journal

J. Am. Ceram. Soc., **83** [6] 1341–45 (2000)

Synthesis of Hydrated Aluminum Sulfate from Kaolin by Microwave Extraction

Seong Soo Park

Department of Polymer Engineering, Pukyong National University, Pusan 608–739, Korea

Eun Hee Hwang

Single Crystal Team2, LG Siltron, Inc., Kumi-city, Kyungsangbuk-do 730–350, Korea

Byoung Chan Kim and Hee Chan Park*

Department of Inorganic Materials Engineering, Pusan National University, Pusan 609–735, Korea

The feasibility of extracting alumina from kaolin via a microwave extraction process was investigated by comparing reaction times, reaction temperatures, and acid concentrations under microwave treatment with the same factors under conventional thermal extraction. The maximum amount of alumina extracted from kaolin under conventional processing at 90°C for 240 min with 1*M* H_2SO_4 was 99.9%; the same amount of alumina was extracted under microwave processing at 90°C for 120 min with 1*M* H_2SO_4.

I. Introduction

Microwave processing technology recently has attracted interest as an alternative to conventional thermal processing, because of the inherent advantages of microwave heating, which is selective, direct, rapid, internal, and controllable.[1] In comparison to conventional thermal processing, microwave processing reduces the environmental impact of materials processing and provides significant cost, energy, and space savings; this processing method also results in unique or enhanced properties. Therefore, microwave processing has been used in various applications such as drying, food processing, polymer synthesis, material processing, joining, and waste treatment.[2–13] The dissolution of inorganic and organic materials by an acid commonly has been used in analytical chemistry to analyze the chemical contents of samples. Several studies on the analytical applications of microwave dissolution have reported that the kinetics of organic and inorganic chemical dissolution can be accelerated significantly using microwaves.[14,15] A sample in the presence of acid, in response to microwaves, acts as a lossy dielectric and exhibits effective internal heating.

Bauxites have been widely used in industry to produce alumina via the Bayer process. On the other hand, nonbauxitic materials, which are more abundant in many countries than bauxite resources, also have been processed in attempts to develop alternative technologies for producing alumina.[16] Some examples of nonbauxitic raw materials are alunite, nepheline, sillimanite, andalusite, kyanite, kaolin, micas, fly ash, and coking residues. Among the methods developed for producing alumina from these materials are a modified Bayer process, an ethylene chloro-hydrin method, hydrolysis of organic aluminum salts, and electrolysis.[17–19] Significant advances in alumina purity have been achieved using materials such as sulfates, nitrates, and chlorides as alumina precursors, to obtain high-purity alumina at low cost. Of all the techniques, the hydrolysis–precipitation of aluminum sulfate by varying such conditions as the addition rate and order of the reactants, the chemical composition, and the temperature and by controlling the pH has proven to be effective for synthesizing high-purity alumina from nonbauxitic materials.[20]

The emergence of microwave processing in the hydrolysis–precipitation method presents an excellent new option for the extraction of alumina from nonbauxitic materials. In the present study, the conventional thermal process and the microwave process for extracting alumina from kaolin via acid treatment were compared, to identify differences in the reaction parameters and product properties that result from the two processes. The ease of extracting alumina from kaolin under the two processes was investigated by comparing reaction times, reaction temperatures, and acid concentrations.

II. Experimental Procedure

Microwave extraction was accomplished in the present study using a system that consisted of a modified 700 W, 2.45 GHz home microwave oven (LG Electronic Co., Changwon, Korea). Modifications included the addition of two 700 W magnetrons (to increase the microwave power) and a mode stirrer (to create a uniform microwave field). Corrosive fumes were removed by an exhaust fan and then vented to a fume hood. The temperature of the aqueous samples was measured using a stainless, shielded K-type thermocouple that was covered by a Pyrex™ (Corning Glass Works, Corning, NY) tube and controlled automatically through feedback control from a programmable controller. A microwave-transparent Pyrex™ flask was used as the reaction vessel.

