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Microwave Caustic Slurry Carbonation of Flue Gas of Coal Power Plants in Double Hot Tube Bed for CO₂ Sequestration

Yıldırım İsmail Tosun

Abstract

There have been very few transport studies of caustic alkali slurry (metal fines-caustic alkali salt mixture). Bath serpentinite particle size changed the heat conductivity to salt bath. A major reason is that the retention time in fixed film processes is longer than in solid–gas processes. This allows more time to the heat absorption for cracking to the desorbed persistent compounds. Furthermore, heavy serpentinite allows an sufficient intimate contact between coal and biomass surface pores and gas atmosphere in the furnace due to more pyrolysis gas desorption. For seeing the sustainability sequestration and environmental concerns in feasibility sight, the microwave heating technologies encompassing natural carbonation, precipitates for soil remediation and toxic gas sorption was offered to be adopted in Şırnak Asphaltite/Batman Oil Fields cases. In many places, amine sequestration techniques can work synergistically for better results. This study determines to a great extent both the high rate and degree of carbonation under pressurized sludge at 5–10 bar so it was found that, a porous sludge bath over 45% sludge was more efficiently conducted even at a low amount serpentinite slime weight rate, below weight rate of 15%.

Keywords: microwave radiation, waste slurries, metal carbonation, carbonation kinetics, sorbent simulation, hybrid sorbent, waste sludge, salt slurries, char composts, shale compost

1. Introduction

This study was searching possibiliy of CO₂ stored in the identification of suitable geological media to and from thermal power plants with installed capacity of over 400 MW in Turkey, cement plants [1] from, the iron and steel industry, sugar involves the calculation of the released CO₂ emissions from the refineries and plants [1]. When the emission sources and possible storage locations were evaluated, Silopi Asphaltitel field was selected and it was decided to use the emissions of a cement plant, which is approximately 130 km away from this field. Injection was modeled into the oil field, where both storage and additional oil production could be obtained, accordingly, technical design was proposed for transportation and injection from the CO₂ source to the storage area and economic evaluation was made.

There are no CO₂ capture facilities in the cement factory, but it was assumed that CO₂ was present in the factory area during modeling.

2. Storage of compressed CO₂

Carbon dioxide storage underground in Turkey has required to determine the suitable geo storage capacity of the rock structures to be chosen [2]. The goal was to examine the details of the storage of carbon dioxide by injecting it underground in a selected area with geological and numerical models and to make an economic analysis.

The work in this study was carried out in steps:

1. To provide the annual fuel amount and fuel types of thermal power plants, refineries, cement factories, iron and steel industry facilities where carbon dioxide emissions are the highest,
2. Calculation of CO₂ emission amounts from fuel consumption according to IGCC method,
3. Oil tank will be in Turkey, natural gas, deep aquifers and examination of structures, such as soda, caves,
4. Modeling the injection and storage of CO₂ in the structure to be selected,
5. Technical and economical feasibility analysis of the storage of CO₂, which is accepted to be separated by holding technology in the industrial facility, in the field to be selected by using the options of transportation by tanker or pipeline,
6. Technical trips to selected facilities and meetings to introduce the project.

2.1 Investment modeling of compressed CO₂ storage from coal and biomass combustion

When the CO₂ emission inventory is examined, it is seen that thermal power plants, cement factories, iron and steel industry and refineries are the main sources of CO₂ emission in high amounts and in centralized areas. Emissions from transport and domestic use are scattered sources and it is thought that they can be reduced by efficiency measures.

The emission statistics in Turkey showed that the high increase in annual emissions [3]. Although it is aimed to increase energy efficiency and the use of renewable energy sources, it is predicted that dependence on fossil fuels will continue in all countries. In this case, another measure that should be taken would be to support technologies that will reduce CO₂ emissions from coal-fired thermal power plants. Since CO₂ is released as a product in all combustion processes, it is still not possible to eliminate CO₂ completely. Therefore, measures should be taken to reduce CO₂ emissions. The reduction of CO₂ emissions will be possible by underground storage of CO₂ in geological structures. Considering that CO₂ emissions from industrial zones around the world are determined as 13.5 Gt/year [4], geological areas other than known oil and gas reservoirs should also be evaluated.

