MIT Concrete Sustainability Hub, Concrete Science Platform
White Paper
Improving Concrete Sustainability through Alite and Belite Reactivity
September 2013

Executive Summary

Calcium silicate phases, alite and belite, are among the main components of modern portland cements. Alite reacts relatively rapidly with water and is responsible for most of the early strength development of concretes. Belite is less reactive at early ages, but can contribute appreciably to strength at later ages. Over time and in response to market demands, portland cements have gravitated toward higher alite contents and lower belite contents, as construction industry professionals sought materials that would allow them to work faster and more efficiently.

However, the manufacture of cements with higher alite contents may have a larger net environmental impact. Compositionally, increased limestone quantities in the raw feed are required to form alite, which results in higher associated CO_2 emissions from calcination. **If cements with higher belite contents could be developed with strength gain characteristics similar to current cements, cements could be manufactured with a reduced environmental impact, which would result in a lower environmental footprint for concrete as a construction material.**

In contrast to this approach is the concept that, because of their more rapid rate of strength development, **cements with higher alite contents can be used in concretes with higher amounts of non-clinker materials—fly ash, slag, and limestone for example, or in blended cements**. Many of these materials are byproducts from other industrial processes that are beneficially used in concrete in lieu of being disposed in landfills. This also has the potential to reduce the environmental impact of cement manufacturing and concrete construction.

Silicate phases also impact finish grinding energy requirements of cements. More reactive alite and belite could lead to grinding energy savings as coarser cements may be able to be used with no loss of early strength development or other performance characteristics.

The MIT Concrete Sustainability Hub's Concrete Science Platform is studying alite and belite phases starting at a fundamental level, that of electrons and atoms, through rigorous computer modeling. The primary goal of the program is to enhance our knowledge about the reactivity of these two phases in order for potential improvements to be developed and implemented. Thus far, the potential impacts on reactivity of substitutions of different elements into alite and belite crystal structures have been evaluated as well as reactivity of their various crystal faces. This work alone would have required decades of research to have been achieved experimentally. Further refinement of these models and validation of model predictions—using alites and belites from commercial clinkers with realistic compositions—is underway.

To be emphasized is that the fundamental nature of this research falls into the "Basic Research" domain of Figure 1.The goal of the project is to provide new knowledge, information and connections so that industrial research teams can provide practical interpretation and innovation to improve the sustainability of cement and concrete through better understanding or optimization of materials or production processes.

The net benefit to the environmental footprint for cement and concrete of improvements developed through these approaches will be further validated through LCA/and LCCA modeling. These benefits are anticipated to lead to lower impacts for buildings and pavements at the time of construction, which will further enhance the long term benefits of concrete in these applications during the use phase already reported (Santero, et al. 2011; Ochsendorf, et al. 2011).
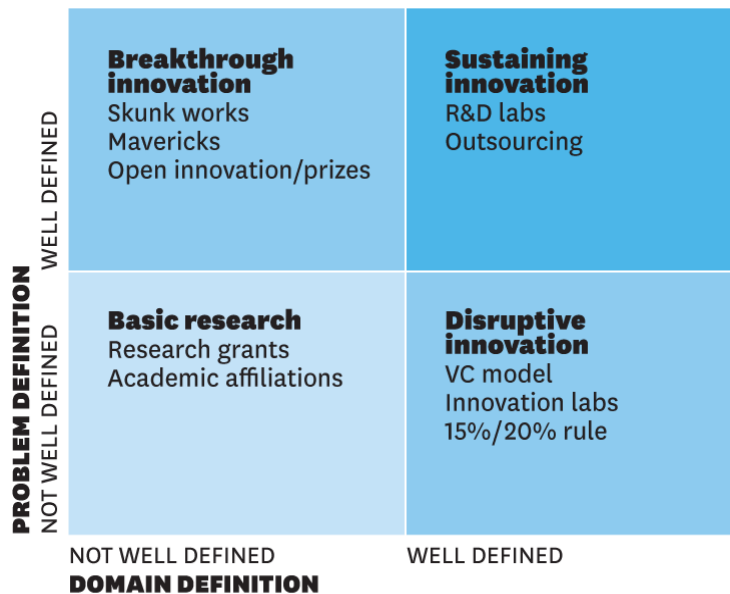

Figure 1. The MIT Concrete Sustainability Hub's Concrete Science Platform performs basic research, which develops fundamental knowledge leading to other types of innovation (Satell 2013).

Alite and Belite Reactivity: An Introduction

Alite and belite are phases (compounds) in portland cement based materials. Alite is impure tricalcium silicate (C_3S) and belite is impure dicalcium silicate (C_2S). The impurities arise as cement is manufactured from natural raw materials (and because alumina and iron are included to form liquids at kiln temperatures to improve the efficiency of kiln reactions) rather than purified chemicals. However, although the word *impurity* may have a negative connotation, in this case impurities are typically a benefit, as they stabilize clinker phases at lower kiln temperatures (reducing kiln energy requirements and related CO_2 emissions) and can make the cement phases more reactive when mixed with water. A range of these impurity elements are found naturally in cement raw materials and they can create clinker phases with a range of compositions and reactivities.

