

Incorporation of waste materials into portland cement clinker synthesized from natural raw materials

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Abstract For every ton of portland cement that is manufactured, approximately half a ton of carbon dioxide is released from calcining limestone. One method of reducing the carbon dioxide from portland cement production is to reduce or eliminate the use of limestone through replacement with calcium oxide-bearing waste materials. In this study, portland cement clinker was synthesized using minimal limestone content and maximal waste material content, specifically fly ash and blast furnace slag. The synthetic cements were characterized using X-ray diffraction, scanning electron microscopy, and isothermal calorimetry. Results show that portland cement clinker can be successfully synthesized from a maximum of 27.5% fly ash and 35% slag. The synthetic cements possessed early-age hydration behavior similar to a commercial Type I/II portland cement. However, the presence of sulfur impurities contained in waste materials significantly affected phase formation in portland cement clinker.

Introduction

Portland cement concrete, the most widely used, and manufactured material in the world, is made primarily from water, mineral aggregates, and portland cement. Portland

cement clinker is produced from high temperature firing and grinding of mineral deposits such as limestone and clay; the clinker is then ground with gypsum to make cement. Portland cement clinker contains four primary phases: Ca_3SiO_5 (C_3S^1), Ca_2SiO_4 (C_2S), $\text{Ca}_3\text{Al}_2\text{O}_6$ (C_3A), $\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$ (C_4AF) [1]. The production of portland cement is energy intensive, accounting for 2% of primary energy consumption and 5% of industrial energy consumption globally [2]. Moreover, portland cement manufacturing contributes significantly to greenhouse gases and accounts for 5% of the global CO_2 emissions resulting from human activity. Half of this CO_2 comes from the use of fossil fuels to heat the kilns, and the other half is produced through the calcination of limestone ($\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$).

One method of reducing CO_2 emissions from portland cement manufacturing is to reduce or eliminate the use of limestone, replacing it with materials high in CaO rather than CaCO_3 . Viable alternatives to limestone are calcium oxide-bearing waste materials such as fly ash from coal burning power plants and blast furnace slag from steel production. The reuse of fly ash and slag as “supplementary cementing materials (SCMs)” to directly replace a portion of the portland cement in concrete has greatly reduced the environmental impact of concrete production. Fly ash and slag have also been used as raw materials for the actual production of portland cement in industry for years, which has reduced the environmental impact of concrete production even further because the cement produced from waste materials can still be replaced with SCMs in concrete. Previous research has shown that waste

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¹ In cement chemistry notation, oxides are abbreviated by the first capital letter: C = CaO , S = SiO_2 , A = Al_2O_3 , F = Fe_2O_3 , H = H_2O , and \$ = SO_3 .

materials such as municipal solid waste, waste gypsum, rice hull, and red mud can be partially used as alternatives to limestone or clay for cement production [3–6]. Some research has shown successful production of portland cement with fly ash and slag incorporated in the raw ingredients [7, 8]. The cements produced from fly ash and slag in those studies showed comparable mechanical properties to commercial portland cement. Nevertheless, a thorough, quantitative investigation on cement phase composition, phase distribution, and hydration behavior was not performed in these studies. This study addresses these gaps in our knowledge.

The primary goal of this research was to synthesize portland cement clinker with minimal limestone content and maximal waste material content. Reagent-grade chemicals were first used to synthesize portland cement clinker in order to establish a baseline for the synthesis procedure and the phase composition. Portland cement clinker was then synthesized using natural raw materials, and then using natural raw materials partially replaced by waste materials. The resulting clinkers were analyzed for phase contents using X-ray diffraction and phase distribution using scanning electron microscopy. The synthesized clinkers were then made into cements by adding gypsum to control hydration reactions. Finally, the early-age hydration behavior of the synthetic cements was investigated using isothermal conduction calorimetry.

Experimental

Materials

The reagent-grade chemicals used to synthesize portland cement clinker were calcium oxide (Acros), silica gel (Fisher), aluminum oxide (Acros), and ferric oxide (Fisher). The natural raw materials used for clinker synthesis were obtained from Texas Lehigh Cement Company (Buda, Texas). These were a gray limestone and an argillaceous yellow limestone that is rich in aluminum and iron; the chemical compositions are shown in Table 1. The industrial waste materials used, specifically fly ash and ground granulated blast furnace slag, were those already marketed and distributed for use as supplementary cementing materials for concrete, meaning that they can be used directly to replace a portion of the portland cement in concrete. The fly ash (Class C; Headwaters/ISG) and slag (Holnam) were chosen for their high calcium oxide, silicon oxide, and aluminum oxide contents which are all necessary for portland cement manufacture (chemical compositions shown in Table 1) [9]. Furthermore, 0.1 wt% boron oxide (Alfa Aesar) and 0.25 wt% lithium borate (SPEX CertiPrep; 75% $\text{Li}_2\text{B}_4\text{O}_7$, 25% LiBO_2) were added to the raw ingredients in

Table 1 Chemical compositions of the natural raw materials and industrial waste materials used

Oxide	Amount in sample (weight %)			
	Gray limestone	Yellow limestone	Fly ash	Slag
SiO_2	5.95	38.44	33.58	34.48
Al_2O_3	1.69	10.51	18.51	11.35
Fe_2O_3	0.64	3.23	6.56	0.67
CaO	49.02	22.74	27.08	41.73
MgO	0.94	0.98	6.10	7.32
Na_2O	0.07	0.23	1.89	0.14
K_2O	0.29	1.66	0.39	0.38
TiO_2	0.04	0.48	1.34	0.46
MnO_2	0.02	0.03	0.03	0.56
P_2O_5	0.08	0.18	1.15	0
SrO	0.07	0.08	0.48	0.10
BaO	0.02	0.06	0.74	0.11
SO_3	0.77	0.08	1.83	1.88
LOI ^a	40.39	21.3	0.34	0.83
Moisture	0.49	0.71	0.07	0.28

^a LOI is mass lost on ignition to 750°C

order to stabilize the desired β - C_2S phase, and to lower the clinkering temperature, respectively [10].

