ORIGINAL CONTRIBUTION

CHEMICAL TREATMENT OF SIMULATED SOLUTION OF EVAPORATOR CONCENTRATE FOR IMMOBILIZATION IN BITUMEN

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ABSTRACT. Studies on the preparation of leach-resistant insoluble boron compound from simulated solution of evaporator concentrate are reported in this work. The insoluble compound $CaB_6O_{10} \cdot 4H_2O$ has been prepared from simulated solution of evaporator concentrate by chemical treatment with calcium chloride solution. Other insoluble compounds $CaB_2O_4 \cdot 6H_2O/Ca_3B_4O_9 \cdot 9H_2O/Ca[B(OH)_4]_2 \cdot 2H_2O$ and $NaCaB_5O_6 \cdot 8H_2O/NaCaB_5O_6 \cdot (OH)_6 \cdot 5H_2O/Ca_2B_6O_{11} \cdot 13H_2O$ have been prepared from simulated solution of evaporator concentrate with calcium hydroxide under controlled conditions of temperature and time. Identification and characterization of these compounds have been done by X-ray diffraction, optical microscopy and differential thermal and thermogravimetric analysis. For low-level radioactive waste treatment, immobilization of insoluble borate compounds in bitumen will produce leach-resistant suitable waste product for safe disposal. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Radioactive liquid and solid wastes are generated from different sections of reactor and radiochemical laboratories associated with nuclear power plants. Liquid radioactive wastes originate from the boric acid control system for safe operation of nuclear power reactors. The boration of reactor coolant for reactor shutdown and during the cooldown operation of reactor coolant for refueling is routine practice. The borated coolant water is contaminated with fission products from the diffusion process and defective fuel elements. Boric acid is separated by evaporation in evaporators and recycled. The concentrated boric acid solution left in the evaporators is considered as low-level radioactive waste contaminated with fission products and corrosion products of reactor components. For economic operation of nuclear plant and to keep the environment and the population free from radioactive contamination, the radioactive wastes should be treated[1-10] by physical and chemical processes for safe disposal.[11-13]

Evaporator concentrate solution contains mainly boric acid and other chemicals such as sodium hydroxide, sodium sulphate, sodium phosphate, ferric sulphate, complexing agents and detergents. It also contains radionuclides of Sr-90, Cs-137, Co-58, Co-60, Mn-54, Fe-59 and Cr-51. The evaporator concentrates are incorporated in cement[1-3,9,10] and bitumen[1-5] for low-level radioactive waste treatment. When evaporator concentrates containing sodium salts are incorporated in cement, the solidified waste product deteriorates due to soluble borate compound present. In an advanced cement solidification process[10] the low-level waste was pretreated to form insoluble compound $CaO \cdot B_2O_3 \cdot 4H_2O$ with calcium hydroxide before incorporation in cement. Immobilization of low-level radioactive wastes of evaporator concentrates in bitumen have been reported by different research workers.[1-5] Recent research work[5] on low-level waste treatment showed that the waste product prepared with bitumen – simulated evaporator concentrates deteriorated during the leaching test.

The objective of the present work is to prepare insoluble boron compounds by chemical treatment of inactive simulated evaporator solution with calcium compound for immobilization in Brazilian bitumen. In a recent investigation[5] three different types of evaporator solutions have been used. In the present work only one type of evaporator solution-1 has been investigated, which is prepared by dissolving boric acid in sodium hydroxide solution.

METHODS AND MATERIALS

The compounds of calcium borate and sodium calcium borate were prepared by chemical reaction of simulated solution-1 of evaporator concentrate with calcium chloride solution and calcium hydroxide under controlled temperature and time. The simulated solution-1 of evaporator concentrate was prepared by dissolving 131 g H_3BO_3 analytical reagent (AR) in 1 litre solution containing 35 g (AR) NaOH at 40°C by agitation magnetically.

The solution of calcium chloride was prepared by dissolving 30 g $CaCl_2$ (AR) in 200 ml deionized water at 96°C with constant agitation for 15 min. The solution of calcium chloride was added to 1 litre simulated solution-1 of evaporator concentrate with constant agitation for 3 h at room temperature. The insoluble compound was separated after standing overnight by vacuum filtration on a buckner funnel using filter paper Whatman No. 40 and dried at 60°C for 3 h.

