

**INVESTIGATION OF CO₂ SEQUESTRATION
POSSIBILITY VIA AQUEOUS PHASE MINERAL
CARBONATION USING INDUSTRIAL WASTE
MATERIALS**

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Degree of Master of Science

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A thesis submitted in partial fulfilment of the requirements for the degree
of Master of Science in Sustainable Process Engineering

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ABSTRACT

Carbon dioxide (CO₂) as the most vital greenhouse gas in the earth's atmosphere plays a major role in maintaining the global temperature. Higher concentrations of CO₂ in the atmosphere, increases amounts of heat entrapped in the atmosphere. Thus, the environmental temperature increases when the CO₂ concentration increases and results in global warming. The global CO₂ emission was approximately 35.3 billion metric tonnes in 2018 and, it is predicted to be increasing up to 43.08 billion metric tonnes by 2050 as per the prevailing trends in statistical analysis. Therefore, maintaining an acceptable concentration of atmospheric CO₂ is required. In this situation, anthropogenic CO₂ capture and storage technologies have emerged to reduce the atmospheric CO₂ concentration. Among the carbon capture methods, post-combustion CO₂ capture technologies are the most common as there is the advantage of ability to retrofitting to existing plants.

Mineral carbonation is considered as a natural and exothermic process among available post combustion CO₂ capture technologies, which gives promising results in CO₂ sequestration by storing as mineral carbonates. Suitable materials for mineralization are natural minerals like silicate rocks, serpentine, olivine minerals or else industrial wastes like oil shale ash, steel slag, paper mill waste, fly ash or mine tailing, etc.

In this study, the existing literature on CO₂ sequestration capabilities through aqueous phase mineral carbonation of industrial waste materials were reviewed and analyzed. Industrial waste materials, such as coal fly ash and steel slag have significant capture capacities and coal fly ash consumes significantly lesser energy and costs to capture one tonne of CO₂. In addition, calcium extraction from Lakvijaya Coal Fired Power Plant fly ash was experimentally investigated to identify the potential for indirect carbonation, to sequestrate CO₂ from coal flue gas. A maximum calcium extraction efficiency of 9.65% was obtained for coal fly ash obtained from Lakvijaya Coal Fired Power Plant.

Keywords: CO₂ sequestration, Mineral Carbonation, Coal Fly Ash, Industrial Waste Materials

DEDICATION

Dedicated to Dr. Mahinsasa Rathnayake, who taught me that teachers go beyond the textbooks and inspire from the heart.

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I would like to express my sincere gratitude to my research supervisor Dr. Mahinsasa Rathnayake for the immense guidance, motivation and knowledge to steer me in the right direction whenever he thought I needed it.

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LIST OF ABBREVIATIONS

Abbreviation	Description
PCC	Post-Combustion Capture
LCPP	Lakvijaya Coal Fired Power Plant
CFA	Coal Fly Ash
VSA	Vacuum Swing Adsorption
PSA	Pressure Swing Adsorption
OSFA	Oil Shale Fly Ash
CBD	Cement Bypass Dust
APMWA	Alkaline Paper Mill Wastes Ash
MSWI	Municipal Solid Waste Incineration
EOR	Enhanced Oil Recovery
EGR	Enhanced Gas Recovery
ECMBR	Enhanced Coal Bed Methane Recovery
XRF	X-Ray Fluorescence spectrometer
SEM	Scanning Electron Microscopy

1. INTRODUCTION

1.1. Effect of anthropogenic CO₂ in atmosphere

Carbon dioxide (CO₂) as the most vital greenhouse gas in the earth's atmosphere plays a major role in maintaining the global temperature and atmospheric equilibrium. Volumetric concentration of CO₂ in atmosphere is approximately 0.04% [1]. This CO₂ content is mostly responsible in thermal regulation of the earth during day and night by absorption and emission of heat from and to the surface of the earth; i.e. greenhouse gas effect. Figure 1.1 elaborates the greenhouse gas effect resulted due to greenhouse gases; mostly CO₂ in atmosphere.

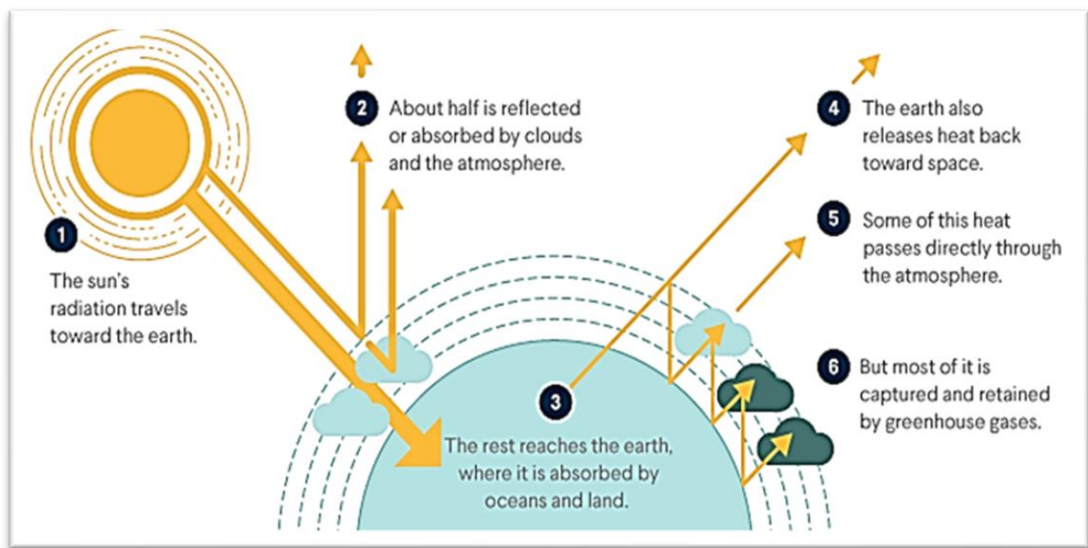


Figure 1.1: Illustration of greenhouse gas effect [2]

Furthermore, higher concentrations of CO₂ in the atmosphere, increases the amount of heat entrapped in the atmosphere. Thus, the environmental temperature increases when the CO₂ concentration increases and results in global warming. Therefore, maintaining an acceptable concentration of atmospheric CO₂ is required [4,5]. Figure 1.2 represents the observed variation of the atmospheric CO₂ concentration since 1960 to 2020. CO₂ has consequently accrued within the atmosphere at an accelerating rate of 0.7 parts per million (ppm) by volume per annum around 1958 – 1959. The observed CO₂ accumulation rate in 1980 and 1990 are 1.5 ppm per annum and 1.6 ppm per annum. The accumulation rate observed since the 2010, for the next 10 years is approximately 2.2 ppm per annum.

However, increment of CO₂ concentration in atmosphere provoke deleterious consequences in humankind including global warming, ocean acidification, and carbon fertilization on all living organisms [1,3,6].

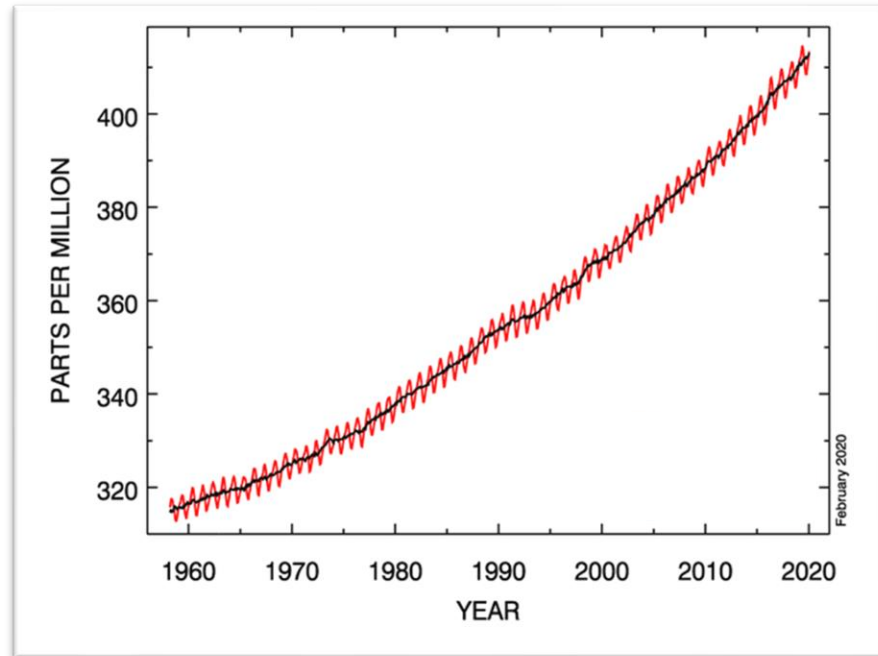


Figure 1.2: Keeling curve for atmospheric CO₂ concentration [6]

The global CO₂ emissions were approximately 35.3 billion metric tonnes in 2018 and, it is predicted to be increasing up to 43.08 billion metric tonnes by 2050 as per the prevailing trends in statistical analysis [7]. Even though green plants absorb atmospheric CO₂ in photosynthesis process, the accelerated CO₂ accumulation rates have increased the atmospheric CO₂ concentration [4]. This inequality is mainly due to the continuous anthropogenic activities; especially fossil fuel combustion, deforestation, and etc. Among them, high energy consuming industries, such as cement industry generates around 4% of the anthropogenic emissions. Deforestation and forest land utilization in agriculture results for 9% of the anthropogenic emissions. Furthermore, the highest amount of atmospheric emissions, approximately 87% is resulted from fossil fuel combustion, especially coal power generation [8].

Fossil fuels including coal, crude oil, and natural gas are the major energy sources utilized throughout the globe. Figure 1.3 forecasts the global energy consumption, with respect to different energy sources. The demand for the fossil fuels has redoubled with the increased demand for energy. Thus, the anthropogenic CO₂ emissions are expected to increase in next five decades. Considering the present statistics, the highest percentage (43%) of CO₂ emission is due to coal combustion followed by crude oil (36%) and natural gases (20%) [8,9].

