International Journal of Engineering Research and General Science Volume 4, Issue 4, July-August, 2016
ISSN 2091-2730

Process Intensification of Colemanite Leaching Using Sulfuric Acid in a Batch Reactor

Ademola S. OLUFEMI[1]*, Mayowa A. AZEEZ[2], and Oluwafemi O. OLAYEBI[3]
[1]Department of Chemical/Petroleum Engineering, Niger Delta University, Wilberforce Island, Bayelsa State, Nigeria.

[2]Department of Chemistry, State University of Ekiti, Ado-Ekiti, Ekiti State, Nigeria.

[3]Department of Chemical Engineering, Federal University of Petroleum Resources, Effurun, Delta State, Nigeria.

E-mails: [1]olufemi.stanford@gmail.com, [2]mayowa.azeez@eksu.edu.ng, [3]olayebi.oluwafemi@fupre.edu.ng

Abstract— This contribution investigated methods of intensifying the leaching of colemanite using sulphuric acid for the improvement of boric acid recovery. Boric acid is one of the most commonly used boron compounds produced by dissolving colemanite ($2CaO\cdot3B_2O_3\cdot5H_2O$) in aqueous sulfuric acid which results in the formation of gypsum ($CaSO_4\cdot2H_2O$) as a by-product and must be separated from the main product. The dissolution of colemanite gives the amount of boric acid formed; the purity and crystallization of boric acid are affected by filtration of gypsum. In this study, and the factors that were examined in this study were stirrer agitation speed, particle size, reaction temperature on the dissolution of colemanite in the reaction of boric acid production. Colemanite having the same elemental chemical composition and particle size, sulfuric acid and distilled water were used as reactants for the boric acid production reaction in this study. The crushing of the colemanites were one in a jaw crusher, ground in a hammer mill and then sieved. The biggest diameter of the colemanite minerals was 150 μm and the experiments were performed at different particle sizes of colemanite (0-150, 0-250 and 250-1000 μm), temperatures (70- 90 °C) and stirring speed (350-500 rpm). The results obtained, showed that increasing the acid concentration results in a significant increase boric acid recovery. The highest recovery was obtained at 85 °C temperature. Increasing the mixing speed form 350 rpm to 500 rpm increased the recovery by 5.5%. Thus, the increase in agitating speed from 350 to 500 rpm resulted in a significant increase in boric acid recovery. Thus, it was concluded that agitation have a significant effect on boric acid recovery above 500 rpm. The batch process proved to be better than the semi-batch process in terms of the amount of boric acid recovered.

Keywords— Colemanite, Boric acid, Sulfuric acid, Batch Reactor, Temperature, Stirring rate, and Particle size.

INTRODUCTION

Boron minerals can be used in some industrial area as crude minerals. In general, their applications after refining and end-products are wider than crude ones. Boron minerals, borates and compounds have a very wide range of applications. With escalating depletion of boron mineral reserve, boron minerals including Tincal [$Na_2B_4O_7.10H_2O$], Kernite [$Na_2B_4O_7.4H_2O$], Ulexite [$NaCaB_5O_9$.$8H_2O$], Probertite [$NaCaB_5O_9$.$5H_2O$], Colemanite [$Ca_2B_6O_{11}.5H_2O$], Pandermite [$Ca_4B_{10}O_{19}.7H_2O$], Boracite [$Mg_3B_7O_{13}Cl$], Szaibelyite [$MgBO_2(OH)$], Sassolite [H_3BO_3], and Hydroboracite [$CaMgB_6O_{11}.H_2O$] are becoming an important source of boric acid (Özbayoğlu et al.,1992).

Colemanite is used as the raw material in the boric acid production. It is one of the most important boron minerals in the world. More than 200 boron minerals have been known but relatively few of them have commercial significance (Roskill, 2002). Colemanite, like other borates, is a complex mineral that is found in desert borax deposits and Tertiary clays in old lake beds. Colemanite is a secondary mineral, meaning that it occurs after the original deposition of other minerals. The mineral borax is directly deposited in regions from the evaporation of water due to run off from nearby mountain ranges. The runoff is rich in the element boron and is highly concentrated by evaporation in the arid climate. Ground water flowing through the borax sediments is believed to react with the borax and form other minerals such as ulexite. It is believed that colemanite may have formed from ulexite. Colemanite is found in geodes within the borax sediment. It's exact means of formation are still not well understood (Amethyst Galleries, 1997). The picture of colemanite mineral is given in Figure 1.1. The basic structure of colemanite contains endless chains of interlocking $BO_2(OH)$ triangles and $BO_3(OH)$ tetrahedrons with calcium, water molecules and extra hydroxides interspersed between the chains (Chuck Brown, 2000).

Figure 1: Picture of colemanite mineral

Colemanite [$Ca_2B_6O_{11}.5H_2O$] is frequently leached by using sulphuric acid, though there are various leaching agents (also called lixiviants). Leaching can be done by different liquids: acids, bases, water and chelating agents.

However, since acidic medium are advantageous for the dissolution of metals, acids are commonly used for the leaching of heavy metals. Sulphuric acid is the most common leaching agent because of its chemical properties and also its relatively low cost (Napo et al., 2011).

The rate of leaching depends on the parameters used such as temperature, time, pH, particle size, concentration of lixiviant, slurry density and agitation speed (Gupta and Mukherjee, 1990).

Boric acid can be viewed as a hydrate of boric oxide and exists both as a trihydrate, orthoboric acid ($B_2O_3{\cdot}3H_2O$ or H_3BO_3), and as a monohydrate, metaboric acid ($B_2O_3{\cdot}H_2O$ or HBO_2). Only the more stable orthoboric acid form is of commercial importance and is usually referred to simply as boric acid. The terms "pyroboric acid" and "tetraboric acid" are sometimes encountered in the literature, but these acids do not actually exist as solid-phase compounds (Ullmann, 2002). Boric acid is white granule or powder. Its density is 1.435 g/cm^3. It melts at 171 °C. Solubility in water at 20 °C is 4.7 g boric acid/ g solution (Patnaik, 2002).

