



**coal combustion and
gasification products**

Coal Combustion and Gasification Products is an international, peer-reviewed on-line journal that provides free access to full-text papers, research communications and supplementary data. Submission details and contact information are available at the web site.

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Web: www.coalcgp-journal.org

ISSN# 1946-0198

Volume# 6 (2014)

Editor-in-chief: Dr. Jim Hower, University of Kentucky Center for Applied Energy Research

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Suggested Citation format for this article:

Duvallet, T., Zhou, Y., Robl, T.L., Andrews, R., 2014, Synthesis and Characterization of High-Iron Alite-Calcium Sulfoaluminate-Ferrite Cements Produced from Industrial By-Products. *Coal Combustion and Gasification Products* 6, 29-34, doi: 10.4177/CCGP-D-14-00007.1

Synthesis and Characterization of High-Iron Alite-Calcium Sulfoaluminate-Ferrite Cements Produced from Industrial By-Products

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ABSTRACT

Ordinary Portland cement (OPC) and calcium sulfoaluminate cement (CSAC) are well-known and commonly used construction materials. The clinker phases mainly responsible for their strength development are C_3S (alite) in OPC, which hydrates to form a calcium silicate gel phase; and $C_4A_3\dot{S}$ (calcium sulfoaluminate) in CSAC, which hydrates to rapidly form ettringite.

The purpose of this work was to produce high-iron alite-calcium sulfoaluminate-ferrite cements, by combining C_4AF (ferrite), from 5% to 50% by weight, to the C_3S and $C_4A_3\dot{S}$ clinker phases. Producing this alite-calcium sulfoaluminate-ferrite cement would decrease the requirement of bauxite in the raw materials, which would consequently reduce its cost. The use of industrial by-products would also reduce the CO_2 emissions and the firing temperature by 200–250°C compared with OPC. This article presents the synthesis and characterization of five compositions produced from industrial by-products (hydrated lime related to carbide lime, fly ash, slag, and red mud) and bauxite, formulated as follows: C_3S from 20% to 50%, C_2S from 10% to 20%, $C_4A_3\dot{S}$ from 10% to 20%, C_4AF from 5% to 50%, and $C\dot{S}$ from 4% to 6% by weight. The clinker with the lowest ferrite content required a higher firing temperature (1275°C) than the compositions with high ferrite contents (1250°C). Impurities, such as MgO and TiO_2 , introduced by the industrial by-products affected the mineralogical compositions. Consequently, some adjustments of the raw mix were necessary to obtain the desired clinker compositions.

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ARTICLE INFO

Article history: Received 13 May 2014; Received in revised form 3 June 2014; Accepted 6 June 2014

Keywords: alite; calcium sulfoaluminate; ferrite; hybrid cements; industrial by-products

1. Introduction

Both ordinary Portland cement (OPC) and calcium sulfoaluminate cement (CSAC) are well-known construction materials, differing in their mineralogical compositions and strength development characteristics.

OPC is produced from common inexpensive materials, such as limestone and shale. The clinker composition includes alite (C_3S), belite (C_2S), tricalcium aluminate (C_3A), and ferrite (C_4AF), and the subsequent cement achieves high compressive strength through

the hydration of alite to form C-S-H gels. Cement abbreviations used in this article are defined in the Appendix Table. The production of OPC has the disadvantage of generating large amounts of carbon dioxide from the calcination of limestone, and requiring a high temperature of synthesis of 1400–1450°C.

CSAC is made from industrial by-products, such as limestone, gypsum, and fly ash, and requires high quantities of aluminum, usually provided from bauxite, which is a very expensive material. The mineralogical composition of CSAC includes belite (C_2S), calcium sulfoaluminate ($C_4A_3\dot{S}$, or Klein's compound), ferrite (C_4AF), and anhydrite ($C\dot{S}$). This material reaches very high compressive strength values very rapidly compared with OPC, as a result of the hydration reaction of $C_4A_3\dot{S}$ to form ettringite. CSAC can be synthesized with

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Table 1

Chemical composition of industrial by-products (BP) from X-ray fluorescence (XRF) analyses, in percentage by weight

