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Title: Sorption of Rare Earth Elements onto Iron oxides

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1. ABSTRACT:

The adsorption experiments of rare-earth elements (REEs) onto Ferrihydrite and Goethite were performed to understand the behaviour of the REEs when they enter in contact with the Fe oxides in different environments. Batch experiments were performed at pH 3, 4, 5, 6, 7 to see the interaction between the REEs with this Fe oxides. The solutions were prepared with 20mg of Fe oxide and a 50µg/L REEs concentration. The solutions were exposed in to different pH conditions and after 36h of pH control were filtrated in order to obtain the solution without Fe oxides and particles. The solutions were analysed with the Inductively Coupled Plasma Mass Spectrometer (ICP MS) to know the concentration of the REEs that weren't absorbed into the Fe oxides. The results revealed that at high pH (pH 7) barely all the REEs were absorbed while at low pH (pH 3) they weren't. At acid environments sorption sites are protonated but if we increase the pH, the sorption sites are deprotonated and disponible for REEs in solution. Cerium anomalies were found in the Ferrihydrite (Fh) due to his oxidation from Ce (III) to Ce (IV) giving one electron to the Fe (III) and reducing it at Fe (II). Also we found some anomalies with europium (Eu) in the Goethite results. The results revealed too that in pH 4,5,6 the Light REEs were easily more absorbed than the Heavy REEs. Finally, due the situation, we couldn't use the Ultraviolet-visible spectroscopy to find the Fe (II) / Fe (III) ratio in the final solution.

2. INTRODUCTION

Rare earth elements (REE) is a group of seventeen chemical elements, metals, with close properties including the scandium (Sc) and yttrium (Y) of group 3 of the periodic table (Figure 1) and the fifteen elements of the lanthanide series (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu).

These elements are usually classified into two categories: light rare earth elements (LREE) and heavy rare earth elements (HREE). The definition of the two groups is according to the electron configuration of each rare earth element:

- Light rare earth elements: lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd).
- Heavy rare earth elements: terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), lutetium (Lu), scandium (Sc), yttrium (Y).

Periodic table of the elements

group 1* 2 13 14 15 16 17 18

period 1 2 3 4 5 6 7

lanthanoid series 6

actinoid series 7

58 59 60 61 62 63 64 65 66 67 68 69 70 71
Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

90 91 92 93 94 95 96 97 98 99 100 101 102 103
Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr

*Numbering system adopted by the International Union of Pure and Applied Chemistry (IUPAC). © Encyclopædia Britannica, Inc.

Figure 1: Periodic table of the elements.

These elements are present in the Earth's crust and cerium is the most abundant of the lanthanides being the 25th most abundant element at 68 mg/kg. They are in a dispersed way and not often found concentrated in rare-earth minerals (Figure 2).

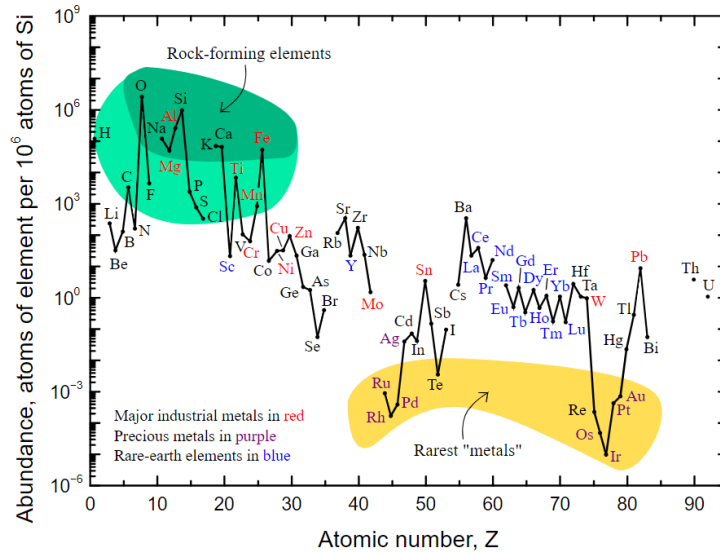


Figure 2: Abundance of elements in Earth's crust per million Si atoms (y axis is logarithmic). ("Rare Earth Elements—Critical Resources for High Technology | USGS Fact Sheet 087-02," n.d.)

The total REE concentrations represent 0.022% of the elemental total budget of Earth's upper crust (Figure 3). Despite their low participation in total budget of Earth's upper crust, the REEs are one of modern-day societies most critical commodities. They are fundamental to today's world economy and with a global shift towards establishing clean and green energy sources, the demand for REEs will only continue to increase.

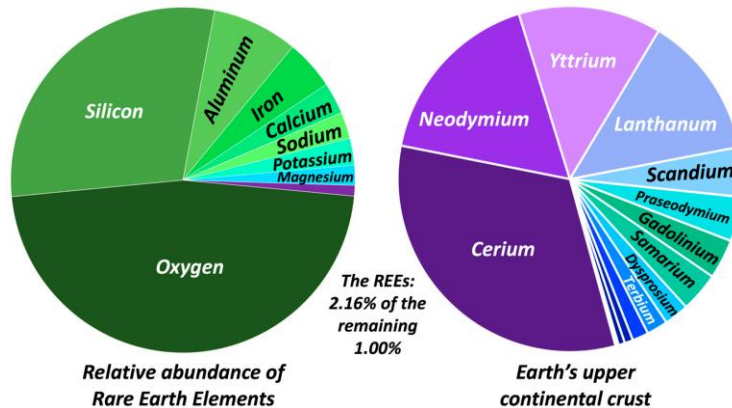


Figure 3: Summary of Earth's upper crustal element budget Silicon and O account for 76%, with Al at 8%, total alkalis (Na, Ca, K) at 8%, and Fe and Mg contributing 6.5% combined. From the remaining 1% (these elements are often referred to as trace elements), the REEs contribute 2.16% with Ce, Nd, Y, and La the most abundant at 32%, 17%, and 13% (Y and La) respectively of the total REE budget. Yb, Ho, Eu, Er, Tm, and Lu collectively comprise 3.2% of the REE budget..

From few years, with advances in new technologies, we are now able to extract them more easily and cheaply. Therefore, the mining production of this elements was multiplied by 2 in the last 15 years starting from 105000 tones/year in 2005 and going to 210000 tones/year in 2019. (Figure 55). In 2019, China was the main producer/extractor of the REEs, following by Australia, Burma and USA (Figure 4).