Synthesis

First, reagent-grade chemicals were used to synthesize portland cement clinker (with 0.1 wt% boron oxide addition). Chemicals were proportioned for a target clinker composition of 50% C_3S , 25% C_2S , 15% C_3A , and 10% C_4AF using the standard Bogue calculation [11, 12]. A portland cement clinker with this composition is classified as Type I according to ASTM C 150 [13]. The C_3A and C_4AF contents are at the maximum limit because this allows for a higher amount of waste material incorporation.

Materials were dispersed in ultra-pure water (1:10 ratio) and mixed by a rotary jar mill (U.S. Stoneware) for 24 h at 120 rpm in a HDPE bottle using 2-mm sphere high-purity ZrO_2 (Y_2O_3 -stabilized) grinding media [14]. The solution was poured in a beaker and dried in a 105°C oven. The resulting product was hand-crushed into fine powder form using a mortar and pestle. The materials were placed in platinum crucibles and fired in an electric muffle furnace (Sentrotech). Two cycles of firing were run, with a 5°C/min heating rate and a 2°C/min cooling rate. In the first cycle, the materials were fired at 850°C for 2 h to dehydrate and calcine the materials. They were then fired at 1200°C for 8 h, from 1200°C to 1250°C for 8 h, and at 1250°C for another 8 h. An intermediate grinding by hand was performed between cycles to homogenize the materials. In the

second cycle, the materials were fired at 1300°C for 8 h, from 1300°C to 1350°C for 8 h, and at 1350°C for another 8 h [15–17]. If the fired product contained excess free lime (>1 wt%, determined by X-ray diffraction), the materials were fired again at 1400°C for 12 h. Finally, the resulting clinker was hand-ground and passed through a #325 sieve (45 µm).

The goal of the laboratory synthesis processes was to mimic the processes that take place in industrial manufacturing. Raw ingredients must be homogenized and then fired at high temperature. The firing time in the furnace was much longer compared to the firing time in a rotary kiln used in industrial manufacturing because the raw ingredients remained stationary inside the crucible during the firing process, which prevented materials from properly reacting with each other. Furthermore, the maximum firing temperature used in the laboratory synthesis processes was 1400°C which is about 50°C lower than the maximum temperature used in industrial manufacturing [1]. Under lower firing temperature, the desired phases may take longer to form.

After successful synthesis of portland cement clinker from reagent-grade chemicals, portland cement clinker was synthesized from gray limestone along with 20–40% yellow limestone (in 2.5% increments) with 0.1 wt% boron oxide and 0.25 wt% lithium borate additions. The goal was to synthesize a portland cement clinker with a similar composition to the clinker sample synthesized from reagent-grade chemicals while keeping the synthesis procedure unchanged. Portland cement clinker can be synthesized by combining only these two natural raw materials because the yellow limestone contained high amounts of silicon, aluminum, and iron (Table 1).

The fly ash and slag used had similar phase compositions to the yellow limestone except for impurities. Several ingredient proportions were fired in the furnace using the same synthesis procedure (gray limestone along with 20–40% fly ash or 20–60% slag; in 2.5% increments; with 0.1 wt% boron oxide and 0.25 wt% lithium borate additions). The primary goal was to synthesize portland cement clinker with minimal limestone content and maximal waste material content.

Analysis

X-ray diffraction

The synthesized clinkers were tested by X-ray diffraction (Siemens D500 Powder Diffractometer; Cu $K_{\alpha 1}$, $\lambda = 1.5046 \text{ \AA}$) to determine phase formation. The instrument was operated under 40 keV and 30 mA, the step size used was 0.02°/6 s, and the scan range was 20–80° 2θ . Test

samples were prepared by dispersing clinkers in ethanol and pouring the solution on quartz low background sample holders. Thin layers of solid materials were left on the sample holders after the samples dried.

Qualitative information of phases present in the sample was obtained using the Hanawalt manual and the Jade program (MDI) [18]. Quantitative information was collected using the Rietveld method which was performed with the TOPAS-Academic software (Bruker AXS) [19–21].

Scanning electron microscopy

Phase distribution in the synthesized clinkers was studied using scanning electron microscopy (LEO 1530 Thermally-Assisted Field Emission SEM). Test samples were prepared by mixing clinker powders with optical-grade epoxy (Epotek 353ND) and casting in cylindrical molds (30 mm diameter). The samples were cured in a 40°C oven for 24 h, and their cross sections were polished and coated with carbon before imaging and compositional examination by energy dispersive spectroscopy [22]. Elemental maps were collected for Ca, Si, Al, Fe, Mg, S, Na, and K. The elemental maps were preprocessed with ImageJ software to reduce noise [23, 24]. Multispectral images were then prepared by overlaying the separate elemental maps and processing using Multispec software (©Purdue Research Foundation), which allowed quantitative assessment of the spatial distribution of phases [25]. The quantitative spatial distribution of phases was later converted to weight distribution by normalizing it with the density of the phases. The quantitative results determined from scanning electron microscopy were compared with those from quantitative X-ray diffraction.

Isothermal conduction calorimetry

To determine if the synthetic cements exhibited similar behavior to traditional cement, the rate of reaction with water was evaluated. The heat produced by cementitious materials in exothermic hydration reactions is a good indication of their early-age hydration behavior [26]. In this study, several selected synthetic cements as well as a commercially produced Type I/II cement (TXI Hunter) were tested for heat-evolution rate using isothermal conduction calorimeter (TAM Air, Thermometric). Cements were made from the synthesized clinkers by adding 12.5 wt% gypsum (Terra Alba ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$); USG) to control the reaction of C_3A [27]. The fineness of cement powders was tested by an air-permeability test, called Blaine fineness, according to ASTM C 204 to assure the uniformity of all synthetic cements [28]. Hydration was

evaluated for 3 days at 23°C using a water-to-cement ratio by weight of 0.45.