	Hydrated lime	Bottom ash	Red mud	Bauxite	Blast furnace slag fines	Class C fly ash	Fluorite
CaO	65.27	45.91	6.96	0.16	38.34	26.28	–
SiO ₂	1.96	15.3	9.41	6.64	37.03	35.24	–
Al ₂ O ₃	1.56	5.95	15.33	58.54	10.25	20.47	–
Fe ₂ O ₃	0.42	3.44	46.50	6.28	1.13	5.13	–
SO ₃	0.07	23.14	0.44	0.24	0.80	1.83	–
LOI	29.83	4.61	12.81	27.60	0.54	0.38	0.30
MgO	2.11	1.99	0.45	0.20	10.99	5.04	–
K ₂ O	0.07	0.47	0.18	0.01	0.39	0.46	–
Na ₂ O	0.11	0.11	1.59	0.01	0.30	1.47	–
P ₂ O ₅	0.01	0.11	0.74	0.22	0.01	1.43	–
TiO ₂	0.07	0.30	5.70	2.18	0.49	1.24	–
CaF ₂	–	–	–	–	–	–	100.00
Sum	101.48	101.33	100.11	102.08	100.27	98.97	100.30
<i>d</i> (0.5) (μm)	9.6	25.2	14.7	17.5	14.8	9.1	1.8 ¹

Note: LOI = loss on ignition.

¹ Data from Fisher website.

much less limestone than OPC and at a lower firing temperature of 1250°C. This procedure generates less CO₂ emissions from limestone calcination and consumes less fuel than OPC production.

The production of a “hybrid” cement including both Klein’s compound and alite phases would combine specific properties from both clinker phases, but it would be difficult to manufacture due to the formation/decomposition temperature incompatibility between C₃S and C₄A₃Š. Indeed, alite begins to form around 1300°C (Taylor, 1997), and C₄A₃Š starts to decompose at 1300–1350°C (Guo and Xie, 2011). However, this difficulty can be overcome by adding CaF₂ and CaSO₄ as fluxes and mineralizers in the raw materials (Blanco-Varela et al., 1995; Odler and Zhang, 1996). Cements containing both of these clinker phases have already been produced and are typically composed of 30–50% by weight of C₃S, 30–40% of C₂S, 5–20% of C₄A₃Š, and 3–10% of C₄AF (Tang and Lu, 2006). This “hybrid” cement has shown great potential but is still at an early stage of development (Zhang and Odler, 1996; Liu and Li, 2005; Ramirez Tovia et al., 2011).

The objective of the present work was to produce high-iron alite-calcium sulfoaluminate-ferrite cements from industrial by-products, such as fly ash, bottom ash, and red mud, which are widely available worldwide and are generally a problem in the concerned regions. The interest in producing a cement with large quantities of ferrite into the alite-calcium sulfoaluminate system is to introduce as much red mud as possible into the raw materials, because it has a very high pH value, and its disposal is a real issue for the environment. Furthermore, the current amount of red mud available worldwide exceeds around 2.7 billion tonnes (Klauber et al., 2009), where only a small amount is being reused, and the rest is stored (Pontikes and Angelopoulos, 2013). This would also decrease the need of aluminum, and thus bauxite required for their production, and consequently the cost would decrease too. The firing temperature, as well as the CO₂ emissions released, would decrease with the production of high-iron cements.

Even though the ferrite phase is known for not contributing much to the strength development of OPC, Quillin (2010) demonstrated that this clinker phase can develop good compressive strength when combined with belite and calcium sulfoaluminate phases.

This paper presents five compositions with different levels of ferrite from 5% to 50% by weight in alite-calcium sulfoaluminate cement, all produced from industrial by-products. Different firing

regimes were tested for each composition, and the parameters were optimized based on free lime determinations and X-ray diffraction (XRD) analyses. The mineralogical composition was determined through Rietveld analyses, which assisted in the correction of the raw mix for each composition.

2. Materials and Experiments

The chemical compositions of the industrial by-products were determined by X-ray fluorescence (XRF) analyses in terms of oxides, and they are displayed in Table 1. The volume median diameter *d*(0.5), representing the diameter where 50% of the distribution is above and 50% is below this specific particle size, is also given in micrometers in Table 1.

