

Dehydration of sodium carbonate monohydrate with indirect microwave heating

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Received 17 August 2005; received in revised form 22 June 2006; accepted 23 June 2006
Available online 29 June 2006

Abstract

In this study, dehydration of sodium carbonate monohydrate ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$) (SCM) in microwave (MW) field with silicon carbide (SiC) as an indirect heating medium was investigated. SCM samples containing up to 3% free moisture were placed in the microwave oven. The heating experiments showed that SCM is a poor microwave energy absorber for up to 6 min of irradiation at an 800 W of microwave power. The heat for SCM calcination is provided by SiC which absorbs microwave. The monohydrate is then converted to anhydrous sodium carbonate on the SiC plate by calcining, i.e. by removing the crystal water through heating of the monohydrate temperatures of over 120 °C. The calcination results in a solid phase recrystallization of the monohydrate into anhydrate. In the microwave irradiation process, dehydration of SCM in terms of indirect heating can be accelerated by increasing the microwave field power.

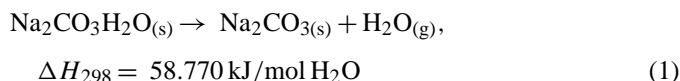
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Keywords: Mineral processing; Sodium carbonate monohydrate; Drying; SiC; Microwaves

1. Introduction

Sodium carbonate, soda ash are used as a source of Na_2O in the glass manufacture, in the production of various sodium chemicals for water treatment, paper production, iron desulphurization, and many other uses. Although, production from brines and fossil trona deposits is becoming increasingly important, soda ash is mostly produced synthetically with Solvay process which requires common salt and limestone by some 60 solvay plants in the more than 40 countries [1]. The sodium carbonate is recovered from its aqueous solution as sodium carbonate monohydrate by atmospheric evaporative crystallization. The monohydrate is then converted to anhydrous sodium carbonate by calcining, i.e. by removing the crystal water through heating of the monohydrate to temperatures of 120 °C or higher (see Eq. (1)). In addition to this Gärtner [2], Garrett [3], Haynes [4], Aitala and Aitala [5] gave excellent reviews of the current state-of-the-art processes and feasible process

alternatives:



The drying and dehydration of the monohydrate is carried out more frequently in steam-tube rotary dryers where the crystals are dehydrated into anhydrous soda ash at 150–200 °C; however, fluidized bed dryers are also used [3,6]. The final product made by the monohydrate process is dense soda ash. Both these dryers have some disadvantages. In rotary dryers, mixing is not good and gas temperatures are low. In fluidized bed dryers, the possibility of powder formation and dusting of the product is quite high as a result of attrition caused by collision of particles [7,8].

Energy transfer as heat from the surrounding environment to the wet solid can occur as a result of convection, conduction, or radiation and some cases as a result of combination of these effects [9]. With this study a new drying technique is exposed as indirect drying with MW, heat is transferred by conduction to the material, through a susceptor. Silicon carbide was chosen as a susceptor due to its absorption characteristics of microwaves (MWs). Earlier studies on MW heating of

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ceramic materials show that SiC absorbs MWs considerably resulting in greater heating in SiC [10,11]. One of the reasons to use ceramic in this study is that the ceramics can withstand high temperature. In addition, the temperature profile within the ceramic materials is uniform due to higher thermal conductivity and these materials may be the perfect choices to be used as supports.

In recent years, microwave energy has found increasing application to the thermal processing of various kinds of materials and products, such as agricultural, chemical, mineral, food, textile, paper and lumber [7,12–14]. MWs propagate through the materials and the accompanying transport processes result in dissipation of electric energy into heat, which lead to the term ‘volumetric heat generation’ due to MW radiations [7]. MWs are widely preferred over conventional heating mainly for shorter processing times. During conventional heating the heat is radiated from the burner to the surface of the material and the material is heated due to surface heat flux whereas during MW heating, the material dielectric loss is responsible to convert electric energy into heat within the entire volume [10]. The unique heating mechanisms of microwaves permit dramatic energy savings in many instances, as well as providing competitive benefits [9,13].

