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Effect of water on behaviour of $Na_2B_4O_7·5H_2O$ and $Na_2B_4O_7$ in HCl-CH_3OH medium

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Abstract: The reactivity of $Na_2B_4O_7·5H_2O$ and $Na_2B_4O_7$ in non-aqueous HCl-CH_3OH solvent system was investigated. The effects of H_2O, CH_3OH/B mole ratio and reaction time on the reaction at room temperature were examined. Experimental results show that when $Na_2B_4O_7·5H_2O$ and $Na_2B_4O_7$ are the reactants, the dissolved B_2O_3 contents are observed to be 98.2% and 99%, respectively, in 5 min at the CH_3OH/B mole ratio of 4. The decrease of water in the reaction medium was observed to increase the crystallization of NaCl in the order of $Na_2B_4O_7$>$Na_2B_4O_7·5H_2O$. It was also observed that the boron solution obtained after the reaction could be hydrolyzed by the addition of H_3BO_3. The results show that HCl-CH_3OH system is a more effective solvent compared to H_2SO_4-CH_3OH both in the reactivity and the shortened reaction time.

Key words: non-metallic ores; oxide ores; hydrometallurgy; leaching

1 Introduction

Trimethyl borate is one of the starting materials used in the production of $NaBH_4$[1−4], which is used as a very mild reducing agent and has a great potential to be an effective hydrogen storage material[5−11]. Trimethyl borate was produced by the reaction of boric acid or boric oxide with methanol[12−14]. Reaction of sodium borate with sulphuric acid and methanol was also studied [13]. Methyl borate-methanol azeotrope was obtained with 8−12 moles of excess methanol in 9 h, thus, it is difficult to prepare methyl borate due to the formation of methyl borate-methanol azeotrope, so the separation methods are needed[15−17].

The authors[18] studied the reaction of $Na_2B_4O_7·10H_2O$ in HCl-CH_3OH system and found that 61.4% B_2O_3 dissolved in 5 min at the CH_3OH/B mole ratio of 4 and the reactivity was further increased to 98.2% and 99.4% at CH_3OH/B mole ratios of 5 and 6, respectively. The aim of this work is to investigate the changes that originate in the reactions between $Na_2B_4O_7·5H_2O$ and $Na_2B_4O_7$ in HCl-CH_3OH system with the crystal water of the borates.

2 Experimental

2.1 Materials

$Na_2B_4O_7·5H_2O$ and $Na_2B_4O_7$ (both 99.5% purity) were supplied by Etibank. Hydrochloric acid, sulphuric acid and absolute methanol were Merck grade reagents and absolute methanol was dried before use.

2.2 Methods

HCl gas was obtained by dropping concentrated hydrochloric acid solution through a capillary tube from a graduated cylinder into concentrated sulphuric acid solution in a flask[19]. Absolute methanol was saturated with the HCl gas in the preparation of HCl-CH_3OH solutions for the following work. The concentration of HCl in HCl-CH_3OH solutions was determined by chloride analysis and adjusted by diluting with absolute methanol.

The 5 g B_2O_3 which was equivalent to $Na_2B_4O_7·5H_2O$ and $Na_2B_4O_7$ were separately added to HCl-CH_3OH solution to keep the CH_3OH/B mole ratio at a required value in a 250 ml beaker at room temperature and was stirred magnetically at a constant speed to keep all the solids in suspension for reaction time of 5−120 min. Experiments were done using $Na_2B_4O_7·5H_2O$ (Eqs. (1)−(3) and $Na_2B_4O_7$ (Eq.(4)) at CH_3OH/B mole ratios of 3, 4 and 8 to keep the amounts of HCl and sodium borates constant of 2 moles and 1 mole, respectively.

$$Na_2B_4O_7·5H_2O+12CH_3OH+2HCl \rightarrow 4B(CH_3O)_3+2NaCl+12H_2O \quad (1)$$

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$$Na_2B_4O_7{\cdot}5H_2O+16CH_3OH+2HCl \rightarrow 4(B(CH_3O)_3{\cdot}CH_3OH)+2NaCl+12H_2O \quad (2)$$

$$Na_2B_4O_7{\cdot}5H_2O+xCH_3OH+2HCl \xrightarrow{x\geqslant 16} 4(B(CH_3O)_3{\cdot}CH_3OH)+(x-16)CH_3OH+2NaCl+12H_2O \quad (3)$$

$$Na_2B_4O_7+16CH_3OH+2HCl \rightarrow 4(B(CH_3O)_3{\cdot}CH_3OH)+2NaCl+12H_2O \quad (4)$$

After the reactions, the residues were separated from the solutions by filtration through Whatman-42 filter paper. No washing with water or methanol was done to the residues to prevent any further reaction. The content of boron in filtrates, wet residues and dried residues were analyzed using sodium hydroxide titration method. The contents of chloride and sodium were determined using Volhard and atomic absorption (Varian Spectra AS) methods, respectively. The XRD patterns were obtained using Rigaku D_{max}2200 X-ray diffractometer. Boron in dry residue was considered to be unreacted; the reacted boron was evaluated considering the boron contents of the dried residue, wet residue and the filtrate.

