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Incorporating Carbon Capture & Storage in Petroleum Coke using Olivine – Converting Liability into Asset

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Abstract—*Boom in petroleum coke production due to industrial shift from fuel oils towards lighter, sweeter petroleum products has raised concerns regarding its disposal. A closer inspection of this waste by-product reveals that it can be turned into a valuable asset which can boost a refinery's bottom line. Recent studies have shown that petroleum coke can displace its contemporaries like coal, biomass and sewage residues because of its higher carbon content. The cheap price and huge production of petroleum coke from refineries has given this entity a powerful economic stimulus to use it for power generation. Although, environmental concerns and rising carbon costs pose a challenge in its utilization at industrial scale. This study aims to provide a solution in the form of mineral carbonation utilizing olivine (Mg_2SiO_4), as a mineral which is rich in calcium/magnesium and reacts with carbon dioxide, thus resulting in metal carbonates as the end product, which is an innovative method of carbon sequestration. A comparative review with various other methods present in the literature exhibits its efficiency and cost effectiveness. Results presented in this study project its wide-ranging industrial scale applications. In this study it is concluded that compared to the other methods of carbon capture and storage, mineral carbonation utilizing olivine proves to be environmentally benign and provide permanent entrapment of carbon dioxide which eliminates the need for post storage surveillance.*

1. INTRODUCTION

Petroleum coke, often termed as petcoke in short is a carbonaceous solid byproduct left after the process of cracking, vacuum distillation of petroleum feed stock in refinery. There are basically two types of petcoke i.e. Calcined and Non – Calcined petcoke. **Calcined petcoke** is made by heating green petcoke at 1200 – 1350°C in rotary kilns. This leads to extraction of moisture and left hydrocarbon in green petcoke due to excess heat. Heating causes modification in existing structure and convert it into more electrically conductive product. Calcined petcoke is mostly used in steel, aluminum and titanium smelting industry. Green coke with excessive metal content is known as **non – calcined petcoke** and is used as a fuel (in furnace) in steel industry. India is the largest importer of petcoke, and hence petcoke serves as the integral part of Indian economy development. Petcoke is more dirtier fuel than coal as it emits 53.6% more CO_2 by weight when burnt (See Table 1). Recently, due to global warming big economy like India is coming forward to reduce its carbon emission.

Table 1: Comparison of petcoke with different coal types[1].

Fuel	CO_2 Emission per unit energy (lbs./MMBtu)	CO_2 by weight (ton CO_2 / ton fuel)
Bituminous Coal	203.99	2.54
Sub – Bituminous Coal	211.91	1.83
Median of Bit./Sub – Bit.	207.95	2.19
Petcoke	222.88	3.36
Percentage Increase	7.2 %	53.6 %

India has banned the use of petcoke but still its use is legal in cement, calcium carbide, lime kiln and gas industries as feedstock [2]. Over dependency on heavy crude oil, which causes production of petcoke in abundance finds its use in power generation and combustion purposes [3]. However, the CO_2 emissions aftermath from petcoke can be suppressed by carbon sequestration techniques. It is a technique of capturing and storing carbon dioxide using methods like **geological storage, ocean storage and mineral carbonation**. Geological storage involves storage of CO_2 in subsurface porous formations. In addition, Enhanced Oil Recovery (EOR) technique also comes under geological storage that aims at pumping CO_2 inside aquifers in order to enhance oil production. However the major drawback of this method is risk of CO_2 leakage hence it will require post storage surveillance. Oceanic storage entails CO_2 injection at shallower depths in ocean, where CO_2 reacts to form carbonic acid. The demerit of this method is lowering of ocean pH due to formation of carbonic acid and lack of permanency. Mineral carbonation is a method in which CO_2 is injected in-situ where it reacts with alkaline minerals to form carbonates. This technique is environmentally benign and provides permanent trapping of CO_2 hence the question of post storage surveillance is ruled out. Present study suggests the use of olivine mineral for carbon storage based on extensive literature survey, which is a mineral carbonation process and its presence in India is abundant, (See Table 2).

