Solubilities of Colemanite, Ulexite, Pandermite And Tunellite Minerals in Different Alkaline Solutions

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SUMMARY

In this work solubilities of four boron minerals and their calcination products in alkaline solutions are investigated. The solubility experiments have been made with NaOH, NH_3, Na_2CO_3 and (Na_2CO_3+$NaHCO_3$) solutions of : 0.5, 2.0 and 5.0 normalities and as well as at room (20° - 30°C) and as at higher (80° - 90°C) temperatures.

The solubility ratios of the minerals in NaOH solutions do increase with the increase of concentrations and temperature. It has been observed that Tunellite mineral dissolves completely in hot NaOH solution. The solubility ratios in ammonia solutions are indirectly proportional with the concentration and directly porportional with the temperature except for Tunellite mineral. The four minerals and their calcination products are almost completely soluble in hot Na_2CO_3 solution as well as in hot (Na_2CO_3+$NaHCO_3$) solution. In order to dissolve the four minerals in Na_2CO_3 and (Na_2CO_3+$NaHCO_3$) solutions at room temperature, it is necessary to make them calcined. The temperature ranges of calcination are; for Colemanite 300° - 350° C, for Ulexite 150°C, for Pandermite 450°C and for Tunellite 250° - 300°C.

INTRODUCTION

In this work it has been aimed to investigate the solubilities of the typical boron minerals, such as Colemanite and Ulexite, the Pandermite mineral, reserves of which has been completely finished in Turkey, and

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the Tunellite mineral which has a different composition, in alkaline solutions.

The solubilities of the above four minerals in water has been the subject of many studies for a long time (1 - 6). The solubilities of Ulexite (7) and Colemanite (8) in waters containing CO_2, have been also thoroughly investigated.

The solubilities of different boron minerals in inorganic acids (9) and the effect of temperature on solubility (10) has been investigated. Also, the rates, kinetics and mechanisms of the solubilities of borates in hydrochloric acid (11, 12), sulphiric acid (13, 14), nitric (15, 16) phosphoric (17), acetic (18) and perchloric (19) acids have been investigated extensively. In addition, it has been shown that the solubilities of Colemanite, Ulexite and Pandermite minerals in disodium EDTA solution are complete (20).

In spite of all these, the solubilities of these four boron minerals in alkaline solutions have not been satisfactorily studied up to now.

In the experiments carried out, solutions of NaOH, NH_3, Na_2CO_3 and (Na_2CO_3+$NaHCO_3$) in various concentrations have been used as alkaline solutions. The solubility experiments have been made both at room temperature (20 - 30°C) and at 80° - 90°C, with the original minerals and with the calcined samples obtained in a series of temperature.

EXPERİMENTAL

Colemanite ($2\,CaO \cdot 3\,B_2O_3 \cdot 5\,H_2O$), Ulexite ($Na_2O \cdot 2\,CaO \cdot 5\,B_2O_3 \cdot 16\,H_2O$), Pandermite ($4\,CaO \cdot 5\,B_2O_3 \cdot 7\,H_2O$) and Tunellite ($SrO \cdot 3\,B_2O_3 \cdot 4\,H_2O$) minerals which were selected as materials for this work, have been obtained from the mines, cleaned carefully analysed. The results obtained indicate the compotion of these minerals as shown in Table I.

Table. I. — Results of the Analysis of Boron Minerals.

Components	Colemanite	Ulexite	Pandermite	Tunellite
B_2O_3	50.86 %	42.60 %	49.70 %	54.10 %
CaO	27.22	14.10	32.20	—
Na_2O	—	7.68	—	—
SrO	—	—	—	27.10
H_2O	21.92	35.60	18.10	18.79

The mineral samples have been then grinded so that they would pass through 100 mesh (0.149 mm) sieve. Both the dhydratation experiments made to obtain calcined products and the solubility experiments of the original minerals have been made with the samples prepared in this manner. The calcined samples were grinded again for a second time so as to pass through 100 mesh sieve.

Preparation of calcined samples: For this purpose the static method has been applied. In this method, each time exactly 5 grams of mineral sample has been taken and heated in a muffle furnace 5 hours. Then the weight losses of the samples have been determined and the B_2O_3 contents of the calcined products determined by the known titration method using alkaline.

The temperature - weight loss curves of each of the four minerals will be given later together with their solubility curves (Fig. 1 - 12).

The values of B_2O_3 content of the calcined products depending on the calcination temperatures are given in Table II.

Table. II. — B_2O_3 contents of the calcined products depending on the temperature.