Results and discussion

Phase composition

Quantitative X-ray diffraction results obtained through Rietveld analysis for the clinker sample synthesized from only reagent-grade chemicals are shown in Table 2 and the refined X-ray diffraction pattern is shown in Fig. 1. The refined X-ray diffraction pattern shows that the calculated pattern from the lattice parameters of the phases present (red line in Fig. 1) agrees with their X-ray diffraction pattern (blue line in Fig. 1) well, which means the quantitative results should be reliable. The gray line that shows negative intensities in Fig. 1 represents the differences in intensities of the two patterns. The quantitative X-ray diffraction results show that all four major clinker phases (C_3S , C_2S , C_3A , and C_4AF) formed in the sample. The free lime content of the sample was low (0.54%), indicating that the materials completely reacted in the furnace. The sample contained 15.49% C_3A and 8.48% C_4AF , which nearly matches the target composition (15% C_3A and 10% C_4AF). In contrast, the sample contained much higher C_3S

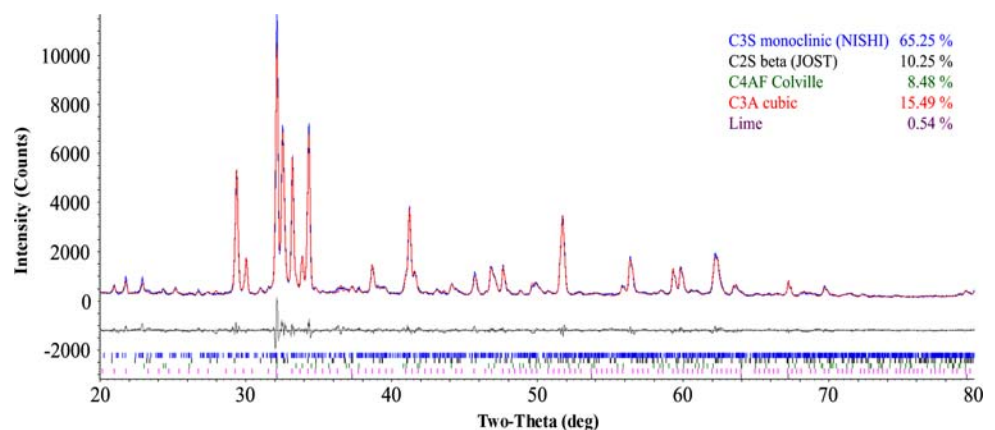
(65.25%) and much lower C_2S (10.25%) than its target composition (50% C_3S and 25% C_2S). The differences may be attributed to errors in the standard Bogue calculation used to proportion the raw materials. The standard Bogue calculation is a method used to estimate the amount of the phases in portland cement clinker from the oxide contents in the raw ingredients using knowledge of phase equilibria and by solving linear equations [11, 12]. This method assumes that the four major clinker phases are in their stoichiometric forms, which is usually not realistic because these phases can accommodate a large amount of substitute ions. Moreover, the synthesis environment is not always in an equilibrium state. Nevertheless, the results demonstrate that the synthesis procedure is appropriate for producing portland cement clinker in the laboratory.

Portland cement clinker was more difficult to synthesize from gray limestone (GLS) and yellow limestone (YLS) than from reagent-grade chemicals and required a higher synthesis temperature. The higher synthesis temperature was due to the large amount of quartz in the YLS, which is less reactive because of its crystalline structure compared to the amorphous reagent-grade silica gel. Therefore, in order to keep the synthesis procedure consistent, 0.25% lithium borate, which is a chemical commonly used as fusion flux for X-ray fluorescence analysis, was added to the system to allow phases to form at a relatively lower temperature.

Table 2 Comparison of Bogue calculation and Rietveld analysis results for clinker samples synthesized from reagent-grade chemicals (RG), GLS with 27.5% YLS, GLS with 27.5% fly ash, and GLS with 35% slag

Sample	Phase (weight %)					
	C_3S	C_2S	C_3A	C_4AF	Lime	Periclase
RG (Bogue)	50	25	15	10	0	0
Rietveld	65.25	10.25	15.49	8.48	0.54	0
GLS + YLS (Bogue)	42.30	33.89	13.29	6.35	0	0
Rietveld	58.58	17.81	16.61	6.32	0.47	0.21
GLS + Fly ash (Bogue)	37.33	26.84	18.26	9.77	0	0
Rietveld	46.10	24.19	16.65	10.21	0.82	2.04
GLS + Slag (Bogue)	45.02	28.24	16.80	2.69	0	0
Rietveld	44.39	31.63	17.56	2.11	0.10	4.21

Fig. 1 Rietveld refinement for a clinker sample synthesized from reagent-grade chemicals



GLS along with 20–40% YLS (in 2.5% increments) were fired in the furnace. The best result is from using 72.5% GLS and 27.5% YLS. Quantitative X-ray diffraction results obtained through Rietveld analysis for this clinker sample are shown in Table 2 and the refined X-ray diffraction pattern is shown in Fig. 2. The four major clinker phases (C_3S , C_2S , C_3A , and C_4AF) formed in the sample. The free lime content of the sample was low (0.47%), indicating that the materials completely reacted in the furnace. The only impurity phase that can be detected by X-ray diffraction was periclase (MgO). However, periclase content (0.21%) is minimal. The maximum amount of periclase in Type I cement allowed by ASTM C 150 is 6% [13]. The sample had a very similar phase composition to the clinker sample synthesized from reagent-grade chemicals, which exactly conforms to the synthesis goal.

