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A Study of Various Aspects of Cement Chemistry and Industry Relevant to Global Warming and the Low Carbon and Low Energy Molten Salt Synthesis of Cement Compounds

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Additional information is available at the end of the chapter

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1. Introduction

Global warming caused by the 'greenhouse effect' is mainly due to the CO₂ emissions from human activities such as fossil fuel use (3/4ers) and land use change (1/4er). The concentration of atmospheric CO₂ has increased from a pre-industrial value of ~280 ppm in 1750 to 391 ppm in 2011. The industrial production of Portland cement clinker involves mixing and heating the raw materials limestone and clay minerals in a rotary kiln up to 1450°C in a complex solid/liquid state reaction process. The decomposition of limestone, the combustion of fuels in the kiln and the power generation required for grinding the raw materials and the product, result in process and energy-related emissions of ~0.8 kg CO₂ / kg of cement produced. Thus, the cement industry contributes ~5% in the global anthropogenic CO₂ emissions. 'ULECeS' EPSRC-funded project involved research on the molten salt synthesis of cement, aiming to reduce significantly these CO₂ emissions.

1.1. Global warming, climate change and the intergovernmental panel on climate change

During the 19th century scientists believed that gases in the atmosphere of the earth cause a "greenhouse effect", thus having a direct effect on the temperature of the planet. A lower level of carbon dioxide in the atmosphere in the distant past was also linked to the ice ages of these periods [1].

At around 1900 the Swedish chemist Svante Arrhenius calculated that CO₂ emissions from the burning of fossil fuels and other combustion processes might someday bring a global warming

[2, 3]. Other scientists dismissed his idea as faulty. In the last few decades accumulating evidence points that the suggestion of Svante Arrhenius might not be faulty at all and that we may indeed face already the first consequences of global warming and of climate change. The need to take some kind of action to tackle global warming and climate change led to the foundation of the Intergovernmental Panel on Climate Change (IPCC) in order to start the study of these phenomena on a worldwide basis.

The tasks and the work undertaken by the IPCC might prove to be of enormous importance for the survival and the future of human species on planet Earth. The rather reluctant response of leading global governments to the suggestions of IPCC seems to be accompanied by an attitude of trying to transfer the responsibility for hard but urgent decisions to the next generations. It is of paramount importance the citizens around the globe to become aware of the work and the scope of IPCC. This is the main reason that in the following paragraphs some relevant information about IPCC will be given, bearing in mind that well informed citizens is the necessary condition to tackle phenomena of huge complexity such as global warming and climate change.

The Intergovernmental Panel on Climate Change (IPCC) is the leading international body for the assessment of climate change [4]. In the official internet site of the IPCC there is the following statement about its founding bodies as well as about its role [5]:

“It (the IPCC) was established by the United Nations Environment Programme (UNEP) and the World Meteorological Organization (WMO) in 1988 to provide the world with a clear scientific view on the current state of knowledge in climate change and its potential environmental and socio-economic impacts. In the same year, the UN General Assembly endorsed the action by WMO and UNEP in jointly establishing the IPCC. The IPCC is a scientific body under the auspices of the United Nations (UN). It reviews and assesses the most recent scientific, technical and socio-economic information produced worldwide relevant to the understanding of climate change. It does not conduct any research nor does it monitor climate related data or parameters. Thousands of scientists from all over the world contribute to the work of the IPCC on a voluntary basis. Review is an essential part of the IPCC process, to ensure an objective and complete assessment of current information. IPCC aims to reflect a range of views and expertise.”

The aim of the IPCC to provide an authoritative international statement of scientific understanding of climate change is implemented by periodic assessments of the causes, impacts and possible response strategies to climate change. These are considered to be the most comprehensive and up-to-date reports available on the subject, and form the standard reference for all concerned with climate change in academia, government and industry worldwide [6].

The IPCC work is shared among three Working Groups, a Task Force and a Task Group [7]:

The IPCC Working Group I (WG I) assesses the physical scientific aspects of the climate system and climate change including: changes in greenhouse gases and aerosols in the atmosphere; observed changes in air, land and ocean temperatures, rainfall, glaciers and ice sheets, oceans and sea level; historical and paleoclimatic perspective on climate change; biogeochemistry,

carbon cycle, gases and aerosols; satellite data and other data; climate models; climate projections, causes and attribution of climate change [7].

The IPCC Working Group II (WG II) assesses the vulnerability of socio-economic and natural systems to climate change, negative and positive consequences of climate change, and options for adapting to it, taking into consideration the inter-relationship between vulnerability, adaptation and sustainable development, while the assessed information is considered by sectors (water resources; ecosystems; food & forests; coastal systems; industry; human health) and regions (Africa; Asia; Australia & New Zealand; Europe; Latin America; North America; Polar Regions; Small Islands) [7].

The IPCC Working Group III (WG III) assesses options for mitigating climate change through limiting or preventing greenhouse gas emissions and enhancing activities that remove them from the atmosphere. The main economic sectors taken into account, both in a near-term and in a long-term perspective include energy, transport, buildings, industry, agriculture, forestry, waste management. The WG analyses the costs and benefits of the different approaches to mitigation, considering also the available instruments and policy measures and the approach is more and more solution-oriented [7].

Within the above three working groups, many hundreds of international experts assess climate change in the published Assessment Reports. A landmark year for this kind of reports was the year 2007 when the Fourth Assessment Report was published. This report including the work of the three Working Groups, showed that the need for drastic action to tackle climate change seems to be getting more and more urgent [8, 9, 10].

According to contemporary atmospheric sciences and the 2007 IPCC reports nearly half of the solar radiation is absorbed by the surface of the earth which gets warm. A certain amount of the infrared radiation emitted by the earth's surface is also absorbed and re-emitted in all directions by the greenhouse gas molecules and clouds in the atmosphere. This results in warming the surface of the earth and the lower atmosphere [11]. The mechanism of the Greenhouse Effect is depicted in Figure 1.

Despite the wealth of evidence pointing to the existence of a Global Warming Effect and of human caused Climate Change, there are still 'climate sceptic' scientists and politicians who have certain objections. A fact that is beyond any doubt is the experimental evidence on the time profile of the concentration of greenhouse gases in the atmosphere for the last two millennia. The experimental data on the concentrations of greenhouse gases (Carbon Dioxide: CO₂, Methane: CH₄ and Nitrous Oxide: N₂O) in the atmosphere for the last 2.000 years, show that there is an evident and profound increase in their concentrations after the beginning of the industrial era in the years after 1750 [12]. This is clearly illustrated in Figure 2.

It is estimated that since the year 1750 and onwards anthropogenic or human-caused CO₂ emissions are mainly due to (nearly 2/3rds) fossil fuel combustion for energy and transport (plus a smaller contribution from cement manufacture) and the rest (1/3rd) is due to land use change (primarily deforestation) [13].

In the Summary for Policymakers in the most recent report of the Working Group I of IPCC, the observed changes in the climate system were summarized as follows [14]:

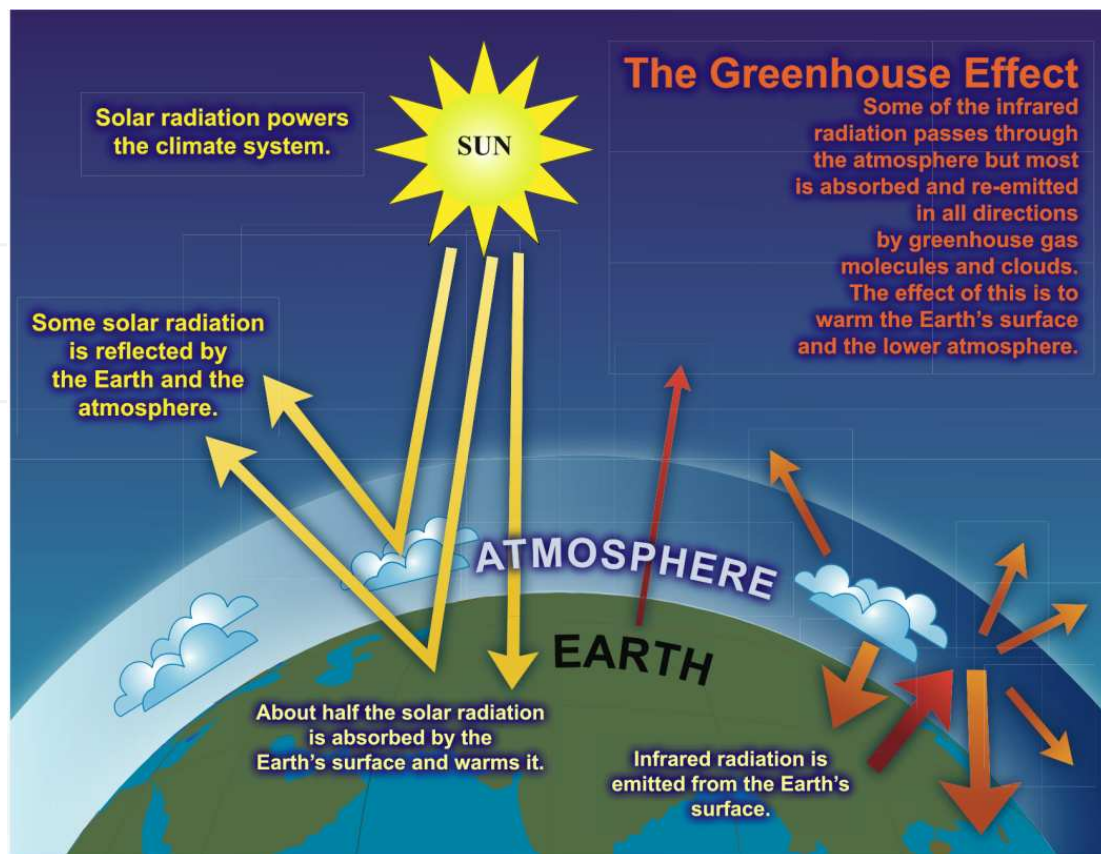


Figure 1. An idealised model of the natural greenhouse effect. From reference 11, p.98. Reproduced by permission from IPCC.

“Warming of the climate system is unequivocal, and since the 1950s, many of the observed changes are unprecedented over decades to millennia. The atmosphere and ocean have warmed, the amounts of snow and ice have diminished, sea level has risen, and the concentrations of greenhouse gases have increased”.

In the same document, some rather alarming details of climate change are reported with particular reference to the individual components of the climate system in our planet [14]:

“**Atmosphere:** Each of the last three decades has been successively warmer at the Earth’s surface than any preceding decade since 1850. In the Northern Hemisphere, 1983–2012 was likely the warmest 30-year period of the last 1400 years (statement of medium confidence).”

“**Ocean:** Ocean warming dominates the increase in energy stored in the climate system, accounting for more than 90% of the energy accumulated between 1971 and 2010 (statement of high confidence). It is virtually certain that the upper ocean (0–700 m) warmed from 1971 to 2010 (see Figure SPM.3), and it likely warmed between the 1870s and 1971.”

“**Cryosphere:** Over the last two decades, the Greenland and Antarctic ice sheets have been losing mass, glaciers have continued to shrink almost worldwide, and Arctic sea ice and Northern Hemisphere spring snow cover have continued to decrease in extent (statement of high confidence).”

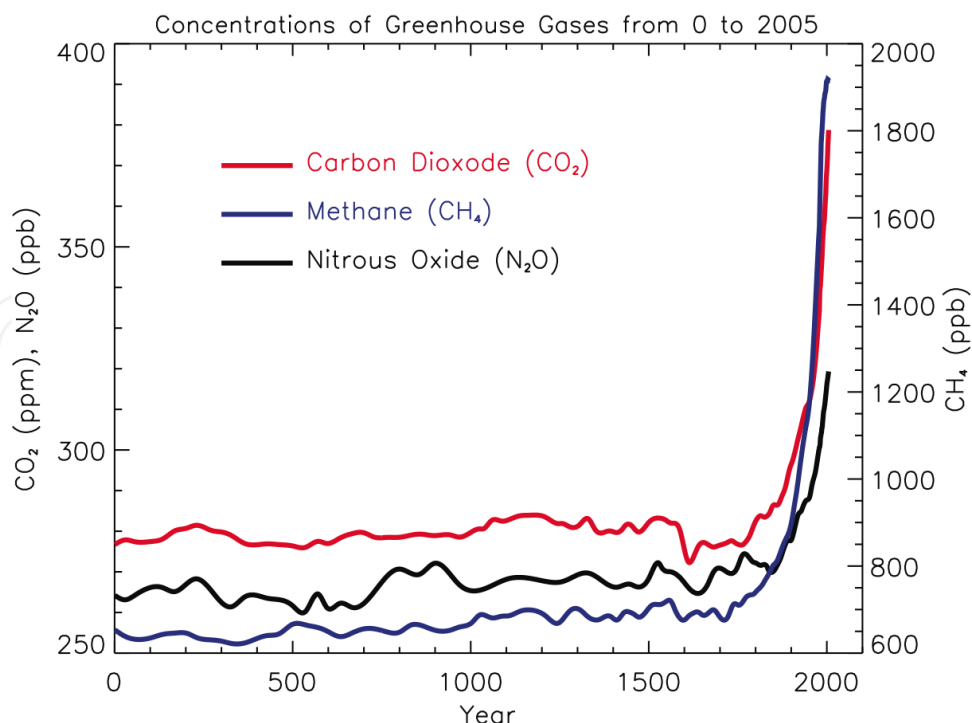


Figure 2. Atmospheric concentrations of important long-lived greenhouse gases over the last 2,000 years. Increases since about 1750 are attributed to human activities in the industrial era. Concentration units are parts per million (ppm) or parts per billion (ppb), indicating the number of molecules of the greenhouse gas per million or billion air molecules, respectively, in an atmospheric sample. From reference 12, p.100. Reproduced by permission from IPCC.

