

EFFECTS OF TEMPERATURE AND CO₂ PARTIAL PRESSURE ON THE DISSOLUTION OF COLEMANITE IN CO₂ - SATURATED WATER

*SICAKLIĞIN VE CO₂ KISMÎ BASINCININ
COLEMANITE'İN CO₂ LE DOYURULMUŞ SUDA
ÇÖZÜNÜRLÜĞÜNE ETKİLERİ*

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ÖZET

Bu çalışmanın amacı karbon dioksit konsantrasyonunun ve reaksiyon sıcaklığının colemanite'in borik asit üretimindeki çözünme hızına etkisini incelemektir. Deneyler atmosferik basınç altında yürütüldü. Çözünme hızının CO₂ konsantrasyonunun ve reaksiyon sıcaklığının yükselmesiyle arttığı gözlemlendi. Ayrıca, reaksiyon sıcaklığının colemanite'in çözünme hızına gerçek etkisi sıcaklığın CO₂'in çözünürlüğüne etkisini ayırarak tespit edildi.

ABSTRACT

The purpose of this work was the investigation of the influence of carbon dioxide concentration and reaction temperature on the dissolution rate of colemanite for the production of boric acid. The experiments were conducted at atmospheric pressure. It was observed that the dissolution rate increased with increase in CO₂ concentration and reaction temperature. Furthermore, the real effect of reaction temperature on the rate of dissolution of colemanite was determined by dissociating the effect of temperature on the CO₂ solubility.

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1. INTRODUCTION

Boron minerals, and in particular colemanite, occur in very few areas of the world, Western Turkey being one such location. It is estimated that about 54% of known world colemanite reserves are in Turkey which has a substantial boron production industry (GONCU, 1982). Elemental boron and its compounds have wide and varied applications in industry, for example in the production of boron nitride and carbide, glass and flame retardants and further applications are likely in the future.

Two particular boron minerals, colemanite ($2\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) and tincal ($\text{JV}^{\wedge}\text{O}^{\wedge}\text{BjOs.1Ojr/jO}$) are especially important as sources of boric acid. The former is used as a feedstock in Europe and Turkey, and the latter in the USA (TOLUN, 1981). In Turkey boric acid is manufactured by leaching calcined colemanite with H_2SO_4 . Gypsum ($\text{CaSO}_4 \cdot \text{H}_2\text{O}$), which is a byproduct of the process, causes difficulties during the filtration stage and is a cause of severe environmental problems (CAKALOZ, 1975) when it finds its way into water courses. There is therefore interest in alternative leaching methods. The dissolution mechanisms of colemanite in various acid solutions have been investigated by several researchers eg (IMAMUTDINOVA, 1967, KOCAKERJM et al, 1988) mostly for geochemical purposes. However, studies of the solubility of colemanite in CO_2 -containing water are limited. In one such study the solubility of colemanite mineral in CO_2 -containing water, in the context of its geological formation, was reported in detail (GULENSOY et al., 1978). In further research directed towards the needs of the boron extraction industry, (ALKAN et al, 1985) investigated the effect of particle size, reaction temperature and calcination temperature on the dissolution of powdered colemanite in carbonic acid. Figure 1 shows some of the results from this study, from which it is seen that considerable time is required to obtain a high degree of boric oxide extraction and the pre-calcination of the mineral produces a large increase in the extraction rate.

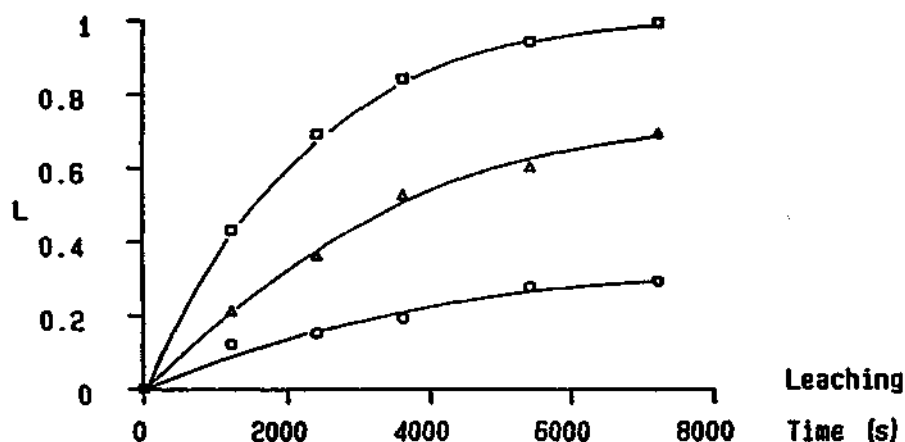


Figure 1. Comparison of leaching rates for normal and calcined colemanite. Data of Alkan et al (1985). \circ - uncalcined colemanite (-100 mesh), \wedge - heated at 380 C for 5 hours, \square - heated at 400 C for 5 hours. L is fraction of boric oxide leached

This paper reports some results of work following on from that of ALKAN et al, (1985) with the objective of examining in more detail the effect of leaching conditions on the leaching rate. In particular, we were interested in looking at the effects of altitude (pressure) and temperature on the performance of a CO_2 -sparged leaching unit.

