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Valorization pathway for solid by-product from the thermal decomposition of phosphogypsum in the cement industry

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Mémoire présenté en vue de l'obtention du diplôme de *Maîtrise ès sciences appliquées*

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Ce mémoire intitulé :

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présenté par **Mona HASSAN**

en vue de l'obtention du diplôme de *Maîtrise ès sciences appliquées*

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RÉSUMÉ

Le phosphogypse (PG) est un sous-produit formé à partir du processus humide de production d'acide phosphorique. Il s'agit principalement de sulfate de calcium dihydraté $CaSO_4.2H_2O$ plus des traces d'impuretés, telles que le silicium, l'aluminium, le fer, les métaux lourds et les éléments radioactifs. Chaque tonne d'acide phosphorique produit environ cinq tonnes de PG, qui sont généralement rejetées sur terre ou dans la mer ou les cours d'eau, provoquant une pollution environnementale dangereuse. Un effort mondial est donc en cours pour valoriser le PG de plusieurs manières bénéfiques ; par exemple, il a des utilisations commerciales précieuses dans l'agriculture, les produits d'alimentation animale, la construction et l'extraction d'éléments de terres rares.

Un type de valorisation des PG est la décomposition thermique dans des conditions réductrices pour produire du dioxyde de soufre (SO_2) et le sous-produit solide de l'oxyde de calcium (CaO), qui est notre objectif dans cette étude. Le CaO est un produit précieux utilisé dans l'industrie du ciment en raison de la similitude de leur contenu chimique.

La recherche actuelle se concentre sur la voie de valorisation du sous-produit CaO de la décomposition thermique de PG dans des conditions réductrices. La réaction de décomposition a été simulée par le logiciel FactSage 7.3. La composition de la réaction a été évaluée en la comparant à la composition du calcaire utilisé dans la production du Ciment Portland Ordinaire.

Les résultats de la simulation démontrent que le sous-produit CaO peut être utilisé comme matière première pour la production de Ciment Portland Ordinaire en ajustant sa composition chimique, par exemple en ajoutant de petites quantités de SiO_2, Al_2O_3 et Fe_2O_3 au sous-produit CaO, en utilisant 50% en poids de sous-produit CaO et 50% en poids de calcaire et d'argile, en ajoutant de l'argile au sous-produit CaO et en l'utilisant comme Ciment Résistant aux Sulfates.

Les résultats indiquent également que les sous-produits du PG (CaO et CO_2) peuvent être utilisés dans le captage et le stockage du dioxyde de carbone comme méthode de valorisation. Cette méthode est utile pour éliminer les émissions de CO_2 dans l'environnement.

ABSTRACT

Phosphogypsum (PG) is a by-product formed from the wet process of phosphoric acid production. It is mainly calcium sulphate dihydrate $CaSO_4.2H_2O$ plus traces of impurities, such as silicon, aluminum, iron, heavy metals, and radioactive elements. Each ton of phosphoric acid produces around five tons of PG, which is usually discharged on land or in the sea or watercourses, causing dangerous environmental pollution. A global effort is therefore underway to valorize PG in several beneficial ways; for instance, it has valuable commercial uses in agriculture, animal feed products, construction, and rare earth elements (REEs) extraction.

One type of PG valorizing is thermal decomposition under reductive conditions to produce sulphur dioxide and the solid by-product of calcium oxide, which is our focus in this study. CaO is a valuable product used in the cement industry due to the similarity in their chemical content.

Current research focuses on the valorization pathway for the CaO by-product from PG's thermal decomposition under reductive conditions. The decomposition reaction was simulated by FactSage 7.3 software. The reaction's composition had been evaluated by comparing it with the composition of limestone used in the production of Ordinary Portland Cement (OPC).

The simulation results demonstrate that the PG by-product (CaO) can be used as a raw material for Ordinary Portland Cement production by adjusting its chemical composition, for example, adding small amounts of SiO2, Al_2O_3, and Fe_2O_3 to the PG by-product (CaO), using 50% of weight PG by-product (CaO) and 50% of weight limestone and clay, adding clay to the PG by-product (CaO), and using it as Sulfate Resistant Cement (SRC).

The results also indicate that the PG by-products CaO and CO_2 can be used in Carbon dioxide Capture and Storage (CCS) as a valorization method. This method is useful in eliminating CO_2 emissions in the environment.

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NOMENCLATURE

ABBREVIATIONS

AEC	Air Entraining Cement
ASTM C	American Society for Testing and Materials calcium-based
BFC	Blast Furnace Cement
Bq/kg	The becquerel is the SI derived unit of radioactivity
C2S	Di-calcium silicate
C3A	Tri-calcium aluminate
C3S	Tri-calcium silicate
C4AF	Tetracalcium aluminoferrite
CaL	Calcium Looping
CCS	Carbon dioxide Capture and Storage
DAP	Di-ammonium phosphate
EC	Expansive Cement
FGDG	Flue Gas Desulfurization Gypsum
GHG	Green House Gases
HAC	High Alumina Cement
HC	Hydrophobic Cement
ICP-MS	Inductively coupled plasma mass spectrometry
IHFBR	Induction Heating Fluidized Bed Reactor
LHC	Low Heat Cement
MAP	Mono-ammonium phosphate
NAA	Neutron Activation Analysis
OPC	Ordinary Portland Cement
PC	Portland Cement
PG	Phosphogypsum
PPC	Portland Pozzolana Cement
PPQ	Part Per Quadrillion
PPT	Part Per Trillion
PSD	Particle Size Distribution
QEMSCAN	Quantitative Evaluation of Materials by Scanning Electron Microscopy
QSC	Quick Setting Cement

REEs	Rare Earth Elements
RHC	Rapid Hardening Cement
SRC	Sulphate Resisting Cement
TENORM	Technologically Enhanced Naturally Occurring Radioactive Material
TSS	Total Suspended Solids
US EPA	The United States Environmental Protection Agency
WC	White Cement

CHAPTER 1 INTRODUCTION

1.1 Problem Statement and Motivation

Phosphogypsum (PG) is a waste by-product of the wet process of phosphoric acid manufacturing. The PG is produced from this process in significant amounts. For each 1-ton of phosphoric acid produced, 5 tons of PG are formed, which is generally disposed of in huge stockpiles on land or discharged into water sources, that cause an environmental catastrophe due to radioactive materials and heavy metals, which pollute the air, land, and water. Humans, animals, and plants have been directly and indirectly affected [1].

Globally, only 14% of PG is treated for re-use in applications, like agriculture and construction. Since the recycling percentage is so low, there is a global effort to find new ways to benefit from PG stacks from valorizing and converting them to a high-value product on the one hand, to minimizing their effect on the environment on the other [1].

Phosphogypsum was recently widely used in the Portland Cement industry due to its immense similarity in appearance and characterization. Many researchers reported different methods for their experiments in this field.

Phosphogypsum is being used commercially as an ingredient, up to five percent, in Ordinary Portland Cement, which will eliminate a significant environmental contamination source. It will also minimize the cost of cement manufacturing. More studies to investigate the possibility of obtaining CaO from PG, which can be used explicitly in the cement industry, are also suggested [2].

However, there is substantial technological potential for eliminating minor components from PG, which are hazardous or have a detrimental effect on the material’s consistency. To achieve this, removal of the hazardous materials from the origins, degradation of residual organics, and separation techniques should be used. Technologies of separation methods usually lead to higher hidden costs, higher waste treatment rates, stricter rules, and higher costs for competitive virgin materials, which could make the use of cleaner phosphogypsum more appealing in building materials [3].

Another issue preventing the use of PG is the trace heavy metals content, which eventually may cause serious health problems and be banned from use in construction [4].

In contrast, phosphogypsum as cementitious binders is extensively used in construction products and materials manufacturing. The use of PG in the construction industry due to product waste could provide low-cost materials and reduce pollution problems [5].

It is recommended to produce cement from phosphogypsum due to its lower energy requirements compared to traditional building materials. The results indicated that heating phosphogypsum to 1000°C could make a stable anhydrite cement [6]. An investigation had been focusing on how PG could be beneficial to the cement industry.

In the present research, the chemical composition of CaO was compared with the limestone's chemical composition used to make Ordinary Portland Cement. Afterward, it was evaluated in three steps: major, minor, and trace elements evaluation. This procedure was used to ensure similarity in the chemical properties.

1.2 Research Objectives

The PG thermal decomposition under reductive conditions at a specific temperature produces sulphur dioxide, SO_2, and the solid by-product, CaO. The SO_2 is re-looped and re-cycled to be used in the sulfuric acid industry. The CaO is analyzed, treated, and evaluated to be used as a cement feedstock.

The main objective of this research is to study, by using FactSage software, the feasibility of using the CaO by-product from the thermal decomposition of PG under reductive conditions in the cement industry as an alternative feedstock in the Portland Cement production.

The following sub-objectives are considered:

- Objective 1: Comparing the CaO produced from the PG thermal decomposition with the typical Portland cement composition by applying three evaluation procedures. The first is the evaluation of the major elements, Ca, Si, Al, and Fe. The second is the evaluation of the minor elements, Mg, Na, K, and SO_3. Finally, the trace metals evaluation, Hg, Cd, Se, and Cr. The evaluations of these elements can be considered for valorization.

- Objective 2: Develop valorization methods to use the CaO by-product as a feedstock in the Portland cement, by replacing the limestone feedstock used in Portland Cement with the CaO solid by-product from PG thermal decomposition.

CHAPTER 2 LITERATURE REVIEW

2.1 Phosphogypsum

2.1.1 What is phosphogypsum?

Phosphogypsum, which is mainly $CaSO_4.2H_2O$, is a waste by-product from the wet method of phosphoric acid manufacturing from phosphate rock [7-9]. It contains variable amounts of phosphoric acid (H_3PO_4), hydrofluoric acid (HF), heavy metals (Cd, Hg, Cu, etc.), which rise depending on the origin of the sample, and natural radionuclides (^{226}Ra, ^{238}U). Eighty-five percent of uranium is present in the phosphate rocks used to produce phosphoric acid. In comparison, 90% of the radium remains in the PG by-product [10]. These elements vary depending on the phosphate's origin, quality, and the process used [10, 11].

Significant quantities of PG are produced every year. It has been estimated the overall production of PG up to 2006 is about 6 billion tons. Worldwide, the annual production of PG is around 160Mt/year and is estimated to grow up to 200-250 million tons per year over the next decades [12]. Noted that, only 14% of the world's waste is re-used, 28% is discarded into water bodies, and 58% is stockpiled, causing tremendous environmental threat [11].

2.1.2 Production of phosphogypsum

PG is generated from the wet process of the phosphate ore chemical reaction with sulfuric acid to form phosphoric acid [13]. In the plant, to produce 1 ton of phosphoric acid, it requires around 3-5 tons of phosphate rocks, which produces approximately 5 tons of PG as a by-product. This treatment produces about 90% of global phosphoric acid [14].

In the wet process, shown in Figure 2.1, phosphoric acid is produced from the digestion of concentrated sulfuric acid with natural phosphate rock, referred to as fluorapatite ($Ca_{10}(PO_4)_6(F, OH)_2$), in presence of water at 75-80°C. The reaction also forms calcium sulfate (named phosphogypsum due to the nature of the material used in the process). The phosphoric acid (26-32%) is then separated from the phosphogypsum by-product in dihydrate filter. The reaction is enhanced by recycling the weak phosphoric acid to the attack tank to allow the phosphogypsum to almost full precipitation. The following equation represents the wet process reaction [15, 16]:

$$Ca_{10}(PO_4)_6F_2 + 10H_2SO_4 + 20H_2O \longleftrightarrow 6H_3PO_4 + 2HF + 10(CaSO_4.2H_2O) \text{ ....…… } (1)$$

H_2SiF_6 is often generated in place of HF, based on the quantity of the soluble SiO_2 in the raw material [16].

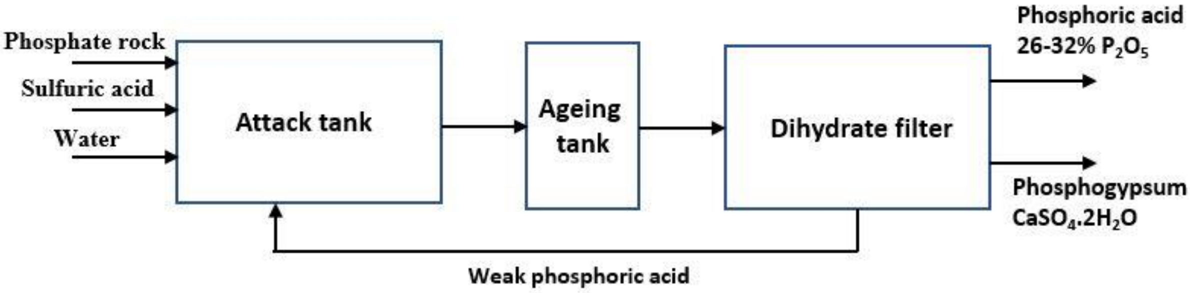


Figure 2.1 Wet process of phosphoric acid production [17]

2.1.3 Properties of phosphogypsum

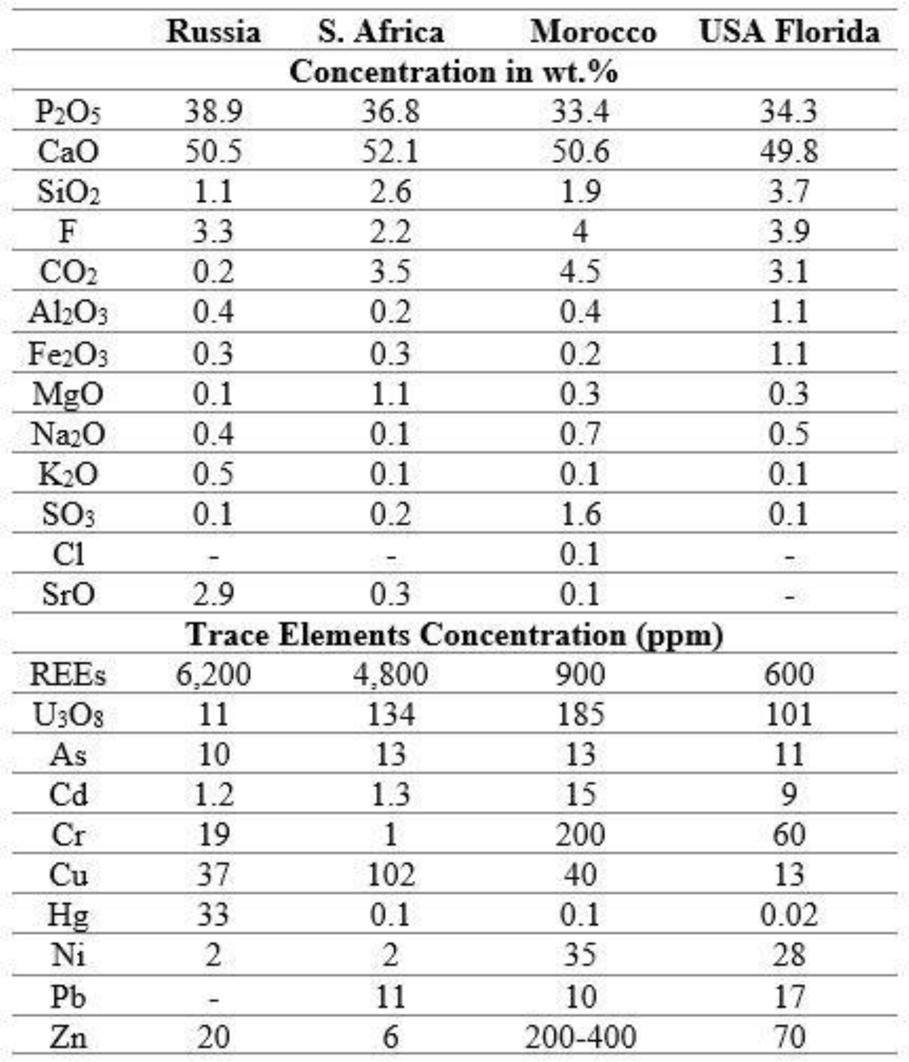
2.1.3.1 Physical properties

PG has specific physical properties, it is a yellowish-brown, sometimes grey powder [14] that is smooth and moist [18]. Morphologically, 75% of its particle size range is between 0.045 and 0.25 mm in diameter, depending on its origin and manufacturing process conditions. It has a specific gravity of around 2.3-2.6 [19]. It consists mainly of calcium sulphate dihydrate. The free moisture content of the PG varies between 25-30% and can be released by heating the PG to 90ºC. On the other hand, the PG core's water content is around 11-25% [20]. The PG solubility varies due to its pH. It is considered an acidic material with an approximate $pH < 3$, and it is highly soluble in saline water (≈4.1 g/l) [21]. PG has a bulk density that varies between 0.9 and 1.7 g/cm^3 [22].

