THE UNIVERSITY OF MANITOBA

SELECTIVE EXTRACTION OF BERYLLIUM OXIDE

A Thesis

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the requirements for the degree of

MASTER OF SCIENCE

by

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ABSTRACT

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The solubility of beryllium oxide and aluminum oxide in saturated solutions of beryllium sulfate was investigated over wide regions of temperature, time, and concentration. The extent of dissolution was one mole of beryllium oxide per two moles of sulfate, with aluminum oxide showing much less molar solubility. The effect of aqueous beryllium sulfate on beryl frit was determined, since specificity with respect to beryllium oxide was indicated. An extraction level of beryllium oxide approaching seventy per cent was attained.

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CHAPTER I

PRESENT INDUSTRIAL PROCESSES

Beryl, a double silicate of beryllium and aluminum - $3BeO \cdot Al_2O_3 \cdot 6SiO_2$ - is the only commercial source of beryllium at present. In pure form this mineral contains approximately fourteen per cent beryllium oxide (BeO), nineteen per cent aluminum oxide (Al_2O_3), and sixty-seven per cent silicon dioxide (SiO_2). Commercial ores rarely contain over 11.5 per cent beryllium oxide.

There are, in commercial operation in United States today, two entirely different methods of extracting beryllium oxide from beryl ore (1).

COPAUX-KAWECKI PROCESS (2)

This is the process used by the Beryllium Corporation, Reading, Pennsylvania. In brief, this process consists of mixing the finely pulverized beryl ore with sodium ferric fluoride, sodium fluosilicate and soda ash and roasting the mixture at 750°C (1382°F). The resulting sinter is ground and leached in water to yield soluble sodium beryllium fluoride and insoluble silicon dioxide, aluminum oxide, and iron oxide. After several decantations through a polishing filter, the liquor is treated with caustic soda. The beryllium is first precipitated and then redissolved as sodium

beryllate. Heating to near boiling causes precipitation of α - beryllium hydroxide which is filtered off, washed, dried, and ignited to beryllium oxide at a temperature of about 1000°C (1830°F).

The sodium fluoride which is formed along with beryllium hydroxide when sodium hydroxide is added to the sodium beryllium fluoride solution, is recovered by the addition of ferric sulfate. The sodium ferric fluoride formed is recycled to the beginning of the process where it is needed to convert the beryl ore into sodium beryllium fluoride.

SAWYER-KJELLGREN PROCESS (3).

This is the process used by The Brush Beryllium Company, Cleveland, Ohio. Beryl ore is completely melted (melting point ~ 1650°C [3000°F]) and then rapidly quenched in cold water. The resulting glassy beryl frit is finely ground and treated with hot, concentrated (93%) sulfuric acid. This treatment will yield only 50 to 60 per cent of the ores' beryllium content. The unreacted beryl frit is subjected to additional heat treatment at moderate temperatures which, after further reaction with sulfuric acid, brings the value up to commercially acceptable levels. (This stage shall be discussed later). After sulfating, the ore is leached, and the bulk of the aluminum sulfate is crystallized out of ammonium alum. Then a suitable chelating reagent (e.g., the disodium salt of ethylenediaminetetraacetic acid) is added to the mother liquor

to hold undesirable impurities (magnesium, calcium, iron) in solution. Excess sodium hydroxide is added to convert the beryllium and remaining aluminum to beryllate and aluminate respectively. Both of these compounds are quite soluble in cold alkaline solution, but they differ in that the beryllate decomposes on boiling to precipitate granular α-beryllium hydroxide, whereas the aluminate is unaffected. Careful control of sodium hydroxide normality during beryllation is necessary in order to insure good recovery of beryllium hydroxide. Some beryllium hydroxide which is too fine to be separated by centrifuging, is filtered off and returned to the alum crystallization step. (See Figure 1).