“Sea Level: The rate of sea level rise since the mid-19th century has been larger than the mean rate during the previous two millennia (statement of high confidence). Over the period 1901 to 2010, global mean sea level rose by 0.19 [0.17 to 0.21] m.”

“Carbon and Other Biogeochemical Cycles: The atmospheric concentrations of carbon dioxide, methane, and nitrous oxide have increased to levels unprecedented in at least the last 800,000 years. Carbon dioxide concentrations have increased by 40% since pre-industrial times, primarily from fossil fuel emissions and secondarily from net land use change emissions. The ocean has absorbed about 30% of the emitted anthropogenic carbon dioxide, causing ocean acidification.”

The following more detailed observations were reported for the carbon and other biogeochemical cycles [14]:

“The atmospheric concentrations of the greenhouse gases carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O) which have all increased since 1750 due to human activity, in 2011 were 391 ppm, 1803 ppb, and 324 ppb, exceeding their pre-industrial levels by about 40%, 150%, and 20%, respectively. The concentrations of CO₂, CH₄, and N₂O now substantially exceed the highest concentrations recorded in ice cores during the past 800,000 years. The mean rates of increase in atmospheric concentrations over the past century are, with very high confidence, unprecedented in the last 22,000 years.”

“The annual CO₂ emissions from fossil fuel combustion and cement production were 8.3 [7.6 to 9.0] GtC·yr⁻¹ averaged over 2002–2011 (statement of high confidence) and were 9.5 [8.7 to 10.3] GtC·yr⁻¹ in 2011, 54% above the 1990 level. Annual net CO₂ emissions from anthropogenic land use change were 0.9 [0.1 to 1.7] GtC·yr⁻¹ on average during 2002 to 2011 (statement of medium confidence).”

“From 1750 to 2011, CO₂ emissions from fossil fuel combustion and cement production have released 375 [345 to 405] GtC to the atmosphere, while deforestation and other land use change are estimated to have released 180 [100 to 260] GtC. This results in cumulative anthropogenic emissions of 555 [470 to 640] GtC.”

“Of these cumulative anthropogenic CO₂ emissions, 240 [230 to 250] GtC have accumulated in the atmosphere, 155 [125 to 185] GtC have been taken up by the ocean and 160 [70 to 250] GtC have accumulated in natural terrestrial ecosystems (i.e., the cumulative residual land sink).”

“Ocean acidification is quantified by decreases in pH ($\text{pH} = -\log_{10} [\text{H}^+]$, where $[\text{H}^+]$ is the concentration of H⁺). The pH of ocean surface water has decreased by 0.1 since the beginning of the industrial era (statement of high confidence), corresponding to a 26% increase in hydrogen ion concentration”

The general trend resulting in the above increase of the acidity of the oceans is clearly depicted in Figure 3.b.

The curve in Fig. 3.a. is the classic “Keeling Curve”. The Keeling Curve is a graph which plots the ongoing change in concentration of carbon dioxide in the atmosphere of the Earth since 1958 [15]. It is based on continuous measurements taken at the Mauna Loa Observatory in Hawaii (and in the South Pole) that began by Charles David Keeling. These measurements were the first significant evidence of rapidly increasing carbon dioxide levels in the atmosphere. The Keeling Curve is considered by many scientists as the graph which brought worldwide attention to the current increase of carbon dioxide in the atmosphere [16].

The Kyoto Protocol was drawn up on 11 December 1997 as an implementary measure to the United Nations Framework Convention on Climate Change (UNFCCC) signed on 9 May 1992 in Rio that set up binding obligations on a number of countries to reduce, below their baselines, emissions of carbon dioxide which are generated mostly by electricity, coal, and steel plants [17]. It is evident from Figure 3.a. that the carbon dioxide emissions have in fact kept increasing with a higher rate after the agreement entailed in the Kyoto Protocol.

The American climatology scientist James Edward Hansen, a pundit of global warming and climate change and a pioneer activist calling for action to mitigate the effects of climate change [18], addressed the reluctance of world leading countries to take drastic measures [19]:

“I have been told by a high government official that I should not talk about “dangerous anthropogenic interference” with climate, because we do not know how much humans are changing the Earth’s climate or how much change is “dangerous”. Actually, we know quite a lot. Natural regional climate fluctuations remain larger today than human-made effects such

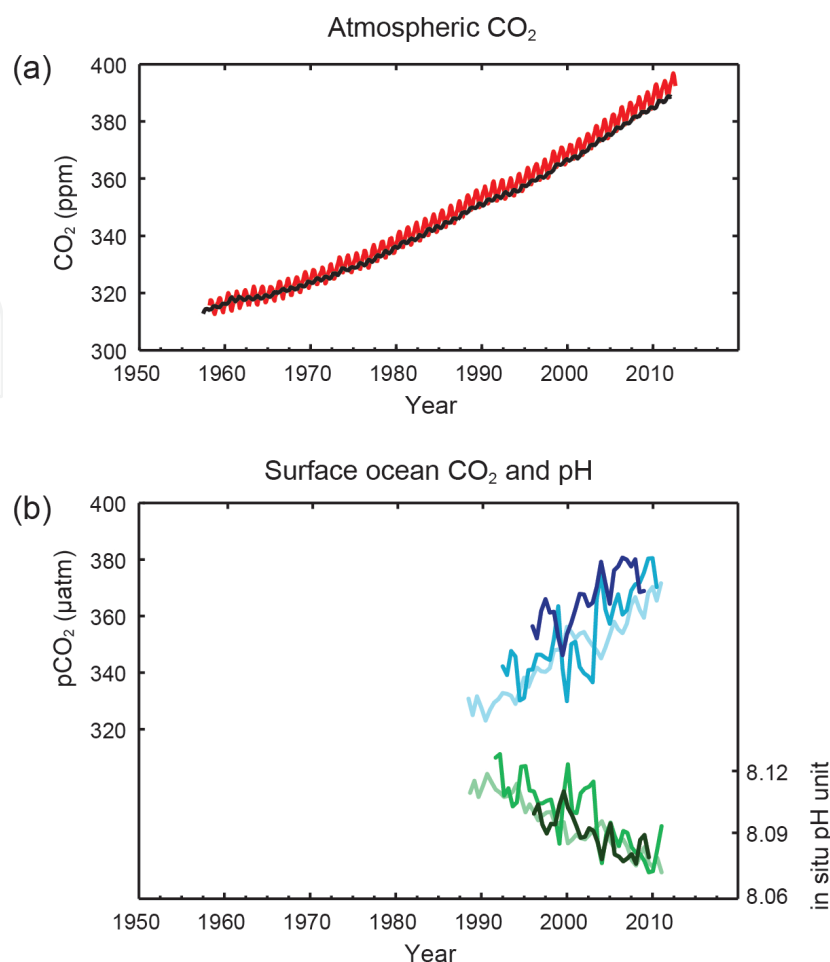


Figure 3. Multiple observed indicators of a changing global carbon cycle: (a) atmospheric concentrations of carbon dioxide (CO₂) from Mauna Loa (19°32'N, 155°34'W – red) and South Pole (89°59'S, 24°48'W – black) since 1958; (b) partial pressure of dissolved CO₂ at the ocean surface (blue curves) and in situ pH (green curves), a measure of the acidity of ocean water. Measurements are from three stations from the Atlantic (29°10'N, 15°30'W – dark blue/dark green; 31°40'N, 64°10'W – blue/green) and the Pacific Oceans (22°45'N, 158°00'W – light blue/light green). Full details of the datasets shown here are provided in the underlying report and the Technical Summary Supplementary Material. {Figures 2.1 and 3.18; Figure TS.5}. From reference 14, p.12. Reproduced by permission from IPCC.

as global warming. But data show that we are at a point where human effects are competing with nature and the balance is shifting.”

The argument of James Edward Hansen that we know quite a lot about the “dangerous anthropogenic interference” with climate, is evidenced by his reported work [20, 21, 22]. In their assessment of “dangerous climate change” James Edward Hansen and his colleagues suggested the required reduction of carbon emissions to protect young people, future generations and nature. According to them the carbon emissions should be such that they fulfill a cumulative industrial-era limit of ~500 GtC fossil fuel emissions and 100 GtC storage in the biosphere and soil which would keep climate close to the Holocene range to which humanity and other species are adapted [22]. The urgency of the situation has also been addressed in the most recent report of IPCC [23].

2. Cement chemistry and industry and its impact on global warming

Concrete is a composite material consisting of an aggregate and a binder phase (hardened cement paste) that is formed by the reaction (hydration) of Portland cement clinker with water [24, 25]. This initially rather rapid reaction can continue for many years resulting in an intimate, micro-porous mixture of several crystalline and poorly crystalline phases. The chemical and physical aspects of the structure, as well as certain properties in concrete materials were outlined [26].

Cement represents a commodity which surpasses any other that our species produces and uses as a construction material. It is also true that cement plants are amongst the biggest human made industrial constructions, simply to mention cement rotary kilns with diameter up to 3.7m (12 feet) and length up to 100m (longer in many instances than the height of a 40-story building) [27]. A state of the art diagram showing in the simplest possible way the very complex succession of reactions taking place during the production of the 'grey' cement powder, the so-called cement clinker was reported in Figure 2.6 in page 79 of reference 25.

The estimated annual production of Ordinary Portland Cement (or simply cement) in 2013 was 4 billion metric tonnes with China producing more than half of it (2.3 billion tonnes) followed by India (0.28 billion tonnes) and by USA (0.0778 billion tonnes) [28]. Most of this portland cement is used in making concrete or mortars. Concrete is the most used construction material in the world, with an annual production of around 11 billion metric tonnes [29], despite the fact that it competes in the construction sector with concrete substitutes, such as aluminum, asphalt, clay brick, rammed earth, fiberglass, glass, steel, stone, and wood [28]. The manufacture of concrete is an industry with a worldwide value of 1 trillion US\$ which employs nearly 30 million workers [29]. The magnitude of the global cement industry and the use of concrete as a building material are such that on our planet we produce annually nearly 0.55 metric tonnes (550 Kg) of OPC or 1.50 metric tonnes (1,500 Kg) of concrete for each one of the 7.239 billion people living on planet Earth [30].

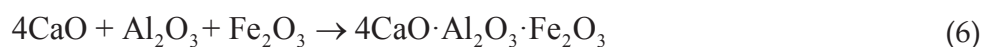
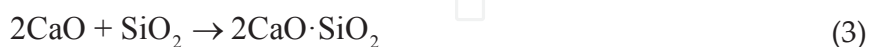
A general overview on hydraulic (mainly portland) cement and, to some degree, concrete, as well as a description of the monthly and annual U.S. Geological Survey (USGS) cement industry canvasses in general terms of their coverage and some of the issues regarding the collection and interpretation of the data therein was reported [31].

The Ordinary Portland Cement (OPC) clinker production is a complex Solid/Liquid State reaction process. Grinded limestone (CaCO_3), Clays (Aluminium Silicates, Al-Si-O), Quartz (SiO_2) and Fe_2O_3 in certain weight ratios are homogeneously mixed in the rotary kiln and heated up to $\sim 1450^\circ\text{C}$. The quenched product is mainly a mixture of 3 compounds (2 calcium silicates and 1 calcium aluminate) and one solid solution (calcium aluminium ferrate) [24, 32]:

1. Tricalcium Silicate, $3\text{CaO} \cdot \text{SiO}_2$ (Alite), C_3S : 45-70 wt.%.
2. β -Dicalcium Silicate, $\beta\text{-}2\text{CaO} \cdot \text{SiO}_2$ (Belite), $\beta\text{-}\text{C}_2\text{S}$: 25-30 wt.%.
3. Tricalcium Aluminate, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ (Celite), C_3A : 5-12 wt.%.

