CO₂ SEQUESTRATION BY BORON MINERALS

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ABSTRACT

Colemanite and ulexite minerals were investigated for CO_2 mineralization in this study. The advantage of boron minerals' use in CO_2 mineralization is that boric acid is extracted from minerals, as well. Thus, this process can be regarded as green process as it replaces the acids in conventional process. The rate of reaction between minerals and CO_2 in aqueous phase was accelerated by increasing the CO_2 pressure in the reactor. 99.0% of colemanite mineral was digested in the reaction for 1 h reaction time at 70°C and 6MPa pressure. 88.7% conversion value was obtained for ulexite reaction at 70°C and 9MPa and for 2 h of reaction time. Experimental CO_2 binding capacities (R_{CO_2}) of colemanite and ulexite were calculated as 0.17kg CO_2/kg colemanite and 0.123kg CO_2/kg ulexite respectively. While boric acid is easily separated and crystallized from colemanite reaction mixture; further separation steps are necessary for obtaining boric acid from the ulexite reaction medium.

INTRODUCTION

CO_2 concentration in atmosphere has been increasing parallel to the fossil fuel consumption of human being in the world. The current CO_2 level reached to 405 ppm [1], that concentration is responsible for significant variations in climate. The most of CO_2 emission is generated by the usage of fossil fuels in power generation, cement industry, iron-steel industry, refinery and petrochemical industry [2]. The annual amount of CO_2 generated by human activities is 7.0 Gtones and 5.4 Gtones is related to fossil fuel consumption [3]. Transportation is another sector that produces CO_2 but it is really difficult to handle CO_2 emitted from vehicles. To bequeath a sustainable world to next generations, we need to find the ways of CO_2 reduction, or its utilization as a raw material. There are two main approaches for CO_2 handling: CO_2 mineralization [4, 5], deep well injection [6] and deep injection into oceans. The major problems reported for deep well injection are CO_2 leakage from the reservoir, variations in aquatic life in the injection zone and long reaction times needed to diminish CO_2. For those reasons, continuous monitoring of CO_2 around the reservoir is necessary.

CO_2 can be used as a raw material in chemical industry to diminish its concentration in atmosphere. Especially, most of the chemical processes are producing its own energy by burning fossil fuels like coal and natural gas. The utilization of CO_2 from those plants can be a real solution for global warming problem. The capture of CO_2 from atmosphere is really challenging problem due to its low concentration. Thus, the recovery of CO_2 from flue gases can be done more easily. CO_2 is a kind of gas which is formed as a by-product in most of the

chemical reactions in industry. It is mostly released to the atmosphere, or it is separated from gas mixture by absorption using potassium carbonate [7] and monoethanolamine (MEA) [8]. Although these chemicals are commercialized, they have some disadvantages, such as MEA degrades at high temperature and it forms very toxic corrosive organic products in the presence of oxygen [9]. Boric acid was used as rate promoter for CO_2 absorption in potassium carbonate solution. The addition of 1.5 M boric acid to the absorption solvent at 80°C has increased the absorption efficiency by 29% [10]. After separation and purification of CO_2, it could be used as raw material or it is converted into stable carbonate forms.

Recently, the most of studies focused on CO_2 mineralization by abundant minerals, such as serpentine, olivine, wollastonite, ankerite, magnesite, siderite [11]. The weathering reaction between CO_2 and minerals occurs naturally in the presence of water. As products formed from the reaction of CO_2 and proposed minerals have low value and/or no value, those processes cannot be commercialized in industry. Boron minerals have commercial importance since they are used in wide range of applications e.g., ceramic and glass industries, polymer industry. Boric acid, which is mainly used in production of boron end product, can be extracted from boron minerals, such as colemanite, ulexite and tincal. If CO_2 is used as a raw material in aqueous phase for this reaction, both boric acid is extracted and CO_2 is sequestrated in a thermodynamically stable carbonate form [12]. The production of boric carbonate and sodium bicarbonate production from sodium borate solutions was investigated by using CO_2 [13]. Experiments were carried out three types of system: an autoclave, a jacketed reactor and an absorption column. Increasing CO_2 pressure in the autoclave has accelerated the rate of reaction and resulted in less reaction time and higher efficiency. However, as the formed by-products, sodium carbonate and bicarbonates, are soluble in water, there are difficulties in the separation of boric acid from that mixture. The use of methanol extraction was proposed for boric acid separation that brings an extra operating cost.