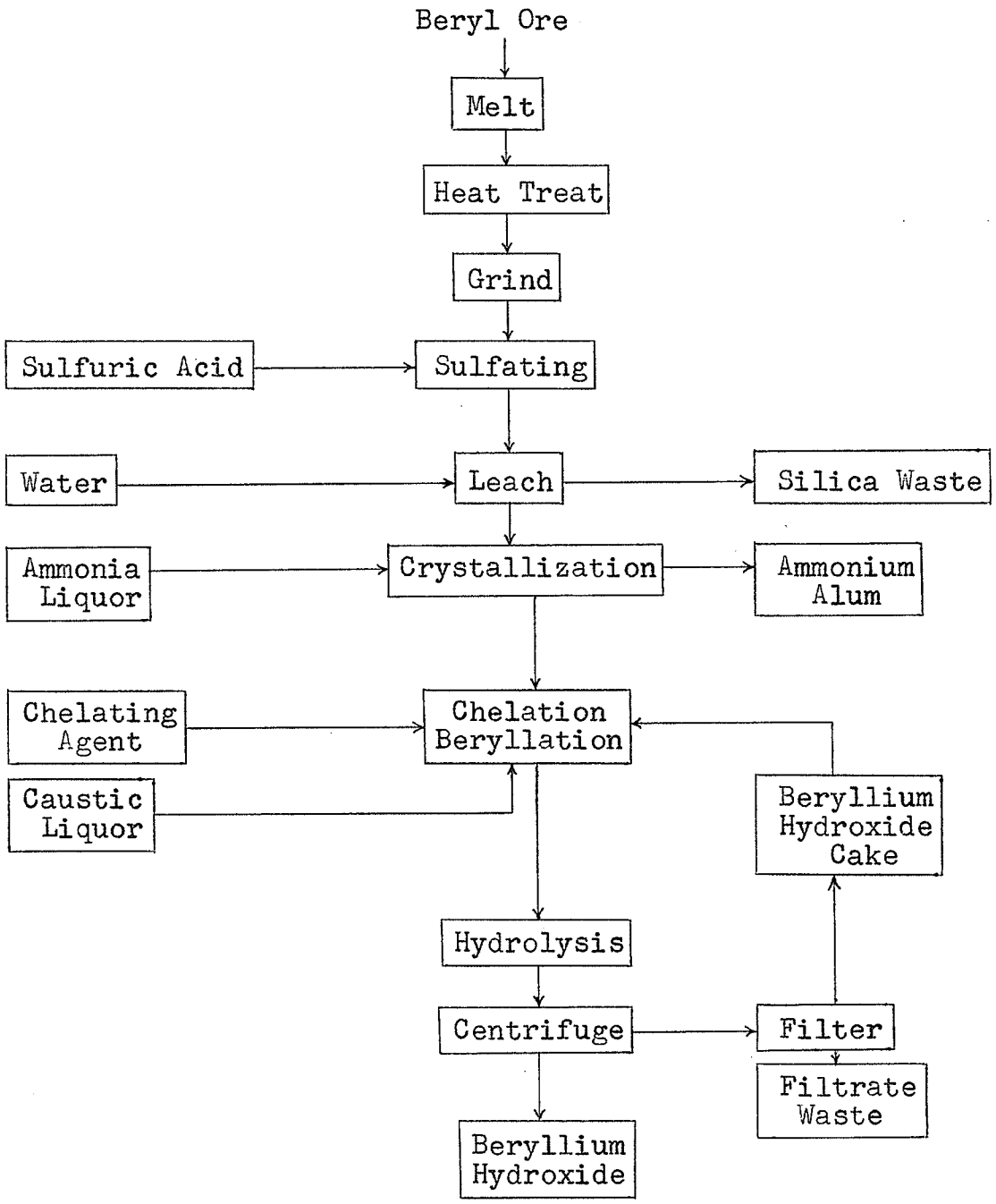


Figure 1. Flow scheme of The Brush Beryllium Company process for beryllium hydroxide production.