The preparation of calcium borate and sodium calcium borate from simulated solution-1 of evaporator concentrate and calcium hydroxide slurry was carried out according to the procedure described by Awwal et al.[14] In each experiment 100 ml of simulated solution-1 of evaporator concentrate was taken and mixed with a stoichiometric amount of calcium hydroxide (AR) in slurry form. The simulated solution-1 of evaporator concentrate was heated at temperature varying from 60 to 95°C for different experiments and the slurry of calcium hydroxide was added to the solution and the solution mixture was agitated for varying period of 1–14 h for different experiments. For the preparation of calcium borate compound two-step chemical reactions were carried out. In the first step the chemical reaction was carried out at a temperature varying from 85 to 95°C for 1–7 h. In the second step the chemical reaction was carried out at temperature of 60°C for 6–8 h. The insoluble compound formed was separated by vacuum filtration using a buckner funnel with filter paper Whatman No. 40 after standing overnight and the solid was dried at 60°C for 3 h.

The preparation of sodium calcium borate compound was carried out in a one-step chemical reaction at a temperature of 85°C for a period of 7 h. The insoluble compound formed was separated by vacuum filtration using a buckner funnel with filter paper Whatman No. 40 after standing overnight and the solid was dried at 60°C for 3 h. Five series of experiments were carried out as a function of varying temperature, time and reagents. The codes used for the experiments were Psol-1 and 1Psol-1, 2Psol-1, 3Psol-1, 4Psol-1, where P stands for pretreatment and sol-1 stands for simulated solution-1 of evaporator concentrate and the prefix 1, 2, 3, 4 stands for different experiments. Table 1 shows the different experimental conditions used for the preparation of different borate compounds.

The concentration of boron and pH of the experimental solution were measured during the preparation of borate compound. Samples of the reaction mixture were taken at 1 h intervals, the pH was measured by pH meter and concentration of boron was determined by spot test[15] with alizarin red S. The profiles of the pH of the reactants during the reaction period are shown in Fig. 1.

The identification of solid borate compounds prepared has been made by crystallographic studies by X-ray diffraction techniques using Geigerflex diffratometer. The characterization of crystal types and sizes was investigated by optical microscopy using Leitz research microscope Othroplan-Pol. The differential thermal analysis and thermogravimetric analysis of the solid compound were performed by Rigaku Thermoflex.

RESULTS AND DISCUSSION

The pH profiles of the reactants are shown in Fig. 1 as a function of reaction time of experiments 3Psol-1 and 4Psol-1 and the experimental conditions are shown in Table 1. The initial pH of the simulated solution-1 of evaporator concentrate was 6.80 which was increased as the chemical reaction proceeded with time. In the case of experiment 3Psol-1,

TABLE 1

The Experimental Conditions for Preparation of Borate Compounds with Simulated Solution-1 of Evaporator Concentrate and Calcium Compound

| Number of experiments	Reagent for chemical reaction	Temperature and time of 1st-step reaction	Temperature and time of 2nd-step reaction	Remark
Psol-1-$CaCl_2$	$CaCl_2$ solution	Room temperature; 3 h	—	Insoluble borate compound
1Psol-1	$Ca(OH)_2$ slurry	95°C; 1 h	60°C; 6 h	No borate compound
2Psol-1	$Ca(OH)_2$ slurry	95°C; 4 h 15 min	60°C; 8 h	No borate compound
3Psol-1	$Ca(OH)_2$ slurry	85°C; 7 h	60°C; 7 h	Insoluble borate compound
4Psol-1	$Ca(OH)_2$ slurry	85°C; 7 h	—	Insoluble borate compound
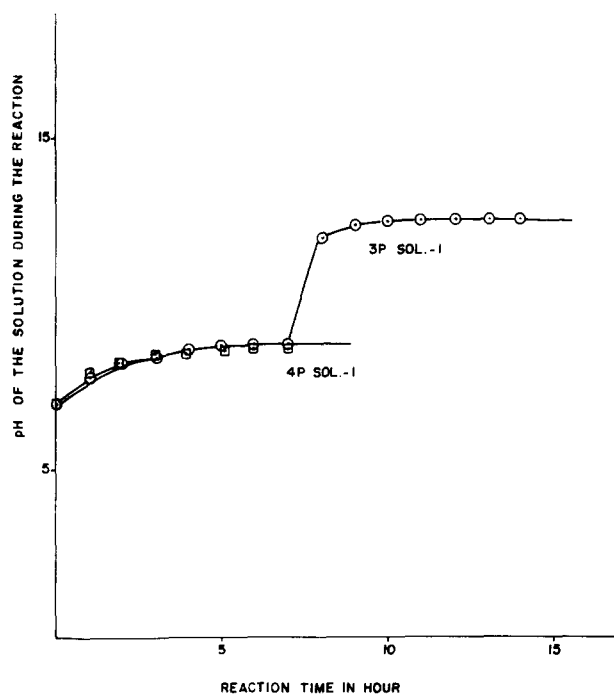
FIGURE 1. The pH profiles of the chemical reaction of calcium hydroxide with simulated solution-1 of evaporator concentrate.