In this study, CO_2 mineralization was investigated using boron minerals of colemanite ($2CaO•3B_2O_3•5H_2O$) and ulexite ($Na_2O•2CaO•5B_2O_3•16H_2O$). Those minerals are significant Ca and Na sources for CO_2 sequestration. The chemical structure of the minerals, the powder crystallized from the filtrate and the filter cake were characterized by FTIR, XRD, TGA.

MATERIALS AND METHODS

Materials: Colemanite and ulexite minerals used in this study were obtained from Eti Mine Inc. in Turkey. Carbon dioxide, CO_2, with 99.9% (vol.) purity (HABAŞ) was used for the experiments. Sodium hydroxide, NaOH, (99% Merck), glycerol, $C_3H_8O_3$, (99% Dalan Chemical Industrial) and phenolphthalein ($C_{20}H_{14}O_4$) and methyl red ($C_{15}H_{15}N_3O_2$) indicators, sulfuric acid, H_2SO_4 (by volume of 96%, Merck), sodium carbonate, Na_2CO_3, (99%, Merck) were used in the analytical determination of B_2O_3 content of aqueous phase and boron minerals. Calibration of sodium hydroxide solution was done by using potassium hydrogen phthalate, $C_8H_4KO_4$ (99.5%, Merck). Potassium bromide, KBr, (99.99% Merck) was used in the preparation of pellets in infrared (IR) analyses. $CaCO_3$ (99.0%) obtained from Merck was used as reference material in IR analysis.

Method: Flow sheet of CO_2 extraction system used in experiments is shown in Fig. 1. Boron

minerals were initially grounded and sieved; the fractions obtained were used in the experiments. A stainless steel reactor with 0.2 dm^3 volume was used in the experiments. The reactor was heated externally by a water bath placed on a magnetic stirrer with temperature controller. Both temperature and mixing were controlled by magnetic stirrer. In order to increase CO_2 capture, parameters, such as reaction temperature, reaction time and pressure were studied in the experiments. 10 g of colemanite mineral and distilled water were added to the reactor for solid/liquid ratio of 0.1.

