

Synthesis of $\text{Ca}(\text{OH})_2$ nanoparticles for rapid treatment of mine waste water

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Abstract $\text{Ca}(\text{OH})_2$ nanoparticles were prepared by a simple hydrolysis method using $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ as the precursor, aqueous NaOH as precipitant, and ethylene glycol as medium. The nanoparticles were characterized by X-ray diffraction analysis (XRD), field emission scanning electron microscopy (FESEM), and transmission electron microscopy (HRTEM). The results showed that the nanoparticles are of about 35 nm in hexagonal structure. A small scale study to treat synthetic acid mine water by synthesized $\text{Ca}(\text{OH})_2$ nanoparticles shows higher efficiency to remove heavy metals than conventional use of lime. XRD results of precipitates show presence of different metal hydroxides and sulfate, precipitated as CaSO_4 .

Key Words $\text{Ca}(\text{OH})_2$ nanoparticle, chemical synthesis, acid mine water, rapid treatment

Introduction

Acid mine drainage (AMD), formed due to the oxidation of sulfide minerals in the presence of oxygen and water, poses an environmental problem to aquatic ecosystems in coal and hard rock mining regions (Williams et al. 2000; Johnson et al. 2003). AMD is characterized as low pH, high acidity effluents with high sulfate content and various dissolved metals such as Fe, Al, Mn, Zn, Cu, Ni, Ca, Mg, and Cr (Kim et al. 2002; Bird et al. 2003). Active AMD treatment involves addition of neutralizing agents (hydrated lime, anhydrous ammonia, sodium hydroxide, limestone and sodium carbonate) to raise the pH of the AMD water and precipitate metal ions. There are passive treatments of AMD also available (Cheong et al. 2010) but it takes more time. Researchers are interested in synthesis of nanosized $\text{Ca}(\text{OH})_2$ for its applications in fundamental and applied science. However, literature on the preparation of moderately water soluble inorganic nanoparticles is rare (Rees 1999), compared to the studies concerning nanoparticles of water insoluble compounds (sulfides, oxides, metals, etc.; Bagwe et al. 1997). $\text{Ca}(\text{OH})_2$ nanoparticles can be used for rapid and high volume water treatment, wall painting and carbonatic stone and wood conservation, etc. (Giorgi et al. 2005; Roy et al. 2010).

Whilhemy et al. (1984) reported that the precipitation of metal hydroxides from corresponding salt solution is affected by temperature. It is also reported that reaction time and temperature affect the precipitation of metal hydroxide (Matijevic et al. 1978). Particularly it has been reported that above 100°C temperature, formation of nano-scale particles is rapid and sizes are found to be uniform. Some studies reported that metal hydroxide precipitation is also affected by concentration of reacting species and types of medium (Hamada et al 1990). Yura et. al. (1990) and Hamada et. al. (1982) reported that selection of organic solvent can influence size and shape of the particles obtained by the precipitation reaction. The present work emphasizes on the preparation and characterization of the nanosized $\text{Ca}(\text{OH})_2$ nanocrystal by hydrolyzing hydrated calcium nitrate by sodium hydroxide in ethylene glycol at 115 °C. A small scale study to treat synthetic acid mine water by synthesized $\text{Ca}(\text{OH})_2$ nanoparticles shows higher efficiency to remove heavy metals than conventional use of lime. Result of treated water shows higher de-acidification and dischargeable concentration of heavy metals in effluent water. XRD results of precipitates show presence of different metal hydroxides and sulfate, precipitated as CaSO_4 .

Experimental Section

Synthesis of $\text{Ca}(\text{OH})_2$

Calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), ethylene glycol (GR), sodium hydroxide, and 2-propanol analytical grade were of Merck (Darmstadt, Germany). Water was purified by a Millipore Organex system ($R > 18\text{MW cm}$). In a typical run, 25ml of ethylene glycol was heated in a conical flask at 115 °C in an oil bath, and then 12 gm of $\text{Ca}(\text{NO}_3)_2$ was introduced into the conical flask. After the calcium salt was dissolved, 12mL NaOH (2.10g) solution was added drop by drop into the above mixture. The mixture was vigorously stirred at same temperature for 10 minutes. In order to get uniform sized particles, after it was stirred, the gel was kept for about 5 minutes at static state, at

room temperature. After the resulting solution was cooled down, supernatant was discarded, and the particles were then separated from the remaining solution by hot vacuum filtration. Filtrated particles were peptized with 2-propanol, and the resulting suspension was discarded. The solids were then dispersed in 2-propanol in an ultrasonic bath. They were separated by centrifugation at 10,000 rpm for 5 minutes. Then the particles were dried under vacuum at temperature 60 °C-70 °C.

