VANESSA DE PAULA FERREIRA

WASTEWATER TREATMENT AND RECOVERY OF URANIUM BY IRON AND ALUMINIUM (HYDR) OXIDES

Dissertação apresentada à Universidade Federal de Viçosa, como parte das exigências do Programa de Pós-graduação em Solos e Nutrição de Plantas, para obtenção do título de *Magister Scientiae*.

VIÇOSA
MINAS GERAIS – BRASIL
2017

Ficha catalográfica preparada pela Biblioteca Central da Universidade Federal de Viçosa - Câmpus Viçosa

T

F383w
2017

Ferreira, Vanessa de Paula, 1989-
Wastewater treatment and recovery of uranium by iron and aluminium (hydr)oxides / Vanessa de Paula Ferreira. – Viçosa, MG, 2017.
vi, 46f. : il. (algumas color.) ; 29 cm.

Inclui apêndice.
Orientador: Jaime Wilson Vargas de Mello.
Dissertação (mestrado) - Universidade Federal de Viçosa.
Referências bibliográficas: f.32-37.

1. Urânio. 2. Águas minerais sulfurosas. 3. Minerais de argila. I. Universidade Federal de Viçosa. Departamento de Solos. Programa de Pós-graduação em Solos e Nutrição de Plantas. II. Título.

CDD 22 ed. 669.2931

VANESSA DE PAULA FERREIRA

WASTEWATER TREATMENT AND RECOVERY OF URANIUM BY IRON AND ALUMINIUM (HYDR)OXIDES

Dissertação apresentada à Universidade Federal de Viçosa, como parte das exigências do Programa de Pós-graduação em Solos e Nutrição de Plantas, para obtenção do título de *Magister Scientiae*.

APROVADA: 31 de março de 2017.

Juscimar da Silva

Leonardus Vergutz

Walter Antônio Pereira Abrahão

Jaime Wilson Vargas de Mello
(Orientador)

AGRADECIMENTOS

Aos meus pais, Maria José e Luiz Carlos, pelo apoio e incentivo a todos meus projetos e sonhos, sempre com todo amor e carinho. À minha irmã, Bárbara, pelo carinho, sinceridade e incentivo incondicionais.

À Universidade Federal de Viçosa, pela formação, vivências e enorme aprendizado.

Ao Departamento de Solos, pelas oportunidades.

A Capes pela concessão da bolsa de mestrado, ao INCT-ACQUA pelo suporte financeiro à pesquisa, ao CDTN/CNEN pela realização das análises de Raio-X.

Ao professor Jaime Wilson Vargas de Mello, pela orientação, amizade, incentivos e confiança depositada durante todos os anos de convivência, desde a iniciação científica.

À professora Ana Cláudia Queiroz Ladeira e ao professor Dean Hesterberg, pela coorientação, o grande auxilio e interesse na pesquisa.

Aos professores Massimo Gasparon e Paulo Vasconcelos da The Universityof Queensland, Austrália e todos da Earth Science School, pela experiência, e oportunidade de desenvolver a pesquisa que instigou e direcionou a realização desse trabalho.

Aos professores do DPS pela formação, ensinamentos e atenção.

Às amigas e amigos, Isabela, Gisely, Tamilis, Júlia, Fábio, Renato, Mateus e Pedro pela ajuda no desenvolvimento do experimento e pesquisa, companheirismo, apoio e pelas importantes e enriquecedoras trocas de ideias. A todos amigos do DPS pela amizade e por tornarem a rotina mais leve e prazerosa.

Aos técnicos e funcionários do DPS, sobretudo Lu, Carol, Rose, Janilson, Zélia, Geraldo Robésio, Adriana, Júlio, Geovane, Jorge, Chico e Beto.

À Maria Lúcia de Oliveira pela correção do texto e todo carinho ao fazê-la.

A todos amigos e amigas que entenderam a falta de tempo, vibraram, torceram, apoiaram, e que tanto contribuíram para paz e tranquilidade em momentos difíceis. Em especial à Chris, Bia, Renata, Bárbara, Mariana Daniel, Camila Leite, Letícia, Camila Alvarenga e Vitória.

BIOGRAFIA

Vanessa de Paula Ferreira, filha de Maria José de Paula e Luiz Carlos Ferreira, nasceu no dia 02 de março de 1989. É natural de Belo Horizonte, Minas Gerais.

Estudou durante o ensino fundamental na escola COOPEN-BH e o ensino médio no Colégio Promove, sempre em Belo Horizonte.

Em março de 2007, ingressou no curso de Engenharia Ambiental na Universidade Federal de Viçosa. Colando grau como Engenheira Ambiental em agosto de 2014.

No Departamento de Solos, estagiou durante a graduação a partir de setembro de 2009. Em 2012, pelo programa Ciências Sem Fronteiras e o INCT-ACQUA, foi bolsista de iniciação científica internacional na The University of Queensland por um ano, de agosto de 2012 a agosto de 2013.

Em março de 2015, iniciou o curso de Mestrado no Programa de Pós-Graduação em Solos e Nutrição de Plantas, também na Universidade Federal de Viçosa.

SUMMARY

ABSTRACT

FERREIRA, Vanessa de Paula, M.Sc., Universidade Federal de Viçosa, March, 2017.**Wastewater treatment and recovery of uranium by iron and aluminium (hydr)oxides** Adviser: Jaime Wilson Vargas de Mello. Co-advisers: Ana Cláudia Queiroz Ladeira and Dean Hesterberg.

Uranium (U) mining and its enrichment process can cause environmental contamination and others problems, especially when acid mine drainage (AMD) occurs. Studies in literature demonstrates the iron (Fe) (hydr)oxides efficiency to immobilize soluble U. However, changes in redox conditions may compromise the efficiency of some minerals, since the ferric hydroxides are unstable under low redox potential (Eh). On the contrary, aluminium (Al) is stable in such environments and could enhance the stability of Fe (hydr)oxides. In this study, the soluble U immobilization was evaluated by the co-precipitation with Fe and Al (hydr)oxides in a U contaminated water. The U recovery and stability in the solid phase were also studied. Solutions of ferric and ferrous sulfate, Al sulfate and a U standard solution were mixed in different proportions in order to obtain 21 treatments, which consisted of a combination of three Fe: Almolar ratio (100:0, 80:20 and 60:40), two valence states of Fe (Fe^{2+} and Fe^{3+}) and one more treatment only with Al (Fe:Al = 0:100), in three concentrations of U(80, 40 e 20 mg L^{-1}). The synthesis lasted 84 days. The pH solution was measured and adjusted to 9 weekly, as well as the sampling of supernatant sample collections. U, Fe and Al concentrations were determined by ICP-OES. The solid phase was characterized by X-ray diffraction (XRD) and the U remobilization potential in the solid phase evaluated discrete extraction and a leaching test. Results demonstrated that all treatments were efficient to immobilize soluble U in the first 24 hours of incubation. In the end of the incubation period, treatments in the presence of Al were more efficient (more than 95%) than the ones only in the presence of Fe. Besides, treatments in the presence of Al only were not as efficient as the ones in the presence of both Al and Fe. The dominant mineralogical phases formed were magnetite and hematite, in the absence of Al and in the presence of Fe^{2+} e Fe^{3+}, respectively; goethite in the presence of Al and Fe^{2+}; ferrihydrite in the presence of Al and Fe^{3+} and gibbsite in the presence of Al and in the absence of Fe. Magnetite, hematite and gibbsite were less stable compared to goethite. Leaching test and discrete extractions procedures confirmed the need of an appropriated mine waste storage facility for the sludge produced by water treatment and a possible U recovery is also suggested, for example, to its enrichment process.

RESUMO

FERREIRA, Vanessa de Paula, M.Sc., Universidade Federal de Viçosa, março de 2017. **Tratamento de água contaminada com urânio por (hidr)óxidos de ferro e alumínio e recuperação de urânio imobilizado.** Orientador: Jaime Wilson Vargas de Mello. Coorientadores: Ana Cláudia Queiroz Ladeira e Dean Hesterberg.

As minerações de urânio (U) e seus processos de enriquecimento podem gerar grandes problemas associados à contaminação ambiental, principalmente quando é gerada drenagem ácida de mina (DAM). Trabalhos comprovam a eficiência dos (hidr)óxidos de ferro na imobilização de U solúvel. Porém, (hidr)óxidos de Fe são instáveis em condições de baixo potencial redox. O Al, ao contrário do Fe, é estável podendo aumentar a estabilidade estrutural dos (hidr)óxidos de Fe. Neste trabalho, avaliou-se a imobilização do U solúvel a partir da coprecipitação de (hidr)óxidos de Fe e Al com U. A estabilidade do U na fase sólida também foi testada. Soluções de sulfato ferroso, sulfato férrico, sulfato de alumínio e solução padrão de U de 10000 mg L^{-1} foram misturadas em diferentes proporções obtendo 21 tratamentos constituídos por combinações de três relações Fe:Al (100:0; 80:20 e 60:40), dois estados de valência de Fe (Fe^{2+} e Fe^{3+}) e mais um tratamento apenas com Al (relação Fe:Al: 0:100), em três concentrações de U (80, 40 e 20 mg L^{-1}). O período experimental foi de 84 dias. O pH do sobrenadante foi aferido semanalmente e quando necessário, ajustado para 9. Além disso, foram coletadas alíquotas para determinação da concentração de U solúvel, por ICP-OES. O resíduo do tratamento de água do foi submetido à caracterização por difratometria de raios X (DRX). O potencial de remobilização do U presente no resíduo foi avaliado por quatro diferentes extrações discretas e pelo teste de lixiviação. Todos os tratamentos se mostraram extremamente eficientes nas primeiras 24h de incubação, porém ao final do período de incubação tratamentos na presença de Al foram mais eficientes em imobilizar U solúvel (eficiência maior que 95%) do que tratamentos apenas na presença de Fe. No entanto, tratamentos apenas com Al não se mostraram tão eficientes. As fases mineralógicas predominantes formadas foram magnetita e hematita, na ausência de Al e presença de Fe^{2+} e Fe^{3+}, respectivamente; goethita na presença de Al e Fe^{2+}; ferridrita na presença de Al e Fe^{3+} e gibbsita na presença de Al e ausência de Fe. Urânio foi facilmente remobilizado nos tratamentos com magnetita, hematita e gibbsita, sendo que a goethita mostrou-se mais estável. O teste de lixiviação e as extrações discretas confirmam a necessidade de um local adequado para disposição da lama gerada e também sugere uma possível recuperação de U para fins comerciais, por exemplo.

1. Introduction

The mining activities play an important role in the social and economic scenario worldwide. In addition to thermoelectric and hydroelectric, the nuclear energy is part of the energetic matrix in many countries and uranium (U) mining is essential for this energy production. In Brazil, such activities are growing and U mining is responsible for 5.3% of total world's uranium (Portal Brasil, 2016). The national reserves were estimated in 309,200 t and the exploitation of U tends to increase. For instance, in the end of 2016, operations of a new Uranium mine started in the city of Caetité, located in Bahia State (INB, 2016).

The waste generated during the exploitation and processing of U ore represents a potential pollution risk to the soil, water and sediment. Uranium production plants can generate a large amount of waste for they generally exceed the volume of the mined ore. Even when the U concentration in the waste piles is not economically or technically viable for exploitation, it may be enough to pollute groundwater and expose the nearby environment and communities to contamination (Fernandes, 2008). The health problems related to U contamination can be due to radiological effects. However, in most cases, chemical effects may cause renal and respiratory problems.

An appropriate mine waste management is essential to avoid contamination, especially if sulfide minerals are exposed to atmosphere. When in contact to atmosphere and rainwater, the weathering of those minerals generates acid mine drainage (AMD) (Ladeira&Gonçalves, 2007). As a consequence, solubilization of metals, metalloids, rare earth elements and radionuclides, such as uranium occurs (Ladeira&Gonçalves, 2007), which can negatively affect water sources as well as human health. Therefore, a suitable wastewater treatment is required.

Immobilization of soluble U by co-precipitation or adsorption by iron and, to a certain extent by aluminium (hydr)oxides is a well known practice and it has been widely indicated to treat contaminated water due to its low cost and high efficiency. Nevertheless, the recovery of U from minerals formed is not explored enough, even though this practice demonstrates to be sustainable and economically viable. Uranium, which is a pollutant, can now be processed as it is an ore.

In view of the above, the present work aims to investigate and test the immobilization of soluble U in AMD effluents by co-precipitation with Fe and Al (hydr)oxides. Moreover, studying a possible way to retrieve the immobilized U from the solids is another important point of this research since it is economically interesting and it may also reduce the need for strategic disposal facilities for keeping products resulting from contaminated water treatment.

2. Literature review

Uranium (U), atomic number 92, is a radionuclide and a heavy metal belonging to the actinide family. It is less hard than steel and more abundant than silver, gold and some rare-earth elements. Moreover, U is found in the rocks of the earth's crust in its natural state, average content of 3 mg kg^{-1} (Meinrath, Schneider &Meinrath 2003). In the soil, it is found in amorphous Si, Fe and Al oxides (Allard et al., 1999). Industrially, Uranium is mainly used as fuel for nuclear reactors, as uranium hexafluoride (UF_6), which is the final product of the ore processing. However, it is also used in medicine and can be found in phosphate fertilizers.

The toxicity of U varies due to its chemical form as well as the route of exposure. The most potent toxicants are the soluble U compounds, e. g. uranyl nitrate ($UO_2(NO_3)_2$), uranium hexafluoride (UF_6), uranyl fluoride (UO_2F_2), uranium tetrachloride (UCl_4) (Keith et al., 2013). The poorly soluble compounds, e.g. uranium tetrafluoride (UF_4), sodium diuranate ($Na_2U_2O_7$) and ammonium diuranate ($(NH_4)_2$U2O7) present moderate to low toxicity, and the insoluble compounds, e. g. uranium trioxide (UO_3), uranium dioxide (UO_2), uranium peroxide (H_2O_4U), triuraniumoctaoxide (U_3O_8) have a much lower potential to cause toxicity, whereas they can cause pulmonary toxicity in case of inhalation (Keith et al., 2013). Ingested uranium is less toxic than inhaled uranium, which may be partly attributed to the relatively low gastrointestinal absorption of uranium compounds. Once natural uranium produces very little radioactivity per mass, the renal and respiratory effects from exposure of humans and animals are usually attributed to the chemical properties of uranium (Keith et al., 2013). Associated to healthy problems related to its radioactive and chemical potential, the World Health Organization (WHO) adopted a threshold of 20 μg L^{-1} of U for drinking water.

Regarding the Brazilian legislation, maximum contaminant levels for U in water are established by the Nuclear Energy National Council (CNEN) and the Environment National Council (CONAMA). The first one states a maximum of 5.6 $x10^3$ Bq m^{-3} of natural U in waste water (CNEM, 2014) for the management of radioactive waste of low and medium radiation levels (Resolution CNEN 167/14). Furthermore, the CONAMA resolution 357/05, determines a maximum total uranium concentration of 0.02 mg L^{-1} for effluent discharge in class 3 water. Class 3 water includes sources destined to human consumption after treatment; irrigation of tree, cereal and forage crops; amateur fishing; recreation and animal feeds (CONAMA, 2005).

This legislation also determines the maximum total uranium concentration in saline water of 0.5 mg L^{-1}.

Uranium is usually found in two valence states: U^{6+} and U^{4+}, therefore it also exists in two other states, U^{5+} and U^{3+}. The hexavalent form is the highly soluble uranyl ion (UO_2^{2+}), which is typically found in oxidizing solutions and soil (Duff et al., 2002; Vandenhove et al., 2014). On the other hand, in its tetravalent state (U^{4+}) uranium is quite insoluble. Uraninite, which is an uranium oxide (UO_2), is an example of U^{4+}compound (Senko et al., 2007). The natural occurrence of uraninite contains some U^{6+} in its structure and it is more precisely represented by the formula $UO_{(2+x)}$ (where $0 \leq x \leq 0.25$) (Bruns, 1999).

Hexavalent uranium, which tends to form relatively soluble compounds is more likely to be a toxicant than tetravalent uranium, which forms relatively insoluble compounds (Keith et al., 2013). Therefore, the reduction of soluble U^{6+} to insoluble U^{4+}, such as uraninite, is a reaction that can be induced to prevent U migration into subsurface and superficial waters (Murphy, 1999) and reduce human health problems.

Under alkaline conditions, quite common in AMD neutralization process, U can precipitate as uranium carbonates, for instance the complex $U_2(CO_3)_3$. It can also occur without carbonate in solution when CO_2, from atmosphere, precipitate. However, this salt is soluble enough, so consequently it is a potential risk at affecting its surrounding environments (Langmuir, 1978).

Different soil properties as pH, phosphorous (P), iron (Fe) and aluminium (Al) (hydr)oxide content, carbonate and organic matter contents and soil colloids also influence the chemical and physical behavior of U (Vandenhove et al., 2014). It is worth noting that U^{4+} concentration in water is also limited by the efficiency of the adsorption process on Fe and Al oxides and hydroxides (Yusan, 2011). The presence of U polluting ground water can rather be related to bicarbonate ions (HCO_3^-), which forms readily soluble uranyl complexes. These complexes are probably transported in the form of hexavalent carbonate complexes (UO_2CO_3) or UO_2^{2+} ions (Choy et al., 2006).

In their study, Duff et al. (2002) presented some mechanism of U immobilization by which U mobility can be retarded in the surface and subsurface of geologic environment. Some of the mechanisms occur by co-precipitation with iron oxides and other minerals, occlusion of

U by clay and metal oxide coatings, reduction of U^{6+}, microbial uptake, sorption of U by organic or inorganic matter, such as humic acids and Fe oxides (fig. 1).

