

Ultrasound-Assisted Removal of Microcrystalline Opal-CT from Ca-Bentonite

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Microcrystalline silica impurities such as quartz and opal-CT commonly associated in bentonite should be controlled and removed as far as possible when bentonite is used as biocompatible raw material because the impurities are hazardous in human health. Since opal-CT contained in Korean Ca-bentonite in trace amounts cannot be well separated by conventional sedimentation method, in this work, the ultrasound-assisted removal of the impurity was attempted. Irradiating ultrasound into bentonite-water suspension promoted the production of fine montmorillonite particles in the suspension and the production markedly increased when montmorillonite was activated by Na₂CO₃. Subsequent centrifugation of the suspension made it possible to recover pure montmorillonite particles as an overflow product. Only 16.2 mass% of total solids was recovered as an overflow from non-activated suspension, whereas 63.5 mass% was recovered from activated suspension at centrifuging speed of 10000 rpm. Increasing sonicating time enhanced the yield of overflow, however, excessive sonication up to 10 min hindered the high purification of montmorillonite. It was observed that the peak reflection of (101) plane of opal-CT in overflow increased as sonicating time increased during prolonged sonication. [doi:10.2320/matertrans.M2016276]

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1. Introduction

Bentonite is clay-rich soft rock generated frequently from the alteration of volcanic ash, consisting predominantly of mineral montmorillonite. Depending on the nature of its genesis, bentonite contains a variety of accessory minerals, which may include mainly quartz, feldspar, opal cristobalite/trydimite (opal-CT), calcite, illite and mica. The presence of these accessory minerals can impact the industrial value of the deposit, reducing its commercial value depending on its applications. Therefore, bentonite is often purified by removing these impurity minerals for special applications where specific properties and characteristics are required.¹⁾ Among the special applications, bentonite is often used in the cosmetic and pharmaceutical industry as both excipient and active ingredient in the forms of liquid (suspensions, emulsions), semi-solid (creams, ointments) and solid (powder, capsules and tablets).^{2–4)} The basic requirements for bentonite to be used as raw material are pure, microbiological and mineralogical inertness. Physical properties such as swelling volume and gel formation are also important. Particularly, microcrystalline silica polymorphs such as quartz, cristobalite and opal-CT should be controlled and removed as far as possible because they show sufficient evidence of carcinogenicity in humans.⁵⁾

In general, the dry processes such as crushing, grinding and air classification are commercially employed to produce the final products of bentonite. On the other hand, wet processes using hydro-cyclone and centrifuge are limitedly adopted to produce extremely fine and pure bentonite for special uses.^{6,7)} Since montmorillonite particles in bentonite are in the size of $\sim 2 \mu\text{m}$, they are disintegrated into finer size, whereas the associated impurity minerals accumulate coarser sizes when bentonite is dispersed in water. Therefore, the dispersion in the form of bimodal particle size distribution can be utilized in the selective removal of impurities by sedimentation method. Although the easy-to-settle coarse impurities

are mostly removed, however, the finely associated impurities like quartz and opal-CT in trace amounts could not be easily removed from the suspension.

It has been well recognized for many years that ultrasonic irradiation causes acoustic cavitation in a liquid medium. When a liquid is irradiated by ultrasound, micro-bubbles appear, grow and oscillate extremely fast and even collapse violently if the acoustic pressure is high enough.⁸⁾ The occurrence of these collapses near a solid surface will generate microjets and shock waves, resulting in cleaning and erosion of the surface and the fragmentation of the solid. Moreover, in the liquid phase surrounding the particles, high turbulence or micro-mixing will increase the heat and mass transfer and even the diffusion of species inside the pores of the solid. Due to this unique characteristic of ultrasound, ultrasonic energy can enhance reaction rates or induce chemical reactions by the formation of highly reactive radical species formed during cavitation.^{9,10)} As an auxiliary energy, ultrasound has been successfully applied in the mining industry as an assistant means to clean mineral surfaces of oxidation products and fine coatings.^{11,12)} Some researchers have reported that ultrasound enhances the flotation performance for difficult-to-process ores.^{13–15)}

In this work, ultrasound-assisted removal of opal-CT from bentonite was attempted. A calcium type bentonite (Ca-bentonite) containing microcrystalline opal-CT was subject to a series of sonicating test in order to develop an effective separation process and identify the technological futures of the separation products. The process variables that influence the separation such as sonicating time, centrifuging speed and soda activation have been examined.

