

# FLUE GAS CO<sub>2</sub> SEQUESTRATION BY TURKISH COAL FLY ASHES AND ANATOLIAN GEOHERMAL HOT WATERS

Yıldırım İ. Tosun

Engineering Faculty, Şırnak University, Şırnak  
\* Corresponding Author. Tel: +90(544) 5896824, Fax:  
(486) 2164844, E-mail: [yildirimosun@sirnak.edu.tr](mailto:yildirimosun@sirnak.edu.tr)

# Aim

- **Sequestration industries with economically competitive and environmentally conscious technology options to produce electricity,**
- **The Sequestration process for Flue Gas of Sırnak asphaltite**
- **The production of carbonates in cost and energy aspect**

# Scope

- Depending on the combustion technology, lignite coal ash contains 10–25% free reactive lime. CO<sub>2</sub> capturing, transport and sequestration by pressurized water dissolution and reacting by natural alkali lime and magnesia in coal fly ash or other sources becomes an industrial advantageous sequestration option resulting in green waste solutions or solid fines. Reactive Mg and Ca containing ash is sufficiently reacting with flue gas CO<sub>2</sub> to form the carbonates. Various types of fly ash materials may react with CO<sub>2</sub> to form carbonate regarding the fly ash composition and reaction parameters. Carbonation of CO<sub>2</sub> will also allow us to produce fine raw materials for cement production industry or as cement filling material in constructions with low cost.
- In this study, the fly ash contains 10–25% free lime of Soma, Yatagan, Afşin Elbistan and Silopi Power Stations were received and transported to wet open-air ponds, by a hydraulic system. Main work used 100,0–200,0 cubic meters of ponds with full of slurry fly ash. This slurry will contain Ca<sup>2+</sup>-ion-saturated alkaline water (pH level 12–13) and easily recycling between the plant and sedimentation ponds.
- This study discussed the results of tests in that the progress on three consecutive column reactors carbonation achieved and search for fast reaction methods using coal fly ash of Soma, Yatagan, Afşin Elbistan and Silopi Power Stations. Other ash materials containing magnesium and magnesium silicates, supercritical CO<sub>2</sub>, steam-slurry, and additives were searched for pretreatment methods to enhance mineral reactivity; and in analyzing the structural changes to identify reaction paths and potential barriers.

# Introduction

- Carbonation of CO<sub>2</sub> gas has many various advantages. Most distinct fact is that carbonates have a lower energy state than CO<sub>2</sub>. Mineral carbonation is 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 CO<sub>2</sub> into the atmosphere is not an issue. However, conventional carbonation reactions are slow under ambient temperatures and pressures.
- 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 CO<sub>2</sub> emissions of approximately 28.8 Gt in 2010 (Minchener and McMullan, 2007, IEA, 2012). 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 CO<sub>2</sub> per annum, representing about 33% of Turkey energy-related CO<sub>2</sub> emissions (TKI, 2009, TTK, 2009).
- Therefore, developing effective CO<sub>2</sub> 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 CO<sub>2</sub> 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.
- Three boreholes, one injection well, and two 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 CO<sub>2</sub>, 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 yr, 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 CO<sub>2</sub> (IPCC, 2005, Stangeland, 2007, Solomon, 2006, Torp and Gale, 2004, Siegenthaler and Oeschger, 1987, Keeling et al., 1995, Plasynski, 1996). The proposed part of the project is restricted to the baseline survey and the injection and basic monitoring of CO<sub>2</sub>. The supply of CO<sub>2</sub> will be provided by near Coal Power Station in Şirnak. Other choice will be the purchase of a pure CO<sub>2</sub> originating from flue gas of hydrocarbon production at an oil refinery. The CO<sub>2</sub> 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 CO<sub>2</sub> at the well head in gaseous phase at a slightly supercritical pressure and slightly supercritical temperature. The anticline at Şirnak -Silopi was used for gas storage in the past in a shallower depth interval in Şirnak-Silopi pit mine field, which also is an mining industry partner in CO<sub>2</sub> sequestration and will be responsible for the CO<sub>2</sub>-injection operations.