Alite and belite account for about 75% by weight of modern cements and dominate the development of properties such as setting time and strength development. Although both are calcium silicates, alite reacts much more quickly than belite when mixed with water. Both alite and belite react to form calcium silicate hydrate (known in cement chemists' shorthand as C-S-H), which is the primary binding material in cement paste, mortar, and concrete. The total amount of alite and belite in cements has not changed appreciably in many decades and is limited by process considerations; however, modern cements are produced in kilns with better control of burning conditions allowing higher percentage of alite in cements, which respond to market demands for higher early strength gains permitted by its relatively rapid reactions.
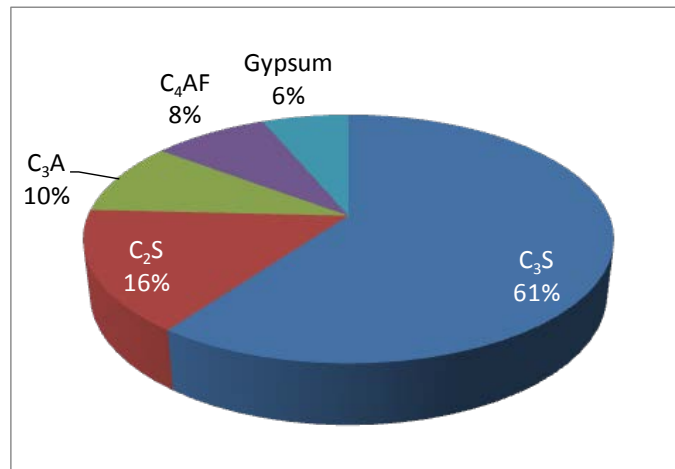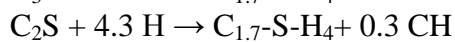

Figure 2. Bogue Composition of a typical Type I portland cement.

The overall reaction of alite and belite can be described chemically (approximately) as:

$$C_3S + 5.3\ H \rightarrow C_{1.7}\text{-}S\text{-}H_4 + 1.3\ CH$$
$$C_2S + 4.3\ H \rightarrow C_{1.7}\text{-}S\text{-}H_4 + 0.3\ CH$$

where H is water (H_2O) and CH is calcium hydroxide. Note that the reaction products of both silicates are C-S-H and CH. C-S-H is the main binding phase in portland cement-based systems

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and primarily responsible for the strength and durability of concrete. CH is a byproduct of the hydration reaction that does not contribute much directly to the strength of concrete (it is a solid, and thus reduces porosity, which of course does improve strength). Calcium hydroxide is beneficial however as it helps maintain a pH at which embedded reinforcing steel is maintained in a passivated state thereby preventing corrosion. CH also reacts with silicates in supplementary cementitious materials (SCMs) like fly ash to produce additional C-S-H via a pozzolanic reaction. Reducing the quantity of CH resulting from hydration of portland cements, however, can improve the potential strength and durability of concrete. Belite produces about ¼ as much CH as alite and thus relatively more C-S-H. It might be expected that cement would therefore be composed of as much belite as practical. However, the early reaction of belite is much slower than alite and therefore a problem for efficient construction cycles. As well, the higher CH contents of cements with higher alite contents may favor use of higher levels of SCMs, which can significantly reduce concrete's environmental footprint.

Some researchers have suggested that the increased amount of calcium hydroxide (CH) resulting from the hydration of modern cements could lead to reduced durability (for example, see Mehta and Monteiro 2005). Calcium hydroxide is relatively soluble in water and can react with sulfate ions to form gypsum in an expansive reaction, which is a secondary sulfate attack mechanism. Since CH provides relatively little contribution to strength compared to C-S-H, stronger, more durable concrete in some applications might be obtained if the quantity of belite is increased relative to the percentage of alite. However, the slow reaction rate of belite makes it less suitable for use as the primary silicate in cement from a practical standpoint. If the reaction of belite could be accelerated, several benefits might be achievable:

1. Relatively more C-S-H per unit quantity of cement, perhaps increasing concrete sustainability as less cement might be needed to achieve necessary strength and durability
2. Since belite forms at lower kiln temperatures and requires less limestone as a raw ingredient in cement manufacture, perhaps 10% to 15% lower CO_2 emissions from calcination and fuel burning, as well as lower energy consumption might be achieved.
3. Improved knowledge about reaction mechanisms could also lead to more reactive alites, which could also improve sustainability.

In contrast, several potentially negative effects of higher belite contents in cements might be observed:

1. Relatively less CH would be formed, limiting the use of SCMs, like fly ash and slag, which partially react with CH to form additional C-S-H (although at a slower rate compared to clinker silicates), and
2. Grinding energy may be increased for cements rich in belite. Although belite is slightly "softer," alite is more brittle. The net result is that alite is generally slightly easier to grind; however a number of other factors also impact clinker grindability.

A primary goal of the MIT Concrete Sustainability Hub is to improve our fundamental knowledge of the reaction mechanisms of alite and belite. In turn, this knowledge may allow industry to improve the reactivity of one or both silicates through commercial innovations. Improving the reactivity of one or both phases might lead to improved cement manufacturing sustainability as cements might be able to be ground to lower fineness and still achieve comparable reaction rates and strength development profiles of current concrete mixtures. Likewise, improved reactivity of the silicates could lead to concretes with lower cement contents, but with the same strength and durability as existing concretes.

Implications of results for cement and concrete industries

Cements that are predominantly alite, like modern portland cements, require higher burning zone temperatures and higher limestone contents in the raw feed, compared to belite-based cements. Burning zone temperatures for producing belite-based cements might be more than 100°C lower, resulting in energy savings as well as lower CO_2 emissions due to fuel combustion. Calcination CO_2 savings can also be significant as less limestone is needed to produce a ton of belite-based clinker as compared to alite-based clinker. Table 1 shows some properties of laboratory produced cements with a range of alite/belite contents.

Table 1. Properties of laboratory-produced cements with different lime saturation factors (LSF)*

LSF	Burning temperature	Alite	Belite	Compressive strength, MPa	
	°C	% by mass	% by mass	7d	28 d
75	1280	0	80	--	15
80	1280	12	68	5	25
85	1290	32	48	18	47
90	1300	46	34	25	55
95	1330	56	24	30	59
100	1380	80	0	42	63

Source: Ludwig and Pöhlman 1986.
*LSF (lime saturation factor) = $(CaO - 1.7SO_3)/(2.80 SiO_2 + 1.18 Al_2O_3 + 0.65 Fe_2O_3)$. This provides an estimate of the maximum amount of C_3S. Values of 92 to 98 are common for modern cements and values above 100 indicate that some free lime will likely be present.

