

## **Compacted bentonite as a source of substrates for sulfate-reducing microorganisms in a simulated excavation-damaged zone of a spent nuclear fuel repository**

Sulfide formed by sulfate-reducing microorganisms (SRM) is a potential safety risk in the geological disposal of spent nuclear fuel (SNF) enclosed in copper canisters because it can corrode copper. The canisters will be isolated from the environment by surrounding them with compacted bentonite. This study shows experimentally that the organic matter naturally present in compacted bentonites can become dissolved and sustain biological sulfate reduction. The experiment was conducted in cell systems consisting of an interface of compacted bentonite (at dry density of 1314–1368 kg m<sup>-3</sup>) and a low-porosity sand layer representing an excavation-damaged zone of the host rock. Some cells were inoculated with SRM and groundwater microorganisms and some were not. Varying concentrations of organic matter and sulfate in the sand layer solution resulted from partial dissolution of the studied bentonites (Wyoming, Indian, and Bulgarian). The dissolved organic matter promoted biological sulfate reduction, as demonstrated by the decrease in sulfate concentration in the sand layer solution and the formation of sulfide iron precipitates in the inoculated cells relative to the uninoculated cells. Other anaerobic microorganisms (e.g., methanogens) also became active in the cells and they along with the SRM were found to grow within the sand and/or bentonite layers of the cells. The findings of this study show that bentonites can sustain biological sulfate reduction in areas with lower density and immobilize possibly formed sulfides. However, the extent of these capabilities seems to be affected by the mineralogy of bentonites in the studied density range.

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## **Editorial**

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### Column leaching of low-grade sulfide ore from Zijinshan copper mine

Abstract Copper and iron dissolution of Zijinshan low-grade copper sulfide ores was investigated in ore-packed columns. At 60 °C and pH 1.0, 37.1 g Fe(III) L<sup>-1</sup> permitted effective copper dissolution and inhibited the activity of iron-oxidizing microorganisms. At 30 °C, microorganisms stimulated Fe(II) and pyrite oxidation, resulting in 85 and 54% of copper and pyrite extraction yields, respectively. Bacteria belonging to the genera Acidithiobacillus and Leptospirillum were dominant as observed by real-time PCR assay. Aeration and inoculation of columns were not necessary. Solutions had a higher pH of 1.7 in the columns operated without recirculation. Under these conditions, copper extraction was not affected and Fe(III) precipitated as jarosite, indicating a novel method for iron control in Zijinshan copper mine.

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Contributors: Zou, G., Papirio, S., Lai, X., Wu, Z., Zou, L., Puhakka, J., Ruan, R.

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### Pre-intercalation of long chain fatty acid in the interlayer space of layered silicates and preparation of montmorillonite/natural rubber nanocomposites

A series of long chain fatty acids was intercalated into the interlayer space of organo montmorillonite (OMt) and a gradual expansion of the interlayer space was observed as the chain length of the fatty acid increased. The fatty acid with 22 carbon atoms (docosanoic acid) was found to offer a highest interlayer space among the fatty acids under consideration. This fatty acid was selected further to modify OMt and subsequently utilized as reinforcing fillers in natural rubber (NR) matrix. Wide angle X-ray diffraction (WAXD), Fourier transform infrared (FTIR) spectroscopy and contact angle measurement indicated successful intercalation of the fatty acid into the interlayer space of the clay minerals. The main objective of such intercalation is to make clay minerals suitable for the preparation of rubber nanocomposites, especially when using non-polar rubbers. Docosanoic acid intercalated Mt was successfully dispersed in NR matrix as confirmed by WAXD and transmission electron microscopy (TEM). As a result, the mechanical properties were found to be improved in a remarkable way. Improvement of ~. 114% in tensile strength and ~. 203% in modulus at 300% elongation was observed. These results were correlated with the morphological data obtained from WAXD and TEM.

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Contributors: Rooj, S., Das, A., Stöckelhuber, K. W., Mukhopadhyay, N., Bhattacharyya, A. R., Jehnichen, D., Heinrich, G.  
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#### A general approach to rubber-montmorillonite nanocomposites: Intercalation of stearic acid

The effect of stearic acid on the properties of different rubbers/montmorillonite composites was studied. We used alkyl quaternary ammonium modified montmorillonite (organo-montmorillonite), which was additionally modified with stearic acid. Premixed with the montmorillonite, the stearic acid expanded the clay mineral layers, thus permitting the rubber molecules to be more easily intercalated into the montmorillonite. We used several kinds of rubbers with different polarities and molecular structures. Both the X-ray diffraction and infrared spectroscopy studies indicated that the stearic acid propped up interlayer space allowing the intercalation of the rubber chains. Measurement of the physical and dynamic mechanical properties, along with studies of the composite morphology by transmission electron microscopy, very clearly showed that mixing the montmorillonite clay with stearic acid yielded various rubber nanocomposites with a high amount of intercalated and exfoliated montmorillonite particles. Either complete intercalation or increased nanostructure formation yielded as compared to the standard rubber-clay mineral composites prepared with a normal dose (2 parts per hundred of rubber) of stearic acid, can be achieved by adding a large amount of stearic acid (10 parts per hundred of rubber in our case) to non-polar rubbers (e.g. natural rubber (NR), ethylene propylene rubber (EPDM), etc.) that are not known to form totally exfoliated structures by simple melt mixing of montmorillonite and rubber.

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Contributors: Das, A., Stöckelhuber, K. W., Jurk, R., Jehnichen, D., Heinrich, G.

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### Zinc removal in anaerobic sulphate-reducing liquid substrate process

Zinc and sulphate removal from synthetic wastewater was investigated by using four laboratory parallel upflow-mode reactors (referred as R1 to R4; R1 contained carriers to retain biomass, whereas R2-R4 were operated as suspended reactors). All reactors were inoculated with anaerobically digested cow manure. R1 and R2 were first fed with glucose- and sulphate-containing feed for 48 days after which all four reactors were fed with wastewater containing  $50 \text{ mg l}^{-1}$  of zinc in R1-R3 and  $200 \text{ mg l}^{-1}$  in R4 and operated for 96 days. In all reactors, hydraulic retention time, organic loading rate, and sulphate load were 5-6 d,  $0.2\text{-}0.4 \text{ kg COD m}^{-3} \text{ d}^{-1}$  and  $3.3\text{-}3.8 \text{ g SO}_4 \text{ l}^{-1} \text{ d}^{-1}$ , respectively, whereas the zinc load in R1-R3 was  $0.074\text{-}0.077$  and in R4  $0.282 \text{ g Zn l}^{-1} \text{ d}^{-1}$ . During the runs, 30-40% of sulphate and over 98% of zinc was removed, and up to 150-200 mg  $\text{H}_2\text{S}$  was produced in all reactors. Effluent pH dropped in all reactors (feed pH 6.5) to 3-5 by the end of the experiment. No significant effects on zinc removal were observed, despite differences in operating conditions and feed. It was only in the latter part of the runs (i.e. between experiment days 120-142) that zinc removal began to fluctuate, showing a negligible decrease in R3 and R4, whereas in R1 and R2 zinc was removed below the limit of detection ( $<0.01 \text{ mg Zn l}^{-1}$ ). Qualitative X-ray diffraction analysis of the reactor sludge at the end of the runs indicated that the compounds precipitated were most probably ZnS (Code 05-0566 Sphalerite), suggesting metal removal through sulphide precipitation; this was supported by the fact that sulphate was reduced and zinc removed simultaneously.

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