FIGURE 2. X-ray diffraction of insoluble borate compound, prepared with calcium chloride solution and simulated solution-1 of evaporator concentrate.

in the two-step reaction, the pH increased to 8.80 when the reaction was carried out for 7 h at 85°C in the first-step reaction and the pH increased steeply when the second-step reaction was started. After 7 h reaction at 60°C, the pH of the solution was 12.5. In the one-step reaction in the experiment 4Psol-1, the pH increased to 8.72 after 7 h reaction at 85°C.

The concentration of boron in the solution of experiments 3Psol-1 and 4Psol-1 decreased as the reaction proceeded with time. The concentration of boron was <0.1 ppm in the solution of experiment 3Psol-1 after 14 h reaction and the concentration of boron in the solution of experiment 4Psol-1 attained <0.1 ppm after 7 h reaction time.

The insoluble calcium borate compound prepared from simulated solution-1 of evaporator concentrate and calcium chloride was identified by X-ray diffraction as $CaB_6O_{10} \cdot 4H_2O^{16}$ and the X-ray diffractogram is shown in Fig. 2. It is a calcium borate compound of 1:3:4 composition of structural formula $CaO \cdot 3B_2O_3 \cdot 4H_2O$. Preparation of a similar compound has been reported by Lehman and Guenther[17] from calcium chloride and sodium borate solution. The optical microscopic studies of this compound have shown that the crystals are needle shaped and radiated fibrous aggregates. The diameters of the crystal grains vary from 0.08 to 0.24 mm. Differential thermal and thermogravimetric analysis of $CaB_6O_{10} \cdot 4H_2O$ have been performed and the thermogram is shown in Fig. 3. Two endothermic peaks are observed. The first peak at 125°C corresponds to the starting of the loss of water of crystallization and the second peak at 700°C may be attributed to final
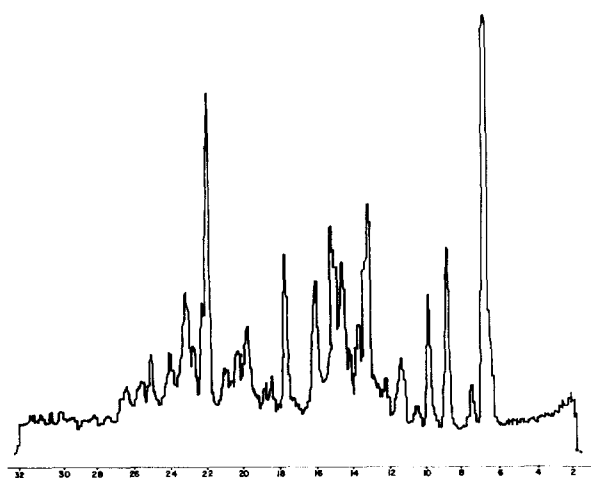
loss of water. An exothermic peak at 780°C indicates the decomposition of borate compound to boric oxide. The total loss of mass corresponds theoretically to 21.3 weight (wt) % but a loss of 15.1 wt% was observed experimentally.

