Stabilization Of Carbon Dioxide In The Flue Gas With Ulexite

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Abstract: Turkey is the country having the largest boron reserves in the world. 72% of the world boron reserves is in Turkey. Commercial boron ores include colemanite, tincal and ulexite in Turkey. +3 mm ulexite fraction produced in ulexite concentration plant is exported, but -3 mm fraction, which has 16.6 % B_2O_3 cannot be sold and is piled up in the mine area.
The Taguchi method has been used to determine optimum conditions for stabilization of CO_2 gas with ulexite. Chosen experimental parameters and their ranges were (i) reaction temperature, 5-40 °C; (ii) solid-to-liquid ratio (in weight), 0.1-0.5; (iii) ; (iv) mean particle size; -600 -150 μm; (v) stirring speed, 300-700 rpm; (vi) reaction time, 15-120 min. The optimum conditions were found to be reaction temperature, 40 °C; solid-to-liquid ratio, 0.1; mean particle size, -150 μm; stirring speed, 500 rpm and reaction time, 90 min. Under these optimum conditions and 29.78 L CO_2/kg ulexite was stabilized.

Introduction

Carbon dioxide (CO_2) emissions have the largest share of anthropogenic emissions of greenhouse gases associated with global warming (IPCC 2001). CO_2 is a effective greenhouse gas and the dominant contributor to anthropogenic climate change. Since the Industrial Revolution (i.e., about 1750), global atmospheric concentrations of CO_2 have risen about 36 percent (IPCC 2007), principally due to the combustion of fossil fuels. Globally, approximately 29,195 million ton of CO_2 were added to the atmosphere through the combustion of fossil fuels in 2006(EPA, 2009). Fossil fuel burning power plants among largest CO_2 emission worldwide(30%); other large sources include cement plants(6%), steel mills(0%) and hydrogen production facilities(1%).
Many studies have been accomplished in favor of CO_2 removal from the gases. A number of CO_2 capturing and removal processes and models have been developed to reduce CO_2 in the fuel gases.

In a research, NH_3 and monoethanolamine (MEA) were used to determine the absorption capacity for CO_2 removal effect. It has been determined that the solution of NH_3 was more effective than that of the MEA solution to remove CO_2 greenhouse gases under similar conditions. The MEA removal process yield was found 94 % and absorption capacity was 0,40 kg CO_2/kg MEA, and the NH_3 removal process yield was found 99 % and adsorption capacity was 1,20 kg CO_2/kg NH_3 (Yeh and Baiu, 1999).

It has been reported that, NH_3 effect and system performance of process parameters have been investigated in a CO_2 absorption removal process at different conditions. The CO_2 gas was supplied to the system continuously, formation of ammonium bicarbonate has been occurred through the trials and removal of the CO_2 has been successfully observed. (Diao, 2004).

A laboratory size spray dryer has been used in another research in different experimental conditions to determine the effecting parameters of CO_2 removal. Best yield was acquired at the conditions of 150 °C 48% spray dryer, 10% NaOH + 5% $Ca(OH)_2$ (Chen, 2005).

Modeling techniques have been used to calculate the cost and performance of capturing and storing of CO_2 from fuel gas of power plants. The research demonstrated that the expenses would be increased to excessive costs to reach the 85-90% yield of CO_2 capture and storage (Rubin, 2007).

Fossil fuels provide a large, affordable source of energy that is limited by environmental impacts rather than resource constraints(Lee, 1976).

As CO_2 removal is getting more and more important, the removal process cost has been found a limiting parameter. The objective of Kyoto Protocol is the "stabilization of greenhouse gas concentrations in the atmosphere at a level that would prevent dangerous anthropogenic interference with the climate system (UNFCC, 2005)

Therefore developing reasonable removal methods have become a purpose for the researchers. In this research a novel reasonable method has been developed for the CO_2 removal by using an unusable squander ulexite ore.

Material Preparation and Experimental Method

Approximately 16.6% ulexide under 3mm sieve from Eti Mine in Bigadiç has been used in the experimental trials. The ulexide samples powdered and sieved. The powders were fractioned to -600 ,-355, -250,-180 and-150 μm. Volumetric and gravimetric methods have been used to determine the chemical compositions of the samples which are given in Table 1.

