Benefaction from Carbonation of Flue Gas CO₂ as Coal Mining Filling

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Abstract

CO₂ capturing, transport and sequestration by pressurized water dissolution and reacting by natural alkali lime and magnesia in coal fly ash or other sources become an industrial advantageous sequestration option resulting in green waste solutions or solid fines. Mg and Ca containing minerals are reacting with CO₂ to form carbonates. Various types of fly ash materials may react with CO₂ to form carbonate regarding ash composition and reaction parameters. Mineral sequestration of CO₂ will also allow using the products in cement industry or as cement material in constructions with low cost. This paper discussed progress on coal mining filling by carbonation method using coal fly ash of Soma, Yatagan, Afşin Elbistan Power Stations. Other filler materials containing coal mine waste shale, fly ashes and foam concrete, and additives were searched for pretreatment methods to enhance cement reactivity; and in analyzing the structural changes to identify reaction paths and potential barriers.

Keywords
Carbon Sequestration, Coal Fly Ash Utilization, Mineral Carbonation, Mineralization, Fly Ash

1. Introduction

Carbonation of CO₂ gas has many various advantages. Most distinct fact is that carbonates have a lower energy state than CO₂. Mineral carbonation thermodynamically occurs in nature (i.e., the weathering of rock over geologic time periods). Further, the raw materials such as magnesium based minerals are abundant on earth. The produced carbonates are basely stable and thus re-evolve of CO₂ into the atmosphere is not an issue. However, conventional carbonation reactions are slow under ambient temperatures and pressures.

Fossil fuels, which account for 80% - 85% of the total of world energy use today, are an important energy source. Fossil fuels have many advantages including abundant supply, high energy density, ease of use and sto-
rate, existing infrastructure, and most importantly, their low cost. Forty percent of global electricity is generated in fossil fuel power plants per annum, with emissions of about 33% (9.5 billion metric tons) of global energy-related CO₂ emissions of approximately 28.8 Gt in 2010 [1] [2]. Over half of the electricity demand of the Turkey is supplied by coal-fired power plants, with emissions of about 16 million metric tons of CO₂ per annum, representing about 33% of Turkey energy-related CO₂ emissions [3] [4].

Therefore, developing effective CO₂ sequestration is one of the critical components in addressing global climate change. Note that improving the efficiency of energy production and utilization, and developing renewable energy sources will certainly play a very important role in reducing CO₂ emissions [5], however these measures alone cannot address the greenhouse emissions issue mainly because world energy consumption will increase significantly as the living standard improves in many parts of the world (Figure 1).

Geothermal power plants on-line today fall into one of three categories of power cycles: dry-steam, flash-steam, or binary; of which only the first two are likely to emit any measurable amounts of GHGs. Non-condensable gas content is a key factor in designing turbines, condensers, gas removal systems, and hydrogen sulfide abatement systems for geothermal power plants. In dry and flash steam plants, non-condensable gases are separated from the steam turbine exhaust in the plant condenser and are either discharged to the atmosphere (air, carbon dioxide, and other nontoxic components) or removed by an abatement system (hydrogen sulfide is usually converted to solid elemental sulfur). These types of plants emit about 5% of the carbon dioxide, 1% of the sulfur dioxide, and less than 1% of the nitrous oxide emitted by a coal-fired plant of equal size. Binary power plants retain non-condensable gases in a closed loop system while the geothermal brine is being utilized for electricity production. Eventually, the geothermal fluid and contained gases are injected back into the reservoir.