Boric acid is used to make variety of glasses comprising fiber glass, heat resistant borosilicate glass and sealing glasses and also used to make porcelain. Major use of boric acid is to prepare a number of boron containing compounds which include inorganic borate salts, boron halides, borate esters, fluoroborates and many boron alloys. The usage of boric acid are: antiseptic, eye washes and ointments; a preservative in natural products; to protect wood against insect damage; in washing citrus fruits; as a catalyst in hydrocarbon oxidation; as a flame retardant in cellulose insulation; in nickel electroplating baths; and as a buffer in ammonia analysis of wastewaters by acid titration (Patnaik, 2002).

Heterogeneous solid-liquid reactions leading to crystallization of the product are widely used in production of many industrial chemicals. Some examples for solid-liquid reaction crystallizations are listed in Table 1.

Table 1: Some examples of solid-liquid reaction crystallizations (Bechtloff et al., 2001)

Reaction System
Calcium citrate + Sulfuric acid → Citric acid + Calcium sulfate
Oxalic acid + Borax → Sodium oxalate + Boric acid
Borax + Propionic acid → Sodium propionate + Boric acid
Colemanite + Sulfuric acid → Boric acid + Gypsum
Sodium sulfide + Benzylchloride → Benzylsulfide + Sodiumchloride

Different type of behavior of reacting solid particles can be seen. Only a solid phase reaction can occur on the surface of the particles if the solid reactant is insoluble in the reaction medium. The shrinking core model developed by Yagi and Kunii (1955, 1961) explains this type of behavior of reacting solid particles. According to this model, the reaction occurs first at the outer skin of the particles. Then, the zone of the reaction moves toward the center of the solid particle leaving behind a solid product layer called as ash (Levenspiel, 1999).

If the solid has a slight or a high solubility, a liquid phase reaction may dominate the process. So, the dissolution of solid reactant and the crystallization of the product happen simultaneously. When the fluid becomes supersaturated, the solid product precipitates. However, the solid product may cover solid reactant. It may lead to a reduced reaction rate or incomplete conversion of solid reactant. (Bechtloff et al., 2001). Table 2 shows the studies on dissolution of colemanite in various mediums, the reaction of colemanite with sulfuric acid is heterogeneous solid-liquid reaction leading to crystallization of the product.

Table 2. Studies on dissolution of colemanite in various mediums

Researchers	**Medium**	**Parameters**	**Results(Empirical formulas)**
Kocakerim and Alkan (1987)	Water saturated with SO_2	Particle size (250-1700 μm) Temperature (11-40 °C) Stirring rate (200-1000 min^{-1})	$1-(1-X)^{1/3}=\frac{bk_s C_g M_B}{\rho_B R}t$
Kum and coworkers (1993)	Ammonium chloride solutions	Calcination temperature(300-460 °C) Solution concentration(1-3 mol L^{-1}) Reaction temperature (25-65 °C) Pre-hydration	$(1-X)^{-1}-1=k[NH_4Cl]^{3/4}t$
Özmetin and coworkers (1996)	Aqueous CH_3COOH solutions	Particle size (0.137- 0.081 mm) Solid-to-liquid ratio (5-35 g mL^{-1}) Temperature (10.6- 50 °C)	$-\ell n(1-X)=$ $56664(D)^{-1.42}(S/L)^{-0.27}$ $\exp(-6193.0/T)t$
Gürbüz and coworkers (1998)	Boric acid solutions	Boric acid concentration (0-20 % wt)	Solubility (1.7- 19.6 g kg $solution^{-1}$)
Temur and coworkers (2000)	H_3PO_4 solutions	Particle size (250-1400 μm) Acid concentration (1.43-19.52 wt %) Solid-to-liquid ratio (0.02-0.08 g mL^{-1}) Stirring rate (300-600 min^{-1}) Reaction temperature (2.5 -35 °C)	$1-(1-X)^{1/3}=$ $(5.87\times10^9)(D)^{-0.744}(S/L)^{-0.453}$ $(C)^{0.328}\exp^{-53.91/RT}t$
Küçük and coworkers (2000)	Water saturated with SO_2	Particle size (0.150- 1400 mm) Solid-to-liquid ratio (0.02-0.06 g mL^{-1}) Stirring rate (300-500 min^{-1}) Reaction temperature(18-40 °C)	$1-(1-X)^{1/3}=$ $(3.423\times10^4)(D)^{-0.7}(S/L)^{-0.65}$ $\exp^{-4754/T}.t$

Tunc and Kocakerim (1998) investigated the dissolution of colemanite in aqueous sulfuric acid. The parameters were temperature (10-60 °C), particle size of colemanite (0.3625-1.5 mm), solid-to-liquid ratio (0.01-0.175 g mL^{-1}), acid concentration (0.25-2 mol L^{-1}) and stirring rate (20.93-62.80 s-1). It was found that temperature and stirring rate had positive effect on the rate. Conversion rate increased with the acid concentration up to 1 mol L^{-1} and decreased with the concentrations above 1 mol L^{-1}. The rate of dissolution reaction was expressed in equation (1).

$$-\ell n(1-x)=82.52(D)^{-0.821}(SR)^{0.426}(S/L)^{-0.383}e^{-3465/T}t \qquad (1)$$

where X is the fractional conversion, D is the particle size of colemanite in mm, SR is the stirring rate in s^{-1}, S/L is the solid-to-liquid ratio g mL^{-1} and t is the time in min.

