

Low-Energy, Low CO₂-Emitting Cements Produced from Coal Combustion By-Products and Red Mud

Tristana Duvallet¹, Robert F. Rathbone², Kevin R. Henke² and Robert B. Jewell²

¹Université De Bourgogne, Ecole Supérieure D'Ingénieurs De Recherche En Matériaux, Aile Des Sciences De L'Ingenieur-9 Avenue Alain Savary-BP 47870-21078 Dijon Cedex;

²University of Kentucky, Center for Applied Energy Research, 2540 Research Park Drive, Lexington, Kentucky, 40511

KEYWORDS: low-energy cement, fluidized bed combustion ash, red mud

ABSTRACT

Over the past 35 years or so, energy conserving or "low-energy" cements have been studied. The research presented herein studied the production and performance of calcium sulfoaluminate (CSA) cement, particularly that containing C₂S ("belite"), termed CSAB, and CSA with calcium aluminoferrite, termed CSFAB. These cements are produced at lower temperatures than Portland cement and require less energy to mill. Furthermore, they require less limestone in the raw mix than Portland cement, so there are less CO₂ emissions. However CSA cement requires a high-alumina raw material such as bauxite which is very expensive. The aim of this study was to formulate CSFAB cement using fluidized bed combustion (FBC) ash and red mud as raw materials and a minimum amount of bauxite. Mortar specimens were prepared from the CSFAB cements for compressive strength and dimensional stability testing.

Several CSFAB cements were fabricated using lime, bauxite, FBC ash and red mud. It was possible to lower the proportion of bauxite in the raw mix by inclusion of red mud and produce a clinker comprising mainly iron-rich C₄AF, C₄A₃S', and C₂S. Good compressive strength and expansion results were achieved on a CSFAB clinker that was formulated with 17% FBC ash and 15% red mud, and which was milled with 30% FGD gypsum. This cement developed strength mainly from the formation of ettringite from the reaction of C₄A₃S', gypsum and water. The aluminoferrite and belite did not react appreciably even after 3 months hydration.

Cement chemistry notation:

C = CaO	S = SiO ₂	S' = SO ₃
A = Al ₂ O ₃	F = Fe ₂ O ₃	H = H ₂ O

INTRODUCTION

The cement industry is an important contributor to global warming because of the substantial CO₂-emissions that originate from fuel combustion and decomposition of limestone. Over the past 35 years or so the interest in energy conserving or “low-energy” cements has been studied. The idea is to decrease the amount of energy required to produce cement and concrete. For example, there is high volume fly ash (HVFA) concrete, blast furnace slag cement concrete and calcium sulfoaluminate cement. The low-energy cements which are described in this study are called calcium sulfoaluminate (CSA) cements, specifically, CSA with dicalcium silicate (“belite”) and calcium aluminoferrite (“ferrite”), termed CSFAB cement. These cements are produced at lower temperatures than Portland cement, require considerably less energy to mill, and can be produced using industrial byproducts as raw materials. Furthermore, these cements need less limestone in the raw mix than Portland cement, so there are less CO₂ emissions. However CSA cement requires a high-alumina raw material such as bauxite which is very expensive in the United States. These cements also have low shrinkage and high early strength but can have durability problems i.e. strength regression after 2-3 years in some cases.

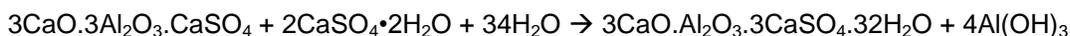
In China, CSA cements have been used primarily to replace Portland cement in mortars and concrete when rapid strength gain, self stressing properties or sulfate resistance is desired. Approximately 1 million tons per year is manufactured in China^[1] which also has special standards for the cements^[2]. CSA type cements have a long history of use in the United Kingdom for specialty applications such as general purpose low shrinkage cement, shrinkage compensated concrete slab, mortar coatings for concrete pipes, rapid repair and setting mortars, anchor bolt grouts and glass fiber reinforced cement products^[3]. The fabrication process for CSA cement is similar to Portland cement, except that the temperature used is lower (e.g. 1250°C), and the clinker is easier to grind. The principal phases in CSFAB clinker are, using cement notation: C₄AF, C₂S and C₄A₃Š (Klein’s Compound).

The reactions during the formation of the clinker are as following:

- at 830°C, CaCO₃ begins to decompose;
- at 1100°C, the formation of C₂AS (gehlenite) and C₄A₃Š occurs;
- at 1150°C, \exists -C₂S forms;
- at 1200°C, the decomposition of C₂AS is observed; and
- at 1250°C, the absorption of lime is complete

Thus at temperatures greater than about 1250°C, the final clinker phases are C₄A₃S’, C₄AF, C₂S and CaSO₄.^[4]

In the presence of calcium sulfate, the major strength forming phase during hydration of CSFAB is ettringite ($C_6A_3S_3H_{32}$)^[5]:



The objective of this study was to formulate CSFAB cement using a maximum amount of industrial byproducts as raw materials and a minimum of bauxite. To do this, we investigated high ferrite cements using alternative calcium, alumina and iron sources. These included red mud, which is a byproduct of aluminum refining, fluidized bed combustion (FBC) spent bed material, which is a coal combustion byproduct (CCB), and flue gas desulfurization (FGD) gypsum. To study these cements, paste samples were prepared for chemical, x-ray diffraction (XRD) and thermogravimetric analysis (TGA) in order to study the hydration phases. Mortar and concrete specimens were prepared from the CSFAB cements for compressive strength and dimensional stability tests.

