Carbon Dioxide Sequestration by Mineral Carbonation Using Alkaline Rich Material

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Abstract. Mineral carbonation is the carbonation of alkaline silicate Ca/Mg minerals, which is replica of the regular weathering processes. Mineral carbonation comprises of the reaction between the minerals and carbon dioxide to form a safe and stable mineral carbonate product. The present investigations deal with the usage of industrial alkaline rich waste (IAW) containing considerable amount of metal oxides as the possible raw material for the carbonation process. The suitability of applying the aqueous scheme of mineral carbonation by using steel slag is studied. The material is economical and is available easily near the large point sources of carbon dioxide emissions, and due to the chemical instability tend to react with carbon dioxide. Various process variables were considered to check the extent of carbonation like the temperature, pressure, liquid to solid ratio, reaction time. Chemical analysis was conducted to check the extent of carbonation. The experiments were carried out in artificial carbonation reactor. The particle size of the samples considered was less than 90 microns and distilled water was used as the medium to carry out carbonation. A maximum of 44% of carbonation was achieved for steel slag at a temperature of 100 ˚C, carbon dioxide pressure of 10 Kg/cm², liquid to solid ratio of 6 and reaction time of 2 hours.

1. Introduction
Carbon dioxide emissions primarily emitted from large area sources like the power plants and other industrial processes involving burning, incineration and combustion processes. The smaller and distributed sources of carbon dioxide include automobile engines emissions, furnaces used in residential and commercial purposes. When carbon dioxide is released in the atmosphere it remains in the atmosphere until it is absorbed in some form. Unlike other Green-house gases carbon dioxide does not absorb the light waves from the sunlight instead when the light waves strike the earth surface it is converted into heat waves which have longer wavelength and carbon dioxide readily absorbs this, thereby preventing the heat waves from escaping the earth’s atmosphere [4, 10].
The increasing carbon dioxide emissions due to various anthropogenic activities have potentially devastating consequences such as global warming and climate change. The main carbon dioxide emissions are due to the burning of fossil fuels and industrial activities. In order to prevent this increasing emission it requires that the net anthropogenic emissions of CO2 be reduced to a small fraction of their current value. To prevent this increasing carbon dioxide emission there arises necessity for a technology that can contribute in capturing these emissions and storing it for a long term in a stable form [4, 14].

The technology of capturing carbon dioxide and its long term storage is called as carbon dioxide sequestration. This technology involves the transportation of carbon dioxide from large point sources to the storage sites where either the emissions are forced deep into the geological formations from which the emissions do not escape into the atmosphere [3]. The carbon dioxide sequestration includes many options in which it can be carried out. The different ways in which the carbon dioxide can be captured and stored include burying the emissions into geological formations, forcing the emissions into the ocean beds, using it in enhanced oil recovery, mineral carbonation.

In mineral storage carbon dioxide is made to react exothermically with available metallic oxides, to produce the end products in the form of stable metal carbonates. Limestone formation is an example for natural mineral carbonation, however in artificial carbonation at high temperatures and pressures carbon dioxide is reacted with the metal oxides to form stable metal carbonates. The basic principle behind the mineral carbonation is to mimic the natural weathering process in which the magnesium and calcium oxides are converted into calcium and magnesium carbonates [9, 15].

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(Ca, Mg)O(s) + CO_2 (g) \rightarrow (Ca, Mg) CO_3 (s)
\]  

(1)

It is based on the principle that the carbon dioxide reacts with the metallic oxides to form their respective carbonates, calcium and magnesium metals are being the common ones [13].

As mineral carbonation is similar to the natural weathering process which proceeds in a slow way, it cannot be relied upon for the sequestration. Hence the mineral carbonation process needs to be accelerated for the capture of carbon. In order to accelerate the process of mineral carbonation aqueous carbonation route is one of the solutions. In this process the carbon dioxide is passed in to the slurry of Ca/Mg rich raw materials. [1, 2]

Industrial waste such as the steel slag is rich in Ca/Mg oxides and is alkaline in nature. The characteristics of the waste make it a potentially possible feedstock for the mineral carbonation process. Major advantage of using steel slag over the ores are it is present near the large point sources of CO₂, by making use of these wastes for CO₂ sequestration it creates an opportunity to reclaim some of the CO₂ emitted during the manufacturing process.

2. Experimental Sequences

2.1 Chemical analysis of steel slag
Steel slag is the industrial waste generated in the iron and steel industry. It is produced in the industry during the separation of molten steel from the impurities. Initially it will be in the molten liquid state which upon solidification on cooling results in complex mix of silicates and oxides. The steel usually consists of 30 to 40% of CaO and 5 to 10% of MgO in its chemical composition. The chemical composition steel slag is alkaline waste with the pH ranging between 8 to10. Due to this chemical composition and natural alkalinity steel slag proves to be a possible feedstock for the mineral carbon sequestration. The steel slag used in this work was procured from the FOSROC pvt limited. The particle size of the procured steel slag obtained was 4.75 mm passing. This slag was tested for its CaO and MgO content in accordance with IS-4032:1985 [5].
2.2 Mineral Carbonation of Steel Slag

The carbonation experiments were carried out in the reactor by varying different parameters. One parameter was varied at a time keeping the remaining parameters constant. 10g of 90 microns passing, moisture free sample was taken and mixed distilled water according to the prior chosen liquid to solid ratio stirred to form the slurry and then poured into the reactor. The reactor was then sealed with lid and made sure it was air tight. The reactor was then heated to the desired temperature once the desired temperature was reached the carbon dioxide was bubbled through the slurry for the desired reaction time. Care was taken to maintain the desired temperature and pressure during the reaction time using the appropriate regulating valves. Figure 1 shows the reactor used for carbonation.

