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Designing particle sizing and packing for flowability and sintered mechanical strength

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Abstract

In this work, alumina powders in five different commercially available size ranges were used to prepare various refractory castable mixtures, defined using the statistical design of mixture experiments (STATISTICA, StatSoft Inc.) and the EMMA 3.3 software (Elkem Materials). Those mixtures were characterized for packing density, Andreasen particle size distribution modulus (q), flowability and after sintering properties, in order to investigate the relationships between these variables. The optimization of matrix and aggregate sizes and matrix-aggregate proportion, subjected to different property requirements, brought to light the relationships between q, specific surface area (SSA) and maximum paste thickness (MPT). Those relationships were investigated for three fundamental processing steps, namely, dry powders, fresh paste and consolidated dried and sintered bodies. The optimized all-alumina castable was found to require 47.5 wt.% of a fine size matrix with high flowability, which provides the necessary flow bed for 52.5 wt.% of coarse aggregates, resulting in a gap-sized particle size distribution, and presented a fresh paste flowability index above 130% with minimum added water (28 mg/m^2) and sintered modulus of rupture above 50 MPa.

Keywords: A. Shaping; C. Strength; D. Al_2O_3; E. Refractories; Particle packing

1. Introduction

Processing of particulate systems (loose powders, slurries, and pastes) is determined by particle packing, hence particle size distribution and particle morphology. These characteristics also greatly affect many properties and the performance of bodies consolidated from powders (dry and sintered powder compacts). However, the particle requirements for consolidated powders are frequently opposed to those for loose powder systems. Refractory concretes, which can be regarded as composite materials containing a mixture of aggregate particles bound by a matrix of fine particles, provide a unique example of this antagonism: fresh castables require easy flow for improved workability and casting into monolithic linings; set and sintered castables require low porosity and high mechanical strength.[1,2] More than a century's work has been dedicated to find the best compromise solution, from Academia (thorough explanations and comprehensive models) and industry (competitive practical solutions) alike, from the spherical particle packing models of Furnas and Andreasen to the development of the latest generation ultra-low cement castables. Still, it is difficult to define the requisites for an adequate new formulation and the last resort is simple adjustment of older ones, based on rule of thumb or virtue of experience.

Refractory castables are supplied as dry mixed materials to which water, or other specified liquid, is added for in situ mixing and application. A self-flowing refractory castable (SFRC) is formed by a broad size group of coarse particles (aggregate) and another group of fine particles, usually <100 μm (matrix). These two groups of different particle sizes are responsible for the properties of the mixture, hence of the SFRC.

The water content in refractory castables, particularly in SFRC, must be kept to a minimum as steam build up during drying can lead to explosive spalling of the lining and excessive porosity hinders the mechanical strength of the sintered concrete.

This means that the flowability and the paste-like fluid state of the castable have to be provided by a matrix of fine powders. Given the low water level and the fineness of the powder matrix, there is a competition between the Van der Waals interaction forces and the capillary forces between particles, and even the water mixing procedure has to be optimized.[3–5] When the water