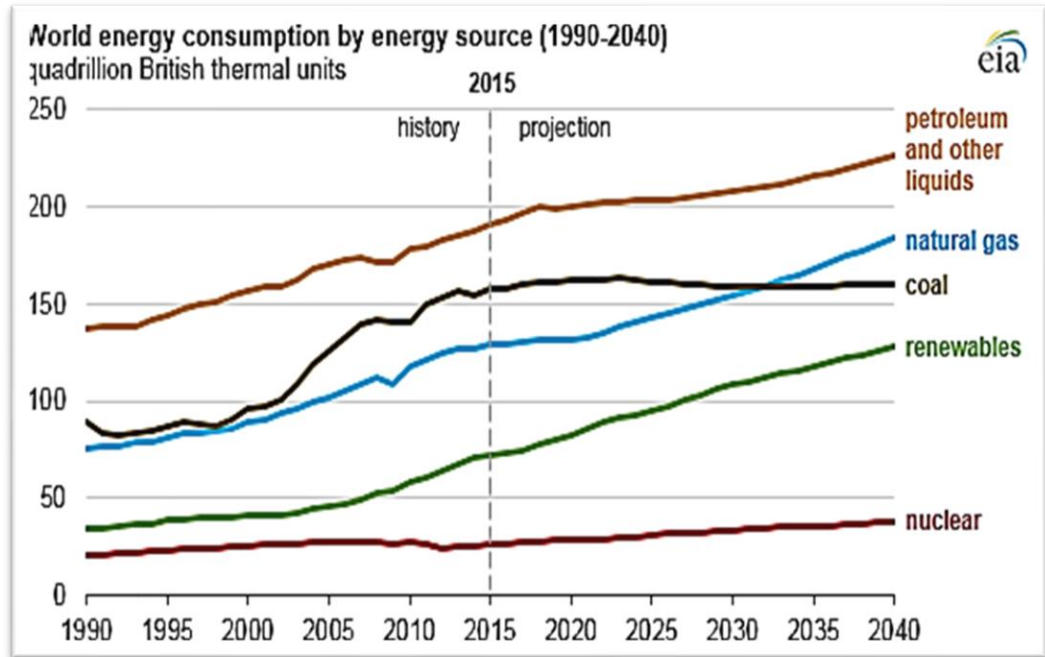


Figure 1.3: Global energy consumption by different energy sources [9]

According to the international statistics of CO₂ emitted based on the sector, 25% of CO₂ emission were due to the power generation around the globe. The transportation and manufacturing industries are accountable for 32.5% of CO₂ emissions.

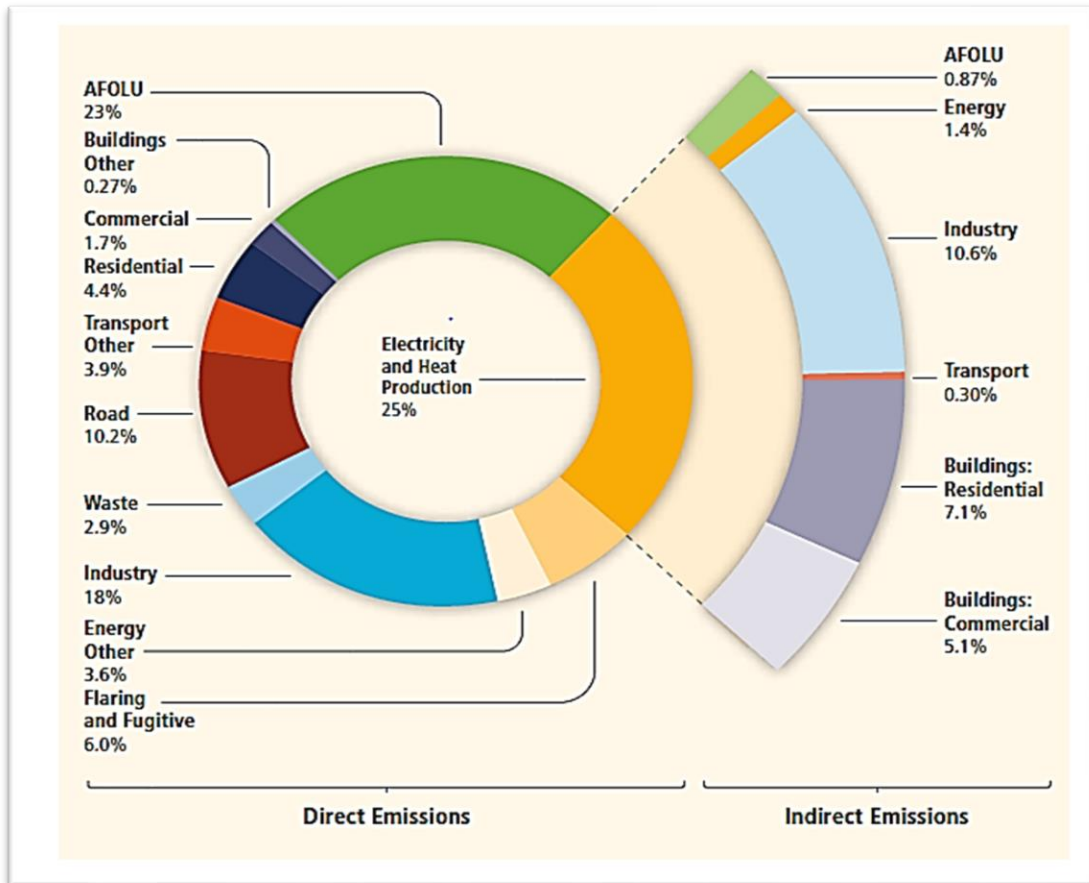


Figure 1.4: Quantification of CO₂ emissions by sector [10]

As stated in Figure 1.4, more energy utilization causes more anthropogenic CO₂ emission to the atmosphere. These statistics are strictly bound with the world population, and the distribution of related high energy consuming industries around the world. Hence, the anthropogenic CO₂ emission rates varies according to the regions in the world.

When considering CO₂ emissions with respect to continents, Asia contributes 53% of global CO₂ emission, whereas, China is the significant emitter who nearly emits 10 billion tonnes per year, which is responsible for more than one quarter of the global emission. The second largest CO₂ emitting continent is North America that represents 18% of global emissions followed by 17% of CO₂ emission is by the Europe. Minimal amount of CO₂ emission is done by African and South American continents and that is nearly 3-4% each of global emissions [11].

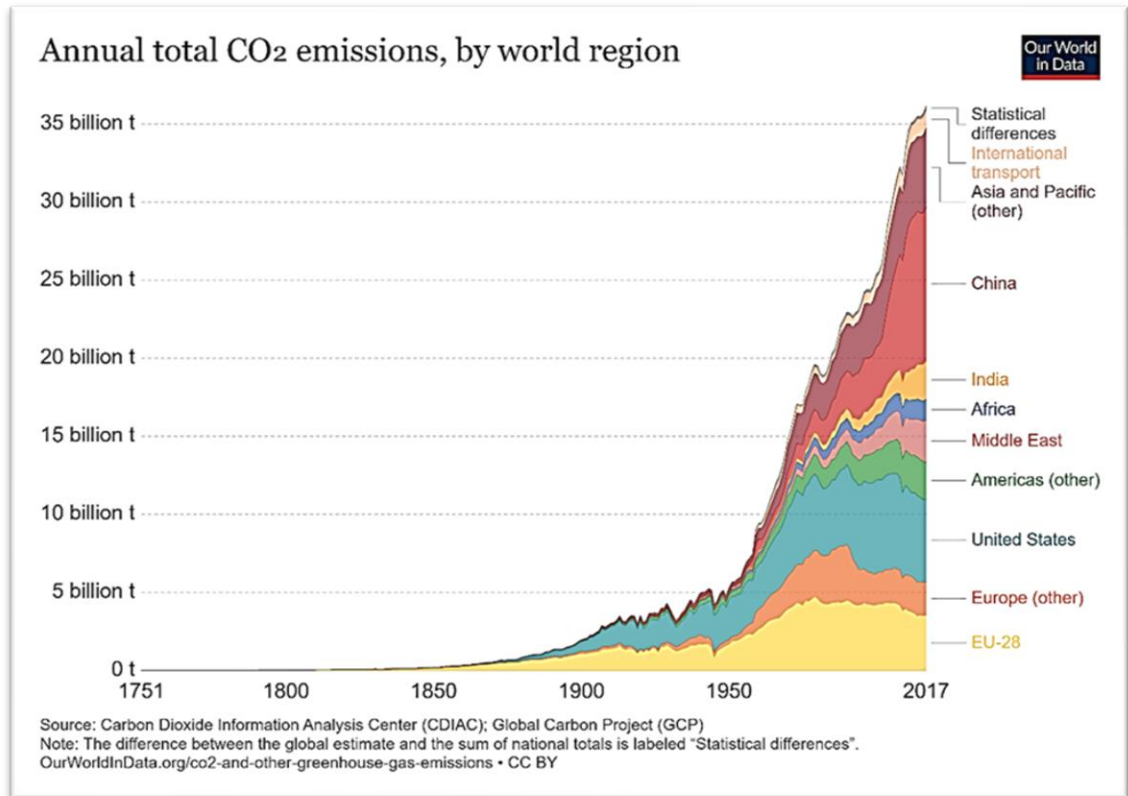


Figure 1.5: Total CO₂ emissions by world region [11]

Considering the statistics mentioned for the anthropogenic CO₂ emissions especially from fossil fuel combustion is expected to increase throughout the world. Hence, the negative environmental impacts are to be worsen in near future. Thus, there is a critical demand for reliable and sustainable technologies to reduce the anthropogenic CO₂ emissions.

1.2. Carbon capture technologies

Pre-combustion capture, oxy-fuel combustion, and post combustion capture are the available three basic CO₂ capturing methods. Pre-combustion is converting solid, liquid, and gaseous fuel into a hydrocarbon mixture by using gasification or reforming [12]. Prior to combustion, oxygen is separated from the air and the fuel is mixed with distilled oxygen flow and flue gas, and the output of the process gives the CO₂ and H₂O rich stream, which is easily purified and this process is called oxy-fuel combustion [13]. Post combustion is the capture of CO₂ from flue gases resulting from combustion by using both physical and chemical processes [14].

Among these three technologies, post-combustion CO₂ capture technologies are the vastly used, as there is an advantage in retrofitting to existing plants [15]. There are four major post-combustion capture techniques available. They are membrane separation, cryogenic separation, absorption by liquid solvents (chemical solvent method), and adsorption by solid sorbents. In all these four techniques, the captured CO₂ is transported and stored through available storage technologies, i.e., geological storage, ocean storage, or storage below seabed (still under experimental stage). These storage technologies appear as temporary storage within eco-system and are required be critically maintained to reduce leakages and other environmental impacts [16]. Therefore, there is a demand for alternative technologies with carbon capture and permanent storage capability.

Anthropogenic CO₂ sequestration through mineral carbonation is an alternative carbon capture technology with permanent CO₂ storage. Mineral compounds containing CaO and MgO are used to capture and store CO₂ in the form of carbonates. Thermal decomposition at high temperatures (around 800 °C) is required to decompose carbonates to release CO₂ again. Thus, mineral carbonation has a capability to safely store CO₂ for thousands of years compared to other technologies. Natural rock minerals, such as wollastonite, serpentinite, and olivine are the most utilized natural feedstocks in mineral carbonation.