Although drying techniques are cornerstones of many industrial applications and also almost universally understood these techniques have undergone dramatic developments over the last 30 years. In this paper, the results of the experimental work to dry off the crystal water from the sodium carbonate monohydrate powder using microwave energy are presented.

2. Experimental

2.1. The indirect microwave heating system

The present system was designed to generate a moderate thermal gradient, providing uniform and sufficient heating of the sample. In this study a Premier, PMO-20 microwave oven was modified as an indirect microwave heating system. It has a frequency of 2450 MHz with a maximum output power of 800 W. Drying experiments were conducted at six different microwave output powers of 136, 168, 264, 440, 616 and 800 W. The heating profile of the oven conducted with water only shows an almost uniform magnetic field. The test was conducted by heating 100 ml water in a beaker and reading its temperature with about 5 s delays, i.e. interrupting the power and reading the temperature.

A β -SiC plate (15 cm diameter) used as the susceptor material, containing the sample forming a layer of 1–2 mm thickness, was placed inside microwave cavity during treatment for absorption of microwave energy. Dehydration experiments were performed with 50.08 ± 0.01 g samples (where \pm shows standard error of the mean, S.E.M.). For the mass determination, a digital balance of 0.01 g accuracy (Sartorius GP4102-OCE) was used. A new sample was used at each microwave output power selected for drying. Each experiment was replicated at least three times.

2.2. Solid phase analysis

As the crystal water of the monohydrate becomes unstable upon heating above ca. 120 °C, it desorbs to the surrounding air and monohydrate recrystallizes to anhydrate (Eq. (1)). The accompanying weigh loss of the sample due to desorption of the water can be used to determine the amount of monohydrate in the sample. The weigh loss for pure sodium carbonate monohydrate is

$$X_{\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}} = \frac{M_{\text{H}_2\text{O}}}{M_{\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}}} = 0.1453 \quad (2)$$

The weigh loss for pure sodium carbonate anhydrate is

$$X_{\text{Na}_2\text{CO}_3} = 0 \quad (3)$$

Whether the dehydration is complete or not is determined by placing the sample in an oven at 150 °C for 24 h. The amount of crystal water in the samples was calculated from the decrease in weight. The identification of a crystal phase was, of course, not only based on the weigh loss of a sample, but also verified either from light microscopy, scanning electron microscopy (SEM) images and powder X-ray diffraction (XRD).

2.3. Temperature measurement

Simultaneous temperature measurement in a continuous electromagnetic field using a thermocouple is a major problem as the thermocouple–field interaction leads to gross errors [9,15]. Some researches found that a very thin metal sheath surrounding the thermocouple could be used to overcome this problem, but contact between the thermocouple tip and the metal sheath must be avoided, while, shielding reduces the response of the thermocouple [15]. To avoid such a problem, the temperature of the irradiated sample was measured by DT-8819 non-contact infrared thermometer immediately after turning off the microwave power.

2.4. Absorption characteristics of SiC and SCM

The rate of MW energy absorption by a material is determined by its dipole rotation and ionic conductance characteristics [16]. Here SiC is absorbed MW energy that provides heating by dipole rotation [15]. The amount of thermal energy deposited into a material due to microwave heating (power absorption density) is dependent on the internal electric field strength within the minerals, the frequency of the microwave radiation, and on the dielectric properties of the material [17]. If the electric field strength is known the power absorption density per unit volume for dipolar rotation of the mineral can be approximated from Eqs. (4) and (5):

$$P_v = kE^2 f \varepsilon' \tan \delta \quad (4)$$

or

$$P_v = kE^2 f \varepsilon'' \quad (5)$$

Table 1

The thermal and dielectric properties of SiC, ZrO₂, Al₂O₃, and sodium carbonate, as collected from [10,11,18]

Material property	Water	SiC	Al ₂ O ₃	ZrO ₂	Na ₂ CO ₃
Density, ρ (kg m ⁻³)	1000	3100	3750	6100	2533 ^a
Thermal conductivity, k (W m ⁻¹ K ⁻¹)	0.609	40	26	2 at 500 °C	0.0418
Heat capacity, C_p (J kg ⁻¹ K ⁻¹)	4190	3300	1046	2468 at 500 °C	1042
Dielectric constant, ϵ' (at 2450 MHz)	78.1	26.66	10.8	–	5.3–8.4
Dielectric loss, ϵ'' (at 2450 MHz)	10.44	27.99	0.1566	0.034 at 25 °C	–

^a Absolute density at 25 °C.

where P_v is the power density (W/m³), f the frequency of the microwave radiation (MHz) current research is on 2.45 GHz, ϵ' the relative dielectric constant or relative permittivity, ϵ'' the dielectric loss factor of the mineral, $\tan \delta$ the loss tangent or dissipation factor, and E is the electric field strength (V/m).

