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Chapter

Microwave Carbonation of Thermal Power Plant Flue Gas/CO$_2$ by Fly Ash/Coal Char for Soil Remediation and Ground Stabilization

Yıldırım İsmail Tosun

Abstract

In this research, the cementing filler material production by microwave carbonation of flue gas of coal combusting thermal power station of Silopi in Şırnak by fly ash/coal char, Şırnak asphaltite char, in molten alkali salts will be investigated. The optimum carbonation was managed in order to provide an overview of stabilization of foundation grounds. In this study, the effect of microwave energy managed the carbonation by salt slurries with flue gas contents in the reactor. By the slurry character of salts in the furnace during that process, the flue gas of Şırnak thermal power plant, salt type and flue content were investigated for carbonation with weight and slurry performances. In this study, the toxic emitted contents were also determined in salt slurry, regarding the amounts and type of salt contents as sorbent agents. As a result, a significant positive effect of microwave energy on the carbonation products was determined at lower gas flow rate and steam rates. Finally, 23% CO$_2$ carbonation could be provided. The oil content in flue gas decreased carbonation fractions. The salt slurry content was primarily settled and coal humus char as by-product was also recovered as solid with a 38.7% recovery rate in microwave carbonation in slurry salt with 20% solid/water rate. The strengths of the ground blocks were dispersed to 0.8–1.2 MPa in shear strength and 3.7–9.4 MPa in compression strength. Thus, with the ideal packing, the strength of the mixed cemented blocks produced from these fine fillers and waste mixtures can also reach 11.2 MPa in compression strength and 3.9 MPa in shear strength.

Keywords: carbonation, microwave carbonating, filler, filler blocks, fly ash/coal char, slope stability, Şırnak province, ground stabilization, salt reactor

1. Introduction

CO$_2$ and HC containing flue gas emissions of thermal power stations pollute the environment and urbanized area, HC emissions of transportation threat hardly and carbonation of flue gas emissions need filtration and carbonization by pressurized water dissolution and reacting by natural alkali lime and magnesia or other alkali sources becomes an industrial advantageous in sequestration. The carbonation sequestration option resulting in green waste solutions or solid fines provided humus or

stabilizing filler materials for land. Mg and Ca containing minerals are commonly reacting with CO_2 to form carbonates. Even by evaporation of salty solutions, similar carbonates and sulfates were precipitated at low temperatures such as 40°C. Various types of hot water sources may react with CO_2 to form carbonate regarding salt composition and reaction parameters. Mineral carbonation of CO_2 will also allow using the products in cement industry or as cement material in constructions with low cost. In this study, the supply of CO_2 will be provided by nearby power stations. Other choice will be the purchase of a pure CO_2 originating from flue gas and hydrocarbon dusty mist of coal combusting industrial furnace at a cement plant. For the pilot plant design, a carbonation unit will contain the compressed flue gas tanks so that sequentially compressed CO_2 will be delivered to carbonation reactor in gas phase, temporarily stored underground at site, and conditioned before carbonation. The carbonation reactions to inject the CO_2 at pressurized microwave radiated heating were effective in reaction gaseous phase with salty molten phase at a slightly high pressure and slightly under supercritical temperature. This paper discussed progress on reactor achieved by tests and search for fast reaction methods using exhaust gas containing sulfur and carbon gases at power stations [1–5]. The alkaline sources containing alkali sodium and magnesium salts, under 10–20 bar pressurized CO_2, salt slurry, and additives were searched for microwave carbonation method to enhance mineral reactivity and to analyze the structural changes to identify reaction kinetics and potential impurity and fouling barriers.

Carbonation products of CO_2 gas were Ca and alkali carbonates even metal iron carbonates. Most distinct sequestration is that carbonization outputs a lower energy compound than calcination [6–9]. Calcium and magnesium carbonates commonly occur in nature (i.e., the weathering of rock over geologic time periods). Moreover, the evaporation outputs such as magnesium-based minerals are dissolved by hot waters and then crystallized at 30–40°C coming out as evaporates on earth. The evaporate carbonates are resistively stable and thus do not re-evolve CO_2 into the atmosphere as an issue. However, settling carbonation evaporates are crystallized very slow under warm temperatures and even saturated in effluent warm waters [10–12].

Natural gas, internal engine combusting and coal fired combusting systems account for almost 80% of the total of world carbon emissions today. There is an important need for carbonation in eliminate carbon gases emission to nature, ease of use and storage, existing filler structure, and most low cost rather than amine absorption. Forty percent of global electricity is generated in fossil fuel power plants per annum, with emissions of about 23% of global energy-related CO_2 pollutes (5.5 billion metric tons) of about 14.7 Gt in 2015 [11, 12]. Over a quarter of the electricity demand of Turkey is supplied by coal-fired power plants, with emissions of about 4 million metric tons of CO_2 as pollutant, among about 23% energy-related polluting gas emissions [13, 14].

Therefore, sequestration with effective CO_2 carbonation method is one of the critical choices in addressing global warming and air pollution. It is improving the efficiency of fuel utilization and curing the environment. The renewable energy sources will certainly play a very important role in reducing CO_2 emissions [15]. Those carbonization and amine absorption methods alone cannot address the greenhouse emission issue mainly because world energy consumption will increase significantly as the living standard improves in many parts of the world. The coal combusting boiler types of power plants and internal vehicle engines still emit over 5% of the carbon dioxide, 1% of the sulfur dioxide, and less than 1% of the nitrous oxide emitted by a coal-fired plant. Similarly, injection of compressed gas to cold back injection to geothermal fields sequestrated less of the carbon dioxide as shown in **Figure 1** [16].

The method for storing CO_2 in deep underground geological formations need adequate porosity and thickness for storage capacity, and permeability for gas injection that are critical as shown in **Figure 2**. The storage formation should be capped by
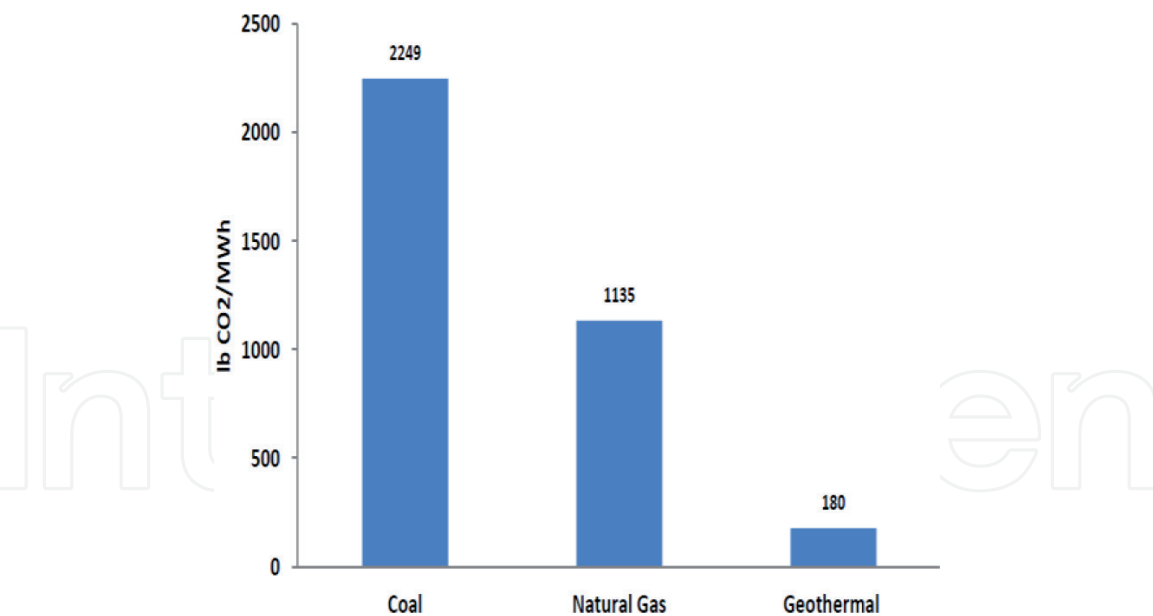
Figure 1.
Comparison of CO$_2$ emissions by coal natural gas and geothermal source.

extensive confining units such as shale, salt caves or anhydrite beds to ensure that CO$_2$ does not escape into overlying, shallower rock units and ultimately to the surface [17].

1.1 CO$_2$ capture and separation from flue gas thermal power plants

The abatement of greenhouse gases is becoming increasingly important. In the last decades, the government issued a White Paper on Energy outlining the national strategies for abating greenhouse gases and filtration systems use in thermal power plants. One of the key options highlighted was the eliminating fly ash and hazardous toxic gas emissions cut and even CO$_2$ from stack emissions and subsequent storage in geological reservoirs (carbon capture and storage can be retrofitted easily onto the tail end of power-plant flue gas streams without requiring complicated integration in Turkey) [18, 19].

