SOLUBILITY OF ULEXITE IN CO_2-CONTAINING WATER

Hüseyin GÜLENSOY and Mehmed Muhtar KOCAKERİM

İstanbul University, Faculty of Chemistry

ABSTRACT. — In this research, the solubility of ulexite samples, in CO2-containing water—whether in original or calcinated form, at a series of temperature conditions—were studied.

For solubility studies the time and temperature were taken as parameters.

The solubilities of the mineral in distilled water were studied in order to be able to compare them with the solubilities in CO_2-containing water.

The general solubility equation for the hydrated boron minerals is:

$xCaO.yB_2O3.zH2O+xCO2+nH_2O \qquad xCaCO_3 + 2yH_3BO_3+[(z—3y) + n]\ H_2O$

Consequently, it was found that this equation was realized for ulexite in the following form:

$Na_2O.2CaO.5B_2O3.I6H_2O+2CO_2 + nH2O \qquad Na_2B4O_7+2CaCO3+6H_3BO3 + (n+7)\ H_2O$

The effect of the increase of the calcination temperature of the mineral upon solubility is negative.

In addition, some information which was considered useful to explain the chemical reactions for the production of boric acid from the ulexite ore was also put forward.

I. INTRODUCTION AND HISTORY

Ulexite ore composed of sodium-calcium-hydroborate is rarely encountered in the earth crust. Rich reserves found in Chile, in association with some other minerals; exposures encountered in the Kazakistan region, USSR; and those discovered in the Bigadiç area, Western Anatolia, Turkey, are the main occurrences.

Studies on ulexite, as compared to other boron minerals, such as pandermite and, especially colemanite, are fewer and it must be noted that very little use is made of this mineral.

Among these the following may be mentioned:

In addition to the work on thermal decomposition of ulexite mineral (14, 15), the most interesting studies in this field are those concerning the solubilities of boron minerals in various acids as well as the study of the mechanics and speed of these solution processes (2-7, 10, II, 16-21). Some studies on the solubility of the ulexite mineral in alkali medium (8, 9, 12) and in ordinary water (13) were also carried out.

Tests on the solubility of original and calcined ulexite samples in different EDTA solutions gave very interesting results (I). Samples of the typical, pure ulexite mineral collected from the quarries in the vicinity of Bigadiç were analyzed according to standard methods. The results obtained are as follows:

Na_2O : 7.65 %
CaO : 13.80 %
B_2O_3 : 42.80 %
H_2O : 35.75 %

Thus, it was confirmed that these samples are expressed with the following formula: $Na_2O.2CaO.5B_2O_3.16H_2O$. The B_2O_3/CaO ratio in this type of ulexite is 3.10.

II. CALCINATION STUDIES

METHODS AND APPARATUS USED

Static method was applied in calcination tests. For this purpose the samples were heated at predetermined temperatures until they reached a fixed weight.