The cost of capturing and deposition as below Eq. 1:

$$u(x, \sigma, c) = (1/\sigma) (1 + k/\sigma (x - \Theta))^{-1-1/k} \quad (1)$$

Figure 1.
Change of the cost of drilling for compressed air/CO₂ storage reservoir.

while exponential distribution $k = 0$, where u is the cost function, σ is the variance, k is hybrid distribution parameter, Θ is the time parameter, x is the flow rate by the following **Figure 1** [5].

3. Carbonation of flue gas at microwave column

The oxygen content and electroopotential of waters adequately accounted in stream flows causing animal feed contamination in the pastoral fields by soil and growing grass nearby this contaminated stream see page [5, 6]. The **Figures 2 and 3** showed the carbonate stability region in the sequestration phase layer and electropotential quality of the sludge.

In the hot streams and acidic mine waters the ferric iron and sulfate tend to be highly common as AMD seepage, alkali resulting from the reduction of these two

Figure 2.
Storage phase layer diagrams for oil and geothermal field - carbonate stability.

Figure 3.
Eh-pH diagrams for metal carbonate stability.

species, a weak base (bicarbonate) and producing a strong base (hydroxyl ions), also generate net alkalinity. The indirect acid production was relatively high rate at higher pH levels over 5 with dissolution of heavy metals in sulphide minerals and neutralization by alkali matters govern the dissolution by the reactions as given below;

Sludge microwave heating was managed by susceptor ferrous slime addition. The Ca ferrite and serpentinite slime were used and heating temperatures are shown in **Figure 4**.

The serpentinite was waste of chromite mines containing high Fe %23–26 and Mg and Al in silicate form. The waste slime of concentration tables of chromite ores of Elazığ chromites contained 36% iron oxide and provided sufficient heating diagram of filter columns for pressurized sludge column as seen in **Figure 4**.

The aerated and oxygen rich waters oxidizing sulphidic character metal precipitates to sulphate and chloride dissolution by unstable forms, but over pH 9 as shown in Figure electropotential matter of waste waters provides hydroxide precipitates in soil mud. Even jarosite form precipitates occurring in hot water streams area with reddish brownish precipitates, however those type residuals stuck over sand may become sweet salty alga fish feed even causing higher heavy metal contamination for fish farming and stream fishing. Batman province copper and lead sulphide deposits and hot streams of high sulphate come out high potential contamination of fresh waters sources at pH Eh diagram stability as given in **Figure 3** following flood.

The dissolution kinetics of soil mud particle for Pb heavy metal is followed by Eq. 2 and 4

$$\frac{dc_{CO2}}{dt} = k_i e^{-t_{ic}} dc \quad (2)$$

Where c_{Pb} Lead/Fe metal contamination mg/l, k the rate of dissolution of lead, i is the reaction style, t is time,

Figure 4.
Carbonation sludge column temperature change by addition weight of microwave susceptor.

The dissolution concentration of accumulated metal in aliquate of lake streams as regarding Pb heavy metal contamination is followed by equations of anion distribution, where n is kinetic order type (Eq. (4) and (5))

$$\frac{dc_{CO_2}}{dt} = k_i c^{tin} dc \tag{4}$$

The dissolution concentration of accumulated metal in aliquate of sulfurous hot water streams as regarding Pb heavy metal contamination is followed by equation, where SO_4^{-2} sulphate concentration in effluent, f_i is concentration rate of sulphate

$$\frac{dc_{SO_4^{-2}}}{dt} = k_i c^{tin} .dc .f_i (SO_4^{-2})^{tin} \tag{5}$$

The dissolution concentration of accumulated metal in aliquate of limestone rocks dissolution by hot water streams in subground lakes with high CO₂ gas dissolved streams as regarding Na metal carbonation is followed by equation, where HCO_3^{-2} bicarbonate concentration in effluent, Bicarbonate sulphate hot streams reduce acidity as below oxygen consumption Eqs. 6 and 7