Cements with high belite contents can be produced with about 120 kg less limestone per ton of clinker and about 220 kJ/ton lower energy needs (enthalpy) for clinker formation (Odler 2000). The lower limestone content in the raw materials leads to a reduction in CO_2 emissions from calcination. As about half of limestone is CO_2, 120 kg/ton translates into roughly 60 kg/ton of reduced CO_2. The net savings in CO_2 emissions might be on the order of 10% to 15%, without considering any grinding energy changes. However, the inherently low reactivity of belite must be overcome to maintain current expectations of cement reactivity and strength gain. Cements with higher belite contents were manufactured in the past (for example see Bhatty and Tennis 2008); however, those cements had slower rate of strength development.

As might be expected in a relatively complex system like cement, there may be tradeoffs involved in optimizing cements for performance and environmental impact. The knowledge developed by the CSHub, in conjunction with practical experience and knowledge developed over the last 100 years or so in industry, will provide a sound basis for those optimizations.

General knowledge about alite and belite reactivity

The term "reactivity" has different meanings. To a cement chemist, it is a measure of how fast the reactions of cement with water occur. This might be measured in overall terms by techniques such as measuring the heat generated when a paste reacts with water (reactions of the primary cement phases with water are exothermic) or by tracking the concentrations of various ions in solution. It might be determined microscopically by measuring the amount of hydration products that form over time or by determining how much clinker has dissolved after a certain amount of time. To a concrete technologist, reactivity may refer to how quickly a cement paste, mortar or concrete reaches initial set or gains strength. All of these definitions are related, because they all depend on the multiple simultaneous chemical reactions that occur when cement comes into contact with water.

A general calorimetry curve for alite displays some of the complex characteristics of the reactions of these phases. Figure 3shows a schematic of the heat released during hydration, which is divided into 6 stages. Stage 0 is usually attributed to wetting of the particles and Stage I is an initial brief reaction period in which perhaps 1% to 2% of alite is reacted.
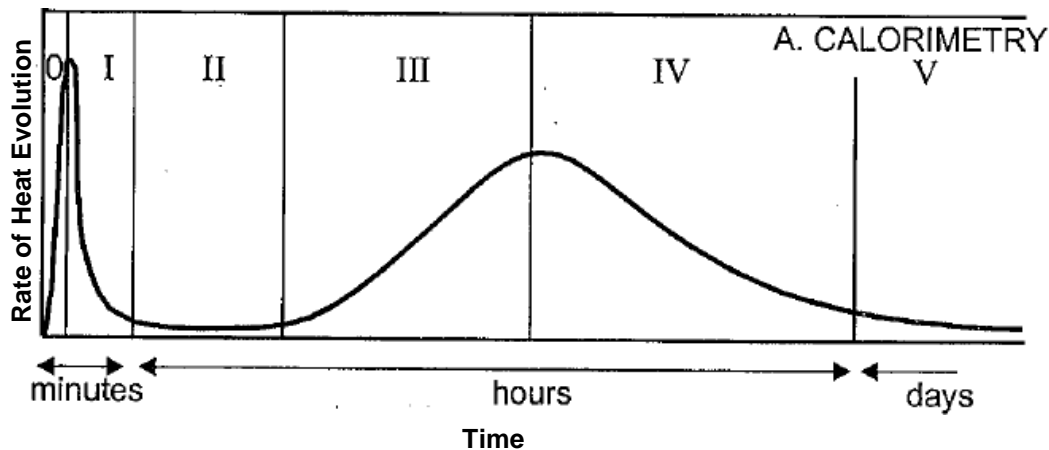
Figure3. Schematic representation of alite hydration (after Gartner et al. 2002).

Stage II is referred to the induction period, a time of very low reactivity shortly after mixing with water. This period is characteristic not only of alite, but also portland cements. The induction period is useful because it provides sufficient working time for concrete or mortar to be placed and consolidated before setting and gaining appreciable strength. There are multiple hypotheses for the cause of the induction period (see for example, Gartner, et al. 2002, and Bullard, et al. 2011), which for alite typically lasts a few hours, while for belite it may last a few days.

Stage III is the period when the hydration reactions begin in earnest and setting and strength development take place. During Stage IV the reactions slow while strength development continues. This may be due to hydration products surrounding cement grains and slowing further dissolution (although other hypotheses exist; see Bullard, et al. 2011). Strength and hydration reactions continue in a slow and decreasing rate in Stage V, provided sufficient water and space for hydration products remain.

Each of these stages of reaction can be better understood, and this understanding could lead to improved control and optimization of cement-based materials.

A primary goal of the Concrete Science Platform at MIT CSHub is to increase the understanding of the mechanisms of cement hydration from a fundamental level: at the level of atoms and electrons. Why does alite react much faster than belite? Can we better control the induction period? Can the reaction rates of all or any of the phases be improved? What is the atomic structure of C-S-H? How can it be modified and optimized for different applications?

Alite has two common polymorphs (different crystal structures for the same phase): M_1-C_3S and M_3-C_3S, both are monoclinic (hence the "M"), which describes the shape of the crystal. These two monoclinic structures are the same crystal shape, but the M_1 and M_3 forms of alite have different spacing of the atoms in the crystals, possibly due to different types or levels of "impurity" atoms in the crystals making those crystal forms stable. Likewise, Belite also has two polymorphs, the common, β-C_2S, is also monoclinic in shape, while the other, (α_H'-C_2S), is triclinic.

Impurities in clinker are often beneficial as they can make the crystals more reactive (and conversely, some can make the crystals less reactive). Thus impurities can impact alite and belite reactivity in two ways: by stabilizing polymorphs that are more (or less) reactive and by making the crystals of specific polymorphs less (or more) stable, and therefore more reactive. This is why they are the subject of intense study at the CSHub. Figure 4 summarizes some initial results of the CSHub on this topic.

For both alite and belite, the modeling effort provides tools to evaluate the reaction of crystals with different types and concentrations of elemental impurities to see how they potentially impact reactivity. This is only a first step because manufacturing alites and belites that include these impurities in commercial clinkers may or may not be feasible. However, acquiring this knowledge is very time consuming to determine experimentally and may be too complex to determine based on first principles without the type of models being developed at the MIT CSHub.