In experiments 1Psol-1 and 2Psol-1, no insoluble borate compound was formed. The pH of the solutions measured during the experiment did not change and the solid separated did not show any
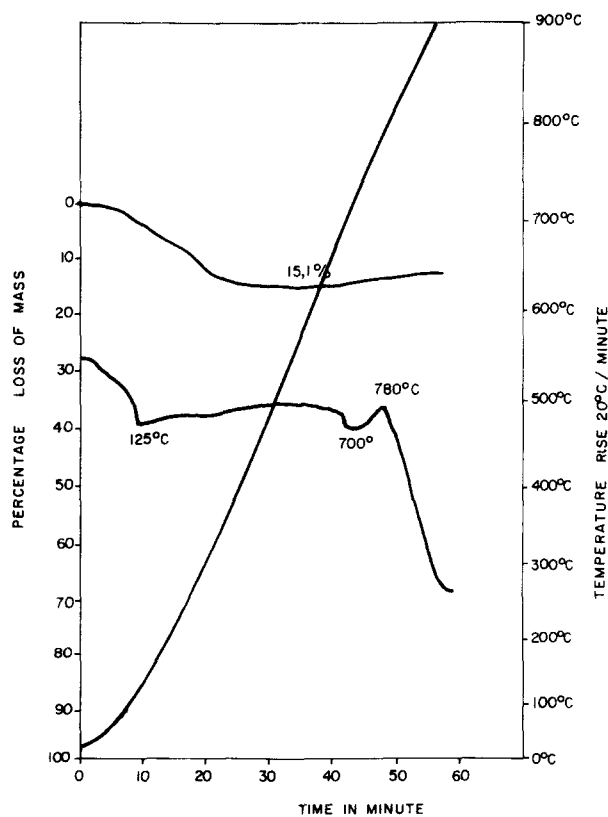

FIGURE 3. Differential thermal and thermogravimetric analysis of $CaB_6O_{10} \cdot 4H_2O$ compound.

borate compound as investigated by X-ray diffraction. The insoluble borate compound formed in experiment 3Psol-1, in a two-step chemical reaction, was identified as $CaB_2O_4 \cdot 6H_2O$[19] and $Ca_3B_4O_9 \cdot 9H_2O$[20] as the predominant phase along with $Ca[B(OH)_4]_2 \cdot 2H_2O$[21] as the minor phase. The X-ray diffractogram of these compounds is shown in Fig. 4. The compound $CaB_2O_4 \cdot 6H_2O$ is a calcium borate of structural formula $CaO \cdot B_2O_3 \cdot 6H_2O$ of $1:1:6$[16] composition. The compound $Ca_3B_4O_9 \cdot 9H_2O$ of structural formula $3CaO \cdot 2B_2O_3 \cdot 9H_2O$ of $3:2:9$ composition is being reported for the first time in the preparation of calcium borate compound from simulated solution-1 of evaporator concentrate with calcium hydroxide in the present work. The formation of $Ca[B(OH)_4]_2 \cdot 2H_2O$ may be attributed to dehydration of $1:1:6$ compound $CaO \cdot B_2O_3 \cdot 6H_2O$.[16] The characterization of crystal type and sizes has been done by optical microscopy. The crystals are prismatic, colourless to slightly brown and the diameters of crystals vary from 0.02 to 0.12 mm. The insoluble calcium borate compound obtained in the present work from simulated solution of evaporator concentrate with calcium hydroxide is different from that of some Japanese workers.[10] Differential thermal and thermogravimetric analyses of $CaB_2O_4 \cdot 6H_2O/Ca_3B_4O_9 \cdot 9H_2O/Ca[B(OH)_4]_2 \cdot 2H_2O$ have been carried out and the thermogram is shown in Fig. 5. Three endothermic peaks at 100°C, 130°C and 140°C were obtained, which correspond to the loss of water of crystallization of the mixed calcium borate compound. The exothermic peak at 720°C indicated the decomposition of calcium borate compound to boric oxide. The total loss of mass that occurred in thermogravimetric studies is 31.1 wt%, but theoretical loss of mass of calcium borates corresponds to 32.0 wt%.

The insoluble borate compound prepared in the experiment 4Psol-1 in a one-step chemical reaction

FIGURE 5. Differential thermal and thermogravimetric analysis of $CaB_2O_4 \cdot 6H_2O/Ca_3B_4O_9 \cdot 9H_2O/Ca[B(OH)_4]_2 \cdot 2H_2O$ compounds.