2. Materials and Methods

2.1 Materials

A Ca-bentonite sample collected from Gampo deposit of Korea was used in this work. The sample was mainly made up of montmorillonite, quartz, feldspar and opal-CT. The chemical composition was found to be as follows: 68.97% SiO₂,

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16.06%, Al₂O₃, 1.57% Fe₂O₃, 2.32% CaO, 3.74% MgO, 0.75% Na₂O, 0.1% TiO₂, 0.05% MnO, 0.02% P₂O₅ and 6.59% of loss on ignition. A sodium carbonate (Na₂CO₃, Junsei Chem., Japan) was used for the soda activation of sample during ultrasonic treatment.

2.2 Sedimentation

Prior to sonicating test, the coarse impurities were firstly removed. The separation of them was conducted by the sedimentation method frequently reported in literatures.^{16,17} An earthy and lumpy form of raw bentonite ore was first crushed in a laboratory-scale cone crusher to pass 3 mm screen. About 500 g of crushed ore was suspended in deionized water (25% by weight mixture) and the suspension was mechanically scrubbed using a laboratory overhead stirrer which is attached to a single axis with a two-bladed impeller (1800 rpm). After scrubbing for 60 min, the suspension was diluted (2.5% by weight mixture) and then left to settling in acryl cylinder to remove easy-to-settle non-clay minerals at coarse fraction. The fine fraction in supernatant were collected by drying at 65°C and used as the starting material for sonicating test.

2.3 Sonication

The fine fraction (starting material) was subsequently subjected to sonicating test. The suspension for sonication was prepared with 28 g of starting material dispersed in 400 ml of deionized water (7% by weight mixture). All the tests were conducted in batch mode where the sonicating time was varied from 2 to 30 min. A tool for irradiating ultrasound was a commercial ultrasonic probe (VCX-1500, Sonics and Materials, USA) that produces acoustic wave at a frequency of 20 kHz with maximum power of 1500 W. The sonic horn made of titanium alloy (tip diameter × length = φ20 mm × 60 mm) was driven by a PZT transducer, and it was dipped into the suspension around 10 mm from the top level. The suspension was subjected to irradiation of ultrasound at optimum sonicating conditions; the sonicating power and amplitude were adjusted to provide the optimum power output of generator. During sonication, cooling water was circulated around the glass vessel constantly in order to prevent excess

temperature increase inside the vessel. The experimental set-up for sonication is illustrated in Fig. 1.

2.4 Centrifugation

After sonication for desired duration, the suspension was transferred into 250 ml falcon tubes for centrifugation. A laboratory-scale centrifuge (Mega 21R, Hanil, Korea) with a swing rotor consisting of six centrifuge tubes was used. The centrifugation was performed at different centrifuging speed varied from 4000 to 10000 rpm for 60 min. Finally, both overflow and underflow products were dried at 65°C and re-ground for analysis.

2.5 Characterization

XRD patterns were collected by X-ray powder diffraction (XRD, RINT-2000, Rigaku, Japan) analysis using CuKα radiation with a scan speed of 3°/min. SEM morphology and the corresponding EDS analyses were performed using field emission scanning electronic microscopy with energy-dispersive spectroscopy (FE-SEM-EDS, JSM-7610F, Jeol, Japan).