Kaolin, which is an abundant mineral in Korea, was used as a starting material. The chemical composition of the kaolin used is shown in Table I. Kaolin powder that was ground in an agate mortar to particles below ~74 μm in size was calcined at 800°C for 3 h in an electric furnace to loosen the alumina components.[20] Then, ~9 g of the calcined sample was charged with 300 mL of a 1*M*–3*M* sulfuric acid (H_2SO_4) solution in a reaction flask. The reaction flask was fitted with a modified thermocouple and a reflux condenser. The mixture of sample and acid was heated to a temperature of 70°–90°C and maintained in that temperature range within the reaction flask for 20–240 min, using a water bath as a conventional heating source or the previously described microwave extraction system as a microwave heating source. Under conventional thermal extraction, the mixture of sample and acid was stirred at a speed of ~450 rpm with a motor-driven stirrer; under microwave extraction, the mixture of sample and acid was

---

P. W. Brown—contributing editor

Manuscript No. 190338. Received April 16, 1998; approved November 30, 1999.

*Member, American Ceramic Society.

Table I. Chemical Content of Kaolin

Component	Content (wt%)
SiO_2	51.52
Al_2O_3	45.00
K_2O	0.81
Fe_2O_3	0.76
CaO	0.52
Na_2O	0.46
MgO	0.32
MnO	0.02
Ignition loss	0.59

stirred naturally by microwaves. After the mixture of sample and acid had been leached, it was cooled to room temperature and filtered to remove the leach residue, which mainly consisted of silica. The filtered leach liquor then was added dropwise at a rate of 5.0 mL/min into 900 mL of ethanol while the ethanol was stirred with a magnetic stirrer.

Ethanol was used as a precipitating agent because Al^{3+} ions can be extracted from ethanol with high selectivity; in fact, precipitates formed immediately after the sample liquor was added into the ethanol in the present study. The precipitates were washed again with the ethanol and with distilled water, then dried at 60°C for 72 h. Finally, the precipitates were calcined at 1000°C for 1 h in an electric furnace.

The efficiency of microwave extraction over conventional thermal extraction was illustrated by the degree of alumina within the synthesized precipitates versus the amount of alumina contained in the starting kaolin. The amount of alumina in the samples was estimated by weighing the alumina residue after the samples were fired at 1000°C for 1 h. The thermal decomposition of the samples was characterized via thermogravimetry/differential thermal analysis (TG-DTA) at a heating rate of 10°C/min. The chemical contents of the samples were analyzed via atomic emission spectroscopy (AES). A BET nitrogen absorption method was used to determine the surface areas of the samples, particle-size analysis was used to measure the size distribution of the particles in the samples, and scanning electron microscopy (SEM) was used to determine the particle size and morphology. Sample phases were identified using X-ray diffractometry (XRD) with nickel-filtered Cu*K*α radiation.

III. Results and Discussion

(1) Effect of Reaction Time

Table II reports the amount (in weight percent) of alumina extracted, as a function of reaction time, which varied from 20 min to 240 min with 1*M* H_2SO_4 at 80° and 90°C, under both conventional thermal extraction and microwave extraction. The data in Table II show that, in the alumina extraction, a short time is required under microwave extraction, in comparison to that required for conventional thermal extraction. Based on the reaction time that was necessary to attain a degree of alumina extraction of 63.1–99.9 wt%, the introduction of microwaves during the reaction increased the kinetics by approximately two orders of magnitude and was a very effective process for the rapid extraction of alumina. The high extraction rate and reduced reaction time exhibited under microwave extraction can be attributed to a significant increase in the rate of dissolution of the reactive species. In response to microwaves, the magnitude of the polarization effect varies with the dipole character of the molecules involved in the interaction; however, this value is particularly high when water molecules are involved. Thus, the present mixture of sample and acid acted as a lossy dielectric and effectively exhibited internal heating. The intense internal heating, together with the differential polarization effect, may have mechanically agitated and ruptured the sample surface, which would expose new surface area to the attacking acid.[14,15] Therefore, microwave extraction can be expected to produce more-efficient sample dissolution by effecting better contact between the acid and the sample.