Calcination Temp. °C	Colemanite	Ulexite	Pandermite	Tunellite
100	50.89 %	46.93 %	49.88 %	54.49 %
150	50.99	51.77	49.94	55.97
200	51.20	59.89	50.39	59.92
250	51.70	61.54	52.02	61.92
300	52.49	62.65	52.52	62.74
350	54.56	63.96	53.38	63.37
400	61.63	64.99	54.83	64.61
450	64.68	65.79	58.84	65.83
500	65.05	66.32	60.61	66.41
550	65.07	66.69	60.85	66.66
600	65.07	66.69	60.89	66.82
650	—	—	—	66.88
700	—	—	—	66.89

The dissolving experiments: The original and the calcined mineral samples have both been dissolved in 0.5 N, 2.0 N and 5.0 N NaOH, NH_3 and Na_2CO_3 solutions, respectively, and also in (1/1) mixture of (0.5 N Na_2CO_3 + 0.5 N $NaHCO_3$) solution. These experiments have been made at room temperature (20° - 30°C) and at 80° - 90°C.

The dissolution procedures have been done as follows: Each time 500 mg of sample has been left to dissolve in 50 ml of solvent for 45 minutes over a magnetic stirrer with constant stirring. At the end of this time, the dissolved part has been filtered through a glass crucible, the insoluble part left in the crucible has been weighed after being dried for 1 hour at 105°C. Besides, the B_2O_3 contents in the filtrates have also been determined volumetrically.

The solubilities in the Na_2CO_3 and (Na_2CO_3+$NaHCO_3$) solutions have not been determined gravimetrically, but they have been determined volumetrically from the B_2O_3 content in the filtrates.

Since the solubility values in 0.5 N Na_2CO_3 solution were 100 %, it was useless to try higher concentrations.

The solubility experiments carried on at hot temperatures have been done under reflux condenser.

RESULTS

The results of the solubility tests of the original minerals and calcined samples in the NaOH and NH_3 solutions as explained in the experimental part are presented in Figures (1 - 8), respectively.

In the graphes the abscissa shows the dehydratation temperatures where the ordinates are :

1. Solubility (Dissolved sample in grams/100 ml of solvent)
2. Loss of water in moles in the dehydratation.
3. Loss of weight in the dehydratation.

The curves presented show respectively :

D : Dehydratation curves of the minerals,

I : Solubility in 0.5 N solution (at 80 - 90°C),

II : Solubility in 2.0 N solution (at 80 - 90°C),

III : Solubility in 5.0 N solution (at 80 - 90°C),

IV : Solubility in 0.5 N solution (at 20 - 30°C),

V : Solubility in 2.0 N solution (at 20 - 30°C),

VI : Solubility in 5.0 N solution (at 20 - 30°C).

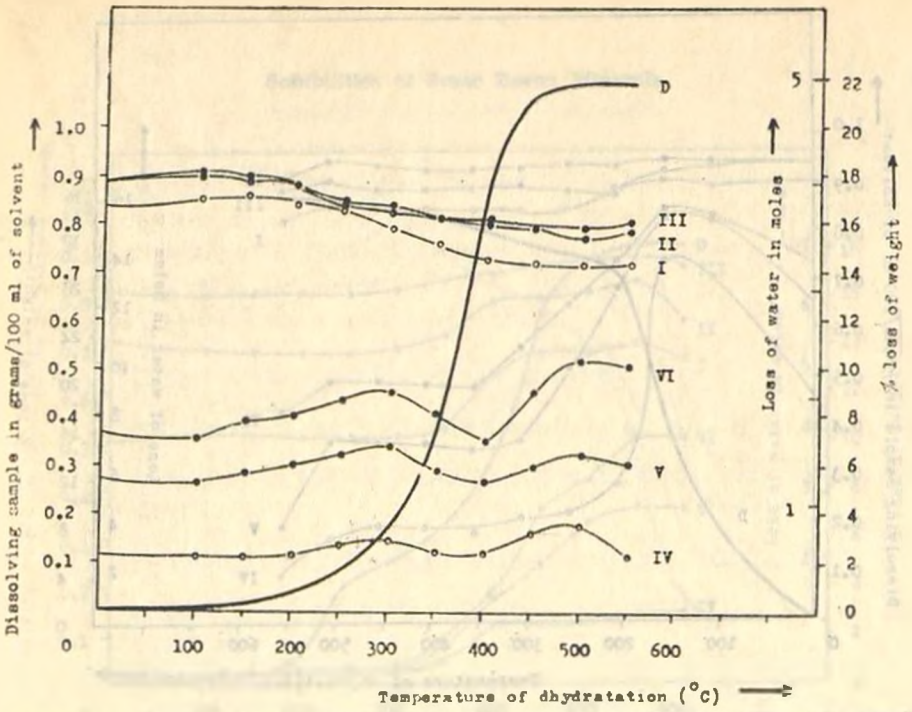

Figure. 1. — The solubities of the original Colemanite mineral and it's calcined products in NaOH solutions.

