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**Issue No. 71, October 2006**

**Combining kinetic investigation with surface spectroscopic examination to study the role of aromatic carboxyl groups in NOM adsorption by aluminum hydroxide**

Guan, XH; Chen, GH; Shang, C

Journal of Colloid and Interface Science, Vol. 301, 2, 2006, pp. 419-427.  
10.1016/j.jcis.2006.05.031

The adsorption of a series of aromatic carboxylic acids, with different numbers and positions of carboxyl groups in the phenyl ring, on aluminum hydroxide was investigated with ATR-FTIR and kinetic analyses to verify the role of aromatic carboxyl groups in the surface complexation of NOM with aluminum hydroxide. It was revealed that the formation of outer-sphere complexes dominated the adsorption of most of the aromatic carboxylates over the pH range examined in this study. Inner-sphere complexes were only detected at some pH levels for some aromatic carboxylates adsorption. The aromatic carboxylates were most likely to be adsorbed onto the first surface layer of hydroxyl groups and water molecules without forming coordinative bonds with the aluminum hydroxide surfaces, but strong hydrogen bonds were formed in this process. The adsorption data fitted the pseudo-second-order kinetic model very well. The activation energies of adsorption calculated from the rate constants of pseudo-second-order kinetics agreed with the ATR-FTIR analysis that the aromatic carboxylates, except pyromellitate, were adsorbed predominantly as outer-sphere complexes on aluminum hydroxide at pH 7. This study revealed that phenolic groups may be more significant than carboxylic groups for the chemical adsorption of NOM onto minerals. The presence of additional carboxylic groups enhanced the adsorption considerably, while the enhancement was limited when there were three or four carboxylic groups on the phenyl ring. The adsorption of aromatic carboxylates was affected by the positions and pK(a) values of the donor groups and the solution pH. (c) 2006 Published by Elsevier Inc.

**Thermodynamic assessment of Hg(II)-gibbsite interactions**

Weerasooriya, R; Seneviratne, W; Kathriarachchi, HA; Tobschall, HJ

JOURNAL OF COLLOID AND INTERFACE SCIENCE, Vol. 301, 2, 2006, pp. 452-460.

10.1016/j.jcis.2006.05.054

As discrete particles and/or as surface coatings on other minerals in natural systems, aluminum hydroxides are efficient sinks for Hg(II). The Hg(II) adsorption on gibbsite was determined as a function of temperature (T), pH, and the type of background

electrolytes, i.e., NaNO<sub>3</sub>, NaClO<sub>4</sub>, and NaCl. When the equilibration time t(E) similar to 2 h, the Hg(II) retention on gibbsite was found to be a reversible process, which was ascribed to adsorption. The Hg(II) adsorption capacity, i.e., Gamma(Hg(II)), varied with the type of electrolyte used in accordance with the following order: Gamma(NO<sub>3</sub>)(Hg(II)) >= Gamma(ClO<sub>4</sub>)(Hg(II)) > Gamma(Cl)(Hg(II)) In all cases, the estimated thermodynamic parameters showed that the Hg(II) adsorption on gibbsite was endothermic and spontaneous. The Hg(II) adsorption data were quantified with the Langmuir or Hill, and Dublin-Radushkevick (DR), isotherms at all temperatures and acidity levels examined. Always, the Hg(II) adsorption data were in compliance with the DR model. However, the Hg(II) adsorption in NaNO<sub>3</sub> or NaClO<sub>4</sub> was interpreted in terms of the Langmuir model. When NaCl was used as electrolyte, the Hg(II) adsorption was modeled well with the Hill equation. The mean free energy values calculated from DR plots concluded that Hg(II)-gibbsite interactions are a result of chemical bonding. (c) 2006 Published by Elsevier Inc.

### **Evaluation of a Turkish low quality oil shale by flotation as a clean energy source: Material characterization and determination of flotation behavior**

Altun, NE; Hicyilmaz, C; Hwang, JY; Bagci, AS

FUEL PROCESSING TECHNOLOGY, Vol. 87, 9, 2006, pp. 783-791.

10.1016/j.fuproc.2006.04.001

Evaluation possibility of a low quality Turkish oil shale from Beypazari, Ankara as an alternative clean solid fuel by froth flotation technique was investigated. Oil shale sample was characterized with mineralogical analysis, XRD and FTIR spectrum studies for its mineral content and surface characteristics. The flotation behavior of the sample and extent of cleaning were determined with respect to non-ionizing and ionizing collectors of anionic and cationic types. The effects of collector dosages and pulp pH on the cleaning performance were investigated. XRD analysis showed that the majority of the inorganic matter was constituted by carbonates, montmorillonite, quartz and feldspar while the sample was poor in organic content. In the FTIR spectrum, strong adsorption bands due to oxygen rich carboxyl groups were observed while the characteristic bands of organic groups were in weak forms. The sample was characterized as a fulvic material with low organic content. Ash content and combustible recovery results showed that cleaning of Beypazari oil shale was a difficult process on accounts of the high inorganic content and fulvic character of the sample. The most effective cleaning was obtained with amine type collectors. With amines, ash could be reduced from 69.88% to 53.10% with 58.64% combustible recovery using 800 g/ton Armoflote 17 at natural pulp pH. (C) 2006 Elsevier B.V. All rights reserved.

### **Reduction roasting of limonite ores: effect of dehydroxylation**

O'Connor, F; Cheung, WH; Valix, M

INTERNATIONAL JOURNAL OF MINERAL PROCESSING, Vol. 80, 2006, pp. 88-99.