2.1.3.2 Chemical properties

The chemical properties of PG differ based on many factors, the most important of which is the origin of the phosphate rocks and their composition [23]. Table 2.1 shows the chemical composition of various phosphate rocks from four different regions: Russia, South Africa, Morocco, and Florida USA [24]. Chemically, PG is mainly gypsum and some components from the wet process, like alkali, fluorosilicates, and fluorides. It contains small amounts of unreacted phosphate from the raw material and some minerals, including quartz, organic waste, and feldspars. As a result, produced acids, such as phosphoric, sulfuric, and hydro-fluosilicic, trapped in the solid residue's pore spaces, accord it its acidic existence in phosphogypsum. Accordingly, these wastes include high amounts of heavy metals and radionuclides [25].

Table 2.1 The chemical composition of various phosphate rocks [24]



	Russia	S. Africa	Morocco	USA Florida
Concentration in wt.%				
P_2O_5	38.9	36.8	33.4	34.3
CaO	50.5	52.1	50.6	49.8
SiO_2	1.1	2.6	1.9	3.7
F	3.3	2.2	4	3.9
CO_2	0.2	3.5	4.5	3.1
Al_2O_3	0.4	0.2	0.4	1.1
Fe_2O_3	0.3	0.3	0.2	1.1
MgO	0.1	1.1	0.3	0.3
Na_2O	0.4	0.1	0.7	0.5
K_2O	0.5	0.1	0.1	0.1
SO_3	0.1	0.2	1.6	0.1
Cl	-	-	0.1	-
SrO	2.9	0.3	0.1	-
Trace Elements Concentration (ppm)				
REEs	6,200	4,800	900	600
U_3O_8	11	134	185	101
As	10	13	13	11
Cd	1.2	1.3	15	9
Cr	19	1	200	60
Cu	37	102	40	13
Hg	33	0.1	0.1	0.02
Ni	2	2	35	28
Pb	-	11	10	17
Zn	20	6	200-400	70

PG consists of specific compounds and those with a high concentration are CaO and SO_3. They make up around 75% of its content. There are other combinations, such as SiO_2, Na_2O, and P_2O_5, which exist in the original ore and occur, after decomposition, in both phosphoric acid and the PG [14, 26]. Table 2.2 presents the chemical oxides analysis of PG.

Table 2.2 Chemical oxides analysis of phosphogypsum in % mass [14]

CaO	**SO_4**	**Na_2O**	**SiO_2**	**Fe_2O_3**	**Al_2O_3**	**P_2O_5**	**MgO**
24-34	48-58	0.12-10	0.5-18	0.01-0.25	0.05-0.6	0.05-8	0.01-0.54

The concentration of heavy metals depends on the phosphate rock type. PG seems however to have a broad tendency for contamination as most trace elements are correlated with it. Between 2 to 12% of each trace element in phosphate rock is transferred to PG during phosphoric acid processing [27]. Transferring metals to PG is divided into three steps: high mobility elements, like Sr and Zn, modest mobility elements, such as As, Ba, Cd, and Cr, and low mobility elements, for example, Cu, Ni, Pb, Se, V, and Zr. Table 3 shows the heavy metals and trace elements in PG in ppm [14, 26].

Table 2.3 Heavy metals and trace elements content in PG in ppm [26, 28]

Cd	**Zn**	**Cr**	**Cu**	**Ni**	**Sr**	**Th**	**F**
0.8-40	4-315	1.6-75	2-195	1.7-250	10-118	0.3-0.77	0.1-1.8
Ba	**Hg**	**Zr**	**Pb**	**As**	**Se**	**V**	**U**
20-236	0.005-10	10-110	0.5-75	1-42	0.5-75	2-40	3-15

Phosphogypsum is loaded with radioactive elements that transferred to it from the phosphate rock. Various radioactive elements occur in PG but vary in their concentrations. The main ones are ^{226}Ra, ^{238}U, and ^{232}Th. Uranium is the principal reason for environmental contamination due to its radiotoxicity behaviour. For PG recycling and re-using purposes in agriculture and construction, radionuclides are considered within the permissible range and accepted in some cases depending on its percentage and the regulations in the area used. On the other hand, some countries have still banned PG’s re-use [29].

2.1.4 Phosphogypsum disposal

Annually, 86% of PG generated is disposed of and stockpiled in stacks or near water sources near the companies and about 14% is recycled [10]. PG is disposed of in dry or wet stacks. The wet stack is commonly used where the produced PG is mixed with water and dumped into settling ponds. The water thus is concentrated, and the solid stacks increased to a vast amount [30].

In dry stacking, the dry PG is transported directly by truck to the area for stockpiling after the filtration stage. In this way, water is not needed to convert the dry PG to a slurry. Dry stacking is used in Jordan, Tunisia, Senegal, and some former Soviet Union countries. However, in North America, wet stacks are more prevalent [31].

According to the US EPA, the disposed of stacks are forming a real threat due to their accumulation and lack of re-use, which categorizes the PG as Technologically Enhanced Naturally Occurring Radioactive Material (TENORM) [32]. PG is considered a waste due to ^{226}Ra because it has been banned from use and directed to stock in stacks. One exception is to use it as a soil amendment if its radioactive concentration is below 370 Bq/kg. While in other countries, like Spain, PG is used in agriculture regardless of its radioactive content [10, 25].

In the past, attempts to find solutions to recover PG and re-use it rarely was made due to the environmental impact and the cost of the treatment. Regulations have tightened and obliged factories to follow waste material disposal laws [33].

2.1.5 Phosphogypsum environmental impact

The phosphate industry dumped the PG by-product into landfills and water, contaminating them with effluent and the threat of air pollution due to the presence of radioactive matters [32]. Furthermore, the inhalation of PG dust uncovered in any process step may cause autoimmune disorders, lung cancer, and liver failure [34].

The phosphogypsum composition varies depending on the nature of origin. It generally includes various harmful elements, like heavy metals, which, if not correctly handled, may be hazardous to the ecosystem and cause significant pollution to the soil and water, especially in areas near burial locations due to its high concentration [12].

For instance, in agriculture, environmental concerns may be threatened by heavy metals that spread underground and affect the food supply of the plants directly and indirectly, which will harm people [19]. Another example are fish, which are affected by PG dumped in water sources. Consequently, people might have been impacted indirectly [33].

2.1.6 Phosphogypsum re-use

PG has limited uses since it poses a serious problem for the environment and people due to its content of heavy metals and radioactive elements [19, 35]. Phosphogypsum requires an extensive disposal in the phosphates sector, which annually bears high costs [36]. Although the beneficial re-use of PG faces several obstacles, positive re-use cases worldwide have shown the potential to reduce the risk of stacking and create benefit instead incurring costs [14, 33].

Around the world, phosphogypsum is increasingly being used in agriculture applications, becoming one of the primary uses in fertilizers and soil amendment since they contain a high concentration of calcium, phosphorus, and sulphur [37]. The main practical uses in agriculture are soil recovery, sodic and saline soil remediation, soil amendment to increase water retention, decreased soil erosion, and fertilization to increase crop yields and additives during the conversion of compost manure [26].

Nowadays, research is focusing on studying the use of PG in agriculture, especially in Ca-amendment. PG was revealed as an amendment for crop production due to its high-volume output and low cost. It is used as a Ca-amendment for sodic and acidic soils due to its high content of calcium and sulphur. Its high solubility makes it absorb quickly when applied in soil [38].

It is known that change in soil hydraulic properties happens since the calcium discharged by dissolved gypsum is exchanged with the sodium fraction of the soil. Garrido and his team [39] demonstrated that PG, as an amendment, enhanced the capacity to maintain metals in soil by controlling the movability of Cd, Cu, and Pb bound to Fe and Al hydroxides and increasing the organic bound part in acid soils. Peregrina et al. [40] treated AP (the top soil) and AB (the subsoil or the soil solum) horizon soils with a mixture of two by-products, phosphogypsum and sugar foam wastes. Together they minimized the Aluminum content in western Spain soil. Moreover, this combination augmented the pH and the commutable Ca, whereas it reduced commutable Al, Na, and Mg. Pavan and his group [41] studied the phosphogypsum effects on apple trees in Brazilian soils. Phosphogypsum substantially increased the rooting density in the high-aluminum soil surface and this effect extended 60 cm in-depth. In contrast, it increased the amount and size of fruits by improving the root and the water supplies to trees.

As the ^{226}Ra in phosphogypsum is known, its radionuclides' influence in agronomic soils as a Ca-amendment should be studied. Applying PG as a soil amendment does not show significant increases in radionuclides concentration in soils [42]. Abril and her team [10] assessed that applying PG for soil alteration in southwest Spain did not significantly increase radioactive doses by inhalation in farmers. Actual exhalation levels of ^{222}Rn from the soil remain within the normal range despite three decades of this practice.

Eventually, various aspects affect the re-use of PG in agriculture: the origin and composition of PG, the type of soil treated, type of crop, and the regulations of the surrounding countryside. Each region must respect their environmental laws and legislation [15].

For decades, PG has been widely investigated for use in construction and building materials. Despite the fast development and growth in the global construction industry, PG can contribute widely in this domain, depending on the similarity in composition between it and cement, bricks, and plaster [3]. Lopez et al. [43] studied the physical, chemical, and radioactive characterizations of PG to produce a PG sulphur polymer cement, which is a new cement used in building materials; it succeeds in obtaining a high strength cement (54–62 MPa) with low porosity (2.8–6.8%).

Thus far, PG's inherent radioactivity may be a significant downside to its use as a construction material. This drawback could be prevented by reducing the portion of PG used during cement preparation. Gasco et al. [44] illustrated in their research the pros and cons of using PG for building purposes from radiological point of view, they concluded that by controlling the PG percentage used in the manufacturing of building material, the downside could be avoided.

Furthermore, to produce reliable building products, specific treatments, including mixing with other products, should be suggested and studied [7]. Folek et al. [45] tested using PG mixed with fly ash and stabilizing binder in road construction by conducting strength tests after six months and 18 months and proved its feasibility.

Manjit Sing [46] proved that the aqueous citric acid solution was leached and purified the PG to be used in the cement and plaster industry. On the other hand, PG was added instead of natural gypsum to the mortar and concrete. Sadiqul Islam et al. [31] investigated that PG performed well when added to the cement clinker. up to 5-10% of PG can be added. Moreover, it achieved better results when PG was washed and dried. Additionally, Antonio and Wen [47] indicated that Phosphogypsum-based roller compacted concrete is acceptable for parking lots without affecting the strength and shrinkage.

One more practical use for PG, depending on the rock type and origin, is the extraction of the rare earth elements (REEs) in PG, which has concentration about 0.04–1.57% in weight [48]. Table 2.4 shows the concentration of REEs in the PG sample used in this study. PG may also be valorized and can theoretically be used as a second valid resource for REEs. Real reviews of cascade leaching methods for recovering REEs from PG are, therefore, of great importance [16].

Table 2.4 Concentration of REEs in PG sample (ppm) [16]

Y	**Sc**	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**
135.59	11.58	61.21	40.1	10.64	46.33	9.74	2.5
Gd	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**
13.7	1.93	12.14	2.81	8.57	1.12	6.54	0.99

Generally, REEs, which are found in PG, have many ways to be extracted by cascade leaching. Decades ago, researchers used several methods of extraction by different types of acids. Nasria et al. [49] double leached the PG sample after washing it with distilled water with sulfuric acid solution 10% at 60-80°C for 2 hours; this method yields optimum REEs after evaporating and filtering the washed residue. Valkova and her team [35] used sulfuric acid at high temperature; they autoclaved the PG sample at 130-150°C to obtain pure PG in a crystal structure. After processing in the reactor, the sample was rinsed with water and then sent to sulfuric acid leaching. Mughda et al. [50] illustrated leaching PG using three acids, HCl, HNO_3, and H_2SO_4 to extract REE's. Their results showed that each acid had its optimum temperature, residence time, molarity, and solid/liquid ratio to perform the perfect extraction. Fransisco et al. [9] extracted the PG with acetic acid for 18 hours and a liquid/solid ratio of 20:1, then centrifuged it and washed it with nitric acid. El-Didamonya et al. [51] added tributyl phosphate, TBP, with Trioctylphosphine oxide to the PG to increase removal efficiency depending on certain residence time factors, molar ratio, and temperature.

2.2 Cement Industry

2.2.1 What is cement?

Cement is a binder that binds aggregates and reinforces materials. Quality and types of cement have changed with the advancement of technology. Therefore, various forms of cement are available for different building works [52]. The most superficial chemical reaction (2) representing the manufacture of cement is the thermal decomposition of calcium carbonate, $CaCO_3$ (limestone), at 1450°C to form calcium oxide, CaO, and carbon dioxide, CO_2, according to the following reaction:

$CaCO_3 \longrightarrow CaO + CO_2$ …………………………………………………………….... (2)

2.2.2 Cement types

Generally, cement can be separated into several divisions depending on the factors dividing them. In one case, cement is divided into two groups based on its hardening and setting. The first type is Hydraulic Cement. It is the kind of cement that hardens when reacting with water forming a water resistance material and its raw materials are lime, clay, and gypsum. The second type is the Non-Hydraulic Cement. It needs a dry condition to harden in the presence of CO_2 in the air, its raw materials are lime, gypsum plasters, and oxychloride [53].

In the other case, there are different cement types classified depending on the cement's composition and characteristics. Due to this classification, the most important type is the Ordinary Portland Cement (OPC). The other types of cement regarding the same classification of composition and characteristics made their applications easily adapted to many different utilizations, such as Portland Pozzolana Cement (PPC), Rapid Hardening Cement, Quick Setting Cement, Low Heat Cement, Sulphate Resisting Cement, Blast Furnace Cement, High Alumina Cement, White Cement, Colored Cement, Air Entraining Cement, Expansive Cement, and Hydrophobic Cement [54].

2.2.2.1 Portland Cement

It is the most commonly used cement all over the world. It is a fine grey powder, sometimes white, and it is the base material that forms concrete when mixed with water and some gravel and sand. It is, therefore, considered a hydraulic cement [55]. Globally, Portland Cement production exceeds 3.6 billion metric tons per year distributed as per the following figure 2.2 [56]:

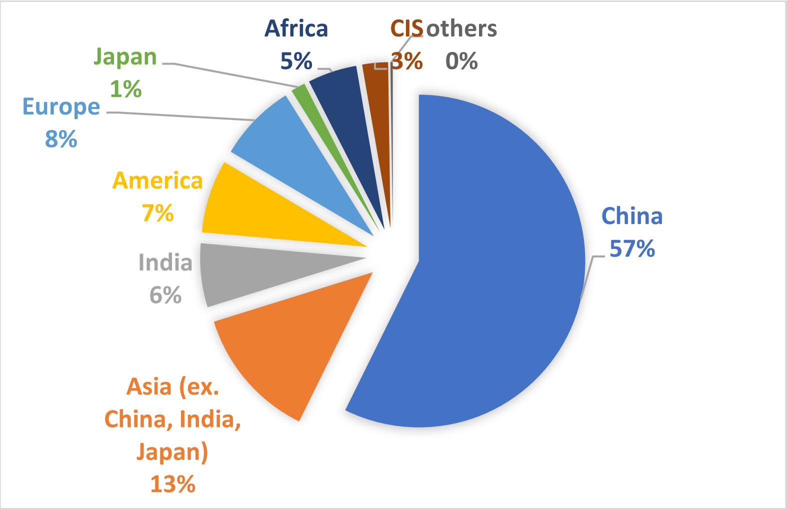


Figure 2.2 World Portland Cement production in 2012 [56]

Chemically, Portland Cement comprises the four main elements: calcium, silicon, aluminum, and iron. They are mixed in the known chemical process to form the Portland Cement. The raw materials of Portland Cement are combined in definite portions: Calcareous materials, which are calcium carbonate and consist of limestone, chalk, and marl, and argillaceous materials, which are silicates of alumina and are usually clay and shale. It has good physical and chemical properties, which allowed it to be used for construction purposes and masonry works [57].

In 1824, Joseph Aspdin issued the patent on the manufacture of cement. He mixed some lime and clay, ground the mixture, and heated it in the furnace to form a powder. The Portland Cement name had been chosen since the produced powder colour reflected Portland Island's rock stockpiles colour [57].

2.2.2.2 Portland Cement industry

Portland Cement production is most generally achieved using a dry process. The first step is to quarry primary raw materials, mainly limestone, clay, and other ingredients in the desired proportion (limestone 65%, clay 32%). The rock gets smashed during quarrying. It comes up with several steps: the first crusher, which lowers the rock size to around 6 inches. The crushed rocks head to the second crusher mills to minimize their particle size to less than 3 inches. The crushed rock then is mixed well with materials like iron ore or fly ash with the help of compressed air to obtain a homogeneous mixture, then it is ground and fed to the kiln through conveyor belts [58].

The cement kiln is a vast, slightly inclined steel rotary cylinder filled with firebrick. It has a diameter of around 3.5 meters. The raw materials of the cement are discharged into the kiln from the upper end. In the bottom end, there are special burners lit with coal or oil to control the temperature to reach 1500°C [59].

The next and most critical step in the Portland Cement industry is the kiln's heating step. It is executed in the tow heating step. Firstly, the fed mixture is preheated to 550°C; at this temperature, all the moisture content is evaporated, and the clay is decomposed to silica, aluminum oxide, and iron oxide. Secondly, in the next zone, the temperature is elevated to 1450°C, where different elements are expulsed in the gas phase, other elements form their oxides. They are combined to form the cement clinker. In this step, the clinker is cooled down in a series of coolers to 200°C; it is in the form of grey nodule balls around 5-25 mm in diameter. The produced heat stream from coolers is sent back to the kiln [60].