Kalafatoğlu and coworkers (2000) stated that if in the reaction of colemanite and sulfuric acid the concentration of sulfuric acid was more, besides the colemanite, some other impurities also dissolved. So, in this study, the most suitable concentration for sulfuric acid was searched and it was shown that if the acid concentration was hold around 5 %, the dissolution of clay and the other impurities was less. Dissolution kinetics of colemanite in sulfuric acid in the absence and presence of ultrasound was studied by Okur and coworkers (2002). An Avrami-type equation was used successfully to explain kinetic data. Activation energy was 30 kJ/mol in both situations. Ultrasound affected the pre-exponential factor in rate constant.

Boric acid is produced from colemanite ($Ca_2B_6O_{11}.5H_2O$) ore by reaction with sulfuric acid. The overall reaction in the reactor is given as below;

$$\begin{aligned}&2CaO.3B_2O_3.5H_2O(s) + 2H_2SO_4\ (l) + 4H_2O\ (l) \rightarrow \\ &2CaSO_4.2H_2O\ (s) + 6H_3BO_3\ (aq)\end{aligned} \qquad (2)$$

This overall reaction consists of two consecutive reactions, dissolution of colemanite and formation of gypsum. In the first reaction boric acid produced and this reaction is a very fast reaction.

Boric Acid Production Reaction:

$$\begin{aligned}&2CaO.3B_2O_3.5H_2O(s) + 2H_2SO_4\ (l) + 2H_2O\ (l) \rightarrow \\ &2Ca^{2+} + 2SO_4^{2-} + 6H_3BO_3\ (aq)\end{aligned} \qquad (3)$$

In the second step, gypsum crystals are formed and stay in the reaction mixture to grow up to a size large enough to be filtered out of the solution.

Gypsum Crystallization Reaction:

$$Ca^{2+} + SO_4^{2-} + H_2O\ (l) \rightarrow CaSO_4.2H_2O(s) \qquad (4)$$

MATERIALS AND METHOD

Materials used

Experiments were conducted using two different reactors; a batch reactor and a leaching cell, colemanite, sulfuric acid, a mechanical stirrer, a heating jacket, a pH meter, a thermocouple, a temperature control unit and a vacuum pump, and distilled water.

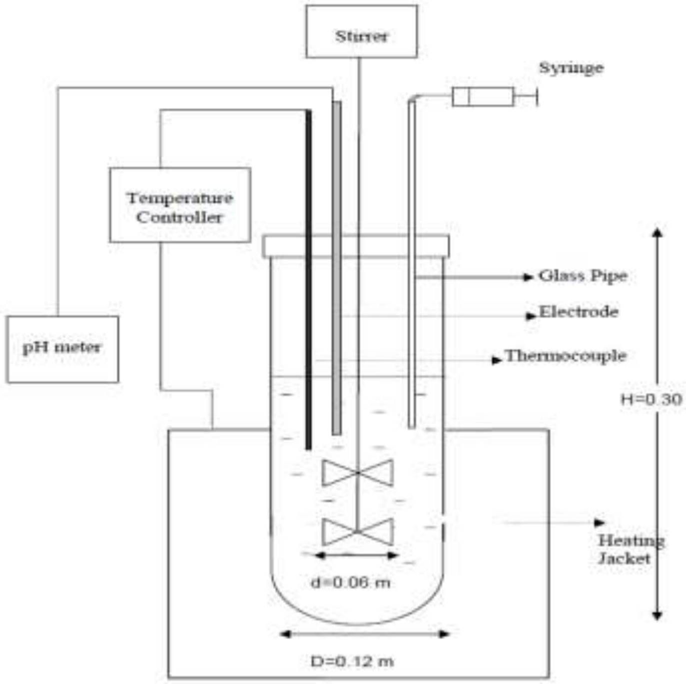

Figure 2: The schematic representation of the batch reactor set-up without filtration Unit

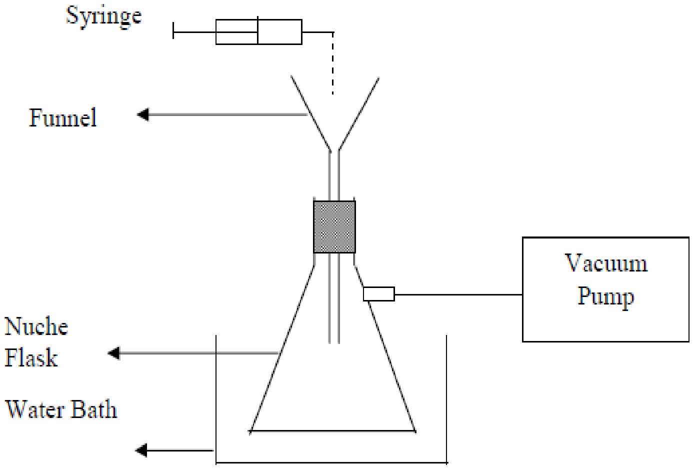

Figure 3: Schematic representation of filtration unit

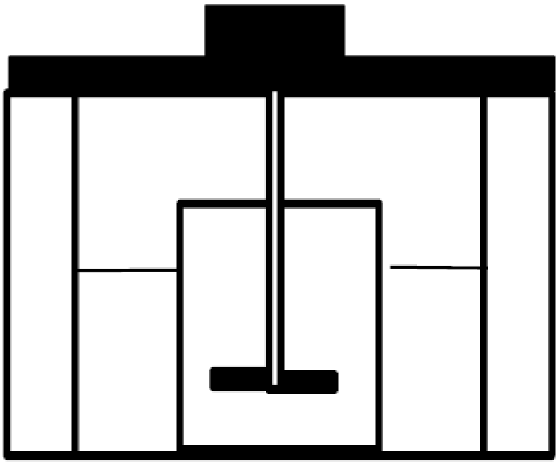

Figure 4: Leaching cell equipment

Method used

The CaO and B_2O_3 contents of the colemanite had to be known to calculate the amount of colemanite added to the reactors according to the CaO/SO_4^{2-} ratio chosen and the conversion of colemanite to boric acid, respectively. Colemanite analysis was done using X-ray Fluorescence (XRF) in Niger Delta University, Chemical Engineering Department. The chemical analysis of colemanite used in the experiments showed that the ore contained between 43.57-43.87 % of colemanite and the remaining percentage is constituted by other oxides as outlined in Table 3.

