Cements in the 21st Century: Challenges, Perspectives, and Opportunities

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In a book published in 1906, Richard Meade outlined the history of portland cement up to that point[1]. Since then there has been great progress in portland cement-based construction materials technologies brought about by advances in the materials science of composites and the development of chemical additives (admixtures) for applications. The resulting functionalities, together with its economy and the sheer abundance of its raw materials, have elevated ordinary portland cement (OPC) concrete to the status of most used synthetic material on Earth. While the 20th century was characterized by the emergence of computer technology, computational science and engineering, and instrumental analysis, the fundamental composition of portland cement has remained surprisingly constant. And, although our understanding of ordinary portland cement (OPC) chemistry has grown tremendously, the intermediate steps in hydration and the nature of calcium silicate hydrate (C-S-H)[*], the major product of OPC hydration, remain clouded in uncertainty. Nonetheless, the century also witnessed great advances in the materials technology of cement despite the uncertain understanding of its most fundamental components. Unfortunately, OPC also has a tremendous consumption-based environmental impact, and concrete made from OPC has a poor strength-to-weight ratio. If these challenges are not addressed, the dominance of OPC could wane over the next 100 years. With this in mind, this paper envisions what the 21st century holds in store for OPC in terms of the driving forces that will shape our continued use of this material. Will a new material replace OPC, and concrete as we know it today, as the preeminent infrastructure construction material?

Keywords: ordinary portland cement; history; admixtures; additive manufacturing, 3-D printing; CO_2 emissions.

[*] Conventional cement chemistry notation will be used throughout this paper where it is convenient to do so: C = CaO, S = SiO_2, A = Al_2O_3, F = Fe_2O_3, \$ = SO_3, H = H_2O.

I. Introduction

In 1824, Joseph Aspdin received a patent[2] for what he called "portland cement," and thereby transformed the way modern infrastructure would be constructed to the present day. Various construction cements had been used, possibly for as many as ten thousand years[3]. None of them, however, were destined to rival Aspdin's cement, which would become the ubiquitous fabric of construction. Originally made by firing clay, a family of natural aluminosilicate minerals, and limestone (calcium carbonate), Aspdin's cement initially bore little resemblance to modern portland cement. However, improvements made by Aspdin and his son William in the latter half of the 19th century would enable the emergence of a product containing the constituents widely recognized in portland cement by the beginning of the 20th century.

Indeed, in 1951, Gonnerman and Lerch[4] reported the analysis of OPC samples collected between 1904 and 1950. They noted that, surprisingly, the composition had changed very little over this time period. In their abstract they stated: "The principal changes have been an increase in… Ca_3SiO_5 (tricalcium silicate; the dominant compound in OPC) content … and fineness… which has contributed to higher concrete strengths…". They reported no other substantive changes in the residual content which contained dicalcium silicate (C_2S), tricalcium aluminate (C_3A), tetracalcium alumino ferrite (C_4AF) and gypsum ($C\$H_2$). More recently, from 1950 until the present time, a survey carried out by Tennis and Bhatty[5] reached the same verdict as Gonnerman and Lerch: other than increasing fineness, OPC has remained essentially unchanged for the last 100 years.

What progress in OPC has been made then, if not in its fundamental chemistry? In his 1999 paper, Mehta summarized the achievements of the previous century, illustrating that both chemical and inorganic admixture utilization has dominated advances in the use of OPC[6], enabling achievements such as effective use of supplementary cementitious materials (SCMs), pumpable concrete, ultra-high strength concrete, self-compacting concrete, sprayable concrete (shotcrete) and unprecedented control of set and early-age strength development.

Foundationally, OPC has emerged as the binder that dominates global construction because of the availability of the natural resources needed and economy of its manufacture along-side properties that enabled convenient, cost-effective construction technologies to thrive (*e.g.*, ready mix concrete production). While OPC-based cementing materials are entrenched in modern construction, the goal of this work is to briefly address where the industry has been and it is today, and then to look to the future in somewhat more detail in an attempt to respond to the question – "What will construction cement(s) look like by the end of the 21st century?" – taking into account those factors that are most expected to drive change in the next 100 years: (1) population and economic growth and global industrialization; (2) climate change; (3) energy sources; (4) natural resource availability; (5) construction technology developments (6) the proliferation of cyber technologies and computational resources; and (7) governmental policy and regulation. Although listed as if they are independent, these seven vectors for change (driving forces) are intimately interconnected, and those interconnections will surface as part of this discourse. Furthermore, these vectors can be mapped to the National Academy of Engineering's Grand Challenges for the 21st Century which call to: make solar energy economical; reverse engineering the brain; restore… urban infrastructure; provide energy from fusion; develop carbon sequestration technologies; and engineer the tools of scientific discovery.

Reasonable estimates placed on the availability of limestone, shale (the more contemporary aluminosilicate resource) and iron ore suggest that these raw materials could last for another 100,000[†], 1,000,000[†] and 600 years at current rates of usage; respectively[7, 8]. Raw material availability is not likely a limitation. Rather, it is the pricing and availability of energy resources needed to manufacture OPC (primarily oil, gas, and coal[9]) together with the CO_2 emitted by combustion of these fuels and by the raw materials themselves that will in large part shape the future.

[†] Based on an estimates of the fraction of the earth's crust that is calcium carbonate or shale, the mass of the earth's crust and accessibility (extractability) of these resources.

CO_2 taxation is an emergent policy-based vector that could dramatically alter the course of what cement will look like and how it will be manufactured over the next century. A number of countries have already implemented CO_2 taxes that range from \$2 (USD) to \$168 per equivalent short ton (tCO_2e) of CO_2 produced; the U.S. and China not among these[10] – although a few US municipalities and California have levied various taxes. A recent study by the International Energy Agency (IEA) places the cost of carbon sequestration at between \$16 and \$64[‡] per short ton of cement produced[11]. Given that about 0.9 tons of CO_2 is released into the atmosphere for every ton of cement produced[12], at a nominal price of \$75 per short ton of cement, a carbon tax in the range of \$70/tCO_2e would expediently motivate a search for alternate cementation solutions. The current CO_2 impact of OPC can be partitioned into three primary categories: 55 % to 60 % to the thermal decomposition of limestone (*i.e.*, to produce lime, the base reagent needed for OPC production), 30 % to 35 % to energy needs of the process, and 10 % to transportation[13]. While the CO_2 burden of energy and transportation could indeed be satisfied by renewable energy sources, managing the CO_2 release associated with limestone decomposition is an unresolved challenge. A vision for cements in the 21st century described by Schneider et al.[14] also suggests that cement production will be forced to change due to environmental factors and that portland-type cements will remain dominate into at least the mid-century.

The world's population is projected to grow from its current level of about 6.6 billion to somewhere between 9.5 billion and 12.9 billion by 2100, with the most frequent projection falling around 11.1 billion[15]. This population growth will come with huge demands for housing, water, food, education and other life essentials, all of which will require huge growth in infrastructure. What is clear, however, is that population growth does not correlate to economic growth[16], and that economic growth is likely a better indicator of future demands for cement. Most economic growth in this century is projected to be in developing countries[17] and statistics already show that these are the same places that are now consuming 93% of the cement produced globally[18]. Consequently, global demand for cement is presently growing at a rate of about 4 % per annum[18]. It is in these places of high growth and need for new infrastructure where aggressive changes in construction practices may also initiate fundamental change in the chemistry of infrastructure cement.

So, how then might cement itself be changed? It seems unlikely that the raw materials and elements that make-up the world's most important construction materials will change, yet it is quite possible and likely that the configuration of the same elements in future cements may change as a response in-part to environmental pressures[14, 19, 20, 21], changes in construction technology and continued economic grown, particularly in the developing world. Possibly the most significant and transformative technology to emerge as a pervasive new manufacturing paradigm for the 21st century is additive manufacturing (AM). Also called three-dimensional (3D) printing, AM is the process of constructing 3D objects, layer-by-layer, using printing or printing-like technologies. This new methodology removes many design tethers, reduces waste and saves time; all goals of construction management as well. Already being demonstrated at moderately large scales, 3D printing of concrete structures is a nascent industry. 3D printing of cement-based materials has potential to change the construction industry, demanding new cementing formulations, new chemical additives, building codes, and testing and specification standards.

The 20th century also ushered in the age of microelectronics which spawned the development of computers and the era of modern instrumental analysis. While other fields have managed to gain molecular- or near molecular-scale control of their materials (*e.g.*, polymer engineering and science, metallurgy, electronic materials and pharmaceuticals), knowledge and control of cement appears to be yet entangled in uncertainties about the structure, composition, and reaction mechanisms at the most fundamental level. Basic questions about how tricalcium silicate reacts with water, and about the structure and properties of calcium silicate hydrate (C-S-H), the chief solid product of portland cement hydration, still have no generally accepted answers[22, 23].

‡ Unless otherwise noted, economic values or estimates will be stated in U.S. dollars.

While the composition of anhydrous OPC has remained largely the same for at least a century, and though the intrinsic mechanisms of OPC hydration and structure of C-S-H remain enigmatic, major advances in the use and performance of cement have come from three fundamental areas: (1) construction technology; (2) the science and engineering of composite materials; and (3) admixture chemistry, both organic and inorganic. 20th century construction technology gave rise to fast-track paving and construction methodologies, the ability to pump concrete over large distances, both horizontally and vertically, and the ready mixed concrete industry. Knowledge of how composite materials work – particularly the behavior of fibers and particulate inclusions[24], fracture processes in brittle materials[25], and of material interfaces at multiple length scales[26] – has given rise to massively steel-reinforced concrete[27] and short-fiber-reinforced ductile-like concrete[28]. The advent and widespread use of organic and inorganic chemical additives has enabled the development of high strength and, more recently, self-consolidating concrete[6]. Collectively, these material innovations have enabled the growth of modern infrastructure, the construction of the world's tallest buildings, roads and railways that connect the farthest reaches of every continent and dams that harness the earth's water resources.

Seven key scientific pathways have been identified by the authors as critical for the development of new cementing agents, and construction solutions for the 21st century encompassing: (1) Additive Manufacturing; (2) Designer Admixtures; (3) Curated Materials Data; (4) Computationally Designed Composites; (5) Big Data and Smart Materials; (6) Alternative Binder Systems; and (7) Next Generation Instrumental Capabilities. These seven pathways link the seven driving forces for change to the cements production industry (Figure 1) in a *tangled* and complex way. Figure 1 is a highly simplified illustration of the relationships neglecting the driving force-driving force and pathway-pathway interactions. What follows are brief reviews, and future expectations and projections, for each of the seven scientific pathways.

II. Reviews

(1) Additive Manufacturing

Likely to be the next revolution in constructed infrastructure technology, additive manufacturing (AM), also known as 3-dimensional or 3D printing, promises to dramatically reduce construction time, increase productivity and safety, improve constructed system reliability, and reduce overall construction cost. AM, a process of making 3D objects from a digital file via robotic placement of successive layers of materials, is expected to not only alter how cement-based structures are constructed but also the very nature of the materials and designs that can be realized.

(1.1) Brief history and today's AM technology for infrastructure materials

Historically, the very first application of AM for infrastructure materials can be attributed to the production of asbestos cement in the 1890's with the development of the Hatschek method[29]. In this technology, which remains to date the most common processing method employed to produce fiber cement boards, a slurry is deposited layer by layer from rotating drums on a felt belt, then cut, pressed, dewatered, and autoclaved. The main disadvantages of the Hatschek method, however, are the large quantity of waste water produced and that it can only produce fiber cement boards in sheet form. Recently, however, new promising pioneering concrete printing processes and automation methods for the construction of large scale structures have been developed[30, 31] and include "Contour Crafting," developed at the University of Southern California[32, 33, 34] "Concrete Printing," developed at Loughborough University[30, 35, 36]and "D-Shape Printing," invented by the founder of Monolite UK Ltd[37, 38§]. The first two methods involve extruding cement-based materials through a nozzle while the last

[§] Certain commercial equipment, instruments, materials, or suppliers are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of method deposits a powder (or granular material), which is selectively bound by cementitious ink. These methods have been demonstrated with mortar and concrete[39]. To date, 3D printing of cements-based materials has been primarily attractive to architects who want to create structures in new shapes and with exotic architectural features, and most of the scarce papers published in the literature on the topic of 3D printing of concrete describe 3D-printed architecture projects[40]. Due to the current size limitation of the 3D printer itself, often a modular approach of producing smaller components that are then assembled like Legos on site has been taken. Nevertheless, successful proof-of-concepts and small- to full-scale demonstrations of 3D printing in construction have been flourishing, and 3D printing of full scale infrastructure is becoming a reality. It is, indeed, now possible to print homes, buildings, and bridges, as well as architectural and art features[41, 42, 43]. Notable examples include: (i) an entirely 3D printed two-story house by a Chinese construction company that was printed on-site, in one-go, in just 45 days and can withstand an 8.0 magnitude earthquake[44]; (ii) the construction of a six-story apartment building in China printed as prefabricated elements off-site using a special ink made from recycled concrete materials[45]; (iii) the construction of a 3 m by 5 m 3D printed concrete *castle* extruded in layers of 3 cm wide and 1 cm thick by a US entrepreneur[46]; and (iv) the recently printed 10.5 m by 12.5 m and 3 m tall dwelling made from indigenous materials (including volcanic ashes) in less than five days as part of an hotel suite in the Philippines ,[47].

NASA and the European Space Agency (ESA) are also exploring 3D printing to build deep space exploration habitats[48, 49, 50]. 3D printing technology is especially appealing for space exploration and extraterrestrial colonization, where it will be expensive and technically difficult to deliver parts from Earth and where on-site manufacturing capabilities will be limited. Already, researchers from the ESA have successfully produced a 1.5 ton building block made of synthetic lunar soil[51]. The Additive Construction for Mobile Emplacement (ACME) project, a collaboration between NASA and the Army Corps of Engineers, has demonstrated the ability to use a feedstock mixture of cement and planetary simulant to build both straight and curved walls[52]. ACME is a gantry system with a nozzle from the Contour Crafting Corporation. In 2016, NASA, Caterpillar, Bechtel, and Bradley University announced the 3D Printed Habitat Challenge, a public prize competition that is part of NASA's Centennial Challenges program to spur development of the fundamental technologies necessary to additively manufacture an off-world habitat using mission recycled materials and/or local indigenous materials[53, 54].

However, despite the recent exciting advances in concrete printing, AM of full-scale construction applications is still in its infancy and an emerging area that has remained limited to the printing of concrete architectural features and empirically formulated mix designs that are minor extensions of existing concrete technology. Notable scientific and regulatory challenges remain to be addressed.

(1.2) Opportunities for AM of cement-based materials

There is increasing pressure to develop more sustainable "green" concrete[55] along with new paradigms for the design and development of high-performance civil infrastructure materials and structures with exceptional mechanical properties, durability, constructability, resilience, and low-cost. However, current cement and concrete development efforts are constrained by the portland cement paradigm and the conventional technologies of casting and precast processing. In contrast, AM provides increased design flexibility and offers a promising new avenue for unprecedented control over the shape, composition, functionality, and embedment of components (*e.g.,* fibers, nanomaterials, and sensors) that are impossible to achieve with current concrete technologies. These unique prospects of 3D printing open new material formulations not conceivable before and the creation of novel cement-based materials that integrate form and function by precisely controlling and shaping the materials' internal structure. This vision was the thrust of the recent workshop sponsored by the US National Science Foundation (NSF) called, Multiscale/3D Cement Printing[56]. The workshop brought together over 30 experts from a broad

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Standards and Technology, nor does it imply that the materials, instruments, or suppliers are necessarily the best available for the purpose.

range of disciplines and backgrounds to discuss the potential of AM technology in the construction industry and to identify opportunities and challenges for 3D printing of cement-based infrastructure materials.

(1.3) AM technology advantages

In addition to the ability to create many shape and geometric features that are impossible with current casting and extrusion methods[42], one of the primary advantages of 3D printing technology for the construction industry is that it blurs the line between masonry and traditional concrete placement and eliminates the need for conventional formwork and molds[35, 57], providing contractors the freedom to build structures without relying on formwork. The cost of molds and formwork represents 35 % to 60 % of the cost of a concrete structure[58], so the possibility of removing the formwork offers tremendous cost savings to the construction industry and a significant increase in productivity. 3D printing is also a unique opportunity to optimize the cementitious binder through use of non-portland (*e.g.,* absence of gypsum), inorganic or mineral based (*e.g.,* geopolymer), and non-hydraulic materials[56]. Formulations that do not rely on water are of high relevance to space exploration applications since imported water will likely be reserved for other mission needs and indigenous water, depending on the planetary surface, may prove difficult to extract. On earth, any opportunities to reduce CO_2 emissions, including use of materials other than limestone-based clinkers or waste materials could have tremendous environmental impacts. Already, powder-based inks made of construction waste materials[43], iron oxide-free portland cement-polymer formulations[58], magnesium oxide mixes[37], and sulfur-based concrete[48, 59, 60] have been formulated and used in the printing of proof-of-concept houses and architectural features. For extraterrestrial applications, recyclable feedstock materials are critical where resupply opportunities are constrained and can have an immense impact on mission logistics and risk mitigation for future planetary missions[61].

Another significant advantage of AM is the potential for building additional functionality into the structure with the inclusion of functional voids or conduits for post printing placement of services (*e.g.*, plumbing pipes, and electrical wires) and reinforcements (*e.g.*, post-tensioning tendons)[57, 62]. At the microstructural level, the additive approach promises to enable the localized control of the chemistry and micro-scale architectures[63, 64] and the inclusion of all manner of co-printed reinforcements and embedded technologies unimaginable with traditional casting or extrusion methods (*e.g.*, embedded fibers and nanoparticles). With the advent of AM, materials design and fabrication processes are merged together. It all begins with the digital design of a three-dimensional electronic model of a building or structure that fully integrates and captures architectural, structural, and functional system details and ends with the push of a button with the rapid fabrication and building of the actual structure from printers. Autonomous and remotely commanded operation of printers is a priority for space use, as many of the habitat construction applications envisioned for planetary surfaces with these technologies would be robotic precursor missions focused on building the infrastructure needed to support human explorers. In 2014, as part of the 3D Printing in Zero G mission, NASA demonstrated the ability to uplink a file to a 3D printer onboard the International Space Station and remotely command the printer's operation with little crew interaction[65].

The rapid iteration of design and manufacturing made possible by 3D printing will enable engineers and designers to more efficiently and cost effectively explore a significantly greater design space and to design and build in one seamless process multi-material structures with varying properties and functional characteristics (*e.g.*, load-bearing, sensing, energy harvesting/storage, self-healing capability, seismic resilience, and recyclability), thus providing greater ease of innovation in cements and concrete compared to traditional methods. AM has also been hailed as one of the most important solutions to achieve sustainable design and reduction in construction material waste and raw material extraction[39].