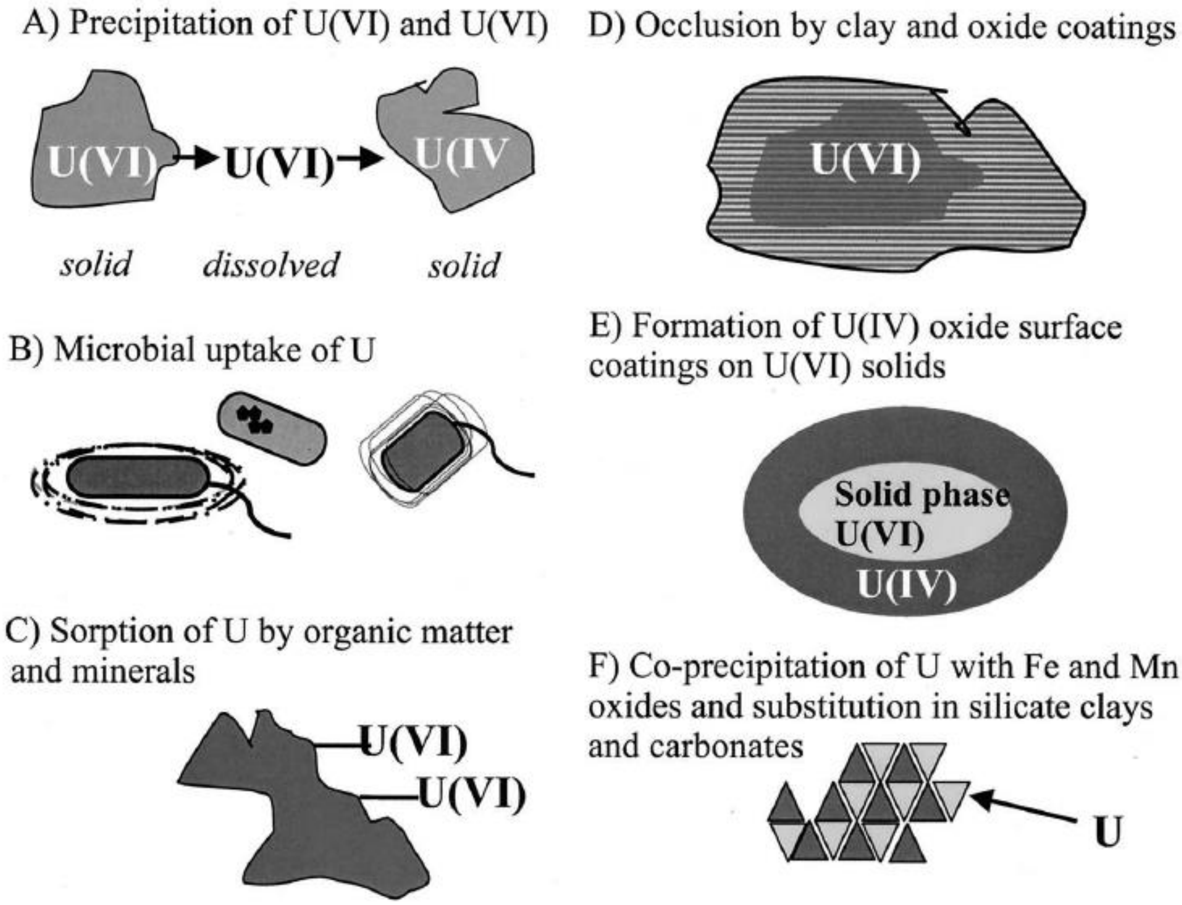

Figure 1. Mechanisms of U immobilization (Duff et al., 2002)

In Brazil, the uranium mine located in the alkaline complex of Caldas, in Minas Gerais State, belongs to the largest complex of alkaline rocks in Brazil. Such complex is altered by metassomatism and hydrothermalist and with phonoliths as their main type of rock. As a result of these processes, pyrite veins with small amounts of galena (PbS) and spharelites((Zn, Fe) S) were formed. In addition, Rare Earth group (ETR) deposits were reported as a result of hydrothermalism and intense weathering (RADAM, 1983). Fifteen years later, (1982 – 1997) uranium mining and milling processes were shut down. However, the waste piles have been generating acid mine drainage (AMD) until today.

The presence of pyrite is considered the main source of AMD in the region of Caldas (Mello et al., 2006). Therefore, the consequences of pyrite dissolution consist of low pH and consequently the dissolution of minerals and the mobilization of their elements, for instance:

arsenic (As), cadmium (Cd), lead (Pb), cobalt (Co) and uranium (U). In order to treat AMD effluent, retention basins are installed on the bases of the rejected piles. According to Fernandes et al. (2008) concentrations between 16.6 mg L^{-1} and 80.2 mgL^{-1}were found in these AMD effluents.

The effluent of AMD is characterized by low pH values, close to 3.5 or less, due to the oxidation of FeS_2 (Ziemkiewics et al., 1997; Mello et al., 2006). As a consequence, there is an increase of ferrous (Fe^{2+}), sulfate (SO_4^{2-}) and hydrogen (H^+) concentrations in solution. The ferrous ion is oxidized to ferric ion, which can precipitate by hydrolysis and enhance the concentration of H^+ ions in solution. According to Singer &Stumm (1970), the kinetic from the precipitation of pyrite is accelerated in the presence of ferric ion. On the other hand, the oxidation of Fe may limit the generation of AMD, once Fe^{3+} precipitates in the surface of the sulfate minerals encapsulating them. This reaction has a half-life of 1000 days. Equations 1, 2 and 3 represent the chemical reactions involved in the process of the oxidation of pyrite (Santos&Ladeira, 2011):

$$4FeS_2\,(s) + 14O_2\,(g) + 4H_2O\,(l) \leftrightarrow 4Fe^{2+}\,(aq) + 8SO_4^{2-}\,(aq) + 8H^+\,(aq) \qquad (1)$$

$$4Fe^{2+}\,(aq) + O_2\,(g) + 4H^+\,(aq) \leftrightarrow 4Fe^{3+}\,(aq) + 2H_2O\,(l) \qquad (2)$$

$$4Fe^{3+}\,(aq) + 12H_2O\,(l) \leftrightarrow 4Fe(OH)_3\,(s) + 12H^+\,(aq) \qquad (3)$$

Studies on literature demonstrate the effectiveness of different Fe(hidr)oxides in soluble U immobilization (Dodge et al., 2002; Duff et al., 2002; Noubactep et al. 2006; Brandy et al., 2008, Nico et al., 2009; Zhang et al., 2009; Dickinson & Scott 2010, Rule et al., 2014). However, changes in redox conditions may compromise the efficiency of some minerals, since the ferric hydroxides are unstable under conditions of low redox potential (Eh). In such environments, the dissimilatory reduction of Fe is an important microbiological process, which depends on ferric minerals as terminal electron acceptors (Bonneville et al., 2006). The microbial reduction can have impacts on the persistence and mobility of U, among other processes, under anaerobic conditions (Lovley et al., 1993; Cumming et al., 1999; Zachara et al., 2001).

The stability of Al under anoxic conditions is already well known. Unlike Fe, this element does not participate in reactions involving the transfer of electrons under natural conditions. For this particular reason, the presence of structural Al increases the stability of the (hydr)oxides of Fe. Slower rates of reductive dissolution, both chemical and microbiological, in the presence of Al in isomorphic substitution to Fe in the structure of the ferric (hydr)oxides were reported by Schwertmann (1984) and Jeanroy et al. (1991). According to Torrent et al. (1987), the isomorphic substitution of Fe by Al was diminishing the reduction dissolution of synthetics goethite and hematite by dithionite bicarbonate solution. Bousserrhine et al. (1999) also demonstrated that the biological reduction rate of Al-substituted goethite decreased as substitution increases. Al-goethite was more resistant to reductive dissolution than another substituted goethite. Similar results were obtained by Silva et al. (2010) who verified that the presence of structural Al increased not only the stability of goethite under reducing conditions, but also its capacity of As adsorption, about three times greater and relative to goethite without substitution. Therefore, the combination of the higher stability of Fe (hydr)oxides under oxidizing conditions with the higher stability of Al under reducing conditions may be an advantageous alternative for the control of AMD.

Structural Al (hydr)oxides are not uncommon and occur under natural conditions, especially in tropical environments. The presence of goethite and, in a less extent, hematite with isomorphic substitution of Fe by Al in soils and sediments is reported by several authors (Schulze and Schertmann, 1984), Torren et al. 1987; Cornell& Schwertmann, 2003).

The co-precipitation of soluble U with Fe and Al (hidr)oxides was investigated in order to analyze the efficiency of U immobilization. Four different Fe:Al molar ratios were tested for two Fe valence (Fe^{2+} and Fe^{3+}). It was expected that in the treatments with higher Al concentration and in the presence of Fe^{2+}, a higher U immobilization would occur. Aluminium would also promote an improved stabilization of the oxides and hydroxides formed, promoting less U desorption and a safe water treatment sludge (WTS). However, a better recovery of U from the sludge/residue of water treatment was expected to occur in the absence of Al. Moreover, for treatments in the presence of Fe^{2+}, a higher U immobilization was expected, once the oxidation of Fe^{2+} to Fe^{3+} could promote the reduction of U^{6+} to U^{4+}, less soluble species.

3. Materials and Methods

The experiment consists of Fe and Al (hydr)oxides precipitates in the presence of soluble U. After an incubation period of approximately three months, the water treatment sludge (WTS) formed were qualitatively and quantitatively characterized.

3.1 Simulating water treatment

The experiment was adapted from the method of Al-substituted goethite described by Schwertmann & Cornell (2000). The main adjustments were made in order to simulate a sulfate-rich water treatment, like AMD. Instead of chloride salts, sulfate salts were used and the pH adjusted to 9 rather than 11. The pH assortment was used according to the Brazilian legislation, CONAMA resolution number 430, which determines that the pH for effluents discharge must be between 5 and 9 (CONAMA, 2011). The total incubation time, 84 days, was chosen in order to obtain a more stable residue (or sludge) of the wastewater treatment.

The precipitation of Al-Fe (hydr)oxides was conducted in polyethylene bottles, which were previously washed in a solution of HCL 1:1, with U contaminated water. Three different concentrations of U were used (80 mg L^{-1}, 40 mg L^{-1} and 20 mg L^{-1}). These concentrations were established based on the literature, especially the study of Fernandes et al., (2008), who found concentrations up to 80 mg L^{-1} of U in AMD contaminated waters at the U mine in Caldas, MG.

The experiment was an incomplete factorial displayed in a randomized block design, the three blocks were the replicates, whose samplings were done in different days of the week (Monday, Wednesday and Friday). Expressing an incomplete factorial of [(3x2) +1] x 3, the treatments consisted of combinations of three Fe:Al molar ratios (100:0, 80:20 and 60:40), two iron valences (Fe^{2+} and Fe^{3+}) and one more treatment only in the presence of aluminium (Fe:Al = 0:100), in three different U concentrations. The Fe:Al molar ratios were determined to test the influence of Fe isomorphic substitution by Al in the immobilization of U, as well as the efficiency of Fe and Al in uranium immobilization.

Summarizing, the experiment consisted on 21 different treatments, and three replicates totalizing 63 experimental units. Those 21 treatments were grouped in four distinct groups, T1; T2; T3 and T4, which express the different Fe:Al molar ratio. To distinguish iron valence number 2 (Fe^{2+}) and number 3 (Fe^{3+}) precede the name of the group. Each group has three different treatments (i.e.: 2T1A, 2T1B and 2T1C), which express the three initial U concentration as described below. (Table 1).

Table 1. Fe:Al molar ratio and U concentrations in treatments.

Fe:Al molar ratio	100:0				80:20				60:40				0:100			
[U] (mg L^{-1})	0	80	40	20	0	80	40	20	0	80	40	20	0	80	40	20
Fe^{2+} treatments		2T1A	2T1B	2T1C		2T2A	2T2B	2T2C		2T3A	2T3B	2T3C				
Fe^{3+} treatments		3T1A	3T1B	3T1C		3T2A	3T2B	3T2C		3T3A	3T3B	3T3C				
Fe^{2+} Blanks	2T1				2T2				2T3							
Fe^{3+} Blanks	3T1				3T2				3T3							
No Fe treatments														T4A	T4B	T4C
No Fe Blanks													T4			

The experiment was performed under oxidic conditions aiming to be as real as possible when compared to the treatment systems performed in a mining waste operation. Initially, for all 63 experimental units, a uranium standard solution of $1x10^4$ mg L^{-1} Assurânce®, SPEXertificate® was diluted into each polyethylene bottles, which already contained 500 ml of Milli-Q® 18 MΩ water, in order to obtain the three different initial U concentrations (80, 40 and 20 mg L^{-1}). In sequence, 200 mL, 160 mL and 120 mL of a $FeSO_4.7H_2O$ PA Merckmillipore 0.645 mol L^{-1} solution were added into the bottles corresponding to Fe^{2+} treatments. To Fe^{3+} treatments 200 mL, 160 mL and 120 mL were added, respectively, of a $Fe_2(SO_4)_3.8H_2O$ PA Merckmillipore 0.323 mol L^{-1}solution. Lastly, 40 mL and 60 mL of a $Al_2(SO_4)_3.18H_2O$ PA Sigma-Aldrich® 0.321 mol L^{-1}solution, were added in the treatment groups T2, T3 for both iron valence state. Treatment T4 was done by addition of 200 mL of $Al_2(SO_4)_3.18H_2O$ PA Sigma-Aldrich® 0.321 mol L^{-1} solution. The volume of all solutions was filled to 900 mL with Milli-Q® 18 MΩ water (Figure 1.-A) and then the pH of each treatment was adjusted to 9 ± 0.5 with a 5 mol L^{-1} KOH PA Sigma-Aldrich® solution (Figure 2.-B), and last of all, to each experimental unit the volume was completed to 1 L.

Figure 2. Experimental units. (A) Before pH first adjust, 0 h. (B) After pH first adjust, 2 h (C) 5 days after pH first adjust.

Oxidation of Fe^{2+} to Fe^{+3+} and possible incorporation of Al $^{3+}$ into the structure of the Fe oxides formed were induced by pumping air through solutions for 1 hour daily over the entire incubation period. Eh and pH were also measured after the supernatant samples collection and before air pumping was applied. pH values were adjusted to 9 whenever necessary.

3.2 Uranium removal from water

In order to evaluate the U removal from the contaminated water, supernatant was sampled periodically, every seven days, throughout the total experimental period. However, during the first week, the samplings were more frequent: 2 hours after adjusting the pH, in the first day, in the third day and in the seventh day of the incubation period. From then on, the samplings were weekly.

Samples of 2 mL from the supernatant solution were collected and saved in micro tubes and stored in a refrigerator as long as the elements are determined. The determination of the U, Fe and Al concentrations were performed by inductively coupled plasma optical emission spectroscopy (ICP- OES) in a Perkin Elmer Optima 8300. Aliquots of 1mL of the supernatant were diluted with 1 mL of 2% HNO_3 to achieve pH lower than 2, which is ideal for ICP-OES analysis. In order to ensure the quality of this analyses, Check solution of 20 mg L^{-1} of U and Spike solutions of 40 mg $L^{-1}$of U plus 1 ml of two samples at random were read between each 10 readings of the experiment samples. Blank samples were also read together with Check and Spike solutions, therefore a better and more realistic detection limit (DL) was calculated. Also, all solutions of the calibration curve had a similar matrix to the samples matrix, a concentrated solution of S and K.

The removal efficiencies were calculated in the end of incubation period by the following equation (Tavengwa et al., 2016):

$$E = \frac{(Co - \ Cf)}{Co} \ x\ 100$$

E = Removal efficiency

Co = Initial concentration of U

Cf = Final concentration of U in the end of the experimental period

3.3 Characterization of water treatment sludge (WTS)

3.3.1 Samples preparation

In the end of the experimental period, the supernatant was siphoned and the water treatment sludge (WTS) transferred to polyethylene pots, which were completely dried in an oven drying at less than 40 °C. According to Schewertmann & Cornell (2000) this temperature is low enough to avoid any phase modification or transformation. After drying, the sludges solid phases were sieved at an opening of 0.088 mm (200 mesh).

The samples of the three replicates, in each treatment, were combined and homogenized forming a single composted sample. Those samples were dialyzed in 30 mL 3,5 kD cassettes with K_2SO_4 solutions at decreasing concentrations (from $4x10^{-2}$ to $4x10^{-6}$ mol L^{-1} approximately) in order to remove soluble salts that precipitated during drying. Dialyses were held until the electrical conductivity dropped to values between 15µS cm^{-1} and 18µS cm^{-1}.

3.3.2 Identification of mineralogical phases

In order to identify the mineralogical phases formed, the X-ray diffractometry technique were performed using Co kα radiation ($\lambda = 0.179$ nm), scanning angle ranging from 0° to 90° and scanning speed of $0.1° \ 2\theta \ s^{-1}$. The diffractograms were interpreted from data in JCPDS (1974) and CHEN (1977).

3.3.3 Evaluation of the stability of U in water treatment sludge (WTS)

A leaching test was performed to evaluate the potential hazardous in the solid phase formed, according to ABNT NBR 10005 (2004). This methodology was applied in order to test the stability of the water treatment sludge/residue so to determine appropriate disposal conditions.

The U stability in the solid phases was also evaluated by two water (Milli-Q® 18 MΩ) sequential extraction, an acid extraction by 0.11 mg L^{-1} CH_3COOH PA Sigma-Aldrich® solution, a reductive extraction by 0.5 mg L^{-1} $NH_2OH.HCl$ PA Merckmillipore and an extraction by 0.5 mg L^{-1} NH_4F PA Sigma-Aldrich® to evaluate U bonded to Al. Extractions were based on the methodology described by Larios & Martínez (2012),but through discrete extractions instead of sequential scheme in order to avoid sample losses between extractions. Baig et al.(2009), who tested both, sequential and discrete extractions concluded there was no significant difference ($p < 0.05$) between them.