2. EXPERIMENTAL

The colemanite samples used in this study were hand-picked from the Espey mine, Turkey. The colemanite was sieved to give a - 150 μ size fraction. The mineral was virtually pure, having a composition determined by both volumetric analysis and flame emission spectroscopy of $J?2O_3, 50.49\%$, $CaO, 27.14\%$, $\#_2O, 22.37\%$ (w/w).

The dissolution experiments were carried out in a spherical 250 ml glass reactor heated by means of a constant temperature bath and equipped with a magnetic stirrer, a gas sparger and a reflux condenser. The essential features are shown in Figure 2.

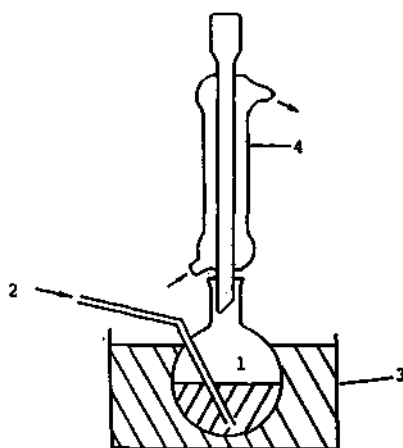


Figure 2. Essential features of the apparatus: 1. Magnetically stirred isothermal reaction flask. 2. Metered supplies of CO_2 and N_2 to gas sparger. 3. Thermostatically controlled water bath. 4- Reflux condenser.

FOT each run, 2g of the mineral sample plus 200 ml of distilled water, presaturated with CO_2 at the desired temperature, were placed in the reactor and a $CO_2 - N_2$ mixture was bubbled through the liquid via a simple sparging device. In the experiments the stirring speed, the total gas flow rate and the initial solid-to liquid weight ratio were kept constant at $9\ s^{-1}$, 200 ml per min and 1:100 respectively. The sparge gas consisted of a mixture of CO_2 and Ar to give various controlled partial pressures of CO_2 , the two gas streams being independently metered.

At the end of each run the reactor contents were filtered and the amounts of Ca^{2+} and H_3BO_3 in the filtrate were determined volumetrically (GULENSOY, 1977). The reacted fraction of the mineral was calculated in terms of B_2O_3 since, during the reaction, the B_2O_3 dissolved from the mineral is equivalent to the H_3BO_3 produced, which was easily determined. The reacted fraction was defined as the ratio of B_2O_3 leached out (as H_3BO_3) to the amount of B_2O_3 originally present in the feedstock.

3. RESULTS AND DISCUSSION

3.1 Effect of CO_2 partial pressure

In these experiments powdered original colemanite samples passing a 150 μ sieve were used. The experiments were carried out at 745, 596, 447, 298 and 149 mm Hg partial pressure of CO_2

(p_{CO_2}) where the partial pressure was adjusted by dilution with N_2 . The dissolved concentrations of CO_2 at various temperatures were calculated by means of Henry's law, allowance being made for water vapour pressure using data taken from PERRY, (1963).

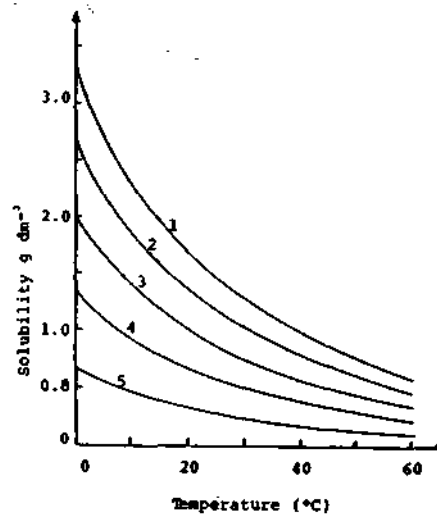


Figure 3. Calculated solubility of CO_2 in water as a function of temperature for various partial pressures of CO_2 - Curve 1, $pp=1$ atm.; curve 2, $pp=0.8$ atm.; curve 3, $pp=0.6$ atm.; curve 4, $pp=0.4$ atm.; curve 5, $pp=0.2$ atm.