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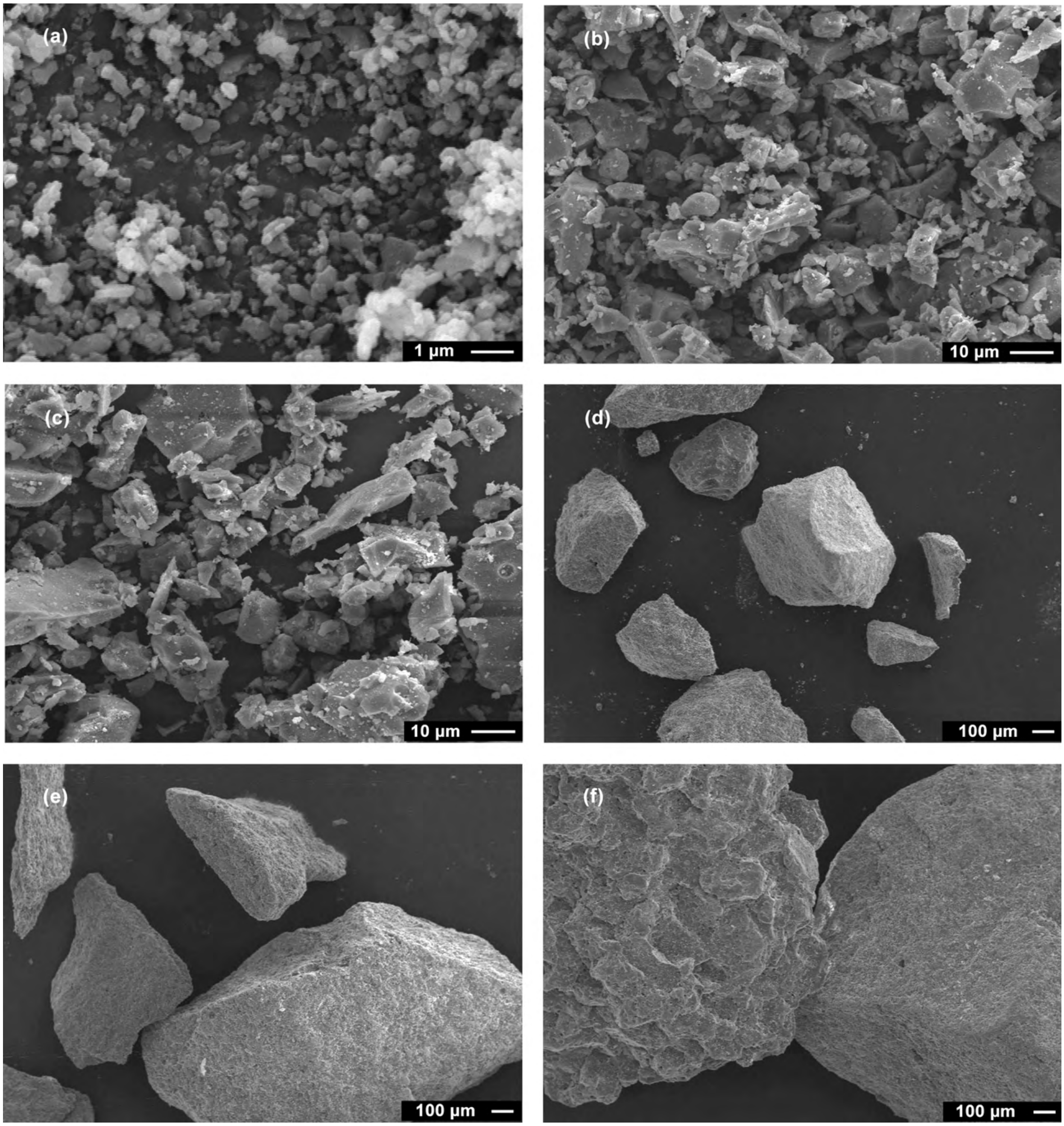

Fig. 1. Comparison of alumina powders used as raw materials, as seen by SEM: (a) reactive alumina CT3000SG; (b)–(f) tabular alumina: (b) <25 μm, (c) <63 μm, (d) 0.2–0.6 mm, (e) 0.5–1 mm and (f) 1–3 mm.

mixing procedure is kept constant, so that all mixtures reach a similar paste-like condition, important properties of the wet castable, such as its flowability, are basically determined by the combination (or mixture) of particle sizes in the fine powder matrix.[6]

The obvious way to reduce the water requirement is to maximise the powders packing density, i.e. to have an Andreasen particle size distribution modulus, q, near 0.37.[7] While modelling particle size distributions (PSD), Andreasen defined the particle size distribution modulus, q, given by Eq. (1), as a measure of the contribution of the various ingredient size classes that compose the mixture to the overall particle size distribution.[8,9] In Eq. (1), CPFT is the cumulative percent of particles finer than a given particle size D, and D_L is the size of the largest particle

$$\mathrm{CPFT} = \left(\frac{D}{D_L}\right)^q \times 100 \qquad (1)$$

The distribution modulus is the slope of the line tangent to the CPFT curve plotted on a logarithmic scale. This is a simple to use tool that allows the control and optimization of the composition of the different size classes in any given particulate system. Using the EMMA 3.3 software (Elkem Materials Mixture Analyzer),[10] mixtures composed of several discrete size classes can be easily “build” as a function of a desired modu-

Table 1
Characteristics of the individual powders used as raw materials.

Alumina powder	Average powder density [g/cm^3]	Average particle size [μm]	SSA [cm^2/g]
CT3000SG	3.963	0.7	80,500
<25 μm	3.879	13.3	7,107
<63 μm	3.924	27.7	8,452
0.2–0.6 mm	3.713	513.0	68.07
0.5–1 mm	3.633	1013	17.50
1–3 mm	3.618	2067	43.27

Table 2
Matrix properties (60 wt.% CT3000SG + 20 wt.% <25 μm + 20 wt.% <63 μm) calculated from the relevant response surfaces (significance level $p < 0.05$, 95% confidence interval)[5].