The percentage of U remobilization was determined by the difference between total U content in the sludge solid phase and the content remobilized by the extractions. The total U content was calculated based on the U initial and final concentration in the solution.

3.4 Statistical analyses

Variance analyses, ANOVA factorial and ANOVA one-way and Tukey tests were performed by the software STATISTICA 8.0 in order to analyze and compare all treatments and their effects (U initial concentration, molar ratio of Fe:Al and Fe valence states) for U removal efficiency results. Results are described in the appendix.

3.5 Visual MINTEQ application

The distribution of the uranium species was calculated by using the freeware chemical equilibrium model Visual MINTEQ ver.3.1 in order to estimate a possible chemical species saturation of such solution in the beginning and in the end of incubation period.

4. Results and discussion

4.1 Uranium immobilization

All treatments were effective to drop soluble uranium concentration to values below detection limit (DL = 0.009 mg L^{-1}) in the beginning of the incubation period (Figures 3, 4 and 5). Only the treatments with ferrous sulfate (Fe^{2+}), in the absence of Al (100:0 Fe:Al molar ratio) and in the presence of Al, at a Fe:Al molar ratio of 80:20, presented an expressive peak of soluble U in the beginning of the incubation period. However, after that period, U concentration in the supernatant dropped and remained so for 28 days. From that period on, U concentration had a general upward trend, which was more expressive in treatments A with the highest initial U concentration (80 mg L^{-1}). However, it was also observed in treatments B and C with initial U solutions of 40 and 20 mg L^{-1}, Figures 2, 3 and 4 respectively. Such results suggest that 24 hours is an ideal incubation period to completely immobilize U from contaminated water by precipitation with Al-Fe (hydr)oxides. Nevertheless, this short time frame is not enough to form stable minerals, as recent precipitated Al-Fe (hydr)oxides are rather poor crystalline. Further, this time frame is not suitable to manage waste in real mining operations and, of course, 2 weeks is not a suitable incubation time to immobilize U. Thus, a safer time frame is from 2 to 3 weeks, when all treatments showed low concentrations of soluble U, though not as low as in the first 24 hours (Appendix Tables A.1 and A.2).

Regarding legal regulations adopted in Brazil, all treatments would fulfill the threshold of 0.02 mg L^{-1} for waste water discharge just during the first day of incubation period. Treatments in the presence of Fe^{3+} and at low U initial concentration comply with this regulation for 21 days of incubation. More specifically, treatments in the presence of Al and Fe^{2+} and the same U initial concentration, 2T2C and 2T3C, maintained U concentration lower than the threshold for 49 and 56 days, respectively. On the other hand, in the end of the incubation period, no treatment achieved the threshold recommended by the CONAMA regulation 357/05 (CONAMA, 2005). It is also worth observing that the World Health Organization (WHO) also suggests the same threshold as uranium maximum concentration in drinking water. Therefore, a suitable waste management time frame of three weeks maximum is reinforced by the legal regulation.

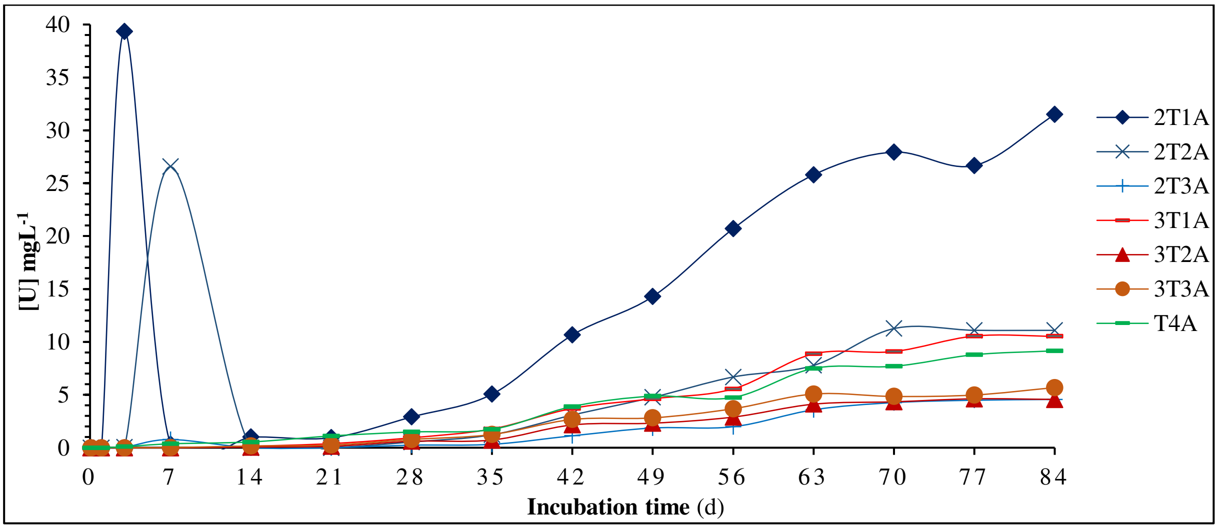

Figure 3. Uranium concentration's during incubation period. Treatments with 80 mg L^{-1} of uranium initial concentration.

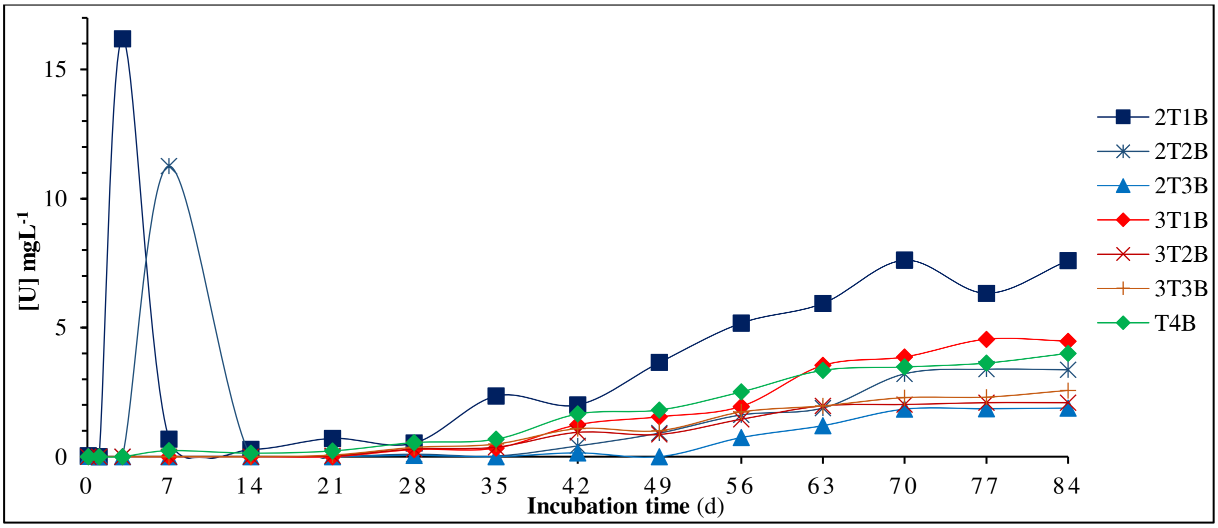

Figure 4. Uranium concentration's during incubation period. Treatments with 40 mg L^{-1} of uranium initial concentration.

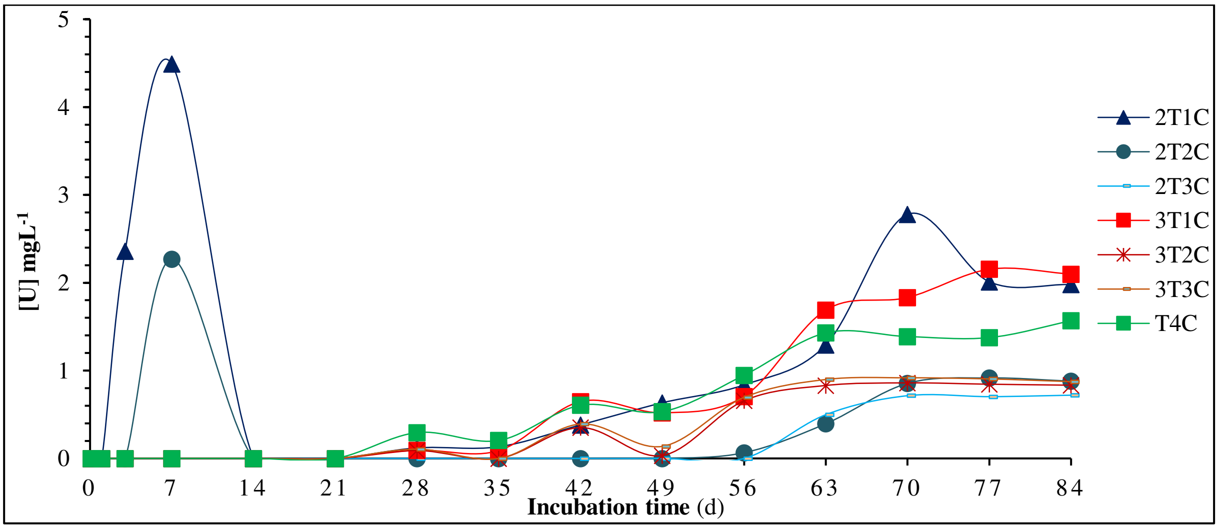

Figure 5. Uranium concentration's during incubation period. Treatments with 20mg L^{-1}of uranium initial concentration.

The most efficient treatment, which immobilized higher amounts of soluble U until the end of incubation period, was treatment 2T3C, in the presence of Fe^{2+} and Al in a molar ratio of 60:40 and low U initial concentration (Figure 5 and 6). In this treatment, U concentration remained lower than the detection limit (DL) within 56 days. From then on, a slight increase in U concentration occurred within incubation period and the final soluble U concentration was around 0.70 mg L^{-1}. On the other hand, treatment 2T1A in the presence only of Fe^{2+}(molar ratio Fe:Al of 100:0) and high U initial concentration was the least efficient ($p < 0.05$). Its soluble U concentration was lower than the DL only on the first day of incubation, and the final U concentration achieved values around 32 mg L^{-1}.

According to Tukey variance analysis (Table 2), treatments containing 80 mg L^{-1} of U in the water presented higher final concentrations of soluble U, independently of the Fe:Al ratio ($p < 0.05$). Therefore, the highest is the uranium concentration in the beginning of the experiment, the lowest is the effectiveness of water treatment by precipitation of Al-Fe (hydr)oxides. Similar results were obtained by Stewart et al. (2009), who achieved higher U immobilization from water with the highest Fe^{2+} concentration (0.01 mg L^{-1}).

As a result of the similarity among the efficiency ($p < 0.05$), treatments can be distinct in two different groups. The group which represents a higher efficiency is totally composed by treatments in the presence of both Fe and Al and low U initial concentration 2T3C; 3T2C; 3T3C; 2T2C; 2T3B and 3T2B (Table 2). The group which represents a lower efficiency in immobilize soluble U is mostly represented by treatments in the presence only of Fe or Al and high U initial concentration 2T1A; 2T1B; 2T2A; 2T1C; 3T1A, T4A and 3T1B.

Therefore, precipitation of Fe (hydr)oxides in the absence of Al was less effective to immobilize soluble U during the entire incubation period ($p < 0.05$) (Table 2). On the other hand, treatments containing Al and Fe tended to maintain lower concentrations of soluble uranium for a longer period, independently of the Fe valence ($p < 0.05$), with removal efficiencies higher than 94% in the end of the incubation period (Figure 6). These data suggest that Al enhances the efficiency of treatments to immobilize U from water in the presence of Fe. However, precipitation of aluminium in the absence of iron, treatments T4 (Fe:Al molar ratio of 0:100), was not as efficient as in Fe presence ($p < 0.05$). Such results suggest that the isomorphic substitution of Fe by Al in octahedral positions plays an important role in uranium immobilization by Fe (hydr)oxides. Silva et al. (2010) also observed similar results, but for arsenic immobilization, which was ascribed to an increase of the arsenic (As) adsorption capacity by goethite containing Al. It is well known that isomorphic substitution of Fe by Al enhances the specific surface due to a decrease in the size of the Fe (hydr)oxides crystallite (Schwertmann & Murad, 1990; Cornell & Schwertmann 2003).

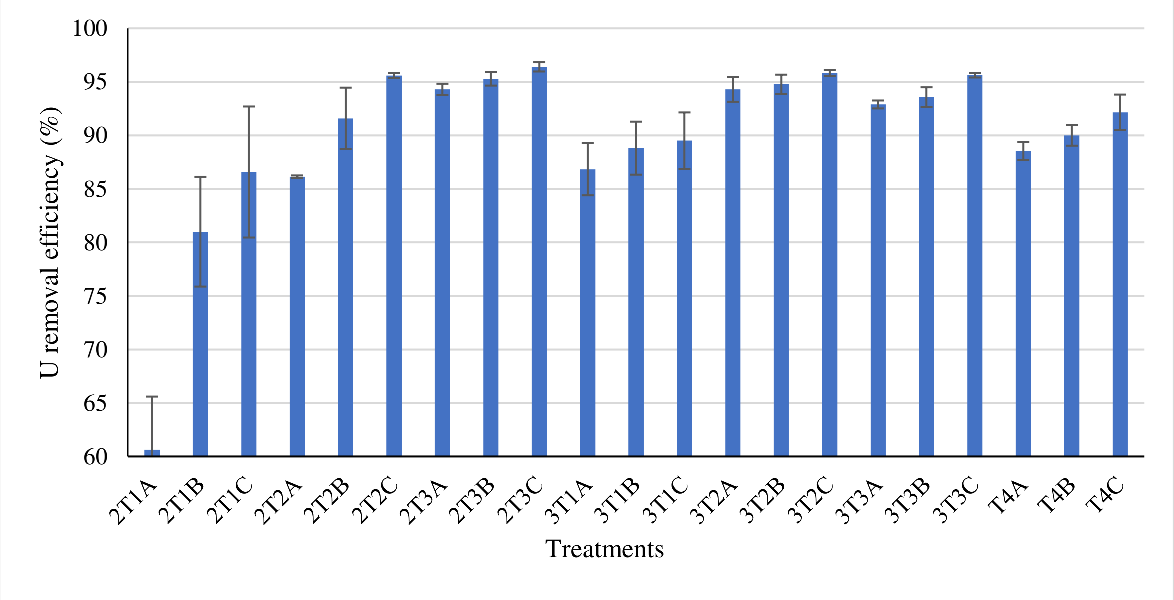

Figure6. Removal efficiency of U in the end of incubation period.

Table 2. Results of variance analyses by Tukey for U removal efficiency

Treatment	**Tukey**	**Treatment**	**Tukey**	**Treatment**	**Tukey**
2T3C	a	2T3A	abc	3T1B	bcd
3T2C	ab	3T2A	abc	T4A	bcde
3T3C	ab	3T3B	abcd	3T1A	cde
2T2C	ab	3T3A	abcd	2T1C	de
2T3B	ab	T4C	abcd	2T2A	de
3T2B	ab	2T2B	abcd	2T1B	e
		T4B	abcd	2T1A	f
		3T1C	abcd		

An interesting behavior of the soluble U during the incubation time is a general upward trend from the 21st day until the end of the experimental period. This trend was more expressive in treatments with higher initial U concentration (80 mg L^{-1}). However, it is also observed in the treatments with initial U solutions of 40 and 20 mg L^{-1}. Dickinson & Scott (2010) reported the same tendency in a study about remediation of uranium contaminated waste effluent with zero-valent iron nanoparticles. They ascribed that results to partial redissolution of uranium previously removed from the zero-valent iron nanoparticles(INP)surfaces. Dissolution of U from carbonate complexes can be another explanation given for that. Vandenhove et al. (2014)

reported formation of uranium carbonates in alkaline conditions, which increases the total solubility of U. Species of uranium carbonate are likely to be present in the solutions, once carbonates were incorporated by the daily air pump in the solutions. According to Visual MINTEQ models some soluble species as $UO_2(CO_3)_2^{-2}$ and $UO_2(CO_3)_3^{-4}$ are probably dissolved in every treatment solution when the pH is 9. However, the concentration estimated by the program is lower than $2x10^{-4}$ mol L^{-1}, therefore it does not explain the whole soluble U. The presence of dissolved uranium sulfate (UO_2SO_4), even at high pH, reinforces the hypothesis that dissolved U species are enhancing total soluble U concentration.

The association of U and SO_4^{-2} occurred once all solutions have more than $1.2x10^4$ mg L^{-1} of sulfate. However, sulfate is also sorbed on iron and aluminum (hydr)oxides and uranium can bound to these complexes. Therefore, uranium sulfate complexes could be adsorbed on minerals formed and by the time desorbed enhancing U concentration. Walter et al. (2003) studied the uranium sorption onto ferric oxides and schwertmannite in a sulfate-rich water. They concluded that U loading occurs due to the release of sulfate from the substrate. They also observed that uranium displace sulfate from the goethite surfaces rather than the schwertmannite surfaces enhancing U stabilization in goethite. These statements can also explain the difference of soluble U concentration among treatments in the end of incubation period. Some complexes of uranium sulfates or only sulfates could be sorbed on Fe and Al (hydr)oxides formed, and depending on the treatment, soluble U could displace more sulfates to solution. Magnetite and hematite were formed by treatments 2T1 and 3T1 only in the presence of Fe^{2+} or Fe^{3+}, which did not immobilize U as well as the treatments in the presence of both Fe and Al that formed goethite.