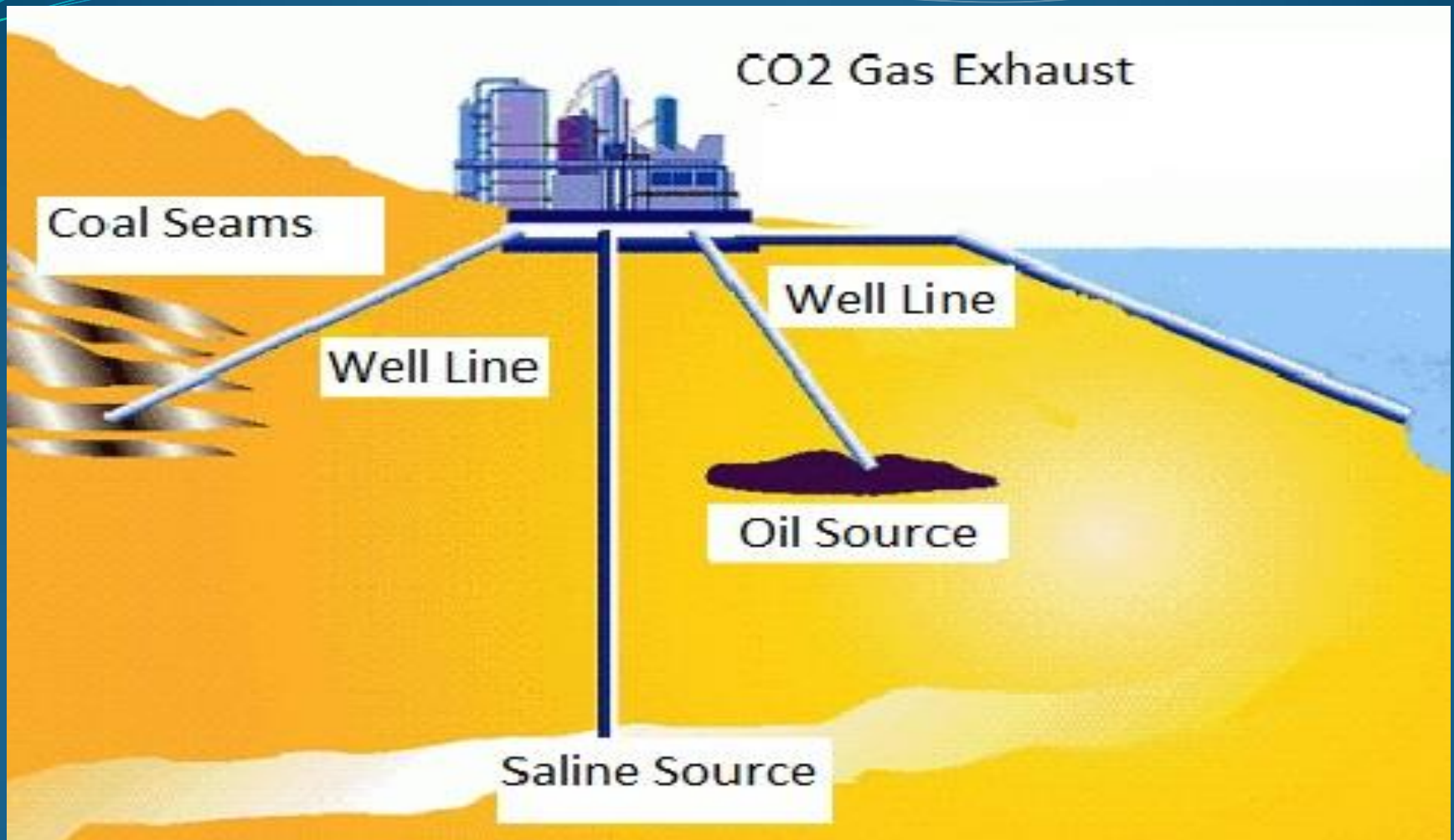


Figure .General Reservoir Storage Path.

# CO<sub>2</sub> SEQUESTRATION AND CARBONATION

- Options for storing CO<sub>2</sub> 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 CO<sub>2</sub> does not escape into overlying, shallower rock units and ultimately to the surface. Geological storage of CO<sub>2</sub> requires compression of CO<sub>2</sub> to allow injection. This is done by compressing the CO<sub>2</sub> to a dense fluid state known as 'supercritical'. This supercritical state is achieved by exposing the CO<sub>2</sub> to temperatures higher than 31.10C and pressure greater than 73.9 bars. The density of CO<sub>2</sub> will increase with depth, until about 800 meters or greater, where the injected CO<sub>2</sub> will be in a dense supercritical state (DOE , 1998, Simbeck, 2004, Burruss, 2004, Oldenburg et al., 2001)
- The mineral carbonation, a process of converting CO<sub>2</sub> into stable minerals - mineralization has been studied extensively to capture and store CO<sub>2</sub> (Stevens et al., 2001). The flue gas treated by fly ash particles, even mineralization hold high mercury (Hg) concentration of 0.22 mg/kg in flue gas (Myer, 2003, Zweigel et al., 2001).
- Geothermal brine waters utilization and using CO<sub>2</sub> as feed material in mineral carbonation produce various environmentally benign products.

# METHOD OF MINERAL SEQUESTRATION

- Mineral sequestration involves the reaction of  $\text{CO}_2$  with minerals to form geologically stable carbonates. This mineralization of  $\text{CO}_2$  was searched by different studies using various materials (Lindeberg, 2003, Rubin and Rao, 2003). General and specific global mineral carbonation reaction pathway is shown in Figure 1. The goals of the current work were to design an ash–water suspension carbonation process in a continuous mode laboratory-scale plant and to search for potential means of intensifying the water neutralization process (Davis, 2004, Seifritz, 1990, Kojima et al., 1997, Gunter et al. 1993, Lackner et al., 1995). The carbonation process was optimized by cascading columns in which the pH progressed from alkaline to almost neutral. The amount of  $\text{CO}_2$  captured from flue gases can reach 0,01–0,12 kg/l at the 500°C temperature and 10 bar pressure level (O'Connor, 1998). Laboratory-scale neutralization experiments were carried out to compare the reactor designs. Sedimentation of carbonate particles was observed and their main characteristics were determined.

