

Studies On Breakdown Of A Beryllium Ore From Sikait Area, Eastern Desert, Egypt

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Summary:- A technological sample of the beryllium ore material of Sikait area, southern eastern desert, was properly collected. The ore minerals involve beryl and bertrandite. Chemical analysis of different sample fractions revealed that BeO content is 6.9%.

Different breakdown procedures have been applied including fluoride and alkali fusion beside sulfuric acid pug and agitation leaching. The best recovery of beryllium in the leach liquor was 83.6%. This was obtained by agitation leaching where the ground ore to –200 mesh was mixed with 939 g/L sulfuric acid at 100 °C for 3 hours in the ore/acid ratio 1/2.

Introduction

Beryllium is naturally found in about thirty minerals, among which beryl is the most important and well-known mineral. It is composed of beryllium aluminum silicate of the theoretical formula $3\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$. The commercial grades of its ore contain approximately 4% beryllium. In Egypt, presence of beryl was reported in different localities, particularly in the Southern Eastern Desert. It is mainly occurs in two geological environments; namely schistose rocks associated with the contacts of pasammitic gneiss and as pegmatite veins and lenses in certain granitic masses which also carry disseminated beryl (1).

Sikait area is considered as one of the most important beryl occurrences in the Eastern Desert. In the latter, beryl occurs within mica schists and is confined to the Nugrus major shear zone forming a long belt extending for more than 50 km in a northwest trend with three main mineralized centers; namely Zabara, Sikait and Um Kabu. The different lithological units in Sikait area are imbricated to form a typical duplex structure, namely the Wadi Sikait Duplex^(2,3).

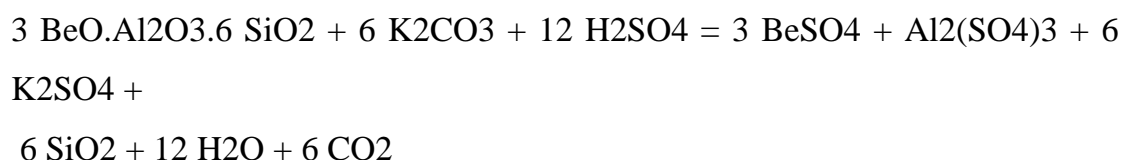
Due to the great importance of beryllium as a nuclear material, many technological studies have been performed for its recovery from the corresponding ores.

Beryllium minerals are normally decomposed by their fusion with acidic and alkaline fluxes. Acids are also used to decompose some beryllium minerals. In acidic aqueous solutions beryllium is in the form of Be^{2+} ions, in subacids solutions BeOH^+ and $\text{Be}_2(\text{OH})_3^+$, and in alkaline solutions $\text{Be}(\text{OH})_4^{2-}$ (4).

Fusion with fluorides or the acidic fluorides of alkaline metals is used to quickly decompose silicate beryllium minerals and remove silicon. Potassium hydrogen difluoride is useful to attack resistant silicates and oxides of elements which form stable beryllium fluoride complexes. Samples are heated at as low temperature as possible with ratios of sample to reagent varying between 1:2 to 1:30 for beryl and the fused cake was then treated with sulfuric acid. Fusion with KF have been preferred to those with KHF_2 as they are less trouble with respect to spitting and foaming(5).

Alkaline fusion of beryllium minerals with NaOH, KOH, Na_2CO_3 , K_2CO_3 , etc. is taken place at high temperature. The temperatures are necessary for acceptable decomposition rates depends upon the alkali used.

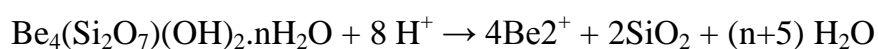
The decomposition of beryl with potassium carbonate at controlled temperatures ranging from 850-1200 °C and leaching the product with sulfuric acid, turns Be, Al and K to soluble sulfates while silica remains in the insoluble residue. This process is given by the following equation(6):



Other beryllium minerals, e.g. bertrandite, phenacite, helvite, etc. are easily decomposed by fusion with potassium carbonate(7).