Treatments with ferrous sulfate (Fe^{2+}), in the absence of Al (100:0 Fe:Al molar ratio) and in the presence of Al, at a Fe:Al molar ratio of 80:20, presented an expressive peak of soluble U in the beginning of the incubation period. It occurred between day 1 to day 7 in the absence of Al and between day 3 to day 14 in the presence of Al (Figures 3, 4 and 5). This behavior can be related to pH data (Figure 7), which showed a corresponding negative peak in the same period. Furthermore, the minimum pH coincide with maximum U concentrations in these treatments. It is worth observing that the same tendencies were not observed in treatments with ferric Fe (Figures 3, 4, 5 and 8). Therefore, these results can be ascribed to oxidation of Fe^{2+} followed by Fe^{3+} hydrolysis, which release H^+ ions. In the formation of goethite from Fe^{2+}, for instance, a total of 8 moles of H^+ are produced as follows (Schwertmann & Cornell, 2000):

Oxidation: $4\ Fe^{2+} + O_2 + 4\ H^+ \rightarrow 4\ Fe^{3+} + 2\ H_2O$

Hydrolysis: $4\ Fe^{3+} + 8\ H_2O \rightarrow 4\ FeOOH + 12\ H^+$

Netreaction: $4\ Fe^{2+} + O_2 + 6\ H_2O \rightarrow 4\ FeOOH + 8\ H^+$

Even though the reaction responsible for pH decrease is the Fe^{3+} hydrolysis, treatments with Fe^{3+} and Al^{3+} pH did not drop as much as in other treatments in the beginning of the incubation period (Figure 8). Consequently, the U concentrations remained low in the same period for treatments with ferric sulfate. An explanation for the difference between treatments with Fe^{3+} and Fe^{2+} is that Fe^{2+} needs to oxidize previously to precipitation. On the other hand, Fe^{3+} immediately precipitates consuming anions OH^-. An evidence to this hypothesis is that treatments with Fe^{3+} consumed almost double the KOH volume compared to treatments with Fe^{2+} in order to buffer pH to 9 in the beginning of the incubation period (Figure 9). After the initial pH correction, the consumption of KOH was higher in Fe^{2+} treatments until the 14th incubation day (Figure 10). These data suggest that Fe^{2+} postpones adsorbent (hydr)oxides formation and also U immobilization.

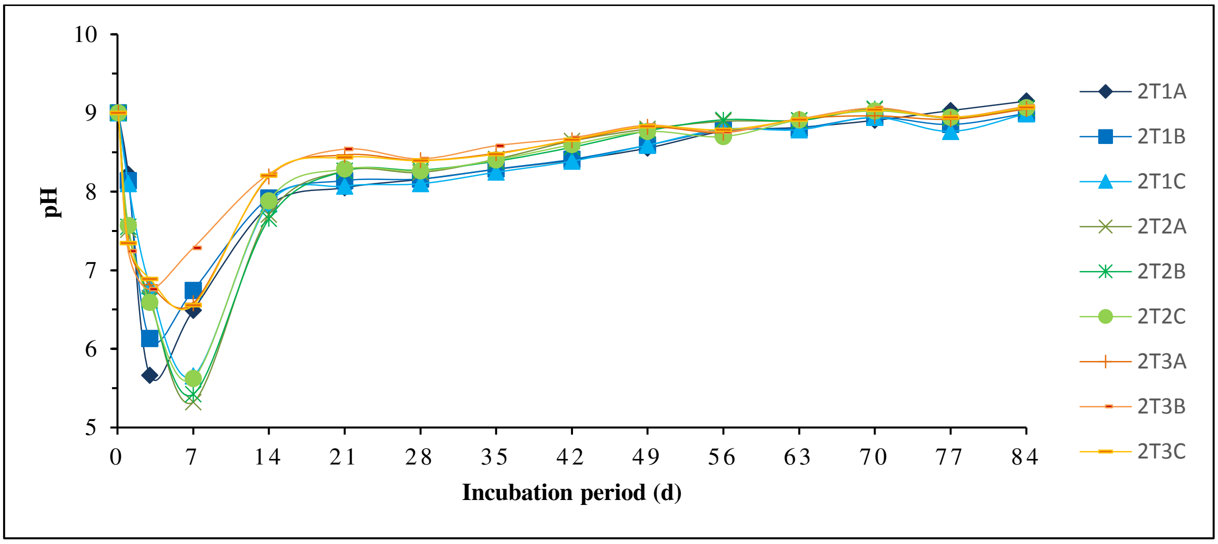

Figure7.pH values during incubation period. Treatments synthesize with Fe^{2+}.

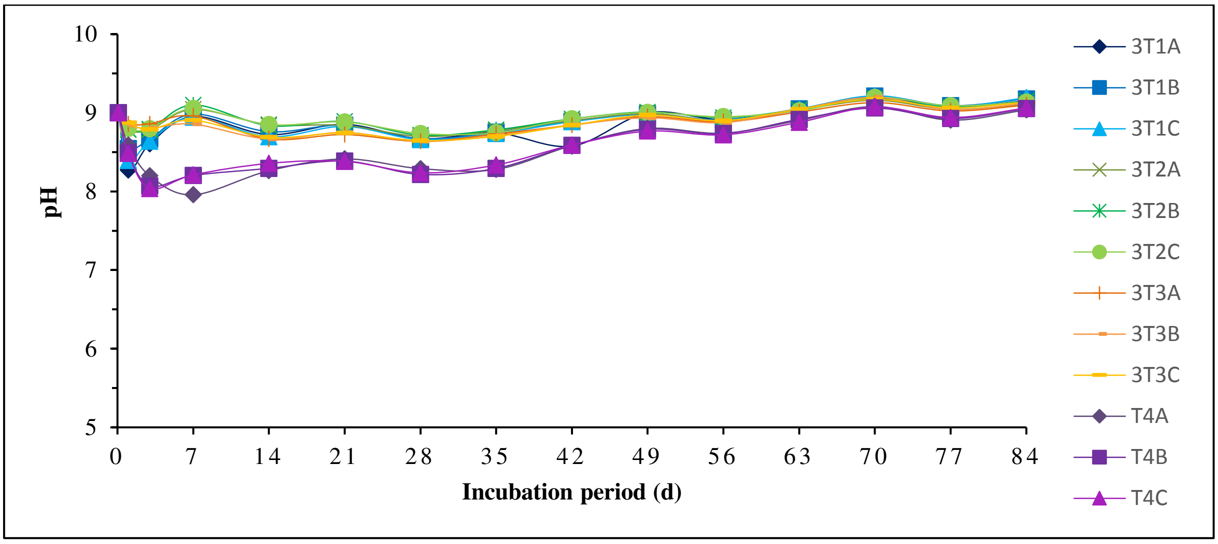

Figure8. pH values during incubation period. Treatments synthesize with Fe^{3+} and only in the presence of Al (T4).

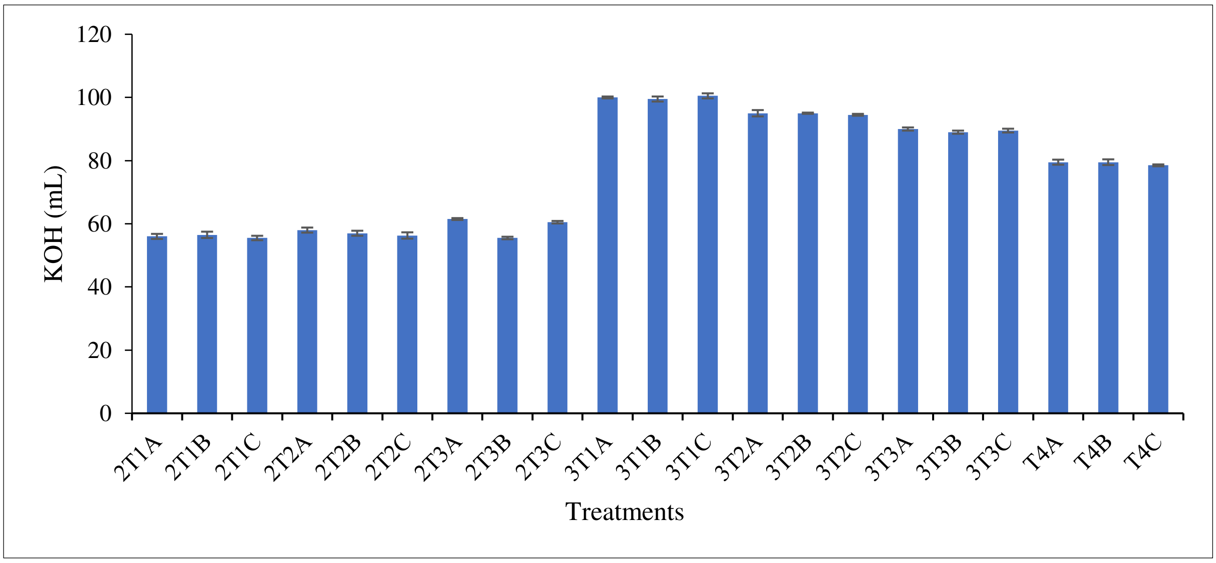

Figure9. Consumption of KOH in the first pH correction.

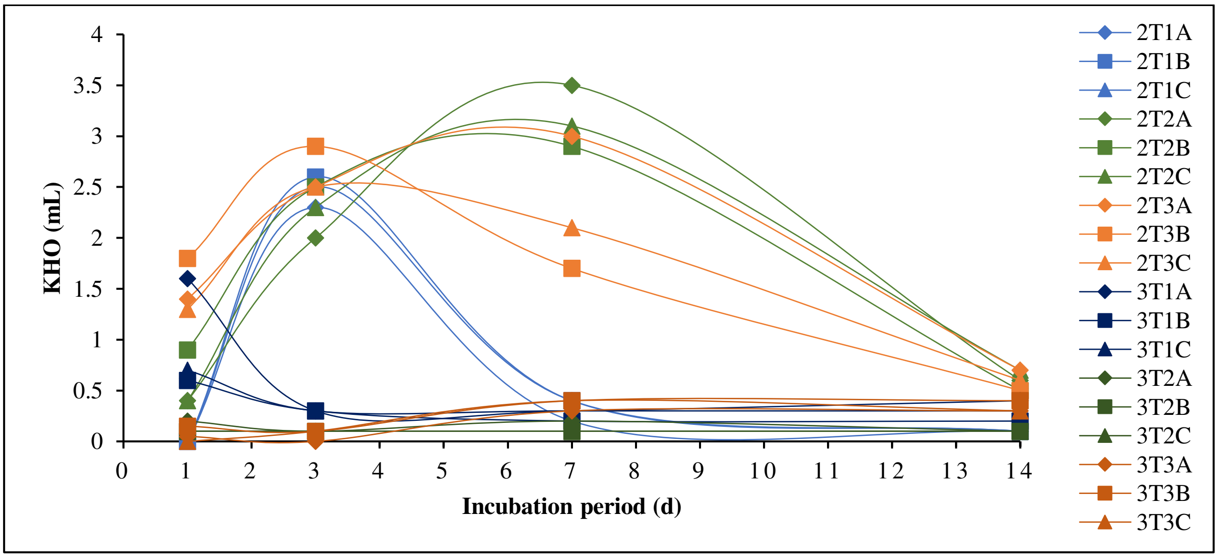

Figure10. Consumption of KOH during incubation period.

Another evidence of Fe^{2+} precipitation delay is the soluble iron during incubation period (Figures 11 and 12). Soluble iron concentrations followed the same tendency of U concentrations. A rapid rise occurred and reached a maximum value and then dropped to values lower than or close to the detection limit (0.013 mg L^{-1}) in treatments with Fe^{2+} (Figure 11). On the other hand, iron concentrations were much lower in treatments with Fe^{3+} (Figure 12). Fe (hydr)oxides solubility, which is minimum around pH 8 (Cornell & Schwertmann, 2003) is the reason for that. The iron and aluminium (hydr)oxides formed in treatments with Fe^{3+}as soon as the pH was firstly buffered to 9, remained more stable than the ones formed in Fe^{2+} treatments. pH of Fe^{3+} treatments remained between 9 and 8 (Figure 8), which explains that. On the contrary, pH dropped to a minimum between 5.5 and 6.5 in Fe^{2+} treatments. Therefore, a higher Fe solubility occurred during the period in which pH was low (Figure 11).

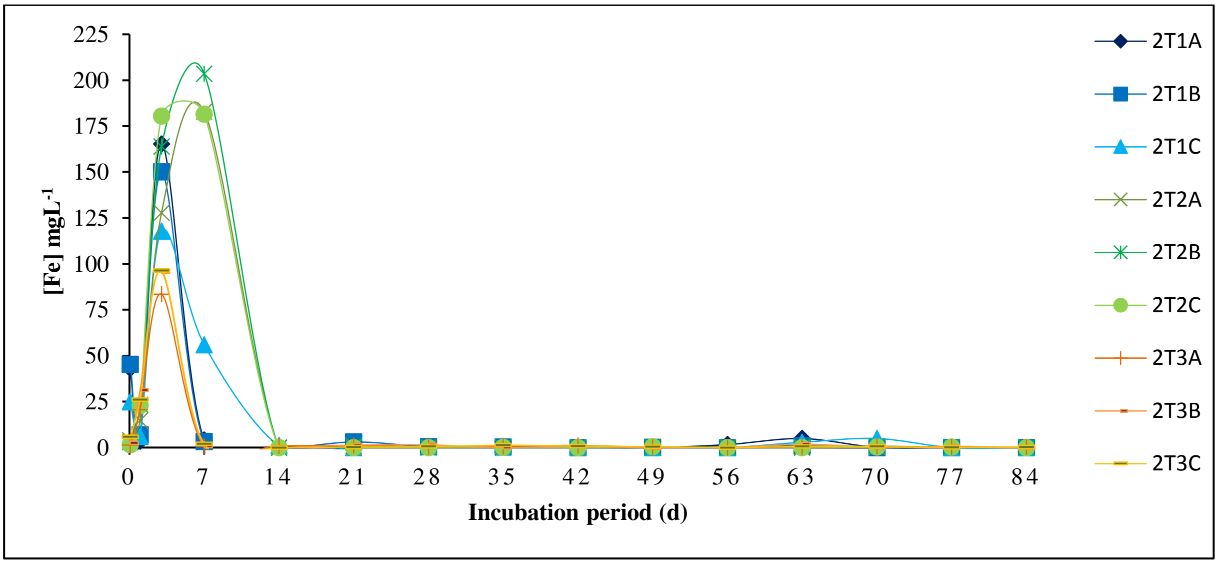

Figure11.Concentration of Fe during incubation period. Treatments synthesize with Fe^{2+}

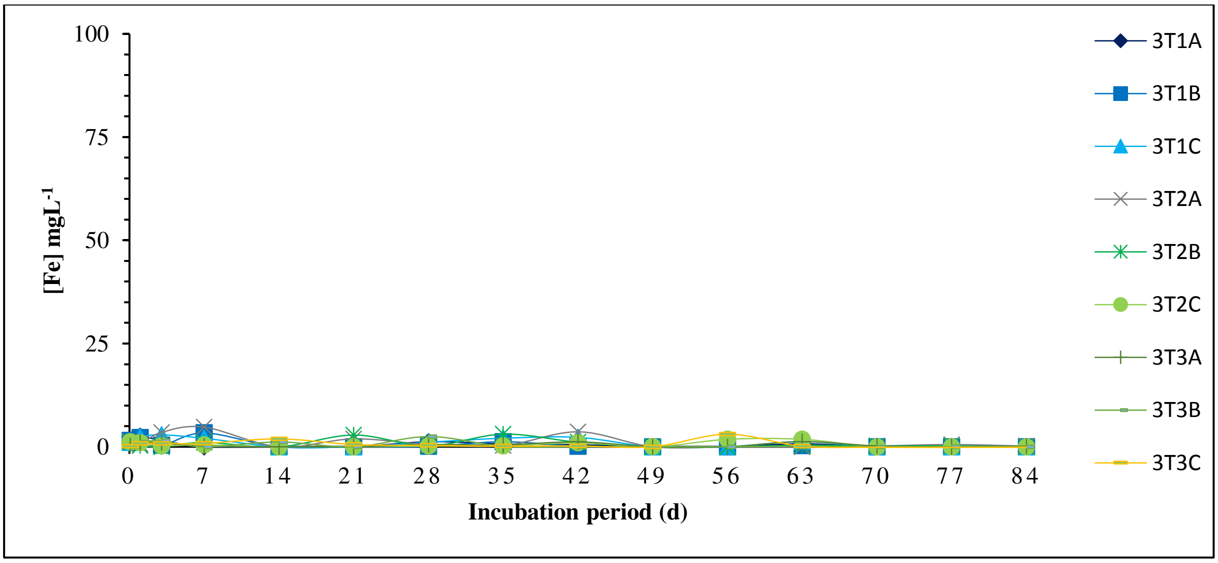

Figure12**.**Concentration of Fe during incubation period. Treatments synthesize with Fe3^{+}

To a certain extent, it was expected a higher efficiency of ferrous (Fe^{2+}) than ferric (Fe^{3+}) ions to immobilize uranium from water. This is because Fe^{2+} oxidation to Fe^{3+}, drives the reduction of uranyl (U^{6+}) to uranate (U^{4+}) ions, which is considered more stable (Dickinson & Scott, 2010). However, in spite of this, treatments with ferrous sulfate were less efficient compared to ferric sulfate, in the absence of Al. The same occurred in the presence of Al at a molar ratio Fe:Al of 80:20, excepted to the lower U concentration (20 mg L^{-1}). On the other hand, there was no significant difference between Fe^{2+} and Fe^{3+} treatments in the presence of Al at a Fe:Al molar ratio of 60:40 (Figure 6). An explanation to those results could be the formation of uranous oxide (UO_2) due to reduction of U^{6+} to U^{4+} in treatments with Fe^{2+}. In the presence of oxygen, UO_2 is less stable resulting in dissolution and release of soluble uranium, as stated by Stewart et al. (2009). In summary, the results mentioned above can be related to interactions of uranium with different mineral phases formed at different Fe:Al:U molar ratios as discussed by Dodge et al. (2002).