The effect of pre-calcination in the reducibility of tropical limonite ore, obtained from New Caledonia, was investigated in this study. A series of reduction tests were carried out with pre-calcined and raw limonite ores. The extent of metallisation was determined from nickel and iron which dissolved in ammoniacal solution. Mineralogical transformations that occurred during reduction were analysed using thermal gravimetric, differential thermal analysis (TGA/DTA) and in situ high temperature synchrotron based X-ray diffraction. Bulk mineral analysis of the raw ore was also obtained using neutron diffraction. This study suggests that there is benefit in the pre-calcination of limonite ores. Pre-calcination of the ores which opens the main gangue mineral structure, goethite, allows a rapid interaction between the reductant gases and the nickel species during reduction. The greater nickel metallisation achieved in reduction of pre-calcined ores resulted in higher dissolved nickel whilst reduced raw limonite showed poorer nickel recovery. Reduction of metal minerals was also accompanied by diffusion of nickel into the reduced iron matrix that resulted in the formation of ferro-nickel alloy (Ni<sub>3</sub>Fe). The formation of this solid solution was monitored by in situ synchrotron based X-ray diffraction and was also reflected by the lower nickel leachability in ammoniacal solution. It was found that incorporation of nickel into the reduced iron oxide resulting from pre-calcination is significantly less in comparison to the diffusion occurring in reduced raw or uncalcined limonite ores. This effect is prevalent in prolonged reduction periods (greater than 20 min), at higher temperatures (> 500 degrees C) and highly reducing conditions (H<sub>2</sub>/CO<sub>2</sub>=1:1). This study showed that optimal nickel recovery can be achieved by controlling the incorporation of nickel into the reduced iron structure by pre-calcination of the limonite ore. (c) 2004 Elsevier B.V. All rights reserved.

#### **Study on the kinetics of iron oxide leaching by oxalic acid**

Lee, SO; Tran, T; Park, YY; Kim, SJ; Kim, MJ

INTERNATIONAL JOURNAL OF MINERAL PROCESSING, Vol. 80, 2006, pp. 144-152.

10.1016/j.minpro.2006.03.012

The presence of iron oxides in clay or silica raw materials is detrimental to the manufacturing of high quality ceramics. Although iron has been traditionally removed by physical mineral processing, acid washing has been tested as it is more effective, especially for extremely low iron (of less than 0.1% w/w). However, inorganic acids such as sulphuric or hydrochloric acids easily contaminate the clay products with SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup>, and therefore should be avoided as much as possible. On the other hand, if oxalic acid is used, any acid left behind will be destroyed during the firing of the ceramic products. The characteristics of dissolution of iron oxides were therefore investigated in this study. The dissolution of iron oxides in oxalic acid was found to be very slow at temperatures within the range 25-60 degrees C, but its rate increases rapidly above 90 degrees C. The dissolution rate also increases with increasing oxalate concentration at the constant pH values set

within the optimum range of pH 2.5-3.0. At this optimum pH, the dissolution of fine pure hematite ( $\text{Fe}_2\text{O}_3$ ) (105-140  $\mu\text{m}$ ) follows a diffusion-controlled shrinking core model. The rate expression expressed as  $1-(2/3)^x-(1-x)^{(2/3)}$  where  $x$  is a fraction of iron dissolution was found to be proportional to  $[\text{oxalate}]^{1.5}$ . The addition of magnetite to the leach liquor at 10% w/w hematite was found to enhance the dissolution rate dramatically. Such addition of magnetite allows coarser hematite in the range 0.5-1.4  $\mu\text{m}$  to be leached at a reasonable rate. (c) 2006 Elsevier B.V. All rights reserved.

### **Reduction of clinkerization temperature by using phosphogypsum**

Kacimi, L; Simon-Masseron, A; Ghomari, A; Derriche, Z  
JOURNAL OF HAZARDOUS MATERIALS, Vol.137, 1, 2006, pp. 129-137.  
10.1016/j.jhazmat.2005.12.053

Valorization of phosphogypsum as mineralizer in the burning of Portland cement clinker was studied in our laboratory. X-ray fluorescence, optical microscope technique and powder X-ray diffraction were then used to characterize the synthesized clinker and its raw mixture in terms of chemical composition and clinker mineralogical composition. The effects of phosphogypsum on structural and morphological properties of clinker minerals and on the presence of alite were followed by scanning electron microscopy combined with microprobe analysis. The addition of phosphogypsum to the cement raw mixture shows that the burning temperature decreases and therefore improves the production process of clinker. The addition of 10% phosphogypsum permits a complete clinkerization at low burning temperature (1200 degrees C), instead of 1470 degrees C, which increases the cement factory efficiency by 25% and extends the service life of furnace fire brick. Structural and morphological analysis of clinker produced under the new conditions show that phosphogypsum preserve perfectly the crystalline structure of silicate phases, which leads to the improvement of physical and mechanical properties of cement. (c) 2006 Elsevier B.V. All rights reserved.

### **Treatment of radioactive liquid waste by sorption on natural zeolite in Turkey**

Osmanlioglu, AE  
JOURNAL OF HAZARDOUS MATERIALS, Vol. 137, 1, 2006, pp. 332-335.  
10.1016/j.jhazmat.2006.02.013

Liquid radioactive waste has been generated from the use of radioactive materials in industrial applications, research and medicine in Turkey. Natural zeolites (clinoptilolite) have been studied for the removal of several key radionuclides ( $\text{Cs-137}$ ,  $\text{Co-60}$ ,  $\text{Sr-90}$  and  $(110)\text{mAg}$ ) from liquid radioactive waste. The aim of the present study is to investigate effectiveness of zeolite treatment on decontamination factor (DF) in a combined process (chemical precipitation and adsorption) at the laboratory tests and scale up to the waste treatment plant. In this study, sorption and precipitation techniques were adapted to decontamination of liquid low level waste (LLW). Effective decontamination was achieved when sorbents are used during the

chemical precipitation. Natural zeolite samples were taken from different zeolite formations in Turkey. Comparison of the ion-exchange properties of zeolite minerals from different formations shows that Gordes clinoptilolite was the most suitable natural sorbent for radionuclides under dynamic treatment conditions and as an additive for chemical precipitation process. Clinoptilolite were shown to have a high selectivity for Cs-137 and (110)mAg as sorbent. In the absence of potassium ions, native clinoptilolite removed Co-60 and Sr-90 very effectively from the liquid waste. In the end of this liquid waste treatment, decontamination factor was provided as 430 by using 0.5 mm clinoptilolite at 30 degrees C. (c) 2006 Elsevier B.V. All rights reserved.