(1.4) AM technology challenges

While the prospects that AM brings to cement-based materials and its construction are seemingly endless, there are many challenges ahead before the premise of 3D printing for industrial-scale applications in construction and the building of large to mega-scale infrastructure like housing complexes, roads and bridges, buildings, and dams can be broadly realized[66, 67]. Most pioneering examples of 3D printing of buildings and structures are on the scale of a few meters and have been printed as prefabricated blocks that were then assembled instead of on-site printing of the entire structure layer-by-layer. Though such demonstrations show glimpses of what is possible, scalability, commercialization, and sustainability of the 3D printing cement technology remain important challenges to be addressed. Additionally, the extrusion and powder deposition-based 3D printers developed to date have low resolution (*i.e.,* layer thickness) that is at best on the order of the centimeter scale. Progress is thus needed for 3D printing cement technologies that allow for printing large size elements and structures in one-go while providing micron-length scale printing resolution without sacrificing shape, strength or productivity. This includes the mechanics of mixing and the technology to continuously mix and deliver the materials (admixture, additives, and fibers) and requires the development of printing media delivery systems (nozzle and extrusion mechanisms) and mixing technologies, in conjunction with a fundamental understanding of the deposition rate, printed element scale, structural build-up of the layering process, and bonding between layers[68, 69, 70]. Despite some of the recent successes and strides in 3D printing concrete-like structures, one significant challenge is the printing material itself, owing to the complex nature and variability of cement-based materials that make them difficult to adapt to 3D printing[56]. Materials and mixtures for extrusion-based AM must have appropriate thixotropy, that is, be sufficiently fluid and pumpable for extrusion, have maximum workability and flowability to be placed in layers, and have a stable shape after being deposited[68, 71, 72, 73]. The cement *ink* of the printing process must set very rapidly and must have high resistance to adhesive failure. This requires employing binders other than portland cement or modifying portland cements' chemistry (*e.g.*, by eliminating gypsum to enhance rapid setting). Durability of the printed material, effect of successive layer deposition, bonding between deposited layers, and environmental impact are some of the technological hurdles that have been identified[56]. Other significant challenges include the development of 3D printing software that can integrate architectural and hierarchical complexity along with structural and material design and seamlessly capture and transmit all this information to printers. Currently available 3D printing software are limited to creating the 3D geometry and do not capture and transmit complex and functional system details at the hierarchical level. The development of software capable of extending the 3D model specifications beyond geometry to include details such as multiple materials, hierarchical complexity within components, embedded reinforcements, or embedded sensors will be essential.

(1.5) AM potential transformative impact

Concrete is the world's most used construction material, so improvements in its use and performance will have far-reaching impacts on the construction industry and global economy. As with any emerging technology, the future of 3D concrete printing in the construction industry is the source of debates, with some experts forecasting it will be disruptive or that it is decades away from viability. While it is difficult to predict the exact impacts that 3D printing will have on concrete and cement, it surely provides the industry with new opportunity. 3D printing technology is poised to have a dramatic impact on how architects, engineers, and designers are using concrete. It provides materials scientists and engineers with the ability to create materials that exhibit paradigm-shifting properties, enabling new functionalities that are not achievable with existing materials, thus opening new product applications wherein concrete has not previously been competitive. Forecasts on potential impacts often mentioned include:

- *Construction industry efficiency and safety*. AM is expected to eliminate the time spent on rebar placement, and mold construction and inspection, making construction faster, cheaper, and easier. It will improve project planning and labor flow reliability, and increase construction flexibility and efficiency[74]. The construction industry has one of the highest fatal injury rates of all industries – 900 fatalities in 2014 in the US alone[75, 76]. Automation of the construction process through the use of AM will shift the workforce demographic to a more skilled, technology oriented workforce, thus significantly reducing the occurrences of fatalities and injuries.

- *A more durable and resilient infrastructure*. The deterioration of cement-based materials is one of the most important infrastructure problems faced by federal, state, and local agencies with more than $20 billion spent each year in the US alone on repair, protection, and strengthening of concrete structures[77, 78]. AM offers a promising new avenue for improved durability and resilience of cement-based materials by reducing human error, enhancing reproducibility, and enabling high-performance, flaw tolerant cement-based materials compared to traditional concrete, thus overcoming one of the major barriers to durability and resilience of infrastructures.

- *Transforming the home and cities*: The 3D printing technology will provide designers and architects with the ability to specify and build complex geometries integrating function, aesthetics, and sustainability. The technology is anticipated to allow affordable housing solutions for low-income areas, customizable homes, and rapid response to large scale natural disaster stricken areas.

- *Environmental impact:* Significant amounts of construction related wastes are produced each year at a high financial cost to the construction industry and a major problem for its environmental impact[79]. 3D printing technology is anticipated to reduce construction waste through precise control of material placement and lower material usage[63].

(2) Designer Admixtures

(2.1) Brief history of concrete admixture development

While the composition of portland cement has not changed significantly in the past 115 years, material performance characteristics have been dramatically altered by the introduction of synthetic admixtures[80]. The key advantage offered by concrete was, and still is, its capacity to flow at early age, a property that allowed the replacement of cut natural stone or fired clay brick with cast-in-place construction. Not surprising, the last century saw great advances in flow properties in-part due to the development of so-called plasticizers. The discovery and design of modern molecules has tailored *rheological* properties, enabled optimization of mix designs, which in-turn led to compressive strengths in excess of hundreds of MPa culminating in ultra-high-performance concretes, and even permitted the stabilization of colloidal C-S-H suspensions used as hardening accelerators[81].

Durability has also been a primary focus of 20th century admixture design[80, 82]. The service life of concrete structures is in many applications dramatically reduced by environmental exposure. Among the most significant additions to the family of organic admixtures to arise in the past 100 years are air entraining agents to minimize freeze-thaw degradation, shrinkage reducers and curing agents to mitigate early-age cracking, corrosion inhibitors, and water-proofers for improving resistance to chemical attack. Notably, plasticizers indirectly also improve durability by enabling the production of concretes with low porosity.

(2.2) Current and future challenges for admixture technologies

The 21st century will likely be marked by continued growth in effectiveness and versatility of synthetic admixtures[83]. This trend will be driven by population growth and economic development, urbanization, changes in construction technology (*e.g.*, the development and wide-spread adaptation of AM technologies for construction), the increasing scarcity and rarefication of raw resources, water and energy.

In response to the seven vectors for change described above, admixture technology in the 21st century should (i) continue to address durability related challenges, (ii) enable minimization of resources consumption, (iii) promote self-healing characteristics, (iv) allow for the better use of alternative raw and recycled materials, (v) respond to the need for fast and easy construction practices, including additive manufacturing, and (vi) enable the development of concretes with better insulating properties and adaptive/reactive qualities in reaction to the environment or interactions with the users. Thus, it is anticipated that admixtures will need to respond to changes in performance expectations for cement-based materials and evolving construction technologies.

So how will such new molecules or new hybrid technologies be discovered? The emergence of and wide-spread adaptation of molecular-scale modeling and computer aided molecular design (CAMD) strategies as well as advances in high-throughput experimental strategies are expected to advance admixture technology this century. The resulting next-generation admixtures are anticipated to impart multi-scale control of hydrate assembly and pore structure development. Yet to achieve this vision, a deeper understanding of cement-admixture interactions is required.

(2.3) Molecular modeling

Molecular modeling has emerged as a main-stream research tool in many fields. Enabling one to conduct what are now referred to as "in-silico" experiments, all atom quantum and molecular dynamic (MD) simulations are rapidly becoming as common-place in molecular-scale research as finite-element analysis is for the engineering-scale. Using tobermorite[84] as a molecular model for C-S-H, Dai et al.[85] estimated the bulk and shear modulus and compressibility of a styrene-methyl acrylate-C-S-H composite. Methods for exploring adsorption potentials of organic molecules on C_3S surfaces were developed in an effort to understand how organic grinding aids work at the molecular scale[86]. Though highly underutilized by the admixture research community at this time, the availability of solid-phase structures for phases relevant to cements[87, 88] along with (MD) force fields[86, 89] is growing. Recent work on the structure of C-S-H, for example, is not only providing insights into the nature of this elusive material[90, 91, 92, 93, 94, 95] but is also making molecular structure files and validated structure models available for use by admixture researchers and designers. And, while the body of literature on admixture-cement molecular-scale model-based research is very small at this time, there exists a huge resource of related studies in other fields, including polymer and surface science, from which to draw methodologies, data sets, insights and inspiration[96, 97, 98].

In an effort to streamline and accelerate the discovery of admixture molecules, Kayello, et al.[99], and Shlonimskaya, et al.[100], introduced an inverse design strategy based on the use of a coarse-grain molecular-scale quantitative structure activity relationship (QSAR). Their inverse QSAR (I-QSAR), a technique *borrowed* from the drug development community, is a focused study on shrinkage reducing molecules, illustrating that new molecules can be discovered *a priori*, with a minimal number of experiments, given the existence of robust structure-activity relationships, in this case between surface tension reduction and shrinkage. Future search strategies of this sort and *spill-over* from other areas of research are expected by 21st century admixture designers along with increasing emphasis on all-atom molecular-scale computational approaches.

(2.4) Bio-inspired hybrids and bio-based molecules

Work over the past two decades has in-part been inspired by the *ingenuity* of nature, through the elaboration of complex architectures seen in living organisms[101] which achieve remarkable mechanical properties through the elaboration of efficient microstructures and composite design. Translating such to man-made infrastructure materials, however, has been difficult, yet should remain a goal for 21st century researchers. For many decades, efforts have been made to intermingle organic matter and cement hydrates at the nano- to the mesoscale[102], the macro-scale being well represented by the use of classical fibers[103]. As an example of natural construction, the hierarchical organization of aragonite crystallites embedded in bio-molecules by shell forming organisms leads to both strength and toughness[104]. In cement pastes, achieving this level of controlled assembly of particles remains challenging due to the way that hydrates are formed and will become increasingly more complex due to the broader use of new binders and supplementary cementitious materials. Yet, first attempts to build ex-situ compact and ordered cement hydrate-polymer structures has been demonstrated producing remarkably flexible materials[105].

The complexity of cement is at least partly the result of staged precipitation of various hydrates at different points in time, each of which exhibits different surface (*e.g.*, cohesive) and filling properties as well as chemical and physical stability. Better control of crystallization rates, habits and packing remains, therefore, key to the development of porosity and mechanical properties upon hydration[106, 107]. The need for highly specific surface interactions is a prerequisite for the control of properties but unlikely with existing admixtures and design strategies since chemists are somewhat limited by the reactivity of traditional monomers. In contrast, bio-based molecules greatly broaden the range of possibilities regarding molecular and polymer complexity and offer higher specificity for interaction with targeted cement phases. Promising properties of cellulose, chitosan and starch have been seen, also as nanoparticles[108]. For C-S-H, specific interactions involving various peptide functional groups have been demonstrated by phage-display[109]. It is noteworthy that this high-throughput technique using huge libraries of peptides opens new routes and ways of thinking about the identification and design of admixture molecules.

Exciting promises from bio-based molecules are anticipated as the market for such grows[110]. Furthermore, a shift to increased use of renewable resources for production of a wider range of synthetic admixtures will become a necessity as fossil carbon sources dwindle or are regulated out of use. Ways to drastically reduce the cost of admixture molecules could create opportunities due to higher affordable dosages.

(2.5) Controlled polymerization, influence of stereochemistry and rationalization of structure activity relationships

Considerable progress has been made in the past two decades on superplasticizer-cement interactions, and has helped identify mechanisms of incompatibility between some cements and some plasticizers[111, 112, 113]. Recent advances have established relationships between polymer activity and molecular structure[114, 115], and have helped to reveal chemical interactions at the solution-mineral interface[116] as well as the roles of dissolved components such as calcium ions[96, 97]. Polymer synthesis will be enabled in the future by a better understanding and control of the polymer structure-cement property relationships[115], guided by all-atom and QSAR modeling.

Despite these advances, rational design of admixtures is still an elusive goal, primarily because of uncertainties about hydration mechanism[22]. Notably, hydration kinetic mechanisms are being scrutinized in much more detail in recent years. Phenomena such as the precipitation of nano-ettringite[117], the nature of dissolution processes[118, 119, 120] and the intercalation of polymers in layered aluminate hydrates[121] or in clays[122] are critical-path information needed to direct the design of future admixtures. The development of tightly controlled polymerization routes will also aid the discovery and marketing of designer organic-cement interactions[123, 124,125]. Finally, manipulation of molecular stereochemistry can lead to huge differences in hydration rates[126, 127]. Stereochemical manipulation, as part of polymer- and small-molecule-based admixture design, should become more common as synthesis methods are introduced to enable such designer molecules to be produced cost effectively.

(3) Computationally Designed Composites

(3.1) Brief History and Prognosis

Starting with the seminal work of Roelfstra *et al.*[128] at the concrete scale, and of Jennings and Johnson at the cement particle scale[129], computer simulations of cement-based materials have been improved and used steadily since then to understand relationships between processing, structure, and properties[130, 131, 132]over the service life of the material. Models for estimating the transport[133, 134] , rheological[135], and mechanical properties[136, 137, 138] of cement-based composites based on their structure, over length scales from nanometers to meters, is now fairly advanced. The much greater challenge is to simulate time-domain *changes* in structure and link them to the consequent changes in properties as the various solid components react either with the interior aqueous solution (*e.g.*, hydration and alkali silica reactions) or with the external environment (*e.g.*, sulfate attack, carbonation, leaching). Furthermore, extending such simulations to accommodate interactions with organic admixtures will be a significant challenge as demands for new cement formulations driven by expected technological changes such as AM place pressure on the research community.

Computer models of structural evolution have been developed with various levels of physical and chemical realism[132, 139, 140, 141, 142], but these models depend on knowledge of the basic material structure, composition, physical properties, and reaction mechanisms, many of which remain poorly understood[22]. Simulations using such models will therefore be limited in their predictive power until these knowledge gaps are narrowed. This is gradually happening with the help of new experimental capability, described elsewhere in this paper, and atomistic-scale computer models of individual solid phases and surfaces[90, 143] , thus models of cement paste microstructure evolution are expected to continue to improve steadily in the future as they incorporate more accurate physics and chemistry.

Perhaps the greatest challenge facing "traditional" computational modeling applications to concrete is that these cement-based composites are becoming more and more complex with the addition of multiple industrial byproducts and organic constituents and additives. Models based on fundamental physics and chemistry can address complex multiphase materials only if detailed information is available about their structure, composition, and reaction mechanisms. These properties may vary greatly among nominally similar materials depending on their source. Materials are chosen primarily based on proximity to the construction site, rather than on particular performance characteristics, and characterizing and accounting for the material variability is a potentially enormous challenge for computational modeling of this kind. Therefore, the accurate design of cementitious composites using computational materials science tools can be effective only if methods are developed for rapidly and accurately characterizing the critical properties of each solid component, including the array of possible solid products that can form during hydration or chemical degradation.

Even with these challenges, the application of such fundamental modeling to cementitious materials has accelerated over the last 30 years, and there is every reason to expect that this trend will continue. However, advances in the existing underlying models will probably be incremental and may be unable to meet the need for reliable design tools for new materials and applications. Therefore, alternative computational strategies should be sought. Among the most promising alternatives are strategies that incorporate one or more forms of artificial intelligence (AI) such as *machine learning* technology[144].

(3.2) Machine Learning (ML)

"Machine learning" (ML) is a general term describing algorithms for efficiently exploring the *property* space of a system. All ML methods use a subset of the available data, called a training set, to discover patterns or relationships among the data. The ML algorithms are broadly classified as *supervised* or *unsupervised*, depending on the nature of the data that are available. The training set for supervised algorithms consists of both input and corresponding output values, and the algorithm's objective is to identify a function that can predict the output corresponding to new input values. Examples of supervised algorithms include various types of least-squares regression[145, 146], neural networks[147, 148] , decision trees[149], and genetic programming[150]. In contrast, the training set for unsupervised algorithms consists only of input values, and the objective is to discover patterns in the input values. Unsupervised algorithms include various types of cluster analysis[151, 152] , Markov random fields[153, 154], and principal component analysis[155].

ML has been used in materials science for at least 15 years to determine phase diagrams from X-ray diffraction data[151, 156, 157] , to predict interatomic potential energy surfaces from quantum mechanical data[158], to use those potential energy surfaces to predict crystal structures of materials that have not yet been synthesized[159], to predict engineering properties from processing data[160, 161] , and to segment metallographic microstructures into their component phases[162, 163].

Some applications of ML to cementitious materials and related chemical admixtures have been made already[99, 100, 164, 165, 166, 167, 168, 169, 170] , and they provide a glimpse of the latent power and flexibility of such methods for designing cementitious composites when sufficient training data are available. Phase segmentation of cement powder microstructures is now routinely accomplished by unsupervised ML, using clustering algorithms[171] trained on subsets of 2D backscattered electron micrographs and X-ray microanalysis data of polished cement powder cross sections[172]. Cross-validation resampling[173] of the data indicate that these methods have prediction errors that are typically less than 2 % for the major phases in portland cement. Genetic programming and neural networks have been used to predict 28 d mortar compressive strength as a function of 19 input variables, including oxide composition, fineness, and the 3 d and 7 d compressive strength[166]. The predictions had about half the error of alternative methods that used a standard multilinear regression among the same variables. Devaney and Hagedorn[168], used unsupervised ML on hydrating plasters, training their models on X-ray microtomography data with unsupervised classification, decision trees, and genetic programming to classify plaster powder and plaster at different hydration times. Wang and Yang[169] even predicted cement paste hydration characteristics with an ML approach, in contrast to the physicochemical microstructure models that have been more often used recently[142]. They used flexible neural trees[171] coupled with genetic algorithms and gene expression programming[172] to evolve the hydration neural tree structure, rules, and parameters. The results are notable; the neural-based hydration model not only fits training data, but also predicts hydration for cements of different composition, fineness and curing conditions. Using a vastly different AI strategy, Cruz, *et al.* demonstrated a crude autoregressive approach for cement microstructure generation[170].

As in other areas of materials science, design of new cementitious mixtures in the future is likely to be increasingly aided by ML. However, realizing the full potential of this approach will require two large and sustained efforts within the industry. One task will be the development and adoption of a complementary suite of supervised and unsupervised algorithms that span the range of challenges from raw material characterization, through the discovery of structure-property relationships, to the final determination of optimized mixture design parameters for a given set of available materials. The second and more challenging task is the design, construction, and curation of a standardized data repository of relevant materials, (*e.g.*, cements, cement phases, aggregates, supplementary cementitious materials, and organic admixtures) that can be used for training and validation of those ML algorithms.