has been identified as $NaCaB_5O_9 \cdot 8H_2O$, ulexite[22] as the predominant phase and $NaCaB_5O_6(OH)_6 \cdot 5H_2O$[23]/ $Ca_2B_6O_{11} \cdot 13H_2O$ inyoite[24] as the minor phase. The X-ray diffractogram of these compounds is shown in Fig. 6. No reference has been cited in the literature on the preparation of these compounds from a simulated solution of evaporator concentrate and calcium hydroxide. The structural formula of ulexite as $NaCa[B_5O_6(OH)_6] \cdot 5H_2O$ has been reported by Ghose *et al.*[23] The presence of $NaCaB_5O_6(OH)_6$
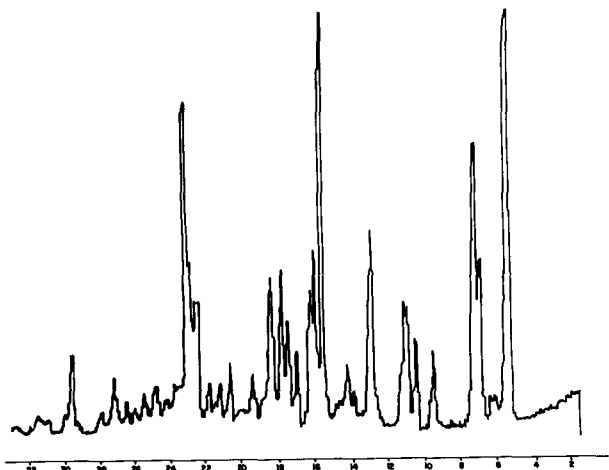

FIGURE 4. X-ray diffraction of insoluble borate compound, prepared with slurry of calcium hydroxide and simulated solution-1 of evaporator concentrate in two steps chemical reaction.
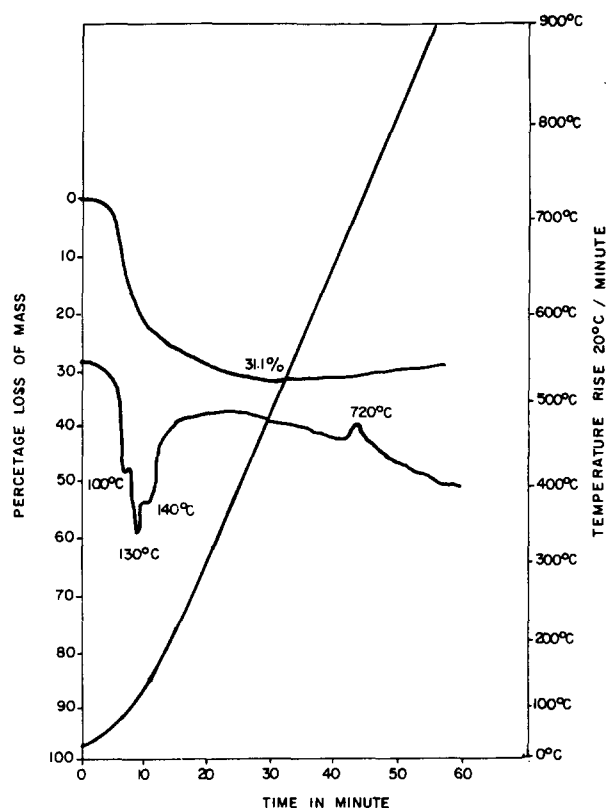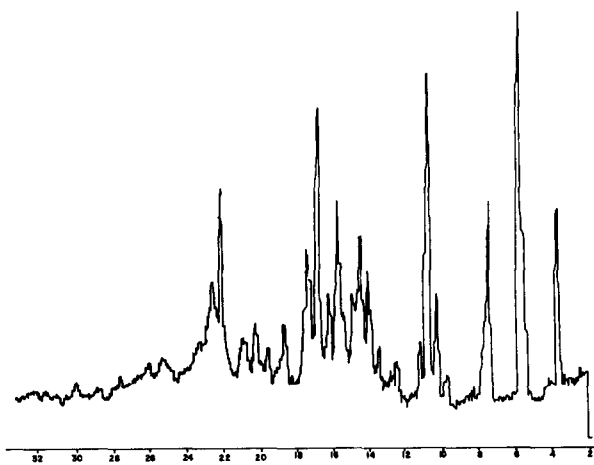

FIGURE 6. X-ray diffraction of insoluble borate compound, prepared with slurry of calcium hydroxide and simulated solution-1 of evaporator concentrate in one step chemical reaction.