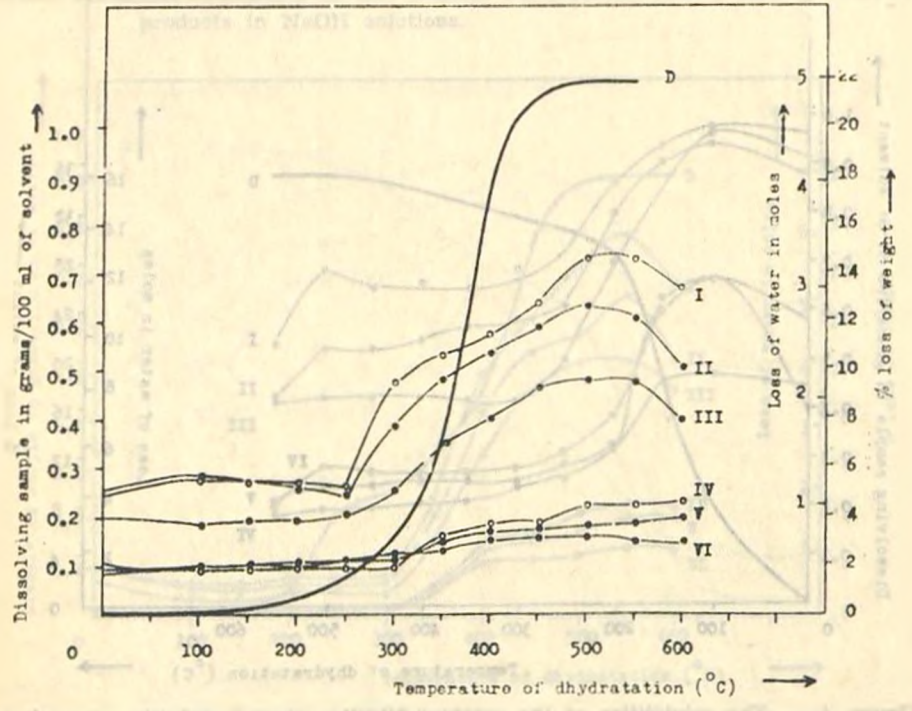

Figure. 2. — The solubilities of the original Colemanite mineral and it's calcined products in NH_4 solutions.

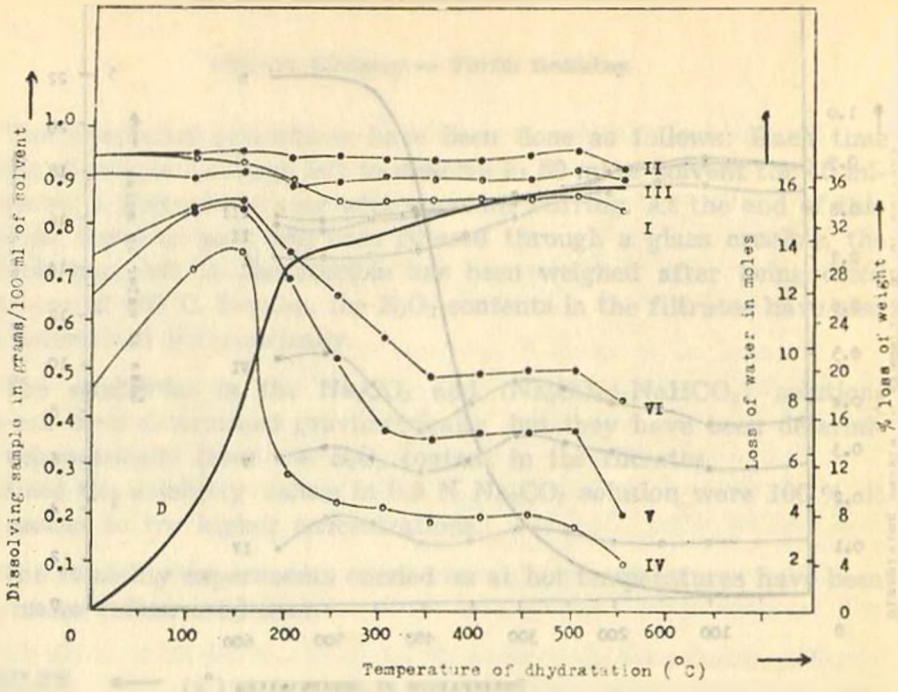

Figure. 3. — The solubilities of the original Ulexite mineral and it's calcined products in NaOH solution.