4. Tetracalcium Alumino Ferrite (solid solution), $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ (Feritte), C_4AF : 5-12 wt. %.

Using a rather simplified picture of the chemistry involved, the following reactions take place during the production of Ordinary Portland Cement (OPC) clinker:

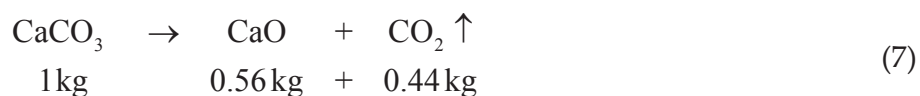


In the industrial process, Portland cement is manufactured by crushing, milling and proportioning the following materials [33]:

1. Lime or calcium oxide, CaO : from limestone, chalk, shells, shale or calcareous rock.
2. Silica, SiO_2 : from sand, old bottles, clay or argillaceous rock.
3. Alumina, Al_2O_3 : from bauxite, recycled aluminum, clay.
4. Iron, Fe_2O_3 : from clay, iron ore, scrap iron and fly ash.
5. Gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$: found together with limestone.

The materials 1-4 are proportioned to produce a mixture with the desired chemical composition and then ground and blended mainly by a dry process. The materials are then fed through a kiln at $2,600^\circ\text{F}$ (1427°C) to produce grayish-black pellets known as clinker. The alumina and iron act as fluxing agents which lower the melting point of the mixture from $3,000^\circ\text{F}$ (1649°C) to 2600°F (1427°C). After this stage, the clinker is cooled, pulverized and gypsum added to regulate setting time. It is then ground extremely fine to produce cement [33].

The CO_2 footprint of cement production causes more than 5% of the total anthropogenic carbon dioxide (CO_2) emissions with nearly 800 kg CO_2 emissions per 1000 kg of cement produced. These emissions are the process emissions due to the chemical reaction of limestone (CaCO_3) decomposition to lime (CaO) (~60%) and the energy-related emissions (~40%) due to the combustion of fossil fuels (to reach the 1450°C reaction temperature) and the power generation needed for grinding the raw materials and the product [34, 35].



The total CO₂ emissions in the production of cement, including process and energy-related emissions were reviewed [34]. The average intensity of carbon dioxide emissions from total global cement production is 222 Kg of C/1.000 Kg of cement or 814 Kg CO₂/1.000 Kg of cement. Emission mitigation options include energy efficiency improvement, new processes, a shift to low carbon fuels, application of waste fuels, increased use of additives in cement making, and, eventually, alternative cements and CO₂ removal from flue gases in clinker kilns [34 and references there in].

According to the America's Cement Manufacturers Portland Cement Association (PCA) Voluntary Code of Conduct, within the Cement Manufacturing Sustainability (CMS) Program, the Environmental Performance Measures translate the Cement Manufacturing Sustainability (CMS) Program Principles into action. Currently there are four goals approved by the PCA members [36]:

1. **Carbon Dioxide (CO₂)** – The U.S. cement industry has adopted a year 2020 voluntary target of reducing CO₂ emissions by 10 percent (from a 1990 baseline) per ton of cementitious product produced or sold.
2. **Cement Kiln Dust (CKD)** – The U.S. cement industry has adopted a year 2020 voluntary target of a 60 percent reduction (from a 1990 baseline) in the amount of CKD landfilled per ton of clinker produced.
3. **Environmental Management Systems (EMS)** – The U.S. cement industry has adopted a year 2006 voluntary target of at least 40 percent implementation of U.S. cement plants using an auditable and verifiable EMS with 75 percent of the U.S. plants implementing an EMS by the end of 2010, and with 90 percent by the end of 2020.
4. **Energy Efficiency** – The U.S. cement industry has adopted a year 2020 voluntary target of 20 percent improvement (from 1990 baseline) in energy efficiency – as measured by total Btu-equivalent per unit of cementitious product.

It is apparent that the target of 10% reduction by year 2020 in Carbon Dioxide (CO₂) emissions from the USA cement industry represents a rather marginal evolutionary approach in tackling the impact of cement industry in global warming. It also stresses the need for development of alternative new technologies and processes for the cement manufacture.

3. Thermodynamic aspects of the synthesis of Ordinary Portland Cement (OPC) clinker with emphasis on calcium silicates and calcium aluminates

The formation of Ordinary Portland Cement (OPC) clinker is a very complex process with reactions involving at least the four oxides CaO, SiO₂, Al₂O₃ and Fe₂O₃. It is generally accepted

that the knowledge of the following phase diagrams is very important for the understanding of the cement production process, especially those involving CaO, SiO₂ and Al₂O₃:

- i. Binary phase diagrams of CaO-SiO₂ and CaO-Al₂O₃.
- ii. Ternary phase diagram of CaO-SiO₂-Al₂O₃.
- iii. Quaternary phase diagram of CaO-SiO₂-Al₂O₃-Fe₂O₃.

All the above phase diagrams were thoroughly reported and assessed in the Slag Atlas [37 and references cited there in].

The existing phase diagrams of the CaO-SiO₂ and of the CaO-Al₂O₃ binary systems [37 and references cited there in] show that the very high melting oxide CaO (m.pt. 2613°C for lime) reacts with SiO₂ (m.pt. 1713°C for vitreous and 1722°C for the cristobalite phase) and with Al₂O₃ (2054°C for corundum phase) [melting points are from reference 38] yielding the following major cement compounds:

1. 3CaO·SiO₂ / Ca₃SiO₅ / C₃S (Mineral Name: Hatrurite) [39] (Cement Chemistry Name: Alite), which melts incongruently at 2150°C and decomposes to CaO and C₂S below 1250°C [37] if not quenched fast, as is the standard practice in the cement industry.
2. β-2CaO·SiO₂ / β-Ca₂SiO₄ / β-C₂S (Mineral Name: Larnite) [40] (Cement Chemistry Name: Belite), which melts at 2130°C [37] and is transformed to γ-C₂S below 500°C if not quenched fast, as is the standard practice in the cement industry.
3. 3CaO·Al₂O₃ / Ca₃Al₂O₆ / C₃A, which melts incongruently at 1539°C and is transformed to another polymorph below 1400°C [37].
4. 12CaO·7Al₂O₃ / Ca₁₂Al₁₄O₃₃ / C₁₂A₇ which is an intermediate compound (Mineral Name: Mayenite) [41] during the synthesis of C₃A, the C₁₂A₇ melts at 1413°C and is transformed to another polymorph below 1400°C [37].

In the current industrial process of production of Ordinary Portland Cement (OPC) clinker an important step is the fast cooling of the clinker product from temperatures around 1500°C to temperatures well below 1000°C. This quenching of the very high temperature clinker product is necessary in order to prevent the decomposition of alite 3CaO·SiO₂ (C₃S) to 2CaO·SiO₂ (C₂S) and CaO (the decomposition of C₃S is taking place below 1250°C) and to avoid the transformation of belite β-2CaO·SiO₂ (β-C₂S) (the desired cement phase of C₂S is the belite β-C₂S) to γ-2CaO·SiO₂ (γ-C₂S), since below 500°C and especially at room temperature the stable phase of C₂S is not β-C₂S but γ-C₂S.

Again it is important to emphasize that the raw meal used in the industrial production of Ordinary Portland Cement (OPC) clinker is composed not only by the 'ideal' CaCO₃, SiO₂, Al₂O₃ and Fe₂O₃ reactants but also there are a lot of other cations and anions present. All these ions and the precise temperature profile of the reactions lead to the formation of more than five polymorphs for the quenched 3CaO·SiO₂ (C₃S) and the presence of some γ-C₂S along with the desired β-C₂S for the 2CaO·SiO₂ (C₂S).

The high temperature reactions taking place in the rotary kiln during cement production and the complexity of the processes involved require a detailed knowledge of these reactions in order to achieve technological advances. An introduction to the topic of cement, including an overview of cement production, selected cement properties, and clinker phase relations was reported [42]. The authors provided an extended summary of laboratory-scale investigations on clinkerization reactions and on the most important reactions in cement production. The formation of clinker by solid state reactions, solid–liquid and liquid–liquid reactions, as well as the influences of particles sizes on clinker phase formation was discussed. In addition, a mechanism for clinker phase formation in an industrial rotary kiln reactor was outlined [42].

In the quest to understand the fundamentals of the cooling process of cement clinker in order to improve the ongoing cooling process, the decomposition of alite (C_3S) in Portland cement clinker was investigated by isothermal annealing [43]. The clinker phases were analyzed by quantitative X-ray diffraction and scanning electron microscopy in order to investigate the microstructure. It was found that the fastest decomposition rate of Ca_3SiO_5 (C_3S) to Ca_2SiO_4 (C_2S) and CaO appeared at 1125–1150°C using a temperature–time–transformation diagram. The combined XRD and SEM study showed that the decomposition of alite (Ca_3SiO_5) primarily occurred at the cracks, edges, and defects of the clinker, while the resulting free CaO segregated and subsequently controlled the decomposition rate of alite. The decomposition kinetics of alite was described by a three-dimensional Jander diffusion model with a non-Arrhenius behavior for the activation energy which exhibited two distinct linear functions with temperature, one above (higher activation energies) and the other below (lower activation energies) the temperature of 1380.65 K (1107.49°C). It was reported that interstitial phases recrystallized during the annealing process were accompanied by an increase of the $3CaO \cdot Al_2O_3$ (C_3A) and $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ (C_4AF) contents and that the recrystallization of C_3A was temperature-dependent, especially above 1000°C [43].

4. Synthesis of Ordinary Portland Cement (OPC) clinker compounds by various methods with emphasis on calcium silicates

A number of methods used in the synthesis of calcium silicates and calcium aluminates, include solid-state reactions, growth from the melt, combustion and sol gel synthesis as well as other more special synthetic methods. The energy characteristics of these synthetic techniques can be compared with the molten salt synthesis used in previous studies and in the present work. A straightforward means of comparison of the molten salt synthesis used in this work with other methods of synthesis involves mainly the reaction temperature, the specific kind of chemical compounds reacting, as well as the kind of reactors used in each method.

4.1. Solid state synthesis of calcium silicates

In a typical solid-state synthesis the two reactants are thoroughly ground in order to increase their reactivity and subsequently are homogeneously mixed in order to increase their contact. The restrictions imposed by the limited mobility of the reacting species as compared to

reactions in solution, dictate the use of rather very high temperatures in order to drive the reaction to the desired product. The nucleation and growth of the product as well as the diffusion of one or both reactants are particularly important factors that affect the outcome of the solid-state reactions. The solid-solid reaction rate and the role of the contact points between particles on the reactivity of solids was studied [44]. Taking into account the exact number of contact points between the two components in a system of solids, their reactivity was expressed in terms of the molar ratio, the particle size ratio and the nature of the reacting system. The theory with a particular emphasis on the Jander model was confirmed by existing experimental data, revealing that the contact points play an important role for wide ranges of reactivity of solids [44]. The basics and mathematical fundamentals of solid-state kinetic models were reviewed [45]. Models used in solid-state kinetic studies were classified according to their mechanistic basis as nucleation, geometrical contraction, diffusion, and reaction order. The authors summarized commonly employed models and presented their mathematical development [45]. There is a wealth of information on the synthesis of calcium silicates by reaction in the solid state done in Europe mainly in Germany more than five decades ago [46, 47]. The formation of the orthosilicate β -2CaO·SiO₂, Wollastonite CaO·SiO₂ and 3CaO·2SiO₂ by solid-state reaction of CaO with H₄SiO₄ (silicic acid) in temperatures of 1000°C and for up to 400 hours was examined by microscopy and XRD [46]. A detailed XRD and DTA study of the solid-state synthesis of calcium silicates (CS, C₂S, C₃S) by the reaction of CaCO₃ or Ca(OH)₂ with amorphous SiO₂ at various temperatures up to 1500°C for 3 hours was reported and a scheme of reaction of CaO with SiO₂ was proposed [47]. The kinetics of the thermal synthesis of calcium silicates by the dynamic reaction of CaO with SiO₂ (2:1 mole ratio) was studied at temperatures up to 1500°C (especially above 1400°C) by simultaneous TG, DTA, high-temperature X-ray diffraction (horizontal sample) and microscopy as well as by dilatometry. The reaction mechanism in the dynamic thermal synthesis of Ca₂SiO₄ was elucidated and confirmed by high-temperature X-ray diffraction [48]. A quantitative kinetics study showed that the reaction between CaO and a SiO₂-rich liquid phase is the rate-determining step. The calculated from the kinetic data activation parameters agree well with the proposed reaction mechanism [49]. The preparation method of β -C₂S powders without stabilizer and their hydration characteristics were studied [50]. The β -C₂S was formed when γ -C₂S was heated at about 1000°C or at even higher temperatures of about 1500°C. The hydration kinetics of β -C₂S produced from α '-C₂S was found to be markedly different from that produced from α -C₂S, with very small amount of Ca(OH)₂ produced in the hydration of β -C₂S without stabilizer and the formed C-S-H had a composition of C/S~2 [50]. The composition of phases in the reaction zones of the CaO-SiO₂ binary system was determined by electron probe microanalysis in the temperature range between 1000 – 1450 °C and the dependence on the time of annealing was investigated [51]. Utilising the diffusion couple technique in combination with a new designed screw loaded sample holder it was suggested that the growth of all product layers obeys the parabolic rate law for diffusion-controlled solid state reactions. The respective reaction rate constants and activation energies were presented and discussed [51]. The solid state synthesis of pure Portland cement phases was reported [52]. The pure clinker compounds are often used to test various aspects of cement chemistry in particular hydration behaviour, mainly due to the fact that they are nearly isostructural to the Ordinary Portland Cement (OPC) clinker phases. The

apparent need of efficient methods to produce big quantities of the pure phases with an affordable cost is well documented by the high prices of these pure phases available from suppliers of chemicals. The authors reported the synthesis of the pure phases as well as a description of phase relations and possible polymorphs of the four main phases in Portland cement, i.e. tricalcium silicate, dicalcium silicate, tricalcium aluminate and tetracalcium aluminoferrite. In addition, details of the process of solid state synthesis were described including state of the art practical advice on equipment and techniques [52]. It is obvious from all the above studies that the solid state synthesis of calcium silicates involves reactions in temperatures well above 1000°C and often up to 1500°C.