- Mineral sequestration involves the reaction of  $\text{CO}_2$  with minerals to form geologically stable carbonates. This mineralization of  $\text{CO}_2$  was searched by different studies using various materials (Davis, 2004, Seifritz, 1990, Kojima et al., 1997, Gunter et al. 1993, Lackner et al., 1995). General and specific global mineral carbonation reaction pathway is given below the reactions.
- Mineral carbonation reactions are known to geologists and occur spontaneously on geological time scales. For example, the reaction of  $\text{CO}_2$  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 (O'Connor, 1998). 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 (Goldberg et al., 2000),  $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ , and  $\text{CO}_2$  into magnesite,  $\text{MgCO}_3$ , silica and water (O'Connor, 1998, Butt et al., 1997, Drăgulescu et al., 1977). Using this ideal case, one ton of serpentine can dispose of approximately one-half ton of  $\text{CO}_2$  (Goff et al., 1997).

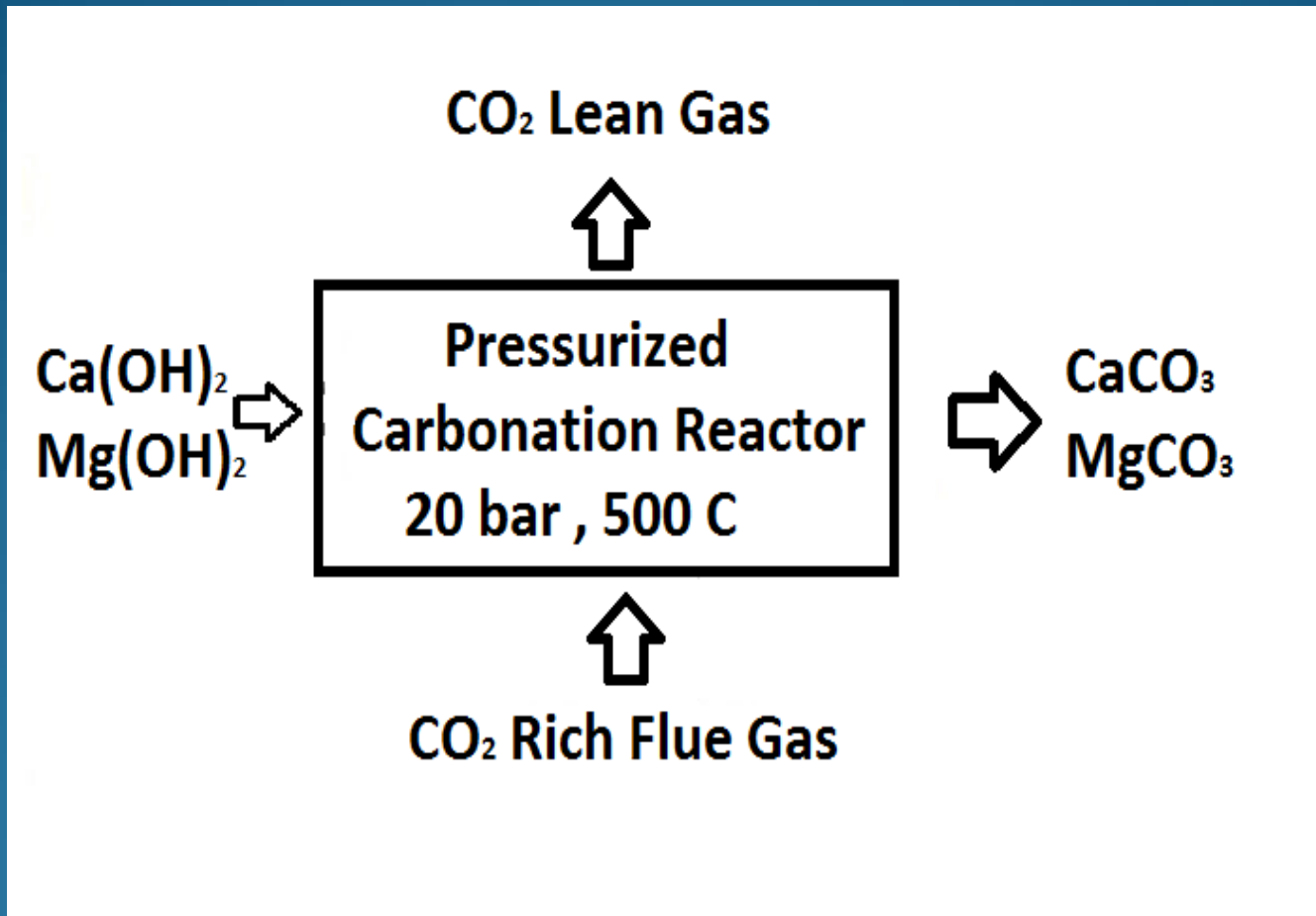


Fig. 1. General Chemical Mineralization Path.