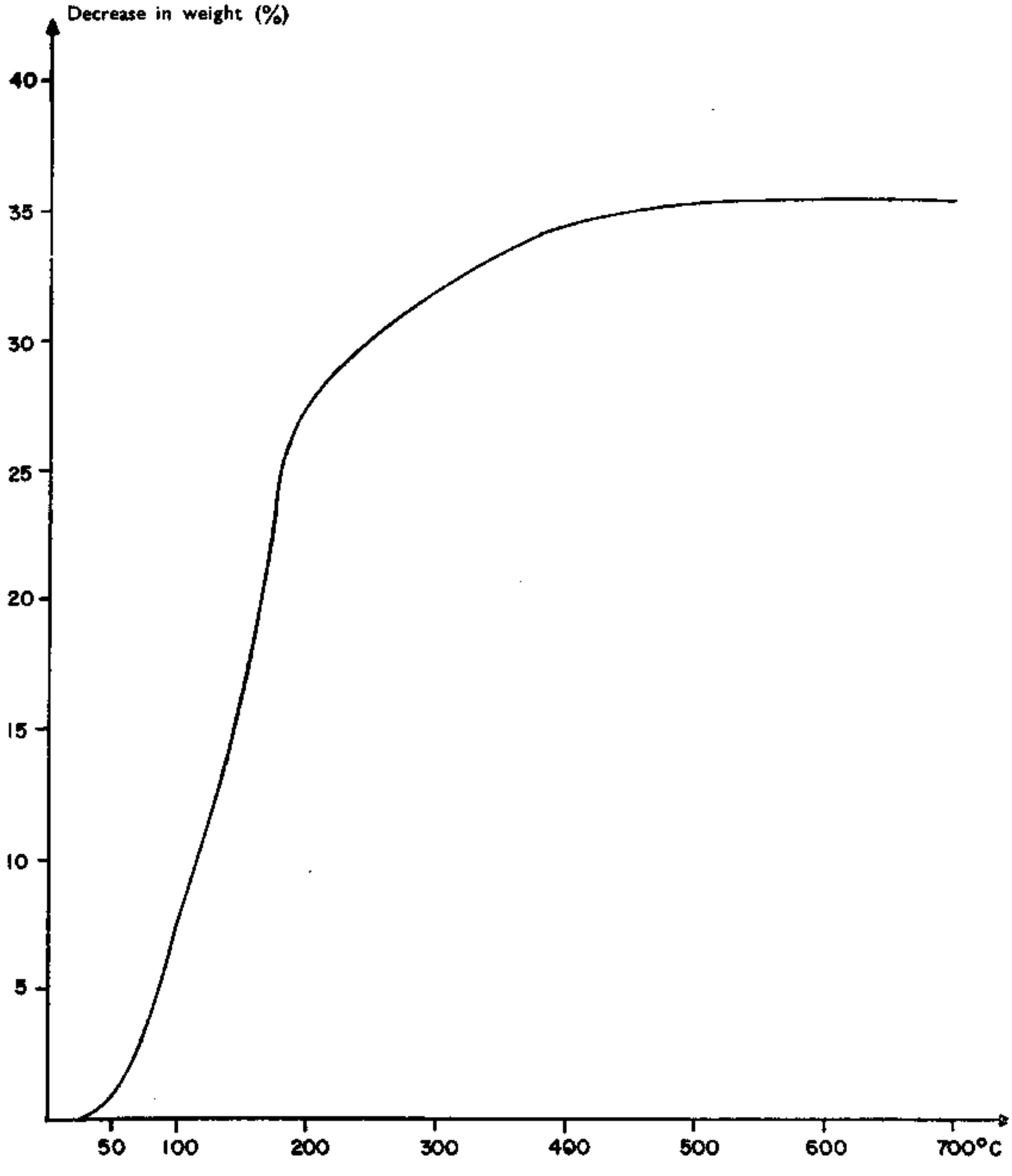

Fig. 1 - Calcination of ulexite.

Heating was conducted in a normal muffle furnace. The aim of this static process was essentially to obtain calcinated ulexite samples which will be used in the determination of the relationship between solubulity and thermal decomposition. It should be noted that thermolysis of the ulexite mineral has previously been studied in considerable detail by some investigators (14, 15).

Calcination temperatures used were 50, 100, I50, 200,250, 300,350,400,450, 500, 550, 600, 650 and 700°C, which were considered to be sufficient.

Loss of water (that is decrease in weight) of ulexite due to temperature changes is shown graphically in Figure I.

During calcination, composition of the remaining sample also changes due to the loss of water. In order to compare the solubilities of the calcination products in detail, the new compositions of calcinated ulexite samples were also determined. The results are given in Table I.

Table - I

Composition of calcinated ulexite samples

Tem. of calcination °C	Na_2O	CaO	B_2O_3	H_2O
Original	7.65	13.84	42.96	35.55
50	7.69	13.92	43.21	34.98
100	8.33	15.07	46.80	27.35
150	9.02	16.33	50.69	20.30
200	10.62	19.22	59.67	7.55
250	10.90	19.73	61.25	5.69
300	11.23	20.32	63.09	3.65
350	11.45	20.71	64.31	2.35
400	11.69	21.16	65.69	0.95
450	11.74	21.25	65.98	0.66
500	11.81	21.36	66.33	0.32
550	11.83	21.41	66.48	0.17
600	11.83	21.41	66.47	0.17
650	11.86	21.46	66.64	0.02
700	11.87	21.49	66.71	—

III. STUDIES ON SOLUBILITY

METHODS AND APPARATUS

1. Solubility in distilled water: Ulexite samples in their original and calcined forms were ground to a 100-mesh fineness, and solubility of 1.0000 gr of the samples in 100 ml of distilled water with a fixed pH value (pH=5.5) was determined.

Solubility tests at moderate rate of stirring and room temperature, during a definite duration of time, were carried out; the residual unsoluble matter was weighed and, thus, the percentage of the dissolved material from 1.0000 gr of sample was determined. These values can also be expressed as «mg sample/100 ml water», if desired.

2. Solubility in CO_2-containing water: This test was carried out under the same conditions with an exception that a CO_2-saturated water was used. The tests were conducted for solutions at room temperature and at 50°C; time of procedure: I, 2 and 3 hours.

3. Similar solubility tests were carried out for 100 ml of NaOH solutions, with pH = l2, with and without CO_2, at room temperature and at 50°C.