If a material does not have significant magnetic properties, only complex permittivity can be considered and defined by the following equations:

$$\epsilon^* = \epsilon' - j\epsilon'' \quad (6)$$

$$\tan \delta = \frac{\epsilon''}{\epsilon'} \quad (7)$$

The complex permittivity, ϵ^* , is related to the ability of material to couple electrical energy from a microwave field. The dielectric constant, ϵ' , is a measure of the ability to store electrical energy in the material, and the loss factor, ϵ'' , is related to the amount of energy a dielectric material can dissipate in the form of heat, and $j = (-1)^{1/2}$. The loss tangent, $\tan \delta$, is the ratio of dielectric loss to dielectric constant.

To explain the influence of microwave heating, the specific heat, thermal conductivity and dielectric properties of materials have to be considered. From Table 1, it is clear seen that SiC is the most suitable susceptor due to its high thermal conductivity and dielectric loss.

At a fixed microwave frequency, only the material properties ϵ^* and $\tan \delta$ determine the total power dissipated within the sample. Both these parameters depend strongly on temperature.

In order to understand interaction characteristics of SCM with MW, SCM powder, was spread on the Teflon line sheet, placed into microwave oven and then irradiated at three power levels of 136, 440 and 800 W. The results of irradiation tests, presented in Fig. 1, show that the SCM was a poor absorber of the microwave energy for up to 6 min of irradiation. The sample's temperature increased to 55.30 ± 3.56 °C during 6 min at the highest power level of 800 W. A few minutes exposure, even at low power levels (136 W), the temperature of SiC plate increased rapidly. The figure clearly indicates the strong absorption of the SiC plate. Experimental time versus temperature curves for SiC and SCM are given in Figs. 2 and 3 for increasing power loadings.

2.5. Penetration depth

The dielectric constant and dielectric loss determine the depth of effective energy penetration into material. The penetration

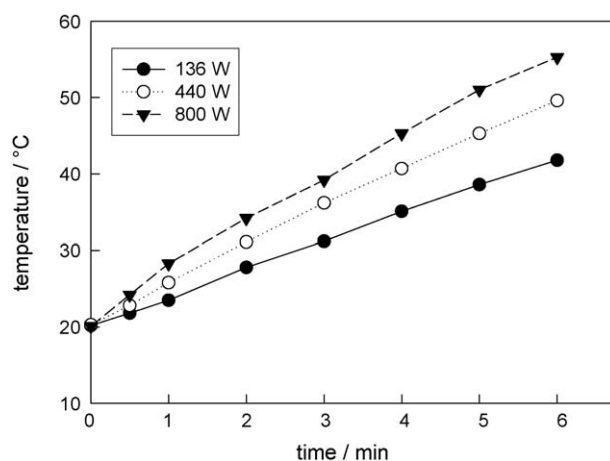


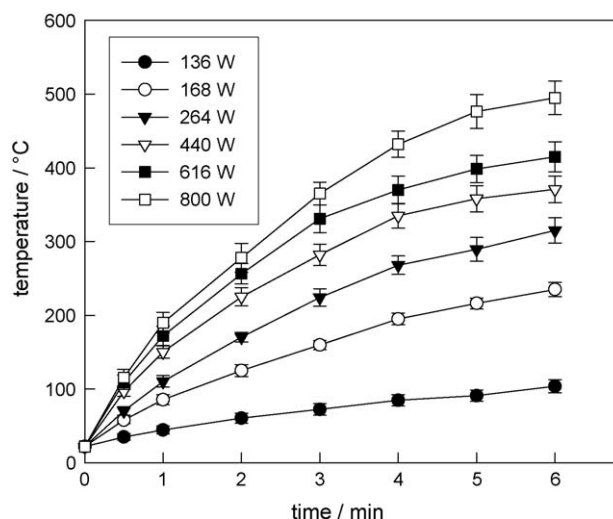
Fig. 1. Heating behaviour of SCM in the microwave oven at 800 W for 6 min.