$$\frac{dc_{Na}}{dt} = k_i c^{tin} .dc .f_i (HCO_3^{-2})^{tin} \tag{6}$$

The dissolution concentration of accumulated metal in aliquate of high fertilizer dissolution by wrong amount of fertilizer use in the agricultural fields discharged to streams as regarding carbonation is followed by equation, where HNO_3^{-2} nitrate concentration in effluent

$$\frac{dc_{Na}}{dt} = k_i c^{tin} .dc .f_i (HNO_3^{-2})^{tin} \tag{7}$$

The dissolution rates of heavy metals in acidic mine waters and sulfurous hot streams occurred in the region of Ilısu Dam, Güçlükonak, Şırnak and Batman Province saline waters in Siirt and Şırnak. The contamination of some accumulated carbonation contents of hot streams and soils in the region are given in **Table 1** [7].

Effluent, mg/l	Şırnak Coal Mine Pool	Şırnak, Hezil Stream	Güçlükonak Hot Stream	Batman Hot Stream	Şırnak Kasrik Laguun	İlisu Dam Laguun1	İlisu Dam Laguun2
Hg	8,11	4,71	12,3	14,11	4,71	4,71	4,71
Pb	10,58	14,53	23,2	12,58	11,53	5,7	5,2
Fe	40,33	70,62	59	93,3	56,2	60,62	67,62
K + Na	7,52	8,46	8,7	8,52	8,6	≥70	≥50
Cd	24,72	19,56	14,1	14,72	19,56	16	15
Mn	33,3	24,1	24,2	43,3	24,1	≤25	≤25
Cu	27,2	30,2	15,7	7,2	10,2	≤15	≤15
As	1,10	2,44	2,8	2,10	2,44	≤5	≤5
CO3	0,57	0,37	1,9	0,67	0,55	≤15	≤15
Soil, ppm							
Hg	34,11	48,71	52,3	54,11	40,71		
Pb	10,58	24,53	23,2	20,58	11,53		
Fe	4,33	7,62	5,9	9,33	5,62		
K + Na	74,52	81,46	81,7	84,52	88,6	≥70	≥50
Cd	24,72	9,56	10,1	4,72	19,56		
Mn	2,72	3,02	1,5	0,72	1,02	≤5	≤5
Cu	3,33	2,41	2,4	4,33	2,41	≤5	≤5
As	1,10	2,44	2,8	2,10	2,44		
CO3	0,57	0,37	1,9	0,67	0,55		

Table 1.
Şırnak and batman province reveals the potential carbonation scale and high saline bi carbonate water source.

The use of water resources (water withdrawal and ordinance) and evaluation for development and community needs have been studied. However, the amount and quality of water that the eco-system will need is not addressed. Everything is built on the theme of “develop-supply-use”. Parameters considered in the planning of water resources were population estimate, per capita water demand, fish farming, agricultural production, economic productivity level.

The agricultural irrigation, and human needs, the amount of water a healthy ecosystem will need, or actual regional water availability. The next step in traditional planning is to identify projects that will reduce the gap between estimated water supply and demand. In every scale, the planning action (region, basin, city) is used for the regular and healthy spatial development uses (housing, commerce, industry, recreation, other social) in the metropolitan cities which are especially migrating in our country and in medium size settlements Such as equipment) as directed by location decisions; It also determines the water demand of the city at the same time with its population and density of buildings and its quality and quantity of usage. While city plans shape the socio-economic and physical structure of the city, with the proposed land use, employment, population and density decisions, the city’s daily water demand is also shaped. Therefore, any kind of urban development outside the plan creates an unhealthy environment that affects the quality of life of the city, as well as poses a serious threat to the water resources [6]. The quality of the water quality will be preserved, improved and monitored. Heavy

