

Review Article

Cement Types, Composition, Uses and Advantages of Nanocement, Environmental Impact on Cement Production, and Possible Solutions

S. P. Dunuweera ^{1,2} and R. M. G. Rajapakse ^{1,2}

¹Department of Chemistry, Faculty of Science, University of Peradeniya, Peradeniya, Sri Lanka

²Postgraduate Institute of Science (PGIS), University of Peradeniya, Peradeniya, Sri Lanka

Correspondence should be addressed to R. M. G. Rajapakse; rmgr@pdn.ac.lk

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We first discuss cement production and special nomenclature used by cement industrialists in expressing the composition of their cement products. We reveal different types of cement products, their compositions, properties, and typical uses. Wherever possible, we tend to give reasons as to why a particular cement type is more suitable for a given purpose than other types. Cement manufacturing processes are associated with emissions of large quantities of greenhouse gases and environmental pollutants. We give below quantitative and qualitative analyses of environmental impact of cement manufacturing. Controlling pollution is a mandatory legal and social requirement pertinent to any industry. As cement industry is one of the biggest CO₂ emitters, it is appropriate to discuss different ways and means of CO₂ capture, which will be done next. Finally, we give an account of production of nanocement and advantages associated with nanocement. Nanofillers such as nanotitania, nanosilica, and nanoalumina can be produced in large industrial scale via top-down approach of reducing size of naturally available bulk raw materials to those in the nanorange of 1 nm–100 nm. We mention the preparation of nanotitania and nanosilica from Sri Lankan mineral sands and quartz deposits, respectively, for the use as additives in cement products to improve performance and reduce the amount and cost of cement production and consequent environmental impacts. As of now, mineral sands and other treasures of minerals are exported without much value addition. Simple chemical modifications or physical treatments would add enormous value to these natural materials. Sri Lanka is gifted with highly pure quartz and graphite from which silica and graphite nanoparticles, respectively, can be prepared by simple size reduction processes. These can be used as additives in cements. Separation of constituents of mineral sands is already an ongoing process.

1. Introduction

This paper is an extended version of the Conference Paper published in the Proceedings of the 28th International Symposium on Transport Phenomena, 22–24 September 2017, Peradeniya, Sri Lanka [1]. As described in it, cement is a powdery substance made with calcined lime and clay as major ingredients. Clay used provides silica, alumina, and iron oxide, while calcined lime basically provides calcium oxide. In cement manufacturing, raw materials of cement are obtained by blasting rock quarries by boring the rock and

setting off explosives [2]. These fragmented rocks are then transported to the plant and stored separately in silos. They are then delivered, separately, through chutes to crushers where they are then crushed or pounded to chunks of ~1/2 inch-sized particles [3]. Depending on the type of cement being produced, required proportions of the crushed clay, lime stones, and any other required materials are then mixed by a process known as prehomogenization and milled in a vertical steel mill by grinding the material with the pressure exerted through three conical rollers that roll over a turning milling table. Additionally, horizontal mills inside which the

TABLE 1: Approximate composition of the cement clinker.

Compound	Formula	Notation	wt.%
Celite (tricalcium aluminate)	$\text{Ca}_3\text{Al}_2\text{O}_6$ [3CaO·Al ₂ O ₃]	C ₃ A	10
Brownmillerite (tetracalcium aluminoferrite)	$\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$ [4CaO·Al ₂ O ₃ ·Fe ₂ O ₃]	C ₄ AF	8
Belite (dicalcium silicate)	Ca_2SiO_4 [2CaO·SiO ₂]	C ₂ S	20
Alite (tricalcium silicate)	Ca_3SiO_5 [3CaO·SiO ₂]	C ₃ S	55
Sodium oxide	Na ₂ O	N	≤2
Potassium oxide	K ₂ O	K	
Gypsum (calcium sulphate dihydrate)	$\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ [CaO·SO ₃ ·2H ₂ O]	CSH ₂	5

Adapted from [2]; <http://www.engr.psu.edu/ce/courses/ce584/concrete/library/construction/curing/Composition%20of%20cement.htm>.

material is pulverized by means of steel balls are also used. It is then homogenized again and calcined, at 1400°C, in rotary kilns for the raw material to be transformed to a clinker, which is a small, dark grey nodule 3-4 cm in diameter. The clinker is discharged from the lower end of the kiln while it is red-hot, cooled by various steps, ground and mixed with small amounts of gypsum and limestone, and very finely ground to produce cement [4].

In the calcination process, in the kiln, at high temperatures, the above oxides react forming more complex compounds [5]. For instance, reaction between CaCO₃, Al₃(SiO₃)₂, and Fe₂O₃ would give a complex mixture of alite, (CaO)₃SiO₂; belite, (CaO)₂SiO₂; tricalcium aluminate, Ca₃(Al₂O₃); and ferrite phase tetracalcium aluminoferrite, Ca₄Al₂O₃Fe₂O₃ with the evolution of CO₂ gas in the Portland cement clinker [6]. However, there can be many other minor components also since natural clay also contains Na, K, and so on. In the chemical analysis of cement, its elemental composition is analyzed (e.g., Ca, Si, Al, Mg, Fe, Na, K, and S). Then, the composition is calculated in terms of their oxides and is generally expressed as wt.% of oxides. For simplicity, if we assume that the clinker contains the above four main oxides, they can be simply represented by the Bogue formulae where CaO, Al₂O₃, Fe₂O₃, and SiO₂ are denoted as C, A, F, and S, respectively [7]. In this notation, alite (tricalcium silicate) [(CaO)₃SiO₂], belite (dicalcium silicate) [(CaO)₂SiO₂], celite (tricalcium aluminate) [Ca₃Al₂O₆ = 3CaO·Al₂O₃], and brownmillerite (tetracalcium aluminoferrite) [Ca₄Al₂Fe₂O₁₀ = 4CaO·Al₂O₃·Fe₂O₃] are represented by C₃S, C₂S, C₃A, and C₄AF, respectively. If we analyze the elemental composition of Ca, Al, Fe, and Si, usually from X-ray fluorescence spectroscopy, then we express them as wt.% of their respective oxides. For example, if the experimentally determined clinker composition is CaO = 65.6%, SiO₂ = 21.5%, Al₂O₃ = 5.2%, and Fe₂O₃ = 2.8%, then Bogue calculations would give C₃S = 64.7%, C₂S = 12.9%, C₃A = 9.0%, and C₄AF = 8.5%, respectively [8]. However, cement contains water (H₂O), sulphate (SO₃), sodium oxide (Na₂O), potassium oxide (K₂O), gypsum (CaSO₄·2H₂O), which are denoted as H, S, N, K, and CSH₂, respectively. Note that gypsum (calcium sulphate dihydrate) is considered as CaO·SO₃·2H₂O and hence its notation is