After successful synthesis of portland cement from natural raw materials, GLS along with 20–40% fly ash and 20–50% slag (in 2.5% increments) were fired in the furnace. The maximum amounts of waste materials that can be used for portland cement clinker synthesis with acceptable compositions were 27.5% fly ash and 35% slag. Quantitative X-ray diffraction results obtained through Rietveld analysis for these two clinker samples are shown in Table 2 and their refined X-ray diffraction patterns are shown in Figs. 3 and 4,

respectively. The four major clinker phases (C_3S , C_2S , C_3A , and C_4AF) formed in these two samples. The clinker samples contained low free lime contents, indicating that the materials completely reacted in the furnace. The clinker sample synthesized from GLS with 35% slag had a low C_4AF content because the slag used contained a low amount of iron. The only impurity phase that can be detected in these two clinker samples by X-ray diffraction was periclase (MgO). The clinker sample synthesized from GLS with 35% slag contained higher periclase content (4.21%) than the clinker sample synthesized from GLS with 27.5% fly ash (2.04%) because the slag used contained higher amount of magnesium than the fly ash (Table 1); moreover, slag was used at a higher amount for portland cement clinker synthesis than fly ash. However, these two synthesized clinkers had periclase contents lower than the ASTM C 150 limit (6%) [13]. Furthermore, even though the clinker samples with waste materials incorporation had lower C_3S , higher C_2S and C_3A contents than an ordinary portland cement clinker, they are still in the acceptable range specified by ASTM C 150. The low C_3S – C_2S ratio in portland cement clinker can be easily increased by increasing the GLS-waste ratio in the raw ingredients.

Rietveld analysis results for the clinker sample synthesized from GLS with 27.5% YLS show that its C_3S content

Fig. 2 Rietveld refinement for a clinker sample synthesized from GLS with 27.5% YLS

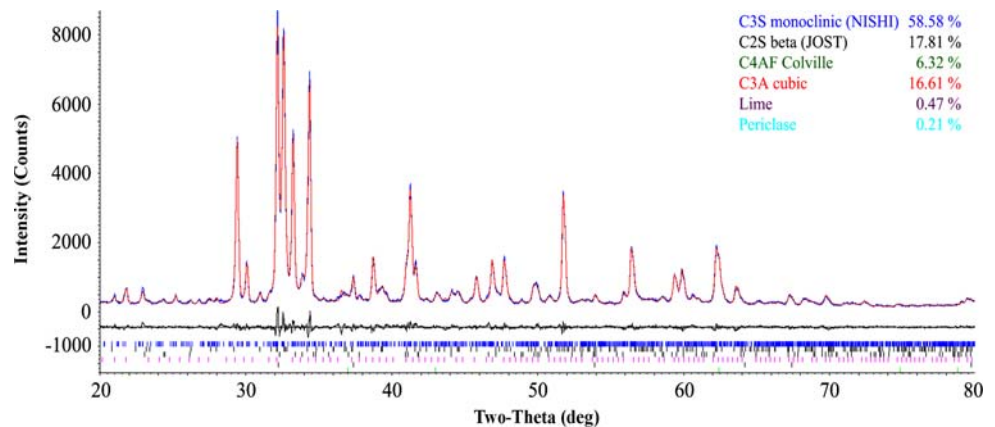


Fig. 3 Rietveld refinement for a clinker sample synthesized from GLS with 27.5% fly ash

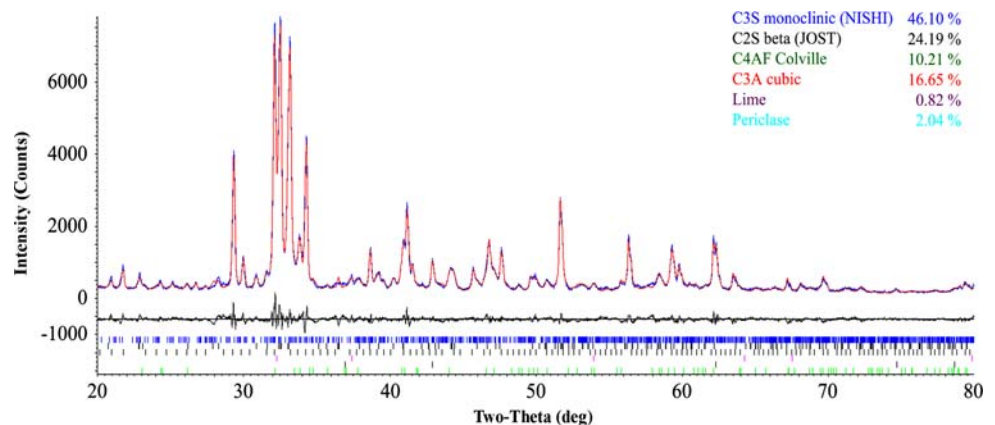
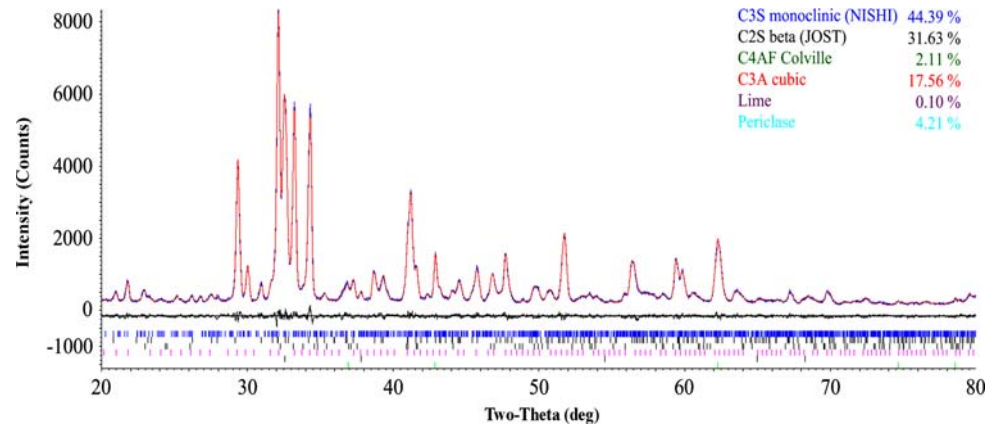