	SiO ₂	Al ₂ O ₂	Fe ₂ O ₂	MgO	K ₂ O	CaO	TiO ₂	LOI*
Kaolin (%)	47.85	37.60	0.83	0.17	0.97	0.57	0.2	11.27
Şırnak Asphaltite Char Shale	27. 54	7.70	10.83	2.17	1.97	10.5	1.74	5.47
Bentonite	50.45	17.80	6.83	12.17	4.97	3.57	0. 4	7.37
Marly Shale	17.85	11.60	0.83	5.17	3.97	20.57	0.4	5.27
Fly ash	27.8	13.60	17.83	4.17	2.97	10.7	1.4	16.27

*LOI: Loss on Ignition at 1000°

Table 2.
Sorbent clay types for waste water treatment.

metal contamination hazard maps will be prepared and an early warning system will be established (Table 2).

3.1 Langmuir Crystallization model

For linear correlated distribution by depending on saturation limit and oxygen content of contaminant levels, the general common method can be given in Table 1.

The first order sorption concentration at three stage cycling counted but the equation below:

$$lnc^{Pb} = 1 + k_1t + f^t, 1ppm < x < 500ppm \tag{8}$$

3.2 Sludge carbonation by microwave radiation

The bentonite sample used in the study was obtained from Unye Madencilik from the Unye region of Tavkutlu mine. The bentonite sample was sieved and a small part of 45 µm was used for the operation. Bentonite samples were activated with 1 and 2 M HCl solutions for 2 h at 90° C using the Batch method (using 100 ml

Figure 5.
Effect of caustic type on carbonation weight as jarosite and gibbsite of gaseous CO₂.

acid solution for 5 g sample). The acid-treated samples were washed with hot deionized water to remove Cl⁻ ions and dried in room condition.

The microwave activated shale and fly ash used in the experimental work was provided from the district of Şırnak province. For the first time, Ünye region bentonite 0.1 M 100 ml CaCl₂ solutions were mixed in the beaker at room temperature for 24 hours. and the filtrate was converted to the ion-exchange by applying the AgNO₃ test. Acid/ clay suspensions were then prepared with bentonite, which was made to be ionized, to give H₂SO₄/clay ratios of 2 M, These were named - bentonite. These suspensions were dried at 150 °C for 3.5 hours. 50 ml of distilled water was added to the hot dry samples. The filtrate was filtered and dried at 80 °C. Finally, 5 ml of chlorite was added to the acid activated bentonite samples, each of which was 0.01 g, and the shale was retained by exposure to methanol vapor at 60° C for 4 hours. In addition, these samples were further dried at the same temperature for 1 hour to remove weak chlorite species. In this research, the caustic slurries microwave radiated cycled on the different bed sorbent types of double tube hot slurries radiated, cycled double washing sodium and calcium caustic content and bicarbonate precipitate samples of 10-20 gr were balanced. Precipitated particle size and weight distributions with fly ash samples are illustrated in **Figure 5**.

4. Results and discussion

The current use of absorbent bentonite and new areas of use increase in demand due to outflow. Especially absorbent claymarket, the cat and cat market A significant improvement in AmericaIt was. For absorbent clay depositsour wealthy country, too, to have a significant share ofthere is no reason why. This, which is gaining in Turkey, absorbant is limited to meet clay consumption [8–10].

This sorbent and carbonation caustic washing is done by compressing the CO₂ to a dense phase as “supercritical”. This supercritical phase is achieved by exposing the CO₂ to temperatures higher than 32° C and pressure greater than 74 bars. The density of CO₂ will increase with geo formation depth, until about 800 meters or greater, where the injection carried into a cap reservoir state [11–21].