depth is defined as

$$D_p = \frac{\lambda_0 \sqrt{2}}{2\pi} \left[\epsilon' \left(\sqrt{1 + (\epsilon''/\epsilon')^2} - 1 \right) \right]^{-1/2} \quad (8)$$

where, D_p is the penetration depth, λ_0 is the free space wavelength defined by $\lambda_0 = c/f$, c being the velocity of light and f being the frequency.

In general, if the penetration depth exceeds sample thickness, the material behaves transparent. Volumetric heating results, if the penetration depth is comparable with the sample thickness.

Fig. 2. Effect of power-dependent microwave absorption on the heating of SiC plate. Error bar represents S.E.M. (95%, $N=3$).

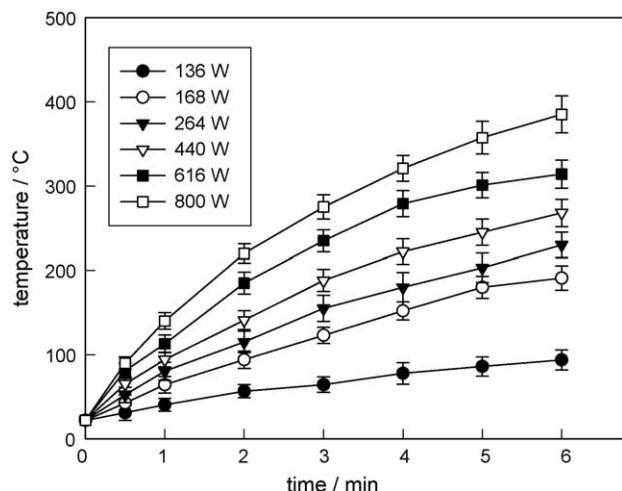


Fig. 3. Effect of power-dependent microwave absorption on the heating of SCM on SiC plate. Error bar represents S.E.M. (95%, $N=3$).

Otherwise, if the sample is too thick, absorption limits to the surface.

The results of irradiation tests, presented in Figs. 2 and 3, showed that while penetration depth exceeds the SCM thickness, it is comparable with the SiC plate. Due to the small penetration depth in SiC, the power decays rapidly from the faces. The property of SiC to rapidly heat in the presence of MWs is exploited to indirectly heat low loss materials like SCM, with SiC being used as a susceptor causing heat to be transferred by radiation to low loss sample. The microwave penetration depth into the SiC plate also decreases as the temperature rises. Similar findings were reported in previous studies [15].

3. Results and discussion

The SCM is a relatively poor microwave absorber (Fig. 1) than the SiC. Since, SiC is an excellent microwave absorber (Fig. 2), it was used to provide the quick warm-up of the SCM and the results are shown in Fig. 3. The samples are processed for 6 min at 136, 168, 264, 440, 616 and 800 W. It can be seen that using SiC plate provided a significant increase in the sample temperature. Thus, a maximum temperature of 385 °C was achieved at 800 W. This strategy may be advantageous for achieving a greater heating rate.

The extent of the temperature increase can be explained rather by the thermal runaway phenomenon than by simple thermal conduction alone. This type of behaviour has been reported by a number of authors [19–21]. Though thermal conduction occurs to some extent, the dielectric loss tangent increases rapidly with temperature and thus steep temperature increases can occur. The area of the sample which interacts with SiC will heat faster than the rest of the sample. Then they will transfer their own temperature to the other parts of the sample and this phenomenon will occur again. Thermal runaway is a complicated phenomenon and depends on sample size, geometry and the relationship between the relative dielectric constant (ϵ') and temperature [21].