Table II. Influence of Reaction Time on the Degree of Alumina Extraction from Kaolin with 1*M* H_2SO_4 Solution under Conventional Thermal Extraction and Microwave Extraction Processes

Reaction time (min)	Degree of alumina extraction (wt%)			
	Conventional process		Microwave process	
	80°C	90°C	80°C	90°C
20			47.0	72.1
40			63.1	83.7
60	48.5	71.9	67.4	86.7
80	65.6	88.3	77.9	93.0
120	75.8	92.5	86.5	99.9
180	81.4	98.9		
240	87.2	99.9		

(2) Effect of Acid Concentration

Figure 1 shows the amount of alumina extracted, as a function of the H_2SO_4 concentration, which varied over a range of 0.5*M*–3.0*M* at 90°C for 60 min under both conventional thermal extraction and microwave extraction. The percentage of alumina extracted under both processes was proportional to the H_2SO_4 concentration, because the oxidation reaction of the acid became quite strong as the acid concentration increased. Clearly, much more alumina was extracted (up to ~20%) in all ranges of acid concentration under microwave extraction, in comparison to conventional thermal extraction.

(3) Effect of Reaction Temperature

Figure 2 shows the amount of alumina extracted as a function of reaction temperature, which varied over a range of 70°–90°C with 1*M* H_2SO_4 for 60 min, under both conventional thermal extraction and microwave extraction. The results from Fig. 2 indicate that the amount of alumina extracted under both processes was proportional to the reaction temperature, because the oxidation reaction of the acid became very strong as the reaction temperature increased. Clearly, the degree of alumina extraction was higher in all reaction-temperature ranges under microwave extraction than under conventional thermal extraction.

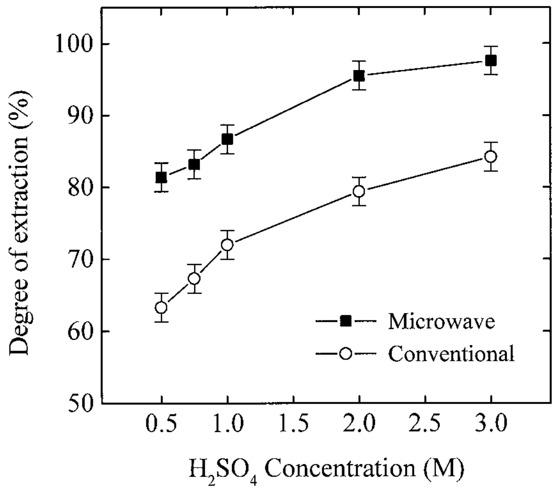

Fig. 1. Influence of acid concentration on the degree of alumina extraction from kaolin at 90°C for 60 min under the conventional thermal process and the microwave extraction process.

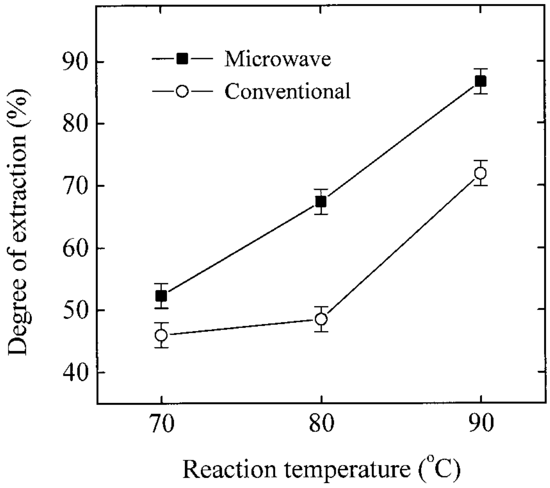

Fig. 2. Influence of reaction temperature on the degree of alumina extraction from kaolin with 1*M* H_2SO_4 for 60 min under the conventional thermal process and the microwave extraction process.

(4) *Characteristics of Precipitates*

The maximum amount of alumina extracted from kaolin under conventional processing at 90°C for 240 min with 1*M* H_2SO_4 was 99.9 wt%; the same amount of alumina was extracted under microwave processing at 90°C for 120 min with 1*M* H_2SO_4. Precipitates synthesized by both processes, under the given conditions, were characterized using XRD and SEM analyses, as shown in Figs. 3 and 4, respectively. The XRD patterns of both samples (Fig. 3) exhibited sharper peaks; these peaks were determined to correspond to crystalline hydrated aluminum sulfate ($Al_2(SO_4)_3{\cdot}12H_2O$). The SEM micrographs (Fig. 4) show that conventionally treated samples consisted of a foamy mass of irregularly shaped aggregates and microwave-treated samples consisted of irregular particles or eggshell-like fragments. Chemical analyses of the leaching residue, which was produced by both processes under the given conditions, are shown in Table III. Vitreous silica without any crystalline phases was observed in both residues, using XRD diffraction. With similar chemical compositions and vitreous silica phases of the both residues, it would be difficult to explain the differences in morphologies of the precipitates obtained from the both conventionally treated and microwave-treated samples. Studies that are intended to explain the different crystal morphologies are now in progress.

