Recovery of boron from the borosilicate tourmaline mineral of Sikait area, Eastern Desert, Egypt.

Galal Mahmoud Abdel Wahab Dabbour

Nuclear Materials Authority, P.O. Box 530 El Maad, Cairo, Egypt.

Summary: A tourmaline ore sample from Sikait area in south eastern desert of Egypt and assaying 10 % B_2O_3 is subjected for boron recovery through an alkali fusion followed by solvent extraction. A flux mixture of Na_2CO_3 + ZnO was used for ore sample fusion in a weight ratio of 1.5 to 1 respectively for 30 minutes at 900^oC before boron was selectively leached. Subsequent solvent extraction of boron was performed using 2-ethyl-1,3-hexandiol (EHD) in benzene however boron extraction efficiency achieved 94.5 %. While boron stripping process was carried out using 1 % NaOH solution with efficiency reached 90 %. The solvent factors of boron extraction and stripping have been adequately studied. From the alkali strip solution borax was crystallized as a final product and its composition was conformed using XRD analysis technique. Overall borax recovery 95 % has actually been realized.

Introduction

Boron is actually a versatile and useful element where it is mainly used in several industries in the form of its many compounds especially borax and boric acid. It is used in glass industries to impact strength and hardness as well as in vitreous enamel besides other industries of soaps, agriculture and chemicals etc. In addition, boron has gained great importance due to its wide applications especially in the nuclear fields. Boron has indeed two isotopes namely ^{10}B and ^{11}B while the former is characterized by its high ability to absorb thermal neutrons due to its large cross section for neutron absorption attains 3850 barns. The cross section of ^{11}B is only 38 barns while the cross section of the natural boron is 755 barns. Accordingly, the isotope ^{10}B has a great importance in controlling the nuclear reactions in the nuclear reactors as well as in shielding of their radiations, El Hazek[1].

Although boron is found in many minerals, only a few is commercially valuable as a source of boron. These mainly include borax ($Na_2B_4O_7.10H_2O$), kernite ($Na_2B_4O_7.4H_2O$), borocalcite ($Ca_2B_6O_{11}.5H_2O$) and sassolite (H_3BO_3) etc. On the other hand, tourmaline [Na $(Mg,Fe)_3Al_6(BO_3)_3(Si_6O_{18})(OH)_4$] which is preumatolytic mineral

in acidic and metamorphic rocks. Tourmaline can be considered as a secondary source for boron.

As a matter of fact, tourmaline has many other functions such as shielding of electromagnetic waves and releasing of negative ions. Therefore, tourmaline minerals are a kind of ecomaterials to purify environment. The later has actually been recorded in different countries. According to Liang Jin et al.,[2] tourmaline recorded in Inner Mongolia, China assays 7.7% B_2O_3 while Marcos et al.,[3] have reported that, a Cu-bearing tourmaline from Paraiba, Brazil contains 10.91% B_2O_3 as has been analyzed with Electron-microprobe analysis. In addition, Cristiane et al.,[4] have studied several tourmaline samples from different sources and were found to contain10% B_2O_3, 43% Al_2O_3 and 38% SiO_2 as their major oxides beside traces of Mg, Fe and Na.

In Egypt, tourmaline has recorded in different locations e.g. in El-Gara El-Hamra Mountain, South East Aswan, Mahmoud[5] as well as in Sikait area, South Eastern Desert, the latter assayed 10% B_2O_3 in some samples, Harraz and Sharkawy[6]. Also, boron can be recovered from other different resources including mainly lead- zinc deposits of Um-Gheig area, Eastern Desert and Qaron Lake brines, Mahdy et al.,[7], the waste of borosilicate glasses industries, Abdel Wahab[8] as well as the processing of the local tourmaline.

Several studies have been published about the chemical processing of high refractory borosilicate tourmaline mineral. Thus, according to, Lihareva et al.,[9] boron in tourmaline was fused with a flux mixture (Na_2CO_3 and ZnO) in the weight ratio 3.5: 0.6 for 30min at 900ºC followed by selective water leaching of boron leaving behind the other matrix elements namely, Si, Mg, Fe and Ca. In the mean time, Gupta et al.,[10] have fused borosilicate glasses containing 32% B_2O_3, 5% (K_2O+Na_2O) and 62% SiO_2 fused at 800-1000ºC. In addition, Abd El Wahab[8] has been succeeded in breaking down borosilicate glasses containing 6.5% B_2O_3, 5% Na_2O, 2.8% Al_2O_3 and 82% SiO_2 by fusion at 800ºC for 15 min with Na_2CO_3 at sample/ reagent weight ratio of 1/2.

