Extraction of boric acid from colemanite mineral by supercritical carbon dioxide

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A B S T R A C T

The use of H2SO4 in boric acid production from colemanite mineral has several problems, related to product impurities, corrosion and environmental discharge limits. To overcome these problems and to increase extraction efficiency of boric acid, heterogeneous reaction between colemanite and CO2 dissolved in H2O was studied at and above supercritical CO2 conditions. Supercritical conditions enhanced the extraction efficiency of boric acid from colemanite mineral, with 96.9% boric acid extraction efficiency being obtained from CO2–colemanite reaction at 60 °C for 2 h of reaction time for particles in the range of +20–40 μm. A powder crystallized from filtrate of reaction was determined as H3BO3 and the solid formed at the end of reaction was characterized mostly as CaCO3 according to FTIR, XRD, TGA and SEM analyses. The use of supercritical CO2 as a leaching agent in colemanite does not only produce boric acid but also helps to reduce the amount of CO2 in the atmosphere. Based on these facts, supercritical CO2 as an extractant makes this process green and sustainable for recovering boric acid from boron minerals.

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1. Introduction

Boric acid (H3BO3) is an important boron chemical which can be produced from different boron minerals, such as colemanite (calcium borate), tincal, kernite (sodium borates), ulexite (sodium and calcium borate) and ascharite (magnesium borate). Although there are more than 200 boron compounds defined in the world, only calcium borates and sodium borates are commercially important and they form 90% of existing reserves [1]. Eti Maden Works (Turkey), which is the second largest producer in the world, produces boric acid from either tincal or colemanite feed stocks. Since the colemanite reserves are greater than the other boron minerals in Turkey, boric acid is mostly produced from colemanite mineral.

Boric acid has been widely used in the production of different boron compounds namely, zinc borate, borate esters, boron carbide, and boron nitride. Boric acid is also found in a small percent as a sassolite mineral in nature. Its normal melting point is 170 °C, however when heated slowly it is converted into metaboric acid (HBO2) by losing water in the range of 100–130 °C. It turns into diboronic trioxide as a result of heating to temperatures higher than 160 °C [2]. Decomposition reactions of boric acid are shown in Eqs. (1) and (2):

\[ 2\text{H}3\text{BO}_3(aq) \rightarrow 2\text{HBO}_2(s) + \text{H}_2\text{O(g)} \] (1)

\[ 2\text{HBO}_2(s) \rightarrow \text{B}_2\text{O}_3(s) + \text{H}_2\text{O(g)} \] (2)

Conventional boric acid production from colemanite ore consists of the following steps: crushing and milling of colemanite ore, dissolution of boric acid in aqueous phase by reaction of colemanite with sulfuric acid, crystallization and filtration of by-product, calcium sulfate (CaSO4·2H2O), and crystallization and filtration of boric acid [3]. The reaction between colemanite and sulfuric acid is given in Eq. (3). It is carried out at 90–98 °C, for period of 3–3.5 h under atmospheric pressure.

\[ \text{Ca}_2\text{B}_2\text{O}_7(s) + 5\text{H}_2\text{O(l)} + 2\text{H}_2\text{SO}_4(l) + 6\text{H}_2\text{O(l)} \rightarrow 2\text{CaSO}_4·2\text{H}_2\text{O(s)} + 6\text{H}_3\text{BO}_3(aq) \] (3)