MATERIALS

The raw mix for CSFAB cement is different that the Portland cement. In this study lime red mud, spent bed ash, pulverized coal combustion (PCC) fly ash and bauxite were used to produce the CSFAB cements. Red mud is produced during the Bayer process, which is the principal means of refining bauxite to produce alumina. It is disposed as slurry having a solid concentration in the range of 10-30%, pH in the range of 13, high ionic strength and it has a high iron content.^[6] The chemical compositions of the raw materials previously presented are in Table 1.

Raw Materials	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	LOI%
Red Mud	9.89	15.03	40.49	6.76	0.22	0.38	1.65	0.20	14.43
FBC Spent Bed	12.77	5.25	3.15	48.23	2.47	27.83	0.05	0.36	2.00
Hydrated Lime	3.86	1.57	0.46	68.98	2.08	0.15	0.12	0.09	23.27
Bauxite	7.66	56.84	3.79	0.20	0.13	1.14	0.01	0.02	27.82
PCC Fly Ash	57.44	29.97	4.94	1.09	0.79	0.11	0.15	2.73	1.61

Table 1: Chemical composition of the raw materials (LOI = Loss On Ignition)

FORMULATION OF CSFAB CLINKER

Several experiments were devised in order to optimize the phase compositions. Different proportions of mineral phases in the clinker were tested:

CSFAB#1: $C_4AF > C_2S > C_4A_3\dot{S}$

CSFAB#2: $C_4AF \approx C_2S > C_4A_3\dot{S}$

CSFAB#3: $C_4A_3\dot{S}' > C_4AF > C_2S$

Modified Bogue equations were first used to estimate proportions of mineral phases in the clinker. Trial batches were then produced by milling the raw materials and firing them in a kiln at 1250°C and the formulations that produced the optimum clinker compositions were selected for further testing. The raw material compositions for the optimized clinkers are shown in Figure 1.

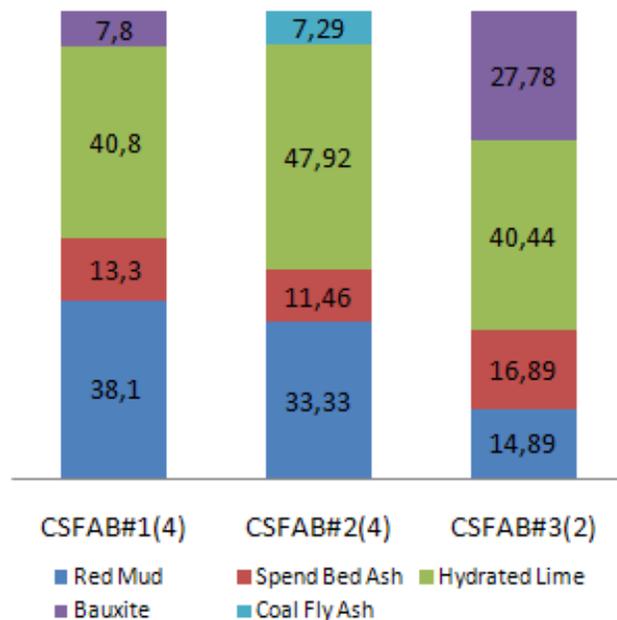


Figure 1: Raw material compositions of CSFAB clinkers.

Production of Clinker and Cement

Prior to milling the raw ingredients, the red mud was dried in a furnace at 80°C for 24 hours. The raw mix was then combined and pre-calcined at 1125°C for 1 hour. At this temperature, all of the clinkering reactions do not occur, but it greatly reduces “caking” in the mill. The pre-calcined mixtures were ground in the ball mill to a median particle size of about 15 µm diameter, and then fired at 1250°C for 1 hour to obtain the clinker. XRD-analysis was completed in order to verify the clinker compositions.

Cements were prepared by milling the clinkers with different proportions of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) as an “activator” for ettringite formation. Gypsum in CSA cements affects not only the setting time, but also the strength development, volume stability, and hydrate composition. The materials were mixed and milled together in a ball mill until a median particle size of approximately 15 µm was achieved.

Mortar Cubes and Expansion Bars for Strength and Length Change Testing

The preparation of mortar cube specimens followed standard methods ASTM C 305^[7] and ASTM C 109^[8]. Dimensional change of mortar bars was studied using ASTM C 157^[9]. Prior to preparing standard 5 cm (2 in) cube specimens, smaller cubes (2.5 cm) were prepared for preliminary testing. These were prepared by placing and compacting mortar into 2.5 cm (1 in) cross-section bar molds and, after setting, cutting the mortar bars into cubes. These are referred to as “small cubes”.

Analysis of Hydrated Phases

Scanning Electron Microscopy (SEM)

SEM analysis was completed for mortar specimens by obtaining a small piece from inside the cube after a compressive strength test. The samples were immersed in acetone and lightly ground in a mortar and pestle to stop the hydration process. After this step, the acetone (and included water) was decanted and the pieces placed in an oven at 55°C for 1 hour. They were then stored in a sealed vessel over silica gel and soda lime until SEM-analysis.

Thermogravimetric Analysis (TGA) and X-Ray Diffraction (XRD)

Cement pastes were prepared for TGA and XRD analysis using the same method as described for SEM analysis, except that the pastes were ground more thoroughly. The dried samples were analyzed with a Netzsch STA 449 C TGA/DSC and a Philips X'Pert x-ray diffractometer.