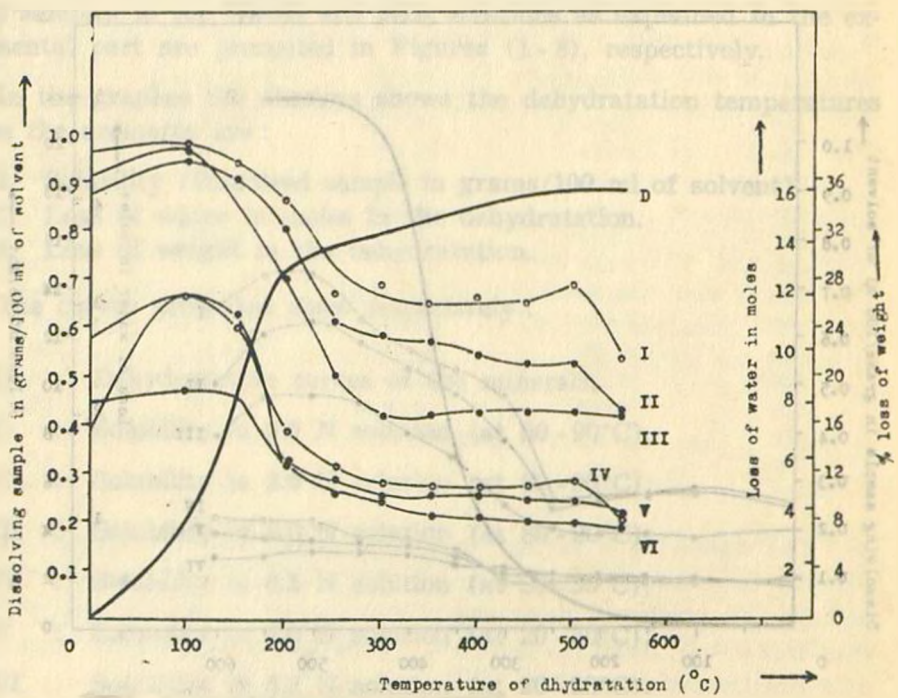

Figure. 4. — The solubilities of the original Ulexite mineral and it's calcined products in NH_4 solutions.

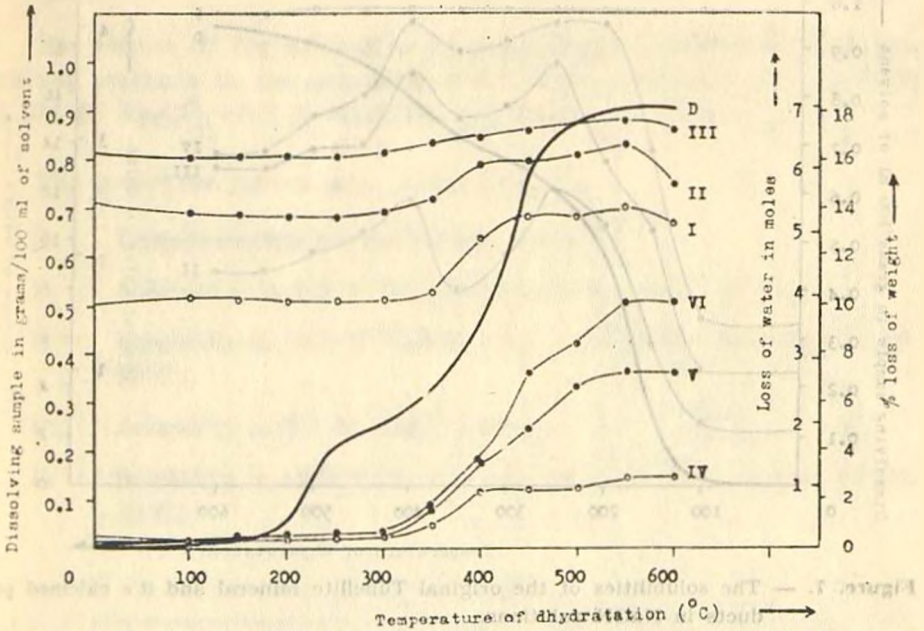

Figure. 5. — The solubilities of the original Pandermite mineral and it's calcined products in NaOH solutions.