Predicted matrix properties	
Modulus of particle size distribution (*Andreasen*)	$0.22 < q < 0.28$
Water for mixture, based on mass [%]	10.59–11.23
Water for mixture, based on specific surface area [mg/m^2]	<30.09
Fresh paste flowability index [%]	>150
Sintered cold modulus of rupture [MPa]	>55
Sintering shrinkage [%]	6.33–6.66
Sintered apparent density [g/cm^3]	3.47–3.50
Sintered bulk density [g/cm^3]	3.20–3.29
Sintered apparent porosity [%]	5.77–8.12
Sintered water absorption [%]	1.91–2.54

lus, q. Small variations in the composition can create significant changes in the model line slope and the properties of the particle size distributions.[11]

However, the work carried out with discrete narrow size classes[6,11,12] showed that maximum particle packing translates into minimum flowability and brought to evidence the effect of the two major factors that promote flowability, namely, the lubricating effect of a high amount of water and the optimization of the PSD. Moreover, the optimization of the PSD for high flowability with minimum added water was shown to be associated with the self-flow character of the castables, which presented a "turning point", and an ideal Andreasen q value near 0.22, which corresponds to a higher maximum paste thickness (i.e. reduced interference between the largest particles).[8] Such an optimized PSD minimises the capillary forces in the presence of a minimum amount of adsorbed water, and the gravity forces associated with the mixture's own weight promote the mixture flowability. The minimum kneading water content, in turn, was shown to be closely related to, and determined by, the particles overall specific surface area (SSA) and should be near 28 mg/m^2 SSA.[12]

For SFRC, because specific surface area is most sensitive to the fine particles content, the self-flow behaviour could be related to a required minimum SSA, close to 2.22 m^2/g, and an optimized matrix content, which translated into an ideal interparticle separation distance and maximum paste thickness (MPT).

The concept of MPT,[9] frequently used in the study of hydraulic castables in civil construction practices and described by Eq. (2), expresses the average distance between coarse particles and relates it to the optimization of the castable rheology

$$\mathrm{MPT} = \frac{2}{VSA_g} \times \left[\frac{1}{V_{sg}} - \left(\frac{1}{1 - P_{ofg}}\right)\right] \quad (2)$$

In Eq. (2), V_{sg} is the volume concentration of coarse particles, VSA_g is the volume surface area of coarse particles (it is the product of the average density by the SSA of coarse particles) and P_{ofg} is the porosity of the coarse particle distribution, calculated by Eq. (3)

$$P_{ofg} = 1 - \frac{1}{V_a} \quad (3)$$

In Eq. (3), V_a is the maximum value assumed by the apparent volume of the mixture of coarse particles, calculated through the Westman and Hugills algorithm,[8] described by Eq. (4). In Eq. (4), a_i is the apparent volume of the size class i, and x_i its mass fraction in the mixture.

$$V_{a1} = a_1 x_1, \quad V_{a2} = x_1 + a_2 x_2, \quad V_{a3} = x_1 + x_2 + a_3 x_3, \quad \ldots \quad V_{ai} = \sum_{j=1}^{i-1} x_j + a_i x_i \quad (4)$$

Accordingly, it is assumed that part of the matrix fills in all the voids formed by the coarse particles, another part covers the aggregates surface and the remaining matrix contributes to increase the distance between coarse particles thus reducing their interference.

It has been shown[11,12] that only a matrix with self-flow character can originate a SFRC with reduced kneading water demand. While controlling the water mixing procedure, it was observed that the quantification of the water that needs to be added to the mixture can be based on the SSA, which is also a measure of the mixture's ability to reach the self-flow "turning point". In the mixture design, it is fundamental to ensure a minimum SSA in order to guarantee a sufficient volume of fine particles in the mixture (matrix), to promote the self-flowing properties and also the fluid paste consistency fundamental to avoid the use of hydraulic cement as binder. Thus, the MPT parameter could be used to select the ideal proportion between matrix and aggregate as the one that presents lower interference among aggregates and, consequently, better flowability.

Nevertheless, there are endless combinations of the same size classes all resulting in nearly the same SSA or MPT. An optimized matrix size distribution can be combined, in optimized proportion, with an optimized aggregate size distribution, leading to the improvement of the properties and the cost of the final castable.[13,14] The optimization of matrix and aggregate sizes and matrix-aggregate proportion, subjected to different property requirements brought to light the relationships between Andreasen size distribution modulus (q), specific surface area (SSA) and maximum paste thickness (MPT). The present work seeks to further understand the relationships among those variables by investigating the prevailing mechanisms for three fundamental processing steps, namely, dry loose powders, fluid fresh paste and consolidated dried and sintered bodies.