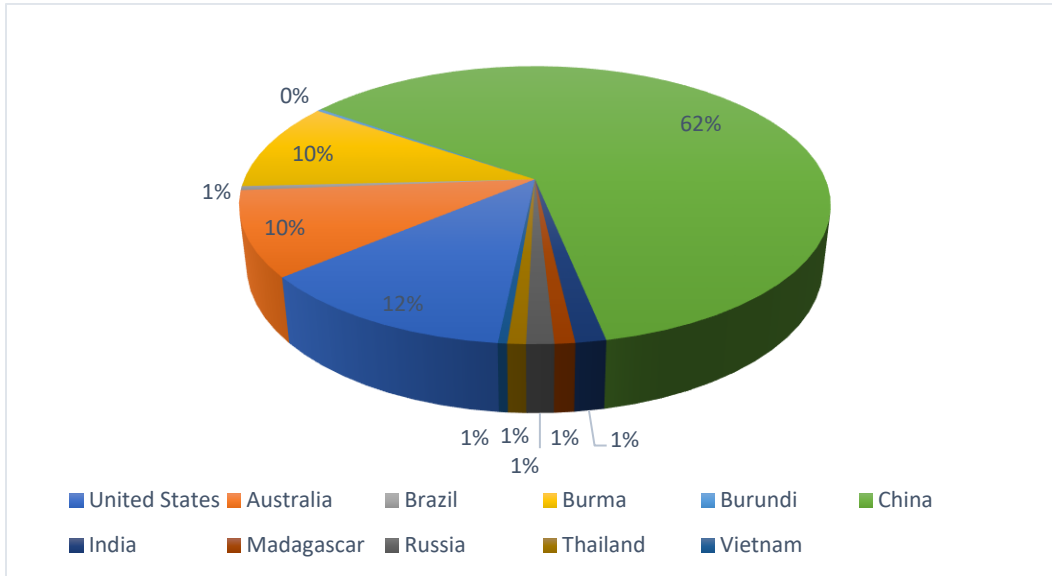


Figure 4: World Mine production of REEs by countries in 2019 according to the U.S. Geological Survey.

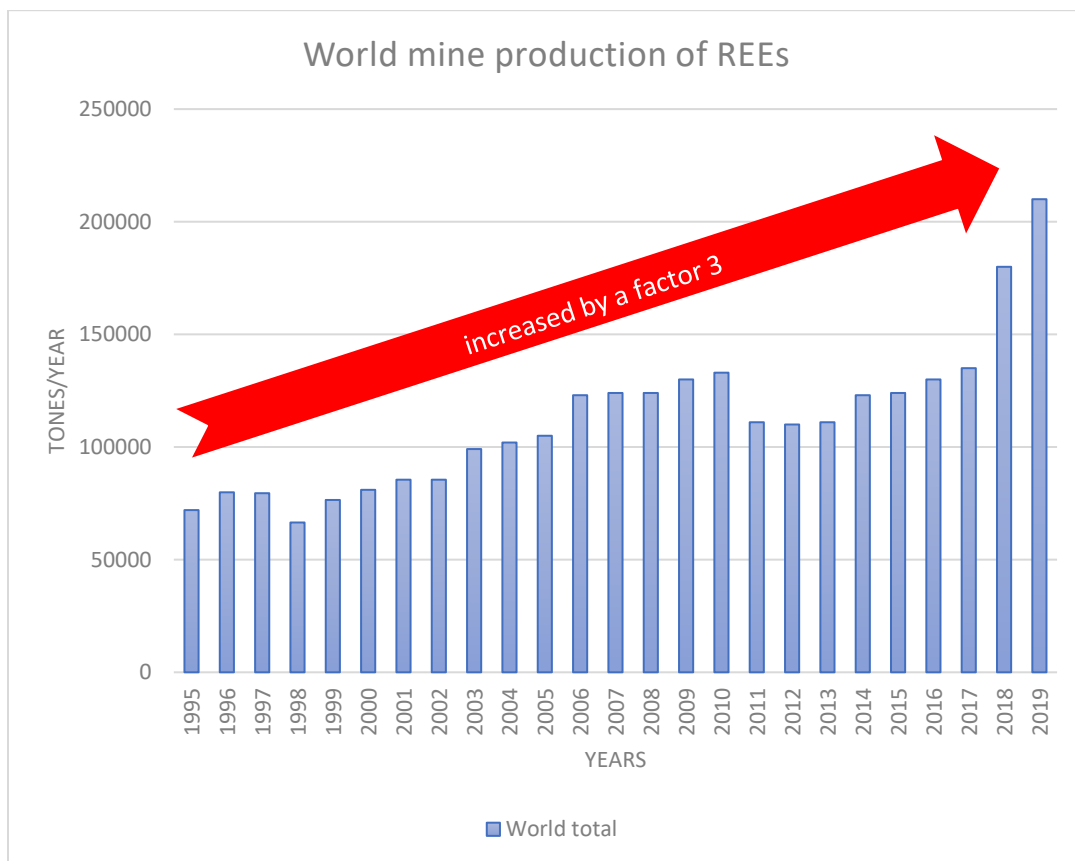


Figure 5: World mine production of REEs according to the U.S. Geological Survey.

The REEs are widely used elements for different fields within new technologies as they have very good properties. Light REEs (LREEs) such as Ce show a strong affinity for elements like phosphorus, making them suitable as water purifiers, while La acts as a hydrogen absorber in rechargeable

batteries. In addition, both of these elements act as stabilizers in catalytic compounds, such as in the process of transforming oil to gasoline. Cerium is also present in catalytic converters in automobiles, sometimes up to 30 wt%. Lanthanum is an important element in hybrid car batteries; each Prius on the road contains about 4.5 kilograms (Koerth-Baker, 2012).

One of the main fields are chemical catalysis, glasses, glass polishing, metallurgy etc... (Figure 66). They can be substituted for other substances in their main uses. REEs such as Eu, Y, and Tb are used to produce more energy-efficient phosphors than halo-phosphors, which are composed of Sb and Mn, in the displays for computers and phones, as well as in compact fluorescent lamps (Tiesman, 2010). However, these substitutes are usually less effective and costly.

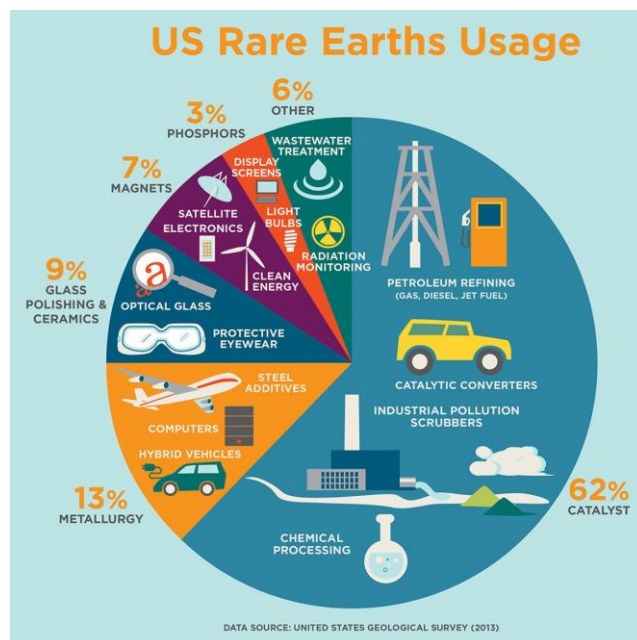


Figure 6: Use of Rare Earth Elements according to US Geological Survey (2013).

Nowadays, REEs usage has been increased by the use of new technologies. That means that it increases the potential release of REEs in the environment and thus in the soil system due to the wastes. Then, they interact with the soil phases, i.e., mainly Fe oxyhydroxides, Mn oxides, clay minerals and organic matter. Their behaviour is driven by the biogeochemical processes and are still few studied. The better understanding of their mobility is crucial to prevent environmental issues.

In the past, experiments were done to understand a little bit more the REEs behaviour. Atsuyuki Ohta and Iwao Kawabe worked in the REEs kinetic adsorption onto Mn dioxide and Fe oxyhydroxide overtime. They found an interesting thing that the Light REEs were easily adsorbed that the others in low pH. Between the Mn oxide and Fe oxide experiment they didn't find a significant systematic difference of REE partitioning coefficients. This result possibly indicates that the coordination states of REEs coprecipitated with Fe oxyhydroxide, are not different from those of REEs adsorbed onto it. They also realised that in low pH not all the REEs evolve the same. (Atsuyuki and Iwao, 2000).