3. Results and Discussion

Figure 2 shows the XRD patterns of fine and coarse particles fractionated by sedimentation as well as raw bentonite. The main mineral of raw bentonite was montmorillonite and minor ones were quartz, feldspar and opal-CT ((a) in Fig. 2). It was observed that the reflections of quartz and feldspar almost disappeared in the fine fraction, indicating the sedimentation was efficient to remove the easy-to-settle coarse particles associated with raw bentonite while the fine particles remained in suspension. Even so, the method could not reach high purification and the satisfactory production of montmorillonite was not given. Obviously the diffractograms verified that opal-CT, which is characterized by broad reflection

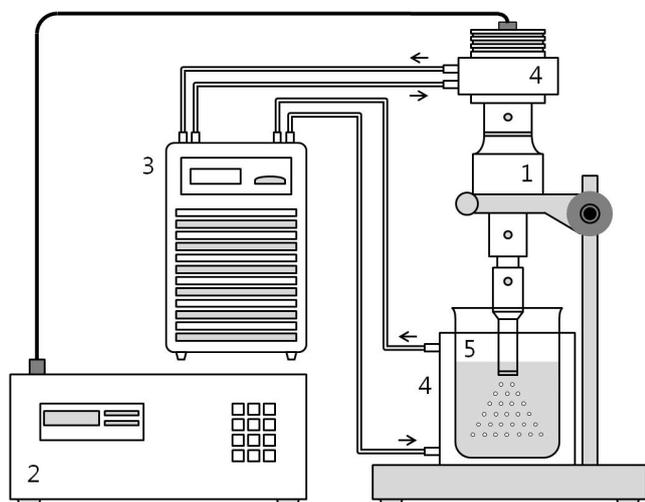


Fig. 1 Experimental set-up for ultrasonic treatment (1: sonic horn, 2: control body, 3: recirculating chiller, 4: cooling jacket, 5: glass vessel).

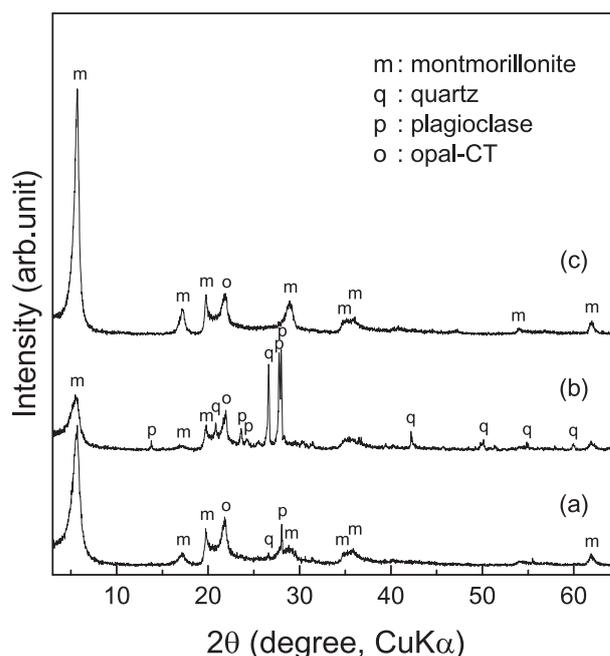


Fig. 2 XRD patterns of raw bentonite and sedimentation products ((a) raw bentonite, (b) coarse fraction and (c) fine fraction).

ranged in 4.05–4.10 Å (ca. 21.7–21.9° at 2θ)¹⁸) still remained in the fine fraction. This implies that the grains of montmorillonite and opal-CT not only are all fine but also co-exist as mixed aggregates quite strongly attached together. So, the mechanical scrubbing employed in this work was probably not strong enough to liberate these co-existing particles and they cannot be well separated each other by conventional sedimentation method.