### **Bioleaching nickel laterite ores using multi-metal tolerant *Aspergillus foetidus* organism**

Le, L; Tang, J; Ryan, D; Valix, M  
MINERALS ENGINEERING, Vol. 19, 12, 2006, pp. 1259-1265.  
10.1016/j.mineng.2006.02.006

Immediate environmental conditions expose the fungi organisms to a multitude of stresses in an in situ bio-leaching process. The most significant abiotic stress is from heavy metals which are dissolved by the metabolic products of the organism. Heavy metal stress can stimulate changes in the fungi metabolism which could inactivate its cellular functions critical in maintaining bio-acid production and leaching of minerals. Gradual acclimatization of the organism to increasing concentration of single metals forms the main method of adapting strains for this process. However in a bioleaching process, several metals are dissolved which exposes the organism to various levels of cation toxicity. In this study *Aspergillus foetidus* was trained using multi metal (Al, Co, Cr, Cu, Fe, Mg, Mn, Ni and Zn) environment to mimic a leaching system. The effect of the metal stress on the fungi metabolism was examined. Bioleaching of weathered saprolite ore using the heavy metal tolerant organism was assessed. (C) 2006 Elsevier Ltd. All rights reserved.

### **Effect of saline stress on fungi metabolism and biological leaching of weathered saprolite ores**

Thangavelu, V; Tang, J; Ryan, D; Valix, M  
MINERALS ENGINEERING, Vol 19, 12, 2006, pp. 1266-1273.  
10.1016/j.mineng.2006.02.007

Biological leaching of nickel laterite ores is based on the use of heterotrophic microorganisms and their metabolic products to dissolve nickel and cobalt from oxide minerals. High salinity of water supplies and soils in the vicinity of nickel laterite ore bodies can be a major challenge in the application of bio-leaching process in situ. Salt stress can imbalance the osmotic potential in fungi cells generating a water deficit and the influx of sodium may lead to metabolic toxicity. The purpose of this study is to examine salt tolerance development of *Aspergillus foetidus* using gradual acclimatization technique to salt concentrations up to 2% and

to assess the use halotolerant microorganisms in leaching weathered saprolite ores under saline conditions. It has been observed that salinity stress affects the growth but not the energy metabolism of the organism. Kinetic of metal leaching, nature of secondary reactions and metal dissolutions were also influenced by salt stress. (C) 2006 Elsevier Ltd. All rights reserved.

### **The role of the reagent suite in optimising pentlandite recoveries from the Merensky reef**

Wiese, J; Harris, P; Bradshaw, D

MINERALS ENGINEERING, Vol. 19, 12, 2006, pp. 1290-1300.

10.1016/j.mineng.2006.04.003

The Platinum group elements (PGEs) in the Merensky Reef in the Bushveld Complex are strongly associated with the sulphide minerals, particularly pentlandite which contains significant amounts of PGEs such as palladium and rhodium in solid solution. The various operations use different reagent combinations in the flotation process to recover PGEs from the Merensky Reef which include primary and secondary collectors, copper sulphate (CuSO<sub>4</sub>) as an activator and depressants, either carboxymethylcellulose (CMC) or modified guar gum (guar). This study examines the effect on two different ores, A and B, using dibutyl dithiophosphate (DTP) as a secondary collector in combination with sodium isobutyl xanthate (SIBX) as primary collector, the point of collector addition (mill or cell), the use of CuSO<sub>4</sub> addition, sequence of CuSO<sub>4</sub> addition and the effect of depressant type on the floatability of pentlandite, and shows that pentlandite floatability in contrast to that of chalcopyrite is reduced when reagents were added to the cell rather than the mill together with CMC. This effect was not observed with the use of guar gum as the depressant. (C) 2006 Elsevier Ltd. All rights reserved.

### **A characterization study of some aspects of the adsorption of aqueous Co<sup>2+</sup> ions on a natural bentonite clay**

Shahwan, T; Erten, HN; Unugur, S

JOURNAL OF COLLOID AND INTERFACE SCIENCE, VOL. 300, 2, 2006, pp. 447-452.

10.1016/j.jcis.2006.04.069

The natural bentonite used in this study contained montmorillonite in addition to low cristobalite. The uptake of aqueous Co<sup>2+</sup> ions was investigated as a function of time, concentration, and temperature. In addition, the change in the interlayer space of montmorillonite was analyzed using XRPD, and the distribution of fixed Co<sup>2+</sup> ions on the heterogeneous clay surface was recorded using EDS mapping. The sorbed amount of Co<sup>2+</sup> appeared to closely follow Freundlich isotherm, with the sorption process showing apparent endothermic behavior. The relevance of the apparent Delta H degrees values is briefly discussed. Analysis of the Co-sorbed bentonite samples using SEWEDS showed that the montmorillonite fraction in the mineral was more effective in Co<sup>2+</sup> fixation than the cristobalite fraction. XRPD analysis

demonstrated that the interlayer space of montmorillonite was slightly modified at the end of sorption. (c) 2006 Elsevier Inc. All rights reserved.

### **Coupled chemical processes at clay/electrolyte interface: A batch titration study of Na-montmorillonites**

Duc, M; Thomas, F; Gaboriaud, F

JOURNAL OF COLLOID AND INTERFACE SCIENCE, Vol. 300, 2, 2006, pp. 616-625.