3 Results

The change of reactivity of $Na_2B_4O_7{\cdot}5H_2O$ at CH_3OH/B mole ratios of 3, 4 and 8 are given in Fig.1. In these experiments, CH_3OH/H_2O mole ratios were 2.4, 3.2 and 6.4 and CH_3OH/HCl mole ratios were 6, 8 and16, respectively. Fig.1 shows that the content of dissolved B_2O_3 increases from 40.6% to 62.4% at reaction time from 5 to 120 min when the CH_3OH/B mole ratio is kept at 3. With the increase of CH_3OH/B mole ratio to 4, maximum reactivity (98.2%) is obtained at a reaction time of 5 min and the reactivity is observed to gradually decrease with increasing reaction time, finally lowering

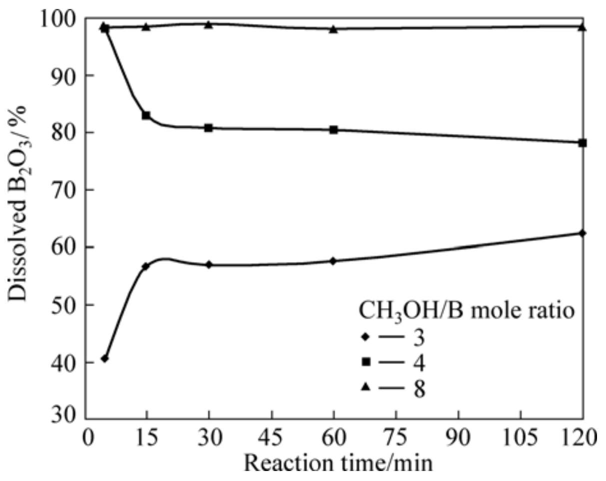

Fig.1 Reactivity change of $Na_2B_4O_7{\cdot}5H_2O$ with different CH_3OH/B mole ratio

to 78.2% at 120 min. When the CH_3OH/B mole ratio is increased to 8, the reactivity irregularly changes at narrow intervals (98.2%−99.0%) at the same reaction time. Consequently, the dissolution value of 98.2% is obtained at CH_3OH/B mole ratio of 4, reaction time of 5 min, which is considered as the optimum condition for the reaction of $Na_2B_4O_7{\cdot}5H_2O$ in CH_3OH-HCl system.

Similar experiments were repeated for $Na_2B_4O_7$ at the same CH_3OH/B mole ratios and reaction time, and the results are given in Fig.2. The main difference in these experiments is that as $Na_2B_4O_7$ contains no crystal water, there is no water present in the reaction medium initially. The data in Fig.2 shows that when the mole ratio of CH_3OH/B is 3, the dissolution value increases from 33.8% to 97.6% with increasing reaction time from 5 to 15 min. For longer reaction time, the reactivity slows down and lowers to 74.40% at 120 min. At CH_3OH/B mole ratio of 4, the dissolution value is 99% at reaction time of 5 min, with slight irregular change, it stays 93.2%−98.6% for reaction time of 15−120 min. With the further increase of CH_3OH/B mole ratio to 8, the dissolution fraction changes in a range of 97.0%−98.6% during the test. As a result, the optimum reactivity for $Na_2B_4O_7$ was determined as 99.0% at a reaction time of 5 min and a CH_3OH/B mole ratio of 4.