The main objective of this project is to analyse the behaviour of REEs in contact with Fe oxides to better understand their mobility in the soil in different environmental conditions (pH, REEs concentration...).

To achieve what we want, we will be setting the internship in two main steps:

(1) Analytical aspect:

Analysis of different solutions at different concentration with the Inductively coupled plasma mass spectrometer (ICP-MS) to obtain accurate results with the calibration curve.

Reduction of the mass interferences caused by the formation of oxides during the ionization.

(2) Experiments:

Conduct REEs sorption experiments with different iron oxides, pH, concentration...

Determination of the chemical composition in solution by ICP MS.

3. MATERIALS AND METHODS:

3.1. Iron oxyhydroxides:

Iron oxides, oxyhydroxides and hydroxides are widely distributed in soils, rocks, lakes, rivers, on the seafloor, air and in organisms). Due to their abundance and reactivity, these minerals play an important role and are extensively studied in numerous disciplines, such as environmental science, geochemistry, geology, engineering and health sciences, in an attempt to understand their different physical, chemical and mineralogical properties (Adegoke et al., 2013).

Iron oxyhydroxides, such as goethite and ferrihydrite, are highly abundant in geochemical environments. Because of their small particle sizes, their surface reactivity is high towards adsorption of anions and cations of environmental relevance. For this reason these minerals are extensively studied in environmental geochemistry, and also are very important for environmental and industrial applications. (Villacís García et al., 2015)

There are different types of iron oxides that have been characterized (Figure 7), for example iron (III) oxide (Fe_2O_3), Fe(II)-deficient magnetite (Fe_2O_3 , $\gamma\text{-Fe}_2\text{O}_3$) and ferrous-ferric oxide (Fe_3O_4). In order to perform our study, we will work on two different Fe oxides (Ferrihydrite and Goethite).

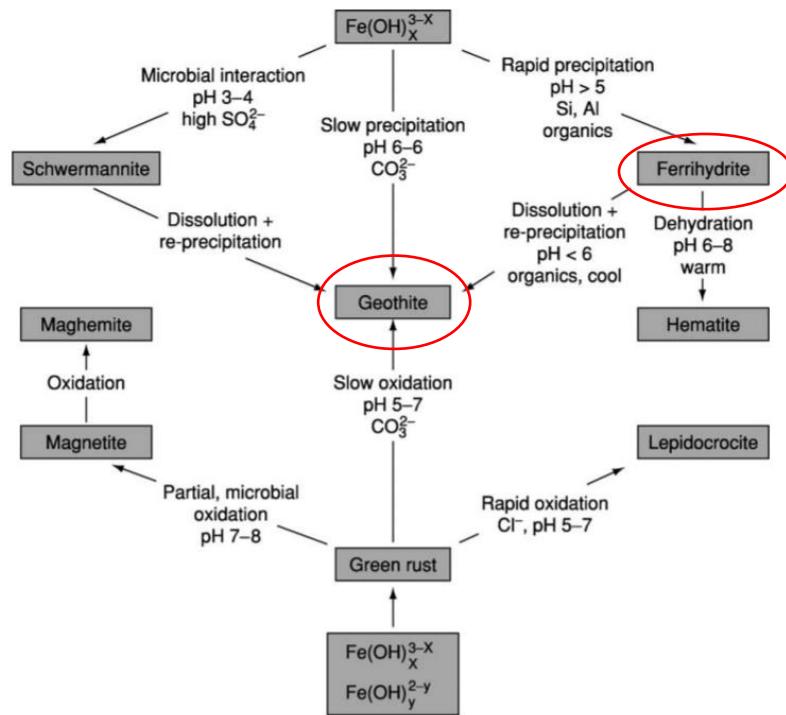


Figure 7: Schematic formation and transformation pathways of common Fe oxides in soils. The precipitation of Fe oxide minerals. (Scheinost, 2005).

3.1.1. Ferrihydrite:

The Ferrihydrite (Fh) that we are using in this analysis is grown in the nature so may contain some impurities such as metal contents or crystallin structures. The specific colour of Fh is dark red-brown.

Ferrihydrite is an amorphous iron oxide with a high absorption capacity due to (i) its small size of the individual nanocrystals and (ii) its amorphous structure (Figure 8).

In addition to having a large surface / volume ratio, Fh also has a high density of local or point defects, such as vacancies. These properties confer a high capacity to absorb many environmentally important chemical species, such as metals, REEs, and organic compounds.

Its strong and extensive interaction with metals is used in industry, on a large scale in water purification plants, such as in northern Germany and to produce city water in Hiroshima, and on a small scale to clean wastewater and groundwater, for example to remove arsenic from industrial effluents and drinking water (R. M. Cornell R.M., U. Schwertammn, Wiley-VCH, Weinheim, Germany (2003)).

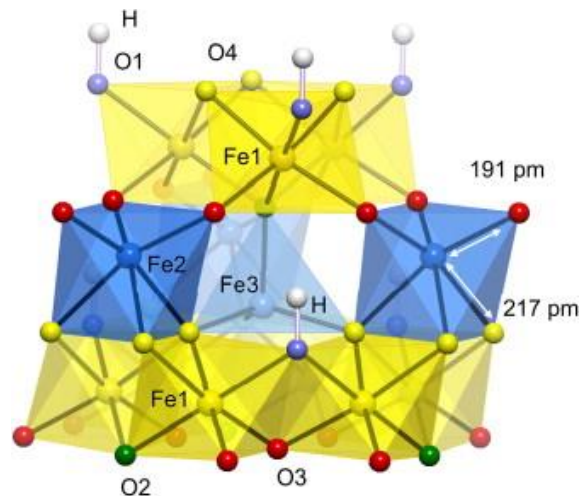


Figure 8: Ferrihydrite chemical structure (Hiemstra, 2013)

3.1.2. Goethite:

The $\text{FeO}(\text{OH})$ is a crystalline iron oxide with a yellowish-brown colour. Goethite often forms through the transformation of other iron-rich (Figure 9).

The formation of goethite is marked by the oxidation state change of Fe (II) (ferrous) to Fe (III) (ferric), which allows for goethite to exist at surface conditions (Suzuki, Akio, 2010). Goethite formation is favoured by slow hydrolysis of Fe (III) hydroxy cations at low temperature. The even distribution of goethite in a soil horizon indicates therefore that this soil has formed under aerated, temperate, humid conditions.

The crystal structure of goethite consists of double chains of edge-shared octahedra that are joined to other double chains by sharing corners and by hydrogen bonds (Figure 9)

It may also be precipitated by groundwater or in other sedimentary conditions, or form as a primary mineral in hydrothermal deposits. Goethite has also been found to be produced by the excretion processes of certain bacteria types.

Goethite is, in varying proportions, virtually ubiquitous in soils, to which, in the absence of hematite, it imparts the typical brown colour developed in moist temperate regions. Hematite usually coexists with goethite, but, due to its greater tinting strength, masks the yellowish colour of goethite even at low concentrations.