Since montmorillonite and opal-CT in bentonite have similar specific gravities (2.4–2.7 g/cm³), gravity based methods are not suitable for the beneficiation of bentonite. The method based on the differences in particle size, therefore, would be a key role for the separation of them. Figure 3 shows the yield of overflow products (fine fractions in supernatant) on centrifugation depends on centrifuging speed at various sonicating time. It was observed that the yield of overflow was only 5.2 mass% at 4000 rpm above which the yield could not be assessed in the centrifugation without sonication (0 min in Fig. 3). Increasing centrifuging speed made it rather difficult to obtain the fine fraction selectively, because most of particles in suspension settled rapidly at higher centrifuging speed. On the other hands, it was interesting to note that the yield of overflow increased noticeably as sonicating time increased in the separation involving sonication-centrifugation process. Although the yield decreased gradually with an increment of centrifuging speed, the result was mainly attributed to the sonication effect that produced not only a cleavage on the (001) plane of montmorillonite but also a breaking of layers in the other directions while the crystalline character of montmorillonite was retained.

On the basis of the result that sonication could enhance the yield of overflow, a comparative sonicating test was performed separately; the irradiating ultrasound into the suspension treated by soda activation using Na₂CO₃. It is well known that one of the well-known characteristics of montmorillonite is its ability to swell in water and it is usually described in

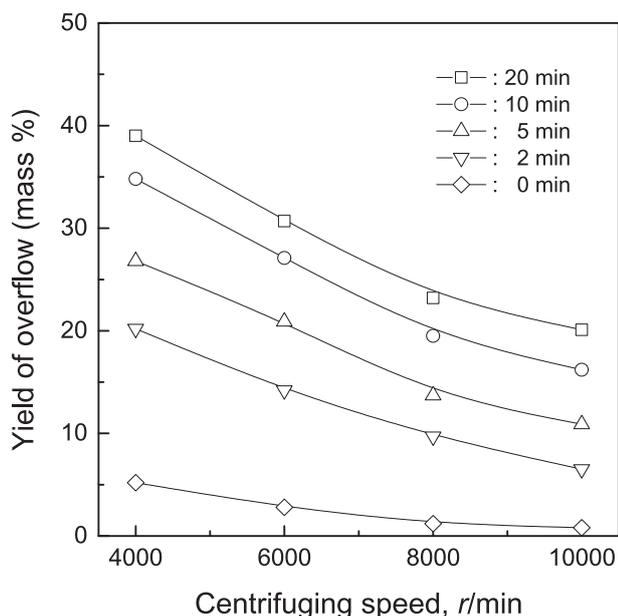


Fig. 3 Yield of overflow on centrifugation depends on centrifuging speed at various sonicating time.

terms of swelling volume. When Na₂CO₃ is introduced into the suspension, the exchangeable cations of interlayer of montmorillonite (mainly Ca⁺⁺ ions in case of Ca-bentonite) are exchanged to Na⁺ ions and the sample behaves like Na-bentonite in the suspension. As such it is water swellable and will hydrate to form stable colloidal structures showing high swelling volume. The preliminary test revealed that the cation exchange capacity (CEC) of starting material was 88.6 meq/100 g and the maximum swelling volume reached when equivalent amount of Na₂CO₃ corresponding to the CEC value of sample was introduced. Therefore, the optimum dosage of Na₂CO₃ for activation was calculated by the following equation;

$$\text{Dosage of Na}_2\text{CO}_3(\text{g}) = \frac{C \times W \times M}{1000} \times \frac{1}{2}$$

where C is the CEC of sample (eq/g), W is the weight of sample (g) and M is the molecular weight of Na₂CO₃, respectively. Figure 4 shows the yield of overflow on centrifugation depends on sonicating time at various centrifuging speed. The result clearly indicated that the increment of yield was significant and the yield reached up to 3 times at higher centrifuging speed when the suspension was activated. This pointed out the effect of high power ultrasound resulting in the enhancement of disintegration of layered montmorillonite particles. Namely, the micro-bubbles produced by ultrasound collapse near the particle surface creating microjets and shock waves and these energetic jets accelerate the destruction of layered structure much more dramatically when montmorillonite particles were expanded in the suspension by soda ac-