The phase analysis and crystallinity were checked with XRD pattern using diffractometer equipped with a Co K α ($\lambda=1.789\text{\AA}$) source and the patterns were recorded at a scan rate 2° min⁻¹. Particle size and morphology were studied with FESEM and HRTEM in the voltage range of 20–200 kV.

Batch experiment with nano Ca(OH)₂

Synthetic AMD was prepared and used for the batch experiment. The aim of these neutralization batch experiments was to note pH and also changes in solution composition due to the addition of nano Ca(OH)₂ and market available lime. At first the analyses of the above mentioned initial parameters of synthetic mine water was carried out by Orion 5 star pH meter and GBC AAS (Atomic absorption spectrophotometer). Two liter reagent bottles were filled with synthetic AMD and an amount of 0.1g of the nano Ca(OH)₂ and lime were added separately and bottle cap was sealed by parafilm. The samples prepared in this manner were put on a vertically rotating shaker and were agitated (0.5 rpm) for 10 minutes. Finally, treated water was again analyzed for pH and metal contain (Tab. 1).

Result and Discussion

Characterization of Ca(OH)₂

Fig. 1 represents the XRD pattern of the material obtained by this method. In figure 1, the patterns of Ca(OH)₂ crystal obtained displays the following diffraction peaks (2θ [°]): 21°, 33.35°, 39.75°, 55.25°, 59.6° and 63.95°, which can be correlated to the (hkl) indices (001), (100), (011), (012), (110) and (111), respectively of pure hexagonal Ca(OH)₂ (JCPDS No. 84–1271). The sharp diffraction peaks of particles indicated that well-crystallized Ca(OH)₂ crystals could be obtained under current synthetic condition. The broadening of the peaks indicated that the particles were of nanometer scale. Estimated from the Sheerer formula, $D = 0.891 \lambda / \beta \cos \theta$, where D is the average grain size, λ is the X-ray wavelength (1.789Å), and θ and β are the diffraction angle and full-width at half maximum of observed peak, respectively, the average size of the particles of sample was 35 nm.

The morphology and size of the samples were investigated by SEM and HRTEM. FESEM of the particles in fig. 2 indicates that the particles were agglomerated and original morphology of the particles was approximately hexagonal, and varying in size approximately between 25–100nm. Fig. 3 represented HRTEM (bright field) images which reveal nearly hexagonal shaped particles of calcium hydroxide.

The size distribution is given in the histogram inserted in fig. 3. Average values included in this histogram were obtained by analyzing several frames of similar bright field images of the specimen. Majority of calcium hydroxide nanoparticles in this histogram are of the average size approximately 39 nm, which is in close agreement with an average D-value 35 nm determined above from the XRD peak broadening. Chemical composition of the resulting nanomaterial was checked by EDX. From EDX result in fig. 4, it was found that chemical constituents of the material were Calcium and Oxygen; Hydrogen perhaps due to low molecular weight was not identified.