CO_2 in the form of dry ice was used in the experiments of ulexite mineral; liquid CO_2 was pumped from cylinder for colemanite mineral experiments. At the end of reaction, remaining CO_2 in the reactor was released and solid-liquid mixture was separated by vacuum filtration at 600 mmHg. The product dissolved in aqueous phase and the formed solid were characterized by gravimetric and volumetric techniques to determine their B_2O_3 content. Filter cake was dried in an oven at 105°C until reaching a constant mass. 0.010 dm^3 of filtrate was evaporated in petri-dish at 50°C so that dissolved boric acid can crystallize. Both powders from filtrate and filter cake were characterized by Infrared Spectroscopy (FTIR), X-ray diffraction (XRD), thermal gravimetric analysis (TGA).
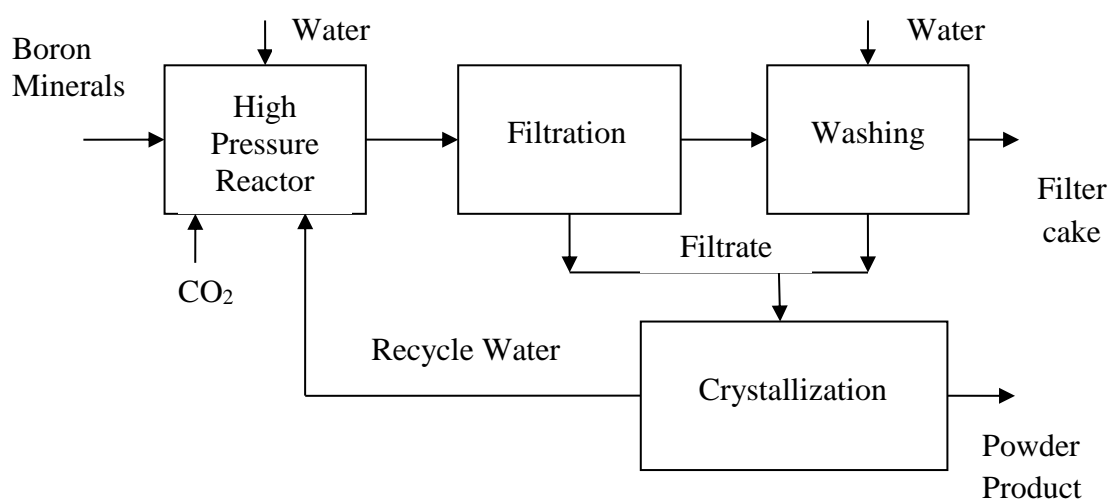

Figure 1. Flow sheet of CO_2 sequestration by boron minerals

The expected overall reactions of colemanite and ulexite with dissolved CO_2 in aqueous phase are represented in Eqn. 1 and Eqn. 2 respectively.

$$(2CaO \bullet 3B_2O_3 \bullet 5H_2O)_{(s)} + 2CO_{2(g)} + 4H_2O_{(l)} \rightarrow 6B(OH)_{3(aq)} + 2CaCO_{3(s)} \qquad (1)$$

$$Na_2O \bullet 2CaO \bullet 5B_2O_3 \bullet 16H_2O_{(s)} + 3CO_{2(g)} \rightarrow 2CaCO_{3(s)} + Na_2CO_{3(aq)} + 10H_3BO_{3(s)} + H_2O_{(s)} \quad (2)$$

Characterization: Solid products obtained at the end reaction as the filter cake and the powder crystallized from aqueous phase were examined by XRD, FTIR, TGA. X-Ray diffractometer (Philips Xpert-Pro) was used to analyze the crystal structures of the colemanite with CuKα radiation at 45 kV and 40 mA. The registrations were performed in the 2θ range of 5-80°. The transmission spectra of KBr pellets prepared by mixing 4.0 mg of sample and 196 mg of KBr in an agate mortar and pressing the mixture under 8 tons were obtained using FTIR spectrophotometer (Perkin Elmer Spectrum BX). TGA were performed in Perkin Elmer-

Diamond TG/DTA. Powder samples (10-15 mg) were loaded into an alumina pan and heated from 20°C to 900°C at 10°C.min^{-1} under N_2 flow (40 ml.min^{-1}).

RESULTS AND DISCUSSION

CaO% content of colemanite and ulexite minerals are 27.0% and 19.0%, respectively which makes them an important candidate for CO_2 mineralization. Those minerals are consumed directly in several industries or digested by acids to produce boric acid. B_2O_3% contents of those minerals vary between 37.0-40.0% [14]. H_2SO_4 is used as a leaching agent for boric acid production from colemanite mineral in Turkey. Thus, $CaSO_4.2H_2O$ is formed as by-product which is insoluble in aqueous phase that makes boric acid separation cost-effective. When CO_2 is used as leaching agent for boric acid dissolution out of those minerals, carbonate anions (CO_3^{2-}) formed in aqueous phase react with Ca^{2+} cations released from the mineral structure to produce $CaCO_3$. In this process, CO_2 is used for boric acid extraction and ultimately converted into stable carbonate form.

