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Dehydration of ulexite by microwave heating

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Abstract

Microwave heating of a solid state reaction is an established application in inorganic chemistry. Dehydration of ulexite samples having different particle sizes were investigated using 150, 300, 450 and 600 W, 2450 MHz microwave radiation energy. The rate and temperature increase with decreasing particle size and increasing microwave power.

Keywords: Microwave; Dehydration; Ulexite

1. Introduction

About 62% of the world's known boron reserves are in Turkey [1,2]. Boron minerals are hydrated borates combined with alkaline-earth and alkaline-boron metals such as Na, Ca, and Mg. The boron reserves commercially recoverable are mostly in the form of hydrated boron minerals such as pandermite $Ca_4B_{10}O_{19}\cdot 7H_2O$, ulexite $NaCaB_5O_9\cdot 8H_2O$, tincal (borax) $Na_2B_4O_7\cdot 10H_2O$ and colemanite $Ca_2B_6\ O_{11}\cdot 5H_2O$ [3].

Dehydration of hydrated boron minerals is important in the production of boron compounds [4]. The dehydration has been investigated generally with thermogravimetric methods. Şener et al. determined the thermal reactions of ulexite by TG, DTG and DTA. Decomposition occurred from 60 to 500 °C with two steps followed by two dehydroxylation stages [4]. Erdoğan et al. analysed the dehydration kinetics of howlite, ulexite, tunellite by DTA and TG methods. Activation energies, rate constants and pre-exponential factors were calculated. The dehydration reactions were first order [2]. Tunç et al. investigated the kinetic parameters of thermal decomposition of ulexite by TGA. The Suziki and Coats–Redfern methods were applied. The process was first-order and the activation energy and frequency factor decreased with decreasing particle size [1]. Okur and Eymir studied calcination kinetics of ulexite by thermogravimetry (TG) with Coats–Redfern and genetic algorithm methods. They concluded that the Coats–Redfern method would not be used for reactions having low activation energies [5]. Davies et al. investigated thermal decomposition of powdered colemanite by flash calcination. The study demonstrated an optimum calcination temperature around 600 °C. Calcines produced at this temperature have a very porous structure, probably caused by explosive dehydroxylation [3]. Çelik and Suner studied the decrepitation properties of colemanite and ulexite. A thermodynamic evaluation of fourteen boron minerals has shown that only colemanite exhibits decrepitation [6].

When boron minerals are heated, the mineral first loses water of crystallization, followed by production of amorphous material or recrystallization into new phases. Colemanite decrepitates as a result of the sudden release of confined water vapour within micropores during thermal treatment, while ulexite does not decrepitate. Instead, it exfoliates as a result of gradual water vapour removal, and the structure becomes amorphous with numerous microcracks and interstices [4].

Recently, the method of microwave heating has been finding wider and wider applications in synthesis and processing of materials because the heating is due to the interaction

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between microwaves and materials [7–11]. During microwave heating, materials having small, polar molecules absorb microwave energy more than others. Microwave heating provides advantages as a volumetric heating rather than the surface heating and thermal diffusion afforded by conventional heating. Very fast heating rates (several degrees per second) can be obtained, depending on the microwave power used in relation to volume [12]. Microwave equipment can be adapted easily to automated systems, can be quickly started and stopped, and its power level can be adjusted electronically [13]. Microwaves can offer considerable energy savings and a shortening of processing times. In addition, in microwave heating it is possible to control the spatial distribution of the energy transferred to the material. That is, it is possible to heat the materials either in selected, localised regions or more uniformly, depending on the specific application [14].

With microwaves, the energy transfer is not primarily by conduction or convection as in conventional heating, but by dielectric loss. Thus, propensity of a sample to undergo microwave heating is highly dependent on its dielectric properties. The dielectric loss factor (loss factor; ε'') and the dielectric constant (ε') of a material are two determinants of the efficiency of heat transfer to the sample (for the ulexite sample used in this study, the dielectric loss factor ε'' and the dielectric constant ε' were measured as respectively 0.2294 and 8.7314). Their quotient ($\varepsilon''/\varepsilon'$) is the dissipation factor ($\tan\delta$), high values of which indicate ready susceptibility to microwave energy. Materials dissipate microwave energy by two main mechanisms: dipole rotation and ionic conduction. At 2450 MHz, the field oscillates 4.9×10^9 times per second, and sympathetic agitation of molecules generates heat. The efficacy of heat production through dipole rotation depends upon the characteristic dielectric relaxation time of the sample, which in turn, is dependent on temperature and viscosity. The second dissipation mechanism, ionic conduction, is the migration of dissolved ions with the oscillating electric field. Heat generation is due to frictional losses which depend on the size, charge, and conductivity of the ions, and their interactions with the solvent [7].