4. The pH values of the solutions obtained by tests I and 2 were determined.

5. Amounts of CaO and B_2O_3 obtained by the tests carried out in water containing CO_2 were determined. For this purpose the following procedures were used:

a. For the test of CaO: The solution containing $Ca^{2}+$ ions was made alkaline by the addition of NH_3 and then titrated by a standard solution of EDTA.

b. For the test of B_2O_3: Titration was carried out by using a standard solution of NaOH in the presence of mannite.

Solubility tests in water containing CO_2 (as well as in alkaline medium) were carried out in an apparatus, diagram of which is given in Figure 2.

CONCLUSIONS

I. Solubility in distilled water

The relationship between the solubility of 1.0000 gr of calcined ulexite sample in 100 ml of distilled water (pH = 5.5) and the calcination temperature, as well as the pH values of the resulting solutions, are summarized in Table 2.

Note: These tests carried out in distilled water were conducted under room temperature, within 1-hour time.

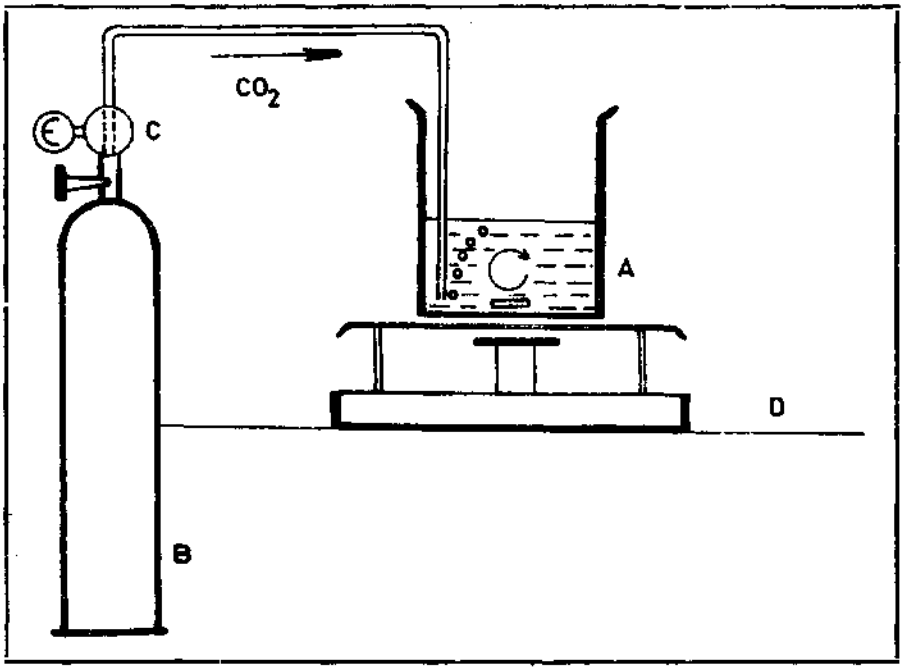

Fig. 2 - Apparatus used in tests.
A - Reaction vessel; B - CO_2 tube; C - Gas regulator; D - Magnetic agitator.

Table - 2

Solubility of ulexite in distilled water

Temp. of calc. °C	*pH*	*Amount of the sample solved (%)*
Original	9.20	34.00
50	9.20	33.00
100	9.20	31.10
150	9.20	29.20
200	9.20	29.20
250	9.20	29.20
300	9.20	29.20
350	9.20	29.20
400	9.20	29.20
450	9.20	29.20
500	8.92	28.80
550	8.80	28.50
600	8.80	28.00
650	8.80	28.00

2. Solubility in CO_2-containing water

A. Tests *performed at room temperature.* — Results obtained from the solubility tests of the original and calcinated ulexite samples m CO_2-containing water, at room temperature, are shown in Table 3. The values given express the solubility tests of I-hour time.

When the values in Table 3 are compared with those in Table 2, it can be concluded that the solubility of ulexite in CO_2-containing water is inversely proportional to the calcination temperature.

However, the solubility of the mineral is rather more in favor of B_2O_3 (as will be seen in the last column of the Table 3). The B_2O_3/CaO ratio in the resulting solutions, indeed, is 12-15 times greater than the same ratio which is only 3.10, in the original mineral. In other words, while the B_2O_3 content dissolves into H_3BO_3, the CaO content of the mineral is partly converted into $CaCO_3$ which keeps its solid form. In fact, the Ca++ions found in the solution result from a bicarbonate formed according to the following equation:

$$CaCO_3 + CO_2 + H_2O \rightleftarrows Ca(HCO_3)_2$$

When similar tests were carried out increasing the time of procedure to 2 or 3 hours, results obtained were not much different. This should be considered normal, because, after a certain time, an equation of $Na_2O.2CaO.5B_2O_3.\ I6H_2O+2CO_2+nH_2O \qquad Na_2B_4O_7 +2CaCO_3+6H_3BO_3+(n+7)H_2O$ will be obtained in the test solutions.