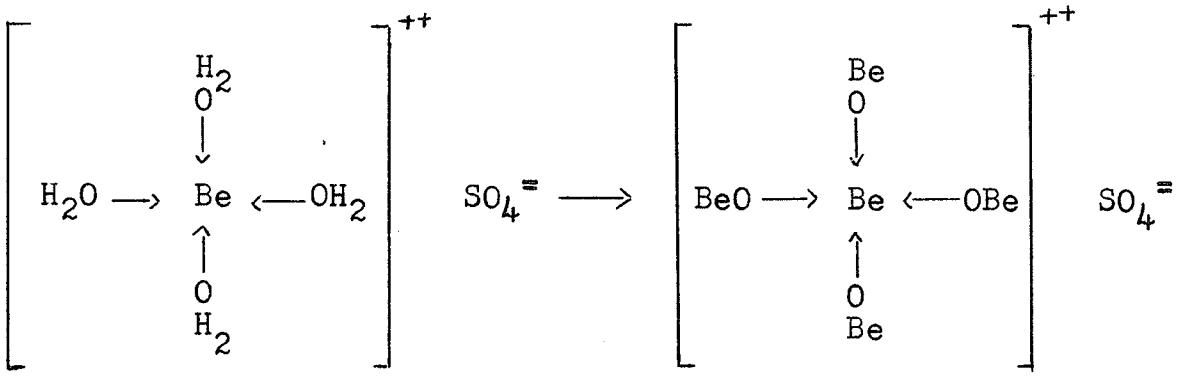
HISTORY

CHAPTER II

HISTORY

Aqueous solutions of beryllium salts are known to dissolve considerable quantities of the "basic carbonate" and the amorphous hydroxide (4) (5) (6). This property appears in mineral acid salts, such as halides, sulfate, selenate, and derivatives of organic acids, such as malonate and tartrate. In fact, the affinity is so strong that a concentrated solution of the beryllium salt of a strong acid continues to dissolve the basic carbonate with a brisk effervescence, even after one mole of base has been added for each mole of salt. Sidgwick and Lewis (5) found that, upon the addition of basic beryllium carbonate (whose composition and physical aspects vary with the nature of the precipitation reaction, concentration of solutions used, and the temperature) to a concentrated solution of beryllium sulfate, followed by boiling to remove carbon dioxide, there was an increase in the solubility of beryllium sulfate. A polynuclear species was postulated in accordance with the datum that one molecule of salt dissolved for every four molecules of oxide added. Sidgwick and Lewis envisaged the formation of complex ions of the type

$Be(BeO)_x(H_2O)_{4-x}$, in which molecules of BeO replace, partially or completely, four molecules of water of hydration on the Be^{++} cation, to form the complex grouping Be ← O = Be -



This formula is also attractive, since it conforms to the normal valence of beryllium.

The hydrates of highly charged metallic ions lose protons readily with the formation of hydroxo complexes

$$M(H_2O)_4^{++} \rightleftharpoons H^+ + \left[M(H_2O)_3OH\right]^+$$

which might dimerize, in the case of beryllium, to form the oxo complex;

$$2\left[Be(H_2O)_3OH\right]^+ \rightleftharpoons \left[(H_2O)_2Be\text{-}O\text{-}Be(H_2O)_2\right]^{++} + 3H_2O$$

or perhaps form the bridged hydroxy complex;

$$2\left[Be(H_2O)_3OH\right]^+ \rightleftharpoons \left[(H_2O)_2\,Be\begin{matrix}\diagup OH\diagdown\\ \diagdown OH\diagup\end{matrix}Be(H_2O)_2\right]^{++} + 2H_2O$$

Attempts have been made throughout the literature (6) (7) to correlate the above mentioned solubility to simultaneous changes in conductivity, freezing-point depression,

and osmotic pressure. Not only are the explanations contradictory but, also, one cannot relate these phenomena to composition in such highly concentrated solutions. Pierre Silber (8) assesses the problem and warns "dans l'état actuel de la question, il semble que l'on doive utiliser les données quantitatives avec circonspection, surtout les données peu recentes".

This behaviour suggested to us that complex formation could occur between ignited beryllium oxide and soluble beryllium salts. Such a reaction, should it be possible to bring about, promised to be relatively specific with respect to attack of beryllium oxide in a mixture of metallic oxides, provided no highly basic oxide were present.

EXPERIMENTAL PROCEDURE

CHAPTER III

EXPERIMENTAL PROCEDURE

Saturated beryllium sulfate solution was prepared by dissolving excess $BeSO_4 \cdot 4H_2O$, supplied by Fisher Scientific Co., in distilled water at 22.5°C. Analysis showed 28.41 grams $BeSO_4$/100 grams of saturated solution, or 0.002704 moles $BeSO_4$/gram of saturated solution (see (9)). The equivalents of beryllium and sulfate were verified to be unity.

The beryllium oxide, supplied by MacKay and Co., was ignited to 900°C to insure the absence of hydroxide. Spectrophotometric analysis, employing 8-hydroxyquinoline in chloroform (10) revealed 0.006% Al_2O_3.

Ignited beryllium oxide, in excess of the amount that, from preliminary work, was anticipated to dissolve and about 0.5 milliliters of saturated beryllium sulfate solution, were weighed into heavy-walled Pyrex tubing of one-half inch outer diameter. The open end of the tube was sealed with a flame, the tube placed into a short length of iron pipe, and the latter sealed with a perforated metal cap. This precaution was intended for the protection of personnel. A number of these assemblies were then placed in an airthermostat, whose

temperature regulation was $\pm 1^{\circ}C$, and then withdrawn after an appropriate time interval.