CSH₂. As such, approximate composition of the cement clinker is different from the above values and is depicted in Table 1.

There are several different types of cements of which Portland cement, Siliceous (ASTM C618 Class F) Fly Ash, Calcareous (ASTM C618 Class C) Fly Ash, slag cement, and silica fume are the major types [9, 10]. They differ from their chemical composition. Table 2 gives the compositions of the above cement types in terms of SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO, and SO₃, and the remaining can be other materials such as Na₂O and K₂O. Note that SO₃ stands for oxide of S, where S is derived from gypsum (CaSO₄·2H₂O). Given in Table 2 are also important physical properties such as specific surface area (surface area per unit mass, SSA) and specific gravity (SG) of these different types of cements [11, 12].

General use of the Portland cement, Siliceous (ASTM C618 Class F) Fly Ash, Calcareous (ASTM C618 Class C) Fly Ash, slag cement, and silica fume in concrete is as primary binder, cement replacement, cement replacement, cement replacement, and property enhancer, respectively [16].

2. Types of Cements and Their Composition and Uses

There are over ten different types of cements that are used in construction purposes, and they differ by their composition and are manufactured for different uses. These are rapid-hardening cement (RHC), quick-setting cement (QSC), low-heat cement (LHC), sulphate-resisting cement (SRC), blast furnace slag cement (BFSC), high-alumina cement (HAC), white cement (WC), coloured cement (CC), pozzolanic cement (PzC), air-entraining cement (AEC), and hydrophobic cement (HpC). RHC has increased the lime content compared to the Portland cement (PC) [17, 18]. Purpose of having high lime content is to attain high strength in early days. It is used in concrete when formwork is to be removed early. Since hardening of cement is due to the formation of CaCO₃ by absorbing atmospheric CO₂ by CaO, increased CaO results in increased CaCO₃ formation even at the early stage to result in rapid hardening [19].

TABLE 2: Composition of components as wt.% used to make different types of cements.

Component	Portland cement	Siliceous fly ash	Calcareous cement	Slag cement	Fume silica
SiO ₂	21.9	52.0	35.0	35.0	85–97
Al ₂ O ₃	6.9	23.0	18.0	12.0	0
Fe ₂ O ₃	3.9	11.0	6.0	1.0	0
CaO	63.0	5.0	21.0	40.0	<1
MgO	2.5	0	0	0	0
SO ₃	1.7	0	0	0	0
SSA (m ² ·g ⁻¹)	0.37 Blaine	0.42 Blaine	0.42 Blaine	0.40 Blaine	15–30 BET
SG	3.15	2.38	2.65	2.94	2.22

SSA = specific surface area; SG = specific gravity. Adapted from [13–15].

QSC is produced by adding a small percentage of aluminium sulphate as an accelerator and reducing the amount of gypsum used with fine grinding. This cement is used when the work is to be completed very quickly as in static and running waters. LHC has reduced the amount of C₃A, which is used to produce massive concrete constructions like gravity dams. LHC has compressive strength to heat of the hydration ratio of at least 7 at the age of 13 weeks. The usual wt. ratio of CaO to SiO₂ is between 0.8 and 1.5, but Al₂O₃ wt.% is less than 10% [20]. This is prepared by grinding the CaO, SiO₂, and Al₂O₃ materials, melting the mixture, quenching the melt, and grinding the quenched matter to have mainly amorphous material of the above composition. Alumina is a hydratable material and reduced alumina gives reduced hydration to produce less heat of hydration. This is important in the construction of large structures to avoid possible thermal cracking during concrete setting [21].

Sulphate attack on concrete is a chemical breakdown mechanism, where sulphate reacts with C₃A and/or Ca(OH)₂ components of the hardened cement forming ettringite, which is hexacalcium aluminate trisulphate hydrate [(CaO)₆(Al₂O₃)(SO₃)₃·32H₂O = C₆ASH₃₂]. Sulphate ions can react with C₃A and/or Ca(OH)₂ in hardened concrete in the presence of water forming gypsum. These newly formed ettringite and gypsum crystals occupy empty spaces of concrete, and as they grow, they tend to damage the paste by cracking. The most important parameters determining the sulphate attack are C₃A, C₃S/C₂A ratio, and C₄AF. It has been reported that the addition of pozzolonic admixtures such as fly ash reduces the C₃A content of cement [22] when sulphate is present in water and soil used; in places like canal linings, culverts, retaining walls, and siphons, it is important to use SRC. SRC is prepared by maintaining C₃A content below 6%.

