MOBILITY MISSION REPORT

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MISSION TITLE

Analysis and discussion of data about mechanisms involved in the U-, Se-sorption and redox behaviour on Fe(II)/Fe(III)-clay minerals.

DESCRIPTION

Concerned organisations

- Research entities:
  - · BRGM (Bureau de Recherches Géologiques et Minières).
  - · CIEMAT (Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas).
- Technical support organisations:
  - · CNRS (Centre National de la Recherche Scientifique).

Concerned infrastructures or facilities

- Other relevant infrastructure or facility to be specified:
  - · Research laboratories at BRGM (Bureau de Recherches Géologiques et Minières).
  - · Research laboratories at CIEMAT (Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas).

· Transmission Electron Microscopy at CNRS (Centre National de la Recherche Scientifique).

Concerned phases

- Phase 1: Site evaluation and site selection.
- Phase 2: Site characterisation.

Themes and topics

- Theme 2: Radioactive waste characterisation, processing and storage (Pre-disposal activities), and source term understanding for disposal:
  - Waste handling, characterisation, treatment and packaging.
  - Radionuclide inventory and source term.
  - Waste acceptance criteria.
- Theme 3: Engineered barrier system (EBS) properties, function and long-term performance:
  - Spent Fuel and high-level waste disposal canisters.
  - Clay-based backfills, plugs and seals.
  - EBS system understanding.
- Theme 4: Geoscience to understand rock properties, radionuclide transport and long-term geological evolution:
  - Long-term stability (uplift, erosion and tectonics).
  - Perturbations (gas, temperature and chemistry).
  - Aqueous pathways and radionuclide migration.

Keywords

Clay minerals; smectites; geochemistry; chemical structure; minerals; mineralogy; redox phenomena; redox reactions; anions; physical and chemical processes; radioactive waste; safety assessment; radionuclide release mechanisms; radionuclide transport; crystallography; X-ray Diffraction (XRD); Transmision Electron Microscopy (TEM); Electron Probe Microanalyzer (EPMA); phenanthroline method for iron estimation.

EXECUTIVE SUMMARY

According to the roadmap of the European Joint Program on Radioactive Waste Management (EURAD), the Engineered Barrier System (EBS) stands out as one of the most critical components to understand in the implementation of any radioactive waste management (RWM) program. In this context, one of the most significant risks within the EBS is container corrosion, potentially linked to iron (Fe) reduction in the clay structure. This is of particular interest due to the role of Fe-rich clays in redox geochemical cycles, especially in the reductive degradation of contaminants. However, uncertainties persist regarding the redox mechanisms coupled with cation adsorption reactions and electron transfers. The title of my thesis, "Geochemical and Redox Processes Influencing the Migration and Retention of Radionuclides in the Context of a Deep Geological Repository

for High-Level Radioactive Waste," can be considered part of the FUTURE work package of the EURAD project. Within this framework, the proposed activities and objectives of my stay involved comparing, discussing, and analyzing Fe(II)/Fe(III)-rich clay materials synthesized at CIEMAT. The goal was to enhance understanding of the mechanisms involved in Fe(II)/Fe(III) sorption and redox behavior on clay minerals. To achieve this, characterization of Fe-rich smectites synthesized at CIEMAT, containing a significant amount of Fe3+, was conducted using techniques not available in our research center, such as Transmission Electron Microscopy (TEM) and Electron Probe Microanalyzer (EPMA). This provided the crystallochemical structure of the samples, revealing that the synthesized smectite particles formed foliated aggregates with crystallized particles exhibiting a laminar structure. Additionally, a study was undertaken involving the mixing of Cu(II)-Triethylenetetramine solutions with ferrous chloride and ferric chloride, testing 20 solutions with different initial Fe/Cu ratios at room temperature and under anoxic conditions. The aim was to investigate potential redox reactions and analyze solid precipitation as a function of the variation of Fe/Cu ratio. The total Fe and Fe2+ amounts in the supernatants of the suspensions were determined, and X-ray Diffraction (XRD) analysis of the precipitated solids is currently underway. During my internship at BRGM, I have felt fully integrated into the team, familiarizing myself with their state-of-the-art laboratories and advanced techniques. The team provided all possible facilities, aiding in my integration and providing the necessary training for full autonomy during my stays. Close collaboration with BRGM experts enriched my knowledge, providing valuable insights and additional skills in the field of geochemistry and redox processes, thereby strengthening my contribution to the project and professional development.