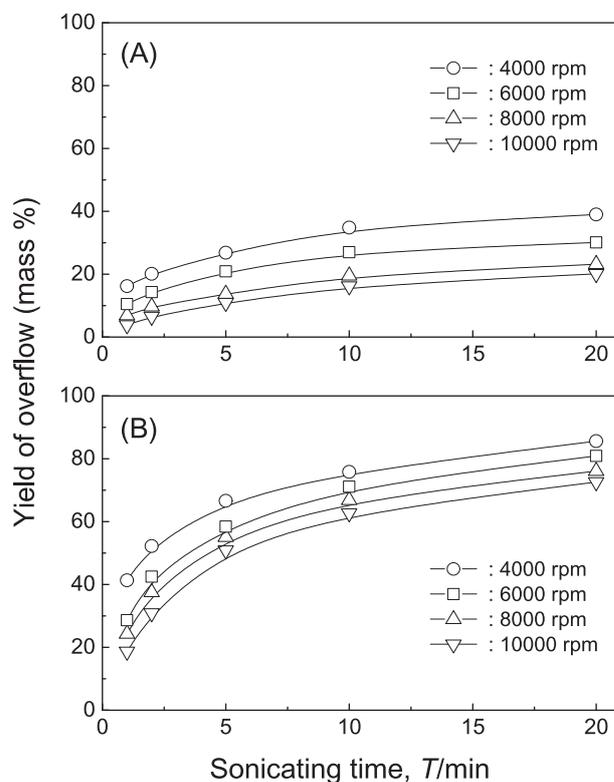


Fig. 4 Yield of overflow on centrifugation depends on sonicating time at various centrifuging speed ((A) non-activated suspension and (B) activated suspension).

tivation.¹⁹⁾

XRD analysis of classified products (both overflow and underflow) more clearly proved the sonication of activated suspension was much favorable for the separation of pure montmorillonite particles as shown in Fig. 5. The XRD patterns of overflows demonstrated that increasing centrifuging speed made it possible to reduce the peak intensity of opal-CT indicating successful separate was possible at high centrifuging speed of 10000 rpm in both cases (Fig. 5(A) and 5(C)). Moreover, they indicated that sonication even without activation also enabled the purification of montmorillonite from the pristine suspension (Fig. 5(A)). The XRD patterns of underflows in Fig. 5(B) showed that opal-CT were shifted toward underflow as centrifuging speed increased; actually a marginal increment of reflection of opal-CT could be detectable. Nevertheless, the diffractogram of underflow at 10000 rpm was similar to that of starting material. This strongly suggested that only sonication cannot provide high selectivity towards the purification of montmorillonite. In the case of activated suspension, on the other hand, intense reflections of montmorillonite (Fig. 5(C)) and opal-CT (Fig. 5(D)) pointed out high efficiency of the purification. Different peak intensities and reflections could be explained by taking into account the yield of centrifugation products from both suspensions as shown in Fig. 6. Only 16.2 mass% of total solids was recovered as an overflow from non-activated suspension at the cen-

trifuging speed of 10000 rpm. This implied that underflow still contained a lot of agglomerated grains of montmorillonite and they settled together with opal-CT particles. On the other hand, 63.5 mass% was recovered from activated suspension indicating sonication accelerated the disintegration of montmorillonite into fine particles remained in the suspension even at higher centrifuging speed. Actually, the reflection of montmorillonite increased, whereas the reflection of opal-CT decreased as centrifuging speed increased. The trend was more clearly observed in the activated suspension. It was also interesting to note that minor impurities of quartz and calcite, which was produced by the reaction between calcium and carbonate ions during activation, were completely moved to underflow after centrifugation. In this work, however, excessive sonication up to 10 min hindered the high purification of montmorillonite. Figure 7 shows the peak intensity of opal-CT in overflow from activated suspension at various sonicating time. The reflection of (101) plane of opal-CT increased slightly as sonicating time increased suggesting that particle size reduction of opal-CT progressed together with montmorillonite particles during prolonged sonication.