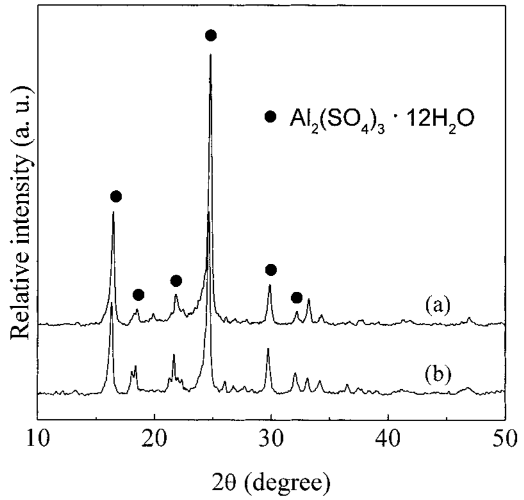

Fig. 3. XRD patterns of precipitates synthesized via (a) conventional thermal extraction at 90°C for 240 min with 1*M* H_2SO_4 and (b) microwave extraction at 90°C for 120 min with 1*M* H_2SO_4.

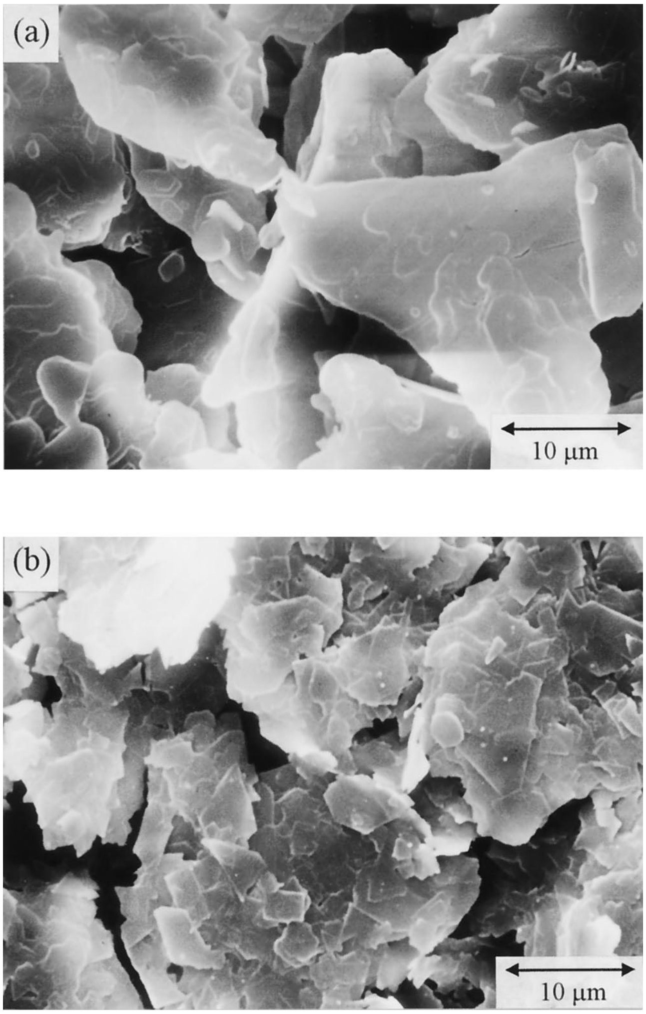

Fig. 4. SEM micrographs of precipitates synthesized via (a) conventional thermal extraction at 90°C for 240 min with 1*M* H_2SO_4 and (b) microwave extraction at 90°C for 120 min with 1*M* H_2SO_4.