Table 2: Reserve of Olivine in India in 1000 tonnes [4]

State	Proved	Probable	Total
Jharkhand	373	570	943
Karnataka	3718	223	3940
Odisha	3337	-	3337
Tamil Nadu	7466	1450	8916

Tier et al.(2006) experimentally observed the stability of calcium and magnesium carbonates when they were exposed to an environment that was acidic in nature. This study was focused on investigating the release of CO_2 in acidic environment as the carbonated mineral are not stable in acidic environment. They concluded that no notable CO_2 release was observed when magnesium and calcium carbonates were leached in solution of pH 2.

Prigiobbe et al. (2009) conducted experimental investigation to characterize dissolution of mineral and precipitation of carbonate separately. He used San Carlos gem-quality olivine crystals ($Mg_{1.82}Fe_{0.18}SiO_4$). Effect of several parameters like temperature, pH and salinity on dissolution kinetics was inquired using flow-through reactor. The modeling was carried out using population balance equation coupled with mass balance equation. However in his mathematical model neither the development of particle breakage nor agglomeration was considered.

Azdarpour et al. (2013) carried out experiments with a purpose to determine best suited temperature and olivine size for CO_2 sequestration process. He took three different sizes (250, 100, 40 µm) of olivine sample to ensure the mineral size which holds maximum efficiency to absorb CO_2. Also, 100 µm of olivine sample was heated for three different temperatures (40, 70, 100 °C) to examine the effect of temperature on carbonation process. He concluded that the smallest size olivine sample exhibits maximum efficiency due to increase in mechanical activation. In addition to it increasing temperature significantly increases the reaction kinetics.

The drive of present work is to enumerate the benefits of using petcoke and discussing the option of reducing harmful gas emission specially carbon dioxide by using mineral carbonation process that incorporates the use of olivine. Based on extensive literature survey, some data which depicts petcoke as an integral fuel, which can fire up the pace of development of Indian economy has been conferred. In addition to that feasibility of using mineral carbonation specially with olivine is discussed in detail with valid data set so as to tap the aftermath of carbon dioxide emissions on human being and environment.

2. PETCOKE – A BOON FOR INDIAN ECONOMY.

According to Indian Oil Corporation Limited (IOCL), a public sector company in India Raw Petroleum Coke (RPC) which is defined as "bottom of the barrel" product of refinery holds numerous uses in different industries. They classify RPC in two distinctive grades, one being Calcination or Green RPC and the other being fuel grade or petcoke.

Table 3. Composition of Petcoke

Carbon (wt %)	81.32 – 83%
Hydrogen (wt %)	3 – 5%
Sulphur (wt %)	4 – 6%
Oxygen (wt %)	0.45 – 5%
Water (wt %)	5 – 8%
Ash (wt %)	0 – 0.46 %
Nitrogen (wt %)	0 – 0.88 %
Heating Value (MJ/kg)	32

Green RPC is produced at Digboi, Barauni, BRPL and Guwahati refineries of IOCL. However fuel grade petcoke is produced at Panipat Refinery of IOCL. In India Green RPC is used for making anodes for aluminum industry. Fuel grade or petcoke is used as fuel requirement to fire up rotary kilns in cement industry. Over 70% of fuel requirements of Indian cement industry is completed by petcoke.

To keep a pace with current development rate, Indian industries like cement industry, aluminium industry needs cheap feedstock like petcoke. Also, aluminium industry needs 0.4 – 0.6 million tonnes of a particular grade and structure of petcoke which is calcined petcoke. Currently there is a clear deficit of this kind of petcoke. The trend shows that the requirement of petcoke is increasing year by year (See Figure 1).