1. MISSION BACKGROUND

1.1. R&D background

According to the European Joint Programme on Radioactive Waste Management (EURAD) roadmap (Theme 3), the engineered barrier system (EBS) is one of the most critical components to be understood for the implementation of any radioactive waste management (RWM) programme. Bentonites, composed of smectite clay minerals, are an essential component of the multi-barrier system securing the long-term safety of the final disposal of nuclear wastes. The efficiency of such engineered clay barrier system (EBS) relies on its physical and chemical confinement properties: low permeability, low diffusivity, high retention and swelling capacity. Therefore, an important issue for performance assessment purposes is to have confidence and demonstrate the preservation of these properties over the long term, i.e., hundreds of thousands of years under real conditions of a repository (e.g., Posiva-SKB (2017)). In this context, one of the most important risks that can occur in the EBS is the corrosion of the canister, which could be coupled with reduction of iron (Fe) in the clay structure. These processes could greatly decrease the long-term stability of the clay and, consequently, of the barriers themselves. Thus, the oxidation state of iron (Fe) in the crystal structures of smectite clay minerals has been found to be a critically important factor underlying the behavior of the clay (Stucki, 2006). The swellability of the clay tends to decrease with an increased Fe reduction level, superimposed layers tend to collapse one upon the other, cation exchange capacity increases markedly upon reduction, the reduction of Fe(III) to Fe(II) may result in an increase in layer charge and ordering in the hk lattice planes and, furthermore, aqueous suspensions of ferruginous smectite have an increased viscosity subsequent to Fe reduction due to increased interparticle attraction (Anastácio et al., 2008 and references herein). Other associated processes also can occur in the barrier such as Si, Al, and Mg release in high pH due to solution leaking from the canisters, with the subsequent formation of new minerals (e.g., zeolites and feldspathoids). The reduction of Fe3+ within the structure of nontronites and ferruginous smectites is a subject of interest due to the role of Fe-bearing clays in geochemical redox cycles and in particular the reductive degradation of contaminants. A range of spectroscopic techniques have been used for iron speciation, structural rearrangements and to investigate the reduction mechanism in clay minerals: Mössbauer (Jaissi, 2005), FTIR (Lee et al., 2006), TG-DSC, XANES-EXAFS (Manceau et al., 2000). In addition, iron, both as structural component of clay minerals or adsorbed to their surfaces, is able to change the oxidation state of contaminants (co-)adsorbed at the clay mineral surface and thereby alters their mobility and/or (bio) availability (Gorski, 2013; Soltermann, 2014). However, there are some uncertainties related to redox mechanisms coupled cation adsorption and electron transfer reactions governing the retention of redox-sensitive elements on iron bearing clay minerals. Different doctoral theses are ongoing to elucidate this issue (e.g., PSI-BRGM studies) in the context of Future workpackage. At CIEMAT we are analysing adsorption reactions governing the retention of uranium, technetium and selenium on iron bearing clay minerals (natural and synthesized clay minerals). For this reason, collaborative works between organizations will be of interest for obtaining final conclusions. BRGM is specialist on clay synthesis tuning the Fe(II)/Fe(III) ratio, and on the characterization of clay minerals from the morphologic to the atomic scales by using different techniques. A further stay at Grenoble or Soleil facilities, will allow to complete the characterization of redox processes by XANES and EXAFS techniques.

1.2. Mission objectives

The title of my thesis is "Geochemical and redox processes influencing the migration and retention of radionuclides in the content of a deep geological repository for high level radioactive waste", can be considered to be integrated within the FUTURE workpackage from the EURAD project. The work plan of my thesis includes the study of U, Se and Tc sorption on both natural and synthetic iron clay minerals with different Fe(II)/Fe(III) contents. Within this framework, the main proposed activity during my stage at BRGM, will be related to the comparison of results, discussion and analysis of Fe(II)/Fe(III) clay rich materials prepared at CIEMAT with the aim of improving the knowledge of the mechanisms involved in the Fe(II)/Fe(III) sorption and redox behaviour on clay minerals, which are important for the analysis of possible alteration of the clay mineral structure, affecting the properties of the bentonite barrier and the redox effects on the radionuclide retention in clays. Special emphasis will be given to the characterization of clay materials by using different techniques, which are not available at CIEMAT as for example Crystal structure analyses by Syroquant or other computer software, resin impregnation for EMPA and RAMAN analyses, etc. During the first two years of my thesis at CIEMAT, a lot of experiments have been performed and it would be of interest to deep my knowledge and discuss about results, as well to improve my capabilities in some techniques not available at CIEMAT laboratories. BRGM people at Orleans are involved in EURAD Project and they are Scientifics of first level. This stay will be a great opportunity for increasing my knowledge in a lot of fields related with nuclear waste disposal and safety assessment.