Five compositions were formulated to study the influence of the addition of ferrite in the alite-calcium sulfoaluminate-ferrite system, and these are displayed in Table 2. The equations followed to formulate these clinkers were derived from a modified Bogue equation, following the same procedure described by Bogue, but for a different final clinker composition. Hypotheses were established as follow. First of all, only five clinker phases are considered to form in these alite-calcium sulfoaluminate-ferrite clinkers, which are alite (C₃S), belite (C₂S), calcium sulfoaluminate (C₄A₃Š), ferrite (C₄AF), and calcium sulfate (CŠ), while all the other minor clinker phases are negligible. The next steps in the determination of the modified Bogue equations are the following: (1) assume all the iron present in the raw mix is used to produce exclusively ferrite (C₄AF); (2) presume all the remaining alumina unused from the previous step is used to form the calcium sulfoaluminate phase (C₄A₃Š); (3) consider all the silica first reacts with calcium to form belite; and finally (4) assume all the remaining lime unused from all the previous steps reacts with belite to form alite.

From these assumptions, the modified Bogue equations are defined as follows:

$$C_3S = 4.07(CaO - f_{CaO}) - 7.60 SiO_2 - 2.24 Al_2O_3 - 4.29 Fe_2O_3 - 2.85 SO_3 \quad (1)$$

$$C_2S = 8.60 SiO_2 + 1.69 Al_2O_3 + 3.24 Fe_2O_3 + 2.15 SO_3 - 3.07(CaO - f_{CaO}) \quad (2)$$

Table 2
The five theoretical clinker compositions (in % by weight) with the three modulus values

		B#1-BP	B#2-BP	B#3-BP	B#4-BP	B#5-BP
Clinker phase composition	C ₃ S	48	41	32	23	15
	C ₂ S	20	18	17	15	13
	C ₄ A ₃ Ŝ	15	14	14	14	13
	C ₄ AF	6	16	27	38	49
	CŜ	5	5	5	5	5
	MgO	5.4	4.53	3.55	2.55	1.87
Modulus values	TiO ₂	0.44	0.84	1.29	1.77	2.2
	LAD	0.9	0.9	0.9	0.9	0.8
	SEC	1.2	1.2	1.3	1.3	1.4
	QLP	0.1	0.1	0.1	0.1	0.1

Note: LAD = lime adequate degree; SEC = sulfur excessive coefficient; QLP = quantity of liquid phase.

$$C_4A_3\hat{S} = 2.00 Al_2O_3 - 1.27 Fe_2O_3 \quad (3)$$

$$C_4AF = 3.04 Fe_2O_3 \quad (4)$$

$$C\hat{S} = 1.70 SO_3 - 0.45 Al_2O_3 + 0.28 Fe_2O_3 \quad (5)$$

Moreover, three modulus values, lime adequate degree (LAD), sulfur excessive coefficient (SEC), and quantity of liquid phase (QLP), established by Zhou (personal communication, 2010), were followed and kept approximately constant for all compositions, respectively, at 0.9, 1.3, and 0.1.

The LAD illustrates the ratio between the remaining lime after forming C₄AF and C₄A₃Ŝ and the lime needed to form C₃S and C₂S.

$$LAD = (C_3S + 0.8835 C_2S) / (C_3S + 1.3253 C_2S) \quad (6)$$

The SEC corresponds to the ratio of the remaining SO₃ in the clinker after reacting to form the liquid phase and the SO₃ needed to form C₄A₃Ŝ.

$$SEC = 1 + 4.4825 \times [(C\hat{S} - 5.2315 CaF_2) / C_4A_3\hat{S}] \quad (7)$$

The QLP represents the percentage of liquid phase in the clinker during the firing process.

$$QLP = 12.8494 CaF_2 \quad (8)$$

The amount of C₄A₃Ŝ and the LAD modulus value were kept approximately constant for each composition at, respectively, 14% by weight and 0.9. The only changes between the five compositions were the amount of C₄AF, which increases, and the total amounts of C₃S and C₂S, which decreases, resulting from this substitution in batches 1 to 5.

CaF₂ and CaSO₄ were added as fluxes and mineralizers to induce a liquid phase at low temperatures in order to increase the reaction rate of C₂S with C and form C₃S in a temperature regime that is compatible with C₄A₃Ŝ phase stability.

The raw materials were mixed in a mortar and pestle until the red-brown color from the iron oxide was visually homogeneous throughout the sample. Small pellets were produced from mixing 10 g of raw materials with 10% by weight of deionized water in a mortar and pestle, to promote good contact between the solid phases and produce uniform pellets. The raw mixes were pressed into 28 × 7-mm pellets with a load of around 36 kN and then dried in an oven at 65°C for 4 hours.