RESULTS

Mortar Compressive Strength and Expansion

Compressive strength data for the small cubes is shown in Figure 2.

For CSFAB#1(4), 10 and 20% percent gypsum addition resulted in a very low compressive strength, about 3 times less than the one without gypsum. Furthermore, the mortar was very red due to the formation of iron hydroxide. For CSFAB#2(4), the 0% gypsum mortar was stronger than mortars with 10% gypsum but at 28 days, the latter became stronger. The mortar containing 20% gypsum is not present in the graph because after 2 weeks it was too weak to be tested.

For CSFAB#3(2), 10% gypsum was not sufficient to prevent flash-setting during mortar preparation. At one day, CSFAB#3(2) with 20% of gypsum had a higher compressive strength than the one with 30% gypsum, but after 1 day the latter gained strength more rapidly. Thus the CSFAB#3(2) with 20 and 30% gypsum were the most promising formulations.

The compressive strength and XRD data indicated that CSFAB#3 clinker, which contained the largest amount of Klein's compound, exhibited the highest strength, while the clinkers containing lesser amounts of Klein's compound exhibited lower strengths. For comparison, mortar strength data for a high-Klein's Compound cement (CSAB#4), which was milled with 35% FGD gypsum, are included in Figure 2. After one day, the CSAB#4 mortar had a compressive strength of about 3600 psi.

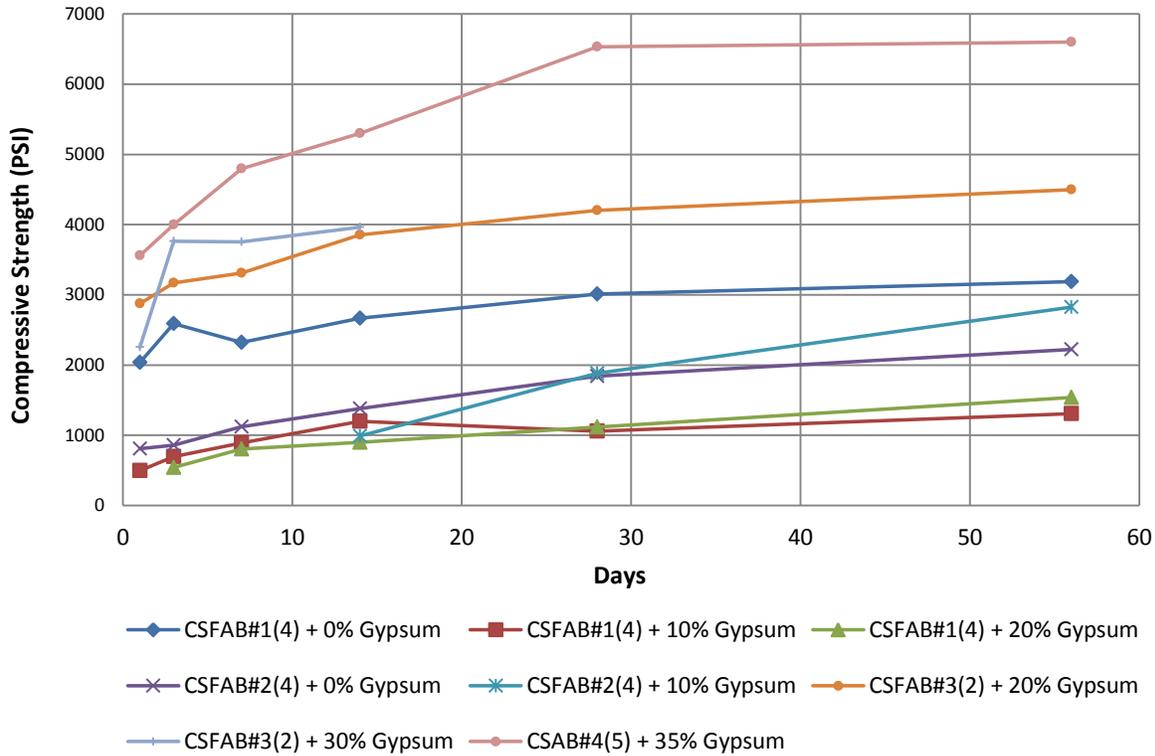


Figure 2: Unconfined compressive strength of 2.5 cm mortar cubes.

Based on the small mortar cube data, the CSFAB#1 and CSFAB#3 + 30% gypsum cement mortars were selected for strength testing using 5.1 cm cubes and ASTM standard mortar. The CSFAB#3+30% gypsum mortar set time was approximately 30 minutes, and the mortar achieved a strength of 1250 PSI (8.6 MPa) in 6 hours. After 1 day the strength was about 2500 PSI (17.2 MPa), which is in good agreement with the preliminary tests. The mortar cube strength eventually increased to 5000 PSI (34.5 MPa) after 56 days. The expansion bars data (Table 2) show that after 15 days the bars expanded 0.0585%. But after this, the expansion of the bars didn't change substantially.