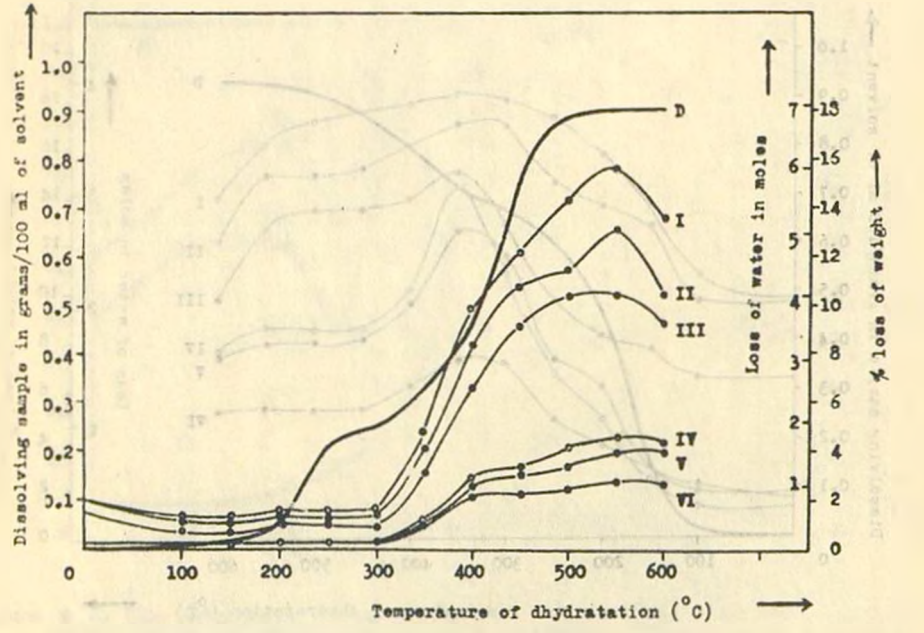

Figure. 6. — The solubilities of the original Pandermite mineral and it's calcined products in NH_3 solutions.

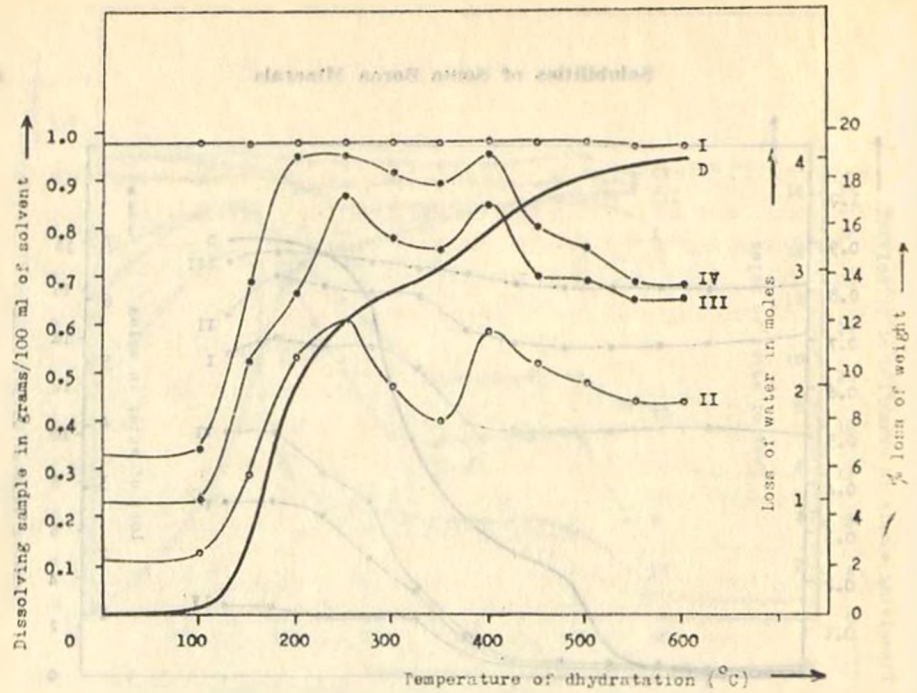

Figure. 7. — The solubilities of the original Tunellite mineral and it's calcined products in NaOH solutions.