1.3. Mission request

The knowledge of the chemical structure and properties of Fe(II)/Fe(III) clay minerals is of great importance in the performance of the EBS and discussion with clay minerals specialist at BRGM will be very useful for increasing my knowledge and for the achievements of the objectives of the project. In a first stage of the stay, discussion about methods and results obtained at CIEMAT regarding iron reduced clay minerals and synthesis of iron smectites with different Fe(II)/Fe(III) contents will be performed. This will allow comparing the obtained results in similar experiments performed with other partners in FUTURE workpackage. In a second stage of the stay, structural and crystallographic characterization of Fe(II)/Fe(III) clay materials prepared at CIEMAT will be performed by using XRD techniques. BRGM scientifics are specialist in the Siroquant program and other DRX software. Working with data obtained at CIEMAT will allow to acquire capacities about the understanding of structural characteristics of Fe(II)/Fe(III) clay minerals. Then, the morphology, mineralogy and structural variation will be analysed by TEM and electron microprobe (EMPA). Solid clay mineral samples will be impregnated with resin and cut with a diamond knife by using a Leia UC7 ultramicrotome. This technique will preserve the texture of the clay material during the preparation for:

a) Imaging the techniques (TEM).

b) Electron microprobe (EMPA) studies

Both techniques are useful for mineralogy, compositional and structural variations at a nanometric scale.

At CIEMAT there is not so much experience about resin impregnations and ultramicrotome cuts. Furthermore, EMPA techniques are not available. Further analysis by RAMAN will be performed on the samples for comparison of methodology and results obtained at CIEMAT when using clay minerals. In addition, Fe(II) ion exchange processes will be analysed by means of some batch type aqueous test experiments, performed at

BRGM or at CIEMAT on FEBEX bentonite, with the aim of to characterize the effects of redox reactions in a representative Fe-bearing barrier clay material in its oxidized and reduced states in order to understand other cation competition under the types of conditions expected in nuclear repository. Finally, surface complexation modelling of redox sensitive elements onto Fe-rich smectites will be made by means of PhreeqC. CIEMAT has experience about modelling, but this experience at BRGM it would be a great opportunity to check results with this program, and acquire capabilities on geochemical modelling.

1.4. Mission composition

Host organisation

BRGM (Bureau de Recherches Géologiques et Minières).

Host facility

French Geological Survey. Direction Eau, Environnement et Ecotechnologies.

Water, Environment, Process Development & Phys-Chem Analyses Division.

Mineralogy, Geochemistry and Modelling of Geological Environments.

Mission dates

16 October 2023 – 15 December 2023.

2. MAJOR PRACTICES, TECHNIQUES, METHODS, TOOLS OR SYSTEMS OPERATED OR STUDIED

2.1. Practice, technique, method, tool or system operated or studied during the mission

Transmission Electron Microscopy (TEM). Sample preparation.

Description

The samples for transmission electron microscopy (TEM) were prepared as follows: solid powders were dispersed in ethanol using an ultrasonic bath and then deposited onto lacey carbon films loaded on copper grids.

Usage

0.5 mL of ethanol is poured into a 15 mL polypropylene tube from Falcon. Subsequently, approximately 0.05 g of each of the samples, previously synthesized at CIEMAT, which are Fe-rich smectites with a high content of Fe3+, are introduced in the ethanol solution using a spatula. This small suspension is then introduced into an ultrasonic bath (Model ELMA P60H Elmasonic P) about 3 times for 3 to 5 seconds each until, finally, it is stirred and left for an additional 10 seconds. Next, the sample is deposited on copper grids for being analysed by TEM. For this, tweezers of the DUMONT model are used to take a lacey carbon film loaded on copper grids, onto which the sample is then deposited. The lacey carbon film should be held by the edge, without the tweezers touching the center of the sheet. Once properly positioned, using a 250-microliter pipette, 2-3 drops of the solution prepared earlier are precipitated and carefully placed on the sheet. The sample is allowed to dry for 10 minutes. If drying is not sufficient, it is placed in the oven at 75°C for approximately 1 minute. This process is repeated with progressively more diluted samples using 3 mL and 5 mL of ethanol, respectively, to obtain three copies.