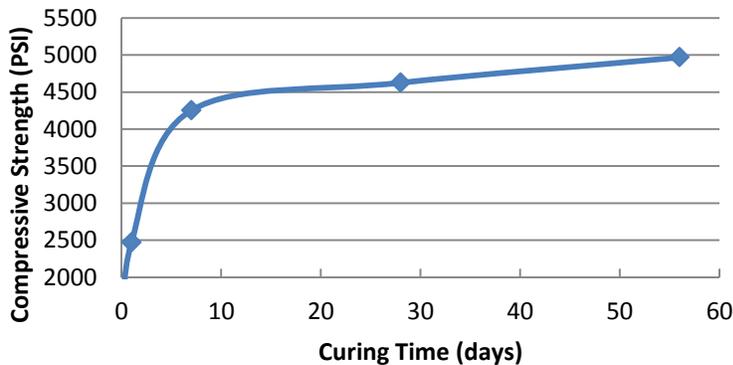


Figure 3: Compressive Strength of CSFAB#3(2) + 30% of Gypsum

Days	Length Change
0	0%
15	0,058%
28	0,059%
56	0,060%
112	0.060%
224	0.061%

Table 2: Percentages of change length for the expansion bars of CSFAB#3(2) + 30% of Gypsum

Compressive strength of the CSFAB#1 mortar cubes is shown in Figure 4 and expansion data are shown in Table 3. The mortar set in less than 15 minutes and achieved a 1 day strength of about 1400 PSI (9.7 MPa). The strength did not increase until after 7 days of moist curing, after which it achieved a strength of only 1800 PSI (12.4 MPa). The expansion (Table 3) was very low, with a maximum length change of approximately 0.01%.

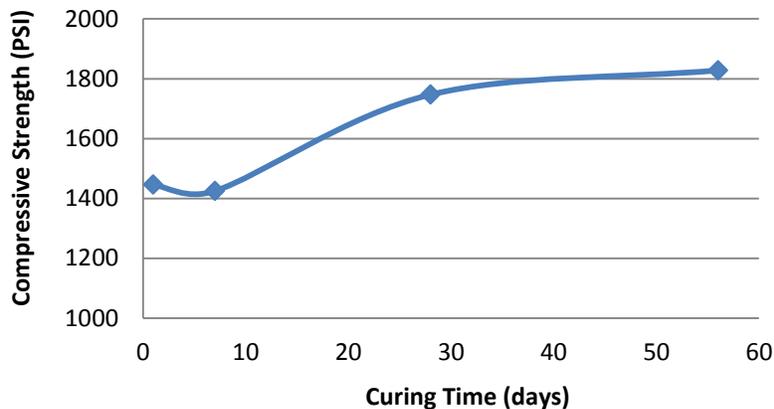


Figure 4: Compressive Strength of CSFAB#1(4) + No Gypsum

Days	Length Change
0	0%
28	0.0032%
56	0.0039%
112	0.006%
224	0.010%

Table 3: Percentages of change length for the expansion bars of CSFAB#1(4) + No Gypsum

XRD and TGA Analysis of Paste Samples

Hydration reactions in the CSFAB#1 and #3 cements were studied using paste samples. These were prepared by mixing 50 g of cement with 16.5 g of water (W:CM = 0.33). The pastes were cured in tightly sealed polyethylene bottles along with a saturated paper towel to maintain 100% RH. Prior to analysis, several grams of paste were treated with acetone in the manner described above to halt hydration.

CSFAB#3 Paste

The XRD analyses showed that ettringite formed rapidly, primarily from the reaction of Klein's compound (yeelimite) with gypsum (Figure 5) and water. Over the course of the experiment, ettringite content increased, Klein's compound decreased, and gypsum content decreased; after approximately 3 weeks curing, only a very small gypsum peak is observed (Figure 5), whereas a substantial quantity of Klein's compound still remained. This suggests that either additional calcium sulfate is required for complete reaction or that the remaining Klein's compound is not able to hydrate. Evidence for the former explanation was provided by an additional experiment wherein a CSFAB#3 paste was prepared without gypsum addition. As Figure 5 shows, after 4 months most of the Klein's compound remained and some calcium aluminum oxide carbonate hydrate $C_4A\dot{C}_{0.5}H_{12}$ are present. Interestingly, the ferrite phase (Brownmillerite) produced strong

XRD peaks throughout the 6 month experiment, suggesting that its hydration rate is very slow.