After cooling, the tubes were removed, broken open and the unreacted beryllium oxide collected on Whatman No. 42 filter paper. Washing with distilled water was continued until complete removal of beryllium sulfate was verified by testing the filtrate with lead acetate solution. The oxide was then ignited to $900^{\circ}C$ and weighed. This mass, when used in conjunction with the masses of the solid and liquid reactants, and the known analysis of the beryllium sulfate solution, permitted a calculation of the ratio of moles of beryllium oxide dissolved per mole of beryllium sulfate in the original charge.

Studies were made to show:

(a) the effect of temperature on the amount of beryllium oxide dissolved, as summarized by the upper curve in Figure 2 (see Table I).

(b) the effect of time on the amount of beryllium oxide dissolved, as summarized by the upper curve in Figure 3 (see Table II). and

(c) the effect of the concentration of beryllium sulfate on the amount of beryllium oxide dissolved, as summarized in Figure 4 (see Table V).

Because aluminum and beryllium generally occur together in nature, and because of the general chemical

similarity of this pair, ignited aluminum oxide was used as a solid reactant in a second series of determinations designed to give some indication of the amount of separation that could be expected. The lower curves of Figures 2 and 3 (see Tables II and IV) summarize the effect of temperature and time, respectively, on the solubility of aluminum oxide in beryllium sulfate solutions.

Next, we wished to investigate whether beryllium oxide could be selectively extracted, by the same technique, from beryl frit (supplied by The Brush Beryllium Company). This had been ground to -325 mesh.

Known amounts of the frit (approximately 100 milligrams) were placed in heavy-walled glass tubing, together with a known weight (approximately 0.5 milliliters) of the saturated beryllium sulfate solution. The tubes were sealed, placed in metal piping as before, and heated in an air-thermostat.

After appropriate time intervals, the tubes were removed, broken open, and the contents washed onto filter paper. The unreacted frit, thus collected, was placed in a platinum crucible, and the filter paper removed by ignition. The method of analysis took advantage of morin (2',4',3,5,7-pentahydroxyflavone)-beryllium fluorescence as described by Riley (11), using a Beckman Model DU spectrophotometer equipped with fluorescence accessory and photo-

multiplier attachment. The more recent paper of Sill and Willis (12) elaborates on modifications of the same procedure, but by the use of chelating agents and the careful consideration of pH, selectivity for beryllium is obtained by the method of Riley.

Reagent grade morin was supplied by K & K Laboratories, Inc. Although Riley found that technical grade morin gave satisfactory results, we found that the use of reagent grade was imperative. The latter gave far more reproducible results, stability of the fluorescence was enhanced, and fading of the fluorescence was almost unnoticeable, even after two hours.

The beryl frit was analyzed by the same method and found to contain 9.8 per cent BeO.

As before, the knowledge of the mass of liquid and solid reactants, BeO content of the frit, fluorometric analysis of the unreacted frit, and the known analysis of the beryllium sulfate solution, permitted a calculation of the ratio of moles of beryllium oxide extracted per mole of beryllium sulfate in the original charge.

Studies, to date, were made to show the effect of time on the amount of beryllium oxide extracted. The data are collected in Table VI, and summarized by Figure 5.

As a comparison, the effect of concentrated sulfuric acid on the frit was determined under similar experimental conditions. At a temperature of 200°C and a time of 24

hours, 0.021 moles of BeO were extracted per mole of sulfuric acid. Referring to Table VI, we see that with beryllium sulfate, under the same conditions, approximately 0.18 moles of beryllium oxide were extracted per mole of beryllium sulfate. Certainly, beryllium oxide seems to dissolve much more readily in beryllium sulfate than in sulfuric acid.

TABLE I

THE EFFECT OF TEMPERATURE ON THE AMOUNT OF BERYLLIUM OXIDE DISSOLVED IN SATURATED BERYLLIUM SULFATE THE TIME IN ALL CASES WAS SIX HOURS

Temperature	Grams BeO/ gram $BeSO_4$ sol'n	Moles BeO/ mole $BeSO_4$
90°C	0.0123	0.182
105°C	0.0166	0.245
120°C	(0.0202 (0.0213	(0.299 (0.314
135°C	(0.0243 (0.0238	(0.359 (0.352
150°C	0.0255	0.378
165°C	0.0292	0.432
180°C	0.0308	0.454
200°C	0.0309	0.457
215°C	0.0307	0.454
230°C	0.0302	0.454