![Figure 1. Reactor for mineral carbonation](image)

After the reaction time elapsed the reactor was depressurized by opening the exhaust valve. Then the reactor was cooled to 30˚ C by passing cold water through the inlet of the cooling system. The reactor lid was opened and the slurry was filtered on a 42 number Whatmann paper. The carbonated sample retained on the filter paper was dried in the hot air oven at 50˚ C overnight. The dried carbonated sample was stored in air tight containers until tested to know the extent of carbonation.

2.3 Analysis of extent of carbonation

Thermal gravimetric analysis (TGA) was carried out on the carbonated sample to know the extent of carbonation. According to the TGA method the change in mass at temperatures of 500˚ C and 1000˚C indicates the percentage of carbonates in the sample. TGA results give the amount of change in weight as the function of temperature. Carbonate decomposition occurs at these temperatures. Hence the change in weight or the loss in weight gives the extent of carbonation.

The carbonated samples were weighed in the silica crucible and heated to temperatures of 500˚ C for 15min and the loss in weight was taken as the organic fraction of CO2 which indicates the presence of carbonates of Magnesium. The same sample was heated for 15min at 1000˚ C and the loss in weight was noted. This fraction of weight loss at 1000˚ C indicates the inorganic CO2 that is the presence of carbonates of calcium.

A clean silica crucible was weighed empty and then 1g of carbonated sample was placed in it and the sample was heated for 15min at each of the temperatures. The loss in weight indicates the extent of carbonation [6].

The steel slag containing CaO and MgO were used for the sequestration of carbon dioxide. The parameters varied and checked for their influence on carbonation are reaction time, pressure, temperature and liquid to solid ratio. The extent of conversion of Ca and Mg oxides into the
carbonates was tested using thermo gravimetric analysis. The influence of various process variables on extent of carbonation are as discussed below.

2.3.1 Effect of reaction time
The time duration for which carbon dioxide remains in contact with the slurry in the reactor at the pre-determined temperature and pressure is called as reaction time. It is the time taken by the gas to interact with the slurry. The reaction time was varied between 1 hour to 4 hours, and the behavior of carbonation is as tabulated below in Table 1.

Table 1. Effect of reaction time on carbonation

| Reaction time in hours | Empty wt | Empty wt + 1g sample | Wt at 500°C | Wt at 1000°C | Loss in wt at 500°C | Loss in wt at 1000°C | % carbonation of MgO | % carbonation of CaO |
|------------------------|----------|----------------------|------------|-------------|-------------------|-------------------|--------------------|-------------------|
| 1                      | 13.29    | 14.29                | 14.28      | 13.92       | 0.01              | 0.372             | 1.08               | 37.2              |
| 2                      | 48.52    | 49.52                | 49.52      | 49.10       | 0.0045            | 0.4171            | 0.45               | 41.71             |
| 3                      | 48.52    | 49.52                | 49.52      | 49.10       | 0.0212            | 0.426             | 2.12               | 42.6              |
| 4                      | 48.52    | 49.52                | 49.51      | 49.10       | 0.0183            | 0.4322            | 1.83               | 43.22             |

2.3.2 Effect of temperature
Temperature is another important process variable. The slurry is heated to the desired temperature and when it reaches the desired temperature the carbon dioxide gas is passed to the slurry. Until the decided reaction time elapses the temperature is maintained by operating the exhaust gas valve and cooling systems. The variation in the extent of carbonation at various temperatures is as tabulated below in Table 2.

Table 2. Effect of temperature on carbonation

| Temperature in °C | Empty wt | Empty wt + 1g sample | Wt at 500°C | Wt at 1000°C | Loss in wt at 500°C | Loss in wt at 1000°C | % carbonation of MgO | % carbonation of CaO |
|-------------------|----------|----------------------|------------|-------------|-------------------|-------------------|--------------------|-------------------|
| 50                | 48.517   | 49.517               | 49.513     | 49.102      | 0.004             | 0.417             | 0.4                | 41.7              |
| 100               | 48.541   | 49.541               | 49.523     | 49.101      | 0.018             | 0.442             | 1.8                | 44.2              |
| 150               | 48.541   | 49.541               | 49.539     | 49.222      | 0.001             | 0.320             | 0.1                | 32                |
| 200               | 48.541   | 49.541               | 49.524     | 49.321      | 0.017             | 0.221             | 1.7                | 22.1              |