Several technologies have been proposed to capture CO$_2$ from power-plant flue gas including absorption, adsorption, cryogenic distillation, and membrane gas separation. The technology examined in this article is polymer-based membrane gas separation. The membranes have been used commercially to refine natural gas and biogas for CO$_2$ [20, 21].
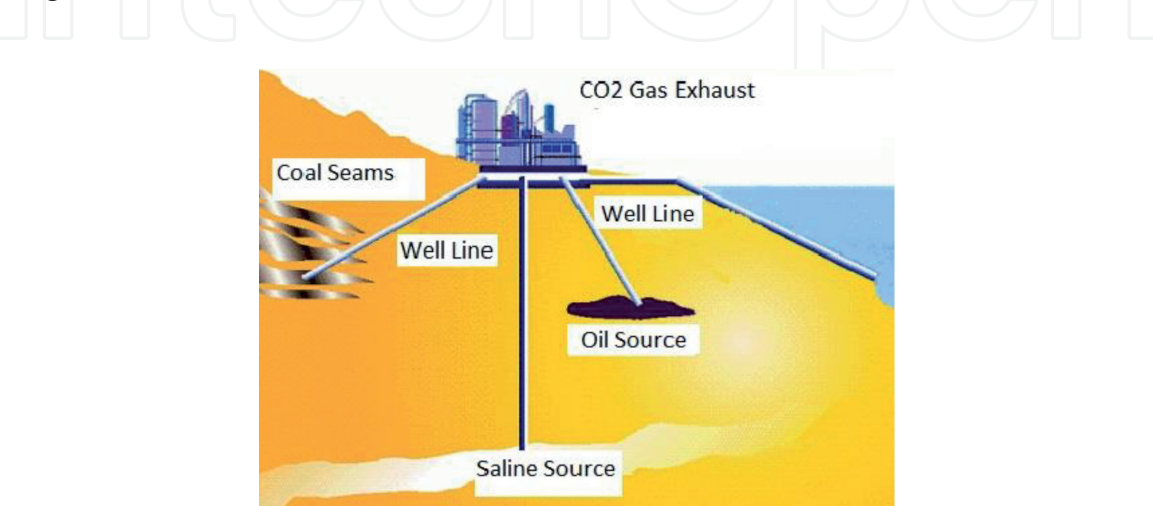

Figure 2.
General chemical carbonation or sequestration path.

1.1.1 Amine absorption

From Fick's law (Eq. (1)), increasing the selectivity of CO_2/N_2 increases the mole fraction of CO_2 in the permeate (y_i) and decreases the mole fraction of CO_2 in the retentate (x_i). Consequently, the driving force across the membrane is also reduced. To obtain the same amount of CO_2 recovered (J_i), the membrane area (A_m) increases and thus the capital costs for membranes also increase. However, as the CO_2 purity of permeate stream (y_i) increases, the flow rate of the permeate decreases, resulting in a smaller post-separation compressor. It is the balance between the cost savings generated by the post-separation compressor and the increase in membrane costs that influences the cost trends [22–24].

1.1.2 Membrane separation

The effective force across a gas-separation membrane is the pressure differential (ΔP) between the feed side and the permeate net, and CO_2 emissions exceeded 550 million tons in 2013. Over 45% were from post-combustion coal-pulverized power plants, and because of this, it is likely that these will be the initial focus of CCS [25–27].

As given below with Fick's law (Eq. (1)), increasing the content of CO_2/flue gas increased the mole fraction of CO_2 in the permeate (y_i) and decreased the mole fraction of CO_2 in the retentate (x_i). Finally, the efficiency of passage across the membrane was decreased. In order to receive high of CO_2 passage (J_i), the membrane area (A_m) increased and thus the capital costs required membrane also increased. Meanwhile, the purity of CO_2 stream (y_i) increased, and the flow rate of the permeate decreased the cost savings generated by the post-separation compressor and the increased the membrane costs that influenced the separation trends [25–29].

Fick's Law:

$$Ji = Yi/Am = -Xi/Am = -Di\, dCi/dt = -Di\, dPi/dt \tag{1}$$

where mass diffusion rate Ji, mass rate of i per area A at diffusion rate constant Di, at pressure or concentrate of permeate change per thickness t.

As the membrane used at atmospheric pressure, compressed feed gas to a high pressure was feasible for CO_2 capture in membrane technology. In our previous work, we have shown that the cost is high because of the high capital costs associated with compressors needed to compress the low-pressure flue gas and the low CO_2 purity product stream. As the feed gas is compressed to 15–20 bar, the recovery of CO_2 was roughly managed [30]. Those case studies showed that the cost for CO_2 capture was at least 30% higher than for CO_2 recovered using amine chemical absorption.

2. Production of reactive coal char and biomass char/char carbon in Şırnak

The energy production by combusting asphaltite, a type of coal, by local alkali rocks such as limestone is advantageous for the development of the South-East Anatolian region and also the industrial construction and diversification [1–5]. As given in **Table 1**, the thermal power station in the region combusting Şırnak asphaltite by addition of 15% limestone şn fluidized bed combustion system emitting much clean exhaust gas out regarding mid power output [31–33].

Flexible and regional targets for a mobile solid waste incineration from an environmental and economic perspective were the following:

- The mobile plant where the waste sorting process is performed can be processed to acquire secondary materials

- Biological treatment of biomass and conversion to compost, which is a market value or energy production by producing methane gas by anaerobic treatment

- Recycling and reducing the amount of waste storage following thermal systems, making it inert and obtaining energy as given in **Table 2**

- Regular land filling and use of landfills for land reclamation and at least the reduction of pollution in the Şırnak Province

Biochar was beneficial in soils around the land as a result of vegetation fires and soil management practices. Intensive study of biochar-rich dark earths in the Amazon (terra preta) has led to a wider appreciation of biochar's unique properties as a soil fertilizer [34–36].

The carbon in biochar resists degradation and can hold carbon in soils for hundreds to thousands of years. Biochar is produced through pyrolysis or torrefaction processes that heat biomass in the absence (or under reduction) of oxygen.

In addition to using soil fertilizers, sustainable biochar dissociation can produce black liquor, oil by-products that can be used as fuel, providing thermal energy. When the biochar is buried in the ground as a soil improver, the natural system may be "carbon negative" [37–39].

Biochar and bioenergy co-production can help combat global climate change by displacing fossil fuel use and by sequestering carbon in stable soil carbon pools. It may also reduce emissions of nitrous oxide **Figure 2**.

Mobile incineration and waste management in Şırnak included energy technologies from recycling, composting and baling waste in order to distribute to long distances. For this, collected waste was classified and iron scrap was send to Iskenderun steel plant. The debris parts were used in road pavements. The combustible waste products controlled organics and plastics. The mayor was aware that the organic products to be obtained from urbanized site should be processed by the sorbent in incineration. These markets are also likely to be sensitive to the quality and quantity of the supply. The distribution of solid wastes in Şırnak Province is shown in **Tables 3** and **4**.

2.1 Pellet char production

Mobile waste management was flexible in terms of incinerating small amounts of waste, as operation, even if it needed to adapt to existing waste type and environmental conditions in the Southeastern Anatolia. Mobile incineration provided the flexible solid waste management of flexible transfer of small amounts of waste to

Thermal power plant size (net)	415 MW
Boiler type	Supercritical
Coal type	Asphaltite
Thermal efficiency (LHV)	38%
Temperature	500
Pressure	85 bar

Table 1.
Processing conditions and composition of a typical supercritical bituminous power-plant flue gas in Şırnak.