Three boreholes, one injection well, and two condensable observation wells will be drilled, about 50 - 100 m (160 - 330 ft) apart, into the flank of an anticlinal structure. A total of up to 1 t/day of CO₂, in gaseous state at the well head, will be injected at about 700 m (2300 ft) depth into a saline mudstone aquifer. Injection is planned to start at the end of 2013 and last for approximately 2 years, during which the distribution and fate of the injected gas will be monitored by surface geophysical surveys and by downhole instrumentation. Various processes and subprojects and work packages address the science and operational aspects of CO₂. The proposed part of the project is restricted to the baseline survey and the injection and basic monitoring of CO₂. The supply of CO₂ will be provided by near Coal Power Station in Şırnak. Other choice will be the purchase of a pure CO₂ originating from flue gas of hydrocarbon production at an oil refinery. The CO₂ will be delivered by truck in liquid phase, temporarily stored at the well site, and conditioned before injection. The project proposed plans to inject the CO₂ at the well head in gaseous phase at a slightly supercritical pressure and slightly supercritical temperature. The anticline at Şırnak-Silopi was used for gas storage in the past in a shallower depth interval in Şırnak-Silopi pit mine field, which also is a mining industry partner in CO₂ sequestration and will be responsible for the CO₂ injection operations.

![Figure 1. Comparison of CO₂ emissions by coal, natural gas and geothermal source.](image-url)
This paper discussed the progress on carbonation filling achieved by tests and searched for fast reaction methods using exhaust gas containing waste sulfur and carbon gases at the stack of Power Stations. Other alkaline sources containing calcium, magnesium and magnesium salts, supercritical CO₂, water slurry, and additives were searched for optimum sequestration methods and also in order to enhance mineral reactivity; and in analyzing the structural changes to identify reaction paths and potential barriers. Carbonation liquid and gaseous products may change to near 20% - 45% yield performances by time increase from 1 hr to 6 hrs.

2. CO₂ Sequestration and Mineralization

Options for storing CO₂ in deep underground geological formations need adequate porosity and thickness for storage capacity and permeability for gas injection are critical. The storage formation should be capped by extensive confining units such as shale, salt caves or anhydrite beds to ensure that CO₂ does not escape into overlying, shallower rock units and ultimately to the surface. Geological storage of CO₂ requires compression of CO₂ to allow injection. This is done by compressing the CO₂ to a dense fluid state known as “supercritical”. This supercritical state is achieved by exposing the CO₂ to temperatures higher than 31.1°C and pressure greater than 73.9 bars. The density of CO₂ will increase with depth, until about 800 meters or greater, where the injected CO₂ will be in a dense supercritical state [5]-[14].

The mineral carbonation, a process of converting CO₂ into stable minerals—mineralization has been studied extensively to capture and store CO₂. However, most of the mineral carbonation studies have been largely investigated at lab scale. Preliminary and pilot scale studies for accelerated mineral carbonation (AMC) were conducted at one of the largest coal-fired power plants (2120 MW) in the USA by reacting flue gas with fly ash particles in a fluidized bed reactor. In the preliminary experiments, flue gas CO₂ and SO₂ concentrations decreased from 13.0% to 9.6% and from 107.8 to 15.1 ppm, respectively, during the first 2 min. of reaction. The flue gas treated by fly ash particles, even mineralization hold high mercury (Hg) concentration of 0.22 mg/kg in flue gas [15]-[18].

Geothermal brine waters utilization and using of CO₂ as feed material in mineral carbonation produce various environmentally benign products. However, many challenges to any solution include technical feasibility, economic viability, environmental soundness and long term sustainability for mineralization of CO₂ [19]-[23].

3. Mineral Sequestration Method of CO₂

Mineral sequestration involves the reaction of CO₂ with minerals to form geologically stable carbonates. This mineralization of CO₂ was searched by different studies using various materials [23]-[26]. General and specific global mineral carbonation reaction pathway is shown in Figure 1.

Mineral carbonation reactions are known to geologists and occur spontaneously on geological time scales. For example, the reaction of CO₂ with common mineral silicates to form carbonates like calcite and magnesite or calcite is exothermic and thermodynamically favored.

