INDUSTRIAL APPLICATIONS OF CLAYS

Monday June 21, 2004

Industrial Applications of Clays	
10:00 – 10:20a	**SYNTHESIS AND CHARACTERIZATION OF LAYERED DOUBLE HYDROXIDES (LDH)/POLYMER NANOCOMPOSITES.** Nilwala S. Kottegoda*[1], Wuzong Zhou[2], and William Jones[1] [1]Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, UK. [2]School of Chemistry, University of St. Andrews, St. Andrews, Fife, KY16 9ST, UK
10:20 – 10:40a	**PHASE CHANGE OF CATALYSTS DERIVED FROM DEOXYCHOLATE PILLARED-HYDROTALCITE-TYPE CLAY AND IMPACTS ON NO_X REDUCTION FROM STATIONARY SOURCES.** Wongkerd, T.[1], Jitkarnka, S.*[1], Luengnaruemitchai, A.[1], and Yang, R.T.[2] [1]The Petroleum and Petrochemical College, Bangkok, Thailand; [2]University of Michigan, Ann Arbor, United States
10:40 – 11:00a	**THE EFFECTS OF ALKALI METAL CATIONS ON KAOLIN SUSPENSION RHEOLOGY.** Ungsoo Kim[*1], Hyojin Lee[1], Mark D. Noirot[2], and William M. Carty[1] [1]New York State College of Ceramics at Alfred University, Alfred, NY 14802; [2]U.S. Borax Inc., 26877 Tourney Road, Valencia, CA 91355-1846
11:00 – 11:20a	**SHORT TERM EXPERIMENTS WITH DIFFERENT BENTONITES IN SALINE SOLUTIONS.** Joern Kasbohm[*1], Roland Pusch[2], and Karl-Heinz Henning[1] [1]Institute of Geography and Geology, University of Greifswald, Greifswald, Germany; [2]Geodevelopment AB, Lund, Sweden
11:20 – 11:40a	**INDUSTRIAL USES FOR NEW ZEALAND HALLOYSITE.** Simon Marsters Imerys Tableware Asia Limited, Auckland, N.Z.
11:40 – 12:00p	**A COMPARISON OF FIBROUS CLAYS AND FIBROUS AMPHIBOLES AS INDUSTRIAL MINERALS.** James L. Post*[1], and Londa Borer[2] [1]740 Zion Street, Nevada City, CA 95959; [2]Chemistry Dept., California State University, Sacramento, CA 95819, USA; jlp.net@jps.net.
Industrial Applications of Clays Poster Session	
5:00p	**UV-PROTECTION CREAMS: FIRST RESULTS FOR SUBSTITUTION OF NON-NATURAL ADDITIVES BY CLAY MINERALS.** Hoang Thi Minh Thao[1], Le Thi Lai[2], Joern Kasbohm[3] [1]Hanoi University of Science (VNU), Hanoi / Vietnam (recently: Institute of Geography and Geology, University of Greifswald/Germany); [2]Institute of Geological Sciences, VAST, Hanoi/Vietnam; [3]Institute of Geography and Geology, University of Greifswald/Germany

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10:00AM

SYNTHESIS AND CHARACTERIZATION OF LAYERED DOUBLE HYDROXIDES (LDH)/POLYMER NANOCOMPOSITES

Nilwala S. Kottegoda*[1], Wuzong Zhou[2], and William Jones[1]