Characterization of Solid Products from Minerals-CO_2 Reaction

FTIR spectra of reference calcite, filter cakes obtained from colemanite-CO_2 reaction, and from ulexite-CO_2 reaction are given in Fig. 2a, Fig. 2b and Fig. 2c, respectively.
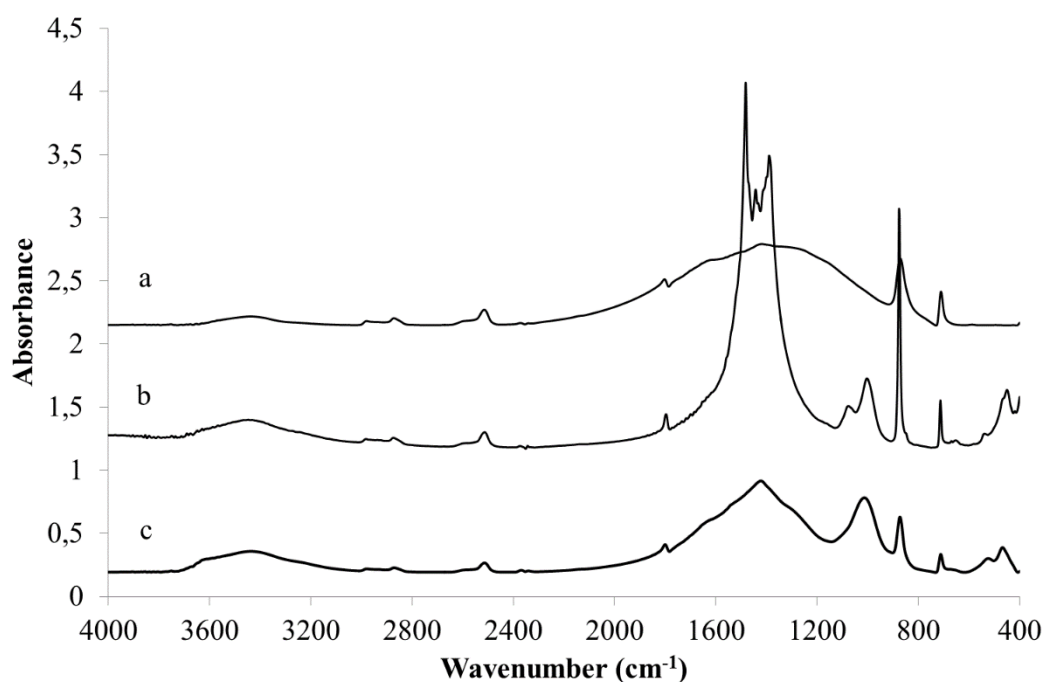

Figure 2. FTIR spectra of a) reference $CaCO_3$ and b) filter cake obtained from CO_2-ulexite reaction, c) filter cake obtained from CO_2-colemanite reaction

Characteristic bands of $CaCO_3$ at 1390, 871 and 711 cm^{-1} wavenumbers are shown in Figure 2-a. the peak at 1390 cm^{-1} is due to the out of phase CO_3 stretching; the medium-weak sharp peak at 871 cm^{-1} is caused by the out-of-plane deformation of the CO_3 ion; a weak peak at 711 cm^{-1} involves CO_3 in-plane deformation [15]. The major peaks in the IR spectrum of the powder formed or remained at the end of colemanite-CO_2 reaction at 1394, 868 and 710 cm^{-1} belong to

the calcium carbonate structure (Fig. 2c). The band at 1000 cm^{-1} is caused by the structures of Si-O and Al-O which present as impurity in colemanite mineral. From the comparison of Fig. 2a and Fig. 2c, calcium carbonate is formed based on the bands observed at 1390, 871 and 711 cm^{-1} wavenumbers.