Eventually, the cooled cement clinker is mixed with 2-3% gypsum and ground to a smaller size range of 5-45 µm. It becomes small in which 1-pound cement approximately includes 150 billion cement particles. The cement is now ready to be packaged and stored in cement bags to be directly used as concrete in the construction plans [61].

Though the dry process of manufacturing the cement is the most common, some US factories used the wet process. Ordinarily, they are the same; the only different step in the wet method is that the products fed to the kiln are mixed with water while grinding [62].

2.2.2.3 Hydration of Portland Cement

Portland Cement, in its standard form, is an anhydrous dry material. When it reacts with water, it forms a hydrated cement. The hydration of cement is an inorganic reaction where the dry powder cement's mineral phases react with water to form a hydrous material. It is a complicated process where silicates (C_2S and C_3S) and aluminates (C_3A and C_4AF) react with water. Each reaction has different reaction rates to produce the binding cement paste, which forms the cement hardness [63].

The cement hydration process takes place in two phases, a setting phase and a hardening phase. The hydration at the setting or stiffness period occurs when the cement and water are combined and react after a few hours based on the outer atmosphere and the cement's properties. The fresh paste gradually becomes stiffer during the setting stage without a significant improvement in intensity. The setting phase is followed by a hardening period where most of the production of strength occurs. Throughout the hardening period, the hydration processes become weaker over time [59].

2.2.2.4 Portland Cement applications and uses

Portland Cement is considered an essential construction material used in the building industry. It has several uses depending on its composition and characterization. Portland Cement is the primary material used as concrete after reacting with water and some sands and gravel in the simplest form. As the concrete is formed, it will be applicable for all types of constructions and building materials.

As long as the chemical composition of the cement is different, the uses of cement will vary. According to this, there are many specific applications for particular benefits of cement. For example, the Ordinary Portland Cement (OPC) is widely used in joint construction projects and seen in masonry applications. The Portland Pozzolana Cement (PPC) is generally used in hydraulic, marine, and seaside construction; it is used in concrete components which are prestressed and post-tensioned, PPC is used in architectural and art installations since it provides a better surface appearance; it is also used for making prefabricated drainage pipes [64]. Rapid Hardening Cement is used when fast and quality strength is required, like pavement construction [65]. If the structure needed to be underwater or in various temperature conditions, where it's very cold or very hot, the Quick Setting Cement is used, because it sets at once [66].

For all coastal construction purposes, groundwater and soil, like bridges, cooling towers, and water storage tanks, Sulphate Resisting Cement is used to resist sulphate attacks in concrete [67]. On the other hand, High Alumina Cement is used in the areas where the concrete might be subjected to high temperature, frost, or acidic actions, like in refractories [68]. White Cement is a kind of Portland Cement, but with a white colour, and it is mainly used for decorative purposes [69].

Some cement and their applications are narrowly used, like Air Entraining Cement, used in shallow temperatures and with high sulphate contents in soil [70]. Expansive Cement has a specific use when constructing various hydraulic systems, sealing joints and grouting anchor bolts [71]. Finally, the Hydrophobic Cement is used in water and underground constructions, like dams and tunnels [72].

2.2.2.5 Properties of Portland Cement

2.2.2.5.1 Physical properties

Physical properties are critical parameters that control the excellent cement quality; thus, the cement blends properties and uses. The following physical properties should be taken into consideration [73-75]:

- The fineness of cement: it is the thickness of cement particles. In the final stage of the cement production cycle, the required fineness of good cement is obtained by grinding the clinker. Since the cement hydration rate is directly proportional to cement particle size, cement fineness is of great importance.

- Soundness: it refers to the cement tendency not to shrink while hardening and after several years. High-quality cement maintains its volume after the setting time without change due to uncombined lime and magnesia.
- Consistency: it is the ability of cement, when reacting with water, to form the concrete paste to flow with consistency and uniformity.
- Strength: three kinds of strength should be considered, compressive, tensile, and flexural. Certain factors control the strength, like the ratios between water/cement and cement/aggregated, the processing conditions, and the raw materials' size and shape.
- Setting time: good cement quality has two setting times: the initial setting, when the paste starts to stiffen within the first 30 min and the final setting, which occurs after 10 hours when the cement begins to harden and endure loads.
- The heat of hydration: when applying water to cement, the reaction is called hydration. Hydration produces heat that can influence the cement's performance and retain the curing temperature in cold weather. However, if the heat produced is high, it will create stress, particularly in large structures. Hydration heat is primarily influenced by the calcium silicate found in cement and the water/cement ratio.
- Bulk density: cement has a variable density that depends on the concentration of the element content in cement. Cement density will range from 62 to 78 lb/ft^3.
- Specific gravity: generally, the specific gravity of the PC is about 3.15. Yet, other types might have a specific gravity around 2.9.

2.2.2.5.2 Chemical properties

Portland Cement consists of four primary compounds: around two-thirds tricalcium silicate ($3CaO \cdot SiO_2$) and dicalcium silicate ($2CaO \cdot SiO_2$), and the rest is tricalcium aluminate ($3CaO \cdot Al_2O_3$) and tetra-calcium aluminoferrite ($4CaO \cdot Al_2O_3.Fe_2O_3$), as well as small quantities of free lime and magnesia together with alkali and small amounts of other impurities. These primary compounds are referred to as C_3S, C_2S, C_3A, and C_4AF in an abbreviated notation, which varies from the standard ones, where C stands for lime or calcium oxide, while S, A, and F stand for silica, alumina, and iron oxide, respectively, as shown in Table 2.5 [57].

Table 2.5 Chemical formula and cement nomenclature for major constituents of PC [57]

Mineral	**Chemical formula**	**Oxide composition**	**abbreviation**
Tricalcium Silicate	Ca_3SiO_5	$3CaO.SiO_2$	C_3S
Dicalcium silicate	Ca_2SiO_4	$2CaO.SiO_2$	C_2S
Tricalcium aluminate	$Ca_3Al_2O_4$	$3CaO.Al_2O_3$	C_3A
Tetracalcium aluminoferrite	$Ca_4Al_nFe_{2-n}O_7$	$4CaO.Al_nFe_{2-n}O_3$	C_4AF

Each of these compounds impacts the cement's chemical properties due to its concentration in the cement. To illustrate this, the tricalcium silicate (C_3S) induces rapid hydration hardening and is responsible for achieving early cement strength by the initial setting as opposed to dicalcium silicate (C_2S), which attains its strength after a week. Tri-calcium aluminate (C_3A) is responsible for part of the strength of the cement. It also releases a lot of heat from hydration in the early stages. The less tricalcium aluminate there is, the more it becomes sulphate resisting cement [76]. Tetracalcium aluminoferrite (C_4AF) is mainly responsible for the cement's grey colour [77] and its role as a fluxing agent in the cement. It decreases the melting points of the ingredients in the kiln from 1650ºC to 1450ºC. However, it has rapid hydration and produces no cement strength [78]. Magnesia (MgO) is needed in limited amounts in the raw materials of cement production to adjust its strength. The amount of magnesia exceeds the 5% by mass [75], which may cause the cement to be unsound and expansive. Controlling the sulfur trioxide SO_3 (from gypsum) within the range of 2-3% by mass will maintain the setting time and the cement soundness. If the gypsum increases, it will prolong the setting time and delay the hardening due to hindering the formation of tricalcium silicate [79]. Lastly, the alkalis, which are the potassium oxide (K_2O) and the sodium oxide (Na_2O), are responsible for setting the cement time as long as they do not both exceed the 0.6% by mass cement. This percentage can be calculated by the equation ($Na_2O + 0.658\ K_2O$) [80, 81].

Ordinary Portland Cement (OPC), the most popular cement, has a specific constituent range of the phase and oxide compositions. In the phase composition in Table 2.6, the tricalcium silicate has the highest concentration value of 40%, followed by dicalcium silicate. They should have both a percentage of around 70% by mass. The C_3A and C_4AF make up about 20% of the total cement mass, while the rest is other materials, like gypsum and alkalis [82].

Table 2.6 The approximate phase composition concentration of the OPC in mass % [82]

Phase composition	Mass%
C_3S	40
C_2S	30
C_3A	11
C_4AF	12

Bogue equations were invented to convert the Ordinary Portland Cement's phase composition to a chemical composition to facilitate the comparison with other chemical compositions and measurements of cement performance. Bogue calculations were invented by Bogue in 1929 to determine the composition of potential oxides for the four major elements by knowing the composition of the four phases or the opposite [83]. The calculations are based on certain assumptions. First, the clinker reactions are considered as completed, and the four cement phases as pure, with no traces of impurities.

There are many forms of Bogue equations depending on the cement considered. In this case, the four equations used are from the ASTM C150 specifications as follows:

$C_3S = 4.0710\ CaO - 7.6024\ SiO_2 - 1.4297\ Fe_2O_3 - 6.7187\ Al_2O_3 - 2.852\ SO_3$ .... (3)

$C_2S = 8.6024\ SiO_2 – 0.75\ C_3S$ .... (4)

$C_3A = 2.6504\ Al_2O_3 - 1.6920\ Fe_2O_3$ .... (5)

$C_4AF = 3.0432\ Fe_2O_3$ .... (6)

The sum of the resulting oxides composition is not equal to 100%; the Bogue calculations do not consider the cement's minor and trace elements. It also does not count the impurities incorporated in the major element. However, it is a potential calculation, as mentioned before [84].

Table 2.7 indicates the oxide composition concentration range assessed from the phase composition [85]. It shows that the lime has more than double the silica, while both have a mass percentage of more than 75%. The lime to silica ratio should be in the range of 2.0 [75].

Table 2.7 The oxide composition percentage range by mass of the PC [82]

Oxide name	Lime	Silica	Alumina	Iron oxide	Magnesia	Sulfur trioxide	Soda $_{eq}$
Oxide formula	CaO	SiO2	Al2O3	Fe2O3	MgO	SO3	Na2O+K2O
Mass%	60-67	17-25	3-8	0.5-6	0.1-4	1-3	0.5-1.3

2.3 FactSage Software

2.3.1 What is FactSage?

FactSage is an extensive software and database computing system for thermodynamics used in the chemical world since 2001. It obtained its name from the fusion of the two well-known software programs, FACT-Win (previously F*A*C*T) and ChemSage (previously SOLGASMIX) thermochemical packages that were formed more than 25 years ago [86].

The FactSage software functions using Microsoft Windows®. It includes a set of information tools, databases, computations, and simulations to model chemical reactions from various databases. From these databases, a vast number of graphs, tables, data, figures, and manipulations are allowed to be computed with the assistance of the database gateway [87].

F*A*C*T, the Facility for the Analysis of Chemical Thermodynamics, was released in 1976 as a combined work between two universities, McGill University and École Polytechnique de Montréal. In the years that followed, the program underwent several updates and expanded on its previous versions and performances. It progressed to perform metallurgy, hydrometallurgy, inorganic chemistry, geochemistry, and environmental science [86].

SOLGASMIX was started by G. Eriksson in 1979. In the first version, it used programming to provide the requisite data. Over time, in the eighties, G. Eriksson began collaborating with K. Hack. They made improvements, until 1999, when ChemSage was fully developed in two-dimensional phase charts for the calculations of phase diagrams.

Early in 2001, F*A*C*T and ChemSage were unified into one major thermodynamics software called FactSage. It became one of the most popular tools installed in hundreds of universities and companies due to its user-friendliness, open access to various databases, and efficient calculation system [87].

In FactSage, there are two primary thermodynamics databases: a pure substances database and a solution database. The latter has the optimal model for phases of the solution, while the former comprises the features of stoichiometric compounds. Whether produced from modifications of phase diagrams or regular recordings, they are authorized to collect data and manipulate the database file for modelling [88].

2.3.2 FactSage in research

FactSage in all its various versions has been used in many research and academic studies during the last three decades, specifically in projects related to PG and cement industry treatment.

In the field of PG, W. M. Song et al. [89] used the reaction module and the Equilib module in FactSage 6.1 to study the viability of using FeS_2 to minimize and decompose the Flue Gaz Desulfurization Gypsum (FGDG) for the preparation of SO_2. J. Yang's team from Yunnan, China [90] focused on the Chemical Looping Gasification of PG with high silicon. They used FactSage 7.1 to analyze the reaction mechanism at various temperatures. In further research, they also [91] computed the impact of impurities in the decomposition of PG with coal by using FactSage simulation. D. L. Zheng et al. [92] used FactSage 7.0 to study PG and lignite decomposition's feasibility to produce pure CaO. L. Zhu et al. [93] introduced using FactSage 6.1 the thermodynamic of the reaction process for preparing CaS from PG with lignite.

FactSage is used in the cement industry and construction research on a wide scale. B. Hokfors et al. [94] conducted a study on the formation of a solid solution of phosphorous Belite and its effect on Alite formation in the cement industry. In their case, the FactSage software database was used to calculate the thermochemical reaction of the clinker. In measuring mineral phases, FactSage was used by W. L. Wang and his team [95] to compute desulfurization residual for Sulpho-aluminate cement production. K. G. Ahari et al. [85] investigated an equilibria estimation on Portland Cement clinker using FactSage numerical simulation.

Many researches inducted the reusing of PG in the cement industry and construction field by FactSage. Ma and her team [96] reviewed by using FactSage 6.1 the mechanism and the impact modelling data to form calcium sulphide in the PG decomposition process. While L. Zhao with his group [95] investigated the results of adding kaolinite on the melting properties of the phosphogypsum-CaS reaction. FactSage is used to determine the phase equilibrium at elevated temperatures to calculate the melting process. Q. X. Dai [97] using FactSage examined the mobility of some aspects in the purification process of CaO from PG's decomposition.

2.4 Key reactions and motivation of the study

The listed literature review and the previous studies did not focus on using the CaO produced from the PG thermal decomposition under reductive conditions as an alternative feedstock in the Portland Cement production. Due to the similarity in their chemical composition, by applying some chemical modification, CaO can be adjusted and used in a large scale in the cement industry. This research gap was the main motivation of this study.

In contrast, there are two main methods of the PG thermal decomposition under reductive conditions:

2.4.1 Thermal decomposition of PG under reductive conditions

The decomposition of PG can be achieved using various methods, such as a reaction with sulphur, additives or carbon. Decomposition of PG by carbon is one of the main ways to decompose PG and produce CaO, although it is a slow chemical process because it is a solid/solid reaction. To accelerate the reaction time, carbon could be gasified to carbon monoxide, according to the reaction below [98].

$C + CO_2 \rightarrow 2CO$ ………………………………………………………………………… (7)

PG's decomposition reaction under reductive conditions occurs in an Induction Heating Fluidized Bed Reactor (IHFBR). In the procedure a carefully weighed sample of dehydrated PG is fed to the IHFBR. A mixture of N_2 and CO gases is injected, and a constant heating rate is applied until the desired isotherm is obtained. The sample is then left for an hour in an isothermal environment to complete the reaction. The reactor is subsequently cooled with N_2 gas and afterward the sample is weighed and kept in a desiccator until completely cooled [99].

Accordingly, two types of reaction can perform the PG decomposition under reductive conditions: the high molar ratio and the low molar ratio of $CO/CaSO_4$.

2.4.1.1 The high molar ratio

The high ratio reaction takes place in two steps. The reduction step, where one mole of the dehydrated PG is reacted with four moles of carbon monoxide, forms one mole of calcium sulphide in the solid state and four moles carbon dioxide as a gas; this reaction took place at 650 °C. The second step is the oxidation step. One mole of the calcium sulphide is reacted with one and a half moles of oxygen to form one mole of the solid by-product of calcium oxide and sulphur dioxide in the gas phase. The second reaction takes place at 1100°C. The two steps are represented as follows:

Reduction step:

$CaSO_4 + 4\ CO \rightarrow CaS_{(s)} + 4CO_{2\ (g)}$ ……………………………………………..………… (8)

Oxidation step:

$CaS + 1.5\ O_2 \rightarrow CaO_{(s)} + SO_{2\ (g)}$ ……………………………………………………….. (9)

2.4.1.2 The low molar ratio

In contrast to the high molar ratio, a low $CO/CaSO_4$ molar ratio requires a temperature near 1200°C and will make the reaction a one-step reaction.

One mole of dehydrated PG and one mole of carbon monoxide react at 1150°C to produce one mole of the solid by-product, calcium oxide, and one mole each of the two produced gases: sulphur dioxide and carbon dioxide, according to the following reaction:

$CaSO_4 + CO \longrightarrow CaO_{(S)} + CO_{2\ (g)} + SO_{2\ (g)}$ …………………………..….………………… (10)

The SO_2 produced is recycled in the system and treated to produce sulfuric acid, which is re-used in the wet process of phosphoric acid production. The carbon dioxide can be used in CO_2 capture and storage, and the CaO solid by-product is treated for use in cement production.