Effective sorption in combustion processes depend on numerous factors including coal rank in carbonization, the volatile gaseous matter of coal such as presence of hydrogen, carbonyl gas and oxidation rate so stabilizing the desorbance, the settings of optimal diffusion conditions including structure defects (nitrogen, phosphorus, sulfur, etc.), temperature, oxygen content of coal, etc. and optimization of carbondioksit concentration ratios added the adsorption–desorption balance, the residence time and the spatial distribution of molecules in coal pores among other factors determining the efficiency of carbonization. as factors affecting the rate and extent of carbonization much dependent on the site activation, its desorption properties and its porosity. As discussed in the previous section, carbonization is a prerequisite step for oil generation from biomass wastes and coal [11, 12, 22, 23].

A major reason is that the retention time in fixed film processes is longer than in solid–gas processes. This allows more time to the carbonization far cracking to the desorbed persistent compounds. Furthermore, high rank coals allows an sufficient intimate contact between surface pores and gas atmosphere in the furnace due to more gas desorptions [13–16].

Potential storage areas are abandoned or in-production oil and natural gas fields, deep aquifers, soda mineral salt caves, methane-containing coal deposits and natural CO₂ fields. **Figure 6** shows the distribution of oil and gas fields in Turkey. In **Figure 2**, the industrial facility and power with CO₂ emissions determined within the scope of the project [24, 25].

Turkey discovered to have the largest natural CO₂ field project, which is already the Field Raman EUR 7 billion Bm³ was produced with CO₂ and used for landfill capacity. For CO₂ storage projects, the properties of geological structures are important and almost all oil and gas fields characterization data are available. Since 1954. As a result of continued exploration work in more than 120 oil and gas fields have been found in Turkey [11, 22, 23]; However, the size of these fields is not very large and the largest field is West Raman, a heavy oil field. When the distribution of oil fields in Turkey is seen that almost all found in the vicinity of the South East Anatolia Region. Most of the natural gas fields are located in the Tigris Region. The target areas in this project are oil fields located in the South East Anatolia Region and close to a power plant or cement factory. Among these areas, Silopi Asphaltite Field was chosen due to its characteristics of having the least depth and highest pore volume, and having little or no cracks. The injected CO₂ will be used as an EOR (enhanced oil recovery) tool to increase the amount of oil that can be produced before the storage phase. Cave of the limestone reservoir is few wells have been drilled in Raman Field so far, and production continues in 3 of these wells.

4.1 Pressurized sequential carbonation by Fly ash compost

The waste water washing provide the main support to the clean water production. The commercial successes in clay mud mentioned in washed bed and its sedimentation ability were described some of the emerging applications in lime use like clean water neutralization, aeration, [12–15]. The figures of statistical potential of washing control with different techniques in waste water cleaning are classified as seen in Figure 11 regarding cycling decantation time.

Some cost evaluations covering security of supply and environmental impacts, climate change evaluations, and technical and economic analysis, may be disused in cycling cost and activities. The jarosite type precipitations regarding sludge eșecropotential of reduction occurred. There was also chloride hydrates formed by salt amount and pH alkalinity as given below:

Figure 6.
The investment rates of compressed air/CO₂ storage in vs capacity of combustion power plant.

Figures 7 and 8 showed The Waste sludge carbonation rates of Different Types of Sorbent Units cycled.

Initially, most of the toxin removal occurs through chemical adsorption of the toxins to the expanded clay where the combustion temperature was in the combustion phase below 750°C that lasts approximately 2–3 mins. The high surface area of fly ash particles and coal char was effective in the caustic slurries of 20 % weight rate Na and Ca caustic slurry with about 34 m²/g highly sufficient in order to react with gaseous CO₂ 10% of weights of fly ash were reacted in 10 bar caustic slurry of Na. Main reactive salt structure is sulphate in the caustic slurry covered widely pores associated active char.

A common industrial combustion to control the emissions pro combustion stage lime washing involves backwashing with air and hydrated lime water rinse. Process variables include the control backwash rate, surface wash rate/duration, time sequence and duration of backwash. Clean filtrate is pumped back into the bottom of the column during backwashing.

The required test and characterization procedures such as pH viscosity measurement, filtration loss and swelling index were applied to all bentonite concentrates obtained and then to products activated with 0.5% soda.