Microwave heating of solid state reaction mixtures is the most established application in inorganic chemistry. Reactions can be considerably accelerated by microwave irradiation. Rate enhancement factors up to over one thousand, in comparison with classical methods of heating, have been recorded. This remarkable rate increase was attributed microwave heating having “specific effects” or “non-thermal effects” [10,15,16]. Thermal analysis using microwave radiation was investigated by Karmazsin et al. [17,18] with differential thermal analysis of calcium hydrogen phosphate dihydrate ($CaHPO_4{\cdot}2H_2O$). The experiments were performed in a single-mode microwave cavity. Bond et al. [19] also used microwave radiation to linearly increase the temperature of a sample within the cavity.

Harrison and Rowson [20] investigated the heating rates of pure minerals and concluded that most valuable minerals are good absorbers of microwave energy, but gangue minerals are not. As most mineral ores do not occur in pure form in nature, but as mixtures of valuable minerals and gangue, the different response of the ore components to dielectric heating causes differential heating. Because minerals expand with an increase in temperature, differential stresses occur at the grain boundaries, thereby weaking the material [21] Spherical composites of Fe_2O_3 and carbon were heated with microwave power (2.45 GHz) and their heating rate was studied by Standish et al. [22]. They improved a mathematical model that described the principal features of heating these solids by microwave energy.

2. Experimental

Ulexite samples used throughout the study were supplied from the deposits around Eskisehir-Kirka in Turkey. Hand picked coarse crystals were cleaned by a brush to remove impurities such as dispersed clay minerals. Cleaned samples were crushed and ground by a jaw-crusher and a laboratory type ball mill. Then samples were screened through 1180 and 212 μm ASTM standard screens. Four different particle sizes (−1180 + 850, −850 + 600, −600 + 425, −300 + 212 μm) of the mineral were used in the experiments. The composition of the sample determined by chemical analysis was 7.14% Na_2O, 13.56% CaO, 42.33% B_2O_3, 35.53% H_2O and 1.44% other.

A laboratory type microwave reactor (Fig. 1) with a frequency of 2450 MHz and a maximum output power of maximum1 kW was used. The apparatus occurs from five sections. The first section of the apparatus includes the generator that can be adjusted with manual and automatic control. The second section consists of a PHILIPS microwave circulator with a frequency of 2.475 GHz. The third section is an R26 standard rectangular waveguide. Three manually adjustable stub tuners inserted in the waveguide section and the tuning plunger of the applicator are used to maximize microwave absorption by minimizing the reflected power. The fourth section consists of an MUFGGE DIR COUPLER MM 1002C model coupler that measures reflected power. The fifth part is the cavity section with two 15 mm holes. The bottom one of these holes is open and the other one closed. Mass was measured by an MW II-300 model scale. For temperature measurements, an optical fiber connected to a transducer (PT-100) and Ni–Cr thermocouples were used. The experimental design is given in Fig. 1.

In the study, two pyrex tubes with diameter of 11 mm were used. Microwave irradiated parts of tubes were filled with 2–2.5 g ulexite and they were installed in the applicator at the position of the highest electric field. To measure loss of weight the bottom of first tube was placed on the scale by a Teflon support. The second tube was installed through the other hole in the cavity. Changes in the temperature were determined by means of a PT-100 thermocouple inserted into the second tube. Weight loss and temperature were recorded as a function of time under constant power.