2.3.3 Effect of liquid to solid ratio
The liquid to solid ratio is the ratio of water to slag. In aqueous path of mineral carbonation water acts as a medium for calcium oxide and magnesium oxide to dissolve in water for reaction with the carbon dioxide. At lower liquid solid ratio good mixing cannot be achieved hence the sequestration of carbon dioxide is not effective. The liquid to solid ratio was varied between 2 to 10 and the results are as tabulated below in Table 3.
Table 3. Effect of liquid to solid ratio on carbonation

| Liquid to solid ratio | Empty wt | Empty wt + 1g sample | Wt at 500°C | Wt at 1000°C | Loss in wt at 500°C | Loss in wt at 1000°C | % carbonation of MgO | % carbonation of CaO |
|-----------------------|---------|---------------------|-------------|-------------|---------------------|---------------------|---------------------|---------------------|
| 2                     | 48.5344 | 49.5344             | 49.5279     | 49.1079     | 0.0065              | 0.4265              | 0.65                | 42.65               |
| 4                     | 48.5344 | 49.5344             | 49.5102     | 49.1094     | 0.0242              | 0.425               | 2.42                | 42.5                |
| 6                     | 48.5344 | 49.5344             | 49.5211     | 49.0928     | 0.0133              | 0.4416              | 1.33                | 44.16               |
| 8                     | 48.5418 | 49.5418             | 49.5233     | 49.1013     | 0.0185              | 0.4405              | 1.85                | 44.05               |
| 10                    | 48.5344 | 49.5344             | 49.5278     | 49.1088     | 0.0066              | 0.4256              | 0.66                | 42.56               |

2.3.4 Pressure

Pressure refers to the pressure of the carbon dioxide inside the reactor. The reactor pressure is maintained by operating the inlet and exhaust gas valves accordingly. Throughout the reaction time the pressure in the reactor should be maintained at the desired constant pressure by operating the necessary valve. At lower temperatures the pressure of the carbon dioxide is of not of much significance however at higher temperature when the dissolution of the carbon dioxide in water becomes difficult higher pressure of the carbon dioxide gas is desired. Usually higher pressure is desirable for the mineral carbonation process. Carbon dioxide was varied between 4 Kg/cm2 to 10 Kg/cm2 and its influence on the extent of carbonation was observed. The variation in carbonation at different pressures of carbon dioxide is as shown below in Table 4.

Table 4. Effect of pressure on carbonation

| Pressure | Empty wt | Empty wt + 1g sample | Wt at 500°C | Wt at 1000°C | Loss in wt at 500°C | Loss in wt at 1000°C | % carbonation of MgO | % carbonation of CaO |
|----------|---------|---------------------|-------------|-------------|---------------------|---------------------|---------------------|---------------------|
| 4        | 48.5315 | 49.5315             | 49.5297     | 49.5012     | 0.0018              | 0.0303              | 0.18                | 3.03                |
| 6        | 48.5312 | 49.5312             | 49.531      | 49.3959     | 0.0002              | 0.1353              | 0.02                | 13.53               |
| 8        | 48.5314 | 49.5314             | 49.5302     | 49.3002     | 0.0012              | 0.2312              | 0.12                | 23.12               |
| 10       | 48.5315 | 49.5315             | 49.5311     | 49.0885     | 0.0004              | 0.443               | 0.04                | 44.3                |

3. Summary and Conclusions

The work demonstrates the suitability of using industrial steel slag for carbon dioxide. The experiments were carried out in a prefabricated artificial carbonation reactor. The samples were exposed to the continuous supply of carbon dioxide at the pre decided temperature, pressure and reaction time. The particle size of the samples was 90 microns passing and was kept constant throughout the work. The process variables temperature, pressure, reaction time and the liquid to solid ratio were studied. The results of this work indicate that steel slag could be an attractive and potential method for carbon dioxide sequestration. The results show that the maximum carbonation of steel slag was achieved of the order 44.3% at temperature of 100 °C pressure of 10 Kg/cm2 for a liquid to solid ratio of 6 and for a reaction time of 2 hours.

It was seen the extent of carbonation increased with high pressure and temperature. However when temperature was increased beyond 100 °C the carbonation decreased this was due to the fact that carbon dioxide dissolution in the water decreases at higher temperature. The carbonation process also needs a good amount of reaction time for the reaction between the slurry and carbon dioxide. The chemical composition of the material showed significant amount of metallic oxides which showed the potential use of these materials. The carbonation was successfully carried out and higher pressures
could not be applied because of the inefficiency of the reactor. More efficiencies of carbonation could be achieved with higher order of pressures of the inlet carbon dioxide pressure.

This approach can result in a breakthrough involving utilization of alkaline rich waste materials like the industrial steel slag waste; the use of such waste also reduces the cost of procurement of raw materials for mineral carbonation. The sites where these material is generated is also the sites where there is large emissions of carbon dioxide hence by using the waste at sites it is possible to reclaim some of the carbon dioxide emitted during their manufacturing process.

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