

Review paper

# Nano-bonded refractory castables

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## Abstract

Calcium aluminate cement (CAC) contents higher than 3 wt% in refractory castables can have some drawbacks in the various processing steps (mainly drying) and also in their refractoriness when in contact with SiO<sub>2</sub>. The use of colloidal silica as an alternative binder has been studied by many researchers in recent years and recently reports have also explored the use of colloidal alumina for the same purpose. This article reviews the recent developments in nano-bonded refractory castables focusing on the use of colloidal silica or alumina. In the first part of the paper, a comparison of different binding systems for refractory castables is shown. The benefits of replacing CAC or hydratable alumina by colloidal binders are discussed. In the second part, the advantages of colloidal silica/alumina as a refractory binder are highlighted. Meanwhile, the characterization techniques and functional mechanisms of these binders are presented in order to understand the behavior of these systems. Finally, in the last section, the challenges for suitable use of colloidal binders are discussed and the future direction of nano-structured refractory castables is outlined.

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## 1. Introduction

Monolithic ceramics have evolved over the years into a widely used class of refractories that associates performance and cost-effectiveness [1]. In the monolithic family, refractory castables comprise a large group of materials whose application has grown significantly in the last 30 years. Progressing from rather simple mixes, today they comprise some very complex and technical formulations, used in a variety of very demanding and harsh industrial applications. Nowadays, their market share has been increasing and, in many instances, has overcome brick and shaped refractories. Furthermore, for many applications it is the most appropriate choice due to better performance and easier installation [2].

Refractory castables can be classified based on different aspects including CaO content, the binder source, chemical composition, fluidity, bulk density, etc [3]. Their binding system plays a relevant role in different processing steps, including workability, dry-out and service performance. Therefore, all efforts are conducted to improve the bonding agents [4,5].

Different sorts of binding systems have been developed throughout the years starting with hydraulic bonding, in which higher amounts of calcium aluminate cement (CAC) were used, towards coagulating binders such as colloidal silica or alumina (Table 1) [4]. Hydraulic bonding via CAC is the most applied mechanism due to its suitable rheological properties and green mechanical strength. Detailed information about this binder has been described in a recent review [6]. Nevertheless, there are some drawbacks related to the use of CAC in systems containing microsilica and/or magnesia, as the presence of CaO coupled with these other oxides results in low melting point phase formation at high temperatures [7,8]. Other important concerns for cement-based castables arise during the curing and dewatering steps, which must be carefully conducted in order to reduce the explosive spalling likelihood [9–12]. In order to minimize these drawbacks, the properties of the refractory castables were improved by decreasing the cement content, giving rise to a shift from regular cement castables towards LCC (low cement castables), ULCC (ultra low cement castables) and lately cement-free castables [13–16].

Table 1  
Progress in binding system for refractory castables [4].

Binding mode	1920s	1930s	1940s	1950s	1960s	1970s	1980s	1990s	2000s	2010s
Hydraulic	Conventional cement bonded castables (Silicate cement, low purity CA cement)				Pure CA cement bonded castables (CA cement with improved purity) High purity CA cement bonded castables (High purity CA cement + uf-Al <sub>2</sub> O <sub>3</sub> ) p-Al <sub>2</sub> O <sub>3</sub> bonded castables Hydratable Al <sub>2</sub> O <sub>3</sub> bonded castables					
Chemical					Phosphate bonded castables [H <sub>3</sub> PO <sub>4</sub> or Al(H <sub>2</sub> PO <sub>4</sub> ) <sub>3</sub> + MgO or CA] Water glass bonded castables [Na <sub>2</sub> O nSiO <sub>2</sub> + Na <sub>2</sub> SiF <sub>6</sub> ] Sulphate, chloride bonded castables [Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> + CA, MgCl <sub>2</sub> or MgSO <sub>4</sub> ] Polyphosphate bonded castables [Na <sub>5</sub> P <sub>3</sub> O <sub>10</sub> or (NaPO <sub>3</sub> ) <sub>6</sub> + MgO, CaO or CA] Resin bonded castables (Phenol resin, Novalac resin + cross linker)					
Polymerization										
Hydraulic + Coagulating					Low cement castables (CA cement + Clay, CA cement + uf-SiO <sub>2</sub> ) Clay bonded castables (Ca-clay or Na-clay + CA) Ultralow cement castables (uf-SiO <sub>2</sub> + uf-Al <sub>2</sub> O <sub>3</sub> + CA ) Cement-free castables (non-cement castables) (uf-SiO <sub>2</sub> , uf-Al <sub>2</sub> O <sub>3</sub> + electrolyte, uf-SiO <sub>2</sub> + MgO) Sol bonded castables (silica sol, alumina sol + electrolyte) MgO–C castables					
Coagulating										
Carbon bonded										
Nano engineered										In progress

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