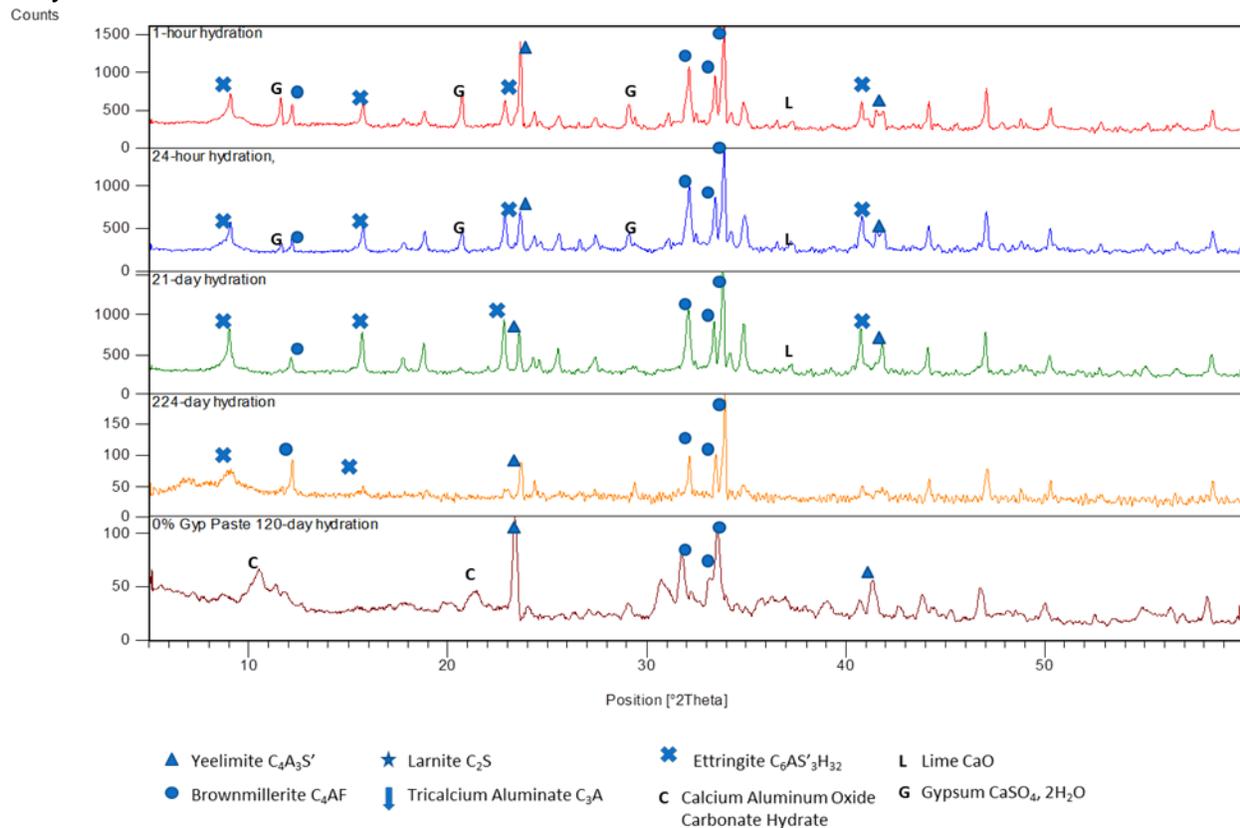


Figure 5: XRD-results for CSAFB#3(2) + 30% gypsum and CSAFB#3(2) with NO gypsum - Hydration results

SEM analysis confirmed that ettringite was abundant in the cement paste. The needles on the Figures 6, 7 and 9 correspond to ettringite. After 1 day, the needles are about 0.5-1 μ m and have a hexagonal shape. At 28-day, new very fine needles grow inside the ones already formed. Furthermore, in Figure 8 plate-shaped hydrates can be seen, which are possibly calcium hydroxide, aluminum hydroxide and/or AFm crystals.

Overall, the TGA analyses (in Fig. 10) indicated that the major cementitious hydrate for CSAFB#3 is ettringite, which is consistent with the XRD data. The data showed an endothermic mass loss from ettringite dehydration at about 150°C. After 1 hour of hydration, an endothermic “shoulder peak” for gypsum dehydration is present at about 160°C. This peak decreased with curing time due to ettringite formation. Furthermore, at about 280°C an endothermic peak representing Al(OH)₃ is present. This is consistent with the known reaction of C₄A₃S̄, gypsum, and water to form ettringite + aluminum hydroxide. After 21-day, an endothermic peak that is possibly attributed to AFm (e.g. monosulfate) appeared, which is a reaction consistent with depletion of gypsum. The XRD data also showed diffraction peaks consistent with monosulfate, but they were very

small and overlap with ettringite peaks. The endothermic TGA peak for ettringite also shifted to higher temperature and became wider with time; this is interpreted to be caused by the ettringite becoming denser and more stable, thus slowing the rate of dehydration within the TGA.

