Recovery of Boron from the Waste Slag of Steel Factories by using Selective Ion Exchange Resin

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Abstract

A process for recovery boron from the waste slag of Helwan Steel Factory was performed. The waste sample assays $0.8\% B_2O_3$ as well as some traces of Mo, Cr, and V ...etc. Recovery of boron from such waste boron bearing materials was carried out by alkali fusion using Na_2CO_3 at optimum fusing conditions; sample/ reagent weight ratio of 1/1.5, fusion temperature of 900°C and fusion time of 30min. The dissolution process of boron from the fused matrix was performed by using diluted alkaline solution.

Boron in the form of boric acid was extracted using boron selective resin Purolite S_{108} with maximum extraction efficiency of 91% at a flow rate of 1ml/min and 9. The elution efficiency of boron (91.2%) was achieved by 3% H_2SO_4 a working flow rate of 1mL / min . The preparation of boric acid was achieved through crystallization of the concentrated boron solution.

1. Introduction

Boron assays 3 ppm in the earth's crust and is consider a useful element used mainly in glass making where its compounds add strength to the glass, soaps, detergent, cleaners, metal fluxing and

agricultural chemicals. Also B in atomic energy control rods, jet and rocket fuels, motor fuel additives, heat and radiations shields and steel hardening as the stiffening agent, in extremely strong, light weight composition structural materials [1]. Boron has a great importance due to its wide applications in the nuclear field. It has two isotopes namely; ¹⁰B and ¹¹B which are characterized by their ability to absorb neutrons. ¹⁰B has a large cross section for neutron absorption reaching 3850 barn as compared to only 38 barn for ¹¹B and 755 barn for the natural boron. For this reason ¹⁰B has a great importance in shielding and controlling chemical reactions in the nuclear reactors, it is quite important to find out new resources for this strategic element. These new resources have actually been discovered in different industrial wastes e.g. borosilicate glasses, pyrexes and steel manufacturing [2].

In this domain, it is worthy to mention here in that, the two main boron compounds namely; borax and boric acid are added during the steel manufacturing to play very different important roles. These include the reduction of the melting temperature (thus to lower the energy consumed) besides increasing the fluidity (as a fluxing agent) and the strength (harden ability) of the steel as well as reducing the corrosion of the refractory material in the furnace. These boron compounds would decompose into boron trioxide (B_2O_3) at the soldering temperatures of 575°C for boric acid and of 765°C for borax (with borax there is also

sodium metaborate produced as a part of the decomposition process). Boron trioxide is the active ingredient in dissolving of metallic oxides where the water soluble the metal metaborates are formed and dissolved away in the pickle after soldering Although neither boric acid nor borax are soldering flux, fire-retardants, they provide protection from oxidation on the rest of the piece while soldering [3]. Almost all of these boron compounds would form borosilicate compounds in the presence of high silica concentration at high temperatures [4]. Accordingly the processing of this type of borosilicate compounds would be achieved by alkali fusion to breakdown such refractory compound

The processing of wastes of different borosilicate compounds by fusion process were reported [5-10] including analysis and leaching of these compounds.

Concerning the recovery of boron from its aqueous solutions, the boron selective resins especially Amberlite IRA₇₄₃ and Purolite S₁₀₈ were applied to extract boron.[11-13]. This resin purolite s 108 has indeed a macroporous polystyrene matrix, on which N-methyl glutamine are attached as the functional group and its chemical formula would thus be as follows [R-N(CH₃)- $C_6H_8(OH)_5$]vis

Accordingly, the active group is a weak base (tertiary amine). On the other hand, boric acid in the solution would dissociate as follows: $B(OH)_3 + H_2O = B(OH)_4^- + H^+$

The exchange mechanism would thus start by a prior amine protonation as follows:

$$-CH_2 - N - (CH_3) - CH_2 - H^+ = -CH_2 - N^+ H(CH_3) - CH_2 -$$

Boron is uptake as borate $B(OH)_4^-$ a matter which can result in boron fixation upon the working purolite resin ,namely



Due to the importance of boron compounds in the nuclear industry as well as the environmental problems of toxic boron compounds, the present work has found interesting to treat the slag product of steel industries to recover the residual boron from the slag of Helwan Steel Factory. Accordingly, the optimum conditions of alkali fusion procedure from the latter were first optimized followed by boron recovery using purolite S108 from the obtained alkali solution. No previous work for boron recovery from waste slag of steel industry has been previously reported.