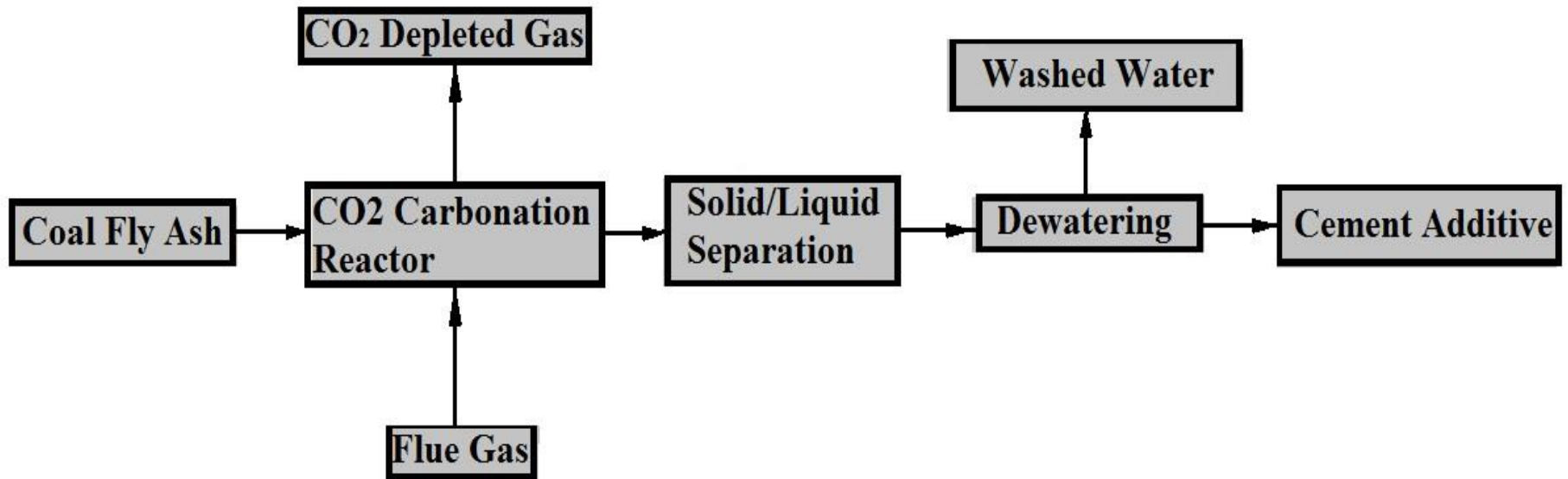


Fig. 2. Chemical Reaction Process of fly ashes for sequestration in the Diagram.

Table 1. Chemical Analysis of Turkish Fly Ash Used in The Experiment

Chemical composition	Soma Fly Ash F	Yatagan Fly Ash F	Silopi Fly Ash F	Afşin Elbistan Fly Ash F
SiO <sub>2</sub> (S)	42.14	52.05	40.4	20.4
Al <sub>2</sub> O <sub>3</sub> (A)	17.12	23.69	4.1	7.1
Fe <sub>2</sub> O <sub>3</sub> (F)	4.34	5.94	5.96	4.96
CS+CAF	63.26	81.68	81	88
CaO	29.6	19.60	24.7	64.7
MgO	1.53	2.38	2.1	3.1
K <sub>2</sub> O	1.15	2.51	1.55	0.55
Na <sub>2</sub> O	1.29	2.56	1.25	0.250
Loss of ignition	0.34	0.90	5.22	4.22
SO <sub>3</sub>	3.43	1.45	2.2	2.4
Density (g/cm <sup>3</sup> )	2.22	2.12	1.9	2.0
Loose unit weight (g/cm <sup>3</sup> )	0.72	0.88	0.71	0.69

Table. 1. Chemical Analysis of Turkish Geothermal Hot Waters

Chemical composition, mg/l	Well 1	Well 2	Well 3	Well st	Well ht
Ca <sup>2+</sup>	55	222	20	953	1760
Fe <sup>2+</sup>	17.12	23.69	7.1	0.2	0.5
K <sup>+</sup>	6.3	7.9	5.9	102	430
Mg <sup>2+</sup>	10.26	33.68	8.0	289	1310
Mn <sup>2+</sup>	0.6	0.02	-	0.01	0.01
Na <sup>+</sup>	15	238	365	16785	90100
F <sup>-</sup>	0.35	0.51	0.55	-	-
Cl <sup>-</sup>	19	122	250	27440	114300
NO <sub>3</sub> <sup>-</sup>	1.34	90	0.92	-	-
SO <sub>4</sub> <sup>2-</sup>	13.43	145	14	1134	3547
HCO <sub>3</sub> <sup>-</sup>	210	502	510	184	40
pH	8,3	8,6	8,4	9,1	9,3