H_2O	B_2O_3	Na_2O	MgO	Al_2O_3	SiO_2	SO_4	CaO	Fe_2O_3	SrO
17.12	16.6	4.20	7.72	0.42	13.22	0.22	25.62	0.18	1.41

Table 1. The chemical composition of ulexite used in study

The commercial CO_2 gas was supplied from HABAS Company-Turkey. The experiments have been carried out in a 500 ml glass reactor under atmospheric pressure. The temperature of the reactor was controlled by a thermostatic controller at predetermined temperatures. 300 ml distilled water was used to for each reaction trial and the water was saturated with CO_2 gas. A water cooled glass cooler was used to recover the vaporized water from the reactor. When the reactor content was reached the desired temperature, a predetermined amount of the fractioned ulexite was added to the saturated aqueous media of the reactor while stirring at predetermined mixing speed and supplying 30 ml/min CO_2 gas into the reactor. At the end of each trial the reaction media was filtered and B_2O_3 analysis has been carried out in solution.

Taguchi method

Taguchi method is a systematic application of design and analysis of experiments for the purpose of designing and improving product quality. There are two differences of this method from other statistical experimental design methods. First, parameters affecting an experiment can be investigated as controlling and not controlling (noise factor). Second, this method can be used to investigate the parameters for more than two levels (Çopur,1997). The use of the parameter design in the Taguchi method to optimize a process with multiple performance characteristics includes the following steps: (a) to identify the performance characteristics and select process parameters to be evaluated; (b) to determine the number of parameter levels for the process and possible interaction between the process parameters; (c) to select the appropriate orthogonal array (OA) and assignment of process parameters to the orthogonal array; (d) to conduct the experiments based on the arrangement of the orthogonal array; (e) calculate the performance characteristic; (f) to analyze the experimental result using the performance characteristic and ANOVA; (g) to select the optimal levels of process parameters; and (h) to verify the optimal process parameters through the confirmation experiment [Nian,1999, Phadke,1989]. The orthogonal array experimental design method was chosen to determine experimental plan, L_{25} (5^5) (Table 4), Because it is the most suitable for the conditions being investigated; five parameters each with five values (Phadke,1989). In order to observe the effects of noise sources on the dissolution process, each experiment was repeated twice under the same conditions at different times. The performance characteristics were chosen as the optimization criteria.

There are three categories of performance characteristics, the larger the- better, the smaller-the-better and the nominal-the-better. The the larger -the- better was evaluated by using the following equation (Pignetiello,1988, Peace,1995):

$$SN = -10\log\left(\frac{1}{n}\sum_{i=1}^{n}\frac{1}{Y_i^2}\right) \quad (1)$$

where SN_L is performance characteristic, n the number of repetition done for an experimental combination, and Y_i the performance value of ith experiment. In Taguchi method, the experiment corresponding to optimum working conditions might not have been done during the whole period of the experimental stage. In such

cases, the performance value corresponding to optimum working conditions can be predicted by utilizing the balanced characteristic of OA. For this, the additive model may be used (Phadke et al., 1983)

$$Y_i = \mu + X_i + e_i \tag{2}$$

If experimental results are in percent (%), before evaluating eqs 2 transformation of the percentage values should be applied first using the following equation. Values of interest are then later determined by carrying out reverse transformation by using the same equation (Taguchi, 1987)

$$\Omega(dB) = -10\left(\frac{1}{P} - 1\right) \tag{3}$$

Run No	A	B	C	D	E
1	1	1	1	1	1
2	1	2	2	2	2
3	1	3	3	3	3
4	1	4	4	4	4
5	1	5	5	5	5
6	2	1	2	3	4
7	2	2	3	4	5
8	2	3	4	5	1
9	2	4	5	1	2
10	2	5	1	2	3
11	3	1	3	5	2
12	3	2	4	1	3
13	3	3	5	2	4
14	3	4	1	3	5
15	3	5	2	4	1
16	4	1	4	2	5
17	4	2	5	3	1
18	4	3	1	4	2
19	4	4	2	5	3
20	4	5	3	1	4
21	5	1	5	4	3
22	5	2	1	5	4
23	5	3	2	1	5
24	5	4	3	2	1
25	5	5	4	3	2