An especially important prerequisite for effective ML modeling is to have a realistic hypothesis space – the range of allowable input parameters and the functional dependence of the model on those parameters – that is informed by materials science knowledge. For example, the current classification scheme for fly ash somewhat arbitrarily depends on bulk oxide composition that does not directly relate to the abundance, composition, and reactivity of the glassy and crystalline components of those materials. Consequently, the Class C or F designation of a fly ash is unlikely to be a useful input variable in the hypothesis space for predicting compressive strength of a high-volume fly ash concrete. This points out the fact that ML by itself is not a panacea for predicting concrete properties. As other sections of this paper have argued, concerted and focused research is still required to determine meaningful characterization of the materials that will more accurately link to performance. High-performance, materials science-based computer modeling at all length scales will inevitably couple to new experimental measurement science to generate that knowledge.

(3.3) Adoption of ML algorithms

The first task, the development and adoption by the cement materials industry of a collection of ML algorithms, is made considerably easier by the fact that much of the development work has been done by others[144]. The challenge for the industry, largely unfamiliar with data-driven methods, is to determine the best ML approaches for each task in the complex endeavor of mixture design. Unsupervised cluster analysis and pattern recognition methods such as dynamic time warping[174] likely will be the workhorses for the automated characterization of material phase composition and microstructure based on microscopy and X-ray diffraction data, whereas supervised methods, especially neural networks and decision trees, may rise to prominence for developing predictive models of engineering properties from chemical and structural input data on the constituent materials. In fact, no one exclusive set of ML methods is likely to be identified because the industry itself is highly distributed and each sector faces different, though related, characterization and prediction challenges. Furthermore, ML algorithms themselves are expected to improve with time. Cement manufacturers will likely adopt unsupervised methods for characterization of their raw materials and final products, as well as supervised methods for discovering relationships among raw material characteristics, clinkering and grinding process variables, and final product characteristics. Chemical additive manufacturers have the same general objectives, but their methods will probably be tailored to molecular design and also may more directly involve atomic and molecular scale simulation models that are accelerated by ML methods (*e.g.*, kernel ridge regression trained by data generated from density functional theory[175]).

(3.4) Building data repositories

The power of ML methods relies entirely on the amount, diversity, and quality of data that are used to train and test them. Recognition of this fact has led to a major thrust within the U.S. Materials Genome Initiative (MGI)[176] toward the design and growth of curated materials data repositories, which are described more fully in Section 7. For cement-based materials, the necessary data will include, but not be limited to, measurements of composition, including oxides and phase abundances, component physical properties such as particle size distribution, densities, and specific heat capacities. The metadata associated with these basic data will need to be captured to help understand variability among materials and the relationships of that variability to processing conditions, and should be sufficiently detailed to enable another researcher to repeat the measurement. Typical metadata for the phase composition of a cement clinker by X-ray diffraction could include the parameters of the measurement itself, such as the instrument settings, analysis software and settings. Other important metadata could be the manufacturing conditions that produced the clinker, such as raw material sources (which themselves will have associated characterization data that can be linked), date and time of production, clinkering temperature, dwell time, quench rate, and grinding conditions. Interoperability will depend on having these data and metadata stored in data repositories in a standardized format that can be rapidly searched and mined to obtain the relevant training and validation data sets for ML models. As various industry sectors gain more confidence in computational materials science calculations, the data repositories could include not only experimental measurement data but also simulation data and metadata, especially for those properties that are currently impossible or inconvenient to measure routinely. Finally, one should expect that ML models themselves, as they become more widely used, will also help determine the most important types of data that are needed because they will automatically identify input data that have little or no impact on a given performance characteristic of the material.

(4) Big Data and Smart Materials

As described in the previous section, effective computational design of cementitious composites will require detailed characterization of material properties, both for the starting components and for the composite itself during its service life. Besides the traditional and emerging lab characterization methods, an increasingly large role in materials measurement will be assumed by continuous sensing technology in the field. Sensors can be embedded within a material component to relay data on its condition wirelessly to a continuous data collection station. Alternatively, the material itself can be endowed with sensing and actuating properties, using conductive fibers, nanowires, or other technologies, to become a "smart" material that can sense and transmit data on its own condition.

The development of AM will likely accelerate the ability to implement smart materials and smart structures that have the potential to generate huge amounts of data or require that large data sets, now referred to as "big data," be processed as part of their ongoing functions. Furthermore, the very development of technologies such as AM, advanced admixture systems and next-generation computational infrastructures will inherently require and be greatly aided by facilities for management and interpretation of large data sets. Despite confusion concerning the etymology and definition of the term "big data," further advances in "smart" materials[**] may result in very large and complex data sets that may be problematic to process using conventional data management or data processing tools (*i.e.*, will result in "big data"). Research on smart materials has often focused on developing materials and sensors that enable a structure to sense stress or strain[177, 178, 179, 180, 181, 182, 183, 184, 185]. However, less research has been performed on developing structural materials (*i.e.*, composite materials, including cements and concretes) that can inherently manifest smart behavior, including sensing and self-healing [186, 187]. The resulting multifunctional behavior could reduce or eliminate maintenance as well as the need for embedded or attached sensors and thereby lower costs and increase the fraction of the functional component to potentially increase durability[††] [186, 188, 189, 190]. The addition of electrically conductive components such as carbon-based powders, carbon fibers, piezoelectric materials, or nanomaterials (*e.g.*, nano-Fe_2O_3, fullerenes, graphene, carbon nanofibers, and nanotubes) to a cement can add "smart" functionality without the concomitant loss of structural integrity; nanoparticle additions can often also improve the structural properties of these materials [179, 191]. Thus nano-engineering smart materials is a promising alternative for large-scale applications[192]. Self-sensing and self-healing "smart" concrete, ideally requiring little or no maintenance, can detect potential defects before failure, making it an important component of smart buildings and infrastructure[193, 194]. Research on brain function, including distributed control, parallel processing, and input-driven event initiation[195] suggests the possibility of changing the paradigm for how to design materials and structures (or systems of structures) for "big data" by designing the structure to accommodate smart materials.

(4.1) Brief history of "big data" and smart materials

No rigorous definition of the term "big data" exists. The first uses of the now ubiquitous term "big data" involved the concept that the amount of information was growing so large that the quantity needed for analysis could not be accommodated in computer storage necessitating changes in the methods and tools needed for analysis[‡‡][196, 197]. One of, if not the first, use of the term "big data" in this context is attributed to John R. Mashey, Chief Scientist at Silicon Graphics, Inc., when he presented a paper entitled "Big Data… and the Next Wave of Infrastress" at a USENIX meeting[§§]. The first published use of the term may be in the paper "'Big Data' Dynamic Factor Models for Macroeconomic Measurement and Forecasting" by F. X. Diebold at the Eighth World Congress of the Econometric Society[198]. Current references to "big data" are based on the relationship of the volume of structured and unstructured data to storage and/or processing capacity and analytical ability using traditional database and software techniques and tools[199]; very few references are to "big data" techniques applied to infrastructure materials or concrete, including smart materials.

"Smart" materials include a wide variety of materials (*e.g.*, piezoelectric, magneto-restrictive, pH-sensitive, chromogenic systems, and shape memory alloys) manifesting varying, "smart" functionalities,

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[**] "Smart" materials are engineered to detect changes in physical parameters (*e.g.*, temperature or strength) and respond appropriately.

[††] The embedding of sensors could lead to the degradation of mechanical properties in the material.

[‡‡] This concept was preceded in terms of knowledge and the assumed proliferation of library volumes as early as the mid-1940's.

[§§] http://static.usenix.org/event/usenix99/invited_talks/mashey.pdf including self-adaptability, self-sensing, and memory[200]. Because of their varied responses to external stimuli, "smart" materials have many applications, including embedded sensors to assess long-term bridge or structural durability or self-healing[201]. Research has often focused on the material science needed to make "smart" sensors and relatively less attention has been given to the development of structural materials (*e.g.*, "smart" concretes) that are able to provide smart functionality. The infrastructure use of these materials would reduce or eliminate the need for maintenance and embedded sensors with the potential for increased strength and lower costs[186].

(4.2) Applications and opportunities of "big data" and smart materials for structural materials

At the nexus of "smart materials" and "big data" is the modification and development of structural materials that inherently manifest "smart" behavior, including transmitting signal information for health monitoring and diagnostics. At one end of the spectrum, there are various sensors made of cementitious materials to measure stress and strain for structural health monitoring (*e.g.*, damage detection) [177, 178, 179, 180, 181, 182, 183, 184, 185, 202, 203, 204, 205, 206, 207]or made of ceramic materials to evaluate early age curing properties [208, 209] where sensing is a fundamental aspect of "smart materials[186]. " Carbon nanotubes and nanofibers are potential candidates as (nano-) reinforcements in cementitious materials; resulting materials exhibit extraordinary strength and have unique electronic and chemical properties[178, 181, 182, 192, 210, 211, 212, 213, 214]. Cement-based, piezoelectric sensors[215] or self-sensing, composite materials incorporating multi-walled carbon nanotubes[216] show promise for real time vehicle detection for a smart traffic monitoring system. Towards the other end of the spectrum is the development of a "smart" cement by incorporating iron oxide nanoparticles to enhance the piezoresistive behavior (allowing for real-time monitoring) while increasing the compressive strength and modulus of elasticity for oil well applications[206, 217]. Monitoring and analysis of the real-time information transmitted by smart materials (especially for large systems) can then leverage extant "big data" techniques (*e.g.*, sampling, on-line, and multiresolution analysis methods)[218, 219].

(4.3) Technology potential and transformative impacts

Efficiently and effectively monitoring cracking, stress-strain, and moisture transport in concrete is paramount for future safe and reliable infrastructure for civil, transportation, and energy applications. Better monitoring and control of the complex processes related to concrete aging and degradation are also critical. "Smart" composites, including cement and concrete, can sense deteriorating structures to allow for immediate response and, in some cases, self-healing resulting in safer and more efficient use. Results from real-time monitoring of infrastructure using "smart" materials can be used to help improve current design techniques and materials for future infrastructure applications. Recent trends in technology over the last decade that have been driven by the demands of the consumer market place have resulted in a massive influx of consumer technology to respond to large and distributed volumes of unstructured and structured data (*e.g.*, mobile computing, full-field imaging, and ad hoc networks).

(5) Alternative Binder Systems

Alternative cements are defined here as inorganic cementitious materials that can be used for building and construction, but whose properties and composition are not yet specified by existing standards and regulations. Efforts to develop new cements have been stimulated by deficiencies in the perceived performance of ordinary portland cement (OPC). Some examples of this include calcium aluminate cement (CAC), and Sorel cement.[220] All cements, traditional or otherwise, have limited elemental composition, primarily comprising Si, O, Ca, Al, Fe, and Mg.[221] This constitution is unsurprising on an economic basis because cementing materials must be composed of materials that are abundant in the Earth's crust.[222] Therefore, while the atomic arrangements of future alternative cements may change, they are expected to continue to contain the elements just listed.

However, in addition to the requirements of low cost and abundance, a new factor has come into prominence: the environmental cost of cement production and use. The global production of OPC is associated with substantial CO_2 emissions, on the order of 0.9 tons per ton of OPC produced.[223] This represents about 7 % of global emissions today, but without constraints the percentage is expected to increase to 25 % of global emissions by 2050.[224, 225] Therefore, a step change is required to produce cements with reduced (or zero) CO_2 impact – a requirement which may force cement manufacturers out of the envelope of compositions defined as OPC.

The evolution of new cement types will need to overcome both technical and non-technical barriers. Requirements for mechanical performance and long-term durability are critical, but standards and specifications, whether prescriptive or performance-based, will also require robust evolution. In addition, confidence in new materials must be acquired by the end user (*e.g.*, contractors) in the field-based deployment of new cements. In each case, some application flexibility will be needed, because new cements may need to be processed and placed in a manner somewhat different from OPC-based concrete. An important concern that arises along with the quest to replace OPC, whether by supplementary cementitious materials or by new cement types, is whether a new formulation can provide high enough pH to passivate the reinforcing steel, which OPC does quite nicely. A shift away from OPC will tend to compromise the calcium buffer, and hence the extent of passivity afforded, but simultaneous changes in reinforcing materials away from ferrous metals (*e.g.*, fiber-reinforced polymers) may reduce the need for corrosion resitance. Nevertheless, because of the driving force to reduce CO_2 emissions, the following alternative cements that may emerge in the next 100 years appear promising.

(5.1) Carbonated cements

Calcium-rich OPC hydrates (*e.g.*, $Ca(OH)_2$, and C-S-H) carbonate spontaneously to form $CaCO_3$, amorphous hydrated silica (if the precursor is siliceous) and water. The carbonation reaction is sensitive to the presence of water which catalyzes the reaction and is favored with increasing pressure and temperature. Based on the tendency of calcium (and magnesium)-rich compounds to carbonate, recently, three propositions for beneficial CO_2 uptake which render cementation have been proposed:

(5.1.1) Carbonation of brackish (Mg, Ca-rich) brines

Concentrated brines that result from the desalination of seawater have magnesium-rich and calcium-rich compositions. When CO_2 is dissolved in such brine compositions – (Mg, Ca) carbonates are spontaneously formed. Pioneering contributions from Glasser *et al.* [226, 227, 228] have recently demonstrated such an approach wherein the formation of nesquehonite results in the formation of stable cementitious formulations. While a range of compositions of (Mg, Ca) carbonates could be formed; thus far only nesquehonite, a hydrated magnesium carbonate, has realized cementing characteristics.

(5.1.2) Carbonation of hydrated lime

Lime mortars “mature” by taking up CO_2 over long periods of exposure to the atmosphere.[229] This process is far too slow to be practical, but recently it has been shown that pressurized CO_2 can carbonate hydrated lime ($Ca(OH)_2$) within a few hours at room temperature if the relative humidity is 20 % or greater.[20] Lime carbonation by such an approach results in the formation of a monophasic $CaCO_3$ end-product (and water) – whose crystal morphology can be controlled by varying the reaction conditions.[230, 231] While stable compacts can be formed, the performance characteristics of the carbonated solids require more in-depth examinations.

(5.1.3) Carbonation of calcium silicates

Hydrated calcium silicates are well-known to carbonate[232]. Based on this idea, there has been some interest in contacting wollastonite ($CaSiO_3$) slurries with carbonated water at elevated pressure and temperature[233]. This approach, which somewhat mimics the process of autoclaving concrete, is a potentially attractive route to activate a wide range of otherwise slightly reactive low-calcium silicates, (*e.g.*, including rankinite and Ca_3SiO_7). Such systems have been shown to produce dense matrices upon carbonation, which offer mechanical properties similar to typical hydrated OPC compositions.[233]

In the latter two cases, the motivation for carbonation is straightforward: it seeks to "reuse" mineralized CO_2 released during the production of the precursors (*e.g.*, portlandite or wollastonite) in the carbonated products. A detailed life cycle analysis (LCA) performed for the case of hydrated lime carbonation suggests that the CO_2 burden is reduced by nearly 60 % compared to an OPC-based concrete of similar compressive strength.[234] To practically exploit such approaches, however, it is necessary to minimize the energy burden associated with the production of the precursor (*e.g.*, $CaSiO_3$, $Ca(OH)_2$). Generally, this implies a need to reduce their lime content or the quantity of SiO_2, the latter of which requires elevated temperatures to react with lime.

Carbonation processing comes with its own unique challenges, too. First, it is sensitive to the presence and state of water, which may be present or liberated over the course of carbonation[235]. The liberated water fills pores and inhibits entry of CO_2 into porosity. Furthermore, the solubility of CO_2 in water diminishes sharply with temperature[236] so the exothermic nature of carbonation could actually slow reaction progress. Second, when it is desired to carbonate a slurry of precursor particles in water, the particle size distribution must be both fine and optimized for the reaction conditions to encourage sufficient carbonation in a short time. Third, carbonation requires a pure and abundant source of CO_2 at the appropriate temperature and pressure for the reaction. Carbonation can be accomplished, in principle, with low-purity CO_2, but the reaction rate increases with purity, so optimization of reaction time requires the highest practical purity of CO_2. [235, 237] Flue gas from coal and natural gas power production has about 5 % to 25 % (v/v) of CO_2. If that purity is adequate, the challenge becomes one of transporting CO_2 to locations of consumption. In the U.S., CO_2 transportation pipelines are already in place in Oklahoma and Texas to convey CO_2 that is useful in enhanced oil recovery applications. However, if a higher purity of CO_2 is desired, the flue gas must be purified using gas separation membranes, sorbents, or other technology.[238] Therefore, carbonation processing is likely best-suited to factory production in the style of precast concrete manufacture today. While the style of such manufacture is evolutionary, encompassing larger and more sophisticated dimensions of additive manufacturing, the promise of carbonation relies on practical cost-effective, industrially viable processing solutions, and the introduction of incentives or credits for cementation agents that take up CO_2.

(5.2) Calcium sulfoaluminate (C$A) cements

Cements based on calcium sulfoaluminate compositions first appeared commercially in China in the 1970s[19], although references to such cements date back to the 1930s.[239] They are gaining relevance due to their ability to be made in a conventional rotary kiln using calcium, aluminum and sulfur-rich precursors. C$A cements are gaining importance due to their lower CO_2 intensity (*i.e.*, CaO content that is approximately 30 % lower than OPC) and ease of grinding.[19] In fact, commercial producers are on the verge of introducing C$A cements for mass-market applications. [20] However, the lower CO_2 intensity comes at the cost of elevated SO_x emissions, potentially elevated NO_x emissions (due to the reduced processing temperatures), and a high-priced product (approximately two or three times more expensive than OPC) since the C$A precursors are more expensive than their OPC counterparts.[239] Compositionally, C$A clinkers contain Klein's compound (ye'elemite, or $C_4A_3\$$), ternesite ($C_5S_2\$$) and belite (Ca_2SiO_4) Soluble sulfate, in the form of anhydrite, is added to regulate dimensional change and to ensure a period of workability similar to OPC. C$A cements also have final strengths similar to OPC compositions, although their initial strength development happens more rapidly.