For boron purification many researchers have studied boron extraction from different aqueous solutions using organic solvents. As has been published by Tural et al.,[11] boron was effectively extracted using alcohols especially those with 1,3 diols due to their

neutral and planar complex formation with boric acid. The distribution coefficient of boric acid between aqueous and these organic solvents was found to exceed10. Also, Poslu and Dudeney[12] have actually noticed that the extraction efficiency of boron with EHD depends mainly on the pH value where boron extraction efficiency is higher at pH 7.5 than at pH 8.5. Moreover, Su et al.,[13] used 50% EHD in kerosene to recover boron from the chloride leach liquor of ascharite mineral ($Mg_2B_2O_5.H_2O$). The loaded solvent has been stripped by water to yield boric acid or else NaOH solution to yield borax. Both extraction and stripping processes have been carried out at 80 ^{o}C. Also, Habashi[14] has been recovered boric acid from the brines of Searles Lake of California, USA assaying 36% total dissolved salts (Na, K, B, Cl$^-$, ….SO$_4^-$) using polyalcohol dissolved in kerosene. In this work, boron is stripped from the organic phase using dilute H_2SO_4 to yield 99.9% pure boric acid with very limited impurities include 0.05% SO_3, and 0.0029% Na.

The main purpose of the present work is to produce pure boron salts from the boron-bearing tourmaline mineral of Sikait area, South Eastern Desert, Egypt. Boron salts were actually the raw material for the production of elemental boron which is quite important in the nuclear industries.

Experimental

Characterization of the ore sample.

For the present work, a weight 200g of tourmaline ore sample was collected from the Sikait, area and was first ground to a grain size less than 0.25 mm. The ground sample was then examined by X-ray diffraction (XRD) technique using Philips instrument for the mineralogical analysis. On the other side, for the chemical composition a weight of 0.2 g was fused into a platinum crucible with 1g of the flux mixture composed of Na_2CO_3 and ZnO in a weight ratio of 3.5-0.6 in a muffle furnace at 900°C for 30min. For the complete dissociation of the fused matrix 30mL of HCl (1:1) was added and the total volume was completed up to100mL with distilled water and subjected to the chemical analysis with different techniques.

Both the major elements (B, Al, Fe) and the trace elements (Mn, Cu, Ni, Pb) were analyzed using the flame atomic absorption Unicam 969 at their respective wavelengths. While Si was determined by UV spectrophotometery at λ 640 nm.. Marczenko [15]. Both Ca and Mg were analyzed by titration against 0.01 M EDTA solution. The flame photometer (Sherwood Model 410) was used for the determination of Na at λ589. The final prepared product has been identified by XRD. The pH values of the aqueous solutions were adjusted with a pH meter (Digimed DM-21).

Optimization of solvent extraction parameters

Extraction of boron was carried out in separating funnel using 2-ethyl-1,3-hexanediol, (EHD) in benzene. The effective boron extraction parameters have been studied to attain their optimum conditions. These parameters were EHD concentrations (25-100%), contact time (5-20 min), temperature (25-90°C) and organic/aqueous volume ratio (O/A). On the other hand, stripping factors of boron from the loaded solvent were also investigated. These factors were stripping agent type, concentration (1-10%) contact time (2.5-10 min), temperature (25-90°C) and aqueous/organic volume ratio (A/O).

Results and Discussion

Mineralogical and chemical composition

The mineralogical analysis of the Sikait tourmaline ore sample has confirmed the presence of two tourmaline mineral types e.g. Fe type, Schorl ($NaFe_3Al_6B_3Si_6O_{27}$ $(OH)_4$), [ASTM cart No., 22-469] and Mg type, Dravite ($NaMg_3Al_6B_3Si_6O_{27}(OH)_4$), [ASTM cart No., 14-76]. On the other hand, the complete chemical analysis of the ore sample revealed the presence of B_2O_3 assays 10%, SiO_2 assays 33%, Al_2O_3 assays 34%, Fe assays 8.5% and Mg assays 7.5%. In the mean time, some trace elements have been analyzed including Pb (100ppm), Mn (400ppm) and Cu (20ppm).