Fig. 4 Rietveld refinement for a clinker sample synthesized from GLS with 35% slag



is about 16% higher than what the standard Bogue calculation estimated. For the cement sample synthesized from GLS with 27.5% fly ash, it is about 9% higher, and for the cement sample synthesized from GLS with 35% slag, the two values are nearly identical. This is because the waste materials used contained higher impurity contents than YLS; moreover, the slag was used at a higher percentage for portland cement clinker synthesis than fly ash. According to the study of Uda et al. [29], this effect could be due to changes in phase equilibria in the CaO–SiO₂–Al₂O₃–Fe₂O₃ system caused by sulfur impurities; the contents of C₂S and CaO will increase, while the content of C₃S will decrease when increasing amount of SO₃ is incorporated in portland cement clinker synthesis. In this study, both the fly ash and the slag used contained approximately 1.8% SO₃ (Table 1). Previous research conducted by the authors using reagent-grade chemicals and waste materials with controlled calcium, silicon, aluminum, and iron oxide contents also showed that the sulfur impurities contained in the waste materials significantly affected formation of the four major clinker phases [30]. The content of C₂S increased, while the content of C₃S decreased when increasing amounts of waste materials were used in portland cement clinker synthesis. Moreover, Uda et al. [29] showed that C₃S no longer formed when the SO₃ content in the raw ingredients exceeded 2.6 wt%. Therefore, it is critical to evaluate the SO₃ content in materials before using them as raw ingredients in portland cement clinker production.

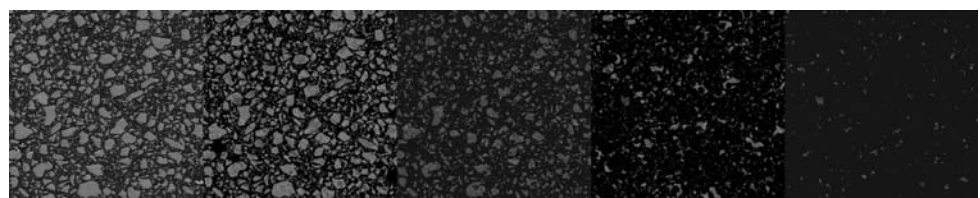
The modified Bogue calculation might be a better method than the standard Bogue calculation to accurately estimate the proportion of phases in portland cement

clinker because it takes into account of the substitute ions in each of the major cement phases instead of assuming their stoichiometric forms [12]. However, performing the modified Bogue calculations is not simple because they require intensive study of the actual contents of CaO, SiO₂, Al₂O₃, Fe₂O₃, and other impurities within each of the major cement phases, which might change when different types of materials are used in portland cement clinker production. Moreover, the modified Bogue equations still will not explain the changes in thermodynamics and kinetics of the CaO–SiO₂–Al₂O₃–Fe₂O₃ system caused by sulfur impurities. Therefore, a model that is more precise than the currently used Bogue methods in addition to empirical experience will be necessary to accurately predict clinker phase compositions when using materials with high SO₃ content as raw ingredients. Finally, because the properties of portland cement are mainly governed by its phase composition, the direct phase proportion quantitative X-ray diffraction technique provides a powerful means for cement manufacturers to better assess their products. Detailed aspects regarding the quantitative X-ray diffraction technique were recently specified by ASTM C 1365 [31].

Microstructure

The synthesized clinkers were examined under a scanning electron microscope to determine the spatial distribution of phases. Elemental maps for the clinker sample synthesized from reagent-grade chemicals are shown in Fig. 5. Only the Ca, Si, Al, and Fe maps are revealed because other elements showed little signal except noise. Multispectral

Fig. 5 Elemental maps for a clinker sample synthesized from reagent-grade chemicals (from left to right: Secondary electron image, Ca, Si, Al, and Fe; field width: 450 μm)



images were obtained from overlaying and processing these elemental maps. Multispectral images for clinker samples synthesized from reagent-grade chemicals, GLS with 27.5% YLS, GLS with 27.5% fly ash, and GLS with 35% slag are shown in Figs. 6, 7, 8, 9. In these multispectral images, colors were assigned to each individual

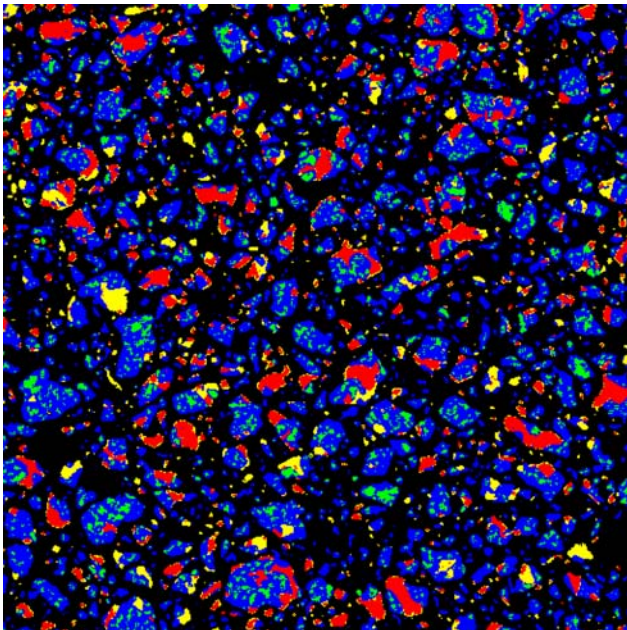


Fig. 6 Multispectral image for a clinker sample synthesized from reagent-grade chemicals (C_3S blue, C_2S green, C_3A red, and C_4AF yellow; field width: 450 μm)