XRD patterns of powders obtained at the end of CO_2-ulexite reaction and CO_2-colemanite reaction in aqueous phase are shown in Figure 3. When the patterns of powders in Fig. 3 were compared to each other, major peaks are same in each pattern. By the comparison of those patterns with the reference XRD data (JCPDS 5-0586) for $CaCO_3$, it was clearly determined that calcite was formed from the reactions of colemanite-CO_2 and ulexite-CO_2 in aqueous phase. The peak with the maximum intensity at 2θ 29.60 in Fig. 3 is attributed to the reflections from (104) plane of $CaCO_3$ [16].
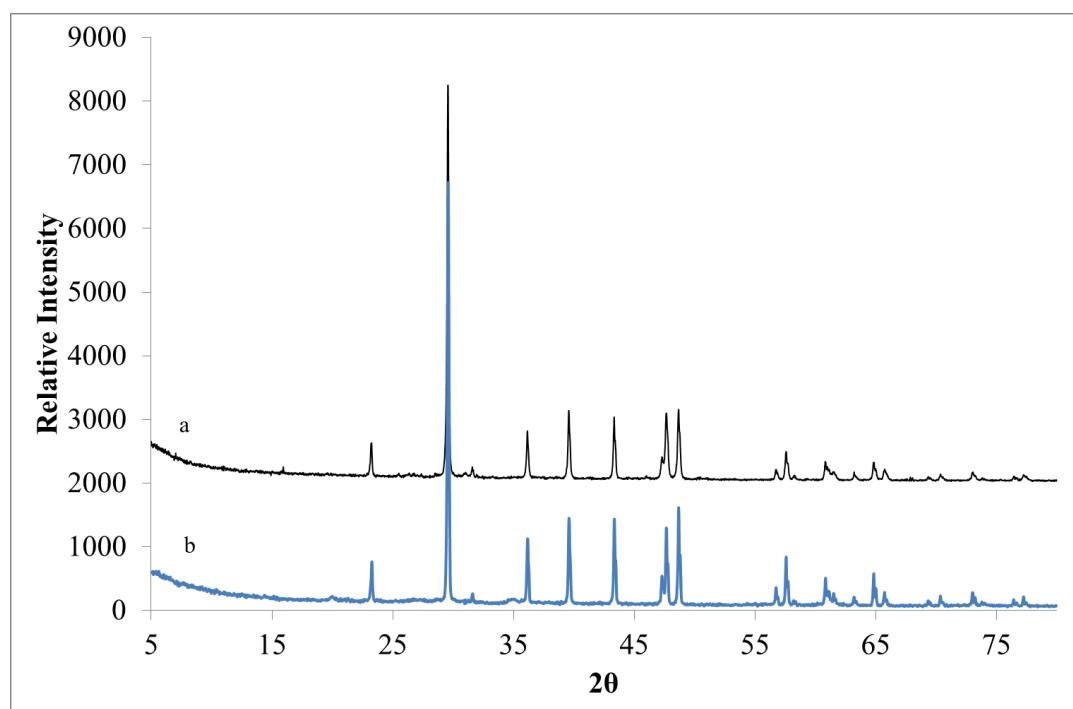

Figure 3. XRD patterns of the powder remained from a) CO_2-ulexite; b) CO_2-colemanite.

Both minerals, ($2CaO•3B_2O_3•5H_2O$) and ($Na_2O•2CaO•5B_2O_3.16H_2O$) were digested by the attack of H^+ proton in water. Cations of Ca^{2+} and Na^+ are present in solution after dissolution of minerals, as well. Carbonic acid formed by dissolution of CO_2 in water reacts with those cations to produce metal carbonates. TG curves of samples produced from CO_2-colemanite and CO_2-ulexite reactions are shown in Figure 4 and Figure 5, respectively. Calcium carbonate begins to decompose at 600°C by releasing CO_2 and the total mass loss is 44% by weight [17]. The mass loss of filter cake was 35% as seen in Fig. 4a which is lower than the theoretical or pure $CaCO_3$. The difference in mass losses of theoretical and filter cake is caused by the impurities (5.9% SiO_2; 3.0% MgO and 1.41% Al_2O_3) presented in the colemanite mineral. The powder crystallized from filtrate of CO_2-colemanite reaction (Fig. 4b) starts to mass loss at 50°C and total mass loss was recorded as 42% in the temperature range of 50 to 200°C. This thermal behavior is in good agreement with pure boric acid having mass loss of 43.8%. TG curves of powder crystallized from filtrate and filter cake obtained from the reaction of CO_2-