The opening-out reaction with potassium hydroxide(8) is usually very rapid, being complete in 5-10 minutes at 600 °C or 15-20 minutes at 500 °C. Dissolution of the solidified melts should be dissolved in ice-cold water to avoid the possibility of precipitation of the beryllium through hydrolysis.

Alternative methods for opening beryllium minerals are performed by digesting the finely powdered mineral by sulfuric acid. One of the currently used method on a commercial scales is based on beryl attack by concentrated sulfuric acid at 400°C in an autoclave for several hours. It gives only 50-60% of the beryllium in a water soluble form(9). Bertrandite as hydrated silicate is readily leached by dilute sulfuric acid, according to the equation(10):



In the light of the above survey, different breakdown techniques are tried in the present work. Thus while fusion is applied using KF and KOH, also pugging and curing the ore sample in the concentrated sulfuric acid and leaching with a moderately acid concentration with continuous stirring have been studied.

Experimental

Fusion breakdown of the studied sample with potassium fluoride and potassium hydroxide was performed in a muffle furnace from Heraeus with the experimental conditions given in Table (1). The fused cake resulted from potassium fluoride was leached for one hour at 100 °C with 50% sulfuric acid to drive off the fluoride, while that obtained by the alkali fusion was first

leached with water for one hour, then with 50% sulfuric acid for another one hour at 100 °C.

Another two sets of experiments were carried out using sulfuric acid. In the first set, pug leaching was done by mixing different volumes of concentrated H_2SO_4 with constant ore weight. The obtained mass was then heated for 2 hours at 180 °C followed by leaching with continuous stirring in 100 ml water at room temperature. The final concentration of sulfuric acid in the leachant varied from 50-175 g/L, Table (2). In the second set, agitation leaching with sulfuric acid was used for opening the ore under the conditions given in Table (2).

The analysis of beryllium and aluminum was done using the flame atomic absorption spectrometer from Unicam model 969.

Table 1: Experimental conditions and recovery efficiencies of beryllium and aluminum upon applying the fusion breakdown on Sikait technological sample.

Fusion Flux	Experimental Conditions			Recovery, %		
	Ratio Wt. Ore/reagent	Time, hr.	Temp., °C	Be	Al	
KF	1/2	1/2	450	26.0	12.4	
	1/4			24.4	13.6	
	1/6			32.0	28.2	
	1/6	1/6	1/2	32.0	28.2	
			1 1/2	13.7	15.7	
			2 1/2	22.9	10.4	
	1/6	1/6	1/2	300	31.0	29.0
			350	31.6	28.7	
			400	32.0	29.0	
			450	32.0	28.2	
	KOH	1/2	1/2	600	36.6	35.6
		1/4			37.0	38.5
1/6		41.2			46.0	
1/6		1/6	1/2	41.2	46.0	
			1 1/2	52.6	66.3	
			2 1/2	36.3	31.6	
1/6		1/6	500	30.0	35.3	
			550	36.5	38.4	
			600	41.2	46.0	

Table 2: Experimental conditions and recovery efficiencies of beryllium and aluminum upon applying sulfuric acid leaching on Sikait technological sample.

Leaching Process	Experimental Conditions				Recovery, %	
	Time, hr.	Temp., °C	Acid Conc. g/L	Ore/H ₂ SO ₄ Wt./Vol. Ratio	Be	Al