TABLE 3: XRF COLEMANITE (%) ELEMENTAL COMPOSITION

Component (%)	Colemanite 0-250 µm	Colemanite 250-1000 µm
B_2O_3	43.57	43.87
CaO	30.90	28.61
Na_2O	0.22	0.79
MgO	0.79	0.45
Al_2O_3	0.22	0.17
SiO_2	0.60	0.21
SO_3	0.14	0.50
Fe_2O_3	0.17	0.31

As_2O_3	0.00	0.03
SrO	0.56	0.64
TiO_2	0.20	0.056
K_2O	0.08	0.059
BaO	0.005	0.015
Li	0.045	*
Others	22.50	17.46

Firstly, a given amount of distilled water was put into the reactor. The mechanical stirrer was started to operate at desired stirring rate. Then sulfuric acid was added slowly into the reactor. An initial sulfate concentration of 0.623 M in solution was used for all experiments. The temperature control unit was adjusted to reaction temperature and kept constant. Certain amount of colemanite was fed into the reactor at once. This time was considered as the starting time of the reaction. The electrode was placed in the reactor to measure the pH of the slurry. The samples were withdrawn by 50 ml syringe attached to a glass pipe. Then, samples were filtered immediately by using vacuum pump connected to 250 ml nuche flask. A funnel was placed on top of flask. Blue band filter paper was put on the funnel. In order to prevent the boric acid solution to crystallize, the flask was placed into hot water. Solid particles and liquid were collected on filter paper and flask, respectively.

The liquid portion was taken from the flask by the help of micropipettes and analyzed for boric acid and calcium ion concentration. The filtrates were analyzed for change of crystal structure of gypsum with respect to time.

RESULTS

In the experiments, particles smaller than 250 μm and greater than 250 μm were used to investigate the effect of particle size on dissolution of colemanite ore, gypsum formation and particle size distribution of gypsum crystals.

Table 4. The screen analysis of Colemanite 0-250 μm

Mesh No	Dpi, μm	Mass Fraction by Weight	Avg. Dpi, μm	Cum. Mass Fraction
60	250	0.280	-	0.720
100	150	0.370	200	0.350
140	106	0.170	128	0.180
170	90	0.075	98	0.105
270	53	0.063	45	0.042
Pan	-	0.042	27	0.000

Table 5. The screen analysis of Colemanite 250-1000 μm

Mesh No	Dpi, μm	Mass Fraction by Weight	Avg. Dpi, μm	Cum. Mass Fraction
25	710	0.193	-	0.807
35	500	0.305	605	0.502
45	355	0.312	428	0.19
60	250	0.176	303	0.014
Pan	-	0.014	125	0.000

