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UTILIZATION OF ALKALINE INDUSTRIAL WASTES FOR CO_2 SEQUESTRATION

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ABSTRACT

There is growing the popularity of the use of carbon capture and storage (CCS) to address the changing climate. CCS can be perceived as a connecting technology that regulates the emission of CO_2 during combustion of fossil fuels. Mineral carbon sequestration has the potential to permanently store CO_2 by converting it into thermodynamically stable solid carbonates. Carbon mineral sequestration is based on natural weathering process of rocks in which CO_2 dissolves in the rainwater and forms thermodynamically stable carbonates by reacting with alkaline rocks. Calcium and magnesium silicates are the most common minerals which are suitable feedstock for carbonation. However, the major challenge for the process is slow reaction rate. The process requires energy demanding pre—treatments of feedstock such as heat treatment, fine crushing and chemical activation using strong acids to offer sufficient conversion and reactions rates. The process can also accelerate at higher temperature and pressure conditions. An alternative source of feedstock for mineral carbonation which is often more reactive than primary minerals are industrial waste residues. The carbonation of waste residues also enhances their chemical stability which increases their environmental acceptance. In the present study, a summary of utilization of industrial wastes for CO_2 sequestration and their available process routes have been discussed.

I. INTRODUCTION

A rise in anthropogenic greenhouse gas (GHG), especially CO_2 has contributed to global warming. An increase in CO_2 can be attributed to emissions from fossil fuel combustion. The consumption of energy are expected to increase with industrialization [1,2]. The CO_2 emissions are likely to increase if proactive mitigation effort is not taken. The changing temperature has a wide range of implications on food and water availability, biodiversity, ecosystems, coastlines and human health [3]. Many governments in the world are making attempts to reduce the emission of anthropogenic CO_2 [4]. This is made possible through regulation and incentives to cap CO_2 emission. Some of the identified CO_2 abatement strategies include improving efficiency in energy utilization, minimizing energy consumption, avoiding carbon—intensive sources of energy, encouraging renewable sources of energy, biological absorption of CO_2 and implementation of CCS [5–7]. CCS comprises of three processes (i) the separation of CO_2 from other flue gasses (ii) the transportation of separated CO_2 to storage points (iii) the permanent isolation of CO_2 from the atmosphere using different sequestration methods [8]. The countries that extensively use fossil fuels to generate electricity such as China and the US, CCS has become a bridging technology that regulates the emission of CO_2 [9]. CCS may be a new idea, but the technology and practices related to CO_2 capture and transportation have been in existence in many industries [10]. The process to capture CO_2 have been set up in coal gasification facilities and power generating plants which use either coal or natural gas [4]. A lot of studies and projects have currently been devoted to exploring the full potential of carbon capture and storage in addressing the climatic change issues [11,12]. In the recent past, it is evident that CCS has received significant attention, but the concept has not been totally integrated with CCS, and hence CCS is still at the beginning stage [13,14]. In each stage during the implementation of carbon capture and storage, there exist several types of technologies. Some of these technologies used to separate CO_2 may include sorbents, cryogenic distillation, membranes and chemical—absorption. However, the most popular method is chemical absorption [15,16]. The separated CO_2 is then stored using ocean, geological and mineral sequestration methods but CO_2 can also be used in several industrial applications [17]. Table 1 highlights the advantages and disadvantages of CCS technologies.

Table 1: Summary of different CO_2 sequestration methods

Storage types	Benefits	Drawbacks	Potential Gt	Cost $	References
Geological	Developed technology Economical Public acceptance	High threat of leakage Requires constant monitoring shortage of suitable sites	1800	0.5—8.0	[4,18]
Ocean	High potential Universal availability No monitoring	High environmental risk Expensive than geo—storage Negative/hostile perception	>1,000	6—31	[4,19]
Biological	Low cost Less environmental issues High potential	Monocultures plantation can imbalance the ecosystem Insufficient capacity Risk of disruption of food chain	100	3—10	[3]
Mineral carbonation	Environmentally safe Exothermic reactions Abundance of feedstock	High costs Pre—treatment Unsecure future potential	>10,000 to 1,000,000	50—100	[4,17]