Ore dissociation

Because the worked ore sample was a borosilicate mineral, its proper breakdown has necessitated an alkali fusion followed by water leaching [.9]. For this purpose, the flux mixture (Na_2CO_3 + ZnO) was thus used for the fusion in a sample/

flux weight ratio of 1/1.5 in a muffle furnace at 900°C for 30min in porcelain crucible followed by hot water leaching. Using an ore sample weight of 50g, it was possible to prepare 1liter of boron alkaline leach liquor of pH11. By the chemical analysis of the latter, boron was found to assay 1.5g/l equivalent to 12.7 g/l $B(OH)_4^-$ with leaching efficiency achieved 93%.

Solvent extraction of boron

Before the extraction experiments, the pH value of the prepared leach liquor was adjusted to pH6 with few drops of concentrated H_2SO_4. The effective and selective boron organic solvent EHD dissolved in benzene was used for this purpose.

Investigation of the extraction parameters

The effective extraction parameters such as: EHD concentrations, contact time, extraction temperature and organic/aqueous (O/A) volume ratio were investigated. The results of the studied parameters were represented and summarized as shown below:

The effect of EHD concentrations was first studied in the range of 25 to 100% by mixing the solvent and the aqueous solution in O/A ratio of 1/1 and shaking the mixtures for 5min at room temperature (25°C) and then separated the aqueous solution and analyzed B. Results shown in Figure (1) showed that, the boron extraction efficiency increases by increasing the EHD concentrations where it attained (96.5%) at 100% EHD concentration. Although 50% EHD concentration gave low boron extraction efficiency of 91%, but it was applied. Indeed, saving the expensive solvent and the boron extraction efficiency will be improved with the other parameters. On the other hand, the investigation of the contact time effect was performed in the range of 5 to 20 min using 50% EHD at O/A ratio of 1/1 and at 25°C. The plotted results shown in Figure (2) indicated that, the maximum B extraction efficiency (94.5%) was achieved at a contact time of 10min where there is no considerable improvement has been occurred. In addition, the studying of the temperature effect at fixed conditions beyond increasing the temperature of the aqueous solution from 25-90°C has no considerable effect upon the B extraction efficiency as shown in Figure (3). It is worthy to mention that, heating

the aqueous solutions up to 90°C does not affect on the organic solvent because its boiling point achieved 133°C, (David)[16]. Finally, the investigation of O/A ratio effect was performed by mixing 50% EHD with the alkali solution at different ratios 3/1, 2/1, 1/1, 1/2, 1/3 at 10 min contact time and at 25°C. The studying of O/A parameter represented the equilibrium states between both organic and aqueous phases and gave the distribution coefficient,(D_A^O) of each O/A ratio as given in Table (1). In addition, it gives the number of theoretical stages required for complete extraction of B as shown in the McCabe Thiele diagram, Figure (4). This diagram indicated that, two stages were theoretically required for complete B extraction from the aqueous solution. While Table (2) showed that, B extraction efficiencies at O/A ratios of 1/3 and 1/2 were low (38% and 49%) compared with O/A ratio of 1/1. In addition, although B extraction efficiencies at O/A ratios of 3/1 and 2/1 were very high (98% and 99.7%) but they were not recommended because they gave B diluted solution.

Extraction distribution coefficient $(D_A^O) = $ [B]or   (1)
[B]aq

The conclusion from the above findings is that, the optimum conditions for the maximum B extraction efficiency, (94.5%) from the alkali leach liquor of tourmaline at pH 6 were 50% EHD concentration, O/A volume ratio (1/1) and 10 min contact
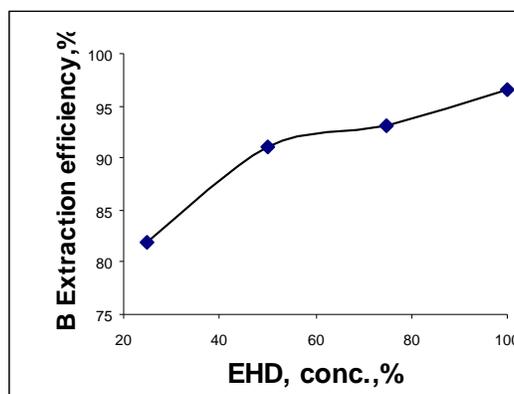

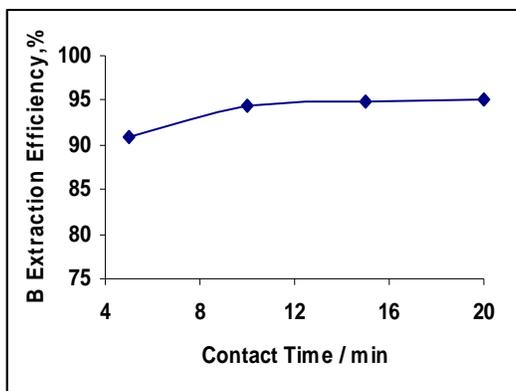**Figure (1):** Effect of EHD concentrations upon B extraction efficiency.