4.2. Growth from the melt synthesis of calcium silicates

The same range of temperatures (1000°C up to 1500°C) seem to be used in the growth from the melt synthesis of calcium silicates. A sample holding technique consisting of a thin platinum wire loop was used for the study of crystal growth in silicate melts (SiO_2 ~49-51 wt.%, Al_2O_3 ~10-15 wt.%, FeO ~9-19 wt.%, MgO ~9 wt.%, CaO ~10-11 wt.%, Na_2O ~0.05-3 wt.%) in gas mixing furnace. The experiments reported were run from 1 hour up to 24 hours at 1250°C [53]. A novel technique of dynamic crystallization used for the directional devitrification from a molten zone have been described by Maries and Rogers [54]. Using this technique it was possible to prepare aligned fibrous crystals by drawing filaments of glass through a supported molten zone. The researchers subsequently modified the method in order the filament to be drawn from a melt through an orifice in the base of a conical platinum crucible [55]. Using this process they crystallized β - CaSiO_3 filaments by continuous drawing from a melt contained in a resistance-heated platinum crucible, whereby the temperature of crystallization was determined primarily by the speed of drawing. The temperatures used were apparently above the 1544°C melting point of $\text{CaO}\cdot\text{SiO}_2$. The authors have also used this technique for the preparation of filaments consisting of aligned fibres of fluoramphiboles, which are synthetic analogues of natural amphiboles by isomorphous substitution of hydroxyl by fluorine anions. The method led to the synthesis of aligned fibrous crystals which bear resemblance with natural amphibole asbestos [56].

The morphology of calcium metasilicate CaSiO_3 produced during the crystallization of glasses and melts of approximately metasilicate composition has been investigated employing isothermal heat treatments and a dynamic crystal-pulling technique [57]. It was observed that the crystallization took place by a dendritic or spherulitic mechanism, depending on which of the crystal polymorphs is stable under the prevailing conditions. It was found that the morphology of the crystals is controlled by the ease with which the anionic groups present in the amorphous phase can be incorporated into the growing crystals. Time-temperature-transformation diagrams have been constructed from the experimental data. It should be noted that the glass compositions used to investigate the crystallization characteristics of calcium metasilicate contained not only CaO (32.5-37.4 mole %) and SiO_2 (51.2-55.4 mole %) but also other oxides such as Al_2O_3 (2.6-7.4 mole %), ZnO (5.7-15.4 mole %) and Na_2O (4.2-4.8 mole %) and in one case a fluoride CaF_2 (5.3 mole %). It should be emphasized that due to the very high melting points of certain compositions, it was necessary to use very high temperatures, well

above 1000°C, i.e. time-temperature-transformation diagram for a certain composition rods nucleated on a β -CaSiO₃ block and on a Pt/Pt 13% Rh thermocouple were reported from T_F=1340°C to 20°C [57].

The rather very high temperatures used in both the solid state synthesis reactions and in the growth from the melt synthesis show the importance of molten salt synthesis for the preparation of calcium silicates in temperatures quite lower than the 1500°C.

4.3. Combustion synthesis of calcium silicates

The low-temperature combustion synthesis of nanocrystalline β -dicalcium silicate (β -Ca₂SiO₄) with high specific surface area was reported [58]. The synthesis of β -Ca₂SiO₄ was achieved for the first time by a simple solution combustion method using citric acid, C₆H₈O₇ (semi-structural formula: HOOCCH₂C(OH)(COOH)CH₂COOH) as fuel. The effect of calcination temperature on the average crystallite size, specific surface area and morphology of the powders were studied by X-ray diffraction (XRD), scanning electron microscopy (SEM) and N₂ adsorption measurements (BET). It was found that when increasing the calcination temperature of β -Ca₂SiO₄ from 650°C to 1100°C this results in the production of crystallites of larger size and lower specific surface area of β -Ca₂SiO₄. It was shown that the highest specific surface area measured was up to 26.7 m² g⁻¹ when the powders were calcined at 650°C [58]. The use of the combustion method for the synthesis of calcium silicates looks very interesting for specific applications of the product which can make affordable the cost of the method.

4.4. Sol gel synthesis of calcium silicates

The synthesis of calcium silicates by a chelate gel route using aqueous solution of citric acid was reported [59]. A number of gel techniques such as the metal-chelate gel method, in situ polymerized complex method and polymer precursor method used in the preparation of ceramics have the potential to yield compositionally homogeneous and fine powders with a narrow particle size distribution [59]. The presence of the various polymorphs and the particle size distribution are particularly important factors since they affect the hydration activity of calcium silicates. A metal-chelate gel route based on gelation of the aqueous solution of citric acid has been successfully applied to the synthesis of calcium silicates (Ca₂SiO₄ and Ca₃SiO₅) for the first time and their phase transformations and particle size were discussed in comparison to the conventional solid-state reaction route [59]. It was found that the novel citrate gel route produces β -Ca₂SiO₄ (the high-temperature phase and favourable cement compound) while the conventional solid-state reaction route produces γ -Ca₂SiO₄ (the low-temperature phase) This result was interpreted in terms of the particle size effect and the energy barrier. It was suggested that the nucleation and propagation of microcracks result in overcoming a comparatively high-energy barrier, $\Delta G^*(\beta \rightarrow \gamma)$ and that the particle size effect governs both the statistic of martensitic nucleation and the propagation of the $\beta \rightarrow \gamma$ transformation. In the case of tricalcium silicate, the triclinic Ca₃SiO₅ (the low-temperature phase) was produced by both the citrate gel route and the conventional solid-state reaction route. It was suggested that the nucleation and propagation do not result in the M-T transformation, pointing that the

energy barrier of the monoclinic (M) to the triclinic (T) transformation, $\Delta G^*(M-T)$ is rather small [59].

The sol-gel synthesis and the textural characterisation of mesoporous calcium silicate glasses having compositions within the liquid-liquid immiscibility dome of the CaO-SiO₂ system was reported [60, 61].

A number of crack-free silica-calcia xerogel monoliths of various shapes and sizes and having compositions of $x\text{CaO} \cdot (1-x)\text{SiO}_2$ ($0 \leq x \leq 0.5$, x =mole fraction), were prepared via the sol-gel processing technique, using tetraethyl orthosilicate, $\text{Si}(\text{OC}_2\text{H}_5)_4$ (TEOS) and calcium nitrate, $\text{Ca}(\text{NO}_3)_2$ reactants [60]. The homogeneous throughout the monolith gel-glasses were characterised by X-ray diffraction, infrared (FTIR) spectroscopy, energy dispersive scanning electron microscopy (SEM-EDS) and by differential thermal analysis (DTA). It was found that they are amorphous even after stabilisation at 600°C, they have crystallisation temperatures above 850°C and they formed crystalline phases present in the CaO-SiO₂ phase diagram only when sintered at 1000°C [60].

The textural characteristics including the surface area and porosity (pore structure and pore volume), of the above monolith gel-glasses were studied by nitrogen adsorption, mercury porosimetry and helium pycnometry [61]. The nitrogen adsorption and the mercury porosimetry methods which study the pore morphology showed that the pore system in these gel-glasses consists of a three-dimensional network of cavities (pores) interconnected by constrictions (throats) in the mesopore range (75–314 Å in diameter) with the pore sizes dependent on the composition of the gel-glasses. It was found that when the CaO content was decreased, then the surface area increased, the pore size decreased, while the skeletal and bulk densities both increased and the gel-glasses were of approximately 30% porosity. [61].

The synthesis of pure cementitious phases by sol-gel process as precursor was reported [62]. The pure phases of calcium silicates and aluminates which are the main constituents of ordinary Portland cement (OPC) and calcium aluminate cements (CAC) are of great importance for the cement research. Due to the demand for big amounts of these pure phases and the fact that their synthesis by solid-state reactions is difficult, there is an obvious need for more efficient synthetic methods. The authors suggested that an attractive alternative to the conventional synthetic route is the sol-gel process. Experimental results on the improved synthesis of calcium silicates and aluminates via sol-gel processes were reported, along with the characterization of the pure clinker phases and studies of their hydration behaviour [62].

The sol-gel synthesis of belite ($\beta\text{-Ca}_2\text{SiO}_4$), one of the major compounds in Portland cement clinker was reported [63]. The authors emphasized the fact that in the conventional preparation with solid state reaction, belite is produced by long lasting sintering of limestone and quartz at temperatures exceeding 1400°C. In the sol-gel synthesis of belite reported, both aqueous and non-aqueous sol-gel routes were applied and the preparation of the precursor mixture and the formation of the ceramic product were monitored using TG/

DTG, XRD, FT-IR and SEM. The combined use of the above techniques led to the recording of all the transformations occurring during the processing of the precursors and the formation of the final products. It was found that both the aqueous and the non-aqueous sol-gel routes can be successful in the preparation of di-calcium silicate and that the final products consisted of very fine spherical crystallites with size in the range 1–3 μm , whose formation required a 3 hours sintering at 1000°C, but in both cases $\beta\text{-Ca}_2\text{SiO}_4$ was obtained without the use of any chemical stabilizers [63].

The sol-gel synthesis of calcium silicates offer a lot of opportunities by controlling the preparation and giving access to tailor made products with specific particle size, shape and morphology. It can be particularly attractive for the synthesis of high price cements for very special applications.

4.5. Other methods of synthesis of calcium silicates

Other methods of synthesis of calcium silicates include rather special techniques such as hydrothermal synthesis, the Pechini method, Ultrasonical – Sonochemical techniques, as well as the so called Organic Steric Entrapment method.

The hydrothermal methods initially produce in a temperature of a just a few hundreds of °C degrees some kind of calcium silicate hydrates, which have to be thermally processed in much higher temperature in order to produce the anhydrous calcium silicates. An example is the microwave-assisted hydrothermal preparation of $\text{Ca}_6\text{Si}_6\text{O}_{17}(\text{OH})_2$ and of $\beta\text{-CaSiO}_3$ nanobelts [64]. The initial step involved xonotlite ($\text{Ca}_6\text{Si}_6\text{O}_{17}(\text{OH})_2$) nanobelts which were synthesized by a microwave-assisted hydrothermal method at 180°C for 90 minutes using a feeding molar ratio of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ to $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ in the range of 0.8–3.0. The crystalline wollastonite ($\beta\text{-CaSiO}_3$) nanobelts were obtained by microwave thermal transformation at 800°C for 2 h of $\text{Ca}_6\text{Si}_6\text{O}_{17}(\text{OH})_2$ nanobelts which were used as both the precursor and the template for the preparation of $\beta\text{-CaSiO}_3$ nanobelts [64].

In the Pechini process the pyrolysis of the polymer matrix leads to the development of the oxide precursor which has a high degree of homogeneity [65]. A relevant study reported involved the hydration kinetics and the phase stability of reactive dicalcium silicate synthesized by the Pechini process [66]. It was found that when increasing the calcination temperature, the amorphous product first crystallized to α'_L -phase and subsequently to the β - and γ -phases. It was also reported that the specific surface area, ranging from 40 to 1 m^2/g , strongly depended on the calcination temperature of 700°–1200°C for 1 hour [66].

