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Critical National Need Idea Title

"Reduction of CO_2 emissions by more efficient cement production"

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Overview:

The **societal challenge** that this white paper addresses is the reduction of carbon dioxide emissions through sustainable and **cleaner chemical processing** of cement. The issue of carbon dioxide reductions justifies **government attention** because carbon dioxide emissions are a well documented contributor to global warming (Kyoto protocol summary http://www.eia.doe.gov/oiaf/kyoto/kyotorpt.html). Global warming is an area of **critical national need** that has been addressed through multiple government funded programs. The societal challenges that are not being addressed by reduction of CO_2 emissions are both current and predicted effects of global warming in the US. The problem of reductions is so vast that it requires significant government attention. Specifically the Obama-Biden administration has launched a comprehensive New Energy for America plan which will implement a program to reduce greenhouse gas emissions 80% by 2050. This plan has the goal of making the US a leader on climate change (http://www.whitehouse.gov/agenda/energy_and_environment/.)

The high risk, high reward **research and technical innovations** that could meet this challenge are the reduction of carbon dioxide emissions through more efficient production of cement. MIT researchers state “Cement is manufactured at the rate of 2.35 billion tons per year; enough to produce 1 cubic meter of concrete every person in the world. If engineers can reduce carbon dioxide emissions in the world’s cement manufacturing by even 10% that would accomplish one-fifth of the Kyoto Protocol goal of a 5.2 percent reduction in total carbon dioxide emissions.” (MIT Tech Talk Vol. 51, No. 17 2007, “Nanoengineering concrete could cut CO_2 emissions” Denise Behm)

Lynn Price and colleagues at Lawrence Berkeley National Labs (LBNL) report that “The production of cement, the primary component of concrete, accounts for a significant 5 to 10 percent of the world’s total carbon dioxide emission.” (http://ies.lbl.gov/node/233 **“**Carbon dioxide emissions from the global cement industry**”**Worrell, Ernst; Price, Lynn; Martin, Nathan; Hendriks, Chris; Ozawa Meida, Leticia Journal, Annual Reviews of Energy & the Environment, v: 26, issue: 8, 2001.

Technological **innovations** to reduce emissions during cement processing include nanoscale analysis of new replacement material, and more efficient process control of the chemical production process. The main area of research and innovation for cleaner chemistry during cement processing currently focuses on flyash and clinker replacement materials (CRMs). Flyash is defined in Cement and Concrete Terminology (ACI Committee 116) as "the finely divided residue resulting from the combustion of ground or powdered coal, which is transported from the firebox through the boiler by flue gases." CRMS are decarbonized, sintered and rapidly cooled limestone particles and are intermediate additives in cement manufacturing. Neither the morphology nor chemical composition of either material is understood on the scale which causes CO_2 emissions during cement production.

Constantines and Ulm from MIT have found that “The source of concrete’s strength and durability lies in the organization of its nanoparticles. The discovery [of new replacement material without CO_2 release] could one day lead to a major reduction in carbon dioxide emissions during manufacturing." (Constantinides, G., Ulm, F.-J., "The nanogranular nature of C-S-H", Journal of Mechanics and Physics of Solids Vol 55, January 2007).

Morphological and chemical analysis and subsequent quality control of flyash, and discovery of new CRMs hold the most potential for impacting CO_2 reduction. CRMs are largely amorphous and their behavior is not well understood. The amount of CRM used in the process is determined by the amount and quality of flyash added in a previous step. Both fundamental research for new materials and more efficient chemical process control have a need for data only attainable by chemical analysis and morphology at the submicron scale, as described in documents available through LaFarge Cement .(http://www.lafarge.com/wps/portal/3_2_5-Sciences_et_materiaux; Cement and Concrete Composites, **26** (8), 957-966 (2004) as well as Paul Stutzman at NIST "Scanning electron microscopy imaging of hydraulic cement microstructure" Paul Stutzman National Institute of Standards and Technology, Gaithersburg, MD 20899, USA).

