

A SUGGESTED PROCEDURE FOR CHEMICAL PROCESSING OF BERYL FROM RECEIVED GEOLOGICAL SAMPLE, EASTERN DESERT, EGYPT BY SOLVENT EXTRACTION TECHNIQUE.

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ABSTRACT

Processing of the beryl from received geological sample collected from Eastern Desert of Egypt has been studied via acidic fusion process using K_2SO_4 under different factors. The recovery of beryllium from the prepared sulfate solution has been accomplished by solvent extraction namely; TOA. The optimum conditions for sulfate fusion for almost complete breakdown of beryllium guarantee 1/3 ore/salt ratio at $550^\circ C$ for 3.5 h. The relevant conditions for the extraction and stripping of beryllium by trioctyl amine determined. The studied optimum extraction conditions involved $8 \times 10^{-3} M$ TOA concentration, 1/1 O/A ratio at a pH of 0.8 and 15 min. Beryllium was stripped by 1.5M H_2SO_4 solution in 1/1 O/A ratio for 20 min. From the corresponding McCabe- Thiele diagrams, it was noticed that 3 theoretical stages for each of the extraction and stripping separately were required. From the stripped solution, beryllium was precipitated as beryllium hydroxide at pH 9 using 10% NaOH solution. The produced beryllium hydroxide has then been properly dried at $150^\circ C$ for 1 hr and analyzed using AAS.

Keywords

Beryl; K_2SO_4 ; fusion; beryllium; extraction.

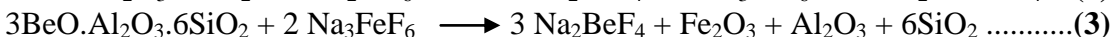
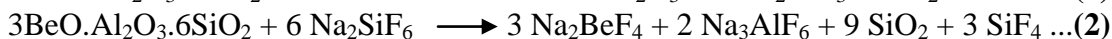
1. INTRODUCTION

One of the metallic elements that are used in the nuclear and aviation industries is beryllium (Be), which is considered light in weight. Beryllium is currently derived from beryl ore ($Be_3Al_2Si_6O_{18}$)^[1-8]. The latter is the principal beryllium mineral found in Umm Addebaa area, the Eastern Desert of Egypt which contains about 1-4% beryllium.^[9, 10]

The processing and dissolution of beryllium from beryl containing geological samples is considerably more difficult process due to the refractory nature of the mineral with mineral acids except hydrofluoric acid. Therefore, dissolution of Be from beryl containing geological samples is generally carried out by two routes; the sulfate pathway or the fluoride pathway.^[11-14]

The sulfate pathway involved ore fusion with sodium (potassium) hydroxide and alkali carbonate as shown in equation 1, and then cooling with water to breakdown the crystal structure of beryl followed by leaching in sulfuric acid. The produced leach liquor contained mainly beryllium beside aluminum and other impurities. Zaki et al., 2005 and Baba et al., 2017 studied the treatment of the aforementioned solution through selective precipitation using ammonia solution and solvent extraction methods to obtain beryllium hydroxide and ammonium alum left behind in the solution.^[1, 15] The fluoride pathway however involved leaching of beryl containing geological samples with

sodium silico fluoride or sodium ferric fluoride as shown in equations 2 and 3. Here, the salt converts the beryllium into water-soluble sodium beryllium fluoride. [4, 6, 16]



Liquid-liquid extraction technique is one of the most important processes used to separate and purify beryllium from its solutions, as it is considered economical, practical and fast. This involved separation of Be from aluminum by di-2-ethylhexyl phosphoric acid (HDEHP) and Cyanex 921 (commercial TOPO) from beryl sulfate solutions and the extraction is affected by changes in pH [1, 17-19]. In addition, TBP, Aliquat 336 and DEHPA are used for separation of beryllium from sulfate and chloride respectively [19- 22]. Cyanex 272 in kerosene is also used for extraction and separation Al and Be from sulfate pregnant solution of a Nigerian beryl ore and the extraction rate is high. With change of pH, Be is separated from the stripping solution through precipitation at pH 3 [23].

The current study dealt with the chemical treatment of beryl from received geological sample collected from Umm Addebaa area, Eastern Desert of Egypt for the recovery of Be metal value. For this purpose, the working sample of beryl ore has been subjected to chemical analysis and processing via potassium sulfate fusion. The relevant factors for the beryllium fusion step were studied, followed by washing the fused cake with distilled water, as the beryllium dissolved with some impurities. Extraction of beryllium in particular requires the use of solvent extraction technique by TOA.