BFSC is prepared by grinding the clinkers with ~60% slag. BFSC resembles properties of the Portland cement and is used for works in which economic considerations are predominant. HAC is obtained by melting a mixture of bauxite and lime and grinding the mixture with the clinker. Since it contains high alumina content, it is rapid-hardening cement with initial and final setting times of about 3.5 h and 5 h, respectively [22]. HAC is used in works where concrete is subjected to high temperatures, frost, and acidic conditions. WC is prepared from raw materials free from iron oxides and oxides of other transition metals such as Cr, Mn, Cu, V, and Ti. The colouring effect takes the order

Cr₂O₃ > Mn₂O₃ > Fe₂O₃ > V₂O₃ > CuO > Ti₂O₃. As such, the amounts of these transition metal ions, particularly Cr³⁺, Mn³⁺, and Fe³⁺, should be minimized to form white cement. Usually, Cr₂O₃, Mn₂O₃, and Fe₂O₃ are kept below 0.003%, 0.03%, and 0.35%, respectively, in the clinker [23]. Cheap quarried raw materials usually contain Cr, Mn, and Fe. For example, lime stones and clays usually contain 0.3–1% and 5–15% Fe₂O₃. Keeping Fe₂O₃ below 0.5% is desirable to make WC, and as such, kaolin and sand are used instead of other clays in making WC. The abrasiveness of sand particles with size <45 μm also ensures less wearing of chrome-steel grinding mill used to grind raw materials, which would otherwise contaminate the mixture with Fe and Cr. Usually, sand is ground separately using ceramic grinding media to avoid chromium contamination. WC is costly and hence used in aesthetic applications such as precast curtain wall and facing panels and terrazzo surface. Contrary to WC, CC is prepared by deliberately adding mineral pigments to cement. CCs are widely used in decorative works on floors. Iron oxides are used to get red, yellow, and black base colours, and several mixed colours such as browns-terracotta-tuscany-sepia-beach. Standard green and blue pigments are chrome oxide and cobalt aluminium oxide, respectively. TiO₂ is the usual white pigment. PzC is prepared by grinding the pozzolanic clinker with the Portland cement [24]. It is used in marine structures, sewage works, and for laying concrete under water such as in bridges, piers, and dams.

AEC is produced by adding air-entraining agents that are surfactants such as alkali salts of wood resins, synthetic detergents of the alkyl-aryl sulphonate type, calcium lignosulphate derived from the sulphite process in paper making, and calcium salts of glues and other proteins obtained in the treatment of animal hides, animal and vegetable fats, oil and their acids, wetting agents, aluminium powder, and hydrogen peroxide, during the grinding of the clinker [25]. They are added in 0.025–0.1% in either solid or liquid form. At the time of mixing, AEC produces tough, tiny, discrete noncoalescing air bubbles of 10–500 μm in diameter in the body of the concrete. These bubbles can compress to some extent, and hence, they can absorb stress created by freezing.

HpC is prepared by adding water-repellent chemicals [26]. They are prepared particularly for use in high-rainfall regions to prevent water absorption during storage. Particles of HpC are coated with nonpolar substances, usually by

TABLE 3: Masses of emitted pollutants from the European cement kilns per year.

Pollutant	Mass emitted (tonnes per year)
CO ₂	1.5456 million
CO	460–11500
SO ₂	Up to 11125
NO _x as NO ₂	334–4670
Dust	0.62–522
TOC/VOC	2.17–267
HCl	0.046–46
HF	0.21–23.0
PCCD/PCDF	0.0000276–0.627 g per year

Adapted from <http://ena.lp.edu.ua:8080/bitstream/ntb/16692/1/55-Stajanca-296-302.pdf>.

adsorbing oleic acid, stearic acid, and so on, to cement particles [27, 28]. When adsorbed, these surfactant molecules self-assemble by coordinating with surface cations through their carboxylic acid groups thereby allowing the nonpolar hydrocarbon chain to extend from the particles. When a water drop falls on them, they are stuck on hydrocarbon chains and stay as spherical particles as does by the lotus leaf. The cement particles are then not wetted, and water drops roll off when slightly slanted. These hydrophobic coatings prevent the attacks by chloride and sulphate ions, and hence, they resist to deterioration of concretes by these ions [29].

3. Environmental Effects of Cement Manufacturing

Measured data of the European cement kiln emissions show that cement industry contributes substantially to environmental pollution. Table 3 lists main environmental pollutants emitted by the European cement kilns in tonnes per year.

TOC/VOC, PCCD, and PCDF indicate total organic compounds including volatile organic compounds, polychlorinated dibenzo-*p*-dioxins, and polychlorinated dibenzofurans, respectively. It has been reported that toxic metals such as Hg, Cd, Tl, As, Sb, Pb, Cr, Co, Cu, Mn, Ni, and V are also emitted in considerable amounts. For example, masses of Hg, Σ (Cd, Tl), and Σ (As, Sb, Pb, Cr, Co, Cu, Mn, Ni, V) emitted in kg per year are 0–1311, 0–1564, and 0–9200, respectively [30]. In addition to material pollutants, noise emission is also associated with almost all the processes involved in cement manufacturing. These environmental impacts contribute to abiotic depletion, global warming, acidification, and marine ecotoxicity [31].

Cement is produced by utilizing an extensive amount of raw materials treated and reacted at extreme conditions such as high temperatures. The high-temperature processes are called pyroprocessing processes where raw materials are heated at high temperatures for solid-state reactions to take place, which utilize fuel sources such as coal, fuel oil, natural gas, tires, hazardous wastes, petroleum coke, and basically anything combustible [32]. Some cement manufacturing plants utilize the organic waste generated in other industries

such as rubber processing industries. As such, cement industry contributes to a significant extent of anthropogenic carbon dioxide emissions, which is in the range of 5–7% of total anthropogenic carbon dioxide emissions [33]. In the clinker burning process, in order to produce 1 tonne of clinkers, 1.52 tonnes of raw materials are used on average. The balance of 0.52 tonne of raw materials is converted mainly to carbon dioxide by the processes such as $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$. This is a serious global environmental problem since increase in carbon dioxide in the atmosphere has direct consequences on global warming. In addition to CO₂, other key polluting substances emitted to air by the cement industry include dust, other carbon oxides such as carbon monoxide (CO), nitrogen oxides (NO_xs), sulphur oxides (SO_xs), polychlorinated dibenzo-*p*-dioxins, dibenzofurans, total organic carbon, metals, hydrogen chloride, and hydrogen fluoride, which are serious health-hazardous substances and some are hilariously odorous [34]. However, the type and amount of air pollution caused by the cement industry depend on various parameters, such as inputs (the raw materials and fuels used) and the type of process used in the industry.