2. Experimental

Commercial (Alcoa) tabular alumina T60, available in four different size classes (<0.2 mm, 0.2–0.6 mm, 0.5–1 mm and 1–3 mm), and reactive alumina CT3000SG (d_{90} = 2.1 μm) were used as raw materials. The aggregate was prepared by combining the three coarser size classes (0.2–0.6 mm, 0.5–1 mm, 1–3 mm), whereas the self-flow matrix was prepared by combining the CT3000SG alumina with two other fine size classes (<63 μm and <25 μm) obtained from the <0.2 mm size class. The <63 μm size class is the powder that passes through a series of vibrating standard Retsch sieves (100, 140, 200 and 230 mesh), in a dry screening separation of the <0.2 mm size class of commercial tabular alumina. The <25 μm size class is the powder that passes through a similar series of vibrating sieves (200, 230, 325 and 500 mesh), in a wet screening separation of the <63 μm size class. After screening, the passing suspension is left to settle, decanted and dried. Powders in each size class were observed by scanning electron microscopy (SEM, Hitachi S2700) and the corresponding specific surface area (SSA) and particle size distributions were obtained using the laser diffraction method (Coulter LS200 particle size analyser, between 0.4 μm and 2000 μm). The powders average density was determined by pycnometry.

The various optimization studies started with the definition of a {3, 2} augmented centroid simplex lattice (ten points), within the relevant particle size composition triangle.[15,16] Each property was experimentally evaluated at those simplex points in various replications and valid models were calculated to describe it (software STATISTICA, StatSoft, Inc.). The models were found to be statistically significant (significance level $p < 0.05$, 95% confidence interval) and were accepted as true descriptions of the real system behaviour after experimental validation.

The proportions between matrix size components were optimized for minimum added water and maximum FI (FI > 150%),[5] hence minimum sintering shrinkage and maximum sintered mechanical strength. The ideal matrix composition was found to be 60 wt.% CT3000SG and 20 wt.% of each of the other size classes (<25 μm and <63 μm). A detailed description of the matrix optimization can be found elsewhere.[5] Thus, this matrix composition was kept constant throughout this work.

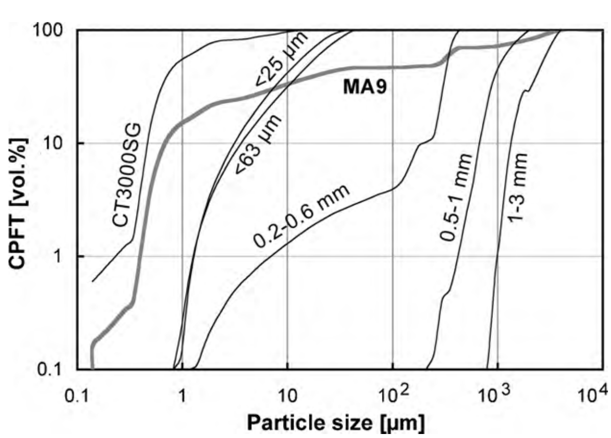

Fig. 2. Particle size distributions of the six classes of alumina powders used as raw materials. Also shown is the particle size distribution of the best castable mixture MA9, discussed further down the text.

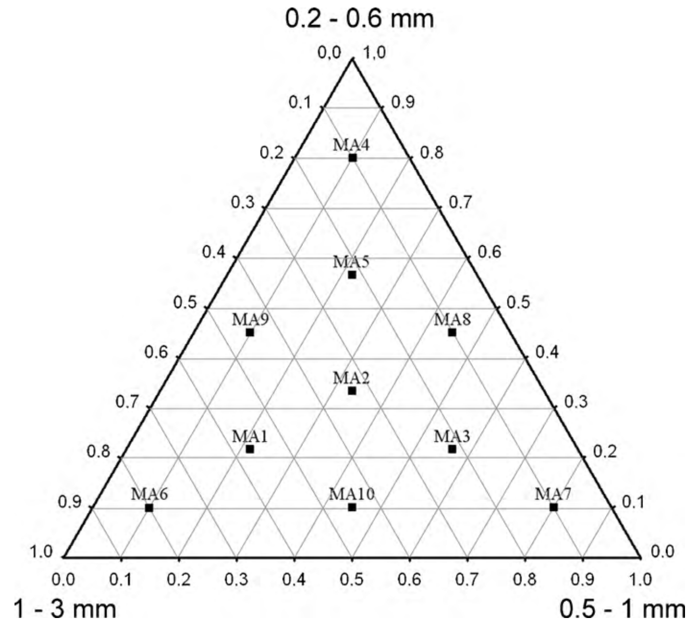

Fig. 3. Aggregate sizes composition triangle with 10 simplex mixtures.