Table 2. L_{25} (5^6) Ortogonal experimental plan table

	Parameters	Levels				
		1	2	3	4	5
A	Reaction temperature (°C)	5	10	20	30	40
B	Particle size (μm)	-600	-355	-250	-180	-150
C	Stirring speed (rpm)	300	400	500	600	700
D	Solid-to-liquid ratio (g/cm^3)	0.1	0.2	0.3	0.4	0.5
E	Time (min)	15	30	60	90	120

Table 3. Parameters and their values corresponding to their levels to be studied in experiments

Since Eq. (2) is a point estimation which is calculated by using experimental data in order to determine whether the additive model is adequate or not, the confidence limits for the prediction error must be evaluated. The prediction error is the difference between the observed Yi and the predicted Yi. The confidence limits for the

prediction error are

$$Se = \pm\sqrt{\left[\frac{1}{n_0}\right]\sigma_e^2 + \left[\frac{1}{n_r}\right]\sigma_e^2} \quad (4)$$

$$\sigma_e^2 = \left[\frac{\text{hatadan dolayı karelerin toplamı}}{\text{hatanın serbestlik derecesi}}\right] \quad (5)$$

$$\frac{1}{n_0} = \frac{1}{n} + \left[\frac{1}{n_{Ai}} - \frac{1}{n}\right] + \left[\frac{1}{n_{Bi}} - \frac{1}{n}\right] + \left[\frac{1}{n_{Ci}} - \frac{1}{n}\right] .... \quad (6)$$

where Se is the two-standard deviation confidence limit, n is the number of rows in the matrix experiment, is the number of repetitions in the confirmation experiment and nAi, nBi, nCi, ... are the replication numbers for the parameter levels Ai, Bi, Ci, ... If the prediction error is outside these limits, the possibility that the additive model is not adequate should be suspected. Otherwise, the additive model can be considered to be adequate (Phadke, 1989).

Result and Discussion

The reactions between ulexide and CO_2 in aqueous solution have been given in equations 7, 8 and 9.

$$Na_2O.2CaO.5B_2O_3.16H_2O_{(k)} + 3CO_2 \rightarrow 2CaCO_{3(k)} + NaHCO_3 + NaB_5O_6(OH)_4 + 5H_3BO_3 + 6H_2O \quad (7)$$

$$Na_2O.2CaO.5B_2O_3.16H_2O_{(k)} + 3CO_2 \rightarrow 2CaCO_{3(k)} + NaHCO_3 + NaB_3O_3(OH)_4 + 7H_3BO_3 + 3H_2O \quad (8)$$

$$Na_2O.2CaO.5B_2O_3.16H_2O_{(k)} + 2CO_2 \rightarrow 2CaCO_{3(k)} + Na_2B_4O_5(OH)_4 + 6H_3BO_3 + 5H_2O \quad (9)$$

The ratios of the borate ions depending on the pH values have been given in Figure 1. The pH value during the chemical reaction was recorded as between 6.5-7. The stochiometric ratio of different borat species according to pH values was given in Figure 1. At the pH value the borate ions were found out as follow $B_5O_6(OH)_4^-$, $B_4O_5(OH)_4^-$, $B_3O_3(OH)_4^-$ and $B(OH)_3$. The amount of captured CO_2 in solution is proportional with the borate ions.

