



# Concrete-A Great Challenge and Role of Nano-Materials



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Submission: 📅 September 11, 2018; Published: 📅 October 17, 2018

## Abstract

The improvement of concrete manufacturing is very essential for efficient utilization of natural resources. The major constituents of concrete are cement and steel. The strength of cement can be improved using Nano-sol of silica which can be generated as a byproduct from chlorination of red-mud. This will open an industrial use of red-mud which is not environmentally friendly. The corrosion of steel is being checked by passivation by chemical or electro-chemical oxidation. The cracks of the passive oxide layer on metal which is produced during fabrication can be healed with a paint produced from silicate, nitric acid and acetic acid.

## Introduction

Nanotechnology is one of the most active research areas for improvement of various technologies. Present day interesting challenging themes amongst many are increase of life of reinforced concrete and its strength. Concrete manufacturing is an age-old process though many attempts are there with some improvement. In general, life of concrete structure is limited to 600yr-800yr without any exotic coating. The technology needs lower level of environmental contamination, cost effectiveness and faster setting time with no deterioration of mechanical properties and should be accomplice through atomic level engineering. Concrete has two components-1) Cement 2) Iron/steel frame. Both have inherent demerits due to poor chemical properties. The hydration of cement produces a lot of micro-voids resulting poor mechanical properties and steel through its inherent corrosion with moisture and diffused oxygen reduces the strength of concrete gradually [1,2]. Cement is produced using enormous amount of fossil fuel generating bulk amount of greenhouse gas. This industry accounts for around 5 percent of global carbon dioxide (CO<sub>2</sub>) emissions. It produces a material so ubiquitous it is nearly invisible. Cement is the primary ingredient in concrete, which in turn forms the foundations and structures of the buildings, roads and bridges. Concrete is the second most consumed substance on earth after water. On average, each year, three tons of concrete are consumed by every person on the planet [3,4]. Concrete is used globally to build buildings, bridges, roads, runways, sidewalks, and dams. Cement is indispensable for construction activity, so it is tightly linked to the global economy. Its production is growing by 2.5 percent annually, and is expected to rise from 2.55 billion tons in 2006 to 3.7-4.4 billion tons by 2050.

## Manufacture of Cement

Though "cement" and "concrete" are often used interchangeably, concrete is actually the final product made from cement. The primary component of cement is CaCO<sub>3</sub> (limestone). To produce cement, limestone and other clay-like materials are heated in a kiln at 1400 °C forming 3CaO, SiO<sub>2</sub> (major) and 3CaO, Al<sub>2</sub>O<sub>3</sub> as lumpy solid substance called clinker; then grounding the clinker and combining with gypsum forms cement. Cement manufacturing is high energy- and emissions-intensive because of the extreme heat required to produce it. Producing a ton of cement requires 4.7 million BTU of energy, equivalent to about 400 pounds of coal, and generates nearly a ton of CO<sub>2</sub>. Given its high emissions and critical importance to society, cement is an obvious place to look to reduce greenhouse gas emissions. It is the great challenge to replace fossil fuel by either Hydrogen burner or efficient electrical furnace using power from nuclear plant. We have observed that microwave is also efficient using CaC<sub>2</sub>O<sub>4</sub> and fumed silica, but bulk production is difficult due to limit of the microwave oven. More over continuous production is difficult in this system. But it is the best option if right technology developed for mega sized micro-wave oven, because it is energy efficient and production rate is high.

One of the interesting developments in concrete-technology is the incorporation of nanomaterials particularly silica which has made a dramatic change in its strength [5-7]. But commercially availability of nanosilica is costly. However, use of diatomous-earth has been attempted but improvement is not that excellent as nano-silica due to its poor mechanical properties. Currently