Other advantages may result from the detailed study of silicate reactivity. Several theories have been postulated to account for the induction period, the period when concrete can be placed and formed/finished before hardening and strength development. Detailed studies of the reaction mechanisms can provide a fundamental understanding of the induction period, and potentially new avenues for the control of this critical period.

Goals/Questions to be addressed by the MIT CSHub Concrete Science Program

Research on atomic scale models at the CSHub have suggested that alite and belite differ in reactivity because alite has a relatively more "defective" crystal structure than belite. This is primarily attributed to the observation that sites in alite crystals that oxygen should occupy are unfilled. This allows water to start reacting with alite (or for alite to start dissolving in water) faster, and thus, the hydration products can form faster. The relatively more "perfect" crystalline structure of belite renders it less reactive.
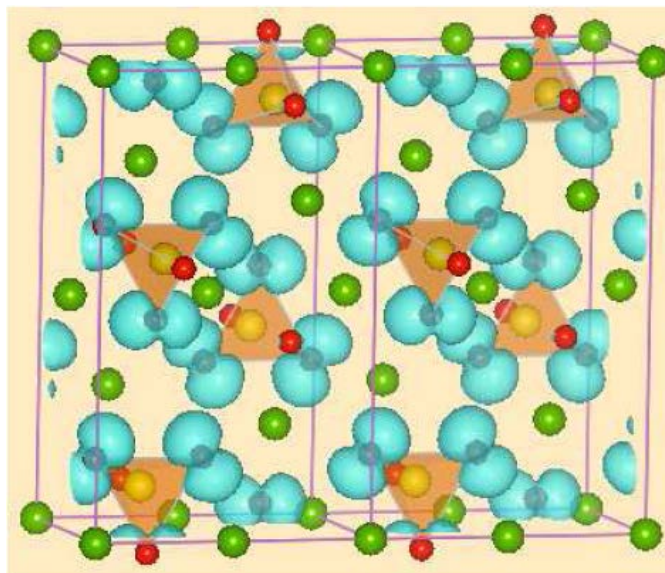
Figure 4. Electron clouds (light blue) in a belite crystal as obtained by quantum simulations. The green, yellow, and red spheres represent Ca, Si, and O atoms, respectively.

Like facets in a cut diamond, crystals have different faces, which also differ in reactivity. The atomic scale modeling efforts offer an advantage here—they can quantify the reactivity of individual faces of the crystals, leading to some interesting possibilities: If clinker could be preferentially ground to expose more of the reactive faces, the resulting cement would be more reactive. If crystals could be made to grow in the kiln such that these more reactive faces are larger, a cement might also be more reactive. The MIT program will provide knowledge about which faces are more reactive, but developing manufacturing technology to take advantage of that knowledge, if sustainable and practical, will require investigation at an industrial level.

Other questions related to alite/belite reactivity that MIT CSHub research can shed light on include improving the extent of reaction (not just the early rate of reaction), but more efficiently or completely hydrating all of the silicates; understanding mechanism(s) that result in the induction period; and understanding the impacts of kiln burning conditions, for example effects of oxidizing or reducing conditions, on alite and belite crystal structures and therefore reactivity. Many of these topics are complex and will require long-term research to complete; however the basis for progress in these areas will be the fundamental atomic scale understanding of alite and belite reactions with water.

Approach used by MIT and Results to Date

The MIT CSHub Concrete Science Platform employs first-principles computational modeling techniques starting at the scale of electrons to fully characterize the structure and reactivity of alite and belite. Researchers analyze how the electron structure of pure alite (C_3S) and belite (C_2S) changes upon introducing different types and amounts of impurities into the system. The most reactive regions are identified by analyzing the charge localization [electron density] in the crystal structure. By quantifying the charge localization, which determines the level of ionic character of the system, the effect of impurities on reactivity of alite and belite can be predicted. Regions of low charge localization will more readily dissolve in water and thus be more reactive. In addition, conducting a wide range of simulations in all possible directions of crystals of varying thickness, the first ever quantum cement surface energy characterization has been achieved. These surface energies provide the critical link between crystallography and reactivity of clinker phases.

The Concrete Science Platform at MIT has made tremendous progress in its ability to model very early age alite and belite reactivity at an atomic scale. A fundamental link between the reactivity of the calcium silicate phases and their electron structure has been developed. Based on first principles, the high reactivity of alite is mainly related to the reactive sites around the more ionic oxygen atoms, which are loosely bound in alite crystals. Calculations indicate that while the *influence* of different types of impurities on crystal properties is similar for alite and belite, their *effect* on the structure at the electron level is very different. These differences are shown to influence the reactivity in these materials, which is consistent with available experimental data. Further validation of these predictions with real-world materials will provide additional insight, as will detailed comparisons with published literature (see Bhatty 1995, for example).

By quantifying the charge localization for a large set of potential substitutions, as shown in Fig. 5, several candidate *impurities* (or pairs of impurities) have been identified that could beneficially influence the reactivity of belite. It is surmised that the kind of fundamental understanding gained here, which relates the reactivity of many minerals to chemical substitutions, can help to accelerate and guide industrial research toward high performance cement with desired properties. Future research may need to consider other effects of substitutions as well, which may include stabilization of different crystal structures, which is not currently taken into account.
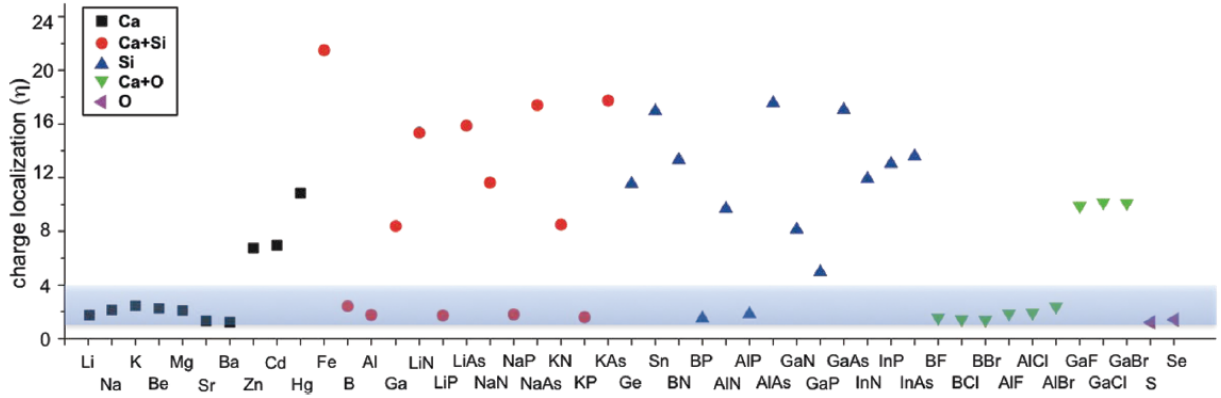
Figure 5. MIT CSHub modeling results for electron charge localization (η) for belite crystals as a function of the type of impurity atom or pairs of atoms. The highlighted region corresponds to values between 1 and 4, where partial charge localization occurs, which could lead to enhanced reactivity. [Adapted from Durgun et al. 2012.]