Among other commercial uses the production of magnetic recording media deserves special mention, goethite being the starting product for the industrial production of maghemite. (Murad E., Cashion J., 2004)

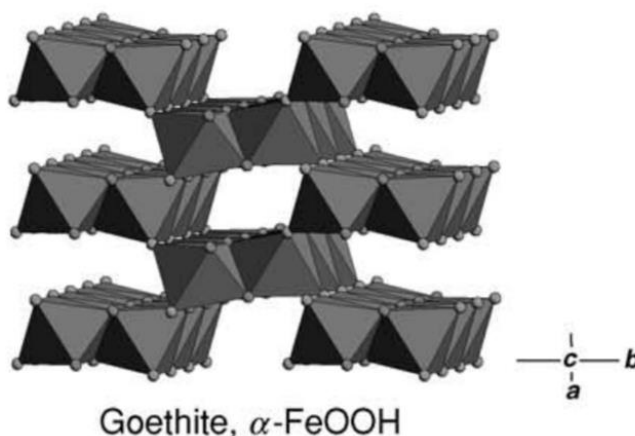


Figure 9: Goethite crystalline structure. (Scheinost, 2005)

3.2. Sorption experiment:

3.2.1. Preparation of the different reactants:

The batch experiments are conducted in 50 mL tubes.

We calculated the volume needed to analyse the samples in both devices (the ICP MS and UV vis, discussed later in the section 2.4). We required a volume of 15 ml (we overcalculated the amount in case of problems) of final sample for each of them, which mean a volume of 30 ml for each of the initial samples.

We set a value of 20 mg for each sample of iron oxide.

First, as we have a standard solution of 50 mg/L REEs (Sigma Aldrich), we need to dilute it in order to be able to grab a reasonable volume to get the concentration we want. To do this, we will prepare a solution A of 100ml of 1 mg/L concentration of REEs from the following equation:

$$V_{STD} = \frac{V_A \times C_A}{C_{STD}} = \frac{100 \text{ ml} \times 1 \text{ mg/L}}{50 \text{ mg/L}} = 2 \text{ ml}$$

As we can see on the equation, we must collect 2 ml from the initial sample of REEs of 50mg/L in a total volume of 100 mL to obtain the solution A.

Then, we can calculate the volume from the solution A that we need to add to each batch sample. The desired concentration of REEs in solution were set at 50 μ g/L with a volume of 30 mL.

$$V_2 = \frac{V_1 \times C_1}{C_2} = \frac{30 \text{ ml} \times 0,050 \text{ mg/L}}{1 \text{ mg/L}} = 1,5 \text{ ml}$$

Therefore, we need to add 1.5 ml from the solution A to each batch sample in order to obtain the desired concentration. Referring to the ICP MS, it allows us to analyse samples with low concentrations. That is why our samples will have a concentration of REEs ranging from 0 to 50 μ g/L.

Moreover, to stabilize the reaction between the different Fe oxides and the REEs we need an electrolyte. We will use NaCl to impose the ionic strength at 0.005 mol L⁻¹. To do this, we will perform the following calculation:

$$30 \text{ ml solution} \times \frac{0,005 \text{ mol NaCl}}{1000 \text{ ml}} \times \frac{58,44 \text{ g}}{1 \text{ mol NaCl}} \times \frac{1000 \text{ mg}}{1 \text{ g}} = 8,76 \text{ mg NaCl}$$

8,76 mg of NaCl were added in each batch samples.

The solid component amount and the volume of solutions for a batch samples are exhibiting in the Table 1.

Table 1: Different components and solution to mix to prepare the samples:

COMPONENTS AND SOLUTION TO MIX		
Iron oxide	20	mg
Solution A of 0,05mg/L of REEs	1,5	ml
NaCl (s)	8,76	mg
distilled water	28,5	ml

3.3. Batch experiments:

The batch experiments were conducted for goethite and ferrihydrite at five different pH: 3, 4, 5, 6 7. Each batch is prepared in 3 replicates as well as one blank for each pH. Therefore, we must prepare 15 samples and 5 blanks for the two iron oxides (Table 2).

A blank is a sample that contains all the components except the REE solution and has been subjected to all the operations of the analytical procedure. If the blank gives signals that contains REEs, it means that the reagents may contain some traces of analyte or that we could have interferences from other species than the analyte or contamination. The blank signal must be subtracted from the response of a real sample before calculating the amount of analyte in the sample.

Table 2: Initial concentration of REEs in the batch experiments prepared for ferrihydrite and goethite at 5 different pH. This concentration has been recalculated after the volume addition of nitric acid or hydroxide sodium to maintain the pH over time.

Ferrihydrite	CONCENCENTRATION OF REEs (µg/L)	Goethite	CONCENCENTRATION OF REEs (µg/L)
pH 7_1 Fh	49,59	pH 7_4 Go	49,84
pH 7_2 Fh	49,67	pH 7_5 Go	49,88
pH 7_3 Fh	49,67	pH 7_6 Go	49,89
pH 6_1 Fh	49,64	pH 6_4 Go	49,80
pH 6_2 Fh	49,29	pH 6_5 Go	49,71
pH 6_3 Fh	49,26	pH 6_6 Go	49,67
pH 5_1 Fh	49,68	pH 5_4 Go	49,86
pH 5_2 Fh	49,67	pH 5_5 Go	49,91
pH 5_3 Fh	49,7	pH 5_6 Go	49,94

pH 4_1 Fh	49,92	pH 4_4 Go	49,88
pH 4_2 Fh	49,92	pH 4_5 Go	49,88
pH 4_3 Fh	49,92	pH 4_6 Go	49,88
pH 3_1 Fh	49,87	pH 3_4 Go	49,98
pH 3_2 Fh	49,97	pH 3_5 Go	49,98
pH 3_3 Fh	49,97	pH 3_6 Go	49,98

The experiment consist in 6 steps:

1. For each batch sample, the pH was monitored and adjusted using pH meter and by the addition of HNO₃ solution or NaOH solution. Depending on whether we need to acidify or basify we will use the nitric acid or hydroxide sodium. We will consider the added volume in order to reach the pH to be more accurate with the final calculations/concentrations. In order to add the acid and the base, we will use a pipette with a range of 10-100 µL.
2. Control of the pH during 36 hours. Once we have all the samples at the desired pH, we let them sit in the automatic shaker (Figure 10). We will have to check the evolution of the pH of the solution until it stabilizes at the pH we want. If it is necessary to add more acid or base again, we must take into account the volume added.



Figure 10: Laboratory shaker with Ferrihydrate samples on the right and Goethite samples on the left

3. Centrifugation of the samples. After about 36 hours, once we have the pH stabilized, we proceed to the centrifugation of the samples at 5000 rpm during 10 mins in order to separate the mixture into two visible phases: solid fraction and solution (Figure 11 11).



Figure 11: Ferrihydrite sample after centrifugation

4. Filtration of the sample with a 25 μ m diameter microfilter to separate the liquid phase from the solid phase. Here, we will focus only on the chemical composition of the solution.
5. Separation of the liquid phase in two fractions to determine (i) the REE chemical composition in solution using ICP-MS and (ii) the Fe (II) concentration in solution by UV-vis spectrometer (not conducted during my internship).

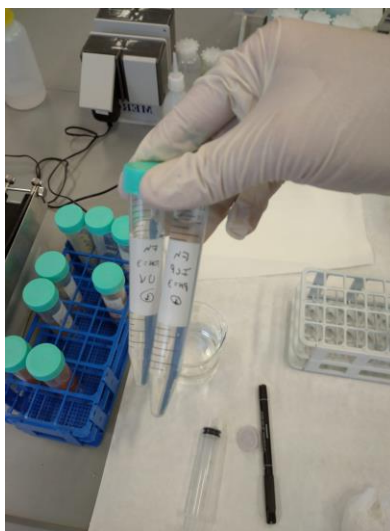


Figure 12: Solution sample after filtration: ready for analyse by ICP MS.

