Available online at www.sciencedirect.com
ScienceDirect
Thermochimica Acta 452 (2007) 49–52
thermochimica acta
www.elsevier.com/locate/tca

Thermal requirements to obtain calcined and frits of ulexite

Horacio R. Flores, Silvana K. Valdez *

Instituto de Beneficio de Minerales (INBEMI), Facultad de Ingeniería, U.N. Salta, INIQUI (CONICET), Buenos Aires 177, 4400 Salta, Argentina

Received 14 February 2006; received in revised form 11 October 2006; accepted 11 October 2006
Available online 20 October 2006

Abstract

Ulexite has a substantial amount of hydration water, which allows using calcination methods to increase the B_2O_3 content from 42.97 to 66.69%, due to the loss of 35.54% of its weight, corresponding to its hydration water.

In this study, determinations of changes in the heat content at each temperature were made using an isoperibol calorimeter. The mean specific heat was calculated from these values. The reaction enthalpy was also determined by DTA methods.

The sample used in the experiments contains 39.04% B_2O_3. The temperature was between 80 and 1000 °C. Curves of weight loss and enthalpy changes are presented and analysed.

The results have industrial application in order to determine the thermal requirements for calcining ulexite at different temperatures, as well as its complete dehydration.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Ulexite; Dehydration; Calorimetry; Specific heat

1. Introduction

The main boron minerals of commercial interest are those of sodium (borax), sodium and calcium (ulexite), calcium (colemanite), and calcium and magnesium (hydroboracite). Of these minerals, all of the commercial boron products, such as concentrated, calcined, frits and refined products are obtained. The more common uses of borates are in ceramics, bleaches, detergents, glasses, micronutrients, and others [1].

The principal borates deposits are placed in Turkey, United States of America and in third place in the South American central Andes. In Argentina, at oriental Puna region, there are "hard borates" deposits formed during the Quaternary period (borax, colemanite and hydroboracite). At altiplano region (Peru, Bolivia, Chile, and Argentina) there are several depressions (playas or brine deposits) where the dominant boron mineral is ulexite ($NaCaB_5O_9{\cdot}8H_2O$) [1]. This mineral shows specific features which allows concentrating it by physical methods (mechanical separation using sieves, washing in trommel or hydrocyclone), or by means of pyrometallurgical methods (calcinations and fusion). Besides, at altiplano region, it is the only mineral used as raw material to produce boric acid.

Salta is the main producer of ulexite in Argentina. Low grade ulexite (<25% B_2O_3) is destined to the production of boric acid, by dissolving it with a mineral acid (sulphuric or hydrochloric acid). High grade ulexite is exported as concentrated ulexite as well as calcined or smelted ulexite. Treating ulexite by pyrometallurgical means has a lot of economical advantages. It permits an important increase of grade (from 42.97 to 66.69% B_2O_3 for pure mineral because 35.56% of ulexite is hydration water), decreases the shipping costs and increases the mineral price.

There is abundant information about the physical and chemical properties of sodium borates (borax) and of boric acid, but the referring data to the species of local interest, such as ulexite are little or null. On the matter, Sener and Özbayoglu [2] determined the structural changes on ulexite and colemanite which are useful to their separation using physical methods. Ruoyu et al. [3] obtained experimental data of molar enthalpies of solution of ulexite. Erdogan et al. [4] studied the dehydration kinetics of howlite, ulexite and tunellite from TG data. Sener et al. [5] presented a study of the changes happened in the structure of the ulexite during its heating. Celik and Suner [6] analysed the thermodynamic data presented by S. Piskin at his doctoral thesis (1982), who pointed that ulexite starts dehydration at 59 °C and decomposes at 449 °C. The change of enthalpy preced-

* Corresponding author. Tel.: +54 387 4255412; fax: +54 387 4255374.
E-mail addresses: hrflores@unsa.edu.ar (H.R. Flores), svaldez@unsa.edu.ar (S.K. Valdez).