Figure 3 shows the calculated CO_2 solubility versus temperature behaviour. It is seen that the solubility of CO_2 in water decreases with increase in temperature and with decrease in CO_2 partial pressure.

The experimental leaching data are shown in Figure 4 as a plot of reacted fraction against time for different partial pressures of CO_2 at $17^\circ C$. It is clearly seen that the reaction rate increases significantly with increase in the partial pressure (solubility) of CO_2 . Also included for comparison are data for a similar experiment carried out in Erzurum, Turkey at an altitude of 2000 m above sea level and for a $p_{CO_2} = 594$ mm Hg.

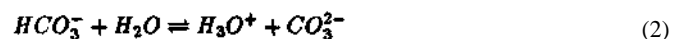
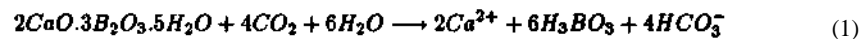
3.2 Real effects of reaction temperature

A series of tests were performed at a total pressure, PT , of 760 mm Hg using powdered original colemanite samples passing a 150 μ mesh. The effect of temperature on the dissolution rate of the colemanite is shown by curve 1 of Figure 5.

As can be seen from this curve an increase in temperature has a positive effect on the dissolution rate despite the decrease in CO_2 solubility with increase in temperature. Curve 2 shows the predicted underlying effect of a rise in temperature on the leaching rate via the fall in solubility of CO_2 in water using Figures 3 and 4. Curve 3 shows the predicted effect on the reaction rate of a rise in reaction temperature at constant $[CO_2]$.

3.3 Leaching process mechanism

The following reactions are thought to occur during the dissolution process



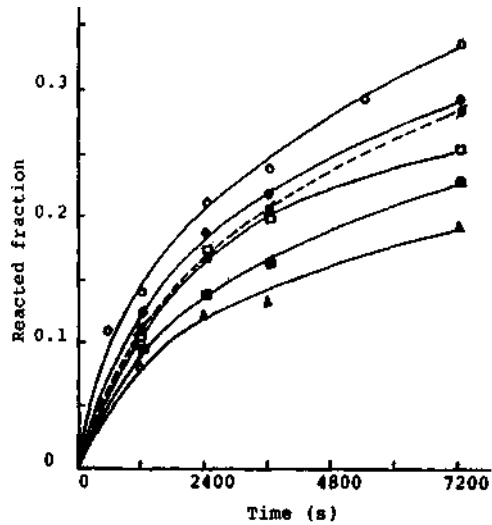


Figure 4. Reacted fraction against time for different CO_2 partial pressures and at a temperature of 17 C. Data from Exeter, UK (sea level): o - $p_{CO_2} = 745$ mm Hg, • - $p_{CO_2} = 596$ mm Hg, a - $p_{CO_2} = 447$ mm Hg, m - $p_{CO_2} = 298$ mm Hg, A - $p_{CO_2} = 148$ mm Hg. Data at 1 atmosphere from Erzvrurf S000 m altitude): f - $p_{CO_2} = 594$ mm Hg.

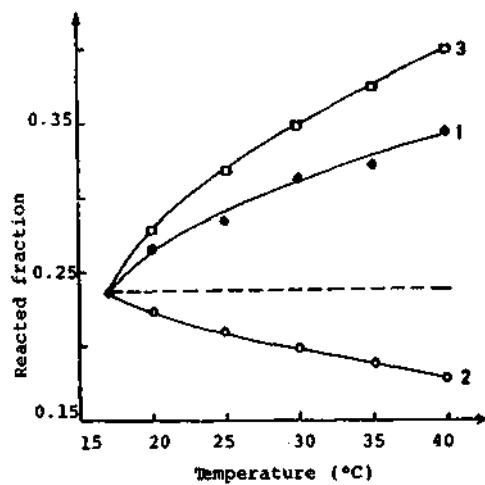


Figure 5. Absolute effect of reaction temperature on leaching rate. $P = 760$ mm Hg, $p_{CO_2} = 745$ mm Hg. • - actual data, o - predicted data accounting for CO_2 solubility decrease with temperature obtained from Figures 3 and 4. a - predicted effect of rise in temperature at constant CO_2 concentration. (Data at 17 C are datum)