In Figure 3 the relationship between the solubility values of calcinated ulexite samples obtained in relation with time and the calcination temperature of the mineral is shown.

Table - 3

Solubility of ulexite in I-hour period at room temperature

Temp. of calc. °C	pH at the end of the test	Amount of the dissolved sample (%)*	Amount of CaO in the sample (mg)	Amount of CaO in the solution (mg)	Solution of CaO in the sample (%)	Amount of B_2O_3 in the sample (mg)	Amount of B_2O_3 in the solution (mg)	Solution of B_2O_3 in the sample (%)	B_2O_3/CaO ratio in the solution **
Original	6.5	77.47	138.38	22.43	16.21	429.62	376.06	87.53	16.77
50	6.4	78.14	139.16	15.70	11.28	432.06	400.43	92.66	25.50
100	6.5	77.43	150.74	20.19	13.39	467.99	407.39	87.05	20.17
150	6.4	75.05	163.28	14.58	8.93	506.92	490.96	96.85	33.67
200	6.4	68.37	192.19	14.58	7.58	596.69	557.12	93.37	38.21
250	6.5	68.21	197.27	15.70	7.96	612.47	564.08	92.10	35.93
300	6.5	66.90	203.20	16.82	8.28	630.86	584.98	92.73	34.78
350	6.1	65.59	207.15	14.02	6.76	643.14	595.42	92.58	42.47
400	6.8	65.32	211.59	16.82	7.95	656.91	644.17	98.06	38.30
450	6.7	62.63	212.53	16.82	7.91	659.83	655.50	99.34	38.97
500	6.6	64.17	213.64	12.90	6.04	663.30	661.58	99.74	51.28
550	6.2	64.50	214.14	16.82	7.85	664.84	644.17	96.89	38.30
600	6.7	51.01	214.11	43.74	20.43	664.73	376.06	56.57	18.41
650	6.7	39.75	214.64	52.71	24.56	666.38	334.27	50.16	6.34

pH of the distilled water used in the test is 5.5.

* Figures represent the soluble part of I-gr sample in percent, under the test conditions.

** B_2O_3/CaO ratio in the sample is 3.10.

It is interesting to note that the temperatures of calcination at which the solubilities of the calcinated samples are maximum, correspond to a rapid water loss in the ulexite mineral. This fact can be easily followed in Figure 3.

B. Tests *performed at* 50°C of *temperature.*— Results obtained from the solubility tests of the original and calcinated ulexite samples in CO_2-containing water, at 50°C of temperature, are shown in Table 4. The values given express the solubility tests of I-hour time.

Table - 4

Temp. of calc. °C	pH at the end of the test	Amount of the dissolved sample (%)*	Amount of CaO in the sample (mg)	Amount of CaO in the solution (mg)	Solution of CaO in the sample (%)	Amount of B_2O_3 in the sample (mg)	Amount of B_2O_3 in the solution (mg)	Solution of B_2O_3 in the sample (%)	B_2O_3/CaO ratio in the solution**
Original	6.4	76.73	138.38	19.07	13.78	429.62	383.02	89.15	20.08
50	6.0	76.12	139.16	11.22	8.06	432.06	383.02	88.65	34.14
100	6.5	76.01	150.74	11.22	7.44	467.99	383.02	81.84	34.14
150	6.6	72.29	163.28	8.97	5.49	506.92	424.80	83.80	47.36
200	6.0	66.53	192.19	5.61	2.92	596.69	494.44	82.86	88.13
250	6.1	66.13	197.27	5.61	2.84	612.47	494.44	80.73	88.13
300	6.1	65.51	203.20	5.61	2.76	630.86	536.23	85.00	95.58
350	6.5	64.36	207.15	5.61	2.71	643.14	543.19	84.46	96.82
400	6.2	63.09	211.59	5.61	2.65	656.91	564.08	85.87	100.55
450	6.1	62.24	212.53	5.61	2.64	659.83	574.98	87.14	102.49
500	6.1	62.22	213.64	5.61	2.62	663.30	567.57	85.57	101.17
550	6.1	61.90	214.14	5.61	2.62	664.84	567.57	85.37	101.17
600	6.0	62.08	214.11	8.97	4.19	664.73	578.01	86.95	64.44
650	6.0	62.34	214.64	11.22	5.23	666.38	605.87	90.92	54.00

pH of the distilled water used in the test is 5.5.

* Figures represent the soluble part I-gr sample in percent, under the test conditions.

