Clay minerals in the natural and built environment: formation, chemistry & applications

Conference Booklet

17 May 2019
Urban Sciences Building
Clay minerals in the natural and built environment: formation, chemistry and applications

The Event Space
Urban Sciences Building, Newcastle University
Newcastle upon Tyne, NE4 5TG

A trans-disciplinary research meeting, co-sponsored and co-organised by the Clay Minerals Group (CMG) of the Mineralogical Society and the Environmental Chemistry Group (ECG) of the Royal Society of Chemistry.

The meeting will explore recent advances in our understanding of how clay minerals – natural and engineered – form, behave and react in the environment, with a particular focus on their effect on the fate of contaminants in natural and built environments, and how this understanding can help us to engineer more sustainable solutions to treat pollution.

We are excited that you join the meeting – to contribute a presentation; to learn more about clay minerals in the natural and built environment; to broaden your horizon; and to meet interesting researchers from academia and industry.

Anke Neumann (CMG) & Laura Newsome (ECG)
– Convenors –
# Programme and Oral Presentations

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Presentation guidelines

Keynotes: 35 minutes (30 min talk + 5 min discussion)
Oral presentations: 20 minutes (15 min talk + 5 min discussion)
Poster presentations: Poster boards will be available to hang posters of maximum size A0 portrait/A1 landscape.

Internet

Eduroam WiFi access is available across the campus.

General information

Registration includes admission to all sessions, lunch, and coffee/tea breaks. We are striving to make this meeting as sustainable as possible, so we encourage you to bring your own cup, bottle, travel mug for water and coffee/tea available during the day.
A printed copy of the program will be available for all participants on the meeting day.
Please bring a printed copy of the abstract book (this one) if you wish to keep it handy during the presentations at the meeting.
Oral Abstracts
Better clays make life easier

Josef Breu

Department of Chemistry, Universität Bayreuth, Germany
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Natural swelling clay minerals suffer of both frequent planar defects and random interstratification, which jointly hamper structural characterization. Reconciliation of intracrystalline reactivity and structural order requires control over compositional homogeneity and a subtle balance of the interaction between the host layers and the interlayer species that allows for sufficient directional bonding assuring a fixed phase relationship. Synthesis from the melt gives rise to micrometer-sized fluorohectorites with tuneable and homogeneous intracrystalline reactivities [1]. With these synthetic materials defects can be reduced to a level where a more detailed look at structural features becomes available even of hydrated phases [2] and microporous organically pillared silicates (MOPS) [3]. They give new insight into crystalline and osmotic swelling, where the separation of individual layers is driven by the electrostatic repulsion and a highly ordered lamellar liquid crystalline phase [4] is obtained. Partial ion exchange inevitably produces ordered interstratifications and these regular heterostructures may then be delaminated into double stacks with any kind of functional molecules or nanoparticles sandwiched between two clay layers [5].

Laponite synthetic clays: new insights from imaging techniques

Kirill Shafran

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Laponite® materials are a growing family of commercial synthetic clays with over five decades of history and a wide variety of technological applications. Already great and constantly increasing number of patents, research articles and reviews is a testament of the enduring legacy of Laponite® in industry and academia.

In order to understand and govern the technological performance of Laponite® materials, one needs to know and control the dimensionality of these synthetic clays, particularly when dispersed in water and other solvents. The extremely fine dimensions of Laponite® platelets (tens of nanometres across and down to one nm in thickness) represent a formidable problem for the measurement of the Laponite® dimensionality in the dispersed state.

Our recent research has been focussing on overcoming the problem of measuring the size distribution of the dispersed Laponite® platelets. We shall discuss some of the approaches to clay size measurements attempted in the literature and tried out in our work. The methods of cryo-transmission electron microscopy (cryo-TEM), scanning electron microscopy (SEM), and atomic force microscopy (AFM) applied to Laponite® will be compared in this report with indirect techniques such as dynamic light scattering (DLS).