10.1016/j.jcis.2006.04.081

The present work addresses the protolytic charge of montmorillonite, which occurs on the broken-bond sites at the particle edges. The purpose is to overcome the general difficulty arising in potentiometric titration due to coupled side reactions, which severely impede the titrant budget (partial dissolution of the clay and of secondary phases, hydrolysis and readsorption of dissolved species, cation exchange). Batch potentiometric titrations were carried out on the montmorillonite fractions extracted from two bentonites (NIX80 and SWy2) to quantify their protolytic charge. The effects of equilibration time (24 h and 7 days), pH from 4 to 10, and ionic strength (0.1 and 0.01 mol L<sup>-1</sup>) were extensively studied for the MX80 sample. Quantification of dissolution was achieved by analysis of the equilibrium solutions for dissolved species and by La<sup>3+</sup> exchange of the readsorbed species. The results clearly show that secondary phases such as iron- or silica-rich minerals contribute to the dissolved species, according to the nature of the raw bentonite. Furthermore, readsorption affects significant amounts of dissolved species. The overconsumption of proton/hydroxide due to dissolution, readsorption, and hydrolysis of dissolved species was evaluated using a self-consistent thermodynamic calculation. The ability of such calculation to correct the raw titration curves in order to extract the titratable surface charge of montmorillonite was evaluated by comparison with the continuous titration procedure. Especially in the alkaline domain, correcting the raw batch titration curves for the measured side reactions failed to reproduce the continuous titration curves. These observations demonstrate the limitations of the batch titration method and the superiority of fast, continuous methods for quantifying the dissociable surface charge of clays. (c) 2006 Elsevier Inc. All rights reserved.

### **Effects of heavy metals and oxalate on the zeta potential of magnetite**

Erdemoglu, M; Sarikaya, M

JOURNAL OF COLLOID AND INTERFACE SCIENCE, Vol. 300, 2, 2006, pp. 795-804.

10.1016/j.jcis.2006.04.004

Zeta potential is a function of surface coverage by charged species at a given pH, and it is theoretically determined by the activity of the species in solution. The zeta potentials of particles occurring in soils, such as clay and iron oxide minerals, directly affect the efficiency of the electrokinetic soil remediation. In this study, zeta potential of natural magnetite was studied by conducting electrophoretic mobility measurements in single and binary solution systems. It was shown that adsorption of charged species of Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Pb<sup>2+</sup>, and Cd<sup>2+</sup> and precipitation

of their hydroxides at the mineral surface are dominant processes in the charging of the surface in high alkaline suspensions. Taking  $Pb^{2+}$  as an example, three different mechanisms were proposed for its effect on the surface charge: if  $pH < 5$ , competitive adsorption with  $H_3O^+$ ; if  $5 < pH < 6$ , adsorption and surface precipitation; and if  $pH > 6$ , precipitation of heavy metal hydroxides prevails. Oxalate anion changed the associated surface charge by neutralizing surface positive charges by complexing with iron at the surface, and ultimately reversed the surface to a negative zeta potential. Therefore the adsorption ability of heavy metal ions ultimately changed in the presence of oxalate ion. The changes in the zeta potentials of the magnetite suspensions with solution pH before and after adsorption were utilized to estimate the adsorption ability of heavy metal ions. The mechanisms for heavy metals and oxalate adsorption on magnetite were discussed in the view of the experimental results and published data. (c) 2006 Elsevier Inc. All rights reserved.

### **Analysis of the gold recovery profile through a cyanidation plant**

De Andrade Lima, LRP; Hodouin, D

INTERNATIONAL JOURNAL OF MINERAL PROCESSING, Vol. 80, 1, 2006, pp. 15-26.

10.1016/j.minpro.2006.01.002

Leaching in the grinding circuit is currently practiced in plants that process gold ores with low content of cyanide consuming minerals. The high gold recovery observed in the grinding-classification section of the plant is commonly explained by the inherent high initial dissolution rate of gold observed in gold ore cyanidation, or by the intense agitation prevailing in grinding mills. For understanding this leaching behavior of gold ores, the grinding, classification and leaching sections of a gold processing plant are analyzed through reconciliation of operating data. It is found that gold circulation in the grinding circuit is quite different from the flow behavior of other species due to the strong gold separation effect in the hydrocyclones, which produces quite large residence time for gold-rich particles. The results presented in this study demonstrate that the residence time of these particles in the grinding circuit can be as long as in the leaching tanks and might be the dominant factor in explaining the high dissolution of gold in this section. (c) 2006 Elsevier B.V All rights reserved.

### **Modeling of flowing film concentrators - Part 1. Water split behaviour**

Majumder, AK; Lyman, GJ; Brennan, M; Holtharn, PN

INTERNATIONAL JOURNAL OF MINERAL PROCESSING, Vol. 80, 1, 2006, pp. 71-77.

10.1016/j.minpro.2006.01.009

A large number of mineral processing equipment employs the basic principles of gravity concentration in a flowing fluid of a few millimetres thick in small open channels where the particles are distributed along the flow height based on their physical properties and the fluid flow characteristics. Fluid flow behaviour and slurry transportation characteristics in open channels have been the research topic

for many years in many engineering disciplines. However, the open channels used in the mineral processing industries are different in terms of the size of the channel and the flow velocity used. Understanding of water split behaviour is, therefore, essential in modeling flowing film concentrators. In this paper, an attempt has been made to model the water split behaviour in an inclined open rectangular channel, resembling the actual size and the flow velocity used by the mineral processing industries, based on the Prandtl's mixing length approach. (c) 2006 Elsevier B.V. All rights reserved.

### **Compositional evolution and cryptic variation in pyroxenes of the peralkaline**

Lovozero intrusion, Kola Peninsula, Russia

Kogarko, LN; Williams, CT; Woolley, AR

MINERALOGICAL MAGAZINE, Vol. 70, 4, 2006, pp. 347-359.

