Refractory castables for civil use: main properties depending on its application

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Abstract

Quick-setting castables for civil use have been developed for the repair of industrial floors, bridges, airport runways, for fixing of metal parts and in those places where quick release is needed for transit. Some characteristics of the castables are quick setting, compensated shrinkage, high mechanical strength and resistance to aggressive agents. After 24 hours, they have high mechanical strength, good thermal shock resistance and at temperatures between 1000\textdegree{}C-1200\textdegree{}C. In this paper it is presented the characterization of three refractory castables with different Al\textsubscript{2}O\textsubscript{3}/SiO\textsubscript{2}/CaO ratios.

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1. Introduction

Castables for civil use have been developed for the repair of industrial floors, bridges, runways, for fixing of metal parts and in those places where quick release for transit is needed. Also, they are used in the cement
plants, chemical, food, ceramics and iron and steel industries, and in incinerators and boilers. They are composed of calcium alumina cement and refractory aggregates with high abrasion resistance.

These castables have quick setting, compensated shrinkage, high mechanical resistance and are resistant to aggressive agents. After 24 hours of its application, they have high mechanical strength, good thermal shock resistance and at temperatures between 1000ºC-1200ºC.

This paper presents the characterization of three refractory castables with different \( \text{Al}_2\text{O}_3/\text{SiO}_2/\text{CaO} \) ratios. Table 1 shows the chemical composition of each castable.

### Table 1. Chemical composition of the quick-setting castables

| Material | \( \text{Al}_2\text{O}_3 \) | \( \text{SiO}_2 \) | \( \text{CaO} \) | \( \text{Fe}_2\text{O}_3 \) | \( \text{TiO}_2 \) |
|----------|----------------|----------------|----------------|----------------|----------------|
| A        | >10            | <52            | <15            | <8             | <2             |
| B        | >30            | <10            | <45            | <16            | -              |
| C        | >68            | <9             | <11            | <6             | <4             |

The characterization of the castables for civil use included the preparation of the castables and casting of specimens in the laboratory; determination of the flowability, the setting time and the hydration curve; determination of the cold crushing strength at different times after the preparation of the castable (2, 6 and 24 hours and 7 days) and of the permanent linear change of specimen dried at 110ºC for 24 hours. Also it was determined the chemical composition by X-ray fluorescence and EDS analysis, and identification of the mineralogical phases by X-ray diffraction of the three castables under study.

### 2. Experimental and Results

The preparation of the castables’ specimens was in accordance to the procedure described in the standard ABNT NBR 8382. Table 2 presents laboratory conditions: water addition, water temperature and room temperature.

### Table 2. Laboratory conditions for the preparation of each material

| Material | Water requirement specified in the technical data sheet (%) | Water (%) | Water temperature (ºC) | Room temperature (ºC) |
|----------|-------------------------------------------------------------|------------|------------------------|-----------------------|
| A        | 7-9                                                         | 11,3       | 28,3                   | 22,1                  |
| B        | <8                                                          | 12,7       | 24,8                   | 19,4                  |
| C        | <7                                                          | 13,6       | 26,7                   | 24,7                  |

### 2.1. Setting time and hydration curve

Once the mixing is completed, a portion of the preparation is placed in a flexible plastic cup, the time is recorded and the material is left until hardening. The flexibility of the body should be monitored regularly until the material reaches rigidity (table 3).
Table 3. Setting time

| Material | A   | B   | C   |
|----------|-----|-----|-----|
| Water (%)| 11.3| 12.7| 13.6|
| Setting time (min) | 99  | 90  | 95  |

Figure 1 presents the hydration curves of the three castables under studied, where the exothermal peak corresponds to the conversion of the cement phase.

Fig. 1. Hydration curves

2.2. Flowability

A conical mold is placed at the center of a flow table and is filled with castable. Then, the mass is tamped several times with the tamper to ensure uniform filling of the mold, castable surface is leveled and is removed from the mold. Immediately after removing the mold, the table is drop 15 times in intervals of 1 second. The flow is the resulting increase in average base diameter of the castable mass, from the measurement of two orthogonal axes (table 4 and figure 2).