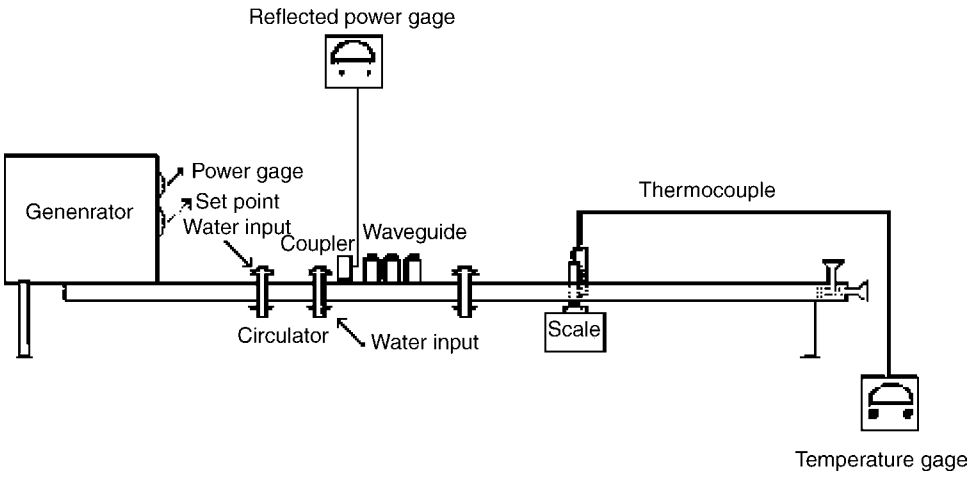

Fig. 1. Microwave experimental design.

During the experiment, real temperature values could not be read because the thermocouple was affected by condensing water vapour. Therefore, at the end of the experiment when the microwave power was off, a Ni–Cr–Ni thermocouple was inserted besides the Pt-100 thermocouple. Then temperatures that both thermocouples displayed were recorded and Pt/Cr–Ni temperature curves were plotted. From these curves, the real temperatures which coincide with the determined temperatures by Pt-100 were obtained.

3. Results and discussion

The dehydration reaction of ulexite is

$$Na_2O \cdot 2CaO \cdot 5B_2O_3 \cdot 16H_2O \rightarrow Na_2O \cdot 2CaO \cdot 5B_2O_3 \cdot nH_2O + (16 - n)H_2O$$

where n is the number of moles of water remaining after dehydration. The fractional decomposition, x, was calculated as the ratio of the mass loss to total mass loss expected from this reaction.

The effect of particle size on the dehydration process of ulexite was investigated with $-1180 + 850$, $-850 + 600$, $-600 + 425$ and $-300 + 212\,\mu m$ fractions at constant microwave power of 300 W. The results are presented in Figs. 2 and 3. To investigate the effect of microwave power on the dehydration process of ulexite, experiments were performed with microwave powers 150, 300, 450 and 600 W at constant particle size $-600 + 425\,\mu m$. Results are shown in Figs. 4 and 5. As the figures show, the fractional decomposition (or rate of the process) and temperatures increase with decreasing of particle size and increasing microwave power.

For comparison conventional heating experiments were conducted in a laboratory type furnace. The furnace was first brought to the temperature reached at the end of 5 min in mi-

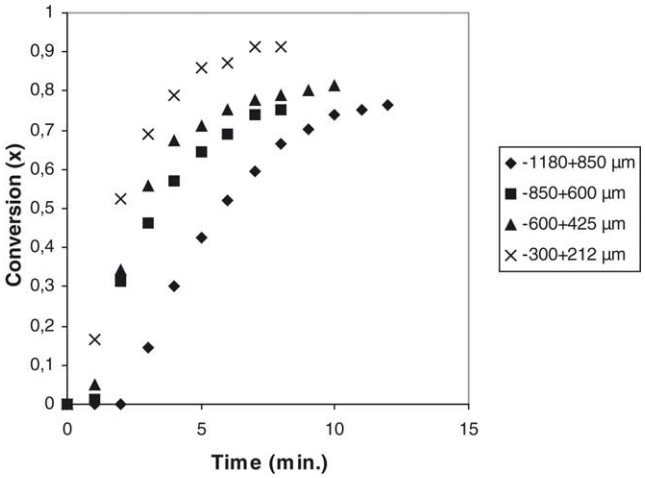

Fig. 2. The effect of particle size on the fractional decomposition (at constant microwave power of 300 W).