6. Addition of HNO₃ before analysing the samples by ICP-MS. We need to add 20 μ L of HNO₃ (65%) in order to maintain an acidic environment in all samples, in this way we avoid the formation of precipitations substances that may cause errors in the sample analysis.

3.4. Chemical analysis: ICP-MS

3.4.1. Principe:

Inductively coupled plasma mass spectrometry (ICP-MS) is an elemental analysis device capable of detecting most of the periodic table of elements at low concentrations (from mg/L to ng/L). It is used in a variety of industries such as environmental monitoring, geochemical analysis, metallurgy, pharmaceutical analysis, and clinical research.

The sample we want to analyse is loaded through a capillary to the plasma where it ionizes the atomic elements. It atomizes the sample and creates atomic and small polyatomic ions, which are then detected and quantified according to their mass (Figure 13).

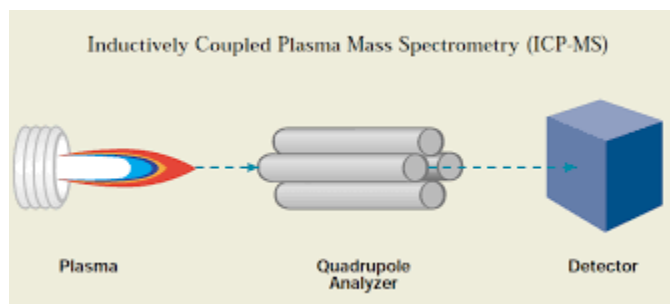


Figure 13: Scheme of the operation of an ICP-MS.

3.4.2. REEs Interferences:

In the case of the REE measurement, mass interferences are the main issues. The method of analysis for REEs must be configured in advance to avoid these mass interferences corresponding to the formation of oxides during the ionization into the plasma (example ^{169}Tm and $^{153}\text{Eu}^{16}\text{O}$). The interferences may be caused by polyatomic ions having the same nominal mass as the analyte, signal or signal suppression. (Barberá et al., 2003)

In order to work with more accurate values, we must work with an oxide formation of less than 2% to consider it as negligible. An uranium (U) and cerium (Ce) standard solutions are used to calibrate the oxide formation into the plasma. That way, we can neglect the formation of oxides and also have an accurate value from the ICP MS.

Standard solutions were prepared with REEs concentrations ranging from 5 to 50 $\mu\text{g/L}$ in order to generate the calibration curve following a linear regression. This will allow us to know exactly the REE concentration of our samples by comparing the ICP-MS intensity results.

3.5. Characterization of the iron oxides: X-ray diffraction

The experiment is designed to observe the behaviour of REEs onto ferrihydrite and. In order to provide robust results, we have to confirm by X-ray diffraction (XRD) that these samples are sufficiently pure and not modified over time.

The X-ray diffractometers are composed of three basic elements: an X-ray tube, a sample carrier and an X-ray detector. X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating electrons to a target by applying voltage, and bombarding the target material with electrons. When the electrons have enough energy to dislodge interior electrons from the target material, characteristic X-ray spectra occur. (Barbara L Dutrow, Louisiana State University, Christine M. Clark, Eastern Michigan University.)

Following the **Bragg's Law**, there is a definite relationship between the angle at which a beam of X rays must fall on the parallel planes of atoms in a crystal in order that there be strong reflection, the wavelength of the X rays, and the distance between the crystal planes : $\sin \Theta = \frac{n\lambda}{2d}$ where Θ is the angle between the incident or the reflected beam and the crystal plane, λ is the X-ray wavelength, d is the crystal plane separation, and n is any integer (Figure 14).

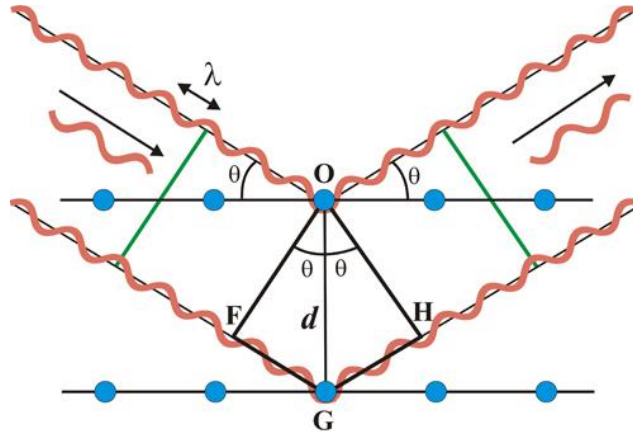


Figure 14: Scattering and Diffraction (Bragg's Law).

To analyse our results, we use a software that contains all the diffractogram (X-ray spectra) of all the known minerals. By comparing our diffractograms with the software we can qualify how pure is it. In this way, we can see the similarity between the spectra and decide which mineral we are talking about.

4. RESULTS AND DISCUSSIONS:

4.1. XRD results:

As we can see in the Figure 15 the diffractogram of the Fh has waves and some pics. The waves from the spectre are characteristic of an amorphous structure, but the defined peak belong to crystalline structures. So, as we can see, if our mineral was pure, the diffractogram should contain only waves. Therefore, the diffractogram is showing us that the sample is not 100% ferrihydrite but some crystalline structures as goethite or lepidocrocite. However, we cannot quantify, but we know that we have some traces of others ferric oxides here. One of the main reasons of that is due to the Fh natural growing conditions. That may cause Fh transformation to other crystallin FeO(OH).

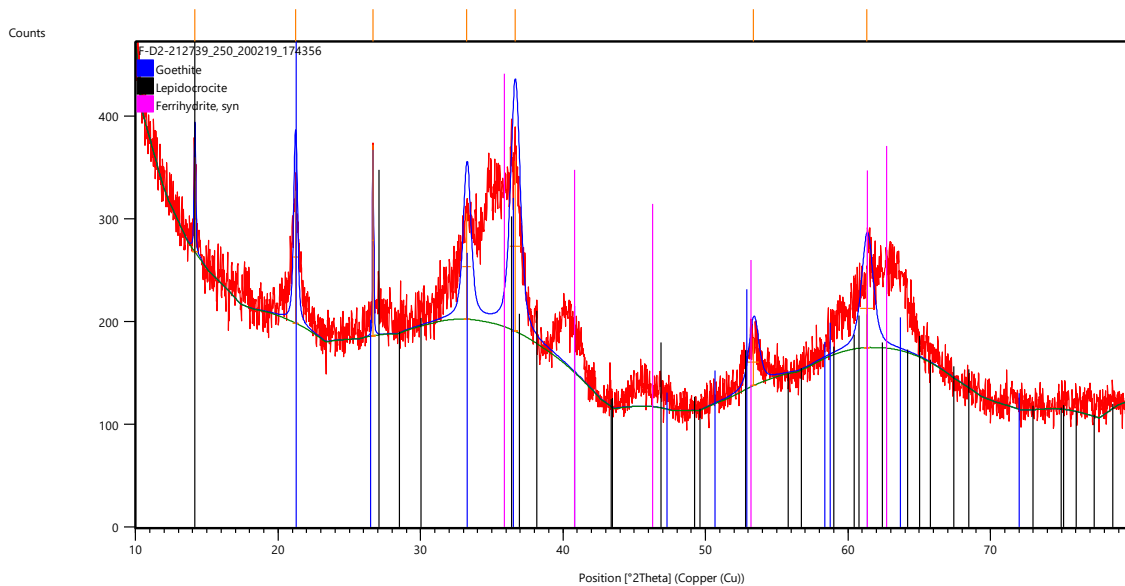


Figure 15: Diffractogram of the Ferrihydrate material/sample

In the Figure 1616 and Figure 1717 we have peaks due to the crystalline spectres of the Goethite and Hematite. If we compare our diffractograms with the reference diffractogram (software base) we can see that the peaks are the same.