Benefits

The major benefit of this procedure or technique is the small amount of sample required and the knowledge of the structural and crystallochemistry of the synthetized clay. Having a small quantity of each of the synthesized clays is crucial for the analysis and characterization of the sample with other techniques.

Limitations

One should not leave the sample in the ultrasonic bath for more than 30 seconds. Another limiting factor is the precision with which 2-3 drops are deposited onto the lacey carbon film and subsequently dried; often, it is necessary to transfer the sample to the oven for 1 minute.

Applicability

Transmission Electron Microscopy (TEM) allows studying the morphology and structure of clay minerals. In this case, TEM and High-Resolution Transmission Electron Microscopy observations were performed with a Philips CM20 operated at 200 kV on iron-rich smectites with a significant amount of synthesized Fe3+ at CIEMAT.

2.2. Practice, technique, method, tool or system operated or studied during the mission

Electron Probe Microanalyzer (EPMA). Sample preparation.

Description

The electron microprobe is essentially a designed and optimized scanning electron microscope that allows for the determination of the chemical composition of a solid substance in very small areas, in this case, on iron-rich smectites with a significant amount of synthesized Fe3+ at CIEMAT. Analyses and the obtained data were calculated from electron probe microanalyses (EPMA; Cameca SX Five electron microprobe). These were carried out on samples embedded in epoxy mounts. After polishing the epoxy mount, a 10–20 nm thick carbon layer was sputter-coated on the samples.

Usage

The epoxy mounts are placed in a crucible for easy transfer to the oven at a later stage. In the initial phase, with the aid of a spatula, a few milligrams of previously synthesized Fe-rich smectites with a high content of Fe3+ at CIEMAT are added to 15 mL polypropylene tubes from Falcon. Approximately 0.25 mL of deionized water is added, and this small solution is introduced into an ultrasonic bath (ELMA P60H Elmasonic P model) three times for 3 to 5 seconds each until, finally, it is stirred and left for an additional 10 seconds. Using a 250-microliter pipette (Eppendorf), a portion of the solution is precipitated onto the epoxy mount (approximately 2 or 3 drops). The samples must be perfectly identified, and it is advisable to create them with different shapes and geometries for proper technician identification. Additionally, they should be as homogeneous as possible. The epoxy mount is hydrophobic, so there is no risk of spillage. The crucible is placed in the oven for approximately 1 hour. Finally, to prevent low-conductivity samples from charging during EPMA analysis, a 10–20 nm thick carbon layer was sputter-coated onto the samples. A carbon evaporator was used for this purpose.

Benefits

The major benefit of this procedure or technique is to know the chemical characterization the samples with a small amount of sample. Having a small quantity of each of the synthesized clays, a low amount of sample for analysis is crucial for the characterization of the same sample with other techniques.

Limitations

One of the limitations or precautions to be taken is to ensure that the samples are deposited onto the epoxy mount with the utmost care, avoiding any mixing. It is important to clearly label each of the samples or keep track of their location to make the technician's

job easier. Exercise caution regarding the time the samples spend in the oven: the longer they remain inside, the higher the probability that the clay will detach from the surface due to shrinking. Lastly, strive for the samples to be as homogeneous as possible and find, for their proper analysis, a surface as flat as possible to apply the technique in the most suitable manner.

Applicability

To determine the chemical composition and find the structural formula of the iron-rich smectites with a significant amount of synthesized Fe3+ at CIEMAT, as our unit does not have this technique.

2.3. Practice, technique, method, tool or system operated or studied during the mission

Validity of the CEC determination with the standard Cu-Trien complex method in clay samples with an iron content and determination of the Fe content in solutions by the 1,10-phenanthroline method.