In the production of boric acid from boron mineral, there are many issues related with the environment, these are an increasing amount of solid by-products with higher boron content, consumption of large quantities of water, and presence of impurities like MgSO4 in the product. On the other hand, since concentrated sulfuric acid is used in the process, corrosion problems occur, especially for equipment used in the reactor. To find a solution to the above problems, different organic and inorganic acids were studied for the
dissolution of boron minerals. For instance, leaching kinetics of tinc-
caling oxalic acid [4]; dissolution kinetics of colemanite in oxalic
acid [5]; extraction of boric acid from colemanite ore by nitric acid
solution [6]; dissolution kinetics of ulexite in acetic acid solution [7]
were investigated. However none of these methods have been able
to replace the sulfuric acid commercially since there are difficulties
in the separation of by-products from the mother solution when
those acids were used and most of them were not cheap enough
to be used in large quantities and they have a very low dissolution
rate. On the other hand, the use ultrasound in solid–liquid hetero-
geneous reaction of colemanite and sulfuric acid was also studied
[8]. Although ultrasonic treatment enhances the dissolution of cole-
manite, commercialization of this method on a large scale seems to
be difficult. At present H2SO4 is the most widely used mineral acid
industrially for producing boric acid from boron ores which forms
a significant amount of boron-containing solid and liquid wastes.

The presence of arsenic in colemanite mineral creates another
problem in boric acid production [9, 10]. Sodium sulfide, hydrogen
sulfide and ammonia have been used to precipitate arsenic, iron
and aluminum impurities in the solution. Since boron level in both
water and soil is critically important for plants and living organ-
isms, boron content of the side streams from production facility
must be monitored and controlled [11]. Instead of treating solid and
liquid waste streams from production side, novel techniques must
be investigated to find a solution to the problems at their source.
For this purpose, the use CO2 and SO2 gases dissolved in aqueous
solution at atmospheric pressure has been studied for extracting
boric acid from colemanite mineral to find alternative ways [12].
Carbon dioxide dissolves in water by forming carbonic acid accord-
ing to Eq. (4). The formed carbonic acid produces proton (Eq. (5))
that is used in acid leaching of the mineral. The formed bicarbon-
ate anion further dissociates into carbonate ion and H+ as shown in
Eq. (6).

\[
\begin{align*}
\text{CO}_2(g) + \text{H}_2\text{O}(l) &\rightarrow \text{H}_2\text{CO}_3(aq) \\
\text{H}_2\text{CO}_3(aq) &\rightarrow \text{HCO}_3^-(aq) + \text{H}^+(aq) \\
\text{HCO}_3^-(aq) &\rightarrow \text{CO}_3^{2-}(aq) + \text{H}^+(aq)
\end{align*}
\]

The solubility of CO2 in water can be raised by increasing pres-
ture and decreasing the temperature. But temperature should not
be below the critical temperature of CO2 (31.1 °C). At 10 MPa and
35 °C, the solubility value of CO2 in water was reported as 29.13 cm³
at standard temperature and pressure (STP)/g H₂O [13]. The pH
of the aqueous solution is also related to the amount of CO2 dis-
solved in aqueous phase. The hydronium ion (H₃O⁺) formed when
CO2 dissolves in water (Eq. (7)) attacks to the colemanite structure
according to the reaction in Eq. (8), and Ca2⁺ cation is formed.
The Ca2⁺ cations and carbonate anions react to produce calcium car-
bonate in Eq. (9). Apart from those reactions, calcium bicarbonate
may be produced from reaction of calcium and bicarbonate ions as
shown in Eq. (10).

\[
\begin{align*}
2\text{CO}_2(g) + 6\text{H}_2\text{O}(l) &\rightarrow 4\text{H}_3\text{O}^+(aq) + 2\text{CO}_3^{2-}(aq) \\
2\text{CaB}_3\text{O}_4(\text{OH})_3 + 3\text{H}_2\text{O}(s) &\rightarrow 3\text{H}_2\text{B}_3\text{O}_3(aq) + 2\text{Ca}^{2+}(aq) + 2\text{H}_2\text{O}(l) \\
2\text{CO}_3^{2-}(aq) + 2\text{Ca}^{2+}(aq) &\rightarrow 2\text{CaCO}_3(s) \\
2\text{HCO}_3^-(aq) + \text{Ca}^{2+}(aq) &\rightarrow \text{Ca(HCO}_3)_2(aq)
\end{align*}
\]