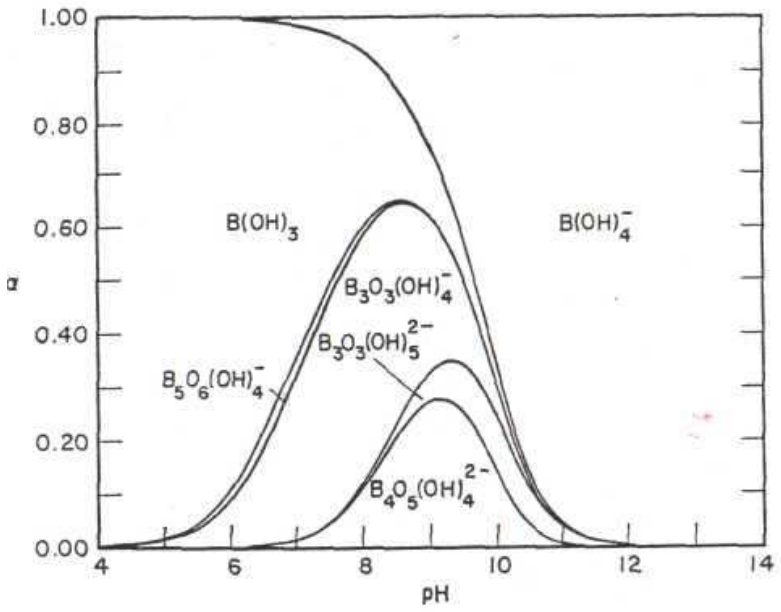

Figure 1. The stochiometric ratio of different borat species according to pH values (Adams, 1964).

The results acquired from the experiments have been analyzed according to optimization criteria and the results have given in Figures 2. Figure 2 was obtained by calculating captured CO_2 by the aqueous media from Equation

6, 7 and 8.

To obtain optimal parameters levels, the larger- the better performance characteristic in Eq. (1) has been taken for stabilization of CO_2. The performance characteristics have been calculated and charted in Figure 5. Figure 5 shows the degrees of the influences of parameter on the performance characteristics. The optimal level of a process parameter is the level with the highest SN. Parameter levels make the performance value maximum as seen in Figure 5 were A5, B5, C3, D1 and E4.