The best proportion between matrix and aggregate was found to be near 50% of each.[11] When working with commercial size classes, however, the finest sizes of the aggregate overlap part of the matrix sizes, meaning that the matrix content can be accordingly reduced. Details of the optimization of the matrix/aggregate proportion can be found elsewhere.[14]

Powders in the selected proportions were mixed with water (28 mg/m^2, constant), in a mortar-blender (Tecnotest, 5 l) using citric acid (0.36 mg/m^2) as deflocculant, as described in the Portuguese Patent 103432 (2008).[17]

Fresh pastes were characterized in terms of FI, as specified by the ASTM C230 Standard (average of four different measurements for each composition), cast into metal moulds (25 mm × 25 mm × 125 mm) and left to dry in the open for 24 h. Test pieces were then demoulded, oven-dried at 110 °C for further 24 h, and sintered at 1600 °C, following the specifications of the ASTM C865 Standard.

Cold mechanical strength (MoR) was evaluated as three-point bending strength (ASTM C133), both for dried and sintered test pieces (average of three different test pieces for each composition).

Apparent porosity, bulk density and water absorption of sintered test pieces were determined using Archimedes water displacement method after 24 h, 48 h and 72 h immersion in water (ASTM C20).

3. Results and discussion

Fig. 1 compares the morphology and typical sizes of the six alumina powders used as raw materials. Table 1 summarizes the individual powders characteristics and Fig. 2 shows the corresponding particle size distributions. The Andreasen modulus,