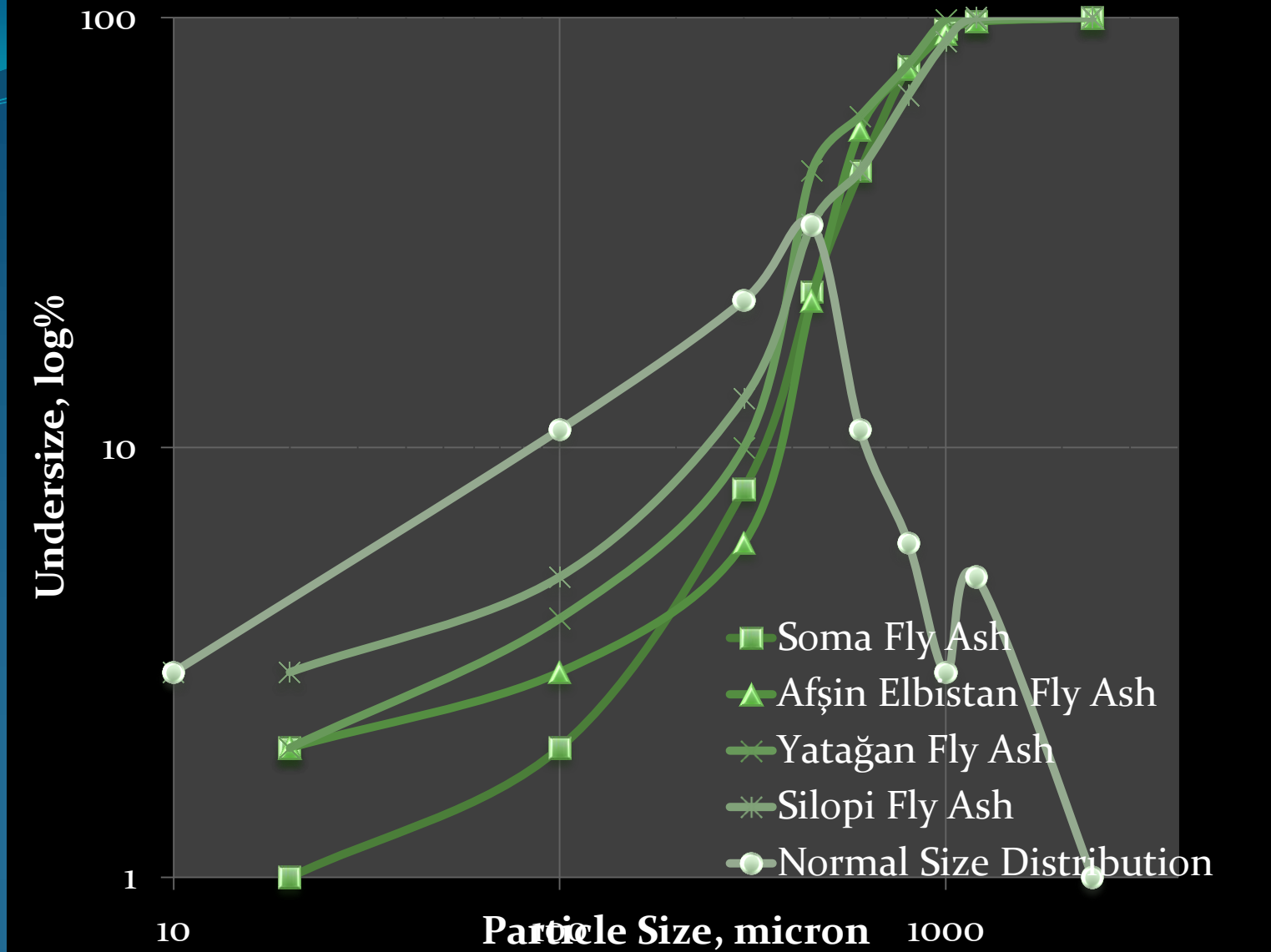


Fig. 3. Particle Size Distribution and Normal Size Distribution of the Fly Ash used in carbonation process.

# RESULTS AND DISCUSSION

The major technical challenge now hindering the use of minerals to sequester CO<sub>2</sub> is their low reaction rate. Weathering of rock is extremely slow. The highest priority is given to identifying faster reaction pathways. The optimized process has to be economical. Although many carbonation reactions are exothermic, it is generally very difficult to recover the low-grade heat while the long reaction time and demanding reaction conditions.