Table 4. Flowability of the castables under study

| Material | A   | B   | C   |
|----------|-----|-----|-----|
| Flow (cm) | 13.7| 12.0| 12.0|
Fig. 2. Castable A after the flow test

2.3. Chemical and mineralogical composition

Table 5 shows the chemical composition of the three materials, determined by X-ray fluorescence and weight loss at 950°C and table 6 presents the mineralogical phases identified by X-ray diffraction. Measurements were performed on ground dry material, passing mesh 120 μm.

Table 5. Chemical composition of the quick-setting castables

| Material | Al₂O₃ | SiO₂ | Fe₂O₃ | CaO | MgO | TiO₂ | K₂O | Weight loss |
|----------|------|------|-------|-----|-----|------|-----|-------------|
| A        | 22,1 | 36,6 | 6,4   | 16,9| 7,2 | 2,4  | 1,6 | 2,5         |
| B        | 36,3 | 10,3 | 12,5  | 36,0| 0,7 | 1,5  | 0,1 | 1,8         |
| C        | 57,3 | 15,7 | 6,4   | 15,4| 0,4 | 2,8  | 0,2 | 1,2         |

Table 6. Mineralogical phases identified in the castables under study

| Phases                                      | A  | B  | C  |
|---------------------------------------------|----|----|----|
| Calcium aluminate – CaO·Al₂O₃               | ✓  | ✓  | ✓  |
| Aluminum oxide (Corundum) – Al₂O₃           | -  | ✓  | ✓  |
| Silicon oxide (Quarzt) – α SiO₂             | ✓  | Traces | ✓  |
| Aluminum silicate (Mullite) – 3Al₂O₃·2SiO₂  | ✓  | -  | ✓  |
| Calcium aluminum silicate (Gehlenite) – 2CaO·Al₂O₃·SiO₂ | -  | -  | ✓  |
| Calcium silicate (Rankinite) – 3CaO·2SiO₂   | ✓  | Traces | Traces |
| Potassium aluminum silicate (Leucite) – KalSiO₆ | ✓  | -  | ✓  |
| Titanium oxide (Rutile) – TiO₂              | ✓  | ✓  | -  |
| Aluminum silicate hydroxide (Pyrophyllite) – Al₃SiO₆(OH)₂ | ✓  | -  | -  |
| Magnesium aluminum silicate (Pyrope) – Mg₃Al₃(SiO₄)₃ | ✓  | -  | -  |
| Iron aluminum silicate (Almandine) – Fe₃Al₃(SiO₄)₃ | ✓  | -  | -  |

2.4. Permanent linear change

The permanent linear change of specimens dried at 110°C during 24 hours is presented in table 7.
Table 3. Setting time

| Material | Specimen 1 | Specimen 2 |
|----------|------------|------------|
| A        | -0,14      | -0,15      |
| B        | -0,12      | -0,11      |
| C        | -0,18      | -0,11      |

2.5. Mechanical properties

The values of cold crushing strength at different times from castable preparation and of specimens dried at 110ºC during 24 hours are shown in table 8. The tests were performed under ABNT NBR 11222: 2010 Standard.

Table 8 Cold crushing strength at different times from preparation of the castables and at 110ºC during 24 hours