Hydrated C$A compositions consist primarily of ettringite, with C-S-H forming more slowly as the belite hydrates. Formation of a mole of ettringite requires 26 moles of water, so the water-to-C$A mass ratio required for complete hydration is on the order of 0.6. Hydration is rapid and is nearly complete in one day or less. While current admixtures, such as water reducing agents, can be used to control the fluidity of C$A formulations, the compatibility of current water reducers with C$A cements needs to be more robustly examined. Significantly, the Chinese Standards Association (CSA) has promulgated standards for these cements and their durability can be appreciated from the elevated motorways around Beijing, some of which were formed from prefabricated sections, and have been in service for nearly 40 years[240]. Looking forward however, C$A cements may be plagued with complexities in sourcing raw materials for their production. For example, the high alumina content of clinkers can best be achieved using bauxite as a component of the raw meal. But worldwide bauxite supplies are relatively limited and grades high in alumina are expensive because bauxite is also needed for aluminum production.[241] To remedy the need for high alumina content, some of the ye'elemite can be replaced by calcium and silica, which react with sulfate to form ternesite, another compound with hydraulic cementing capability.[242] Thus a range of belite-ternesite-ye'elemite clinkers may be produced using lower cost reactants.

C$A cements have significant future potential, but understanding of the kinetics and equilibrium of synthesis is poor. Even now a critical knowledge gap is the understanding of which mineralogical components, and in what quantities, are desirable in the clinker. Recent studies have shown that gas fugacities of S-O species affect sulfate phase formation and the balance between anhydrite, ternesite and ye'elemite,[243] but numerous inconsistencies still need to be resolved before optimized clinkers with specific mineral compositions and engineering properties can be manufactured.

(5.3) Geopolymer Cements

While incapable of precise definition, geopolymers are formed by reaction of an aluminosilicate solid (*e.g.*, clay, fly ash, or slag) with an alkali source, typically sodium or potassium hydroxide or silicate, or mixtures thereof, with water.[244] The main bonding phase formed is a hydrous gel with poor long-range order that contains sodium (or potassium), and oxides of aluminum and silicon (abbreviated as N-A-S-H).[27] This gel is analogous to, but not continuously miscible with, the C-A-S-H gels formed in hydrated OPC. For example, sodium is strongly bonded in the gel, unlike sodium in C-A-S-H, which is readily leached.[245, 246]. Alkalis in geopolymers are linked into a rather open and negatively-charged Al-Si framework.[246] Calcium has also been used to replace part of the alkalis to produce a hybrid cementing matrix.[247] The principle concern about geopolymers is their inability to react sufficiently to produce early-age strength unless significant heat curing and elevated alkali concentrations are used. The N-A-S-H gel is thermally fragile and crystallizes at temperatures exceeding 60 °C. This results in the formation of phases similar to sodalite, which have inferior binding characteristics compared to the original gel.[248] The interest in geopolymers is based on the supposedly low CO_2 emissions associated with their production and use. However, it is difficult to foresee an overall CO_2 savings because of the highly CO_2-intensive nature of alkali production, the limited abundance of alkalis in the Earth's crust, and questions regarding the future availability of fly ash in an economy where coal power is penalized. This latter issue will be even more problematic if fly ash use itself incurs a CO_2 economic penalty because its status changes from "coal combustion waste" to "valuable SCM".

(5.4) Active belite

The belite compound in cement (Ca_2SiO_4, abbreviated as C_2S) is known to contribute significantly to the strength of hydrated OPC especially after the first few days or weeks of hydration. Since belite can be produced at a lower temperature, and with one formula unit less lime than alite (Ca_3SiO_5), it can be produced with a lower CO_2 impact.[249] Significant value could therefore be realized if belite could be made more reactive with water. The search for reactive belite is facilitated by the fact that belite has several polymorphs. The olivine structured γ-C_2S structure is essentially unreactive with water, but the β-C_2S

structure that is stabilized by foreign ions in technical clinkers is much more reactive with water.[250] The alpha polymorphs are reported to be reactive, although efforts to stabilize them at lower temperatures have not been successful. However, the origin of belite and, more broadly, of clinker reactivity is still a matter of debate. The thermodynamic stability differences among the different polymorphs are important because phase transformations that occur during cooling can produce twinning, exsolution, and mechanical strain. Furthermore, ionic substitutions that occur at elevated temperatures may result in the formation of both point and extended defects.[251] So far, it has not been possible to deconvolute the many factors controlling belite reactivity, but recent work[252, 253, 254] shows systematic approaches by which the role of defects and clinker processing could be decoupled to render new understanding. This renews the potential for controlling reactivity enhancement, making belitic cements a valuable target for reducing the industrial reliance on alite-dominant clinkers for early strength.

(5.5) Prognosis for alternative cements

OPC will probably be produced for at least the next 100 years, but likely in an evolved form, at a reduced scale, and by processes that utilize renewable energy and carbon sequestration technologies. The composition of OPC clinker will likely move towards lower CO_2 emissions per ton, principally by formulating reactive belite chemistries, by better exploitation of the ability of impurities to manipulate clinker reactivity, and by bringing new efficiencies to the clinkering cycle, the latter of which will become less empirical through close integration of kinetic and thermodynamic data.

Among alternative cements, formulations that take up CO_2, or that are even CO_2 negative, are principle targets for further development. An important aspect of such cements is the possibility they offer to realize beneficial utilization of CO_2. However, all current propositions for cement compositions that sequester CO_2 are not yet competitive with OPC. Substantial progress must still be made, scientific and otherwise, before these cements can be manufactured at industrial scales. On the other hand, C$A cements appear to be emerging as a leading alternative cement over the next decade. Indeed, near-term commercial entry of C$A cements appears to be imminent in the Western world.

In broader terms, the stimulus and time scale to innovation and evolution of alternative cements depends on public policy. CO_2 taxes can be regarded as either an opportunity or a threat. Scientific developments and technology can inform debates, but if the cement industry is to remain competitive in the face of possible policy-driven mandates, it needs to present realistic, viable and impactful alternatives to traditional OPC.

(6) Next Generation Instrumental Capabilities

Advanced instrumentation is a critical part of supporting the cement research community's efforts to develop data that can inform modeling initiatives, and ultimately will be key to discovering new and innovative cements and organic admixtures. And, while the cements research community has done a good job utilizing big science instruments and keeping pace with state-of-the-art laboratory tools, the future seems equally bright as new tools come on-line and others are planned to be built and are envisioned for this century. Such tools are urgently needed to complete the fundamental physical and chemical description of the processes that determine the materials properties of infrastructure cements. Increased specialization and performance specifications will also drive the need for better measurements and more understanding.

The heterogeneity of cement and concrete varies over ten orders of magnitude, from nanometers to meters, which imposes unique challenges for analytical methods. The measurement time scales also have an enormous range. For example, there are important chemical changes (reactions) that are observable on the order of seconds, such as C_3S dissolution and C_3A hydration, while others persist or are delayed for months or years (*e.g.*, C_3S hydration, carbonation and alkali silica reaction). In addition, the vulnerability of the hydrated cement paste to sample preparation and environmental conditions during analysis is a particularly great challenge. Artifacts can be introduced by the hard-vacuums or localized heating by particle beams required for many measurement techniques that can dehydrate the sample and destroy the microstructure in fractions of a second. These challenges, however, will likely be overcome by emergent techniques.

The trends in the development of analytical techniques have led to a distinction between instruments located in an individual investigator's laboratory and those at centralized multi-user materials science centers. The latter comprise a small number of large dedicated facilities around the world that have multiple instrument stations (*e.g.*, photon beam lines) where experiment time is allocated through a formal user application process. This approach is sometimes referred to as the "Big Science" of materials in analogy to the "Big Science" of high energy particle physics.[255]

Among *big materials science* facilities of primary interest to the cement science community are synchrotron radiation (low energy X-rays) and neutron sources. Since neutrons interact with the nucleus of atoms and X-rays interact with the surrounding electron cloud, they are complementary techniques. Typically, X-rays are more suitable for elements with higher atomic numbers and neutrons for the lighter elements, particularly hydrogen.

Analytical methods involving both X-ray and neutron radiation can be classified into three main categories: diffraction, spectroscopy and imaging. For the diffraction category, conventional one-dimensional single detector goniometer-based methods are being replaced by 2-D image plates that record numerous Debye-Scherrer rings simultaneously (enabling advanced texture analysis), and 3-D diffraction techniques[256]. Moreover, the much higher data acquisition rates of the 2-D and 3-D techniques will make possible time-resolved diffraction studies on much finer timescales, especially with the very high brilliance of future sources such as free electron lasers. These advances will make possible microstructure characterized in terms of parameters such as colloidal particle size, fractal surface areas and total surface area[257] by small angle scattering methods (SAS) in which the coherent scattering becomes dominated by the dimensions of microstructural features rather than by interatomic distances. A unique capability of small angle neutron scattering (SANS) is contrast matching. This involves adjusting the hydrogen/deuterium ratio of the pore water in order to highlight or fade out selected phases such as CH[258]. Finally, the pair distribution function (PDF) which is the Fourier transform of the diffraction pattern, can be used to characterize amorphous or disordered materials in terms of nearest neighbors and bond lengths[259].

As new spectroscopy facilities come on line, including the Advanced Photon Source Upgrade (APS-U)[260], existing X-ray fluorescence (XRF) measurements will be supported by X-ray absorption (XAS) techniques that provide information on chemical state along with X-ray emission spectroscopy (XES) and inelastic X-ray scattering[261]. New neutron spectroscopy facilities are expected to include increasingly resolved quasi-elastic neutron scattering (QENS)[262, 263] and inelastic neutron scattering (INEL). Such new techniques should be applied to quantify the states of water (*i.e.*, reacted verses unreacted) in hydrating cement pastes and to measure phonon distributions in solid phases in order to investigate the role of factors such as internal relative humidity[264] in controlling hydration reaction kinetics of innovative cement systems including the effects of chemical additives, respectively.

As noted above, X-rays and neutrons have different attenuation properties. This makes combined imaging systems of interest. These can produce 2-D grayscale histogram plots that can significantly improve the segmentation of images into individual phases that could not be recognized using either type of radiation alone. This should eliminate the need for simultaneous diffraction in some applications, especially for identifying hydrogen-bearing phases. Simultaneous X-ray and neutron imaging has been implemented by installing a conventional tube-based X-ray system in the Neutron Imaging Facility at NIST[265]. In the future, combined systems utilizing electronic neutron generators (ENG)[266] in the beamlines of synchrotron radiation sources are expected.

Since synchrotron and neutron methods do not require destructive sample preparation or hard-vacuums, it is possible to make repeated measurements on the same sample over time using 4-D (3-D + time) CT, enabling the quantification of materials evolution and behavior. The capability to perform *in situ* imaging is expected to be extended by the development of experimental cells in the form of micro-reactors using nanotechnology fabrication methods. These micro-reactors can be either batch operation[265, 266] or single-pass flow-through environments that would permit complete control of solution chemistry and temperature in, for example, the investigation of cement hydration kinetics[267]. These imaging-based methods may also be enhanced by the introduction of nanoparticles with multiple functionalities to serve as contrast agents or as tags to track chemical species of admixtures.

Unfortunately, the number of new Big Science user facilities will be limited for the foreseeable future[268, 269]. Consequently, shorter-term strategies for increasing the throughput of research at existing facilities are expected to emphasize increasing the number of instruments per source, increasing the radiation flux at each instrument through improved detector efficiency and adding more detectors per instrument. This will drive the development of higher performance new detector technologies such as superconducting micro-calorimeters for X-ray detection that can improve energy resolution to less than 10 electron-volts[270], or excimer scintillation detectors for neutrons to increase detection efficiency[271].

Ion beam analysis (IBA) techniques fall in between big materials science and individual-investigator lab-based science. Although ion beam accelerators are not found in every materials lab, there are still hundreds available in both academic and industrial facilities, making competition for beam time on them much less intense then for the big science facilities. The IBA approach uses beams of charged particles in a wide variety of techniques involving different combinations of incident particle types and detected signal[272]. A major application of IBA to cement chemistry might be the nuclear resonance reaction analysis (NRA) based on $^{15}N(^{1}H,\gamma)^{12}C$ reaction to probe the development of the surface layers that may control cement hydration kinetics during the critical early period prior to solid-phase percolation[273].

Finally, Big Materials Science techniques are expected to migrate to individual-investigator laboratories through the introduction of table top synchrotrons[274], advanced electronic neutron generators and miniaturized particle accelerators. This will enable the ultimate vision of a lab-based materials characterization system that can simultaneously perform diffraction, spectroscopy and imaging at relevant time and length scales and make such devices widely and affordably available. And, while the primary focus here has been on the multi-user Big Science facilities to be, it is likely that most advances in the future will come from individual investigator laboratories that use miniaturized particle accelerators. Many of the techniques described above will be generally applicable for such instruments as particle flux and detector capabilities improve with time.

(7) Curated Materials Data

The common needs of the preceding six focal areas for 21st century research on cements culminates in the need for high quality material properties and structure characterization and broad sharing of such data sets. Furthermore, the complex stoichiometry, heterogeneity, and hierarchical structure of cement and concrete make the design and discovery of new cementitious materials quite challenging. These features, combined with variability in manufacture, processing, placement, testing, and field environment, call for a unified materials data platform (so-called Curated Materials Data) to facilitate the design and engineering of concrete products in the century ahead. Creating and sharing a meticulously curated materials dataset including various processing (*e.g.*, mixing ingredients, temperature), structure (*e.g.*, electron microscopy data, atomic structure), properties (*e.g.*, thermodynamic data), and testing (*e.g.*, strength according to ASTM standards) data will significantly impact modern engineering of concrete, especially in light of rapid advancements in computational discoveries, big data science and analytics, cloud systems and machine learning. As an example, recent curated data-based discovery and advancements in biological materials (*e.g.*, mapping of DNA and its characteristics such as folding patterns) has put biology on a sound footing compared to a few decades ago. This section briefly highlights some of the opportunities that hold great promise for creating a globally-accessible curated materials dataset for advancing concrete science and technology.

Looking at the past century, the Long-Time Study of Cement Performance in Concrete,[275] was an ambitious, large-scale, nation-wide effort starting in 1940 to combine laboratory and field studies on cement performance in concretes in different exposure conditions. Cements were selected that represented a range of physical and chemical properties as well as methods of manufacture, and were extensively characterized. Their data, archived on paper, consists of a detailed accounting of the cement manufacture, the bulk chemistry, descriptive and quantitative microscopy, physical characteristics such as specific gravity, fineness, specific surface, water demand, time of set, strength development, and phase composition. These cements were subsequently used in the construction of test pavement sections, walkways, parapet walls, beams, prisms, and blocks in different locations using local aggregates to assess performance in outdoor exposure experiments in distinct climatic regions across the US and in lab environments. This exhaustive testing and exposure site monitoring undoubtedly helped in the development of ASTM C150 in the early 1940s and refinements made subsequently in existing ASTM tests and in the development of new test methods. The archived cements were used for many years after, for example in Frohnsdorff's automated quantitative X-ray diffraction routine in the mid-1960s calibrated using the Long-Time cements.[276]

Although the above advancements and standard protocols established by the American Concrete Institute (ACI) and the American Association of State Highway Transportation Officials (AASHTO) helped in the preparation of a sort of virtual databank and design manuals associated with basic cement/concrete manufacturing and testing, they still have significant shortcomings when it comes to new materials and innovation. More precisely, despite all the successes of test and specification standardization, it may have inadvertently limited innovation and acceptance of novel materials in the construction industry through creation of a *cookbook* for the manufacture of cement and, perhaps, materials that are a compromise in performance to satisfy a range of construction conditions. With the demands of sustainability and emergent new technologies such as AM in the 21st century, there is an urgency to develop new cementitious systems (see Section 5), inclusive of mineral and organic constituents, with improved properties that entail low energy consumption, minimal field maintenance and reduced or zero CO_2 emissions. To this end, unified and curated materials data for cement and concrete science and technology can have a significant impact.

The last decade has seen a remarkable increase in high performance computing, big data and machine learning. A prime example in the context of materials science is the Materials Genome Initiative (MGI) – initially started by the US Department of Energy (DOE) and later supported by other organizations and industries – which initiated a new era of materials innovation, serving as a foundation for strengthening materials-related industries. The cement-related sciences have also witnessed a dramatic improvement in computationally-enabled design and understanding across many length scales. Examples include detailed molecular-level understanding of the defects and screw or edge dislocations in cement crystals (alite and belite),[277, 278, 279] and tobermorite[280] (see Figure 2) , origin of nanoscale friction in cement hydrates,[281] understanding and tuning the behavior of hybrid and nanostructured cementitious materials,[282, 283, 284] and development of atomic force field potentials enabling the study of a much broader range of properties in cementitious materials,[285, 286, 287] , along with the many advances mentioned in the preceding six sections. This notable computationally-fueled growth has also amplified the need for better data-related tools. Given the current technological trends, in the next century, massive quantities of scientific data in cement and concrete will be continuously produced, thus rendering the past modes of communication (print/email) and collaboration inadequate. Essential to the success of such computationally-powered data as well as emerging advances in manufacturing of concrete (*e.g.*, AM of concrete) is the development of a curated data infrastructure. The diversity of materials data, processing, testing conditions, and properties require that this data infrastructure be built to accommodate a variety of user needs, data types and complexity of the data structures. Such a curated materials dataset in cement and concrete would ideally have three key components: Data Curation, Ontology Development, and Semantic Infrastructure.

(7.1) Data curation

This is an essential component as the benefits of more computational and experimental data presumes that the necessary information is available in a machine readable format. Data can be of different types – numerical, categorical, Boolean (true or false), or structured. Note that data must come with associated information (*e.g.*, provenance and quality). When were the data generated? What was the source of the data? What kind of tests or protocols were used to generate the data? By necessity, data curation must include i) a user interface to curate, search, and retrieve data, ii) support for semantic queries, scientific images and graphics, and integration with registry systems, and iii) integration with scientific workflows. The American Concrete Institute took a prescient and significant step in this direction 18 years ago with the publication of a guide for formatting a database of concrete material properties, and future data curation efforts could build upon the foundation of that work.

(7.2) Ontology development

The second component, which will be the focus of increasing scientific and technical communities, is the ontology development**.** Ontologies provide a foundation for semantic document processing and advanced analytics, large-scale combination of diverse information from multiple sources and accelerating quantitative-knowledge activities such as modeling, simulation, processing, fabrication, design and engineering. An ontology is a shared understanding of basic objects, concepts, and their relationships. These ontological features provide the structural framework for the underlying database. Akin to software development, ontology development is tractable only with an understanding of the domain in which it will be embedded. Obtaining this domain knowledge is usually a difficult and error-prone process. Automation is key to properly extract the knowledge. Such automation, categorized as *ontology learning*, is the automation of ontology development including the extraction of knowledge and data from texts. An example is the use of modern computer languages to analyze a rich body of several thousand cement/concrete-related scientific articles, more specifically, the creation of a distributed system for text extraction from PDF files of scientific articles via optical character recognition, combined with machine learning-based de-noising techniques. These smart methods and strategies will help towards collecting and consolidating a vast range and amount of data in appropriate ontologies.