Figure (2): Effect of contact time upon B extraction efficiency.
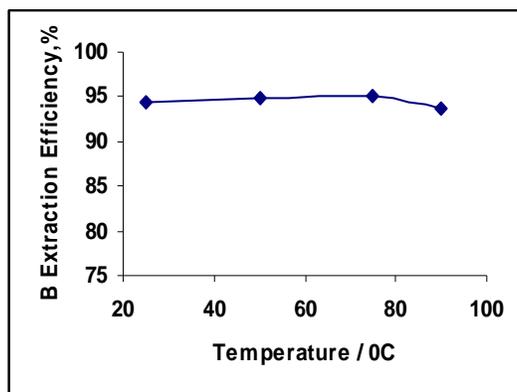

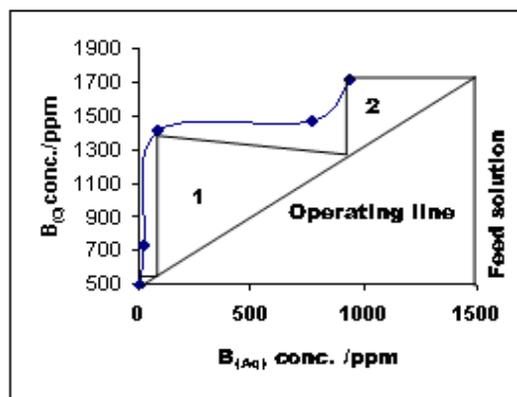**Figure (3):** Effect of temperature upon B extraction efficiency.

Figure (4): Extraction McCabe Thiele   diagram

time at room temperature. By applying these conditions, it could have an organic solvent loaded by 1.7 g/l of B which subjected to the stripping stage.

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Table (1): Effect of O/A ratio upon B extraction efficiency

O/A ratio	Aqueous phase conc., ppm	Organic phase conc., ppm	D_A^O	B Extraction efficiency,%
1:3	930	1710	1.83	38
1:2	765	1470	1.92	49
1:1	82.5	1417.5	17.18	94.5
2:1	30	735	24.51	98
3:1	4.5	498.5	110.77	99.7

Investigation of the stripping parameters

Different effective parameters have been investigated to regenerate B from the loaded EHD through the stripping process. Different stripping agents e.g., H_2O, 5% of HNO_3, H_2SO_4 and NaOH were applied at A/O ratio of 1/1 and shacked for 5min at 25°C. It was found that, 5% NaOH gave the best B stripping efficiency,(80%) compared to 5% H_2SO_4 (54%) and hot distilled H_2O (28%) and cold distilled H_2O (15%) . Thus, it was decided to study the other different affecting factors for achieving the maximum B stripping efficiency by using NaOH solution. These factors were NaOH concentrations, contact time and stripping temperature.

Firstly, the effect of NaOH concentration was conducted by mixing both the loaded EHD and NaOH solution in different concentrations ranged from 1 to 10% at A/O ratio of 1/1 and shacked for 5 min at 25°C. It can be infered from Figure (5) that, B stripping efficiency decreased by increasing the concentration of NaOH solution however the maximum B stripping efficiency,(90%) was given at NaOH concentration of 1% compared to the others. On the other hand, results in Figure (6) clarify that, the best B stripping efficiency 90% was given at the stirring time of 5min compared to 2.5, (86%), 7.5, (88%) and 10min (85%) at A/O ratio of 1/1 and at 25°C.In addition, the effect of stripping temperature was applied by heating the NaOH solution to different temperatures ranged from 25 to 90°C at A/O ratio of 1/1 and at 5min contact time. It was observed from Figure (7) that, increasing the temperature of

the stripping agent has an opposite effect upon the B stripping efficiency. It decreased from 90% at 25°C to achieve 55% at 90°C. Moreover, the effect of A/O ratio was studied by mixing different volumes of 1% NaOH and the loaded EHD in the range 3/1,…,1/1,….1/3. Results in Table (2) represented the equilibrium states between both aqueous and organic phases at different A/O ratios and gave the distribution coefficient, (D_O^A) of each A/O ratio. While Figure (8) showed McCabe Thiele diagram which represented that, two main stages were required for complete B stripping from the loaded EHD. On the other hand, observations revealed that, B stripping efficiencies at 1/3, 1/2 ratios (55% and 40%) were low compared with 1/1 ratio. Furthermore, B stripping efficiencies at A/O ratios 3/1 and 2/1 were 93% and 99%, respectively but it was not recommended because it gave diluted B strip solutions.