Total	Landfill	Incineration	Energy recovery	Backfilling	Recycling	
(million tons)			(%)			
EU-28	2319.5	47.4	1.5	4.7	10.2	36.2
Belgium	42.8	8.2	4.3	13.6	0.0	73.9
Bulgaria	175.7	97.9	0.0	0.1	0.0	2.0
Czech Republic	19.9	17.3	0.4	5.1	29.1	48.1
Denmark	17.7	21.7	0.0	20.7	0.0	57.6
Germany	370.7	19.2	2.3	10.5	25.3	42.7
Estonia	20.7	65.6	0.0	2.5	11.9	20.0
Ireland	10.0	42.6	0.1	7.2	37.4	12.7
Greece	67.1	88.4	0.0	0.2	8.1	3.2
Spain	103.4	47.9	0.0	3.4	12.6	36.1
France	299.7	29.3	2.0	4.5	10.7	53.6
Croatia	3.5	51.1	0.0	1.4	2.0	45.5
Italy	129.2	16.0	5.2	1.6	0.2	76.9
Cyprus	1.8	58.9	0.0	1.7	25.9	13.5
Latvia	1.9	34.8	0.0	8.7	0.9	55.5
Lithuania	4.5	67.6	0.1	4.1	2.5	25.8
Luxembourg	8.5	38.3	0.0	2.5	16.0	43.3
Hungary	13.7	39.4	0.7	8.9	3.7	47.3
Malta	1.6	28.9	0.4	0.0	37.5	33.3
The Netherlands	130.6	45.4	1.0	7.9	0.0	45.7
Austria	53.9	38.6	0.2	6.5	20.1	34.7
Poland	182.4	24.9	0.4	2.7	21.5	50.5
Portugal	9.9	31.8	10.0	3.1	0.0	55.0
Romania	172.2	94.4	0.0	1.3	0.6	3.7
Slovenia	5.4	9.2	0.6	4.9	33.5	51.8
Slovakia	7.1	53.8	0.8	4.4	0.0	40.9
Finland	93.3	80.9	0.5	4.8	0.0	13.8
Sweden	163.3	84.4	0.1	4.7	1.6	9.3
The United Kingdom	209.0	41.5	3.6	0.9	10.4	43.6
Iceland	0.5	30.7	0.0	2.7	0.6	66.0
Norway	11.7	17.9	0.5	35.8	5.3	40.5
Montenegro	1.0	98.8	0.0	0.1	0.0	1.0
Form. Yug. Rep. of Macedonia	1.5	98.7	1.3	0.0	0.0	0.0
Albania	1.2	74.8	3.1	0.5	0.0	21.6
Serbia	49.4	97.3	0.0	0.1	0.0	2.6
Turkey	79.3	70.2	0.0	0.7	:	29.0

Table 2.
Distribution of urban wastes conversion and energy generation by European countries, Eurostat waste management Statistics 2016 [40].

Waste type	Theoretical amounts, tons per annum		
	Regular	%	Heat value, kcal/kg
Agricultural waste	13,000	14.5	2100
Cardboard	12,000	12	2100
Poultry	9000	9	1100
Sewage	32,000	33	1100
Dairy	1000	1.2	1700
Forest	32,000	33	3100

Table 3.
Biomass waste type of Şırnak Province and distribution in quality.

Biomass char	C, %	Ash, %	Moisture, %	S, %	P, %	Na + K, %	Mg,%	Ca
Agricultural waste char	13	3.4	69	0.1	1.1	1.1	1.1	1.1
Cardboard char	12	0.5	44	0.1	0.1	0.1	0.1	0.1
Poultry char	9	8.9	65	0.9	5.1	3.1	2.1	3.1
Sewage char	2–3	77–87	11–19	0.3	2.1	2.1	2.1	2.1
Dairy char	1	4–5	88	0.2	4.1	4.1	1.1	4.1
Forest waste char	32	1	55	1.3	1.1	1.1	2.1	1.1

Table 4.
Chemical carbonation quality of biomass waste char of Şırnak Province and distribution in quality.

direct treatment systems as much hard environmental conditions [41]. The drying and torrefaction were packing and pelleting of biomass wastes managed for Biomass/Waste Drying System Pelleting System/Cooling /Sieving/Bagging System, Wood Char Pelleting (**Figure 1**).

2.2 Mobile coal char pelletization in Şırnak

In the Project, the scope of this study is 5 MW with regional biomass waste and Şırnak asphaltite primary energy source to evaluate Şırnak's biomass for electricity generation. The common burning of biomass resources within the special firearms is designed and proposed by providing legal and institutional, economic and environmental impact assessment. However, the use of Şırnak biomass energy source is to develop solutions against technological coal burning pollution. Biomass wastes for most of Anatolia, Southeastern Anatolia Region and Şırnak Province in Eastern Anatolia and Southeastern Anatolia region, which mostly contains high elevation figures in Turkey, and solid fuels are consumed. In addition, energy production is realized with thermal power plants especially Şırnak asphaltite and Afşin Elbistan lignite [42, 43] in the analysis, as the coal slime Sırnak asphaltite slime samples was used and the char as shown in **Figure 4**, the reduction of the coal samples was shown in semi pyrolysed fractions. The chemical analysis temperature was continuously weighed and the combustion analysis was carried out in the bath oven. The test results are shown in **Figure 5** for biomass pellets and coal sample. As shown in **Figure 6**, the effect of addition is determined in combustion experiments, the lime on desulfurization and emission is hydrated, and the reactor temperature was 500°C and only 10% MgO char pellet at weight rate. The temperature varied
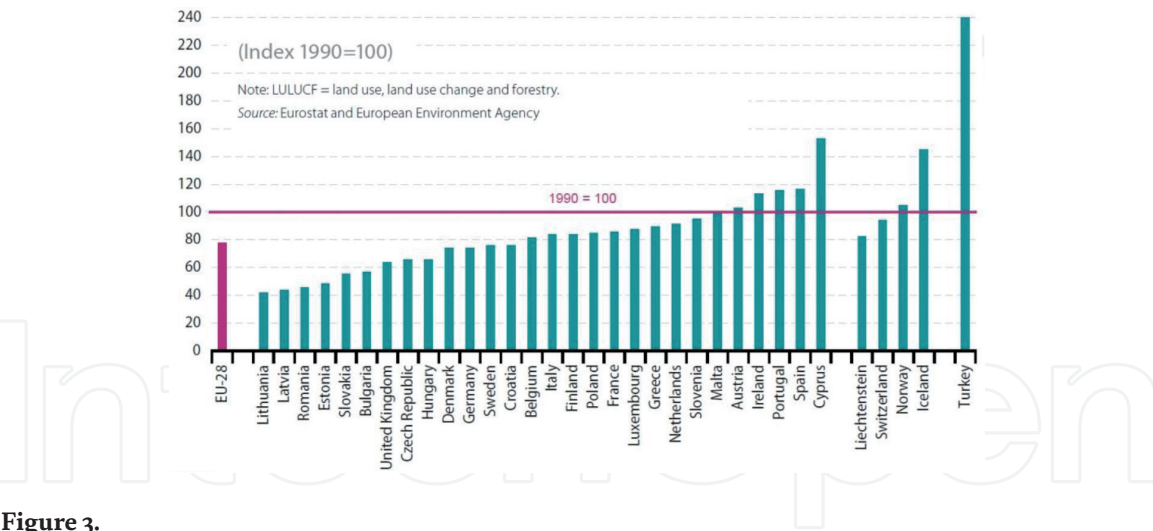
Figure 3.
Green gas CO₂ emission to environment in EU28, Eurostat 2016 [40].

to 550°C and solid waste mixture samples were analyzed for sulfur content on semi pyrolysis char samples. Experimental results are shown in **Figure 6**. For the production of pyrolysis oil from a mixture of waste at weight rate, 50% animal manure and 50% human manure at three production stages were put in the kiln at 1 h, 8 h, 14 h and at total 50 h pyrolysis completed. The pyrolysis oil product was in total over 9 kg/100 kg. The production was executed using a feed rate of 150 kg/h, with average pyrolysis temperature of 500°C (**Figure 4**).

The mass, energy and carbon balance for the pyrolysis of animal manure and human manure compared by Şırnak asphaltite in char production was presented in **Table 3**. The pyrolysis oil and char yield (carbon basis) were significantly lower for the manure compared to coal. That was for the reason of higher moisture content of the type manure wastes so was over than 80%, far optimal processing, which often resulted in greatly disturb the black liquor oil production. Especially the char yield was higher for the manure pyrolysis even providing phosphate ash, which could very likely be advantageous in emission control sorbent production. In a full-scale pyrolysis plant, the energy value from the char was not lost, but will be recovered via decantation systems. The high yield of water phase for the manure waste types was not a suitable indirect char output as the result of the weight of char next to high moisture content evaporated hardly from the feedstock. Indirectly, the phosphate content of manure types also increased high ash content of the char due to phosphate ash. Ash components such as phosphor and potassium were known to enhance the sorption gaseous components as the desulfurizing components. The gas yield was not higher for the manure pyrolysis case, and this was about the lower pyrolysis temperature, in combination with a lower mass balance output received as given in **Table 5**. The analysis showed that soot formed
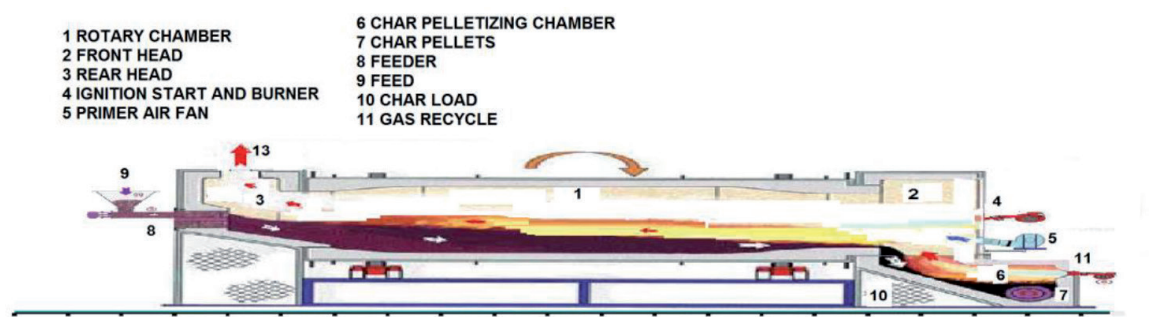