10.1180/0026461067040340

The Lovozero alkaline massif is the largest of the world's layered peralkaline intrusions (similar to 650 km<sup>2</sup>). We describe the evolution of clinopyroxene from the liquidus to the late residual stage throughout the whole vertical section (2.5 km thick) of the Lovozero Complex. Microprobe data (similar to 990 analyses) of the clinopyroxenes define a relatively continuous trend from diopside containing 15-20% hedenbergite and 10-12% aegirine components, to pure aegirine. The main substitutions during the evolution of the Lovozero pyroxenes are (Na,Fe(3+),Ti) for (Ca,Mg,Fe(2+)). The composition of the pyroxene changes systematically upwards through the intrusion with an increase in Na, Fe(3+) and Ti and decrease in Ca and Mg. The compositional evolution of the Lovozero pyroxene reflects primary fractionation processes in the alkaline magma that differentiated in situ from the bottom to the top of the magma chamber as a result of magmatic convection, coupled with the sedimentation of minerals with different settling velocities. The temperature interval of pyroxene crystallization is very wide and probably extends from 970 to 450 degrees C. The redox conditions of pyroxene crystallization in the Lovozero intrusion were relatively low, approximating the QFM buffer.

### **REE zoning in allanite related to changing partition coefficients during crystallization: implications for REE behaviour in an epidote-bearing tonalite**

Beard, JS; Sorensen, SS; Giere, R

MINERALOGICAL MAGAZINE, Vol. 70, 4, 2006, pp. 419-435.

10.1180/0026461067040337

Allanite is present in most samples of the tonalitic Bell Island Pluton, with an average mode near 0.05 wt.%. Allanite occurs as cores in igneous epidote-clinozoisite and exhibits characteristic and consistent zoning patterns. REE-rich cores (All(40-70)) grade out towards epidote-clinozoisite with REE below electron microprobe detection limits. La, Cc and Pr contents are highest in the REE-rich cores of zoned crystals. Nd and Sm contents both initially increase as total REE decreases and are highest in intermediate zones. Y contents are generally low throughout, but tend to

be highest in analyses with All(5-20). The zoning behaviour exhibited by the allanite, specifically the rimward increases in Nd, Sm, and Y, cannot be accounted for by simple fractionation and are best explained by increases in allanite/ melt partition coefficients (K-d values) for these elements during crystallization. We propose that the variation in K-d values reflects modification of the allanite structure with changing REE content. These modifications are manifested by changes in colour, extinction, and pleochroism within the zoned crystals and include changes in unit-cell volume and dimensions. The changes in K-d values are large enough to result in crossing REE patterns within single allanite crystals. Fractional crystallization of zoned allanite can have noticeable effects on LREE contents and La/Sm (and almost certainly La/Lu) in magmas. In the Bell Island pluton, 80% of La, but < 3% of Y is contained in allanite. Although some of the variation in the LREE chemistry of the pluton is attributable to statistical sampling error, much of it appears to reflect petrogenetic processes that controlled LREE abundance and, ultimately, allanite mode. One sample of Bell Island tonalite is depleted in LREE and has low La/Lu and La/Sm. These chemical features can be modelled by fractionation of zoned allanite.

#### **DEM simulation of the flow of grinding media in IsaMill**

Yang, RY; Jayasundara, CT; Yu, AB; Curry, D  
MINERALS ENGINEERING, Vol. 19, 10, 2006, pp. 984-994.  
10.1016/j.mineng.2006.05.002

IsaMill is a high speed stirred mill for high efficiency grinding of mineral ores and concentrates. A numerical model based on the discrete element method (DEM) was developed to study flow of grinding media in IsaMill. The DEM model was first verified by comparing the simulated results of the flow pattern, mixing pattern and power draw from those measured from a 1:1 scale lab mill. Then the flow properties were analysed in terms of flow pattern, flow velocity, force field and power draw. The effects of parameters relating to particle material (i.e., sliding friction coefficient and damping coefficient) and operational conditions (i.e., rotation speed and solid loading) were investigated. While the damping coefficient showed a negligible effect for the range considered, other three parameters had strong effects on the flow properties. Increasing the sliding friction caused the flow velocity and compressive force to have minimum values due to the competitive mechanisms for energy transfer and dissipation, but increased the power draw. The increase in the rotation speed and solid loading also increased the flow velocity, compressive force and power draw of mill. The particle scale, information obtained would be useful to understand the fundamentals governing the flow of grinding media in IsaMill. (c) 2006 Elsevier Ltd. All rights reserved.

#### **Study of flow behaviour in a three-product cyclone using computational fluid dynamics**

Mainza, A; Narasimha, M; Powell, MS; Holtham, PN; Brennan, M  
MINERALS ENGINEERING, Vol. 19, 10, 2006, pp. 1048-1058  
10.1016/j.mineng.2006.03.014

Simplicity in design and minimal floor space requirements render the hydrocyclone the preferred classifier in mineral processing plants. Empirical models have been developed for design and process optimisation but due to the complexity of the flow behaviour in the hydrocyclone these do not provide information on the internal separation mechanisms. To study the interaction of design variables, the flow behaviour needs to be considered, especially when modelling the new three-product cyclone. Computational fluid dynamics (CFD) was used to model the three-product cyclone, in particular the influence of the dual vortex finder arrangement on flow behaviour. From experimental work performed on the UG2 platinum ore, significant differences in the classification performance of the three-product cyclone were noticed with variations in the inner vortex finder length. Because of this simulations were performed for a range of inner vortex finder lengths. Simulations were also conducted on a conventional hydrocyclone of the same size to enable a direct comparison of the flow behaviour between the two cyclone designs. Significantly, high velocities were observed for the three-product cyclone with an inner vortex finder extended deep into the conical section of the cyclone. CFD studies revealed that in the three-product cyclone, a cylindrical shaped air-core is observed similar to conventional hydrocyclones. A constant diameter air-core was observed throughout the inner vortex finder length, while no air-core was present in the annulus. (c) 2006 Elsevier Ltd. All rights reserved.

