French Polytech network form for PhD Research Grants from the China Scholarship Council

This document describes one of the PhD subjects proposed by the French Polytech network. The network is composed of 15 engineering schools/universities. The document also provides information about the supervisor. Please contact the PhD supervisor by email for further information regarding your application.

Supervisor information	
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PhD information	
Title	From hydration to solubilization of Fe bearing LDH: electronic structure and reactivity in environmental conditions
Main topics regards to CSC list (3 topics at maximum)	IV-7. Materials for environment and ecology

	IV-12. Environmental behavior and failure of materials
Required skills in science and engineering	The profile sought for this position is that of a chemistry, physics or mineralogy student with a strong interest in physical chemistry, characterization of solids and environmental applications.

Subject description (two pages maximum including biblio)

Layer double hydroxide (LDH) is a class of synthetic and natural materials made up of brucitic sheets which are themselves composed of octahedra of hydroxides of cations di (M^{II}: Mg^{2+}, Fe^{2+}, Ni^{2+} ...) and trivalent (M^{III}: Al^{3+}, Fe^{3+} ...) cations. The positive electrical charge of the sheets due to the trivalent cations is compensated by hydrated anions (A^{n-}: Cl^-, SO_4^{2-}, NO_3^-...). With great compositional flexibility, LDHs have the general formula $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}[(A^{n-})_{x/n},y\ H_2O]$ with a charge density (x) in the range 0.20-0.33 for most cation couples. The applications of these nano-materials already cover various fields (heterogeneous catalysis, flame retardant, etc.). New applications, based on their anion- and cation-sequestration/exchange/leaching properties, are now being considered. Thus, LDH could be exploited for its antimicrobial action[1] or for agronomic applications[2] (controlled fertilizer leaching).

The development of such processes is hampered by a lack of understanding of the behaviour of LDH in environmental environments and in the presence of water. Indeed, the water content of the interlayer space is largely dependent on the relative humidity and influences the anion mobility as well as the electronic properties of HDL to ultimately affect their reactivity. Beyond water adsorption, the solubilization of HDL in aqueous solution has given rise to little work: the dynamics of (non-congruent) solubilization phenomena and the subsequent mineralogical transformations remain poorly understood. Recent measurements of NAP-XPS (Near Ambient Pressure X-ray Photoemission Spectrocopy) conducted at LCPME have explored for the first time the evolution of the electronic properties of an Mg^{2+}-Al^{3+} LDHas a function of its water content.[3,4] At the same time, NAP-XPS has been shown to be a new tool for probing the early dissolution stages of a solid.

Environmental applications of aluminum compounds are questionable and the use of iron-based LDH (i.e. Mg^{2+}-Fe^{3+}) is therefore to be preferred due to the abundance and safety of this element. In addition, Fe^{2+}-Fe^{3+} LDH are minerals found in hydromorphic soils where their reactivity contributes to nitrate abatement[5] and soil chemistry[6,7].

The PhD student will focus on describing the electronic structure of iron-based HDL. To do this, he will implement photoemission techniques (XPS, UPS) and Mössbauer spectrometry of ^{57}Fe available at the laboratory. In particular, she/he will be able to explore the effects of the composition (sheets, inorganic [Cl^-, NO_3^-, ...] or organic interlayer anions) and size of (nano-)crystals on Fe-Fe interactions. The modulation of electronic structure upon hydration would necessitate NAP-XPS measurements on synchrotron facilities. The mineralogical transformations in aqueous solution of these HDLs will be elucidated by solid state characterization techniques (Mössbauer spectrometry, XRD, FTIR) coupled with chemical analysis of the liquid phase (ICP-MS, chromatography). Particular attention will be paid to the leaching of phosphate by these compounds as well as their reactivity for agronomic or environmental applications.

The PhD student will be part of the Laboratoire de Chimie Physique et Microbiologie pour les Matériaux et l'Environnement (LCPME) located in Nancy (France). LCPME is a multidisciplinary unit focusing on the study of mineral and biological interfaces in aqueous media. The main objective is to better understand the reactivity of solid surfaces (mineral phases, organo-mineral hybrids, nanomaterials or biological objects) in contact with aqueous media, with the aim of taking into account the structural and reactional heterogeneities of the systems studied at different spatial scales, and with potential spin-offs in the environmental and materials fields. The unit combines disciplines from the fields of physical chemistry (spectroscopy and electrochemistry) and microbiology (microbial interfaces and adhesion).

(1) Awassa, J.; Soulé, S.; Cornu, D.; Ruby, C.; El-Kirat-Chatel, S. Understanding the Role of Surface Interactions in the Antibacterial Activity of Layered Double Hydroxide Nanoparticles by Atomic Force Microscopy. *Nanoscale* **2022**, *14* (29), 10335–10348. https://doi.org/10.1039/D2NR02395D.
(2) Borges, R.; Wypych, F.; Petit, E.; Forano, C.; Prevot, V. Potential Sustainable Slow-Release Fertilizers Obtained by Mechanochemical Activation of MgAl and MgFe Layered Double Hydroxides and K2HPO4. *Nanomaterials* **2019**, *9* (2), 183. https://doi.org/10.3390/nano9020183.
(3) Coustel, R.; Boucly, A.; André, E.; Di Bitetto, A.; Bournel, F.; Gallet, J.-J.; Rochet, F.; Carteret, C. NAP-XPS Probes the Electronic Structure of the Mg–Al–Cl Layered Double Hydroxide upon Controlled Hydration. *J. Phys. Chem. C* **2023**, *127* (8), 4144–4153. https://doi.org/10.1021/acs.jpcc.2c05362.
(4) Tissot, H.; Coustel, R.; Rochet, F.; Boucly, A.; Carteret, C.; André, E.; Bournel, F.; Gallet, J.-J. Deciphering Radiolytic Oxidation in Halide Aqueous Solutions: A Pathway Toward Improved Synchrotron NAP-XPS Analysis. *J. Phys. Chem. C* **2023**, *127* (32), 15825–15838. https://doi.org/10.1021/acs.jpcc.3c03676.

(5) Etique, M.; Zegeye, A.; Grégoire, B.; Carteret, C.; Ruby, C. Nitrate Reduction by Mixed Iron(II-III) Hydroxycarbonate Green Rust in the Presence of Phosphate Anions: The Key Parameters Influencing the Ammonium Selectivity. *Water Res.* **2014**, *62*, 29–39. https://doi.org/10.1016/j.watres.2014.05.028.
(6) Cornu, D.; Coustel, R.; Renaudin, G.; Rogez, G.; Renard, A.; Durand, P.; Carteret, C.; Ruby, C. Synthesis and Characterization of a New Monometallic Layered Double Hydroxide Using Manganese. *Dalton Trans.* **2022**, *51* (31), 11787–11796. https://doi.org/10.1039/D2DT01835G.
(7) Doggaz, A.; Coustel, R.; Durand, P.; Humbert, F.; Ruby, C. Birnessite: A New Oxidant for Green Rust Formation. *Materials* **2020**, *13* (17), 3777. https://doi.org/10.3390/ma13173777.