As for water pollution, the contribution from cement industry may be insignificant through the storage and handling of fuels that may contribute to soil and ground-water contaminations [35]. In order to reduce the amount of raw materials, particularly in the manufacturing of specialized cement types as described above, supplementary cementitious materials such as coal fly ash, slag, and natural pozzolans such as rice husk ash and volcanic ashes are used. This will not only reduce the waste materials generated for landfilling but also the cost of cement production [36].

However, cement is an essential material for human survival nowadays. As such, there is no alternative, but the production of cement is mandatory. At the same time, controlling pollution created by cement industry is also very important. In the next section, we discuss ways and means of controlling pollution resulting from cement industries.

4. Pollution Control in Cement Manufacturing

The air pollution occurs in the excavation activities, dumps, tips, conveyer belts, crushing mills, and kilns of cement industry. Minimizing air pollution is a mandatory legislative requirement, which also contributes to minimizing wastage and survival of the industry [37]. Dust particles emitted at sites other than kilns can be captured using a hood or other partial enclosure and transported through a series of ducts to the collectors. The dust collected can be fed to the kiln provided that it is not too alkaline not exceeding 0.6% as per the Na₂O (N) content. However, if the alkalinity is higher than this value, then the dust must be either discarded or pretreated before feeding to the kiln. Flexible pulse jet filters, electrostatic precipitators, wet scrubbers, and baghouse method can be used to collect dust from flue gas [38]. The US Environmental Protection Agency has reviewed the available and emerging technologies for reducing greenhouse gas emissions from Portland cement industry. The primary greenhouse gas emitted in the cement industry is carbon

dioxide, but in lower quantities, NO_x s and SO_x s are also emitted as detailed in Table 3 [39].

4.1. Carbon Capture and Storage. This involves separation and capture of carbon dioxide from the flue gas, pressurization, and transportation via pipelines, injection, and long-term storage. In regard to this, several processes have been developed as detailed below.

4.1.1. Calera Process. This involves capture of CO_2 from flue gas and conversion to carbonates. This utilizes a scrubber containing high-pH water with calcium, magnesium, sodium, hydroxide, and chloride as the scrubbing liquid. CO_2 captured by this water is converted to CaCO_3 and MgCO_3 , which are precipitated out of the solution. The precipitates can be filtered, washed, and dried for reuse as feed material for the kiln to make blended cement. Water used may be seawater or reject brine. Capture efficiency of over 90% has been reported in a 10-MW coal-fired pilot plant. It is interesting to note that when captured carbon is reused, the overall carbon footprint becomes negative since the carbon emissions avoided from the cement manufacturing process could be greater than those of carbon emissions from the power plant [39, 40].

4.1.2. Oxy-Combustion Process. In the oxy-combustion process, fuel is burnt with pure or nearly pure oxygen instead of air. Since there is no nitrogen gas, the fuel consumption is reduced due to the fact that there is no need to heat and burn nitrogen gas. Since air contains nearly 79% nitrogen gas and any combusted nitrogen comes as NO_x in flue gas, the volume of flue gas and NO_x in it is significantly reduced when pure oxygen is used for combustion [39, 41]. This process should utilize an air separation process to separate out nitrogen gas, which can be used for other processes such as for inflating vehicle tires. Nitrogen-removed air basically contains majority of oxygen, and it can be used for the oxy-combustion process. When oxy-combustion is used, the resulting kiln exhaust contains over 80% CO_2 gas, which can be recovered by the Calera process. There are several technical issues as laid down in [42] that have to be tackled before implementing this process in cement industry.

4.1.3. Monoethanolamine (MEA) Process. When flue gas is passed through a column containing monoethanolamine, CO_2 gas is selectively absorbed. High-pressure, low-temperature conditions favour the absorption. When CO_2 -rich MEA solution is subjected to low-pressure, high-temperature conditions, it releases absorbed CO_2 which can be converted to some other product like CaCO_3 or MgCO_3 and the solvent recovered can be reused. One of the problems with this method is that acidic gases such as SO_x and NO_x present in the flue gas can react with MEA. Therefore, levels of these gases must be kept below 0.001% prior to absorption by MEA. Instead of regular amines, hindered amines can also be used. Hindered

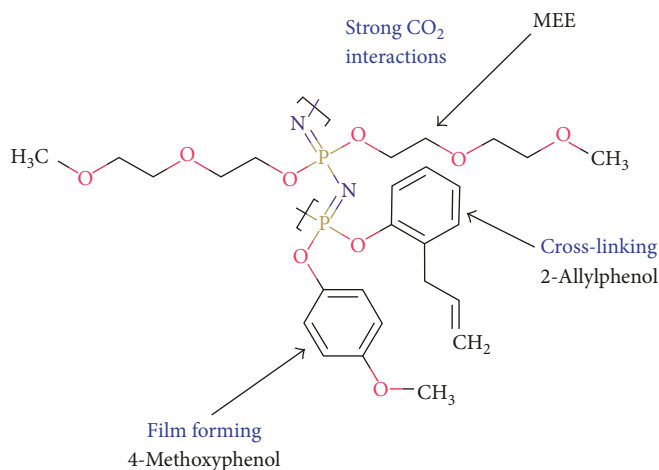


FIGURE 1: General structure of stabilized poly(methoxyethoxy) ethanol phosphazene hollow fibre membrane.

amines have special functional to prevent degradation of the amine [43].

4.1.4. Flue Gas Desulphurized Mixture. Flue gas contains SO_x , which could be separated using limestone-based compounds. They are then converted to slurries to use as CO_2 absorbents. This way, both SO_x and CO_2 can be removed from flue gas [43].