2. EXPERIMENTAL

2.1. Chemical Characterization

To determine the chemical composition, about 50 g sample weight was separated by quartering from the finely crushed representative sample before being ground down to – 200 mesh size. The sample was opened by a mixture of acids (HF, HCl and HNO₃). The pulverized sample was then analyzed using the conventional wet chemical procedures given by Shapiro and Bannock (1962), [24] where SiO₂, Al₂O₃ and P₂O₅ were spectrophotometrically analyzed. Na was determined by flame photometry. CaO, MgO and total Fe₂O₃ were determined titrimetrically through murexide, Eriochrome black T and sulfosalicylic acid indicators respectively. Known sample weights were used to estimate the loss of ignition at various temperature degrees. On the other hand, beryllium was analyzed using atomic absorption technique in the Egyptian Chemical Warfare laboratories.

2.2. Experimental Procedures

2.2.1. Potassium sulfate fusion of the beryl ore

Multiple fusion experiments were carried out on a sample of beryl ore using K₂SO₄. For this purpose, different amounts of K₂SO₄ were mixed with a constant weight of the ore sample (10 g) in a nickel crucible for variable periods of time at variable temperatures. The resulted melt was then cooled, washed by a sufficient amount of hot distilled water,

filtered and made up to volume for beryllium analysis, which the leaching efficiency was calculated.

2.2.2. Solvent extraction of beryllium

To study the beryllium extraction, a 500 g sample weight of the working beryl ore was subjected to K_2SO_4 fusion under the best fusion conditions followed by cooling and specific washing of the slurry. From the resulted sulfate liquor, Be was extracted using TOA as organic solvent. Different concentrations of the solvent are prepared by diluting it in kerosene. After each extraction experiment, an aliquot sample of the aqueous phase was analyzed for its remaining metal content in order to calculate the extraction efficiency.

Factors related to solvent extraction were studied, namely TOA concentration, the contact time, the leach liquor pH and aqueous/ organic ratio (A/O). On the other hand, a sample of solvent loaded was prepared for studying the stripping behavior of the beryllium.

2.3. Control Analysis

In all the experiments, beryllium was analyzed in all the working stream solutions using atomic absorption technique (AAS), as well as a high-purity beryllium product.

3. RESULTS AND DISCUSSION

3.1. Material Characteristics

Chemical composition of the beryl ore shown in table 1 indicated that the main content of the ore material is SiO_2 beside Al_2O_3 and Fe_2O_3 that attained 14.35% and 5.35% respectively as well as high MgO content (3.09%). In the meantime, a total loss of ignition of about 3.33% was obtained at $1000^\circ C$. On the other hand, analysis of BeO assayed 1.4%.

Table (1): Chemical composition of Umm Addebaa beryl ore material.

Component	wt.,%
SiO_2	65.42
Al_2O_3	14.35
CaO	2.04
MgO	3.09
Na_2O	2.06
MnO	2.94
Fe_2O_3	5.35
L.O.I.	3.33
BeO	1.4
Total	99.98

3.2. Processing of Beryl Ore Material

As mentioned earlier, the potassium sulfate fusion has been used for the breakdown of the beryl mineral. Improving factors relevant of this method are the fusion time and temperature as well as the beryl ore / K_2SO_4 ratio. After water leaching of the melt, the

leached Be was analyzed and the dissolution efficiency determined followed by recovery of beryllium via solvent extraction technique using TOA.

3.2.1. K_2SO_4 fusion of Be

3.2.1.1. Effect of the fusion time

To study the effect of fusion time on dissolution of beryllium from the working beryl ore, a series of experiments was carried out in the range of 1 to 4.5 hrs. Other conditions were fixed at a beryl ore / K_2SO_4 ratio of 1:1 and a temperature of 300°C. Then dissolution for Be analysis to the final efficiency of dissolution.

From the obtained results listed in table 2, it is illustrated that increasing the fusion time from 1 to 3.5 h has increased the dissolution efficiency of Be where it reached 39.1 % at 3.5 h. Further increasing the fusion time to 4 h and 4.5 h has not shown any perceptible increase in beryllium dissolution thereafter.