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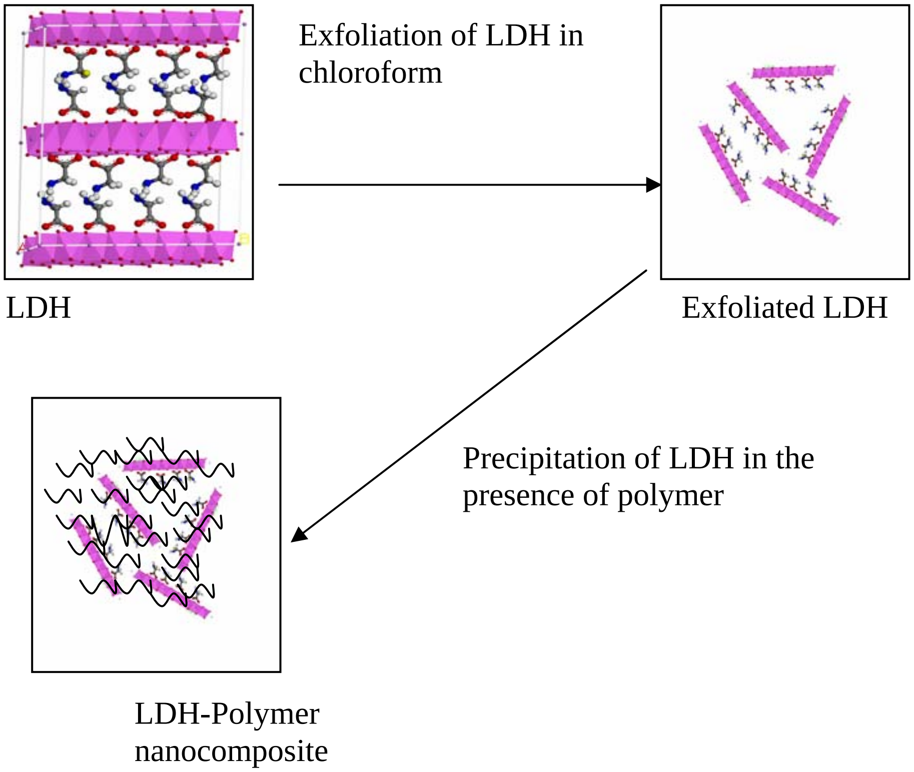
Layered Double Hydroxides (LDHs) are a class of layered materials which are suitable for the preparation of nanocomposites, in which ultra fine nano-particles of LDH are homogeneously dispersed within a polymer matrix. Nanocomposites are prepared either by (i) intercalation of a polymer material between the layers of an inorganic material or (ii) by exfoliation of a layered material in a suitable solvent followed by precipitation in a polymer matrix.

Nanocomposites based on exfoliated Li-Al-glycine LDHs and polyethyleneglycol (PEG) are described in this presentation. The products have been characterised by PXRD, FTIR and HREM and the properties of the composite materials have been studied using thermogravimetry and by mechanical testing. Results suggest that the LDH plates are individually dispersed in the polymer matrix and that the properties of the composite materials are superior to the parent polymer, proving that the exfoliated clay state is effective in improving the properties of parent polymer.



PHASE CHANGE OF CATALYSTS DERIVED FROM DEOXYCHOLATE PILLARED-HYDROTALCITE-TYPE CLAY AND IMPACTS ON NO_X REDUCTION FROM STATIONARY SOURCES

Wongkerd, T.[1], Jitkarnka, S.*[1], Luengnaruemitchai, A.[1], and Yang, R.T.[2]

[1]The Petroleum and Petrochemical College, Bangkok, Thailand; [2]University of Michigan, Ann Arbor, United States.

Selective catalytic reduction (SCR) of NO by NH_3 forming nitrogen and water is the commercial technology for removing nitric oxides in power plants. Clay is intensively interesting for this technology. In this study, catalysts from a hydrotalcite-type clay were prepared and used for SCR of NO by NH_3 over excess oxygen. Deoxycholate pillared-hydrotalcite-type clay (DA-clay) was synthesized by hydrothermal method. It showed over 99% N_2/N_2O selectivity at all testing temperatures. The change in structure, phase transition, surface morphology, and surface area of pillared-clay upon temperature were studied by XRD, TGA, SEM, and BET techniques. The characterization results showed that this pillared-clay has different thermal transition behaviors in the different stages of calcination temperatures, which affected to the SCR activity. The magnesium-aluminium mixed oxide phase from pillared-clay calcined at 500°C, which possessed Brønsted acid sites and high surface area, gave higher activity than the others.

THE EFFECTS OF ALKALI METAL CATIONS ON KAOLIN SUSPENSION RHEOLOGY

Ungsoo Kim[*1], Hyojin Lee[1], Mark D. Noirot[2], and William M. Carty[1]

[1]New York State College of Ceramics at Alfred University, Alfred, NY 14802; [2]U.S. Borax Inc., 26877 Tourney Road, Valencia, CA 91355-1846

The effect of alkali metal cations on commercial kaolin suspension rheology was studied across a concentration range of 1.0 to 500 mM. The kaolin slurries were all dispersed with sodium polyacrylic acid (Na-PAA) at 0.2 mg/m^2 (the amount necessary for surface coverage). The critical coagulation concentration (CCC) was determined for Li^+, Na^+, K^+, Rb^+, and Cs^+ using viscosity measurements. Also, diluted suspensions (~10 vol.%) were prepared to examine the coagulation effects on kaolin suspensions at different pH levels (pH = 4, 7, and 9). Adsorption isotherms of cations on the kaolin were measured for all the samples. The critical coagulation concentration of M^+ was determined to be identical for Li^+, Na^+, K^+, Rb^+, and Cs^+, but the maximum viscosity scaled with ion size. In addition, the larger metal ions demonstrated significant specific adsorption on the surface of the clay modifying the viscoelastic properties of the coagulated system. Dispersion stability is eventually overcome by cation affects as the CCC is approached. The rheology of highly loaded suspensions is sensitive to combined alkali concentrations at the tens of millimolar level which is occasionally of concern for industrial ceramic production.