ulexite reaction is shown in Fig. 5a and Fig. 5b, respectively. Decomposition of the crystallized product occurs between 80-400°C (Fig. 5a) with a mass loss of 25%. Crystallized product could be mixture of boric acid and some sodium borate. On the other hand, filter cake remained in the reactor may include impurities presented initially in the mineral. Because of this, mass loss (35%) on Fig. 5b is lower than the corresponding mass loss (43.8%) of calcite.
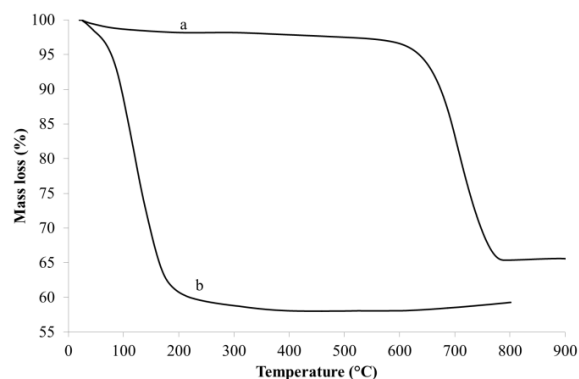
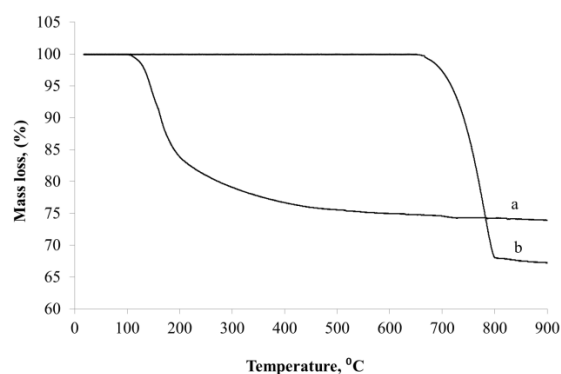**Figure 4.** TG curves of the samples from CO_2-colemanite reaction.