#### **Computational modeling of reactive multi-phase flows in porous media: Applications to metals extraction and environmental recovery processes**

Cross, M; Bennett, CR; Croft, TN; McBride, D; Gebhardt, JE  
MINERALS ENGINEERING, Vol. 19, 10, 2006, pp. 1098-1108  
10.1016/j.mineng.2006.05.004

A computational modeling framework is described for the analysis of multi-phase flows in reactive porous media targeted at the metals recovery through stockpile leaching and in environmental recovery processes. These systems involve a complex suite of interacting fluid, thermal and chemical reaction physics in complex geometries, which in the case of heap leaching actually grow with time, and varying environmental conditions. The computational models of such processes need to account for variably saturated liquid flow in porous media, gas flow through porous media, together with the transport of many species in one of these fluid phases plus multi-phase heat transfer and mass transfer arising from a range of phase change and gas-liquid-solid chemical reaction processes. This contribution describes just such a development of a three dimensional modeling framework which is applied to the heap leaching of gold, silver and copper in a variety of contexts. (c) 2006 Elsevier Ltd. All rights reserved.

#### **The development of a CFD model of a submerged arc furnace for phosphorus production**

Scheepers, E; Adema, AT; Yang, Y; Reuter, MA

MINERALS ENGINEERING, Vol. 19, 10, 2006, pp. 1115-1125  
10.1016/j.mineng.2006.05.003

A computational fluid dynamics (CFD) based model of a submerged arc furnace for the production of phosphorus was developed. The model was constructed to investigate the influence of changing operating conditions on energy distribution within the burden and reaction characteristics such as the position of the solid-gas reaction zone. Two user-developed models generate a volumetric distribution of the mass sources and energy sinks within the packed bed region. Boundary conditions, initial values and material specifications are provided by industrial measurements, laboratory experiments and a combination of empirical and thermodynamical data. The results provide three-dimensional furnace characteristics of gas flow, energy distribution and chemical reactions that will give decision support for a predictive, Dynamic-CFD hybrid model [Scheepers, E., Yang, Y., Reuter, M., Adema, A., 2006. A dynamic-cfd hybrid model of a submerged arc furnace for phosphorus production. Minerals Engineering 19 (3), 309-317]. (c) 2006 Elsevier Ltd. All rights reserved.

#### **Statistical monitoring of a grinding circuit: An industrial case study**

Groenewald, JWD; Coetzer, LP; Aldrich, C  
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With the increasing availability of large amounts of real-time process data and a better fundamental understanding of the operation of mineral processing units, statistical monitoring of mineral processing plants is becoming increasingly widespread. Process plants are typically too complex to model from first principles and therefore models based on historical process data are used instead. Multivariate methods such as principal component analysis are indispensable in these analyses and in this paper, it is shown how the statistical analysis of process data from a grinding circuit and a sound fundamental knowledge of the operation of mineral processing plants complement one another. For this purpose a philosophy for the statistical monitoring and cause and effect analysis of a process was outlined. It was shown how a well defined process hierarchy with complementing performance measures can effectively be used to detect a shift in the operation of a mineral processing plant and find the root cause of the shift. Visualisation of the results was found fundamental in communicating the findings of the statistical analysis to the processing plant. This resulted in the requirement for multidimensional visualisation of the process for which principal component analysis plots and process performance graphs in the form of two-dimensional histogram plots and parallel plots were found to be the most effective. Data availability, process variable selection, process hierarchy definition and performance measure selection were also found to be critical factors directly impacting on the success of statistically monitoring a process. (c) 2006 Elsevier Ltd. All rights reserved.

#### **Kernel-based fault diagnosis on mineral processing plants**

Jemwa, GT; Aldrich, C  
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Safe operation, environmental issues, as well as economic considerations all form part of the wide range of driving forces for the development of better fault diagnostic systems on process plants. The continuous search for novel methods for fault detection and identification resulting from these incentives has recently drawn attention to support vector machines as a means towards improved fault diagnosis. These kernel-based methods are in theory capable of better generalization, particularly as far as large systems are concerned, since their performance is not dependent on the number of variables under consideration and recent studies underlined their promising role in diagnostic systems. However, integration of these methods into the classical multivariate statistical process control framework is complicated by difficulties in the identification of the original variables associated with detected faults. In this paper, a general strategy for process fault diagnosis is proposed. First, kernel methods are used to remove nonlinear structure from the data, if present, after which the residuals from the data are used to monitor the process. A novel element of the strategy is the use of one-class support vector machines to estimate nonparametric confidence limits for these residuals. Using these limits in conjunction with Gower and Hand biplots and standard statistics collectively constitute a powerful approach to monitoring process systems, as demonstrated by several case studies on mineral processing systems. (c) 2006 Elsevier Ltd. All rights reserved.

#### **Recovery of feldspar from trachyte by flotation**

Bozkurt, V; Ucbas, Y; Koca, S; Ipek, H  
MINERALS ENGINEERING, Vol. 19, 11, 2006, pp. 1216-1217  
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In this study, recovery of feldspar from trachyte by flotation was studied. A feldspar concentrate containing 5.72% K<sub>2</sub>O, 5.33% Na<sub>2</sub>O, 0.321% Fe<sub>2</sub>O<sub>3</sub> and 0.080% TiO<sub>2</sub> was obtained from a feed containing 5.20% K<sub>2</sub>O, 3.37% Na<sub>2</sub>O, 1.778% Fe<sub>2</sub>O<sub>3</sub> and 0.253% TiO<sub>2</sub> with an overall recovery of 22.4% by weight. (c) 2005 Published by Elsevier Ltd.

#### **Removal of methylene blue from aqueous solution by fibrous clay minerals**

Hajjaji, M; Alami, A; El Bouadili, A  
JOURNAL OF HAZARDOUS MATERIALS, Vol. 135, 2006, pp. 188-192  
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Kinetics and equilibrium processes of the methylene blue (MB) retention from aqueous solution by a mixture of fibrous clay minerals, which was isolated from a naturally occurring clay, were investigated. For these purposes, the effects of contact time, initial adsorbate concentration, adsorbent content, pH and ionic

strength were determined. The results show that the MB retention obeys a pseudo-first order equation and the process is a diffusion controlled solid-state reaction. Moreover, the isotherm data fitted the Langmuir equation and the MB binding process became more energetic with the increase of the adsorbent concentration. In addition, the augmentation of the clay content or the initial MB concentration reduced the adsorption capacity, presumably because of the clay particles microaggregation and/or the occurrence of MB deriving species. On the other hand, it is observed that the MB uptake limit is reduced in low acid pH, particularly below the PZC, as well as in ionic strength solutions. These facts are linked to the silanol group protonation and to the reduction of the electrostatic forces induced by the clay particles, respectively. (c) 2005 Elsevier B.V. All rights reserved.