II. MINERAL SEQUESTRATION

The process is established on the knowledge derived from natural rock weathering [19,20]. The CO_2 dissolves in the rainwater to form carbonic acid, and these acids are neutralized when comes in contact with alkaline minerals and form mineral carbonates [21]. Mineral carbonation results in the formation of thermodynamically stable solid carbonates and hence, no CO_2 is released after the process [22,23]. The release of CO_2 from these carbonates requires a high amount of energy [4,24]. Mineral carbon sequestration can be achieved either *in—situ* or *ex—situ* [15]. There are several advantages associated with mineral sequestration when contrasted with geological, ocean and biological sequestration [3]. The products of mineral sequestration can be sold, they are environment friendly and provide a permanent CO_2 storage [9].

III. MECHANISM FOR MINERAL CARBONATION

Rocks rich in magnesium and calcium silicates such as wollastonite and olivine are most suitable feedstock for mineral carbonation. The carbonated products such as dolomite, calcite, and magnesium are thermodynamically more stable than their primary minerals. The following equations can illustrate the carbonation reactions of calcium and magnesium silicates.

$CaSiO_3 + CO_2 \rightarrow CaCO_3 + SiO_2$ $\Delta H = -90$ kJ/mol

$Mg_2SiO_4 + CO_2 \rightarrow 2MgCO_3 + SiO_2$ $\Delta H = -89$ kJ/mol

$Mg_3SiO_5(OH)_4 + 3CO_2 \rightarrow 3MgCO_3 + 2SiO_2 + 2H_2O$ $\Delta H = -64$ kJ/mol

No additional energy is essential to the system since the process is exothermic, but the cost of processing silicates is adversely affected by pre—treatment required. It is paramount to take into account the cost involved in grinding of minerals when evaluating the viability of the process [25,26]. Mineral sequestration can be realized either by *ex—situ* where raw materials are transported to the site or *in—situ* where CO_2 diffuse into the rocks rich in calcium and magnesium [27–29]. There are three stages involved in *ex—situ* carbonation and they include:

[1] Pre—treatment of the minerals such as thermal and mechanical activation.
[2] Carbonates formation by reaction of activated minerals and CO_2
[3] Storage and reuse of the finished carbonated products

It is desirable to locate carbonation plant to be adjacent to the natural mineral resources to reduce the cost involved if the CO_2 emitters are far from the actual location of the mineral resources. This is a challenge since most CO_2 emitter sources are situated far from the mineral resources [9,18].

IV. CARBONATION OF WASTE RESIDUES

The solid waste residues can react with CO_2 as a substitute to natural minerals. The advantage that waste residues carbonation possesses over mineral carbonation is evident when it comes to pre—treatment in that it is not mandatory to conduct pre—treatment in waste residues and closeness to the sources of CO_2. Most of the waste products such as cement waste, iron and steel slag, municipal solid waste incinerator ash and bauxite processing have worldwide availability in large quantity [9,19,30,31]. The process streams generate a substantial amount of waste residues with prospective for carbonation are discussed in the Table 2.

Table 2: Characteristics of alkali waste [18]

Main Category	Sub—category	Waste
Wastes resulting from exploration, mining, dressing and further treatment of minerals and quarry	Wastes from further physical and chemical processing of metalliferous minerals	Bauxite residues
Inorganic wastes from thermal processes	Wastes from power stations and other combustion plants	Coal FA
	Wastes from the iron and steel industry	Steel slags
	Wastes from manufacture of cement, lime and plaster and articles and products made from them	CKD
Wastes from waste treatment facilities, offsite waste water treatment plants and the water industry	Wastes from incineration or pyrolysis of waste	MSWI BA MSWI FA

5.1. bauxite residue

Bauxite residues are also known as ‘red mud’ and they are the waste products generated during extraction of alumina from bauxite ores using Bayer process [9]. It is difficult to transport, dispose or reuse bauxite residue due to their high level of alkalinity and also high sodium concentration [32]. Carbonation of red mud is also beneficial for neutralization of its alkalinity which involves the reaction between the solutions of bauxite residue and CO_2 [32,33].

5.2. Cement kiln dust

Cement kiln dust (CKD) is a mixture of fine particles, partially and unburnt raw materials and impurities which formed when manufacturing cement clinker at high temperatures (1400 °C). Most of the industries which manufacture cement usually recycle cement kiln dust. CKD which are recycled depends on various parameters such as the required standards to be achieved, alkali content and composition of the dust. Cement kiln dust can be a potential source for CO_2 sequestration.

