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ADVANCES IN CLAY SCIENCE IN CHINA

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Reports of scientific investigations published in *Clays and Clay Minerals* address a wide range of topics covering virtually every physical and natural science and thousands of industrial products and processes worldwide. Even though these nano-sized materials occur naturally throughout the Earth's crust, a large proportion of the studies carried out in the past regarding their origins, nature, and uses, as reported in *Clays and Clay Minerals*, have arisen predominantly from North America and Europe. In recent years, however, manuscript submissions from China have increased appreciably (Figure 1). In the current issue, a number of those studies were selected for a compilation in order to highlight the contributions being made by Chinese colleagues, which gives a glimpse into the types of clay research under way in that country. The manuscripts selected do not, of course, represent a comprehensive treatise of clay research in China, but rather an opportune emphasis that is intended to call attention to the work being done there.

China has a long history of using clay minerals for various applications, but scientific research on clay minerals did not start until the 1950s. Early studies centered largely on the purification of clay minerals and their crystal structure and chemistry. Rapid economic development in China over the past 20 years has led to a large demand for natural resources. Concerted efforts in mineral exploration have discovered abundant clay and clay mineral resources in China. In addition to common kaolinite, smectite, and vermiculite, large deposits of other clay minerals, such as rectorite in Hubei Province and hydrobiotite in Xijiang Autonomous Region, have also been discovered.

With advances in terms of characterization techniques, such as modern spectroscopy and electron microscopy, Chinese scientists have made important contributions to clay science research (Figure 1). They are actively involved in a number of professional organizations and international conferences. Current clay-mineral research in China is multi-faceted. In addition to traditional research on crystal structure, crystal chemistry, clay genesis, and occurrence, many Chinese scholars are heavily engaged in the characterization of clay-surface chemistry. In particular, the Chinese clay-minerals community is active in finding new applications of traditional clay minerals through surface or structural modification. Modified clays and clay minerals have found wide applications in environmental remediation, catalysis, and materials engineering.

Two papers in this issue describe new methods to synthesize various types of clay-organic and metal-intercalated nanocomposites. Fan *et al*. (2011) synthesized zerovalent iron/montmorillonite nanosized heterostructures through a hybridization process in which montmorillonite was impregnated with ferric ions followed by chemical reduction. The hybridized iron nanoparticles were well dispersed on the montmorillonite surface and resistant to reoxidation. These nanomaterials are expected to have promising applications in heterogeneous catalysis, adsorption, and environmental remediation. Wang, Y. *et al*. (2011) report a method to intercalate poly(oxypropylene) (POP) amine hydrochlorides into the interlayer space of montmorillonite. The basal spacing of modified montmorillonite increased with the hydrophobic chain length of the POP ammonium ions. After intercalation into the montmorillonite

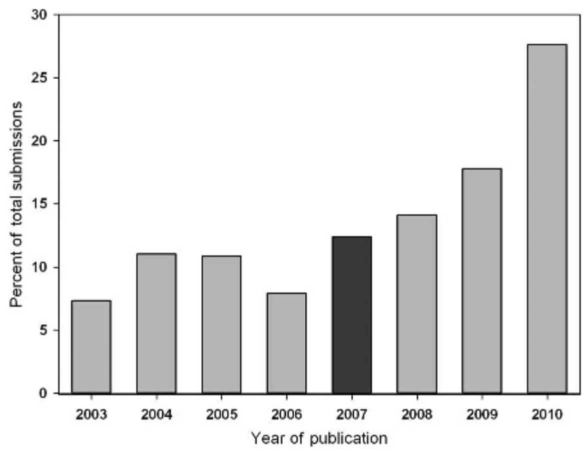

Figure 1. Proportion of manuscripts submitted for possible publication in *Clays and Clay Minerals* by Chinese scientists (value for 2007 is estimated).

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interlayer spacing, the thermal stability of the POP ammonium ions was decreased. These findings are important in providing understanding of the application of modified montmorillonite to pollution prevention, environmental remediation, and clay-polymer nanocomposites.

Several papers in this collection investigated the applications of synthetic clay nanocomposites in environmental remediation. The study by Li *et al*. (2011) evaluates the effectiveness of hydroxyl-Fe/Al-intercalated montmorillonite (Fe/Al-Mt) as a photo-Fenton catalyst. Intercalation was achieved *via* an ion-exchange method and brilliant orange X-GN, a toxic dye, was the test compound for photodegradation by hydrogen peroxide (H_2O_2) under visible light irradiation in the presence of Fe/Al-Mt. The photocatalytic activity of the Fe/Al-Mt was significant due to the presence of the hydroxy-Al/Fe surface, bringing about near-complete degradation within 3 h. The study by Wang, M. *et al*. (2011) reports the adsorption of low concentrations of ammonium in wastewater by vermiculite from Hebei Province, as a function of adsorption time, particle size, adsorbent dose, pH, and temperature. Optimal adsorption was found at pH 6–7 and a temperature of 60ºC, which yielded an adsorption capacity of 18 mg of ammonium g^{-1} of vermiculite after 3 h of equilibration. Cation exchange was the mechanism for ammonium uptake into the vermiculite structure. Ling *et al*. (2011) investigated the possibility of using organically modified bentonite (OMB) to treat municipal landfill leachate. The OMB, synthesized based on a modified version of a previously published procedure, was found to be very effective (90% efficiency) in degrading organic pollutants in leachate.

