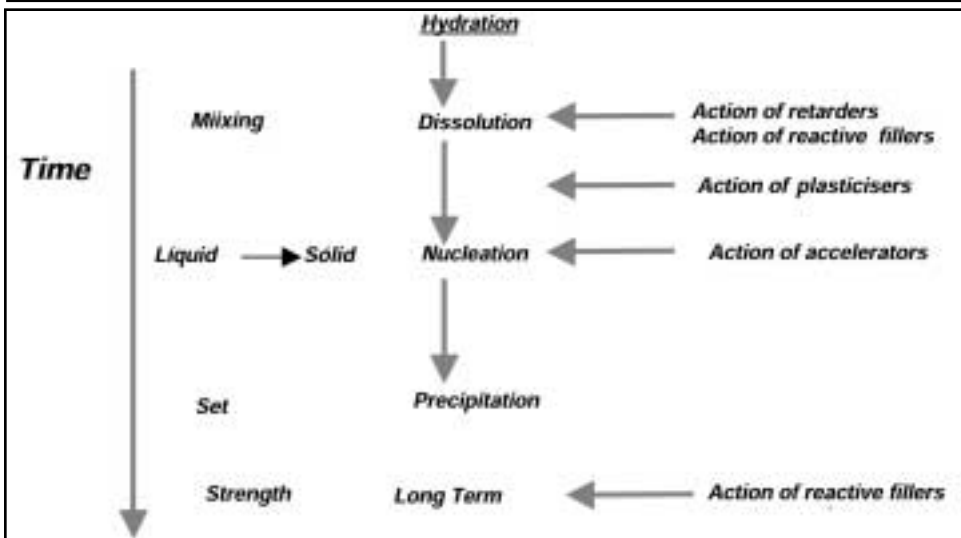


Figure 7. Action of additives on the hydration of calcium aluminate cements

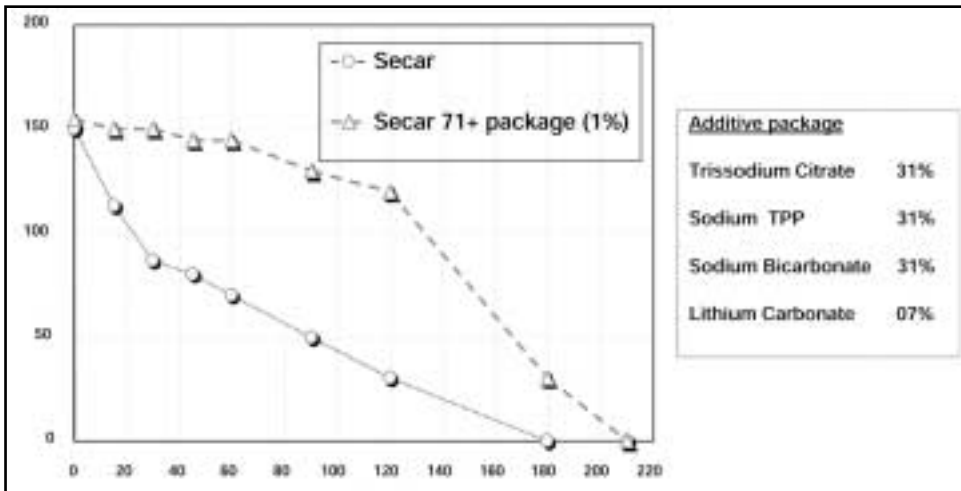


Figure 8. Influence of additives on calcium aluminate cement

AFNOR independently of the temperature. It is possible to adjust the setting time by varying the amount of lithium carbonate. The workability time can be controlled with Sodium TPP dosage.

5. THE ACTION OF THE FILLERS

Fume silica and reactive aluminas are the main components used as fillers in deflocculated systems. In the case of the fume silica, factors such as pH, amount of free carbon, and the moisture content respectively influence the setting time, the mechanical properties, the water demand and the ageing and stability of the properties of the

concrete. Reactive and calcined aluminas influence the properties of concrete due to their specific surface area, crystal size, particle size and soluble alkalis. The main properties affected are the water demand, the workability time, the mechanical resistance, the sinterability, the cementing time and the additive adjustment.

6. BEHAVIOR OF CALCIUM ALUMINATE CEMENTS

The calcium aluminate cements exert a basic role in deflocculated systems and in each stage of the application process they have a well-defined function: (Table 2).

STAGE	NECESSARY ACTION
Mixture	Compatibility with additives Ease of dispersion and low water consumption
Installation	Controlled reactivity to maintain workability
Setting, Hardening	To promote setting and hardening
Final performance	Good mechanical resistance and refractoriness

Raw materials		(%)
Tabular Alumina	6 - 10 mesh	22
	8 - 14 mesh	10
	14 - 28 mesh	19
	48 mesh	29
Reactive Alumina	P 152SB	10
Fume Silica	Elkem 971U	5
Cement	Secar 71	5
Additives	TPP	0.015
	D7S	0.03
	Na-Bicarbonate	0.0045
	Citric Acid	0.0045
	Water	5.2

This behavior is obtained by using pure calcium aluminate cements with adequate specifications and control of mineralogical phases. In applications of deflocculated systems, pure cements (without additives) of 70% of Al_2O_3 containing CA and CA_2 phases in appropriate proportions are recommended for better control of the reactivity during all phases of placing.

7. OPTIMAL FORMULATION OF FREE FLOW CASTABLES

Table 3 shows an optimized standard formulation for free flow castables, using a particle size distribution according to Andreasen and using the additives package already cited, where sodium bicarbonate exerts the function of controlling the pH of the system.

Table 4 shows the resulting characteristics.

Flow at time 0	(%)	110
Flow at 30 sec	(%)	95
Workability Time	(min)	66
Compression strength at 24h	(MPa)	29
Compression strength at 110°C	(MPa)	110
Compression strength at 800°C	(MPa)	140
Compression strength at 1100°C	(MPa)	160
Apparent Density 110°C	(kg/m ³)	3.2
Apparent Density 800°C	(kg/m ³)	3.1
Apparent Density 1100°C	(kg/m ³)	3.1

The final properties that are obtained with free flow castables, show good levels of performance coupled with a facility of use during installation. The attainment of such properties is the result of the study of the individual influence of each component, as well as controlling the different interactions between each component.

8. CONCLUSIONS

Free flow behavior is obtained through the correct selection of the components of the refractory matrix and of the volume ratio between matrix and aggregates. It is necessary to optimize the additives for each specific system. A system of multiple additives with an optimized addition results in

total control of the installation properties. The use of pure calcium aluminate cements is a basic point to obtain free flow castables.

9. REFERENCES

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