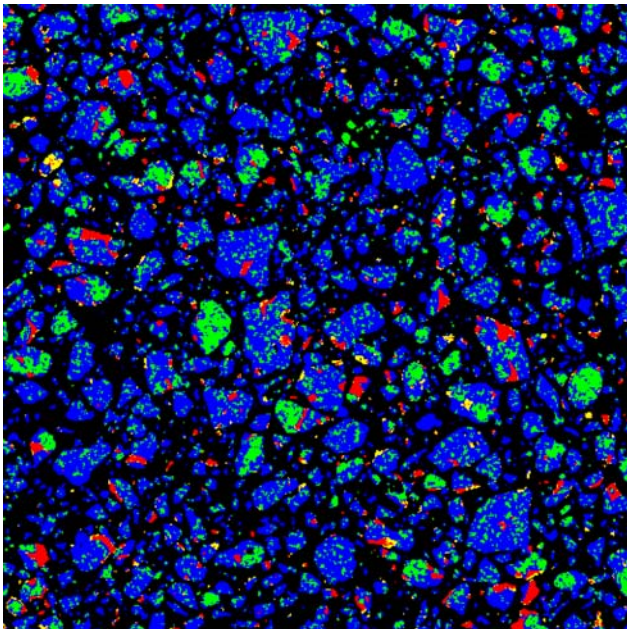


Fig. 7 Multispectral image for a clinker sample synthesized from GLS with 27.5% YLS (C_3S blue, C_2S green, C_3A red, C_4AF yellow, and periclase purple; field width: 450 μm)

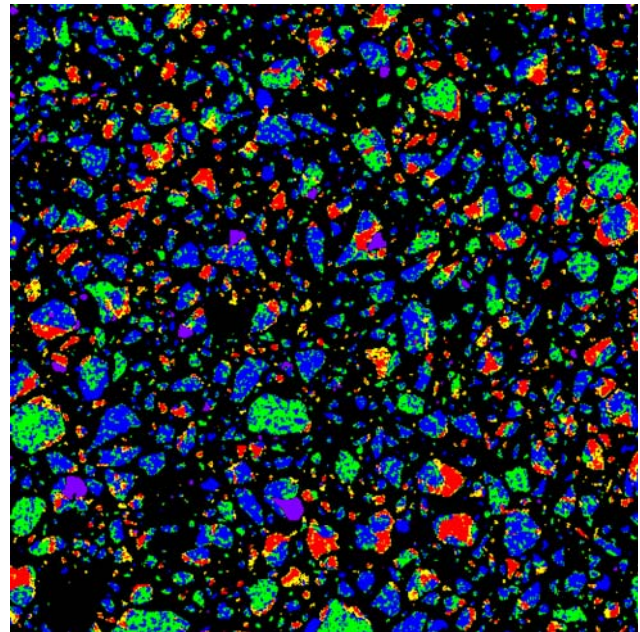


Fig. 8 Multispectral image for a clinker sample synthesized from GLS with 27.5% fly ash (C_3S blue, C_2S green, C_3A red, C_4AF yellow, and periclase purple; field width: 450 μm)

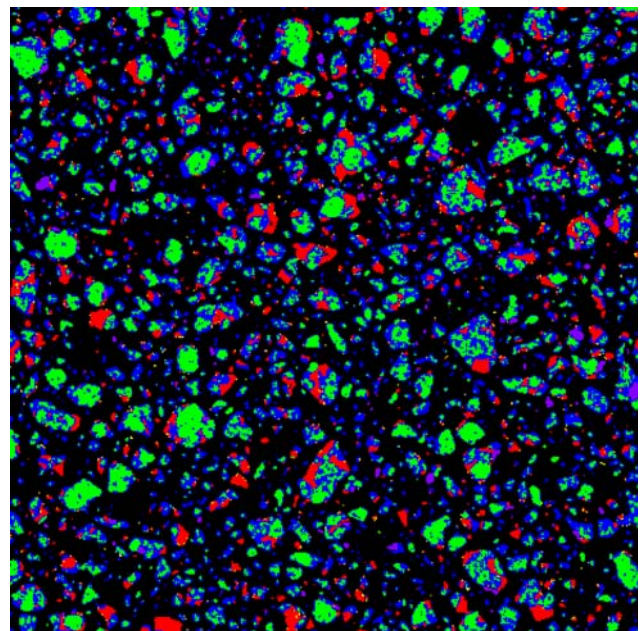


Fig. 9 Multispectral image for a clinker sample synthesized from GLS with 35% slag (C_3S blue, C_2S green, C_3A red, C_4AF yellow, and periclase purple; field width: 450 μm)

phase (from light to dark: C_3S , C_2S , C_3A , C_4AF , and periclase). Periclase was the only impurity phase that can be identified in the clinker samples with waste materials incorporation. The content of other impurities may have been too low to be identified. The clinker samples synthesized from reagent-grade chemicals and natural raw

Table 3 Comparison of multispectral (MS) and Rietveld analysis results for clinker samples synthesized from reagent-grade chemicals, GLS with 27.5% YLS, GLS with 27.5% fly ash, and GLS with 35% slag