TABLE II

THE EFFECT OF TEMPERATURE ON THE AMOUNT OF ALUMINUM OXIDE DISSOLVED IN SATURATED BERYLLIUM SULFATE THE TIME IN ALL CASES WAS SIX HOURS

Temperature	Grams Al_2O_3/ gram $BeSO_4$ sol'n	Moles Al_2O_3/ mole $BeSO_4$
180°C	0.00974	0.0353
200°C	0.00953	0.0345
215°C	0.0104	0.0377
230°C	0.0109	0.0396

TABLE III

THE EFFECT OF TIME ON THE AMOUNT OF BERYLLIUM OXIDE DISSOLVED IN SATURATED BERYLLIUM SULFATE THE TEMPERATURE IN ALL CASES WAS 180°C

Time	Grams BeO/ Gram $BeSO_4$ sol'n	Moles BeO/ mole $BeSO_4$
3 hours	0.0210	0.310
5 hours	0.0282	0.417
6 hours	0.0308	0.454
8 hours	0.0306 0.0310	0.452 0.458
19 hours	0.0325	0.480
24 hours	0.0331 0.0337	0.489 0.497
96 hours	0.0333	0.492
134 hours	0.0339	0.501

TABLE IV

THE EFFECT OF TIME ON THE AMOUNT OF ALUMINUM OXIDE DISSOLVED IN SATURATED BERYLLIUM SULFATE THE TEMPERATURE IN ALL CASES WAS 180°C

Time	Grams Al_2O_3/ gram $BeSO_4$ sol'n	Moles Al_2O_3 mole $BeSO_4$
3 hours	0.00596	0.0216
5 hours	0.00719	0.0261
6 hours	0.00974	0.0353
8 hours	0.00857	0.0311
19 hours	0.0110	0.0399
24 hours	0.0105	0.0382
144 hours	0.0137	0.0496

TABLE V

THE EFFECT OF CONCENTRATION OF BERYLLIUM SULFATE ON
ON THE AMOUNT OF BERYLLIUM OXIDE DISSOLVED
THE TEMPERATURE IN ALL CASES WAS 180°C;
THE TIME WAS SIX HOURS

Concentration*	Grams BeO/ gram $BeSO_4$ sol'n	Moles BeO/ mole $BeSO_4$
70.9%	0.0176	0.355
75.1%	0.0300	0.589
84.4%	0.0234	0.410
92.3%	0.0247	0.396
95.5%	0.0287	0.444
100.0%	0.0308	0.454

*reckoned as percentage by weight.

TABLE VI

THE EFFECT OF TIME ON THE AMOUNT OF BERYLLIUM OXIDE EXTRACTED FROM BERYL FRIT BY SATURATED BERYLLIUM SULFATE. THE TEMPERATURE IN ALL CASES WAS 200°C.

Time	Moles BeO extracted/ mole $BeSO_4$ sol'n	Percentage BeO extracted
4 hours	0.110 0.112 0.087	30%
8 hours	0.114 0.136	46%
24 hours	0.195 0.173 0.175	64%
48 hours	0.227 0.230 0.216	68%