Figure 4.
Biomass/waste drying system pelleting system/cooling /sieving/bagging system, wood char pelleting.

from the light hydrocarbons within the reactor or unconverted char particles formed during the conversion of the pyrolysis oil. Animal manure and human manure could be converted into pyrolysis oil at laboratory scale. The pyrolysis oils were converted into syngas in a fluid bed flow gasifier, which was operated at a capacity of 2 kg/h pyrolysis oil input. Temperatures around 950°C were obtained, yielding a methane-rich syngas product with volume fractions of 26% CO, 10% H$_2$ and 10% CH$_4$, 13% CO$_2$ on dry, and N$_2$ free basis for both pyrolysis oils. Animal and human manure-derived pyrolysis oil was successfully converted into methane-rich syngas by Şırnak asphaltite.

In the pyrolysis experiments with addition of hydrated lime, reactor temperature changed between 400°C and 650°C and asphaltite samples mixed only by %10 lime. Products received from pyrolysis of coal specimens were subjected to analysis for sulfur holdup managed effectively (**Tables 5** and **6**).

The reactive contents of produced semi carbon char pellets are given in **Table 6**.

With the mobile pyrolysis system in Şırnak Province, the urbanization organic waste transformed into energy and fertilizer. For direct heating systems used in Şırnak, thermal insulation and coal boilers feed reduced 4–5% by weight of fuel. The boiler bottom ash could be used as filler material in cement and lime plants close to the locality, 10% by weight potentially. The fly ash of Silopi thermal coal power plant was used as sorbent in fluidized combusting system in order to reduce hazardous gas pollution at stack of plants.

Figure 5.
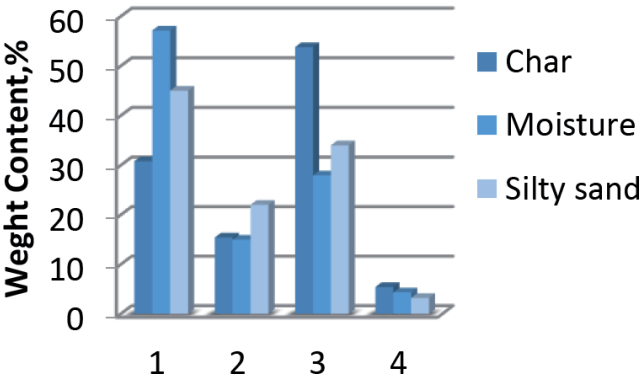*Reactive biochar picture for carbonation and carbon use.*

Figure 6.
The component distribution of reactive char of different biomass waste sources for Şırnak biomass and asphaltite coal. (1) Coal Slime, (2) Municipal Sewage Sludge, (3) Forest Biomass Waste, and (4) Mixture semi Char.

	Animal manure	Human manure	Asphaltite
Pyrolysis oil			
Mass (g kg^{-1})	84.1	55.7	143
Energy (J J^{-1})	0.588	0.553	0.47
Carbon (mol mol^{-1})	0.582	0.420	0.382
Water phase			
Mass (g kg^{-1})	457	526	25
Gas			
Mass (g kg^{-1})	154	132	334
Energy (J J^{-1})	0.068	0.049	0.068
Carbon (mol mol^{-1})	0.120	0.13	0.120
Char			
Mass (g kg^{-1})	97	87	140
Energy (J J^{-1})	0.166	0.141	0.266
Carbon (mol mol^{-1})	0.073	0.070	0.163
Ash (g kg^{-1})	54	94	360
Total			
Mass (g kg^{-1})	999	977	999
Energy (J J^{-1})	0.924	0.960	0.924
Carbon (mol mol^{-1})	0.979	0.935	0.979

Table 5.
Mass, energy and carbon balances for the products in char production for carbonation/carbon use of flue gas of thermal power plants.

Şırnak asphaltite + sewage content, %	P, g	C, g	N, g	K, g	Na + K, g	Ca, g	Mg, g
A. 82 + 18	323.3	1123.3	23.3	23.3	323.3	323.3	323.3
B. 70 + 30	744.5	2214.5	445	44.5	744.5	744.5	744.5
C. 50 + 50	2122.2	4442.2	2220	162.2	2122.2	2122.2	2122.2

Table 6.
The humus chemical contents for carbonation activity of produced semi char pellets from sewage sludge and Şırnak asphaltite mixture chars used in microwave carbonation tests.

3. CO_2 sequestration and carbonization

Sequestration deposits of CO_2 require salt or geothermal space underground for compressed CO_2 to allow injection. The compressed CO_2 reaches a phase known as 'supercritical.' This state is achieved by exposing the CO_2 to temperatures over 31.1°C and pressure over 73.9 bars. The sequestration density of CO_2 will be managed by geological deposition depth, until about 800 m or over a dense supercritical state [15, 16].

The mineral carbonation, a process of converting CO_2 into stable sequestration, was studied extensively to capture and store CO_2. However, most of the Ca and Mg, forsterite sequestration studies were investigated at lab scale. Preliminary and pilot scale studies for accelerated mineral carbonation (AMC) were conducted at
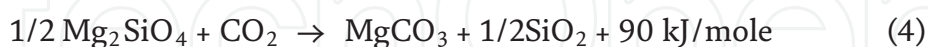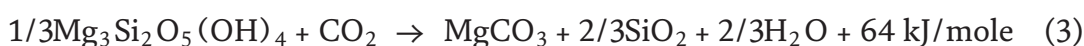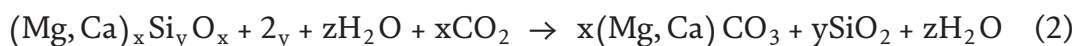
one of the largest coal-fired power plants (2120 MW) in the USA by reacting flue gas with fly ash particles in a fluidized bed reactor. In the preliminary experiments, flue gas CO$_2$ and SO$_2$ concentrations decreased from 13.0 to 9.6% and from 107.8 to 15.1 ppm, respectively, during the first 2 min 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 (**Figure 3**) [15, 16].

Fly ash utilization and using CO$_2$ 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 CO$_2$ [13–15].

4. Method of microwave carbonation

Mineral carbonation reactions are known to geologists and occur spontaneously on geological time scales [43–64]. For example, the reaction of CO$_2$ with common mineral silicates to form carbonates like calcite and magnesite or calcite is exothermic and thermodynamically favored [64–78]. The design for carbonation microwave furnaces is shown in **Figure 7**.

The reactions given below transformed as that the CO$_2$ gas to Ca carbonates by Reaction 1 has the potential to convert naturally occurring silicate minerals to hydrated and carbonated minerals of silica and silicates. The process followed natural chemical formations such as altering of rocks to form carbonates over million year time periods. Reaction 2 illustrates the transformation of the common silicate mineral serpentine, Mg$_3$Si$_2$O$_5$(OH)$_4$, and CO$_2$ into magnesite, MgCO$_3$, silica and hydrate. At theoretical case, a unit of serpentinite can dispose of approximately one-half of CO$_2$. Reaction 3 illustrated the conversion of forsterite and was the final common silicate mineral olivine. A unit of olivine can dispose of approximately two-thirds of CO$_2$. Again, the reaction is exothermic and releases 90 kJ/mole of CO$_2$.

$$(Mg, Ca)_x Si_y O_x + 2_y + zH_2O + xCO_2 \ \rightarrow \ x(Mg, Ca)CO_3 + ySiO_2 + zH_2O \quad (2)$$

$$1/3Mg_3Si_2O_5(OH)_4 + CO_2 \ \rightarrow \ MgCO_3 + 2/3SiO_2 + 2/3H_2O + 64\ kJ/mole \quad (3)$$

$$1/2\ Mg_2SiO_4 + CO_2 \ \rightarrow \ MgCO_3 + 1/2SiO_2 + 90\ kJ/mole \quad (4)$$

An illustrated in the process shown in **Figure 8** of the searched the carbonization process as presented in **Figure 3**. CO$_2$ from one or more power plants is transported to a carbonation reactor, combined with fly ash slurry treated at certain appropriate reaction conditions until the desired degree of carbonation was reached. The resulted solution chemistry yielded olivine conversions of 90% in 24 h and 83% within 6 h. The study shows that further modifications of the same basic reaction can achieve 65% conversion in 1 h and 83% conversion in 3 h [16]. A recent literature review indicated that weak carbonic acid treatments had also been suggested for Mg extraction in the prior literature [17]. Carbonation tests at ARC resulted in heat pretreated serpentinite conversion up to 83% conversion in 30 min lower than 115 bars [18]. By increasing sodium bicarbonate concentration, the carbonation reaction of serpentinite can reach 62% conversion under 50 bars.