The family of reactions represented by Reaction 1 has the potential to convert naturally occurring silicate minerals to geologically stable carbonate minerals and silica. This process follows natural chemical transformations such as weathering of rocks to form carbonates over geologic time periods. Reaction 2 illustrates the transformation of the common silicate mineral serpentine, Mg₃Si₂O₅(OH)₄, and CO₂ into magnesite, MgCO₃, silica and water. Using this ideal case, one ton of serpentine can dispose of approximately one-half ton of CO₂. Reaction 3 illustrates the transformation of forsterite, which is the end member of the common silicate mineral olivine. One ton of olivine can dispose of approximately two-thirds of a ton of CO₂. Again, the reaction is exothermic and releases 90 kJ/mole of CO₂.

\[
\begin{align*}
(Mg, Ca)_x Si_y O_z + 2y + zH_{2z} + xCO_2 &\rightarrow x(Mg, Ca)CO_3 + ySiO_2 + zH_{2O} \\
\frac{1}{3}Mg_3Si_2O_5(OH)_4 + CO_2 &\rightarrow MgCO_3 + 2/3 SiO_2 + 2/3 H_2O + 64 kJ/mole \\
\frac{1}{2}Mg_2SiO_4 + CO_2 &\rightarrow MgCO_3 + 1/2 SiO_2 + 90 kJ/mole
\end{align*}
\]

A conceptual illustration of the projected Fly ash mineralization process is presented in Figure 2. As illustrated, CO₂ from one or more power plants is transported to a carbonation reactor, combined with fly ash slurry tank and held at the appropriate reaction conditions until the desired degree of carbonation is reached. Careful
control of solution chemistry yielded olivine conversions of 90% in 24 hrs and 83% within 6 hrs. The most recent results show further modifications of the same basic reaction can achieve 65% conversion in 1 hour and 83% conversion in 3 hours. A recent literature review indicated that weak carbonic acid treatments had also been suggested for Mg extraction in the prior literature [12]. Carbonation tests performed at ARC employing heat pretreated serpentine have resulted in up to 83 % conversion in 30 minutes lower than 115 bars [13]. Indeed, by increasing sodium bicarbonate concentration the carbonation reaction of serpentine can reach 62% completion under 50 bars [27]-[29].

Then products of the reaction, which might be slurry of carbonated minerals and residues and lean gas CO₂ in aqueous, are separated. The residual CO₂ is recycled. Useful materials are collected for construction works or the carbonated materials and residue are returned to the mine site. Almost calcium and magnesium oxide (MgO) content in the magnesium silicate ore mineral of 40% and 60% - 70% chemical efficiency of the carbonation reaction; mass balance of Equation (1). A 100 MW power plant in Şırnak-Silopi, generating approximately 200 tons/day of CO₂, would require just over near 80 tons/day of calcium and magnesium containing fly ash. Several fly ash types in Turkey containing sufficient calcium and magnesium oxide quantity in silicate mineral to provide raw materials for the mineral carbonation.

4. Experimental Work

In this research, representative specimens the different types of Turkish fly ashes Soma, Yatağan and Aşşin were classified to calcium content by chemical analysis. Gas samples of 10 - 20 kg tubes from each different coal power stations were used. Chemical analysis of the fly ash used in the experiments is given in Table 1. Chemical reactivity of fly ash sources as lime compound is given in Table 1. Ashes contain various alkali elements. Substantial fractions of these elements in springs could be lost during clay rock pores leak. Even 50% - 60% of arsenic, lead, manganese, mercury and selenium could be removed by salt transforming in cooling.

Turkish fly ash was reacted by waste gas in the process reactor (Figure 2) and solution distributions were investigated at each stage of sequestration. Screen analysis of Turkish fly ash samples were made by standard Tyler Screens regarding ASTM 4749 and particle size distributions and normal distributions of Turkish fly ash samples are respectively illustrated from Figure 3. Particle Size Distribution and Normal Size Distribution of Turkish fly ashes used in gaseous CO₂ medium changed mainly surface pore reaction process. Main reactive ash structure is widely distributed and porous structures are associated with clay minerals. Coarse alkali oxides are also seen. Screen analysis of carbonate samples were made by standard Tyler Screens regarding ASTM 4749 and particle size distributions and normal distributions of lignite samples are respectively illustrated from Figure 4. Specific surface area yielded carbonate crystals was about 2.6 - 4.2 m²/g determined by BET surface analyzer and highly sufficient in order to react with gaseous CO₂. As seen from Figure 4, 80% of weights of carbonates size distribution under 4 mm. In order to determine strengths in cure through a concrete block, the laboratory scale studies were conducted at a controlled medium.