A quantum mechanical surface analysis and surface energy characterization of calcium silicate phases can be obtained, which can serve as benchmark for further studies. Surface energies for all possible directions of crystals of varying thickness are used to calculate the most stable and reactive surfaces. Lower surface energies indicate more stable surfaces. Dicalcium silicate (C_2S) surfaces are more stable than tricalcium silicate (C_3S) surfaces as quantitatively shown in Fig. 6. In addition to surface energies, the calculated energy required to detach (dissolve) Ca atoms from belite is significantly larger than alite, which provides a link between crystallography and low dissolution rates of belite.
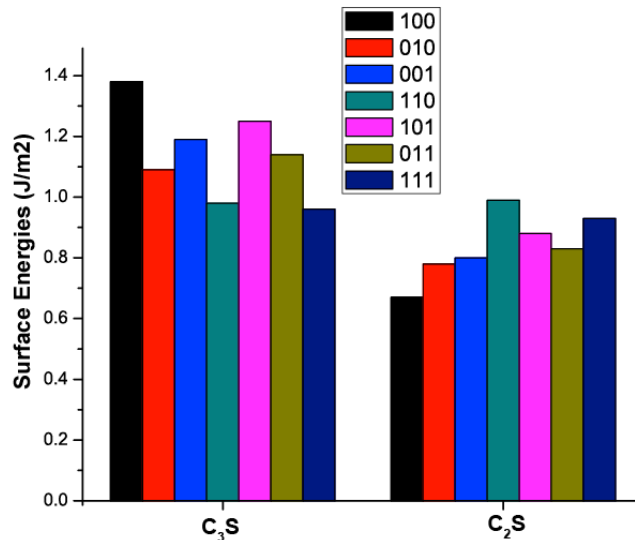
Figure 6. The calculated surface energies for different directions of pure C_3S and C_2S crystals, which can be compared to those calculated for alites and belites with different impurities.

Surface energy characterization can also be used to predict the equilibrium shape of a crystal (Wulff diagram) that determines the thermodynamically stable surfaces and the percentage of area they cover. The sharp edges of alite and more cylindrical shape of belite predicted by models and, as shown in Fig. 7, are in agreement with experimental results and indicate the power of the technique. Interestingly, the most reactive surfaces of C_3S (100) and C_2S (110) occupy relatively small areas of the total surface. However, if clinker could be preferentially ground to expose more of these faces, the resulting cement would be more reactive.
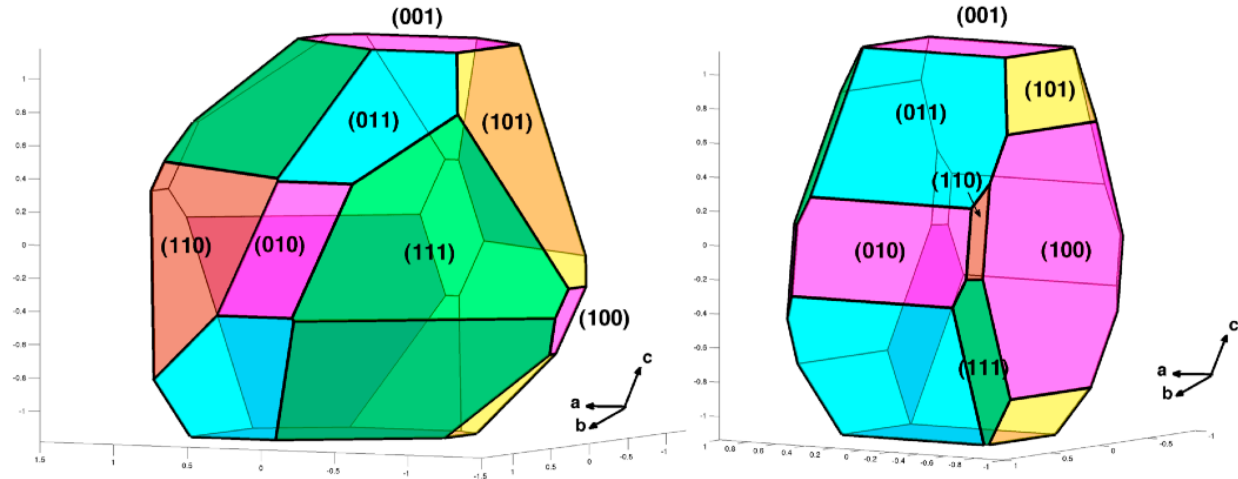
Figure 7. The equilibrium crystal structure (Wulff diagram) of pureC_3S and C_2S.

Future research plans of the CSHub include continuing to evaluate impacts of substitutions, initiating research on the reactivity of other phases (especially aluminate and ferrite), studying the influence of alkalies and sulfates, looking at longer time and larger length scales, and comparisons between the predictions of materials characteristics based on modeling and those determined using real-world materials and analysis techniques. The current results of the Hub form the building blocks at the molecular scale that can validate (or refute) previous research and modeling that has been conducted on a larger scale.