Table III. Chemical Analyses of Leaching Residues under Conventional Thermal Extraction (1*M* H_2SO_4, 90°C, and 240 min) and Microwave Extraction (1*M* H_2SO_4, 90°C, and 120 min) Processes

	Content (wt%)	
Component	Conventional process	Microwave process
SiO_2	90.24	91.24
Al_2O_3	0.00	0.00
Potassium	0.36	0.47
Sodium	0.36	0.32
Calcium	0.17	0.19
Magnesium	0.06	0.11
Iron	0.00	0.00
Ignition loss	8.81	7.67

The DTA curves of both samples are shown in Fig. 5. The conventionally treated and microwave-treated samples desulfurized at temperatures of ~804° and ~782°C, respectively, via dehydration at ~125°C. Desulfurization of the microwave-treated sample occurred at a relatively lower temperature, possibly because the eggshell-like fragmentary structure in the microwave-treated sample was very small.

(5) *Characteristics of Calcined Precipitates*

The powders obtained by calcining both conventionally treated and microwave-treated samples at 1000°C for 1 h were characterized via XRD and SEM analyses, as shown in Figs. 6 and 7,

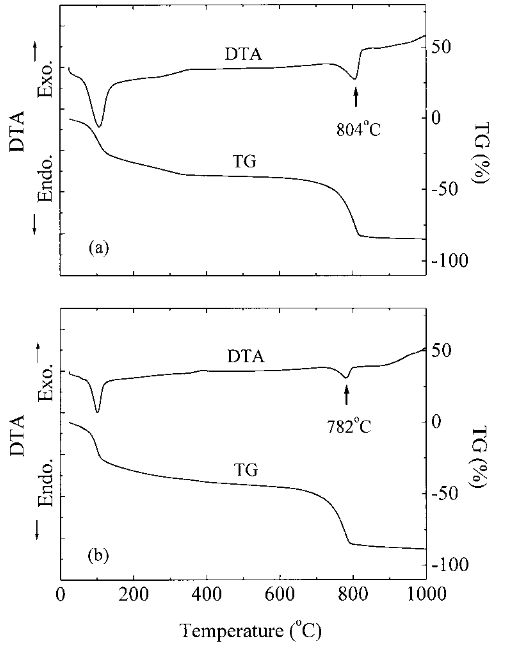

Fig. 5. TG-DTA curves of precipitates synthesized via (a) conventional thermal extraction at 90°C for 240 min with 1*M* H_2SO_4 and (b) microwave extraction at 90°C for 120 min with 1*M* H_2SO_4.

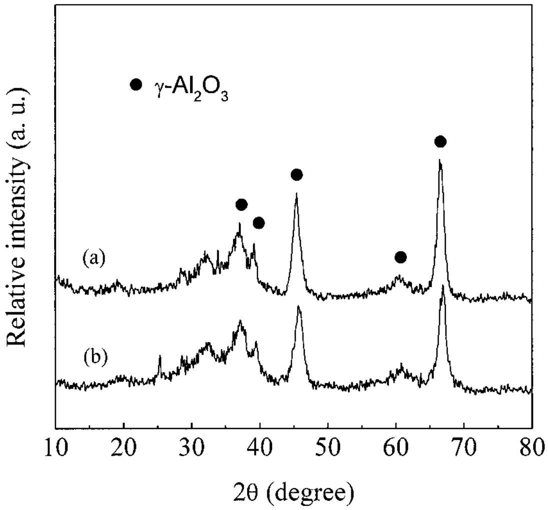

Fig. 6. XRD patterns of (a) the conventionally treated (90°C, 240 min, and 1*M* H_2SO_4) sample and (b) the microwave-treated (90°C, 120 min, and 1*M* H_2SO_4) sample; both were obtained by calcining at 1000°C for 1 h.

respectively. The XRD patterns of both calcined powders (Fig. 6) identified them as being γ-Al_2O_3. The SEM micrographs of the calcined powders (Fig. 7) indicate that a different morphology was not observed in both samples, except for a clear surface of particles in the microwave-treated sample.

Typical powder characteristics and chemical analyses results are shown in Table IV. The calcined powders of the microwave-treated sample had different impurity contents, in comparison with those of the conventionally treated sample. Apparently, the leach solution that was obtained from the microwave extraction process had different impurity contents, because of microwave-enhanced dissolution rates. The calcined powders of microwave-treated sample had a larger surface area and a smaller particle size than did those of the conventionally treated sample. Therefore, the characteristics of calcined powders are affected greatly by the morphology of the precipitates. However, further studies will be necessary to define how the precipitate parameters can be changed to control the particle size.