Phase	Amount in sample (weight %)							
	RG		GLS + YLS		GLS + Fly ash		GLS + Slag	
	MS	Rietveld	MS	Rietveld	MS	Rietveld	MS	Rietveld
C ₃ S	64.61	65.25	65.65	58.58	46.68	46.10	49.82	44.39
C ₂ S	10.30	10.25	21.61	17.81	27.77	24.19	31.95	31.63
C ₃ A	16.46	15.49	10.16	16.61	15.07	16.65	15.75	17.56
C ₄ AF	8.63	8.48	2.57	6.32	9.01	10.21	0.84	2.11
Lime	N/A	0.53	N/A	0.47	N/A	0.82	N/A	0.10
Periclase	N/A	N/A	N/A	0.21	1.67	2.04	1.64	4.21

materials contained more C₃S and less C₂S than the clinker samples with waste materials incorporation (images appear lighter), which agrees with the X-ray diffraction results that showed a lower C₃S–C₂S ratio in clinker samples with waste materials incorporation. Furthermore, quantitative information of the spatial distribution of phases in these multispectral images was obtained by calculating the number of pixels of the different colors. The space fraction was later converted to weight fraction by normalizing it with the density of the phases. The comparison of multispectral and Rietveld analysis results for the synthesized clinkers are shown in Table 3. The multispectral and Rietveld analysis results agree with each other well except that the multispectral analysis results showed a higher C₃S and C₂S, and a lower C₃A, C₄AF, and periclase contents. This is because the multispectral analysis method quantifies the spatial distribution of phases which were later converted to weight distribution by normalizing it with the density of the phases. However, space distribution may not represent volume distribution due to the different morphology of the phases, and therefore may have caused errors in the analysis. Furthermore, C₃S and C₂S, C₃A and C₄AF formed together and are sometimes really difficult to differentiate due to the resolution of the elemental maps, which may have also induced errors in the analysis. Nevertheless, all of these samples showed similar spatial distribution of phases.

Early-age hydration behavior

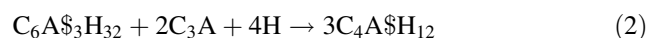
The reactivity of cement is strongly affected by its particle size. Therefore, in order to compare hydration behavior between commercial portland cement and the synthesized clinkers, the synthesized clinkers were first ground to a comparable fineness and tested for Blaine fineness. The Blaine fineness values for the synthesized clinkers ranged from 275.1 to 311.0 m²/kg and are shown in Table 4. The differences in Blaine fineness between the synthesized clinkers are perhaps caused by the grinding and sieving

Table 4 Blaine fineness values for a commercial Type I/II portland cement (control) and clinker samples synthesized from reagent-grade chemicals, GLS with 27.5% YLS, GLS with 27.5% fly ash, and GLS with 35% slag

Sample	Specific surface area (m ² /kg)
Control	405.5
RG	298.4
GLS + YLS	275.1
GLS + Fly ash	311.0
GLS + Slag	304.9

process. However, the differences are about 10% and should not seriously affect the early-age hydration behavior. All of the clinker samples were hand-ground and passed through a #325 sieve (45 μm); however, their Blaine fineness results were still significantly lower than the commercial Type I/II portland cement (405.5 m²/kg).

The synthesized clinkers were then made into cements by adding 12.5 wt% gypsum. The gypsum addition content was determined by adding a range of gypsum content to the synthesized clinkers and testing for early-age hydration behavior using isothermal conduction calorimetry. The addition of 12.5 wt% gypsum was considered as the optimum gypsum content. The optimum gypsum content represents the lowest amount of gypsum that results in only one hydration peak from the hydration reaction of C₃S, and the shape of the peak no longer changes with additional amount of gypsum added [32]. An additional hydration peak generally indicates the formation of calcium monosulfaluminate (C₄A\$H₁₂) from ettringite (C₆A\$₃H₃₂) due to insufficient gypsum in the system:



The rates of heat-evolution for a commercial Type I/II portland cement and the synthetic cements are shown in Fig. 10, and the curves for the cumulative heat evolved are

Fig. 10 Rate of heat-evolution for a commercial Type I/II portland cement (control) and cement samples synthesized from reagent-grade chemicals (RG), GLS with 27.5% YLS, GLS with 27.5% fly ash (F), and GLS with 35% slag (S)

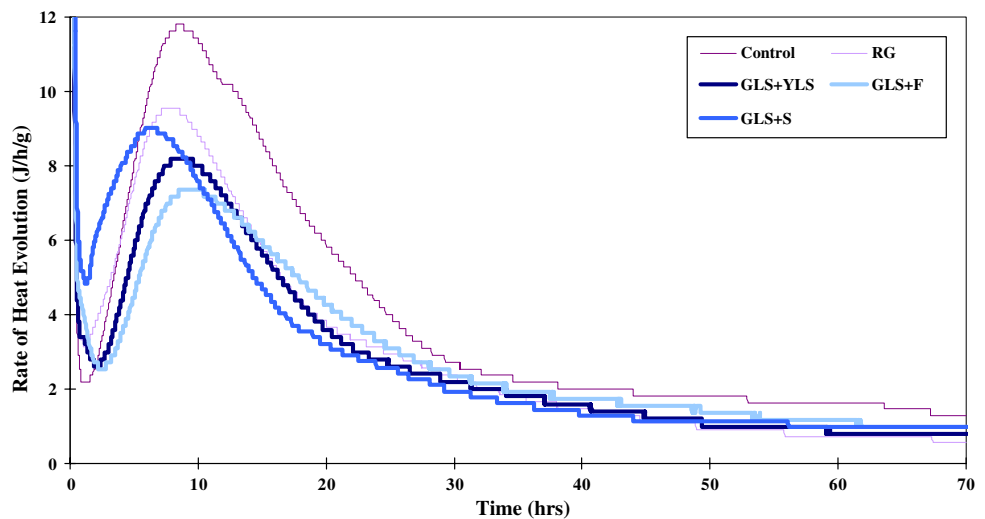
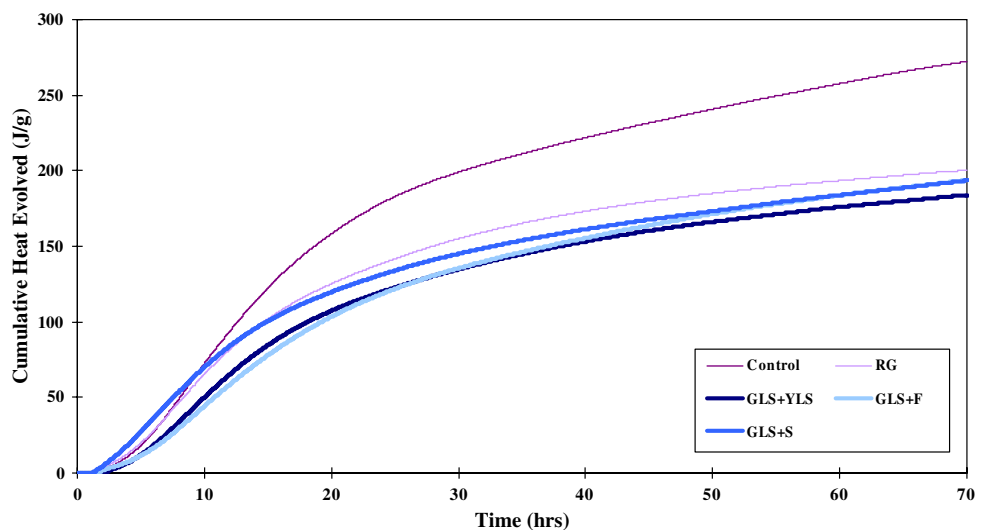