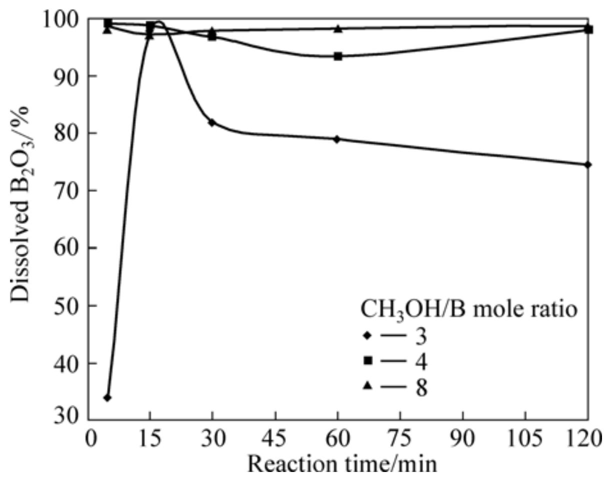

Fig.2 Reactivity change of $Na_2B_4O_7$ with different CH_3OH/B mole ratio

Considering the data given in Figs.1 and 2, the experiments were done using $Na_2B_4O_7{\cdot}5H_2O$ and $Na_2B_4O_7$, respectively, for a reaction time of 5 min at CH_3OH/B mole ratios of 3, 3.5, 4, 5 and 8 in order to determine the optimum CH_3OH/B mole ratio, and the results of these experiments are given in Fig.3. At a CH_3OH/B mole ratio of 4, without requirement of any excess methanol, the dissolved B_2O_3 content of $Na_2B_4O_7{\cdot}5H_2O$ reaches 98.2% in 5 min, while the dissolved B_2O_3 content reaches a higher value of 99% when $Na_2B_4O_7$ is used at the same condition.

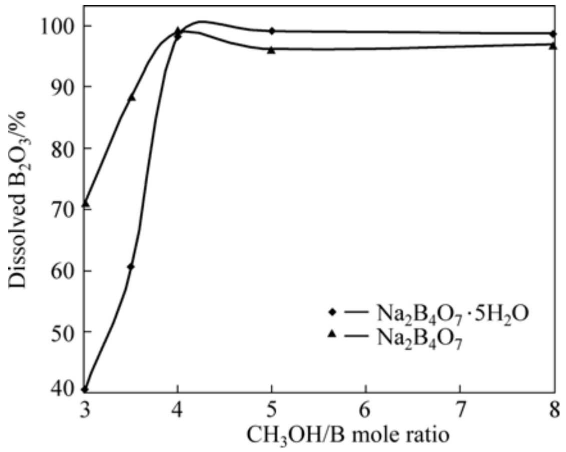

Fig.3 Reactivity change of $Na_2B_4O_7 \cdot 5H_2O$ and $Na_2B_4O_7$ at different CH_3OH/B mole ratios

Experiments were repeated with $Na_2B_4O_7 \cdot 5H_2O$ and $Na_2B_4O_7$ at the optimum CH_3OH/B mole ratio of 4 and reaction time of 5 min, and the residues (R-5, R-0) and the filtrates obtained were collected for analyses. The first half of the aliquots in the filtrates were diluted with water at a filtrate/water ratio of 2, cooled in a refrigerator for 1 h then filtered. B, Cl, Na and XRD analyses were done on the residues (W-5, W-0) dried at 105 °C. The second half of the aliquots of the filtrates were dried, B, Cl, Na and XRD analyses were done on the residues (E-5, E-0). The chemical compositions of the unreacted residues and the residues obtained from the filtrates are given in Table 1. The XRD patterns of the unreacted residues and the residues obtained from the filtrates for $Na_2B_4O_7 \cdot 5H_2O$ and $Na_2B_4O_7$ are given in Figs.4 and 5, respectively.

Table 1 Chemical compositions of residues obtained in $Na_2B_4O_7 \cdot 5H_2O$/HCl-CH_3OH and $Na_2B_4O_7$/HCl-CH_3OH systems (mass fraction, %)

Sample	B	Na	Cl
R-5	3.11	32.66	48.27
W-5	22.22	0.21	0.15
E-5	19.43	10.88	5.86
R-0	3.12	32.63	39.53
W-0	22.22	0.06	0.70
E-0	20.11	8.62	7.24

The data in Table 1 and the XRD patterns in Fig.4 from the $Na_2B_4O_7 \cdot 5H_2O$/HCl-CH_3OH system (R-5) show that NaCl is crystallized and separated as a solid phase with the formation of $Na_2B_2O_4 \cdot 8H_2O$. As 1 mole of sodium borate contains 5 moles of crystal water, CH_3OH/H_2O mole ratio in the medium reaches 3.2 and the reaction is completed without requirement of excess