Stripping distribution coefficient (D_O^A) = $\dfrac{[B]aq}{[B]or}$ (2)
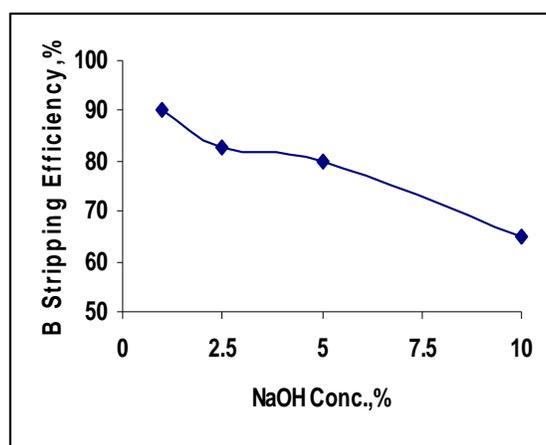

Figure (5): Effect of NaOH concentrations   upon B stripping efficiency
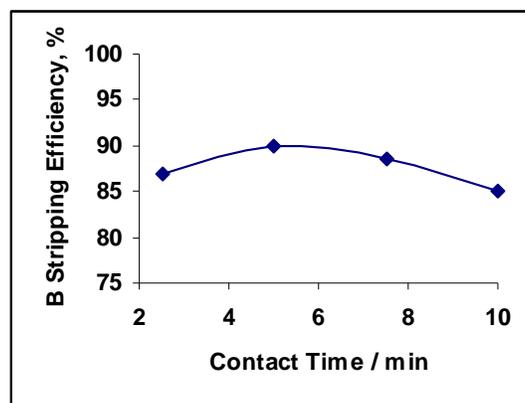

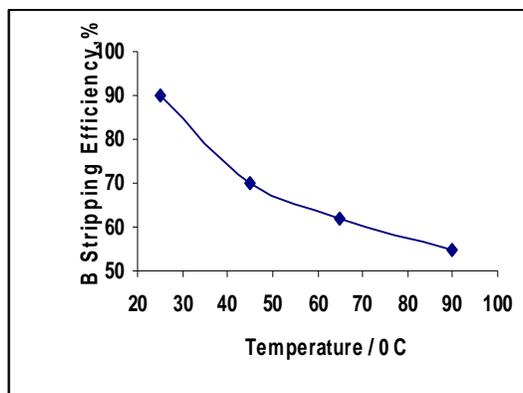**Figure (6):** Effect of contact time upon B   stripping efficiency
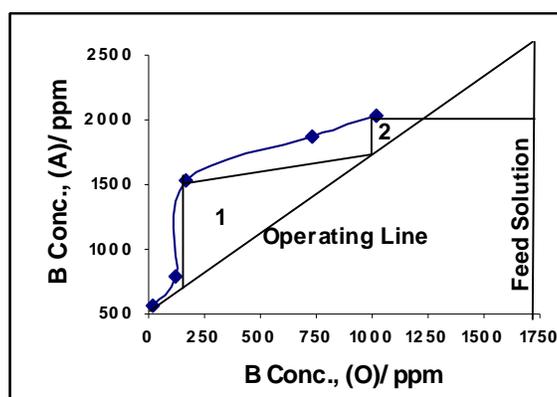
Figure (7): Effect of temperature upon B stripping

Figure (8): Stripping McCabe Thiele diagram

Table (2): Effect of A/O ratio upon B stripping efficiency

A/O ratio	Aqueous phase conc., ppm	Organic phase conc., ppm	D_O^A	B Stripping efficiency, %
1:3	2040	1020	2	40
1:2	1870	735	2.54	55
1:1	1530	170	9	90
2:1	790	119	6.64	93
3:1	561	17	38.3	99

It was concluded from the perivious study that, 90% of the loaded B was transfered to the aqueous solution in two stripping stages. The optimum stripping conditions were 1% NaOH, 5 min contact time, A/O ratio of 1/1 and room temperature.