The products of carbonation, which were slurries of hydrated and carbonated minerals and lean gas CO$_2$ in aqueous, were followed by decantation separation. The exhaust CO$_2$ is recycled. The finer solid matter was transferred as filler for
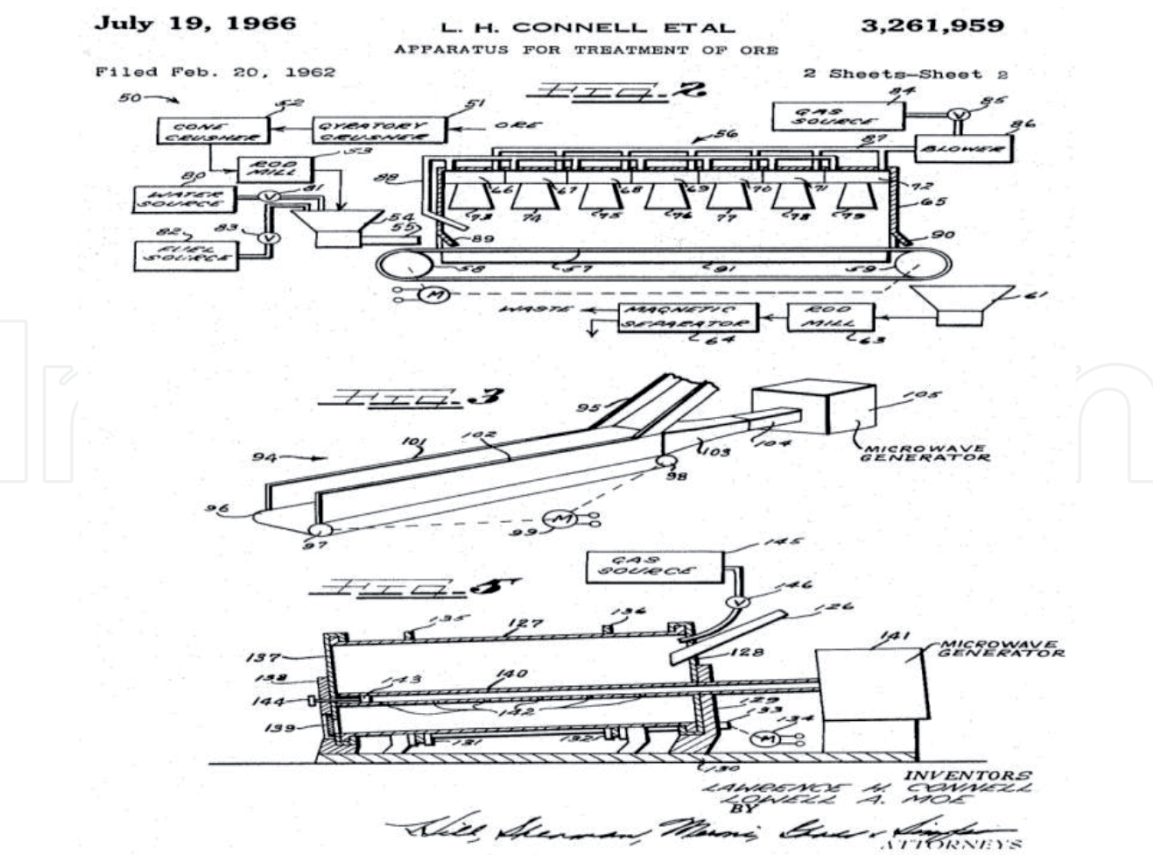
Figure 7.
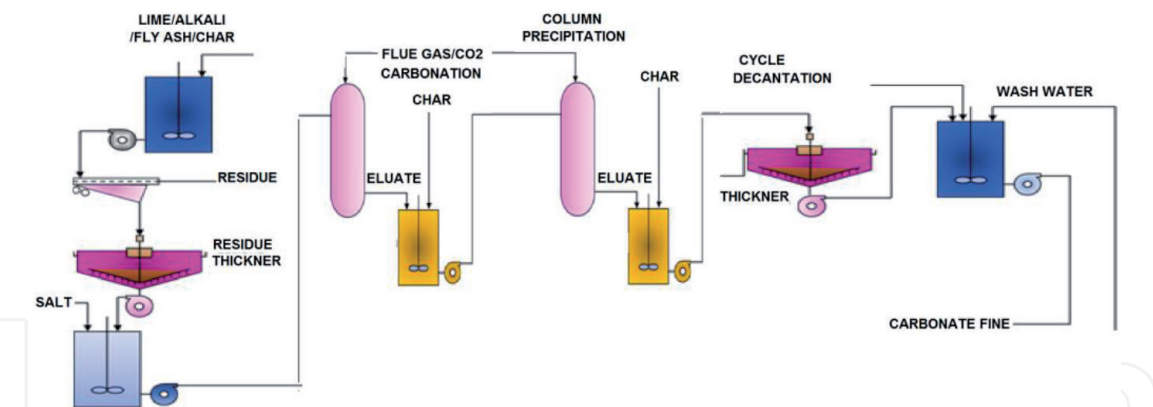*Types of CO_2 microwave carbonation furnace for sequestration path by fly ash.*

Figure 8.
CO_2 carbonation or sequestration path by fly ash.
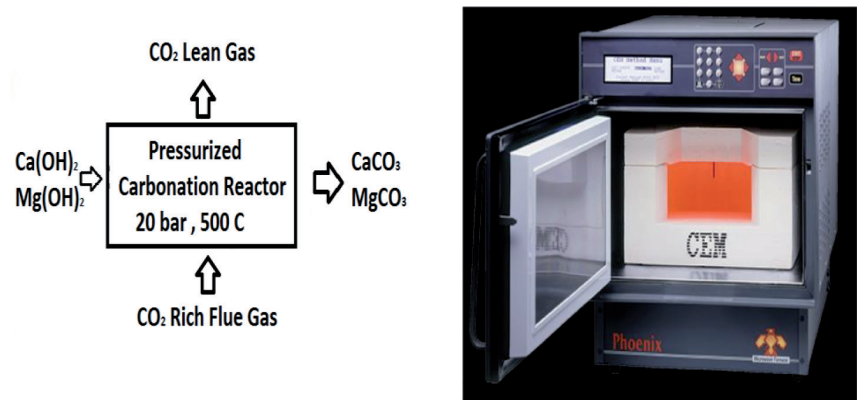

Figure 9.
(a) Microwave laboratory steel jar CO_2 carbonation by fly ash/coal char and (b) microwave ash laboratory furnace.

construction works or the carbonated materials were returned to the caving in mine site. Almost calcium and magnesium oxide (MgO) content in the magnesium silicate minerals were of 40% and 60–70% reactive efficiency for the carbonation regarding mass balance of Eq. 1. A 100 MW power plant in Şırnak, generating approximately 200 tons/day of CO$_2$, would require just over 100 tons/day of calcium and magnesium containing fly ash. Several fly ash types in Turkey contain sufficient calcium and magnesium oxide quantity in silicate mineral to provide raw materials for the mineral carbonation (**Figure 9a** and **b**).

5. Experimentation method of microwave carbonation

In this research, representative specimens of the different types of Turkish fly ash/coal char sources in Şırnak were classified to calcium content and bicarbonate by chemical analysis. Gas samples of 10–20 kg tubes from Silopi coal power stations were used. Chemical analyses of salt mixtures used in the experiments are given in **Table 7**.

Chemical reaction of molten salt sources is illustrated in **Figure 6**. Carbonation salt mixtures contain reactive 25, 35 and 45% hydrated lime and rest reactive caustic, respectively. Salt mixtures contained microwave radiation emitter 2.2, and 5.7% serpentinite and also non reactive, respectively. The crystal waters and moisture of salt hydrates dissociate under microwave radiation and salt mixtures resulted in various sulfate compounds. Substantial fractions of these compounds in carbonates could be stuck during clay dissociation to pore leaks. Fifty–sixty percent of arsenic, lead, manganese, mercury and selenium could be removed by solid salt oxides in transforming during cooling.