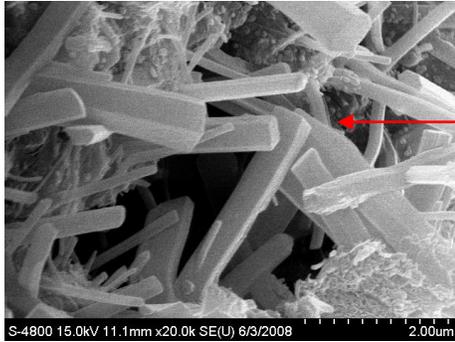


Figure 6: 1-day hydration of CSFAB#3(2)+30%gypsum paste cement

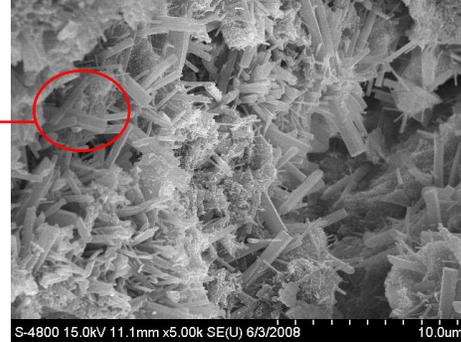


Figure 7: 1-day hydration of CSFAB#3(2)+30%gypsum paste cement

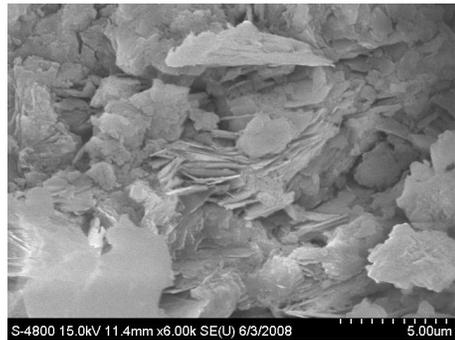


Figure 8: 1-day hydration of CSFAB#3(2)+30%gypsum paste cement

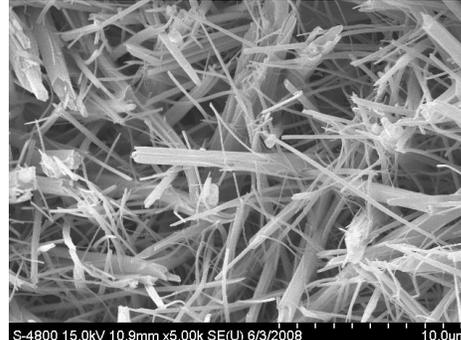


Figure 9: 28-day hydration of CSFAB#3(2)+30%gypsum paste cement

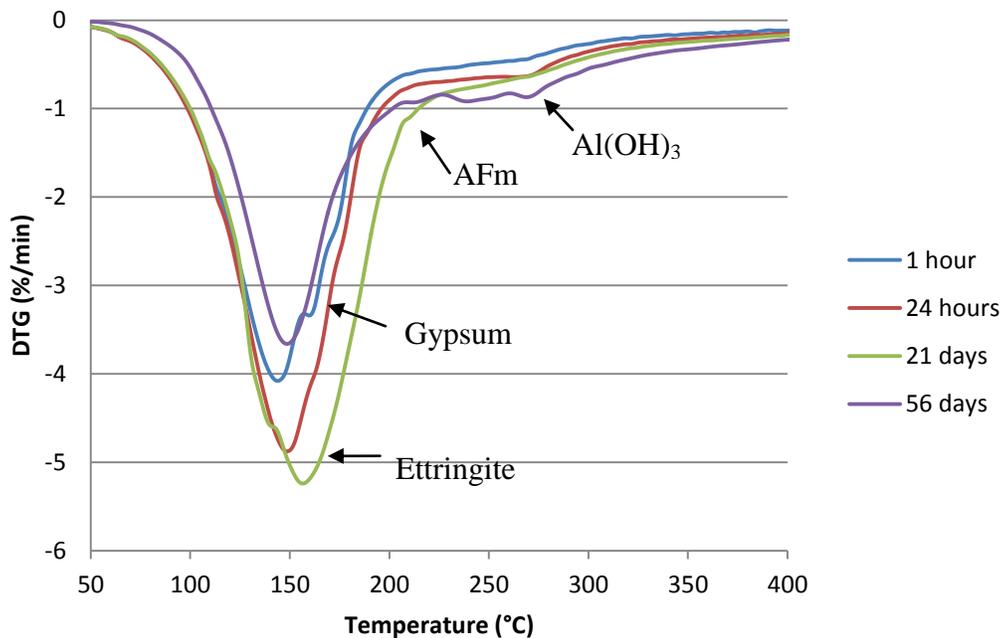


Figure 10: Results of TGA-analysis for CSFAB#3(2) + 30% Gypsum

CSFAB#1 Paste

The XRD-analyses show that during the first day (1 and 24-hour results), brownmillerite, yeelimite, tricalcium aluminate (C_3A) and larnite (C_2S) were present. Within 21 days, most of the brownmillerite hydrated to form hydrogarnet. Larnite and some brownmillerite remained. After almost 4 months of hydration, peaks of hydrogarnet and calcium aluminum oxide carbonate hydrate are present. Thus the hydration rate of this cement is very fast, because after 21 days after, essentially hydrogarnet was remained. For comparison, another experiment was done with CSFAB#1(4) + 20% of gypsum. The data showed that after 4 months the gypsum addition caused ettringite formation, while the brownmillerite was still abundant with no trace of hydrogarnet.

