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NANO, BIO AND MINERAL TECHNOLOGIES—MUTUAL LEVERAGING FOR PRODUCT AND PROCESS INNOVATIONS

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ABSTRACT

Particle engineers, primarily trained in disciplines such as mineral, chemical, materials, and mechanical engineering, have made important contributions to basic and applied nanotechnology advances, especially involving nanostructured particulate materials. These include flotation chemistry inspired reagent schemes for selective polishing in microelectronic manufacturing, multifunctional particles for diagnosis and therapies for cancer, nanocomposites for enhanced photocatalysis, functional nano particles for odor control. At the same time, concepts from other technologies such as nano and bio technologies are being adapted for advances in mineral and materials processing technologies. Notably among them are the new measurement and characterization tools that involve sensors and robots. For example, high throughput or combinatorial methodologies employed for screening of chemical/biological/drug have the potential of identifying potential surface active chemical or biological entities for advanced separation purposes. Similarly targeted drug delivery platforms could be adapted for delivering microencapsulating leachants on specific sites on mineral surfaces for extracting the desired metal component. These developments may not only decrease processing costs, but also waste disposal costs. In order to achieve these goals, researchers with interdisciplinary expertise and technology integration skills are needed for developing disruptive solutions to long standing challenges in mineral and materials processing. This paper illustrates attempts for adapting technological innovations across industry sectors.

Keywords: *Minerals and materials processing, Nanotechnology, Biotechnology, Photocatalysis, Nanoclays.*

INTRODUCTION

Conventional processing techniques have contributed significantly to mineral/material production; and efforts to further improve current technologies are continually made for incremental advances. On the other hand, applying new processing technologies can produce a quantum leap in the types, quality, and economics of the new products and processes. For example, nanotechnology derived concepts may be used in producing value added products from existing minerals or waste streams. Currently, nanomaterials have found applications in fields spanning from aerospace, electronics to biomedical and advanced materials. Examples of various commercial applications of nanoparticles derived from natural resources are given in Table 1.

Nanoscale particles exhibit new properties, phenomena, processes, and functionalities. New material properties, at nanoscale, are manifestation of either quantum or combination of quantum and classical phenomena. Recently, electronic properties of materials have dominated the scientific interest and industrial application of nanotechnology. However, many other novel combinations of properties are being examined to produce value added products for a wide range of materials. In this regard, researchers at the Particle Engineering Research Center (PERC) at the University of Florida have been investigating nanotechnologies that can lead to the development of new products/processes. Specific efforts are made to cross fertilize products and processes innovations across a spectrum of industries—from mining to microelectronics. Mineral flotation concepts have resulted in innovative ideas in computer chip manufacturing; similarly specificity and selectivity observed in biological systems is being explored to design new mineral separation reagent schemes. Highlights of select projects are summarized below.

Table 1: Various commercial applications of nano particles derived from natural materials

Material	Uses as nano material
Alumina	Nano alumina powders are used in many applications including ceramics, coatings, polishing slurries, catalysis
Carbon	Carbon black is used in fillers, inks, pigments, building products
Carbon	Carbon nanotubes started to have a wide application in electronic devices, drug delivery
Clays	Organically modified nanoclays are used in nanocomposites, utilized in many industries
Iron oxide	Iron oxide nano powders are of wide applications in cosmetics, paints, pigments, ferrofluids
Silica	Silica and mesoporous silica are used in catalyst support, “soft” silica-paints, foundry facings, polishing slurries, filtration media
Titanium Dioxide	For its unique properties, TiO_2 is of wide usage in photocatalysis self-cleaning surfaces, paints, paper
Zinc oxide	Is currently used in cosmetics, coatings, catalyst, textiles
Zirconia	Catalysis, fuel cells, bio-implants