Figure 8 shows SEM images of centrifugation products obtained from activated suspension. The observed morphology and EDS analysis of overflow revealed the presence of main components constituting montmorillonite; Si, Al and O, and traces of Mg and Na ((a) in Fig. 8(A)). EDS analysis of un-

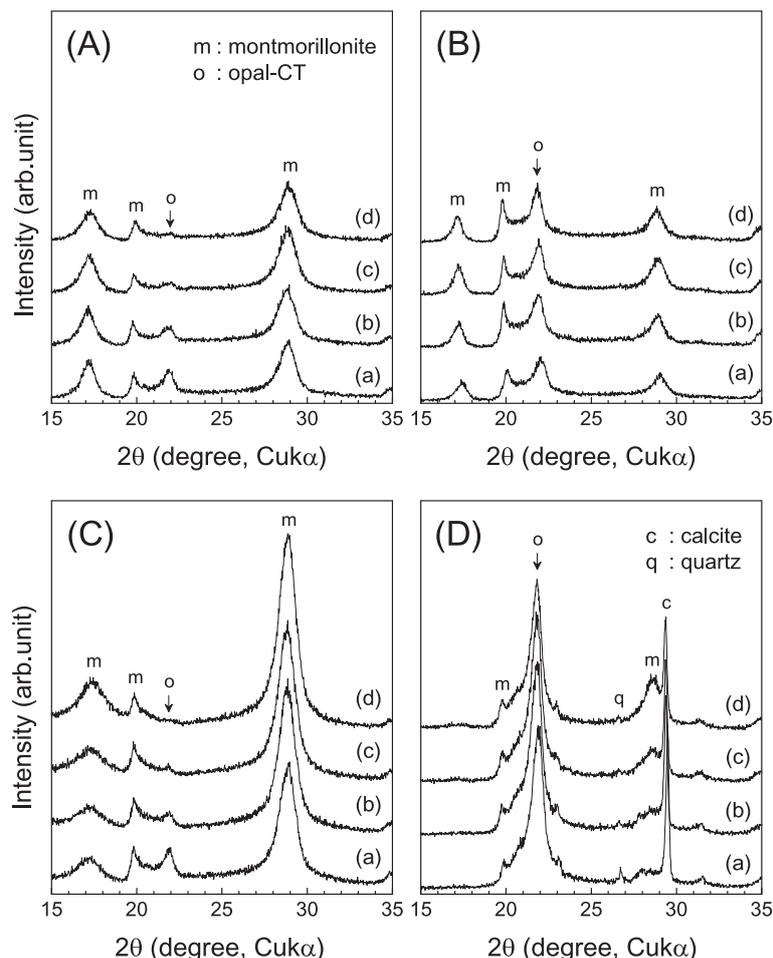


Fig. 5 XRD patterns of centrifugation products obtained from non-activated suspension ((A) overflow, (B) underflow) and activated suspension ((C) overflow, (D) underflow) at sonicating for 10 min ((a) 4000 rpm, (b) 6000 rpm, (c) 8000 rpm and (d) 10000 rpm).