Mapping Goals to national needs selection criteria

The **research and technologies** that need to be developed to reduce CO_2 emissions through more efficient and cleaner chemical processing of cement are described by NIST, LBNL, MIT and others. They include new processes, shift to low carbon fuels, application of waste fuels, increased use of additives in cement making, and alternative cements and CO_2 removal from flue gases in clinker kilns. The Battelle Analysis March 2002 ("Towards a Sustainable Cement Industry – an independent study commissioned by the World Business Council for Sustainable Development" www.wbcsd.org/web/publications/toward-a-sustainable-cement-industry.pdf) states that fundamental research needs to address the nanoscale particle analysis of flyash and CRMs. Once this is understood, the data can be used for 'feedforward' process control, as well as to provide nanoscale analysis of new materials used in cement processing. Since 5-10% of the global CO_2 emissions occur during cement processing, and since CRMs are the highest carbon producing components during cement processing, it is obvious that more efficient and innovative chemical processing of CRMS and the precursor flyash hold the highest chance for reduction of CO_2 emission.

Paul Stutzman at NIST, and scientists at LaFarge Cement (the world's largest cement manufacturer) have studied cement morphology, and found that flyash and CRMs are largely amorphous and their behavior is not well understood nor are the associated properties predictable. The composition on the macro, micro and even nano scale fluctuates and there are no raw materials standards in their composition. (Stutzman http://ciks.cbt.nist.gov/~garbocz/monograph/tablecontents.html, www.lafarge.com). The MIT group of Ulm and Constantinides, reported by Behm in MIT Techtalk states that nanoengineered concrete could cut CO_2 emissions.
Specifically the chemistry and morphology of particles and materials produced by processing would provide knowledge about the composition, subsequently reducing fluctuations during processing, and eventually providing feedforward information for

more efficient real time process control. And, a detailed offline chemical and morphological analysis on the nanoscale would allow development of new materials with greatly reduced composition fluctuations. In the January 2009 Journal of Mechanics and Physics of Solids, Ulm etal reports that “the source of concretes strength and durability lies in the organization of its nanoparticles. …If everything depends on the organizational structure of the nanoparticles that make up concrete, …we can conceivably replace it with a materials that has concrete’s other characteristics – strength, durability, mass availability and low cost – but does not release so much CO_2 into the atmosphere during manufacture.”

The goals map to the 3 critical national needs selection criteria as follows:

1. **Administration Guidance**

Documents such as the Kyoto Protocol and Batelle SWOT analysis, as well as academic publications such as the MIT Journal Tech Talk, have documented that reduction of CO_2 emissions is an essential element of reduction of global warming. LBNL, NIST and cement manufacturers including LaFarge Cement recognize that 5-10% of worldwide CO_2 emissions are a product of cement production. To the best of FEI’s knowledge there are no existing policies or funding programs that address this problem. At present, technologies are unavailable to do a complete morphological and chemical analysis of the submicron particles that are both critical components and polluting byproducts of cement processing. Analysis of shape, size, chemistry, phase distribution, etc at the submicron level is essential for both identifying new materials to replace the offending materials, as well as to provide real-time database driven information to do feed forward corrections on cement processing to reduce CO_2 emissions as the process exists today.

2. **Justifies Government Attention**

As shown in the following figures from the Battelle SWOT analysis, the annual growth rate of cement demand is increasing (Figure 1) and the United States is the one of the highest consumers of cement. (Figure 2).