(7.3) Semantic infrastructure

Other fields, particularly biomedical sciences, have had success with semantic technologies such as the Semantic Web to help the broad access, sharing and use of their data. Cement and concrete communities can also create a similar *semantic infrastructure* for their data and promote widespread access and collaboration in the 21st century. For instance, a starting strategy might be to learn from other Semantic Libraries, such as the National Library of Medicine's Semantic Medline, and apply what is learned to cement and concrete materials literature. An interesting feature of the Semantic Medline is that it allows users to see search results as an interconnected graph of knowledge-based relationships and perhaps unveil valuable hidden connections. Such a capability would be extremely helpful in supporting curated materials data in cement and concrete field.

Despite decades of intensive research on cement and concrete materials to date, the majority of the documented data are fragmented and there is no unified international, searchable curated databank such as that described above. Although there are databanks (*e.g.*, Crystallographic Database for Minerals[288]) that partially cover select characteristics of cementitious minerals, a much more focused and global effort is needed to create a comprehensive curated materials dataset for all aspects of cement and concrete materials. The initial platform of such curated materials data would likely take a decade to assemble but what is important is that it should be updated dynamically as new information and data becomes rapidly available in the next century.

In summary, given the wide phase-space of variables in cementitious materials and concrete technology including compositions, processing, testing and predicted and measured properties, a curated materials dataset based on modern database structure and ontological concepts would serve as a key source of information, transparency, sharing and broader collaboration in the century ahead. The advantage of such a comprehensive database system is that it would rapidly increase knowledge of advanced modeling, computations and experiments, and would allow industry and academia to better embrace and contribute to the concept of open innovation (*e.g.*, of hybrid multifunctional cementitious materials) in the field of cement and concrete science and technology.

III. Discussion and Concluding Remarks

So, what will the next 100 years of cementitious materials look like? Based on the discourse presented above, a picture emerges that anticipates transformative changes in the way research on cements happens and the way that constructed infrastructure is built, both of which are expected to impact what a cement will be by 2117, 100 years from now. Getting to that point will be an integrated network of pathways crudely illustrated by Figure 3. It is not too speculative to say that additive manufacturing will have huge impacts. And, while there are research-based challenges ahead, it appears that new cements formulations with respect to both the inorganic and organic fractions will emerge, driven primarily by the need for tailored rheological properties and the potential to implement hierarchically engineered structures across many length scales. Furthermore, while it is somewhat unclear how well additive manufacturing will scale, it is quite clear that large sectors of the construction industry will be impacted and projections suggest that even structures as large as high-rise buildings and expansive bridges will be additively constructed at some point. Increasing environmental concerns will likewise transform both how we manufacture cements and the composition of their inorganic fraction, though, the final outcomes will most surely continue to utilize the Earth's most abundant resources, limestone and shale. Transformations in how constructed infrastructure is built and what defines a cement (both inorganic and organic components) will be dramatically influenced by rapidly emerging computational resources including artificial intelligence, molecular-scale computational chemistry, big data and curated digital data sets. The implementations of additive manufacturing and smart material technologies will symbiotically emerge because AM will enable smart materials and smart structures to be ubiquitously built. Finally, the micronization of big science and standardization of all-atom molecular scale modeling will further accelerate progress and both provide inputs for big data and curated resources and utilize their data sets. In summary, we cannot live as we know it, nor project life into the future without constructed infrastructure across great length scales requiring massive amounts of matter. The matter we assemble in the future, however, must be sustainable. How we utilize the limited resources of the Earth to produce next generation cements will be shaped by human ingenuity manifested as construction technologies, computers, digital resources and analytical tools. Let us see what happens.

List of Figures

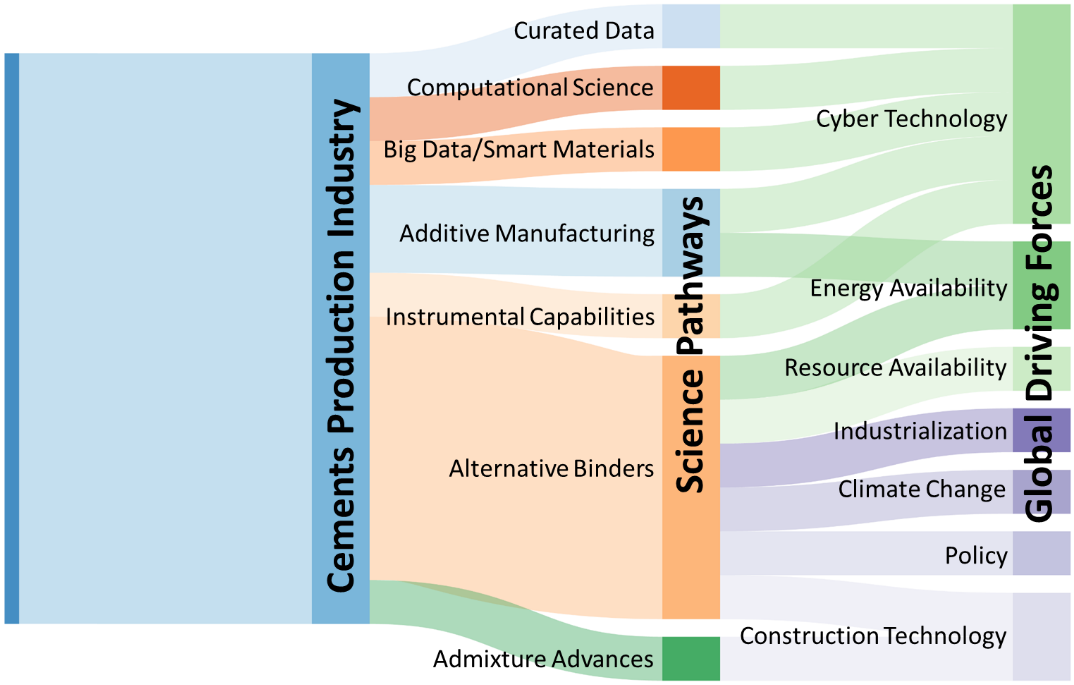

Figure 1. Sankey diagram illustrating the relationship between the seven vectors for change (driving forces) and the seven key scientific pathways expected to enable future developments in construction cements. Note that the width of the lines are proportional only to the number of interactions and do not necessarily indicate relative importance.

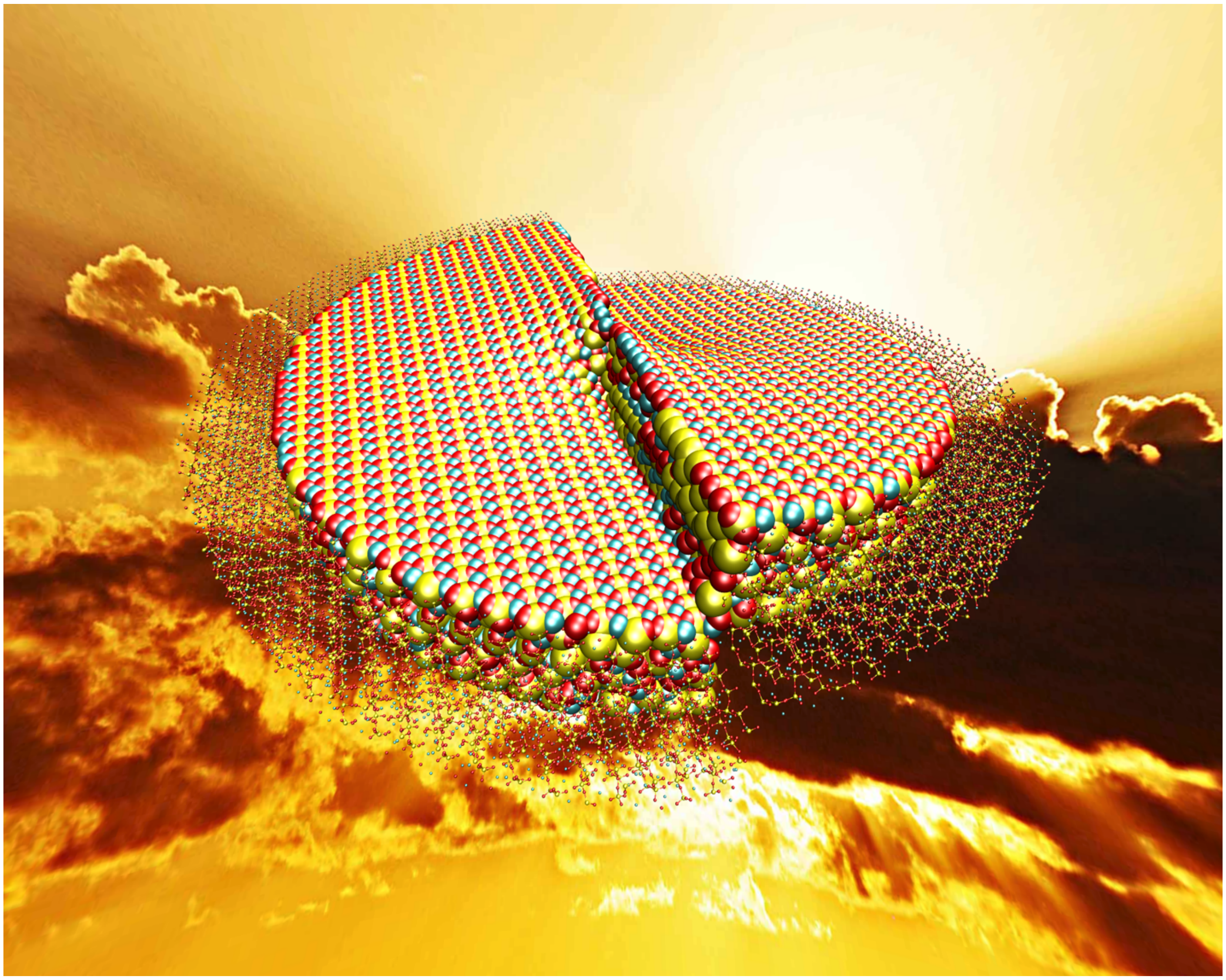

Figure 2. Atomistic configuration of tobermorite with a screw dislocation, which impacts mechanical properties.[280]

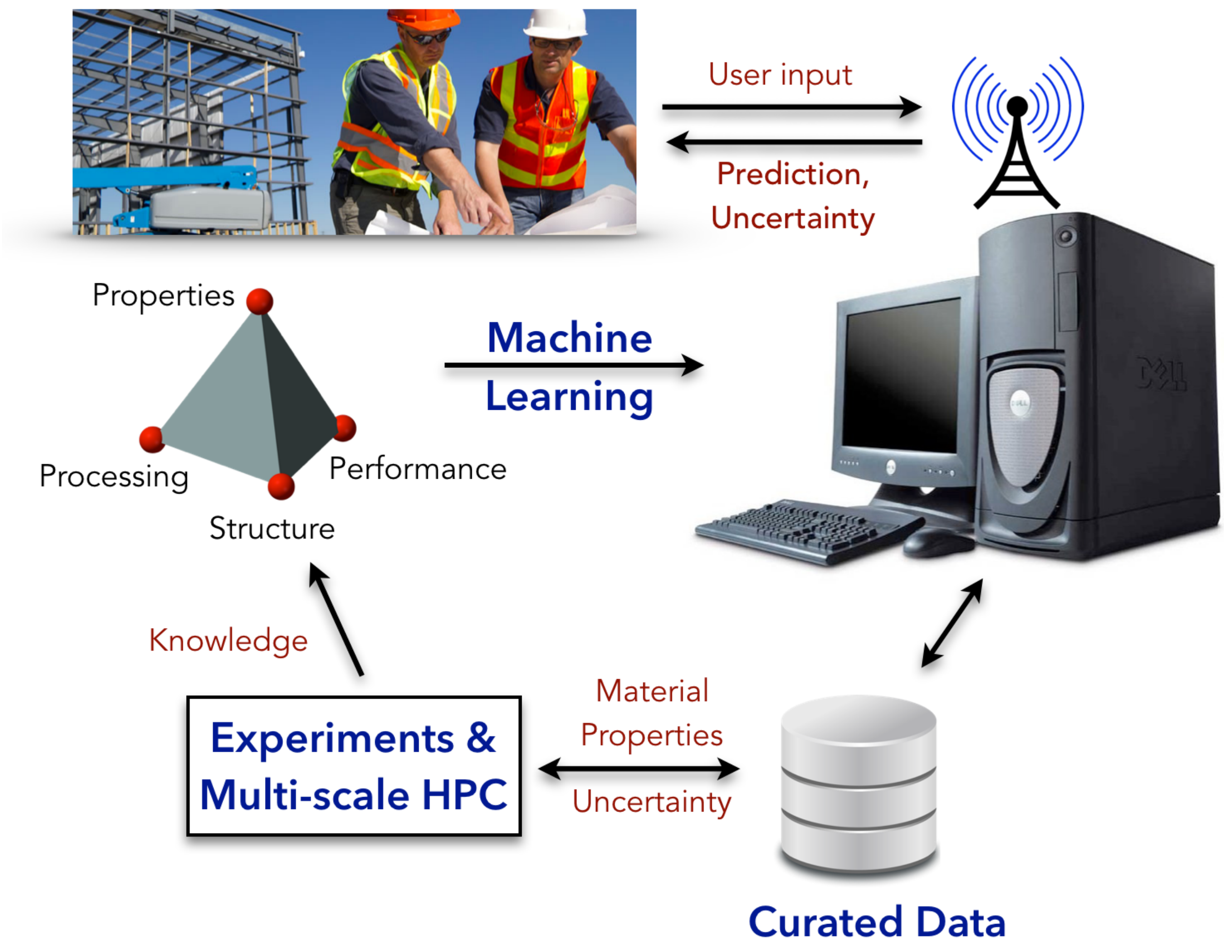

Figure 3. Integration of seven key scientific pathways illustrating anticipated relationships and feedback loops between computational, experimental and development sectors. Note that the width of the lines are proportional only to the number of interactions and do not necessarily indicate relative importance.

References

1. R. K. Meade, "PORTLAND CEMENT Its Composition, Raw Materials, Manufacture, Testing and Analysis," (1911).
2. J. Aspdin, "An improvement in the modes of producing artificial stone," *Brevet britannique BP,* 5022 1824 (1824).
3. H. Kanare, I. Milevski, H. Khalaily, N. Gezov, and J. Nasvik, "How old is concrete?," *Construction Management*, (Januvary 2009) [Online]. Avaailable: http://www.concreteconstruction.net/business/management/how-old-is-concrete_o, [Accessed on 19 07 2016].
4. H. Gonnerman and W. Lerch, "Changes in characteristics of portland cement as exhibited by laboratory tests over the period 1904 to 1950." *ASTM International,* (1952).
5. P. Tennis and J. Bhatty, "Portland cement characteristics-2004," *Concr. Tech. Today,* 26 [3] 1-3 (2005).
6. P. K. Mehta, "Advancements in concrete technology," *CONCRETE INTERNATIONAL-DETROIT-,* 21, 69-76 (1999).
7. "The Earth's Crust," [Online]. Available: http://butane.chem.uiuc.edu/pshapley/Environmental/L26/1.html, [Accessed on 19 07 2016].
8. J. W. Miller, "Exhausting the Earth's Resources? Not So Fast," *Wall Street Journal, June,* 5 (2012).
9. J. DesJardins, "A forecast of when we'll run out of each metal," *Visual Capitalist*, (September 2014) [Online]. http://www.visualcapitalist.com/forecast-when-well-run-out-of-each-metal/, [Accessed on 19 07 2016].
10. "Putting a price on carbon with a tax, World Bank," [Online]. Available: http://www.worldbank.org/content/dam/Worldbank/document/SDN/background-note_carbon-tax.pdf, [Accessed on 19 07 2016].
11. "CO_2 capture in the cement industry, International Energy Agency (IEA), Technical Study Report No. 2008/3, July 2008" [Online]. Available: http://ieaghg.org/docs/General_Docs/Reports/2008-3.pdf, [Accessed on 19 07 2016].
12. G. Habert, F. Pacheco-Torgal, S. Jalali, J. Labrincha, and V. John, "Environmental impact of Portland cement production," *Eco-efficient concrete,* 3-25 (2013).
13. J. Ke, M. McNeil, L. Price, N. Z. Khanna, and N. Zhou, "Estimation of CO 2 emissions from China's cement production: methodologies and uncertainties," *Energy Policy,* 57, 172-81 (2013).
14. M. Schneider, M. Romer, M. Tschudin, and H. Bolio, "Sustainable cement production—present and future," *Cement and Concrete Research,* 41 [7] 642-50 (2011).
15. "United Nations Population Division, World population prospectus, the 2015 revision," [Online]. https://esa.un.org/unpd/wpp/, [Accessed on 19 07 2016].
16. R. Florida, "The great growth disconnect: population growth does not equal economic growth", *The Atlantic CityLab*, (September 2013) [Online]. http://www.citylab.com/work/2013/09/great-growth-disconnect-population-growth-does-not-equal-economic-growth/5860/, [Accessed on 19 07 2016].
17. "PricewaterhousCoopers LLP, The world in 2050, will the shift in global economic power continue?", (February 2015) [Online]. Available: https://www.pwc.com/gx/en/issues/the-economy/assets/world-in-2050-february-2015.pdf, [Accessed on 19 07 2016].
18. "Portland Cement Association, World cement consumption, PCA Market Intelligence", (August 2013) [Online]. Available: http://www.betonabq.org/images/imguser/WorldReport_Aug_2013final__01__cement.pdf, [Accessed on 19 07 2016].
19. C. Shi, A. F. Jiménez, and A. Palomo, "New cements for the 21st century: the pursuit of an alternative to Portland cement," *Cement and concrete research,* 41 [7] 750-63 (2011).
20. K. Vance, G. Falzone, I. Pignatelli, M. Bauchy, M. Balonis, and G. Sant, "Direct Carbonation of Ca (OH) 2 Using Liquid and Supercritical CO2: Implications for Carbon-Neutral Cementation," *Industrial & Engineering Chemistry Research,* 54 [36] 8908-18 (2015).