0040-6031/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2006.10.007

ing dehydration (between 25 and 59 °C) has been calculated as 27.04 J mol^{-1}. However, C_p determinations at different temperatures and dehydration and fusion heat have not been determined with accuracy due to the fact that dehydration process occurs in several steps and ulexite has not got a defined change when transforming solid into liquid (it has glass behaviour).

The results of thermogravimetric determinations are affected strongly by heating rate, which was proved by Sener and Özbayoglu [2]. Sener et al. [5] show the loss of 1.5 mol of water up to 118 °C, 6 mol up to 260 °C and the last 2 mol between 260 and 500 °C; partial fusion starts at 850 °C. Erdogan et al [4] found out that 1.9 mol of water are lost at 100 °C, 6 mol at 300 °C and the loss is completed at 530 °C. Ersahan et al. [7] observed that dehydration starts at 100 °C and it is really fast at temperatures higher than 230 °C; they pointed that 6 mol of water are lost at 210 °C and there is no weight loss after 530 °C. In Fig. 2 are included the results of weight loss determinations tested on furnace and kiln by Flores [8]. They were tested at constant temperature until the weight loss was constant. The residence time was between 5 and 20 h. In such conditions 2 mol of water are lost at 87 °C, 4 mol up to 148 °C, one up to 230 °C and the last one at 510 °C. The dehydration reaction can be expressed with the equation:

$$NaCaB_5O_9{\cdot}8H_2O \rightarrow NaCaB_5O_9(8-n)H_2O + nH_2O \quad (1)$$

At temperatures higher than 600 °C ulexite particles first agglomerate weakly keeping their shape and individuality, then this union gets stronger and takes the appearance of a sinter. Fusion process occurs after 800 °C and the viscous liquid obtained occupies the same volume as the original solid. This feature is lost at 900 °C.

Because of the observations above, the temperature of calcination furnaces is about 600 °C, whereas in fusion furnaces it is 1000 °C or higher to obtain an homogeneous and fluid liquid (easy to discharge) [8].

This paper describes the experimental techniques and shows the results of pyrometallurgical tests carried out to obtain the change of enthalpy between 25 and 1000 °C of a commercial sample of concentrated ulexite.

2. Materials and methods

The selected sample used throughout the study came from Centenario deposit (Salta, Argentina). The previous preparation of the sample was made at the deposit itself and consisted of grinding to −2″ and mechanical classification by sieves of 3 mm to eliminate gangue with fines. This pre-concentrated sample was washed with water to eliminate soluble gangue (mainly sodium chloride) and dried in a laboratory furnace at low temperature (50 °C). Then it was ground to 1 mm. Thus, the sample prepared contains L = 39.04% B_2O_3, 5.41% Na_2O and 12.39% CaO expressed on a dry basis. This corresponds to a purity of 90.85% (purity $P = 100L/43$).

To determine the heat of dehydration a thermobalance was made with an electrical furnace and a balance. The furnace, trade mark Indef I^2r, is provided with a temperature controller DHACEL DH 15. The balance, METTLER PB 3002-S, was placed above the furnace. It was connected to a data acquisition system, TerminalLab 2000. A holder hangs from the balance into the furnace. It allows setting two stainless steel sample vessels inside the furnace and measuring their weight continuously (at the test temperature). Each vessel has a K type thermocouple which measures the temperature inside the sample. The data are registered on thermometer Data Logger Delta Ohm DO9416, for thermocouple probe input.

One of the vessels is filled with anhydrous ulexite (which has been previously calcined at 600 °C). This is the inert substance and its weight is W_I. The other one contains the sample to test, which weighs W_{So}. The weights are about 150 g each.

The system was heated to the desired temperature at 3.4 °C/min. This temperature remained constant until the sample weight (W_S) remained constant and the difference of temperature between the sample and the inert was null. The temperature of the sample θ_S and temperature of the inert θ_I as well as total weight W_T were registered every 30 s.

