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# Precipitation and characterization of zinc borates from hydrometallurgical processing of zinc ash

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ABSTRACT

Zinc ash has been used as a zinc source for precipitation of zinc borates through leaching–purification–precipitation route. Zinc ash containing about 71% Zn, 0.6% Fe, 28% $Cl^-$, 0.2% Pb, and traces other elements such as Cu, Cd, As etc. in ppm level were leached in sulfuric acid. The leach solutions generated were purified by pH adjustment, followed by precipitation of borates using borax ($Na_2B_4O_7 \cdot 10H_2O$). It has been observed that, the phase compositions of precipitated zinc borates as well as their morphologies are quite sensitive to B/Zn molar ratio, solution pH, precipitation temperature and ageing period. Precipitation of particular zinc borate phase of interest ($3ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$) was found to be facilitated at higher precipitation temperature ($\geq 95$ °C) and in the pH range 5.5–6.0 with B/Zn molar ratio $> 4.0$.



## 1. Introduction

Zinc forms number of borates/hydrated borates, such as $2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$, $4ZnO \cdot B_2O_3 \cdot H_2O$, $ZnO \cdot B_2O_3 \cdot 1.12H_2O$, $ZnO \cdot B_2O_3 \cdot 2H_2O$, $6ZnO \cdot 5B_2O_3 \cdot 3H_2O$, $2ZnO \cdot 3B_2O_3 \cdot 7H_2O$, $2ZnO \cdot 3B_2O_3 \cdot 3H_2O$, $3ZnO \cdot 5B_2O_3 \cdot 5H_2O$ and $ZnO \cdot 5B_2O_3 \cdot 4.5H_2O$ [1,2]. Zinc borates have versatile applications as fire/flame retardant additive, antibacterial agent to protect wood composites, animal feed, smoke, afterglow suppressant [3–5] etc. Among these zinc borates, the tri-borate composition [$2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$] have been extensively used as fire and flame retardant additive in polymers/rubbers due to its favorable high onset dehydration temperature (290 °C).

Preparation of different types of borates according to their end-uses has been the subject of much attention [2–10,12]. It has been observed that, the phase compositions, morphologies, etc. of precipitated zinc borates are greatly influenced by precipitation conditions (temperature, pH, duration etc.), type of zinc and boron salts used [2,3,6,8], as well as through use of surface modifying reagents [7–12]. Most of the reported precipitation studies employ pure zinc salts such as $ZnSO_4 \cdot 7H_2O$ and $Zn(NO_3)_2 \cdot 7H_2O$. In this study we tried synthesis of zinc borates from an industrial discard material such as zinc ash and the main objective is to thoroughly correlate the phase compositions of zinc borates with that of their precipitation conditions.

## 2. Experimental

*Materials*: Zinc ash used in this study found to contain about 71% Zn, 27.5% $Cl^-$, 0.6% Fe, 0.3% Si, 0.2% Pb, and traces of other metals such as Cu, Mn, As and Cd. XRD analysis of the sample indicated ZnO, $Zn(ClO_4)_2 \cdot 6H_2O$ and $Zn_2OCl_2 \cdot H_2O$ as the major phases. For zinc borate precipitation, lab distilled water and chemically pure borax ($Na_2B_4O_7 \cdot 10H_2O$, Loba Chemie, India) was used. Other chemicals used for leaching, purification and analyses were of analytical grade (E-Merk, India).

*Leaching and purification*: Zinc ash samples were first washed with lab distilled water to remove soluble chlorides including any zinc chlorides. The washed and dried zinc ash was leached in sulfuric acid for dissolution of $> 98\%$ Zn under the following optimized conditions: $H_2SO_4 = 3.56$ N, Temp. = 80 °C, Time = 3 h and *S*/*L* ratio = 15. The leach solution was heated to 50 °C, and its pH was adjusted to 3.5–3.8 by adding1 N NaOH solution followed by addition of $H_2O_2$ to precipitate most of the dissolved Fe, Mn, Cu, Cd, etc. The purified leach solutions taken for borate precipitation studies have the composition Zn ~ 71 g/L, $Cl^-$ ~ 55 ppm and all other metallic impurities $< 10$ ppm.

*Precipitation and characterization of zinc borates*: Zinc borate precipitation experiments were conducted with purified leach solutions and borax as the boron source. Experiments were conducted at varying B/Zn molar ratio, temperature and ageing time. Precipitation experiments were carried out inside a 500 ml three-necked flat bottom flask placed on a temperature controlled hot plate-*cum*-magnetic stirrer (Schot). Borax solutions of pre-determined concentration were taken inside the flask, heated to

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desired temperature. To this solution quantitative amount of purified zinc leach solutions were added drop-wise through a buret. Solution pH was adjusted after addition of zinc solution by 10% NaOH solution and the whole mixture was kept for specific time period at desired (precipitation) temperature. Various experimental conditions maintained and corresponding sample codes are presented in Table 1.

Zinc borates were analyzed for their phase composition by Bruker D 8 Discover X-ray diffractometer employing Ni-filtered Cu Kα radiation ($\lambda = 1.5406$ Å) at a scanning rate of 2°/min with $2\theta$ ranging from 10–80°. Few precipitated borates were digested and analyzed by ICP-OES/AAS to determine their exact chemical composition. Morphological investigations were carried out by a table top electron microscope (Model: TEM-1000, Hitachi). Selected samples were also analyzed by scanning electron microscope (FEI 430 SEM, 15 kV), fitted with energy dispersive X-ray spectrometer (EDS).TGA were performed by using a SDT-Q600 analyzer. Heating rates of about 10°/min were employed in air atmosphere for recording.