$\cdot 5H_2O$ as a minor phase in the calcium borate compound obtained in 4Psol-1 may be attributed to the dehydration of $NaCaB_5O_9\cdot 8H_2O$. The compound $Ca_2B_6O_{11}\cdot 13H_2O$, inyoite, of structural formula $2CaO.3B_2O_3\cdot 13H_2O$ of 2:3:13 composition, of calcium borate has been reported by Farmer.[16] The preparation of $2CaO\cdot 3B_2O_3\cdot 13H_2O$ by reacting calcium chloride with ammonium pentaborate solution or calcium iodate with borax at 30°C was investigated by Wieder et al.[26] The types of crystals and their sizes were investigated by optical microscopy. The crystals are granular, needle-shaped and the diameters of the crystals vary from 0.04 to 0.11 mm. Differential thermal and thermogravimetric analyses of $NaCaB_5O_9\cdot 8H_2O/NaCaB_5O_6(OH)_6\cdot 5H_2O/Ca_2O_6O_{11}$ $\cdot 13H_2O$ have been investigated and the thermogram is shown in Fig. 7. Two endothermic peaks are observed, the first one at 110°C corresponds to the loss of water of crystallization and the second endothermic peak at 175°C may be attributed to the loss of the hydroxyl group of the compound $NaCaB_5O_6(OH)_6\cdot 5H_2O$. An exothermic peak is observed at 675°C which corresponds to decomposition of the compound. When $NaCaB_5O_9\cdot 8H_2O$ is thermally decomposed, it may form a calcium borate compound of composition $2CaO\cdot 3B_2O_3\cdot x\ H_2O$[16] and $Na_2O\cdot B_2O_3$. If we consider the formation of the lowest

member of the borate compound due to thermal decomposition of series 2:3:1 of composition $2CaO\cdot 3B_2O_3$ $\cdot H_2O$, which has been reported by Hart and Brown,[27] then the decomposition of ulexite may be written as

$$2NaCaB_5O_9\cdot 8H_2O \rightarrow Na_2O\cdot 2B_2O_3\cdot 2CaO\cdot 3B_2O_3\cdot H_2O.$$

According to the reaction the total weight loss due to thermal decomposition should have been 33.3%, but our studies showed a constant weight loss of 27.2% at 440–600°C which is 6.1% less than the theoretical weight loss; this may be considered as experimental error.
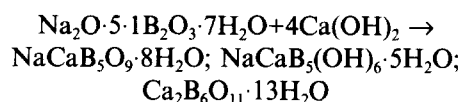
The simulated solution-1 of evaporator concentrate prepared in this work may be composed of dibasic sodium pentaborate of composition $Na_2O\cdot 5\cdot 1B_2O_3\cdot 7H_2O$ based on studies of the solubility isotherm.[18] Studies of IR spectra of the $Na_2O-B_2O_3-H_2O$ system[28] have also shown the presence of polyborate species of mole ratio of $B_2O_3:Na_2O$ of 5:1 at pH 6.5 at 26°C. The pentaborates of sodium are the stable phase in the $Na_2O-B_2O_3-H_2O$ system at 40–90°C.[16] The reaction temperatures of the experiments were 60–85°C for the preparation of the insoluble compound of borate. Considering the mode of preparation of the simulated solution-1 of evaporator concentrate, the borate compound present was sodium pentaborate of composition $Na_2O\cdot 5\cdot 1B_2O_3\cdot 7H_2O$.[18,28] The most common sodium pentaborate has the structural formula $Na_2O\cdot 5B_2O_5\cdot 10H_2O$ and some workers[25] have also cited sodium pentaborate as $Na[B_5O_6(OH)_6]\cdot 3H_2O$.

The formation of different borate compounds during the chemical treatment of simulated evaporator concentrate solution-1 with calcium compounds may be attributed to the following schematic chemical reactions:
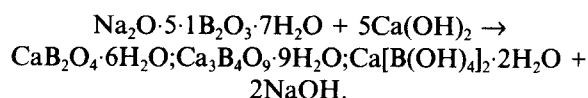
Borate compound formed with $CaCl_2$:

$$Na_2O\cdot 5\cdot 1B_2O_3\cdot 7H_2O + CaCl_2 \rightarrow$$
$$CaB_6\cdot O_{10}\cdot 4H_2O + 2NaCl$$
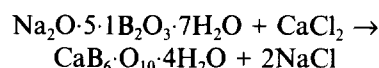
Borate compounds formed with $Ca(OH)_2$ in the one-step reaction process:

$$Na_2O\cdot 5\cdot 1B_2O_3\cdot 7H_2O + 4Ca(OH)_2 \rightarrow$$
$$NaCaB_5O_9\cdot 8H_2O;\ NaCaB_5(OH)_6\cdot 5H_2O;$$
$$Ca_2B_6O_{11}\cdot 13H_2O$$