Description

CEC in bentonites is usually determined by the Cu-Trien method. Howerver, in samples with high iron content some interferences may invalidate the method. For checking the method, different solutions varying the Fe/Cu ratios were prepared from initial Cu(II)-Triethylenetetramine and ferrous/ferric chloride solutions. After reaction inside anoxic glove box, the determination of iron by the 1,10-phenanthroline method was performed in each sample. In this method, 1,10-phenanthroline is added to the iron-containing solution, forming colored complexes with the metal. The intensity of the formed color is directly related to the concentration of iron in the sample. The process involves preparing a 1,10-phenanthroline solution and adding this solution to the sample being analyzed. After the formation of the iron-1,10-phenanthroline complex, the absorbance of the formed color is measured using a spectrophotometer. The absorbance reading is compared to a previously established calibration curve with known concentrations of iron solutions.

Usage

Firstly, all necessary reagents for the initial solutions (ammonium acetate, 100% acetic acid, hydroxylamine hydrochloride, and 1,10-phenanthroline hydrochloride) are gathered. Once the reagent solutions are prepared following the method, different standards are prepared for the calibration curve with the assistance of the spectrophotometer (Cary 60 Agilent) and Agilent Cary WinUV software (Concentration). In total, 12 standards are used with Fe concentrations ranging from 0 mg/L to 4 mg/L. After creating the calibration curve, the sample solutions were prepared. In this particular case, the total Fe and Fe2+ of 20 samples with different Fe/Cu ratios from an initial solution of Cu(II)-Triethylenetetramine with a proportion ferrous chloride solution were measured. Besides, other 20 samples from an initial solution of Cu(II)-Triethylenetetramine mixed with ferric chloride. For both measurements, the method is followed, incorporating the initial reagent solutions in appropriate quantities and proportions (for Fe2+ measurement, the volume of hydroxylamine is replaced with the equivalent volume of deionized water).

Benefits

Check the validity of the CEC determination with the standard method of Cu-Trien complex. These methods (Cu-Trien complex and 1,10-phenanthroline methods) have the advantages of being quite simple, fast, cost-effective, and applicable to different fields.

Limitations

Oxidation of samples by air contact. Protect all solutions with reagents and all standard solutions in the fridge when not in use. They can be affected by light and by evaporation, leading to a loss of volume if flasks are not properly sealed with an appropriate stopper.

Applicability

This method has been used to check the standard determination of CEC by Cu-Trien method and define their applicability in samples with high iron content. The total amount of Fe and Fe2+ in each of the 20 samples with different initial Fe/Cu ratios from the mixture of Cu(II)-Triethylenetetramine solutions with ferrous chloride and ferric chloride have been measured and the possible neoformation of solid phases during the process have been checked.

2.4. Practice, technique, method, tool or system operated or studied during the mission

Replace this entire field with the name of the practice, technique, method, tool or system that is the object of this mission.

Description

Replace this entire field with a description of the implementation of this practice, technique, method, tool or system at the host organisation.

Usage

Replace this entire field with a description of your operation or study of this practice, technique, method, tool or system during the mission.

Benefits

Replace this entire field with a description of the benefits for implementing this practice, technique, method, tool or system.

Limitations

Replace this entire field with a description the limitations of this practice, technique, method, tool or system.

Applicability

Replace this entire field with a description of how this practice, technique, method, tool or system could be implemented in or adjusted to your home context.

3. MISSION FINDINGS AND CONCLUSIONS

3.1. Lessons learned and conclusions

My internship at BRGM has been a rich and insightful experience, providing valuable lessons and conclusions. Collaborating with top-notch researchers and utilizing state-of-the-art equipment has significantly contributed to my professional growth. The interdisciplinary nature of the research projects at BRGM allowed me to expand my knowledge and skills beyond my initial scope.

Highlighting the simplicity with which the entire BRGM team showed me their laboratories, the various equipment they had in their institution, how to use them, the different operating protocols, and where the necessary materials were located for the proper development of my work. They provided the necessary assistance through two laboratory training courses ("Health and Safety of BRGM Employees" & "The Risks of Analytical and Experimental Activities at BRGM") to enable me to be completely independent in their facilities.