4.1.5. Cryogenic Distillation. Cryogenics is the science that addresses the production and effects of very low temperatures. In the cryogenic separation, all other gases except CO_2 and N_2 have to be removed prior to subjecting to low-temperature conditions. The triple point for CO_2 is 256.68°C and 7.4 atm, and when these conditions are maintained, CO_2 will condense while N_2 will remain as a gas. N_2 gas is then escaped through an outlet at the top of the chamber, and the dense liquid is taken from the bottom of the chamber. Refrigeration under pressure is an alternative method to cryogenic distillation but utilizes even harsh conditions such as higher pressures and lower temperatures. Cryogenic methods have distinct advantages over other separation methods. Since CO_2 is separated as a liquid, it can be transported via pipelines for sequestration. Also, the recovery and purity of CO_2 is very high (CO_2 purity after distillation can exceed 99.95%) [43].

4.1.6. Membrane Separation. Suitable membranes can be used to separate or adsorb CO_2 in the kiln exhaust gas. Poly(methoxyethoxy)ethanol phosphazene (MEEP) hollow fibre membranes are excellent CO_2 separation and storing membranes, where (methoxyethoxy)ethanol groups attached P have strong interactions with CO_2 [44–46]. One such example is given in Figure 1.

Polymer blends with required properties such as strong interaction with CO_2 can be used as CO_2 -selective membranes. For example, cross-linked thin-film composite of poly(vinylalcohol) (PVA)/polyvinylpyrrolidone (PVP) blend

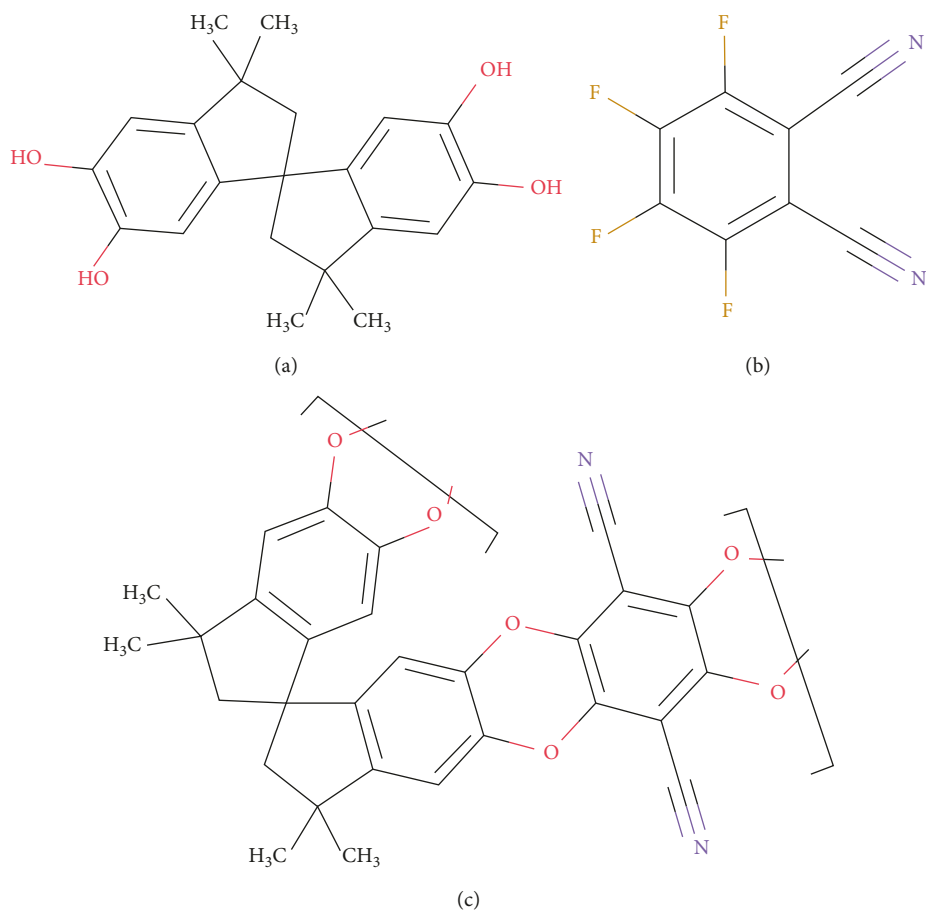


FIGURE 2: Chemical structures of (a) 5,5,6,6-tetrahydroxy-3,3,3,3-tetramethylspiro-bisindane, (b) tetrafluorophthalonitrile, and (c) polycondensate polymer PIM-1 [49].

membranes doped with suitable amine carriers are excellent CO_2 -selective membranes as reported by Mondal and Mandal. The CO_2 permeability of this membrane is 1396 Barrer at 2.8 atm and 100°C [47]. Combination of grafting and cross-linking is an advanced technique capable of suppressing plasticization. In this respect, Achoundong et al. developed cellulose acetate (CA) membranes and grafted vinyl-trimethoxysilane (VTMS) to $-\text{OH}$ groups, which due to subsequent condensation of hydrolyzed methoxy groups on the silane form cross-linked polymer networks. The modified membranes have an order of magnitude higher CO_2 permeability than neat cellulose acetate membranes [48].

Polymers of intrinsic microporosity (PIMs), thermally rearranged polymers (TRPs), polyimides, and polyurethanes are advanced polymers with high selectivity for CO_2 and hence are suitable membranes for CO_2 separation. PIMs are ladder polymers with high free volume and high selectivity for CO_2 . These ladder polymer backbones can be prepared by polycondensation reaction of tetrahydroxy monomers containing spiro- or contorted centres with tetrafluoromonomers. One such example is the PIM-1 prepared by the polycondensation reaction of commercial monomers such as 5,5,6,6-tetrahydroxy-3,3,3,3-tetramethyl-1,1'-spiro-bisindane with tetrafluorophthalonitrile. Chemical structures of the monomers are given in Figure 2.