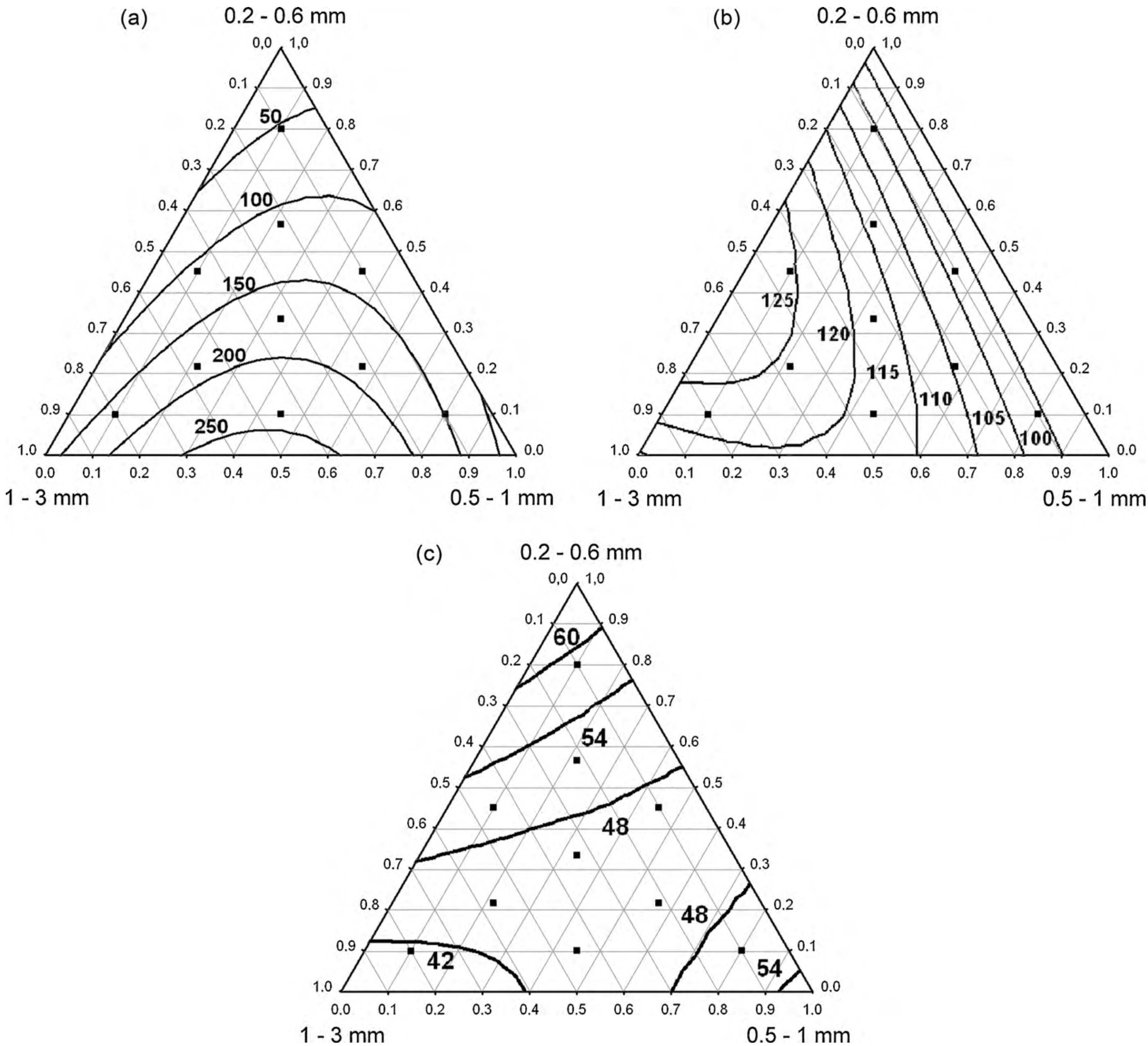

Fig. 4. Castables properties contour plots as functions of the aggregate size composition: (a) MPT [μm]; (b) fresh paste FI [%]; and (c) sintered MoR [MPa].

q, of each distribution is the slope of the tangent to the corresponding CPFT curve. Also shown in Fig. 2 is the particle size distribution of the best castable mixture MA9, discussed further down the text.

Using the three finest size classes (CT3000SG, <63 μm and <25 μm) and the Andreasen particle size distribution modulus, the matrix size composition was optimized for highest flowability with minimum added water, as described in detail elsewhere.[5] Table 2 summarizes the characteristics of the ideal matrix composition (60 wt.% CT3000SG + 20 wt.% <25 μm + 20 wt.% <63 μm), which was kept constant throughout the work.

In an earlier work,[11] aggregates were prepared by combining coarser size classes, so that the distribution modulus, q, varied between 0.18 and 0.28. Using the MPT concept, the best proportion between matrix and coarse aggregate for maximum FI was found to be near 50% of each, corresponding to $q = 0.22$. It was observed that the water requirement decreases when the matrix content increases, in spite of the increase in total SSA. This is no doubt the contribution of the reduced interference between the aggregate particles (i.e. higher MPT) provided by the higher matrix content. Although the increase in the broadness of the mixture particle size distribution reduces the overall flowability, it also decreases the kneading water content, enables better dimensional stability and increases the SFRC sintered mechanical strength.[13]

When working with commercial size classes (0.2–0.6 mm, 0.5–1 mm, and 1–3 mm), however, and as shown in Fig. 2, the finest sizes of the aggregate overlap part of the matrix