2. Experimental

2.1. Material characteristics

A weight 50kg waste slag sample of Helwan Steel Factory was crushed and ground to a mesh size ranging between -100 to -150 mesh. A representative 5g waste slag sample portion was prepared by quartering and further ground to a size mesh of -200 before being subjected to complete chemical analysis. The major elements were estimated by wet chemical analysis. For this purpose a sample weight of 1g portion of the fine ground sample was digested with a concentrated acid mixture of (97%) H_2SO_4 , (65%) HNO₃ and 40%HF for complete dissociation of the sample followed by dissolution with 1:1HCL and the final volume made up to a volume of 100ml [14].

On the other hand, for Si analysis another small portion of 0.1g was directly fused with 1g of NaOH pellets in a nickel crucible for 20 min on Bunsen flame followed by leaching with 1:1 HCl and closed up to a volume of 100ml. The colorimetric molybedate was then used for the analysis of Si by using UV-vis spectrophotometer (Shemadzu 610) at λ 640nm [15].

With respect to B analysis in the waste slag sample, a weight of 0.2g sample portion was fused into a platinum crucible with 1g of a flux mixture composed of Na₂CO₃ and ZnO in a weight ratio of 3.5-0.6 in a muffle furnace at 900°C for 30min. The produced fused matrix was left to cool and then washed with 50ml of distilled H₂O for dissolution of its B content which then determined by atomic absorption (unicam 969) at their proper wavelengths [16]. On the other hand the final H₃BO₃ product which prepared from the waste sample was identified by means of X ray diffraction,(XRD), PHILIPS. In the processing work, control analysis of B in all the stream solutions has also been determined by the flame atomic absorption and all experiments have indeed been duplicated to ensure both accuracy and precision. The precision and accuracy of this method is tested against the (SRM-951) boric acid standard (U.S National institute of standards and Technology),with completely independent chemical extractions of boron in each case. Other chemicals used during the experiments and analysis were reagent–grade Merck products.

2.2. Optimization of the alkali fusion parameters

Extraction of B from the refractory borosilicate compounds in the working waste slag of Steel Factories was performed through alkali fusion followed by washing the obtained fused matrix with different aqueous solutions to dissolve its B content. For optimizing the fusion parameters (type of fusion reagents, sample /reagent (S/R) weight ratio, fusion time and fusion temperature) by using a constant weight of 5g from the working waste slag sample.

2.3. Optimization of ion exchange parameters for boron recovery.

The free base B selective resin Purolite S_{108} , which does not show any swelling when immersed in water. A volume 15 ml of this wet settled resin (wsr) was then packed into a glass column of 50 cm in length and 1 cm in diameter to optimize the B loading process from the prepared alkaline solution. Because B in the alkaline leach liquor exits as borate anion $B(OH)_4$ thus the utilized B selective resin should be converted to its anion form. For this purpose a volume of 25ml of 3% HCl solution was passed through the resin column in a working flow rate of 1ml/min. The full capacity of the wet settled Purolite S_{108} resin is 3 g of B/ L of resin [13]. Optimization of B loading parameters includes the study of the effect of pH value and the working flow rate of the prepared alkaline solution. While the optimization of B elution parameters includes the investigation of different eluate solutions, concentration of the chosen eluant and the flow rate

3. Results & Discussions

3.1. Chemical composition of the studied B waste slag sample

The complete chemical analysis of the studied B waste slag sample. Table (1) reveals that it is more enriched in Si, Mg, Fe, Mn and Ca elements as well as considerable concentration of valuable elements such as: B, Mo and V. Also B and Si at the working high temperatures would form refractory borosilicate and other compounds B_2 (SiO₃)₃ and B₂O [4]. The dissolution of B from such refractory compounds would be achieved by applying the alkali fusion procedures followed by washing the fused matrix with diluted alkaline solution to dissolve its B content. The reaction can be represented as follows:

$$\begin{array}{c} B_2\,(SiO_3)_3 + 4Na_2CO_3 {\longrightarrow}\, 3Na_2\,SiO_3 + 2Na\,BO_2 + \\ 4\,CO_2 \end{array}$$