Initially we expected to work with the three Fe oxides, Hematite, Goethite and Fh, but because of the situation we could only get results of Fh and Goethite. Another part of the experiment that we were unable to do was to work with different REE concentration and work on the kinetic experiments to see the evolution of the sorption overtime.

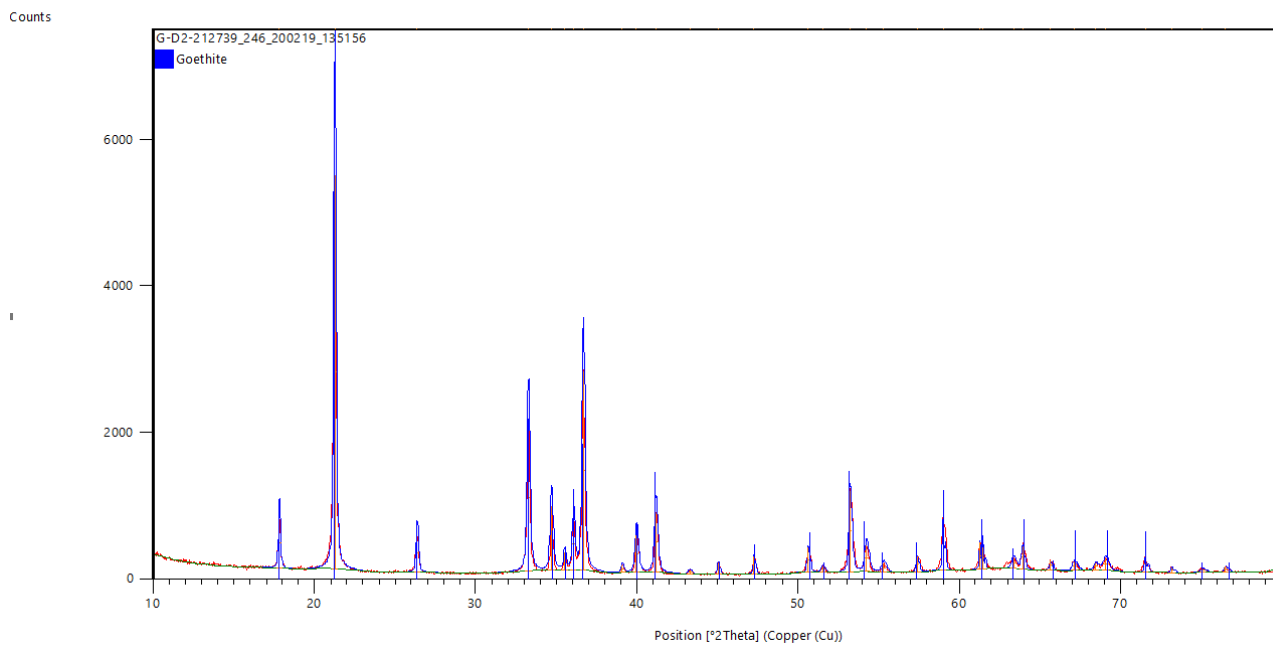


Figure 16: Diffractogram of the goethite material/sample.

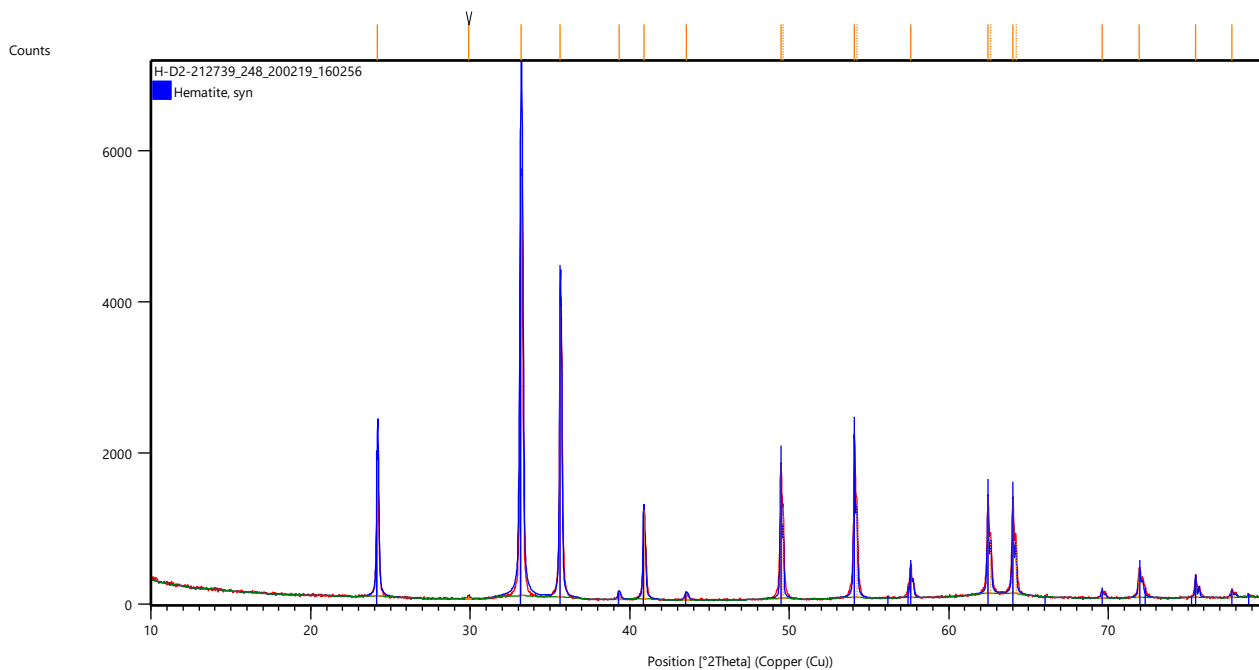


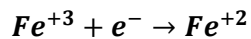
Figure 17: Diffractogram of the hemathite material/sample

4.2. Sorption of REEs onto Fe oxides:

- The Figure 18 represents the REEs concentrations in the solution after the batch experiments conducted for Fh.
- Description of the REE pattern according to the pH variations:
The REEs concentrations in solution decrease with the pH increasing. At high pH (pH 7), almost 100% of REEs are adsorbed to the ferrihydrite. At low pH, sorption sites are protonated but if you increase the pH, the sorption sites are deprotonated and disponible for REEs in solution. According to the equation ($\text{pH} = -\log [\text{H}^+]$) we know that acidic pH has a higher concentration of protons than at high pH (basic). These protons interact with the surface of iron oxides, affecting the percentage of oxidized REEs and subsequently reducing iron.
- Description of the REE pattern trend for the different pH:
At pH 4 and 5, the general trend of the REE pattern shows that HREE are more adsorbed than LREE. At pH 7, a positive Ce anomaly is observed in solution. As we know, elements such as cerium (Ce) that are tetravalent are in the Ce (III) state and when absorbed by the iron oxide they oxidize to Ce (IV). In this way, they yield an electron that will capture the iron and cause it to reduce to Fe (II).