A practical implication of these results is the need of a safe facility to dispose the resulting sludge/residue of the sulfate-rich water treatments. A one-day-old mud disposal produced by such treatments may arise environmental risks due to the instability of co-precipitated U, as Al-Fe (hydr)oxides are rather amorphous. On the other hand, this period should be a suitable time frame when the objective of the treatment is the enrichment to recover U from the resulting water treatment sludge/residue. These two statements will be further considered when discussing solid phase characterization.

4.2 Solid phase characterization by XRD diffraction

According to previous discussion and Cornell & Schwertmann (2003), each group of treatments formed different Fe-Al (hydr)oxides. The authors claim that many different types of factors influence on iron (hydr)oxides formation. Different ions concentration in solution, iron oxidation state, concentration and oxidation rate, presence and Al concentration, pH, Eh and temperature are the most important factors that fulfill the minerals formation. However, in general, the presence and U concentrations did not influence in different minerals formation when compared to control treatments. Control treatments have the same Fe:Al molar ratio of each group of treatment though, and they were synthesized in solution without the presence of uranium.

In treatments of 100:0 Fe:Al molar ratio, a formation of goethite was observed. However, the goethite peaks were really short and wide, implying in poor crystallinity (Figure

13). Barcelos (2014) and Poyares (2014) stated that in their study, the presence and concentration of lanthanum (La) and cerium (Ce), respectively influenced on the minerals formed. However, they used a much higher Fe:La or Fe:Ce molar ration rather the Fe:U molar ratio used in this study. Therefore, the U concentrations were not enough to change the minerals formation, since control diffractograms do not differ from treatments (Figures 13, 14 and 15).

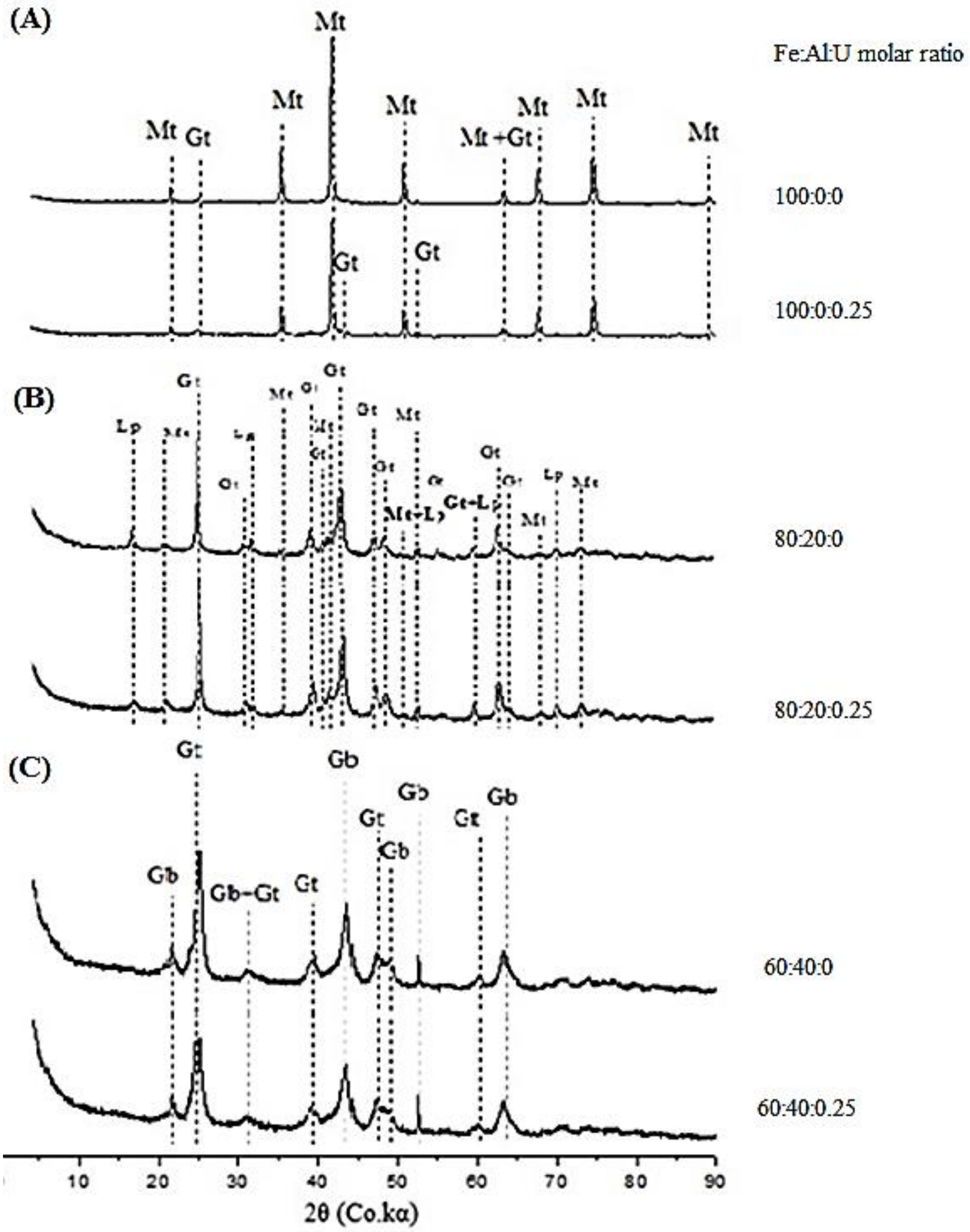

Figure 13. XRD of treatments in the presence of Fe^{2+}. Gt -Goethite; Mt -Magnetite, Lp- Lepidocrocite, Gb – Gibbsite. (A) Treatments of group T1 (Fe: Al = 100:0). (B) Treatments of group T2 (Fe: Al = 80:20). (C) Treatments of group T3 (Fe: Al = 60:40)

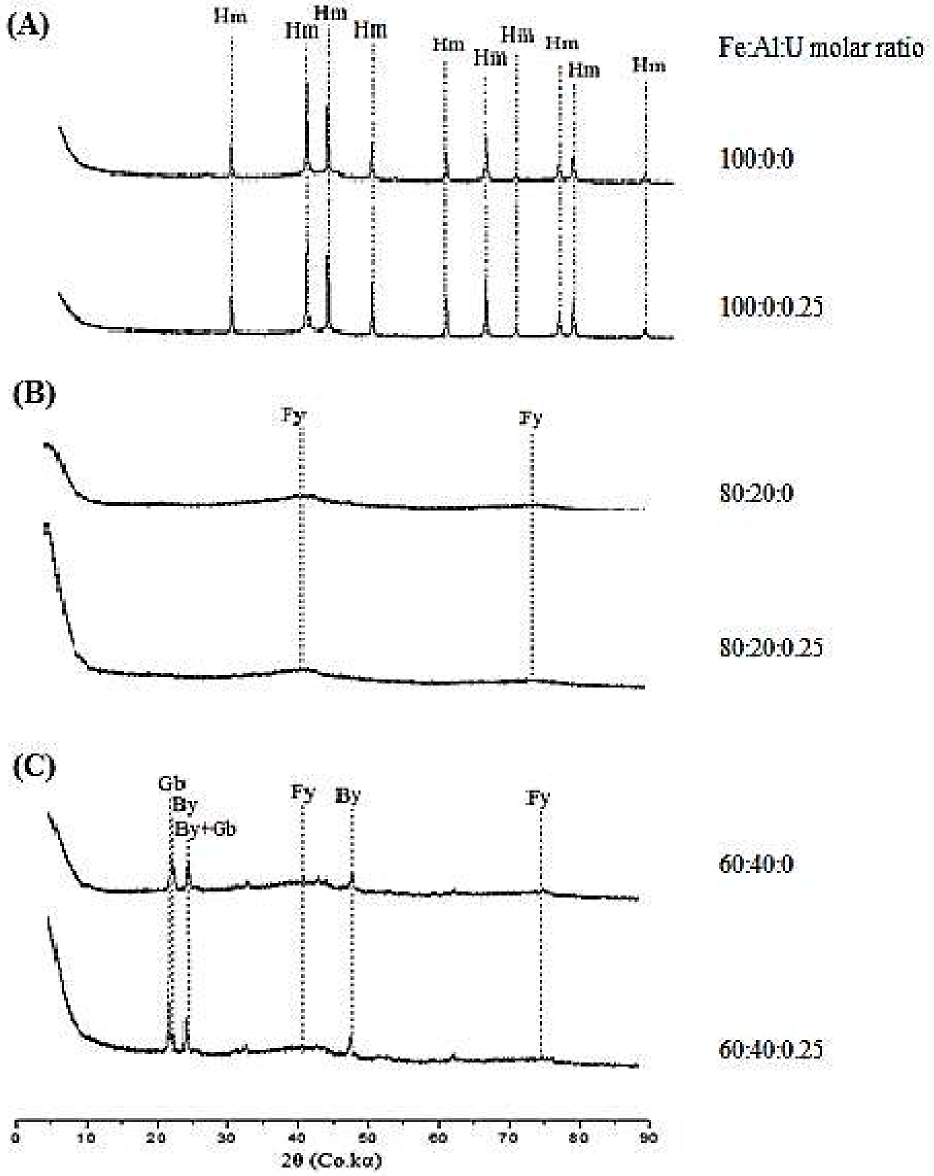

Figure 14. XRD of treatments in the presence of Fe^{3+}. Hm – Hematite; Fy – Ferrihydrite; Gt - Goethite; Gb – Gibbsite. (A) Treatments of group T4 (Fe: Al = 100:0). (B) Treatments of group T5 (Fe: Al = 80:20). (C) Treatments of group T6 (Fe: Al = 60:40)

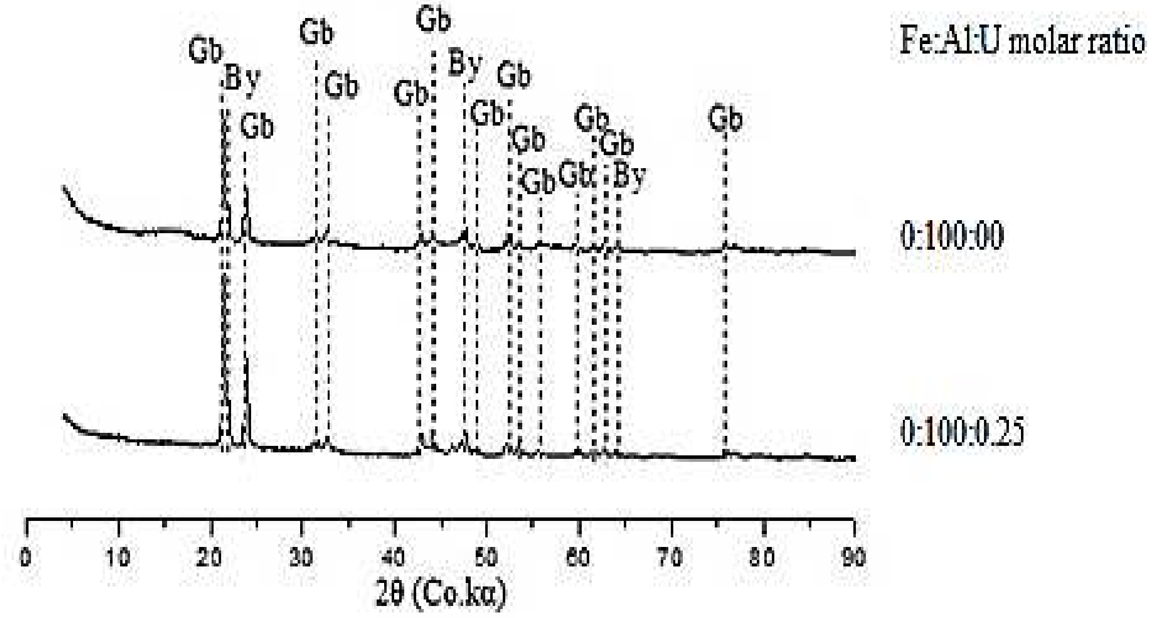

Figure 15. XRD of treatments only in the presence of Al. By – Bayerite; Gb – Gibbsite. Treatments of group T7 (Fe: Al = 0:100).

In the presence of Fe^{2+} and in the absence of Al, Fe:Al molar ratio of 100:0, magnetite was mostly formed (Figure 13-A). Treatments in the presence of Fe^{2+}, with Fe: Al molar ratio of 80:20, also formed magnetite. However, goethite is the dominate mineral (Figure 13-B). Higher Al concentration, (Fe:Al molar ratio of 60:40), mostly formed goethite and also gibbsite in a lesser extent (Figure 13-C).

On the other hand, treatments in the presence of Fe^{3+}, but in the absence of Al (molar ratio of 100:0) formed only hematite (Figure 14-A). The presence of Al provoked a poorly crystallization of Fe (hydr)oxides. X-ray diffraction patterns did not show defined peaks, instead, it presented two broad reflections attributed to ferrihydrite formation (Figure 14-B and C). A higher Al concentration, also promoted the formation of gibbsite and bayerite (Figure 14-C). The presence of Al only, (Fe:Al molar ratio of 0:100) formed Al hydroxides, gibbsite and bayerite.

According to previous treatments efficiency discussion, Al presence enhanced the efficiency of U immobilization by Fe (hydr)oxides. Therefore, goethite and ferrihydrite were the most efficient minerals to immobilize soluble U. Poorly crystalline minerals have a higher superficial area than crystalline minerals, increasing adsorption capacity. On the contrary, magnetite and gibbsite were the least efficient. They were not able to immobilize as much U as other Fe (hydr)oxides formed.

Magnetite formation in Fe^{2+} treatments (Fe: Al molar ratios of 100:0 and 80:20) was expected once these treatments were synthesized by precipitation of ferrous sulfate. They also presented a magnetic activity and a dark color. According to Latta et al., (2014), at low U concentrations mononuclear U^{6+}complexes are formed on magnetite surface. Such complexes can nucleate the precipitation of uraninite (UO_2) as more magnetite precipitates. This final complex remained stable for at least 4 months, under anoxic conditions. Dodge et al., (2002) and Scott et al., (2005) also state that magnetite can remove U^{+6} from solution through reduction to U^{+4} coupled to Fe^{+2} oxidation. However, UO_2 is adsorbed in the magnetite surface and this U phase is easily remobilized under oxidizing and even in slightly reducing conditions (Senko et al, 2002). It explains a higher U remobilization in magnetite treatments (Fe: Al molar ratios of 100:0 and 80:20 in the presence of Fe^{2+}). In addition, Marshall et al., (2013) observed the same behavior of U remobilization during oxidation process. They explain that a structure re-orders occurs and U is likely to be expelled from the particle core. Uranium has a larger ionic radius compared to Fe (Marshall et al., 2013). The ions U^{+4} and U^{+6} in octahedral coordination have radius of 0.87 Å and 1.03 Å, respectively, whilst Fe^{+3} and Fe^{+2}, in the same coordination, have 0.785 Å and 0.92 Å, respectively (Shannon, 1976).

Formation of lepidocrocite and goethite (Figure 13- B and C) enhanced the uranium incorporation. According to Dodge et al. (2002), those two minerals could immobilize all the soluble U during iron oxides formation. Also, they claimed that U was predominantly present in the hexavalent form when associated with the minerals, which did not remobilize under oxidizing environments. Lepidocrocite structure was maintained after co-precipitation and association of uranyl (UO^{2+}). This ion is attached to goethite surfaces sites as an inner-sphere bidentate complex during the crystallization process. Uranium may also become encapsulated into the oxides as a microcrystalline phase (Dodge et al., 2002). Uranium incorporation enhancement could also be related to the well-known fact that the unit cell size decreases with the Fe isomorphic substitution by Al the goethite structure (Schulze and Schertmann, 1984). Therefore, the specific surface area increases, and so the adsorption capacity.

Hematite formation is promoted by high Fe^{3+} concentration (Cornell& Schwertmann, 2003) (Figure 14-A). Formation process begins with ferrihydrite aggregation followed by recrystallization within the aggregate via dissolution and reprecipitation processes (Marshall et al., 2014). The crystallization involves a variety of processes: dehydration of the ferrihydrite particles, deprotonation of hydroxyl groups, creation of oxy-linkages, and redistribution of cation vacancies. During these process, adsorbed uranium has the potential to be incorporated into the structure of the hematite (Shaw, 2005).

The precipitation of Al hydroxides, gibbsite and bayerite did not improve the efficiency of U immobilization. Treatments in the absence of Fe only formed these two minerals phase (Figure 15). They were not as efficient in immobilizing soluble U as treatments in the presence of both Fe and Al. Treatments which the Fe:Al molar ratio is 60:40 also formed these minerals, but in a lesser amount. Cornell & Schwertmann (2003) state that in a [Al/(Al + Fe)] ratio of 0.3 and at 22 °C, goethite and gibbsite will be formed. According to Karamalidis & Dzombak (2010), at pH 9.7 uranyl dimmers [$(UO_2)_2(OH)_2^{+2}$] can form corner-sharing complexes at the gibbsite surface.

4.3 Uranium remobilization potential

4.3.1 Leaching test

In order to qualify the water treatment sludge (WTS) to their environmental hazards, leaching test based on NBR 10005 Brazilian regulation was realized. Leaching concentrations data of U, Fe and Al are described in Table 4.

All solid phase of WTS formed after U immobilization are hazardous. The concentration of U remobilized by the extractor were always higher than the threshold values determined by legislation, 0.02 mg L^{-1} (CONAMA, 2005). Therefore, the solid phase of WTS or precipitates must be disposed in an appropriated mine waste storage facility. On the other hand, these data suggest that part of U can be recovered from the WTS, once Fe and Al concentrations leached were lower than the detection limit or really low. Consequently, the U that was a water pollutant first will now be recovered to its enrichment.