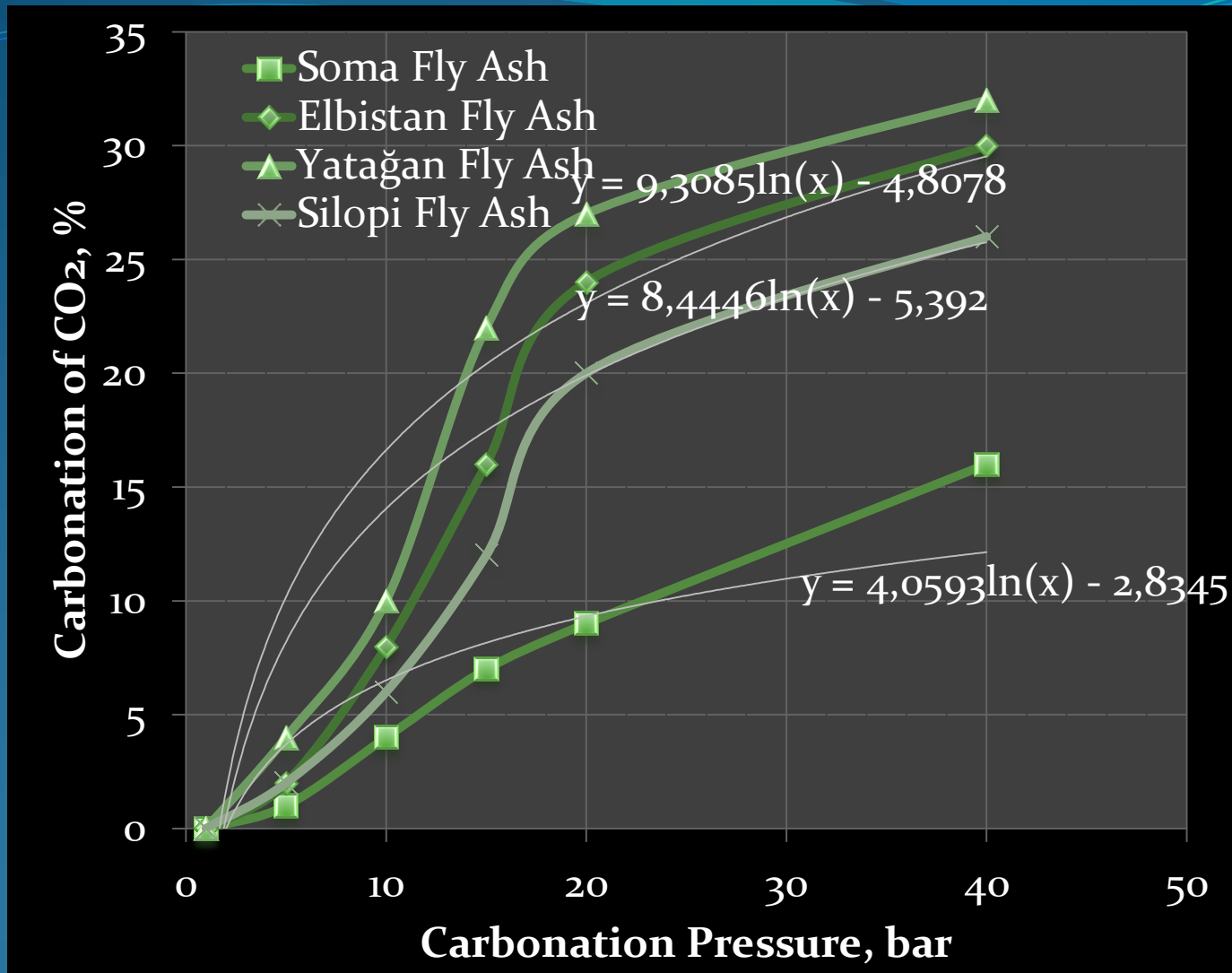


Fig. 4. Effect of carbonation time over conversion yield rates in hot 500 °C steam used.