Figure 1 Annual Growth Rate of Cement Demand

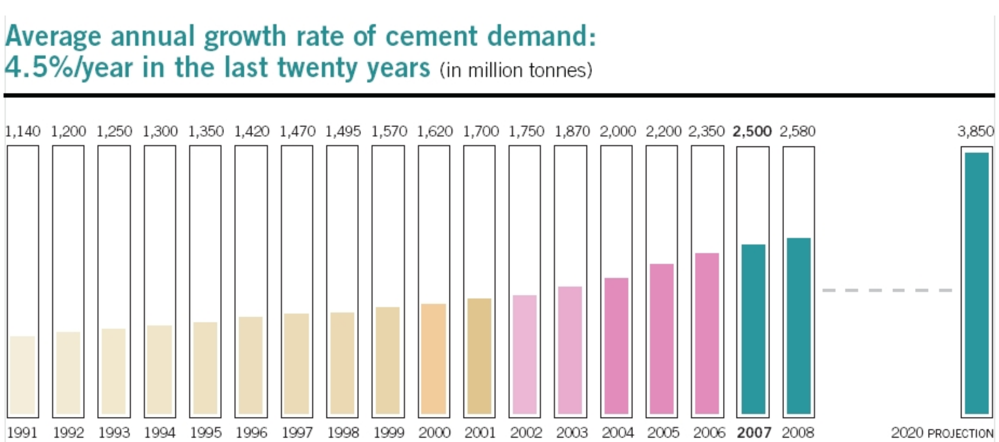
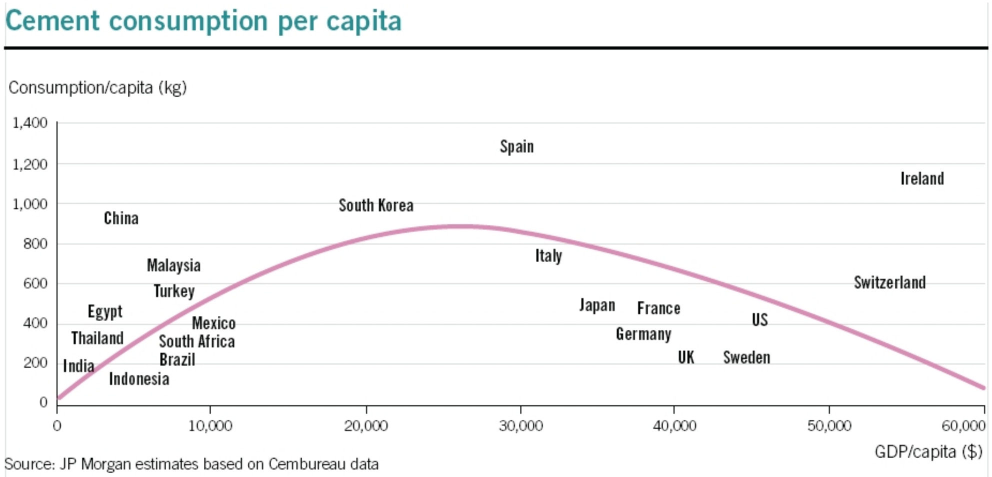
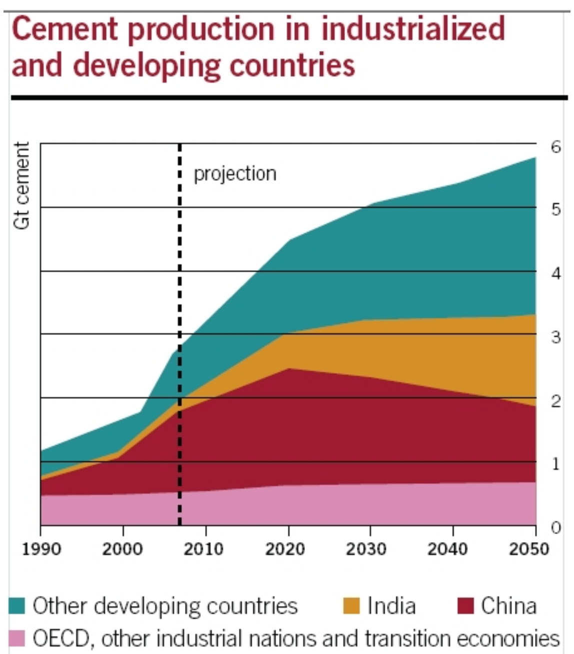


Figure 2 Cement Consumption per Capita



The production of cement (Figure 3) is growing concurrent to the growth of developing and industrial nations, which consequently continues to increase the amount of CO_2 emissions. The reduction of CO_2 emissions justifies government attention because the problems to solve and the impact to society are too vast to be addressed on a local level. The government has the resources to make a singular impact on global warming, (an international problem) by focusing on a major global contributor. Even the cement manufacturers such as LaFarge and Ashgrove recognize that improvement of the cement process has a global societal benefit. (www.ashgrove.com, www.lafarge.com)

Figure 3 Cement Production



Essentials for TIP Funding

Reduction of CO_2 emissions via cleaner chemical processing of cement is a **critical national need** that justifies **government attention** because the magnitude of the problem is large - world production of cement in 2007 totaled 2.6 billion tons (Battelle SWOT). The societal challenges of this problem can not be solved by individuals on a grassroots level, and thus require a top level approach funding high risk high reward research.