It has been seen that the complete drying or conversion occur at 440 W and upper power levels as shown in Fig. 4 from the

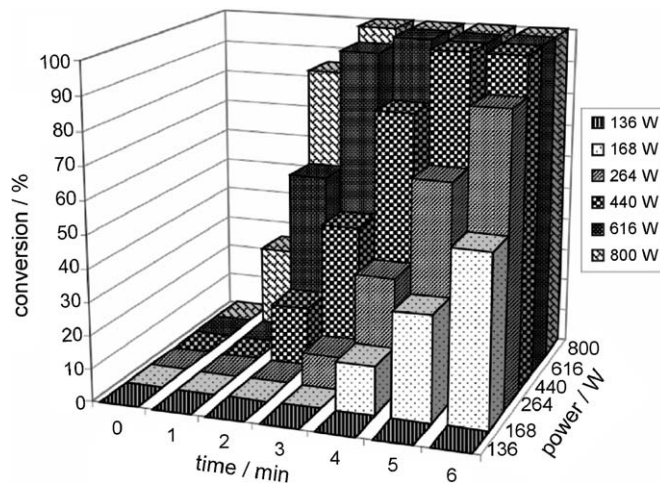


Fig. 4. Sodium carbonate ratios after MW irradiation of SCM at different microwave energy levels.

heating weight loss analysis with heating in an oven at 150 °C for 24 h. It was shown that the dehydration began almost immediately under microwave energy at a bulk temperature of 140 °C. Eighteen percent of SCM was converted within only 2 min at 440 W. At 136 W no dehydration was observed, most probably because the temperature did not increase significantly.

In an attempt to understand the effect of the different drying techniques on the quality of the produced sodium carbonate anhydrate, a comparison was made between dehydration and drying in a fluidised bed versus indirect microwave heating using with the excellent study of Chen et al. [6]. According to this study monohydrate conversion begins approximately 100 s after the operation commences, a steady-state conversion of about 0.33 is reached after about 10^4 s. As seen from Fig. 4 in MW heating complete conversion of SCM was achieved within only 2 min at 800 W. In addition to this the results of the microwave versus conventional heating experiments are clearly shown in Fig. 5 as conversion of the SCM versus time. Moreover, microwave heating provides great time savings, compared with conventional drying.

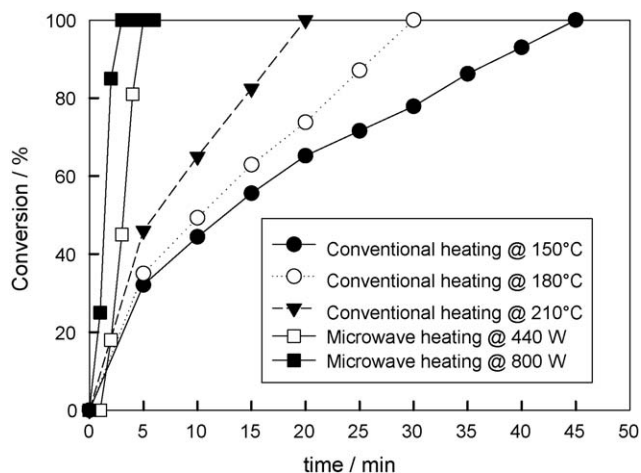
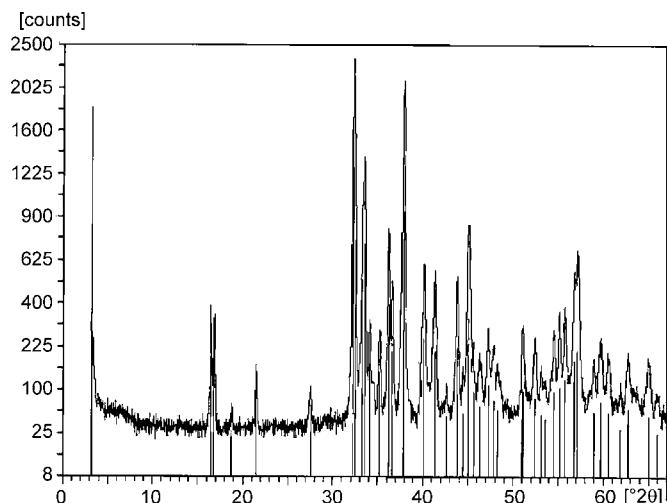
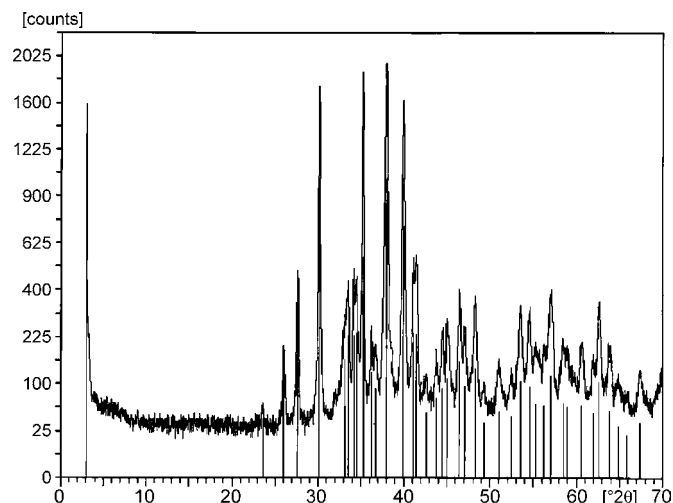