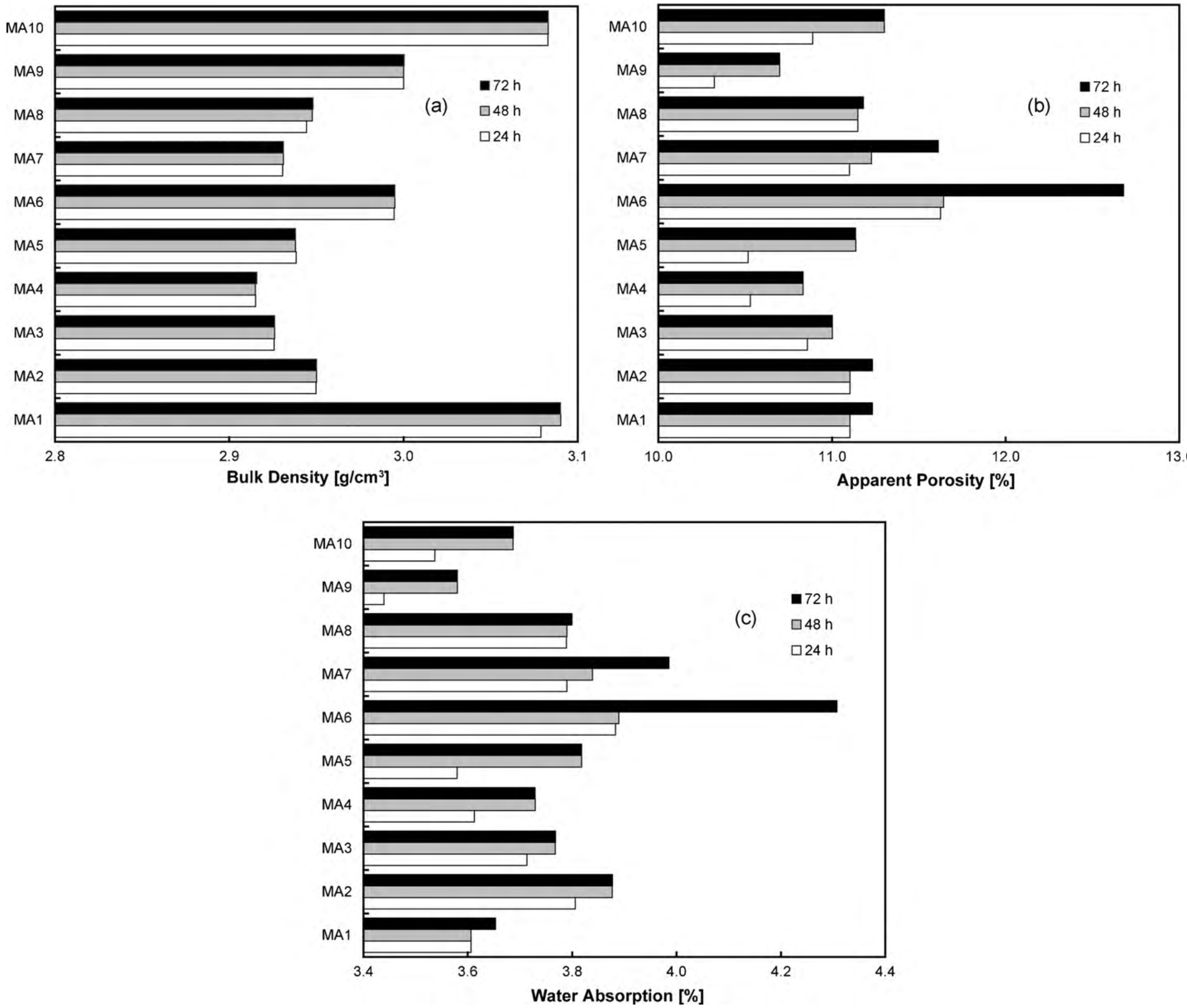

Fig. 5. Properties of sintered castables (24, 48 and 72 h water immersion): (a) bulk density; (b) apparent porosity; and (c) water absorption.

sizes (2.90 vol.% below 44 μm), meaning that the matrix content can be accordingly reduced to 47.5 wt.%. In this way, the required minimum of 2.466 m^2/g SSA and 227 μm MPT were guaranteed. Details of the optimization of the matrix/aggregate proportion can be found elsewhere.[14]

For this matrix content, the proportions between aggregate size components can be optimized to produce a SFRC with high flowability, hence of easy industrial application, without hindering the castable's final mechanical strength. To this aim, a new simplex design of experiments was established (Fig. 3) to define the ten aggregate size combinations to be investigated.

The ten castables were prepared as described earlier and characterized in the paste-like condition (FI, three replications) and after sintering (cold MoR, five replications). Also, the MPT values were calculated using Eqs. (2)–(4) as a function of the changes in the aggregate size composition while keeping the matrix sizes constant. From the results obtained in the various replications, statistically optimized regression equations were calculated subjected to a probability degree of 95% and 0.05 maximum error, to describe the properties as functions of the aggregate size composition, and experimentally validated (Table 3).[15,16] For easier visualization, the final quadratic equations are plotted as constant property contour plots (response surfaces) in Fig. 4.

The diagrams in Fig. 4 clearly show that there is a non-linear dependence of properties on the aggregate size composition. From the MPT contour plot (Fig. 4a), it can be observed that the finest aggregate size (0.2–0.6 mm) has the greatest effect on MPT: increasing this size class content leads to a steep decrease in the MPT value, meaning that the aggregate particles are nearer each other. Therefore, it is not surprising that an increase in the (0.2–0.6 mm) class content also leads to an increase in MoR (Fig. 4c), which can exceed 60 MPa. However, an increase in FI is better achieved by a reduction in the (0.5–1 mm) class content

Table 3
Property equations (quadratic) calculated from experimental results (significance level $p<0.05$, 95% confidence interval[15,16]). X, Y and Z are the contents (wt.%) of the size classes 1–3 mm, 0.5–1 mm, 0.2–0.6 mm, respectively.