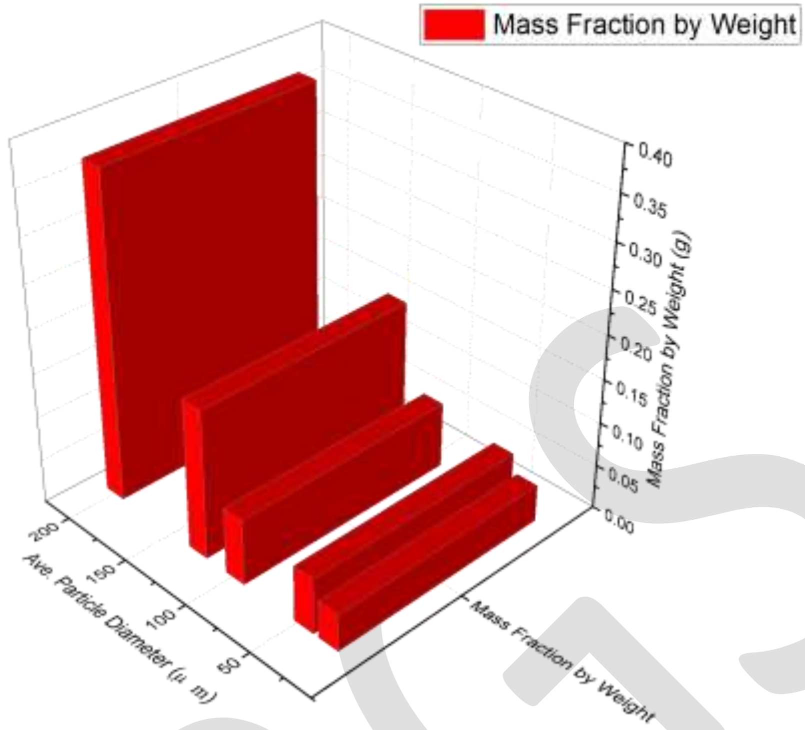

Figure 5: Differential particle size distribution of Colemanite 0-250 μm

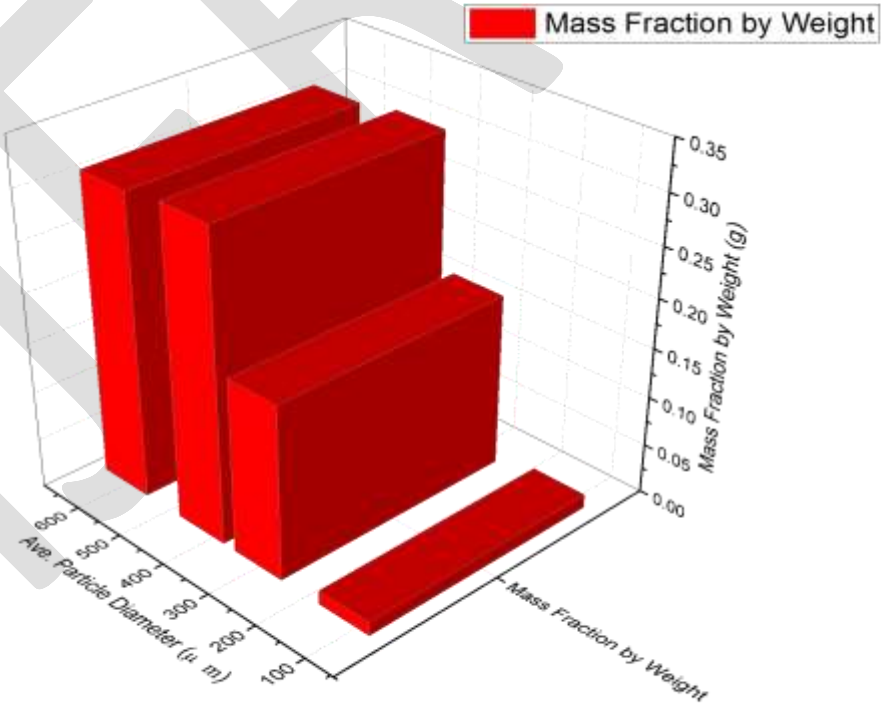

Figure 6: Differential particle size distribution of Colemanite 250-1000 μm

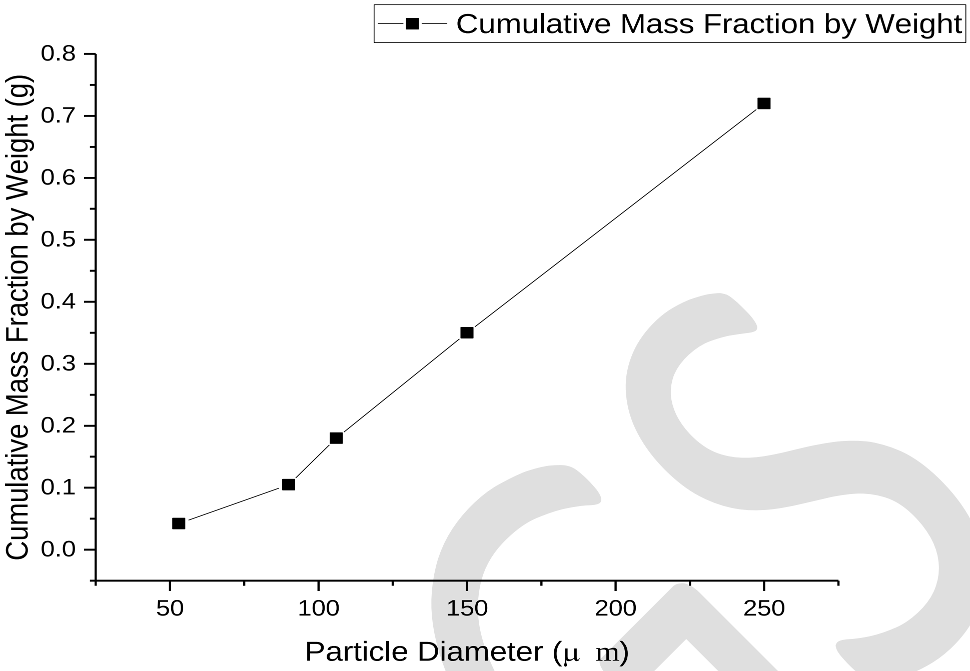

Figure 7: Cumulative particle size distribution curve for Colemanite 0-250 μm

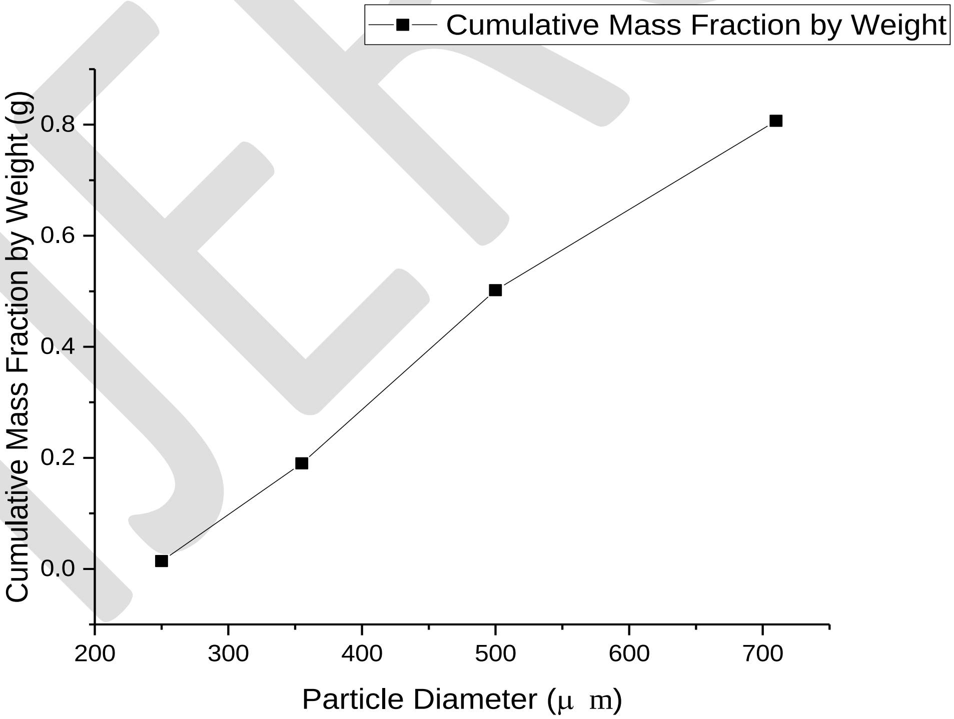

Figure 8: Cumulative particle size distribution curve for Colemanite 250-1000 μm

Originally, sieve analysis was performed to separate the particles larger than 250 μm. The 60 mesh sieve (corresponding to 250 μm) was used for this drive, and was seen that nearly 35 percent of the colemanite was left on this sieve. In other words, nearly 35 percent of the colemanite particles were larger than 250 μm. The screen analyses of the colemanite lesser and larger than 250 μm are given in Table 4 and Table 5, respectively. In these tables, the mass fractions of the colemanite on each sieve and the cumulative mass fractions of the colemanite under that sieve were represented. The particle diameter is the maximum diameter of the particles that could pass the former sieve. The average particle diameter stands for the arithmetic mean of the minimum and maximum diameter of the particles on that sieve. Figures 5 and 6 present the differential particle size distribution of the colemanite particles smaller and greater than 250 μm, respectively. The mass fractions of the colemanite particles on each sieve according to their average particle diameters were