Crystallization of Borax

A strip solution measured 200mL and assayed 1.6g/Lof B was subjected to prepare 2.12g of $Na_2B_4O_7.5H_2O$ by crystallization through gentle thermal evaporation at 60°C. The product was identified by using XRD technique as shown in XRD pattern Figure (9). On the other hand, the obtained borax was chemically analyzed and was found to attain a purity of 95% with impurities of Na, Mg and Al.
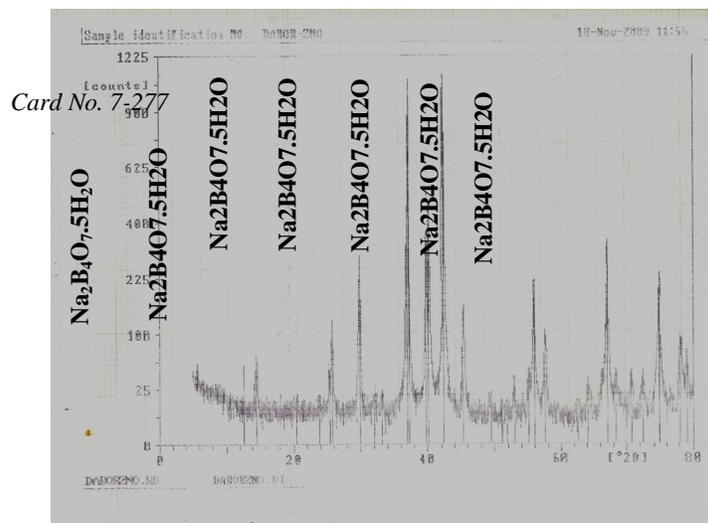

Figure (9): XRD pattern for the identification of pure borax.

Conclusions

1- A flux mixture (Na_2CO_3 + ZnO) has successfully been used for the breaking down of the refractory tourmaline ore sample at sample/flux weight ratio of 1/1.5 at fusion temperature of 900 °C for 30 min. Subsequent water leaching was applied to separated more than 93% of tourmaline boron content from the other matrix elements such as: Fe, Mg, Al, and Si.

2- The prepared leach liquor was then taken with 50% EHD in benzene for boron extraction. The corresponding parameters were optimized at contact time of 10 min and O/A ratio of 1/1 at room temperature (25°C). The extraction efficiency of B achieved 94.5%. A solution of 1% NaOH was found effective to carry out the stripping process of B. The B stripping efficiency reached 90% at A/O ratio of 1/1 and contact time of 5min at room temperature.

3- Borax was recovered from boron concentrated strip solution by crystallization through thermal evaporation at 60ºC with recovery achieved 95%. On the other hand, the obtained borax was chemically analyzed and was found to attain a purity of 95% with impurities of Na, Mg and Al.

4- Figure (10) shows a working flow-sheet for the processing of Sikait tourmaline ore sample to produce pure borax
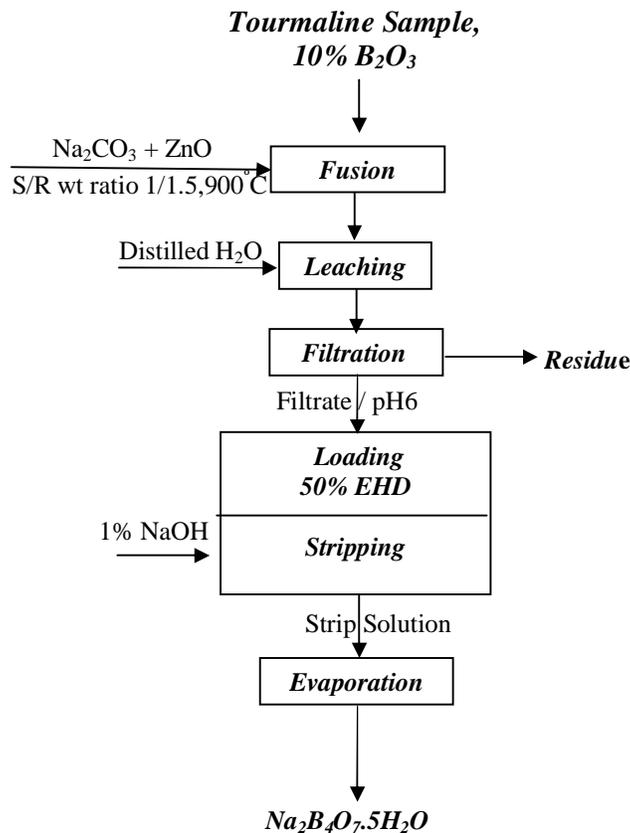
Figure (10): A worked flow sheet for processing Sikait tourmaline ore sample for producing pure Borax

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