Screen analysis of Turkish lignite fly ash samples was done by standard Tyler screens and particle size distributions and normal distributions of lignite samples were tested. Specific surface area fly ash/coal char samples were about 1.76–4.2 m^2/g determined by BET surface analyzer and highly sufficient in order to react with gaseous CO$_2$. About 80% of weights of samples were 0.1 mm. Ash particles in lignite samples were mainly distributed below 40 and 100 μm size fractions. Main reactive silicate structure is widely distributed and pore structures are associated with ash minerals. Coarse alkali oxides are also seen in the picture shown in **Figure 10**.

Salt mixture composition, g/kg	Ca1	Ca2	Ca3	Mg1	Mg2
Ca^{2+}	550	422	220	43	26
Fe^{2+}	7.12	3.69	1.1	0.2	0.5
K$^+$	63	79	59	102	130
Mg^{2+}	10.6	6.7	3.0	489	310
Mn^{2+}	0.6	0.02	—	0.01	0.01
Na$^+$	15	18	6	16	9
F$^-$	0.35	0.51	0.55	—	—
Cl$^-$	19	122	250	27,440	114,300
NO$_3^-$	1.34	0.9	0.92	—	—
SO$_4^{2-}$	13.43	14.5	14	11.34	35.47

Table 7.
Chemical analyses of salt mixtures used in the microwave carbonation experiments.
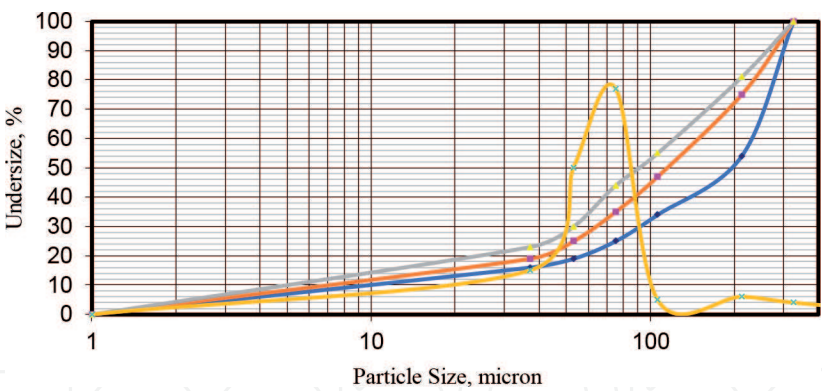
Figure 10.
Particle size distributions and normal size distributions of fly ash/coal char samples tested.

6. Results and discussions

The major technical challenge was hindering the use of carbonation method for CO_2 due to low reaction rate. The reactivity of rock was extremely slow. The priority was given to improving faster reaction pathways. The optimized process should be economical. Although the carbonation reactions were exothermic, it is generally very low-grade heat with the long reaction time and demanding uncontaminated reaction conditions (**Figure 11**).

The environmental impact from mining, mineralization and carbonation processes must be considered in carbonation. We succeeded in achieving shortened carbonation reaction times employing fly ash/coal char containing lime and calcium magnesium silicates such as gehlenite and mehlenite. Reaction took 4 h to reach 40–50% completion of carbonation with fly ash/coal char. The reaction required microwave temperatures of 450–550°C, pressures of 10–20 bar (**Figure 12**), and mineral particles in the −100 μm size range.

Because the high pressure requirement of the carbonation reaction will certainly lead to high process costs, the team is modifying solution chemistry to allow reaction to proceed at a lower pressure and temperature. The research showed that the concentration of sud caustic in the solution was critical to the reaction rate. The high CO_2 pressure will lead to increased CO_2 absorption in the solution and thus enhance the liquid concentration. Adding bicarbonate such as sodium bicarbonate in the solution will significantly increase the liquid concentration even at a relatively lower CO_2 pressure (**Figure 13**).

In the carbonation experiments with addition of fly ash/coal char, reactor temperature changed between 400°C and 650°C and Silopi fly ash/coal char samples mixed only by 10% rate. Products received from carbonation of ash specimens were subjected to analysis for gas holdup determination. Test results of carbonation by fly ash/coal char and also salt mixtures are seen in **Figure 10**.
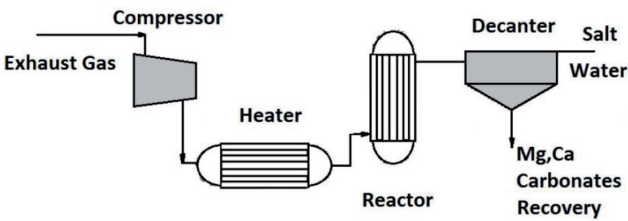

Figure 11.
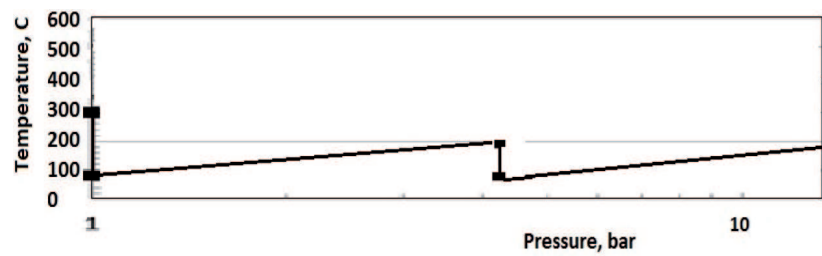*Reaction diagram of molten salt mixtures and fly ash/coal char used in carbonation process.*

Figure 12.
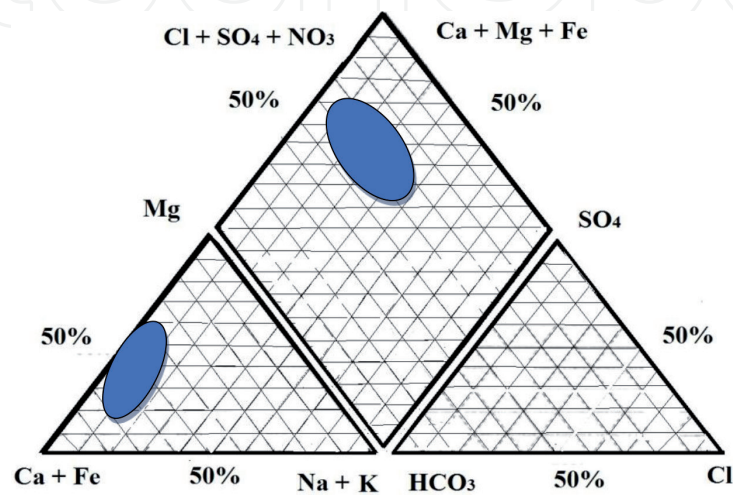*Pressure-temperature steps for microwave carbonation process.*

Figure 13.
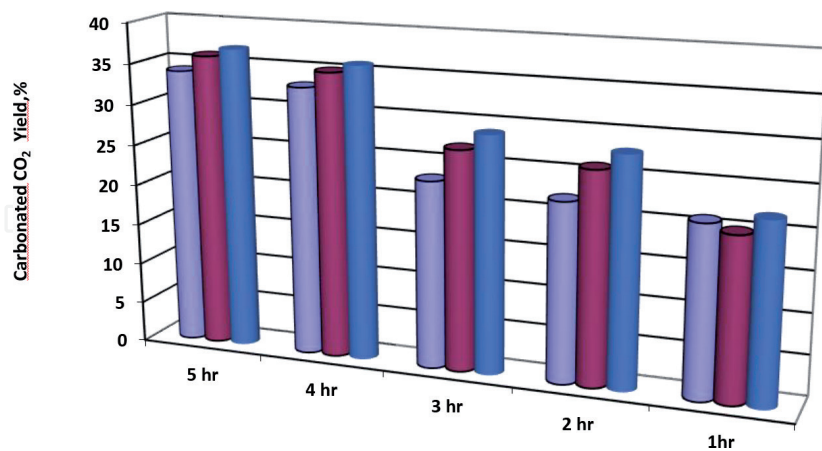*Piper diagram of salt mixtures used in microwave carbonation process.*

Figure 14.
Effect of carbonation time for microwave carbonation over conversion yield rates in salt mixtures used.

From the point of view of carbonation experimentation, Silopi flue gas carbonation value was significant. The quantity in the carbonation chambers for flue gas samples was determined for different source evaluation and for reducing the effect of ash content of coal samples in order to optimize carbonation rates of fly ash/coal char samples. As given in **Figure 14**, gas conversion yield for salt mixtures and alkali caustic acts were distinctly improved.

7. The column reactor of microwave carbonation process

In the carbonation experiments with addition of fly ash/coal char, reactor temperature changed between 400°C and 650°C and Silopi fly ash/coal char samples mixed only by 10% rate. Products received from carbonation of ash specimens were subjected to analysis for gas holdup determination. Test results of carbonation by fly ash/coal char and also salt mixtures are seen in **Figure 15**.