Figure 5. TG curves of the samples from CO_2-ulexite reaction

The effect of pressure was investigated on the reaction of colemanite and CO_2 in aqueous phase. As the solubility of CO_2 in water is directly proportional to the pressure, the reaction was carried out at higher pressures. As shown in Figure 6, the conversion increased with rising pressure up to 8MPa; further increase of the pressure did not make a significant change on the reaction. This result can be explained by the critical pressure of CO_2 (7.39MPa), when this threshold value is exceeded, mass transfer limitations diminishes at the temperatures greater than critical value (31.1°C). The solubility power of supercritical CO_2 is greater than the solubility of CO_2 at lower pressures. Solubility power is related to pH of the solution where CO_2 dissolves to produce proton. Formed proton is responsible for dissolution of boron minerals.
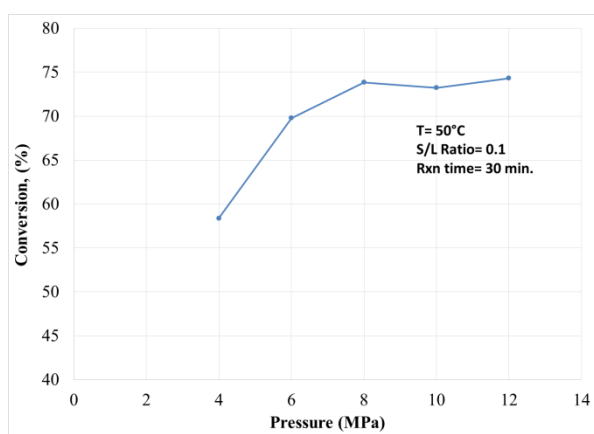
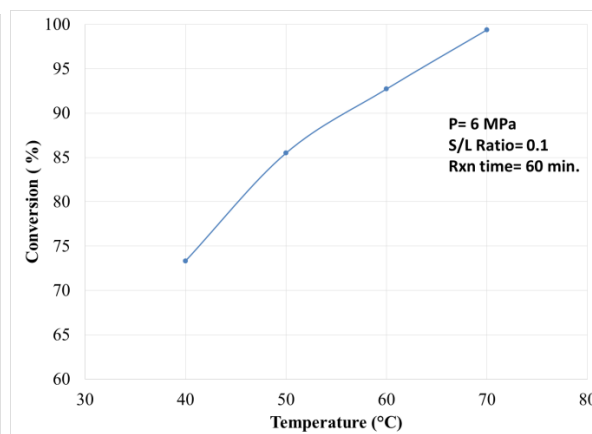**Figure 6.** Effect of pressure on the CO_2-colemanite reaction.

Figure 7. Effect of temperature on the CO_2-colemanite reaction

The effect of the temperature above critical temperature of CO_2 (40-70°C) was investigated on CO_2 colemanite reaction as shown in Fig. 7. When temperature is increased from 40°C to 70°C, conversion increased from 70% to 99% at 6 MPa pressure and for 60 minutes of reaction time.

Reaction rate usually increases with rising temperature as given by Arrhenius equation. On the other hand, solubility of gases is inversely proportional to the temperature rise. For the reaction of colemanite and CO_2 in aqueous phase, temperature rise brought a significant increase in conversion. Another important derivation from the Fig. 7 is that both reaction time (1h) and reaction temperature (70°C) are lower than the commercial process which is carried out at 88-92°C for 3-3.5 h. The cost of CO_2 pressurization in a new process can be compensated from the energy cost of commercial process. From the comparison of Fig. 6 and Fig. 7, it was clearly seen that conversion was increased from 70% to 85% by increasing reaction time from 30 min. to 60 min. at 6 MPa and 50°C.

CONCLUSION

The experimental CO_2 binding capacity (R_{CO_2}) for colemanite is 0.17 kg CO_2/kg mineral, whereas R_{CO_2} of ulexite is 0.123 kg CO_2/kg mineral. Thus less colemanite is need for the same amount of CO_2 that will be sequestrated. The use of carbon dioxide in the boron industry will provide a more sustainable and efficient process and will help to reduce CO_2 emissions from the boric acid production process. The solid phase crystallized from filtrate was boric acid as inferred from its FTIR spectrum and XRD pattern according to the JCPDS 30-0199. The filtrate phase obtained at the end of reaction and washing solutions were analyzed for boric acid using volumetric titration in which glycerol and phenolphthalein were present. Filter cakes obtained at the end of both reactions are calcium carbonate and mixture of unreacted impurities. 99.0% of colemanite mineral was digested in the reaction for 1 h reaction time at 70°C and 6MPa pressure. 88.7% conversion value was obtained for ulexite reaction at 70°C and 9MPa and for 2 h of reaction time.

REFERENCES

[1] Dr. Pieter Tans, NOAA/ESRL (www.esrl.noaa.gov/gmd/ccgg/trends/) and Dr. Ralph Keeling, Scripps Institution of Oceanography (scrippsco2.ucsd.edu/).

[2] IPCC, 2005: IPCC Special Report on Carbon Dioxide Capture and Storage. Prepared by Working Group III of the Intergovernmental Panel on Climate Change [Metz, B., O. Davidson, H. C. de Coninck, M. Loos, and L. A. Meyer (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 442 pp.