The best option for the analysis of the dimensionality of Laponite® synthetic clays from our perspective appears to be the AFM imaging method in combination with advanced image analysis. It seems to provide a statistically sound distribution of Laponite® platelet sizes. In addition, the AFM enables one to measure the thickness of each exfoliated particle, which renders it an excellent tool for evaluating the degree of dispersion of Laponite® materials.
Bentonite clay has been used to improve paper making and clean up waste water from paper making processes. The presentation discusses the benefits of bentonite when used with polymers of both modified natural and synthetic origin.
Na-Ca cation exchange isotherms in reduced iron-bearing clay minerals and implications to low-salinity water flooding

Nikolaos Apeiranthitis¹, H. Chris Greenwell¹, Anke Neumann²

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²School of Engineering, Newcastle University
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Clay minerals can play a significant role during oil production from a conventional reservoir, because they exhibit a structural variety which will induce different physical and chemical behaviour, such as swelling, oil adsorption, cation selectivity, during oil production processes.

All these should be taken into account during an enhanced oil recovery method, such as low-salinity waterflooding, where injected water is of lower salinity than that originally in the reservoir, with very low divalent cation content. The main functioning mechanisms involved for this process are multi-ion exchange, local pH increase, fines migration, double layer expansion, all associated with clay minerals, and leading to wettability changes from mixed-wet to more water-wet. However, none of the above methods conclusively explain low salinity enhanced oil recovery.

One factor that is least examined is the presence and possible influence of iron (Fe) in some clay minerals that can be found in sandstone reservoirs. As iron is a redox-active element, its redox state can affect the behaviour of clay minerals, i.e. cation exchange capacity. Conceptually, a sandstone reservoir should be in a reduced state just prior to production and any intervention, such as waterflooding, can cause a shift towards more oxidising conditions. Targeting on better understanding of the underpinning mechanisms for low-salinity waterflooding it is essential to examine and compare how Fe-bearing clay minerals behaving in these two different redox states.

For this project, cation exchange isotherms are produced using three iron smectites, under reduced conditions, for Na and Ca. This can give us insights on the clay mineral preference towards these cations and how this can be changed or affected during low-salinity waterflooding. Sodium-Potassium (Na- K) is also to be examined during future work, as well as the effect of these three different cations on oil adsorption using carboxylates, after FTIR analyses.
Smart reactive sorbents for the removal of emerging contaminants

Wojciech Mrozik, Anke Neumann

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Pollution of water resources is one of the major worldwide concerns and is often due to the accidental release of various toxic and persistent substances into water bodies. In addition, classical wastewater treatment plants (WWTPs) treat domestic wastewaters to regulated standards but often fail to remove emerging contaminants, or micropollutants, which are released mostly from households and health care facilities. Micropollutants comprise various groups of chemicals, including pharmaceutical and personal care products (PPCPs) and Endocrine Disrupting Compounds (EDCs). Even though these pollutants are found in very low concentrations (<1 ng L⁻¹), they are potent chemicals, thus causing harm to the aquatic natural environment and posing a threat to human health.

To meet the requirements for the removal of micropollutants, energy, cost, and maintenance intensive technologies such as advanced oxidation or nanofiltration are applied. Another, much simpler approach is the efficient elimination of organic micropollutants by adsorption, which is used frequently to treat industrial wastewaters. As feasible alternatives to mentioned processes natural materials such as clay minerals are under investigation. Surface modification of clay minerals with amphiphilic entities, or surfactants, provide organic surfaces with greater affinity for non-polar groups, making organo-clays efficient and promising sorbents for the removal of pollutants.

To design a truly smart and sustainable adsorbent, removal of pollutants needs to be combined with in situ transformations of pollutants to benign products. Redox transformations of organic contaminants by structural iron in clay minerals are well known and usually lead to products which are more benign or more readily transformed by microorganisms. In this proof of concept, we first tested clay pillared with ionic liquids for the removal of selected EDCs from the aqueous phase. We studied both normal and reduced clay and various loadings of the surface modifiers.
Using Fe-bearing clay minerals to remove antibiotic resistance genes from domestic wastewater

Panagiota Adamou, James Entwistle, Anke Neumann, David W. Graham
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Only in recent years has it become apparent that antimicrobial resistance is widely spread in the environment and has reached alarming levels worldwide. Antibiotic resistance bacteria (ARB) and genes (ARGs) have been detected in samples from a range of different environments and wastewater discharges have been identified as one of the main sources of AR dissemination. Although conventional wastewater technologies are efficient at treating both (macro)contaminants and pathogens, including ARB, additional treatment steps may be required to further improve water quality to comply with standards for discharge and/or re-use, or be applied to highly contaminated waste streams, such as hospital wastes. Thus, innovative technologies are currently explored as additional steps to conventional treatment or as a more cost-effective option.