Other than rock minerals, industrial wastes containing alkaline earth metal oxides like CaO and MgO also have a capability to capture CO₂. Coal fly ash, steel slag, cement kiln dust, etc. are some key industrial wastes utilized for mineral sequestration of CO₂. Above-mentioned industrial wastes have significant CO₂ sequestration capacities according to their process conditions and the mineralization pathways. These industrial wastes are abundantly available throughout the world, as they are resulted from large scale high energy consuming processes (coal powerplants, steel manufacturing, cement production plants). On the other hand, the utilization of these wastes to capture CO₂ through mineral sequestration (mineral carbonation) enhances the environmentally- benign performance of the CO₂ capture process as well.

1.3. Significance of coal fly ash as a CO₂ sequestrating agent through mineral carbonation in Sri Lankan scenario

36.5% of the Sri Lankan electricity demand is supplied through Lakvijaya Coal Power Plant (LCPP), Norochcholei, Sri Lanka [17]. The power plant has a power output capacity of 900 MW. This power plant generates fly ash 30 tonnes per hour, which is a significant amount of fly ash. The possibility to utilize this fly ash to sequester emitted CO₂ by the power plant and reduce the anthropogenic emissions is very interesting to be investigated. The literature reveals that the CO₂ sequestration capacity depends on the free lime (free CaO) composition in fly ash [55]. There is a lack of reliable/published data on the free CaO composition in LCPP fly ash. Thus, determination of CaO composition in LCPP fly ash composition, leads to determine the theoretical carbon capture capacity optimized mineral carbonation techniques to be utilized in future.

1.4. Objectives of the study

The objectives of this study can be split up as follows.

01. To compare CO₂ sequestration capabilities through mineral carbonation of selected waste materials, reported in the literature.

02. To investigate the experimental calcium (free CaO) extraction efficiency for the possibility of indirect mineral sequestration of CO₂ (carbonation) using coal fly ash from Lakvijaya Coal Fired Power Plant, Norochcholei.

2. LITERATURE REVIEW

In this chapter, detailed literature review was conducted for post-combustion CO₂ capture capabilities through mineral carbonation of selected waste materials, reported in the existing studies.

2.1. Post combustion CO₂ capture technologies

In post combustion capture technologies, CO₂ is sequestered from flue gases, which are released from combustion processes [14]. Post-combustion CO₂ capture technologies are essentially required as the pre-combustion techniques and oxy-fuel or efficient combustion methods could not control the majority of CO₂ emissions from existing plants and processes [15]. There are four major post-combustion capture techniques available.

- Membrane separation
- Adsorption by solid sorbents
- Cryogenic separation
- Absorption by liquid solvents (Chemical solvent method)

2.1.1. Membrane separation

Thin polymeric film membranes and inorganic membranes are the two types of membrane materials available for CO₂ capture. Polyimide, poly-dimethyl-phenylene oxide, poly-ether-sulfone and poly-acrylonitrile with poly-ethylene glycol are examples for polymeric films whereas alumina, activated carbon, silicon carbide, and zeolites are examples for inorganic membranes [22].

The membrane should complete following requirements that one may capture CO₂ from flue gas including high CO₂ permeability, high CO₂/N₂ selectivity, high thermal and chemical stability, and acceptable cost in large-scale application. Thus, polymer-based membranes are the only economically viable membrane materials for a CO₂ capture process [23]. The advantages of this process include simple application, easily operative equipment, and cost effectivity. However, the technology lacks the ability to use in the presence of high flow rate and selectivity of the membrane according to the process even though this process considered as a relatively mature process [20].

Table 2.1: CO₂ sequestration capacity of polymer membranes [24]

Membrane	CO ₂ / N ₂ Selectivity	Temperature (°C)	Permeance ^a (mol s ⁻¹ m ⁻² Pa ⁻¹) or Permeability ^b (mol s ⁻¹ m ⁻¹ Pa ⁻¹)
Cellulose Acetate	40.17	-	2.48 × 10 ^{-7 a}
Polycarbonates-FBPC	25.5	35 °C	4.76 × 10 ^{-11 b}
Polymides-TMeCat	25	30 °C	6.30 × 10 ^{-10 b}
PolysulfoneTMPSF-HBTMS	21.4	35 °C	2.27 × 10 ^{-10 b}
Polysulfone-HFPSF-O-HBTMS	18.6	35 °C	3.31 × 10 ^{-10 b}
Polymides-IMDDM	18.1	-	6.17 × 10 ^{-10 b}
Polysulfone-HFPSF-TMS	18	35 °C	3.47 × 10 ^{-10 b}

2.1.2. Adsorption by solid sorbents

Weak intermolecular forces (Van der Waals forces) with the gas molecule is promoted by the porous sites available on solid sorbents, which is referred as physical adsorption (physisorption) [25]. Physisorption is a reversible process that is reversed due to pressure reduction or temperature increase (desorption), and as a result, adsorbed gas molecules leave the solid surface [26]. Certain compounds available in the solid sorbent are foamed irreversible chemical reactions with the gas molecules by either covalent or ionic bonding and this process is known as chemical adsorption (chemisorption), which is occurred in addition to the physisorption [27]. Surface reaction, internal diffusion, and external diffusion are the reaction steps those take place during the mechanism of a chemisorption process [28].

Adsorption technology is a very attractive and practical method that uses low energy, maintenance, and operational-friendly, flexible sorbents, such as zeolites, activated carbon, metal oxides, porous silicates, etc. in chemical and environmental processes. Temperature swing adsorption reported in the literature, which can be used in coal-fired plants is a profitable process due to its inexpensiveness and less thermal energy consuming process. Yet, longer cooling and heating time is essential for CO₂ capturing.

There are two types of swing adsorptions namely Vacuum Swing Adsorption (VSA) and Pressure Swing Adsorption (PSA). Although VSA is more economically feasible than PSA, VSA has its own negatives, such as sensitivity to feed gas temperature, excessive heat required before injecting flue gas to VAS, which causes the separation efficiency of the process. Besides, PSA used as a capable technology in recent days due to minimum energy usage and its capability to operate in broad spectrum of temperatures and pressures. Another advantage of adsorption technology is that it requires lower investment costs than other previously mentioned technologies.

The adsorption technology also has some disadvantages, such as poor heat transfer, and slow kinetics. However, disadvantages of this technology are negligible compared to its advantages [15].

Table 2.2: CO₂ adsorption capacity of different adsorbents

Feedstock	Process Conditions	Adsorption Capacity mg CO₂/g_{sorbent}	Ref.
Activated carbon	65 °C, 3 atm	134.2	[29]
	25 °C, 1 atm	108	[29]
Zeolite	25 °C, 1 atm	169.84	[30]
Coal fly ash	90 °C, 1 atm	145	[31]
Coal bottom ash	90 °C, 1 atm	20	[32]
Bagasse	60 °C, 1 atm	159.28	[33]
Coffee grounds	25 °C, 1 atm	132	[33]

2.1.3. Cryogenic separation

Multistage compression is done to separate CO₂ from the gas phase by cooling down CO₂ in the flue gas to liquefy or solidify CO₂, which is proceeded with a distillation column to remove any available impurities in CO₂. This process is known as cryogenic distillation [22, 33]. High energy consumption and high operating cost is integrated with cryogenic distillation because of CO₂ condensation and separation.

Cryogenic distillation refers to the cryogenic air liquefaction process used to separate gases from air. It uses low temperatures for condensation, separation, and purification of CO₂ from flue gases. So, the components of the process go through a series of compression, cooling, and expansion steps to extract pure component. Hence, this process directly produces liquid CO₂, which will be stored or seized at high pressure via liquid pumping. Direct production of liquid CO₂, which is easy to store or utilized in enhanced oil recovery is a comparatively straight forward process without involving solvents and easy scaled-up to industrial-scale utilization are the advantages of this process. The foremost disadvantage of this process is massive energy requirement for cooling [34].

2.1.4. Absorption by liquid solvents

A reaction between CO₂ and a chemical solvent is formed a weakly-bonded intermediate compound and by adding heat to the process it regenerates original chemical solvent and CO₂ [33, 35]. Mono-ethanol-amine (MEA) and di-isopropanol amine (DIPA) are corrosive chemical solvents which are used in this method [33]. Preferred component in mixed gasses that comes out from flue gas are dissolved in a solvent, then CO₂ rich solvent is fed into a heater to release high purity CO₂ which is suitable for compression and transportation to respective CO₂ storage. Then, the regenerated absorbent solution is cooled and recycled to the process accordingly [37].

This process is considered as the most-matured CO₂ capture technology and mostly applied in large scale plants to capture CO₂ at a higher efficiency. However, deficiencies of the process include corrosive nature, intensive use of energy in regeneration process and cost ineffectively discourage the application of the above said technology [15]. Energy intensive regeneration process and storage of CO₂ after regeneration are another two drawbacks of this method. Therefore, CO₂ capture by chemical solvent absorption also undergoes several disadvantages like solvent degradation due to SO₂ and O₂ in flue gas, high equipment corrosion rate and high operational cost due to high energy consumption [33, 36].

Table 2.3: Comparison for post-combustion CO₂ sequestration technologies [37]

Technology	Advantages	Disadvantages	Plant Scale in Use
Absorption	<ul style="list-style-type: none"> • Rapid reactions • Higher absorption capacities • Flexible 	<ul style="list-style-type: none"> • Material degradation of the equipment • High energy requirement for solvent regeneration 	Industrial/ Large scale
Adsorption	<ul style="list-style-type: none"> • Low energy consumption and CO₂ capture cost • Suitable for separating CO₂ from dilute stream 	<ul style="list-style-type: none"> • Low adsorption capacities (in flue gases conditions) 	Pilot
Cryogenic Distillation	<ul style="list-style-type: none"> • Liquid CO₂ production • Not requiring solvents or other components • Easy scaled-up to industrial-scale application 	<ul style="list-style-type: none"> • Higher energy requirement compared with other technologies 	Pilot
Membrane Separation	<ul style="list-style-type: none"> • Clean and simple process • Continuous, steady-state technology 	<ul style="list-style-type: none"> • Require high energy for post-combustion CO₂ capture 	Experimental

2.2. Available CO₂ storage technologies

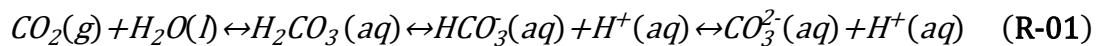
2.2.1. Geological storage

Geological storage is the direct injection of captured CO₂ into abandoned gas, oil, coal, or any other similar underground reservoir. There are three major types of geological storage, namely, Enhanced Oil Recovery (EOR), Enhanced Gas Recovery (EGR), and Enhanced Coal Bed Methane Recovery (ECBMR). In EOR and EGR, CO₂ is flooded over shale oil/gas fields and the remaining oil/gas is recovered. In ECBMR, trapped methane in abandoned coal mines

is recovered by injecting CO₂ into the mine. Geological storage has been implemented throughout the world in significant level even though, geological storage comprises large scale CO₂ capture capacities (in Giga tonnes of CO₂ per year) and it requires thorough monitoring on storage sites over thousands of years. Otherwise, there is a probability to CO₂ effusion back into the atmosphere. [16, 18]

2.2.2. Ocean storage

Injecting CO₂ into deeper ocean to accumulate CO₂ in the form of carbonic acid is known as ocean storage. In deep-down ocean, the partial pressure of gaseous CO₂ increases due the elevation. Then CO₂ reacts with water and form carbonic acid and prepares an equilibrium condition with hydrogen, bicarbonate, and carbonated ions. (As represented in reaction 01). [16]



Even though this technology provides better carbon storage facility, it decreases the ocean pH level. Hence, this technology has not been implemented due to the resulting environmental issues [16, 19].