With these data it was calculated for each interval j:

$$\text{sample weight (g)}: \; W_S = W_T - W_{acc} - W_I$$
$$\text{with } W_{acc}: \text{ weight of all accessories} \quad (2)$$

$$\text{accumulative weight loss (\%)}: \; \Delta W = 100 \times \frac{W_{So} - W_S}{W_{So}} \quad (3)$$

$$\text{moles } H_2O \text{ lost/mol ulexite}: \; -nH_2O = \frac{8\Delta W \times 100}{35.56\,P}, \quad 0 \le n \le 8 \quad (4)$$

$$\text{difference of temperature (°C)}: \; \Delta\theta_j = (\theta_I - \theta_S)_j \quad (5)$$

$$\text{partial area } \Delta A_j(°\text{C min}): \; \Delta A_j = \Delta\theta_j \Delta t, \quad \text{with}$$
$$\Delta t = 0.5\,\text{min} \quad (6)$$

$$\text{accumulative area, } \Delta A\ (°\text{C min}): \Delta A = \sum_1^j \Delta A_j \quad (7)$$

The area ΔA is proportional to the heat involved in the thermal decomposition which occurred in the sample. To determine this proportional constant C the thermobalance was calibrated by heating two samples of anhydrous ulexite. One of them acted as inert material and the other was moisturized with a certain mass of water W_W. Therefore:

$$W_W\,[C_{pW}\,(100-25) + \lambda_{vap}] = C\Delta A, \quad (8)$$

where C_{pW} = 4.18 J/g °C and λ_{vap} = 2257.2 J/g.The mean value of C for five calibrations was: $C = 10.99 \pm 0.50$ J °C^{-1} min^{-1}.

Taking into account that ulexite is the only reactant, the reaction heat up to j interval would be:

$$Q_r = \frac{100C\sum_1^j \Delta A_j}{PW_S}, \text{ J/g ulexite} \quad (9)$$

To this method, each vessel has to be heated at the same rate, the sample and inert have to occupy approximately the same volume, the specific heat must be similar and other considerations pointed out by Currel [9].

The heat content at different temperatures was determined considering the hydration grade and the aggregation state of sample. The temperatures were 82 and 93 °C (solid samples, $n < 2$), 253 and 264 °C (solid sample, $n = 7$), 522, 711, and 750 °C (anhydrous solid, $n = 8$), 840 °C (doughy anhydrous sample) and 900 and 1000 °C (liquid samples).

To measure the amount of heat absorbed during heating at each temperature an isoperibol calorimeter was used, where the temperature of the surrounding was constant. It consists of a 2000 cm^3 plastic container with a cover of the same material, covered externally by an insulating wall made of expanded HD polystyrene of 3.5 cm thick. This container was fill with water. Suspended of the edges and partially submerged in the water, there is a vessel made of stainless steel. The test sample was heated to the desired temperature in the thermobalance, registering weight and temperature at each time, and then, rapidly dropped into the metal vessel inside the calorimeter. The temperature of the water inside the calorimeter was measured before, during and after finalizing the test, by means of K type thermocouples.

First, the water equivalent of the calorimeter was measured. The water equivalent is the heat capacity of the calorimeter and corresponds to the sum of the heat capacities of all the constituent parts of the calorimeter: isolated container, agitator, thermocouple and support glass [10]. The calibration was made by electrical heating. The heat was given by a submerged resistor to which a voltage V was applied. The circulating current and the time needed to reach a certain increase in the temperature of the water ($\Delta\theta$) were measured. As the electrical heat input is equal to the sum of the heat absorbed by the water and the heat absorbed by the calorimeter, the water equivalent K was calculated.

Five different determinations of $\Delta\theta$ (between 40 and 50 °C) were made, obtaining an average value of 172.1 ± 7.0 cal/°C. As verification, the specific heat of the stainless steel container was measured warming it up in the electrical furnace until a temperature of about 620 °C and measuring the heat yielded to the water of the calorimeter. A value of specific heat of 0.1 cal/g °C was obtained, concordant with data for stainless steel given in the bibliography [11].