PARTICLE CONSTRUCTS FOR MULTIMODAL CONTRAST AGENTS

Clinicians/surgeons would like to employ complimentary imaging modalities to enhance prognosis and enable early and accurate detection of tumors. This concept has led to the emergence of nano particle based multimodal contrast agents that are capable of generating contrast by different imaging modalities (*e.g.*, fluorescence, magnetic resonance, x-rays), simultaneously. Researchers have been developing nano particle based contrast agents that overcome limitations faced by conventional contrast agents, such as detection limits, and chemical and photostability.[1, 2]

COPPER COATED NANOPOROUS SILICA PARTICLES FOR ODOR REMOVAL

Nanoscale particles of copper compounds when deposited in the pores of silica particles significantly improved the catalytic decomposition of model odor causing molecules – ethyl mercaptan. Surface area, pore size distribution and electron paramagnetic resonance spectroscopy analyses revealed that at lower copper concentrations, copper species preferentially adsorb in 20Å pores of silica. Nature of the copper species, their site of adsorption, as well as state of dispersion are important processing parameters for optimal performance in a number of applications such as deodorization, removal of sulfur compounds from crude oil, hydrogenation and antimicrobial activity.[3]

FULLERENE—TiO_2 NANOCOMPOSITES FOR ENHANCED POTOCATALYSIS

Photocatalytic destruction of environmentally hazardous chemicals and microbes results in complete mineralization without generation of toxic byproducts. Titanium dioxide by itself exhibits self-cleaning properties; however, its photocatalytic efficacy is limited to 10% of the theoretical value due to electron-hole pair recombination.

Fullerenes are known for their unique electronic properties including high electron scavenging capabilities. Although use of fullerenes for scavenging photo-generated electrons from titanium dioxide particles has been known, its application for increasing the photocatalytic efficiency has been limited until recently. Studies at PERC have demonstrated that coating of water-soluble polyhydroxy fullerenes (PHF) on titanium dioxide (anatase) particles enhanced photocatalytic degradation of a model organic dye.[4]

NIPPING IN NANO-MILLING FOR ENERGY EFFICIENT COMMINUTION

One of the primary challenges encountered in nano-milling industrially is the re-aggregation and increased energy consumption limiting grinding below specific sizes. It is hypothesized that this apparent grinding limit of the materials can be manipulated by effective use of grinding aids (e.g. surfactants, polymers) and media. In particular, the role of surfactant/polymer interactions with the media and milled material interfaces is being explored for designing grinding aids for nanomilling processes.

Particle-media interaction force measurements (nipping forces!), using atomic force microscopy, indicated these (attraction) forces to be dependent on the chemical nature of the surfactant/ polymer used. Attractive forces were measured to be highest with Pluronic F-68—a block copolymer nonionic surfactant followed by polyvinyl pyrrolidone (PVP) and minimum with Tween-80 (nonionic surfactant). Particle size reduction mimicked this trend with maximum reduction in particle size with F-68, and least with Tween-80 indicating that nipping plays an important role in particle reduction processes.

A CASE STUDY: NANOCLAYS

Nanoscale manipulations of clays have been practiced much longer than the advent of "nanotechnology." An attempt to highlight some of the past advances in nanoclays and their potential as a particulate material platform for new applications is presented to illustrate how a commodity mineral can be converted into new useful products by using new tools and processing methodologies perfected in other industry sectors.

Clays are typically hydrous alumino-silicates with particle size usually less than 4 μm. The layer structure of clays imparts moldablility in wet state and rigidity in dry state. During the last few decades, clay nanoparticles or "nanoclays" have received many researchers' attention especially as fillers for polymers. They have the ability to enhance mechanical, thermal and optical properties of polymers composites. In this regard, nanoclay filled polymers have weight advantage as the filler does not significantly change the density of nanocomposite and nanosize of clay maintains the optical transparency. Polymer-clay nanocomposites have found extensive applications in packaging, automobile and aerospace industries.