illustrated. Figures 7 and Figure 8 show the cumulative particle size distribution of the colemanite particles smaller and greater than 250 μm, respectively. For each particle diameter, cumulative mass fraction of the colemanite smaller than that diameter was represented. When the particle size distribution of the colemanite mineral was examined, it was seen that most of the particles had had average particle size between 2.5 and 10 cm. Therefore, the colemanite was crushed in the jaw crusher, then grinded in a hammer mill.

The Effect of Particle Size of Colemanite

The experiments were performed at 80 °C and 85 °C at 500 rpm stirring rate. Colemanite minerals smaller than 250 μm and 160 μm were used in the first group. The initial CaO/SO_4^{2-} molar ratio was 0.95. In the second group of the experiments, particles smaller and greater than the 250 μm were used. The initial CaO/SO_4^{2-} molar ratio was 1.0.

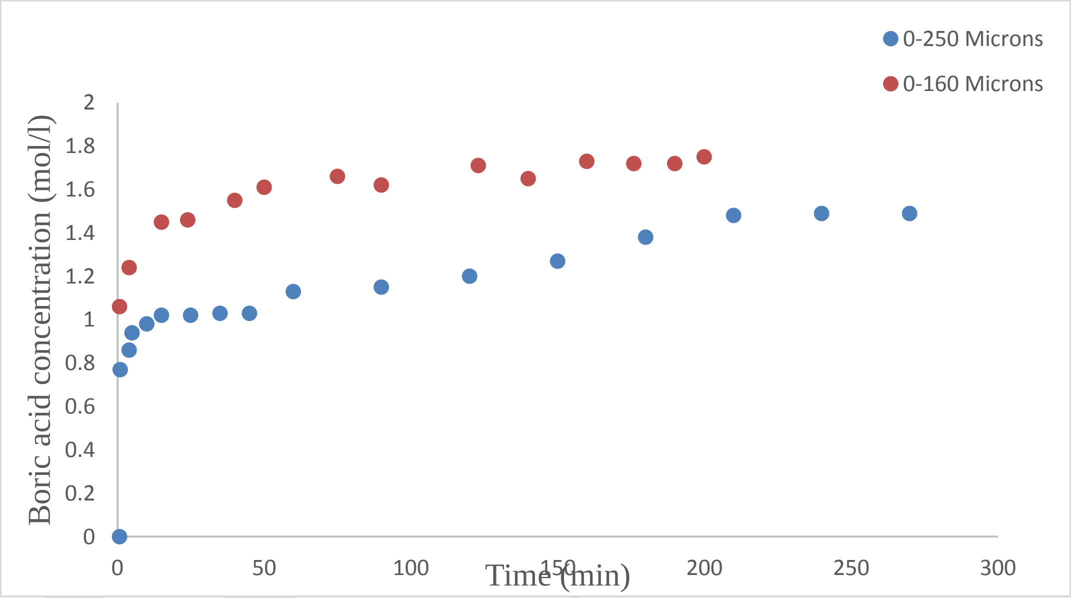

Figure 9: Variation of boric acid concentration in liquid with respect to time of particle size 0-160 and 0-250 microns at 80 ^{0}C

In the first group, the effect of particle size on dissolution of colemanite and formation of gypsum reactions were analyzed. Figure 9 shows that, the change of the boric acid concentration in the liquid phase with respect to time is slower for colemanite particles smaller than 250 μm. Also, a slightly inclined plateau is observed between 15 and 50 minutes only for these particles. Obviously, the colemanite particle size affects the dissolution reaction rate.