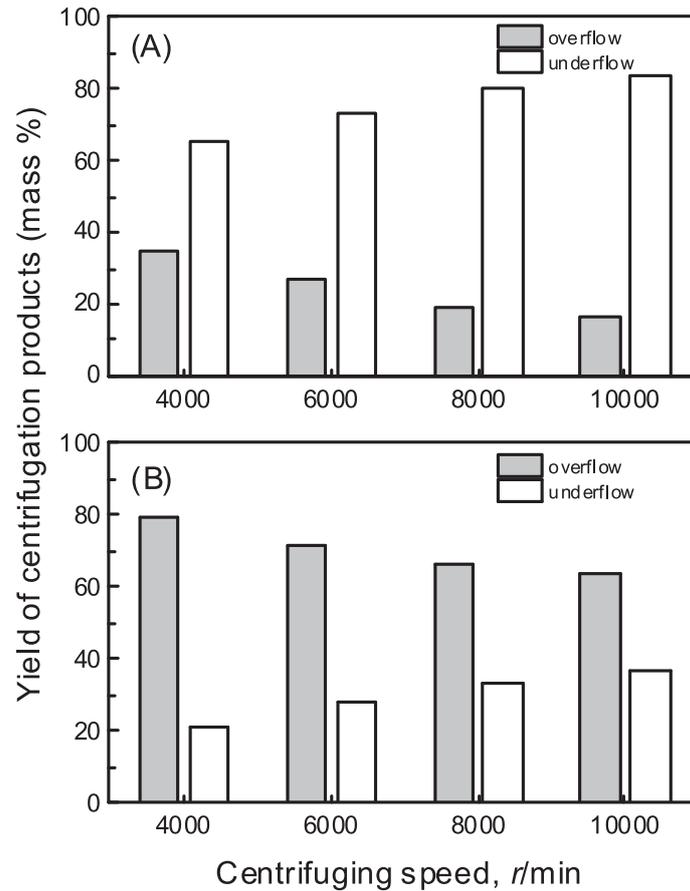


Fig. 6 Yield of centrifugation products depends on centrifuging speed at sonicating for 10 min ((A) non-activated suspension and (B) activated suspension).

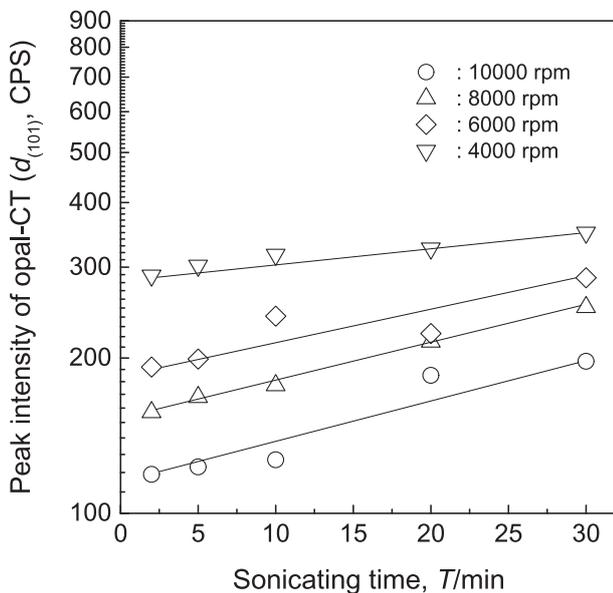


Fig. 7 XRD peak intensity of (101) plane of opal-CT depends on centrifuging speed at various sonicating time.

derflow showed the compounds containing mainly Si and O in different ratio indicating the presence of quartz and opal-CT, which is characterized by small crystallites that commonly form agglomerates of blade-shaped crystals so-called lepispheres²⁰ ((b) and (d) in Fig 8(B)). A trace of Ca was also

detected in the underflow identified as (c) confirming that calcite produced during activation was removed by centrifugation.

4. Conclusion

Irradiating ultrasound into bentonite-water suspension could result in particle size reduction of montmorillonite by cavitation effect of sonication leading to microjets and shock wave impacts on montmorillonite surface together with interparticle collisions. The production of fine montmorillonite particles increased as sonicating time increased in the suspension. Moreover, the production increased markedly when the suspension was activated by Na_2CO_3 . It was possible that pure montmorillonite particles were collected as an overflow product whereas opal-CT and other impurity particles were shifted towards underflow by centrifugation. The separation became more efficient when sonication was employed to the activated suspension. Increasing centrifuging speed made it possible to separate pure montmorillonite particles. Only 16.2 mass% of total solids was recovered as an overflow from non-activated suspension whereas 63.5 mass% was recovered from activated suspension at centrifuging speed of 10000 rpm. In this work, 10-min sonication was best, however, sonicating up to 10 min deteriorated the purification of montmorillonite due to particle size reduction of opal-CT during prolonged sonication.