21. A. Heath, K. Paine, and M. McManus, "Minimising the global warming potential of clay based geopolymers," *Journal of Cleaner Production,* 78, 75-83 (2014).
22. J. W. Bullard, H. M. Jennings, R. A. Livingston, A. Nonat, G. W. Scherer, J. S. Schweitzer, K. L. Scrivener, and J. J. Thomas, "Mechanisms of cement hydration," *Cement and Concrete Research,* 41 [12] 1208-23 (2011).
23. K. L. Scrivener, P. Juilland, and P. J. Monteiro, "Advances in understanding hydration of Portland cement," *Cement and Concrete Research,* 78, 38-56 (2015).
24. R. F. Zollo, "Fiber-reinforced concrete: an overview after 30 years of development," *Cement and Concrete Composites,* 19 [2] 107-22 (1997).
25. R. de Borst, "Fracture in quasi-brittle materials: a review of continuum damage-based approaches," *Engineering fracture mechanics,* 69 [2] 95-112 (2002).
26. A. Bentur and M. Alexander, "A review of the work of the RILEM TC 159-ETC: Engineering of the interfacial transition zone in cementitious composites," *Materials and structures,* 33 [2] 82-87 (2000).
27. J. G. MacGregor, J. K. Wight, S. Teng, and P. Irawan, "Reinforced concrete: mechanics and design," Vol. 3. Prentice Hall Upper Saddle River, NJ, (1997).
28. M. Teutsch, "CONCRETE. REINFORCEMENT-Development of ductile, steel-fibre-reinforced, high performance concrete," *Betonwerk und Fertigteiltechnik,* 67 [4] 56-63 (2001).
29. B. Mobasher, "Mechanics of fiber and textile reinforced cement composites." CRC press, (2011).
30. S. Lim, R. A. Buswell, T. T. Le, S. A. Austin, A. G. Gibb, and T. Thorpe, "Developments in construction-scale additive manufacturing processes," *Automation in construction,* 21, 262-68 (2012).
31. Y. W. Tay, B. Panda, S. C. Paul, M. J. Tan, S. Qian, K. F. Leong, and C. K. Chua, "Processing and Properties of Construction Materials for 3D Printing," in Materials Science Forum. Vol. 861.
32. B. Khoshnevis, "Automated construction by contour crafting—related robotics and information technologies," *Automation in construction,* 13 [1] 5-19 (2004).
33. B. Khoshnevis, D. Hwang, K.-T. Yao, and Z. Yeh, "Mega-scale fabrication by contour crafting," *International Journal of Industrial and Systems Engineering,* 1 [3] 301-20 (2006).
34. "Contour Crafting," 27 9 2016. [Online]. Available: http://www.contourcrafting.org/. [Accessed 2016].
35. S. Lim, T. Le, J. Webster, R. Buswell, S. Austin, A. Gibb, and T. Thorpe, "Fabricating construction components using layered manufacturing technology," pp. 512-20 in Global Innovation in Construction Conference.
36. S. Lim, R. A. Buswell, T. T. Le, R. Wackrow, S. A. Austin, A. G. Gibb, and T. Thorpe, "Development of a viable concrete printing process," (2011).
37. G. Cesaretti, E. Dini, X. De Kestelier, V. Colla, and L. Pambaguian, "Building components for an outpost on the Lunar soil by means of a novel 3D printing technology," *Acta Astronautica,* 93, 430-50 (2014).
38. "D Shape," [Online]. Available: http://d-shape.com/. [Accessed 2016].
39. I. Hager, A. Golonka, and R. Putanowicz, "3D printing of buildings and building components as the future of sustainable construction?," *Procedia Engineering,* 151, 292-99 (2016).
40. J. Gardiner, "Exploring the emerging design territory of construction 3D printing-project led architectural research," (2011).
41. L. Y. Feng, "Study on the Status Quo and Problems of 3D Printed Buildings in China," *Global Journal of Human-Social Science Research,* 14 [5] (2014).
42. "Emerging objects - Our 3D printed design & material innovations," [Online]. Available: http://www.emergingobjects.com/portfolio/. [Accessed 29 9 2016].
43. "3DPrint.com: Shanghai-based WinSun 3D prints 6-story apartment building and an incredible home," (Januvary 2015). [Online]. Available: https://3dprint.com/38144/3d-printed-apartment-building/. [Accessed 30 9 2016].

44. "3DPrint.com: Chinese Construction Company 3D Prints an Entire Two-Story House On-Site in 45 Days," [Online]. Available: https://3dprint.com/138664/huashang-tengda-3d-print-house/. [Accessed 29 9 2016].
45. "3DPrint.com: Shanghai-based WinSun 3D Prints 6-Story Apartment Building and an Incredible Home," (Januvary 2016). [Online]. Available: https://3dprint.com/38144/3d-printed-apartment-building/. [Accessed 29 9 2016].
46. "3ders.org: Minnesotan man builds the world's first 3D printed concrete castle in his own backyard, designing a kit that can print two-story houses," (August 2014). [Online]. Available: http://www.3ders.org/articles/20140826-minnesotan-world-first-3d-printed-concrete-castle-in-his-own-backyard.html. [Accessed 29 9 2016].
47. "EXCLUSIVE: Lewis Grand Hotel Erects World's First 3D Printed Hotel, Plans to Print Thousands of Homes in the Philippines Next", (September 2015). [Online]. Available: https://3dprint.com/94558/3d-printed-hotel-lewis-grand/. [Accessed 29 9 2016].
48. "NASA Technology Roadmaps Technical Area 7 Human Exploration Destination Systems," [Online] Available: http://www.nasa.gov/sites/default/files/atoms/files/2015_nasa_technology_roadmaps_ta_7_human_exploration_destination_final.pdf. [Accessed 31 10 2016].
49. B. Khoshnevis, M. P. Bodiford, K. H. Burks, E. Ethridge, D. Tucker, W. Kim, H. Toutanji, and M. R. Fiske, "Lunar contour crafting—a novel technique for ISRU-based habitat development," pp. 7397-409 in 43rd AIAA Aerospace Sciences Meeting and Exhibit—Meeting Papers.
50. F. Ceccanti, E. Dini, X. De Kestelier, V. Colla, and L. Pambaguian, "3D printing technology for a moon outpost exploiting lunar soil," in 61st International Astronautical Congress, Prague, CZ, IAC-10-D3. Vol. 3.
51. S. Bhandari and B. Regina, "3D Printing and Its Applications," *International Journal of Computer Science and Information Technology Research ISSN,* 378-80 (2014).
52. "ACME Fact Sheet," [Online]. Available: https://www.nasa.gov/sites/default/files/atoms/files/fs_acme_factsheet_150910.pdf. [Accessed 31 10 2016].
53. "NASA's 3D Printed Habitat Challenge," Available: http://bradley.edu/challenge. [Accessed on 31 10 2016].
54. "STMD: Centennial Challenges - NASA's Centennial Challenges: 3D-Printed Habitat Challenge," NASA, 2015. [Online]. Available: http://www.nasa.gov/directorates/spacetech/centennial_challenges/3DPHab/index.html. [Accessed 29 9 2016].
55. M. S. Imbabi, C. Carrigan, and S. McKenna, "Trends and developments in green cement and concrete technology," *International Journal of Sustainable Built Environment,* 1[2] 194-216 (2012).
56. F. Sanchez, J. Biernacki, J. Olek and P. Zavattieri, "Grant NSF CMMI-1239979. Multiscale/3D Cement Printing," Vanderbilt University, Nashville, Tenn., (July 2015).
57. R. A. Buswell, R. Soar, A. G. Gibb, and A. Thorpe, "Freeform construction: mega-scale rapid manufacturing for construction," *Automation in construction,* 16 [2] 224-31 (2007).
58. R. Rael and V. San Fratello, "Material Design and Analysis for 3D-printed Fiber-reinforced Cement Polymer Building Components," *PROCEEDINGS 2011 BORÅS SWEDEN EDITORS: LARS HALLNÄS, ANNIKA HELLSTRÖM, HANNA LANDIN* 136.
59. H. Toutanji, D. Tucker, and E. Ethridge, "New Fiber Reinforced Waterless Concrete for Extraterrestrial Structural Applications," (2005).
60. H. Toutanji, B. Glenn-Loper, and B. Schrayshuen, "Strength and durability performance of waterless lunar concrete," pp. 10-13 in 43rd AIAA Aerospace Sciences Meeting and Exhibit.
61. A. Owens and O. De Weck, "Systems Analysis of In-Space Manufacturing Applications for the International Space Station and the Evolvable Mars Campaign," pp. 5394. in AIAA SPACE (2016).

62. C. Gosselin, R. Duballet, P. Roux, N. Gaudillière, J. Dirrenberger, and P. Morel, "Large-scale 3D printing of ultra-high performance concrete–a new processing route for architects and builders," *Materials & Design,* 100, 102-09 (2016).
63. N. Oxman, J. Duro- Royo, S. Keating, B. Peters, and E. Tsai, "Towards robotic swarm printing," *Architectural Design,* 84 [3] 108-15 (2014).
64. N. Oxman, S. Keating, and E. Tsai, "Functionally graded rapid prototyping," pp. 483-89 in 5th International conference on advanced research in virtual and physical prototyping, VR@ P. Vol. 28.
65. "3D Printing in Zero G," [Online]. Available: http://www.nasa.gov/mission_pages/station/research/experiments/1115.html. [Accessed on 31 10 2016].
66. B. PANDA, Y. TAY, S. C. PAUL, T. M. JEN, K. LEONG, and I. GIBSON, "CURRENT CHALLENGES AND FUTURE PERSPECTIVES OF 3D CONCRETE PRINTING."
67. P. Wu, J. Wang, and X. Wang, "A critical review of the use of 3-D printing in the construction industry," *Automation in Construction,* 68, 21-31 (2016).
68. A. Perrot, D. Rangeard, and A. Pierre, "Structural built-up of cement-based materials used for 3D-printing extrusion techniques," *Materials and Structures,* 49 [4] 1213-20 (2016).
69. R. Wolfs, "3D printing of concrete structures" Department of the Built Environment, Eindhoven University of Technology, (2015).
70. T. T. Le, S. A. Austin, S. Lim, R. A. Buswell, R. Law, A. G. Gibb, and T. Thorpe, "Hardened properties of high-performance printing concrete," *Cement and Concrete Research,* 42 [3] 558-66 (2012).
71. T. Di Carlo, B. Khoshnevis, and Y. Chen, "Manufacturing Additively, With Fresh Concrete," pp. V02AT02A007-V02AT02A07 in ASME 2013 International Mechanical Engineering Congress and Exposition.
72. A. Perrot, Y. Mélinge, D. Rangeard, F. Micaelli, P. Estellé, and C. Lanos, "Use of ram extruder as a combined rheo-tribometer to study the behaviour of high yield stress fluids at low strain rate," *Rheologica acta,* 51 [8] 743-54 (2012).
73. Z. Malaeb, H. Hachem, A. Tourbah, T. Maalouf, N. El Zarwi, and F. Hamzeh, "3D CONCRETE PRINTING: MACHINE AND MIX DESIGN," *International Journal of Civil Engineering,* 6 [6] (2015).
74. "National Research Council, Advancing the Competitiveness and Efficiency of the U.S. Construction Industry," National Academies Press., Washington, DC, (2009).
75. "Bureau of Labor Statistics. Industries at a Glance: Construction: NAICS 23," 15 10 2015. [Online]. Available: http://www.bls.gov/iag/tgs/iag23.htm#fatalities_injuries_and_illnesses. [Accessed 2015].
76. "Occupational Safety & Health Administration," 15 10 2015. [Online]. Available: https://www.osha.gov/.
77. K. Kesner, K. Conroy and L. Kahn, "ACI 562– Evaluation, Repair and Rehabilitation of Concrete Buildings," *Structure Magazine,* 18-21 (2014).
78. P. H. Emmons and D. J. Sordyl, "The state of the concrete repair industry, and a vision for its future," *Concrete repair bulletin,* 7-14 (2006).
79. S. A. Dajadian and D. C. Koch, "Waste management models and their applications on construction sites," *International Journal of Construction Engineering and Management,* 3 [3] 91-98 (2014).
80. P.-C. Aïtcin and R. J. Flatt, "Science and Technology of Concrete Admixtures." Woodhead Publishing, (2015).
81. L. Nicoleau, T. Gädt, L. Chitu, G. Maier, and O. Paris, "Oriented aggregation of calcium silicate hydrate platelets by the use of comb-like copolymers," *Soft Matter,* 9 [19] 4864-74 (2013).
82. J. Plank, E. Sakai, C. Miao, C. Yu, and J. Hong, "Chemical admixtures—Chemistry, applications and their impact on concrete microstructure and durability," *Cement and Concrete Research,* 78, 81-99 (2015).

83. D. Van Gemert and Ö. Cizer, "Merging cement concrete, concrete-polymer composites and inorganic polymer technologies for sustainability in construction and restoration," *Advanced Materials Research,* 1129 (2015).
84. S. Hamid, "The crystal structure of the 11 Ä natural tobermorite Ca2. 25 [Si3O7. 5 (OH) 1.5]· 1H2O," *Zeitschrift für Kristallographie-Crystalline Materials,* 154 [1-4] 189-98 (1981).
85. W. Dai, Z. Shui, and P. Duan, "Molecular Dynamics Simulation on Calcium Silicate Hydrate Doped Organic Molecules," pp. 155-60. in Intelligent Computing and Information Science**.** Springer, 2011.
86. R. K. Mishra, R. J. Flatt, and H. Heinz, "Force field for tricalcium silicate and insight into nanoscale properties: cleavage, initial hydration, and adsorption of organic molecules," *The Journal of Physical Chemistry C,* 117 [20] 10417-32 (2013).
87. H. Manzano, J. S. Dolado, and A. Ayuela, "Structural, mechanical, and reactivity properties of tricalcium aluminate using first- principles calculations," *Journal of the American Ceramic Society,* 92 [4] 897-902 (2009).
88. H. Manzano, A. Ayuela, A. Telesca, P. Monteiro, and J. Dolado, "Ettringite strengthening at high pressures induced by the densification of the hydrogen bond network," *The Journal of Physical Chemistry C,* 116 [30] 16138-43 (2012).
89. R. T. Cygan, J.-J. Liang, and A. G. Kalinichev, "Molecular models of hydroxide, oxyhydroxide, and clay phases and the development of a general force field," *The Journal of Physical Chemistry B,* 108 [4] 1255-66 (2004).
90. R. J.-M. Pellenq, A. Kushima, R. Shahsavari, K. J. Van Vliet, M. J. Buehler, S. Yip, and F.-J. Ulm, "A realistic molecular model of cement hydrates," *Proceedings of the National Academy of Sciences,* 106 [38] 16102-07 (2009).
91. M. Bauchy, M. A. Qomi, F.-J. Ulm, and R.-M. Pellenq, "Order and disorder in calcium–silicate–hydrate," *The Journal of chemical physics,* 140 [21] 214503 (2014).
92. M. A. Qomi, K. J. Krakowiak, M. Bauchy, K. Stewart, R. Shahsavari, D. Jagannathan, D. B. Brommer, A. Baronnet, M. J. Buehler, and S. Yip, "Combinatorial molecular optimization of cement hydrates," *Nature communications,* 5 (2014).
93. G. Kovačević, B. Persson, L. Nicoleau, A. Nonat, and V. Veryazov, "Atomistic modeling of crystal structure of Ca 1.67 SiH x," *Cement and Concrete Research,* 67, 197-203 (2015).
94. G. Kovačević, L. Nicoleau, A. Nonat, and V. Veryazov, "Revised Atomistic Models of the Crystal Structure of C–S–H with high C/S Ratio," *Zeitschrift für Physikalische Chemie*.
95. L. Pegado, C. Labbez, and S. V. Churakov, "Mechanism of aluminium incorporation into C–S–H from ab initio calculations," *Journal of Materials Chemistry A,* 2 [10] 3477-83 (2014).
96. M. Turesson, A. Nonat, and C. Labbez, "Stability of negatively charged platelets in calcium-rich anionic copolymer solutions," *Langmuir,* 30 [23] 6713-20 (2014).
97. M. Turesson, C. Labbez, and A. Nonat, "Calcium mediated polyelectrolyte adsorption on like-charged surfaces," *Langmuir,* 27 [22] 13572-81 (2011).
98. I. Pochard, C. Labbez, A. Nonat, H. Vija, and B. Jönsson, "The effect of polycations on early cement paste," *Cement and Concrete Research,* 40 [10] 1488-94 (2010).
99. H. M. Kayello, N. K. Tadisina, N. Shlonimskaya, J. J. Biernacki, and D. P. Visco, "An Application of Computer- Aided Molecular Design (CAMD) Using the Signature Molecular Descriptor—Part 1. Identification of Surface Tension Reducing Agents and the Search for Shrinkage Reducing Admixtures," *Journal of the American Ceramic Society,* 97 [2] 365-77 (2014).
100. N. Shlonimskaya, J. J. Biernacki, H. M. Kayello, and D. P. Visco, "An Application of Computer-Aided Molecular Design (CAMD) Using the Signature Molecular Descriptor–Part 2. Evaluating Newly Identified Surface Tension- Reducing Substances for Potential Use as Shrinkage-Reducing Admixtures," *Journal of the American Ceramic Society,* 97 [2] 378-85 (2014).
101. C. Sanchez, K. J. Shea, and S. Kitagawa, "Recent progress in hybrid materials science," *Chemical Society Reviews,* 40 [2] 471-72 (2011).