At this point, supercritical fluids or supercritical conditions may
provide alternative solutions. Supercritical fluids (SCF) have been
widely used for the last few decades in the synthesis of novel
materials. The use of SCF processes has been increasing as the envi-
ronmental and food regulations become more and more important
for human being. The most important feature of supercritical fluid
is that its properties can be adjusted from gas to liquid with small
variations in pressure and temperature [14, 15]. Design of inorga-
nic materials using supercritical fluid methods is accomplished
through two distinctive processes. In the first one, the driving force
for particle formation is a physical transformation of matter by a
rapid depressurization or antisolvent effect. The detailed informa-
tion about these processes can be found in literature. In the
second group of processes, supercritical fluids are used as a reac-
tion media to synthesize a number of different materials, such as
oxides, metals, or semiconductors [14]. It is expected that the reac-
tion between CO2 and colemanite in the aqueous phase would be
enhanced at supercritical conditions of CO2.

The aim of this study is to use environmentally friendly solvent,
supercritical CO2, for extracting boric acid from colemanite mineral
and to determine the optimum parameters for boric acid produc-
tion at supercritical CO2 conditions. The solid by-product formed
at the end of reaction and powder crystallized from filtrate of reac-
tion were characterized by FTIR, XRD, TGA and SEM analyses. B₂O₃
contents of solid phase remained/former at the end of reaction and
filtrate were determined by volumetric analyses.

2. Experimental

2.1. Materials

Colemanite used in this study was obtained from the Bigaçı-
Balıkesir plant of Eti Maden Works in Turkey. Carbon dioxide, CO2
(99.9% v/v, Habas), was used for the experiments at supercritical
conditions. Sodium hydroxide, NaOH (99.0% w/w Merck), glycerol,
C₃H₇O₃ (99.0% w/w, Dalan Chemical Industry) and phenolphthalein
(C₂₀H₁₄O₄, Merck) and methyl red (C₁₅H₁₃N₃O₂, Merck) indicators,
sulfuric acid, H₂SO₄ (96% w/w, Merck), sodium carbonate, Na₂CO₃
(99%, w/w, Merck) were used in the analytical determination of
B₂O₃ content of aqueous phase and initial raw colemanite min-
eral. The factor value of NaOH solution was determined by using a
potassium hydrogen phthalate (KHP) C₄H₄KO₄ (99.5% w/w, Merck),
which is not affected by the humidity in air during weighing. So a
solution prepared by KHP can be used to determine the precision
of the NaOH solution in the titration procedure. Potassium bromide,
KBr (99.9% w/w, Merck) was used in the preparation of pellets in IR
analyses. CaCO₃ (99.0% w/w, Merck) was used as reference material
in IR analyses.

2.2. Raw material characterization and analysis of B₂O₃

Chemical analysis of colemanite mineral (Table 1) was per-
formed by using X-ray fluorescence spectrometer (Spectro

Table 1

<table>
<thead>
<tr>
<th>Oxide formula</th>
<th>Theoretical composition, %</th>
<th>Colemanite by XRF, % (w/w)</th>
</tr>
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<tbody>
<tr>
<td>B₂O₃</td>
<td>50.8</td>
<td>43.4*</td>
</tr>
<tr>
<td>CaO</td>
<td>27.3</td>
<td>19.3</td>
</tr>
<tr>
<td>SiO₂</td>
<td>-</td>
<td>5.9</td>
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<tr>
<td>MgO</td>
<td>-</td>
<td>3.0</td>
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<tr>
<td>Al₂O₃</td>
<td>-</td>
<td>1.4</td>
</tr>
<tr>
<td>SiO</td>
<td>-</td>
<td>0.9</td>
</tr>
<tr>
<td>Na₂O</td>
<td>-</td>
<td>0.7</td>
</tr>
<tr>
<td>K₂O</td>
<td>-</td>
<td>0.6</td>
</tr>
<tr>
<td>As₂O₃</td>
<td>-</td>
<td>0.5</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>-</td>
<td>0.5</td>
</tr>
<tr>
<td>Others</td>
<td>-</td>
<td>0.4</td>
</tr>
</tbody>
</table>

* Determined by analytical titration.