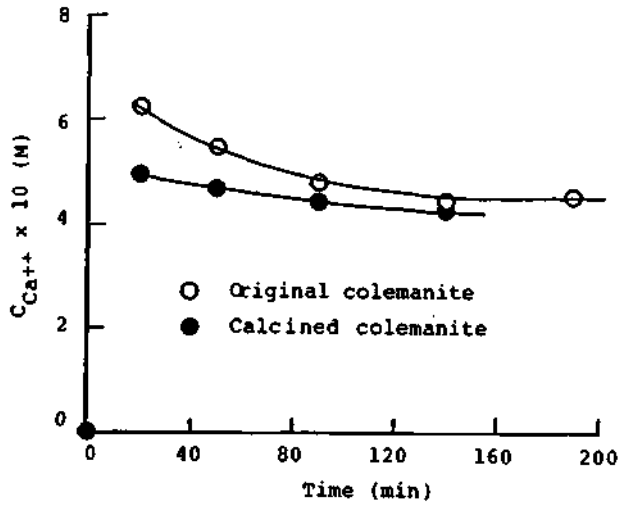
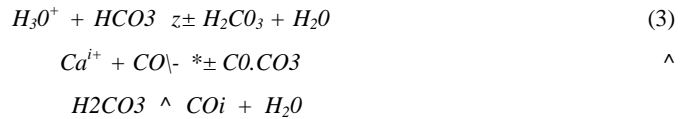
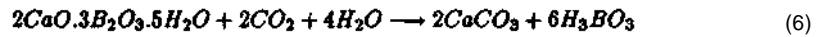


Figure 6. Plots of Ca^{++} in solution vs time for original and soak calcined colemanite samples under identical leaching conditions showing attainment of equilibrium Ca^{++} concentration. Calcination temperature 400 C, calcination time 130 minutes, o - original colemanite B2O3 = 50-4996, • - calcined colemanite B2O3 = 54-52%.



The overall reaction equation may be written as:



At the beginning of the process the concentration of Ca^{2+} in solution increases due to reaction (1) until $[Ca^{2+}][CO_3^{--}] > K_{sp}$, where K_{sp} is the solubility product, whereupon the concentration of Ca^{++} decreases, following equation (4) until it reaches an almost constant equilibrium value. The attainment of this equilibrium value is shown in Figure 6 both for an uncalcined and a calcined colemanite sample.

As can be seen from equation (6) the end products are H_3BO_3 and $CaCO_3$.

The sequence of scanning electron microscope pictures in Figure 7 shows the change in appearance of the colemanite during the operations of calcination and leaching under conditions close to those associated with the upper curve of Figure 1. After calcination the colemanite powder was resieved to -150 μ prior to leaching.

Figure 7(a) shows the original feedstock colemanite. The scale bar is 10 μ m and all pictures in the sequence are at this scale. Figure 7(b) shows the appearance of the particles after calcination at 400 C for 4 hrs (colemanite undergoes extensive dehydroxylation at this temperature with an associated structural disruption). Figure 7(c) shows a honeycombed particle of colemanite after leaching in carbonic acid for 50 minutes. The cubic crystals are calcite (calcium carbonate)