These polymers have high CO_2 solubility and spirocentres, such as thianthrene [50], 9,10-dimethyl-9,10-dihydro-9,10-ethanoanthracene [51], ethanoanthracene [52], and pyrazine [53], and could be incorporated in PIM membranes for adjusting the gas permeation properties.

Thermally rearranging polymers (TRPs) are prepared by a thermal postmembrane conversion process of functionalized polyimides. They have uniform cavities with tailored free-volume elements with well-connected morphology in the amorphous state [54]. For example, thermal rearrangement of poly(hydroxyimide)s is shown in Figure 3.

TRPs have good CO_2/CH_4 separation performance, good resistivity to CO_2 -induced plasticization, and high chemical resistivity [55].

4.2. Adsorption of CO_2 into Advanced Sorbents. Separation of CO_2 from a gas mixture by selective adsorption involves both thermodynamics (adsorption) and kinetics (diffusion selectivity), and designing adsorbents for CO_2 in the presence of gases such as CH_4 and N_2 is challenging since all three gases have similar kinetic diameters of 3.30 Å, 3.76 Å, and 23.64 Å, respectively [55]. In this sense, sorbents such as zeolites and metal-organic frameworks (MOFs) stand out as adsorbents of CO_2 .

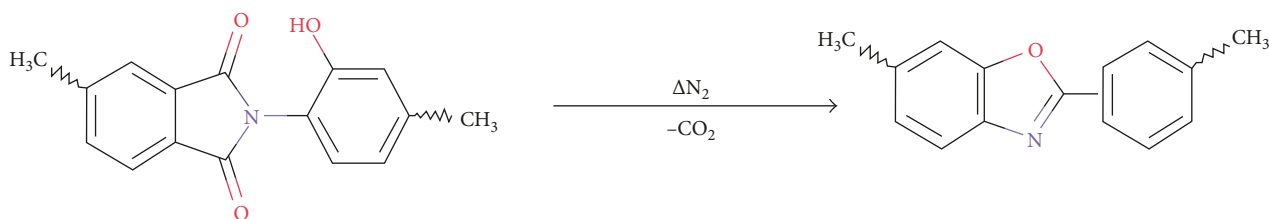
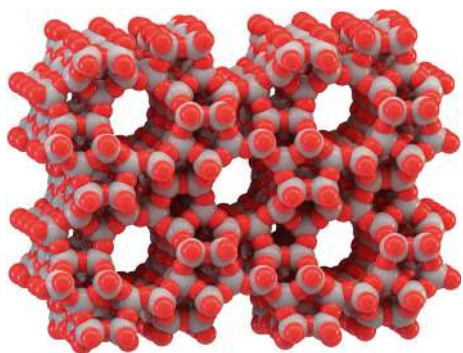


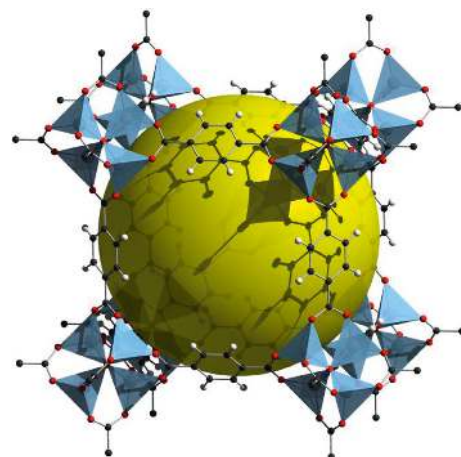
FIGURE 3: Thermal rearrangement of poly(hydroxyimide)s.

FIGURE 4: The microporous molecular structure of zeolite, ZSM-5. (Thomas Spletstoeser (www.scistyle.com), own work, CC BY-SA 4.0, File:Zeolite-ZSM-5-vdW.png (created: 23 June 2015); <https://en.wikipedia.org/wiki/Zeolite> (accessed: June 11, 2017)).

4.3. *Zeolites*. Zeolites are microporous aluminosilicate minerals such as analcime, chabazite, clinoptilolite, heulandite, natrolite, phillipsite, and stilbite. Figure 4 shows the microporous molecular structure of zeolite, ZSM-5. Synthetic zeolites are prepared by the slow crystallization of a silica-alumina gel in the presence of alkalis and organic templates.

Zeolites are added to the Portland cement as a pozzolan and water reservoir to reduce chloride permeability and to improve workability. Siriwardane et al. have studied competitive gas adsorption properties of zeolites 13X, 4A, 5A, UOP-WE-G 592, and UOP APG-II with gas mixtures containing CO₂ and found that all of them have good CO₂ adsorption capacities down to ppm levels from a gas mixture containing 15% CO₂, 3% O₂, and 83% N₂ [56]. Zeolites are microporous and aluminosilicate minerals commonly used as commercial adsorbents. Zeolite has been used for trapping CO₂ from ice or air [57]. A zeolite trap was also used as an alternative to a cryogenic trap for collecting CO₂ from oxidation of organic carbon. The selective gas absorption and desorption characteristics of zeolite as a function of temperature will be useful for simplifying the system for trapping CO₂ and transferring the gas to a graphitization reactor [58].

4.4. *Metal Organic Frameworks (MOFs)*. Metal organic frameworks (MOFs) are yet another good sorbents for CO₂. Their structures are composed of metal-containing nodes linked by organic ligand bridges, which are assembled through strong coordination bonds (Figure 5) [59].

FIGURE 5: An example for MOF: MOF-5. Large pore is shown with the yellow ball (Tony Boehle, own work: https://en.wikipedia.org/wiki/Metal-organic_framework#/media/File:IRMOF-1_wiki.png).