** B_2O_3/CaO ratio in the sample is 3.10.

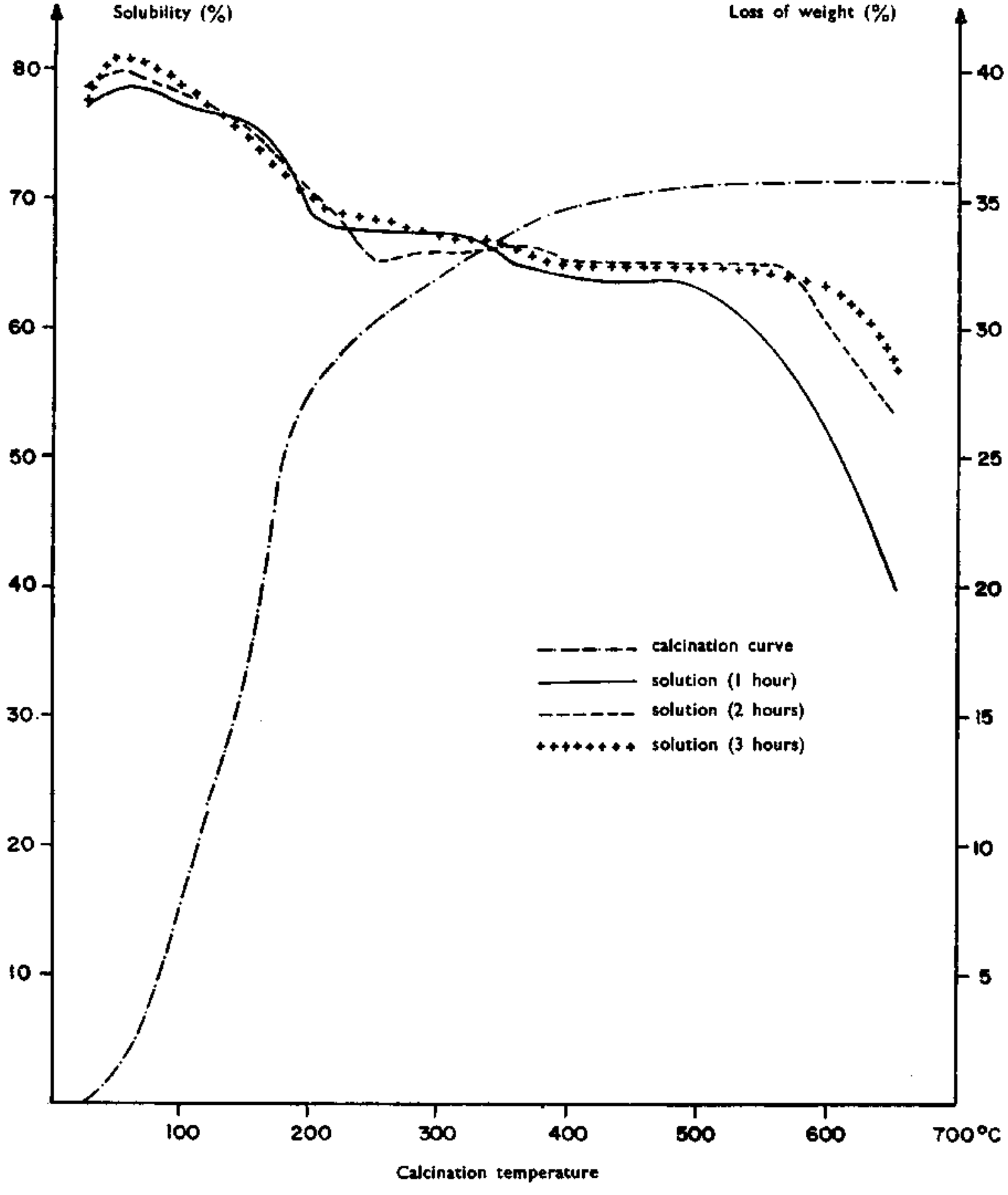

Fig. 3 - Solubility of ulexite at room temperature.

It is apparent that the effect of temperature upon the solubilities of both original and calcinated ulexite minerals in CO_2-containing water is very slight, as it is observed in the comparison of Tables 4 and 3.

However, the temperature has important effect on the solution of B_2O_3 which is also observed from the investigation of B_2O_3/CaO ratio in the tables. For example, in solid ulexite sample calcinated at 400-550°C, the B_2O_3/CaO ratio is 3.10, while the same ratio is 38-50 for room temperature, and it is 100-105 for 50°C solutions.

The solution period of 2 or 3 hours lowers the value of this ratio B_2O_3/CaO. The reason being that the $CaCO_3$ form in the beginning is dissolved as Ca $(HCO_3)_2$ with CO_2. Thus, Ca^2+ ion concentration increases while the B_2O_3/CaO ratio diminishes (Fig. 4).

