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Short communication

Laboratory synthesis of C_3S on the kilogram scale

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ABSTRACT

An optimized process using amorphous silica for efficient C_3S synthesis in the laboratory is reported: an estimated production capacity of ~2 kg C_3S within a week is possible. Amorphous silica (fumed silica) was used as raw material and inter-ground with $CaCO_3$ and water for C_3S synthesis, the dried raw mixture has sufficient green strength to be self-supporting, which allows large cylinders to be placed in Platinum crucibles. The mineral composition of the sintered sample was quantified with X-ray powder diffraction using Rietveld analysis. C_3S with < 0.4 wt% of free CaO was sintered at a shortened residence time (≤ 5 h) when temperatures ≥ 1550 °C. The efficiency of the C_3S synthesis was dramatically enhanced because of 1) increased burnability of the raw mix due to amorphous silica and very fine $CaCO_3$ particles after grinding, 2) simplified sample preparation process avoiding pressing discs and 3) improved capacities of the crucible and furnace.

1. Introduction

C_3S (tricalcium silicate) is the major phase in Portland cement, as such many studies have been focused on the reaction of this phase alone. However, more extensive work is hindered by the difficulty in obtaining high quality C_3S. It is important to realise that C_3S, like Portland cement will tend to age, due to humidity in the atmosphere, if stored for too long. The best quality materials can be obtained if it is synthesized fresh for each study. Furthermore, local synthesis allows adjustment of the minor elements to obtain alite with grain growth similar to alite in Portland cement, which can then be ground to have a particle size distribution resembling Portland cement. However, most of the standard methods for preparing C_3S are very time-consuming.

The methods typically reported for C_3S synthesis are: solid reaction [1–14] (summarized in Table 1), sol-gel method [15–17]. Pechini or modified Pechini process [18] and the so-called organic steric entrapment method [19,20] were also used to synthesize C_3S. For massive synthesis, the solid reaction using calcium carbonate and SiO_2 (quartz or silica) is more practical and widely used. The procedures, as well as the main limitations for C_3S synthesis are summarized in Table 2. The main factors hindering the C_3S synthesis are: 1) disc pressing is time-consuming; 2) long sintering time is required (> 10 h); 3) capacity of Pt crucibles and furnaces are limited.

Here we report the straightforward synthesis of kilogram quantities of C_3S which adapts the solid reaction method [1,21] and can be used in any laboratory equipped with a high-temperature furnace. The solid reaction routine was modified by changing the raw materials and procedures to maximize the furnace efficiency and decrease the workload of the procedures. The sintering parameters were optimized to maximize the amount of C_3S which could be produced within working hours.

2. Materials and equipment/tools

2.1. Materials and mix design

Calcium carbonate (VWR) and SiO_2 (silica fumed, Sigma-Aldrich) were used as raw materials for C_3S synthesis. The characteristics of the raw materials and the C_3S raw mix are shown in Table 3. The source for SiO_2 was amorphous fumed silicas (see Fig. 1) with a nominal diameter of 0.007 μm and 0.2–0.3 μm indicated by the supplier. These two fumed silicas with different particle size distribution (PSD) were used to check the feasibility to produce C_3S using coarser silica (0.2 μm) instead of using 0.007 μm fumed silica for nano safety reasons. After grinding, both raw mixes made with 0.007 μm and 0.2–0.3 μm fumed silica have similar PSD (see Table 3).

A correction of the mix design was needed based on actual mineral composition detected by X-ray powder diffraction (XRD) or the actual chemical composition by X-ray fluorescence (XRF) of the trial mix design. The reason for the deviation in chemical composition was moisture/solvent residue in fumed silicas so there was less SiO_2 than expected in the weighed quantity. Extra amount silica will be needed to react with the excess f-CaO to compensate for this effect. The excess 3.7 wt% of CaO (by mass 476.67 g × 0.037 = 17.80 g) was compensated by 6.44 g of silica in the mix to form C_3S, resulting 133.11 g of

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Table 1
Summary of the reported raw materials and procedures used for C_3S/alite synthesis.