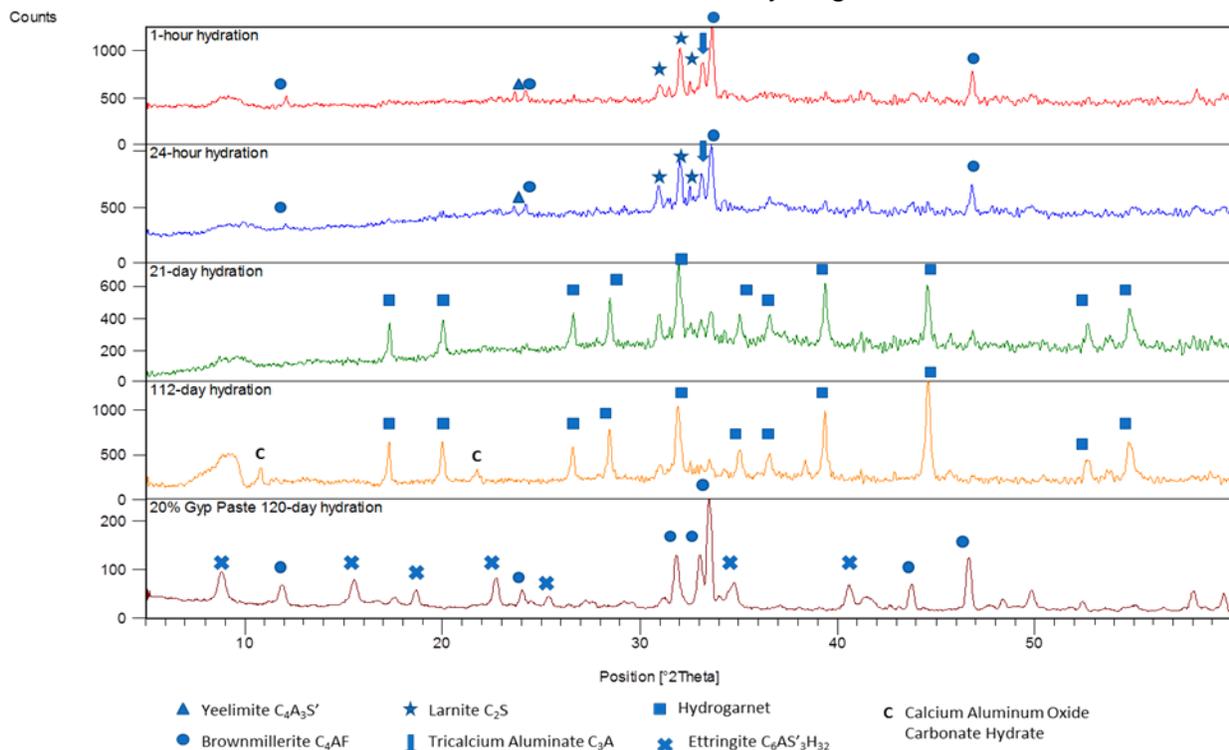


Figure 11: XRD-results for CSAFB#1(4) + No gypsum and CSAFB#1(4) with 20% of gypsum - Hydration results

SEM analysis confirmed that some ettringite was present during the first day of hydration (Figure 12), but not longer present after the 7-day of hydration. From 7-day to 56-day of hydration, only hexagonal plates of AFm phases and hydrogarnet can be seen.

TGA-analyses show the strong peak of ettringite at about $100^\circ C$ after the first hour. The peaks of AFm and hydrogarnet were present too. After 24 hours, the largest mass loss rate occurred from dehydration of AFm, possibly monosulfate. After 21 days, decomposition of hydrogarnet was the major mass loss from the sample. This is consistent with the XRD data; that ettringite transforms into monosulfate in 3 days, followed by brownmillerite transformation to hydrogarnet.