Polymer-clay nanocomposites

Since Toyota research group reported the greatly improved tensile properties and the enhanced heat distortion temperature of nylon-6 nanocomposites[5], polymer nanocomposites containing layer-structured, inorganic nanoparticles (clay) have been the focus of several studies in many laboratories. Three general types of composites can result as clay particles are dispersed in the polymer matrix. Namely, (a) conventional composites; the clay fraction in conventional clay composites plays little or no functional role and acts mainly as a filling agent for economic considerations, (b) intercalated nanocomposites; it is formed when one or a few molecular layers of polymer are inserted into the clay galleries with a fixed interlayer spacing, (c) exfoliated nanocomposites; the individual silicate layers are separated and dispersed in the polymer matrix and the gallery structures are completely destroyed. Both the last two categories (intercalated and exfoliated nanocomposites) offer improvement in physical and mechanical properties as compared to the conventional composites.[6, 7]

To achieve good dispersion and adequate adhesion of the clay particles to the polymer matrix, surface modifications have been commonly used. For instance, ion exchange of the clay gallery cations (Na^+ or Ca^{2+}) by alkylammonium ions is generally chosen to modify the clay interlayer from hydrophilic to hydrophobic and to reduce the physical or electrostatic bonding force between clay interlayers. As an example, natural sodium Montmorillonite is hydrophilic in nature. When the cation site is exchanged by cationic surfactants such as quaternary ammonium surfactants), the lattice spacing of clay increases from 12 to 18 Angstrom and the hydrophilic nature of montmorillonite changes to organophilic nature, allowing dispersion in organic solvent. When this an organo-montmorillonite is mixed with polymer (epoxy), the monomer of epoxy resins or a curing agent was diffused into the galleries, resulting in the increase of the gallery spacing even further (up to 35 Angstrom). This exfoliation resulted in a substantial improvement in the mechanical properties of the composite over the polymer matrix by itself.[8] For instance, adding 7% by weight clay to the polymer matrix improved the modulus of elasticity by 65%.

Modification of Clays for Toxins Removal

Mycotoxins represent a threat to both the human and animal health. Zearalenone (ZEN) represents one of these mycotoxins. The addition of nonnutritive adsorptive materials to the feeds of livestock animals to reduce the bioavailability of mycotoxins in the gastrointestinal tract is a successful method for protection against the smaller and more water soluble aflatoxins. On the other hand, previous attempts to use adsorbents to prevent the effects of zearalenone in livestock have been largely ineffective due to the hydrophobic character of this toxin. The aluminosilicate clays which were quite successful in binding aflatoxin were much less successful at extracting ZEN.[8-10] In studies at PERC, hydrated sodium calcium aluminosilicate clays (HSCAS) modified with cationic surfactant -tri-capryl-methyl- ammonium chloride (TCMA) were used to render the clays hydrophobic, increase the intergallery spacing, and thus increase the ZEN binding capacity. The results shown in Table 2 (at two pH values simulating the conditions in different parts of the animal stomach) indicate that above 99% of the toxin can be removed using the modified clays depending on the interacting factors as listed in the table.

Table 2: Selected ZEN experimental runs and extraction results

Cation Exchange Capacity (CEC) replaced by surfactant	Amount of clay	ZEN dosage	ZEN removal at pH 3	ZEN removal at pH 7
(%)	(mg)	(ppm)	(%)	(%)
70	87.5	14	96.9	96.5
100	50	8	98.3	98.8
100	125	8	99.5	100.0
100	50	20	99.4	98.1
		std dev:	1.34	1.9

ADAPTING TECHNOLOGICAL INNOVATIONS ACROSS INDUSTRY SECTORS

Illustrative examples of adapting innovations across industry sectors are outlined below.