3. Solution of crystals

Besides the previously described studies, solution tests were also carried out with ulexite crystals, approx. I gr each in weight. The methods applied and the apparatus used were the same. The tests were conducted at room temperatures and at 50°C, during 1,2 and 3 hours. Results of the tests are given in Table 5.

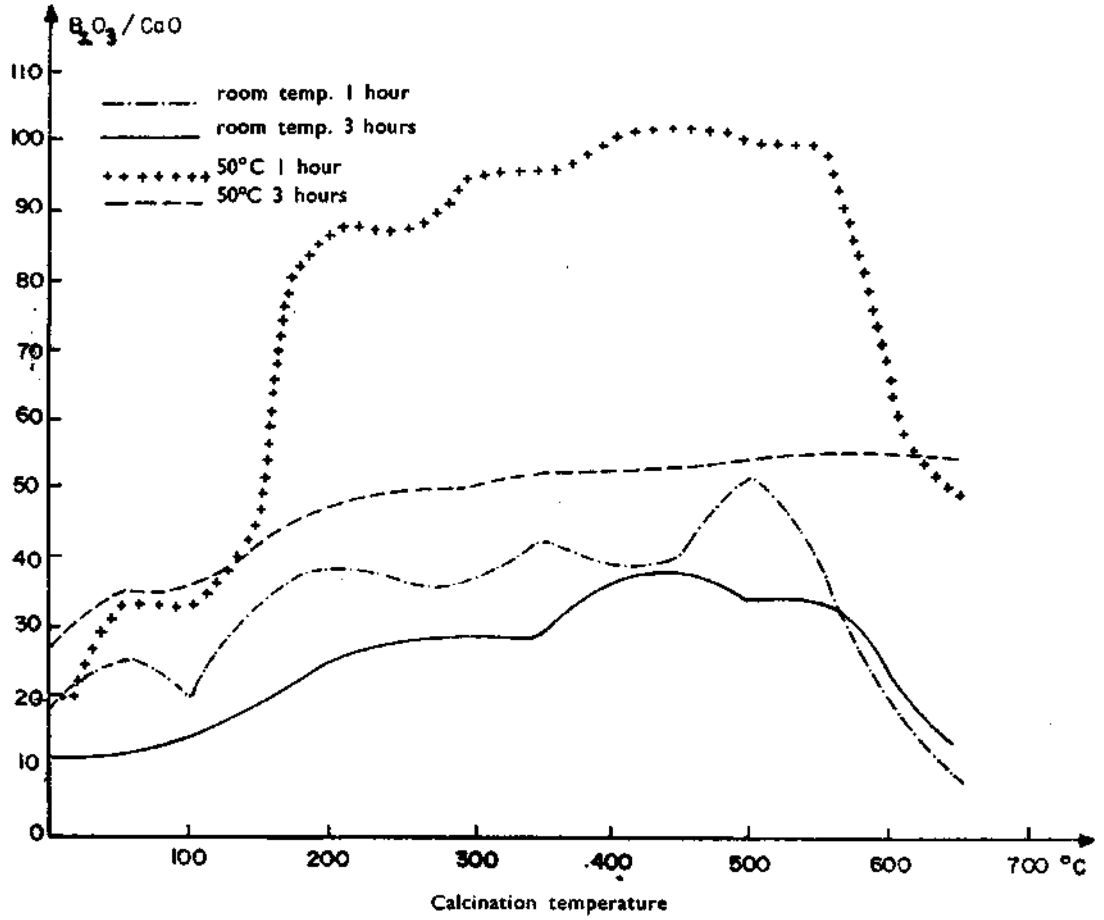

Fig. 4 - Effect of the temperature upon the solubility of ulexite.

The figures in Table 5 indicate that the solubility of ulexite crystals is directly proportional to temperature and time. However, this is not the case for the rate of solubility. Because, while the solubility rate at 50oC during 1-hour period is 71 % more than that at room temperature (13.44-23.86 %), it decreases to 60 % and 37 % during 2- and 3-hour periods, respectively. Moreover, it can be said that the temperature of solution is rather more in favor of B_2O_3 solution (see column «B_2O_3/CaO» in the Table).

4. Tests of continuous solubility

Solubility tests so far carried out for max. 3 hours time indicated that, when conditions are right, crystals could be dissolved completely. For this purpose, some tests were made in order to attain complete solution of the ulexite crystals at room temperature by using an apparatus shown in Figure 5.

A crystal sample of approx. 5-gr weight is placed in vessel (A), where distilled water flows from reservoir (B) with a flow rate of 50 ml/hour. A carbon dioxide flow, supplied by a CO_2-tube, is sent to vessel (A) at a stable rate. The overflow from vessel (A)—which is regularly agitated—passes through pipe (C) and is gathered in vessel (D), where, previously, some NaOH was placed. When vessel (D), which is I liter in volume, is filled, it is replaced by an empty one, and the amount of B_2O_3 in the vessel is measured.