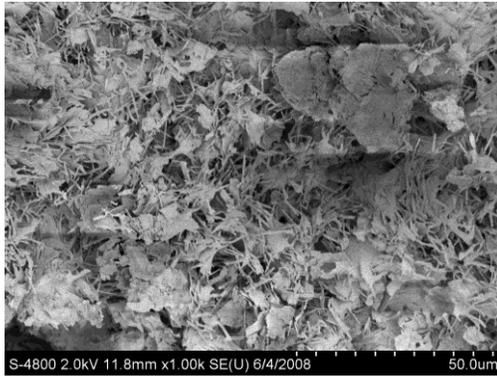


Figure 12: 1-day hydration of CSFAB#1(4)+no gypsum paste cement

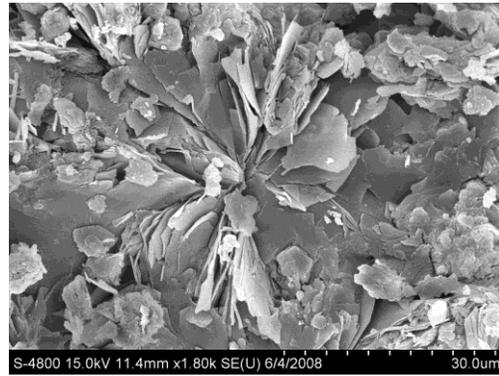


Figure 13: 7-day hydration of CSFAB#1(4)+no gypsum paste cement

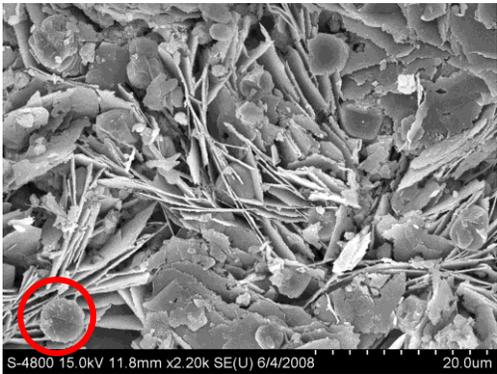


Figure 14: 28-day hydration of CSFAB#1(4)+no gypsum paste cement

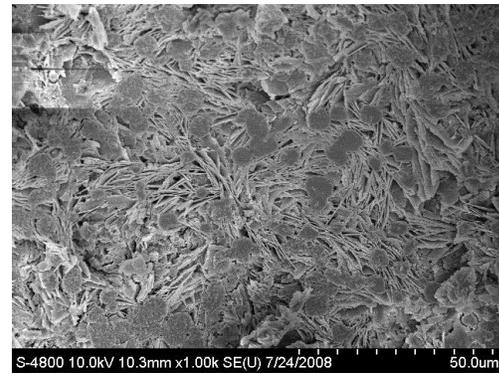


Figure 15: 56-day hydration of CSFAB#1(4)+no gypsum paste cement

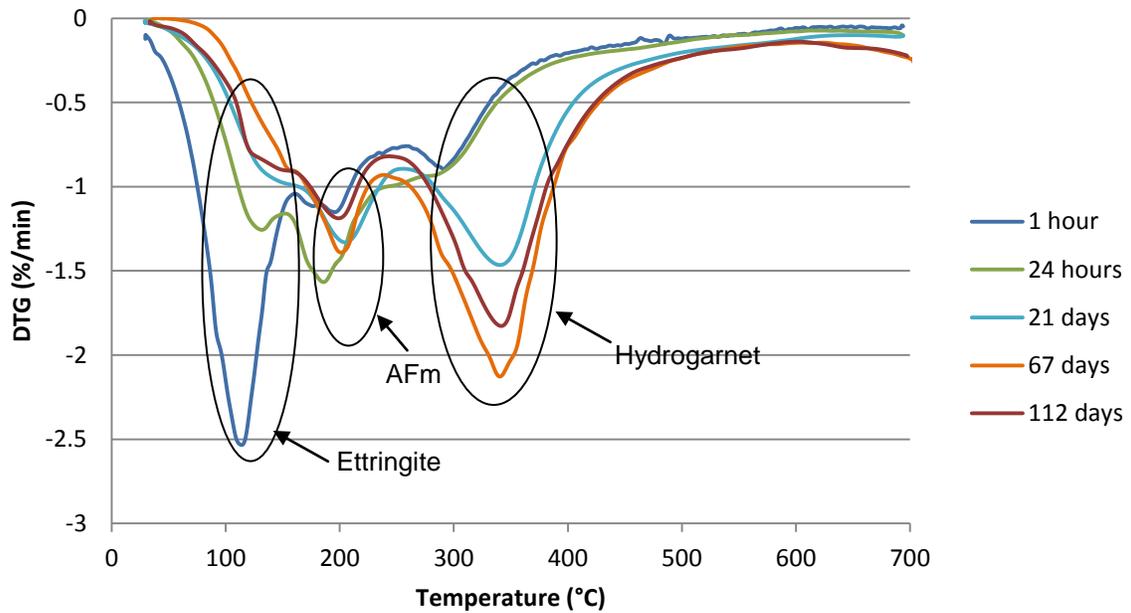


Figure 16: Results of TGA-analysis for CSFAB#1(4) with NO Gypsum

Conclusion

Several rapid hardening cements were fabricated using lime, bauxite, coal combustion byproducts and red mud. It was possible to lower the proportion of bauxite in the raw mix by inclusion of red mud and produce a cement comprising mainly iron-rich C_4AF , $C_4A_3\dot{S}$, and C_2S (belite). However, replacement of bauxite with red mud resulted in a lowering of compressive strength, compared to high- C_4A_3S' cement, and can only be achieved to a limited degree before compressive strength gain and durability are substantially compromised.

Three compositions of CSFAB were initially formulated and the strongest ones chosen for more detailed testing. The main selection criteria were strength gain and dimensional stability (i.e. presence of expansion and cracking). The CSFAB#3(2) with 30% gypsum addition exhibited a compressive strength of 2500 PSI the first day and reached 5000 PSI within 2 months. Its strength was derived from the formation of ettringite in large amounts as seen on SEM results. Furthermore, XRD and TGA-analysis showed that within several months, ettringite formation consumed nearly all the gypsum.

The cement prepared using less bauxite (CSFAB#1) formed ettringite rapidly, which then transformed to monosulfate within 3 days. Subsequently, the brownmillerite hydrated to hydrogarnet. Although expansion and cracking was not observed when the cement was cured in sealed plastic bottles or submerged in water, after approximately 6 months of moist curing (i.e. exposure to 100% RH, but not submerged) this cement exhibited pronounced expansion cracking that was apparently caused by carbonation. Further research will focus on increasing ettringite formation in the CSFAB#1 cement and improving dimensional stability. In fact, preliminary experiments using ultrafine fly ash indicated that expansion and cracking could be controlled by milling fly ash with the clinker as a process addition.

Based on the experiments in this study, the CSFAB#3 cement has potential as a rapid hardening cement that can be produced using greater than 35% byproducts in the raw materials. As regards the rate of compressive strength development, set time, and expansion in water it could qualify as a "medium rapid hardening" cement according to ASTM C1600^[10]. However, further testing on drying shrinkage and autoclave expansion would need to be conducted. In addition, an effective set retarding admixture needs to be identified if this cement were to be used in general construction.

Bibliography

- [1] Zhang, L. and Glasser, F.P., 1999, *in* Modern Concrete Materials: Binders, Additions and Admixtures, Proceedings of the International Conference held at the University of Dundee, Scotland, September 1999, R. K. Dhir and T. D. Dyer, ed., pp. 261-274.
- [2] Zhang, L., Su, M. and Wang, Y., 1999, *Advances in Cement Research*, 11, pp 15-2.
- [3] Brown, A.D.R., 1993, *in* Concrete 2000: Economic and Durable Construction Through Excellence, Proceedings of the International Conference held at the University of Dundee, Scotland, UK, September 1993
- [4] Wang Yanmou, Deng Jun'an, Su Muzhen, "An investigation into cement CaO-SiO₂-Al₂O₃-Fe₂O₃-SO₃ system"
- [5] M. Marroccoli, M. Nobili, A. Telesca, G. L. Valenti, "Early hydration of calcium sulfoaluminate-based cements for structural applications", *Sustainable Construction Materials and Technologies – Chun, Claisse, Naik & Ganjian (eds), © 2007 Taylor & Francis Group, London, ISBN 978-0-415-44689-1.*
- [6] W. Kurdowski, F. Sorrentino, "Waste Materials Used in Concrete Manufacturing", p. 290-308, Edited by Satish Chandra, William Andrew Publishing/Noyes, 1997
- [7] ASTM C305 – 82 (Reapproved 1987)
Standard Practice for Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency.
- [8] ASTM C109 – 90
Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 2-in. or 50-mm Cube Specimens)
- [9] ASTM C157 / C157M – 99
Standard test Method for Length Change of Hardened Hydraulic-Cement Mortar and Concrete
- [10] ASTM C1600 / C1600M – 08
Standard Specification for Rapid Hardening Hydraulic Cement