a) Pug	2	180	Conc. Acid (1840)	10/2.7	13.6	30.2	
				10/4.0	15.1	36.0	
				10/5.6	29.0	41.1	
				10/7.1	30.9	46.2	
				10/8.6	44.6	60.0	
				10/10.1	38.6	59.8	
b) Agitation	1 2 3 4 5 6	100	1782.5	1/2	26.8	61.4	
					30.5	66.4	
					49.9	70.9	
					41.1	69.5	
					35.8	68.2	
					31.0	62.9	
	3	100	1782.5	1/2	35	12.1	22.5
					70	33.5	58.8
					100	49.9	70.9
					150	53.3	72.1
					180	60.0	75.0
	3	100	1782.5 1502 1220 939 469	1/2	49.9	70.7	
					54.5	80.7	
					61.7	83.0	
					83.6	82.5	
					80.3	85.7	
3	100	939	1/1 1/2 1/3 1/4 1/6 1/8	64.7	79.1		
				83.6	82.5		
				80.0	76.0		
				78.6	74.7		
				66.3	74.1		
				54.7	73.3		

Results and Discussion

I. Ore Analysis

A fraction of the collected Sikait technological sample ground to –200 mesh was subjected to X-ray diffraction analysis (using Philips-PW 1140/90 XRD) to identify its mineral composition. The obtained data revealed the presence of beryl [$\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$] and bertrandite [$\text{Be}_4(\text{OH})_2\text{Si}_2\text{O}_7$] as the principle ore minerals of beryllium and the aluminum mineral montmorillonite (Table 3) beside traces of feldspar. The ground ore was analyzed for its chemical composition as shown in Table (4).

II. Fusion Breakdown Studies

In the fusion process both fluoride and alkali reagents, namely potassium fluoride and potassium hydroxide were mixed with the ground ore to –200 mesh to study the effect of ore to reagent ratio as well as the fusion time and temperature. The results are given in Table (1).

II.A. Fluoride Fusion

Decomposition with KF at different ore to reagent weight ratios (1/2 to 1/6) shows a low yield for both Be and Al by leaching the fused cake with H_2SO_4 . At a weight ratio of ore/KF = 1/6, the recovery percent of both Be and Al was improved to 32.0 and 28.2 % respectively when using fusion time of ½ hour at 450 °C, Table (1). Increasing the fusion time from ½ hour to 2½ hours at ore:KF weight ratio of 1/6 and 450 °C results in decreasing the recovery of Be and Al to 22.9 and 10.4%, respectively. It was reported by Dolzer et al(11) that a fusion time of 15-20 minutes are sufficient to achieve complete ore decomposition by fluoride fusion.

Trials to raise the temperatures from 300 to 450°C while fixing the ore ratio with KF at 1/6 and the fusing time at ½ hour, shows no improvement in the recovery of both Al and Be.

Although the studied minerals exhibit weak response to potassium fluoride fusion and the subsequent leaching with H_2SO_4 , Be recovery seems to be slightly higher than that of Al. This may be attributed to the difficulty of opening silicates minerals of high Al_2O_3 content by potassium fluoride where the element oxide remains insoluble in the solidified melt after leaching ⁽⁵⁾.

II.B. Alkali Fusion

Alkali fusion breakdown was tried in the present work with potassium hydroxide under different conditions of ore sample/reagent weight ratio at different fusion time and temperature. Studying the effect of increasing the amount of potassium hydroxide with respect to ore sample at 600 °C for ½ hour shows a fairly improvement in both beryllium and aluminum, Table (1). The relatively low yield of beryllium in presence of excess amounts of KOH might be due to a relatively large amount of beryllium hydroxide remaining as precipitate after leaching the fused cake⁽¹²⁾.

Extension of the fusion time to 1½ hours at the fixed ore sample:KOH ratio of 1/6 at 600 °C resulted in a better reaction of the ore sample where Be and Al yield increased to 52.6 and 66.3% respectively, however, increasing the fusion time to 2½ hours has an adverse effect upon the recovery of both elements. This may be due to the formation of some refractory compounds of Be and Al in the fused cake that are difficult to dissolve during the next leaching step. Trials to increase the fusion temperature from 500 to 600 °C for ½ hour and at

1/6 ore sample/KOH ratio resulted in slight improvement in both Be and Al recovery, Table (1).

III. Sulfuric Acid Breakdown Studies

III.A. Pug leaching.