This test was successfully conducted until the total B_2O_3 content of a 5-gr crystal in vessel (A) was transported to vessel (D). After the process of solution was completed, i.e. the total B_2O_3 content of the crystal sample in vessel (A) was transported to vessel (D), it was analytically proved that a $CaCO_3$ mass, equivalent to the CaO content of the crystal, remained in vessel (A).

Table - 5a

Solubility of ulexite crystals at room temperature

Time (hour)	pH at the end of tests	Amount of the soluble sample (%)*	Amount of CaO in the sample (mg)	Amount of CaO in the solution (mg)	Solution of CaO in the sample (%)	Amount of B_2O_3 in the sample (mg)	Amount of B_2O_3 in the solution (mg)	Solution of B_2O_3 in the sample (%)	B_2O_3/CaO ratio in the solution**
1	6.1	13.44	138.38	11.22	8.11	429.62	34.82	8.10	3.10
2	6.2	21.25	138.38	28.04	20.26	429.62	90.53	21.07	3.23
3	6.2	24.72	138.38	33.65	24.62	429.62	111.42	25.93	3.31

Table - 5b

Solubility of ulexite crystals at 50°C

Time (hour)	pH at the end of tests	Amount of the soluble sample (%)*	Amount of CaO in the sample (mg)	Amount of CaO in the solution (mg)	Solution of CaO in the sample (%)	Amount of B_2O_3 in the sample (mg)	Amount of B_2O_3 in the solution (mg)	Solution of B_2O_3 in the sample (%)	B_2O_3/CaO ratio in the solution**
1	5.8	23.86	138.38	22.43	16.21	429.62	83.57	19.45	3.72
2	5.8	33.86	138.38	28.04	20.26	429.62	118.39	27.56	4.22
3	5.6	33.60	138.38	29.14	21.04	429.62	153.21	35.66	5.26

pH of the distilled water used in the tests is 5.5.

* Figures represent the soluble part of I gr of the sample in percent, under the test conditions.

** B_2O_3/CaO ratio in the sample is 3.10.

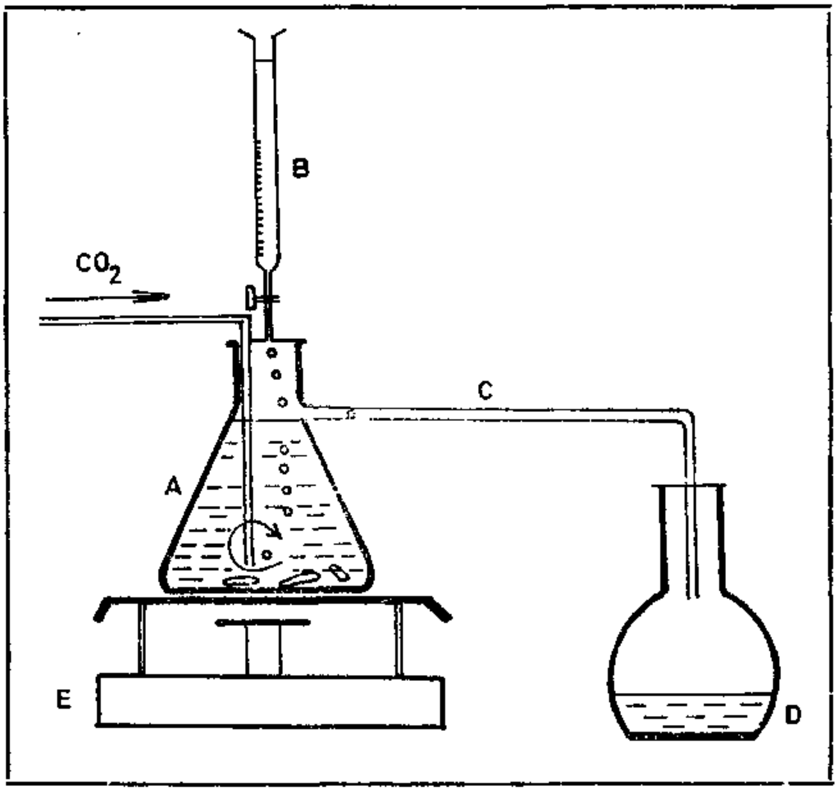

Fig. 5 - Apparatus in which continuous solution tests are performed.

A - Reaction vessel; B - Reserve of distilled water; C - Flow pipe; D - Collecting vessel.