Compared to other CO₂ sorbents such as zeolites and activated carbon, MOFs have higher pore volume and surface area and hence have higher CO₂ sorption capacity [60, 61]. Adsorption is the process of entrapping atoms or molecules which are incident on a surface; hence, the adsorption capacity of a material concerned increases with respect to its surface area. In 3D nature, the maximum surface area would be obtained by a structure that is highly porous such that molecules and atoms can access internal surfaces of the materials. It clearly suggests that the highly porous metal organic frameworks (MOFs) should have to have an excellent ability of entrapping CO₂. Generally, the most successful MOFs demonstrate extremely high BET surface areas of 4,000–7,000 m²·g⁻¹ with many also possessing coordinatively unsaturated metal sites [62]. In order to gain high efficiency of CO₂ entrapment inside the MOF and for the development of higher performance MOFs, the interior part of MOFs should be designed to have coordinative porosity, hydrophobicity, defects and embedded nanoscale metal catalysts, unsaturated metallic suitable sites, specific heteroatoms, and other building unit interactions [63]. Some examples of MOFs capable of CO₂ sorption are Ni^{II}₂Ni^{III}(μ₃-OH)(pba)₃(2,6-ndc)_{1.5} (MCF-19; pba = 4-(pyridin-4-yl)benzoate, 2,6-ndc = 2,6-naphthalenedicarboxylate), Zn₄O(bdc)₃ (MOF-5 or IRMOF-1, bdc = 1,4-benzenedicarboxylate), Zn₄O(btb)₂ (MOF-177, btb = benzene-1,3,5-tribenzoate), and Zn₄O(bte)_{14/9}(bpdc)_{6/9} (MOF-210, bte = 4,4,4-(benzene-1,3,5-triyltris(ethyne-2,1-diyl))tribenzoate, bpdc = biphenyl-4,4-dicarboxylate) [64–66].

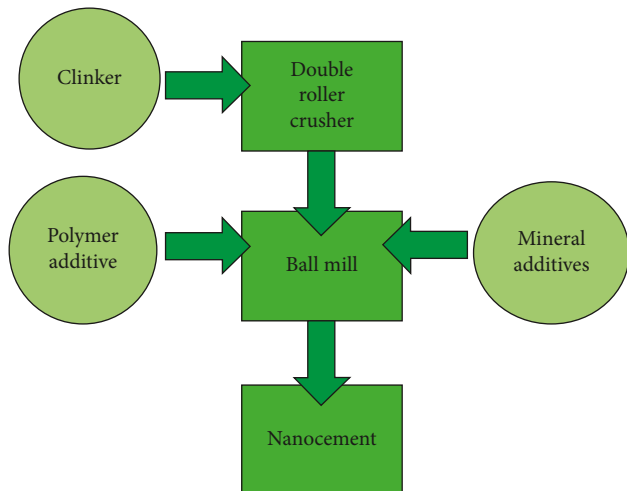


FIGURE 6: Schematic representation of the nanocement production process.

5. Nanocement

Nanocement is the cement produced by mechanical activation of nuclear cement particles in the size range 2–3 μm by coating with 10 to 100 nm-thick membranes of modifier materials. More than 65% of mineral supplements such as sand, ash, slag, and tuff and polymer additives are used as modifier materials [67]. The development of modern cement and concrete industry seeks for the improvement of the durability of the materials by the addition of required amount of nanoparticles, or nano-based structure of cement-based materials can be improved. Frequently used nanoparticles are nanosilica, nanoclay, and carbon nanotubes [68, 69]. Improvement of durability of the materials is approached through alteration of the physicochemical properties of the binder. In addition, usages of nanoclay and carbon nanotubes can decrease the transport property, optimize microstructure, and decrease the volume instability of cement-based materials. The process of nanocement production is shown schematically in Figure 6. It has been reported that nanocement can be used to produce 500–800 brands of high-strength concretes and 1300–1500 brands of heavy-duty concretes [70]. “US Patent on Method for producing nano-cement, and nano-cement” [71] deals with the procedure developed to produce nanocement, which involves mechanochemical activation of dispersed grains of the Portland cement in the presence of a polymeric modifier. They used at least 60% by wt. of sodium naphthalenesulfonate and mineral siliceous additive containing at least 30 wt.% SiO_2 and gypsum to form nanoshells around cement grains. Capsules of 20–100 nm thickness are formed around Portland cement grains, which are made of sodium naphthalenesulfonate and structured by calcium cations. Subsequent to mechanochemical activation, the resultant material is ground to a specific surface area of 300–900 $\text{m}^2\cdot\text{kg}^{-1}$. Nanocement improves the technical quality of the Portland cement, reduces cost of production due to the use of 70 wt.% mineral additives, 1.2–2 times reduction of the fuel cost, and

2–3 times reduction of emission of NO_x , SO_2 , and CO_2 per tonne of cement. Nanocement has very high performance; for instance, the deflection strength of nanocement-based concrete and ordinary Portland cement-based concrete at 2-day hardening are around 6.3–7.1 MPa and 2.9 MPa with corresponding compressive strengths of 49.3–54.7 MPa and 21.3 MPa, respectively. At 28-day hardening, deflection strength improves to 8.2–8.7 MPa and 6.4 MPa, respectively, while compressive strength improves to 77.5–82.7 MPa and 54.4 MPa, respectively [72].

Use of nano-graphite as an additive in cement is also currently under investigation. Use of graphite nanoparticles in cement is expected to not only improve mechanical properties but also improve faster curing time, inhibition of premature failure in concretes, and ability to withstand large external forces produced in earthquakes and explosions [73]. The use of less concrete is also possible which means eventual contribution to the production of less Portland cement and hence reduction of consequent environmental problems associated with Portland cement manufacturing [74]. Other nanofillers used to improve properties of Portland cement include nanotitania (TiO_2), carbon nanotubes, nanosilica (SiO_2) and nanoalumina (Al_2O_3), nanohematite/iron oxide (iii) (Fe_2O_3), nano-magnetite/iron oxide (ii) (Fe_3O_4), nano- ZnO_2 , nano- ZrO_2 , nano- Cu_2O_3 , nano- CuO , nano- CaCO_3 , as nanotubes or fibres (carbon nanotubes and carbon nanofibers, and nano-clay).