From the point of view of carbonation experimentation, Silopi carbonation value was significant. The quantity in the carbonation chambers for Ca 2 samples were determined for different source evaluation and for reducing the effect of ash content of coal samples in order to optimize carbonation rates of fly ash/coal char samples. As given in **Figure 15**, gas conversion yield for salt mixtures and alkali caustic acts were distinctly improved.

The tests with the microwave carbonation by fly ash packed bed under the high-pressure feed column process were carried out. As shown in **Figure 15**, for column permeate systems, the gases were recycling at three steps. As shown in **Figure 16**, the melted salt types affected greatly carbonation conversion under microwave radiation as giving the products of 36 gr sodium and Ca carbonates by fly ash added at weight rate of 10%.

At the design stage of the unit, it was decided that the overall capital cost of the sequential column system was much higher than that for the high-pressure feed packed bed column method (**Figure 17**). The column permeates on the recycling gas stages were at the largest cost, accounting for over 10% of the total equipment costs. In comparison, for the high-pressure feed process, the cycling time cost accounts for less than 70% of the total equipment costs. For the microwave carbonation by coal char tests under column gas flow conditions, the results were shown in **Figure 18**. As shown in figure, the melted salt types affected greatly carbonation conversion under microwave radiation giving the products of 64 gr sodium and Ca carbonates by coal char, Şırnak asphaltite char type A, added at weight rate of 10%.

Over 10 bar pressure, the weight percent increases in salt mixtures for pressurized column processes. First, without the feed-gas compression, the overall total carbonate conversion decreased. Second, the column pressure difference in caustic permeate steps was less than 2 bar that for the high-pressure feed process at 12 bar. In this analysis, the amount of CO_2 recovered per second (J_i) was fixed at 85–90% of the flue gas or 2.49 kmol/s. In addition, P_i^* and δ were constant. Because ΔP is reduced for the column rough stage, Fick's law (Eq. (1)) showed that the required membrane area (A_m) should increase to maintain a fixed value for J_i. Hence, the cost of the microwave carbonation three step stream column unit increased under pressurized cycling conditions.

The second-largest conversion step was the post-cycling conversion, also shown in **Figure 18**. The rough column unit and scavenger CO_2 column together accounted
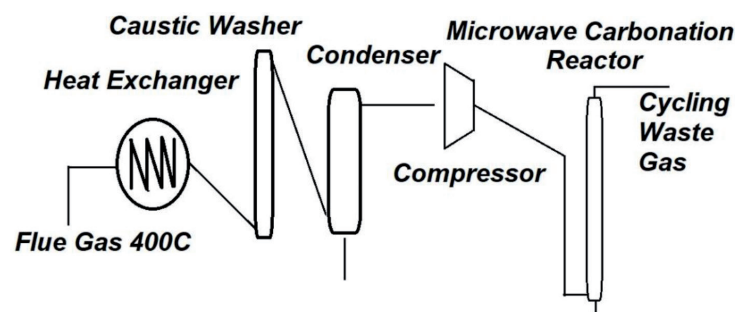

Figure 15.
Simplified diagram of caustic washing and following microwave carbonation with pressurized conditions.
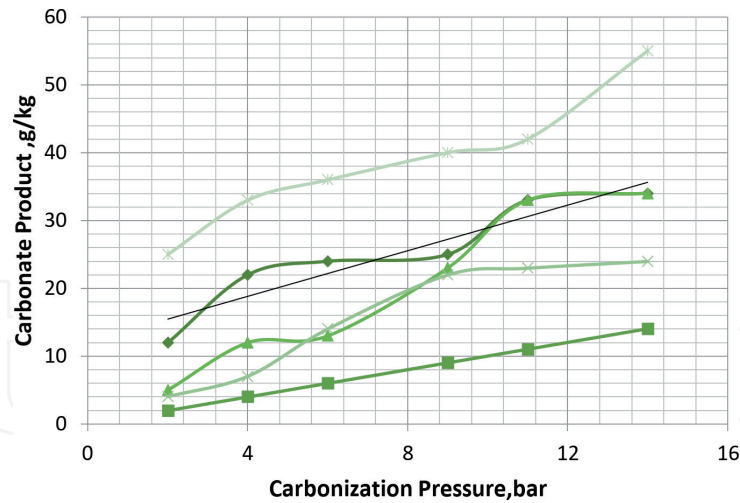
Figure 16.
Percentage melted salt carbonate product by column pressurized feed in microwave carbonation by Şırnak asphaltite char at 10 wt% systems under high pressure (HP) feed conditions.
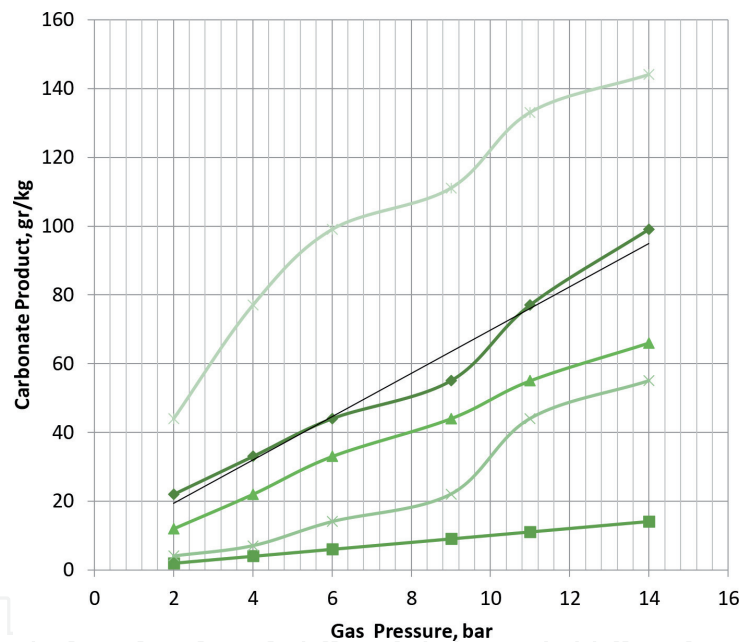

Figure 17.
Percentage melted salt carbonate product by column pressurized feed in microwave carbonation by Şırnak asphaltite char at 10 wt% systems under high pressure (HP) feed conditions.

for approximately 75% of the total salt melting system. **Figure 19** illustrates that the two most expensive items are replacing the membranes and the energy required for compression. The results from **Figures 17** and **18** indicate that carbonate weight could be achieved by the following:

The effect of CO$_2$ content was ascertained as depended on flue gas type. The CO$_2$ content will influence the rate at which CO$_2$ is carbonated from the feed gas. For a fixed flux of CO$_2$ across the thermal column, increasing the membrane's CO$_2$ conversion will decrease the required melting area and thus reduce the conversion time.

The main parameters that affect carbonation under microwave-radiated salt mixtures were the CO$_2$ purity and the impact on capture cycling time.

The parameters that affect the CO$_2$ purity are the pressure ratio and the column CO$_2$/HC selectivity. Regarding Fick's law, the ratios of the fluxes for the CO$_2$ are determined as 60 g carbonate conversion under 10 bar in 11 h cycling time (**Figure 19**).
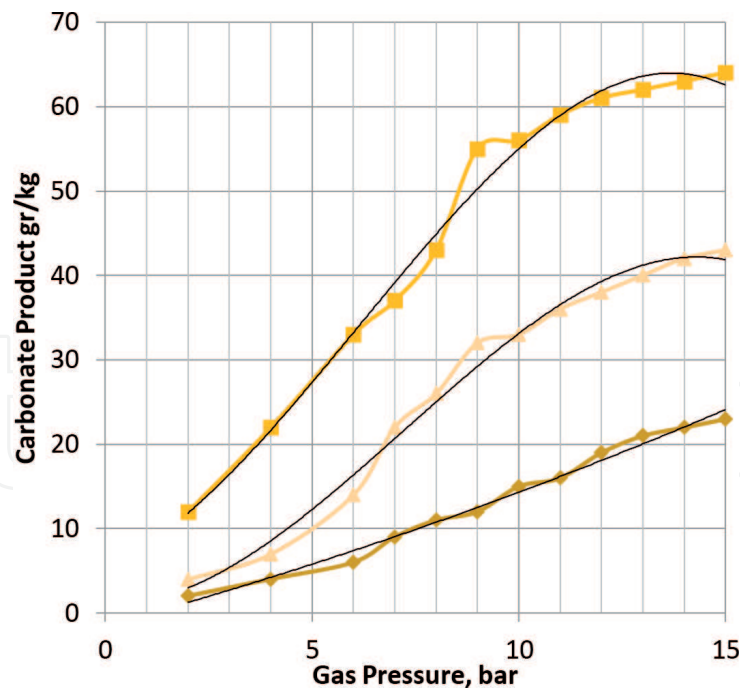
Figure 18.
Effect on CO_2 content with changes in the CO_2/HC of misty flue gas selectivity at pressure ratios of 2–14 bar.
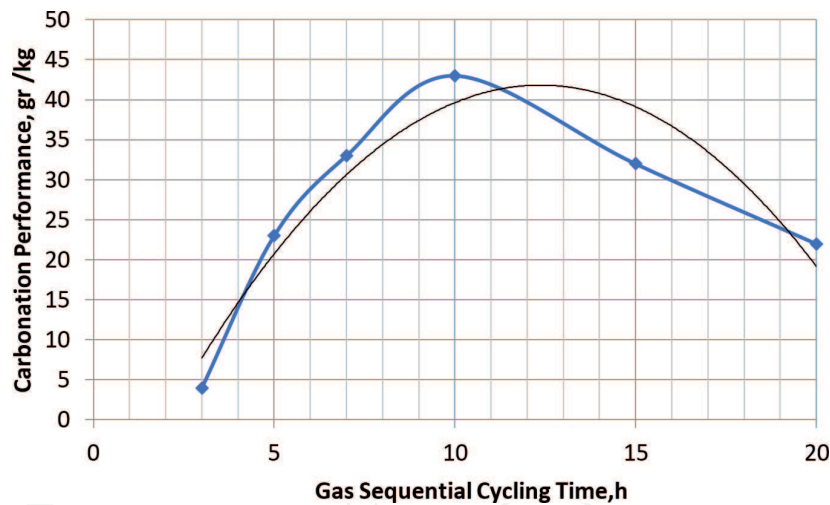