CHAPTER 3 MATERIALS AND EXPERIMENTAL PROCEDURE

This chapter introduces the material used in the study, the material's sampling, the different analytical characterizations of the material, the FactSage software used, and the simulation procedures.

3.1 Materials

The phosphogypsum used in this study came in a batch of 20 kg directly from the stockpile of PG stored at Al-Jadida, Morocco, in 2019. It had a grey-brown colour with a particle size range between 5-200 µm.

3.2 The sampling of the PG

The ASTM C702 method for stockpile sampling is used to guarantee the sample homogeneity and obtain a representative PG sample. This method is defined in the following four steps [100]:

3.2.1 Mixing the sample

In the beginning, an amount of 5 kg of PG was mixed thoroughly to homogenize the sample and prepare it for the separation techniques.

3.2.2 Coning and quartering separation method

The first step in this method was to spill a cone of the PG sample, which uniformly shaped a cone. The sample was divided into quarters, like in Figure 3-1. Then two opposite quarters were discarded. The remaining two quarters were merged and poured into another conical sheet, which was again flattened and separated. The quartering cycle was continued until the required quantity of the sample of around 1 kg was achieved [101].

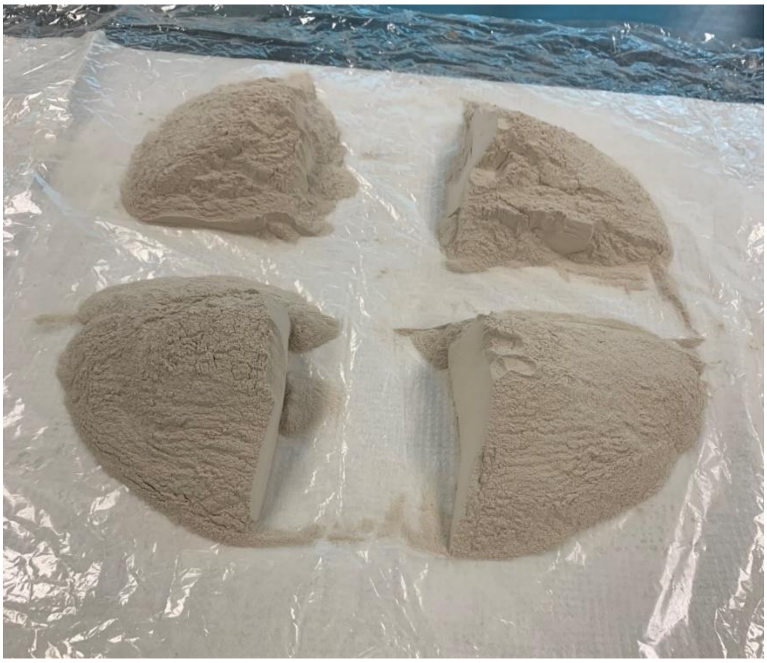


Figure 3.1 The PG sample divided into quarters for the quartering separation method

3.2.3 Riffle splitter method

According to the quartering method, the Riffle splitter method was used to continue sampling the PG by reducing the mass up to 50 g for each sample. As shown in Figure 3-2, the sample was split into two equal portions; each portion was taken separately to be split until the desired sample mass was reached [102].

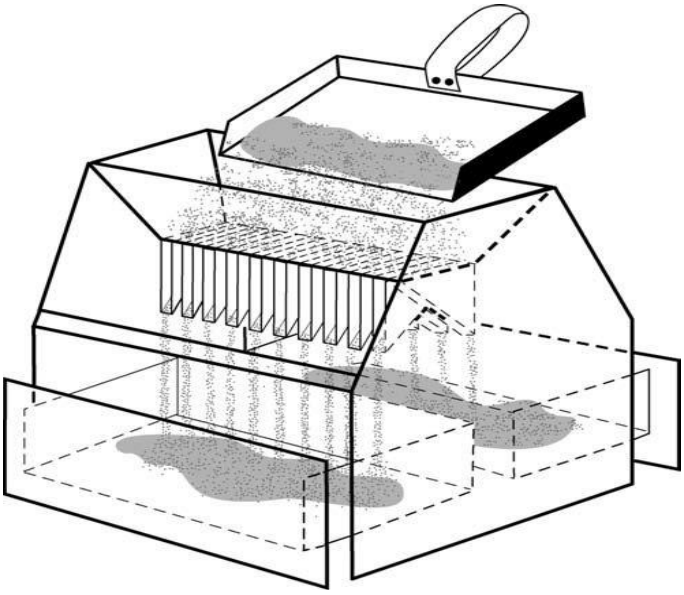


Figure 3.2 The Riffle splitter method [102]

3.2.4 Drying the Sample

The drying process was an important step to evaporate all the humidity and free water present in the PG sample. In contrast, PG was subjected to a gentle drying cycle in a furnace at 90-100°C for approximately 24-48 hours to ensure a completely dried sample.

3.3 Characterization of PG Sample

The PG sample was analyzed and characterized using several analytical techniques to determine and ensure correct analysis and data were provided. The analytical methods used were:

3.3.1 Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)

Inductively Coupled Plasma Optical Emission Spectrometry model Agilent 5100 SVDV ICP-OES was used to determine the PG sample's elemental concentration. For the preparation step before analysis, the PG sample was passed through the fusion digestion process in the Claisse LeNeo Fluxer. A dried PG sample was mixed with a strong acid mixture (10% nitric acid) at 1050°C.

ICP-OES is commonly used in many areas of science. The basic theory is that the component elements are excited when plasma energy is supplied to the sample from outside, then moved to low energy states, where emission rays are emitted. The spectrometer defines the ones corresponding to the photon wavelength. Based on the photon rays' location, the element type is measured, and the component of each element is calculated based on the intensity of the rays. ICP-OES is an effective and highly sensitive method for detecting specific and unknown compounds [103].

3.3.2 Neutron Activation Analysis (NAA)

Neutron activation analysis (NAA) is quite effective as a flexible analytical method for conducting a multi-element qualitative and quantitative study of major, minor, and trace elements in solid samples. The PG sample was analyzed with the NAA SLOWPOKE reactor to characterize the sample's elements and impurities.

NAA is widely known as the "referee method" of choice; due to its consistency and effectiveness when new protocols are being developed or other approaches produce results that do not agree. It is generally used as a reference for other forms of analysis. NAA usage is so common that nearly 100,000 samples are analyzed annually [104].

3.3.3 Quantitative Evaluation of Materials by Scanning Electron Microscopy (QEMSCAN)

QEMSCAN is shorthand for the Quantitative Evaluation of Materials by Scanning Electron Microscopy. The mineralogical analysis was performed on the PG sample by QEMSCAN to indicate the bulk mineralogy variation and liberation of gypsum based on its chemistry.

QEMSCAN is the most active mineralogical analysis tool used in the minerals industry. Based on its versatile process, QEMSCSAN can be used for ore samples and metallurgical products. The information collected by the QEMSCAN instrument can quantify the mineralogy, indicate the mineral species in each particle and its degree of mineral liberation [105].

3.4 Thermal decomposition of PG under reductive conditions

The decomposition of PG under reductive conditions can be achieved in this study using two types of reaction: the high molar ratio and the low molar ratio of $CO/CaSO_4$.

3.4.1 The high molar ratio

The high ratio reaction which takes place in two steps as described in section 2.4.1.1.

3.4.2 The low molar ratio

The low $CO/CaSO_4$ molar ratio which requires a temperature near 1200°C and will make the reaction a one-step reaction as described in section 2.4.1.2.

In this study, the two methods had been simulated to ensure and indicate that both methods produce CaO and SO_2, although only the low molar ratio is implemented to the major, minor and trace elements evaluation procedure of this study; in order that it is a one-step reaction, so it is easier to follow and calculate, moreover, the high molar ratio requires to higher amount of CO in the reaction and produced higher amount of CO_2, even though they produce the same amount of CaO and SO_2. Further, the high molar ratio needs lower heat temperature than the low molar ratio.

3.5 FactSage simulation

In this study, the reactions were simulated to study the results of PG decomposition. The reactions that were simulated were the Portland Cement formation and the reactions of PG decomposition in high and low molar ratios under reductive conditions. A comparison between the two results for major, minor, and trace elements was performed. Based on the comparison, appropriate methods to valorize CaO in the cementitious process were simulated by modelling in FactSage 7.3 software.

3.5.1 FactSage simulation of the thermal decomposition of limestone to form Portland Cement

Simulation of limestone and clay's thermal decomposition as the raw materials of Portland Cement production is considered an important step in studying the phases and the chemical composition of its components. Afterward, the resulting phases are compared with the typical Portland Cement phases to ensure similarity and validate the FactSage results.

3.5.2 FactSage simulation of PG thermal decomposition

For this study, PG's thermal decomposition in both high and low molar ratios will be simulated in FactSage to identify the results produced from each reaction. Only the low molar ratio, however, will be selected to study its valorization. It is a one-step reaction to produce CaO; however, tracking the reaction products will be easier.

The CaO by-product produced from the PG thermal decomposition is then compared with the Portland Cement composition by evaluating the major, minor, and trace elements. Eventually, solutions will be proposed to valorize the feasibility of CaO in the production of the Portland Cement.

3.5.3 FactSage simulation of different methods for CaO valorization

In determining the elemental composition of the CaO solid by-product, effective methods are then proposed to adjust the concentration and obtain feasible compounds to be used in the cement industry. Each method was simulated and studied in FactSage to ensure its suitability.

CHAPTER 4 RESULTS AND DISCUSSION

4.1 PG Characterization Results

4.1.1 ICP-OES results

The ICP-OES analysis determined the chemical composition content of the PG sample in this study after using fluxer diffusion to digest the PG sample in 10% nitric acid. The benefit of this method is its lower uncertainties and standard errors range which increase its reliability. The representative PG sample was characterized three times. Table 4.1 presents the average concentration of the elements produced in the PG sample in ppm.

Table 4.1 The elemental concentration in the PG sample by ICP-OES

Element	ppm	Element	ppm
Ca	239550 ± 383.79	**Cr**	28.8 ± 2.42
Fe	2088 ± 7.84	**Cd**	3.5 ± 0.47
Se	6941 ± 76.17	**Mn**	2.5 ± 1.11
Al	746.4 ± 16.27	**Ni**	143 ± 9.32
Si	37678 ± 274.69	**Co**	4.2 ± 0.69
P	5952 ± 268.03	**V**	1.6 ± 0.15
Mg	159 ± 11.41	**Ag**	1.8 ± 0.24
Ba	167 ± 9.86	**As**	0.099 ± 0.004

4.1.2 NAA results

NAA is an accurate and appropriate method used to analyze the PG sample. The reasonable standard errors range of this analysis makes it reliable and trustworthy to use in the simulation of this study. Table 4.2 shows the average elemental concentration of the three analysis conducted in the PG sample in ppm.

Table 4.2 The elemental concentration in the PG sample by NAA

Element	ppm	Element	ppm	Element	ppm
Ca	233338 ± 374.61	**Ba**	157 ± 20.21	**U**	8.81 ± 1.12
S	182377 ± 189.25	**Zn**	110 ± 2.89	**Th**	5.31 ± 0.38
Si	40000 ± 288.75	**Mg**	100 ± 2.83	**Co**	5 ± 00
F	8706 ± 238.73	**Sn**	90 ± 5.77	**V**	4.67 ± 0.43
Fe	1900 ± 86.60	**K**	85.2 ± 18.99	**Cd**	4 ± 0.29
Zr	1300 ± 121.24	**Rb**	50 ± 00	**Cs**	3 ± 00
Na	1251 ± 38.79	**Cu**	30 ± 00	**Mn**	2.2 ± 0.14
Al	727 ± 64.67	**Cr**	30 ± 2.89	**Hg**	0.8 ± 00
Cl	403 ± 26.98	**Se**	20 ± 00	**Sc**	0.771 ± 00
Ni	150 ± 37.53	**Ag**	9 ± 0.29	**Au**	0.007 ± 00

4.1.3 QEMSCAN results

The QEMSCAN mineralogical analysis of PG shows the mineral mass percentage of the PG sample. Table 4.3 shows the average of the phase content of five representative samples of phosphogypsum varies in their particle size. This analysis provides a high reliability method due to the narrow standard errors range to be considered in the simulation of this study.

Table 4.3 The mineral mass percentage in the PG sample by QEMSCAN

Mineral	Chemical formula	Mineral mass (% in PG)
Gypsum	$CaSO_4.2H_2O$	92.3 ± 0.78
Apatite	$Ca_5(PO_4)_3(F,Cl,OH)$	0.76 ± 0.25
Quartz	SiO_2	6.08 ± 0.84
Ca Silicate	$CaSiO_3$	0.64 ± 0.38
Fe Metals	Fe^{+2}, Fe^{+3}	0.18 ± 0.43
Other		0.03 ± 0.02

4.2 Characterization results conclusion

The PG characterizations by ICP-OES and NAA had been analyzed three tests each, they show that the results obtained from the two methods are reliable and in good agreement. The measurement had been taken from the average of three different representative PG samples. These results helped to simulate the PG's thermal decomposition reaction in FactSage accurately by adding the gypsum with its associated elements in their specific concentration.

The QEMSCAN analysis provides low standard errors range for its phase composition concentration, the average of the five-analysis conducted by the representative phosphogypsum samples were used in the FactSage simulation.

The decomposition process was simulated twice, once elementally and the other using the mineral content. The first simulation was by adding the gypsum associated with the concentration of each element; the data were obtained from ICP-OES and NAA. The second simulation conducted by inserting the mineral component with its concentration provided from QEMSCAN data. This procedure ensures, due to the similarity of the results, that entering the input data of the reaction with either of these methods will not affect the modelling results.

4.3 FactSage simulation results

4.3.1 The thermal decomposition of limestone to produce the Portland Cement

In this section, the Ordinary Portland Cement (OPC) formation reaction was simulated in FactSage software to guarantee that the simulated composition results match the typical Ordinary Portland Cement composition. These results were used to reference the PG thermal decomposition and conveniently study it in the cement industry.

Two main ingredients entered the kiln in appropriate portions to form the Ordinary Portland Cement; the Calcareous and Argillaceous materials. Limestone comes from the Calcareous materials and is the main source of calcium. The Argillaceous material, which we can find in clay, shale, and sand, is the exporter of silicon alumina and iron oxides. Finally, the gypsum added to the clinker in the desired amount resulted after the thermal reaction [106]. The distribution portions of these elements are shown in Figure 4.1:

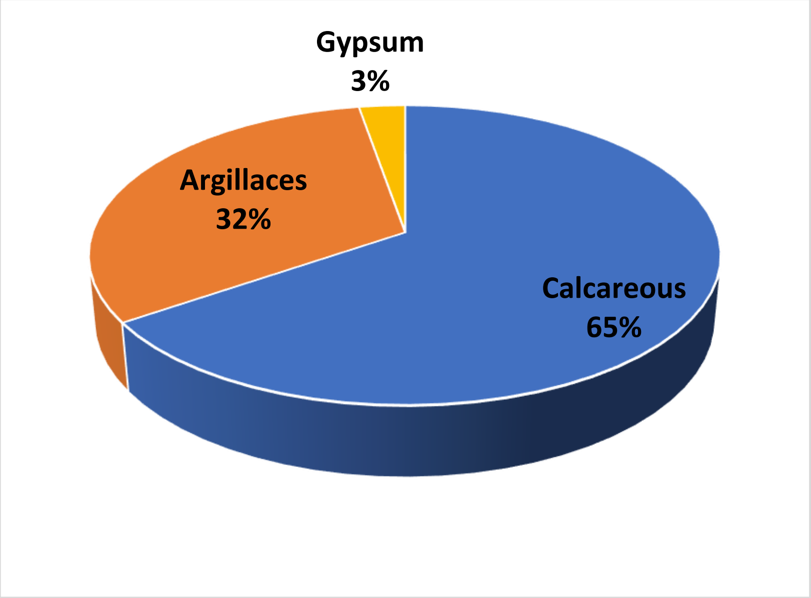


Figure 4.1 The raw material portions in percentage used to form the Portland Cement

Table 4.4 presents the chemical composition of the typical limestone used for the simulation of the Portland Cement; the average values of the obtained ranges given in Table 4.4 were considered in the simulation.

Table 4.4 The limestone chemical composition [106]

	CaO	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**MgO**	**SO_3**	**K_2O**	**Na_2O**	**Loss On Ignition**
wt. %	50-55	5-8	0.7-1.2	0.4-1.3	0.5-7	0-0.3	<0.4	<0.1	33-38

Table 4.5 shows the chemical composition of the typical clay used for the simulation of the Portland Cement; the average values of the obtained ranges given in Table 4.5 were considered in the simulation.

Table 4.5 The clay chemical composition [107]

	SiO_2	**Al_2O_3**	**Fe_2O_3**	**CaO**	**MgO**	**K_2O**	**Na_2O**	**SO_3**	**TiO_2**
wt. %	52-65	15-19	1-6	8-12	3-5	1.4-2	0.4-1.5	0.1-1	0.1-1

The limestone ratio to clay, which is used in Ordinary Portland Cement to react in the kiln, is 2:1. Where the limestone is 65% by weight while the clay is around 32% by weight at 1450°C.