R^2	$R_{Adj}{}^2$	Model equation
0.8912	0.8042	MPT [μm] = $132.945X+72.926Y+6.087Z+665.561XY+279.702YZ$
0.7598	0.5676	FI [%] = $121.183X+99.854Y+95.438Z+85.393XY$
0.9605	0.9110	MoR [MPa] = $38.455X+52.710Y+66.736Z-70.157YZ$

(Fig. 4b). In other words, a high MPT value is necessary for good fresh paste flowability, but it might not be enough. As an example, there is a large range of aggregate size combinations with MPT values between 100 μm and 150 μm but only a restricted area within that range presents adequate flowability.

To produce a SFRC with easy industrial application and good sintered mechanical behaviour, a fresh paste FI > 110% and a cold MoR > 50 MPa after sintering are desirable. Among the mixtures investigated, MA5 and MA9 fulfil these requirements.

The diagrams in Fig. 5 show other properties of the sintered castables, namely, bulk density, apparent porosity and water absorption, which enable further comparison of mixtures MA5 and MA9. Although the two mixtures present similar MPT and MoR values, mixture MA9 presents better flowability, which results in a sintered castable with ∼4% less porosity, hence ∼7% less water absorption, and the corresponding ∼2% higher density.

Fig. 6 shows the changes in particle packing density as the system goes from dry loose powders to fluid fresh paste, to consolidated dried and sintered body (apparent density).

The addition of water to the loose powders causes the expected increase in packing density (lubricating effect). As the consolidated body dries out, porosity replaces the evolved water (decrease in packing density, evaluated as apparent density). Sintering mechanisms contribute to reduce the dried body porosity and the apparent density reaches the maximum value.

When the particle size distribution curve of mixture MA9 is plotted in comparison with those of the individual powders (Fig. 2), and the Andreasen distribution modulus, q, is calculated, a gap-sized distribution is clearly visible, roughly between 40 μm and 250 μm. Thus, the mixture that presented the best results contains a matrix fraction (<40 μm) with a PSD modulus $q=0.275$ ($R^2=0.988$) and an aggregate fraction (>250 μm) with

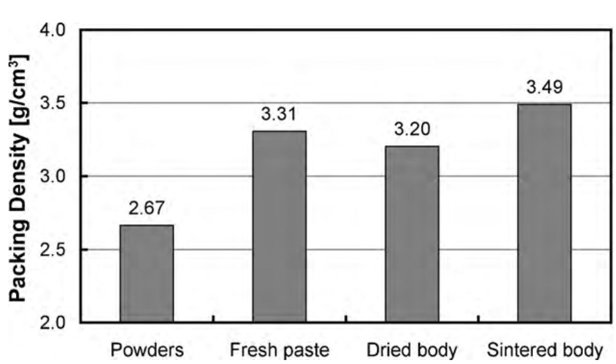

Fig. 6. Changes in packing density in mixture MA9: dry loose powders, fluid fresh paste and consolidated dried and sintered bodies.

a PSD modulus $q=0.169$ ($R^2=0.934$), both much lower than the Andreasen distribution modulus that corresponds to maximum particle packing ($q=0.37$). Moreover, it is interesting to note that the ideal continuous PSD with maximum flowability, i.e. minimum interference between aggregate particles, has $q=0.22$,[8] which is in between the q values now obtained for the matrix and aggregate fractions of the ideal gap-sized PSD.

4. Conclusions

The present work was aimed at further understanding the relationships among the Andreasen particle size distribution modulus (q), specific surface area (SSA) and maximum paste thickness (MPT) in self-flow refractory castables (SFRC) containing no cement. Practical experience and previous studies have shown that it is not possible to conciliate maximum fresh castable flowability with highest sintered castable mechanical strength, not to mention castable cost. However, a compromise solution can be determined (optimized composition) so that the best property values are reached. Using the Andreasen q modulus and MPT concepts, an optimized matrix size distribution can be combined, in optimized proportion, with a combination of commercial aggregate sizes, leading to the improvement of the properties and the cost of the final castable. Still, the results obtained showed that there are endless combinations of the same aggregate size classes all resulting in nearly the same SSA (∼2.466 m^2/g) or MPT (100–150 μm), but many among them will present limited flowability.

The optimization studies carried out with commercially available alumina powders brought to light that the best results for easy industrial application (fresh paste FI = 130%) and high sintered mechanical strength (MoR = 51 MPa) and reduced porosity were reached when there was a clear particle size gap between matrix and aggregate sizes, roughly between 40 μm and 250 μm. Both matrix and aggregate fractions present Andreasen distribution modulus much lower than that corresponding to maximum particle packing ($q=0.37$) and the Andreasen q modulus of the ideal continuous PSD with maximum flowability ($q=0.22$) lies in between the two.

Acknowledgement

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