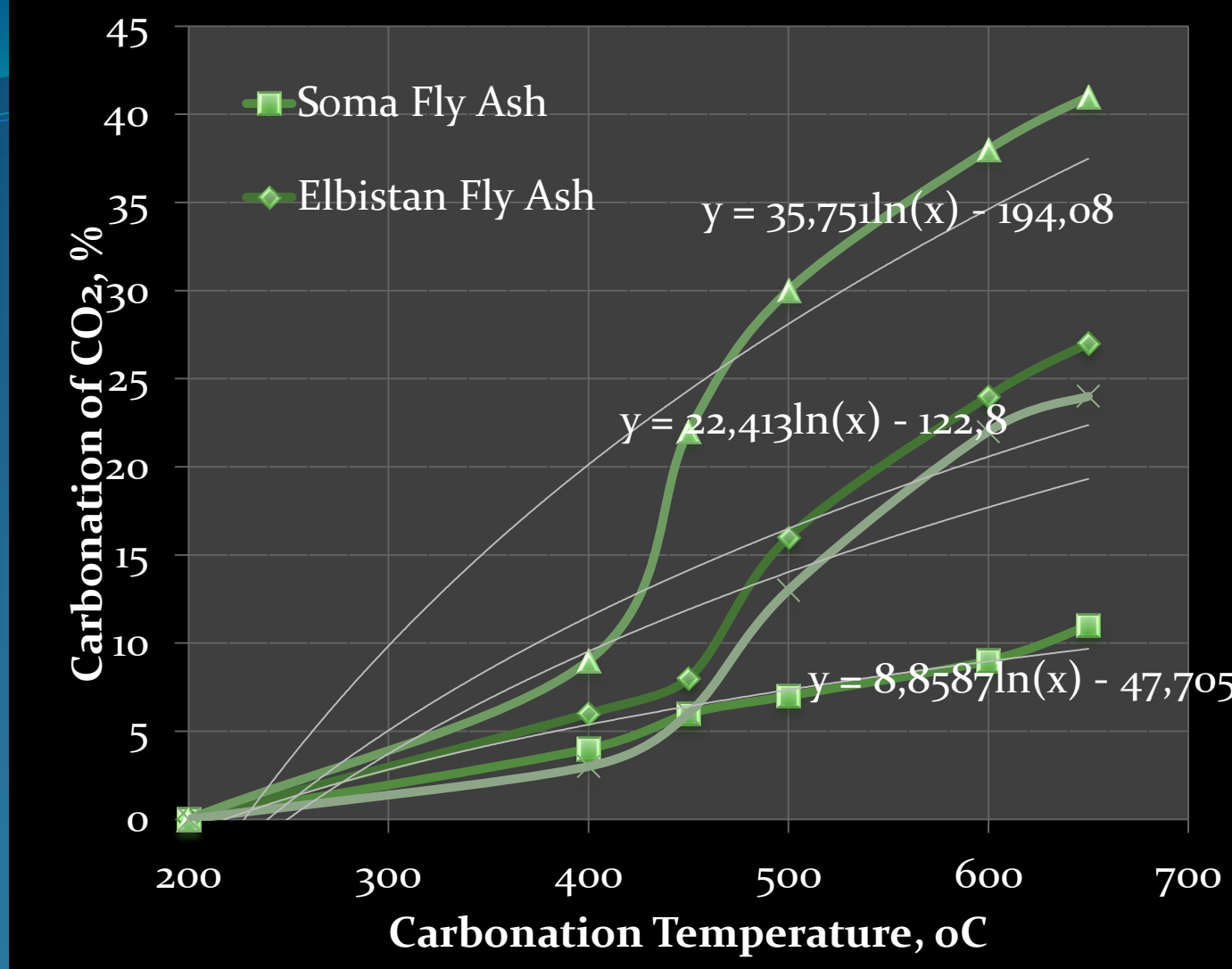


Fig. 5. Effect of time of carbonation over conversion yield rates in steam with 10% additional lime used at 20bar .