4.3.1.1 Simulation of Portland Cement production by FactSage

The procedure used in FactSage was to choose the "Equilib" module on the front page of the FactSage 7.3 software and the compound (pure substance) databases, which were "FactPS" and "FT oxides" and then add to the simulation the element species of limestone and clay in a 2:1 ratio, including impurities and trace metals concentrations. Next, the temperature and pressure are chosen using the same as in the real reaction to be simulated. The reaction takes place at 1450°C and ambient pressure. The required gas and solid phases are then selected to be studied.

The simulated Portland Cement phase composition results by FactSage, indicates that C_3S is tricalcium silicate, C_2S is dicalcium silicate, C_3A is tricalcium aluminate, and C_4AF is tetracalcium aluminoferrite.

4.3.1.2 The phase composition of Ordinary Portland Cement

The results show that the phase composition simulated by FactSage is in good agreement with the phase composition of typical Ordinary Portland Cement (OPC). The tricalcium silicate concentration is ideally more than double the dicalcium silicate. Similarly, the tricalcium aluminate and tetracalcium aluminoferrite are less than 10% in weight. At the same time, the alkali minerals are always within the acceptable range of 1-5%.

Table 4.6 shows the results for both simulated and typical phase compositions. The tricalcium silicate, C_3S, is 54% by weight or the highest percentage overall. The dicalcium silicate, C_2S, is around 22% by weight, and the tricalcium aluminate, C_3A, and the tetracalcium aluminoferrite, C_4AF, are less than 10% each. The gypsum content is very low; however, 3% of gypsum is added to the Portland Cement after its formation. Alkali oxides, K_2O and Na_2O, are 2.7% [106].

The typical Portland Cement which is used as a reference is obtained by a similar process and conditions of temperature and pressure used in this study. The raw materials used are also the same; limestone which mainly forms CaO and CO_2 during thermal process, and Clay which is mainly consist of SiO_2, Al_2O_3 and Fe_2O_3. The CaO is then reacted with the oxides to form the four phases composition of Portland Cement. Regarding the reference [106]; which used the X-ray diffraction to analyze the phase and chemical composition of the reference typical Portland Cement.

Table 4.6 The phase composition of the typical and simulated Ordinary Portland Cement

Chemical name	**Tricalcium Silicate**	**Dicalcium Silicate**	**Tricalcium Aluminate**	**Tetracalcium Alumino-ferrite**	**Gypsum**
Formula	$3CaO.SiO_2$	$2CaO.SiO_2$	$3CaO.Al_2O_3$	$4CaO.Al_2O_3.Fe_2O_3$	$CaSO_4$
Notation	C_3S	C_2S	C_3A	C_4AF	CSH_2
OPC wt.% [106]	50-70	15-30	5-10	2-15	2-3
FactSage wt.%	54.2	22.7	6.1	9.3	0.3

Figure 4.2 illustrates the upper and lower weight percentage presented in Table 4.6 of typical Ordinary Portland Cement (OPC) phase composition compared with the simulated composition by FactSage. The results show that the four phases simulated by FactSage are within the Ordinary Portland Cement phase composition range.

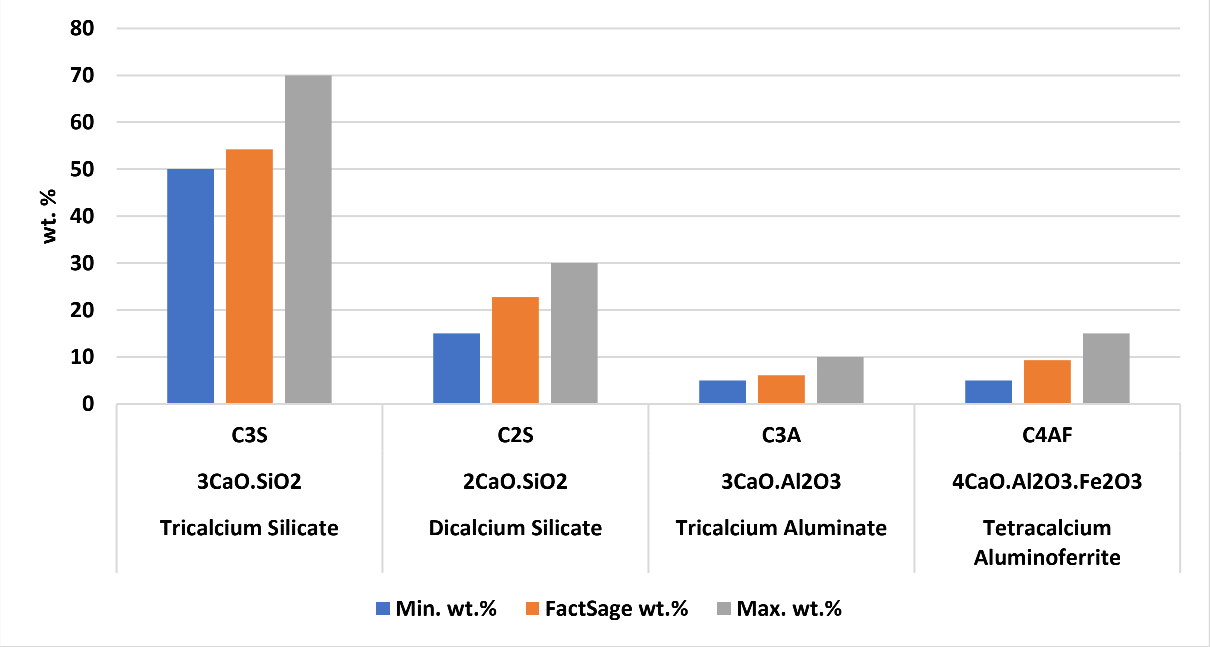


Figure 4.2 Max and Min ranges of the simulated phase composition of Ordinary Portland Cement

4.3.1.3 The chemical composition of Ordinary Portland Cement

Applying the Bogue equations to the resulting phase composition from FactSage produce the oxide composition of the portland cement for the four major elements: Ca, Si, Al and Fe.

4.3.1.3.1 Chemical composition of major elements in Ordinary Portland Cement

According to Bogue calculations, the percentage of major element oxides indicated that CaO is dominate by more than 60% by other major elements, followed by SiO_2 as the second element with a percentage of 22%, and aluminum and iron oxides at around 4% and 3%, respectively.

Table 4.7 compares the chemical composition of typical Ordinary Portland Cement with the chemical composition simulated by FactSage and calculated from Bogue calculations.

Table 4.7 The simulated oxide composition of the major elements in Portland Cement

Chemical name	**Calcium Oxide**	**Silicate**	**Aluminum Oxide**	**Iron Oxide**
Formula	**CaO**	**SiO_2**	**Al_2O_3**	**Fe_2O_3**
OPC wt.% [106]	63-67	19-23	3-7	1-6
FactSage wt.%	64.5	22.1	4.3	3.2

Figure 4.3 illustrates the maximum and minimum chemical composition weight percent presented in Table 4.7 of typical and simulated Ordinary Portland Cement for the major elements. The results show that the four major elements simulated by FactSage are within the Ordinary Portland Cement chemical composition range.

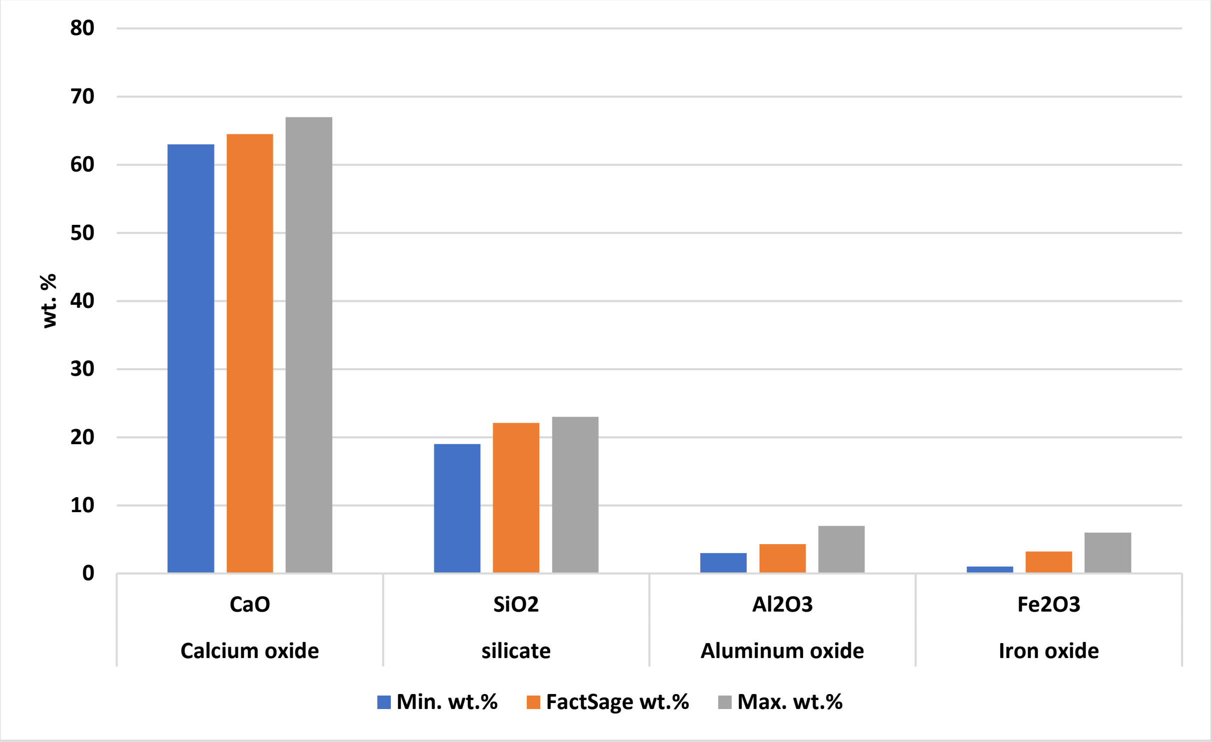


Figure 4.3 Max. and Min. range composition of the major elements of Portland Cement

4.3.1.3.2 The chemical composition of minor elements in Ordinary Portland Cement

Table 4.8 shows that the minor elements make up a smaller concentration of the Portland Cement composition than the major elements. Indeed, they do not contribute to the Portland Cement's quality except if their indicated concentration were exceeded, they might adversely affect the cement's quality. For example, MgO should remain under 5% in cement weight, preferably between 2 to 3 percent, to avoid hardening cracks. The alkali oxides must not exceed 1% cement weight so that the cement retains its quality and setting time [106] and SO_3 is important to maintain the durability of the cement. The desired amount of 3% is added to the clinker in the grinding step [52, 108].

The minor oxides composition of the typical Portland Cement which is used as a reference is obtained by a similar process and conditions of temperature and pressure simulated in this study. They are produced from the firing of the limestone and clay to form the major and minor oxide composition. The chemical composition ranges obtained in Table 4.8 are considered for the simulation’s comparison [109].

Table 4.8 The chemical composition of the minor elements of typical and simulated Ordinary Portland Cement

Chemical name	**Magnesium Oxide**	**Sodium Oxide**	**Potassium Oxide**	**Titanium oxide**	**Sulphur Trioxide**
Formula	**MgO**	**Na_2O**	**K_2O**	**TiO_2**	**SO_3**
OPC wt.% [109]	1-3	0.1-0.5	0.5-1	0.1-1	2-3.5
FactSage wt.%	2.9	0.17	0.73	0.23	3

Figure 4.4 illustrates the values in Table 4.8 where the maximum and minimum chemical composition weight percent of typical and simulated Ordinary Portland Cement for minor elements. The results show that all the elements simulated by FactSage are within the Ordinary Portland Cement's chemical composition range.

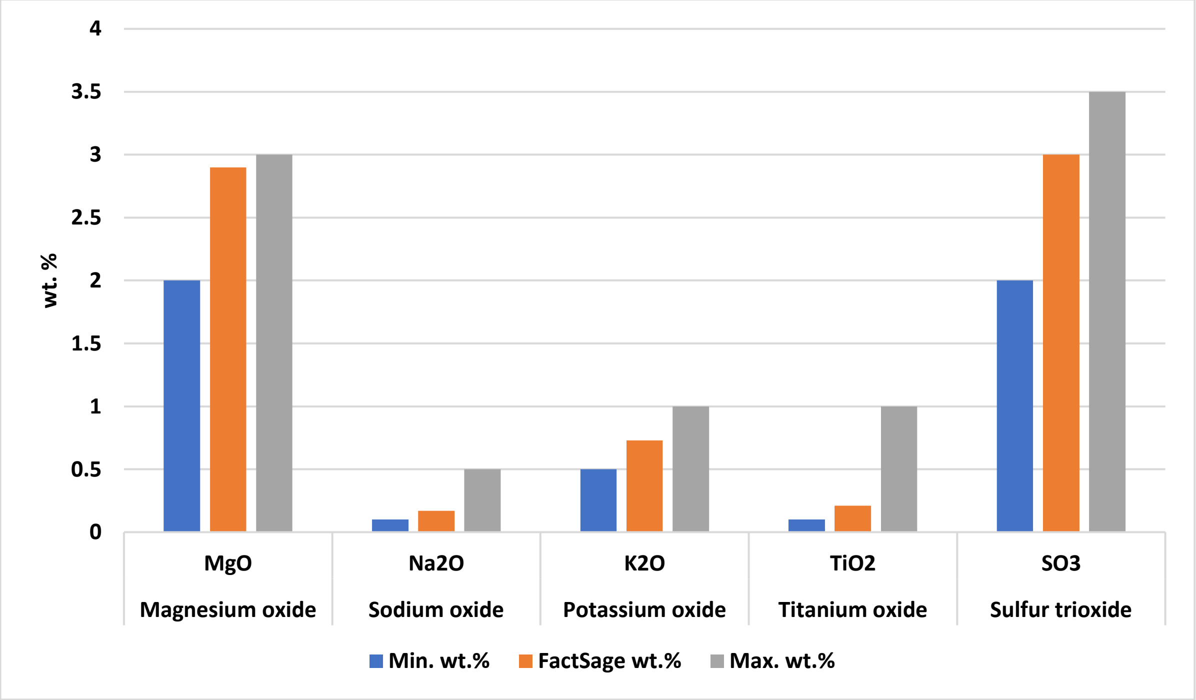


Figure 4.4 Max and Min range for the chemical composition of minor elements of Ordinary Portland Cement

4.3.2 The simulation of the thermal decomposition of PG under reductive conditions

The PG thermal decomposition reaction in either high or low molar ratios was studied and simulated in the FactSage 7.3 software to ensure and indicate that in both methods produce CaO.

4.3.2.1 The high molar ratio reaction

In FactSage, the reaction was set by adding 100 g of gypsum and the required amount in grams for 4 moles of CO. The temperature was set between ambient temperature and 1100⁰C for 100-degree temperature intervals to observe the reaction at different temperatures and determine the exact temperature where the products occur. Ideal gas, pure liquid and pure solid were the compound species chosen. Figure 4.5 shows the reaction between $CaSO_4$ and CO at a molar ratio 1:4. In this figure, at a temperature less than 300°C; the CO oxidized with air to form CO_2, and due to the thermodynamics; part of $CaSO_4$ were split to form $CaCO_3$. At temperature between 300°C and 900°C; CaS started to form, $CaCO_3$ concentration went down with slightly increase in $CaSO_4$ and CO_2. At temperature between 900°C and 1100°C; the CaO, SO_2 formed and the $CaSO_4$ and CaS were deformed and almost reacted. Table 4.9 presents the weight in grams for each product from the simulation of the high molar ratio reaction at 1100⁰C according to the two-step reactions (8-9) which explained in section 2.4.1.1.