In addition to their importance in environmental remediation, clay minerals are also used widely in materials science and engineering, such as in the development of new materials used for thermal insulation, noise reduction, and retention of heat. Montmorillonite, kaolinite, and sepiolite, modified by inorganic and organic nanomaterials, exhibit superior properties in terms of their resistance to heat and salinity, due largely to the complex tunnel structures and large surface areas. Two papers in this compilation report applications of clay minerals in materials science and engineering. Wang, J. *et al*. (2011) studied the effect of organo-montmorillonite (OMMT) and modified OMMT on the flame-retardance and mechanical properties of natural rubber composites. These investigators synthesized novel flame-retardant hyper-branched organic montmorillonite (FR-OMMT), natural rubber-OMMT, and natural rubber-FROMMT. Through various testing, they found that organic montmorillonite is an effective filler for improving the mechanical and flame-retardance properties of natural rubber composites. Surface modifications of OMMT further improve the tensile and flame-retardant properties of natural rubber. He *et al*. (2011) applied first-principles theory to calculate the formation energy of kaolinites when structural Al is replaced by two other elements. The implication of this work is a better understanding of the chemical and physical properties of natural kaolinite in engineering applications.

Other clay-sized minerals have received increased attention by Chinese clay scientists, among which natural or synthetic layered double hydroxides (LDH) and Mn oxides are two examples. Layer double hydroxides, also called anion clays (in contrast to phyllosilicates which are cation clays), possess large surface area, strong anion exchangeability, and adjustable layer spacing, and can be modified readily by inorganic and organic agents. For example, insertion of various anion surfactants into the LDH structure increases the layer spacing and changes its hydrophilicity to hydrophobicity. Various active catalysts are synthesized by inserting metal oxides into the layer spacing of LDH, such as Mo, W, and Si oxides. These metal oxide-intercalated LDH are highly catalytic and are promising 'green' catalysts. Two papers in this issue address special applications of LDH and birnessite, a Mn oxide. Wu *et al*. (2011) synthesized LDH with varying molar ratios of Mg/Al and used this material to remove reactive brilliant orange X-GN, a toxic dye material. The mechanism of removal was *via* its intercalation into the interlayer space of the LDH. The high molar ratio of Mg/Al favored the removal of X-GN. The optimal intercalative adsorption occurred at pH 3.0 and the adsorption mechanism was described by monolayer adsorption. Liu *et al*. (2011) synthesized hexagonal and triclinic birnessites in acidic and alkali media and used these materials to study the influence of the crystal-structure properties of birnessites on the oxidative polymerization of hydroquinone. The catalytic mechanism of birnessites in the abiotic formation of humic-like polymers is elucidated. The authors found that the crystal structure and surface chemistry of birnessites have significant influence on their oxidative activities and the degree of polymerization of hydroquinone, but they have little effect on the abiotic formation mechanism of humic-like polymers.

One recent research direction among Chinese clay scientists is clay mineral-microbe-DNA interactions, such as the interactions between various clay minerals and extracellular DNA molecules and the stability and activity of DNA molecules on the surfaces of soil minerals. These studies are important to understanding the origin of life on Earth and medical applications of clay minerals. One paper in this issue, by Zhu *et al*. (2011) on clay mineral-microbe interaction, fits broadly into this category. The authors studied the interactions between a smectite-rich bentonite, and silicate-weathering bacterium, *Bacillus mucilaginosus*, and characterized the consequences of such interactions. Certain elements were released from bentonite, and mineralogical changes were observed.

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Lastly, one paper in this issue represents a sub-discipline of clay mineralogy, *i.e.* applications of clay minerals in paleo-environment reconstruction. Hong *et al*. (2011) studied interstratified illite-smectite and kaolinite from the Permian-Triassic boundary (PTB) sediments between the Meishan section (the Global Stratotype Section and Point of the PTB) and the Xiakou section, southern China. The crystal chemistry and genesis of these clay minerals was used to infer the temporal link between volcanism and mass extinction at the Permian-Triassic boundary.

In summary, Chinese scientists are making novel and pioneering contributions in clay research that merit international scrutiny, attention, and admiration. The Clay Minerals Society is pleased to recognize their work by the emphasis given with this issue of *Clays and Clay Minerals*. The Editorial Staff hopes this will encourage and foster even greater contributions from and collaborations with colleagues in China.

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