cement particle sizes range from 50 nano-meter to 100 micrometers. A Portland cement particle has sizes less than 0.5 micron (500nm) as a cementing agent. Attempts have been made to improve the mechanical properties with a) Polycarboxylate polymer [8-10] b) Nanosilica [5-7] c) Nanocarbon allotropes (nano-tube and graphene) [11,12]. Nano-tube may have several millimeters in length having tube structure with single layer or multiple layers of carbon. Graphene is a single graphite sheet. It is also available with multiple layers. Carbon nano-tube is the stiffest and strongest fibers and it is till now the strongest fibre with flexibility. But all these applications of carbon allotropes are not commercially viable due to high cost. In that respect organic polymer is cheap but it needs further improvement. Through the detailed investigation it is found that Nano-Silica is better than silica (mostly sand) with outstanding improvement. It is saving 35-45% of cement. It can fill up all macro and micro pores improving compressibility of concrete and having high workability with reduced water/cement ratio. This admixture is very suitable for under water anti-wash out concrete. The higher dose of nano-silica produces self-compacting concrete and lower dose reduces water consumption. Poly acrylic acid or its derivative makes high range water reducing (HRWR) admixture. We found that for better mixing of polymer with the cement, ethanolamine or its higher analogs are very suitable. The low addition polymer (1 to 1.5% of cement weight) produces high resistance and with high proportion (>2.5%) produces self-compacting characteristics. Resistance to compression reaches 50-90MPa in one day and the value increases to 80-120MPa after 28 days. Addition of propylene glycol (<1%) accelerates the process through complex formation with  $\text{Ca}(\text{OH})_2$ . This introduces 70% less use of additives like traditional silica, super-plasticizer or traditional fibre meeting the norms of environmental protection. This protocol produces concrete having good workability with high initial and final compressive and tensile strength. It has also lower cost per building site. Moreover, the concrete with these protocols improves toughness, shear strength, tensile strength and flexural strength. It also introduces better bonding between aggregates and cement paste accelerating hydration. The well dispersed nano-particles of polymer or silica increase viscosity of liquidous phase improving the segregation and workability of concrete admixture.

It is well known that nano-silica is the most wonderful material in composite formation due to its high surface and more reactivity. In the concrete industry nano-silica has made a breakthrough introducing the increase of mechanical properties by 300% using particles of size 30nm or less. However, the industries are looking for lower manufacturing cost and safe handling. Handling of nanosilica is problematic because of low density of the powder. However, some industries are trying to sell as an admixture of cement and nano-silica. We found that bulk production of Ethyl orthosilicate can lower the cost of production if manufacturing is attempted from Red mud [13,14] using chlorination process producing  $\text{SiCl}_4$  (57.65C b.p),  $\text{AlCl}_3$  (180C b.p),  $\text{FeCl}_3$  (315C) and  $\text{TiCl}_4$  (136.4C b.p).  $\text{SiCl}_4$  and  $\text{TiCl}_4$  are liquids and can be separated easily from the mixture of products and finally by fraction distillation  $\text{SiCl}_4$  (major) and  $\text{TiCl}_4$  (minor) can be recovered independently.  $\text{SiCl}_4$  by simple

reaction with ethanol we get ethyl ortho-silicate and liberated HCl may be reused for chlorination. Otherwise  $\text{SiCl}_4$  can be decomposed with oxygen of air to produce  $\text{Cl}_2$  and nano-silica.  $\text{Cl}_2$  can be reused for generation of halide mixture. Red-mud is a great environmental problem of the aluminum industry throughout the globe and no suitable bulk use is available. Use of  $\text{TiO}_2$  from  $\text{TiCl}_4$  is very essential in the future due to fast depletion of Titanium minerals. We observed that Ethyl orthosilicate (10% in water) on hydrolysis gives a sol of  $\text{H}_4\text{SiO}_4$  or its condensed products. The sol can be stabilized with amino-silane (<0.5%). The material is highly efficient to replace nano-silica. As it will be a byproduct of chlorination so cost will be permissible. This material is very useful to make various classes of composite with other metal oxides.

The passivation of steel rods is an age-old process [15-18]. The people used many chemical reagents like  $\text{K}_2\text{Cr}_2\text{O}_7$ , nitric acid,  $\text{H}_2\text{O}_2$  and efficient passivation was done also by electrochemically in the presence of various electrolytes. So far amongst reported methods the best electrolyte is borate salt in alkaline condition. One major problem remains with the workability of efficient electrochemical methods. In construction sites the metal rods are deformed or scratched, and these cracks become seeds of corrosion. So, there is an immediate need for healing of cracks. We found that paint made of silicate, nitric acid and acetic acid generates a passive layer without any dissolution of the generating passive oxide layer. After cleaning with a dilute solution of soda-ash followed by a mild stream of water it can be safely imbedded in concrete structure. The protocol is under field testing. Last but not the least; major challenge lies with the availability of lime stone. However, it is expected to be solved through harnessing  $\text{Ca}(\text{OH})_2$  from sea water and development of high temperature heating systems without any emission of greenhouse gas.

### Acknowledgement

I am grateful to my university GLA University for financial support and other collaborating universities Jadavpur University (Salt Lake campus) Kolkata, Indian Statistical Institute, Department of Agriculture and Ecology Kolkata. I also express my thanks to Susmita Pradhan for helping me to write this manuscript.

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