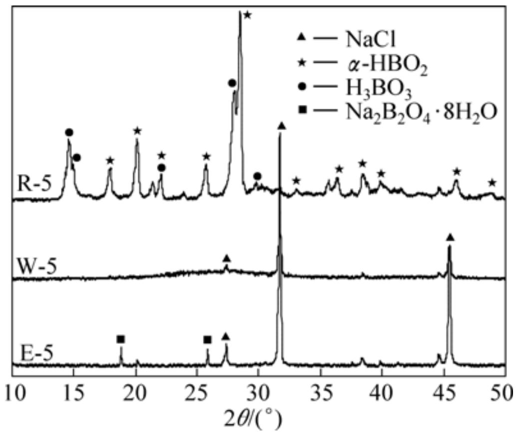

Fig.4 XRD patterns of samples R-5, E-5 and W-5

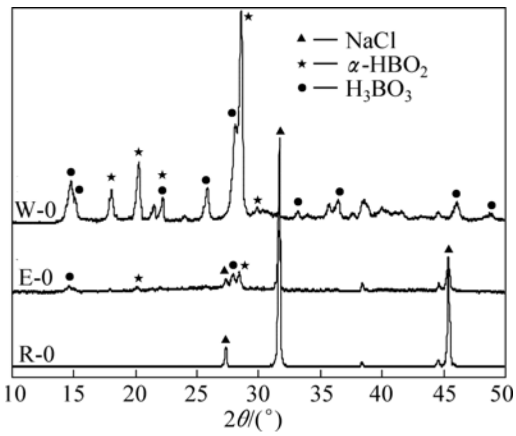

Fig.5 XRD patterns of samples R-0, E-0 and W-0

methanol, which is in accordance with Eq(2). However, low water content in the medium compared to aqueous hydrochloric acid solution leads to the crystallization of NaCl, 61.3% (mass fraction) of the total NaCl expected from the reaction. In $Na_2B_4O_7$/HCl-CH_3OH system, only NaCl peaks are detected in the residue (R-0) obtained after the reaction with some excess sodium, as evidenced from the chemical analysis (Fig.5). $Na_2B_4O_7$ contains no crystal water and the reaction starts at non-aqueous conditions without the requirement of excess methanol (Eq(4)). Although some water is formed as the reaction proceeds, more NaCl is crystallized (65.8% of the theoretical expectation) compared to that in $Na_2B_4O_7 \cdot 5H_2O$/HCl-CH_3OH system. No other crystalline phases were detected in the XRD patterns, showing that the sodium borate compound(s) formed would be amorphous.

Upon dilution of the dissolved phase obtained in $Na_2B_4O_7 \cdot 5H_2O$/HCl-CH_3OH system with water, H_3BO_3 is precipitated and when the precipitate is dried at 105 °C (W-5), part of H_3BO_3 is transformed into α-HBO_2. Evaluation of the chemical analysis result shows that the residue contains 0.25% (mass fraction) NaCl and the ratio of α-HBO_2/H_3BO_3 is around 2/1. When the dissolved phase is evaporated (E-5), the only crystalline phase is NaCl (the calculated value is 9.7%) with some excess Na present in the evaporate. The chemical analysis result shows the possibility of formation of some amorphous sodium borate(s).

Similar to $Na_2B_4O_7{\cdot}5H_2O$/HCl-CH_3OH system, the precipitate obtained upon dilution of the filtrate with water (W-0) in $Na_2B_4O_7$/HCl-CH_3OH system contains H_3BO_3 and α-HBO_2, the α-HBO_2/H_3BO_3 ratio is calculated as 2.3/1. The chloride in the precipitate proves some NaCl of nearly 1.2% (mass fraction). On the other hand, H_3BO_3, α-HBO_2 and NaCl peaks are observed in the residue obtained by evaporation of the filtrate (E-0). Evaluation of the chemical analysis shows that the NaCl content of the residue obtained after evaporation of the filtrate is around 11.9% and the α-HBO_2/H_3BO_3 ratio reaches to 3/1.

4 Conclusions

1) Previous study shows that the dissolved B_2O_3 content of $Na_2B_4O_7{\cdot}10H_2O$ reaches to 98.2% in 5 min when the CH_3OH content in the reaction medium is in excess of 4 moles (CH_3OH/B mole ratio of 5) in $Na_2B_4O_7{\cdot}10H_2O$/HCl-CH_3OH system. If the reaction in the same system is performed using $Na_2B_4O_7{\cdot}5H_2O$ and $Na_2B_4O_7$, the dissolved B_2O_3 contents are observed to be 98.2% and 99%, respectively, without the requirement of excess CH_3OH.

2) Experimental results show that the reaction is affected from the water content in the medium. Although water is one of the reaction products, the crystal water contents of the sodium borates play a dominating role and the reactivity follows the order $Na_2B_4O_7$> $Na_2B_4O_7{\cdot}5H_2O$>$Na_2B_4O_7{\cdot}10H_2O$.

3) NaCl is one of the reaction products, and due to its low solubility in CH_3OH, sodium chloride is crystallized and separated as a solid phase with decreasing water in the reaction medium in the order $Na_2B_4O_7$>$Na_2B_4O_7{\cdot}5H_2O$>$Na_2B_4O_7{\cdot}10H_2O$, which causes gradually decreasing contamination of the dissolved phase with NaCl.

4) The reactivity of sodium borates in HCl-CH_3OH system is faster and more efficient compared to that in H_2SO_4-CH_3OH system. The differences in the reactivities of sodium borates originating from the water contents in the HCl-CH_3OH medium seem favorable to the production of H_3BO_3, HBO_2 and $B(CH_3O)_3{\cdot}CH_3OH$.

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