The pellets were then fired at 800°C for 30 minutes, followed by different clinkering temperatures from 1250°C to 1300°C with a

dwelling time of 30 or 60 minutes. The clinker compositions were air quenched, ground in a shatter box, and analyzed by several characterization methods described later. The furnace used was a “tube furnace,” from Carbolite, which was able to reach temperatures up to 1500°C, and which was mapped. Consequently, the samples were placed in the optimum region determined from the temperature mapping.

The selection of an optimum firing regime for each composition was determined by the study of the contents of free lime (CaO) and tricalcium aluminate (C₃A) in each clinker sample. These two phases characterize a firing regime as “under-” or “overfired” depending on the phases identified in the clinker composition. An underfired system is confirmed if CaO is detected in an excessive amount (i.e., >2.0%), as CaO is not entirely consumed and indicates an incomplete reaction (Newman and Choo, 2003). An overfired system is identified if C₃A is detected, as C₄A₃Ŝ decomposes to C₃A and CŜ at elevated temperatures (Odler, 2003).

The presence of CaO was identified through XRD analyses and free lime determinations, and the presence of C₃A was determined through XRD analyses.

XRD analyses were performed with a Philips X’Pert diffractometer operating at 45 kV and 40 mA. The samples were dry mounted in aluminum holders and scanned with a size step of 0.017° at 0.035°/s over 7–60°-2θ with Cu K-α radiation. Free lime determinations were performed following the alternative test method B, also called rapid Sr(NO₃)₂ method (ASTM International, 2006).

The appropriate firing regime for each composition was selected by determining the clinker phases in each sample through Rietveld analyses. This procedure was used to confirm the theoretical mineralogical compositions and, if necessary, to identify the modifications required to attain the theoretical clinker compositions.

Rietveld analyses were performed with a Philips X’Pert diffractometer operating at 45 kV and 40 mA. The samples were dry mounted in aluminum holders and scanned at 8–90°-2θ with Cu K-α radiation. The X’Pert HighScore Plus from PANalytical software was used to process the XRD data and quantitatively determine the clinker phases.

3. Results

3.1. Selection of the appropriate firing regime for each composition

We use composition #3-BP (from industrial by-products) as an example to explain the approach taken to derive the optimal firing regime for all the other compositions.

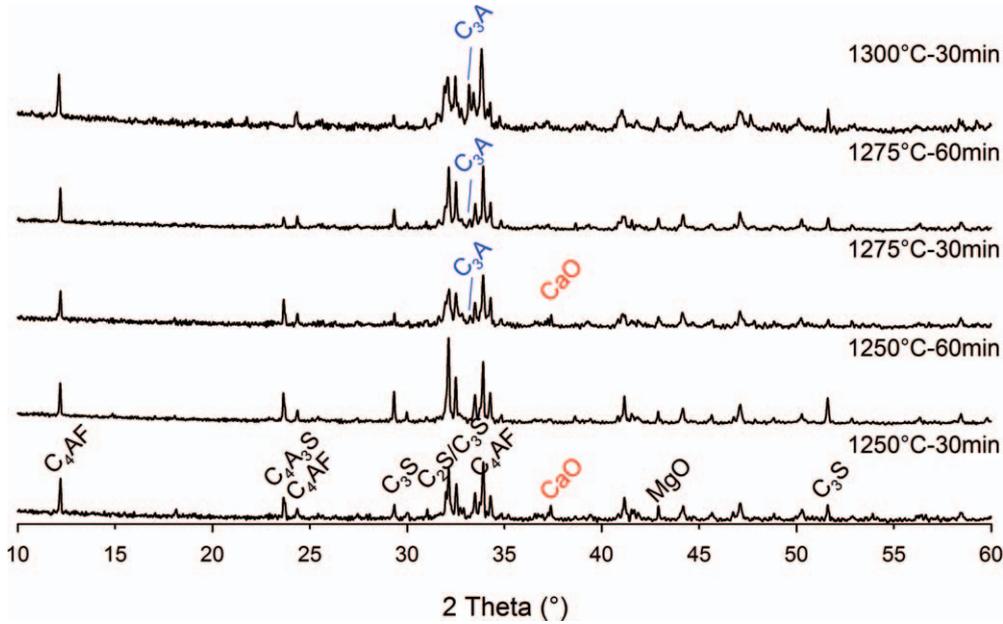


Fig. 1. X-ray diffraction (XRD) graphs for batch #3-BP for firing temperatures and dwelling times tested.