### **Reaction kinetics of FEBEX bentonite in hyperalkaline conditions resembling the cement-bentonite interface**

Sanchez, L; Cuevas, J; Ramirez, S; De L, DR; Fernandez, R; Dela Villa, RV; Leguey, S  
APPLIED CLAY SCIENCE, Vol. 33, 2, 2006, pp. 125-141  
10.1016/j.clay.2006.04.008

Bentonite of the Serrata de Nijar (Almeria, Spain) and concrete made with an ordinary portland cement (OPC) are candidate materials to be used as engineering barriers in the high level radioactive waste disposal in argillaceous rock. This experimental alteration study has been conducted in order to determine the kinetics of alteration of a montmorillonitic bentonite under hyperalkaline conditions (NaOH 0.5 to 0.1 M) in the presence of portlandite. The amount of montmorillonite destroyed and the secondary minerals formed have been measured by means of X-Ray Diffraction (XRD) in the solid phase after the performance of batch reactions carried out in airtight cells (3/1 liquid/solid) during 30 to 540 days. Scanning Electron Microscopy (SEM-EDX) and chemical analysis of a <0.5  $\mu\text{m}$  Ca-bromoionized fraction have been used to characterize the reaction by-products, mostly zeolites (analcime and phillipsite type); calcium silicate hydrates (amorphous and 11 angstrom-tobermorite type) and saponite. The nature of the solution chemistry determined in the aqueous phase has allowed us to calculate the chemical speciation and the saturation indices for the observed minerals. The evaluation of the equilibrium state in the system supports the dissolution of montmorillonite from undersaturation conditions as the driving process for the alkaline reaction of bentonite. The rate of montmorillonite dissolution has been calculated from the mineralogical quantification of smectite in the 75-200 degrees C tests. The global kinetics for the conversion of montmorillonite can be fitted to  $R \text{ (mol s}^{-1}) = A \text{ (n}^{(2)}) k[\text{OH}^-]^{(0.5)}$ ;  $\ln k = (-20.09 \pm 1.37) - (2731 \pm 543) \cdot (1/T)$ ;  $E_a = 22.7 \pm 4.4 \text{ kJ/mol}$ . These data are in close agreement with the rate of dissolution of montmorillonite obtained by methods based on solution chemistry. (C) 2006 Elsevier B.V. All rights reserved.

### **Some aspects about the adsorption of quinoline on fibrous silicates and Patagonian saponite**

Vico, LI; Acebal, SG  
APPLIED CLAY SCIENCE, Vol. 33, 2, 2006, pp. 142-148  
10.1016/j.clay.2006.03.012

Adsorption of quinoline (Q, C<sub>9</sub>H<sub>7</sub>N) on aqueous suspensions of sepiolite, palygorskite and saponite was determined experimentally in a wide pH range. The enhancement of adsorption with increasing pH and some release of OH<sup>-</sup> were observed. The clay minerals showed, at short reaction times, a higher adsorption and then this decreased along the time. Displaced Mg<sup>2+</sup> from octahedral sheet decreased when the Q adsorption happened. The surface of the mineral covered by the molecules at a 20 mM Q total concentration practically coincided with the BET surface for sepiolite and palygorskite. In the case of saponite, it coincided with the EGME surface. The obtained data suggest three possible mechanisms that could be involved in the interaction between Q and the surface of the mineral. 1) Adsorption of Q on surface sites (SiOH, AlOH, MgOH, FeOH) on the broken edges of the mineral via the donation sigma of the N electron pair of the Q. 2) Adsorption via T links on the external surface (sepiolite and palygorskite) and on the external and interlayer surface (saponite). 3) A process of ion exchange in which protonated Q (QH<sup>(+)</sup>) replaces Na<sup>+</sup>. (C) 2006 Elsevier B.V. All rights reserved.

#### **A novel dispersion method comprising a nucleating agent solubilized in a microemulsion, in polymeric matrix I. Dispersion method and polymer characterization**

Libster, D; Aserin, A; Garti, N  
JOURNAL OF COLLOID AND INTERFACE SCIENCE, Vol. 299, 1, 2006, pp. 172-179  
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This is the first of a two-part study focusing on a novel dispersion method which enables increasing the crystallization rate of polypropylene (PP) through the incorporation of nucleating agent HPN-68 into the molten polymer using a microemulsion as a nanovehicle. The cycle time for processing the PP is significantly reduced and thus the effectiveness of its production is increased. Our concept is based on creating an advantage in dispersion capability of the nucleator that is dissolved in a nanoreactor vehicle in comparison with its conventional introduction as a crystalline powder. The microemulsions were introduced to the target PP using a mixer. By the end of the mixing, when the water phase had evaporated, only the nucleator and the surfactant remained in the matrix. The microemulsion components that solubilized the HPN-68 were mineral oil, alcohol, surfactant, and water. DSC results showed a 24% improvement in nucleation efficiency of PP by this method. WAXS results showed that HPN-68 is a gamma-nucleator. It causes polymorphism by significantly raising the gamma-phase concentration in the PP. SEM results showed a four-fold decrease in the PP spherulite size due to the improved dispersion of HPN-68 within the matrix via microemulsion compared to conventional nucleator incorporation. (c) 2006 Elsevier Inc. All rights reserved.