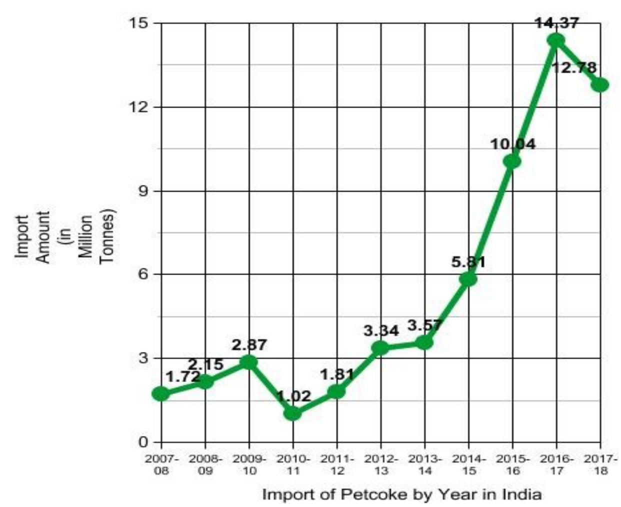

Figure 1: Total import of petcoke in India from 2007-2018. (Source: EXIM database, Ministry of Commerce & Industry)

Use of petcoke in different industry is depicted in Figure 2. It can be concluded that cement industry is highly dependent on petcoke as its feedstock. The installed cement capacity in India is 465 million tonnes, and it is expected to grow by a rate of 7% annually [10]. Indian government policies like Pradhan Manti Awas Yojana is expected to constitute a remarkable of 30% of total cement requirement in India.

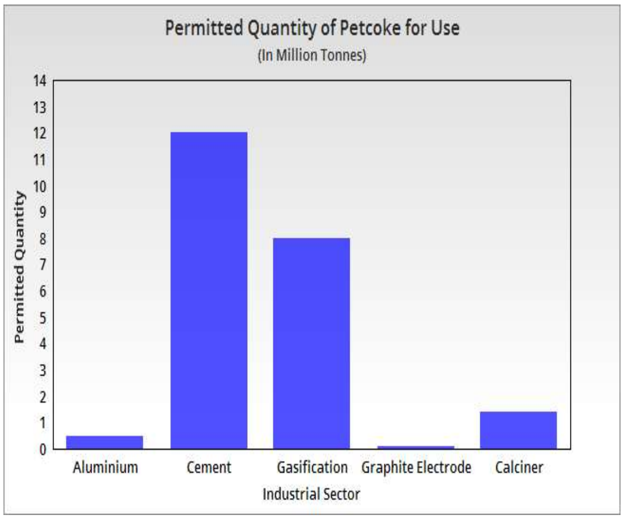

Figure 2: Permitted quantity for use of Petcoke in India [12].

3. CHARACTERIZATION OF OLIVINE.

As the name depicts, olivine is green in color and occasionally it can be greenish yellow or brown in appearance (See Figure 3). Olivine is referred to a group of rock forming minerals found in mafic igneous rocks like basalt and gabbro. As compared to other minerals olivine possess high crystallization temperature.

Figure 3: Sample of Olivine from Naran-Kagan Valley, Kohistan District, North-West Frontier Province, Pakistan. [8]

The general chemical and physical information about olivine is described in Table 4.

Table 4. Chemical & Physical Characteristic of Olivine

Chemical Formula	$(Mg, Fe)_2 SiO_4$
Molecular Weight	153.31 grams
Composition	Magnesium – 25.37% Iron – 14.57% Silicon – 18.32% Oxygen – 41.74%
Density	3.27 – 3.37
Hardness	6.5 – 7
Luster	Vitreous
Streak	White

Olivine has also been found in meteorites that orbit near Mars and Jupiter.