Five samples of the same composition of #3-BP were produced and fired at different firing temperatures and dwelling times. XRD graphs obtained from these tests are displayed in Figure 1.

Both samples, fired at 1250°C and 1275°C with a dwelling time of 30 minutes, contained some unreacted free lime, as a strong CaO peak was detected at around 37.3°.

Moreover, the presence of tricalcium aluminate was detected in the samples fired at 1275°C for 30 and 60 minutes, and in the sample fired at 1300°C for 30 minutes. In all these samples, the diminishing of the $C_4A_3\dot{S}$ peak is clearly observed as this phase decomposes into C_3A and $C\dot{S}$.

By elimination, the optimum firing regime for the composition #3-BP was 1250°C for 60 minutes, as no CaO and no C_3A were detected. In addition, the C_3S peak was better defined with this firing regime than with all the others. This demonstrates the importance of a necessary longer retention time while developing high levels of C_3S .

In order to confirm these data, free lime determinations were performed on all samples, except for one sample fired at 1250°C for 30 minutes, as the presence of CaO was clearly noticeable from Figure 1.

As shown in Figure 2, the free lime contents for batch #3-BP samples were all below the maximum limit of 2.0% by weight, meaning that all the free lime initially present in the raw mixes had completely reacted with the other raw materials. These data confirmed the earlier XRD graphs, further demonstrating that the temperature of 1250°C with a dwell time of 60 minutes was the optimal firing parameter, as a very low level of CaO (0.7%) was present in this clinker.

All the other compositions (#1, #2, #4, and #5-BP) were submitted to the same methodology used for composition #3-BP (Figure 3), and the optimal firing regime of 1250°C for 60 minutes was identified for batches #2 to #5, while batch #1 was best formed at a firing temperature of 1275°C for 60 minutes.

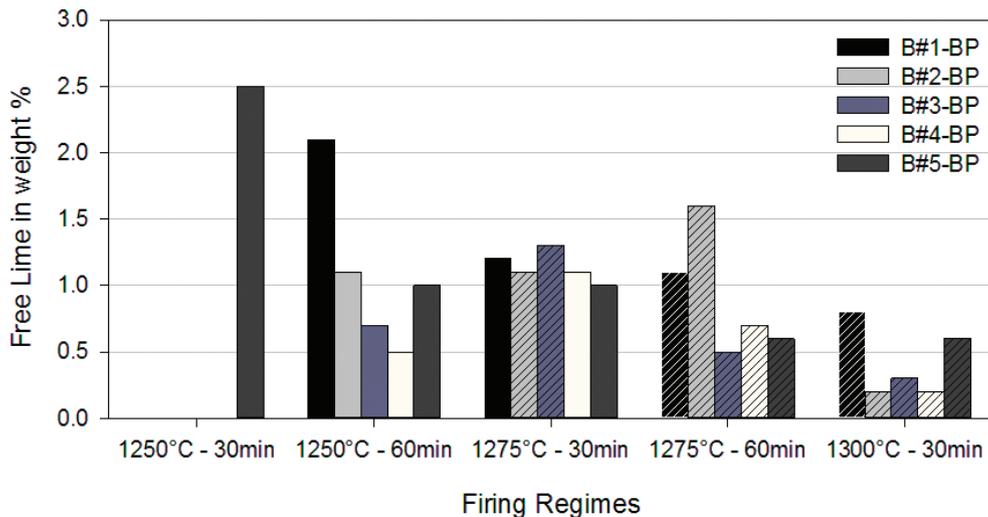


Fig. 2. Free lime determinations for compositions #1 to #5, fired under different firing regimes. The hatched bars illustrate the presence of C_3A in clinker samples observed during XRD analyses.