### **Influence of sodium thiosulphate on oxidation of sulphide minerals during selective flotation of copper-nickel ores**

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The studies of sulphur distribution in oxidation products of pyrrhotite and chalcopyrite being components of Cu-Ni ores showed that the elementary sulphur - sulphoxide ion ratio on the mineral surface and in the liquid phase of mineral suspensions changes in the presence of sodium thiosulphate. Sodium thiosulphate exhibits properties of a reducing agent and prevents formation of hydrophobic elementary sulphur on pyrrhotite surface due to oxygen absorption and oxidation of thiosulphate-ions to sulphates. The decrease in pyrrhotite floatability is observed, and more favorable conditions are provided for selective flotation of chalcopyrite on copper-nickel ore processing.

### **Material balance and stream sampling errors**

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MINERAL PROCESSING AND EXTRACTIVE METALLURGY REVIEW, Vol. 27, 3, 2006, pp. 215-230

10.1080/08827500600564234

This article investigates the influence of the data variation on sampling errors throughout a two-stage flotation circuit. The material balance technique is used to upgrade the measured variables. The sampling errors are evaluated before and after material balance. In one case, the covariance terms between the components in a stream and between the streams in the flotation circuit are included. In the other case, these terms are not included. This article proves that by including the covariance terms in the calculation, the variances of the sampling errors are reduced and, therefore, the reliability of the material balance is improved.

### **An evaluation of different models of water recovery in flotation**

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MINERALS ENGINEERING, Vol. 19, 9, 2006, pp. 871-882

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Water recovery is one of the key parameters in flotation modelling for the purposes of plant design and process control, as it determines the circulating flow and residence time in the individual process units in the plant and has a significant effect on entrainment and froth recovery. This paper reviews some of the water recovery models available in the literature, including both empirical and fundamental models. The selected models are tested using the data obtained from the experimental work conducted in an Outokumpu 3 m(3) tank cell at the Xstrata Mt Isa copper concentrator. It is found that all the models fit the experimental data reasonably well for a given flotation system. However, the empirical models are either unable to

distinguish the effect of different cell operating conditions or required to determine the empirical model parameters to be derived in an existing flotation system. The model developed by [Neethling, S.J., Lee, H.T., Cilliers, J.J., 2003, Simple relationships for predicting the recovery of liquid from flowing foams and froths. Minerals Engineering 16, 1123-1130] is based on fundamental understanding of the froth structure and transfer of the water in the froth. It describes the water recovery as a function of the cell operating conditions and the froth properties which can all be determined on-line. Hence, the fundamental model can be used for process control purposes in practice. By incorporating additional models to relate the air recovery and surface bubble size directly to the cell operating conditions, the fundamental model can also be used for prediction purposes. (C) 2005 Elsevier Ltd. All rights reserved.

### **Mechanism of di-isobutyl dithiophosphate adsorption onto galena and pyrite**

Pecina, E.T.; Uribe, A.; Finch, J.A.; Nava, F

MINERALS ENGINEERING, Vol. 19, 9, 2006, pp. 904-911

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The interaction of sodium-di-isobutyl dithiophosphate (DTPiNa) with galena and pyrite in alkaline media (pH 9) was examined using cyclic voltammetry, open circuit potential and contact angle techniques. Analysis of results suggests that the collector interacts with the minerals by chemical and electrochemical mechanisms according to the following steps: a chemisorption process (without electron transfer) that takes place when the collector interacts with metal species (e.g., of lead) that shows chemical affinity towards the collector; an electrochemical-chemical process developed by the galena that involves two steps: the oxidation of the mineral (electrochemical step) and the formation of a metal-collector precipitate (chemical step); and an electrochemical process (adsorption of collector and dimer formation) that occurs when pyrite is held at a redox potential sufficiently anodic to produce oxidation of the collector. (C) 2005 Elsevier Ltd. All rights reserved.

### **Adsorbing flocs in expanded/fluidised bed reactors: A new basis for pollutants removal**

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The present work describes studies concerning a new adsorption technique based on the use of adsorbent flocs in an expanded/ fluidised bed reactor for the removal of pollutants from aqueous solutions. The technique, based on flocculation of aqueous suspensions of powdered adsorbent materials, when conducted in an expanded/fluidised bed reactor takes advantage of conducting adsorption and solid-liquid separation in one single stage. Studies were performed using flocculated powdered activated carbon and natural zeolites, alone and in mixtures, for phenol and ammonia adsorption. A reactor with cylindrical-conical geometry

was used for the pollutants adsorption in floes beds (pure and mixed), as well as the regeneration/recycle of the exhausted adsorbents. Results proved the high adsorption efficiency of powdered natural zeolites and activated carbon floes for the uptake of ammonia (11 mg NH<sub>3</sub>-N g<sup>-1</sup>) and phenol (132 mg g<sup>-1</sup>), at 38 and 19 m h<sup>-1</sup> loading rates, respectively. Regeneration/recycle of the pollutant-saturated beds was possible for the ammonia/natural zeolites adsorption case, using sodium sulphate as regenerator. Use of mixed floes beds was efficient, showing advantages such as multiple-pollutants adsorption in one single stage, higher loading rates when using light materials (activated carbon) combined with heavier ones (natural zeolites) and use of small adsorbent concentrations (not possible otherwise). Economical and environmental issues regarding the technique are also discussed in the paper. The new technique shows great potential as an alternative physicochemical adsorption process for pollutant removal from aqueous solutions using low-cost and highly-available powdered adsorbent materials. (C) 2005 Elsevier Ltd. All rights reserved.

### **Nonlinear data reconciliation in gold processing plants**

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Data reconciliation in hydrometallurgy process is less common than in mineral processing, due to the more complex mathematical formulation of the problem to describe the process balances that can include multiphase and multi-component reactions and mass transfer. In this case, to avoid thermodynamic violations, the use of inequality constraints, in addition to the classical equality mass and energy balances, can be mandatory. This paper presents two case studies of data reconciliation for a gold extraction plant using the direct optimization of a nonlinear objective function and nonlinear constraints that includes equality and inequality equations. The problems are solved using a sequential quadratic programming algorithm and the results demonstrate the applicability of this approach to data reconciliation in hydrometallurgical processes generating reliable results, without mass balance or thermodynamic violations. (C) 2005 Elsevier Ltd. All rights reserved.