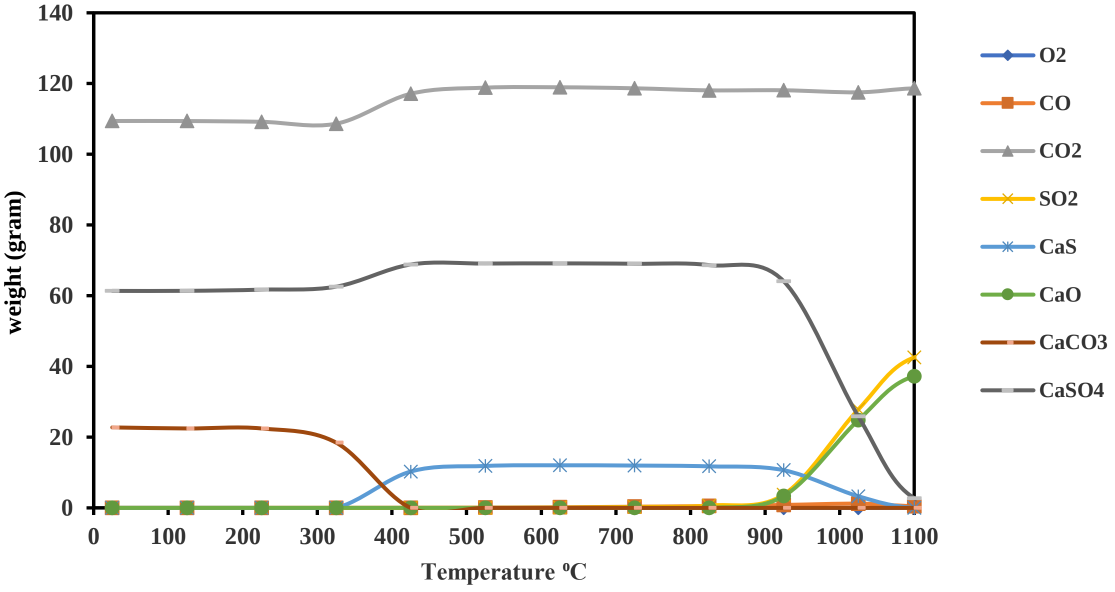


Figure 4.5 The thermal decomposition of PG at the high molar ratio

Table 4.9 The products of the thermal decomposition of PG under reductive conditions at high molar ratio

Concentration at 1100ºC	**O_2**	**CO**	**CO_2**	**SO_2**	**CaS**	**CaO**	**$CaCO_3$**	**$CaSO_4$**
Weight (gram)	2.2E-6	0.48	118.64	42.53	0.0	37.89	0.0	2.76

4.3.2.2 The low molar ratio reaction

The thermal decomposition of PG was simulated in FactSage for a 1:1 mole gypsum/CO ratio at 1150ºC. Theoretically, the products obtained when one mole of gypsum (equal to 136g) reacts with one mole of carbon mono-oxide (equal to 28g) to produce one mole of calcium oxide and one mole sulphur dioxide and carbon dioxide (57g, 64g, and 44g, respectively), according to the reaction (10)

The chemical composition simulated for PG's thermal decomposition under reductive conditions at 1150ºC in the low molar ratio are passed through the three levels of evaluations.

4.3.3 Element evaluation of the CaO solid by-product

The elemental evaluation of the CaO solid by-product was carried out in three steps. Firstly, the major elements, Ca, Si, Al, and Fe, were evaluated and determined to be the cement's main components. Secondly, after verifying that the major elements were within the typical Ordinary Portland Cement (OPC) chemical composition range, the minor elements' evaluation of Mg, Na, K and SO_3 took place. Finally, after completing the evaluation of the major and minor elements, the evaluation of trace metals, which is mandatory, was carried out to verify that the heavy metals are below the permissible value in the cement industry and due to environmental issues.

4.3.3.1 The chemical composition of major elements evaluation

In this evaluation step, the data collected from the FactSage software shows that the major elements' chemical composition does not correspond to the typical Ordinary Portland Cement (OPC) chemical composition values. According to Table 4.10 below, the CaO concentration is much higher than in the typical Portland Cement. SiO_2 concentration is less than the acceptable range, and the Al_2O_3 and Fe_2O_3 concentrations are considerably less than the typical Portland Cement composition.

Table 4.10 The major elements evaluation of the CaO solid by-product and typical OPC

Chemical name	**Calcium oxide**	**silicate**	**Aluminum oxide**	**Iron oxide**
Formula	**CaO**	**SiO_2**	**Al_2O_3**	**Fe_2O_3**
OPC wt.% [106]	63-67	19-23	3-7	1-6
FactSage wt.%	80.6	14.2	0.3	0.6

Figure 4.6 illustrates that the major oxide composition's values indicated in Table 4.10 are within their acceptable range indicated by the Portland Cement Association.

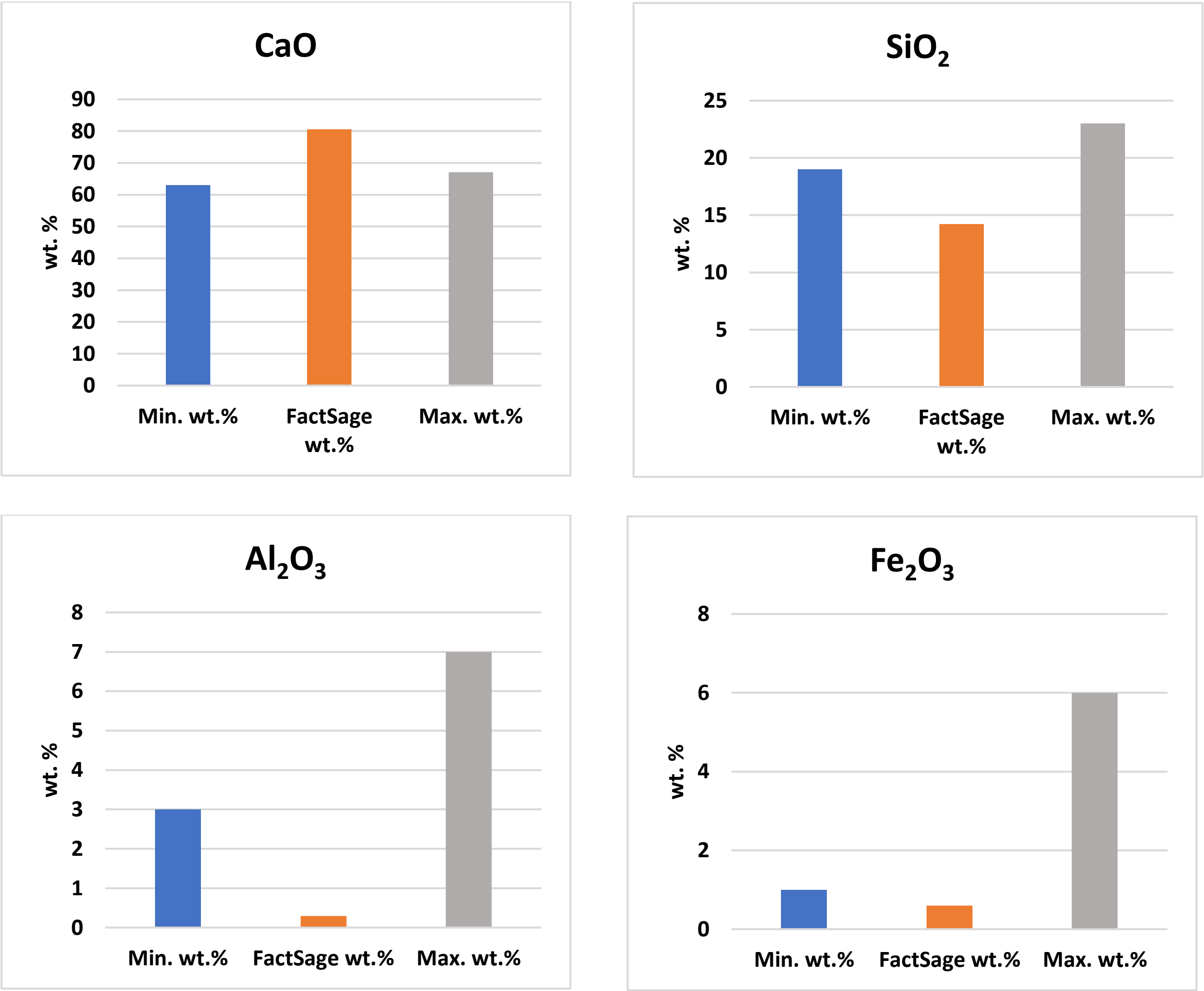


Figure 4.6 The major elements oxide range evaluation for CaO by-product

4.3.3.2 The chemical composition of minor elements evaluation

This is the second step in the procedure, where the minor elements oxide evaluation was done by FactSage software. Note that the elements should not be more than a few percent of the cement weight. The results in Table 4.11 demonstrate good agreement with the same oxides in Portland Cement. The concentration of MgO is 1.85%, where in Ordinary Portland Cement it is between 1-3%. The alkali oxides, Na_2O and K_2O, which do not exceed 1.5% in Ordinary Portland Cement, are 0.85% in the CaO solid by-product. For SO_3 concentration, it comes from PG's source and the results show that its mass percentage is 2.7%, which is the desired percentage.

Table 4.11 The minor elements evaluation of the CaO solid by-product with typical OPC

Chemical name	**Magnesium Oxide**	**Sodium Oxide**	**Potassium Oxide**	**Sulphur Trioxide**
Formula	**MgO**	**Na_2O**	**K_2O**	**SO_3**
OPC wt.% [109]	1 – 3	0.1 – 0.5	0.5 – 1	2 - 3.5
FactSage wt.%	1.85	0.22	0.63	2.7

Figure 4.7 demonstrates the results in Table 4.11 to show that the minor elements oxide evaluation matches the Ordinary Portland Cement chemical composition.

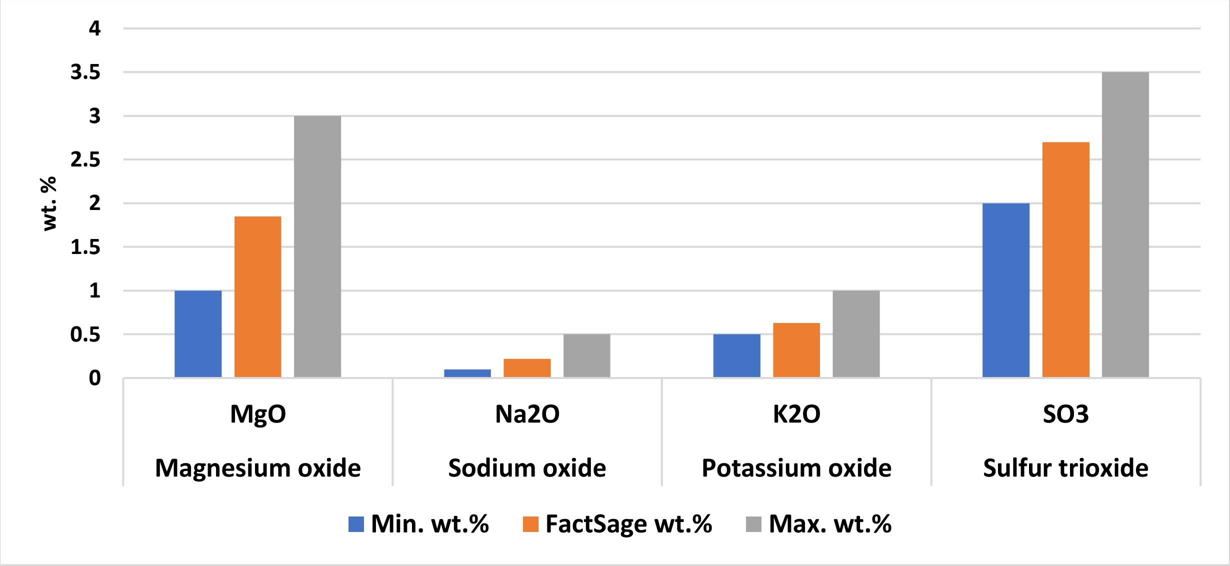


Figure 4.7 The minor elements oxide range evaluation for PG solid by-product

4.3.3.3 The chemical composition of the trace elements evaluation

The last step in the evaluation procedure, the trace elements evaluation, reveals the solid by-product's heavy metals concentration. It is an important step due to regulations banning cement if heavy metals and radioactive materials are present. The trace elements obtained from the typical Ordinary Portland Cement are compared with the concentration of trace elements obtained from the FactSage simulation of the PG thermal decomposition under reductive conditions at a low molar ratio. Table 4.12 presents the concentrations of the trace elements found in the product used in this study [110].

Table 4.12 The trace elements evaluation of the CaO solid by-product with typical OPC

Chem. name	**Mercury**	**Cadmium**	**Arsenic**	**Antimony**	**Lead**
Formula	**Hg**	**Cd**	**As**	**Sb**	**Pb**
OPC wt.% [110]	<0.001	<0.005	<0.05	<0.01	<0.05
FactSage wt.%	0.000	0.000	0.00	0.00	0.00
Chem. name	**Nickel**	**Selenium**	**Vanadium**	**Chromium**	**Uranium**
Formula	**Ni**	**Se**	**V**	**Cr**	**U**
OPC wt.% [110]	<0.05	<0.01	<0.001	<0.05	<0.001
FactSage wt.%	0.009	0.00	0.0003	0.002	0.000

As shown in Figure 4.8, the concentration of trace elements in the CaO solid by-product are permissible for all elements. Some elements do not exist in the final solid by-product at around 1200°C because they were diverted to liquid or gaseous phases during the thermal reaction depending on their boiling or melting points [111]. The gaseous elements are appeared in the stack gas stream which is emitted to the atmosphere causing environmental issue. While liquid phase and volatile elements are incorporated with the kiln dust and are stuck in the internal dike of the equipment which is after a while may spoil the equipment. Further investigations and research concerning the emissions of these metals.

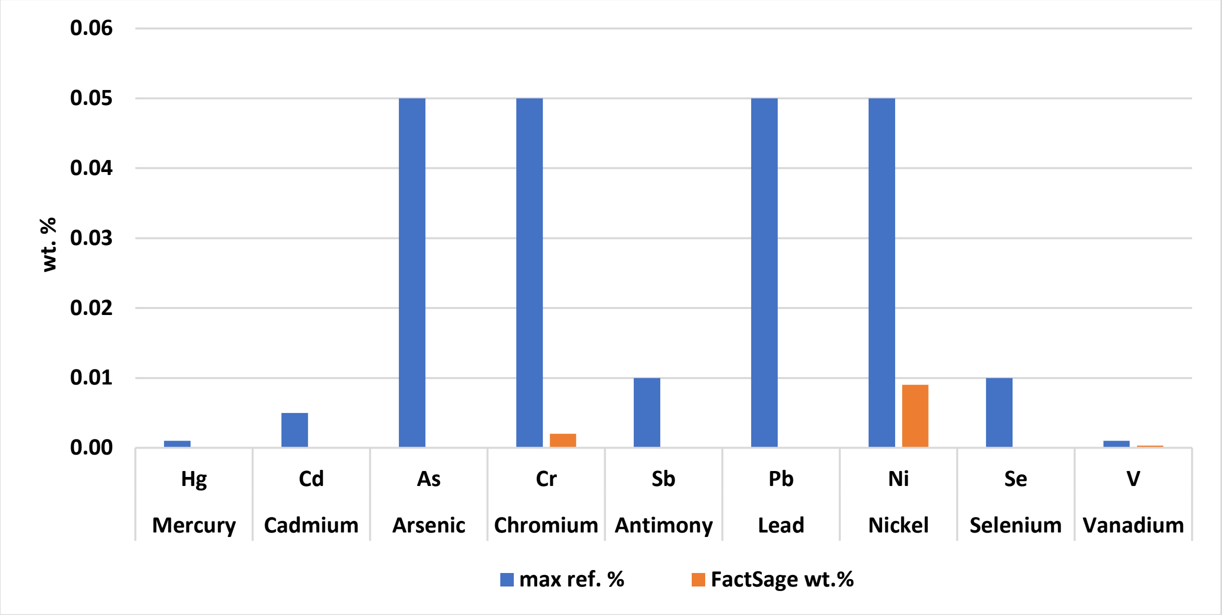


Figure 4.8 The oxides of trace elements range evaluation for PG solid by-product

4.4 Methods of valorizing the CaO by-product from PG thermal decomposition

The evaluation procedure ends with acceptable concentrations for minor and trace element oxides, as they are all within the range of the elements in typical Ordinary Portland Cement (OPC) concentrations. In contrast, major element oxides show that elementally Ca content is high, whereas Si, Al, and Fe are low.

Consequently, the CaO product is not comparable with Portland Cement due to the dissimilarity in major element oxide concentration unless modified and adjusted. To do that, proposed solutions to valorize the solid by-product from PG thermal decomposition are as follows:

4.4.1 Using CaO by-product as Sulfate Resistant Cement

The CaO solid by-product produced from the thermal decomposition of PG under reductive conditions at a low molar ratio is used as is to obtain type five of Portland Cement, which is Sulfate Resistant Cement (SRC).

The CaO by-product in Table 4.13 shows a high similarity in its composition with the SRC on account of the low C_3A content. In this type of cement, the amount of tricalcium aluminate

(C_3A) is restricted to lower than 5% by weight, and the ($2C_3A + C_4AF$) ought to be lower than 25% in weight [112].

Due to the low C_3A concentration, a very small quantity of calcium aluminate is formed in the hydration process, reducing the production of sulpho-aluminates, which is the main reason for concrete crack. Thus, the resistance to concrete against sulphate attack will increase.

Despite the lack of tricalcium aluminate in SRC, the latter is used on a large scale for constructions in contact with soil or groundwater. For instance, it is used when concrete is exposed to the risk of deterioration (spoil) due to sulphate attacks, like foundations, piles, basements, underground structures, sewage and near coastal work constructions [113].

The SRC is considered more expensive than OPC because it is not commonly available due to its special composition and its specific uses.

Table 4.13 The phase composition of CaO by-product and SRC

	C_3S	C_2S	C_3A	C_4AF
SRC wt.% [114]	51- 70	21 -28	0-0.5	0-0.75
CaO by-product wt.%	68.7	21.6	0.1	0.3

4.4.2 Adjustment of CaO to meet Portland Cement composition (3 methods):

4.4.2.1 Adding Al_2O_3, Fe_2O_3 and SiO_2 to the PG product

According to the simulation results, alumina and iron oxide have a lower concentration than in OPC, and the silica needs to be adjusted to be in the range of the OPC composition. Adding these compounds to the CaO by-product and reacting them at 1300ºC will yield the same phase composition. The minor and trace element oxides are maintained at the same concentration during the thermal treating.