Table (2): Effect of the fusion time upon the dissolution efficiency of beryllium.

Time, h	Dissolution Efficiency of Be, %
1	13.61
1.5	19.00
2	24.80
2.5	28.00
3	34.50
3.5	39.10
4	39.30
4.5	39.60

3.2.1.2. Effect of the fusion temperature

The effect of fusion temperature upon the dissolution efficiency of beryllium from working beryl ore material was studied in the range of 300 to 650°C. Other conditions were fixed at a beryl ore / K_2SO_4 ratio of 1:1 for 3.5 h. The dissolution efficiency of Be after water dissolution given in table 3, give a gradual increase by increasing the fusion temperature from 300 to 550°C where it estimated 69.5% at 550°C. Further increase in the fusion temperature did not improve the beryllium dissolution thereafter.

Table (3): Effect of the fusion temperature upon the dissolution efficiency of beryllium

Temp., °C	Dissolution Efficiency of Be, %
300	39.10
350	45.80
400	52.50
450	58.00
500	62.30
550	69.50
600	69.70
650	70.00

3.2.1.3. Effect of beryl ore / K₂SO₄ ratio

To study the effect of ore / K₂SO₄ ratio upon the dissolution efficiency of beryllium, a set of experiments was performed using ratios ranging from 1:1 to 1:4 while the other fusion conditions were fixed at 550 °C for 3.5 h. The results recorded in table 4, illustrate that the dissolution efficiency of Be has reached 97.3% at 1/3 beryl ore / K₂SO₄ ratio.

Table (4): Effect of beryl ore / K₂SO₄ ratio upon the dissolution efficiency of beryllium.

Beryl Ore / K ₂ SO ₄ Ratio	Dissolution Efficiency of Be, %
1/1	69.50
1/1.5	78.00
1/2	84.90
1/2.5	91.00
1/3	97.30
1/3.5	97.40
1/4	97.50

From the above-mentioned fusion factors of the beryl ore material, it can be decided that the best conditions for dissolution of beryllium include:

Fusion time : 3.5 hrs.
Fusion temperature : 550°C.
Beryl ore / K₂SO₄ ratio : 1/3

3.2.2. Preparation of the sulfate leach liquor

The sulfate solution of beryl ore sample of Umm Addebaa area, Eastern Desert of Egypt was prepared by applying the above optimum factors followed by washing and filtration the slurry with distilled water to attain up to volume 2 L. Analysis of the prepared sulfate liquor is shown in table 5. From the latter, the produced solution pH is 1.6 and estimates 0.73 g/l Fe₂O₃, 1.43 g/l Al₂O₃ and 3.40 g/l BeO with almost complete dissolution of the latter. The reaction of beryl mineral with potassium sulfate represented in the following equation 4:



Table (5): Chemical analysis of the produced sulfate liquor.

Component	Concentration, g/l
Fe ₂ O ₃	0.73
Al ₂ O ₃	1.43
BeO	3.40
pH	1.6

3.2.3. Extraction of Be

3.2.3.1. TOA extraction of Be

The prepared sulfate solution is presented for the extraction of beryllium by TOA/kerosene. The studied relevant factors affecting the beryllium extraction have involved TOA concentration, the contact time and the leach liquor pH as well as the aqueous/ organic ratio (A/O).

(i) Effect of contact time

Four experiments have been conducted to study the effect of contact time upon the extraction efficiency of Be using TOA at different contact time periods ranging from 5 to 20 min. Other extraction factors were fixed at an O/A of 1:1 and using 3×10^{-3} M TOA in kerosene at pH 1.6. From the obtained results shown in table 6, it is clear that increasing the contact time from 5 to 15 min, increased the Be extraction efficiency from 56.3 to 69.8 % respectively. Extending the contact time to 20 min resulted in a decrease in the extraction efficiency of beryllium to 65.4 % and an optimum contact time of 15 min was thus considered as the optimum value.

Table (6): Effect of contact time on the extraction efficiency of Be.

Contact Time, min.	Be Extraction efficiency, %
5	56.30
10	64.30
15	69.80
20	65.40

(ii) Effect of pH of the prepared sulfate liquor

Six experiments have been conducted to study the effect of pH upon the extraction efficiency of Be at different pH values ranging from pH 1.6 to 0.6. Other conditions were fixed at an A/O of 1:1 and using 3×10^{-3} M TOA in kerosene for a contact time of 15 min. From the results shown in table 7, it is clear that the maximum Be extraction efficiency (76.5 %) was reached at pH 0.8 and which was found to decrease thereafter.