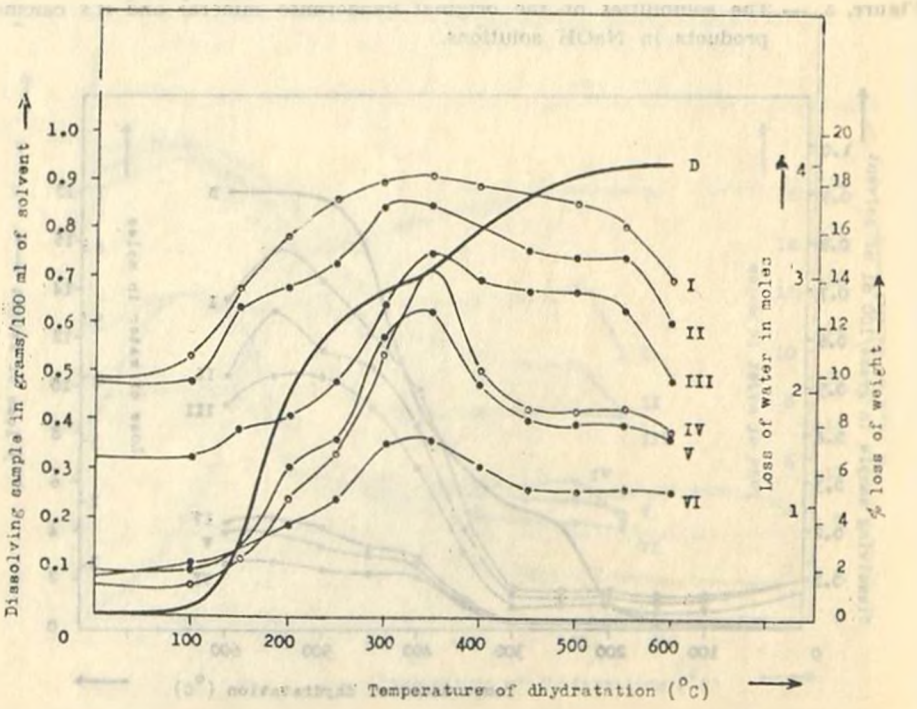

Figure. 8. — The solubilities of the original Tunellite mineral and it's calcined products in NH_3 solutions.

The results of the solubilities of previously mentioned minerals and calcined products in the solutions of 0.5 N Na_2CO_3 and (1 1) mixture of (0.5 N Na_2CO_3 + 0.5 N $NaHCO_3$) are shown in Figures (9 - 12).

The presented curves are, respectively :

D : Dehydratation curves of the minerals,

I : Solubility in 0.5 N Na_2CO_3 solution (at 80 - 90 C).

II : Solubility in (0.5 N Na_2CO_3 + 0.5 N $NaHCO_3$) solution (at 80 - 90 C),

III : Solubility in 0.5 N Na_2CO_3 solution (at 20 - 30 C),

IV : Solubility in (0.5 N Na_2CO_3 + 0.5 N $NaHCO_3$) solution (at 20 - 30°C).

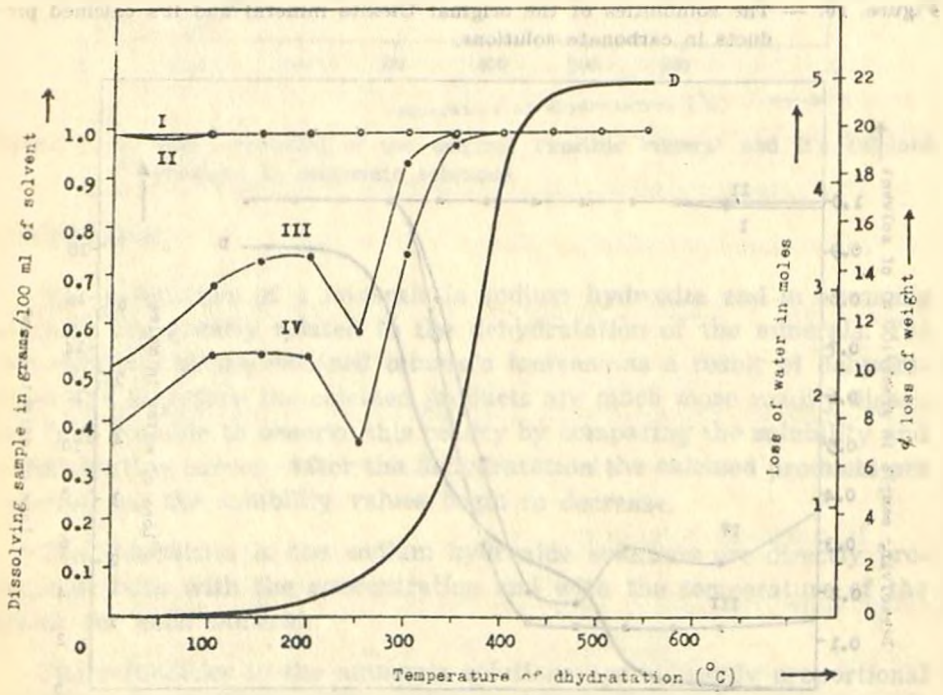

Figure 9. — The solubilities of the original Colemanite mineral and it's calcined products in carbonate solutions.