In the ultrasonic or sonochemical methods at some stage of the process the reaction mixture is sonicated in an ultrasonic bath. A relevant work was on the synthesis and characterization of hydration behaviour of manganese oxide-doped dicalcium silicates obtained from rice hull ash [67]. In this work the authors reported that the syntheses were performed using silica obtained from rice hull ash and the solids SiO_2 , CaO and MnO were weighed in stoichiometric proportions to prepare silicates having a ratio $(\text{Ca}+\text{Mn})/\text{Si}=2$, with the amount of manganese varying from 1 to 10 mole %. The ground solid reactants after the addition of water formed aqueous suspensions which were sonicated for 60 minutes in an ultrasonic bath. This was

followed by drying, and the resulting solids were ground and burned at 800°C producing calcium silicates containing up to 10% of manganese oxide [67].

The synthesis and hydration study of Portland cement components prepared by the organic steric entrapment method was reported [68]. The major four components of Portland cement; dicalcium silicate (Ca_2SiO_4), tricalcium silicate (Ca_3SiO_5), tricalcium aluminate ($\text{Ca}_3\text{Al}_2\text{O}_6$), and tetracalcium aluminate iron oxide ($\text{Ca}_4\text{Al}_2\text{Fe}_3\text{O}_{10}$) were synthesized by the PVA, $[\text{CH}_2\text{CH}(\text{OH})]_n$ (Polyvinyl Alcohol) complexation process. The authors stated that powders prepared by this new method can make relatively high yields of pure, synthetic, cement components of nano or sub-micron crystallite dimensions, high specific surface area, and extremely high reactivity at relatively low calcination temperatures in comparison with conventional methods. It is obvious that the above advantages can enhance setting speed, increase strength, and lead to other desirable characteristics of Portland cement [68].

All the above special methods of synthesis yield calcium silicates with very specific properties and are indeed offering a great deal of control over the outcome of the reaction. They are the choice to be considered for special applications that can pay off their production cost. In the question if these special methods can be used in the manufacture of cement on an industrial scale, an obvious answer is that this will only be possible if their cost per unit volume of product becomes comparable to the cost of cement produced with the current industrial process.

4.6. Previous studies on the molten salt synthesis of calcium silicates

Reactions in molten salt media [69] have been used in the synthesis of refractory [70], nuclear [71, 72] and advanced engineering materials [73] as well as in the preparation of low-dimensional solid-state compounds [74] and of semiconductors [75]. In recent years nanomaterials are prepared by molten salt reaction routes [76, 77]. Previously reported successful preparations of dicalcium silicate in molten salt media include the following:

1. Growth of Ca_2SiO_4 crystals in extremely fine ($0.01 \times 0.1 \mu\text{m}$; surface area $120 \text{ m}^2/\text{g}$) acicular form from the reaction of CaCl_2 flux with SiO_2 at 1000°C for 2 hours and at 1200°C for 1 hour [78].
2. Growth of prismatic Ca_2SiO_4 crystals with edge lengths up to 20 mm from a CaCl_2 flux [79, 80, 81].
3. Formation of needle-like $\beta\text{-Ca}_2\text{SiO}_4$ crystals upon melting a CaO-SiO_2 mixture in an alkali-halides flux [82]. The crystal growth of Monticellite (CaMgSiO_4) and Akermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$) using alkali chlorides was also reported [83].
4. Growth of Mn-doped mono-crystals of Ca_2SiO_4 in a CaCl_2 flux at 1060-1300°C using raw mixes (2CaCO_3 , SiO_2 , 3CaCl_2) with different contents of MnCO_3 and 1% $\text{Ca}_3(\text{PO}_4)_2$ equivalent to 0.46% P_2O_5 stabilizer [84].

The growth of Ca_2SiO_4 crystals [85] and $\text{Ca}_3\text{Si}_2\text{O}_7 \cdot 1/3\text{CaCl}_2$ single crystals [86] from fluxes were reported. The crystal growth of calcium silicates from melts, hydrothermal solutions and from fluxes was reviewed by Hermoneit and Ziemer [87].

5. The use of low carbon low energy molten salt synthesis method to prepare cement compounds

5.1. The 'ULECeS': Ultra low energy cement synthesis: A radical process change to achieve green and sustainable technologies EPSRC EP/F014449/1 project in University College London. Main targets and summary of results

The basic concept of 'ULECeS' project, that is the idea of cement production using synthesis in molten salt solvents, was conceived by Alan Maries, following the work on 'Making ceramic powders from molten salts' of Douglas Inman and his research team in 1996. The focus of the study of low carbon low energy molten salt synthesis of cements within the 'ULECeS' project in UCL was mainly the energy-related emissions of the cement industry. The 'ULECeS' project involved research in new processes in molten salt media for the Ultra Low Energy Cement Synthesis. The target was to attempt a revolutionary rather than an evolutionary approach in improving the environmental impact of the cement industry. Experiments were undertaken to produce cement and cement compounds in molten salt media at much lower reaction temperatures than the 1450°C of the currently used worldwide process.

The 'ULECeS': Ultra Low Energy Cement Synthesis: A Radical Process Change to Achieve Green and Sustainable Technologies EPSRC EP/F014449/1 project had the following targets:

1. Synthesis of cements/cement compounds (Ca_3SiO_5 , $\beta\text{-Ca}_2\text{SiO}_4$, $\text{Ca}_{12}\text{Al}_7\text{O}_{33}$, $\text{Ca}_3\text{Al}_2\text{O}_6$) in molten salt solvents at lower temperatures than the current industrial process.
2. Preparation of cements/cement compounds with desired particle size distribution, which would reduce the energy needed for grinding the product.
3. The current 'fossil fuel' energy powered process involves a lot of waste of energy. If the molten salt synthesis of cements/cement compounds (Ca_3SiO_5 , $\beta\text{-Ca}_2\text{SiO}_4$, $\text{Ca}_{12}\text{Al}_7\text{O}_{33}$, $\text{Ca}_3\text{Al}_2\text{O}_6$) is achieved in lower temperatures (e.g. below 1000°C) then this will pave the way to potential 'electric' energy powered cement production processes.

Experiments on the synthesis of the major cement compounds **Tricalcium Silicate** (Ca_3SiO_5 , C_3S), **β -Dicalcium Silicate** ($\beta\text{-Ca}_2\text{SiO}_4$, $\beta\text{-C}_2\text{S}$) and **Tricalcium Aluminate** ($3\text{CaO} \cdot \text{Al}_2\text{O}_3$, C_3A) were attempted in molten alkali chloride (ACl , $\text{A}=\text{Na}$, K , Na-K binary eutectic) and CaCl_2 solvents. To simulate the real life industrial process the reactants used were CaCO_3 (calcite), SiO_2 (α -quartz), Al_2O_3 (corundum) and NaAlO_2 ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3$). The thermodynamics of the formation of calcium silicates and aluminates, made it necessary to use solvents with melting points higher than 700°C, which at the same time are not reactive towards the desired product(s). The above prerequisites pointed to the use of alkali and alkaline earth chlorides.

In the next section the results on the attempted molten salt synthesis of the calcium silicates, namely **Tricalcium Silicate** (Ca_3SiO_5 , C_3S) and **β -Dicalcium Silicate** ($\beta\text{-Ca}_2\text{SiO}_4$, $\beta\text{-C}_2\text{S}$) in molten NaCl will be reviewed from the published work on the raw reaction products [88]. The published work on the attempted molten salt synthesis of dicalcium silicate and of tricalcium silicate probed mainly by powder XRD and reported in reference 88, was on the raw 'unprocessed' reaction products. New results of processing the raw reaction products will be reported

here and compared with the results published in reference 88 on the raw reaction mixes. It is worth mentioning that within the ULECeS project attempts were made to prepare calcium aluminates in molten salt media, with emphasis on Tricalcium Aluminate. This represents approximately the 10 wt% of Ordinary Portland Cement clinker and considerably more of calcium aluminate cements. In all attempts to prepare **Tricalcium Aluminate** ($3\text{CaO} \cdot \text{Al}_2\text{O}_3$, C_3A) by the reaction of CaCO_3 with Al_2O_3 in molten alkali chloride solvents at temperatures from 900°C up to 1140°C , the main product was **Dodecacalcium Heptaaluminate** ($12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$, C_{12}A_7) which is an intermediate compound apparently reacting with CaO well above 1140°C to produce **Tricalcium Aluminate** ($3\text{CaO} \cdot \text{Al}_2\text{O}_3$, C_3A) [89, 90].

5.2. Studies of low carbon low energy molten salt synthesis of calcium silicates cement compounds and the effect of processing on the reaction product

In this section the published results [88] on the raw ‘unprocessed’ reaction product of the molten salt synthesis of calcium silicates will be reviewed and compared with new results on the ‘processed’ reaction product. The processing of the samples involved the removal of the NaCl molten salt solvent by two methods. The first method involved the use of water to remove the NaCl molten salt solvent from the raw reaction product using filtration of the aqueous solution. The second method involved the use of a high temperature filtration technique called ‘cupellation’, suggested by Douglas Inman. The details of the experimental procedures about the chemicals used, the sample preparation method, and the characterization techniques (Raman spectroscopy / microscopy, powder XRD and SEM) can be found in reference 88.

The study of the low carbon low energy synthesis of calcium silicates involved experiments on the attempted molten salt synthesis of Dicalcium Silicate Ca_2SiO_4 (C_2S) and of Tricalcium Silicate Ca_3SiO_5 (C_3S) by the reaction of CaCO_3 (calcite) with SiO_2 (α -quartz) (mole ratios 2:1 and 3:1 for the production of C_2S and C_3S respectively) in molten NaCl and at temperatures from 908°C up to 1140°C using different concentrations of the reactants in the molten salt solvent (Table 1) [88]. The following reactions take place during the formation of C_2S and of C_3S respectively:



The raw reaction products were characterized by Powder X-Ray Diffraction, Raman Spectroscopy and Scanning Electron Microscopy (SEM). It was reported that in all experiments the major product was $\beta\text{-Ca}_2\text{SiO}_4$ ($\beta\text{-C}_2\text{S}$) even in the case when the intended product was Ca_3SiO_5 (C_3S) [88]. In these samples intended to produce Ca_3SiO_5 (C_3S) a certain amount of CaO that has not reacted with SiO_2 was always detected in the reaction mixture. This finding pointed the need of using temperatures definitely higher than the maximum temperature of 1140°C used in this study in order to produce Ca_3SiO_5 (C_3S) [25]. The reaction of $\beta\text{-Ca}_2\text{SiO}_4$ with CaO is a classic Lux-Flood type Acid-Base reaction:

Sample number/target compound	CaCO ₃ /SiO ₂ /NaCl mole ratios	Reaction temperature/time	Reaction products detected by XRD
1.A/ β -Ca ₂ SiO ₄	2.0:1.0:19.2	908°C/2h	β -Ca ₂ SiO ₄ , CaO
1.B/ β -Ca ₂ SiO ₄	2.0:1.0:19.2	908°C/2h	β -Ca ₂ SiO ₄ , CaO, CaCO ₃ *
2.A/Ca ₃ SiO ₅	3.0:1.0:19.8	908°C/2h	β -Ca ₂ SiO ₄ , CaO
2.B/Ca ₃ SiO ₅	3.0:1.0:19.8	908°C/2h	CaO, Ca ₅ (SiO ₄) ₂ CO ₃ *
2.C/Ca ₃ SiO ₅	3.0:1.0:19.8	1000°C/1h	β -Ca ₂ SiO ₄ , CaO, trace Ca ₃ SiO ₅
3 / β -Ca ₂ SiO ₄	2.0:1.0:20.4	1140°C/3h	β -Ca ₂ SiO ₄
4 / β -Ca ₂ SiO ₄	2.0:1.0:13.5	1140°C/3h	β -Ca ₂ SiO ₄
5 / β -Ca ₂ SiO ₄	2.0:1.0:10.3	1140°C/3h	β -Ca ₂ SiO ₄
6 / β -Ca ₂ SiO ₄	2.0:1.0: 8.0	1140°C/3h	β -Ca ₂ SiO ₄
7 /Ca ₃ SiO ₅	3.0-1.0:20.0	1140°C/3h	β -Ca ₂ SiO ₄ ,CaO, trace Ca ₃ SiO ₅
8 /Ca ₃ SiO ₅	3.0:1.0:14.0	1140°C/3h	β -Ca ₂ SiO ₄ , CaO, trace Ca ₃ SiO ₅
9 /Ca ₃ SiO ₅	3.0:1.0: 9.9	1140°C/3h	β -Ca ₂ SiO ₄ , CaO, trace Ca ₃ SiO ₅
10 /Ca ₃ SiO ₅	3.0:1.0: 8.1	1140°C/3h	β -Ca ₂ SiO ₄ , CaO, trace Ca ₃ SiO ₅

*Reaction product in the upper part of the sample crucible only.