[3] LIU, Z.; Zhao, J. Contribution of carbonate rock weathering to the atmospheric CO_2 sink, Environmental Geology 39/9, 1053, (2000).

[4] R.M. Santos, W. Verbeeck, P. Knops, K. Rijnsburger, Y. Pontikes, T.V. Gerven, Integrated Mineral Carbonation Reactor Technology for Sustainable Carbon Dioxide Sequestration: 'CO$_2$ Energy Reactor', Energy Procedia, 37, 2013, 5884-5891.

[5] N.A. Kojima, Ueno, N. & Uemiya, S., Absorption and fixation of carbon dioxide by rock weathering, Energy Conversion and Management 38, 1997, S461-S466.

[6] B. Metz, O. Davidson, H. C. de Coninck, M. Loos, L.A. Meyer, IPCC Special Report on Carbon Dioxide Capture and Storage. Prepared by Working Group III of the Intergovernmental Panel on Climate Change, Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 2005, 442 pp.

[7] Benson, H.E., Field, J.H. and Jimeson, R.M., CO_2 absorption employing hot potassium carbonate solutions. Chemical Engineering Progess,. 50: p. 356-364, (1954).

[8] S. Reddy, J. Scherffius, S. Freguia, and R. C., 2003. Fluor's Econamine FG PlusSM Technology: An Enhanced Amine-Based CO2 Capture Process, in Second National Conference on Carbon Sequestration. Alexandria, VA.

[9] Bello, A., and Idem, R., (2005). Pathways for the formation of products of the oxidative degradation of CO_2-loaded concentrated aqueous monoethanolamine solutions during CO_2 absorption from flue gases Ind.Eng.Chem.Res. 44. 945-969.

[10] H. Thee, K. T. Smith, G. D. Silva, S. E. Kentish, G. W. Stevens, 2012. Carbon Dioxide Absorbtion into Unpromoted and Borate Catalyzed Potassium Carbonate Solutions, Chem. Engineering J., 181–182, 694–701.

[11] X. Wang, V. Alvarado, N. Swoboda-Colberg, J.P. Kaszuba, Reactivity of Dolomite in Water-Saturated Supercritical Carbon Dioxide: Significance for Carbon Capture and Storage and for Enhanced Oil and Gas Recovery, Energy Conversion and Management, 2013, 564-573.

[12] Gönen, M., E. Nyankson, and R. Gupta, Boric acid production from colemanite together with ex-situ CO_2 sequestration. Ind. Eng. Chem. Res. Vol. 55. 2016.

[13] Yılmaz O., Ünlü F., Karakoç G., Maraşlıoğlu D., Gökçek S., Production of Boric Carbonate and Sodium Bicarbonate from Sodium Borate Solvents, World Intellectual Property Organizastion, WO 2010/140989 A1 (2010).

[14] Web, http://www.etimaden.gov.tr/files/files/SPEKT%20KATALOG%202016.pdf (Access date: March 07, 2018).

[15] N.B. Colthup, L.H. Daly, S.E. Wiberley, Introduction to Infrared and Raman Spectroscopy, Third Edition ed., Academic Press. Inc., San Dieogo, 1990.

[16] B.P. Bastakoti, S. Guragain, Y. Yokoyama, S.-i. Yusa, K. Nakashima, 2010. Synthesis of Hollow $CaCO_3$ Nanospheres Templated by Micelles of Poly (styrene-b-acrylic acid-b-ethylene glycol) in Aqueous Solutions, Langmuir, 27 379-384.

[17] J.P. Sanders, P.K. Gallagher, 2002. Kinetic Analyses Using Simultaneous TG/DSC Measurements: Part I: Decomposition of Calcium Carbonate in Argon, Thermochimica Acta, 388, 115-128.