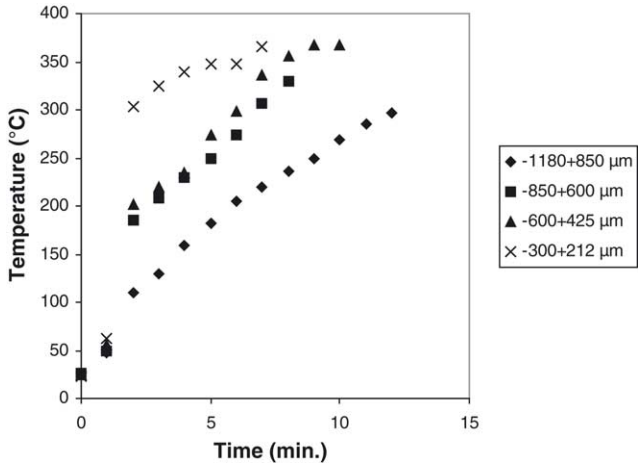

Fig. 3. The effect of particle size on the temperature (at constant microwave power of 300 W).

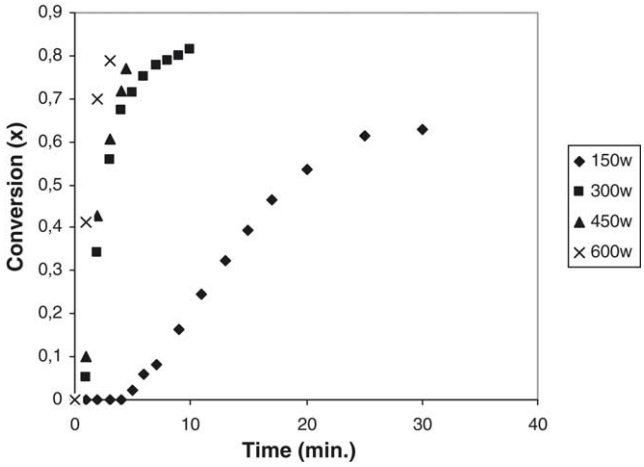

Fig. 4. The effect of power on the fractional decomposition (at constant particle size −600 + 425 μm).

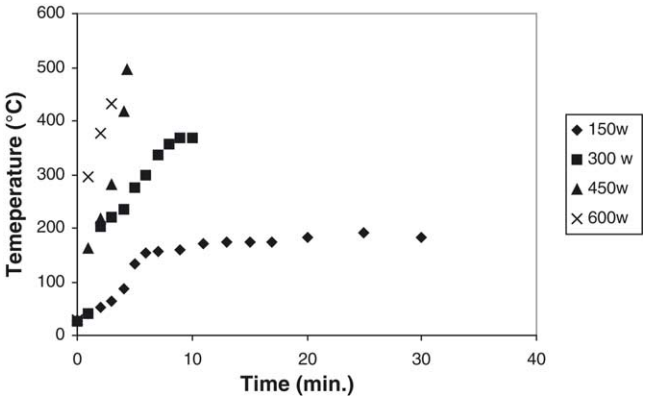

Fig. 5. The effect of power on the temperature (at constant particle size −600 + 425 μm).

crowave experiments. A porcelain crucible with 2–2.5 g ulexite sample was placed in the furnace. At the end of 5 min, the crucible was taken out and weighed to determine the water loss. The results of these tests are presented in Table 1. The increasing fractional decomposition with decreasing particle size is caused by the decreasing intra particle resistance to the escape of water. As seen in Table 1, microwave heating is more effective than conventional heating because of the microwave heating mechanism. The increasing temperature with decreasing particle size arises because there is less void space among little particles. This means more oscillated molecules and more heat produced per unit volume. At the same time it can be said that fewer void space causes fewer heat loss. Microwaves provide heating from center [23]. Heating from center provides a suitable environment for evaporation and diffusion toward the surface. Therefore, it can be said that thermal diffusion is easier in decreasing particle sizes.

Table 1
Comparison of microwave and conventional heating on fractional decomposition at 5 min

Particle size (μm)	T (°C)	x (mw) (%)	x (conventional) (%)
−1180 + 850	182	0.424	0.275
−850 + 600	250	0.643	0.515
−600 + 425	274	0.712	0.580
−300 + 212	348	0.858	0.673

As seen from Figs. 4 and 5, temperature and fractional decomposition increase with increasing microwave power. At an applied power of 150 W, no mass loss was observed until 5 min, and temperature was only 133 °C. When the power was 600 W, a fractional decomposition of 42% and a temperature of 295 °C were obtained. Because of the energy carried by the microwaves increase in the condition of the power increase, the oscillation of the molecules increase as well. As a result, the molecule which oscillate faster occur more heat.

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