Table 3. Uranium, iron and aluminium concentrations in TCLP supernatant

Treatment	Molar Ratio	U	Fe	Al	U Remobilization
	Fe:Al:U	---------------- mg L^{-1} ----------------			%
2T1A	100:0.00:0.25	47.739 ± 5.155	0.096 ± 0.105	<DL	13.34
2T1B	100:0.00:0.13	26.026 ± 1.720	<DL	<DL	14.10
2T1C	100:0.00:0.06	13.076 ± 1.967	<DL	<DL	15.51
2T2A	80:20:0.25	40.655 ± 2.455	<DL	0.186 ± 0.028	8.26
2T2B	80:20:0.13	15.384 ± 0.859	<DL	0.157 ± 0.026	11.98
2T2C	80:20:0.06	5.332 ± 1.065	<DL	0.142 ± 0.031	16.19
2T3A	60:40:0.25	29.008 ± 3.387	<DL	0.169 ± 0.015	10.76
2T3B	60:40:0.13	11.118 ± 0.861	<DL	0.191 ± 0.009	12.37
2T3C	80:20:0.06	4.845 ± 0.085	<DL	0.154 ± 0.008	15.62
3T1A	100:0.00:0.25	34.537 ± 2.079	<DL	<DL	24.20
3T1B	100:0.00:0.13	17.535 ± 2.032	<DL	<DL	26.26
3T1C	100:0.00:0.06	7.683 ± 0.433	<DL	<DL	27.19
3T2A	80:20:0.25	20.782 ± 0.34	<DL	0.120 ± 0.012	13.78
3T2B	80:20:0.13	9.216 ± 3.579	<DL	0.184 ± 0.008	15.16
3T2C	80:20:0.06	4.3012 ± 0.221	<DL	0.137 ± 0.068	16.16
3T3A	60:40:0.25	26.983 ± 1.177	<DL	0.064 ± 0.005	15.42
3T3B	60:40:0.13	13.679 ± 0.541	<DL	0.104 ± 0.029	18.55
3T3C	80:20:0.06	5.774 ± 1.530	<DL	0.134 ± 0.012	18.64
T4A	0.00:100:0.25	77.032 ± 4.282	<DL	0.752 ± 0.115	38.37
T4B	0.00:100:0.13	33.227 ± 4.333	<DL	0.972 ± 0.143	40.15
T4C	0.00:100:0.06	15.44 ± 1.770	<DL	0.905 ± 0.094	45.61

[*] DL = Detection Limit = (U): 0.02 mg L^{-1}; (Fe): 0.02 mg L^{-1}; (Al): 0.05 mg L^{-1}

Data suggests that some treatments immobilize U more strongly than others, once U concentrations values varied among the groups of treatment and among treatments (Table 3). Treatments synthesized with a higher initial U concentration, presented higher concentrations of soluble U in the extraction solution, which is the same pattern of U concentrations in the immobilization period.

Surprisingly, treatments in the presence of Fe^{3+} and Al at the Fe:Al molar ratio of 80:20 (3T2A, 3T2B and 3T2C) released a lower U concentration for all treatments when compared to all other treatment groups. Such result was not expected, once the Fe (hydr)oxide formed in these treatments was the poorest crystalline, consequently the most instable releasing higher U concentrations in solution, as well as iron and aluminium.

On the contrary, T4 group released a higher U concentration for all treatments. These data indicate that Al hydroxides were the most instable minerals and could not retain U as expected.

4.3.2 Extraction of easily soluble uranium phase

Easily soluble U was evaluated by two consecutively water extractions. In the first extraction, U concentrations were determined in all groups of treatments (Table 4). However, the percentage of U remobilization was low to the most of treatments. These data suggest that some U phases are not co-precipitate in iron and aluminium (hydr)oxides. They should be slightly adsorbed on the minerals surfaces as in sulfate complexes sorbed onto minerals surfaces.

Even with the formation of a well crystalline hematite, as showed in X-ray diffraction (Figure 14 - A), this Fe oxide was not efficient to keep U stable. Regardless of the fact that U could be incorporated in hematite structured via ferrihydrite aggregation followed by recrystallization (Shaw, 2005), the U remobilization was higher in these treatments. Therefore, the U association to hematite occurred in a different process, once the element was easily extracted by water, but presented higher soluble U immobilization efficiency (Figure 6). Consequently, hematite precipitation is the best treatment to clean uranium polluted water and recover it from the water treatment sludge.

The association of U with lepidocrocite demonstrated to be an efficient mechanism of immobilization, once all treatments in the presence of Fe^{2+} in the Fe:Al ratio of 80:20 presented a lower U concentration in the first extraction. On the other hand, even enhancing the U immobilization, Al hydroxides by itself could not efficiently adsorbed U phases. Treatments in the absence of Fe released the second higher U concentration in solution. This data corroborates with the XRD discussion.

The easily soluble U phases was almost all extracted with the first water extraction. In the second extraction, most of all treatments presented U concentration lower than 1 mg L^{-1}. However, hematite treatments continued to release a considerable U concentration, values close to the ones of other groups of treatments in the first extraction. Therefore, hematite is definitely not an efficient mineral to maintain U incorporated. However, it is an appropriate option for U immobilization and further recovery.

Table 4. Concentrations and remobilization of uranium in water extractions

Treatment	Molar Ratio	First extraction	U Remobilization	Second extraction	U Remobilization
	Fe:Al:U	mg L^{-1}	%	mg L^{-1}	%
2T1A	100:0.00:0.25	9.486 ± 0.669	1.22	1.611 ± 0.754	0.20
2T1B	100:0.00:0.13	0.772 ± 0.317	0.16	0.393 ± 0.100	0.08
2T1C	100:0.00:0.06	0.316 ± 0.109	0.13	0.215 ± 0.009	0.09
2T2A	80:20:0.25	5.832 ± 0.328	0.93	0.319 ± 0.038	0.05
2T2B	80:20:0.13	1.654 ± 0.019	0.51	0.223 ± 0.043	0.07
2T2C	80:20:0.06	0.557 ± 0.065	0.35	0.202 ± 0.013	0.13
2T3A	60:40:0.25	7.330 ± 0.573	1.58	0.294 ± 0.020	0.06
2T3B	60:40:0.13	3.569 ± 0.255	1.58	0.223 ± 0.015	0.10
2T3C	80:20:0.06	1.247 ± 0.273	1.10	0.193 ± 0.004	0.17
3T1A	100:0.00:0.25	75.996 ± 1.400	23.93	8.689 ± 2.460	2.72
3T1B	100:0.00:0.13	46.180 ± 6.669	27.62	3.940 ± 0.625	2.36
3T1C	100:0.00:0.06	20.635 ± 2.209	26.03	1.638 ± 0.538	2.05
3T2A	80:20:0.25	7.450 ± 1.782	2.34	0.356 ± 0.065	0.11
3T2B	80:20:0.13	3.029 ± 0.284	1.99	0.265 ± 0.040	0.17
3T2C	80:20:0.06	1.715 ± 0.173	2.19	0.218 ± 0.001	0.28
3T3A	60:40:0.25	8.553 ± 0.080	2.36	0.361 ± 0.033	0.10
3T3B	60:40:0.13	3.63 ± 0.350	1.97	0.256 ± 0.018	0.14
3T3C	80:20:0.06	1.425 ± 0.173	1.53	0.206 ± 0.012	0.22
T4A	0.00:100:0.25	28.202 ± 2.139	6.66	0.597 ± 0.122	0.14
T4B	0.00:100:0.13	14.198 ± 3.002	6.90	0.249 ± 0.022	0.12
T4C	0.00:100:0.06	2.075 ± 1.884	2.06	0.208 ± 0.026	0.21

*Uranium detection limit of 0.019 mg L^{-1}

4.3.3 Extractable soluble, reductive and Al associated uranium phases

In order to evaluate possible mechanisms of U recovery, samples that were extracted by two sequential extractions with water were freeze-dried and then weighed for three different extractions. The extraction solutions were: solutions of 0.11 mg L^{-1} of acetic acid (CH_3COOH), 0.5 mg L^{-1} of hydroxylamine chlorate ($NH_2OH.HCl$) and 0.5 mg L^{-1} ammonium fluoride (NH_4F)

Table 5. Remobilization of uranium by different extractors.

Treatment	Molar RatioFe:Al:U	U Remobilization by CH_3COOH	U Remobilization by $NH_2OH.HCl$	U Remobilization by NH_4F
		%	%	%
2T1A	100:0.00:0.25	35.22	48.43	34.35
2T1B	100:0.00:0.13	34.19	41.89	34.23
2T1C	100:0.00:0.06	26.73	33.80	28.06
2T2A	80:20:0.25	37.32	70.85	63.92
2T2B	80:20:0.13	27.54	54.93	48.63
2T2C	80:20:0.06	18.28	38.05	31.86
2T3A	60:40:0.25	37.32	93.23	73.61
2T3B	60:40:0.13	30.03	91.38	61.94
2T3C	60:40:0.06	25.09	86.62	56.14
3T1A	100:0.00:0.25	43.99	61.01	60.18
3T1B	100:0.00:0.13	36.62	53.25	51.16
3T1C	100:0.00:0.06	44.80	62.37	65.08
3T2A	80:20:0.25	73.21	47.07	71.69
3T2B	80:20:0.13	75.13	40.78	74.09
3T2C	80:20:0.06	69.53	32.80	70.00
3T3A	60:40:0.25	81.83	51.83	56.81
3T3B	60:40:0.13	78.65	75.96	50.04
3T3C	60:40:0.06	73.69	45.27	39.29
T4A	0.00:100:0.25	81.55	100.00	100.00
T4B	0.00:100:0.13	71.68	1000.00	100.00
T4C	0.00:100:0.06	66.43	97.33	93.09

The soluble uranium phases were extracted by CH_3COOH and treatments in the presence of Fe^{2+} are more stable, by Tukey test ($p > 0.5$) (appendix Table A.11). U remobilization in those treatments was lower compared to Fe^{3+} treatments and the ones only in the presence of Al (Table 5). Treatments 3T1, in the presence of Fe^{3+} only, differ ($p > 0.5$) from treatments 3T2 and 3T3, which are in the presence of Fe^{3+} and Al. Mineralogical phases are different among those treatments and hematite. After water extraction, they showed to be more stable than ferrihydrite, which is poorly crystalline. Therefore, U associated to ferrihydrite and also to gibbsite is probably weakly adsorbed on the minerals surface and U associated to hematite, goethite and magnetite is by adsorption and probably also by co-precipitation.

Extraction by $NH_2OH.HCl$ corroborates with the hypotheses of U co-precipitation. This extraction reduces Fe (hydr)oxides liberating U that was bonded to the Fe^{3+}. The remobilization of U was higher in this extraction compared to extraction by CH_3COOH in all treatments, except in treatments 3T2 and 3T3 (Table 5). Uranium remobilization in treatment 2T1 was not expressive once magnetite (Fe_3O_2) is the main mineralogical phase in this solid phase and already has iron its structure Fe^{2+}. Consequently, U is probably bounded to Fe^{2+}in magnetite. The presence of Al in the Fe^{2+} treatments improved iron oxidation. Therefore, treatments in the presence of Fe^{2+} and high Al concentration (Fe: Al molar ratio of 60:40) significantly differ from the others ($p > 0.05$). Remobilization around 90% in treatments 2T3 explains a high efficiency in immobilizing U by co-precipitation with goethite and the solid phase stability (Table 5). Treatments only in the presence of Al presented an elevated U remobilization but it is probably related to the low pH (4.2) of the extraction solution.

In order to analyze U bonded to Al (hydr)oxides, NH_4F was used as an extractor. Acid pH of the extraction solution remobilizes U form treatments in the absence of Al as well. However, the difference among treatments with and without Al is clear ($p > 0.5$) (Table 5). Therefore, U is also associated to Al, which reinforces the efficiency of Fe-Al (hydr)oxides and not only Fe (hydr)oxides in U immobilization.

Data of U remobilization (Table 5) suggest that any of the extractors can be used to recover U from the solid phase produced by the sulfate-rich water treatment. Thus, water treatment was only effective to immobilize U and not to produce a stable water treatment sludge. This result demonstrated a sustainable mechanism to treat and then recover U for economic use.

5. Conclusions

1. Treatments with iron and aluminium (hydr)oxides precipitation were efficient to clean uranium contaminated water to values below the thresholds stablished by legislation, but only within 24 hours after precipitation.
2. Treatment 2T3C, in the presence of Fe^{2+} and Fe:Al:U molar ratio of 60:40:0.06 was the most efficient indicating that U immobilization is enhanced with Fe isomorphic substitution by Al.
3. Al improved U immobilization in all treatments compared to the ones without the element by the precipitation of Fe (hydr)oxides. Nevertheless, the efficiency of the treatments depends on the U initial concentration.
4. The oxidation of $Fe^{2+}$to Fe^{3+} did not improve U immobilization. Treatments synthesized with Fe^{3+} were more efficient.
5. Precipitation of goethite, ferrihydrite and at lesser extent lepidocrocite enhances U immobilization rather than magnetite and gibbsite.
6. Hematite could not keep U stable in the water treatment sludge, even though efficient treatments in immobilizing soluble were high. However, it is an ideal treatment in order to recover U from the mud produced the water treatment.
7. Uranium associated with gibbsite demonstrated to be a less stable mineral phase.
8. Incubation period of 3 weeks is the most appropriated for contaminated water treatment and U recovery.
9. Uranium recovery can be done by extraction with acetic acid, hydroxylamine chlorate or ammonium fluoride.

6. Reference

ABNT NBR 10005. Procedimento para obtenção de extrato lixiviado de resíduos sólidos. Associação Brasileira de Normas Técnicas.16 p.2004.

ALLARD, T.; ILDEFONSE, P.; BEAUCAIRE, C.; CALAS, G. Structural chemistry of uranium associated with Si, Al, Fe gels in granitic uranium mine. Chemical Geology. v. 158, p.81-103. 1999.

BAIG, J. A.; KAZI, T. G.; ARAIN, M. B.; SHAH, A. Q.; SARFRAZ, R. A.;AFRIDI, H. I.; KANDHRO, G. A.; JAMALI, M. K.; KHAN, S. Arsenic fractionation in sediments of different origins using BCR sequential and single extraction methods. Journal of Hazardous Materials. v.167, p.745–751. 2009.

BARCELOS, G.S. Imobilização de Lantânio por precipitação com ferro e alumínio. 2014. 53 f. Dissertação (Mestrado em Solos e Nutrição de Plantas) - Departamento de Solos, Universidade Federal de Viçosa, Viçosa.

Brasil. CNEN- Conselho Nacional de Energia Nuclear. Resolução CNEN No 167, de 30 de abril de 2014. Estabelece os critérios gerais e requisitos básicos de segurança e proteção radiológica relativos à gerência de rejeitos radioativos de baixo e médio níveis de radiação, bem como de rejeitos radioativos de meia-vida muito curta. Diário Oficial da República Federativa do Brasil. Brasília, DF, 2014.

Brasil. CONAMA- Conselho Nacional do Meio Ambiente. Resolução CONAMA No375, de 17 de março de 2005. Dispõe sobre a classificação dos corpos de água e diretrizes ambientais para o seu enquadramento, bem como estabelece as condições e padrões de lançamento de efluentes, e dá outras providências. Diário Oficial da República Federativa do Brasil. Brasília, DF, 2005.

Brasil. CONAMA- Conselho Nacional do Meio Ambiente. Resolução CONAMA No430, de 16 de maio de 2011. Dispõe sobre as condições e padrões de lançamento de efluentes, complementa e altera a Resolução no 357, de 17 de março de 2005, do Conselho Nacional do Meio Ambiente-CONAMA. Diário Oficial da República Federativa do Brasil. Brasília, DF, 2011.

BONNEVILLE, S., BEHRENDS, T., CAPPELLEN, P.V., HYACINTHE, C. AND ROLING, W.F.M. Reduction of Fe(III) colloids by *Shewanella putrefaciens*: A kinetic model. Geochimica et Cosmochimica Acta. v.70, p.5842-5854. 2006.

BOUSSERRHINE N., G.U., JEANROY E., BERTHELIN J. Bacterial and chemical reductive dissolution of Mn^-, Co^-, Cr^-, and Al-substituted goethites. Geomicrobiology Journal. v.16, p.245-258. 1999.

BRANDY, D.; PETERS, N.; SCOTT. F. Stability of Uranium Incorporated into Fe (Hydr)oxides under Fluctuating Redox Conditions. Environmental Science & Technology. v. 43, p. 4922-4927. 2008.

BURNS, P. C. The crystal chemistry of uranium. Rev. Mineral. v. 38, p. 23-90. 1999.

CHEN, P.Y. Table of Key Lines in X-ray Powder Diffraction Patterns of Minerals in Clays and Associated Rocks. Bloomington. Department of Natural Resources. Geological Survey. v. 1, 67 p, 1977.

CHOY, C. C.; KORFIATIS, G. P.; MENG, X. Removal of depleted uranium from contaminated soils. Journal of Hazardous Materials. v. 136, p. 53–60. 2006.

CORNELL, R.M. AND SCHWERTMANN, U. The iron oxides: Structure, Properties, Reactions, Occurrences and Uses. Wiley-VCH, Weinheim. Cambridge. 2003.

CUMMINGS, D. E.; CACCAVO, JR. F.; FENDORF, S.; ROSENZWEIG, F. Arsenic mobilization by the dissimilatory Fe(III)-reducing bacterium *Shewanella alga BrY*. Environmental Science & Technology. v.33, p.723-729. 1999.

DICKINSON, M.; SCOTT, T. B. The application of zero-valent iron nanoparticles for the remediation of a uranium-contaminated waste effluent. Journal of Hazardous Materials. v. 178, p. 171-179, 2010.