Eq. 1: Cerium oxidation



Eq. 2: Iron reduction

Therefore, the more protons there are on the adsorbed surface, the more saturated the iron molecule will be and the less REEs it can capture. That's why in the Figure 2018, we can see how in the basic pH's the concentration of REEs in solution is lower than acid pH's.

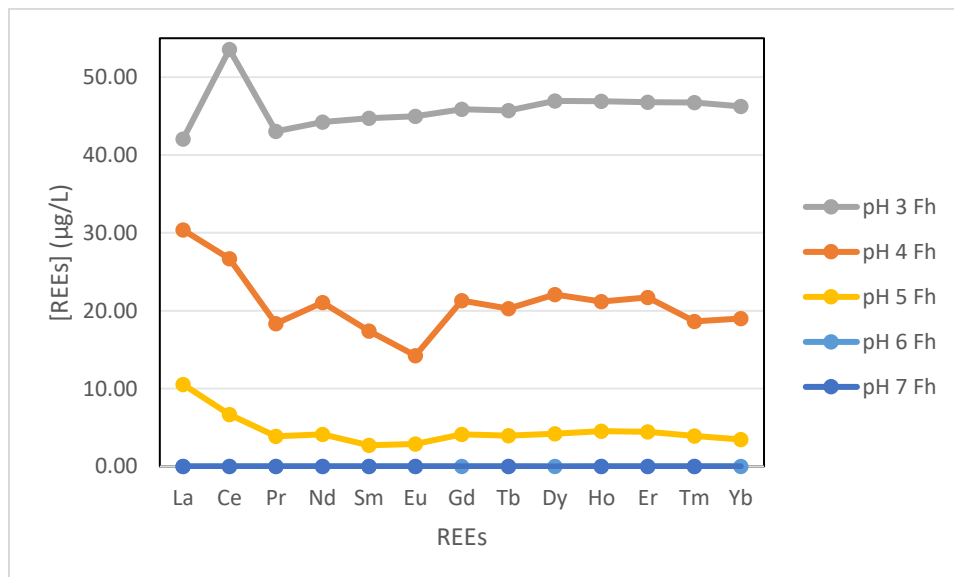


Figure 18: Results of the [REEs] onto Fh by the ICP MS at the different pH's.

- The Figure 19 represents the REEs concentrations in the solution after the batch experiments conducted for Goethite.
- Description of the REE pattern according to the pH variations:
The REEs concentration in solution follows the same pattern as it happens with the Fh. At pH 4 and 5, the concentrations are barely the same. That could be due to an error in the pH monitoring step during the experiment.
- Description of the REE pattern trend for the different pH:
At pH 4, a negative Eu anomaly is observed in solution. I don't know which could be the reason of that.

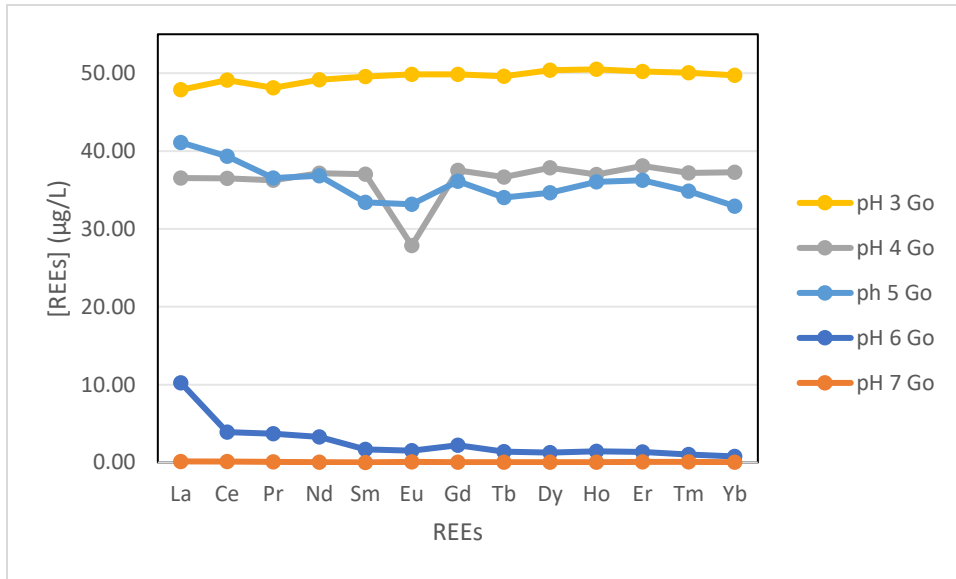


Figure 19: Results of the [REEs] onto Goethite by the ICP MS at the different pH's

Comparing Figure 18 and Figure 19, we can assume that Fh has better sorption trend than Goethite due to the results of the REEs concentration in solution at pH 4 and 5. At high pH's the sorption of the REEs onto this Fe oxides are barely the same, as it is with the pH 3.

In order compare our results with other studies, we will normalise them by the mass of the Fe oxides. We will use the distribution coefficient of REE, $K_d[REE]$, between the solid and solution. The $K_d(REEs)$ is a way to normalize the data with the published data to normalize with the mass of Fe oxides that we used and the volume of the solution.

To define this coefficient we will use the following equation:

$$K_d (REE) = \frac{[REE]_{init} - [REE]_{fil}}{c[REE]_{fil}} \left(\frac{mL}{g} \right)$$

where $[REE]_{fil}$ is the concentration of REEs in the filtrate, while $[REE]_{init}$ is the initial concentration of each dissolved REE. The term c (g/mL) is the ratio of solid to solution. Therefore, the term c is $20 \text{ mg}/30 \text{ mL} = 6,667 \times 10^{-4} \text{ (g/mL)}$. (Tanaka et al., 2010).

If we take a look at the results (Table 3 Table 3 Distribution coefficient of concentration, K_d (REE), between the solid and solution:) we can see that some REEs weren't detected by the ICP MS (pH 6 Fh) so we had to remove it from the analysis. In order to graph the results obtained we used the $\log K_d$ [REEs].

The Figure 20 and Figure 21 represents the concentration of the REEs in solution in the K_d factor onto both Fe oxides. Comparing to other experiments where they realised that they had positive anomalies with the Ce, we only found that in the pH 3 Ferrihydrite. Once again, the graph shows us that the Fh has absorbed more REEs than the Goethite.