		<u> </u>		
	Major Oxides	Concentration %	Trace Elements	Concentrat ion, mg/Kg
	CaO	45.9	В	2500
	Fe ₂ O ₃	28.7	Мо	500
	SiO ₂	10.8	V	300
	MnO	7.6	Cr	200
	MgO	2.2	Al	10
	Na ₂ O	0.45	Со	*nil
	K ₂ O	0.2	Ni	*nil
	Total	95.85	Cu	*nil

Table (1): The chemical composition of the working B waste slag of Helwan Steel Factory.

*(nil) under detction limit

Born in the prepared alkaline solution exists as borate anion $[B(OH)_4]$. It was found to recover the latter by the application of B selective resin, Purolite S₁₀₈.

3.2. Optimization of alkali fusion parameters and dissolution of B.

Optimization of alkali fusion parameters and dissolution of B from the present B waste slag sample required the investigation of several parameters such as: type of fusion reagents, sample/reagent (S/R) weight ratio, fusion time and fusion temperature

3.2.1. Effect of alkali fusion type. A 5g weight of different alkali fusion reagents e.g. Na₂CO₃, NaOH, KOH, NaHCO3 and a mixture of (Na₂CO₃+ NaHCO₃) was mixed in a porcelain crucible with the B waste slag sample at S/R ratio of 1/1 and fused at 800°C for 15 min. The fused matrix was then cooled and washed with 100 ml of hot distilled H₂O during filtration. The dissolved B in the obtained filtrate was analyzed and its dissolution efficiency was calculated. The obtained data, which are represented in Table (2) emphasized that either Na₂CO₃ or NaHCO₃ are the most effective reagents for B dissolution. They gave the maximum B dissolution efficiencies of 85% and 85.1%, respectively. Sodium carbonate was preferred because it has a high solubility which facilitates rapid aqueous leaching of the resulting fusion cake besides; it's available and lower cost. These characteristics also renders it's preference with respect to K₂CO₃ in addition to its lower melting point 850 $^{\circ}$ C with respect to K₂CO₃ (893°C) [17]

Table (2): Effect of the alkali fusion reagents upon B dissolution efficiency from the studied B waste

sumpte				
Type of reagent	B Dissolution efficiency, [%]			
Na ₂ CO ₃ + NaHCO ₃	57			
КОН	68			
NaOH	76			
Na ₂ CO ₃	85			
NaHCO ₃	85.1			

3.2.2. Effect of sample / reagent (S/R) weight ratio. A constant weight of 5g from the B waste slag sample was mixed in a porcelain crucible with Na₂CO₃ at different weight ratios of $1 \setminus 0.5$ 1/1, 1/1.5 and 1/2 and fused in a muffle furnace at 800°C for 15min. After cooling, each fused matrix was washed with 100 ml of hot distilled H₂O during filtration and the dissolved B was then analyzed in the obtained filtrate. Data represented by Figure (1) reveals that, the two S/R weight ratios 1/1.5 and 1/2 have recorded the maximum value of B dissolution efficiency of 88%, these results indicate that in case of S/L ratios of 1/0.5 and 1/1, the alkali reagent was not adequate for high boron fusion and in turn its alkali dissolution. Thus; the former was indeed applied and preferred from the economic point of view.



Figure 1. Effect of S/R weight ratios upon B dissolution efficiency from waste slag sample

3.2.3. Effect of the alkali fusion time period. The effect of the alkali fusion time periods ranging from 10 to 60 min on the fusion of the B waste slag sample for its B dissolution by using Na₂CO₃ was studied at a constant S/R weight ratio of 1/1.5 and a fusion temperature of 800°C. Each fused matrix was then washed with 100ml of hot distilled H₂O during filtration and its B content was analyzed in the obtained filtrates. The obtained data shown in Figure (2) indicate that the alkali fusion time periods of 30 and 40 min are quite adequate for the maximum B dissolution efficiency of 90%. It was also noticed that as the alkali fusion time period was increased to 60 min the B dissolution efficiency was decreased to 79%. This matter could be explained as that the increase in the alkali fusion time periods at 800^oC behind 40 min has increased the solidification of the obtained fused matrix in a manner that subsequent dissolution of B by washing with hot H₂O has become more difficult. [18]



Figure 2. Effect of fusion time upon B dissolution efficiency from waste slag sample.