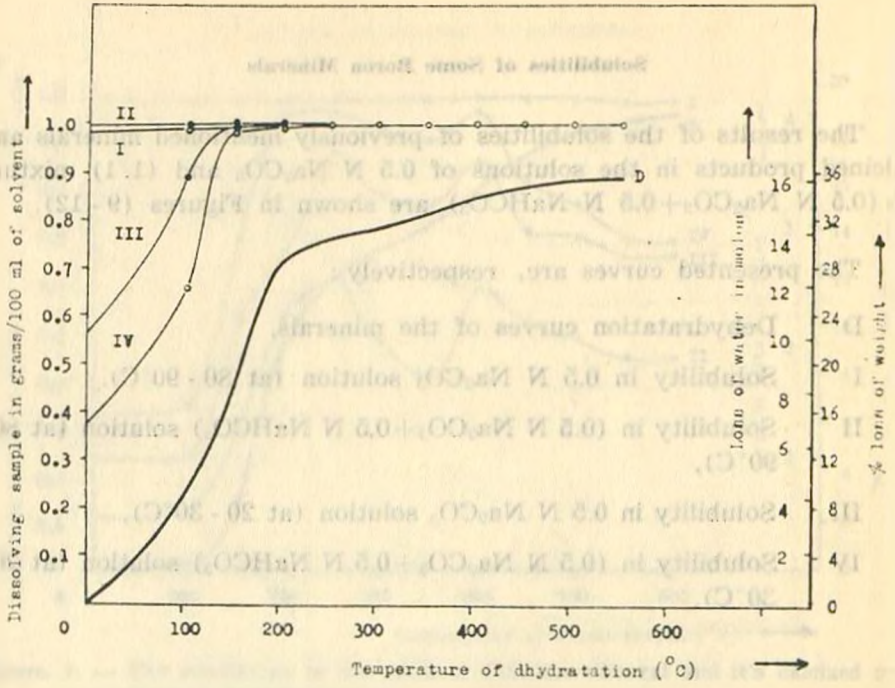

Figure. 10. — The solubilities of the original Ulexite mineral and it's calcined products in carbonate solutions.

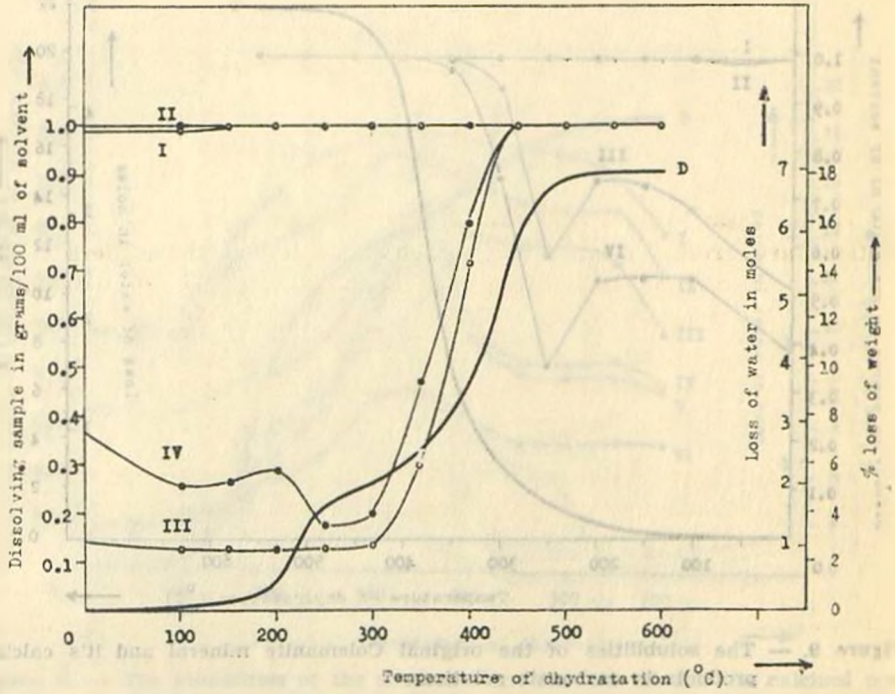

Figure. 11. — The solubilities of the original Pandermite mineral and it's calcined products in carbonate solutions.