The amounts of Al_2O_3, SiO_2 and Fe_2O_3 were obtained from a trial and error method indicated from the concentrations of the raw materials of limestone and clay used in the Portland Cement formation.

The approximate cost for the alumina, iron oxide, and silica added per ton of CaO solid by-product to reach the same OPC chemical composition depends on the data sources provided, as shown in Table 4.14. From the data, the total additives cost per ton CaO by product produced is an average of US $136.

Table 4.14 The amount of alumina, iron oxide and silica added per ton CaO produced with the cost

	Al_2O_3	Fe_2O_3	SiO_2
Kg added/ton	50	30	20
US $/ton in 2020	≈400 [115]	≈1400 [116]	≈3700 [117]

4.4.2.1.1 FactSage results

Figure 4.9 emphasizes the products produced from reacting alumina, silica and iron oxide with the CaO by-product, and by simulating the reaction in FactSage at intervals of 100°C to indicate the temperature when the phase composition products are produced. The graph shows the completion of the reaction at 1300°C.

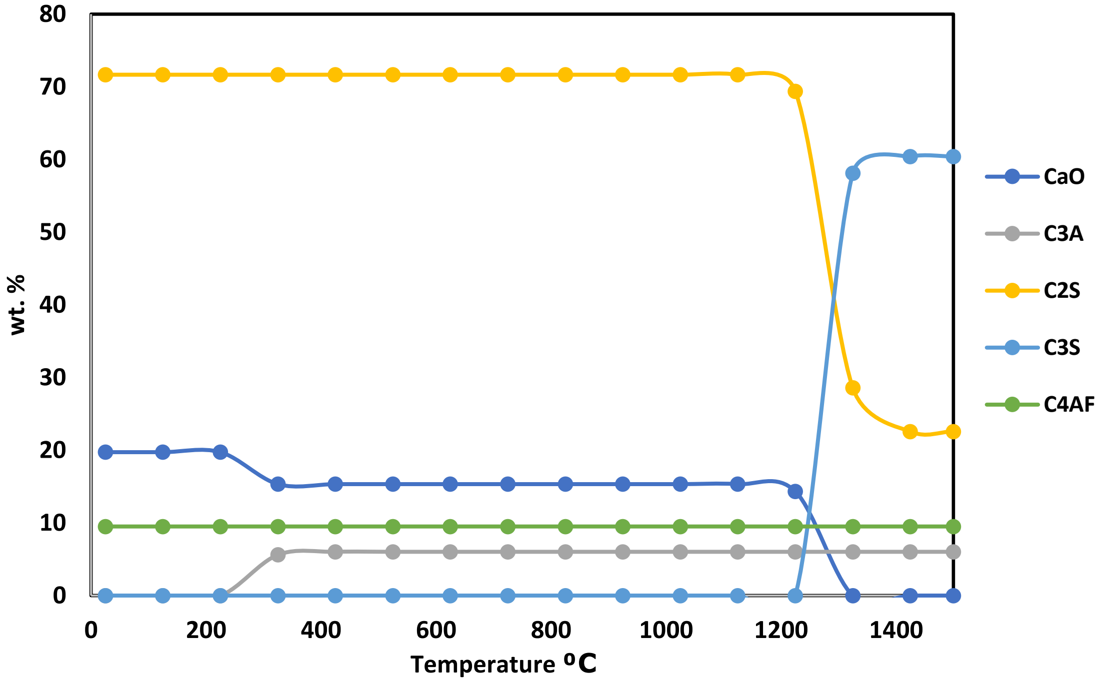


Figure 4.9 The phase composition after adding alumina, iron oxide and silica to the CaO by-product by FactSage

Table 4.15 clarifies the phase composition concentration at 1300℃ after adding alumina, silica and iron oxide to the CaO by-product, compared with the typical Portland Cement composition.

Table 4.15 The phase composition after adding alumina, iron oxide and silica to the CaO by-product

Chemical name	**Tricalcium Silicate**	**Dicalcium Silicate**	**Tricalcium Aluminate**	**Tetracalcium Aluminoferrite**
Notation	C_3S	C_2S	C_3A	C_4AF
OPC wt.% [106]	50-70	15-30	5-10	2-15
FactSage wt.%	60.4	20.7	6.01	9.5

4.4.2.2 Adding Clay to the CaO by-product

Clay is an important raw material used in OPC formation. It compensates for the lack of alumina, silica and iron oxide in the limestone, which gives OPC its good quality. In the CaO by-product form, due to alumina and iron oxide insufficiency, it is highly recommended to add clay in proportion with the CaO by-product and react them at 1300°C to adjust the composition to form Ordinary Portland Cement.

By adding 75% CaO by-product by weight and 25% clay by weight and simulating them in the FactSage software at 1300ºC, it will give the composition of Ordinary Portland Cement as presented in Figure 4.10:

These percentages are obtained from a trial and error method indicated from the concentrations of the raw materials of limestone and clay used in the Portland Cement formation.

4.4.2.2.1 FactSage results

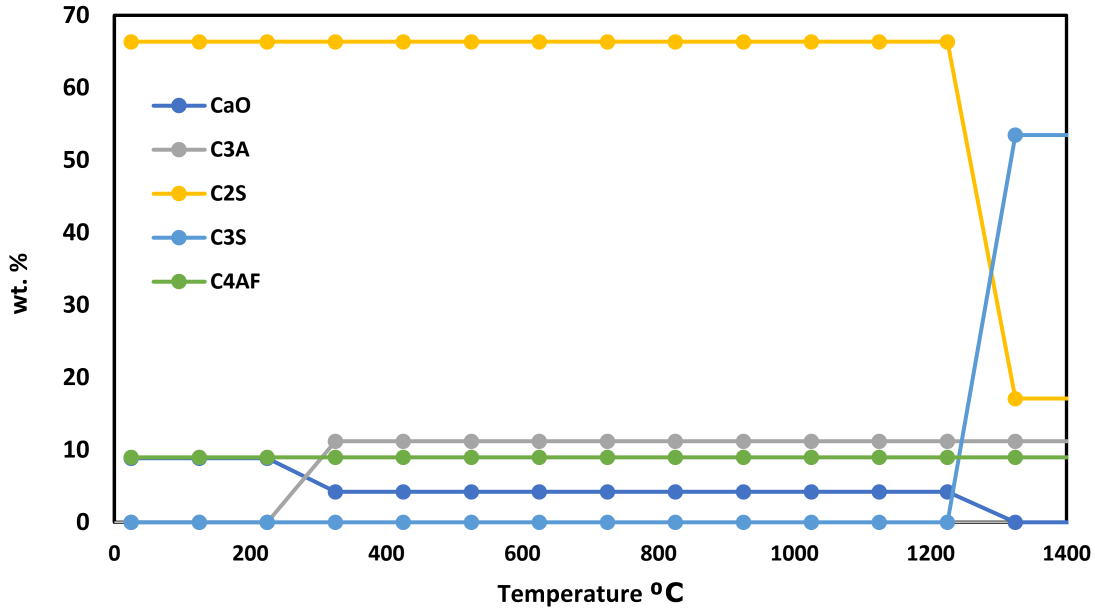


Figure 4.10 The phase composition after adding clay to the CaO product by FactSage

4.4.2.2.2 The phase composition of the CaO by-product with Clay

The phase composition of the CaO by-product reacted with clay in 3:1 ration at 1300°C. It was collected by FactSage software and is presented in Table 4.16.

Table 4.16 The phase composition of CaO by-product reacted with clay

Chemical name	**Tricalcium Silicate**	**Dicalcium Silicate**	**Tricalcium Aluminate**	**Tetracalcium Aluminoferrite**
Notation	**C_3S**	**C_2S**	**C_3A**	**C_4AF**
OPC wt.% [106]	50-70	15-30	5-10	2-15
FactSage wt.%	53.8	17.3	9.25	8.9

Figure 4.11 demonstrates the concentrations of the four-phase compositions of Portland Cement and how the CaO by-product after reacting with clay is adapting these ranges.

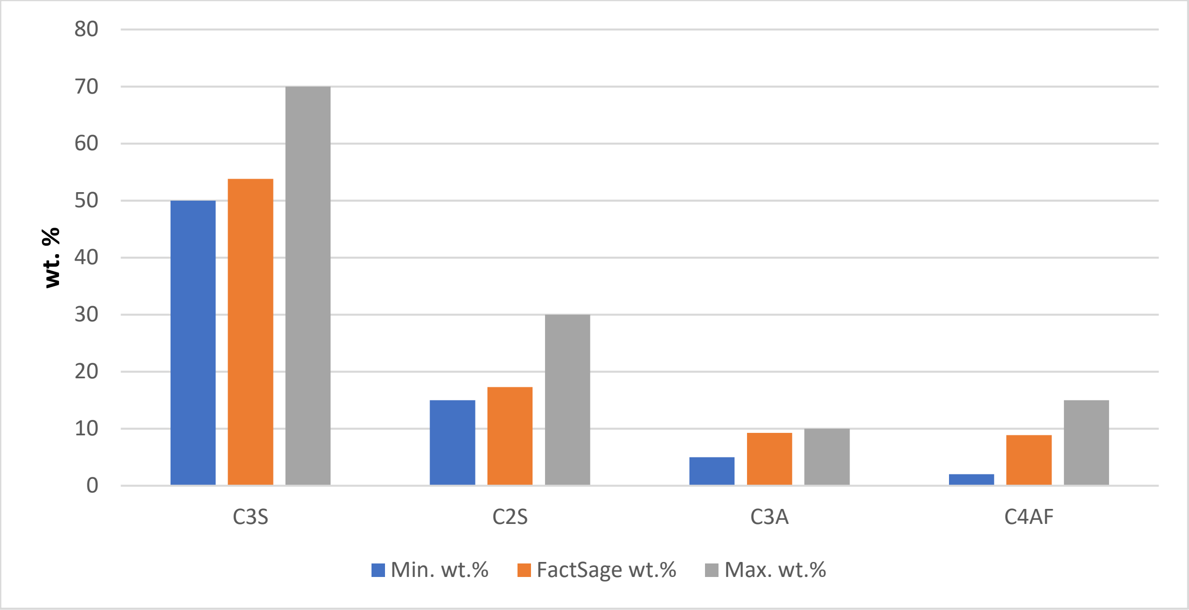


Figure 4.11 The phase composition range of CaO by-product reacted with clay

4.4.2.2.3 Chemical oxides composition of CaO with Clay

The chemical oxide composition of CaO reacted with clay should be calculated using Bogue calculations to evaluate the major, minor and trace elements and verify a similarity between the CaO by-product reacted with clay and the Ordinary Portland Cement composition.

Table 4.17 indicates all the major and minor chemical oxides produced by the reaction in 3:1 ratio between the CaO by-product and clay at 1300°C.

Table 4.17 The chemical oxide composition of CaO by-product reacted with clay

	CaO	**SiO_2**	**Fe_2O_3**	**Al_2O_3**	**MgO**	**Na_2O**	**K_2O**	**SO_3**
OPC wt.% [106] [109]	63-67	19-25	1-6	3-7	1-1.8	0.2-0.3	0.5-0.6	2-3.5
PG product wt.%	64.1	23.12	1.45	4.7	1.01	0.22	0.58	2.7

Figure 4.12. a and 4.12. b show that all the major and minor element oxide evaluations meet the acceptable range of the Portland Cement chemical composition. Thus, trace elements and heavy metals are lower than the max acceptable range.

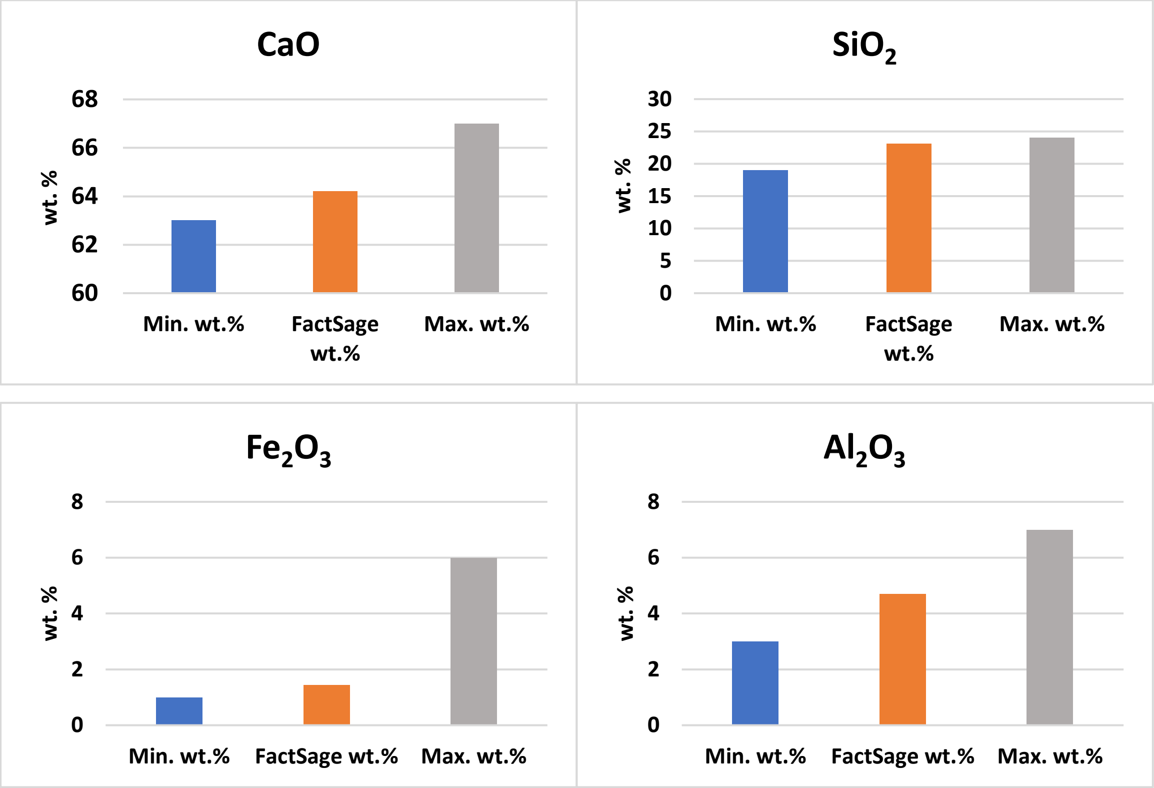


Figure 4.12-a Major element oxide composition range of CaO reacted with Clay

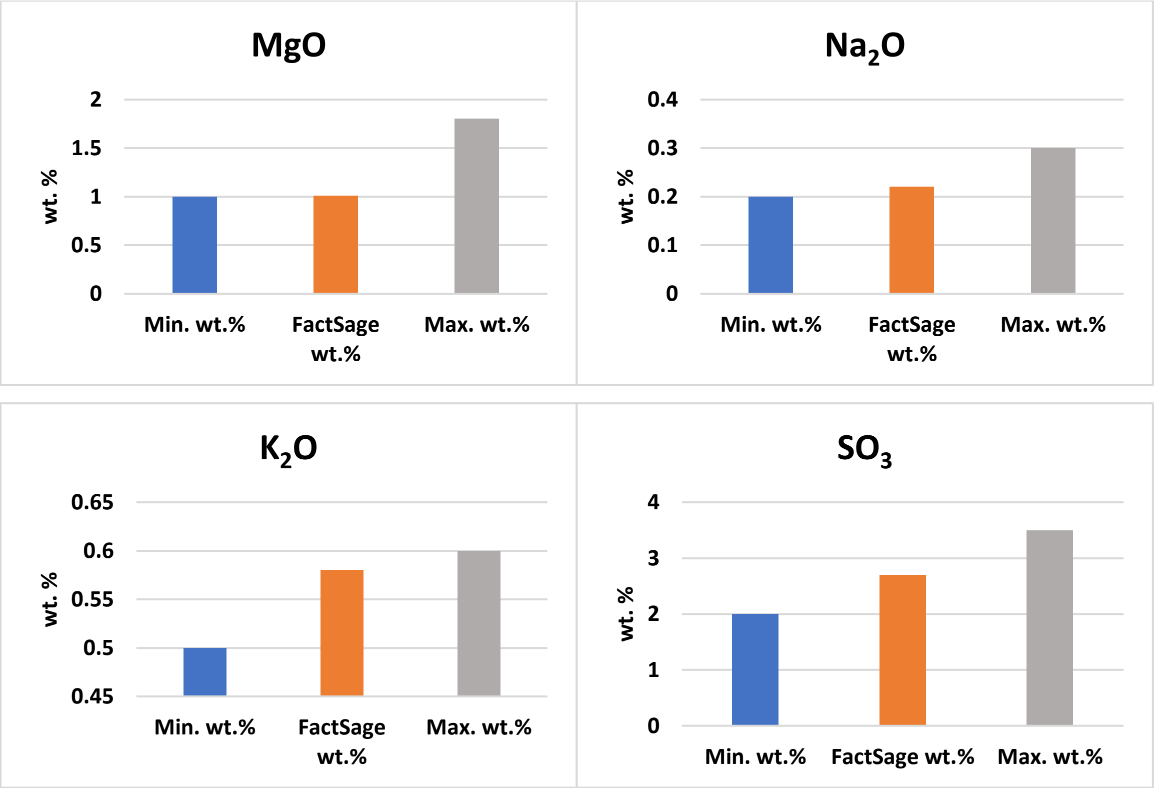


Figure 4.12-b Minor element oxide composition range of CaO reacted with Clay

4.4.2.3 Adding CaO to the mixture of limestone and Clay

It is known that limestone and clay are the main raw materials added to the rotary kiln to form Portland Cement clinker. In this method, the CaO by-product will replace half the weight of these raw materials. Therefore, adding 50% CaO by-product and 50% limestone and clay by weight in a 2:1 ratio and reacting them at 1300°C will result in the same Ordinary Portland Cement composition as the FactSage modelling shown in Figure 4.13.