| Time      | Sample | Material | A   | B   | C   |
|-----------|--------|----------|-----|-----|-----|
|           |        |          | 2 hours |       | 6 hours |           | 24 hours | 7 days | 110ºC x 24 hours |
|           | 2      | 2        | 7,3 | 15,7 | 7,7 | 23,5 | 16,2 | 10,8 | 20,8 | 14,1 | 11,3 | 27,6 | 16,5 | 12,4 |
|           |       | 2        | 6,4 | 15,0 | 7,5 | 26,4 | 17,8 | 18,6 | 28,1 | 16,9 | 12,8 | 24,5 | 17,1 | 11,7 |
|           | Average|          | 7,9 | 15,3 | 6,6 | 25,1 | 17,2 | 13,6 | 25,5 | 18,3 | 13,5 | 24,5 | 17,0 | 12,2 |
|           | 2      | 2        | 8,1 | 15,3 | 4,4 | 26,1 | 17,6 | 13,4 | 24,5 | 17,1 | 11,7 | 24,5 | 17,0 | 12,2 |
|           | Average|          | 9,7 | 15,2 | 6,7 | 24,5 | 17,1 | 11,7 | 24,5 | 17,1 | 11,7 | 24,5 | 17,0 | 12,2 |
|           | 2      | 2        | 9,7 | 15,2 | 6,7 | 24,5 | 17,1 | 11,7 | 24,5 | 17,1 | 11,7 | 24,5 | 17,0 | 12,2 |
|           | Average|          | 9,7 | 15,2 | 6,7 | 24,5 | 17,1 | 11,7 | 24,5 | 17,1 | 11,7 | 24,5 | 17,0 | 12,2 |
|           | 2      | 2        | 23,5 | 16,2 | 10,8 | 28,1 | 16,9 | 12,8 | 29,7 | 18,3 | 15,3 | 29,1 | 21,5 | 15,1 |
|           | Average|          | 25,1 | 17,2 | 13,6 | 25,5 | 18,3 | 13,5 | 29,0 | 21,3 | 16,0 | 29,0 | 21,3 | 16,0 |
|           | 2      | 2        | 23,8 | 22,4 | 15,2 | 29,1 | 21,5 | 15,1 | 29,0 | 21,3 | 16,0 | 29,0 | 21,3 | 16,0 |
|           | Average|          | 25,5 | 18,3 | 13,5 | 29,0 | 21,3 | 16,0 | 29,0 | 21,3 | 16,0 | 29,0 | 21,3 | 16,0 |
|           | 2      | 2        | 24,5 | 17,0 | 12,2 | 24,5 | 17,0 | 12,2 | 24,5 | 17,0 | 12,2 | 24,5 | 17,0 | 12,2 |
|           | Average|          | 24,5 | 17,0 | 12,2 | 24,5 | 17,0 | 12,2 | 24,5 | 17,0 | 12,2 | 24,5 | 17,0 | 12,2 |
|           | 2      | 2        | 23,5 | 16,2 | 10,8 | 28,1 | 16,9 | 12,8 | 29,7 | 18,3 | 15,3 | 29,1 | 21,5 | 15,1 |
|           | Average|          | 25,5 | 18,3 | 13,5 | 29,0 | 21,3 | 16,0 | 29,0 | 21,3 | 16,0 | 29,0 | 21,3 | 16,0 |
|           | 2      | 2        | 23,8 | 22,4 | 15,2 | 29,1 | 21,5 | 15,1 | 29,0 | 21,3 | 16,0 | 29,0 | 21,3 | 16,0 |
|           | Average|          | 25,5 | 18,3 | 13,5 | 29,0 | 21,3 | 16,0 | 29,0 | 21,3 | 16,0 | 29,0 | 21,3 | 16,0 |
|           | 2      | 2        | 24,5 | 17,0 | 12,2 | 24,5 | 17,0 | 12,2 | 24,5 | 17,0 | 12,2 | 24,5 | 17,0 | 12,2 |
|           | Average|          | 24,5 | 17,0 | 12,2 | 24,5 | 17,0 | 12,2 | 24,5 | 17,0 | 12,2 | 24,5 | 17,0 | 12,2 |
|           | 2      | 2        | 23,5 | 16,2 | 10,8 | 28,1 | 16,9 | 12,8 | 29,7 | 18,3 | 15,3 | 29,1 | 21,5 | 15,1 |
|           | Average|          | 25,5 | 18,3 | 13,5 | 29,0 | 21,3 | 16,0 | 29,0 | 21,3 | 16,0 | 29,0 | 21,3 | 16,0 |
|           | 2      | 2        | 23,8 | 22,4 | 15,2 | 29,1 | 21,5 | 15,1 | 29,0 | 21,3 | 16,0 | 29,0 | 21,3 | 16,0 |
|           | Average|          | 25,5 | 18,3 | 13,5 | 29,0 | 21,3 | 16,0 | 29,0 | 21,3 | 16,0 | 29,0 | 21,3 | 16,0 |
|           | 2      | 2        | 24,5 | 17,0 | 12,2 | 24,5 | 17,0 | 12,2 | 24,5 | 17,0 | 12,2 | 24,5 | 17,0 | 12,2 |
|           | Average|          | 24,5 | 17,0 | 12,2 | 24,5 | 17,0 | 12,2 | 24,5 | 17,0 | 12,2 | 24,5 | 17,0 | 12,2 |
3. Discussion