Figure 19.
Change in the capture cost gas sequential cycling time, a function of the three-step column systems under high-pressure carbonation system.

The effect of CO_2 selectivity was not as effective on carbonation due to pressurized carbonation system. By changing to column permeate conditions, the salt/coal char carbonation CO_2, especially for the 10 h column scavenge ring configuration, was significantly improved. However, one disadvantage was that the purity of the CO_2 in the column gas stream was low. It was less than 20% for the rough salt column and less than 80% for scavenger. In the sorption column with salt mixtures, to compete with other CO_2 capture technologies such as chemical absorption and man should also produce high conversion by microwave salt melting and carbonation of CO_2 in coal char.

8. Stabilization quality: geotechnical properties carbonate filler

American Standard (ASTM 3080) experiments were carried out in the fill area. The specimens were tested to determine the geotechnical properties based on the

Component%	Şırnak carbonate	Volcanic slag	Tatvan pumice
SiO$_2$	33.48	50.50	60.13
Al$_2$O$_3$	9.10	14.61	17.22
Fe$_2$O$_3$	4.52	24.30	4.59
CaO	22.48	2.30	2.48
MgO	9.80	1.28	2.17
K$_2$O	2.51	2.51	3.51
Na$_2$O	1.35	1.35	4.35
Ign. loss.	10.9	0.21	4.12
SO$_3$	3.32	0.12	0.52

Table 8.
The chemical composition values of Şırnak carbonate, volcanic cinder and Tatvan pumice.
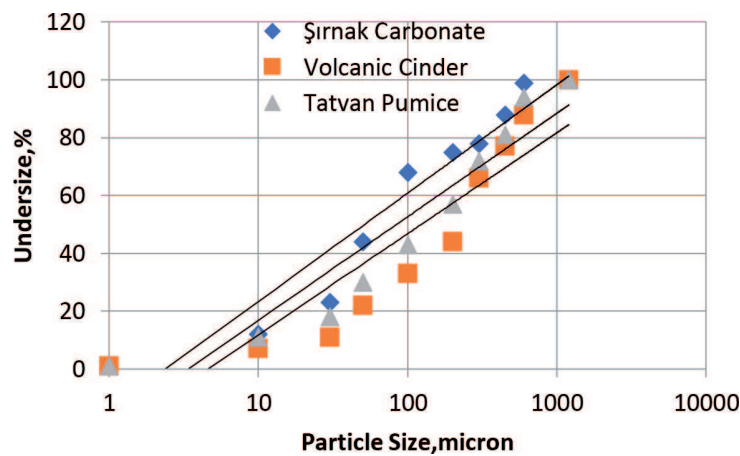

Figure 20.
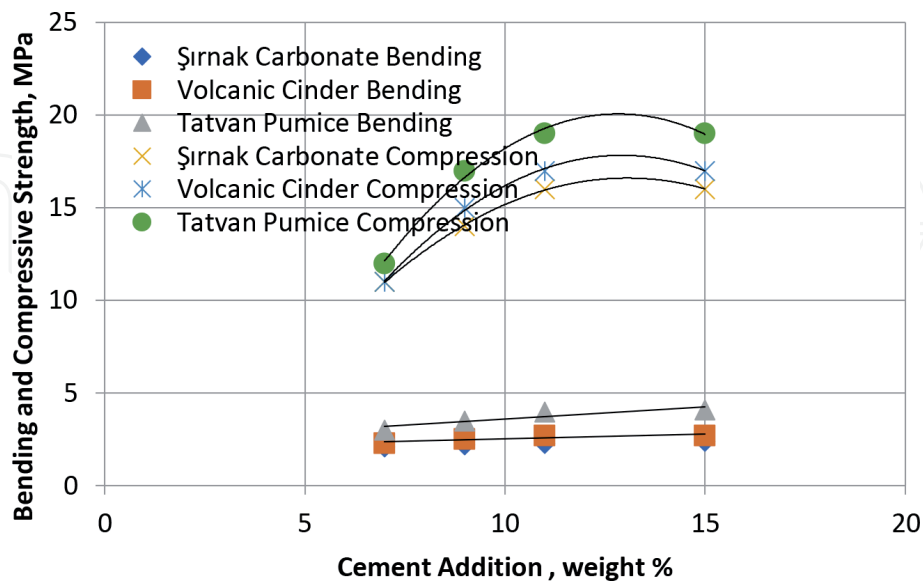*The grain size distributions of the carbonate output material.*

Figure 21.
The tensile and compressive strength of the carbonate cemented block materials.

representative masses in the study area, where the soundings of content are given in **Table 8**. The grain size distributions of the carbonate output material used in stabilization is shown in **Figure 20**. The stabilization cementing blocks of 7 cm cubes

were subjected to uniaxial compression strength tests at 28 curing time period. The results for stabilization as bottom layer in the landfill were shown in **Figure 21**. The cemented blocks used Şırnak carbonate and volcanic cinder and pumice were tested as seen from **Figure 21**.

The stability by cement type puzzolane, but local wastes such as fly ash or mid ash of power plants, was used for ground strengthening. The discharge hazardous risk landfill was practiced for contaminated soil area for preventing stabilization and remediation. The strengths of the ground blocks were dispersed to 0.8–1.2 MPa in shear strength and 3.7–4.4 MPa in compression strength. Thus, with the ideal packing, the strength of the mixed cemented blocks produced from these fine fillers and waste mixtures can also reach 11.2 MPa in compression strength in 3.9 MPa in shear strength.

9. Conclusions

This study reveals suitable large-scale operating units in order to achieve the carbonation method as a viable carbonation tool at industrially relevant scales by using fly ash/coal char. Carbonation liquid and gaseous products with fly ash/coal char may change to near 20–45% yield performances with time increase from 1 h to 12 h.

While there is a potential to utilize other types of flue ashes in mineralization, lime or similar alkali can be evaluated to sequester CO_2 allowing clearly significant amounts. There are even researches that succeeded using serpentine and olivine [34–38]. Consequently, the flue gas should be continuously monitored to measure flue gas flow at depleted gas outlet in order to reprocess it.

Other harmful emissions caused by flue gas containing high sulfur (S) and mercury (Hg) content can be eliminated by this method. In that study, results suggested that an appreciable amount of flue gas CO_2 and significant amounts of SO_2 and Hg can be directly captured and mineralized by the fly ash/coal char particles.

Even with progress made so far, to develop an economical method to sequester CO_2 with minerals is still a challenging task, because the process is still relatively slow, and most reactions require high pressure and moderately elevated temperature.

Figure 9 illustrates for the 11 h carbonation period show that cost of carbonation of CO_2 with increasing CO_2 salt carbonation at 65 g by coal char. The results show that the capture cost can be reduced to almost U.S. $20/ton CO_2 avoided when the CO_2 permeability was at high pressure columns 300 bar in the CO_2/N_2 selectivity.

Coal char with CO_2/soot preference of 40–60 mg soot and tar content reduces the carbonation from flue gas to salt reaction below 20%. After the tests, a small quantity of char and soot material was found in the melted salt column scavenger due to coal dissolution reactivity. This material was mainly soot carbon (%99C). Further work is required to determine the soot concentration and compare that with the soot use into gas carbonation.

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