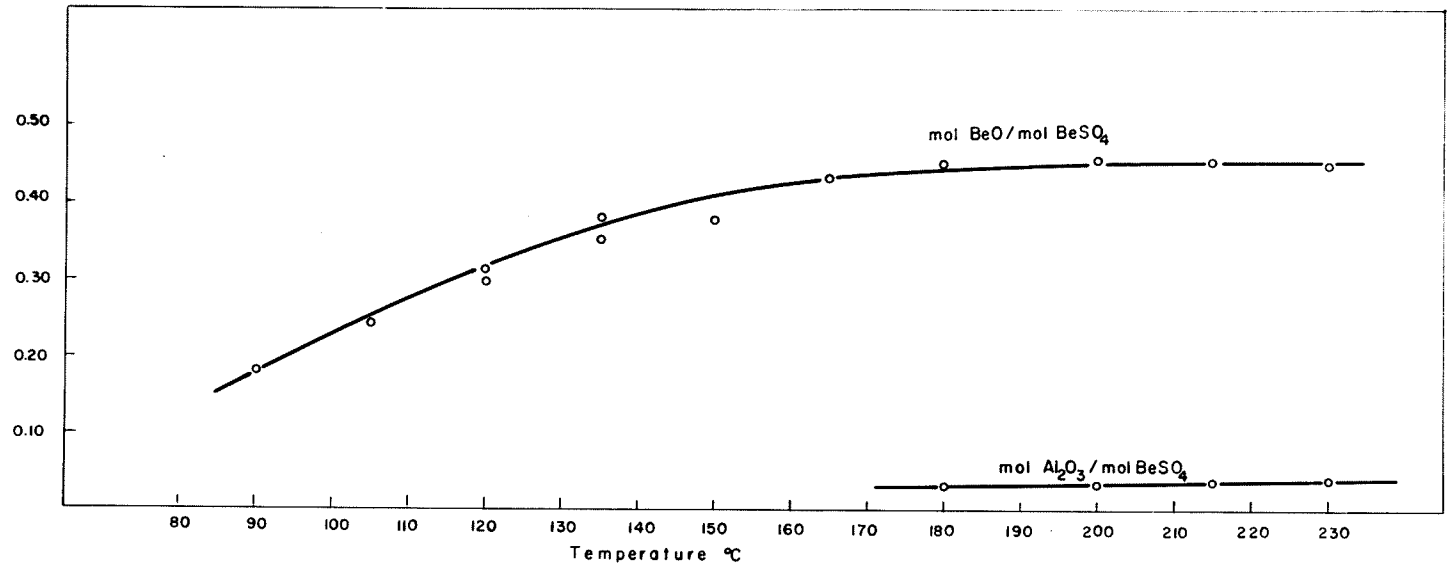


Figure 2. The effect of temperature on the number of moles of beryllium oxide and on the number of moles of aluminum oxide dissolved per mole of beryllium sulfate. The time in all cases was six hours.

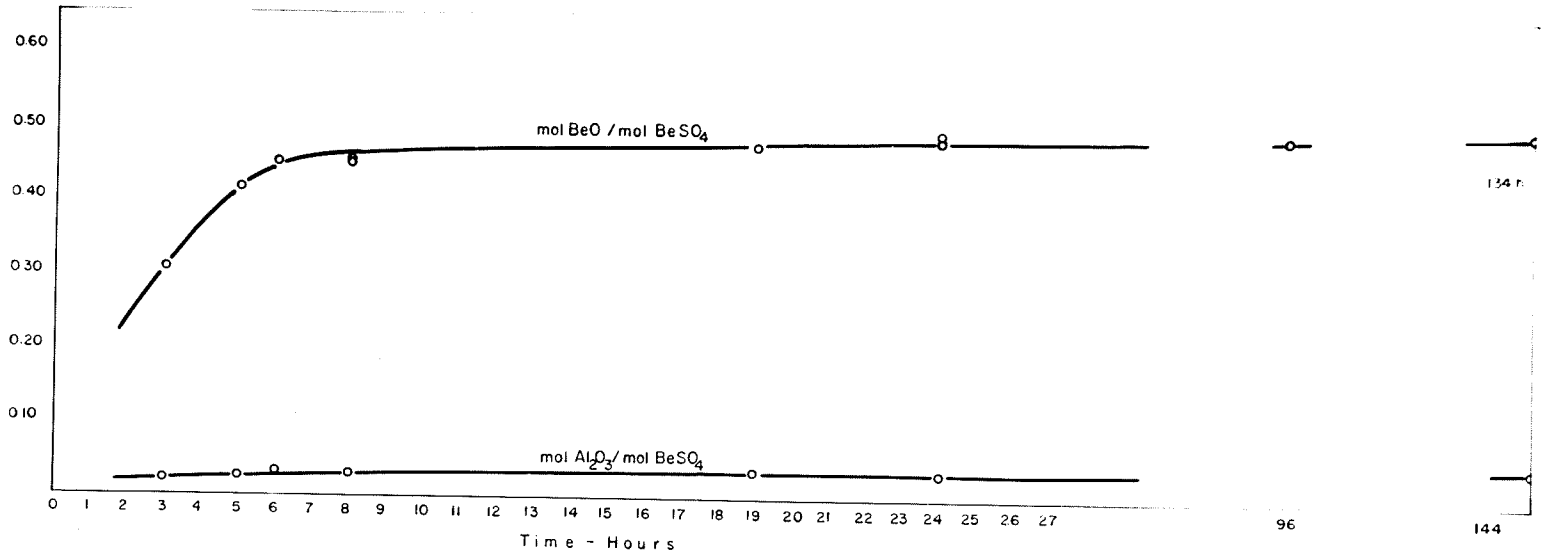


Figure 3. The effect of time on the number of moles of beryllium oxide and the number of moles of aluminum oxide dissolved per mole of beryllium sulfate. The temperature in all cases was 180°C.