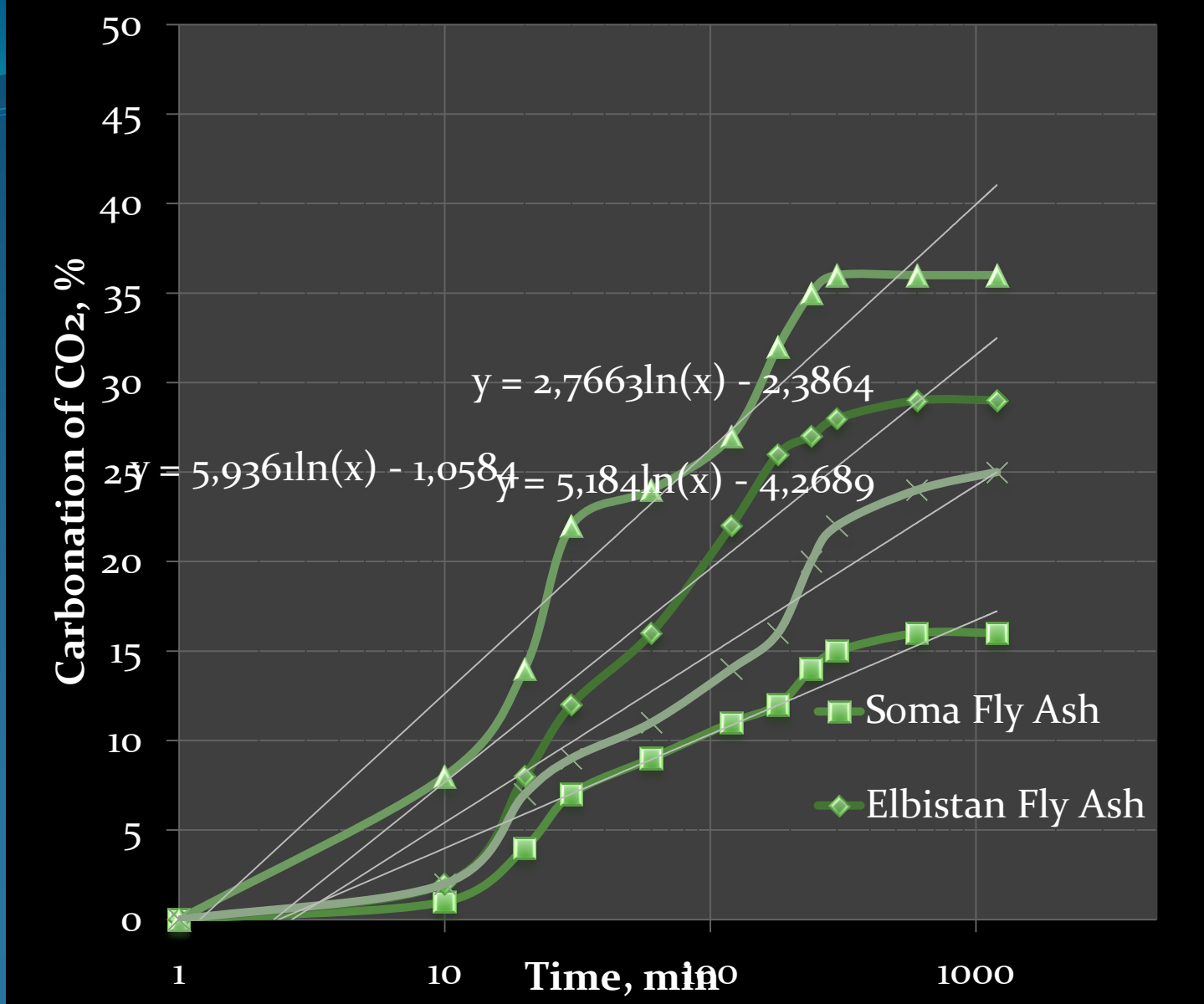


Fig. 6. Effect of time of carbonation over conversion yield rates in hot waters used at 500 °C and 20bar.

The environmental impact from mining, mineralization and carbonation processes must be considered in sequestration. We succeeded in achieving shortened carbonation reaction times employing fly ash containing lime and calcium magnesium silicates such as gehlenite, mehlenite. Reaction took 4 hours to reach 40-50% completion of carbonation. The reaction required temperatures of 450-550°C, pressures of 10-20 bar, and mineral particles in the -100 micron 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  $\text{HCO}_3^-$  in the solution is critical to the reaction rate. The high  $\text{CO}_2$  pressure will lead increased  $\text{CO}_2$  absorption in the solution and thus enhance the  $\text{HCO}_3^-$  concentration. Adding bicarbonate such as sodium bicarbonate in the solution will significantly increase the  $\text{HCO}_3^-$  concentration even at a relatively lower  $\text{CO}_2$  pressure.

In experiments with 3 hours reaction period at reactor temperature of 500°C and fly ash slurries were kept under changing CO<sub>2</sub> pressure ranged 5 bar to 40 bar. Products were subjected to analysis for carbonate yield determination. Test results of yields for different Turkish fly ash sources were seen in Fig. 4.

That quantity in the carbonation amounts were determined for different source evaluation and reduce the effect of gas content of waste gas in order to optimize carbonation rates. As given in Fig. 4 gas conversion yield for steam and ash samples were greatly differed. Yatağan and Elbistan Fly ash showed high carbonation yields reaching 32% and 30% respectively. Because of active lime amounts were over 20% and even alkali Na and K contents were over totally over 5%, the higher carbonation yields were sufficiently provided by three consecutive carbonation columns at 20 bar.

In the carbonation experiments with addition alkali, reactor temperature changed between 200°C and 650°C and ash slurries were mixed with active lime additionally by 10% rate. Products received from carbonation of ash specimens were subjected to analysis for gas hold-up determination. Test results of carbonation by fly ash and also alkali lime contained over active lime at 10% weight rate were investigated.

In experiments with 3 hours reaction period of ash specimens, at reactor temperature changed between 200°C and 600°C and all ash samples contained over active lime at 10% weight rate. Products were subjected to analysis for carbonate yield determination. Test results of carbonation yields of Turkish fly ash sources and additional 10% lime were seen in Fig. 5.

# CONCLUSIONS

The qualitative comparison of the carbonation for three different Turkish fly ash reactants and products revealed a complete MgO, CaO– MgO to Mg CO<sub>3</sub>-CaCO<sub>3</sub> conversion. The carbonation efficiency of CaO was dependent on the initial pressure of CO<sub>2</sub> of 20bar. This was significantly affected by reaction temperature 500 °C and by the fly ash dose 100 gr/l. The kinetic data demonstrated that the initial rate of CO<sub>2</sub> transfer was enhanced by carbonation process for our experiments. The precipitate calcium carbonate was characterized by isolated micron sized particles and micron agglomerates of calcite.

This study reveals suitable large scale operating units in order to achieve the carbonation method as a viable sequestration tool at industrially relevant scales by using Turkish fly ashes in 500-600 °C waters. Carbonation liquid and gaseous products may change to near 20%-40% yield performances by time increase from 1hr to 6hr.

.

While there is a potential to utilize other types of flue ashes in mineralization, lime or similar alkali can be evaluated to sequester CO<sub>2</sub> allowing clearly significant amounts. Even there are researches succeeded usage of serpentine and olivine. Consequently, the flue gas should be continuously monitored to measure flue gas flow at depleted gas outlet in order to reprocess it.

Carbonation of the ash slurries and carbonation yield products changed to 37%, 29%, 25% and 19% for Yatağan, Elbistan, Silopi and Soma Fly ash, respectively, by time increase from 1hr to 6 hr.

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<sub>2</sub> and significant amounts of SO<sub>2</sub> and Hg can be directly captured and mineralized by the fly ash particles.

Even with progress made so far, to develop an economical method to sequester CO<sub>2</sub> with minerals is still a challenging task, because the process is still relatively slow, and most reactions require high pressure and moderately elevated temperature.

**Thanks for attention.**

**Şirnak University, Turkey**