102. J. Rieger, M. Kellermeier, and L. Nicoleau, "Formation of Nanoparticles and Nanostructures—An Industrial Perspective on CaCO3, Cement, and Polymers," *Angewandte Chemie International Edition,* 53 [46] 12380-96 (2014).
103. J. J. Beaudoin, "Handbook of Fiber-Reinforced Concrete. Principles, Properties, Developments and Applications,*"* (1990).
104. J. Sun and B. Bhushan, "Hierarchical structure and mechanical properties of nacre: a review," *Rsc Advances,* 2 [20] 7617-32 (2012).
105. A. Picker, "Influence of Polymers on Nucleation and Assembly of Calcium Silicate Hydrates." in., 2013.
106. F.-J. Ulm, "Nano-engineering of concrete," *Arabian Journal for Science and Engineering,* 37 [2] 481-88 (2012).
107. H. M. Jennings and J. W. Bullard, "From electrons to infrastructure: Engineering concrete from the bottom up," *Cement and Concrete Research,* 41 [7] 727-35 (2011).
108. Y. Cao, P. Zavaterri, J. Youngblood, R. Moon, and J. Weiss, "The influence of cellulose nanocrystal additions on the performance of cement paste," *Cement and Concrete Composites,* 56, 73-83 (2015).
109. A. Picker, L. Nicoleau, A. Nonat, C. Labbez, and H. Cölfen, "Identification of binding peptides on calcium silicate hydrate: a novel view on cement additives," *Advanced Materials,* 26 [7] 1135-40 (2014).
110. F. Pacheco-Torgal, V. Ivanov, N. Karak, and H. Jonkers, "Biopolymers and Biotech Admixtures for Eco-efficient Construction Materials.*"* Woodhead Publishing, (2016).
111. C. Jolicoeur and M.-A. Simard, "Chemical admixture-cement interactions: phenomenology and physico-chemical concepts," *Cement and Concrete Composites,* 20[2] 87-101 (1998).
112. K. Yamada, S. Ogawa, and S. Hanehara, "Controlling of the adsorption and dispersing force of polycarboxylate-type superplasticizer by sulfate ion concentration in aqueous phase," *Cement and Concrete Research,* 31 [3] 375-83 (2001).
113. R. J. Flatt and Y. F. Houst, "A simplified view on chemical effects perturbing the action of superplasticizers," *Cement and concrete research,* 31 [8] 1169-76 (2001).
114. D. Marchon, P. Juilland, L. Frunz, M. Palacios and R. J. Flatt, "Effect of molecular structure of polycarboxylate superplasticizers on polyphased clinker hydration," in *14th International Conference on Cement Chemistry*, Beijing, China (2015).
115. F. Dalas, S. Pourchet, A. Nonat, D. Rinaldi, S. Sabio, and M. Mosquet, "Fluidizing efficiency of comb-like superplasticizers: The effect of the anionic function, the side chain length and the grafting degree," *Cement and Concrete Research,* 71, 115-23 (2015).
116. C. Labbez, I. Pochard, B. Jönsson, and A. Nonat, "CSH/solution interface: Experimental and Monte Carlo studies," *Cement and Concrete research,* 41 [2] 161-68 (2011).
117. M. R. Meier, A. Rinkenburger, and J. Plank, "Impact of different types of polycarboxylate superplasticisers on spontaneous crystallisation of ettringite," *Advances in Cement Research,* 28[5] 310-19 (2016).
118. L. Nicoleau and M. A. Bertolim, "Analytical model for the alite (C3S) dissolution topography," *Journal of the American Ceramic Society* (2015).
119. L. Nicoleau and A. Nonat, "A new view on the kinetics of tricalcium silicate hydration," *Cement and Concrete Research,* 86, 1-11 (2016).
120. T. Sowoidnich, "A study of retarding effects on cement and tricalcium silicate hydration induced by superplasticizers," *University of Weimar* (2015).
121. C. Giraudeau, J. B. D'Espinose De Lacaillerie, Z. Souguir, A. Nonat, and R. J. Flatt, "Surface and intercalation chemistry of polycarboxylate copolymers in cementitious systems," *Journal of the American Ceramic Society,* 92 [11] 2471-88 (2009).
122. S. Ng and H. Justnes, "Influence of dispersing agents on the rheology and early heat of hydration of blended cements with high loading of calcined marl," *Cement and Concrete Composites,* 60, 123-34 (2015).

123. S. Pourchet, S. Liautaud, D. Rinaldi, and I. Pochard, "Effect of the repartition of the PEG side chains on the adsorption and dispersion behaviors of PCP in presence of sulfate," *Cement and Concrete Research,* 42 [2] 431-39 (2012).
124. X. Wang, Q. Ran, Y. Yang, X. Shu, and C. Yu, "Influence of Sequence Structure of Polycarboxylate Superplasticizers on Early Age Properties of Cement Paste," *Journal of Materials in Civil Engineering* 04016112 (2016).
125. D. Rinaldi, S. Pourchet, F. D'Agosto, Dalas F., I. Pochard, "Role of the microstructure of the PCP in the relationship to adsorption-dispersion", in *10^th^ Int. Conf. on Superplasticizers and other chemical admixtures in concrete*, Prague (CZ), Suppl. Papers, 188 (2012)
126. L. Zhang, L. J. Catalan, R. J. Balec, A. C. Larsen, H. H. Esmaeili, and S. D. Kinrade, "Effects of saccharide set retarders on the hydration of ordinary Portland cement and pure tricalcium silicate," *Journal of the American ceramic society,* 93 [1] 279-87 (2010).
127. C. Nalet and A. Nonat, "Effects of functionality and stereochemistry of small organic molecules on the hydration of tricalcium silicate," *Cement and Concrete Research,* 87, 97-104 (2016).
128. P. Roelfstra, H. Sadouki, and F. Wittmann, "Le béton numérique," *Materials and Structures,* 18 [5] 327-35 (1985).
129. H. M. Jennings and S. K. Johnson, "Simulation of microstructure development during the hydration of a cement compound," *Journal of the American Ceramic Society,* 69[11] 790-95 (1986).
130. E. Garboczi and D. Bentz, "Computer simulation of the diffusivity of cement-based materials," *Journal of materials science,* 27 [8] 2083-92 (1992).
131. P. Feng, E. J. Garboczi, C. Miao, and J. W. Bullard, "Microstructural origins of cement paste degradation by external sulfate attack," *Construction and building materials,* 96, 391-403 (2015).
132. D. P. Bentz, "Three- Dimensional Computer Simulation of Portland Cement Hydration and Microstructure Development," *Journal of the American Ceramic Society,* 80 [1] 3-21 (1997).
133. E. Samson, J. Marchand, K. Snyder, and J. Beaudoin, "Modeling ion and fluid transport in unsaturated cement systems for isothermal conditions," *Cement and Concrete Research,* 35 [1] 141-53 (2005).
134. N. S. Martys and J. G. Hagedorn, "Multiscale modeling of fluid transport in heterogeneous materials using discrete Boltzmann methods," *Materials and structures,* 35[10] 650-58 (2002).
135. N. S. Martys, "Study of a dissipative particle dynamics based approach for modeling suspensions," *Journal of Rheology (1978-present),* 49 [2] 401-24 (2005).
136. G. Constantinides and F.-J. Ulm, "The effect of two types of CSH on the elasticity of cement-based materials: Results from nanoindentation and micromechanical modeling," *Cement and concrete research,* 34 [1] 67-80 (2004).
137. C.-J. Haecker, E. Garboczi, J. Bullard, R. Bohn, Z. Sun, S. Shah, and T. Voigt, "Modeling the linear elastic properties of Portland cement paste," *Cement and Concrete Research,* 35 [10] 1948-60 (2005).
138. K. Maekawa, T. Ishida, and T. Kishi, "Multi-scale modeling of concrete performance," *Journal of Advanced Concrete Technology,* 1 [2] 91-126 (2003).
139. S. Bishnoi and K. L. Scrivener, "μic: A new platform for modelling the hydration of cements," *Cement and Concrete Research,* 39 [4] 266-74 (2009).
140. J. W. Bullard, E. Enjolras, W. L. George, S. G. Satterfield, and J. E. Terrill, "A parallel reaction-transport model applied to cement hydration and microstructure development," *Modelling and Simulation in Materials Science and Engineering,* 18 [2] 025007 (2010).
141. J. W. Bullard, B. Lothenbach, P. E. Stutzman, and K. A. Snyder, "Coupling thermodynamics and digital image models to simulate hydration and microstructure development of portland cement pastes," *Journal of Materials Research,* 26 [04] 609-22 (2011).
142. J. J. Thomas, J. J. Biernacki, J. W. Bullard, S. Bishnoi, J. S. Dolado, G. W. Scherer, and A. Luttge, "Modeling and simulation of cement hydration kinetics and microstructure development," *Cement and Concrete Research,* 41 [12] 1257-78 (2011).

143. J. S. Dolado, M. Griebel, and J. Hamaekers, "A molecular dynamic study of cementitious calcium silicate hydrate (C–S–H) gels," *Journal of the American Ceramic Society,* 90 [12] 3938-42 (2007).
144. T. Mueller, A. G. Kusne, and R. Ramprasad, "Machine learning in materials science: Recent progress and emerging applications," *Rev. Comput. Chem* (2015).
145. A. N. Tikhonov and V. Y. Arsenin, "Solutions of ill-posed problems," (1977).
146. A. E. Hoerl and R. W. Kennard, "Ridge regression: Biased estimation for nonorthogonal problems," *Technometrics,* 12 [1] 55-67 (1970).
147. W. S. McCulloch and W. Pitts, "A logical calculus of the ideas immanent in nervous activity," *The bulletin of mathematical biophysics,* 5 [4] 115-33 (1943).
148. D. F. Specht, "A general regression neural network. IEEE Transactions on Neural Networks," *vol,* 19, 1560-68 (1991).
149. S. K. Murthy, "Automatic construction of decision trees from data: A multi-disciplinary survey," *Data mining and knowledge discovery,* 2 [4] 345-89 (1998).
150. J. R. Koza, "Genetic programming: on the programming of computers by means of natural selection," Vol. 1. MIT press, (1992).
151. C. Long, J. Hattrick-Simpers, M. Murakami, R. Srivastava, I. Takeuchi, V. L. Karen, and X. Li, "Rapid structural mapping of ternary metallic alloy systems using the combinatorial approach and cluster analysis," *Review of Scientific Instruments,* 78 [7] 072217 (2007).
152. K. Fukunaga and L. Hostetler, "The estimation of the gradient of a density function, with applications in pattern recognition," *IEEE Transactions on information theory,* 21 [1] 32-40 (1975).
153. S. Z. Li, "Markov random field modeling in image analysis." Springer Science & Business Media, (2009).
154. R. Kindermann and L. Snell, "Markov random fields and their applications," (1980).
155. H. Abdi and L. J. Williams, "Principal component analysis," *Wiley Interdisciplinary Reviews: Computational Statistics,* 2 [4] 433-59 (2010).
156. M. L. Green, I. Takeuchi, and J. R. Hattrick-Simpers, "Applications of high throughput (combinatorial) methodologies to electronic, magnetic, optical, and energy-related materials," *Journal of Applied Physics,* 113 [23] 231101 (2013).
157. A. G. Kusne, T. Gao, A. Mehta, L. Ke, M. C. Nguyen, K.-M. Ho, V. Antropov, C.-Z. Wang, M. J. Kramer, and C. Long, "On-the-fly machine-learning for high-throughput experiments: search for rare-earth-free permanent magnets," *Scientific reports,* 4 (2014).
158. J. Behler, "Neural network potential-energy surfaces in chemistry: a tool for large-scale simulations," *Physical Chemistry Chemical Physics,* 13 [40] 17930-55 (2011).
159. C. C. Fischer, K. J. Tibbetts, D. Morgan, and G. Ceder, "Predicting crystal structure by merging data mining with quantum mechanics," *Nature materials,* 5 [8] 641-46 (2006).
160. E. W. Bucholz, C. S. Kong, K. R. Marchman, W. G. Sawyer, S. R. Phillpot, S. B. Sinnott, and K. Rajan, "Data-driven model for estimation of friction coefficient via informatics methods," *Tribology Letters,* 47 [2] 211-21 (2012).
161. Y. Lin, J. Zhang, and J. Zhong, "Application of neural networks to predict the elevated temperature flow behavior of a low alloy steel," *Computational Materials Science,* 43 [4] 752-58 (2008).
162. S. R. Kalidindi, S. R. Niezgoda, and A. A. Salem, "Microstructure informatics using higher-order statistics and efficient data-mining protocols," *Jom,* 63 [4] 34-41 (2011).
163. J. Simmons, P. Chuang, M. Comer, J. Spowart, M. Uchic, and M. De Graef, "Application and further development of advanced image processing algorithms for automated analysis of serial section image data," *Modelling and Simulation in Materials Science and Engineering,* 17 [2] 025002 (2008).
164. A. H. Gandomi, A. H. Alavi, and M. G. Sahab, "New formulation for compressive strength of CFRP confined concrete cylinders using linear genetic programming," *Materials and Structures,* 43 [7] 963-83 (2010).

165. E. Ozbay, M. Gesoglu, and E. Güneyisi, "Empirical modeling of fresh and hardened properties of self-compacting concretes by genetic programming," *Construction and Building Materials,* 22 [8] 1831-40 (2008).
166. A. Baykasoğlu, T. Dereli, and S. Tanış, "Prediction of cement strength using soft computing techniques," *Cement and concrete research,* 34 [11] 2083-90 (2004).
167. P. E. Stutzman, P. Feng, and J. W. Bullard, "Phase Analysis of Portland Cement by Combined Quantitative X-Ray Powder Diffraction and Scanning Electron Microscopy," *Journal of Research of the National Institute of Standards and Technology,* 121 47-107. (2016).
168. J. E. Devaney and J. G. Hagedorn, "Discovery in Hydrating Plaster Using Multiple Machine Learning Methods." pp. 47-58 in *Discovery Science*, Volume 2534, Springer, New York, 2002.
169. L. Wang, B. Yang, Y. Chen, X. Zhao, J. Chang, and H. Wang, "Modeling early-age hydration kinetics of Portland cement using flexible neural tree," *Neural Computing and Applications,* 21 [5] 877-89 (2012).
170. D. Cruz, D. A. Talbert, W. Eberle, and J. Biernacki, "A Neural Network Approach for Predicting Microstructure Development in Cement," pp. 328 in Proceedings on the International Conference on Artificial Intelligence (ICAI).
171. Y. Chen, B. Yang, J. Dong, and A. Abraham, "Time-series forecasting using flexible neural tree model," *Information sciences,* 174 [3] 219-35 (2005).
172. S. J. Russell, P. Norvig, J. F. Canny, J. M. Malik, and D. D. Edwards, "Artificial intelligence: a modern approach," Vol. 2. Prentice hall Upper Saddle River, (2003).
173. D. Landgrebe and L. Biehl, "MultiSpec©," *School of Electrical and Computer Engineering, Purdue University, West Lafayette, Indiana, USA* (2002).
174. H. Sakoe and S. Chiba, "Dynamic programming algorithm optimization for spoken word recognition," *IEEE transactions on acoustics, speech, and signal processing,* 26 [1] 43-49 (1978).
175. M. Rupp, A. Tkatchenko, K.-R. Müller, and O. A. Von Lilienfeld, "Fast and accurate modeling of molecular atomization energies with machine learning," *Physical review letters,* 108[5] 058301 (2012).
176. "Materials Genome Initiative". www.mgi.gov [Accessed 2016-09-13].
177. K. Sobolev, "Modern developments related to nanotechnology and nanoengineering of concrete," *Frontiers of Structural and Civil Engineering,* 10 [2] 131-41 (2016).
178. J. Hoheneder, I. Flores-Vivian, Z. Lin, P. Zilberman, and K. Sobolev, "The performance of stress-sensing smart fiber reinforced composites in moist and sodium chloride environments," *Composites Part B: Engineering,* 73, 89-95 (2015).
179. N. Banthia, "Fiber reinforced concrete for sustainable and intelligent infrastructure," pp. 337-50 in First International Conference on Sustainable Built Environment Infrastructures in Developing Countries, Algeria.
180. D. Nevers, J. Zhao, K. Sobolev, and G. Hanson, "Investigation of strain-sensing materials based on EM surface wave propagation for steel bridge health monitoring," *Construction and Building Materials,* 25 [7] 3024-29 (2011).
181. M. S. Konsta-Gdoutos and C. A. Aza, "Self sensing carbon nanotube (CNT) and nanofiber (CNF) cementitious composites for real time damage assessment in smart structures," *Cement and Concrete Composites,* 53, 162-69 (2014).
182. K. Sobolev and M. F. Gutiérrez, "How nanotechnology can change the concrete world," *American Ceramic Society Bulletin,* 84 [10] 14 (2005).
183. T.-C. Hou and J. P. Lynch, "Electrical impedance tomographic methods for sensing strain fields and crack damage in cementitious structures," *Journal of Intelligent Material Systems and Structures* (2008).
184. D. Chung, "Piezoresistive cement-based materials for strain sensing," *Journal of Intelligent Material Systems and Structures,* 13 [9] 599-609 (2002).
185. S. Wen and D. Chung, "Electrical-resistance-based damage self-sensing in carbon fiber reinforced cement," *Carbon,* 45 [4] 710-16 (2007).

186. D. Chung, "Cement-matrix composites for smart structures," *Smart materials and Structures,* 9[4] 389 (2000).
187. D. M. Addington and D. L. Schodek, "Smart materials and new technologies: for the architecture and design professions." Routledge, (2005).
188. S. Wen and D. Chung, "Piezoelectric cement-based materials with large coupling and voltage coefficients," *Cement and concrete research,* 32 [3] 335-39 (2002).
189. D. D. Chung, "Self-monitoring structural materials," *Materials Science and Engineering: R: Reports,* 22 [2] 57-78 (1998).
190. C. Stephens, L. Brown, and F. Sanchez, "Quantification of the re-agglomeration of carbon nanofiber aqueous dispersion in cement pastes and effect on the early age flexural response," *Carbon* (2016).
191. M. Etman, S. Shebl, A. Mosallam, and M. El-Dimerdash, "Effect of carbon nanotubes addition on mechanical properties of cement paste," in International conference on nano-technology for green and sustainable construction, Cairo-Egypt.
192. F. Sanchez and K. Sobolev, "Nanotechnology in concrete–a review," *Construction and Building Materials,* 24 [11] 2060-71 (2010).
193. C. Dumoulin, G. Karaiskos, J.-Y. Sener, and A. Deraemaeker, "Online monitoring of cracking in concrete structures using embedded piezoelectric transducers," *Smart materials and structures,* 23 [11] 115016 (2014).
194. A. M. Shelvay, "Reinforced concrete: applicability of smart materials." in. Massachusetts Institute of Technology, 2012.
195. B. Whitworth and H. Ryu, "A comparison of human and computer information processing," (2008).
196. R. B. Downs and F. Rider, "The Scholar and the Future of the Research Library; A Problem and Its Solution." in. JSTOR, 1945.
197. V. Mayer-Schönberger and K. Cukier, "Big data: A revolution that will transform how we live, work, and think." Houghton Mifflin Harcourt, (2013).
198. F. X. Diebold, "'Big Data'Dynamic factor models for macroeconomic measurement and forecasting," pp. 115-22 in Advances in Economics and Econometrics: Theory and Applications, Eighth World Congress of the Econometric Society,"(edited by M. Dewatripont, LP Hansen and S. Turnovsky).
199. N. Kulkarni and P. Puri, "Big Data Analytics – Business Benefits and Technical Challenges". *International Journal of Modern Computer Science and Applications* (IJMCSA), 3 [2] 19-24 (2015).
200. S. Kamila, "Introduction, classification and applications of smart materials: an overview," *American Journal of Applied Sciences,* 10 [8] 876 (2013).
201. D. A. Rade and V. Steffen Jr, "Introduction to Smart Materials and Structures," pp. 121-34. in Dynamics of Smart Systems and Structures**.** Springer, 2016.
202. B. Han, X. Guan, and J. Ou, "Electrode design, measuring method and data acquisition system of carbon fiber cement paste piezoresistive sensors," *Sensors and Actuators A: Physical,* 135[2] 360-69 (2007).
203. B. Han, Y. Yu, B. Han, and J. Ou, "Development of a wireless stress/strain measurement system integrated with pressure-sensitive nickel powder-filled cement-based sensors," *Sensors and Actuators A: Physical,* 147 [2] 536-43 (2008).
204. H. Xiao, H. Li, and J. Ou, "Modeling of piezoresistivity of carbon black filled cement-based composites under multi-axial strain," *Sensors and Actuators A: Physical,* 160[1] 87-93 (2010).
205. H. Xiao, H. Li, and J. Ou, "Strain sensing properties of cement-based sensors embedded at various stress zones in a bending concrete beam," *Sensors and Actuators A: Physical,* 167[2] 581-87 (2011).
206. E. Teomete, "The effect of temperature and moisture on electrical resistance, strain sensitivity and crack sensitivity of steel fiber reinforced smart cement composite," *Smart Materials and Structures,* 25[7] 075024 (2016).