Borate compounds formed with $Ca(OH)_2$ in the two-step reaction process:

$$Na_2O\cdot 5\cdot 1B_2O_3\cdot 7H_2O + 5Ca(OH)_2 \rightarrow$$
$$CaB_2O_4\cdot 6H_2O;Ca_3B_4O_9\cdot 9H_2O;Ca[B(OH)_4]_2\cdot 2H_2O +$$
$$2NaOH.$$

The borates of alkali and alkaline earth metals give an alkaline reaction in solution as they are formed to give a compound of lower boron-to-metal ratio than those of the initial solution.[29]
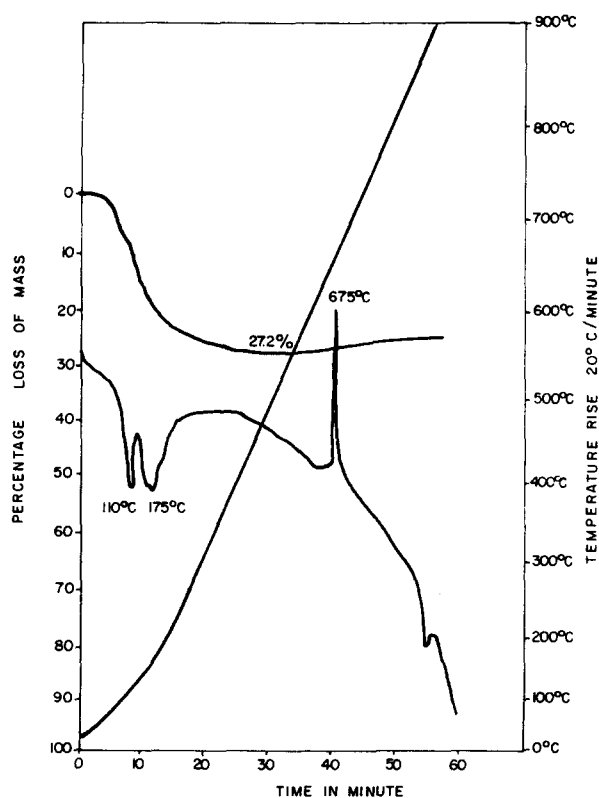

FIGURE 7. Differential thermal and thermogravimetric analysis of $NaCaB_5O_9\cdot 8H_2O/NaCaB_5O_6(OH)_6\cdot 5H_2O/Ca_2O_6O_{11}\cdot 13H_2O$ compounds.

CONCLUSIONS

The insoluble compound $CaB_6O_{10} \cdot 4H_2O$ is prepared from simulated solution-1 of evaporator concentrate with calcium chloride solution. Sodium chloride formed during the chemical reaction will be a secondary waste. This chemical treatment process will not be economic for waste management.

In two-step preparation, insoluble compounds $CaB_2O_4 \cdot 6H_2O / Ca_3B_4O_9 \cdot 9H_2O / Ca[B(OH)_4]_2 \cdot 2H_2O$ are obtained from simulated solution-1 of evaporator concentrate and calcium hydroxide. A large amount of calcium hydroxide is consumed and the reaction time is very long in this process. Sodium hydroxide is formed during the chemical reaction and the pH of the filtrate solution is 12.5. The solution of sodium hydroxide cannot be liberated into the environment without further treatment and the waste management will be expensive.

Insoluble compounds $NaCaB_5O_9 \cdot 8H_2O / NaCaB_5O_6$ $(OH)_6 \cdot 5H_2O / Ca_2B_6O_{11} \cdot 13H_2O$ are formed from simulated solution-1 of evaporator concentrate with calcium hydroxide in the one-step reaction process. Since the pH of the filtrate solution is 8.72, this can be liberated as such into the environment. The major component of the compound formed is $NaCaB_5O_9 \cdot 8H_2O$, which is identical to stable boron-bearing mineral ulexite. Immobilization of sodium calcium borate compounds in bitumen will produce a leach-resistant waste product for safe disposal. Since the insoluble boron compound contains calcium and sodium, the retention of fission products Sr-90 and Cs-137 will be good.

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