Table (7): Effect of pH of the sulfate liquor on the extraction efficiency of Be.

pH	Be Extraction efficiency, %
1.6	69.80
1.4	71.90
1.2	74.00
1.0	76.90
0.8	79.50
0.6	73.40

(iii) Effect of TOA concentration

Six experiments have been conducted to study the effect of TOA concentration upon the Be extraction efficiency by shaking equal volumes of the sulfate leach liquor with TOA solvent of different concentrations ranging from 3×10^{-3} to 8×10^{-3} M in kerosene at pH 0.8 for 15 min contact time.

Table (8): Effect of TOA concentration on the extraction efficiency of Be.

TOA Conc., M	Be Extraction efficiency, %
3×10^{-3}	79.50
4×10^{-3}	82.30
5×10^{-3}	86.80
6×10^{-3}	90.40
7×10^{-3}	94.30
8×10^{-3}	98.90

From the obtained results shown in table 8, it is decided that extraction efficiency of Be has increased from 79.50 to 98.90 % when the TOA concentration was increased from 3×10^{-3} to 8×10^{-3} M respectively. The latter was thus considered as the best concentration for beryllium extraction from the prepared sulfate liquor of the working beryl ore sample.

(iv) Construction of McCabe-Thiele extraction diagram

Investigation the effect of the aqueous / organic (v/v) phase ratio upon the extraction of Be in the range of 3:1 down to 1:3 was studied depending on the prepared sulfate liquor. Other extraction factors were fixed at their determined optimum values (8×10^{-3} M TOA, 15 min. as contact time at room temperature and the pH value of the aqueous phase of 0.8). On the other hand, the produced equilibrium data have been presented to construct the extraction McCabe-Thiele diagram (figure 1). From the latter, 3 theoretical stages were required for almost complete extraction of Be from the sulfate liquor prepared from the beryl ore, Eastern Desert, Egypt.

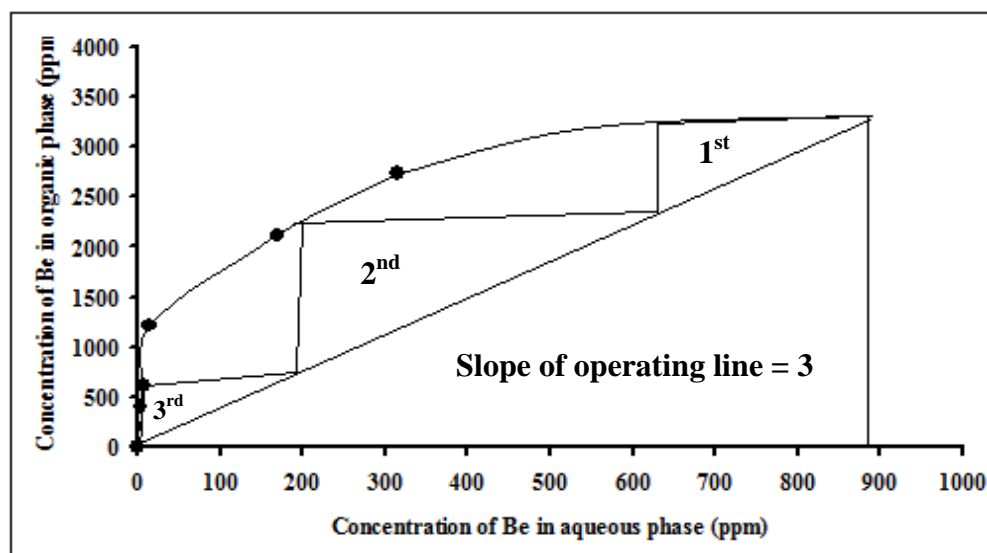


Fig. 1: McCabe-Thiele diagram for Be extraction.

3.2.3.2. Stripping of Be

A loaded TOA/kerosene liquor assaying 1.21 g Be /l and prepared to strip beryllium was treated with H_2SO_4 solution under different conditions. The latter included the acid concentration, the contact time and different A/O ratios.

