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Review Article

The development of a novel process for the production of calcium sulfoaluminate: A review

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Abstract

In an industrial climate where the reduction of carbon emissions is paramount to meeting industry standards for a sustainable future, the cement industry is looking for alternative and creative solutions to reducing its carbon footprint and energy consumption. The title thesis develops a novel process for the production of calcium sulfoaluminate (CSA) cement, a material produced in the Chinese construction industry for use as a rapid hardening binder for 5 decades; but now undergoing rapid change.

The novelty of the proposed process lies partly in its source of sulfur. Typically provided by gypsum in conventional raw feeds, the novel process instead sequesters sulfur into the cement solids through the combustion of elemental sulfur. This combustion event, in turn, contributes towards the calorific value required to heat and maintain kiln temperatures by burning fossil fuel, e.g. natural gas. The combustion of sulfur also provides various added benefits. The resultant sulfur-containing atmosphere in the reaction system provides a protective environment which represses S volatilisation at the operating temperatures used for CSA production, ca 1200–1300 °C.

The novel process was developed with the intention for eventual commercial production in Doha, Qatar. The combustion of sulfur would be additionally beneficial due to the nation's production of vast quantities of natural gas; elemental sulfur is a by-product of the Claus process, used for the desulfurisation of natural gas or sour crude. The proposed novel process would thereby utilise a waste product, i.e. sulfur, for the production of a low carbon cement product.

Keywords: Sustainability; Low energy cement; Calcium sulfoaluminate

Contents

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1. Introduction

1.1. An industry focused on carbon emission reductions

In recent decades, climate change has become an issue of global importance and its mitigation has become a major focus across all industry sectors. Responsible for the generation of 5% of the world's anthropogenic carbon emissions, the cement industry has been no exception. This has led to active efforts to seek alternative solutions to reduce its excessive carbon emissions. In an attempt to build an organised, worldwide drive towards the objective of a "greener" industry, the cement sustainability initiative was established by industry leaders, operating under the umbrella of the world business council for sustainable development (WBCSD). This global consortium was led by 25 of the industry's major cement producers, representing over half of the world's cement production outside of China (World Business Council for Sustainable Development, 2002; The World Business Council for Sustainable Development, 2007). Another initiative launched by the WBCSD was "the low carbon technology partnership initiative" (LCTPi) which operates in many industry sectors including the cement industry. The goal of the LCTPi is to accelerate the research and development of low-carbon technology solutions to keep the increase of the global average temperature to below 2 °C above pre-industrial levels. The LCTPi aims to achieve this by reducing CO2 emissions in the range of 20–25% by 2030 (World Business Council for Sustainable Development). It is certain that the cement industry will need to play a crucial role if this target were to be achieved.

1.2. Calcium sulfoaluminate (CSA) as an alternative low carbon cement

Calcium sulfoaluminate (CSA) cements are not new to the cement industry. The first mention of the use of CSA as a cementitious phase in literature dates back to the early 1960s. Klein (1964) filed a patent which described the use of a calcium sulfoaluminate cement as an expansive alternative to Portland cement or as an addition to produce a cement composition with little to no net shrinkage. This calcium sulfoaluminate portion of the proposed cement was thereby named "Klein's Salt". However, it was not until the 1970s that CSA saw the majority of its development when it was introduced into the Chinese construction industry. Known as the "third series cement", CSA was developed by the China Building Materials Academy who defined two types of CSA compositions, sulfoaluminate, containing ye'elimite and belite as major constituents, and ferroaluminate clinker which consisted of a greater portion of ferrite, $Ca_2(Al,Fe)2O_5$, in addition to ye'elimite and belite. The third series cement was introduced into the Chinese construction industry as a high-performance cement with rapid, high early age strength development (Zhang et al., 1999).

In the European construction industry as well as cement research, there was limited attention given to CSA based cements until recent decades. The increased attention on Calcium Sulfoaluminate cements, was due to CSA being a low CO_2 alternative to Portland cement in an industry in which there was a new global initiative to lower carbon emissions (World Business Council for Sustainable Development, 2002). Its resultant popularity has led to great strides in its development. Various research groups studied the influence of the formation of CSA clinker in air and the performance of the resultant cement. The formation of CSA clinker was studied with respect to the influence of factors such as raw mix design and clinker cooling rates (Ali et al., 1994; Arjunan et al., 1999; Bullerjahn et al., 2014; Martín-Sedeño et al., 2010). Authors also reported that CSA clinker could be synthesised from a range of waste materials and industrial by-products such as blast furnace slag, fly ash, kiln dust, etc. (Arjunan et al., 1999).

Consequent to the cement research conducted, CSA proves to be a very promising low carbon alternative to OPC (Gartner, 2004). However, whereas Portland cement compositions are well known and covered by codes and standards to provide a quality assurance of OPC products, there is no compositional framework equivalent for CSA outside of China. The lack of European CSA standard has inhibited the possibility of CSA being widely adopted by the commercial cement industry. One of the reasons could be attributed to the volatility of SO_3 in sulfate cement phases such as ye'elimite and anhydrite. This leads to an uncertainty when predicting clinker compositions compared to the more kinetically stable calcium silicates and calcium aluminates present in Portland cement. This loss of sulfur at high temperature is also an issue when considering that its loss leads to lower ye'elimite yields in clinkers giving lower early age strengths than could potentially be achieved without SO_3 losses. While this could potentially be compensated, there is a general loss of control over clinker mineralogy.

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