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Short communication

International Summit on Cement Hydration Kinetics and Modeling Special Edition Québec City, July 27, 28 and 29, 2009

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ABSTRACT

The performance of portland cement concrete relies upon a series of complex events that begin with raw minerals and end many years after the concrete is placed. Between these points, the life of this dynamic material is dominated by chemical reactions called hydration. While much is known about hydration, unfortunately, there is no unifying theory that describes the kinetics (rates) of these complex transformations from anhydrous cement to hydrous cement paste. Other industries including metalugy, petrochemicals, pharmaceuticals and semiconductors have asserted process control by developing a fundamental, mechanistic understanding of the kinetics of the chemical reactions and phase transformations that define their products. Might the concrete industry be moving along a similar trajectory?

The cement and concrete industry is presently faced with a singular challenge, driven by our responsibility to the world community to produce a more sustainable and environmentally benign product: we *must* find new ways to reduce the lifecycle impact of concrete use on the environment. The answer to a more sustainable concrete infrastructure is, however, not likely a single product or technology, but rather a multiplicity of alternatives. Among the potential technologies are *designer* clinkers that have smaller carbon footprints, advanced admixtures that ultimately improve concrete lifecycle performance, and new protocols for more effective utilization of waste and by-product supplementary cementitious materials. Unfortunately, discovering and developing such technologies are difficult challenges with today's knowledge about hydration kinetics and how to engineer new cement-based materials.

The scientific community at large has invested heavily in the study of chemical kinetics; the discipline that quantifies how fast and by what pathway or mechanism a particular chemical or physical transformation takes place. Is it, however, so important to quantitatively understand the transition pathways and the rates at which they occur? Isn't the final result what matters? If the history of materials technology has anything to teach us then, yes, kinetics is a foundational, solution-enabling framework for the development of new and improved materials. Our understanding of kinetics has unlocked nature's resources and permitted mankind to take control of chemical and physical transformations in diverse areas of materials science including the nano-processing of thin film electronic devices, synthesis of advanced polymers and biomimetic materials and, yes, Portland cement.

Through kinetics, we now understand how to refine ores and to tailor the properties of metallurgical materials by controlling their solidification, crystallization and solid-state phase transformations. This knowledge has given us super-alloys, stainless steel, lightweight alloys, corrosion resistant metals and high temperature refractory metallurgy. Understanding the kinetics of organic interactions now enables us to hypothesize the structure of macromolecules and pharmaceuticals never before synthesized and to construct and test those molecules at will. This has lead to mega-ton production of polymers, the invention of designer co-polymers, liquid crystals, strong lightweight matrix materials for composites and new drugs. Without kinetic control of low-level doping of semiconducting materials, modern computers as we know them would be impossible. Detailed knowledge of how fast various dopants react with and move through semiconductors such as silicon, spawned what is without debate mankind's single most rapid intellectual transformation and has propelled us into the “Communication Age” of cell technology and satellites that have imaged virtually every inch of the plant. And, it is through kinetic control that modern man has converted our most controversial resource into energy that has powered the 20th Century — without knowledge of chemical kinetics, modern crude oil processing would be impossible. Kinetic control of petrochemical reactions permits our refineries to be *agile machines* that can move between product distributions in response to rapidly changing market demands, crude prices and availability, and changing chemistry of crude resources.

So what does all of this have to do with Portland cement concrete? Consider a few examples of how kinetics matter for the concrete

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industry. The so called dormant or induction period that is characteristic of portland cement hydration makes it possible to mix concrete off-site, transport it and place the material at will, after which it sets and gains strength rapidly. This kinetic property of Portland cement concrete makes it a unique and versatile construction material. Silica sand is largely inert as a cementitious material. Even in the presence of calcium hydroxide, bulk silica sand is mostly inert, that is, the rate of reaction is very, very slow, in fact, negligible — this property makes ordinary sand and quartz-bearing rock suitable aggregates. It is well known, however, that some forms of silica, e.g. naturally occurring volcanic ash, fumed silica and even very finely divided (ground) crystalline silica can be reactive with calcium hydroxide, a characteristic we call pozzolanic reactivity. Why is this? The answer is quite simple: the structure of the material matters. Whereas bulk crystalline silica is effectively insoluble in calcium hydroxide solution, amorphous forms such as fumed silica (silica fume) and some silica-based volcanic ashes are. By pulverizing quartz, even crystalline silica can be made more reactive by increasing its surface area and introducing surface and bulk defects. Similarly, whereas tricalcium silicate (C_3S) is hydraulic, dicalcium silicate (C_2S) is less reactive and calcium silicate (wollastonite, CS) is kinetically non-reactive with water at standard conditions of temperature and pressure. Furthermore, even the different crystalline forms of C_3S vary in their degree of hydration reactivity, the formation process of which is mediated by the introduction of various impurities including Mg, Fe and Al to form the tricalcium silicate clinker *polyphase* mineral known as alite, a mixture of monoclinic polymorphs. In fact, alite is a kinetically trapped metastable form of tricalcium silicate. If during clinkering the hot clinker is cooled too slowly, the more stable triclinic forms of C_3S will form and if cooled very slowly, C_2S and CaO will precipitate. And, for that matter, even calcium silicate hydrate (C-S-H) is metastable — in the presence of CO_2 C-S-H presents as stable only because the kinetics of carbonation is slow relative to the lifespan of most concrete structures. So, it appears that kinetics is indeed quite important in both the manufacturing of cement and in its application as a binder for making concrete.

As illustrated above, other industries, however, have a far better command of the theoretical basis upon which chemical change and transport phenomena occur in systems of interest to them. The cement and concrete community needs the same. Admittedly, many advances have been made — new cement systems are being developed, good admixture protocols are available and new multi-modal fiber reinforced concretes have modified and improved the ductility of concrete in remarkable ways; but on-demand design of materials is not yet possible. Understanding kinetic transformations, mechanisms and pathways is the key.

Indeed, the cements community has been hard at work investigating the kinetics of cement hydration. This special volume includes six papers, commissioned as part of the International Summit on Cement Hydration Kinetics and Modeling, a multi-national event sponsored by the US National Science Foundation (NSF), the US Federal Highway Administration (FHWA), the Canadian Research Center on Concrete Infrastructure (CRIB), the Natural Science and Engineering Research Council of Canada (NSERCC) and industry interests, which summarize the present knowledge base on cement hydration kinetics. New computational and experimental strategies are suggesting that some of what we had previously accepted might well be quite incorrect and those new hypotheses are in contention. Yet, a more focused and concerted effort is still needed to transition from an industry that by-and-large develops its next product by heuristics, experience and trial and error, to an industry comparable to those mentioned earlier. Unraveling the processes that control hydration kinetics and reducing the knowledge to quantitative theories is a “Grand Challenge” for the cements community, one that must be met.