Although significant progress has been made in a relatively short time frame, exciting possibilities for future work remain:

- Applying modeling to clinker compositions with multiple impurities, more closely simulating real-world systems;
- Studying effects of impurities on different polymorphs (crystal structures) on reactivity
- Including studies of the interstitial phases (aluminate and ferrite); and
- Providing data to larger scale models to investigate effects like C_2S dissolution inhibition by C_3S hydration.

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Appendix.

Evaluation of Lab Cements Consisting of Clinker with Different Reactivity

Clinker reactivity is mainly affected by its composition and individual clinker mineral's (phase's) reactivity. It has been often observed that clinker samples with similar mineralogical composition (estimated by Bogue calculation) have different behavior regarding their reactivity. This may be due to either presence of different clinker mineral polymorphs, deviation from actual phase content (from estimated values), or to other factors such as mineral size or presence of minor constituents (alkalies, sulfates etc) in clinker phases. Based on the above, it is necessary to follow detailed characterization techniques in order to correlate observed cement performance with the above mentioned parameters.

Mineralogy

Recently a commercially-produced clinker with moderate alite content (Plant A) was observed to have higher reactivity than that of two other clinkers with higher alite content, based on their 28-day compressive strength (EN 196-1 mortar prismatic specimens). This observation runs counter to the normal trend of 28-day strength being strongly dependent on alite content.

Bogue phase composition can be calculated by either direct chemical composition or by taking into account free CaO content as well as CaO combined with SO_3 (based on Peray-corrected (1979) Bogue formulas for clinker constituents) as $CaSO_4$. The mineralogical composition of clinker samples from the three plants (A, B and C) is presented in Table A1. In most cases Bogue analysis underestimates the composition of clinker minerals relative to the composition determined using Rietveld analysis of XRD data. Furthermore, Plant B clinker mainly consisted of the less reactive alite M2 polymorph while clinkers produced at Plants A and C contained both M1 and M2 alite polymorphs.

Table A1. Composition of clinkers used in this program, % by mass.

		Plant A	Plant B	Plant C
Bogue	C_3S	60.0 (64.5)*	72.8 (77.7)*	64.1 (69.0)*
	C_2S	17.7 (14.4)*	5.2 (1.5)*	11.9 (8.2)*
	C_3A	5.2	1.3	4.1
	C_4AF	12.3	15.7	12.2
Rietveld	Alite	12.5(M1) + 47.2(M2)	4.8(M1) + 70.4(M2)	31.9(M1) + 36.1(M2)
	Belite	19.3	5.7	9.3
	Aluminate	2.0(cubic) + 3.4(ortho)	0.1(cubic) + 1.4(ortho)	1.8(cubic) + 0.1(ortho)
	Ferrite	13.1	14.4	15.6
	free CaO	0.3	0.3	0.6

*Bogue calculated values have been corrected for free lime content and CaO combined with SO_3 (uncorrected Bogue values provided in parentheses).

All Bogue calculations were based on the XRF analysis of clinker samples reported in Table A2.

Table A2. XRF Analyses of Clinkers, % by mass.

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	f. CaO
Plant A	21.98	4.55	4.04	65.82	0.61	0.43	0.06	0.24	1.1
Plant B	20.97	3.78	5.16	66.29	1.00	0.63	0.07	0.39	1.2
Plant C	21.03	4.11	4.01	64.65	3.84	0.58	0.20	1.09	1.2

Amorphous Phase Determination

Clinker samples were thoroughly examined by means of Rietveld analysis in order to evaluate their crystallinity. The analysis of all clinker samples was performed after subjecting all samples to three different methods of treatment.

These methods were:

XRD-1: Dry grinding of clinker, selective extraction (by salicylic acid in methanol and KOH-sugar) of silicate and interstitial phases, XRD on both extracts.
XRD-2: Wet grinding (with cyclohexane) of clinker as received
XRD-3: Wet grinding and use of internal standard (α-Al_2O_3) of known concentration for the determination of amorphous content of clinker as it is.

By comparing the results, some significant qualitative and quantitative differences were obtained. More specifically, it was found that:

1. Contrary to C_2S and C_3A, in all clinker samples, after grinding, part of C_3S and C_4AF becomes amorphous, due to their crystal structure distortion, indicating that those mineral phases are easier to grind.
2. Plant A clinker with the smaller alite size (results are shown later in the text) can be ground easier since a significant fraction (about 15%) of C_3S becomes amorphous.
3. Plant C clinker with micro-crystallized liquid phase when ground to perform XRD analysis, results in higher amorphous content.

Table A3. X-ray Diffraction Analyses of Clinkers Treated with Different Techniques.

|	Plant A				Plant B				Plant C			
	Extr.*	XRD-1	XRD-2	XRD-3	Extr.	XRD-1	XRD-2	XRD-3	Extr.	XRD-1	XRD-2	XRD-3
C_2S		18.7	19.5	17.3		3.4	5.7	4.8		9.2	9.3	7.8
C_3S		60.3	59.7	50.9		73.8	75.2	69.6		65.4	68	60.1
C_3A		5.5	5.4	5.1		1.5	1.5	1.8		2.5	1.9	2.0
C_4AF		13.6	13.1	10.4		18.2	14.4	14.4		17.4	15.6	13.9
$C_3A+C_4AF+Amorphous$		19.1	18.6	29.3		19.7	15.9	22.0		19.9	17.4	28.3
C_3S+C_2S	80	79.0	79.2	68.2	80	77.2	80.9	74.4	77	74.6	77.3	67.9
C_3A+C_4AF	20	19.1	18.5	15.5	20	19.7	15.9	16.2	23	19.9	17.5	15.9
Amorphous				13.8				5.8				12.4

*Extr: clinker phases extraction

Sulfates

It is known that cement strength is also affected by sulfate form and content as well as by cement particle size distribution. For that reason, the effect of sulfate content was assessed using the three different clinkers that were co-ground with gypsum in a laboratory mill. As it has been reported in the literature since the 1940s when Lerch (1946) investigated the influence of gypsum on the hydration and properties of portland cement pastes, there is an optimum SO_3 content beyond which compressive strength decreases, particularly at early ages. It is generally believed that maximum strength values are obtained at an optimum gypsum content depending on clinker characteristics, cement fineness and hydration time. However, as shown by the following strength results (see Table A4 and graphs of Fig. A1), the compressive strength correlation of these lab-produced cements with gypsum addition is not clear. One of the complicating factors is that at a constant fineness, the clinker content is slightly coarser and slightly diluted by the addition of gypsum.