Fig. 5. SCM conversion of conventional and microwave heating.

Fig. 6. XRD pattern of $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ before MW irradiation.Fig. 7. XRD pattern of Na_2CO_3 after MW irradiation of SCM.

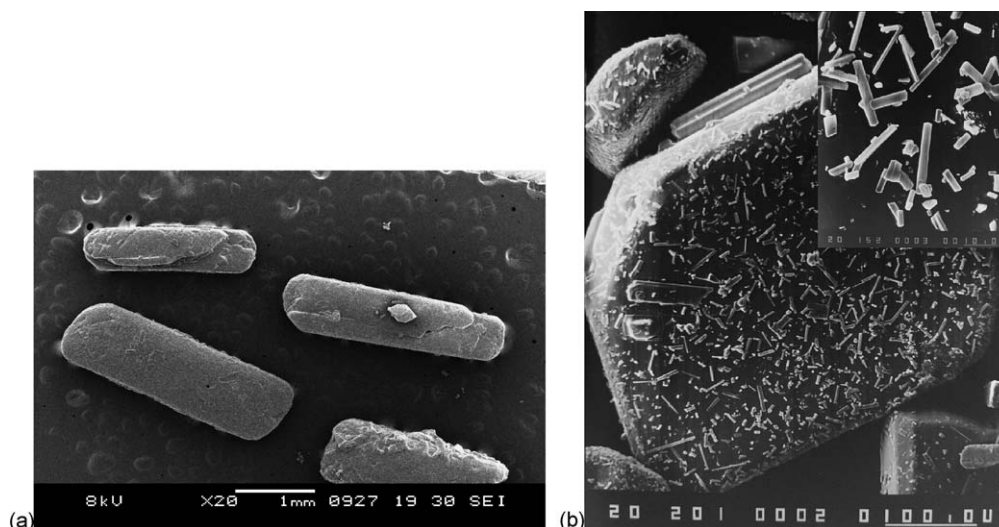
This observation was confirmed by the analysis of the XRD-patterns of the samples. While powder X-ray diffraction of sample essentially showed peaks corresponding to SCM in Fig. 6, in Fig. 7 powder X-ray diffraction of the microwave-irradiated product essentially showed peaks corresponding to anhydrous sodium carbonate.

SEM photographs are depicted in Figs. 8(a and b) and 9(a and b). While in the first picture, monohydrate crystals, orthorhombic, long needle-shaped crystals are visible (see Fig. 8(a)), monoclinic structure of the anhydrate crystals can be seen very clear in Fig. 9(a).

Calcination (i.e. thermal solid-state recrystallization) of SCM usually results in agglomerates (pseudomorphs) of micron size anhydrate crystals (Fig. 9(b)). As seen in this image, the shape of the original crystal is maintained, but it is composed of tiny anhydrate crystals. The crystal structure of the monohydrate differs significantly from the anhydrate—so the anhydrate does not simply form by taking the water out of the monohydrate. The monohydrate crystals have to dissolve, while anhydrate crystals

have to nucleate and grow. The pseudomorphs form, because there is no medium, in which the ions (the building blocks of the crystal) can move easily (like a solution). Therefore, the recrystallization occurs usually in the solid state (short diffusion paths, high super-saturation, and high degree of nucleation). A solid phase recrystallization is very unlikely to produce well-shaped, comparatively large anhydrate crystals.