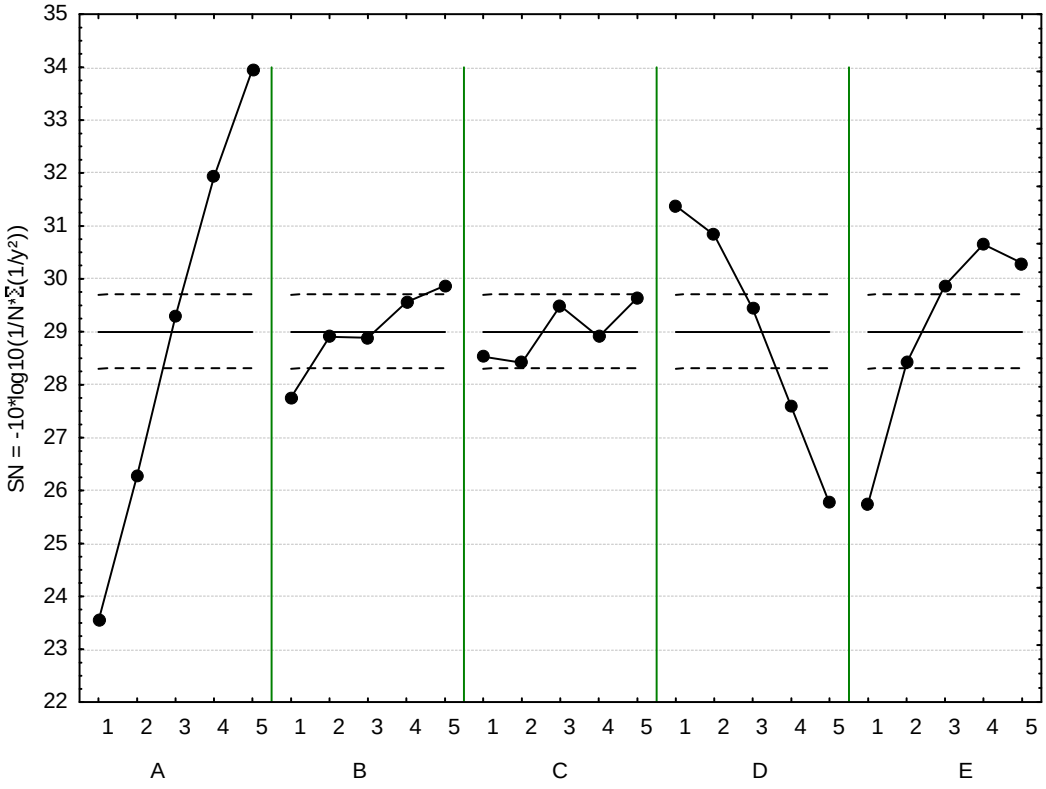

Figure 5. The effect of each parameter on the optimization criteria for carbon dioxide stabilization

In the working range, optimum conditions have found to be the temperature of 40 °C, particle size 15 μm, stirring speed 500 rpm, solid/liquid ratio 0.1 g/cm^3 and the time 90 min. Under these optimum conditions and 29.78 L CO_2/kg ulexite was stabilized.

Variance analysis was performed to determine the effective parameters and their confidence level for CO_2 absorption. Statistical ANOVA table has been established to see the process parameters statistically important or not. F-test is a tool to see which process parameters have a significant effect on the stabilization of CO_2. Usually, the larger the F-value, the greater the effect on the process due to the change of the process parameter. Optimal combination of the process parameters can be predicted with ANOVA analyses and performance characteristics. The results of variance analysis are given in Tables 4. As can be seen in Table 4 and Figure 5 for stabilization of CO_2, it has been found that respectively the temperature, the solid-to-liquid ratio and time have significant effects on the absorption process while the stirring speed and particle size having no significant effect within the working range.

Parameters	SS	Df	MS	F
A	324.6316	4	81.15791	41.62341
B	18.0640	4	4.51600	2.31612
C	10.9688	4	2.74219	1.40638
D	130.1742	4	32.54356	16.69060
E	59.0990	4	14.77475	7.57752
Error	7.7993	4	1.94981	

Table 4. Result of the analysis of variance for the carbon dioxide stabilization

A verification experiment is a powerful tool for detecting the presence of interactions among the control parameters. If the predicted response under the optimum conditions does not match the observed response, then it implies that the interactions are important. If the predicted response matches the observed response, then it implies that the interactions are probably not important and that the additive model is a good approximation [16]. It has been estimated that carbon dioxide can be captured in optimal conditions and were found to be 29.41 L CO_2/kg ulexide. In order to test the predicted results, confirmation experiments were carried out twice at the same working conditions. Experimental value was obtained as 29.78 L CO_2/kg ulexite. The fact that the CO_2 absorbtion values from confirmation experiments are within the calculated confidence intervals shows that experimental results are within ± 5% in error. This case states that there is a good agreement between the predicted values and experimental values, and interactive effects of parameters are indeed negligible. It may be concluded that the additive model is adequate for describing the dependence of this CO_2 stabilization process on the various operational parameters (Phadke, 1989).

It was observed that the temperature is much more effective than stirring speed on reaction between CO_2 and ulexide. For a heterogeneous reaction system, the mechanism controlling the reaction rate can be determined by taking into consideration the parameters which affect the reaction rate. Accordingly, it can be deducted that for the processes in which stirring speed is more effective, the rate of the process is controlled by diffusion while for the processes in which temperature is more effective, the rate is controlled by a chemical reaction. Therefore, for the present work it can be stated that carbon dioxide capturing process is controlled by chemical reaction.

Conclusion

The results can be drawn from this research:

1) It has been determined that-3 mm ulexide was an effective reactive to capture CO_2 gas.
2) The important parameters are temperature, solid-liquid ratio and time.
3) The optimum conditions were found to be, 40 °C, 0.1 g cm^{-3}, 500 rpm, 90 min, particle size 150 µm.
4) 29.78 L CO_2/kg ulexide was stabilized under optimum conditions.
5) Predicted and observed B_2O_3 values were related each other. The experimental model process is adequate to determine the relations.

Acknowledgements

It is a great pleasure to thank TUBITAK (The Scientific and Technological Research Council of Turkey) for their financial support during our project (107Y170).

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