DODGE, C. J.; FRANCIS, A. J.; GILLOW, J.B.; HALADA, G. P; ENG, C and CLAYTON, R. Association of Uranium with Iron Oxides Typically Formed on Corroding Steel Surfaces. Environmental Science & Technology. v. 36, p. 3504-3511. 2002.

DUFF, M. C.; COUGHLIN, J. U.; HUNTER, D. B. Uranium co-precipitation with iron oxide minerals. Geochimica et Cosmochimica Acta. v. 66, p. 3533-3547. 2002.

FERNANDES, H.M.; FRANKLIN, M.R.; GOMIERO, L.A. Critical analysis of the waste management performance of two uranium production units in Brazil – part I: Poços de Caldas production centre. Journal of Environmental Management. v. 87, p.59-72. 2008.

INB. INB inicia mais uma etapa para retomada da produção de urânio. Available at: <http://www.aben.com.br/noticias/inb-inicia-mais-uma-etapa-para-retomada-da-producao-de-uranio>. Accessed in: 02 de fev. 2017.

JCPDS, Joint Committee on Powder Diffraction Standards. Selected Powder Diffraction Data for Minerals. 1st. Ed., 833 p. JCPDS, Pennsylvania, U.S.A.1974.

JEANROY, E., RAJOT, J.L., PILLON, P. AND HERBILLON, A.J. Differential Dissolution of Hematite and Goethite in Dithionite and Its Implication on Soil Yellowing. Geoderma. v.50, p. 79-94. 1991.

KEITH, S.; FAROON, O.; RONEY, N.; SCINICARIELLO, F.; WILBUR, S.; INGERMAN, L.; LLADOs, F.; PLEWAK, D.; WOHLERS, D.; DIAMOND, G. Toxicological Profile for Uranium. Agency for Toxic Substances and Disease Registry (U.S.): Atlanta, GA, 2013.

KARAMALIDIS, A. K.; DZOMBAK, D.A. Surface Complexation Modeling – Gibbsite. Wiley-VCH. New Jersey. 2010.

LADEIRA, A.C.Q.; GONÇALVES, C.R. Influence of anionic species on uranium separation from acid mine water using strong base resins. Jounal of Hazardous Materials. v. 148, p.499-504. 2007.

LANGMUIR, D. Uranium solution-mineral equilibria at low temperatures with applications to sedimentary ore deposits. Geochimica et Cosmochimica. Acta v. 42, p. 547-569. 1978.

LARIOS, R., FERNÁNDEZ R., RUCANDIO, I. Comparison of three sequential extraction procedures for fractionation of arsenic from highly polluted mining sediment. Anal Bioanal Chem. v.402, p.2909-2921. 2012.

LATTA, D. E.; MISHRA, B.; COOK, R. E.; KEMNER, K. M.; BOYANOV, M. I. Stable U(IV) complexes form at high-affinity mineral surface sites. Environmental Science & Technology. v. 48, p. 1683–1691. 2014.

LOVLEY, D.R., RODEN, E.E., PHILLIPS, E.J.P. AND WOODWARD, J.C. (1993) Enzymatic iron and uranium reduction by sulfate-reducing bacteria. Marine Geology. v.113, p.41-53. 1993.

MARSHALL, T.A.; MORRIS, K.M.; LAW, G.T.W.; LIVENS, F. R.; MOSSELMANS, J.F.W.; BOTS, P.; SHAW, S. Incorporation and retention of 99-Tc(IV) in magnetite under high pH conditions. Environmental Science & Technology. v. 48, p. 11853–11862. 2013.

MARSHALL, T.A.; MORRIS, K.M.; LAW, G.T.W.; LIVENS, F. R.; MOSSELMANS, J.F.W.; BOTS, P.; SHAW, S. Incorporation of Uranium into Hematite during Crystallization from ferrihydrite. Environment Science & Technology. v. 48, p. 3724-3731. 2014.

MEINRATH, A., SCHNEIDER, P. MEINRATH, G. Uranium ores and depleted uranium in the environment, with a reference to uranium in the biosphere from the Erzgebirge/Sachsen, Germany. Journal of Environmental Radioactivity. v.64, p.175-193. 2003.

MELLO, J.W.V., ROY, W., TALBOTT, J. AND STUCKI, J. “Mineralogy and Arsenic Mobility in Arsenic-rich Brazilian Soils and Sediments”. Journal of Soils and Sediments. v.6, p.9-19. 2006.

MURPHY, W.M and SCOCK, E. L. Environmental aqueous geochemistry of actinides. Rev. Mineral. v. 38, p.221-253. 1999.

NICO, P.S.; STEWART, B. D.; FENDORF, S. Incorporation of Oxidized Uranium into Fe (Hydr)oxides during Fe(II) Catalyzed. Environmental Science & Technology. v. 43, n.19, p. 7391-7396. 2009.

NOUBACTEP, C.; SCHONER, A.; MEINRATH, G. Mechanism of uranium removal from the aqueous solution by elemental iron. Journal of Hazardous Materials. v. B132, p.202–212. 2006

PORTAL BRASIL. Brasil possui 5ª maior reserva de urânio no mundo. Available at<http://www.brasil.gov.br/infraestrutura/2016/09/brasil-possui-5-maior-reserva-de-uranio-no-mundo>. Accessed in: 02 de fev. 2017.

POYARES, L. C.; Imobilização do Cério por óxidos de ferro sintéticos. 2014. 43 f. Dissertação (Mestrado em Solos e Nutrição de Plantas) - Departamento de Solos, Universidade Federal de Viçosa, Viçosa.

RAURET, G.; et al. Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials. Journal of Environmental Monitoring. v.1, p. 57-61. 1998.

RULE, P.; BALASUBRAMANIAN, K.; GONTE, R.R. Uranium(VI) remediation from aqueous environment using impregnated cellulose beads. Journal of Environmental Radioactivity. v. 136, p.22-29, 2014.

SANTOS, L. R., SBAMPATO, M. E., SANTOS A. M. Characterization of electrodeposited uranium films. Journal of Radio analytical and Nuclear Chemistry. v.261, p.203-209, 2004.

SANTOS, E. A.; LADEIRA, A. C. Q. Remoção e concentração de urânio de rejeito de mina. Tecno-Logica. Santa Cruz do Sul, v.15, p.34-41. 2011.

SCHULZE, D.G. AND SCHWERTMANN, U. The Influence of Aluminum on Iron-Oxides.10. Properties of Al-Substituted Goethites. Clay Minerals.v.19, p. 521-539. 1984.

SCHWERTMANN, U. The Influence of Aluminum on Iron-Oxides .9. Dissolution of Al-Goethites in 6m HCl. Clay Minerals. v.19, p. 9-19. 1984.

SCHWERTMANN, U. AND CORNELL, R.M. Iron oxides in the laboratory: preparation and characterization, Wiley-VCH, Weinheim ;Chichester. 2000.

SCHWERTMANN & MURAD, E. The influence of aluminum on iron oxides: XIV. Al-substituted magnetites synthesized at ambient temperatures. Clays & Clay Minerals. v. 38, p. 196-202, 1990.

SCOTT, T.; ALLEN, G.C.; HEARD, P.J.; RANDELL, M.G. Reduction of U(VI) to U(IV) on the surface of magnetite. Geochimica et Cosmochimica Acta. v. 69, p.5639–5646. 2005.

SENKO M. J.; ISTOK, J. D.; SUFLITA, J. M.; KRUMHOLZ, L.R. In situ evidence for uranium immobilization and remobilization. Environmental Science & Technology. v .36, p. 1491–1496. 2002.

SENKO, M. J.; KELLY, S. D.; DOHNALKOVA, A.C.; McDONOUGH, J.T.; KEMNER, K. M.; BURGOS, W.D. The effect of U(VI) bioreduction kinetics on subsequent reoxidation of biogenic U(IV). Geochimica et Cosmochimica Acta. v. 71, p.4644-4654. 2007.

SHANNON, R.D. Revised effective ionic-radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Crystallographica. v. 32, p. 751–767. 1976.

SHAW, S. The Kinetics and Mechanisms of Goethite and Hematite Crystallization under Alkaline Conditions, and in the Presence of Phosphate. Am. Mineral. v. 90, p. 1852–1860. 2005.

SINGER, P. C. AND STUMM, W. Acid mine drainage: the rate determining step. Science. v.167, p.1121-1123. 1970.

SILVA, J., MELLO, J.W.V., GASPARON, M., ABRAHÃO, W.A.P., CIMINELLI, V.S.T. AND JONG, T. The role of Al-Goethites on arsenate mobility. Water Research In Press. v.44, p.5684-5692, 2010.

STEWART, B.D, NICO, P. S., FENDORF, S. Stability of Uranium Incorporated into Fe (Hydr)oxides under Fluctuating Redox Conditions. Environmental Science & Technology. v. 43. p. 4992-4927. 2009.

TORRENT, J., SCHWERTMANN, U. AND BARRON, V. The Reductive Dissolution of Synthetic Goethite and Hematite in Dithionite. Clay Minerals. v.22, p.329-337. 1987.

VANDENHOUVE, H.; VANHOUDT, N.; DUQUÈNE, L.; ANTUNES, K.; WANNIJN, J. Comparison of two sequential extraction procedures for uranium fraction in contained soils. Journal of Environmental Radioactivity. v. 137, p. 1-9, 2014.

YUSAN, S.; ERENTURK, S Sorption behaviors of uranium (VI) ions on α-FeOOH. Desalination. v.269, p.58-66. 2011.

ZACHARA J.M., F.J.K., SMITH S.C., GASSMAN P.L. Solubilization of Fe(III) oxide-bound trace metals by a dissimilatory Fe(III) reducing bacterium. Geochimica et Cosmochimica Acta. v.65, p.75-93. 2001.

ZHANG, G.; SENKO, J. M.; KELLY, S. K.; TAN, H.; KEMNER, K. M.; BURGOS, W.D. Microbial reduction of iron (III)-rich nontronite and uranium(VI). Geochimica et Cosmochimica Acta. v. 73, p.3523-3538. 2009.

ZHANG, F.; WU, W., PARKER, J. C.; MEHLHORON, T.; KELLY, S.K.; KEMNER, K.M.; ZHANG, G.; SCHADT, C.; BROOKS, S. C.; CRIDDLE, C.S.; WATSON, D. B.; JARDINE, P. M. Kinect and modeling of oleate and ethanol stimulated uranium (VI) bio-reduction in contaminated sediments under sulfate reduction conditions. Journal of Hazardous Materials. v. 183, p.482-489. 2010.

ZIEMKIEWICS, P.F.; SKOUSEN, J.G.; BRANT, D.L.; STENER, P.L. E LOVETT, R.J. Acid mine drainage treatments with armored limestone in open limestone channels. Journal of Environmental Quality.v.26, p. 718-726. 1997.

APPENDIX

TableA.1. Uranium concentration during incubation period from time zero to 35th day.

Treatment	Molar Ratio Fe:Al	Initial U conc.	2h	24h	3rd day	7th day	14th day	21st day	28th day	35th day
		---------- mg L^{-1} ----------								
2T1A	100:0	80	0.019 ± 0.008	<DL	39.334 ± 7.794	0.317 ± 0.165	1.005 ± 0.645	0.940 ± 0.336	2.908 ± 0.659	5.057 ± 0.776
2T1B	100:0	40	0.075 ± 0.077	<DL	16.194 ± 0.118	0.680 ± 0.612	0.282 ± 0.259	0.469 ± 0.778	0.527 ± 0.136	2.350 ± 0.814
2T1C	100:0	20	<DL*	<DL	2.359 ± 1.213	1.475 ± 0.492	<DL	<DL	0.12 ± 0.044	0.133 ± 0.020
2T2A	80:20	80	<DL	<DL	0.042 ± 0.01	26.566 ± 5.503	<DL	<DL	0.542 ± 0.099	1.224 ± 0.460
2T2B	80:20	40	0.014 ± 0.018	<DL	<DL	11.260 ± 0.726	<DL	<DL	0.095 ± 0.023	0.025 ± 0.004
2T2C	80:20	20	<DL	<DL	<DL	2.269 ± 0.758	<DL	<DL	<DL	<DL
2T3A	60:40	80	0.033 ± 0.000	<DL	0.047 ± 0.006	0.776 ± 0.127	<DL	<DL	0.242 ± 0.030	0.482 ± 0.026
2T3B	60:40	40	0.013 ±0.007	<DL	<DL	<DL	<DL	<DL	0.048 ± 0.001	<DL
2T3C	60:40	20	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
3T1A	100:0	80	<DL	<DL	<DL	<DL	0.145 ± 0.010	0.389 ± 0.025	0.941 ± 0.168	1.77 ± 0.332
3T1B	100:0	40	<DL	<DL	<DL	<DL	<DL	<DL	0.276 ± 0.037	0.328 ± 0.020
3T1C	100:0	20	<DL	<DL	<DL	<DL	<DL	<DL	0.140 ± 0.021	0.089 ± 0.046
3T2A	80:20	80	<DL	<DL	<DL	<DL	0.061 ± 0.017	0.132 ± 0.016	0.611 ± 0.233	0.726 ± 0.044
3T2B	80:20	40	<DL	<DL	<DL	<DL	<DL	0.056 ± 0.038	0.293 ± 0.039	0.367 ± 0.134
3T2C	80:20	20	<DL	<DL	<DL	<DL	<DL	<DL	0.090 ± 0.028	<DL
3T3A	60:40	80	<DL	<DL	<DL	0.013 ± 0.002	0.156 ± 0.001	0.254 ± 0.036	0.783 ± 0.110	1.248 ± 0.276
3T3B	60:40	40	<DL	<DL	<DL	<DL	<DL	0.062 ± 0.015	0.358 ± 0.127	0.487 ± 0.035
3T3C	60:40	20	<DL	<DL	<DL	<DL	<DL	<DL	0.105 ± 0.017	<DL
T4A	0:100	80	<DL	<DL	0.099 ± 0.002	0.37 ± 0.104	0.545 ± 0.0531	1.113 ± 0.172	1.488 ± 0.287	1.727 ± 0.120
T4B	0:100	40	<DL	<DL	<DL	0.232 ± 0.051	0.234 ± 0.171	0.222 ± 0.027	0.545 ± 0.123	0.676 ± 0.178
T4C	0:100	20	<DL	<DL	<DL	<DL	<DL	<DL	0.294 ±0.035	0.204 ± 0.063

*DL = Detection limit = 0.009 mg L^{-1}

Table A.2. Uranium concentration during incubation period from 42th day to 84th day.

Treatment	Molar Ratio Fe:Al	Initial U conc.	42th day	49th day	56th day	63th day	70th day	77th day	84th day
		------------------	------------------	------------------	------------------	mg L^{-1}	------------------	------------------	------------------
2T1A	100:0	80	10.654 ± 3.416	14.29 ± 1.869	20.698 ± 3.163	25.793 ± 4.861	27.94 ± 8.237	26.674 ± 9.521	29.234 ± 0.676
2T1B	100:0	40	2.003 ± 0.668	3.647 ± 1.370	5.172 ± 1.895	5.936 ± 1.827	7.612 ± 2.085	6.328 ± 1.573	8.700 ± 0.753
2T1C	100:0	20	0.382± 0.044	0.634 ± 0.016	0.838 ± 0.006	1.293 ± 0.152	2.779 ± 1.024	2.011 ± 0.050	1.980 ± 0.101
2T2A	80:20	80	3.087 ± 0.779	4.763 ± 0.518	6.686 ± 0.743	7.778 ± 1.097	11.261 ± 0.550	11.098 ± 0.208	11.092 ± 0.101
2T2B	80:20	40	0.416 ± 0.056	0.913 ± 0.177	1.671 ± 0.537	1.884 ± 0.465	3.209 ± 0.942	3.388 ± 1.155	2.704 ± 0.125
2T2C	80:20	20	<DL*	<DL	0.065 ± 0.013	0.395 ± 0.039	0.854 ± 0.118	0.916 ± 0.152	0.879 ± 0.044
2T3A	60:40	80	1.129 ± 0.040	1.866 ± 0.170	1.981 ± 0.590	3.586 ± 0.658	4.266 ± 0.486	4.487 ± 0.494	4.563 ± 0.428
2T3B	60:40	40	0.146 ± 0.042	0.404 ± 0.267	0.738 ± 0.112	1.201 ± 0.421	1.84 ± 0.287	1.855 ± 0.195	2.029 ± 0.019
2T3C	60:40	20	<DL	<DL	<DL	0.498 ± 0.172	0.714 ± 0.074	0.703 ± 0.079	0.719 ± 0.086
3T1A	100:0	80	3.716 ± 0.390	4.627 ± 0.136	5.559 ± 0.841	8.870 ± 1.798	9.091 ± 1.376	10.555 ± 1.805	11.597 ± 0.621
3T1B	100:0	40	1.237 ± 0.104	1.546 ± 0.171	1.948 ± 0.283	3.535 ± 0.185	3.862 ± 0.703	4.549 ± 1.001	3.967 ± 0.452
3T1C	100:0	20	0.648 ± 0.122	0.52 ± 0.126	0.707 ± 0.077	1.690 ± 0.160	1.832 ± 0.376	2.154 ± 0.545	1.795 ± 0.045
3T2A	80:20	80	2.155 ± 0.396	2.318 ± 0.710	2.895 ± 0.404	4.118 ± 0.357	4.34 ± 0.961	4.624 ± 0.754	4.076 ± 0.360
3T2B	80:20	40	0.943 ± 0.040	0.861 ± 0.102	1.448 ± 0.124	1.968 ± 0.255	2.020 ± 0.272	2.090 ± 0.404	2.090 ± 0.360
3T2C	80:20	20	0.351 ± 0.038	0.033± 0.005	0.657 ± 0.002	0.830 ± 0.119	0.860 ± 0.176	0.845 ± 0.100	0.833 ± 0.056
3T3A	60:40	80	2.671 ± 0.186	2.82 ± 0.074	3.685 ± 0.260	5.077 ± 0.632	4.845 ± 0.507	4.982 ± 0.442	5.687 ± 0.298
3T3B	60:40	40	1.087 ± 0.259	1.007 ± 0.286	1.731 ± 0.301	1.968 ± 0.210	2.287 ± 0.458	2.307 ± 0.374	2.357 ± 0.021
3T3C	60:40	20	0.392 ± 0.033	0.137 ± 0.050	0.695 ± 0.043	0.898 ± 0.071	0.918 ± 0.067	0.905 ± 0.088	0.874 ± 0.044
T4A	0:100	80	3.898 ± 0.180	4.878 ± 0.330	4.749 ± 0.168	7.496 ± 0.618	7.696 ± 0.682	8.790 ± 0.945	8.800 ± 0.260
T4B	0:100	40	1.652 ± 0.288	1.807 ± 0.441	2.508 ± 0.363	3.345 ± 0.677	3.473 ± 0.439	3.626 ± 0.392	3.791 ± 0.118
T4C	0:100	20	0.605 ± 0.217	0.533 ± 0.067	0.947 ± 0.230	1.429 ± 0.221	1.387 ± 0.262	1.376 ± 0.223	1.377 ± 0.032

*DL = Detection limit = 0.009 mg.L^{-1}

Table A.3. Eh during incubation period from 1st day to 35th day.