Hydration of the cement is an important step and has great influence on the subsequent application of refractory castable, transforming the anhydrous cement to different hydrated phases. As shown in Table 9, monocalcium aluminate (CaAl$_2$O$_4$) is the main active ingredient in all aluminous cements. Cements with lower alumina contain additional phases, such as brownmillerite (Ca$_4$Al$_2$Fe$_2$O$_{10}$) and gehlenite (Ca$_2$Al$_2$SiO$_7$), due to high iron and silica levels. High-alumina cements contain $\alpha$-Al$_2$O$_3$ as additional phases.

Table 9. Hydration rates of the different phases present in calcium aluminate cements

| Relative hydration rate | Low  | Medium | High |
|-------------------------|------|--------|------|
|                         | 35-50| 55-60  | 70-90|
| Fast                    | CA, C4A3S, | CA, C12A7, | CA, C12A7, |
|                         | CA2, C   | CA, C12A7, | CA2  |
| Slow                    | C2S, C4AF, C2AS | C2S, C4AF | - |
| Non-hydration           | CT, A | CT, A | A |

C: CaO; A: Al$_2$O$_3$; S: SiO$_2$; F: Fe$_2$O$_3$; T: TiO$_2$

Although the hydration of cement is the sum of the hydration of each phase, the different anhydrous calcium aluminates react with water in different ways. When the more reactive phases hydrate, significant amounts of heat are developed that increase the temperature in the paste. This promotes the reactivity of the inert phases. In general, the higher the lime contents in the calcium aluminate, higher the reactivity with water (Pena et al., 1999).

In the three refractory castables under study, monocalcium aluminate is the main active ingredient (table 6). The hydration of the calcium aluminate is very complex as different hydration-reaction products may appear. As the temperature and/or time increases, metastable hydrates transform to stable hydrates. At temperature above 30°C alumina gel crystallized giving rise to gibbsite. Every transformation from one hydrate to another takes place with significant volume change that generates porosity in the hydrated mass. The hydrates C$_3$AH$_6$ and AH$_3$ are thermodynamically stables at temperatures higher than 30°C. This phenomenon, known as conversion, takes place at any temperature; but, at a temperature below 20°C, it is a kinetically slow process and it accelerates at higher temperatures.

Unlike conventional castables, which reach conversion after more than 8 hours of the hydration of the cement, the exothermic peaks in the civil castables under study were achieved after two hours for material A and after three hours for materials B and C. Material C (with the highest lime-content) took 90 minutes to harden; meanwhile, material A and C, with similar lime-contents, took almost the same time to harden (95-99 and 95 minutes, respectively).

Figures 3, 4 and 5 show the mechanical properties determined in the laboratory and those indicated in the technical sheet of the refractory castables under study. Material A has lower mechanical strength in comparison to the specification and the greater difference was obtained after 2 h, 24 h and 7 days of preparation. Cold crushing strength of material B, after 24 h and 7 days of preparation, is within the specified values, but at 110°C the value of cold crushing strength is half of the one provided by the supplier.

Comparing the three tested castables for civil use, A material exhibits better mechanical strength after 6 hours from the setting time. Figure 6 shows the cold crushing strength for the three materials under study. It
can be seen that material B presents the lowest value of cold crushing strength (after 2 hours) of the three materials.

Fig. 3. Cold crushing strength at different times from material A mixing

Fig. 4. Cold crushing strength at different times from material B mixing

Fig. 5. Cold crushing strength at different times from material C mixing
4. Conclusion

Refractory castable A has a setting time of 99 minutes and acquires strength after two hours (exothermal peak in the hydration process); meanwhile, materials B and C set within 90-95 minutes and the exothermal peak appeared after three hours.

After six hours, material A showed an improved mechanical strength compared to the other refractory castables.

Material B had good mechanical strength (15 MPa) after 2 hours of castable preparation, which remained almost constant in time.

References

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