In this study, we expand on the seminal work on antibacterial properties of clay minerals, which has demonstrated that antimicrobial clays applied as topical treatment for skin lesions can kill or inhibit the growth of bacteria, including anti-microbial resistance strains. Here, we explore whether clay minerals can also be an alternative treatment option for removing ARB and ARGs from treated secondary effluents. We specifically investigated the potential of reactive oxidizing species such as hydroxyl radicals formed in the presence of iron-bearing clay mineral NAu-1 for removing ARB and ARGs. We monitored removal of target ARGs from real secondary effluent by (a) OH radicals formed from H₂O₂ and native, Fe(III)-bearing NAu-1 in a Fenton reaction, and (b) in situ production of H₂O₂, and subsequently OH radicals, during oxygenation of reduced, Fe(II)-bearing NAu-1. We systematically varied H₂O₂ doses and contact times and gained promising results suggesting that clay minerals should be considered as a novel solution for reducing antimicrobial resistance in wastewater effluent.
Clays in nature as functional nanoparticles

Susan L. Svane Stipp

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Nature has given us a palette of natural clay minerals and clay size particles, nanoparticles. These have existed at the Earth’s surface for billions of years but there is promise of more to be done through deeper understanding of their properties and creativity about how to tailor them. Soil scientists have known about the cation exchange capacity of clay minerals for generations and geologists have known for well over 100 years that clay size particles carried organic compounds into the black shales, which have served as oil source rocks throughout the ages, but there is more we can learn about clay behaviour that can help for solving current problems in nature and in industry. Any consulting engineer knows that contaminants in clay bearing formations are deadly difficult to remove, be they organic or inorganic, but can we learn enough more about the processes that control the composition and structure of clay particle surfaces to allow us to engineer better remediation methods for soil and groundwater? Or to develop filtration techniques that would allow us to mine our garbage dumps? Ultrahigh resolution techniques, the instrument facilities that spawned the field of nanoscience, offer new insight into what really goes on at the mineral-fluid interface and provide clues we can use to solve some of society’s challenges.
Assessing the sustainability of Fe-bearing clay mineral redox reactions for applications in engineered systems

Harry L. Brooksbank, Anke Neumann

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Fe can be substituted into the clay mineral structure, and structural Fe in its reduced state (Fe$^{2+}$) has been shown to be able to reductively degrade a range of organic contaminants. Because the oxidation state of structural Fe can be repeatedly altered without causing significant loss of Fe from the clay mineral framework, it could act as a renewable source of environmental reduction equivalents for the long-term natural attenuation of pollution. However, recent studies showed that clay minerals can be irreversibly altered by recurrent redox cycling. Interestingly, marked differences in Fe reduction extents and reversibility of structural alterations has been observed for chemically (dithionite) and microbially reduced clay minerals, as well as for clay minerals with low and high Fe content. Here, we will systematically investigate the impact of multiple cycles of reduction and oxidation on the structure and reactivity of Fe-bearing clay minerals.

We subjected clay minerals of different Fe contents (high: NAu-1; low: SWy-3) to three cycles of reduction and oxidation (by hydrogen peroxide). We have been studying the effect of reduction via three different reduction pathways: chemical reduction by dithionite, microbial reduction using a commonly found electron shuttling compound (electrochemically reduced form of AQDS (2,6-anthrahydroquinone disulfonate)) as a proxy, and microbially mediated abiotic reduction with aqueous Fe(II). Our preliminary kinetic results from dithionite-reduced NAu-1 with high (75%) and low (20%) reduction extent suggest an increase in reactivity of clay mineral Fe with increased redox-cycling. This effect was more pronounced with higher extents of reduction. The presentation will also discuss findings from preliminary microscopy and spectroscopy analysis. This data will be compared with reaction kinetics from clay mineral samples reduced by aqueous Fe(II), as well as the potential preliminary data from NAu-1 cycled with electrochemically reduced AQDS.
Basalt amendment for organic carbon stabilisation in soil: rationale and basalt characterisation

Amy Lewis¹, Binoy Sarkar¹, Mark Hodson², Simon Kemp³, David Beerling¹

¹Animal and Plant Science, University of Sheffield
²Environment and Geography, University of York
³British Geological Survey
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Natural weathering of silicate minerals, which comprise most of the Earth’s solid rocks, consumes carbon dioxide (CO₂) from the atmosphere and deposits it in the ocean as bicarbonate. With the need to identify solutions to increasing CO₂ levels, scientists have been investigating how this natural process can be accelerated in a process coined enhanced weathering. Amending cropland soils with a finely crushed basalt, an abundant rock with a reasonably fast weathering mineral assemblage, is one such proposed enhanced weathering deployment strategy.