2.2.3. Storage below seabed

CO₂ becomes denser than water, when the depth of the ocean level is more than 3,000 m. According to this phenomenon, CO₂ is stored under the marine sediment, which is approximately 1,000 m below the ocean floor [21]. Also, these stored CO₂ should be trapped to prevent possible leakages from ocean currents and earthquakes. The stored CO₂ has a possibility to form CO₂ hydrates under high pressures and low temperatures. These hydrates block the pores of the ocean floor and would trap the CO₂ more effectively. Even though, this technology overcomes the issues in geological storage and ocean storage, is still under experimental conditions [23].

2.3. CO₂ sequestration through aqueous phase mineral carbonation

Mineral carbonation is a reaction which forms insoluble carbonates after reacting CO₂ with metal oxides bearing materials. Calcium and Magnesium are the most attractive metals. Suitable materials for mineralization are natural minerals like silicate rocks, serpentine, olivine minerals or else industrial wastes like steel slag, paper mill waste, oil shale ash, mine

tailing or fly ash [38,39]. It is considered as a natural and exothermic process among available post combustion CO₂ capture technologies, which gives promising results in CO₂ sequestration by storing as mineral carbonates [40].

During the CO₂ capture process, the adsorption of CO₂ and the carbonation reaction can take place between CaO (free lime) and CO₂ to form CaCO₃ [41]. Figure 2.1 illustrates different approaches available for mineral carbonation with their expected CO₂ capture efficiencies.

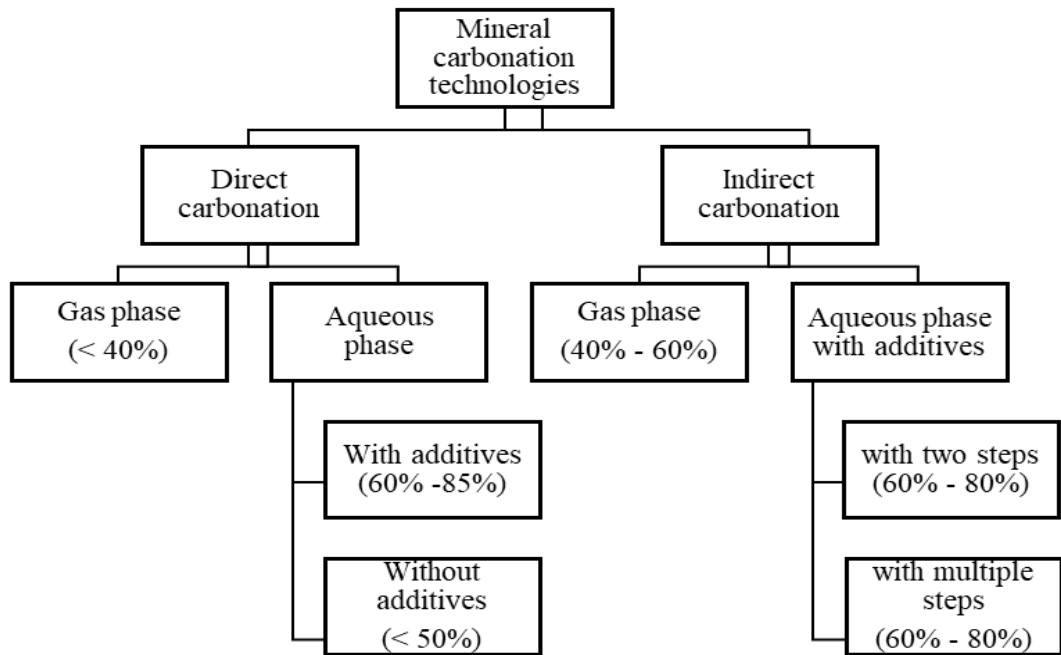


Figure 2.1: Different approaches available for mineral carbonation with their expected CO₂ sequestration efficiencies

There are two methods for mineralization called direct carbonation and indirect carbonation. Gas phase and aqueous phase are the two phases of direct carbonization [42]. Reaction 02 indicates gas phase carbonation reaction of CO₂ and free lime, which caused to increase the capture performance [43].

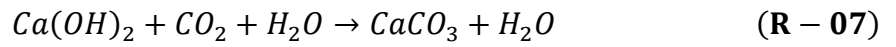


Aqueous phase carbonation, which is the most effective carbonation method due to attainability of high carbonate amount at the end of the process. It has two ways either by simple carbonation or additive enhanced carbonation. Complex agents and acids are added to react with CO₂ to foam carbonates is known as additive enhanced carbonation. In other words,

this is a method, which is used to increase the efficiency of a simple carbonation process [40]. In aqueous carbonation reaction CO_2 reacts with water and produce carbonic acid as in Reactions 03 to 06 [43].



When partial pressure increases dissolution in water also increased, but dissolution is inversely proportional to the temperature and Reaction 07 is the overall reaction of solid phase with CaO and H_2CO_3 [43].



According to the analysis, aqueous carbonation reaction is dependent on the amount of water present in the system and it says aqueous carbonation requires less energy than dry carbonation [43].

Indirect carbonation involves two or more steps. During the first step reactive components (Ca or Mg) are extracted from the mineral as an oxide or hydroxide and then it is reacted with CO_2 to form carbonate in the second step [39].

There are several advantageous characteristics of CO_2 sequestration through mineral carbonation when compared to other carbon capture and storage techniques. Hence the carbonation pathways are a thermodynamically stable reaction, resulting mineral carbonates are stable geologically end products. These products are environmentally benign, as CO_2 is permanently stored and inherently safe. Furthermore, the carbonation reaction is exothermic, where the released heat can be integrated to optimize the process efficiency. Also, there is a high abundancy in these materials (both natural mineral resources and waste materials) throughout the world. Thus, mineral carbonation has the highest potential to sequester post-combustion CO_2 .

Wollastonite, Olivine, and Serpentinites are some of the key mineral rocks which can be utilized in CO_2 mineral carbonation. Table 2.4 represents some selected mineral rocks with their CO_2 sequestration capacities.

Table 2.4: CO₂ sequestration capacities of mineral rocks [44]

Rock Mineral	CaO (wt %)	MgO (wt %)	CO ₂ Sequestration Capacity (kg/kg)
Basalt	9.4	6.2	7.1
Talc, Mg ₃ Si ₄ O ₁₀ (OH) ₂	-	31.9	2.9
Wollastonite	43.7	0.8	2.9
Talc	0.0	34.7	2.6
Wollastonite, CaSiO ₃	48.3		2.6
Serpentinite	-	40	2.3
Serpentinites, Mg ₃ Si ₂ O ₅ (OH) ₄	-	48.6	1.9
Dunite	0.3	49.5	1.8
Olivine, Mg ₂ SiO ₄	-	57.3	1.6

2.4. Utilization of industrial wastes for CO₂ sequestration via mineral carbonation

Apart from the available mineral rocks for carbonation, largely available industrial waste with a significant CaO and MgO can also be utilized in mineral carbonation. The required characteristics of such an industrial waste material are as follows.

- Having an inorganic nature with pH > 8 in the waste material
- Availability of the solid form of the waste material
- Containing free calcium or magnesium minerals (non-carbonated) in the waste material for a considerable carbonation potential.

The large-scale industrial processes involving with minerals, such as power generation, iron and steel manufacturing, cement manufacturing, and waste incineration, generates solid residues at higher flowrates. Hence, these processes include raw materials containing Ca and Mg compounds and related with oxidation at higher temperatures, their wastes contain a

significant amount of CaO and MgO. Thus, MSWI bottom ash, MSWI fly ash, steel slag, blast furnace slag, coal fly ash and other mine tailings are readily available waste feedstocks for mineral carbonation [44].

A detailed literature analysis was conducted based on the recently published studies (within last 10 years), and the carbon capture capacities and carbonation efficiencies of different waste materials are summarized in the tables 2.5 to 2.11.

2.4.1. Iron and steel slag

Table 2.5: CO₂ sequestration capacities and carbonation efficiencies of iron and steel slag

Waste Material	CaO (%)	MgO (%)	Maximum CO ₂ uptake (%) / Capture capacity (kg CO ₂ /tonne) / Carbonation efficiency (%)		Process Conditions	Ref.
			Theoretical	Experimental		
Blast furnace slag	15 – 42	5 – 11	<i>CO₂ uptake</i> = 20% – 44%	<i>CO₂ uptake</i> = 22.7%	Indirect aqueous carbonation: Step 01; T = 70 °C, treated with CH ₃ COOH Step 02; T = 30 °C, P = 1 bar, treated with NaOH	[50]
				<i>CO₂ uptake</i> = 7%		Direct aqueous carbonation: P = 5 bar, L/S = 0.15, 100% CO ₂ feed stream, t = 2 h
Basic oxygen furnace slag	34 – 56	2 – 6	<i>CO₂ uptake</i> = 29%–52%	<i>CO₂ uptake</i> = 28.9%	Direct aqueous carbonation: T = 60 °C, P = 1.47 bar, L(DI)/S = 20, 100% CO ₂ feed, t = 30 min	[52]
				<i>Capture capacity</i> = (277–290) kgCO ₂ /tonne <i>Carbonation efficiency</i> = 91% – 94%	Direct aqueous carbonation: T = 65°C, L/S = 20 mL/g, t = 30 min	[45]