4. METHODOLOGY OF MINERAL CARBONATION BY OLIVINE.

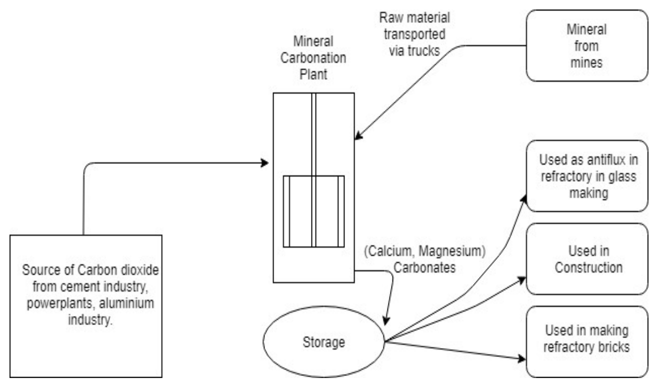

Figure 4: Depicting a workflow of mineral carbonation and uses of carbonates.

Trapping CO_2 in the form of carbonates can be accomplished by numerous methods which ranges from weathering of limestone to indirect carbonation processes. Figure 4 depicts a general process flow diagram of the whole carbonation process which includes CO_2 transportation to carbonation plant and then after carbonation the use of metal carbonates in various type of industries. The presence of olivine reserves in huge amount makes olivine the best suited candidate for mineral carbonation as compared to other minerals like Wollastonite and Serpentine. The conversion of olivine to mineral carbonates is represented by following chemical equation [6]:

$$Mg_2SiO_4 + CO_2 \rightarrow 2\ MgCO_3 + SiO_2 + 89\ KJ\ mol^{-1}\ CO_2$$

Table 5. Optimum pressure & temperature of carbonation [11]

Mineral	Temperature (°C)	Pressure (atm)	Carrier Solution	Carbonation, 1hr (%)
Olivine	185	150	0.64 M $NaHCO_3$, 1 M NaCl	49.5

Broadly there are two ways by which carbonation can be achieved i.e. direct and indirect mineral carbonation (See Figure 5). **Direct carbonation** is a one step mineral carbonation process in which the carbonation is accomplished in a single reactor by bringing the metal oxide in contact with gaseous CO_2 at an ambient temperature and pressure. The main constraint with this method is that the reaction rate is too slow. Indirect carbonation process is a multi-step method in which first the metal part of mineral, like magnesium in case of olivine is extracted followed by carbonation process. This process is carried out at a temperature higher than in direct carbonation.

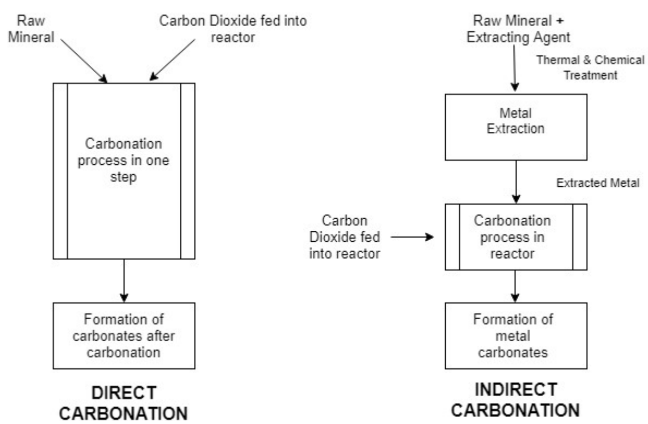

Figure 5: Direct & Indirect carbonation process

5. RESULTS & DISCUSSIONS

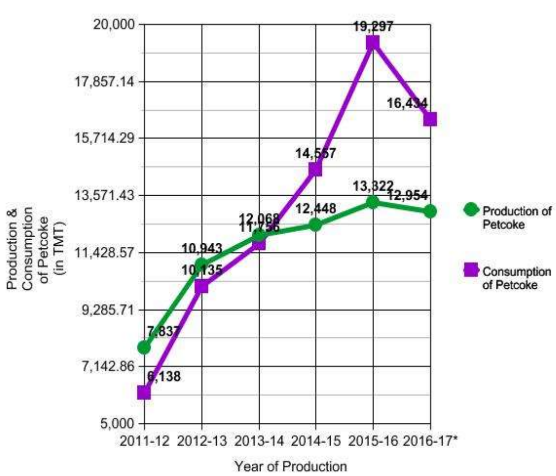

Figure 6: Production & Consumption of petcoke in India.