5.3. Coal combustion ash

Coal fly ash and bottom ash are the by—products of the coal combustion and they are categorized as either class C or class F depending calcium contents [34,35]. The higher composition of calcium in the ash is favorable for CO_2 sequestration.

5.4. Steelmaking slags

During the manufacture of steel, slag consists of elements such as calcium, magnesium, silicon, manganese, and iron which can react with CO_2 to form stable carbonates are produced. Hence, these slags have a high potential to sequester CO_2 [23,36,37].

VI. CARBONATION ROUTES

The carbonation routes can be categorized into two major groups, namely direct and indirect routes of carbonation. The reaction between calcium or magnesium silicates and CO_2 either in aqueous or gaseous form occurs in a single step in the case of direct route. On the other hand, indirect route involves extraction of minerals and their carbonation in separate multiple steps [23,38,39].

Table 3: Carbonation routes

Route	Description	Advantages	Disadvantages
Gas—solid	Solid feed directly reacts with CO_2	Straightforward Production of steam and electricity Utilization possibility of waste steam	Sluggish reaction Thermodynamic limitation non-viable
Aqueous	Carbonation reaction under aqueous medium. Additive chemicals are also used to enhance carbonation rate	High capacity	Energy intensive Needs additives No additive recovery Expensive
HCl extraction	HCl employed to extract reactive components	Easy recycling of HCl	Energy intensive Costly
HNO_3 extraction	HNO_3 used to extract reactive components	Energy efficient Low cost	Non recovery of chemicals
Molten Salt	Molten salt used as extraction agent	Energy efficient than HCl	Highly corrosive Unwanted by—products
Ammonia extraction	Ammonium salts employed to extract reactive components	Pure products Fast reaction Recyclable	Expensive Limited literatures

VII. CARBON SEQUESTRATION POTENTIAL

In the case of waste residues carbonation, there is no additional transportation and also monitoring costs [9]. The cost involved with waste residues carbonation is lower than mineral carbonation since the average cost of waste residues carbonation is approximate $67/tone of CO_2 [18]. The reaction process generally involves low temperature and pressure. It is significant to perform some pre—treatment due to the presence of radioactive elements in some residues and also the complexity of waste systems [12,17].

Table 4: Alkali waste for carbonation

Waste types	Annual worldwide production, Mt	Sequestration potential, kg CO_2/ton of waste	Sequestration capacity, Mt
Bauxite	120	53	6.36
CKD	990	15—115	14.85—113.85
PFA	600	8—264	4.8—158.4
MSWI BA	80	247—475	19.76—38
MSWI FA	20	30—120	0.6—2.4
Steel slags	400	227—300	90.8—120

VIII. COMMERCIAL APPLICATIONS

A lot of valuable products are produced by several companies while utilizing mineral and waste residues carbonation. Some of these products include aggregates and secondary building materials [37,40]. The carbonate products such as calcium carbonate can be used as filter papers or coating materials [41,42].

IX. CONCLUSIONS

Anthropogenic CO_2 emissions since industrial time begun have tremendously contributed to rapidly changing climate across the globe. CO_2 is one of the major contributor greenhouse gas which is emitted from the burning of the fossil fuel. In the recent past, carbon capture and storage have been considered the best approach to address the changing climate since it regulates the emission of CO_2 during fossil fuel combustion. There exist direct and indirect carbonation process routes, but direct aqueous carbonation is a more popular process. The minerals which are used for carbonation process consist of magnesium calcium silicates are expensive, and much energy is required to convert them into carbonates with acceptable kinetics. However, mineral carbon sequestration using waste residues not only absorb CO_2 but also improves their stability by neutralizing the reactive components present in the waste. Hence, the carbonation also enhances environmental acceptance of waste residues. Carbonation also used to convert waste residues into valuable products such as calcium carbonates. It is cumbersome to distinguish various types of waste because each waste has its own unique merits and demerits and hence, the different carbon sequestration capacity. The waste such as cement contains a high percentage of CaO, and they are available in huge quantities although the sequestration capacity is limited when carbonates dominate the waste.

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