Cont'd Table 2.5,

Electric arc furnace slag	25 – 47	4 – 19	<i>CO₂ uptake</i> = 24%–48%	<i>CO₂ uptake</i> = 12%	Direct aqueous carbonation: P = 5 bar, L/S = 0.15 ml/g, 100% CO ₂ , t = 2 h	[51]
Larnite furnace slag	42 – 58	6 – 15	<i>CO₂ uptake</i> = 42%	<i>CO₂ uptake</i> = 24.7%	Direct aqueous carbonation: T = 20 °C, P = 1 bar, L/S = 10 ml/g, 15% CO ₂ feed, t=40h, diameter = 38–106 μm	[49]
Argon oxygen decarburization slag	41 – 61	4 – 7.5	<i>CO₂ uptake</i> = 31%–54%	<i>CO₂ uptake</i> = 27 %	Direct aqueous carbonation: T = 50 °C, L/S = 10 ml/g, 10% CO ₂ feed, t = 240 min	[53]
				<i>Capture capacity</i> = 260 kg CO ₂ /tonne	Direct aqueous Carbonation: T = 180°C, P = 30 bar, S/L = (25-250) g/L, t = 120 min, diameter = 46μm	[50]
Continuous casting slag				<i>Capture capacity</i> = 310 kg CO ₂ /tonne	Direct aqueous Carbonation: T = 180°C, P = 30 bar, S/L = (25-250) g/L, t = 120 min, diameter = 46 μm	[50]
Red gypsum				<i>Carbonation efficiency</i> = 41.1%	Direct Carbonation: P=70bar, treated with NH ₄ OH (1 M), L/S = 5 mL/g, diameter < 45 μm	[54]

2.4.2. Cement waste

Table 2.6: CO₂ sequestration capacities and carbonation efficiencies of cement waste

Waste Material	CaO (%)	MgO (%)	Maximum CO ₂ uptake (%) / Capture capacity (kg CO ₂ /tonne) / Carbonation efficiency (%)		Process Conditions	Ref.
			Theoretical	Experimental		
Cement kiln dust	34 – 48	1 – 1.5	CO ₂ uptake = 10% – 30%	CO ₂ uptake = 10%	Direct aqueous carbonation: T=25 °C, P = 2 bar, H ₂ O to form a paste, 100% CO ₂ feed, t = 72 h	[55]
				Capture capacity = 180 kg CO ₂ / tonne	Indirect aqueous carbonation: Treated with NH ₄ NO ₃ / CH ₃ COONH ₄ (1 M), S/L = 50 g/L, CO ₂ flow rate = 200 mL/min	[56]
Cement bypass dust	66	1	CO ₂ uptake = 50%	CO ₂ uptake = 25%	Direct aqueous carbonation: T=25 °C, P = 2 bar, 100% CO ₂ feed, t = 72 h	[55]
Waste Cement, Recycled concrete aggregate	25 – 63	0.3 – 2	CO ₂ uptake = 20%	CO ₂ uptake = 8.9%	Direct aqueous carbonation: T = 20 °C, L/S = 0.26, 20% CO ₂ feed, t = 60 min	[58]

2.4.3. Municipal solid waste incineration ashes

Table 2.7: CO₂ sequestration capacities and carbonation efficiencies of municipal solid waste incineration ashes

Waste Material	CaO (%)	MgO (%)	Maximum CO ₂ uptake (%) / Carbonation efficiency (%)		Process Conditions	Ref.
			Theoretical	Experimental		
Municipal solid waste incineration bottom ash	22 – 53	2.8	CO ₂ uptake = 25%	CO ₂ uptake = 4%	Direct aqueous carbonation: T=25 °C, P = 2 bar, 100% CO ₂ feed, t = 72 h	[59]

Cont'd Table 2.7,

Municipal solid waste incineration fly ash				<i>CO₂ uptake</i> = 58.6% <i>Carbonation efficiency</i> = 56.9%	<i>Indirect carbonation:</i> Two step carbonation using ammonia, pH = 6.95, t = 5 min	[60]
Air pollution control residue	36 – 60	1 – 2.5	<i>CO₂ uptake</i> = 50% – 58%	<i>CO₂ uptake</i> = 25%	<i>Direct carbonation:</i> T = 650 °C – 500 °C, P = 1 bar, 10–50% CO ₂ feed	[61]

2.4.4. Fuel combustion ashes

Table 2.8: CO₂ sequestration capacities and carbonation efficiencies of Fuel combustion ashes

Waste Material	CaO (%)	MgO (%)	Maximum CO ₂ uptake (%)/ Capture capacity (kg CO ₂ /tonne)/ Carbonation efficiency (%)		Process Conditions	Ref.
			Theoretical	Experimental		
Coal fly ash	1.3 – 10	1–3	<i>CO₂ uptake</i> = 6% – 9%	<i>CO₂ uptake</i> = 26%	<i>Direct aqueous carbonation:</i> T = 20 °C – 60 °C, P = 10–40 bar, 100% CO ₂ feed, L/S = 10, particle diameter = 40 µm, t = 18 h	[62]
				<i>Capture capacity</i> = 27.1 kg CO ₂ /tonne <i>Carbonation efficiency</i> = 13.9%	<i>Direct aqueous carbonation:</i> T = 40°C, P = 3 MPa, L/S = 0.2–0.3 (w/w)	[63]
Lignite FA	27.5	6.5	<i>CO₂ uptake</i> = 43%	<i>CO₂ uptake</i> = 23%	<i>Direct aqueous carbonation:</i> T = 75 °C, P = 1 bar, 10% CO ₂ feed, L/S = 20, t = 4.5 h, particle diameter < 250 µm	[64]

Cont'd Table 2.8,

Oil shale fly ash	38–50	5–12	<i>CO₂ uptake</i> = 26% – 49%	<i>CO₂ uptake</i> = 29%	<i>Direct aqueous carbonation:</i> T=25 °C, P = 1 bar, L/S = 10, 15% CO ₂ feed, t = 65 min	[65]
Wood ash	24–46	8–9	<i>CO₂ uptake</i> = 50%	<i>CO₂ uptake</i> = 8%	<i>Direct aqueous carbonation:</i> T= 25 °C, P = 2 bar, 100% CO ₂ feed, t = 72 h	[55]

2.4.5. Mine tailings

Table 2.9: CO₂ sequestration capacities and carbonation efficiencies of mine tailings

Waste Material	CaO (%)	MgO (%)	Maximum CO ₂ uptake (%)		Process Conditions	Ref.
			Theoretical	Experimental		
Asbestos Tailings	0.2	39	43	0.5	<i>Direct aqueous carbonation:</i> T = 375 °C, P = 1 bar, 56% CO ₂ , 10% H ₂ O feed, particle diameter = 37 µm – 75 µm, t = 5 h	[67]
Ni Tailings	3.4	21–40	43	29	<i>Indirect aqueous carbonation:</i> Step 01: T = 70 °C, treated with 4 M HCl, HNO ₃ , L/S = 10, t = 2 h, particle diameter < 0.5 mm Step 02: T = 30 °C, 100% CO ₂ feed, treated with NaOH, t = 0.5 h	[68]
Red mud	2–7	<1	7–19	7.2	<i>Direct aqueous carbonation:</i> T= 25 °C, P = 2 bar, 100% CO ₂ feed, particle diameter = 0.1 µm – 160 µm, three carbonation cycles (each having t = 5 h)	[55]

2.4.6. Paper mill waste

Table 2.10: CO₂ sequestration capacities and carbonation efficiencies of paper mill waste

Waste Material	CaO (%)	MgO (%)	Maximum CO ₂ uptake (%)		Process Conditions	Ref.
			Theoretical	Experimental		
Alkaline paper mill wastes ash	45 – 82	1 – 5	42 – 55	10 - 26	<i>Direct aqueous carbonation:</i> T= 25 °C, P = 2 bar, 100% CO ₂ feed, t = 72 h	[70]

2.4.7. Waste mixtures

Table 2.11: CO₂ sequestration capacities and carbonation efficiencies of waste mixtures

Waste Material	Capture capacity (kg CO ₂ /tonne)/ Carbonation efficiency (%)	Process Conditions	Ref.
Cement kiln dust, spray dryer absorber ash, and circulating dry scrubber ash	<i>Capture capacity</i> = (101 – 123) kg CO ₂ /tonne <i>Carbonation efficiency</i> = 77% - 93%	<i>Indirect carbonation:</i> Solvent leaching using NaHCO ₃ (0.5 M), t = 24 h	[75]
Steel slag, phosphate slag, and blast furnace slag	<i>Carbonation efficiency</i> = 59% - 74%	<i>Indirect carbonation:</i> (pH swing) Dissolution using NH ₄ SO ₄ , T = 65°C, pH = 8.2–8.3, S/L = 15 g/L, Particle diameter = 75–150 μm, t = 1 h	[57]

2.5. Significance of coal fly ash in Sri Lankan context

Lakvijaya Coal Power Plant (LCPP), Norochholei, Sri Lanka, has a total power output capacity of 900 MW. This power plant generates fly ash at a rate of 30 tonnes per hour, which is a highly significant amount of fly ash accumulation [17]. It is interesting to study the possibility of utilizing this fly ash in order to sequester CO₂ emissions from the same power plant and reduce the anthropogenic emissions. The CO₂ sequestration capability depends on the free lime (free CaO) composition in fly ash.

Fly ash mostly consists of amorphous and crystalline compounds like SiO₂, Al₂O₃, FeO, CaO, MgO and free lime, which cause to increase the surface area of fly ash and thermal stability with uniform properties [46]. Table 2.12 represents the CaO and MgO composition in different types of coal.

Table 2.12: Average CaO/MgO composition of CFA in different types of coal [46]

Component	Bituminous coal (wt %)	Sub-bituminous coal (wt %)	Lignite coal (wt %)	Anthracite coal (wt %)
CaO	1 – 12	5–30	15–40	0.5–0.9
MgO	0 – 5	1–6	3–10	0.7–0.9

There is a lack of reliable published data on the CaO composition in LCPP fly ash. Thus, determination of CaO composition in LCPP fly ash composition, leads to determine the theoretical CO₂ sequestration capability of LCPP fly ash.

3. METHODOLOGY

In this chapter, materials and methods which were used to conduct this research are discussed.

3.1. Literature analysis

A comprehensive search and systematic literature review were carried out through the Google Scholar, ScienceDirect, SpringerLink, etc. research databases until 08th February 2020, using the following search terms:

- (a) (Post Combustion OR post combustion CO₂ sequestration technology) AND storage methods. Filters: From 2000/01/01 to 2020/02/08
- (b) (CO₂ sequestration OR mineral carbonation OR aqueous phase mineral carbonation OR CO₂ sequestration through aqueous phase mineral carbonation) AND storage methods. Filters: From 2000/01/01 to 2020/02/08
- (c) Rock minerals AND CO₂ sequestration AND aqueous phase mineral carbonation AND storage methods. Filters: From 2000/01/01 to 2020/02/08
- (d) Industrial waste materials AND CO₂ sequestration AND aqueous phase mineral carbonation AND storage methods. Filters: From 2000/01/01 to 2020/02/08
- (e) (Coal fly ash AND CO₂ sequestration AND aqueous phase mineral carbonation AND Lakvijaya coal fired power plant) OR (Norochholei) AND storage methods. Filters: From 2000/01/01 to 2020/02/08

3.1.1. Eligibility criteria

The review included computational, experimental, and review studies on post combustion CO₂ sequestration and storage methods, CO₂ sequestration through mineral carbonation, utilization of industrial waste materials and rock minerals for CO₂ sequestration through mineral carbonation, and CO₂ sequestration possibility via aqueous phase mineral carbonation for coal fly ash from LCPP. In addition, editorials, letters to the editor or comment publication types were excluded due to lack of information.