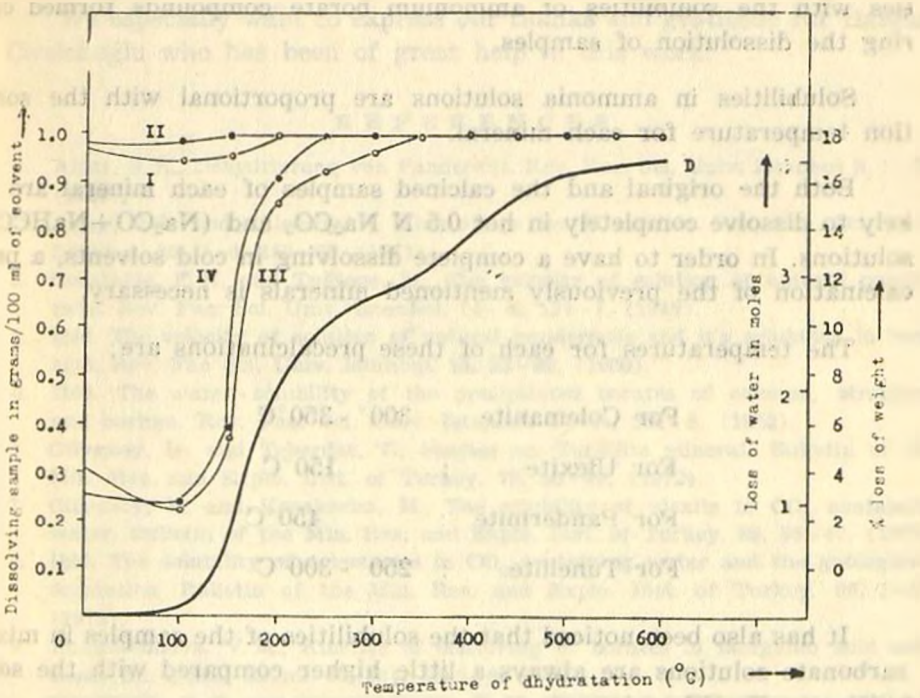

Figure. 12. — The solubilities of the original Tunellite mineral and it's calcined products in carbonate solutions.

DISCUSSION

The solubilities of 4 minerals in sodium hydroxite and in ammonia solutions are greatly related to the dehydratation of the minerals. The heat contents of the calcined minerals increase as a result of dehydratation and therefore the calcined products are much more readily dissolved. It is possible to observe this reality by comparing the solubility and the calcination curves. After the dehydratation the calcined products are cindered and the solubility values begin to decrease.

The solubilities in the sodium hydroxide solutions are directly proportional both with the concentration and with the temperature of the solvent for each mineral.

The solubilities in the ammonia solutions are indirectly proportional with the concentration of the solvent for all the minerals except Tunellite. It is possible to explain this indirect proportionality of the solubili-

ties with the solubilities of ammonium borate compounds formed during the dissolution of samples.

Solubilities in ammonia solutions are proportional with the solution temperature for each mineral.

Both the original and the calcined samples of each mineral are likely to dissolve completely in hot 0.5 N Na_2CO_3 and ($Na_2CO+NaHCO_3$) solutions. In order to have a complete dissolving in cold solvents, a precalcination of the previously mentioned minerals is necessary.

The temperatures for each of these precalcinations are;

For Colemanite	:	300° - 350°C
For Ulexite	:	150°C
For Pandermite	:	450°C
For Tunellite	:	250° - 300°C

It has also been noticed that the solubilities of the samples in mixed carbonate solutions are always a little higher compared with the solubilities in Na_2CO_3 solutions.

The maximum solubilities obtained can be summarized as below :

In sodium hydroxide solutions:

Colemainte	:	Calcined sample at 100°C, in 2N hot solution;	91.00 %
Ulexite	:	Calcined sample at 150°C, in 2N hot solution;	96.20 %
Pandermite	:	Calcined sample at 550°C, in 2N hot solution;	88.60 %
Tunellite	:	All samples in 0,5 N hot solution;	100.00 %

In ammonia solutions:

Colemanite	:	Calcined sample at 500°C, in 0.5 N hot solution ;	73.10 %
Ulexite	:	Calcined sample at 100°C, in 0.5 N hot solution ;	97.50 %
Pandermite	:	Calcined sample at 550°C, in 0.5 N hot solution ;	78.50 %
Tunellite	:	Calcined sample at 350°C. in 0.5 N hot solution ;	91.10 %

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