In the soil-plant system, however, basalt not only interacts with the high CO₂ concentrations in soils. The basalt and its weathering products also interact with a diverse range of organic compounds including the plant root exudates. During these interactions, fresh surface area provided by basalt and its weathering products may bond with organic molecules, stabilising the organic carbon and thus preventing it from being directly accessible to respiring microorganisms.

Basalt composition can also be diverse, and initial characterisation of chemistry and mineralogy of the rock is important for understanding the mechanisms and success of carbon stabilisation. X-ray Diffraction (XRD) was conducted to determine the whole rock and clay mineralogy of 5 basalt samples, and the elemental compositions of the basalts were determined through inductively coupled plasma optical emission spectrometry (ICP-OES) following a hydrofluoric acid (HF) digestion. At this meeting, I will briefly discuss the rationale behind my PhD project and the initial mineralogical and chemical characterisations of the basalt samples.
Bulk X-ray spectroscopy is a powerful tool for understanding oxidation state, speciation and coordination environment of elements under probe. X-ray microscopy, on the other hand, provides unparalleled information regarding the distribution and localisation of the key species driving the reaction dynamics. Integration of the two results in what is often called X-ray spectromicroscopy, which embodies the strengths of both X-ray spectroscopy and microscopy techniques.

Taking advantage of some of the recent developments in synchrotron X-ray science, our research combines x-ray microscopy (µ-XRF, tomography, and STXM) and X-ray spectroscopy (NEXAFS, XANES, EXAFS, and X-ray Raman) techniques to understand the mechanisms of coupled (biotic and abiotic) reaction pathways in order to integrate molecular constraints with modelling efforts. Lack of molecular-level insight hinders the development of accurate reaction networks in models, which in turn limits the predictive ability of the global elemental cycles.

There is an increasing evidence that reactions occurring at the surfaces and interfaces of cells and clay minerals are central to many, perhaps most, processes of environmental importance – understandably so because the microenvironment at and adjacent to cell surfaces and clay/mineral particulates can be significantly different from the bulk environment.

This talk will elucidate the role of cell surfaces, clays, and mineral colloids in a range of natural processes, from the fate and transport of contaminant metals to nutrient cycling in terrestrial and aquatic ecosystems. Examples presented in this talk would demonstrate that an in-depth understanding of molecular-scale processes affecting elemental speciation is a critical research need for modelling the global cycling of elements in order to advance fundamental understanding of coupled reaction processes in complex natural environments and enable system-level environmental prediction and decision support.
Interaction of molybdate (MoO$_4^{2-}$) with hematite and magnetite

Jing Zhang, Victoria Coker, Frederick W. Mosselmans, Samuel Shaw

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Molybdenum (Mo) is an essential trace element in the environment. However, at high levels Mo can become toxic to plants and animals, including humans. Mo commonly exists as the tetrahedral oxyanion molybdate (Mo(VI)O$_4^{2-}$) in oxic environments in soils associated with mining, steel waste and other extractive industries and in high concentrations in soils can lead to molybdenosis in ruminants resulting in copper deficiency. Iron oxide minerals (such as hematite (Fe$_2$O$_3$) and magnetite (Fe$_3$O$_4$)) are ubiquitous in subsurface soils and sediments and can strongly impact the mobility of contaminant metals; in particular through absorption to these high surface area minerals.