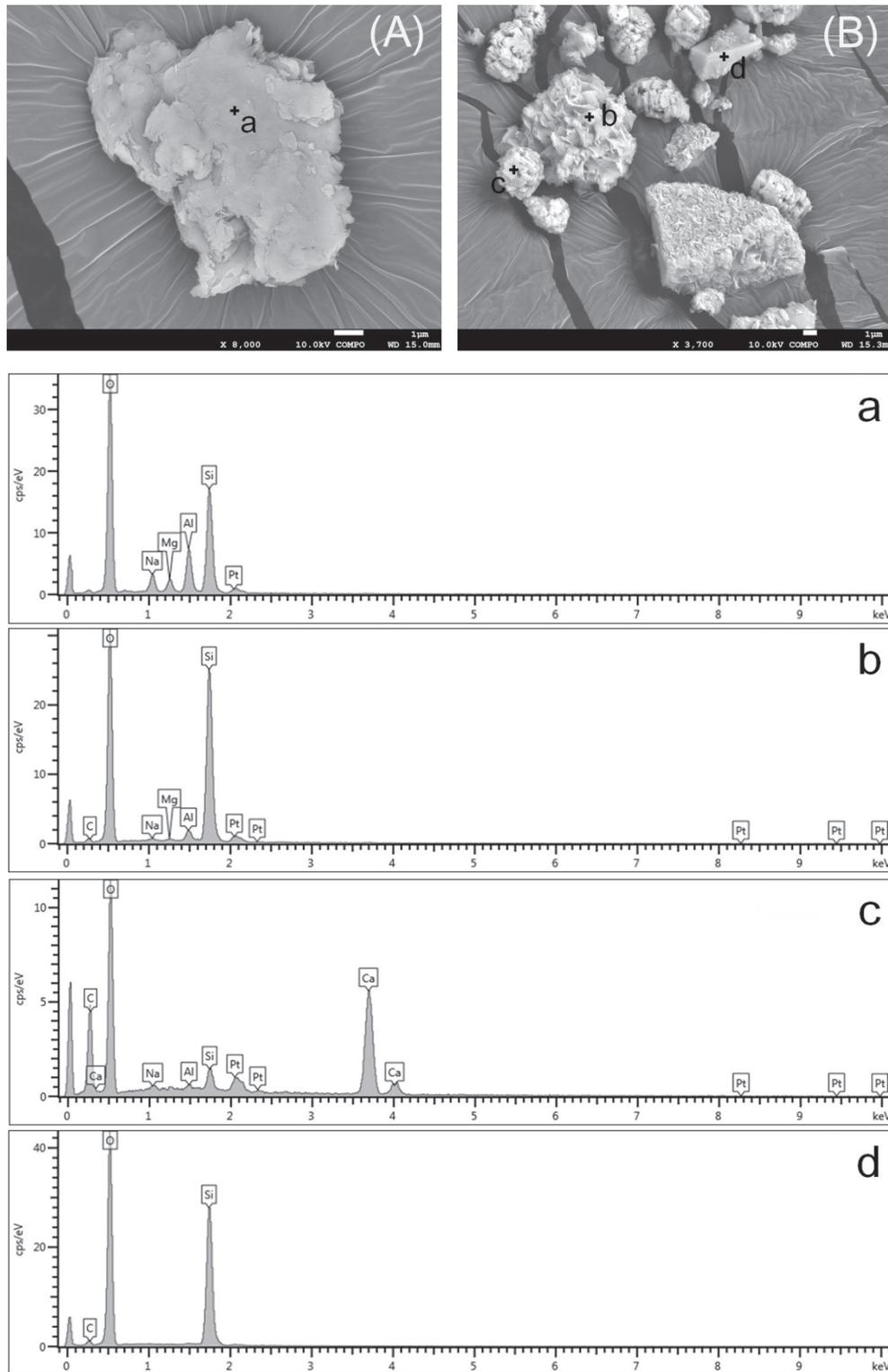


Fig. 8 SEM images and corresponding EDS analyses of centrifugation products at centrifuging speed of 10000 rpm ((A) overflow and (B) underflow).

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