(i) Effect of acid concentration

A series of stripping experiments were carried out for Be stripping using H₂SO₄ solution of different concentrations ranging from 0.5 to 2 M at a contact time of 5 minutes and using an O/A ratio of 1/1 at room temperature. The obtained results are tabulated in table 9, where it is obvious that 1.5 M H₂SO₄ gave a Be stripping efficiency of 90.7% and which has remained almost constant thereafter.

Table (9): Effect of acid concentration on the stripping efficiency of Be.

H ₂ SO ₄ Conc., M	Be Stripping efficiency , %
0.5	41.20
1.0	69.60
1.5	90.70
2.0	90.80
2.5	90.90

(ii) Effect of stripping time

The effect of the stripping time upon Be stripping efficiency was studied in the range from 5 to 20 min. at 1.5M H₂SO₄ and an O/A ratio of 1/1. From the obtained results shown in table 10, it is found that 20 min. is sufficient as a stripping time where the stripping efficiency exceeded 99%.

Table (10): Effect of time upon the stripping efficiency of Be.

Contact Time, min.	Be Stripping efficiency , %
5	90.70
10	93.60
15	96.10
20	99.65

(iii) Construction of McCabe-Thiele stripping diagram

Construction McCabe-Thiele diagram was depended on the equilibrium stripping data under different A/O ratios using 1.5M H₂SO₄ solution for a contact time 20 min and represented in figure 2. From the diagram, three theoretical stripping stages would be required for almost complete beryllium stripping.

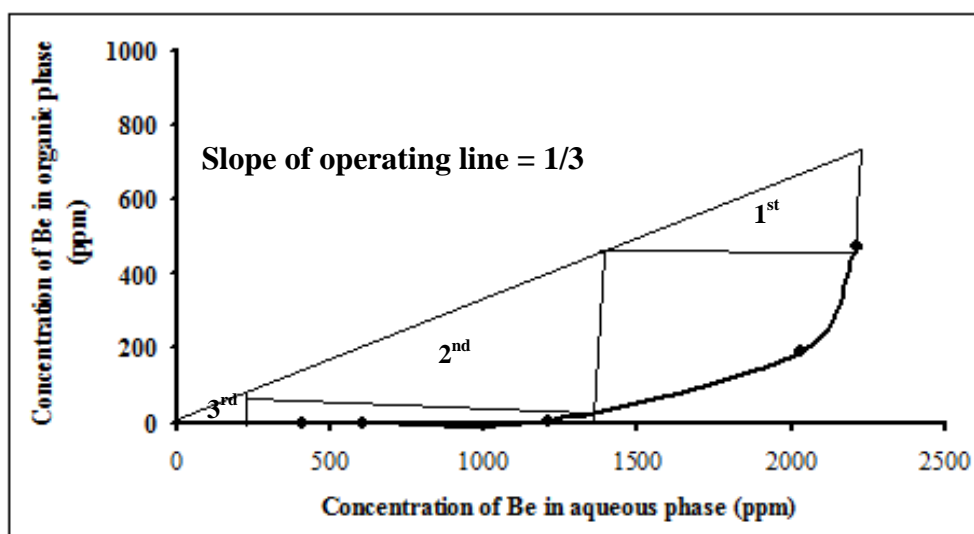


Fig. 2: McCabe-Thiele diagram for Be stripping.

3.2.3.3. Be product precipitation

By adding 10% NaOH solution on the beryllium strip solution, Be precipitated completely at pH of 9 as beryllium hydroxide. After drying at 150°C, a highly pure Be(OH)₂ was obtained and subjected to chemical analysis using atomic absorption spectrometry which its purity 92%.

4. CONCLUSION

The fusion method by potassium sulfate was applied for processing the beryl from received geological sample of Eastern Desert followed by leaching of the obtained cake in water for beryllium extraction. The best conditions of the sulfate fusion for almost complete dissolution included 1/3 ore / salt ratio at 550 °C for 3.5 hr. From the prepared liquor, beryllium was recovered using the tertiary amine (TOA) in kerosene. The studied optimum extraction conditions involved 8×10^{-3} M TOA concentration, 1/1 O/A ratio at a pH of 0.8 and 15 min. Beryllium was stripped by 1.5M H₂SO₄ solution in 1/1 O/A ratio for 20 min. From the corresponding McCabe- Thiele diagrams, it was noticed that 3 theoretical stages for each of the extraction and stripping separately were required. From the stripped solution, beryllium was precipitated as beryllium hydroxide at pH 9 using 10% NaOH solution. The produced beryllium hydroxide has then been properly dried at 150 °C for 1 hr and subjected to an AAS analysis. Finally, all the obtained results have properly been formulated in a generalized flow sheet as shown in figure 3.