Previous studies on the absorption characteristics of Mo onto iron minerals have focused primarily on goethite and ferrihydrite, and to some extent hematite, with little information on the associations of Mo with magnetite. The aim of this project is to characterise the adsorption behavior of Mo(VI)O$_4^{2-}$ to hematite and magnetite under varying environmental conditions including pH (4-14), adsorbent concentration and ionic strength, as well as identify any changes in chemical state. X-ray Absorption Near Edge Structure (XANES) indicates the oxidation states of Mo associated with hematite or magnetite is different depending on pH and suggests that Mo(VI) is partially or fully reduced to Mo(IV) when adsorbed to magnetite and may not be reduced when adsorbed to hematite. Further work using Extended X-ray Absorption Fine Structure (EXAFS) analysis of Mo sorbed to hematite and magnetite provides a detailed molecular scale understanding of the Mo adsorption mechanisms. This is associated with solution analysis and geochemical modelling (PHREEQC) to provide a comprehensive dataset for determining the environmental mobility of Mo in a variety of geochemical scenarios. CD-MUSIC and constant capacitance model (CCM) etc. will also needs to be applied to fit the data.
Water quality dynamics and clay minerals – An example from a hyper-arid Andean river basin subject to large-scale mining

D. H. Nimalika Perera¹, Luis De Los Santos Valladares¹, David R. M. Arvidsson-Shukur¹, E. P. G. Barnes¹, P. J. Newton¹, E. Escobedo Pacheco, Patrick Byrne² and Crispin H. W. Barnes³

¹ Cavendish Laboratory, Cambridge University
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Water quality dynamics upstream and downstream of a large-scale copper mine in a hyper-arid region was studied. It showed that heavy rain resulted in change in river water composition downstream of the mine. Contrary to the expected acidity associated with acid mine drainage, water was found to be alkaline downstream of the mine. However, elevated concentrations of Al, Fe, Mn and a few trace metals (Li, Cu, Pb) were found during rainy season. These elements were found in lower concentrations upstream of the mine. River sediment analysis showed the presence of clay minerals in both upstream and downstream sites. This region’s hyper-aridity, which greatly reduces soil mineral mobility, is a probable cause for absence of acid mine drainage by the large-scale open-pit copper mine. However, owing to the elevated metal concentrations and arsenic concentrations above safe limits for potable use, this river water was not suitable for human consumption. Hyper-arid Andean river basins are severely strained by large-scale mining activities. The investigation of water quality in these remote regions, complicated by topographical constrains and limited infrastructure, is important to mitigate the impacts of hyper-aridity, climate change and industrial expansion on these precious water resources.
Poster Abstracts
Investigating the Antibacterial Properties of Azerbaijani Clays

Elshan Abdullayev¹, Anke Neumann², H. Chris Greenwell³, Gary J. Sharples⁴

¹ French-Azerbaijani University (UFAZ), Baku, Azerbaijan
² School of Engineering, Newcastle University
³ Department of Earth Sciences, Durham University
⁴ Department of Biosciences, Durham University
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The first use of medicinal clay was recorded in ancient Mesopotamia. Indigenous peoples around the world, such as in France and Africa, still use natural clays in traditional medicine and the antibacterial effect of such clay deposits have been validated in numerous published articles. Clay minerals found at various localities in Azerbaijan have also been used for their therapeutic benefits. Green Surakhany clays are used for internal and external treatments. Gilabi clays are only employed externally because they contain alkali elements, which can be harmful, especially for the stomach, when applied internally.

Clays are used in wound care to stop bleeding due to their propensity to adsorb fluids. In addition, some 'healing clays' have been identified as antibacterial and the modes of antibacterial action of such clays have started to be investigated. For example, investigation of the antibacterial properties of clay minerals, a study of green clays from France, have found that clay minerals can inhibit bacteria by physical attack or by a chemical inactivation. The clay platelets can envelop bacteria which can result in blocking of the uptake of nutrients and expulsion of waste products.

The main aim of our study is to investigate clay minerals assemblages of the Surakny and Gilaby clays in order to understand their medicinal and bioactive antibacterial properties. We will determine the mineralogical composition of the clays, their elemental composition and morphology, redox chemistry and surface properties that may contribute to their therapeutic role. In parallel, the antibacterial activity of these clay samples will be evaluated in assays with representative bacterial species. We will include Gram-negative and Gram-positive bacteria, which can be susceptible to different modes of antibacterial action exerted by clay minerals of different mineralogical composition. Our long-term aim is to develop novel clay therapies.
An investigation into stone decay at Jedburgh Abbey

Marli De Jongh, Martin Lee, Maureen Young

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One of four 12th C. Augustine abbeys situated in the Scottish borders, Jedburgh Abbey forms an integral part of Scotland’s historic past and built heritage. Over the past decade, Historic Environment Scotland (HES) have observed signs of delamination and disintegration of its clay-rich, heterogenous Carboniferous period sandstone. Clay minerals pose a potential threat to building stones; particularly smectites, which enhance weathering through intracrystalline swelling. By focussing on clay mineral content, this project explores the dynamic relationship between stone and the environment through careful mineralogy and petrophysical characterisation.