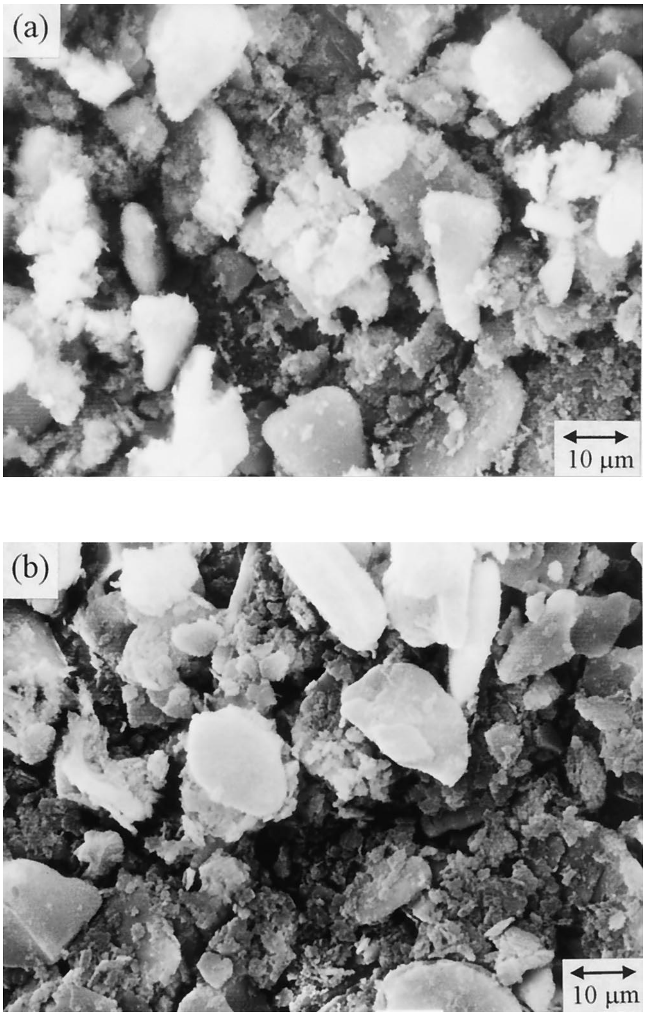

Fig. 7. SEM micrographs of (a) the conventionally treated (90°C, 240 min, and 1*M* H_2SO_4) sample and (b) the microwave-treated (90°C, 120 min, and 1*M* H_2SO_4) sample obtained by calcining at 1000°C for 1 h.

Table IV. Chemical Analyses and Powder Characteristics of Powders Obtained by Calcining Both Conventionally Treated Samples (90°C, 240 min, and 1*M* H_2SO_4) and Microwave-Treated Samples (90°C, 120 min, and 1*M* H_2SO_4) at 1000°C for 1 h

	Value	
Property	Conventional process	Microwave process
Alumina content	98.53 wt%	98.61 wt%
Impurity content		
Potassium	0.82 wt%	0.68 wt%
Calcium	0.39 wt%	0.42 wt%
Sodium	0.08 wt%	0.14 wt%
Magnesium	0.08 wt%	0.10 wt%
Iron	0.00 wt%	0.00 wt%
Total impurities	1.37 wt%	1.34 wt%
Mean particle size	25.74 μm	9.31 μm
BET specific surface area	91.75 m^2/g	159.00 m^2/g

IV. Conclusions

The microwave extraction process that has been described in the present paper has proven to be quite effective, in comparison to conventional thermal extraction, for the rapid extraction of alumina from kaolin. Microwave processing probably accelerates alumina extraction, because of its intense internal heating.

References

[1] W. H. Sutton, "Microwave Processing of Ceramic Materials," *Am. Ceram. Soc. Bull.*, **68** [2] 376–86 (1989).

[2] I. J. Chabinsky, "Application of Microwave Energy Past, Present and Future"; pp. 17–29 in Materials Research Society Symposium Proceedings, Vol. 124, *Microwave Processing of Materials*. Edited by W. H. Sutton, M. H. Brooks, and I. J. Chabinsky. Materials Research Society, Pittsburgh, PA, 1988.