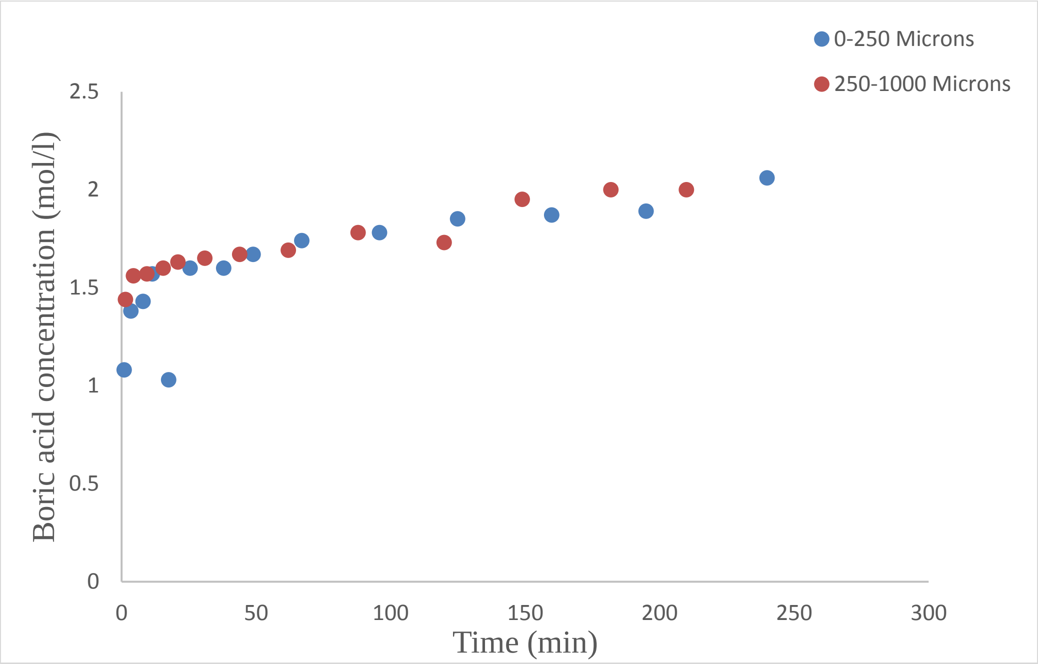

Figure 10: Variation of boric acid concentration in liquid with respect to time of particle size 0-250 and 250-1000 microns at 85 ^{0}C

Figure 10 illustrates the change in boric acid concentration in the liquid phase versus time at 85 °C, 500 revolution per minute (rpm) and initial CaO/SO_4^{2-} molar ratio of 1.00 for particle sizes greater than 250 µm of colemanite. The reaction mixture was stirred by using two propellers. As seen from the figure, the variation of boric acid concentration shows same trends for both particle sizes. In other words, insignificant effect of particle size of colemanite is observed if the experiments are performed with stirrer having two propeller. It means that stirrer type affects the dissolution.

The saturation concentration of calcium ion is the same for both experiments. Because, the saturation concentration is depend on temperature. In these experiments, the temperature was kept constant at 85° C.

Effect of particle size of colemanite on dissolution reactions becomes negligible if the stirrer used has two propellers. This showed that the stirrer type used is a critical parameter for boric acid production.

The Effect of Stirring Rate

Three experiments were performed at the initial CaO/SO_4^{2-} molar ratio of 1.00 and at 85 °C. The effect of stirring rate on dissolution of colemanite reaction were analyzed at 350, 400 and 500 stirring rates. During the experiments, variation of the boric acid concentration with respect to time were determined at different stirring rate is shown in Figure 11. As seen from the figure, the boric acid concentration at certain time increases with increasing stirring rate. This means that the dissolution of colemanite reaction is limited by the rate of diffusion of sulfate ions through the surface of the solid colemanite particles. The increasing stirring rate increases the mass transfer of H+ ions in solution through colemanite particles so the boric acid concentration increases with increasing stirring rate. The maximum boric acid concentration is obtained as 2.06 mol L^{-1} at 500 rpm stirring rate.

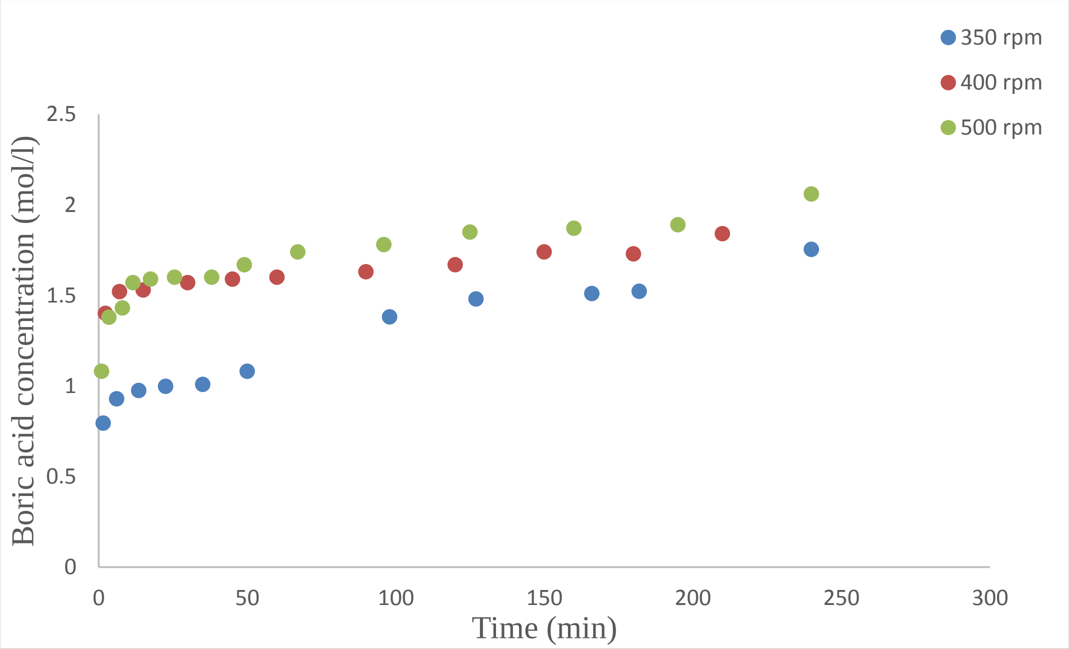

Figure 11: Variation of boric acid concentration in liquid with respect to time of different stirring rate at 85 ^{0}C

The Effect of Temperature

Two different types of colemanite were used. Experiments were performed at 70, 80, 85 °C for the particle size of colemanite greater than 250. Three experiments were performed at the initial CaO/SO_4^{2-} molar ratio of 1.00. In these experiments, stirring rate was kept constant at 400 rpm. During the experiments, variation of the boric acid concentration with respect to time were determined as shown in Figure 12. From the figure, the boric acid concentration at certain time increases with increasing temperature. Temperature affects the dissolution rate of colemanite. In this range of temperature, the dissolution rate increases with increasing temperature. This means that the rate of boric acid production depends on the reaction temperature.