Table A4. Compressive strength of EN 196-1 cement mortars made from clinkers interground with different amounts of gypsum.

	Blaine (m^2/kg)	Clinker (%)	Gypsum (%)	1d (MPa)	2d (MPa)	7d (MPa)	28d (MPa)
Plant A	377	97.5	2.5	9.8	20.4	43.4	61.5
		96.5	3.5	11.9	22.9	43.9	61.0
		95.5	4.5	14.2	24.9	42.4	60.7
		94.5	5.5	14.6	26.8	44.9	59.2
Plant B	402	98.0	2.0	8.8	19.7	42.6	58.3
		97.0	3.0	11.9	21.7	42.9	56.6
		96.0	4.0	14.6	25.1	44.6	57.7
		95.0	5.0	15.6	25.7	44.3	56.3
		94.0	6.0	15.1	29.5	46.6	56.3
Plant C	398	95.0	5.0	13.9	24.4	40.6	51.8
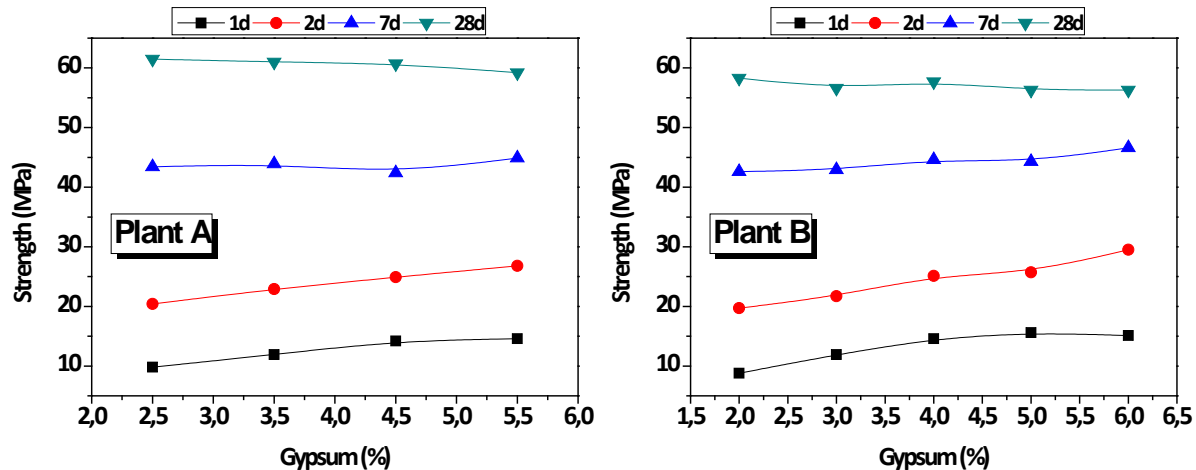
Figure A1. Compressive strength of cements made with clinker from Plant A and Plant B with various gypsum contents.

Alite Size

In the past, several research groups have investigated the correlation between cement strength performance and clinker mineral size using optical microscopy. Dr. Y. Ono's method (Ono 1995) has become a widespread tool for predicting cement strength performance through analyzing clinker phase characteristics by means of optical microscopy. Even though the effect of alite size on cement strength has been recognized, opinions regarding the relationship between these two parameters differ. In the present study, the microstructural characteristics (size, geometry, etc.) of the main clinker phases were also characterized by optical microscopy.
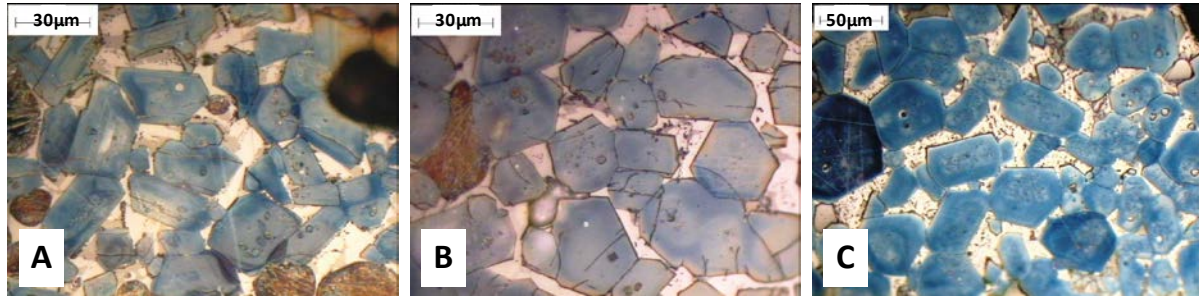
Figure A2. Optical micrographs of clinkers from Plants A, B, and C.

Optical microscopy images taken from a significant number of polished clinker nodules etched with nital (mixture of alcohol and nitric acid) revealed that clinker of Plant A and B consisted of relatively small alite crystals forming a well-defined structure. On the other hand, Plant C's clinker contained mainly coarse alite crystals having a mean size greater than 50 μm. The average size of belite crystals in all clinker samples calculated from optical microscopy image analysis (from many images) varied between 25 μm and 30 μm. As shown by the images of the polished clinker samples (Fig. A2), the degree of liquid phase crystallization of the three clinkers varied. The C_3A crystals of the Plant C clinker were well dispersed in the interstitial phase matrix and small, whereas C_3A of the other two clinkers was better crystallized and clearly visible.