Fig. 11 Cumulative heat evolved for a commercial Type I/II portland cement (control) and cement samples synthesized from reagent-grade chemicals (RG), GLS with 27.5% YLS, GLS with 27.5% fly ash (F), and GLS with 35% slag (S)



shown in Fig. 11. The rates of heat-evolution results show that the synthetic cements possessed hydration behavior similar to a commercial Type I/II portland cement because the shapes of the curves are similar.

The synthetic cements had lower maximum heat-evolution rates and cumulative heat than the commercial cement. The lower heat-evolution rate is most likely caused by the differences in particle size; the Blaine fineness of the synthetic cements is about 25% lower than that of the commercial cement. Previous research has shown that coarser cements reach lower degree of hydration than when compared with finer cements even after a long period of time, which agrees with the hydration results of the synthetic cements, which showed an overall lower heat released than when compared with the commercial cement [33].

The cement samples synthesized from GLS with 27.5% YLS, GLS with 27.5% fly ash, and GLS with 35% slag had lower heat-evolution rates and lower cumulative heat than

the synthetic cement synthesized from reagent-grade chemicals. The phase composition of the clinker sample synthesized from GLS with 27.5% YLS is similar to the clinker sample synthesized from reagent-grade chemicals. However, the Blaine fineness of the cement sample synthesized from GLS with 27.5% YLS is about 8% lower than the cement sample synthesized from reagent-grade chemicals which may be the primary reason that causes its lower heat-evolution rate and cumulative heat. On the other hand, the cement samples synthesized from GLS with 27.5% fly ash and GLS with 35% slag also had lower heat-evolution rates and lower cumulative heat than the synthetic cement synthesized from reagent-grade chemicals. Since the hydration of C_3S dominates the early-age hydration behavior of cement, this phenomenon agrees with the X-ray diffraction results that showed a lower C_3S and higher C_2S in clinker samples with waste materials incorporation.

Conclusions

Portland cement clinker was successfully synthesized from reagent-grade chemicals, gray limestone (GLS) with yellow limestone (YLS), GLS with fly ash, and GLS with slag. The maximum amounts of waste materials that can be used for portland cement clinker synthesis with acceptable compositions were 27.5% fly ash and 35% slag. The clinker samples synthesized from GLS with 27.5% fly ash and GLS with 35% slag had lower C_3S-C_2S ratios than the clinker samples synthesized from reagent-grade chemicals and GLS with 27.5% YLS. However, the phase compositions of all the synthesized clinkers still conformed to the compositional specifications in ASTM C 150 for Type I cement. The low C_3S-C_2S ratio in the synthesized clinkers with waste materials incorporated can be easily increased by increasing the GLS-waste ratio in the raw ingredients. The synthesized clinkers with waste materials incorporated had high periclase (MgO) contents; however, the quantities formed were less than the limit specified in ASTM C 150. On the other hand, the incorporation of waste materials had little to no effect on the spatial distribution of phases. The quantitative multispectral and Rietveld analysis results agree with each other well. Finally, the synthetic cements had similar early-age hydration behavior to commercial cement; however, their heat-evolution rates and cumulative heat were lower.

Manufacturing portland cement with waste materials incorporation can reduce the consumption of natural raw materials, CO_2 emissions, and landfilling of wastes, thereby reducing the environmental impact of the portland cement production. Moreover, manufacturing portland cement from waste materials does not preclude it from being replaced with SCMs in concrete. These two methods can be applied simultaneously to further reduce the environmental impact of the concrete production. However, the presence of sulfur impurities in waste materials can significantly affect phase formation in portland cement clinker. The contents of C_2S and CaO will increase, while the content of C_3S will decrease when increasing amount of SO_3 is incorporated in portland cement clinker synthesis due to the changes in phase equilibria in the $CaO-SiO_2-Al_2O_3-Fe_2O_3$ system, which renders the standard and modified Bogue method inaccurate. Therefore, it is critical to evaluate SO_3 content in materials before using them as raw materials in portland cement clinker production. Furthermore, a model that is more precise than the currently used Bogue methods in addition to empirical experience will be necessary to accurately predict clinker phase compositions when using materials with high SO_3 content as raw ingredients. Finally, because the properties of the portland cement are mainly governed by its phase composition, the direct phase proportion quantitative X-ray

diffraction technique provides a powerful mean for cement manufacturers to better assess their products.

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