Illite, kaolinite, and chlorite were identified in Jedburgh Abbey sandstone by X-ray diffraction. The absence of smectitic clay minerals rules out the possibility of intracrystalline swelling as a predominant mechanism for stone decay. Scanning electron microscopy reveals that clays are concentrated on bedding planes creating a localised microporous texture. Furthermore, analyses of petrophysical stone properties reveal that capillary absorption of water is more effective along bedding planes. This directional dependence associated with bedding planes was also found during hygric swelling experiments with physical swelling occurring perpendicular to bedding planes.

Results suggest that a concentration of aligned clay minerals leads to a localised microporous texture around bedding planes. Microporosity and mineral alignment may then enhance capillary absorption along bedding planes. During moisture ingress, disjoining pressure within micropores and intercrystalline swelling of aligned clays can lead to hygric swelling of stone perpendicular to bedding. Moreover, concentrated stress near the bedding plane may lead to preferential mechanical weathering of bedding planes, in the case of Jedburgh Abbey, manifesting as delamination. These findings highlight the importance of studying the mineralogy of clays present, and that we must consider how textural properties and distribution of clays can influence weathering and subsequent decay of historically significant stone buildings.
Characterisation of Complex Adsorbed Layers

Belinda Fonseka, Stuart Clarke

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Only 40% of oil is recovered from sandstone reservoirs. The remainder is trapped on reservoir rock. Reservoir rocks have physical (grain size/porosity) and chemical (adsorption and absorption) properties. Our main interest is the surface chemistry.

Currently, in industry, testing additives for enhanced oil recovery is expensive as it requires extraction of reservoir core plugs. Easily accessible outcrop rock is used as a model reservoir rock, but doesn’t behave the same as reservoir rock. Can a realistic model be created.

Previous literature has shown that oil may be adsorbed on to the rock plug by an intermediate organic layer containing pyridine-type and other organic structures. Can new techniques further characterise the organic layer?

This work has shown a range of new techniques complimenting current literature, as well as opening up a range of further study towards understanding the mechanism behind enhanced oil recovery, with regards to surface chemistry.
Microbial community of MX80 bentonite and their interaction with iron

*Katie Gilmour, Neil Gray, Colin Davie*

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MX80 bentonite is a montmorillonite clay that has been selected as the buffer and backfill material in a proposed method of long-term deep geological storage of nuclear waste; however, it is not clear what effect microbes may have on its ability to function as an effective barrier. Microbes could affect the mineralogy or clay structure leading to changes in the geomechanical properties. Of particular concern are interactions with the steel waste canisters (corrosion), the fate and effect of corrosion products on the clay/microbe system and changes to the swelling capacity of the clay, which is key to the sealing properties of the barrier. The indigenous microbial community of MX80 bentonite was found to include iron-interacting bacteria and silicate solubilising bacteria. Experiments were carried out with the indigenous MX80 community and various iron substrates. Direct and indirect interactions were observed through a series of plate and liquid experiments. The concentration of Fe(II), Fe(Total), and silicate were measured throughout the respective experiments and XRD, SEM and EDX analyses were carried out on resulting products. Significant differences in structure and appearance were seen in all indirect iron-interaction experiments. This could prove a significant issue in the repository because reduced pore size would not be an obstacle as secreted metabolites would be small enough to travel through the barrier. Etching experiments showed evidence of micropitting and surface colonisation. Silicate bacteria also affected the silica content of the clay, which could significantly affect the swelling capacity.
Bentonite-Chitosan beads: as a promising candidate for purification of metal-contaminated water