To study the potentiality of pug leaching of Sikait Be ore sample, different volumes of concentrated sulfuric acid (1840 g/L) were mixed with constant weight of the ore sample ground to –200 mesh and cured at 180 °C for two hours, (Table 2). The cured mass was then extracted with 100 ml water where the acid concentration varied from 50 to 175g/L. The obtained leaching efficiencies of beryllium and aluminum under the mentioned conditions are shown in Figure (1). As the acid concentration increased, the leaching efficiency of both elements increased. The recovery of either beryllium or aluminum did not exceed 45% and 60%, respectively. Such a partial attack of Be from Sikait ore sample after curing with concentrated sulfuric acid, may be due to the refractory nature of beryl which needs preliminarily opening by heat treatment at 1650 °C to increase its reactivity before treated with sulfuric acid at 250-300 °C to convert Be and Al to water soluble sulfates⁽¹³⁾ or else by proper alkali or silicofluoride fusion prior to sulfuric acid leaching⁽⁹⁾. On the other hand, the ability of bertrandite to be attacked by the concentrated sulfuric acid was not recommended⁽¹⁰⁾.

III.B. Agitation leaching

The ore ground to –200 mesh was subjected to agitation leaching studies with sulfuric acid under mild concentration and at different conditions to find the efficiency of this method to transfer both beryllium and aluminum metal values to soluble sulfates, Table (2).

III.B.1.Effect of leaching time

The influence of increasing the leaching time on the solubility of both beryllium and aluminum was studied using sulfuric acid concentration of 1782.5 g/L in an ore/acid solution ratio of 1/2 at 100 °C. Elongating the leaching time from 1 to 3 hours resulted in a leaching efficiency of Be and Al of 50 and 71% respectively, Figure (2). After 3 hours, the leaching efficiency of both metals decreases; a matter which is most probably due to saturation and/or precipitation of some samples forms. It was reported by Grunig and Anderson⁽¹⁴⁾ that the additional time exceeding 8 hours is not harmful in terms of either acid consumption or dissolution of impurities

III.B.2.Effect of temperature

Fixing the leaching time at 3 hours and raising the leaching temperature from 35 °C to 180 °C using the same conditions of acid concentration and ore /acid ratio, has good influence in transferring beryllium and aluminum to their soluble sulfates. The obtained results are shown in Figure (3). Bertrandite as one of the ore components is leached with sulfuric acid at moderate temperature of 95 °C to solubilize Be⁽¹⁵⁾. The ore sample contains also the aluminum mineral montmorillonite other than beryl which are attacked by hot sulfuric acid.

III.B.3.Effect of sulfuric acid concentration

Investigation of the obtained experimental data plotted in Figure (4) indicates that the acid concentration has a great influence on leaching extent

of both beryllium and aluminum when using the acid solution in the ratio of 1/2 at 100 °C for 3 hours. Moderately concentrated sulfuric acid is actually more preferred than concentrated acid especially bertrandite⁽¹⁰⁾. At sulfuric acid concentration of 939g/L the recovery of beryllium attained up to 83.6% while the maximum recovery of aluminum revealed 85.7% at 469g/L sulfuric acid.

III.B.4 Effect of ore/acid solution ratio

The effect of increasing the ore/acid solution ratio (weight/volume) was studied in the range 1/1 to 1/8, while using 939 g/L sulfuric acid and fixing leaching time and temperature at 3 hours and 100 °C respectively, Figure (5). The obtained maximum recovery of both beryllium and aluminum was at the ratio of the ore to acid solution of 1/2. Increasing the volume of the acid with respect to ore weight did not improve the leaching ability of both elements.

From the aforementioned results it is possible to say that the alkali fusion process has good influence than the fluoride fusion in bringing out beryllium and aluminum into the leach liquor from the fused mass. On the other hand, treatment by acid pugging was not efficient to solubilize more than 45 and 60% of Be and Al, respectively. It could be improved by preheating the ore in carbon arc furnace at 900-950 °C for short time to increase the reactivity of beryl toward the subsequent sulfuric acid leaching at 300 °C⁽¹⁶⁾.