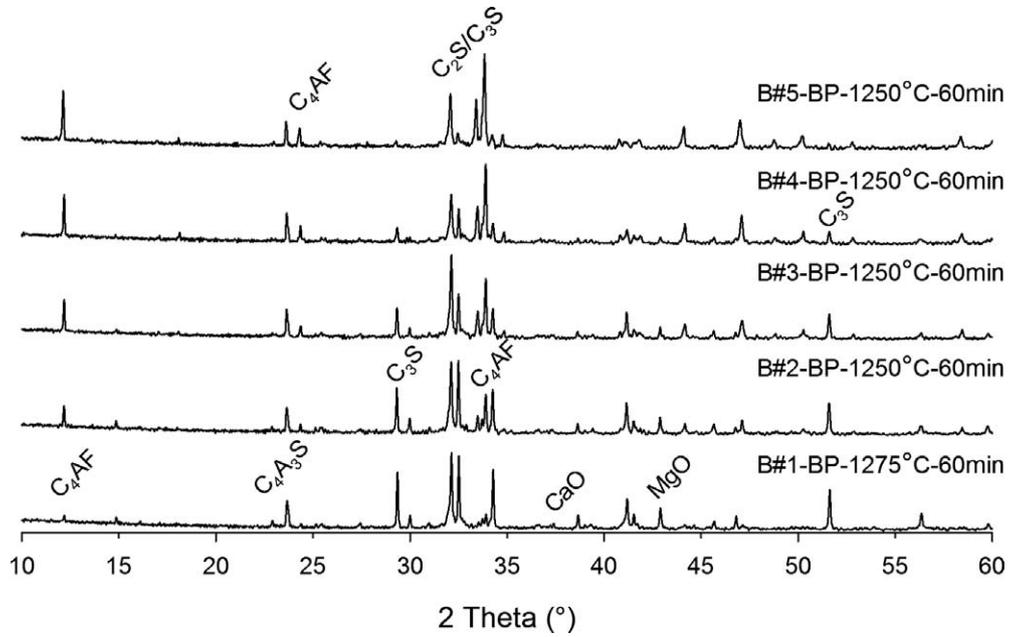


Fig. 3. XRD graphs of the optimum firing regime for each composition produced from industrial by-products (BP).

3.2. Rietveld analyses

Figure 4 displays the Rietveld analyses performed on each sample (all fired at 1250°C for 60 minutes) compared with the theoretical clinker compositions established in section 2.

Some differences could be observed by comparing the theoretical and Rietveld data. The total amounts of silicates in each batch were the same in theoretical and experimental samples, but the amounts of alite were lower and amounts of belite were higher than expected. Besides, the quantities of calcium sulfoaluminate were lower than anticipated and those of ferrite were higher than estimated.

3.3. Modification of the raw material compositions

When the quantities of ferrite and belite in each batch were identified as too high in the original batches, a modification of the raw material compositions was performed by substituting amounts of red mud with bottom ash.

The samples were all produced and fired at 1250°C for 60 minutes. The Rietveld data are presented in Figure 5 and compared with the theoretical compositions.

The quantities of alite and calcium sulfoaluminate were higher in the compositions produced using the modification of the industrial by-products (MBP) than from the original BP batch in section 3.2. On the other hand, the amounts of belite were close to the anticipated compositions, whereas the amounts of ferrite were lower compared with those in section 3.2.

By reducing the quantity of red mud and replacing it with bottom ash to decrease the quantities of belite and ferrite originally formed from by-products, the compositions were closer to the theoretical compositions.

4. Conclusions

Iron-rich alite-calcium sulfoaluminate-ferrite cements, containing 5% to 50% by weight of ferrite, can be produced from