An additional result can be obtained from liquid samples due to the fact that the heat released into the calorimeter includes the fusion heat. So, subtracting the curve of heat content of solid samples, Q_s, from that of heat content of liquid samples, Q_{s+fus}, the fusion heat can be obtained:

$$\lambda_{fus}\,(J/g) = \frac{[Q_{s+fus}(\text{liquid}) - Q_s(\text{solid})]_{\theta_s=\theta_{fus}}}{W_S} \quad (10)$$

Note that both curves are extrapolated to the fusion temperature $\theta_S = \theta_{fus}$.

Knowing Q_s, Q_r, $-nH_2O$, θ_S, as time function the curves $Q_S(\theta_S)$, $Q_r(\theta_S)$, and $-n_{H_2O}(\theta_S)$ can be determined and, with them, the change of enthalpy of the samples at any temperature:

$$\Delta H(J/g) = Q_s(\theta_S) + Q_r(\theta_S) + \lambda_{fus} \quad (11)$$

3. Results and discussion

Fig. 1 shows the curves obtained from a test on thermobalance. It shows the dependence on time of the inert temperature, sample temperature, difference $\Delta\theta = \theta_I - \theta_S$ and loss of weight.

Note that the weight loss occurs between 31 and 169 min, when the sample temperature varies between 57.2 and 501 °C. The curve of difference of temperature starts at 34 min and ends at 207 min. The fact that θ_I is higher than θ_S indicates that the dehydration reaction is endothermic.

Fig. 2 shows the reaction heat Q_r, calculated with Eq. (9), with $34 \le j \le 207$ min. It also shows the weight loss expressed as mol of water per mol of ulexite compared to that obtained by Flores [8].

From an industrial point of view, it is interesting to determine Q_r at the lowest temperature, but suitable with a high dehydration. For instance, to eliminate 7 out of 8 moles of hydration water of ulexite it requires a temperature $\theta_S \ge 263.8$ °C, and $Q_r = 923.78$ J/g ulexite. This value could be smaller than the true

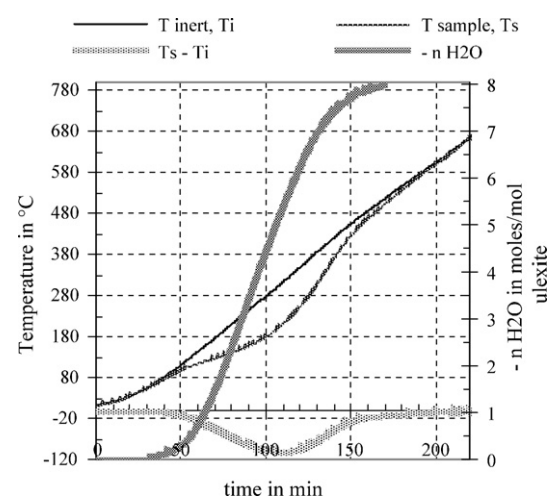

Fig. 1. Temperature of inert and sample, and weight loss vs. time.

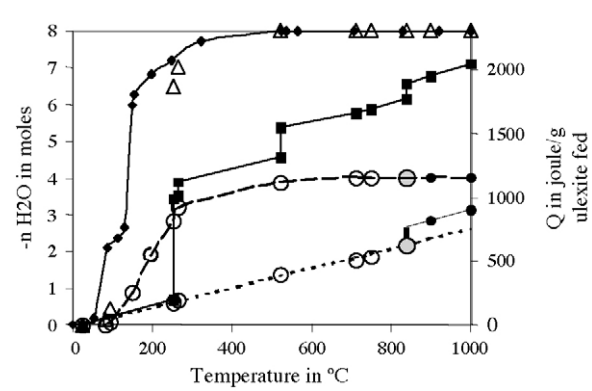

Fig. 2. TG, heat content, heat of reaction and enthalpy vs. temperature curves for ulexite. (♦) TG by Flores [8]; (■) enthalpy; (—) Q fusion (•) liquid; (△) $-nH_2O$; (◯) Q reaction; (· · ·) heat content; (◯) doughly solid.

value, because of the delay of the loss of weight curve respect to the difference of temperature $\Delta\theta$ as time function. Total dehydration occurs with temperatures higher than 522 °C, it requires 1152.63 J/g ulexite, calculated with Eq. (9) with $j = 207$ min, when $\Delta\theta = 0$ and $-n_{H_2O} = 8$.