SHORT TERM EXPERIMENTS WITH DIFFERENT BENTONITES IN SALINE SOLUTIONS

Joern Kasbohm[*1], Roland Pusch[2], and Karl-Heinz Henning[1]

[1]Institute of Geography and Geology, University of Greifswald, Greifswald, Germany;
[2]Geodevelopment AB, Lund, Sweden

Compacted bentonites are candidate materials for sealing elements of technical barriers in repositories for radioactive and chemical wastes. For a long term guarantee of such barriers we have to describe beforehand the possible alteration processes of applied bentonite in interaction with different types of solutions.

In our previous work, pyrophyllitization/kaolinitization was characterized as the main thermodynamic pathway of alteration in high saline solutions (low pH) for MX-80 bentonite. These results were valid mainly for “closed” reaction systems. This work also suggested that beidellitization, vermiculitization and illitization might occur in ”dynamic” systems.

To test these predictions, short term experiments (20 days) were carried out with different bentonites (Belle Fourche, Pioche, Chambers, Otay; Garfield nontronite; Friedland IS-mixed layers). These experiments were conducted with powder samples in 1 n NaCl-solution (solid-liquid ratio = 1:4), at ambient temperature, and arranged in an overhead-shaker equipment (= “dynamic”). Experiments with compacted MX80-bentonite (dry density 1200 – 1300 kg/m^3) in percolating 10% and 20% NaCl-solutions for 30 days (110°C) were also conducted to visualize possible alteration processes under more realistic conditions. Run products were characterized by X-ray diffraction and transmission electron microscopy (morphology, electron diffraction, element distribution).

After the short reaction time of 30 days smectite was still the main compound in the run products of compacted MX-80 bentonite and retained full expandability under ethylene-glycol solvation (16.9 Å). Montmorillonite was formed by Al-enrichment in the octahedral layers (as shown by TEM-EDX). This process decreased the layer charge. Otherwise, remarkable amounts of beidellite were identified by TEM. A small 10 Å-interference was seen but we could not distinguish between illite/brammalite neoformation or irreversible collapsed layers. Saline solutions increased the rate of changes for the mineralogical and technical parameters (hydraulic conductivity, swelling pressure) compared to distilled water.

‚Closed’ System *(up to 600 days)*	
pyrophyllitization	*MX-80 bentonite*
‚Dynamic’ System *(in 20 days)*	
unchanged	*Belle Fourche bentonite*
beidellitization	*compacted MX-80 bentonite*
vermiculitization	*nontronite of Garfield*
illitization	*Chambers bentonite completely to IS; Pioche bentonite partially; Otay bentonite in first steps*

It is possible to describe different rates of hydrolytic reactions for different montmorillonites in “dynamic” systems. Different rates should also be expected for different bentonites in a compacted design.

INDUSTRIAL USES FOR NEW ZEALAND HALLOYSITE

Simon Marsters

Imerys Tableware Asia Limited, Auckland, N.Z.

Imerys Tableware New Zealand Limited mines halloysite from several deposits located in Northland, New Zealand. The halloysite is processed and then sold to export markets around the world, mainly to the manufacturers of high quality and high value tableware. A significant proportion of sales are to manufacturers of technical ceramics such as molecular sieves and honeycomb catalyst supports. The paper will briefly examine the physical and chemical properties of the halloysite and then look at market applications for this unique product.

A COMPARISON OF FIBROUS CLAYS AND FIBROUS AMPHIBOLES AS INDUSTRIAL MINERALS

James L. Post*[1], and Londa Borer[2]

[1]740 Zion Street, Nevada City, CA 95959; [2]Chemistry Dept., California State University, Sacramento, CA 95819, USA; jlp.net@jps.net.

The identification of fibrous clays and fibrous amphiboles are compared using their near-infrared (NIR) and fundamental OH bands. A palygorskite clay from Los Angeles Co. is included along with a new source of richterite from Trinity Co. and a new source of eckermannite from Placer Co.