Reduction of CO_2 emissions during cement production requires **innovative collaborations in the United States between US nanotechnologists, national labs and endusers**. The innovation will be imbedded expertise of databases from NIST, LBNL Energy Lab, Michigan Tech Transportation Institute, applied to large scale chemical processing to reduce both a US and global problem of global warming.

This extremely **diverse approach** requires integration of imbedded learning from national research into onboard database assisted particle analysis - the end user takes the risk to incorporate and build from that knowledge into scale up process. The approach is t**ransformationa**l **–** if successful, the **reward** is cleaner chemical processing, via linking nanoscale information into macrochemical manufacturing for a cleaner environment. This will be a **disruptive change** to the current methods of impacting global warming (eg looking for alternative energy, creating and policing emissions and pollutants, encouraging grass roots efforts). The flip side to the diversity is that this problem doesn't fare well in the traditional peer review process due to the infrastructure gap between the researchers and the end users in the cement industry. The gap could be bridged by technology that imbeds the research learning in a very usable, realtime form for the cement manufacturers.

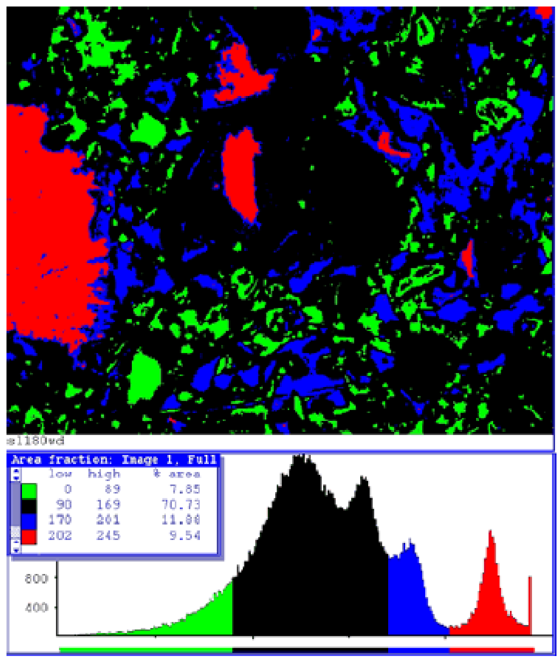
The fundamental research fits **within the area of NIST**, specifically the Building and Fire Research Laboratory's (BFRL) microstructure laboratory operated by Paul Stutzman. The equipment used in the lab includes a scanning electron microscope with energy dispersive x-ray analysis, computer image analyzer, light microscopy, and an automated x-ray powder diffractometer. Personnel at BFRL conduct research on the microstructural and chemical characterization of cement clinker, cement paste, cement paste/aggregate interfacial regions, high performance concrete, concrete, and mortar.

Tapping into the **nation's expertise at NIST**, LBNL, and MIT, for example, would stimulate further research into submicron events which have rapid benefits to the United States such as reduction of carbon dioxide emissions and consequently an impact on global warming. The **success or failure** of the approach to emission reduction will be a measure of how well the microstructural and chemical analysis of flyash and CRMs will impact the production of cement, thus a clean chemistry issue.

Although there are some internal research efforts being conducted by cement processors (www.lafarge.com and MIT) the impact to society is marginal. This is a result of the gap between fundamental research and the end users. A 'blackbox' approach which imbeds the research in such a way to be immediately useful to the enduser cement producers would bridge the gap.

The **risks are high** because the current technologies used to analyze the intermediate materials are slow but high resolution (electron microscopy and xray analysis), poor resolution but relatively fast (optical microscopy), and do not make use of the extensive libraries of information created by research institutes. The only existing technique that can resolve the phases in the amorphous materials depends on a qualitative estimate of gray scale information and is not quantitative. (Figure 3) Petrographic Methods of Examining Hardened Concrete: A Petrographic Manual Chapter 14, FHWA-HRT-04-150 written by Paul Stutzman, NIST http://www.fhwa.dot.gov/pavement/pccp/pubs/04150/chapt14.cfm.