As far as the consumption of petcoke is considered, there is a substantial amount of gap when its is compared to the production of petcoke in India (See Figure 6). Also the requirement of aluminium industry sticking to a particular grade and structure of petcoke has led to an extra burden on the imports. From all these data it is clear that petcoke requirements is going to increase in near future. The use of a dirtier fuel like petcoke requires extra attention and such king of fuel is irreplaceable because of its low cost. Capping the CO_2 which is emitted after burning petcoke becomes obligatory. In this study, such a method i.e. mineral carbonation is explained with valid data set to justify its use in carbon capture and storage.

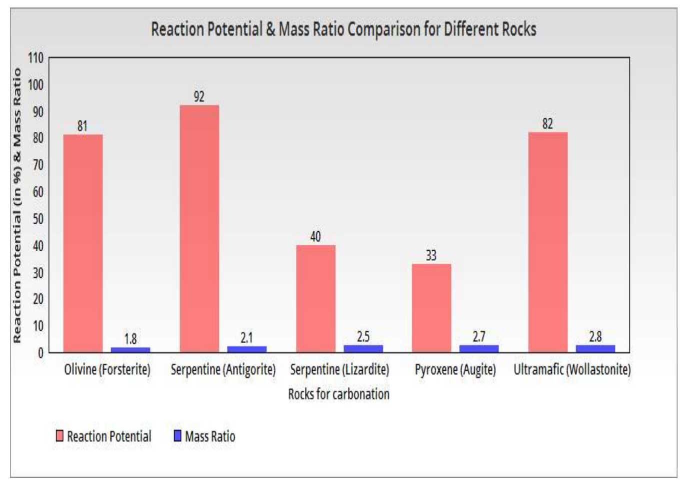

Figure 7: Reaction potential & mass ratio comparison for different rock.

In this study, olivine is chosen for mineral carbonation process owes to the reason that it is present in huge amount in the Indian states of Jharkhand, Karnataka, Odisha and Tamil Nadu. In addition to that, reaction potential of carbonation of olivine is around 81% which is descent when compared to other mineral carbonation rocks like serpentine and pyroxene. The advantage of using olivine is also hidden in the fact that mass ratio of olivine is least among different rocks (See Figure 7). Mass ratio is the tonnes of mineral required to carbonate a unit mass of CO_2. Mass ratio of olivine means that least amount of mineral is required to carbonate carbon dioxide. This will lead to less burden on mining activities of this mineral.

6. CONCLUSIONS

In this study, extensive literature survey was done to describe the importance of a dirtier fuel petcoke in Indian context. In addition to that, method for capping the environmental effects after burning this fuel is explained. Mineral carbonation is the best technique to tackle this problem. This study becomes significant because in the recent past the use of petcoke is only allowed for limited industrial sector and for rest its use is banned. From this study, following conclusion is drawn:

1) Based on the observation of trends of consumption and production of petcoke, it is clear that the consumption of petcoke is going to increase at a substantial rate in the near future.
2) Petcoke is an integral part of feedstock for various industrial sector in India, especially the cement sector which depends on petcoke to fulfill its 70% fuel feedstock necessity.
3) Mineral carbonation technique holds an upper hand from other carbon sequestration technique like oceanic storage and geological storage.
4) Due to the abundance of olivine in India, and on top of it possessing a descent reaction potential and good mass ratio makes it the best candidate among other minerals for performing mineral carbonation.
5) The practice of mineral carbonation using olivine is encouraging because of its low cost of 60 euros per ton of CO_2 avoided.
6) Petcoke is more dirtier fuel than coal but due to less price of petcoke it can replace coal as a fuel provided an state of art carbon capture and storage technique like mineral carbonation should be used.

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