According to the Feldman–Sereda model, the cement paste consists principally of gel pores, capillary pores, and an interlayer of water. In the concrete, there is an interfacial transition zone between the cement paste and the aggregates, which establishes a weak link in the concrete, basically the site at which the first cracks occur. Hence, it is significant to generate crack-free concrete with the possible incorporation of nanosilica to pursue [75]. Chen et al. demonstrated that TiO_2 is an inert and stable compound during the cement hydration process, in which the total porosity of the cement pastes decreased, so that the pore size distribution is also changed. Normally, the acceleration of the hydration rate and the change in the microstructure also affected the physical and mechanical properties of the cement-based materials. The nano- TiO_2 role is to work as a catalyst in the cement hydration reactions. Water absorption and capillary absorption show a significant decrease when TiO_2 nanoparticles are included in the concrete, as the nanoparticles represent as nanofillers and thereby improve the concrete’s resistance to water permeability. Moreover, TiO_2 nanoparticles can progress the filler effect, and also the great pozzolanic action of fine particles substantially rises the quantity of strengthening gel formed [76]. Nanomontmorillonite (NM) is the most common member of the smectite clay family, which is sometimes referred to as nanoclay. This kind of clay belongs to a general mineral group of clays, which have particles with a sheet-like structure in which the dimensions in two directions far exceed the thickness.

We have investigated the production of these nanoparticles from both top-down and bottom-up approaches. Top-down approach is more industrially viable since large quantities of bulk materials found naturally can be used to

produce corresponding nanomaterials through particle size reduction. The top-down approach relies on reducing the size of bulk materials to the size of the nanorange of 1–100 nm. This can be done by crushing bulk materials to make powders, sieving to different fractions, further crushing of large size fractions, and finally milling to obtain sizes in the nanorange. Sri Lanka is gifted with very high-purity quartz, which contains almost 100% SiO₂. This quartz can be used to obtain nanosized SiO₂ particles. Our ongoing research in collaboration with the Sri Lanka Industrial Technology Institute (ITI) is very successful, and we are able to produce 50 nm size SiO₂ nanoparticles in large quantities by this top-down approach. We have also attempted converting ilmenite obtained from Sri Lanka Mineral Sand Corporation to produce nanotitania with great success. Birgisson et al. [77] summarized the key breakthroughs in concrete technology most probable to result from the usage of nanotechnology. Basically, it has shown the development of high-performance cement and concrete materials as measured by their mechanical and durability properties, development of sustainable concrete materials and structures through engineering for different adverse environments, reducing energy consumption during cement production and enhancing safety, improvement of intelligent concrete materials through the integration of nanotechnology-based self-sensing and self-powered materials and cyber infrastructure technologies, advancement of novel concrete materials through nanotechnology-based innovative processing of cement and cement paste, and also development of fundamental multiscale model(s) for concrete through advanced characterization and modeling of concrete at the nano-, micro-, meso-, and macroscale [78]. The frost resistance of concrete comprising nano-Al₂O₃ is better than that comprising the same amount of nano-SiO₂. The compressive strength of normal concrete containing nano-SiO₂ is higher than that of the same amount of nano-Al₂O₃. The frost resistance of the concrete mixtures can be improved significantly by adding either nano-Al₂O₃ or nano-SiO₂. These nanomaterials not only promote the pozzolanic reaction, but they also act as fillers, thereby improving the pore structure of the concrete and densifying the microstructure of the cement paste. The frost resistance of the concrete containing nano-Al₂O₃ is better than that containing the same amount of nano-SiO₂.

Nanoparticles have a large surface area to volume ratio than their bulk counterparts, and due to their small size, they can fill in small cavities of the cement matrix, densifying the structure to result in improved strength and faster chemical reactions such as hydration reactions associated with cement setting. Further, the material requirement can be reduced drastically thus saving fast depleting natural resources and energy requirements for cement manufacturing and reducing associated adverse environmental consequences.

6. Conclusion

Basically, different types of cements and their chemical composition and applications in the current engineering and chemical world have been discussed in detail. Different types

of enhancing materials and fillers developed using nanotechnology for the productive and effective cement manufacturing have been mentioned with the chemical background. The mechanical defects when concrete is concerned and possible solutions that can be given through chemistry and nanotechnology have been deliberated in detail. In addition, CO₂-entrapping chemical compounds such as zeolites and metal organic framework and their contribution in making durability of the cement manufacturing have been illustrated with their chemistry. Environment effects of cement manufacturing and how to control the pollution of the environment when manufacturing processes that are being executed have been discussed using several standard processes, including the Calera process, oxy-combustion process, and monoethanolamide (MEA) process. Currently, the applications of nanoscience and nanotechnology have been gaining popularity in different fields of science and technology. The potential of nanotechnology to progress the performance of concrete and to lead to the development of novel, sustainable, advanced cement-based composites, and smart materials with unique mechanical, thermal, and electrical properties is promising, and many novel opportunities are expected to arise in the future. So finally, the newest trend of making nanocement and its development towards current developing and updating world is described in advance.

Conflicts of Interest

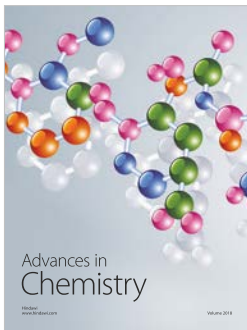
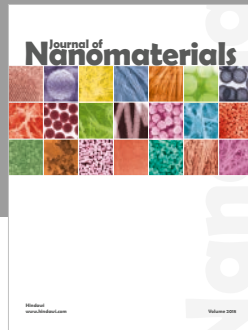
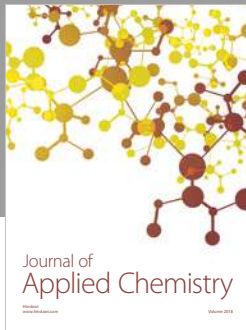
The authors declare that there are no conflicts of interest.

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