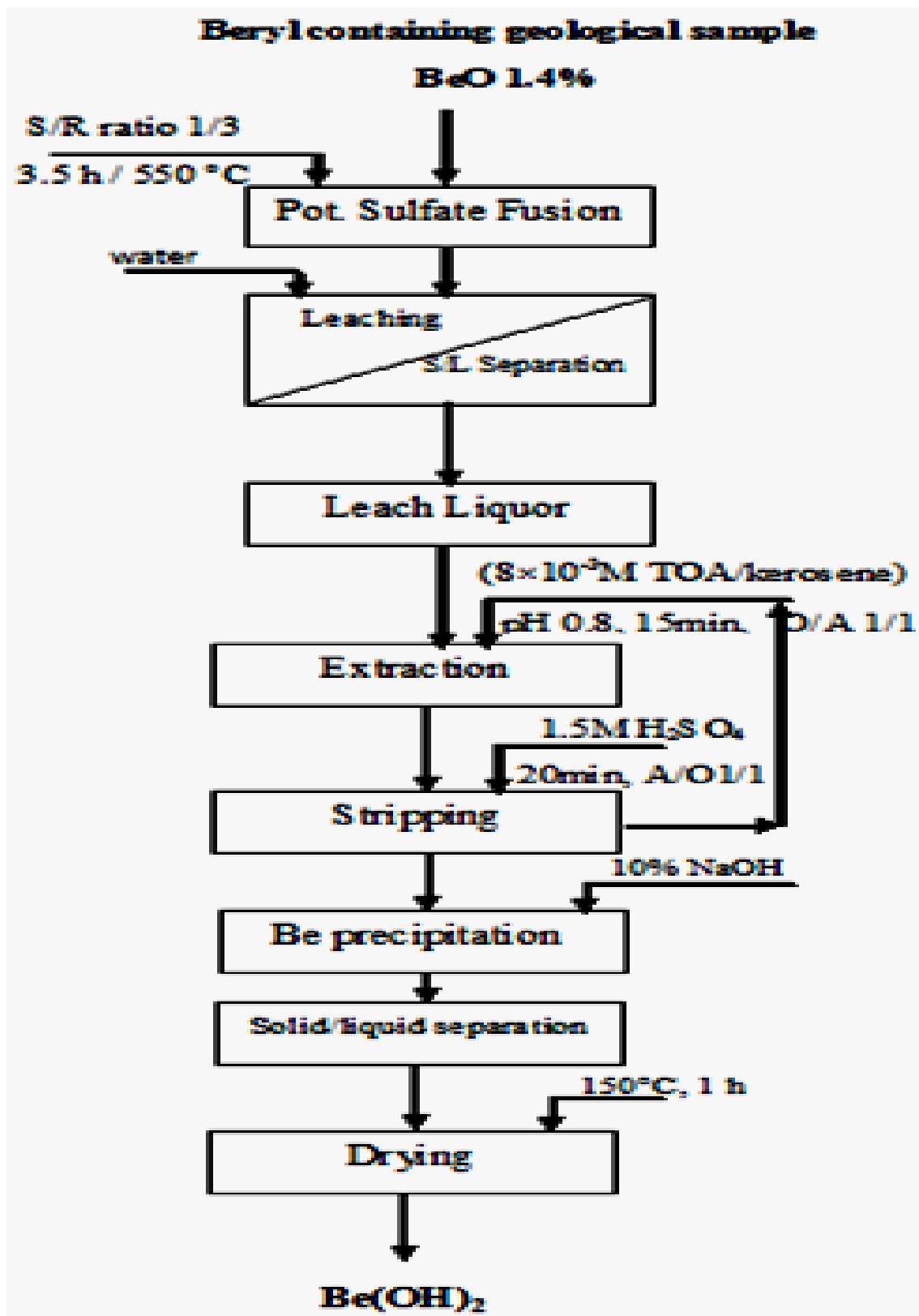


Fig. 3: Generalized flow sheet for the processing of beryl containing geological sample of Umm Addebaa (Eastern Desert, Egypt).

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