Thus, the following results were obtained:	Gr
Weight of the ulexite crystal	5.009
CaO content of the crystal	0.692
Equivalent of $CaCO_3$: 0.692×(100/56)	1.235
Weight of $CaCO_3$ in vessel (A)	1.220

Results obtained from continuous solubility tests are given in the following table:

5-gr crystal compound of $Na_2O.2CaO.5B_2O_3.16H_2O$	*Theoretical amount (mg)*		*Time of solution*	
	CaO	B_2O_3	B_2O_3 (mg) solved in the 1st week	B_2O_3 (mg) solved in the 2nd week
	692	2149	2143	—

It was determined that ulexite mineral is completely solved in one week and is converted into CaO. However, in another test it was shown that it takes more than three weeks to dissolve the same amount of colemanite mineral.

The solubility tests on ulexite mineral in CO_2-containing water, with a pH value of 12, were repeated both at room temperature and at 50°C, and it was established that pH of the solvent did not produce any noticeable effect on the solubility procedure.

CONCLUSION

These tests show that the solubility of ulexite mineral in water can be increased by addition of CO_2. However, the degree of solubility of this mineral in water containing CO_2 is inversely proportional to the calcination temperature of the mineral.

Provided that when the tests are carried out in a stable medium, the time has practically no effect on solution. In a stable medium the solution process is observed to develop rather in favor of B_2O_3 content of the mineral. In the solubility tests carried out in this way, the CaO content of the mineral is converted into $CaCO_3$ which is partly soluble, as seen in the following equation:

$$CaCO_3+CO_2+H_2O \rightleftarrows Ca\,(HCO_3)_2$$

It has been noted that the temperature of the solvent did not produce any noticeable change at the solubility of the mineral.

Finally it was proved that, provided the solution is continually renewed, the ulexite mineral in the form of $Na_2O.2CaO.5B_2O_3.16H_2O$ compound can be entirely converted into $CaCO_3$.

Thus, it seems possible that under favorable conditions of exploitation, production of boric acid from the ulexite mineral, using the CO_2-treatment method, is feasible.

Manuscript received January 26, 1977

Translated by: Leyla OKAY

REFERENCES

1 — GÜLENSOY, H. & SAVCI, H. (1976): Solubilities of calcium minerals and compounds In EDTA. *M.T.A. Bull.,* no. 86, Ankara.

2 _ IMAMULDINOVA, V.M. (I967a): *Zh. Prikl. Khim.* 40 (II), 2593-6.

3 ————(19676): *Zn. Prikl. Khim.* 40 (II), 2596-8.

4 ————(1970): *Zh. Prikl. Khim.* 43 (2), 425-8.

5 ————& BIRKCHUROVA, A.Kh. (1967): *Zh. Prikl. Khim.* 40 (7), 1616-18.

6 ————& VLADYKINA, A.M. (1965): *Zh. Prikl. Khim.* 42 (5), 1172-5.

7 — KIM, G.E.; BEREMZHANOV, B.A. & KARAZHANOV, N.A. (1973): *Tr. Inst. Khim. Nefti. Prir. Solei. Akad. Nauk. 5,* 19-23.

8 — LAWRENCE, L. (2 Aug. 1974): Ger. Offen. 2,337,506 21 Feb. 1974. Appl. 277, 347.

9 — MARDENENKO, V.K.; KARAZHANOV, N.A. & KALACHEVA, V.G. (1974): *Zh. Prikl. Khim.* 47 (2), 439-41.

10 _ MUNN, A.I.; RADINOVA, M.A. & LUKONINA, Z.N. (1973): *Tr. Inst. Khim. Nauk.* 36, 70-5.

11 _ NAURUZOVA, G.Kh. & BEN'KOVSKII, V.G. (1973): Tr. *Inst. Khim. Nefti. Prir. Solei.* 5.41-53.

12 — Solvey et Ciebolg. Appl. 797, 137. 21 Mar. 1973, 9 pp.

13 — SPIRYAGINA, A.I. (1953): *Inst. Galurjii.* 27, 77-83.

14 _ TUĞTEPE, M. & SANIGÖK, Ü. (I962a): Rev. Fac. Sci. İ*st.* 27-2, 98-114.

15——————&————(I962b): Rev. Fac. *Sci. İst.* 27-2, 114-37.

16 — ZDANOVSKII, A.B. & BIKTAGIROVA, L.G. (1967): *Zh. Prikl. Khim.* 40 (12), 2659-63.

17——————& IMAMULDINOVA, V.M. (I963a): *Zh. Prikl. Khim.* 36 (8), 1675-80.

18——————&————(I963b): *Zh. Prikl. Khim.* 37 (5), 1095-9.

19—————(I965o): Sb. Statei. 12-17.

20—————(I965b): Sb. Statei. 17-21

21—————; STREZHNEVA, I.I. & TKACHEV, K.K. (1973): *Zh. Prikl. Khim.* 46 (10), 2303-5.