The dominant NIR bands of Two Crows sepiolite, at 4324 cm^{-1} and 4363 cm^{-1}, are comparable to those of talc, at 4323 cm^{-1} and 4365 cm^{-1}, and that of palygorskite, at 4503 cm^{-1} is close to that of muscovite, which ranges from 4505 cm^{-1} to 4550 cm^{-1} with varying $Al_2 0_3$ content. Richterite, with NIR bands at 4320 cm^{-1} and 4211 cm^{-1}, is also similar to eckermannite, with bands at 4320 cm^{-1} and 4208 cm^{-1}. Their fundamental bands also are similar with the strongest bands at 3729 cm^{-1}. The fundamental OH band shift of these alkali amphiboles is about 55 cm^{-1} from those of actinolite, at about 3674 cm^{-1}. The XRD spectra of richterite and eckermannite are similar to those of actinolites.

Tremolite and richterite are thermally stable to about 1045°C, whereas sepiolite and palygorskite are stable to about 820°C. The fibrous clays may hold large amounts of Pb and As whereas the fibrous amphiboles seldom contain either.

Concerning the use of these fibrous minerals, no adequate methods have been established for determining the relative health hazards from mining, fabrication, and use of these different fibrous minerals.

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POSTER SESSION

5:00PM

UV-PROTECTION CREAMS: FIRST RESULTS FOR SUBSTITUTION OF NON-NATURAL ADDITIVES BY CLAY MINERALS

Hoang Thi Minh Thao[1], Le Thi Lai[2], Joern Kasbohm[3]

[1]Hanoi University of Science (VNU), Hanoi / Vietnam (recently: Institute of Geography and Geology, University of Greifswald/Germany); [2]Institute of Geological Sciences, VAST, Hanoi/Vietnam; [3]Institute of Geography and Geology, University of Greifswald/Germany

We used clay minerals to substitute for common compounds in UV-protection skin creams, e.g. TiO_2. Clay minerals are relatively inert in comparison to photocatalytic TiO_2 [Dunford et al., 1997, FEBS Letters 418:87-90]. Experiments from Elsner (2003; unpublished report) have demonstrated, that UV rays kill Escherichia coli bacteria colonies on skin covered by TiO_2-bearing sun creams. Previous work with clay minerals has mostly focused on Na-montmorillonite (Vicente et al., 1989, Clays Clay Miner. 37:157-163; Del Hoyo et al., 2001, Clay Miner. 36:541-546). Our investigations have been carried out with kaolins (from Saxonia/Germany), bentonites (Wyoming, Chambers, Nontronite Garfield), and clays (from Saxonia/Germany) to recognize advantageous factors. Clay samples were identified by XRD, TEM, XRF and their UV-absorption abilities were studied by UV-spectrophotometry from 250-400 nm (passing a 3 µm thick cream layer). The transmission data are shown for 3 wavelengths: 280 nm (beginning of UV B area), 300 nm (responsible wavelength for sunburning), and 400 nm (end of UV A area).

Sample	Fe_2O_3 (%)	Transmission (%) at Wavelength cream + 10 % clay			Transmission (%) at Wavelength cream + 20 % clay		
		280 nm	300 nm	400 nm	280 nm	300 nm	400 nm
Kaolins							
Wolfka	0,34	29,61	21,42	34,18	22,76	16,57	25,54
Caminau	1,25	27,07	18,71	30,51	23,11	16,06	25,26
Seilitz	1,29	33,17	28,35	42,85	23,66	19,03	33,90
Clays							
Teistungen	4,52	13,94	10,86	21,42	9,54	5,84	15,99
Teistungen (dithionite)	4,06	13,94	11,86	28,54	8,95	7,48	20,41
Thierfeld	7,89	7,29	7,02	15,08	4,06	2,06	8,53
Thierfeld (dithionite)	4,11	17,23	20,02	35,05	10,77	13,42	25,29
Bentonites							
Na-Wyoming	3,35	35,68	35,74	48,37	13,97	21,46	37,49
Garfield (nontronite)	31,79	23,41	13,77	36,65	5,48	3,72	23,41

The Teistungen and Thierfeld clays show the best results for decreasing the intensity of UV radiation. This property seems to be connected with the amount of Fe in these clays. Both clays are red colored and thus are not commonly suitable for pharmaceutical purposes. Fe-rich smectite (nontronite from Garfield) offers similar protection against UV radiation as demonstrated for Thierfeld and Teistungen. The absorption of Garfield nontronite greatly exceeds that of the commonly used Na-Wyoming bentonites.