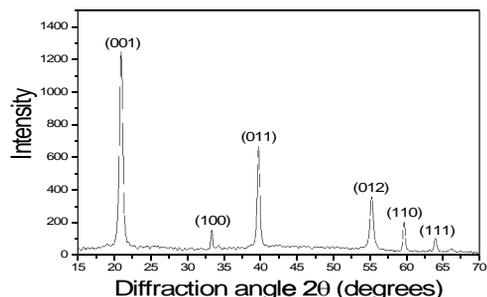


Figure 1 XRD patterns of Ca(OH)₂ nanocrystals

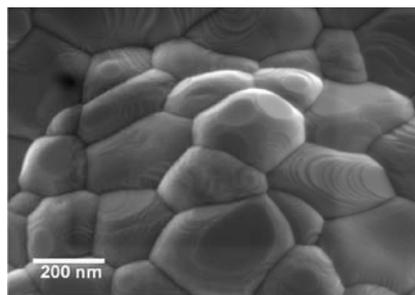


Figure 2 FESEM image of nanoparticles

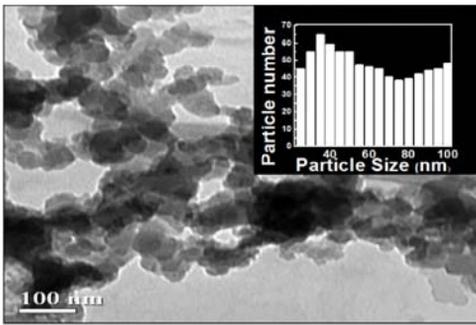


Figure 3 HRTEM micrograph of nanocrystals

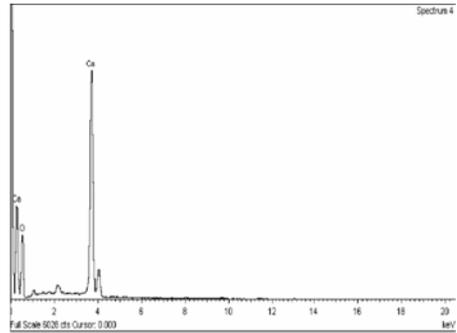


Figure 4 EDX spectrum of nano Ca(OH)₂

Batch experiment

Tab. 1 shows chemical composition of feed and treated water when synthetic acid mine water was treated with nano Ca(OH)₂ and lime. After 10 min shaking treated water was analyzed by AAS for heavy metal measurement and sulfate concentration was measured by spectrophotometric method. As nanoparticles have high surface by volume ratio, it is more reactive, high chemical specificity and fast sorption capacity. Heavy metal removal capacity of the synthesized nano Ca(OH)₂ higher than lime treatment and takes very less time.

Precipitate was collected and characterized by XRD. XRD spectrum (fig. 5 and 6) of precipitates shows heavy metals were precipitated as metal hydroxide and sulfate was removed by precipitation of gypsum (Ca(SO₄)). XRD spectrum in fig 6 shows good amount of metal were precipitated and also sulfate (SO₄²⁻) were precipitated as gypsum which was not found in the fig. 5. Lime removes heavy metals but it seems to have less ability to remove sulfate from AMD. Nano Ca(OH)₂ was able to remove heavy metals as well as sulfate.

Table 1 Comparison of pH and selective ions of synthetic AMD and treated synthetic AMD with nano Ca(OH)₂ and lime

	pH	Fe (ppm)	Cu (ppm)	Mg (ppm)	Mn (ppm)	Sulfate(mg/L)
Synthetic AMD	2.56	166.5	63	28.9	2910	1001
Synthetic AMD + lime	8.5	125	49	21	2102	950
Synthetic AMD + nano Ca(OH) ₂	10.2	49	13	12	1050	256

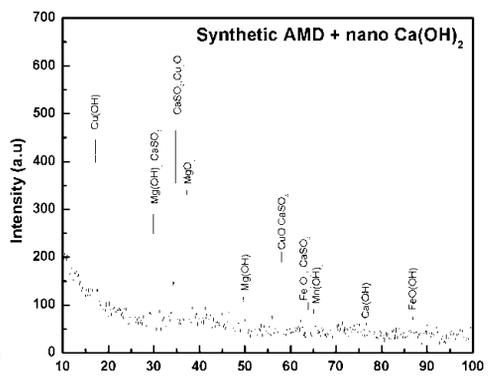
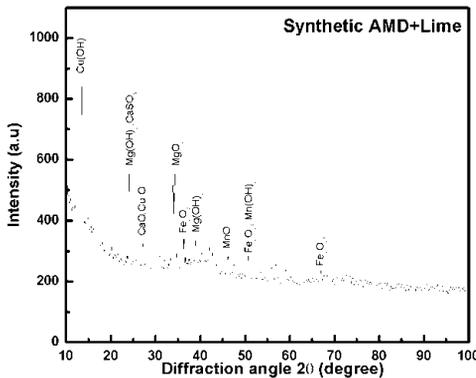


Figure 5 XRD of precipitate from lime treatment

Figure 6 XRD of precipitate from nano treatment

Conclusion

This study describes a simple method for the preparation of nanosized $\text{Ca}(\text{OH})_2$ particles by simple chemical method. The crystal phase of $\text{Ca}(\text{OH})_2$ was hexagonal. A novel approach toward the removal of heavy metals from AMD water is presented. It is proved that the addition of nano $\text{Ca}(\text{OH})_2$ into acid mine water leads to a pH increase of the solutions with the consequence of reduction of targeted anions and cations. Such processes involve mechanisms like reductive mineral precipitation and coprecipitation, insoluble hydroxide formation and adsorption.

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