These sorbents need to be accurately mixed with combustion matter and to optimize the combustion process. Reliable models, based on the above results, need to be combustion chamber construction far the estimation of kinetic parameters for toxic stream control. Such toxic stream circulation models would aid in the

Figure 7.
The column carbonation sludge sequent in microwave activation as sorbent compost.

Figure 8.
The column carbonation sludge sequent in microwave activation as sorbent compost. The waste sludge carbonation.

microwave activated shale clay sorbent use in waste water treatment systems as shown in **Figure 5**.

The country needs the cleanest fuel to be produced providing the essential oils and gases. For this reason, acidic mine waters as heavy metal contamination to control fish farming were mixed with expanded clay at 1-2 mm size soaked with slurries of different alkali sorbents such as bentonite, shale fine, NaCl, CaCl₂ and KCl were tested in the packed bed column washing and the test results were illustrated in **Figure 5**.

A carbonation bed column was used in compost sorption process was tested at a scale of 2–3 kg/h; collecting operational and design data to build an industrial installation. A technological diagram of the compost washing at three stage process developed unit was made. Activated shale destruction almost observed at third cycled end. Carbonate jarosite concentration change increased from 2nd cycle with performance of 30–40% and also simultaneous dilution of waste mud products by sedimented. it is necessary to optimize the cycling stages on metal circulation without the metal concentration change.

5. Conclusions

Reviews of the world shows that Turkey is responsible for only 1% of CO₂ emissions. The establishment of the Carbon Market will ensure that the sectors and activities to be included in the evaluations will be determined.

- This study shows that, due to their low volume, known oil and gas reservoirs can only preserve the CO₂ emissions of small industrial sites.
- In such a case, it is seen in this project that transportation of CO₂ by tankers is more feasible.
- Silopi and Şırnak limestone a natural CO₂ reservoir, can be considered as a suitable high-volume reservoir, currently with a suitable volume of 2 billion Sm³.

- The possibility of storage in deep saltwater aquifers should also be considered. A suitable pilot project will allow the parties to examine their eligibility.
- One of the most important elements of carbon capture and storage practices is incentives for CO₂ storage.

The pH increased at washing was efficient in heavy metal sorption, the swelling index decreased, the loss of filtration increased negatively, and viscosity decreased by the addition of sodium.

In the obtained data, it was observed that sorption manner of bentonite has negatively effected by foreign ions in washing water for the activation especially total iron ion.

This result also indicated that the properties of the irrigation and fish farming water to be used during wet soil amendment of agricultural organic soil and lake muds with wet bentonites, on waste water treatment units which friendly mud should be controlled, otherwise the contamination after discharge would be harm human health, toxicology of animal and fish feed.

Abbreviations

Greek symbols

a	affinity parameter of the Langmuir isotherm (L mg^{-1})
b	stoichiometric constant defined by
B	reactant solid defined
Bi_m	Biot number for mass transfer
C_i	concentration of manganese in the bulk external phase of stage i (mg L^{-1})
C_0	feed concentration of manganese in the column (mg L^{-1})
D_{ef}	effective diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)
F	objective function
h	fixed bed height (m)
k_e	mass transfer coefficient in the bulk external phase (m s^{-1})
k_r	reaction rate constant for heterogeneous systems (m s^{-1})
N	number of stages
Q	volumetric flowrate ($\text{m}^3 \text{s}^{-1}$)
q_i	concentration of immobilized manganese within the adsorbent particle at stage i (mg g^{-1})
q_m	theoretical maximum adsorption capacity of the Langmuir isotherm (mg g^{-1})
r	radial distance from the center of the particle, $0 < r < R_p(\text{m})$
R	radius of column (m)
R_p	radius of adsorbent particle (m)
R^2	determination coefficient (—)
$r_{c,i}$	unreacted core radius at stage i (m)
t	time (s)
V_i	volume of stage i (L)
α	backmixing coefficient (—)
φ	column hold-up (—)
ρ	density of adsorbent particle (g m^{-3})
τ	mean residence time of fluid in the column (s)

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