3.2.4. Effect of the alkali fusion temperature. Accoring to the previous determined optimum conditions S/R weight ratio of 1/1.5 and fusion time of 30 min, the effect of alkali fusion temperature was studied in the range from 800 to 950° C. The obtained results in Figure (3) showed that, as the alkali fusion temperature increased to

900 °C the B dissolution efficiency has increased to 91.8%, However, a further increase in the alkali fusion temperature to 950 °C decrease the B dissolution efficiency to 88% This may be attributed to the conversion of some water soluble borate anions insoluble B_2O_3 at such higher fusion temperatures [4].



Figure 3. Effect of fusion temperature upon B dissolution efficiency, % from waste slag sample

3.2.5. Effect of the washing solution type. In a trial to increase B dissolution efficiency more than 91.8% which has been obtained at the optimum fusion conditions: (S/R weight ratio of 1/1.5, fusion temperature of 900 °C and fusion time of 30 min) from the B waste slag sample using Na₂CO₃ the fused matrix was washed during filtration with 100ml of different washing solutions to dissolve its B content. For this purpose the fused matrix was washed besides cold and hot H₂O with 0.1M of HNO₃ acid solution (pH1) and 0.1M of Na₂CO₃ solution. The obtained data in Table (3) clear that 0.1 M Na_2CO_3 solution gave the maximum B dissolution efficiency of 94% because it would also dissolve a percentage of Si in the fused matrix.

Table (3): Effect of washing solution upon Bdissolution efficiency, % from B waste slag sample.

Washing solutions	B dissolution efficiency,	
wasning solutions	[%]	
0.1 M HNO ₃	88	
Distilled cold water	77	
Distilled hot water	91	
0.1 M Na ₂ CO ₃	94	

3.3. Ion exchange extraction of B.

The extraction procedure of B from the alkaline solution of the working B waste slag was studied by using Purolite S_{108} , the B selective ion exchanger resin. For this purpose a 200g weight of the working B waste slag sample was fused in a porcelain crucible using Na2CO3 at the studied optimum fusion conditions S/R weight ratio of 1/1.5, a fusion temperature of 900 °C and a fusion time period of 30 min. The fused matrix was left to cool and then washed with 1000 mL of 0.1M Na₂CO₃ solution to dissolve its B content as borate anions, B(OH)₄. The prepared alkaline leach liquor was found to have a pH11.5 and assaying 0.4 g/l of B and 3 g/l of Si with achieved dissolution efficiencies of 80% and 30%, respectively. The relatively decrease in the B dissolution efficiency of B attributed to increase the weight of the fused sample. By adjusting the pH value of The prepared alkaline leach liquor at adjust pH9 using drops of conc H₂SO₄. Si ions was directly precipitated as sio₂ - gel. This precipitate was washed with 25ml of distilled H₂O during filtration to avoid the loss of 20% from the dissolved B by adsorption on its outer surface. The washing solution was then added to the filtrate of the alkaline B feed solution. The precipitate of SiO₂-gel should be removed because it might coat the exchange sites of the B ion selective resin. The precipitate of SiO₂-gel was ignited at 850°C for 1h and left to cool and then washed. After dryness a 6.4g weight of SiO₂ was recovered with achieved recovery efficiency upto 99%. The produced SiO₂ was identified using XRD analysis. The total volume of the alkaline B solution after the precipitation of Si ions was increased to 1025 mL and assaying 0.39g/l of B. This B solution was directed to the ion exchange column which packed with 15 mL wet settled resin of B selective resin, Purolite S_{108} in the chloride form to recover its B content.

3.3.1. Ion exchange loading of B. The affecting factors namely; pH value and the working flow rate were studied to achieve the maximum B loading efficiency from the working B alkaline solution.