Table 1. Powder XRD results for light green grain raw product of Molten Salt Synthesis of Calcium Silicates. Republished with permission of Maney Publishing, from *Advances in Applied Ceramics*, G. Photiadis et al., 110, 3, 2011 [Reference 88]; permission conveyed through Copyright Clearance Center, Inc.



The outcome of the reactions was fully confirmed by Raman spectroscopy which showed the absence of any peaks of Ca₃SiO₅ in the raw reaction product [91] in the samples intended to produce Ca₃SiO₅ (C₃S). This is particularly important since in the analysis of the XRD data of the above samples, it always appears the possibility of the existence of trace amounts of hatrurite (Ca₃SiO₅), something which is not confirmed by Raman spectroscopy.

Relevant to the molten salt synthesis of Ca₂SiO₄ at ~900°C in 2 hours in this work, it is worth mentioning that the preparation of Ca₂SiO₄ by solid-state reaction of CaCO₃ and SiO₂ at 800°C for 10 hours at N₂ atmosphere was reported recently [92]. An important result of the reported work on the raw reaction product was the successful preparation of the cement compound β -Ca₂SiO₄ (β -C₂S) (belite) at a temperature of 908°C [88] which is lower than all other previous molten salt synthesis reaction temperatures published so far. This temperature is also lower than the 1000°C (for 12 hours) and 1200°C (for 3 hours) used in a typical solid-state reaction synthesis of belite [93].

A representative Powder XRD measurement of the precipitated raw product of the reaction mixture 1.A is shown in Figure 4 [88]. Assignment of the peaks was after comparison with the XRD data for NaCl and CaO from Wyckoff [94] and for β -Ca₂SiO₄ from Tsurumi [95] respectively.

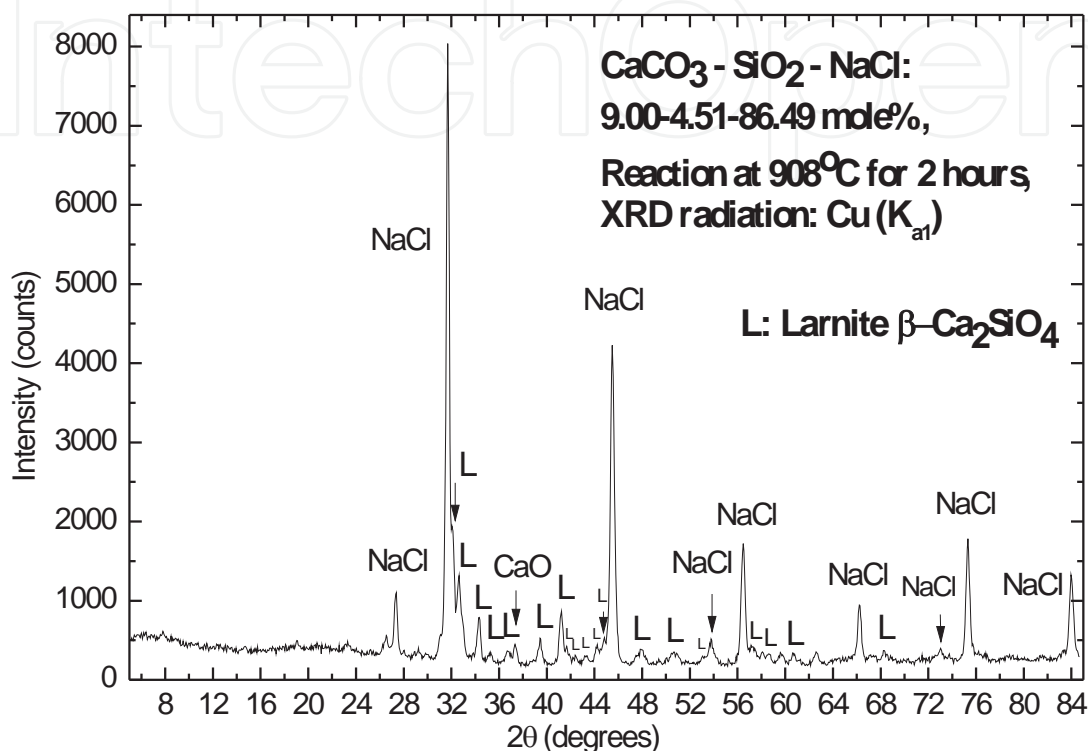


Figure 4. XRD pattern of the raw product of sample 1.A. Republished with permission of Maney Publishing, from *Advances in Applied Ceramics*, G. Photiadis et al., 110, 3, 2011 [Reference 88]; permission conveyed through Copyright Clearance Center, Inc.

The Raman spectrum of the raw reaction product of sample 1.A measured in that work and depicted in Figure 5 [88] showed that the major raw reaction product was larnite (β -Ca₂SiO₄). The Raman-active modes of β -Ca₂SiO₄ having the highest intensity are the internal modes of vibration of the tetrahedral [SiO₄]⁴⁻ orthosilicate molecular anion. The Raman peaks were attributed to the following normal modes of vibration [96]:

Stretching: ν_1 (A₁) = 860 and 845 cm⁻¹.

Bending: ν_2 (E) = 426 and 415 cm⁻¹.

Stretching: ν_3 (F₂) = 978, 914 and 897 cm⁻¹.

Bending: ν_4 (F₂) = 557, 539 and 519 cm⁻¹.

In addition, the Raman spectrum showed a pronounced effect of the atmospheric CO₂ on the sample of the raw reaction product, leading to the conversion of a certain amount of CaO (lime)

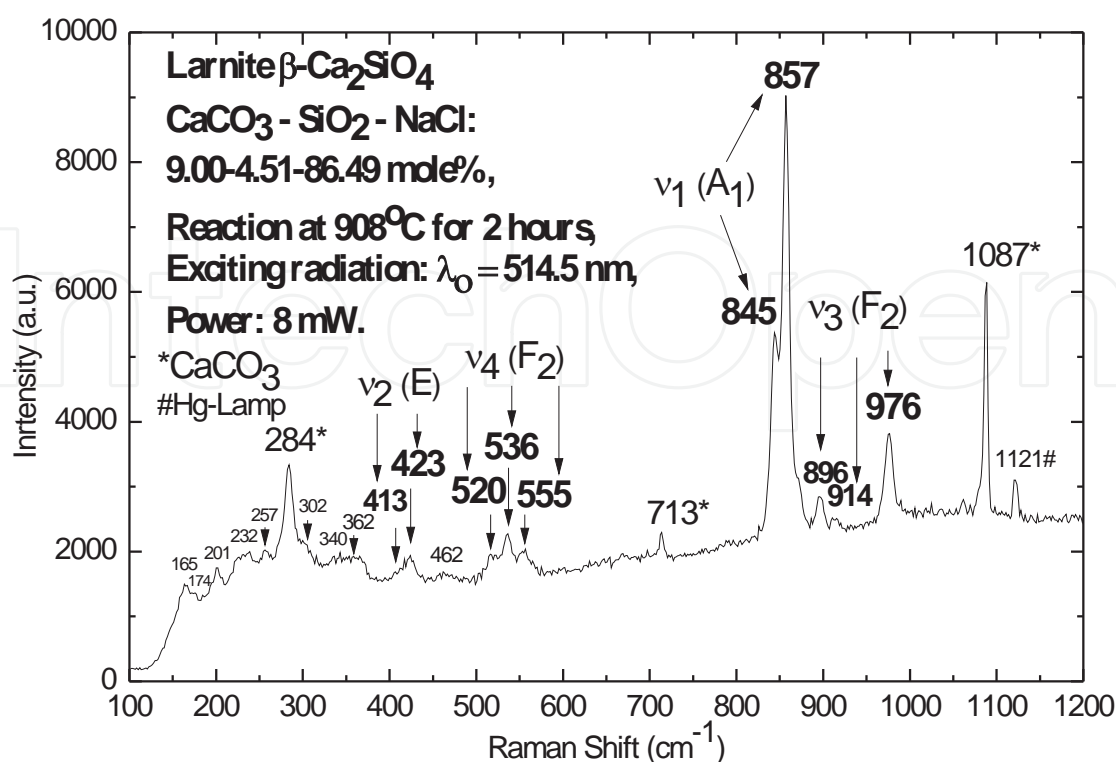


Figure 5. Raman spectrum of raw product of sample 1.A. Republished with permission of Maney Publishing, from *Advances in Applied Ceramics*, G. Photiadis et al., 110, 3, 2011 [Reference 88]; permission conveyed through Copyright Clearance Center, Inc.

to CaCO_3 (calcite). Similar data measured in this work show the potential of Raman spectroscopy as a fast and reliable probe of the molten salt synthesis of cement compounds.

The SEM microphotographs of the raw reaction product show that the $\beta\text{-Ca}_2\text{SiO}_4$ ($\beta\text{-C}_2\text{S}$) has the shape of milky droplet globules (Figure 6).

The individual cement compounds are mixed oxides. If their component oxides have very low solubility in a molten salt solvent, the same is approximately the case for the mixed oxide cement compound. That means that the product does not dissolve in the molten salt solvent and can be separated by a technique such as molten salt filtration. Simultaneously the very low solubility of the reactants in the molten salt solvent does not impose an important problem because even this very low solubility is adequate to drive the reaction in completion in a few hours, e.g in 3 hours at 900°C as compared to the 12-24 hours at 1400°C needed in solid-state reaction synthesis.

The solubility of CaO in NaCl is approximately 0.001 mole % at 850°C [97]. The solubility of SiO_2 in molten NaCl is estimated to have a value of similar order of magnitude [98]. Thus since the solubilities of both CaO and SiO_2 in molten NaCl are very low and the solubility of Ca_2SiO_4 in fused NaCl is anticipated to have a value of an approximately similar order of magnitude. This fact explains clearly the absence of any calcium silicate chloride in the raw reaction product.

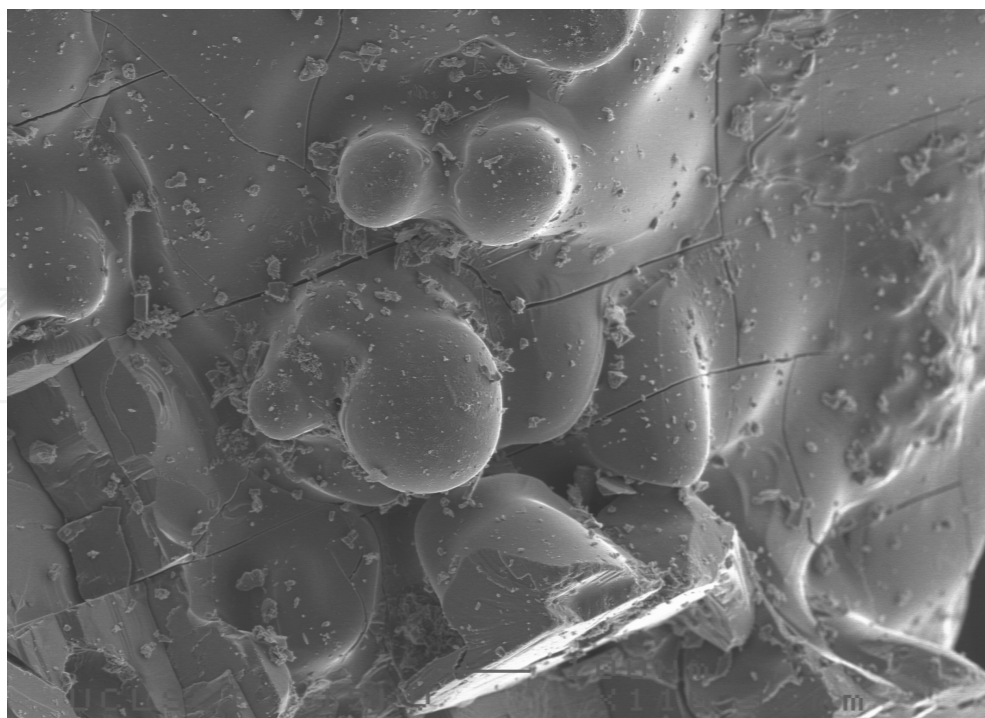


Figure 6. SEM microphotograph of raw product of sample 1.A. The globules of the dicalcium silicate product have size in the order of 50 micrometers.