207. X. Fu and D. Chung, "Self-monitoring of fatigue damage in carbon fiber reinforced cement," *Cement and concrete research,* 26 [1] 15-20 (1996).
208. J. Zhu, Y.-T. Tsai, and S.-H. Kee, "Monitoring early age property of cement and concrete using piezoceramic bender elements," *Smart Materials and Structures,* 20 [11] 115014 (2011).
209. Y. B. Lin, C. L. Pan, Y. H. Kuo, K. C. Chang, and J. C. Chern, "Online monitoring of highway bridge construction using fiber Bragg grating sensors," *Smart Materials and Structures,* 14 [5] 1075 (2005).
210. J. Makar, J. Margeson, and J. Luh, "Carbon nanotube/cement composites-early results and potential applications."
211. A. Peyvandi, L. A. Sbia, P. Soroushian, and K. Sobolev, "Effect of the cementitious paste density on the performance efficiency of carbon nanofiber in concrete nanocomposite," *Construction and Building Materials,* 48, 265-69 (2013).
212. M. S. Konsta-Gdoutos, Z. S. Metaxa, and S. P. Shah, "Multi-scale mechanical and fracture characteristics and early-age strain capacity of high performance carbon nanotube/cement nanocomposites," *Cement and Concrete Composites,* 32 [2] 110-15 (2010).
213. Z. S. Metaxa, M. S. Konsta-Gdoutos, and S. P. Shah, "Carbon nanofiber cementitious composites: effect of debulking procedure on dispersion and reinforcing efficiency," *Cement and Concrete Composites,* 36, 25-32 (2013).
214. F. Sanchez and C. Ince, "Microstructure and macroscopic properties of hybrid carbon nanofiber/silica fume cement composites," *Composites Science and Technology,* 69 [7] 1310-18 (2009).
215. J. Zhang, Y. Lu, Z. Lu, C. Liu, G. Sun, and Z. Li, "A new smart traffic monitoring method using embedded cement-based piezoelectric sensors," *Smart Materials and Structures,* 24 [2] 025023 (2015).
216. B. Han, X. Yu, and E. Kwon, "A self-sensing carbon nanotube/cement composite for traffic monitoring," *Nanotechnology,* 20 [44] 445501 (2009).
217. C. Vipulanandan and K. Ali, "Smart Cement Piezoresistivity Characterization with Sodium Metasilicate under Temperature and Curing Environments for Oil Well–Cementing," *Journal of Materials in Civil Engineering* 04016180 (2016).
218. C. P. Chen and C.-Y. Zhang, "Data-intensive applications, challenges, techniques and technologies: A survey on Big Data," *Information Sciences,* 275, 314-47 (2014).
219. J. Han, J. Pei, and M. Kamber, "Data mining: concepts and techniques." Elsevier, (2011).
220. B. Tooper and L. Cartz, "Structure and formation of magnesium oxychloride sorel cements," (1966).
221. G. C. Bye, "Portland cement: composition, production and properties." Thomas Telford, (1999).
222. P. J. Hart, "The Earth's crust and upper mantle: structure, dynamic processes, and their relation to deep-seated geological phenomena," Vol. 13. American Geophysical Union, (1969).
223. E. M. Gartner and D. E. Macphee, "A physico-chemical basis for novel cementitious binders," *Cement and Concrete Research,* 41 [7] 736-49 (2011).
224. P. K. Mehta, "Concrete. Structure, properties and materials," (1986).
225. R. Snellings, "Assessing, Understanding and Unlocking Supplementary Cementitious Materials," *RILEM Technical Letters,* 1, 50-55 (2016).
226. F. P. Glasser, G. Jauffret, J. Morrison, J.-L. Galvez-Martos, N. Patterson, and M. S.-E. Imbabi, "Sequestering CO2 by Mineralization into Useful Nesquehonite-Based Products," *Frontiers in Energy Research,* 4, 3 (2016).
227. J. Galvez-Martos, J. Morrison, G. Jauffret, E. Elsarrag, Y. AlHorr, M. Imbabi, and F. Glasser, "Environmental assessment of aqueous alkaline absorption of carbon dioxide and its use to produce a construction material," *Resources, Conservation and Recycling,* 107, 129-41 (2016).
228. J. Morrison, G. Jauffret, J. L. Galvez-Martos, and F. P. Glasser, "Magnesium-based cements for CO 2 capture and utilisation," *Cement and Concrete Research,* 85, 183-91 (2016).
229. “The Use of Lime Mortar in Historic Structures”. *CADW*, Wales, UK (2004).

230. O. Regnault, V. Lagneau, and H. Schneider, "Experimental measurement of portlandite carbonation kinetics with supercritical CO 2," *Chemical Geology,* 265 [1] 113-21 (2009).
231. Ö. Cizer, C. Rodriguez-Navarro, E. Ruiz-Agudo, J. Elsen, D. Van Gemert, and K. Van Balen, "Phase and morphology evolution of calcium carbonate precipitated by carbonation of hydrated lime," *Journal of Materials Science,* 47 [16] 6151-65 (2012).
232. A. Morandeau, M. Thiery, and P. Dangla, "Investigation of the carbonation mechanism of CH and CSH in terms of kinetics, microstructure changes and moisture properties," *Cement and Concrete Research,* 56, 153-70 (2014).
233. Q. Li, S. Gupta, L. Tang, S. Quinn, V. Atakan, and R. E. Riman, "A Novel Strategy for Carbon Capture and Sequestration by rHLPD Processing," *Frontiers in Energy Research,* 3, 53 (2016).
234. G. Sant, "unpublished".
235. S.-M. Shih, C. u.-S. Ho, Y.-S. Song, and J.-P. Lin, "Kinetics of the reaction of Ca (OH) 2 with CO2 at low temperature," *Industrial & Engineering Chemistry Research,* 38 [4] 1316-22 (1999).
236. J. G. Speight, "Lange's handbook of chemistry," Vol. 1. McGraw-Hill New York, (2005).
237. P. De Silva, L. Bucea, D. Moorehead, and V. Sirivivatnanon, "Carbonate binders: reaction kinetics, strength and microstructure," *Cement and Concrete Composites,* 28 [7] 613-20 (2006).
238. D. Aaron and C. Tsouris, "Separation of CO2 from flue gas: a review," *Separation Science and Technology,* 40 [1-3] 321-48 (2005).
239. M. Aranda and A. De la Torre, "Eco-efficient concrete: 18. Sulfoaluminate cement." Elsevier Inc. Chapters, (2013).
240. R. K. Dhir and T. D. Dyer, "Modern concrete materials: binders, additions and admixtures: proceedings of the international conference held at the University of Dundee, Scotland, UK on 8-10 September 1999." Thomas Telford, (1999).
241. S. H. Patterson, "Bauxite reserves and potential aluminum resources of the world." in. US Govt. Print. Off., (1967).
242. F. Bullerjahn, D. Schmitt, and M. B. Haha, "Effect of raw mix design and of clinkering process on the formation and mineralogical composition of (ternesite) belite calcium sulphoaluminate ferrite clinker," *Cement and Concrete Research,* 59, 87-95 (2014).
243. T. Hanein, M. S. Imbabi, F. P. Glasser, and M. N. Bannerman, "Lowering the carbon footprint and energy consumption of cement production: A novel Calcium SulfoAluminate cement production process."
244. J. L. Provis and J. S. J. Van Deventer, "Geopolymers: structures, processing, properties and industrial applications." Elsevier, (2009).
245. O. Burciaga-Díaz, L. Y. Gómez-Zamorano, and J. I. Escalante-García, "Influence of the long term curing temperature on the hydration of alkaline binders of blast furnace slag-metakaolin," *Construction and Building Materials,* 113 917-26 (2016).
246. R. J. Myers, S. A. Bernal, R. San Nicolas, and J. L. Provis, "Generalized structural description of calcium–sodium aluminosilicate hydrate gels: the cross-linked substituted tobermorite model," *Langmuir,* 29 [17] 5294-306 (2013).
247. I. García- Lodeiro, A. Fernández- Jiménez, A. Palomo, and D. E. Macphee, "Effect of calcium additions on N–A–S–H cementitious gels," *Journal of the American Ceramic Society,* 93 [7] 1934-40 (2010).
248. M. Criado, A. Fernández-Jiménez, and A. Palomo, "Alkali activation of fly ash. Part III: Effect of curing conditions on reaction and its graphical description," *Fuel,* 89 [11] 3185-92 (2010).
249. K. Quillin, "Performance of belite–sulfoaluminate cements," *Cement and Concrete Research,* 31 [9] 1341-49 (2001).
250. A. Chatterjee, "High belite cements—present status and future technological options: part I," *Cement and concrete research,* 26 [8] 1213-25 (1996).
251. K. Morsli, Á. G. De La Torre, S. Stöber, A. J. Cuberos, M. Zahir, and M. A. Aranda, "Quantitative Phase Analysis of Laboratory- Active Belite Clinkers by Synchrotron Powder Diffraction," *Journal of the American Ceramic Society,* 90 [10] 3205-12 (2007).

252. P. Guo, B. Wang, M. Bauchy, and G. Sant, "Misfit Stresses Caused by Atomic Size Mismatch: The Origin of Doping-Induced Destabilization of Dicalcium Silicate," *Crystal Growth & Design,* 16 [6] 3124-32 (2016).
253. J. Huang, B. Wang, Y. Yu, L. Valenzano, M. Bauchy, and G. Sant, "Electronic Origin of Doping-Induced Enhancements of Reactivity: Case Study of Tricalcium Silicate," *The Journal of Physical Chemistry C,* 119 [46] 25991-99 (2015).
254. E. Durgun, H. Manzano, R. Pellenq, and J. C. Grossman, "Understanding and controlling the reactivity of the calcium silicate phases from first principles," *Chemistry of Materials,* 24[7] 1262-67 (2012).
255. R. P. Crease and C. Westfall, "The New Big Science", *Physics Today,* 69 [5] 30-37 (2016).
256. K.-D. Liss and K. Chen, "Frontiers of synchrotron research in materials science," *MRS BULLETIN,* 41 (2016).
257. W. Bumrongjaroen, R. A. Livingston, D. A. Neumann, and A. J. Allen, "Characterization of fly ash reactivity in hydrating cement by neutron scattering," *Journal of Materials Research,* 24 [07] 2435-48 (2009).
258. A. J. Allen, J. J. Thomas, and H. M. Jennings, "Composition and density of nanoscale calcium–silicate–hydrate in cement," *Nature materials,* 6 [4] 311-16 (2007).
259. T. Proffen, K. L. Page, S. E. McLain, B. Clausen, T. W. Darling, J. A. TenCate, S.-Y. Lee, and E. Ustundag, "Atomic pair distribution function analysis of materials containing crystalline and amorphous phases," *Zeitschrift für Kristallographie-Crystalline Materials,* 220 [12] 1002-08 (2005).
260 "APS Upgade" [Online]. Available: https://www1.aps.anl.gov/aps-upgrade, [Accessed on 20 12 2016].
261. X. Liu and T.-C. Weng, "Synchrotron-based x-ray absorption spectroscopy for energy materials," *MRS Bulletin,* 41 [06] 466-72 (2016).
262. S. FitzGerald, D. Neumann, J. Rush, D. Bentz, and R. Livingston, "In situ quasi-elastic neutron scattering study of the hydration of tricalcium silicate," *Chemistry of materials,* 10 [1] 397-402 (1998).
263. T. Gutberlet, H. Hilbig, R. Beddoe, and W. Lohstroh, "New insights into water bonding during early tricalcium silicate hydration with quasielastic neutron scattering," *Cement and Concrete Research,* 51 104-08 (2013).
264. N. M. Nemes, D. A. Neumann, and R. A. Livingston, "States of water in hydrated C 3 S (tricalcium silicate) as a function of relative humidity," *Journal of Materials research,* 21 [10] 2516-23 (2006).
265. J. LaManna, D. L. Jacobson and D. Hussey, "Simultaneous X-ray and Neutron Computed Tomography Facility", *Nuclear Instruments and Methods* in press (2016).
266. D. L. Chichester, "Production and Applications of Neutrons Using Particle Accelerators," *Industrial Accelerators and Their Applications* 243 (2012).
267. Y. Inagaki, S. Mitsui, H. Makigaki, K. Idemitsu, T. Arima, T. Banba, and K. Noshit, "Measurement of HLW glass dissolution/alteration kinetics by using micro-reactor flow-through test method," pp. 219 in MRS Proceedings. Vol. 1193.
268. "Lightsources of the World." [Online]. Available: http://www.lightsources.org/regions, [Accessed on 20 12 2016].
269. "Neutron Sources," *NIST Center for Neutron Research,* (2016). [Online]. Available: https://www.ncnr.nist.gov/nsources.html, [Accessed on 20 12 2016].
270. D. Wollman, K. D. Irwin, G. C. Hilton, L. Dulcie, D. E. NEWBURY, and J. M. MARTINIS, "High- resolution, energy- dispersive microcalorimeter spectrometer for X- ray microanalysis," *Journal of Microscopy,* 188 [3] 196-223 (1997).
271. J. C. McComb, M. A. Coplan, M. Al-Sheikhly, A. K. Thompson, R. E. Vest, and C. W. Clark, "Noble gas excimer scintillation following neutron capture in boron thin films," *Journal of Applied Physics,* 115 [14] 144504 (2014).

272. Y. Wang and M. A. Nastasi, "Handbook of modern ion beam materials analysis." Materials Research Society Warrendale, Pennsylvania, (2009).
273. R. Livingston, J. Schweitzer, C. Rolfs, H. Becker, and S. Kubsky, "Characterization of the induction period in tricalcium silicate hydration by nuclear resonance reaction analysis," *Journal of Materials Research,* 16 [03] 687-93 (2001).
274. C. Ding, "Bright Coherent Ultrafast Tabletop Light Sources Development and the Application on EUV to Soft X-Ray Absorption Spectroscopy." in. University of Colorado, 2014.
275. W. Lerch and C. Ford, "Long-time study of cement performance in concrete," pp. 745-96 in Journal Proceedings. Vol. 44.
276. G. FROHNSDORFF and P. HARRIS, "USE OF DIGITAL TECHNIQUES IN THE PHASE ANALYSIS OF PORTLAND CEMENT BY X-RAY DIFFRACTION," pp. 320 in Analysis of Calcareous Materials: Comprising Compilation of Basic Methods of Analysis, and Papers (with Discussions) Read at a Symposium Held on 18-19 April, 1963, at the Imperial College of Science and Technology, London, SW 7.
277. R. Shahsavari and L. Chen, "Screw dislocations in complex, low symmetry oxides: core structures, energetics, and impact on crystal growth," *ACS applied materials & interfaces,* 7 [4] 2223-34 (2015).
278. R. Shahsavari, L. Tao, and L. Chen, "Structure, Energetics, and Impact of Screw Dislocations in Tricalcium Silicates," *Journal of the American Ceramic Society* (2016).
279. R. Shahsavari, L. Chen, and L. Tao, "Edge dislocations in dicalcium silicates: Experimental observations and atomistic analysis," *Cement and Concrete Research,* 90, 80-88 (2016).
280. N. Zhang, P. Carrez, and R. Shahsavari, "Screw Dislocation-Induced Strengthening-Toughening Mechanisms in Complex, Layered Materials: The Case Study of Tobermorite," *ACS Applied Materials & Interfaces* (2017).
281. S. Jalilvand and R. Shahsavari, "Molecular mechanistic origin of nanoscale contact, friction, and scratch in complex particulate systems," *ACS applied materials & interfaces,* 7 [5] 3362-72 (2015).
282. M. A. Rafiee, T. N. Narayanan, D. P. Hashim, N. Sakhavand, R. Shahsavari, R. Vajtai, and P. M. Ajayan, "Hexagonal boron nitride and graphite oxide reinforced multifunctional porous cement composites," *Advanced Functional Materials,* 23 [45] 5624-30 (2013).
283. N. Sakhavand, P. Muthuramalingam, and R. Shahsavari, "Toughness governs the rupture of the interfacial H-bond assemblies at a critical length scale in hybrid materials," *Langmuir,* 29 [25] 8154-63 (2013).
284. S. E. Moghaddam, V. Hejazi, S. H. Hwang, S. Sreenivasan, J. Miller, B. Shi, S. Zhao, I. Rusakova, A. R. Alizadeh, and K. H. Whitmire, "Morphogenesis of cement hydrate," *Journal of Materials Chemistry A* (2017).
285. R. Shahsavari, R. J.-M. Pellenq, and F.-J. Ulm, "Empirical force fields for complex hydrated calcio-silicate layered materials," *Physical Chemistry Chemical Physics,* 13 [3] 1002-11 (2011).
286. R. Shahsavari, M. J. Buehler, R. J. M. Pellenq, and F. J. Ulm, "First- principles study of elastic constants and interlayer interactions of complex hydrated oxides: Case study of tobermorite and jennite," *Journal of the American Ceramic Society,* 92 [10] 2323-30 (2009).
287. N. Zhang and R. Shahsavari, "Balancing strength and toughness of calcium-silicate-hydrate via random nanovoids and particle inclusions: Atomistic modeling and statistical analysis," *Journal of the Mechanics and Physics of Solids,* 96, 204-22 (2016).
288. "Crystallographic Database for Minerals," [Online]. Available: http://database.iem.ac.ru/mincryst/index.php, [Accessed on 20 12 2016].