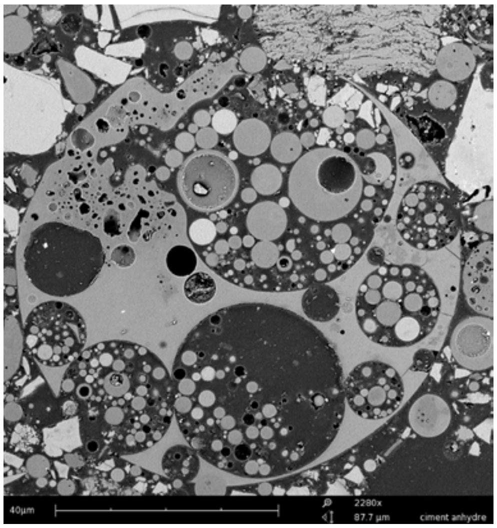
Figure 3 Pseudocolored image based on BE gray scale of figures 199 and 200 (red = residual cement, blue = CH, black = CSH, and green = coarse porosity).Counting the number of pixels for each color allows an **estimate** of the phase area fractions for this field of view.



The ideal tools to capture rapid morphological and chemical analysis of flyash and CRMs would be an electron microscope coupled with onboard chemical analysis such as xray analysis, correlated with an onboard database obtained from basic research a “cement data generator”). These **fundamental technologies** are the only way to evaluate the amorphous and reactive surfaces at the submicron level of the intermediate materials. At present only optical microscopy images the amorphous phases but lacks the resolution required to improve the chemistry of cement processing any further.

For example, Figure 4 is an SEM image of flyash and CRMS in cement (courtesy of FEI, www.fei.com). All of the spherical particles are flyash and the non-spherical particles are CRMS. The diameters range from several microns to below 1 micron. From the grey level intensity it is obvious that there is a large variation in chemical composition and hence also in reactivity which controls the surface chemistry. If the information in the SEM image was coupled with onboard databases and corresponding chemical analysis, the number to come out of an automated analysis is a measure for the reactivity and in the ideal case, a real time tool for quality control focused on reduction of CRMs and hence reduction in CO_2 emissions.

Figure 4 SEM image of flyash imbedded in cement, 2280x magnification



C. Barriers preventing the successful development of solutions

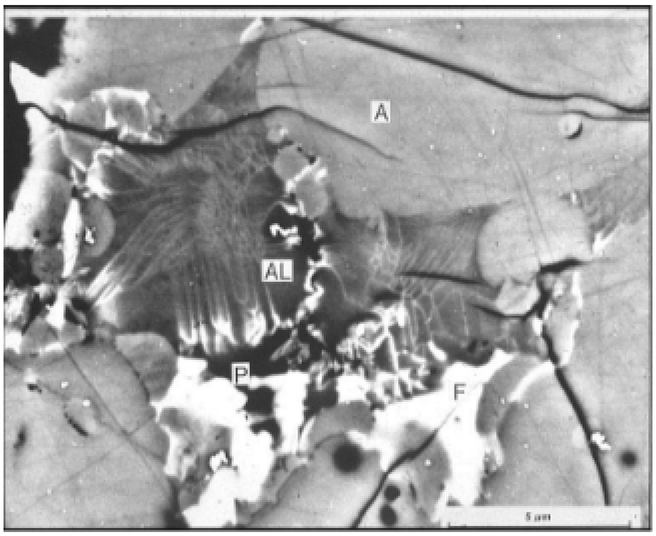
The current techniques used to analyze chemical components of cement processing include optical microscopy, x-ray analysis and electron microscopy. The typical flyash and CRM particles are 1-5 um in diameter, and one of the key areas of interest is the amorphous phase areas. However particle structure in the 30-70 nm regimes will ultimately determine the critical structure of materials (MIT, Behm).

According to Stutzman, NIST technical Note 1441, **optical microscopy** is "very time- and labour-consuming and attempts for its automation have failed so far. The results are also not accurate for the …minor phases…the phases can not be counted on…as the crystals are crushed to an average particle size of just a few micrometers during milling." Thus optical microscopy, though rapid, does not have the resolution required, or the chemical analysis capability.