In order to have a successful synthesis in a molten salt medium it is not a necessary condition to have both reactants absolutely dissolved in the molten salt solvent. In a recent publication on the molten salt synthesis of MgAl_2O_4 in molten AlCl solvents, SEM pictures of the MgAl_2O_4 product show a close resemblance to the SEM pictures of the Al_2O_3 reactant which acts as a template, indicating a 'template' reaction mechanism [73]. Despite the fact that both the CaO and the SiO_2 reactants have a very low solubility in molten AlCl ($\text{A}=\text{Na}, \text{K}$) solvents, their solubility is high enough to yield with high efficiency the Ca_2SiO_4 product in approximately a few hours in a typical experiment at $\sim 900^\circ\text{C}$. This is a major progress compared to a typical solid-state reaction where tens of hours and reaction temperatures well above 1200°C are necessary in order to produce Ca_2SiO_4 . The advantages of molten salt synthesis compared to solid-state reaction synthesis lies in the fact that in the former case the reactants are brought much easier into close contact with each other resulting in higher reaction rates in lower temperatures. It is natural to expect the diffusion of an ion (Ca^{2+} or O^{2-}) to be faster in a liquid medium than in a solid medium. The following reaction mechanism seems to take place. The O^{2-} anions from CaO dissolved in molten NaCl solvent diffuse in the melt and react with SiO_2 forming SiO_4^{2-} molecular anions. In the next stage the Ca^{2+} cations from CaO dissolved in molten NaCl solvent diffuse in the melt and are attached to the SiO_4^{2-} molecular anions to fulfil the electro-neutrality principle, thus forming the Ca_2SiO_4 crystals.

In order to separate the reaction product ($\beta\text{-Ca}_2\text{SiO}_4$) from the molten salt solvent (NaCl) two methods were used:

1. Dissolution of the raw reaction product in water and subsequent filtration of the aqueous solution resulting in the removal of NaCl.
2. High temperature filtration of the raw reaction product, exploiting the fact that at temperatures of $\sim 900^\circ\text{C}$ the $\beta\text{-Ca}_2\text{SiO}_4$ product is solid while the NaCl molten salt solvent is liquid.

The so-called 'wet' method using a solvent like water to wash out the NaCl molten salt solvent is applicable only in the case of $\beta\text{-Ca}_2\text{SiO}_4$ ($\beta\text{-C}_2\text{S}$) samples, because $\beta\text{-Ca}_2\text{SiO}_4$ ($\beta\text{-C}_2\text{S}$) is well known to be much less hygroscopic than Ca_3SiO_5 (C_3S).

Typical X-Ray diffractograms obtained for the water filtered samples are shown in Figure 7 and in Figure 8.

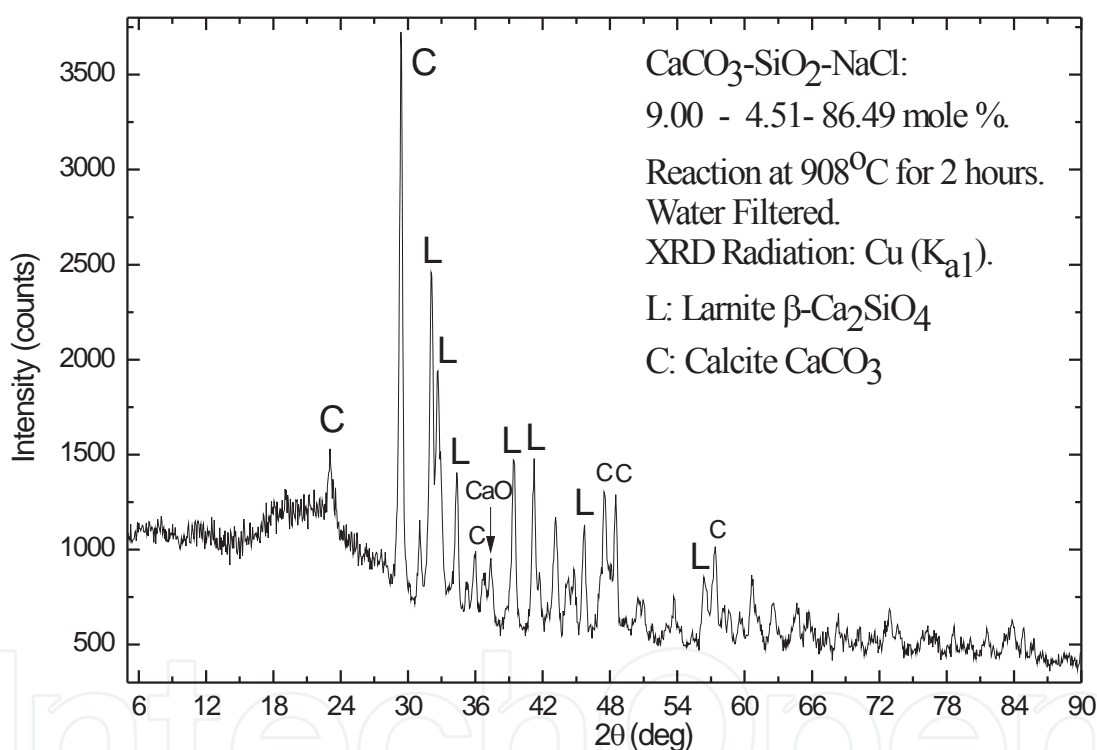


Figure 7. XRD pattern of the water filtered powder product of sample 1.A. The aqueous solution was heated at 80°C in the ultrasonic bath for ~ 30 minutes and the precipitate having the form of light green grains was dried at 100°C for 3 hours and 45 minutes.

It is evident from the diffractogram in Figure 7 that the excess CaO in the raw product sample has reacted with carbon dioxide (CO_2) forming calcite (CaCO_3). The presence of peaks of medium to very strong intensity due to calcite (CaCO_3) in the XRD pattern in Figure 7 shows that the reaction was not complete but was not far from full completion, taking into account that the reaction time was just 2 hours. In an incomplete reaction the amount of free lime CaO which has not reacted with SiO_2 , readily absorbs atmospheric CO_2 and transforms to calcite CaCO_3 .

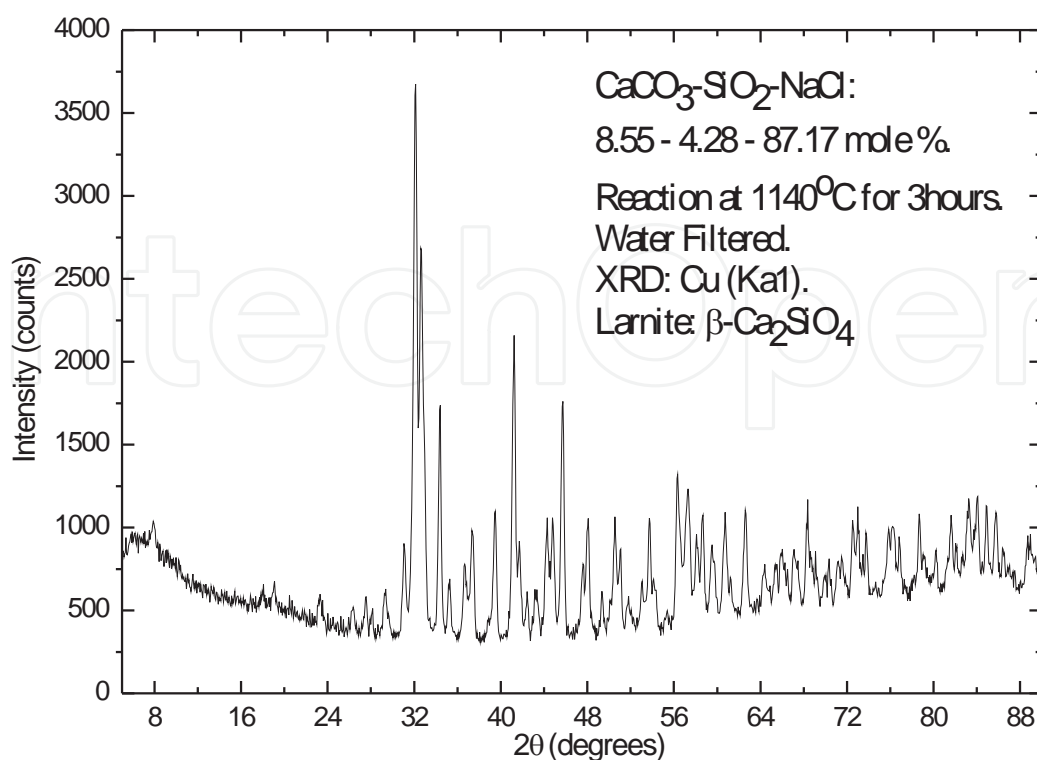


Figure 8. XRD pattern of the water filtered powder product of sample 3. Adding water to the reaction mixture the solution had pH=11 (compared to the pH=14 of water filtered sample 1.A) showing the absence of free lime which would give calcium hydroxide. The aqueous solution was heated at 80°C in the ultrasonic bath for ~30 minutes. The filter paper was glass microfibre FB59407, MF100 (Fisherbrand, Fisher Scientific UK Ltd) made from 100% borosilicate glass, with a retention of 1.6 µm. The precipitate having the form of light green grains was dried at 107°C overnight.

In the XRD pattern of Figure 8 it is evident that the diffractogram is dominated by the peaks of larnite. The absence of peaks due to lime CaO or to calcite CaCO₃ confirms that the reaction is complete as is anticipated from the very high reaction temperature.

In the so-called 'dry' method involving "cupelling" the separation of the precipitated product from the molten salt solvent is implemented using Magnesia (MgO) 'cupels' which absorb the molten NaCl with the β-Dicalcium Silicate remaining on the surface of the cupel. It is highly recommended to use 'cupelling' only after the reactions products are known, because cupel may absorb not only the molten salt solvent but also the CaO and SiO₂ powders that have not reacted. In general physical methods of separation including molten salt filtration / centrifugation techniques and high-vacuum sublimation/distillation) are indeed simpler than chemical methods. The X-Ray diffractogram of sample 1.A after cupellation at 850°C for 4 hours is shown in Figure 9. It is evident from comparison of Figure 7 to Figure 9 that cupellation seems to be a not so efficient separation method as is water filtration. The presence of medium to strong intensity peaks of NaCl is obvious in Figure 9, while these peaks are either absent or of very weak intensity in the case of the water filtered sample in Figure 7.

A comparative view of the XRD diffractograms for the raw product, the cupelled and the water filtered sample 1.A. is presented in Figure 10. The differences between the 'processed' product

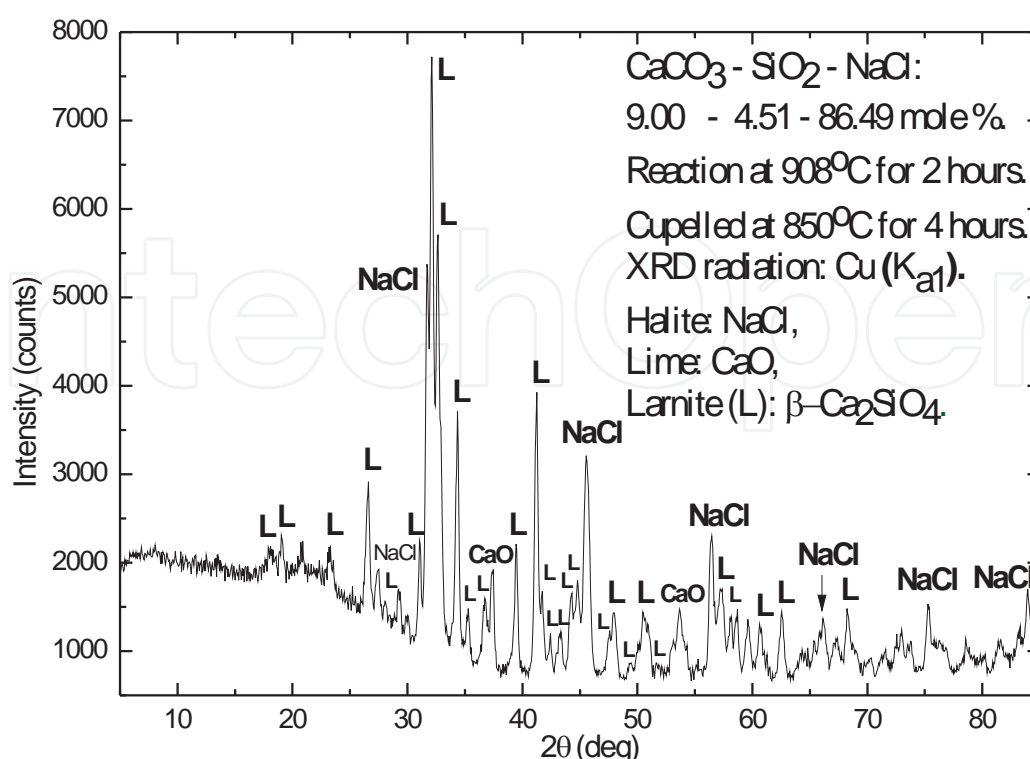


Figure 9. XRD pattern of the cupelled sample 1.A. Cupellation at 850°C for 4 hours.

employing the two separation methods and between them and the raw reaction product are clearly visible in the relative intensities of the peaks of the individual components in Figure 10. Similar XRD patterns of the raw product, the cupelled and the water filtered of other samples provide important information on the influence of the separation technique on the outcome of the reaction.