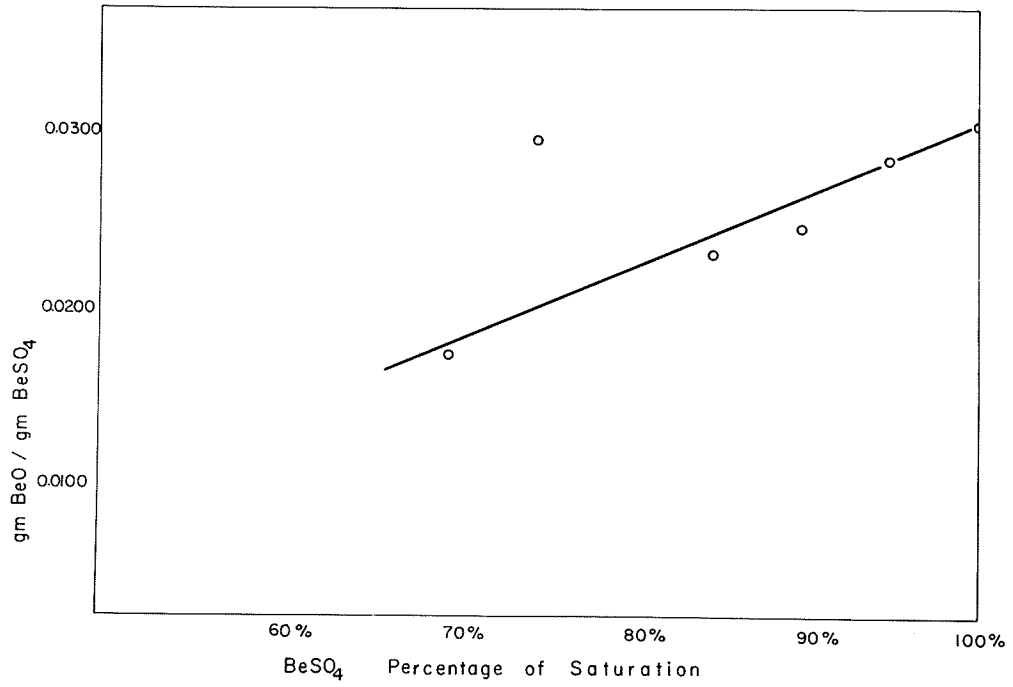


Figure 4. The effect of concentration of beryllium sulfate solution on the number of moles of beryllium oxide dissolved per mole of beryllium sulfate. The temperature in all cases was 180°C; the time was six hours.