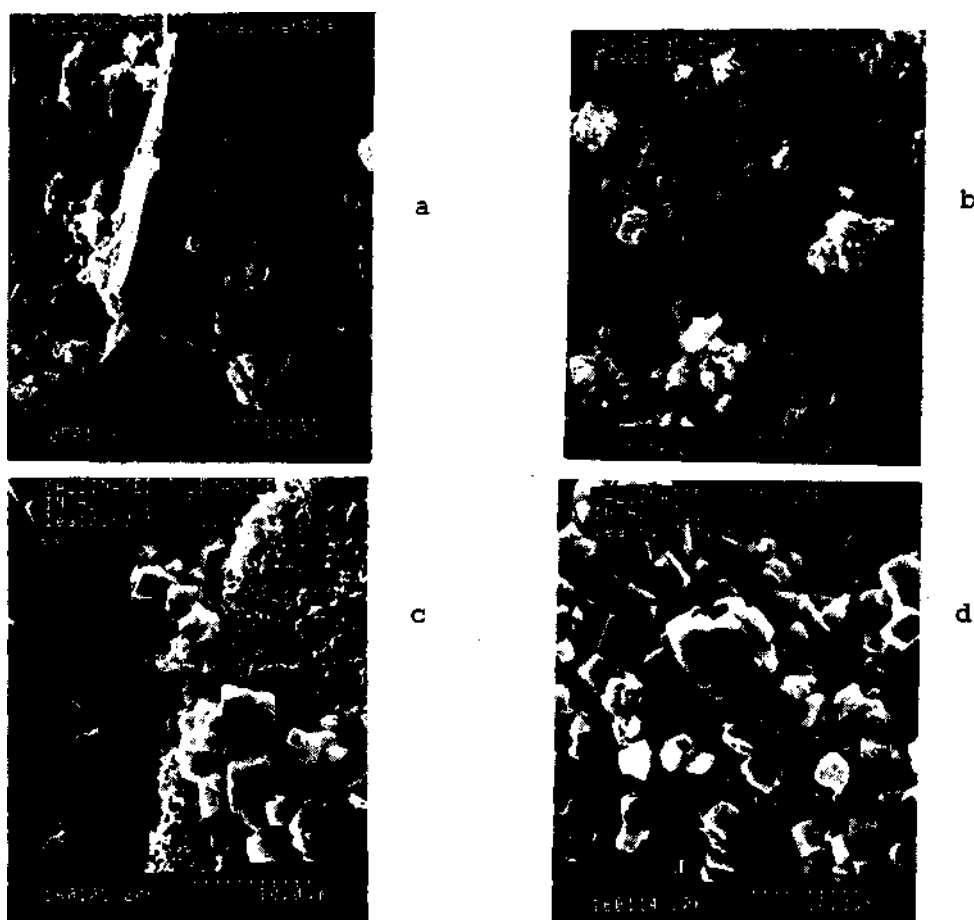


Figure 7. Scanning electron microscope photographs, *a*) original colemanite sample, *b*) calcined colemanite (at 400 C for 4 hours), *c*) leached calcine filtrate (50 minutes at 17 C), *d*) leached calcine filtrate (140 minutes at 17 C)

precipitated out of the leach solution. Figure 7(d) shows the appearance of the filtrate from the leaching vessel after 140 minutes of reaction time, from which it will be noted that the solid content of the filtrate is mostly calcite. This precipitated calcite has commercial potential as a filler in the paper industry.

4. CONCLUSIONS

In investigations of the leaching of natural colemanite it has been shown that colemanite can be dissolved in CO_2 -saturated water. The dissolution rate increased with increase in partial pressure of CO_2 and reaction temperature as expected. Although the solubility of CO_2 decreases with temperature (Figure 1), and this is reflected in a detrimental effect on leaching (curve 2 of Figure 4), the positive effect of temperature on the reaction rate more than compensates for this decreasing concentration effect.

Precalcination of feed material greatly improves the rate of subsequent acid leaching. The extent of precalcination can be optimised to minimise energy consumption and maximise boric acid production.

5. REFERENCES

- ALKAN, M., KOCAKERIM, M.M., and COLAK, S., 1985, Dissolution Kinetics of Colemanite in Water Saturated by Carbon Dioxide, J. Chem. Tech. Biotechnol., 35A 382-386.
- CAKALOZ, T., 1975, Kalsine Kolemanitten Karbonasyon Yolu ile Borik Asit Üretimi, TÜBİTAK Yayınları, 279, MAG-26, Ankara, p.1.
- GONCU, N., 1982, Dünyada ve Türkiye'de Metal ve Mineral Kaynakların Potansiyeli, Ticareti, Beklenen Gelişmeleri, MTA Yayınları, 187, Ankara.
- GULENSOY, H., 1977, Kompleksometrinin Esasları ve Kompleksometrik Titrasyonlar, İstanbul Üniversitesi Yayınları, İstanbul, 144.
- GULENSOY, H. and KOCAKERIM, M.M., 1978, Solubility of Colemanite Mineral in CO_2 - containing Water and Geological Formation of This Mineral, Bull. Miner. Res. Explor. Inst. Turk., 90, 1-19.
- IMAMUTDINOVA, V.M., 1967, Kinetics of Dissolution of Borates in Mineral Acid Solutions, Translated from ZhPKh, 40, 11, pp.2593- 2596.
- KOCAKERIM, M.M., and ALKAN, M., 1988, Dissolution Kinetics of Colemanite in SO_2 - saturated water., Hydrometallurgy, 19, 385-392.
- PERRY, J.H., 1963, Chemical Engineer's Handbook, 4th Ed., McGraw-Hill, New York, NY, 3:43, 14:3-4.
- TOLUN, R., 1981, Anorganik Bor Bileşikleri ve Üretim Teknolojisi, TÜBİTAK Marmara Bilimsel ve Endüstriyel Arastırma Enstitüsü, Kimya Arastırma Bölümü, Gebze-Kocaeli, p.36.