Treatment	**Molar Ratio Fe:Al**	**Initial U conc.**	**1st day**	**3rd day**	**7th day**	**14th day**	**21st day**	**28th day**	**35th day**
		----------	----------	----------	---------- **mg L^{-1}** ----------	----------	----------	----------	----------
2T1A	100:0	80	-46.00 ± 51.16	95.33 ± 74.33	133.33 ± 61.44	53.33 ± 40.92	7.33 ± 24.01	35.00 ± 134.58	103.66 ± 33.55
2T1B	100:0	40	-29.67 ± 54.00	55.33 ± 146.03	122.33 ± 67.04	31.33 ± 23.46	27.33 ± 26.31	50.00 ± 117.84	106.67 ± 19.73
2T1C	100:0	20	-12.67 ± 23.71	75.33 ± 125.88	168.67 ± 14.50	27.67 ± 39.50	28.33 ± 6.81	57.33 ± 110.21	90.00 ± 16.52
2T2A	80:20	80	-15.67 ± 19.55	40.67 ± 25.71	131.67 ± 5.13	40.33 ± 14.22	32.6 ± 32.537	77.67 ± 96.57	77.00 ± 17.06
2T2B	80:20	40	-10.00 ± 2326	54.00 ± 20.07	127.67 ± 35.92	52.67 ± 12.66	35.667 ± 18.93	77.00 ± 98.74	79.33 ± 12.86
2T2C	80:20	20	-8.00 ± 15.72	53.67 ± 18.50	113.00 ± 28.84	54.00 ± 14.73	35.67 ± 12.74	77.67 ± 98.74	80.67 ± 9.86
2T3A	60:40	80	-4.33 ± 38.50	5.67 ± 33.08	116.67 ± 11.02	40.33 ± 24.37	41.67 ± 14.47	78.67 ± 97.50	73.33 ± 10.02
2T3B	60:40	40	4.67 ± 28.02	4.67 ± 22.30	112.33 ± 11.06	33.33 ± 3.21	42.67 ± 15.28	79.00 ± 82.61	57.00 ± 9.54
2T3C	60:40	20	-14.00 ± 13.75	5.67 ± 29.54	110.67 ± 19.55	38.00 ± 4.58	46.00 ± 11.53	89.33 ± 77.70	65.00 ± 7.81
3T1A	100:0	80	46.33 ± 10.21	34.67 ± 26.10	31.33 ± 28.29	29.67 ± 11.37	39.67 ± 11.02	74.33 ± 62.40	60.33 ± 10.69
3T1B	100:0	40	48.00 ± 9.54	47.33 ± 23.75	25.67 ± 25.11	33.33 ±10.26	36.33 ± 12.34	76.33 ± 62.40	53.67 ± 29.26
3T1C	100:0	20	57.33 ± 12.86	58.33 ± 37.87	31.67 ± 12.50	39.00 ± 9.64	46.00 ± 10.58	70.00 ± 53.01	55.67 ± 25.93
3T2A	80:20	80	53.00 ± 16.82	64.67 ± 42.71	28.33 ± 15.82	38.33 ± 8.32	58.33 ± 22.19	73.33 ± 49.66	58.33 ± 22.03
3T2B	80:20	40	51.33 ± 16.82	61.00 ± 45.31	24.00 ± 11.27	43.00 ± 13.08	80.33 ± 34.24	76.67 ± 46.48	56.33 ± 26.50
3T2C	80:20	20	49.33 ± 31.72	55.00 ± 61.65	23.00 ± 22.00	45.33 ± 14.36	65.00 ± 22.27	73.67 ± 41.02	56.33 ± 25.89
3T3A	60:40	80	75.67 ± 48.81	30.67 ± 84.68	26.00 ± 11.14	47.67 ± 21.50	66.00 ± 18.68	78.67 ± 42.72	57.67 ± 30.62
3T3B	60:40	40	112.67 ± 24.01	92.67 ± 132.08	27.00 ± 14.73	52.00 ± 18.35	70.00 ± 19.08	77.00 ± 42.33	58.67 ± 26.76
3T3C	60:40	20	101.67 ± 15.95	83.00 ± 97.04	28.33 ± 11.68	53.67 ± 15.70	67.33 ± 21.55	75.67 ± 42.72	60.67 ± 26.41
T4A	0:100	80	96.67 ± 63.69	93.00 ± 97.02	47.33 ± 12.66	62.00 ± 19.29	77.00 ± 19.29	90.67 ± 39.25	70.00 ± 28.35
T4B	0:100	40	78.00 ± 62.39	101.00 ± 85.75	56.33 ± 13.65	66.00 ± 19.08	82.33 ± 23.69	96.33 ± 37.45	73.00 ± 27.49
T4C	0:100	20	86.00 ± 66.09	95.67 ± 85.17	56.67 ± 8.96	64.33 ± 15.95	80.67 ± 23.97	96.33 ± 38.42	72.33 ± 27.93

Table A.4. Eh during incubation period from 42th day to 84th day.

Treatment	Molar Ratio Fe:Al	Initial U conc.	42th day	49th day	56th day	63th day	70th day	77th day	84th day
		----------	----------	----------	----------	mg L^{-1}	----------	----------	----------
2T1A	100:0	80	49.67 ± 32.15	36.67 ± 99.01	112.50 ± 62.93	145.67 ± 49.33	170.00 ± 18.52	174.33 ± 11.59	171.00 ± 35.34
2T1B	100:0	40	11.33 ± 23.71	45.67 ± 83.24	109.00 ± 29.70	118.67 ± 65.58	165.33 ± 14.01	165.67 ± 8.74	183.33 ± 35.73
2T1C	100:0	20	12.00 ± 1.73	45.67 ± 74.90	107.50 ± 23.33	108.00 ± 59.73	156.67 ± 8.96	153.00 ± 13.23	186.67 ± 36.35
2T2A	80:20	80	2.33 ± 22.85	49.67 ± 62.42	99.00 ± 16.97	110.33 ± 50.46	149.00 ± 6.08	148.67 ± 13.65	179.00 ± 44.80
2T2B	80:20	40	10.67 ± 23.12	47.67 ± 65.90	96.00 ± 14.14	108.67 ± 46.31	146.00 ± 5.57	144.67 ± 11.67	178.67 ± 44.43
2T2C	80:20	20	14.67 ± 22.50	48.00 ± 63.17	92.00 ± 7.07	105.00 ± 51.39	142.67 ± 10.69	141.67 ± 12.06	170.67 ± 43.39
2T3A	60:40	80	23.00 ± 14.80	58.67 ± 52.20	92.00 ± 16.97	107.00 ± 49.79	143.67 ± 7.09	136.33 ± 16.01	184.67 ± 50.52
2T3B	60:40	40	12.33 ± 12.01	58.67 ± 47.16	84.50 ± 20.351	105.00 ± 45.74	140.33 ± 7.51	131.67 ± 17.79	183.67 ± 50.06
2T3C	60:40	20	18.00 ± 20.00	60.00 ± 42.04	83.50 ± 24.75	96.00 ± 46.16	140.33 ± 7.51	130.33 ± 22.05	184.00 ± 49.96
3T1A	100:0	80	12.33 ± 16.65	43.67 ± 41.88	72.00 ± 25.46	87.33 ± 40.70	130.33 ± 6.66	106.33 ± 21.39	169.67 ± 57.71
3T1B	100:0	40	20.00 ± 15.13	44.33 ± 40.08	70.00 ± 21.21	85.33 ± 38.84	126.33 ± 6.66	103.00 ± 22.00	178.00 ± 64.37
3T1C	100:0	20	23.67 ± 14.19	48.00 ± 39.36	68.00 ± 24.04	84.67 ± 37.07	125.00 ± 4.36	99.67 ± 23.03	177.00 ± 64.78
3T2A	80:20	80	29.67 ± 16.17	70.33 ± 51.33	67.5 0 ± 21.92	85.00 ± 33.87	115.00 ± 10.58	97.33 ± 20.84	179.67 ± 67.65
3T2B	80:20	40	31.00 ± 12.53	68.67 ± 51.39	72.5 ± 27.58	83.67 ± 30.44	115.33 ± 9.07	93.67 ± 19.86	174.67 ± 65.12
3T2C	80:20	20	33.33 ± 10.69	70.33 ± 49.74	72.00 ± 28.28	81.00 ± 31.00	117.33 ± 8.50	93.33 ± 20.03	178.33 ± 66.98
3T3A	60:40	80	34.33 ± 10.97	71.00 ± 51.26	41.00 ± 72.12	67.67 ± 53.80	116.00 ± 8.54	92.67 ± 20.31	176.33 ± 68.19
3T3B	60:40	40	36.00 ± 18.74	76.00 ± 54.51	56.50 ± 51.62	71.67 ± 46.80	116.67 ± 7.57	92.00 ± 22.72	181.67 ± 61.92
3T3C	60:40	20	35.67 ± 20.82	76.67 ± 55.03	59.00 ± 45.25	74.00 ± 42.93	117.33 ± 6.43	90.67 ± 21.36	176.00 ± 68.79
T4A	0:100	80	38.33 ± 32.75	84.33 ± 53.08	70.00 ± 41.01	88.67 ± 29.50	123.00 ± 5.57	95.33 ± 30.98	184.67 ± 57.18
T4B	0:100	40	43.00 ± 31.58	86.33 ± 53.63	72.00 ± 38.18	84.67 ± 41.43	122.67 ± 8.51	97.67 ± 19.86	182.67 ± 59.34
T4C	0:100	20	37.67 ± 36.47	88.00 ± 52.26	71.00 ± 37.20	91.33 ± 28.22	123.33 ± 3.79	97.00 ± 20.95	184.67 ± 59.18

Tables of ANOVA factorial between all treatment effects (uranium initial concentration, Fe:Al molar ratio and Fe valence state) and the depended variables (U immobilization efficiency, U remobilization of leaching test, U remobilization of water extraction, U remobilization of acetic acid extraction, U remobilization of hydroxylamine chloride extraction and U remobilization of ammonium fluoride extraction). Tukey test Tables between treatments (interaction of all effects) and the depended variables.

Table A.5. ANOVA between efficiency and effects

Effect	**DF***	**SS**	**MS**	**F**	**p**
U initial concentration or [U]	2	513.4	256.7	47.9	0.000000**
Fe:Al	3	1648.6	549.5	102.5	0.000000**
Fe Valence	1	248.9	248.9	46.4	0.000000**
U*Fe:Al	6	314.4	52.4	9.8	0.000001**
U* Fe Valence	2	192.9	96.5	18.0	0.000001**
Fe:Al* Fe Valence	3	507.9	169.3	31.6	0.000000**
U*Fe:Al* Fe Valence	6	308.1	51.3	9.6	0.000001**
Error	48	257.3	5.4		
Total	71	3991.3			

*DF = Degree of freedom; ** p significant value <0.05

Table A.6. ANOVA between leaching test and effects

Effect	**DF**	**SS**	**MS**	**F**	**p**
U initial concentration or [U]	2	498.54	249.27	29.847	0.000000**
Fe:Al	3	8531.52	2843.84	340.519	0.000000**
Fe Valence	1	393.43	393.43	47.109	0.000000**
U*Fe:Al	6	113.29	18.88	2.261	0.053072
U* Fe Valence	2	36.56	18.28	2.189	0.123078
Fe:Al* Fe Valence	3	242.26	80.75	9.670	0.000042**
U*Fe:Al* Fe Valence	6	24.50	4.08	0.489	0.813315
Error	48	400.87	8.35		
Total	71	10240.99			

*DF = Degree of freedom;** p significant value <0.05

Table A.7. Tukey between leaching test and treatments

Treatment	**Tukey**	**Treatment**	**Tukey**	**Treatment**	**Tukey**	**Treatment**	**Tukey**
T4C	a	3T1A	def	2T3C	gh	2T2A	h
T4B	ab	2T1C	defg	2T1B	gh		
T4A	bc	3T3C	efg	3T3A	gh		
3T1C	cd	3T3B	efg	2TIA	gh		
3T1B	cde	3T2B	efg	3T2A	gh		
		2T2C	fgh	2T3B	gh		
		3T2C	fgh	2T2B	gh		
				2T3A	gh		

Table A.8. ANOVA between water extraction and effects

Effect	DF	SS	MS	F	p
U initial concentration or [U]	2	28.922	14.461	11.174	0.000104**
Fe:Al	3	2141.262	713.754	551.549	0.000000**
Fe Valence	1	1069.607	1069.607	826.532	0.000000**
U*Fe:Al	6	46.713	7.785	6.016	0.000095**
U* Fe Valence	2	4.098	2.049	1.583	0.215838
Fe:Al* Fe Valence	3	2613.762	871.254	673.256	0.000000**
U*Fe:Al* Fe Valence	6	14.100	2.350	1.816	0.115842
Error	48	62.116	1.294		
Total	71	5980.580			

*DF = Degree of freedom; ** p significant value<0.05

Table A.9. Tukey between water extraction and treatments

Treatment	**Tukey**	**Treatment**	**Tukey**	**Treatment**	**Tukey**
3T1B	a	T4A	c	2T3B	c
3T1A	a	3T3C	c	2T3C	c
3T1C	a	3T2A	c	2T3A	c
T4B	b	3T2C	c	2T2C	c
T4C	b	3T2B	c	2T2B	c
		3T3B	c	2T2A	c
		2T1C	c	2T1B	c
		3T3A	c	2T1A	c

Table A.10. ANOVA between acetic acid extraction and effects

Effect	DF	SS	MS	F	P
U initial concentration or [U]	2	1238.9	619.5	7.690	0.001268**
Fe:Al	3	12161.0	4053.7	50.319	0.000000**
Fe Valence	1	11684.4	11684.4	145.042	0.000000**
U*Fe:Al	6	243.4	40.6	0.504	0.802528
U* Fe Valence	2	161.0	80.5	0.999	0.375688
Fe:Al* Fe Valence	3	7864.7	2621.6	32.542	0.000000**
U*Fe:Al* Fe Valence	6	234.5	39.1	0.485	0.816114
Error	48	3866.8	80.6		
Total	71	37454.8			

*DF = Degree of freedom; ** p significant value <0.05

Table A.11. Tukey test between acetic acid extraction and treatments

Treatment	**Tukey**	**Treatment**	**Tukey**	**Treatment**	**Tukey**
3T3C	a	T4B	ab	2T1C	c
T4C	a	3T2A	ab	2T1B	c
3T3B	a	T4A	ab	2T3B	c
3T2B	a	3T1A	bc	2T2B	c
3T3A	a	3T1C	bc	2T1A	c
3T2C	a	2T3C	c	2T3A	c
		2T2C	c	2T2A	c
		3T1B	c		

Table A.12. ANOVA between hydroxylamine chloride extraction and effects

Effect	DF	SS	MS	F	p
U initial concentration or [U]	2	2535.6	1267.8	7.037	0.002090**
Fe:Al	3	40205.6	13401.9	74.384	0.000000**
Fe Valence	1	986.3	986.3	5.474	0.023504**
U*Fe:Al	6	1675.1	279.2	1.550	0.182613
U* Fe Valence	2	297.3	148.7	0.825	0.444304
Fe:Al* Fe Valence	3	6143.4	2047.8	11.366	0.000009**
U*Fe:Al* Fe Valence	6	910.8	151.8	0.843	0.543507
Error	48	8648.3	180.2		
Total	71	61402.5			

*DF = Degree of freedom; ** p significant value <0.05

Table A.13. Tukey between hydroxylamine chloride extraction and treatments

Treatment	Tukey	Treatment	Tukey	Treatment	Tukey
T4C	a	2T3A	abcd	2T1C	def
T4B	ab	3T3B	bcde	3T2C	def
T4A	ab	2T2C	bcdef	3T3A	def
2T3C	abc	2T1A	bcdef	2T1B	ef
2T3B	abc	3T1C	bcdef	3T2B	ef
		2T2B	cdef	2T2A	ef
		3T1B	cdef	2T1A	ef
		3T3C	cdef	3T2A	f

Table A.14. ANOVA between ammonium fluoride extraction and effects

Effect	DF	SS	MS	F	p
U initial concentration or [U]	2	2692.7	1346.3	21.438	0.000000**
Fe:Al	3	36846.2	12282.1	195.568	0.000000**
Fe Valence	1	1394.1	1394.1	22.199	0.000021**
U*Fe:Al	6	1001.9	167.0	2.659	0.026191**
U* Fe Valence	2	335.5	167.7	2.671	0.079457
Fe:Al* Fe Valence	3	5373.2	1791.1	28.519	0.000000**
U*Fe:