The surface of anhydrate crystals looks rather rough (see Fig. 9(a)). The prism-shaped crystals have noticeable pores. For high calcination temperature, the anhydrate size becomes even smaller and the pseudomorphs even denser, as the crystallites sinter together. Also it can be seen that there is no caking formation occurred from Fig. 9(a). There is also no distinct influence of the operating conditions in this hybrid system on the bulk density of the product. It was found that approximately 1000 kg m^{-3} after complete dehydration was achieved which is the same value of the product that produced with the conventional drying methods.

Fig. 8. SEM images of $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ before MW irradiation: (a) long needle-shaped crystals, (b) small crystallites adhered to the surface of the SCM.

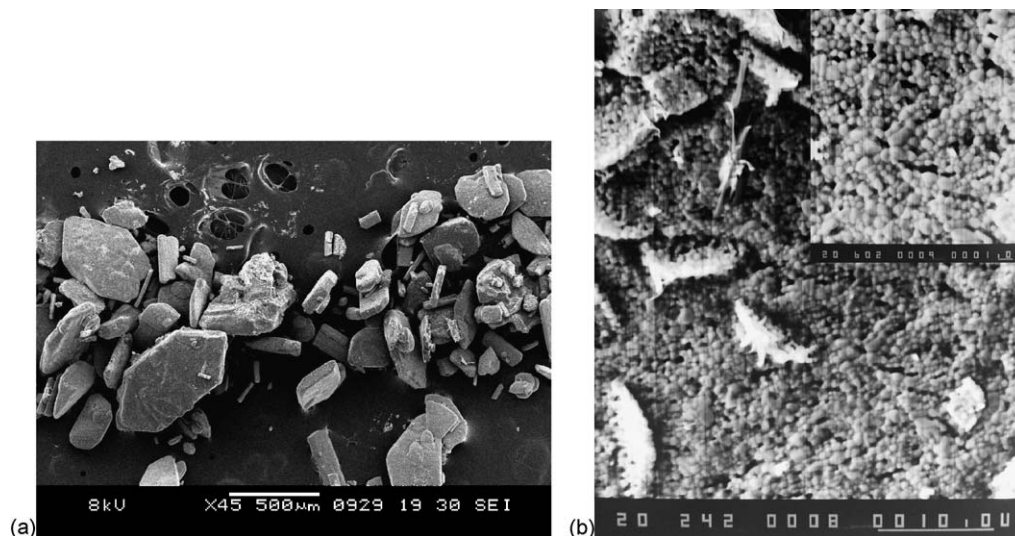


Fig. 9. SEM images of Na_2CO_3 after MW irradiation of SCM: (a) anyhydrate crystals, (b) agglomerates (pseudomorphs) of micron size anyhydrate crystals.

4. Conclusions

In many processes, the drying of the finished product has a major influence on the production duration. To increase the output of system, however, the production duration must be reduced. Conventional drying methods offer little scope for acceleration. Finding applications for the microwave processing methods in these well-established and highly competitive industries is extremely difficult. However, microwave drying is fast and gentle on the product. This assures it a place among the drying techniques of the future. In this investigation, the influence of microwave heating on the modification of dehydration properties SCM was experimentally confirmed and the expressive shortening of the exposing time observed in comparison to the conventional heating. With the susceptor, SCM was converted to sodium carbonate with indirect microwave heating. The increase in microwave power and air temperature significantly reduced the drying time of the SCM crystals.

Acknowledgements

The authors gratefully thank Mr. Ismail Ceylan and Mr. Ali Ugurelli from Eti Soda Production Marketing Transportation & Electricity Generation Industry & Trade Inc. and Dr.-Ing. Robert S. Gärtner, Laboratory for Process Equipment, Delft University of Technology, for their helpful discussions.

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