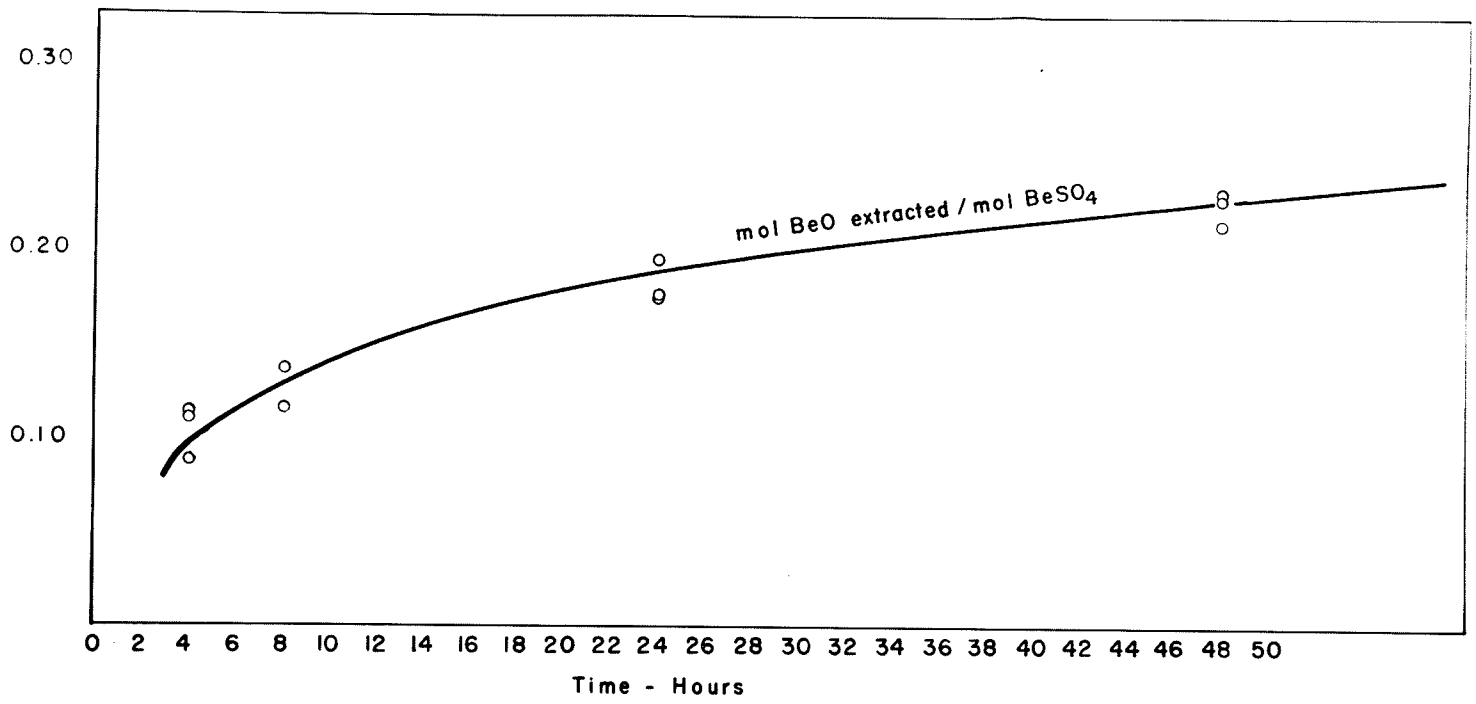


Figure 5. The effect of time on the amount of beryllium oxide extracted from beryl frit by saturated beryllium sulfate. The temperature in all cases was 200°C.

DISCUSSION OF RESULTS

CHAPTER IV

DISCUSSION OF RESULTS

The data collected indicate that the optimum conditions for dissolving pure beryllium oxide in beryllium sulfate solutions are 180°C, a time of six hours and that a high concentration of beryllium sulfate increased the rate of reaction considerably. Figure 3 and some isolated runs not included here, indicate that some species, very stable in solution, with an empirical formula $2BeSO_4 \cdot BeO \cdot xH_2O$ is formed, the rate of formation being favored by high temperatures. The region of stability of this compound must be fairly extensive since highly diluted solutions obtained in washing the undissolved beryllium oxide onto a filter show no tendency to reprecipitate the dissolved beryllium oxide, even when allowed to stand for several months at room temperature. It seems unlikely that this apparent stability can be explained in terms of the inertness sometimes observed with polynuclear species.

The limited solubility of aluminum oxide is most likely due to its having a basicity similar to that of beryllium oxide and simply displacing some of the aquoberyllium ions from solution, the displaced beryllium then entering

into polynuclear formation.

With regard to the results on the beryl frit, we would not expect to attain an extraction level of 0.5 moles of beryllium oxide per mole of beryllium sulfate (the maximum value reached with the pure oxide), since a slight excess of beryllium sulfate was present in all cases.

In the straight fusion process used by The Brush Beryllium Company, the opening of the ore is based entirely upon crystallographic changes in the ore molecule. The non-reactive beryllium oxide content of the quenched frit after the first treatment with sulfuric acid is believed to be present in solid solution in the silica. By heat treating the frit, this additional beryllium oxide can be caused to precipitate out of solid solution. If, in this study, we have approached the maximum extraction level of beryllium oxide, it may indeed be due to the same cause.

Referring to Figure 5, the data at 48 hours indicate beryllium oxide extraction approaching 70 per cent. It does not seem unlikely that a 90 per cent extraction, or better, could easily be reached. But the question of selectivity with respect to beryllium oxide is yet undetermined. This information can only be acquired by a complete analysis of the beryl frit, and analysis of solid, and solution, after reaction. Further studies should be continued in this direction.

The existence of a preferential solvent for beryllium oxide, with suitable experimental conditions established, could be used to advantage in specific metallurgical situations. In the Brush process, for example, (see Figure 1) considerable simplification could be introduced. Reaction of the ground heat treated beryl frit with saturated beryllium sulfate solution, followed by decantation or filtration, would eliminate sulfating with sulfuric acid, leaching with water, and removal of aluminum by ammonium alum crystallization. Even the addition of chelating agents might be avoided, or at least the amounts reduced.

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