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Absorption of combustion gases in boron solutions and recovery as industrial products

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ABSTRACT

In this study, it is aimed that to reduce environmental effects of CO_2 (as a greenhouse gas), to achieve absorption of CO_2 in boron solutions and to yield a mixture product with boron compounds and the $NaHCO_3$ which is raw material input especially in glass industry. In the laboratory scale experiments using autoclave, with different pressure, solid/liquid ratio, and different reaction times, absorption of CO_2 in the boron solutions were examined and the Na-borate compounds containing $NaHCO_3$ were produced. The characterization of the products was determined by XRD inspections and chemical analysis. In the studies, maximum 92.4% $NaHCO_3$ bearing borate compounds was obtained. As a result of the purification of these products it was reached pure $NaHCO_3$ by 99%.

Introduction

Today, the biggest environmental problems such as global warming and climate change, along with the quest for a global solution require urgent measures to be taken. However, at present the amount of high quality and easily accessible fossil fuels is shrinking due to their high demand, as a result of the depletion of reserves in accessible areas and to a great population growth. This has led to the use of heavy and dirty fossil fuel reserves that contain higher amounts of contaminants such as sulfur (S), which harm the environment, besides the large amounts of CO_2, mainly resulting from the combustion thereof [1]. Carbon dioxide is the most important greenhouse gas that cause global warming and it has a share of 50%. Atmospheric concentration of carbon dioxide, which is the most important greenhouse gases, was 280 ppm in the pre-industrial era, today has reached 370 ppm and is expected that it will be 500 ppm by the end of this century [2,3]. In order to keep global warming to less than 2 °C, some state that the atmospheric CO_2 concentration should not exceed 450 ppm CO_2-equivalent [4].

To mitigate the continuous increase of carbon dioxide (CO_2) content in the atmosphere, mostly due to energy production, Carbon Capture and Storage technologies (CCS) are being implemented [5]. Absorption of carbon dioxide in the atmospheric air with alkaline solutions was investigated during last half a century [6,7]. Large-scale scrubbing for the absorption of CO_2 in ambient air was suggested by Lackner et al. firstly [8,9]. In this way, adding calcium hydroxide obtained from quenching of quick lime, carbon dioxide was precipitated as calcium carbonate. Then, by means of sodium

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Table 1 – Properties of commercial Borax decahydrate ($Na_2B_4O_7{\cdot}10H_2O$).

Content	Unit	Value
Purity	min%	99.9
B_2O_3	min%	36.4
Na_2O	min%	16.2
SO_4	min%	70
Cl	min%	50
Fe	min%	10

hydroxide solution, conversion of sodium carbonate was carried out [10]. The general process of carbonation of $Ca(OH)_2$ in the aqueous phase was studied by Jukevar et al. [11]. Then, Lackner et al. proposed the use of sodium hydroxide instead of calcium hydroxide [9]. Storaloff et al. [12] proposed an alternative process in which used a fine spray tower providing large surface for open-air flow to enhance absorption. Researchers have focused on lime, Na_2CO_3 and NaOH conversion and the absorption of CO_2 in the air on the NaOH solution by a set of well-known solid–liquid reactions [12–14]. In a patent taken by Nelson et al. $NaHCO_3$ and H_3BO_3 were obtained by using $Na_2B_4O_7$, H_3BO_3, CO_2 and H_2O [15]. Also, Steven et al. obtained Na_2CO_3, $NaHCO_3$ and B_2O_3 by using $NaBO_2$, H_3BO_3, CO_2 and H_2O in another patent [16]. Harold and Otto obtained Na_2CO_3 and $NaBO_3$ by using $Na_2B_4O_2$, Na_2O_2, CO_2 and H_2O in their studies resemble to that mentioned above [17,18]. George et al. produced trimethyl borate, methanol and some Na_2CO_3 from using several amount of $Na_2B_4O_7$, methanol and H_2O in their study [19]. In Paul and his colleagues' study that was patented in USA, for the first time, $NaHCO_3$ and Na-borate containing products that are important raw material input in the industry was intended to produce together or separately by through the absorption of carbon dioxide by reacting synthetic borax solutions [20]. Also, Park and Yi found that the combined co-precipitation and hydration method is considered to be effective for producing highly stable CaO-based CO_2 absorbents [21].

However, CO_2 capture and storage have not reached their maturity as proven technologies from the technical and commercial points of view. Therefore, further research and development on the processes of CO_2 absorption and separation are required [22].

In this work, for the first time it is aimed to achieve the products together or separately containing $NaHCO_3$ and Na-Borate which is important raw material in industry by reacting through the absorption in synthetic borax solutions. Especially $NaHCO_3$, which is produced by holding CO_2 with sodium is important product in glass industry. Also boron compounds are indispensable raw material for the glass industry. These products could be offered as raw material for glass industry by mixing them in desired amounts according to the needs of industry.

Table 3 – Used pure commercial carbon dioxide features.

Pure	99.9%
Density (liquid)	0.7949 kg/dm^3
Density (gas °C, 1 atm)	1.25001 kg/m^3
Specific gravity (air = 1)	0.9676

Material and method

Synthetic solutions used in works are produced from commercial borax decahydrate supplied from Eti Mine Works Bandırma Plant Works and 99.9% pure CO_2 is supplied from Oksan Kollektif company. The chemical features and the solubility of used borax decahydrate are given in Table 1 and Table 2 accordingly. The features CO_2 gas used in this study is also given in Table 3.

In experimental works, an autoclave (pressured reactor) that has 1 L reactor volume up to 4400 psi and 500 °C is used. Under these conditions borax is reacted with CO_2 and NaHCO3 and H_3BO_3 are formed as products according to chemical reaction (1). According to reaction conditions $NaB_5O_6(OH)_4(H_2O)$ (Sborgite) may be formed instead of H_3BO_3 according to chemical reaction (2).

$$3Na_2B_4O_7 + 7H_2O + 2CO_2 \rightarrow 2NaHCO_3 + 4H_3BO_3 \quad (1)$$

$$Na_2B_4O_7 + 6H_2O + 6/5\ CO_2 \rightarrow 6/5NaHCO_3 + 7/5H_2O + 4/5NaB_5O_6(OH)_4(H_2O) \quad (2)$$

Optimum conditions are defined in different parameters as pressure, reaction time, solid/liquid ratio (gram Na_2O/gram solution which calculated by soluble/solution = Na_2O (g)/[Na_2O + water amount]) according to reaction equation (1) and (2)

Produced $NaHCO_3$ by feeding CO_2 to prepared solutions in autoclave is analyzed. Obtained solution after reaction time is filtered as 7% ≤ moisture products and dried at 30–40 °C in drying-oven. If needed, for purification process methyl alcohol is used, the product is mixed for 1 h by solving in more than 5% methyl alcohol at 30 °C and the obtained solution is filtered. Composed cake is dried between 30 and 40 °C in drying-oven. Determination of B_2O_3 and Na_2O and obtained products are achieved by wet method, CO_2 gas analyze is achieved by Orsat method. The crystal structures of obtained solids are characterized by XRD model of Shimadzu. Process diagram of work is in Fig. 1.

Table 2 – Solubility of $Na_2B_4O_7$ in water (g substance/100 g solution).

0 °C	10 °C	20 °C	30 °C	50 °C	60 °C	70 °C	80 °C	90 °C	100 °C
1.3	1.6	2.7	3.9	10.5	20.3	24.4	31.5	41	52.5