3.1.2. Data extraction

An abstracted data spreadsheet was developed by using Excel version 2016 (Microsoft Corporation, Redmond, Washington, USA). Full-text articles were selected under following information such as topic, DOI number, and type of CO₂ sequestration, findings/efficacy of the CO₂ sequestration, conclusion and limitations of the study, remarks and full text accept/reject. The data was extracted and were independently assessed.

3.2. Experimental methodology

3.2.1. Determination of LCPP fly ash characterization

Coal fly ash samples were physically collected from the fresh ash heap of an electrostatic precipitator outlet in one of the three 300 MW power generation units at Lakvijaya coal-fired power plant (LCPP), Norochcholai, Sri Lanka (Figure 3. 1).



Figure 3.1: Collected fresh LCPP fly ash samples

The compositions of major constituents in LCPP fly ash were analyzed using an X-ray fluorescence (XRF) spectrometer, HORIBA Scientific XGT-5200 X-ray analytical microscope. Morphological analysis of LCPP fly ash was performed using the scanning electron microscope (SEM), Zeiss EVO 18 Research. Analysis of particle size distribution of LCPP fly ash was obtained using the particle size analyzer, FRITSCH Analysette 22, with a measurable range of 0.08 μm – 2000 μm .

3.2.2. Extraction of free lime content in LCPP fly ash

For calcium extraction from LCPP fly ash, deionized water was taken as the solvent. In each initial experiment, 400 ml of deionized water was taken into a laboratory beaker (1 L full capacity) and a fly ash sample of 20 g was mixed in the solution in the beaker at a solid-liquid ratio of 50 g/L. The prepared coal fly ash solution was well mixed by a magnetic stirrer (Model: Jenway 1000) with a controlled temperature of 30 °C and a fixed stirring rate of 800 rpm. To ensure perfect mixing, 4 baffles with 15 mm width and 1.5 mm thickness were used (Figure 3.2).

Initial experiments were performed to investigate the effect of the residence time (0 –120 min) on the efficiency of calcium extraction into the solution. A series of experiments were conducted by varying the solid-liquid ratio between LCPP fly ash and deionized (DI) water in a range of 10g/L–200g/L in order to study the influence of solid/liquid ratio for the efficiency of calcium extraction. Temperature was maintained for each experiment at 30 °C. In each experiment, a liquid quantity of 10 mL was taken with a sampling syringe (precleaned with DI water) and a 0.22 µm syringe filter unit was used to filter the liquid sample, immediately. The sampled liquid was considered as a homogeneous solution, because of the drastic mixing along with the use of baffles for all experiments. At the end of each experiment, the amount of Ca²⁺ extraction in the leachate (sampled liquid) was measured by the EDTA titration method.



Figure 3.2: Laboratory mixer for calcium extraction from fly ash

3.2.3. EDTA titration and calculation methodology

The amount of Ca^{2+} ions leached into the solution from dissolved fly ash was determined by the EDTA (Ethylene diamine tetra acetic acid) titration method. Each solid sample of 20 g of fresh fly ash was diluted in 400 ml of distilled water and the mixture was set on a stirrer to get a sample for the titration process. 4.65g of ethylene diamine tetra acetic acid disodium (EDTA) was diluted in a 500 ml volumetric flask with distilled water in order to prepare EDTA solution at the concentration of 0.025M ($\text{mol}\cdot\text{dm}^{-3}$). 90 g of Ammonium chloride and 375 ml of ammonium hydroxide were diluted in a 500 ml volumetric flask distilled water as the buffer solution with a pH value of 10. An amount of 200 mg of Eriochrome Black T (EBT), 15 ml of triethanolamine and 5 ml of absolute ethanol were mixed in order to make the indicator. 1 ml of the buffer solution and a drop of the indicator were added per 10 ml of sample solution and, titration was carried out for the sample solution with the EDTA solution. The volume of the EDTA solution consumed to change purple colour of the sample into blue colour in each titration was marked. The amount of Ca^{2+} in fly ash sample and the time taken to reach the stability was determined.

The reaction which take place during the titration is shown in equation (1).



The extractable amount of Calcium ($m_{\text{Ca-ext}}$ (g)) was calculated using the equation (2). The concentration of Ca^{2+} in the solution ($X_{\text{Ca}^{2+}}$ (mg/L)) at time t (min) was calculated using the consumed amount of EDTA and the equation 1. Total volume of the solution was taken as Vol (mL).

$$m_{\text{Ca-ext}} = \frac{X_{\text{Ca}^{2+}}}{1000} \times \frac{Vol}{1000} (g) \quad (2)$$

Total calcium amount in the fly ash sample ($m_{\text{Ca-total}}$ (g)) was calculated using equation (3). Here, weight percentage of Calcium in the raw fly ash sample (X_{Ca} wt%) was determined by the XRF analysis results and m (g) is the weight of the raw fly ash sample.

$$m_{\text{Ca-total}} = \frac{X_{\text{Ca}}}{100} \times m(g) \quad (3)$$

Hence, experimental calcium extraction efficiency (e) prior to indirect mineral sequestration of CO_2 was calculated using the equation (4).

$$e = \frac{m_{Ca-ext}}{m_{Ca-total}} \times 100 \quad (4)$$

Detailed calculation procedure is shown in Appendix A.

4. RESULTS AND DISCUSSION

4.1. Literature comparison results

4.1.1. Selection and identification of studies

Two hundred forty-nine research articles were initially acquired from the Google Scholar, ScienceDirect and SpringerLink databases, and 118 duplicate research articles were eliminated. The remaining 131 research articles were re-examined by reading titles and abstracts, and 92 studies did not match with selection requirements. The full texts of the remaining 39 studies were re-examined in detail, but 16 studies did not meet the criteria and were further eliminated. This systematic review was consisted remaining twenty-three (n=23) studies matched with selection requirements. Figure 4.1 illustrates the flow chart of systematic review process consist article elimination and selection in this study.

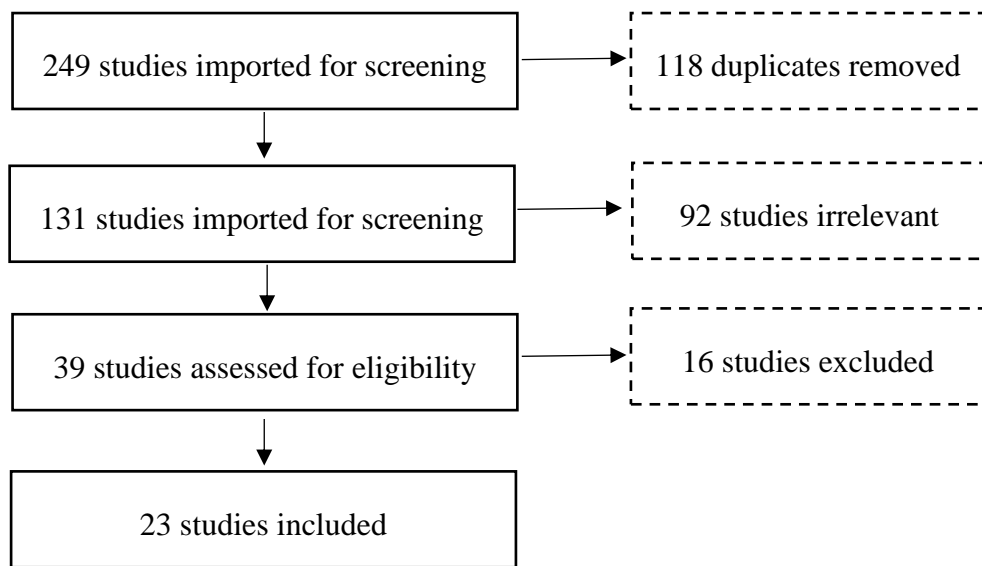


Figure 4.1: Flowchart of systematic review process in this study

4.1.2. Study Characteristics

The current search was able to extract 23 articles that dealt with CO₂ sequestration capacities via direct aqueous mineral carbonation in different industrial materials and rock minerals. Twenty-two of these articles dealt with CO₂ sequestration capacities via direct aqueous

mineral carbonation in different industrial materials [45,49-65,67-68,70,72]. Remaining one focused on CO₂ sequestration capacities via direct aqueous mineral carbonation in rock minerals [44]. However, CO₂ sequestration capacities in rock minerals have not been tested in many of the articles searched. The characteristics of the selected studies are listed in Table 4.1, Table 4.2, Figure 4.2, Figure 4.3, and Figure 4.4.

Table 4.1: CO₂ sequestration capacities via direct aqueous mineral carbonation of different industrial wastes

Waste material	Average free CaO composition (wt %)	Average free MgO composition (wt %)	Maximum CO₂ uptake (Experimental) (wt %)
Oil shale fly ash (OSFA)	44.0	8.5	29.0
Coal fly ash (CFA)	5.7	2.0	26.0
Cement bypass dust (CBD)	66.0	1.0	25.0
Larnite furnace slag (LAFS)	50.0	10.5	24.7
Alkaline paper mill wastes ash (APMWA)	63.5	3.0	18.0
Cement kiln dust (CKD)	41.0	1.3	10.0
Waste cement, recycled concrete aggregate (WCRCA)	44.0	1.2	8.9
Wood ash (WA)	35.0	8.5	8.0
Red mud (RM)	4.5	0.5	7.2
Municipal solid waste incineration bottom ash (MSWIBA)	37.5	2.8	4.0

Table 4.1 reports CO₂ sequestration capacities of available wastes compared along with their CaO and MgO composition in identified waste materials from the literature. They were utilized for CO₂ sequestration via direct aqueous mineral carbonation. The operation conditions were, temperature range of (20 – 25) °C, pressure range of (1 – 2) bar.

The selected waste materials have a considerable CO₂ sequestration capacity when they are used in direct mineral carbonation at closer ambient conditions. The highest CO₂

sequestration capability was observed in OSFA, with 44% CaO and 8.5% MgO, which is 29%. According to Table 4.1 both CBD and APMWA have 66% and 63.5% of free CaO composition, but both of them have lower CO₂ uptake efficiencies compared to OSFA. Literature says CO₂ sequestration capability is depended on the total free lime content of the selected material. However, there can be minerals which contains calcium, but not reactive with CO₂. Therefore, CO₂ uptake efficiency would be low though wastes contains higher free calcium amount in its composition [55].

Other than this, CO₂ sequestration capability is affected by factors like porosity, surface area, particle size, other minerals and properties of the composition, etc. Therefore, there can be seen variations in CO₂ uptake efficiencies for different waste materials.