Xray Analysis provides a measure of phase abundance and bulk chemical analysis but analysis of CRMs is difficult because the multiple phases of the material result in peak overlap, and there are no pure phase reference standards. Similarly the Rietveld method allows standardization of power diffraction and the ability to get crystal structure models, which may be related to phase abundance but it is slow, and inaccurate based on modeling not actual data. (Microstructure Analysis in Materials Science, Freiberg, June 15 – 17, 2005 1 Application of the Rietveld method in the cement industry, M. Paul Dyckerhoff AG., and Stutzman, NIST 1441).

Electron microscopy coupled with back scattered and secondary electron analysis provides high resolution on the nanometer scale which is the bulk xray limit. This is the only technique which can image phases not observable by optical microscopy. (Figure 5, from Stutzman, NIST)

Figure 5. SEM backscattered electron image of the interstitial phase of RM 8487 shows the inter-mixing of ferrite (F, bright phase) and aluminate (AL, dark) not observable by optical microscopy.



Thus the barriers to rapidly incorporating high resolution chemical analysis information of components of cement processing which determine the properties of the material are lack of a single easy to use ‘black box’ or a ‘cement data generator’.

Defined path to achieving the goals

A proposed path to achieve the goal of CO_2 emissions during cement processing is to create a ‘cement data generator’ where the output is data that allows stricter quality control of flyash and real time optimization of process parameters to reduce the amount of CO_2 producing CRMs. The first step would be to import existing databases and libraries of chemical analysis and morphological studies into an SEM. A tool manufacturer such as FEI would work closely with entities such as NIST, LBNL and MIT to develop reusable applications and software tools to imbed learning from basic research into a tool that could be deployed into manufacturing.

Once a prototype tool was developed, a cement manufacturer such as the US company Ashgrove would then take the tool and test it in the actual cement process.

Potential research partners include NIST's Paul Stutzman who is currently involved with a similar project for mineral liberation analysis in the mining industry. Paul is also a member of a member of ASTM C01. The ASTM C01 (Cement) Committee formed a task group to investigate quantitative X-ray powder diffraction analysis that resulted in the ASTM C 1365 standard test for X-ray powder diffraction of [standard] cement clinker and [standard] cement. ("Development of an ASTM Standard Test Method on X-Ray Powder Diffraction Analysis of Hydraulic Cements" Paul Stutzman, Proceedings of the 52nd Annual Denver X-Ray Conference, Steam Boat Springs, CO, August 4-7, 2003).

Larry Sutter at the Michigan Tech Transportation Institute is also a member of ASTM C01, ASTM C618 (Coal Fly Ash) and is a chair of the International Cement Microscopy Association (ICMA). His research has focused on the forensic analysis of concrete, concrete petrography, cement and clinker characterization, and advanced methods of materials characterization using microscopy and xray diffraction. (www.misti.mtu.edu/pdf/resume/lawrence_sutter_resume.pdf)

Another potential partner could be Lynn Price, LBNL Energy Analysis Department (http://industrial-energy.lbl.gov/node/29). She is a member of the China Energy group and is an expert on the cement-greenhouse connection. Her skills would be very valuable for analyzing the outcome of the a 'cement data generator' on the cement process.

The only US based SEM company is FEI (www.fei.com) in Oregon, although there are other non US SEM companies such as JEOL (www.jeol.com) , Hitachi (www.hitachi.com) and Zeiss (www.zeiss.com).

Ashgrove is the largest US cement company is the only US cement company to "join the World Business Council for Sustainable Development's Cement Sustainability Initiative. Sustainability means building for today and tomorrow without depleting future resources. It seeks to balance the economic, social, and environmental impacts of society's actions, recognizing that population growth will continue.Ash Grove management and other leaders in the cement industry believe concrete is an important product in achieving sustainable development." (www.lafarge.com) Thus they would be an ideal cement manufacturer to work with.

Additional feedback to NIST/TIP on how to improve the process for identifying societal challenges

Continue to embrace and support diverse partnerships – grass roots organizations may have ideas that could be incorporated into larger businesses with greater impact.