## 3. Results and discussion

Typical purified leach solutions containing about 71 g/L of zinc (~1.1 M $Zn^{2+}$) and other impurities in ppm level were taken for borate precipitation. Initial precipitation experiments were conducted at different temperatures (70–95 °C) by maintaining B/Zn molar ratio 4 and pH 7.5–8.0. It was observed that, lower reaction temperature (< 85 °C) resulted thick viscous slurries difficult to filter/handle. Also, precipitation at lower B/Zn molar ratios (< 3.5) resulted zinc hydroxy-sulfate species as impurities in addition to formation of amorphous borate phases. Therefore, further precipitation trials were conducted at temperature > 90 °C and B/Zn molar ratio 4.0.

*Effect of pH*: The effect of pH on the type of precipitation products obtained was studied in the range pH = 5.0 to 8.0 keeping other reaction conditions constant viz. samples ZB-1, ZB-2 and ZB-3 (*cf.* Table 1). Fig. 1 shows the XRD pattern of these samples, which indicate that, ZB-1 which is precipitated at a lower pH is being less crystalline in comparison to the precipitates obtained at higher pH (ZB-2 and ZB-3). The major phase detected in ZB-1 is $3ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$ (JCPDS-0350433), with other impurity phases such as $Zn_4O_3(SO_4) \cdot 7H_2O$ (PDF file No: 00-0003-0797) and $Zn_4SO_4(OH)_6 \cdot H_2O$ (PDF file No: 00-039-0690). Hydroxy-sulfate species were also reconfirmed through EDS analysis of this sample (not shown). On increasing the precipitation pH to 6.5–7.0 (ZB-2), almost a pure borate phase of composition $Zn_8(BO_3)_3O_2(OH)_3$ (PDF file No: 04-013-6367) was obtained with very minor impurity phase $Zn_6(BO_3)_3O(OH)$ (PDF file No: 04-013-4389). On further increasing pH to 7.5–8.0 (ZB3) a pure borate phase of composition $Zn_6(BO_3)_3O(OH)$ (PDF file No: 04-013-4389) was obtained.

**Table 1**
Precipitation conditions of zinc borates from purified leach solutions of zinc ash.

| Sample code | pH | Temperature (°C) | Time (h) | $n$(B)/$n$(Zn) |
|---|---|---|---|---|
| ZB-1 | 5.5–6 | 95 | 3.5 | 4:1 |
| ZB-2 | 6.5–7 | 95 | 3.5 | 4:1 |
| ZB-3 | 7.5–8 | 95 | 3.5 | 4:1 |
| ZB-4 | 6.5–7 | 95 | 7 | 4:1 |
| ZB-5 | 7.5–8 | 95 | 7 | 4:1 |

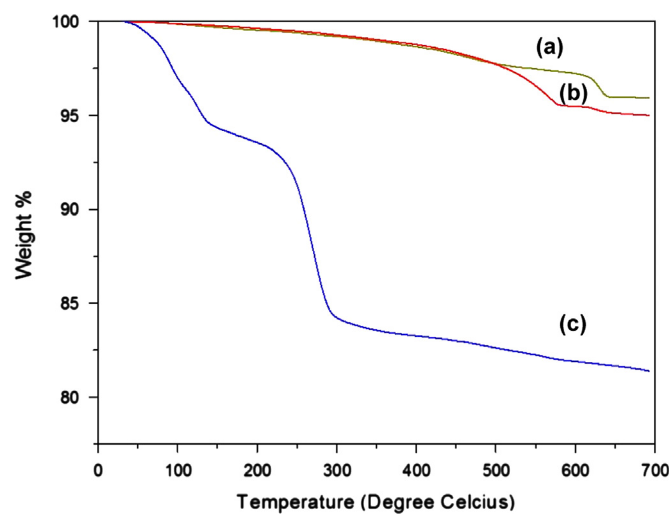


**Fig. 2.** TGA curves of zinc borates precipitated at different pH conditions: (a) ZB-3, (b) ZB-2, and (c) ZB-3.

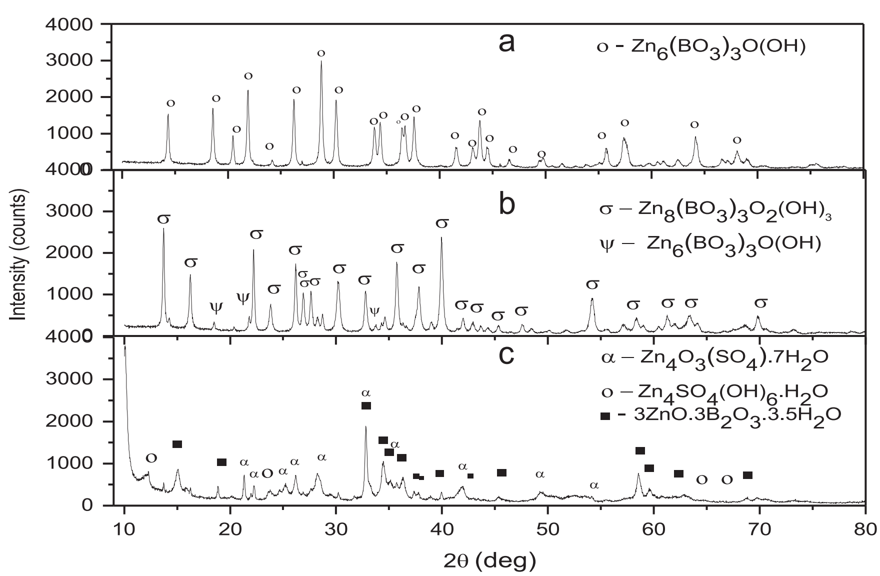


**Fig. 1.** XRD of zinc borates precipitated at different pH conditions: (a) ZB-3, (b) ZB-2, and (c) ZB-1.