Among the methods applied for breaking down the studied ore minerals, agitation leaching with sulfuric acid was the most effective method for realizing high leaching efficiency of Be and Al especially when moderately concentrated acid was used.

The relatively high leaching efficiency of Be and Al is mainly due to the presence of bertrandite and montomorillonite minerals in the ore sample and not to beryl. The latter would require more severe breakdown conditions. The low breakdown of both beryllium minerals using fusion by KF and KOH or by pug leaching is most probably due to interference from other ore components.

For economic reasons, successful ore breakdown at the proper conditions must be preceded by concentrating its minerals by suitable physical beneficiation.

Conclusion

The breakdown of the studied Sikait ore sample containing two beryllium minerals beryl and bertrandite was performed by different methods. It may be concluded that:

- 1- Fusion with potassium hydroxide is preferred to potassium fluoride for the partial decomposition of the ore sample. The maximum recovery of Be and Al was 52.6 and 66.3%, respectively. This result was obtained when the ground ore sample to –200 mesh was mixed with KOH in the ratio 1/6 and fused the mixture at 600 °C for 1½ hours.
- 2- Pug leaching shows slight improvement in decomposing the ore sample by increasing the quantity of sulfuric acid with respect to the ore weight.
- 3- The best conditions of breakdown the beryllium ore sample was attained by applying agitation leaching with sulfuric acid. These include mixing the ground ore to –200 mesh with 939 g/L sulfuric acid in ore/ acid ratio 1/2 then heating the mixture at 100 °C for 3hours.
- 4- The recovery of Be and Al under the best conditions of agitation leaching was 83.6 and 82.7% respectively.

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Table 3: X-ray diffraction pattern of beryl, bertrandite and montmorillonite minerals from ore sample of Sikait area, Southern Eastern Desert, Egypt.

Sample		Beryl , (9-430) $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$		Bertrandite, (17-515) $\text{Be}_4(\text{OH})_2\text{Si}_2\text{O}_7$		Montmorillonite (3-0009) $\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_2 \cdot 2\text{H}_2\text{O}$	
d	I/I _o	d	I/I _o	d	I/I _o	d	I/I _o
14.84	5					15.3	100
7.83	38	7.98	90	7.56	10		
5.01	3					5.15	80
4.56	8	4.60	50	4.38	100	4.5	100
4.31	30			3.94	40		
3.93	21	3.99	45	3.19	90		
3.22	95	3.254	95	2.93	10		
3.00	73	3.015	35	2.88	10	3.07	100
2.85	95	2.867	100				
2.64	19	2.660	3			2.61	100
2.59	10	2.523	30	2.54	80	2.55	100
2.41	1					2.41	40
2.28	4	2.293	11	2.28	60	2.24	20
2.19	5	2.208	3	2.22	60		
2.14	7	2.152	15	2.18	2	2.16	20
1.99	8	1.9926	20	1.98	20	1.91	20
1.82	4	1.83.8	7				
1.79	10	1.7954	17	1.787	6		
1.73	10	1.7397	20				
1.71	5	1.711	13	1.698	16	1.71	60
1.62	9	1.6265	17	1.650	10	1.68	100
1.60	6	1.5953	7	1.579	4		
1.57	5	1.5710	9	1.555	30		
1.53	9	1.5320	7				
1.51	100	1.5138	15			1.50	100

Table 4: The chemical composition of the beryllium ore sample obtained from Sikait area.

Major Elements	Concentration, %.	Trace Elements	Concentration, ppm
SiO ₂	69.70	F	260
Al ₂ O ₃	18.90	Sn	11
Cr ₂ O ₃	0.04	Zn	19
FeO	0.12	Ga	20
MgO	3.80		
BeO	6.90		
Na ₂ O	0.50		

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