To represent the heat absorbed during heating the same criterion was used. Temperatures below 250 °C were not considered because dehydration is small. Between 250 and 840 °C (incipient fusion) a linear variation was obtained. It can be represented by:

$$Q_s(\text{J/g fed}) = C_{p_s}(\theta_S - 25) \quad (12)$$

where $C_{p_s} = 0.765 \pm 0.021$ J/g °C, it is the mean value calculated from Eq. (12) with the experimental data.

Eq. (12) is also suitable for temperatures higher than 840 °C adding 147.97 J/g ulexite fed. This value corresponds to the heat required for fusion process.

The change of enthalpy of a sample of concentrated ulexite which has no other volatile compounds, with a purity P (%) and specific heat C_{p_s} is:

$$\Delta H(\text{kJ/kg}) = C_{p_s}(\theta_S - 25) + 9.24P, \quad 264 \le \theta_S \le 522 \quad (13)$$

$$\Delta H(\text{kJ/kg}) = C_{p_s}(\theta_S - 25) + 11.54P, \quad 522 \le \theta_S \le 840 \quad (14)$$

$$\Delta H(\text{kJ/kg}) = C_{p_s}(\theta_S - 25) + 11.54P + 147.97, \quad \theta_S > 840\,^\circ\text{C} \quad (15)$$

These equations correspond to the thermal requirements to heat 1 kg of ulexite with P purity up to θ_S temperature and attain an 87.5% dehydration, total dehydration and dehydration followed by fusion, respectively.

4. Conclusions

The average specific heat of ulexite is $C_{p_s} = 0.765 \pm 0.021$ J/g °C between 250 and 840 °C.

The heat of fusion of the ulexite was determined as 147.97 J/g ulexite.

The heat required for eliminate 7 out of 8 mol of water is 923.78 J/g ulexite. And the heat needed for total dehydration is 1152.63 J/g ulexite.

The amount of heat required to raise the temperature of 1 kg of ulexite to a temperature θ can be determined with Eqs. (13)–(15) depending on the temperature.

These results have industrial importance because they allow knowing the thermal requirements for a specific pyrometallurgycal treatment of ulexite.

References

[1] D.E. Garret, Handbook of Deposits, Processing, Properties and Use, Academic Press, San Diego, CA, USA, 1998, pp. 183 401–427.
[2] S. Sener, G. Özbayoglu, Miner. Eng. 8 (6) (1995) 697–704.
[3] C. Ruoyu, L. Jun, X. Shuping, G. Shiyang, Thermochim. Acta 306 (1997) 1–5.
[4] Y. Erdogan, A. Zeybek, A. Sahin, D. Demirbas, Thermochim. Acta 326 (1999) 99–103.
[5] S. Sener, G. Özbayoglu, S. Demirci, Thermochim. Acta 362 (2000) 107–112.
[6] M.S. Celik, F. Suner, Thermochim. Acta 245 (1995) 167–174.
[7] H. Ersahan, M. Tunc, A. Ekmekyapar, S. Yapici, Thermochim. Acta 250 (1995) 125–135.
[8] H.R. Flores, El Beneficio de los Boratos, Crisol (Ed.), Salta Arg., 2004, pp. 125, 278, 280.
[9] B.R. Currel, in: F.S. Robert, Paul Garn (Eds.), Application of Thermal Analysis to the Quantitative Measurement of Enthalpy Changes in Thermal Analysis, vol. 2, Academic Press, Inc., United States of America, 1969, pp. 1185–1188.
[10] O. Kubaschewski, C.B. Alcock, Metallurgyical Thermochemistry, 5th ed., Pergamon Press, 1979, pp. 70–88.
[11] R.H. Perry, D.W. Green, J.O. Maloney, Manual of the Chemical Engineer, vol. 1, 6th ed., McGraw Hill, 2000, pp. 3–176.