The size distributions of alite crystals that were present in clinker samples are presented in the following graph. It is clear that for Plant C clinker, the alite crystal size followed a normal distribution, while the other two clinkers' alite crystals followed a bimodal size distribution.
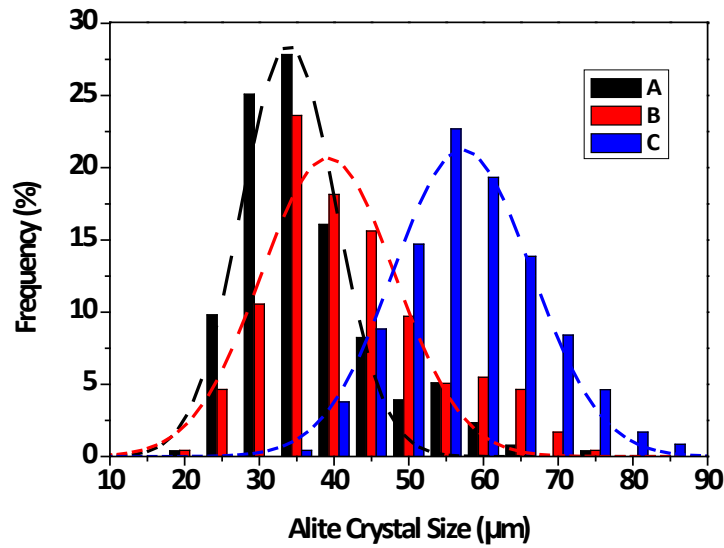
Figure A3. Alite crystals size distribution of clinkers form Plants A, B and C.

The median size (d_{50}) of alite crystals based on the above distributions was correlated with the strength performance of lab produced cements. A strong dependence between alite size and 28-d strength of the tested lab cements was observed. More precisely, the average 28-d strength of the cements seemed to increase linearly with decreasing alite crystal size (Fig. A4).
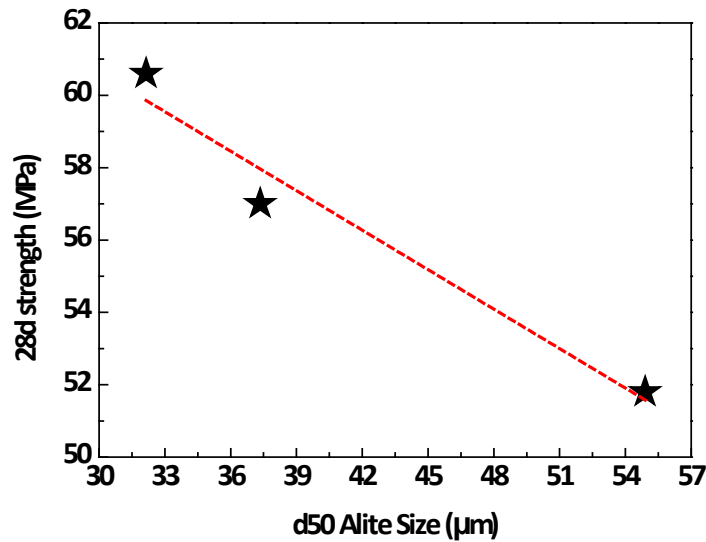

Figure A4. An inverse relationship between mean alite crystal size and 28-day compressive strength of cement was observed.

The appearance of dendritic belite (left side of micrograph B in Fig. A2) typically suggests exposure to excessive temperatures, which can result in slower clinker cooling inside the kiln, in turn resulting in leaching of the substituted ions back into the liquid phase (typically MgO and alumina). This will tend to result in less reactive C_3S (lower surface energy). Typically these types of clinkers must be ground finer to reach equivalent strength potential. The appearance of periclase grains surrounding/adjacent to some of the alite crystals in micrograph B supports that conclusion in a low total MgO containing clinker. Rapid quenching retains the MgO in solid solution.

Minor Constituents
It has been generally acknowledged that cement hydration is mainly affected by Ca/Si ratio in clinker phases. However, the presence of certain minor constituents in the clinker, originating from raw mix components or fuels, can also impact either early or late strength (either through reactions with the hydrating cement phases, or, if substituted in the clinker crystals, by impacting the reactivity of the phases). On the other hand, it has been observed that the effect of these impurities on overall cement performance (strength, setting time etc.) might vary. Using SEM/EDX chemical elemental analysis indicated that isolated alite or belite crystals contain significant amounts of Al, Fe, Mg, K, and Na apart from the dominant Ca and Si constituents.

Table A5. Elemental microanalysis of Alite and Belite Crystals in studied Clinkers, % average by mass.

Plant		SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O
A	alite	24.8	2.5	1.8	68.0	0.7	0.4	0.4	0.1
	(belite)	(29.9)	(3.8)	(2.4)	(59.0)	(0.9)	(0.7)	(1.3)	(0.5)
B	alite	24.6	2.1	2.3	67.7	0.8	0.4	0.6	0.2
	(belite)	(28.1)	(4.3)	(3.8)	(58.9)	(1.0)	(1.0)	(1.2)	(0.2)
C	alite	24.5	2.5	1.9	66.4	2.1	0.7	0.4	0.2
	(belite)	(28.1)	(3.4)	(2.4)	(58.4)	(3.9)	(1.3)	(0.7)	(0.4)

Of the various minor constituents, the effect of alkalies has been studied more extensively. Depending on the form and quantity in which they are present in the clinker, alkalies' effect on cement performance varies. On the other hand the partial substitution of Ca and Si constituents in alite and belite crystals by Mg and S is highly related to clinker phases' polymorphism as well as with crystal size.

Based on the above it is apparent that the specific clinker performance poses a challenge to be explained by MIT Concrete Sustainability Hub's Concrete Science Platform, which is investigating the factors that affect clinker mineralogical components' reactivity, especially alite and belite reactivity. For that reason, an extended analysis route should include the following:

-   Characterization of individual clinker mineralogical phases (dissolution)
-   Determination of chemical composition of each clinker mineral polymorph
-   Characterization of hydrated cement pastes
-   Examination of setting time (precipitation/setting)

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