[3] W. H. Sutton, "Microwave Processing: Steps to Successful Commercialization"; pp. 3–5 in Ceramic Transactions, Vol. 59, *Microwaves: Theory and Application in Materials Processing III*. Edited by D. E. Clark, D. C. Folz, S. J. Oda, and R. Silberglitt. American Ceramic Society, Westerville, OH, 1995.

[4] E. R. Peterson, "Seal Formation Rates of Microwave Heated Ethylene Carbon Monoxide Copolymers"; pp. 697–703 in Materials Research Society Symposium Proceedings, Vol. 347, *Microwave Processing of Materials IV*. Edited by W. H. Sutton, M. H. Brooks, and I. J. Chabinsky. Materials Research Society, Pittsburgh, PA, 1994.

[5] J. Herz, J. Chang, and M. Brodwin, "Microwave Induced Polymerization of Monomer Impregnated Hardened Cement"; *ibid*, pp. 711–15.

[6] M. J. Kennedy, "Commercialization of Microwave Processes"; see Ref. 3, pp. 43–54.

[7] J. Jacob, L. H. L. Chia, and F. Y. C. Boey, "Thermal and Non-Thermal Interaction of Microwave Radiation with Materials," *J. Mater. Sci.*, **30**, 5321–27 (1995).

[8] S. S. Park and T. T. Meek, "Microwave Processing of Zirconia–Alumina Composite in a 2.45 GHz Electromagnetic Field," *J. Mater. Sci.*, **26**, 6309–13 (1991).

[9] S. A. Nightingale, H. K. Wormer, and D. P. Dunne, "Microstructural Development during the Microwave Sintering of Yttria–Zirconia Ceramics," *J. Am. Ceram. Soc.*, **80** [2] 394–400 (1997).

[10] F. L. Paulauskas and T. T. Meek, "Processing of Thermoset Prepreg Laminates Via Exposure to Microwave Radiation"; see Ref. 4, pp. 743–51.

[11] J. G. P. Binner, P. A. Davis, T. E. Cross, and J. A. Fernie, "Microwave Joining of Engineering Ceramics"; see Ref. 3, pp. 335–46.

[12] S. J. Oda, "Microwave Remediation of Hazardous Waste: A Review"; see Ref. 4, pp. 371–82.

[13] G. G. Wicks, D. E. Clark, R. L. Schulz, and D. C. Folz, "Microwave Technology for Waste Management Applications Including Disposition of Electronic Circuitry"; see Ref. 3, pp. 79–90.

[14] L. B. Fischer, "Microwave Dissolution of Geologic Material: Application to Isotope Dilution Analysis," *Anal. Chem.*, **58**, 261–63 (1986).

[15] H. M. Kingston and L. B. Jassie, "Microwave Energy for Acid Decomposition at Elevated Temperatures and Pressures Using Biological and Botanical Samples," *Anal. Chem.*, **58**, 2534–41 (1986).

[16] H. Juárez M., J. M. Martínez R., J. M. Ruvalcaba L., O. A. Vargas P., and J. Serrato R, "Aluminum Oxide and Hydroxides from Non-Bauxitic Sources," *Am. Ceram. Soc. Bull.*, **76** [6] 55–59 (1997).

[17] D. W. Johnson Jr., "Nonconventional Powder Preparation Techniques," *Am. Ceram. Soc. Bull.*, **60** [2] 221–24, 243 (1981).

[18] J. E. Blendell, H. K. Bowen, and R. L. Coble, "High Purity Alumina by Controlled Precipitation from Aluminum Sulfate Solutions," *Am. Ceram. Soc. Bull.*, **63** [6] 797–802 (1984).

[19] T. Sato, F. Ozawa, and S. Ikoma, "Thermal Decomposition of Aluminum Salts—Hydrates of the Chloride, Nitrate, and Sulphate and of Ammonium Alum," *J. Appl. Chem. Biotechnol.*, **28**, 811–22 (1978).

[20] H. K. Kang, K. H. Kim, and H. C. Park, "Preparation of Fe-free Alumina Powder from Kaolin," *J. Mater. Sci. Lett.*, **14**, 425–27 (1995). □