T (°C)	Resistance time (h)	Repetition	f-CaO (%)	SiO_2 source	Ions	Mixing/grinding	Pretreatment	Ref.
1650	–[b]	–	0.2	–	Al_2O_3, Fe_2O_3, and MgO mixed with C_3S	–	–	[3]
1600	10	1	< 0.5	silica fumed	–	24 h, wet ball mill	φ 70 mm pressed disc	[1]
1600	2	2	Invisible in XRD	Quartz	–	Mixed by lab mixer	1000 °C calcination	[2]
1600	5	2	–	quartz	ZnO and La_2O_3 were introduced with C_3S	–	–	[4]
1550[a]	24	2	< 3	Gel Silica	–	Milled	–	[5]
1520	2 12	3	0.45–1.18	–	Cr, Ni, and Zn in raw mix	–	–	[6]
1500–1550	12–24	3	–	quartz	–	Mixing in ethanol,	in 1000 °C, 1100 °C,	[7]
1500	6	2	–	–	ZnO, MgO in raw mix	3 h dry homogenize	–	[8]
1500	2	> 1	–	–	–	Milled	–	[9]
1500	2	≥2	< 0.5	Silica gel	ZnO in raw mix	–	–	[10]
1500	6	> 1, until no f-CaO detected	f-CaO non-detectable by XRD	Quartz	γ-Al_2O_3 in raw mix	30 min, ball mill at 1200 rpm	1000 °C 6 h, then press discs	[11]
1050	4	1	–	–	$Mg(OH)_2{\cdot}4MgCO_3{\cdot}5H_2O$, γ-$Al_2O_3$	30 min ball mill at 200 rpm after each burn	pressed to disc	[12]
1450	6	1						
1500	6	1						
753	2	2	–	–	–	–	φ 10 mm pressed disc	[13]
1400	3							
1400	1	3	< 0.5	–	CaF_2	–	–	[14]

Notes:
[a] Tubular furnace.
[b] Details not available.

Table 2
Summary of the detailed procedures and limitations for classic C_3S/alite synthesis based on solid reaction.

	Detailed procedures	Limitations
Raw mix preparation	Step 1: mix/grind the raw mix in wet/dry grinding Step 2: dry the ground paste Step 3: powder the dried paste Step 4: press raw powder into discs	● Disc pressing always time-consuming
Sintering	Step 5: sintering	● Long sintering time required (> 10 h) ● Repeated sintering needed ● Limited capacity of the Pt crucible and furnace

Table 3
Characteristics of the raw materials and raw mix.

Samples	D_{v10} (μm)	D_{v50} (μm)	D_{v90} (μm)	Notes
Fumed silica	–	0.007[a]	–	Amorphous
	–	0.2–0.3[a]	–	
$CaCO_3$	4.41	16.11	29.55	Chemical pure
Raw mix (0.007 μm SiO_2)	1.04	3.54	8.30	Wet milled for 24 h
Raw mix (0.2 μm SiO_2)	1.10	4.05	10.30	

Notes:
[a] Reported data from the supplier.

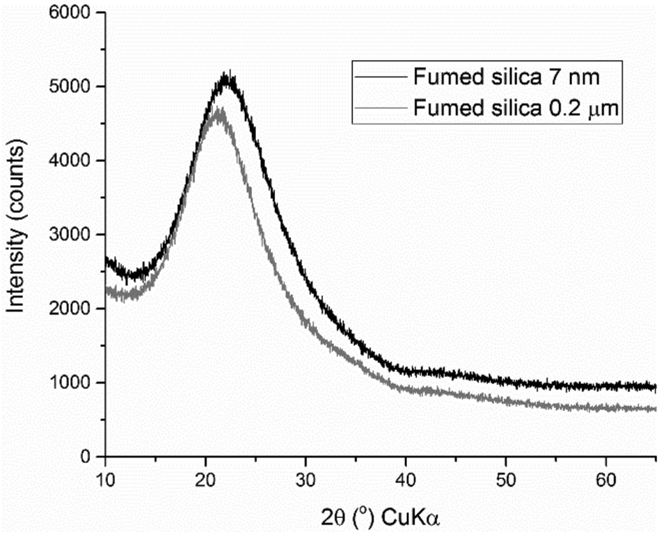

Fig. 1. XRD pattern of the fumed silica, data collection was done using zero background sample holder.

silica.

2.2. Equipment and tools

The required equipment/tools are (see Fig. 2):

- ball milling jar up to 3 L
- milling balls (ZrO_2) with diameter ~30 mm
- rolling machine to grind by rotating the ball milling jar
- cylinder moulds[1]
- ladles, filters and containers (i.e. salad spinner) to separate the ball and mixed raw materials
- high-temperature furnace (up to at least 1600 °C)
- *Pt* crucible
- strengthened crucible tongs with extra-long handle and a fire proof base
- fan for cooling process (cleaned compressed air can be used as well)
- a full set of protection such as heat resistance gloves, welding glasses

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[1] Depend on the size of the platinum crucible and the inside height of the furnace, in this paper the ASTM moulds with the dimension of φ70mm × 140 mm for mortar test was used