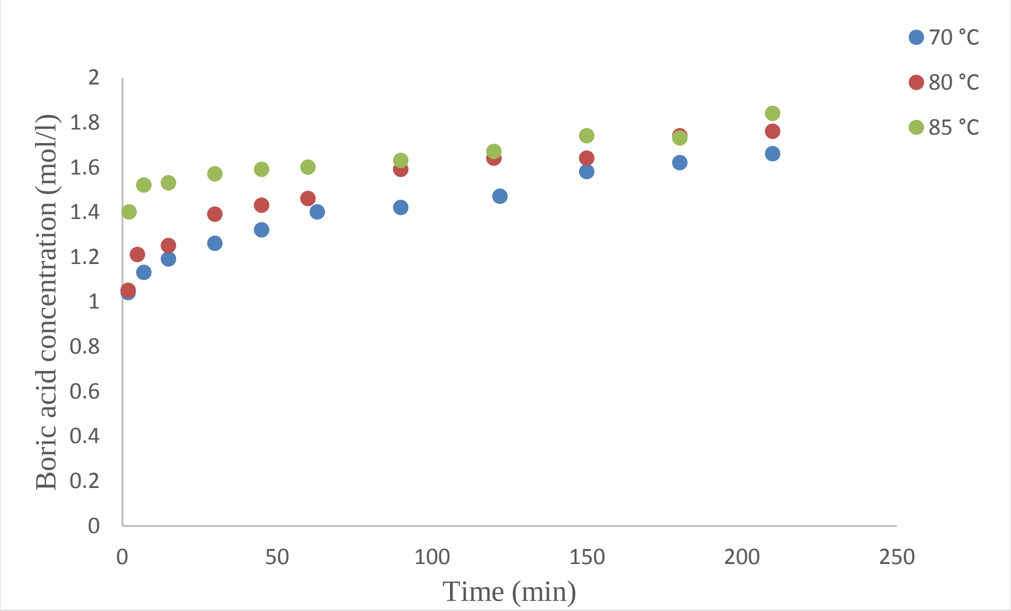

Figure 12: Variation of boric acid concentration in liquid with respect to time of different temperatures at 400 rpm.

CONCLUSION

In this study it is aimed to examine the effects of particle size of colemanite, stirring rate and reaction temperature in the reaction of colemanite in boric acid production.

Boric acid concentration increases and reaches an asymptotic value as the colemanite dissolves. From the material balance calculation, it is observed that nearly 90 % of the colemanite dissolves during first few minutes in the experiments performed with colemanite particle size of greater than 250 µm. So, the dissolution of colemanite is a fast reaction and the rate equation cannot be found from the obtained data. Also, it was seen that, the colemanite dissolution rate increases with decreasing particle size of colemanite (0-150 µm,0-250 µm, 250-1000 µm) because of increasing surface area, increasing stirring rate (350-500 rpm) due to increasing the mass transfer of H^+ ions in solution through colemanite particles and increasing temperature up to 85 °C. The dissolution rate of colemanite was faster at 85 C. Therefore, the optimum temperature for the production of boric acid should be between 80 and 85 °C.

REFERENCES:

1) Özbayoğlu G. and Poslu K., “Mining and Processing of Borates in Turkey”, Mineral Processing and Extractive Metallurgy Review, Vol. 9, pp. 245-254, 1992
2) Chuck Brown,”Minerals-n-More”, 2000
URL:http://www.minerals-n-more.com/Colemanite_Info.html
3) Roskill, “The Economics of Boron”, 10th Ed., pp.11-20, 2002
4) Amethyst Galleries, 1997
URL: http://mineral.galleries.com/minerals/carbonat/colemani/colemani.htm
5) Napo D., Ntuli F., Muzenda E., and Mollagee M., “Process Intensification of Zinc Oxide Leaching Process Using Sulphuric Acid” *Proceedings of the World Congress on Engineering and Computer Science*, 2011 Vol II WCECS 2011, October 19-21, 2011, San Francisco, USA
6) Bechtloff B., Jüsten P., Ulrich J., “The Kinetics of Hetergenous Solid-liquid Reaction Crystallizations-An Overview and Examples”, Chemie Ingenieur Technik, Vol.73, pp.453-460, 2001
7) Gupta C. K. and Mukherjee T.K., “*Hydrometallurgy in extraction processes”*, CRC Press, 1990, vo. 2, pp.39-78.
8) Ullmann, “Ullmann’s Encyclopedia of Industrial Chemistry”, 6th Ed., USA, 2002
9) Patnaik P., “Handbook of Inorganic Chemicals”, Mc. Graw-hill Handbooks, New York, pp. 119-120, 2002
10) Levenspiel O., “Chemical Reaction Engineering”, 3rd Ed., pp.566-585, 1999
11) Tunç M. and Kocakerim M.M., “Kolemanitin H2SO4 Çözeltisinde Çözünme Kinetiği”, UKMK 3, Erzurum, 2-4 Eylül, pp. 1235-1240, 1998
12) Kalafatoğlu İ.E., Örs N. and Özdemir S.S, “Hisarcık Kolemanitinin Sülfürik Asitle Çözünme Davranışı”, UKMK 4, İstanbul, 4-7 Eylül, 2000
13) Okur H., Tekin T., Ozer A.K., Bayramoğlu M., “Effect of Ultrasound on Dissolution of Colemanite in H2SO4”, Hydrometallurgy, Vol. 67 pp. 79-86, 2002