Flotation chemistry inspired selective chemical mechanical polishing (CMP) of silicon wafers

Shallow Trench Isolation (STI) processes during microelectronic device fabrication require selective removal of material during Chemical Mechanical Polishing (CMP) steps for optimum processing and quality control. To improve the selectivity of STI CMP processes, application of selectively adsorbing surfactant (sodium dodecyl sulfate -SDS) resulted in a 10-fold increase in polishing selectivity over conventional colloidal silica slurry. Adsorption measurements revealed preferential adsorption of SDS on silicon nitride rendering it to be passive due to the formation of a surfactant mediated lubrication layer, thus resulting in selective polishing.[11]

CMP slurry dispersion chemistry for processing of minerals using sea/ brackish water

CMP slurries for polishing of silicon wafers require dispersing nano abrasive particles under extreme ionic strength conditions. Dispersing chemistries developed for CMP slurries could be helpful in designing reagents schemes that are effective for processing of minerals using sea/brackish water.

Kidney stone formation mechanisms and phosphogypsum filtration

Phosphate fertilizer manufacturing involves filtration of phosphogypsum from the phosphoric acid. Enhancing filtration efficiency and reducing the loss of phosphoric acid in the phosphogypsum residue remains an important goal for the fertilizers and a number of other industries that encounter solid-liquid separations. Literature studies have indicated that modifying the precipitated particle morphology can result in higher filtration efficiency. In a kidney stone study conducted at PERC, it was determined that blocking the calcium sites on a specific crystal face changed the particle morphology significantly. This concept was later extended to phosphogypsum filtration research, where blocking the calcium sites on precipitated particles resulted in notably enhanced filtration of phosphogypsum in laboratory studies.

Protein surface interactions for the bioprocessing of minerals

The use of microorganisms or biologically derived biopolymers for the concentration or selective separation of minerals has received increased interest over the past two decades. Gene manipulation combined with technology for the economical bulk production of microorganisms and their byproducts has the potential for producing a wide variety of highly selective flotation or flocculation aids from biological sources. Whole organisms with a specific mineral affinity can be grown in situ or produced in large bioreactors. Bioorganisms often interact with mineral surfaces through hydrophilic or hydrophobic interactions under specific conditions of pH and ionic strength. For example, in a study on the selective separation of hematite and quartz under various conditions, concluding that the attachment and detachment of bacteria to mineral surfaces can be manipulated to achieve high levels of separation.[13] Perhaps more exciting is the prospect of harnessing microbes to create very specific binding of biopolymers to surfaces by genetically modifying them to synthesize the desired sequence of amino acids and protein conformation. Biological techniques used for biomemetics research use combinatorial techniques such as phage libraries to generate large numbers of candidate proteins which are then tested for their molecular binding affinity to mineral surfaces. Successful candidates are identified and amplified such that the kinetics and stability of the interactions can be characterized. Subsequently, these bio inspired compounds can be mass produced either through microbial culture or synthetically to provide surface specific separation aids.[14]

CONCLUDING REMARKS

Mineral processing inspired particle technology concepts have played an important role in a number of nano advances over the last several decades. At the same time nano and bio technology research over the last three decades has led to numerous new processing methodologies including engineered particles for targeted drug delivery and multimodal contrast agents to name a few. These particulate platform design skills could be adapted to synthesize smart delivery systems for plant nutrients ("smart fertilizers") with capabilities of on-demand delivery of nutrients/pesticides/water with significant cost savings and environmental benefits. Nanoscale analytical tools such as atomic force microscopy are advancing the science underlying mineral processing technologies. Advances in comminution for controlled shape and size reduction capabilities could lead to more efficacious minerals based traditional medicines—a multibillion dollar industry with significant growth potential.[12] TiO_2 based photocatalysts are being developed for self-detoxifying paints and dye synthesized solar cells.

Processing of complex low grade ores, with minimal environmental footprint, will require developing new mineral processing paradigms inspired by nanobio, computational/IT and other technologies already commercialized, or on the horizon. Interdisciplinary research would play an ever significant role in tackling complex engineering problems, and scientists and engineers that have expertise to bridge interdisciplinary language and skill set gaps would play ever more critical roles in developing disruptive solutions to outstanding technological challenges.

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