3.3.1.1. Effect of pH. The pH value of the alkaline feed solution is the most important factor that affects the B extraction efficiency. This effect was studied by passing 150 mL of the feed solution with different pH values ranged between 5–12 with a fixed working flow rate of 1ml/min. B in the out put bed volumes is analyzed to calculate its extraction efficiency percentage. The

obtained data, Figure (4) indicates that, B extraction efficiency increased from 67.4 % to 91% when the pH value of solution increased from 5 to 9. At pH values higher than 9, B extraction efficiency decreased to 74% because at higher pH values an amount of other interfering species especially the excess (OH)⁻ could be retained by resin. Therefore, a selective B separation should be performed at a pH 9. The obtained data can be explained that, B exists in the form of H_3BO_3 in acidic and neutral media but in alkali medium H_3BO_3 transform to $B(OH)_4^-$, according to the following equation [19]:

 $H_3BO_3 + H_2O \leftrightarrow B(OH)_4 + H^+$

When the pH increases $B(OH)_4^-$ concentration rises and the extracted B amount increases to a maximum at a pH 9. At a pH value below 7, H_3BO_3 is the dominant species which has a low electrical activity and the extracted amount is less [20].



Figure 4. Effect of pH values of the working solution upon B loading efficiency.

3.3.1.2. Effect of the applied flow rate. The effect of working flow rate upon B extraction efficiency was studied by passing 150 mL of the alkaline feed solution at pH 9 at different working flow rates varying from 0.5mL / min to 2ml/min. Determination of B in the out put bed volumes shows its extraction efficiency indicates that, as the working flow rate increased from 0.5mL/min to 2mL/min, the maximum B extraction efficiency decreased from 92.5% to 66%, Figure (5).



Figure 5. Effect of applied flow rate upon B loading efficiency.

This is attributed to when the flow rate is higher, the extraction solution does not have enough time to react with the resin and vise verse [21]. Although the working flow rate of 0.5ml/min gave the maximum B extraction efficiency (92.5%) but that of 1ml/min (91.2%) was used for the extraction process. This is due to the lower difference in B extraction percentage which is unsuitable with the long time of the working flow rate of 0.5mL/min.

From the optimization study of B loading process from the alkaline feed solution, it can be concluded that, the maximum loading efficiency of 91.2% was achieved at pH 9 and working flow rate of 1ml/min. At these optimum loading conditions, 150ml of the alkaline working feed solution which assays 390ppm of B could saturate a column packed with 15ml of wet settled Purolite S_{108} resin. B. Figure (6) show that the quantity of the loaded B (42.8 mg) achieved a percentage of 95.1% of the theoretical capacity of the working resin (3g B/L resin). Once the B loaded resin has been saturated, it is directed to the elution stage to bring out the loaded B to the aqueous solution.



Figure 6. Adsorption loading Curve of the prepared alkaline feed solution (pH9 and flow rate, 1 mL/min).

3.3.2. Elution of the B loaded resin. This stage is not only used to regenerate the used resin but also to prepare concentrated B solution suitable for the preparation of pure H_3BO_3 . To optimize the elution stage, different elution parameters e.g. eluant type, eluant concentration and the applied flow rate were investigated. These parameters were performed upon 15mL resin saturated with 0.0428g of B which was firstly washed with a suitable volume of distilled H_2O at a relatively fast flow rate to get rid of any impurities that have been left from the working B alkaline solution.

3.3.2.1. Effect of the eluant type. Different eluant solutions includin both cold and hot distelled H_2O , 1%HCl, 1% H_2SO_4 and 1%

NaOH,(25mL each) were investigated. These eluant solutions were passed through the B satrated resin at a flow rate of 1mL/min and B in the collected eluant solutions was analyzed to calculate its elution efficiency. The obtained data in Table (4) showed that, the maximm B elution efficiency of 81% was obtained by using 1% H_2SO_4 .