According to Figure 4.2, coal fly ash has a significant CO₂ sequestration capacity, compared to the other wastes when it is used in direct mineral carbonation at closer ambient conditions.

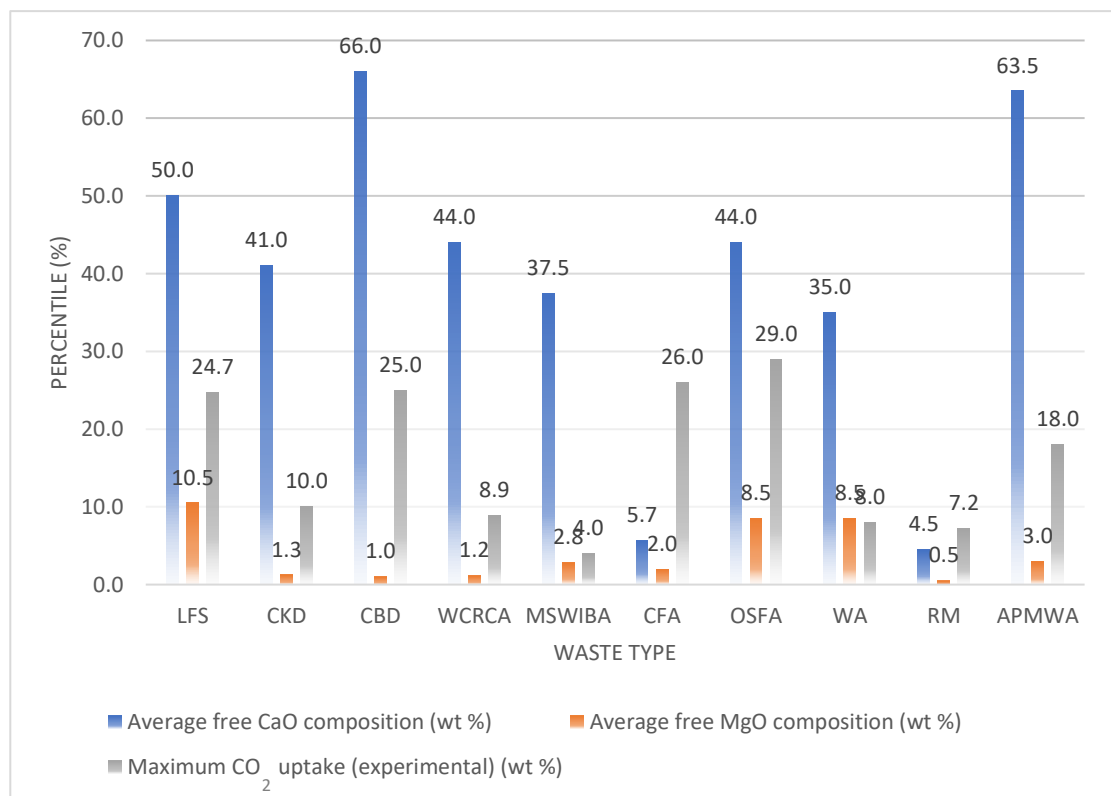


Figure 4.2: CaO and MgO compositions, and experimental CO₂ sequestration efficiencies for different industrial wastes

Table 4.2: Average energy and cost consume by each feedstock per CO₂ sequestration of tonne per CO₂

Feedstock	Average energy consumption (kWh per tonne of CO ₂)	Average cost (USD per tonne of CO ₂)	Ref.
<i>Natural resources</i>			
Serpentine	NA	70	[45]
Wollastonite	591	133	[44]
Olivine	643	54.5	[47]
<i>Waste materials</i>			
Coal fly ash	NA	15.85	[73-74]
Steel slag	404	100	[44]
Basic oxygen furnace slag	485	57	[48]
Mixed waste (Steel slag and concrete)	15.6	8	[75]

Figure 4.3 and 4.4 represents the average energy consumption and average cost per tonne of CO₂ via direct aqueous mineral carbonation for different waste materials.

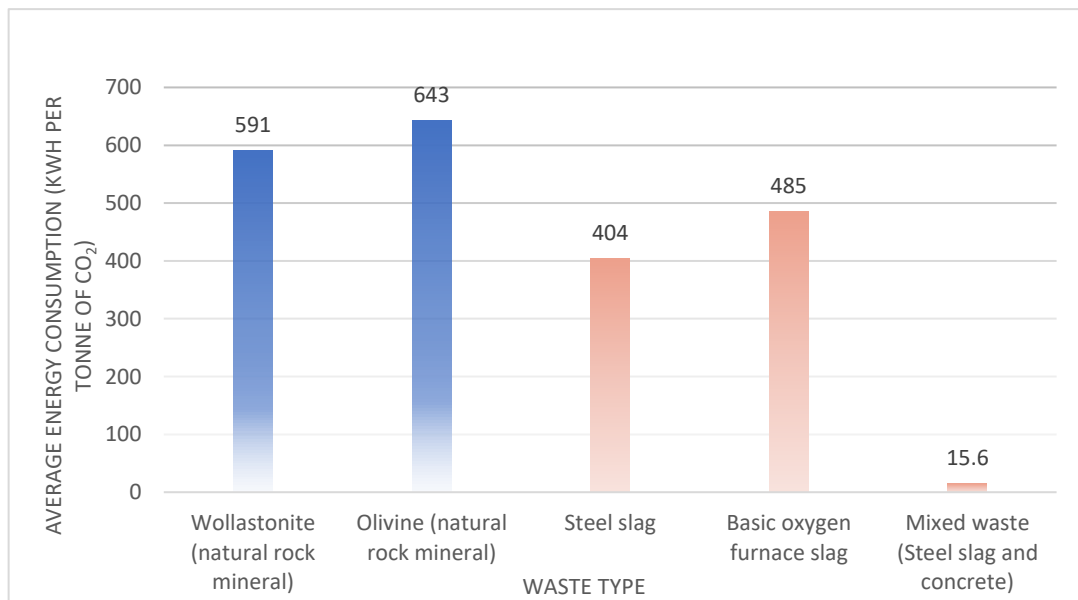


Figure 4.3: Average energy consumption according to waste type

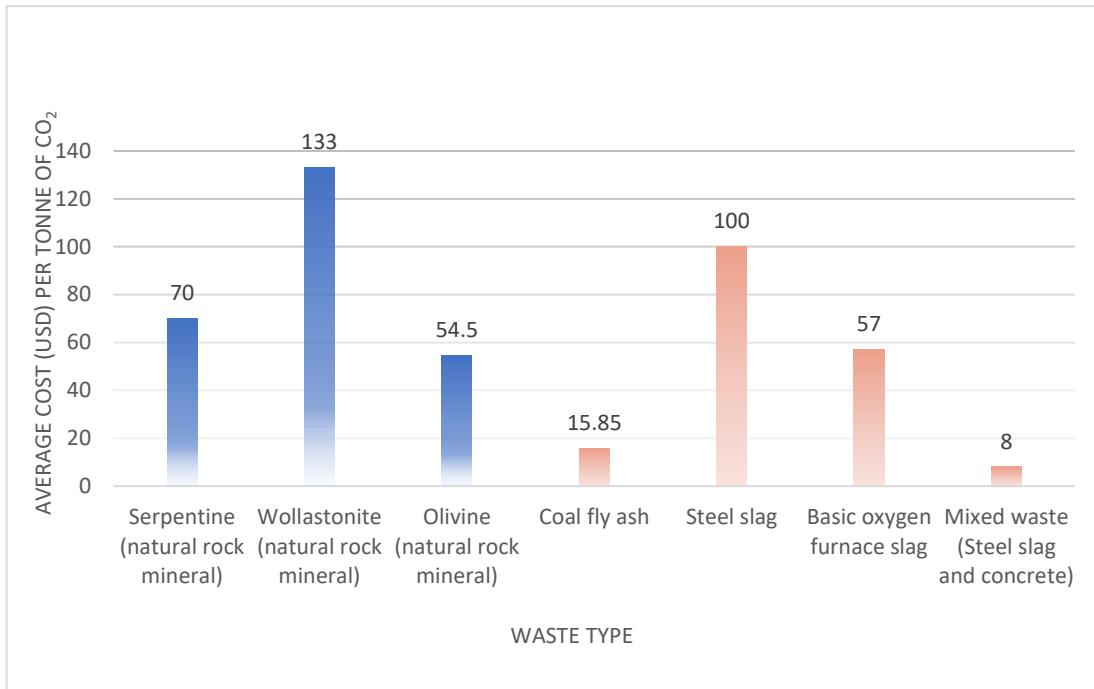


Figure 4.4: Average cost per tonne of sequestered CO₂ according to waste type

When compared to the natural rock minerals the average power consumption and average cost to sequester one tonne of sequestered CO₂ via direct aqueous phase mineral carbonation, are lesser in selected industrial waste materials. Most of the natural rock minerals mentioned in Table 4.2 required pre-treatments for use as the solid feedstock. Pre-treatments conducted to reduce particle size, activate heat, separate components, maintain pressure, etc. in order to increase CO₂ sequestration rate. These pre-treatment methods are energy intensive and it caused to enhance average energy consumption. Other than this, necessity of different chemicals enhanced average cost. So, natural rock minerals consumed more power and cost.

Compared to other waste types, coal fly ash consumed lesser energy and overall cost in mineral carbonation via direct aqueous phase carbonation because coal fly ash didn't require transportation and pre-treatments, simple operational processes.

4.2. Experimental results

4.2.1. Composition of LCPP fly ash

Table 4.3 lists the composition of major components in fly ash acquired from LCPP, which was analyzed by the X-ray fluorescence spectrometer (XRF). According to the XRF results, it can be observed that CaO content in LCPP fly ash is 5.81%, which is comparatively lower Calcium content relative to coal fly ashes, reported in the global average. In addition, the results show that MgO is absent, which makes LCPP fly ash quite different in composition compared to coal fly ashes from worldwide. Furthermore, XRF results exhibit that LCPP fly ash has Al₂O₃ and SiO₂ content at above 80 wt%, which integrates high thermally stable properties for different applications.

Table 4.3: XRF Results for composition of major components in LCPP fly ash

Element	Mass%
SiO ₂	56.01
Al ₂ O ₃	28.65
CaO	5.81
Fe ₂ O ₃	3.52
P ₂ O ₅	2.10
TiO ₂	1.91
SO ₃	1.14
K ₂ O	0.77

4.2.2. Physical properties of LCPP fly ash

Figure 4.5 shows the results of the particle size distribution analysis of LCPP fly ash. The results show that 90% of the distribution lies below 47.4 μm value, 50% of the distribution lies below 22.8 μm value, and 10% of the distribution lies below 0.2 μm value.