From these results, we designed and developed laboratory scale filling unit consisting a mold (0.3 mΦ × 0.7 m) to mixture mineralized cement with cement/ash rate 5/1 and cement/water slurry rate at about 2/7. The decanter unit separates ash and fine aqueous water in molding. The cured at 28 days effect of fly ash and shale were provided higher strengths in slurry through a concrete block. The laboratory scale studies were conducted at a controlled pressure.

5. Results and Discussion

Turkish Fly ashes and Mine Waste Shale thrown as waste in Şırnak City of Turkey were used with foam con-
Table 1. Chemical analysis of Turkish fly ash.

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>Soma Fly Ash F</th>
<th>Yatagan Fly Ash F</th>
<th>Afşin Elbistan Fly Ash F</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂ (S)</td>
<td>41.14</td>
<td>51.05</td>
<td>22.4</td>
</tr>
<tr>
<td>Al₂O₃ (A)</td>
<td>16.12</td>
<td>21.69</td>
<td>9.1</td>
</tr>
<tr>
<td>Fe₂O₃ (F)</td>
<td>4.34</td>
<td>5.94</td>
<td>4.96</td>
</tr>
<tr>
<td>CS + CAF</td>
<td>64.6</td>
<td>78.0</td>
<td>84.2</td>
</tr>
<tr>
<td>CaO</td>
<td>30.6</td>
<td>11.60</td>
<td>54.7</td>
</tr>
<tr>
<td>MgO</td>
<td>1.3</td>
<td>2.2</td>
<td>3.1</td>
</tr>
<tr>
<td>K₂O</td>
<td>1.15</td>
<td>2.1</td>
<td>0.7</td>
</tr>
<tr>
<td>Na₂O</td>
<td>1.29</td>
<td>2.56</td>
<td>0.250</td>
</tr>
<tr>
<td>Loss of ignition</td>
<td>0.34</td>
<td>0.90</td>
<td>4.22</td>
</tr>
<tr>
<td>SO₃</td>
<td>3.43</td>
<td>1.45</td>
<td>2.4</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>2.22</td>
<td>2.12</td>
<td>2.0</td>
</tr>
<tr>
<td>Loose unit weight (g/cm³)</td>
<td>0.72</td>
<td>0.88</td>
<td>0.69</td>
</tr>
</tbody>
</table>

Figure 3. Particle size distribution and normal size distribution of fly ash.

Figure 4. Particle size distribution and normal size distribution of carbonate fillers.
concrete. Waste mixture at certain proportions decreasing instead of cement used, fine aggregate in specific proportions decreasing instead of fly ash used improved mechanical strength and porosity. Even fine aggregate reducing porosity rather than fly ash, such as using three different methods were performed in foam concrete production. Effects on mechanical properties of fly ash in concrete were studied intensively. Uniaxial and triaxial compression strength of foam concrete landfills was carried out in the ELE type laboratory press.

The purpose of this study, in ready-mixed foam concrete industry, Şırnak Coal Mine Waste shale and fly ash contribution were widely determined and effective amount of clay and ash on workability of the foam concrete and the curing time were determined. For this purpose in the mixture of foam concrete fine aggregate of 5%, 10%, 20% and 65% shale and 5%, 10%, 20% and 30% of fly ash were prepared with the foam concrete mixture substitution. In conclusion, depending on the amount used the fly ash in foam concrete, workability significantly changed and even significant the pressure increase.

Compression strength values depending on the amount of fly ash and foam substituent were reduced. Also in the mixture of fly ash used concrete curing time depending on the amount of substitution was found to reduce the porosity.

Soil rock samples were taken from the construction foundation and strengths with the bulk density are shown in Table 2. For determination of rock types based on logging were carried out and the results showed poor and good rock classification as given in Table 2.

In this study, the strength and the mechanical parameters of 10% mixture shale and foam concrete were determined and are given in Table 2. The amount of fly ash on properties of water discharges in the landslide risk area were also investigated and briefly given in Table 2. Some control coal mine rooms were accessed in order to optimize filling use with carbonation fills as given in Figure 5. The yield strengths for fly ashes and shale fill without foam concrete filling with different Turkish fly ash were tested and the results of samples were given in Figure 6. At shale fill blocks the strength increased to the higher levels of 19 MPa. At carbonate filling foam concrete blocks the strength significantly increased and even significant the pressure increase.