These percentages are obtained from a trial and error method indicated from the concentrations of the raw materials of limestone and clay used in the Portland Cement formation.

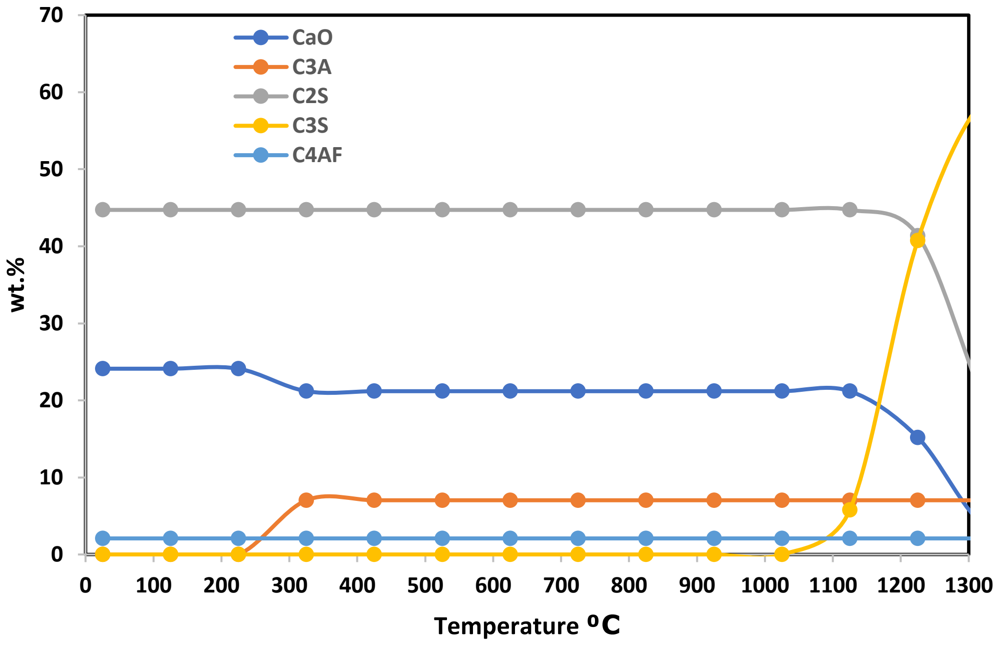


Figure 4.13 The phase composition of CaO and a mixture of limestone and Clay

The phase composition resulting from the FactSage simulation shows good agreement with the typical Ordinary Portland Cement (OPC) phase composition, as shown in Table 4.18:

Table 4.18 The phase composition of CaO by-product reacted with limestone and clay

	C_3S	C_2S	C_3A	C_4AF
OPC wt.% [106]	50-70	15-30	5-10	2-15
FactSage wt. %	59.28	25.27	6.04	3.08

4.4.2.4 The Advantages of the adjustment method

The CaO by-product adjustment method shows valuable advantages in the cement industry, the most important regarding the environment and the cost are:

4.4.2.4.1 Reduce CO_2 emissions

Reducing emissions from the cement production process means looking to an alternative feedstock other than limestone that can react to form Portland Cement, which releases greenhouse gas emissions directly and indirectly.

The heating of limestone releases CO_2 directly, through calcium carbonate breaks down to CaO and CO_2. This process accounts for around 50% of all cement production emissions. CaO by-product can replace the limestone. Hence, prohibit direct CO_2 emissions to the maximum.

The fossil fuel combustion to heat the kiln emits indirectly around 40% of the total cement emissions; because of the extreme heat requires to produce it. CaO from PG decomposition can decrease the reaction heat from 1450°C to 1300°C, which reduces the indirect CO_2 emissions around 10%.

Generally, to manufacture one ton of cement, it takes 4.7 million BTU of heat, equal to around 400 pounds of fossil fuel, which produces about 1.25 tones CO_2 [118, 119]. Cement industry is responsible for 5-8% of the global CO_2 emissions [120]. The CaO from PG decomposition could reduce 40-50% of the total cement CO_2 emissions, which means, if globally applied, will reduce the CO_2 emissions to 2-4%.

4.4.2.4.2 Save heat energy

Cement manufacturing is an energy intensive process; due to the high reaction temperature needs to produce clinker. The CaO from PG decomposition can replace the limestone and reduce the thermal energy needed in the cement making kilns from 1450°C to 1300°C; thus, afford considerable energy cost reduction.

4.4.2.4.3 Economize limestone processing cost

The CaO from PG decomposition particle size is quite similar to the Portland Cement particle size. CaO from PG decomposition shows considerable feasibility to economize the cost of extraction, transportation, crushing, and grinding of the limestone rocks to be used as a raw material for the cement reaction.

4.4.2.5 Industrial case study

The reaction between the CaO from PG decomposition and the additives (for example Clay) in the adjustment method to form Portland Cement is formed at 1300°C according to FactSage. To find a way to reduce this temperature, three procedures are suggested and simulated by FactSage:

First procedure is to add the Clay to the CaO from PG decomposition and mix them without any heat, according to FactSage this way will never end up with any reaction or phase composition because the cement needs high temperature to be formed.

The second procedure is to add the Clay to the PG in the beginning of thermal decomposition under reductive condition and simulate it in FactSage, Figure 4.14 presents the result of the simulation, it clearly shows that by adding Clay to PG and expose them to thermal decomposition will generate some phase composition which are not valuable in cement industry, it will lead to ineffectual products that are not related to the phase composition concentration of the Portland Cement.

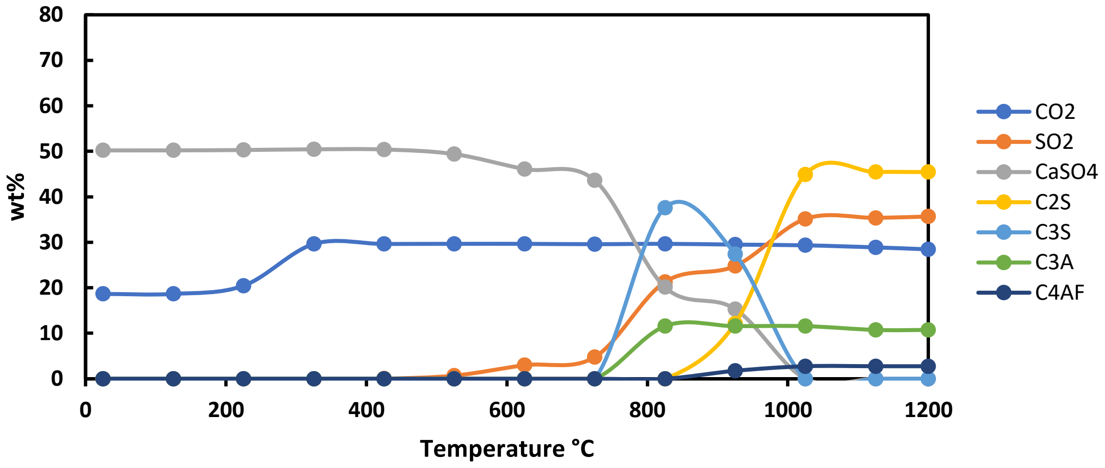


Figure 4.14 Simulation of Clay and PG thermal decomposition under reductive condition

The third procedure is to react the Clay with the CaO solid by-product after the thermal decomposition in appropriate ratio at 1300°C. According to FactSage simulation, this method will ensure the formation of the Portland Cement's phases composition. In this case, to reduce the energy consumed in heat; the Clay can be fed to the thermal decomposition reactor after releasing the produced gases. The Clay will react with the remained CaO from the PG decomposition to form Portland Cement. This method among all shows the most considerable acceptance.

4.4.3 Carbon dioxide Capture and Storage (CCS)

The Carbon dioxide capture and storage (CCS) technology decreases and eliminates CO_2 emissions from industrial processes by reacting CaO (in the case of the present study it is the CaO by-product) with emitted CO_2 to form $CaCO_3$ and sink it.

The thermal decomposition of PG under reductive conditions produces CaO, SO_2 and CO_2, according to reaction (11). SO_2 is separated and re-looped to be used in the production of H_2SO_4. In contrast, CaO is used as a calcium-based absorbent to capture the CO_2 emitted from either the PG thermal decomposition reaction or even the CO_2 released from the Portland Cement formation by limestone's thermal reaction.

$CaSO_4 + CO \xrightarrow{1150^oC} CaO_{(S)} + CO_{2\,(g)} + SO_{2\,(g)}$………………………………………. (11)

4.4.3.1 Ca-Looping process (CaL)

The operation in Figure 4.15 [121] starts when CO_2 is produced from an industrial process and fed to the carbonator to react with CaO; it is used as a calcium-based absorbent and forms $CaCO_3$. According to reaction (12), this step is called the Carbonator, and it occurs at a temperature between 400-650ºC. The $CaCO_3$ formed is passed to calciner. The $CaCO_3$ is decomposed at a high temperature between 850 – 900ºC in a Calcinator according to reaction (13) to form CaO. The CaO must be generated to reactivate it. Pure CO_2 is then emitted, which can be sequestered and stored. The spent CaO can be used in the feedstock of the cement production industry [122].

Carbonation: $CaO + CO_2 \longrightarrow CaCO_3$ ……………………………………………… (12)

Calcination: $CaCO_3 \longrightarrow CaO + CO_2$ ………………………………………………… (13)

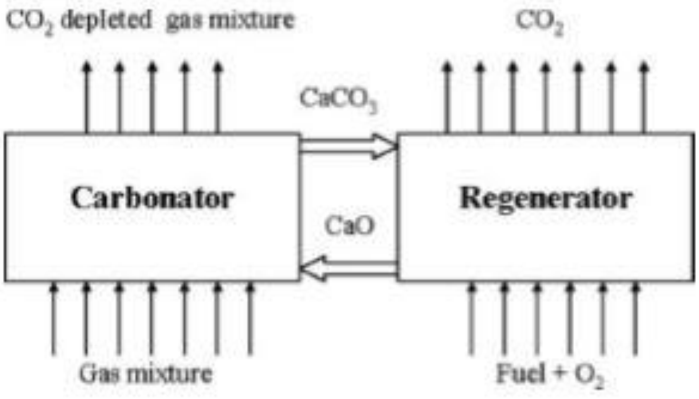


Figure 4.15 Carbonation/calcination cycle process for CO_2 capture [121]

For the CO_2 capture and storage of this study, only the carbonation step will occur where CaO settles in a fluidized bed reactor, and a stream of CO_2 passes and forms $CaCO_3$ and sink it at a temperature of 650ºC, as presented in Figure 4.16 [123].

An alternative to traditional CCS methods, which are already employed in some plants, CO_2 emissions can be captured after it is produced through carbon capture and storage (CCS). CaO from the PG thermal decomposition can use their product as a sink for CO_2. As a mitigation technology, carbonation can be achieved by exposing CaO with CO_2 concentrations to form $CaCO_3$ and sink it. The result is stable, long-term CO_2 storage [124].

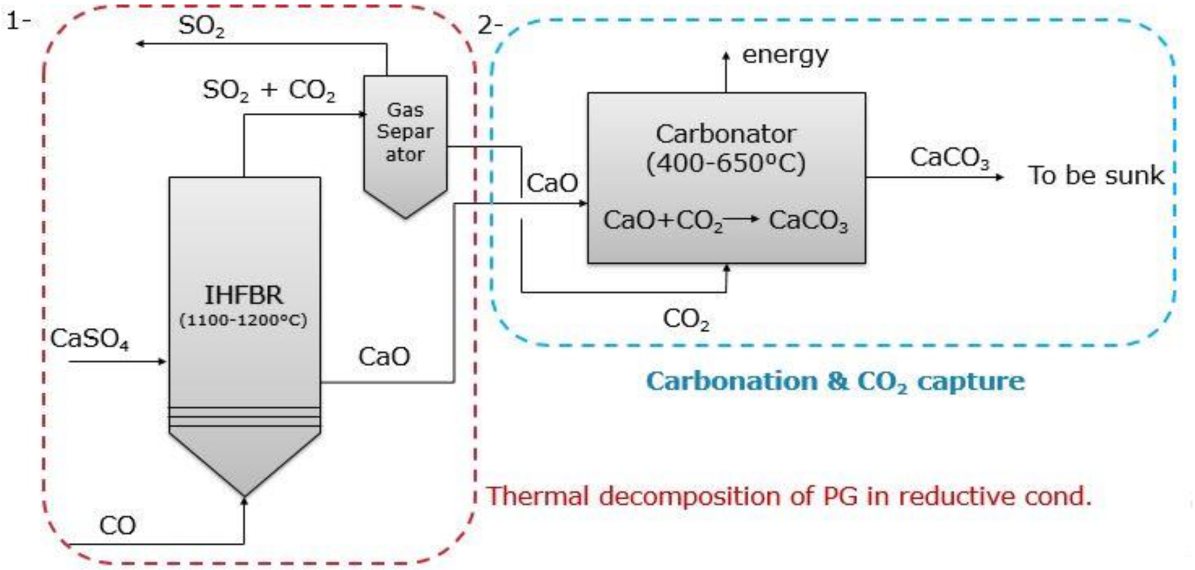


Figure 4.16 The process flowsheet of the thermal decomposition of PG and the CO_2 capture

CHAPTER 5 CONCLUSION, UNCERTAINTIES AND RECOMMENDATION

5.1 Conclusion

In this study, the results achieved from the simulation using the FactSage software provide a good indication of how to valorize the solid by-product (CaO) of PG after its thermal decomposition under reductive conditions. The proposed points below highlight the conclusion to valorize the solid by-product of PG in the present study:

Method 1: Using it as Sulfate Resistant Cement

An alternative solution is to use the CaO solid by-product as Sulfate Resistant Cement (SRC), due to its high similarity with the phase composition of SRC and its low C_3A content.

Method 2: Adjustment of the CaO by-product to meet Portland Cement composition using three methods:

1. **Adjusting the content of the CaO by-product**
   Adding adequate amounts of Al_2O_3, Fe_2O_3, and SiO_2 to the PG solid by-product to react at 1300°C and form Ordinary Portland Cement. The results of FactSage show a high similarity in their phase composition.
2. **Adding Clay to the CaO by-product**
   Adding clay, which is rich with Si, Al, and Fe, to the PG solid by-product in a ratio of 1:3 and then reacting them at 1300°C will form a composition in the acceptable range of Ordinary Portland Cement.
3. **Using 50% CaO by-product and 50% limestone and clay**
   Using 50% of PG by-product with a portion of 50% limestone and clay will form Ordinary Portland Cement when reacting at 1300°C.

Method 3: CaO in Carbon dioxide Capture and Storage (CCS)

The CaO by-product can be used to eliminate CO_2 emissions from industrial processes. Where CaO reacts with CO_2 at 650°C to form $CaCO_3$, which then will be sunk and stored after cooling down.

5.2 Uncertainties

This study was based mainly on simulation and modelling and has not yet been tested on a laboratory scale. Due to this fact, there are some uncertainties and limitations when applied to a particular industrial field. This study mainly shows to what extent the reaction could take place and how it happens under equilibrium conditions. It also serves as a reference for designing the process. The following main points should be taken into consideration before granting a study based on these results:

1. FactSage results might indicate a difference between the simulated and experimental results.
2. The mechanical and physical properties of the Ordinary Portland Cement are not examined on CaO by-product. They must be studied and examined practically in the laboratory using the recommended tests and equipment.
3. Bogue calculations give the potential composition only and not real values. However, the difference between the real and the calculated values should be considered.

5.3 Recommendation for future work

This study delivered a successful and great opportunity to valorize and benefit from the CaO solid by-product in the cementitious field, based on the modelling by FactSage software of PG thermal decomposition under reductive conditions.

Based on this study and literature reviews, upon completion of this work and after obtaining a more precise and specific understanding of the use of the CaO solid by-product in the cement industry, the recommendations below may be the subject of future studies:

1. Produce CaO solid by-product on a laboratory scale to test at real cement production conditions.
2. Implement and apply all the Ordinary Portland Cement tests and measurements to study its mechanical and physical properties and verify its quality and performance.
3. Perform process and cost analysis to investigate the feasibility of implementing the valorization processes.
4. Further investigations and studies should be done on CO_2 capture and storage to perform a well-designed process.

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