Among all the lessons learned, it is worth noting: a) the sample preparation for studying the morphology and structure of Fe-rich smectites synthesized at CIEMAT using Transmission Electron Microscopy (TEM), allowing me to see the equipment and gain a deeper understanding of the technique with explanations from the technicians present; b) the sample preparation for studying the chemical composition and finding the structural formula of Fe-rich smectites synthesized at CIEMAT through Electron Probe Microanalyzer (EPMA), enabling me to see the equipment and gain a more in-depth understanding of the technique with explanations from the specialist technician in charge of the equipment; and c) conducting a new study about the CEC determination with Cu-Trien complex when iron is involved in the aqueous system. This study involved the mixing of solutions of Cu(II)-Triethylenetetramine with ferrous chloride and ferric chloride, respectively, testing 20 initial solutions of different Fe/Cu atomic ratios at room temperature and under anoxic conditions to investigate potential redox reactions and analyze the spontaneous precipitation of a solid based as a function of the Fe/Cu ratio in the solution; and determining the amount of Fe2+ and Fe3+ in these samples using the 1,10-phenanthroline method.

In conclusion, being part of the EURAD mobility program and having this experience at BRGM has been a great opportunity to promote the internationalization of the scientific results obtained and give them a more significant impact. Additionally, this has contributed to strengthening CIEMAT's collaborations with other EURAD partners. It has been a fantastic professional and personal experience.

3.2. Relevant findings and conclusions for home organisation

Currently, data obtained from various techniques and procedures conducted at BRGM are being compiled and analyzed. For CIEMAT, thanks to the analyses and data provided by TEM and EPMA, it will be possible to study the morphology and structure of iron-rich smectites with a significant amount of synthesized Fe3+ in our laboratories. This includes understanding the chemical composition and, consequently, determining the structural formula of the different samples. Additionally, experiments conducted with FeCl2+4H2O and FeCl3+6H2O solutions combined with Cu(II) Triethylenetetramine solution, in which

the ratio of Fe to Cu was varied, will allow the study of mechanisms involved in the redox behavior during a CEC determination with Cu-complex when iron is involved in the system.

3.3. Relevant findings and conclusions for host organisation

Similarly, for BRGM, data obtained from various techniques and procedures conducted at their institution are being compiled and analyzed. All results obtained will be shared between both institutions, highlighting their collaboration throughout the process.

3.4. Relevant findings and conclusions for other organisations

The study of the valididy of the CEC determination with the standard Cu-Trien method will be of interest for other organizations and the scientific community related with clay mineralogy.

4. POTENTIALS FOR IMPROVEMENT OR DEVELOPMENT

4.1. Generic potentials

Honestly, the level of satisfaction during my stay at BRGM has been very high, being able to collaborate with the best people and researchers and having access to top-notch equipment. At all times, I have been provided with all possible facilities, and in this document, I do not suggest any generic improvements or developments for the practices, techniques, methods, tools, or systems operated or studied during the mission. However, the stay was too short for completing of the objectives and a further collaboration in the future with BRGM team woul be of great interest.

4.2. Potentials for home organisation

According to my supervisor's opinion and considering the equipment available at BRGM, the exchange of ideas and research work would be more straightforward. CIEMAT should adapt some laboratory conditions (for example, a centrifuge, balance, and oven within the glove box) for improving analysis and results. Publication of results in collaboration with BRGM.

4.3. Potentials for host organisation

New collaboration and join works between BRGM and CIEMAT. Exchange of PhD students between BRGM AND CIEMAT. Publication of results in collaboration with CIEMAT.

APPENDICES

Mission journal

This section has been completed every day during the stay at BRGM. Since it is a 60-day stay and an important part of the report, we have tried to synthesize it as much as possible to avoid exceeding the maximum length. It has been decided to fill it in day by day with their corresponding dates:

16/10/23: Arrival at BRGM. Completion of personal data. Creation of the access card to the center. Creation of a personal account for WiFi. First meeting with Dr. Sylvain Grangeon. 17/10/23: Second meeting with Dr. Sylvain Grangeon with the aim of contextualizing the work carried out so far at CIEMAT and possible avenues of research and activities to be carried out during this period. Given the short available time, it was important to decide which activities were a priority or essential among those initially proposed in the mobility application and mission request document. 18/10/23: Visit to BRGM laboratories. 19/10/23: Review of literature before the study to be carried out, analyzing possible redox effects on the measurement of cation exchange capacity with Fe-rich smectites synthesized at CIEMAT. 20/10/23: Meeting with Dr. Ana María Fernández (CIEMAT), Dr. Mathieu Debure (BRGM), and Dr. Sylvain Grangeon (BRGM) to define the work that will be carried out. 23/10/23: Meeting with Dr. Sylvain Grangeon and Dr. Esra Orucoglu from BRGM to define work, times, and space in the laboratory. 24/10/23: Calculation of the initial concentrations of ferric chloride, ferrous chloride, and Cu(II)-Triethylenetetramine solutions. 25/10/23: Calculation of concentrations and different Fe/Cu ratios of the 20 solutions of ferric chloride and ferrous chloride with Cu(II)-Triethylenetetramine. 26/10/23: Preparation of samples for TEM. 27/10/23: TEM analyses. 30/10/23: Download TEM images and DM3 Software for image processing. 31/10/23: Completion of the Laboratory Training course at BRGM, "The Risks of Analytical and Experimental Activities at BRGM." 01/11/23: Public holiday in France. 02/11/23: Preparation of samples for TEM. 03/11/23: Completion of the Laboratory Training course at BRGM, "Health and Safety of BRGM Employees." 06/11/23: Preparation of samples for TEM. 07/11/23: Preparation of samples for EPMA. 08/11/23: Second TEM session. 09/11/23: First EPMA session. 10/11/23: Rest day. 13/11/23: Preparation of initial solutions of ferrous chloride, ferric chloride, and Cu(II)-Triethylenetetramine. 14/11/23: Preparation of 20 solutions with different Fe/Cu ratios of ferric chloride and Cu(II)-Triethylenetetramine. 15/11/23: Preparation of 20 solutions with different Fe/Cu ratios of ferric chloride and Cu(II)-Triethylenetetramine. 16/11/23: Preparation of 20 solutions with different Fe/Cu ratios of ferrous chloride and Cu(II)-Triethylenetetramine. 17/11/23: Preparation of 20 solutions with different Fe/Cu ratios of ferrous chloride and Cu(II)-Triethylenetetramine. 20/11/23: Separation of solid and supernatant using vacuum filtration system within glove box. 21/11/23: Separation of solid and supernatant using vacuum filtration system within glove box. 22/11/23: Separation of solid and supernatant using vacuum filtration system within glove box. 23/11/23: Separation of solid and supernatant using vacuum filtration system within glove box. 24/11/23: Separation of solid and supernatant using vacuum filtration system within glove box. 27/11/23: Download TEM images, second session. 28/11/23: Meeting with Dr. Ana María Fernández to evaluate progress. 29/11/23: Preparation of two new solutions at a higher volume by mixing the initial solutions of ferrous chloride and Cu(II)-Triethylenetetramine. 30/11/23: Preparation of two new solutions at a higher volume by mixing the initial solutions of ferrous chloride and Cu(II)-Triethylenetetramine. 01/12/23: Rest day. 04/12/23: Preparation of reagents for Fe tot and Fe2+ measurements. 05/12/23: Preparation of standards for Fe tot and Fe2+ measurements. 06/12/23: Calibration curve for Fe tot and Fe2+ measurements. 07/12/23: Fe tot measurements of the 20 samples with different

Fe/Cu ratios from the initial solutions of Cu(II)-Triethylenetetramine and ferrous chloride. 08/12/23: Fe2+ measurements of the 20 samples with different Fe/Cu ratios from the initial solutions of Cu(II)-Triethylenetetramine and ferrous chloride. 11/12/23: Fe tot measurements of the 20 samples with different Fe/Cu ratios from the initial solutions of Cu(II)-Triethylenetetramine and ferric chloride. 12/12/23: Fe2+ measurements of the 20 samples with different Fe/Cu ratios from the initial solutions of Cu(II)-Triethylenetetramine and ferric chloride. 13/12/23: Preparation of samples for XRD (FeCl3-Cu(II)-Triethylenetetramine). 14/12/23: Preparation of samples for XRD (FeCl3-Cu(II)-Triethylenetetramine). 15/12/23: Preparation of samples for XRD (FeCl2-Cu(II)-Triethylenetetramine).

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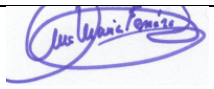
REPORT APPROVAL

Date	Beneficiary	Home mentor/supervisor	Host mentor/supervisor
14/02/2024	Francisco Javier León Vicente	Ana María Fernández Díaz	Sylvain Grangeon
			VISA