Table(4): Effect of eluant type solutions on the Belution efficiencyfrom the saturated purolite S_{108} resin

Eluant type solutions	B Elution efficiency, %
Cold distilled H ₂ O	5
Hot distilled H ₂ O	21.3
1% NaOH	23.3
1% HCl	34
1% H ₂ SO ₄	81

3.3.2.2. Effect of H₂SO₄ acid concentration. The effect of sulphuric acid concentration upon B elution efficiency from the satrated Pourlite S₁₀₈ resin was studied by using 25mL of H₂SO₄ solution in different concentrations at 1% to 10% range at the applied flow rate of 1mL/min. B in the collected eluant solutions was analyzed to calculate its elution efficiency. The obtained data represented in Figure (7) it was easily indicated that increasing the acid concentration from 1% to 3% increases the B elution efficiency from 81 to 91%. Further increase in the acid concentration more than 3% has resulted in an oppesit effect upon B elution efficiency which was decreased down to 62 and to 51% at the acid concentrations of 6 and 10%, respectively. This decrease in the elution efficiency could be interpreted as due to decrease in the acid dissociation.



Figure 7. Effect of H₂SO₄ concentration on B elution efficiency,%

3.3.2.3. Effect of eluant solution flow rates. The effect of rate flow of 3% H₂SO₄ as eluant solution on B elution efficiency from the saturated Pourlite S₁₀₈ resin was investigated by passing 25mL of the eluant at different flow rates varying from 0.5 to 2 mL/min. However, B in the collected eluant solutions was analyzed to calculate its elution efficiency. From the obtained date shown in Figure (8) it was found that, as the applied flow rate increased from 0.5 to 2 ml/min, the maximum B elution efficiency decreased from 92.5 to 62%. This can be explained by the fact that at higher flow rates, the contact time between the eluant solution and the loaded resin would decrease and the eluant would not have adequate time for B elution. However, as perviously mentiomed, an oprating flow rate of 1mL/min wold be applied to avoid a long period time of From these results, it can be eltion stage. concluded that the optimum B elution efficiency of 91% was achieved by using 3% H₂SO₄ solution and applying a flow rate of 1ml/min. The detailed results obtained under these conditions are plotted in Figure (9). The preparation of the final boric acid product required the chosen of the eluate samples that assaying the highest B content.



Figure 8. Effect of flow rate on the B elution efficiency from the saturated Purolite S_{108} resin



Figure 9. B elution curve at the optimum elution conditions of $3\% H_2SO_4$ and 1mL/min

3.4. Preparation of boric acid product

A volume of 30mL from the obtained B eluated solution which containing 0.039g of B was subjected to prepare a weight of 0.22 g of boric acid through gentle thermal evaporation. The application of the B extraction process on the remained B alkaline feed solution leads to extract more than 95% of the presented $B(OH)_4$ as pure boric acid. The obtained boric acid was identified by using X-ray diffraction technique as shown in XRD pattern, (Figure 10). Summing up, it was found interesting to formulate the obtained data in a working flow-sheet as shown in Figure (11).



Figure 10. XRD pattern for the identification of pure H₃BO₃ which produced from the processed B Waste Slag Sample Of Helwan Steel Factory





4- Conclusions

Chemical analysis of the working waste slag sample of Helwan Steel Factory reveals the

presence of 0.8% of B_2O_3 and the goal of this work is the recovery of this B content. Alkaline fusion of the present waste sample with Na₂CO₃ followed by aqueous alkaline washing was found quite effective to dissolve both of B and Si with dissolving efficiencies of 94% and 30%, respectively. This is due to the fact that B is found in the waste slag as refractory borosilicate compounds. The performed optimum fusion conditions involved sample/reagent (S/R) weight ratio of 1/1.5, fusion time of 30min and fusion temperature of 900°C. The fused matrix was washed with 0.1M of Na₂CO₃ to dissolve its B content in a manner that the pH value of the alkaline solution attained a value of 11.5.

The dissolved silica in the prepared alkaline solution was successfully separated in the form of SiO₂-gel by adjusting its pH value to pH7 using few drops of conc. H_2SO_4 with an achieved precipitation efficiency of 99%. Boron in the form of boric acid was then extracted from the filtrate alkaline solution using B selective resin Purolite S₁₀₈ where with an achieved B extraction efficiency of 91.2%. Subsequent elution process of the loaded B was applied by using 3% H_2SO_4 with an achieved elution efficiency of 91%. The structure of the produced boric acid was confirmed using XRD analysis.

5. References

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