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Water contamination with pollutants such as heavy metals is of significant concern because the toxicity exhibited by these metals can pose a severe threat to human health and the environment. Conventional water purification is costly and is usually not affordable by developing nations due to financial implications. In recent years, research has shifted towards the use of geological materials (such as clays) and biodegradable polymers as a promising class of adsorbents for domestic water purification and industrial wastewater treatment. These materials not only offer a cost-benefit but are also interesting materials from sustainability and environmental aspects. The combination of the biopolymer chitosan with clay has been reported to improve its chemical and mechanical stability, which in turn also enhances its adsorption capacity. However, studies which investigate the complementary advantage when both clay and chitosan are added together to form a composite are still limited in the literature. This study will develop and investigate a range of stable bentonite-chitosan composite beads through immobilisation of chitosan biopolymers onto bentonite clay focusing on changing the composition, preparation method and subsequent chemical modification. Initial investigations involve the combination of bentonite (Cloisite® Na+) with two different chitosans (medium and high molecular weight) in the weight ratio of 90%/10%, 70%/30% and 50%/50%. The composites beads have been characterised using a range of techniques including X-ray diffraction, Thermogravimetric analysis and Fourier transform infrared spectroscopy. The prepared composites will be used to test for adsorption of heavy metals via batch and column procedures. It is with our utmost expectation that this remediation technology could be a cheaper and more eco-friendly method in the treatment of metal-contaminated water at the domestic and industrial scale.
Revealing the interfacial reactions between green rust and arsenic species at the nanoscale

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Green rust (GR) phases are redox-active materials consisting of alternating FeII-FeIII hydroxide sheets and hydrated interlayer anions (e.g., Cl−, CO3^2−, SO4^2−). They are excellent sorbents for toxic oxyanions such as arsenic (As) due to their nanoparticulate nature and a zero point of charge around pH 8. We have recently shown that synthetic GR sulfate (GRSO4) is capable of taking up high amounts of As(III) and As(V), and are among the best performing Fe-bearing mineral phases in subsurface environments [1]. To date, most of the studies have focused on synchrotron X-ray absorption spectroscopy (XAS) and have shown that As(III) and As(V) are adsorbed to GR surfaces as inner sphere complexes [2-4]. However, the exact mechanisms for the interaction between As species and GR phases are still poorly understood.

Here, we investigated the removal mechanism of As(III) and As(V) (500 ppm) by synthetic GRSO4 using scanning transmission electron microscopy (STEM) coupled with energy dispersive X-ray (EDX) imaging, high energy X-ray diffraction (HEXRD), pair distribution function (PDF) analysis and As K-edge XAS. The STEM-EDX maps showed redox state-dependent As distribution and morphological changes in the GRSO4 surfaces. Meanwhile, HEXRD patterns and PDF analysis revealed that the initial GRSO4 did not transform to other Fe-bearing phases, and XAS analyses of the same samples indicated that both As(III) and As(V) were bound as bidentate, binuclear inner-sphere surface complexes. Overall, these results give new important insights on how As species are sequestered on the surface of GR, and on the potential role of GR phases in controlling the mobility of As in contaminated environments.

The Effect of Salt and Clay on Wettability

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The study of the wettability of surfaces is of great interest to many industries; for this work, we concentrate on concepts surrounding the injection of fresh water or brine into sandstone reservoirs. Here we consider the wettability by contact angle measurement of brine droplets on both glass and 3D printed surfaces. It is known that the presence or absence of various cations in the brine may have an effect on the detachment and movement of fine, usually clay, particles in the sandstone pore spaces. Will the presence of the clay particles in the brine droplet have an effect on the measured contact angle?
In oil and gas exploration and production, the chemical and physical properties of reservoir clay minerals can have an effect on drilling operations, reservoir quality and oil recovery rates. Various methods have been used to optimise the recovery of oil from reservoirs, through technologies that are more economical, easier to apply and environmentally friendly, culminating in the development of low salinity water flooding (LSWF). LSWF is a chemical method whereby the concentration of cations, especially multivalent cations, in the injected water is carefully reduced and controlled. LSWF is used in secondary and tertiary enhanced oil recovery (EOR) operations.

In this present study, we explore a new frontier in EOR research by examining the wettability and swelling capacity of reservoir clay minerals as a function of reduction potential ($E_H$) at different scales. We investigate how changes in Eh and salinity during a LSWF impact on the wettability of iron rich clay minerals. In further work, we will study how this in turn impacts the swelling of the clay minerals, surface adhesion changes and, ultimately, the migration of fines. Following the mineralogy studies, core floods will be undertaken and the changes in iron mineral and oil production in the outflow water assessed. Data gained will be modelled along with results obtained by confining pressure and temperature gradient experiments on sandstones. By scaling up the geochemistry data and combining them with the P, T conditions of the reservoir, we are going to create a tool for better constraining reservoir suitability for EOR applications that could potentially set the basis for optimising the operations.