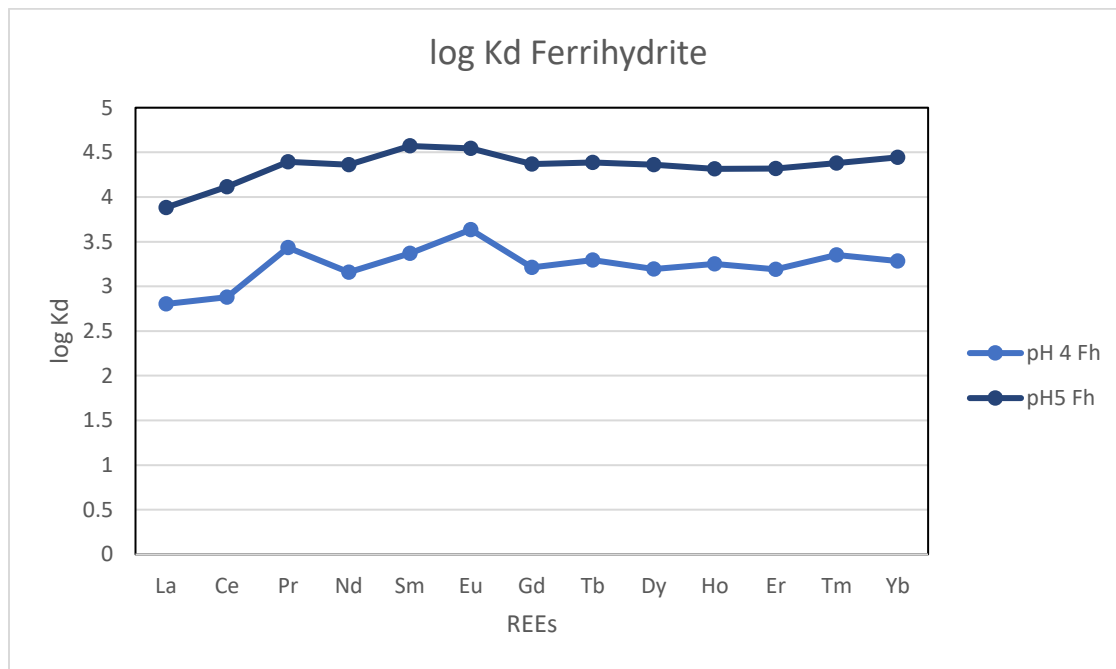


Figure 20: Sorption of the REEs onto Ferrihydrite at different pH's

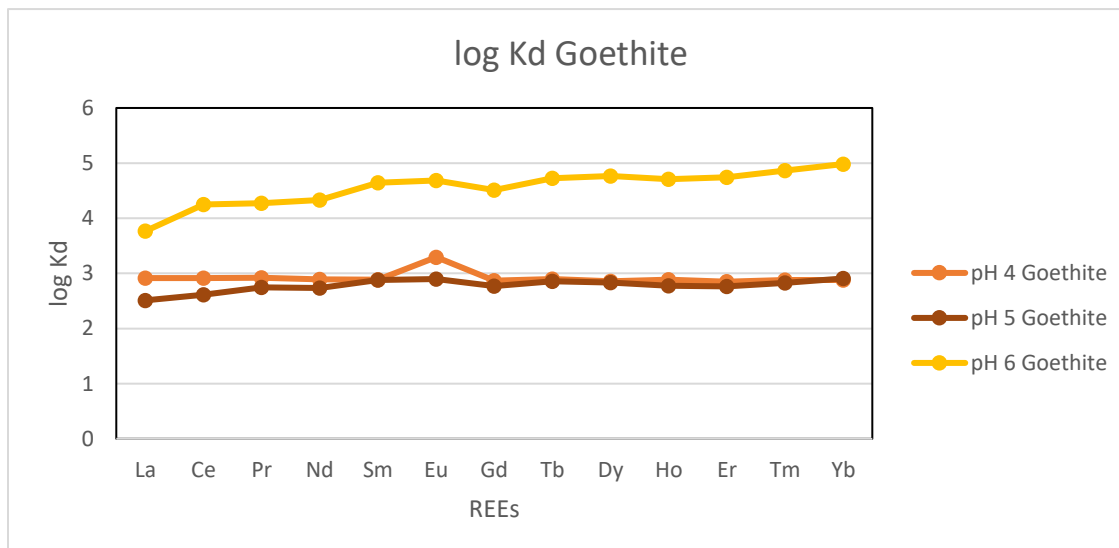


Figure 21: Sorption of the REEs onto Goethite at different pH's

As we have seen in previous results, the sorption of several REEs induces a reduction of Fe (III) as Fe (II) in solution by REEs oxidation onto the Fe oxides surface. It could be interesting to find the ratio of Fe (II) / Fe (III) with the help of the UV-vis spectrometer. The determination of Fe (II) in solution will give us some clues to identify redox processes during the REEs sorption onto Fe oxides.

Table 3 Distribution coefficient of concentration, Kd (REE), between the solid and solution:

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
Kd	mL/g	mL/g	mL/g	mL/g	mL/g	mL/g	mL/g	mL/g	mL/g	mL/g	mL/g	mL/g	mL/g
pH3 Goethite	66,33	26,12	58,73	25,30	13,00	4,36	3,81	11,74					7,89
pH4 Goethite	820,90	817,92	834,21	774,27	768,49	1971,87	742,97	793,18	722,31	770,29	706,96	757,21	762,52
pH5 Goethite	324,28	409,94	558,76	543,89	759,67	784,96	586,21	722,68	685,70	595,34	581,99	672,96	808,46
pH6 Goethite	5848,91	17776,23	18841,74	21379,31	44205,97	48606,47	32561,85	53227,45	58339,90	51087,34	55047,03	73585,69	96157,19
pH7 Goethite	1423848,43	783072,02	1435505,73	1957838,94	22759707,05	811447,54	2550191,10	1842524,12	2623838,35	1964509,44	1251712,64	1454457,91	5148962,57
pH3 Fh	283,01		239,96	193,73	174,11	164,85	132,06	138,50	95,52	96,73	101,44	101,76	119,23
pH4 Fh	635,43	754,44	2713,17	1439,71	2335,26	4312,16	1632,78	1965,81	1569,08	1780,62	1551,68	2241,49	1928,23
pH5 Fh	7637,02	13012,00	24823,05	23064,39	37285,17	35111,96	23394,81	24406,08	22969,11	20637,97	20919,07	23978,93	27807,85
pH6 Fh													
pH7 Fh	1423848,43	783072,02	1435505,73	1957838,94	22759707,05	811447,54	2550191,10	1842524,12	2623838,35	1964509,44	1251712,64	1454457,91	5148962,57

Table 4: Distribution coefficient of concentration, log Kd (REE), between the solid and solution:

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
log Kd	mL/g	mL/g	mL/g	mL/g	mL/g	mL/g	mL/g	mL/g	mL/g	mL/g	mL/g	mL/g	mL/g
pH3 Goethite	1,82	1,42	1,77	1,40	1,11	0,64	0,58	1,07					0,90
pH4 Goethite	2,91	2,91	2,92	2,89	2,89	3,29	2,87	2,90	2,86	2,89	2,85	2,88	2,88
pH5 Goethite	2,51	2,61	2,75	2,74	2,88	2,89	2,77	2,86	2,84	2,77	2,76	2,83	2,91
pH6 Goethite	3,77	4,25	4,28	4,33	4,65	4,69	4,51	4,73	4,77	4,71	4,74	4,87	4,98
pH7 Goethite	6,15	5,89	6,16	6,29	7,36	5,91	6,41	6,27	6,42	6,29	6,10	6,16	6,71
pH3 Fh	2,45		2,38	2,29	2,24	2,22	2,12	2,14	1,98	1,99	2,01	2,01	2,08
pH4 Fh	2,80	2,88	3,43	3,16	3,37	3,63	3,21	3,29	3,20	3,25	3,19	3,35	3,29
pH5 Fh	3,88	4,11	4,39	4,36	4,57	4,55	4,37	4,39	4,36	4,31	4,32	4,38	4,44
pH6 Fh													
pH7 Fh	6,15	5,89	6,16	6,29	7,36	5,91	6,41	6,27	6,42	6,29	6,10	6,16	6,71

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