In experiments with different filler types for yield strengths of fly ash and shale fill within foam concrete filling were tested and the results of samples were given in Figure 7. At shale fill blocks the strength increased to the higher levels of 19 MPa. At carbonate filling with foam concrete blocks the strength yields are seen satisfying unit resistance to in-situ stress in filling rate of 40% - 50% with foam concrete.

Table 2. Effect of mixture rates used on filling strength yield and water discharge in 28 curing time.

<table>
<thead>
<tr>
<th>Mixture in Foam Concrete</th>
<th>σ, Strength MPa</th>
<th>γ, Unit Weight, g/cm³</th>
<th>Water Discharge (%)</th>
<th>Without Foam Concrete σ, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shalestone, 5%</td>
<td>13.9 - 14.9</td>
<td>1.74</td>
<td>45.2</td>
<td>24.9 - 25.2</td>
</tr>
<tr>
<td>10%</td>
<td>14.4 - 15.9</td>
<td>1.85</td>
<td>35.5</td>
<td>23.1 - 24.5</td>
</tr>
<tr>
<td>20%</td>
<td>16.5 - 17.5</td>
<td>1.97</td>
<td>32.4</td>
<td>22.5 - 23.5</td>
</tr>
<tr>
<td>30%</td>
<td>18.2 - 19.0</td>
<td>2.15</td>
<td>27.7</td>
<td>18.2 - 19.0</td>
</tr>
<tr>
<td>Fly Ash, 5%</td>
<td>9.6 - 9.9</td>
<td>1.25</td>
<td>64.3</td>
<td>14.3 - 14.9</td>
</tr>
<tr>
<td>10%</td>
<td>11.5 - 12.5</td>
<td>1.38</td>
<td>62.7</td>
<td>13.4 - 13.9</td>
</tr>
<tr>
<td>20%</td>
<td>13.4 - 13.9</td>
<td>1.42</td>
<td>61.2</td>
<td>11.5 - 12.5</td>
</tr>
<tr>
<td>30%</td>
<td>14.3 - 14.9</td>
<td>1.58</td>
<td>60.3</td>
<td>9.6 - 9.9</td>
</tr>
</tbody>
</table>

Figure 5. Filling of carbonates coal mine room.
In the carbonation experiments, the experimental conditions are calculated on the basis of the gas composition in the ambient state. So neither the contained water vapor nor the others are taken into account. Carbonation solid products may change to filler strength of 45% - 20% by time increase from 14 days to 28 days.

6. Conclusions

Various faces characterize the mining open rooms in coal mining in Şırnak Coal Mine excavation seam of Lower Eocene that had been named formations which include the Cudi Mountain Formation. It is one of the four lateral equivalents of the Siirt Group and consists of shale and marls with abundant limestone. In this paper, we report on the filling matter on settlement and strength of the Coal Mining Rooms during operation. Settlement values were satisfying in the formation from nine outcrop cross sections in central and northern Coal Mine Site. The total strength (σ) values and Rock-Classification analysis showed that this formation had preserved coal rooms in operation. Locally, such as at 50 - 75 mm are very high. These values are reliable to the structural framework in subsiding during the excavation of the coal. Laboratory analysis showed that this total strength (σ) is very great in these shale carbonate compounds. Our results exposed that the fly ash use in carbonation and filling in coal rooms were strong as other fillers by an open site tests as revealed by the relative stability of the Shale fill (37% - 43%), Carbonate fill (26% - 31%), and Fly ash-Foam Concrete fill (30% - 34%).

The compounds for all the samples were good preservations of the roof formation which has been evidenced by the high abundance. Under preserved conditions in central Mine Site, we interpreted that the development of
mine had been induced by water flow in winter climate. These results in concord with the structural and the settling where the roof formation in central deposited coal excavation area in highly subsiding separated from the open west hill site. In northern excavation site, eastern upwelling waters enhanced primary settlement and the development of abnormal conditions.

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References