Preliminary Raman results show that there is some very small amount of γ - Ca_2SiO_4 present along with the dominant phase of β - Ca_2SiO_4 (a Raman peak at 814 cm^{-1} shows the presence of trace γ - Ca_2SiO_4), in the water filtered product.

5.3. The potential reductions in CO_2 emissions using the method of molten salt synthesis for the production of cement compounds on an industrial scale

The cement industry is responsible for 5% of the global anthropogenic CO_2 emissions [34]. The Ordinary Portland Cement (OPC) consists of 95 wt.% Clinker ($3\text{CaO}\cdot\text{SiO}_2$, $2\text{CaO}\cdot\text{SiO}_2$, $3\text{CaO}\cdot\text{Al}_2\text{O}_3$, $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$) and of 5 wt.% Gypsum ($\text{CaSO}_4\cdot 2\text{H}_2\text{O}$) [34]. The average intensity of carbon dioxide emissions from the total global cement production was reported to be 222 kg of C/t of cement or 814 kg of CO_2 /t of cement [34]. The highly energy-intensive process of cement production consists of three major steps: raw material preparation, clinker making in the kiln and cement making [34]. The preparation of raw material involving crushing and grinding the reactants is a process consuming electricity. The clinker kiln uses nearly all of the fuel in a typical cement plant and the production of clinker is the most energy-intensive

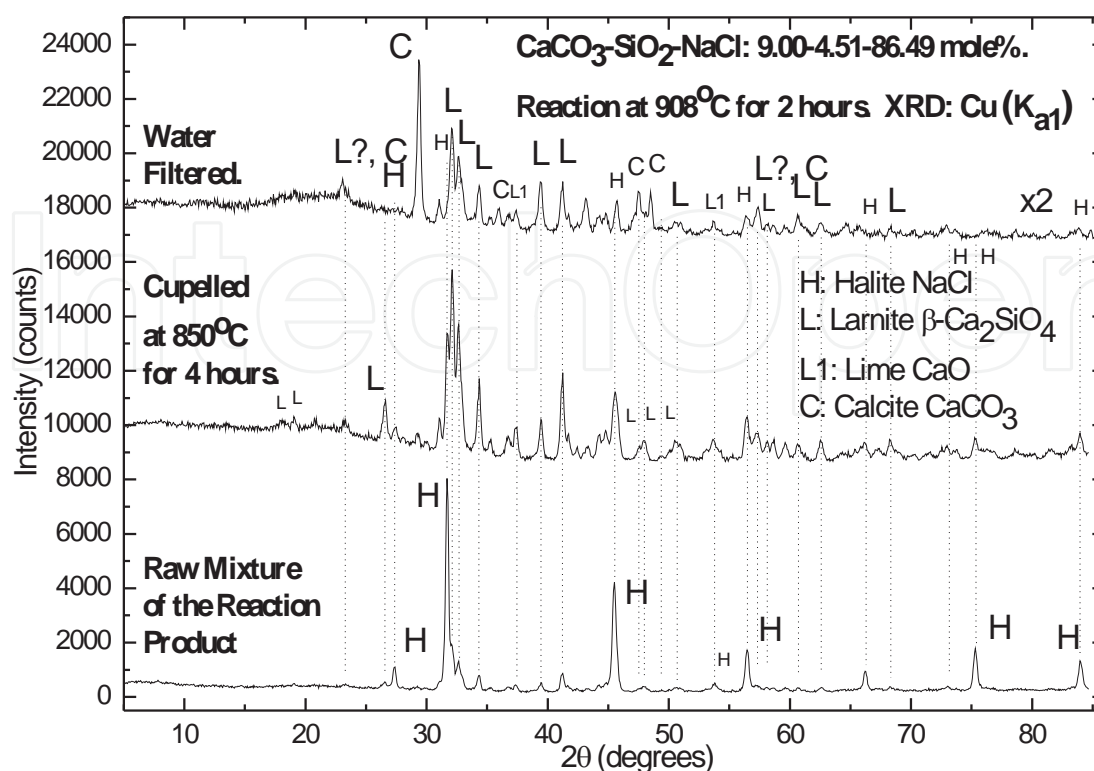


Figure 10. XRD patterns of the raw product, of the cupelled and of the water filtered sample 1.A.

production step, responsible for about 70%–80% of the total energy consumed. The cement making involving finish grinding is a process consuming electricity [34]. The process related CO₂ emissions are due to the decomposition of limestone (CaCO₃) to lime (CaO) and to carbon dioxide (CO₂). These process related CO₂ emissions from clinker production amount to about 0.5 kg CO₂/kg of clinker [34] and represent roughly 60% (500/814) of the total emissions. The remaining 40% are the energy related emissions of the cement production process in all of the three major steps of cement manufacture mentioned above.

The suggested low carbon low energy molten salt synthesis of cement compounds has the potential to lead to reductions in both process and energy related carbon dioxide emissions.

Concerning the process related carbon dioxide emissions, the molten salt synthesis method has the potential to use technology enabling the total capture and storage of all carbon dioxide emissions from the calcination of limestone (CaCO_3). A precalciner molten salt reactor is a realistic option to achieve the decomposition of limestone (CaCO_3) to lime (CaO) and to carbon dioxide (CO_2) in a molten salt solvent and the capture of all carbon dioxide (CO_2). Thus it will be possible to eliminate the process related emissions and to reduce the carbon dioxide emissions of the cement industry by 60%. The elimination of process related emissions within a Molten Salt Synthesis method means a cement industry capable of reducing its impact from 5% to 2% (0.60x0.05 equal to 3% process related emissions gone, 0.40x0.05 equal to 2% energy related emissions left) of the global anthropogenic CO_2 emissions.

The estimation of reduction in carbon dioxide emissions relevant to the energy related emissions is far more complex and has to take into account the production of the individual cement compounds. In the following paragraphs some rough estimates will be attempted by doing some calculations. A rough assumption made is that the temperature, the energy and the carbon dioxide emissions involved in generating the necessary energy to achieve a certain reaction temperature bear all a linear dependence to each other.

The production of β -2CaO·SiO₂ with molten salt synthesis at ~900°C (1173 K) represents a reduction of nearly 550°C from the temperature of 1450°C (1723 K) used in a cement kiln. Since β -2CaO·SiO₂ is 25-30 wt.% of OPC clinker and the production of clinker is responsible for about 70%–80% of the total energy consumed, and the energy related emissions are the 40% of the total emissions, then the roughly calculated reduction in carbon dioxide emissions can be from 2.23% [(550/1723)×0.25×0.70×0.40] up to 3.06%[(550/1723)×0.30×0.80×0.40] of the emissions of the cement industry or from 0.11% [(550/1723)×0.25×0.70×0.40×0.05] up to 0.15% [(550/1723)×0.30×0.80×0.40×0.05] in the global anthropogenic CO₂ emissions of the cement industry

The production of 12CaO·7Al₂O₃ with molten salt synthesis at ~900°C (1173 K) represents a reduction of nearly 550°C from the temperature of 1450°C (1723 K) used in a cement kiln.

The 12CaO·7Al₂O₃ compound is an intermediate compound during the synthesis of 3CaO·Al₂O₃. The 12CaO·7Al₂O₃ compound is formed with molten salt synthesis at ~900°C (1173 K) while the synthesis of 3CaO·Al₂O₃ in the kiln is taking place at ~1250°C (1523 K). The ratio 0.77 of the two temperatures of the reactions of syntheses can be used as a very rough estimate of how the low carbon low energy molten salt synthesis of 12CaO·7Al₂O₃ may facilitate the formation of 3CaO·Al₂O₃ [0.77=(1173/1523)]. Since 12CaO·7Al₂O₃ is an intermediate compound during the synthesis of 3CaO·Al₂O₃ which is 5-12 wt.% of OPC clinker and the production of clinker is responsible for about 70%–80% of the total energy consumed, and the energy related emissions are the 40% of the total emissions, then the roughly calculated reduction in carbon dioxide emissions can be from 0.34% [(550/1723)×0.05×0.70×0.40×0.77] up to 0.94% [(550/1723)×0.12×0.80×0.40×0.77] of the emissions of the cement industry. or from 0.02% [(550/1723)×0.05×0.70×0.40×0.77×0.05] up to 0.05% [(550/1723)×0.12×0.80×0.40×0.77×0.05] in the global anthropogenic CO₂ emissions of the cement industry

Thus the use of molten salt synthesis in the production of β -2CaO·SiO₂ and of 12CaO·7Al₂O₃ can lead to a roughly estimated reduction of the carbon dioxide emissions of the cement industry from 2.57% (2.23%+0.34%) up to 4% (3.06%+0.94%). The use of molten salt synthesis method for the production of the above two compounds represents a potential reduction of up to 0.2% (0.04×0.05) in the global anthropogenic CO₂ emissions of the cement industry. It is also possible to achieve further progress by attempting the molten salt synthesis of 3CaO·SiO₂ and of 3CaO·Al₂O₃ at temperatures above the 1140°C used in the studies reported here, but below the temperature of 1450°C used in the kiln. In a rough calculation a potential molten salt synthesis of 3CaO·SiO₂ and of 3CaO·Al₂O₃ at 1250°C could reduce the global anthropogenic CO₂ emissions of the cement industry by up to 0.13% [(200/1723)×0.70×0.80×0.40×0.05] for 3CaO·SiO₂ and by up to 0.02% [(200/1723)×0.12×0.80×0.40×0.05] for 3CaO·Al₂O₃.

It is also suggested that the controlled molten salt synthesis of cement compounds with desired particle size distribution can reduce the energy needs (and the associated carbon dioxide emissions) for the finish grinding in the final step of cement making.

The above rough but not far from reality calculations show that the adoption of the molten salt synthesis method in the production of cement compounds offer a realistic alternative option and a complementary to other approach to mitigate the environmental impact of the cement industry. It can lead to a cement industry responsible for less than 1.8% (5%-3%-0.2%) of the global anthropogenic CO₂ emissions which is a figure much better than the current 5%.

6. Conclusion

The compound β -Ca₂SiO₄ (β -2CaO·SiO₂) which is an important constituent of Portland cement and a major component of belitic cements was synthesized by the reaction of CaCO₃ (calcite) with SiO₂ (α -quartz) in molten NaCl solvent at ~900°C [88, 89]. This is the lowest reaction temperature in molten salt media in which this product has been formed when using CaCO₃ and SiO₂ as reactants. The β -Ca₂SiO₄ polymorph has been stabilized at room temperature without the need to use any kind of doping with B₂O₃, Al₂O₃ or sulfates to prevent its inversion to γ -Ca₂SiO₄. The synthesis of β -Ca₂SiO₄ was also achieved using a slow cooling rate of the reaction mixture, just a few °C/minute (e.g. 3°C/minute) which is much slower than the quenching used in the industrial process of cement manufacture. The effect of two separation methods on removing the molten salt solvent from the reaction product was studied by powder XRD. This is of particular importance since it is necessary to have a β -Dicalcium Silicate product with the minimum amount of NaCl present. Similar very promising results have been reported for the synthesis of Ca₁₂Al₁₄O₃₃ (12CaO·7Al₂O₃) in molten NaCl at ~900°C [89, 90]. The Dodecacalcium Heptaaluminate (12CaO·7Al₂O₃) is an intermediate product during the formation of Tricalcium Aluminate (3CaO·Al₂O₃) which is a major component of calcium aluminate eco-friendly cements.

The energetically efficient synthesis of β -C₂S and of C₁₂A₇ in molten alkali chloride solvents at temperatures as low as 900°C is very promising and paves the way for electric energy powered cement production processes. This is a breakthrough result which can lead to a much more efficient use of energy in the production of cement. It can also pose much less technological challenges for the decomposition of limestone to lime and the efficient capture and storage of the emitted CO₂, thus enabling the use of a molten salt reactor precalciner which can reduce directly the global carbon dioxide emissions of the cement industry from 5% to 2%. The benefits of using a molten salt synthesis process for cement manufacture are that it can reduce both the process and the energy related emissions of carbon dioxide. It can result in a cement industry responsible for less than 1.8% (5%-3%-0.2%) of the global anthropogenic CO₂ emissions, a figure which represents not a simple step change but a significant improvement compared to the 5% of the current cement industry. The strategies to mitigate climate change already in use or planned for use in the future by the cement industry were assessed in the report of the IPCC in 2007 on Mitigation of Climate Change [reference 10, page 467]. In this report it was emphasized that the cement industry is capital intensive and the equipment has a long lifetime, which is a factor limiting the economic potential in the short term. In this respect, an industrial process

using the method of the molten salt synthesis of cements has the potential on a medium to longer term to be a realistic novel technology.

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