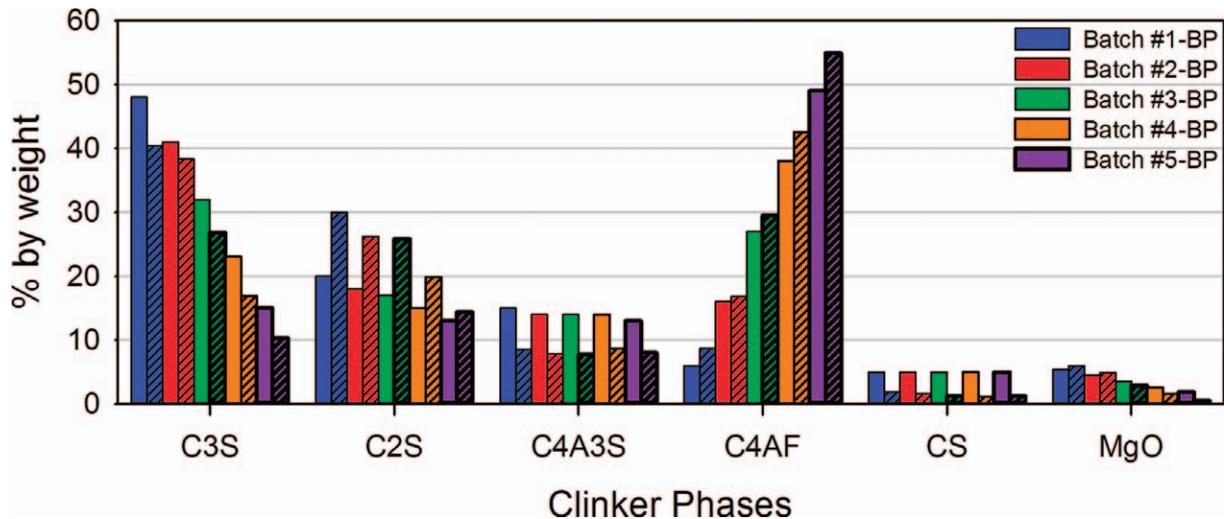


Fig. 4. Theoretical (plain bars) and Rietveld data (hatched bars) of the clinker composition of each batch.

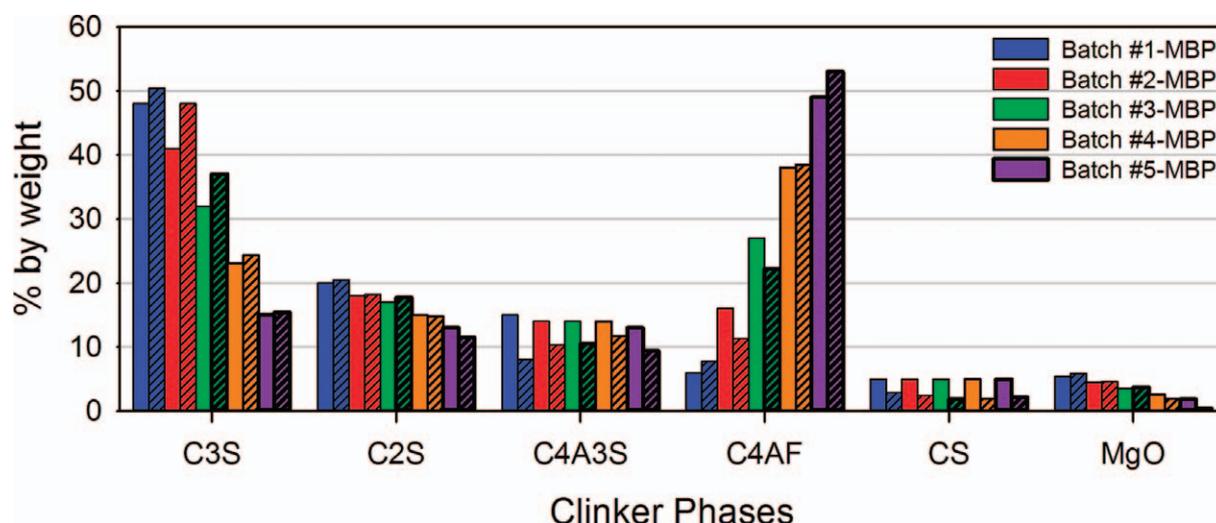


Fig. 5. Theoretical (plain bars) and Rietveld data (hatched bars) of the clinker composition of each batch produced from the modification of the original composition with industrial by-products (modification of the by-products = MBP).

industrial by-products by following specific modulus values, with the aid of mineralizers and fluxes, and by selecting the optimum firing regime for each composition. As demonstrated in this paper, the composition with a low amount of ferrite (5% by weight) has to be fired at a higher firing temperature of 1275°C for 60 minutes, whereas all the others compositions, with a content of ferrite from 15% to 50% by weight, required a firing regime of 1250°C for 60 minutes. Moreover, Rietveld analyses indicated that impurities present in the raw materials can affect the clinker compositions and that small modifications to the raw mix were necessary to obtain the desired mineralogical compositions.

These iron-rich alite-calcium sulfoaluminate-ferrite cements are expected to present great mechanical properties due to the combination of the highly active clinker phases present, such as alite and calcium sulfoaluminate. Further experiments are in progress to demonstrate the chemical and physical properties of these cements.

Acknowledgments

The authors would like to thank Shelley Hopps and Dr. Kevin Henke for their valuable help.

This work was supported in part by a grant from the National Institute for Hometown Security (NIHS).

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Appendix Table

Cement abbreviations

Cement notation	Actual formula	Name
C	CaO	Calcium oxide
S	SiO ₂	Silicon dioxide
A	Al ₂ O ₃	Aluminum oxide
F	Fe ₂ O ₃	Iron oxide
S̄	SO ₃	Sulfur trioxide