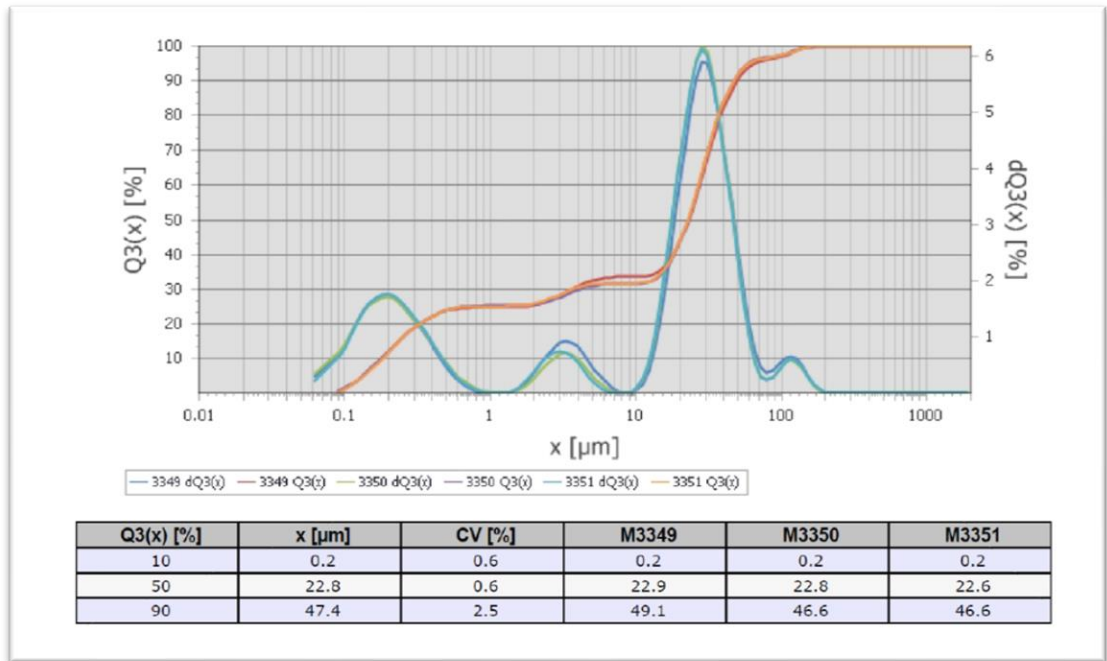


Figure 4.5: Particle size distribution of LCPP fly ash

Based on the results, it can be stated that the particle size of LCPP fly ash lies in the range of 0.1 – 100 μm. Observation of the morphology of raw fly ash samples using SEM images was performed to further confirm the particle size/diameter.

Morphology of the raw fly ash samples were observed by using the Scanning Electron Microscopy (SEM) technique as shown in Figure 4.6. The SEM image analysis also provides evidences that the particle diameter of LCPP fly ash lies in the range of 0.1 – 100 μm. In addition, it is evident that the LCPP fly ash particles are almost spherical in the shape with a shape factor value close to 1.

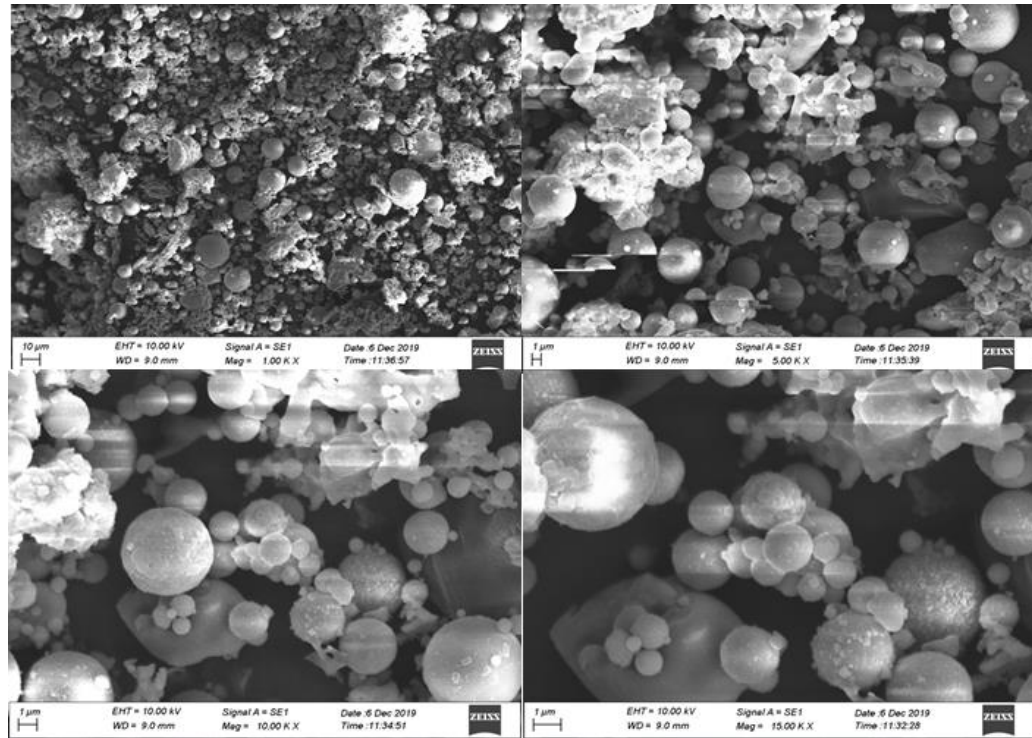


Figure 4.6: SEM images for morphology of LCPP fly ash

4.2.3. Calcium extraction for indirect CO₂ sequestration

Figure 4.7 indicates the variation of the calcium extraction efficiency against time. A fly ash solution at solid-liquid ratio of 50g/L was used for this experiment, in a baffled mixer. It was observed that Ca²⁺ extraction occurs at an increasing rate within the first few minutes of mixing, which decelerates and reaches a constant after about 45 minutes mixing time. Similar variations are reported in the literature [76], which further validate this experimental result in this study. A maximum extraction efficiency of 9.65% was achieved within the observed time range. The results implied that Ca²⁺ amount is around 0.5 wt% of the total composition of LCPP coal fly ash. However, the fly ash compositions from other origins, reported in the literature show higher free CaO composition, which is 1.0-10.0 wt% of total fly ash composition. Thus, it can be concluded that LCPP fly ash consists of a comparatively lower free CaO compared to other fly ashes reported in the literature, and this could be a reason for the lower Ca extraction efficiency of LCPP fly ash, compared with other origins of coal fly ashes.

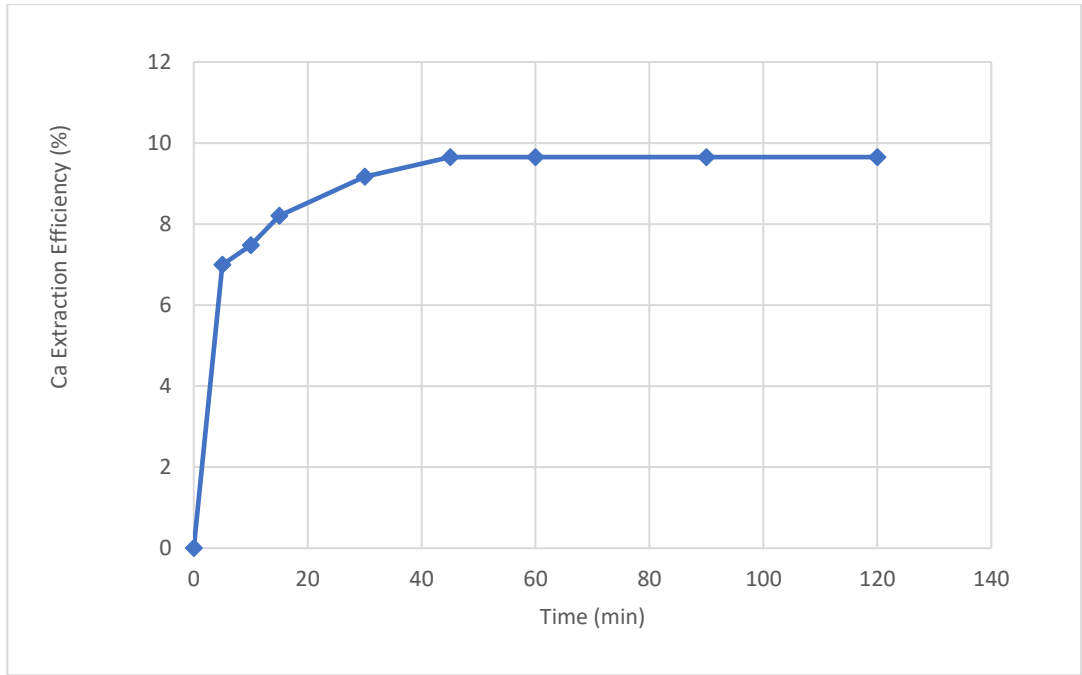


Figure 4.7: Variation of calcium extraction efficiency with mixing time (30°C, Solid/Liquid ratio 50g/L, 800 rpm, baffled, 120 min)

5. CONCLUSION

CO₂ sequestration capabilities of industrial waste materials through aqueous phase mineral carbonation, reported in the literature were analyzed to determine and compare their performances. The literature review results indicated that industrial waste materials, such as coal fly ash and steel slag also have significant capture capacities, compared to natural mineral rocks. When compared with the natural mineral rocks, coal fly ash also requires significantly lower energy consumption and costs to sequester one tonne of anthropogenic CO₂. Experimental capability of calcium extraction efficiency from LCPP fly ash was investigated to identify the possibility for indirect carbonation, to sequester CO₂ from coal flue gas. A maximum calcium extraction efficiency of 9.65% was obtained for LCPP fly ash. Based on these findings, future investigations would be possible to test for scaled-up calcium extraction from LCPP fly ash and CO₂ sequestration capacity (efficiency) via indirect mineral carbonation.

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APPENDIX A

Calculation procedure for EDTA titration results

Calculation of Ca^{2+} ions available in each fly ash sample,

Concentration of Ca^{2+} ions in fly ash sample solution (C1) ($\frac{\text{mol}}{\text{L}}$);

$$C1 = \frac{\text{Concentration of EDTA solution } (\frac{0.025 \text{ mol}}{\text{L}}) \times \text{Titration volume of EDTA (V1)}}{\text{Titration volume of fly ash sample solution (V2)}}$$

Ca^{2+} ions available in total fly ash sample ($\frac{\mu\text{mol}}{\text{g}}$)

$$= \frac{C1 (\frac{\text{mol}}{\text{L}}) \times \text{Total volume of fly ash sample solution (L)}}{\text{Mass of the fly ash sample (g)}} \times 10^{-6} (\frac{\mu\text{mol}}{\text{mol}})$$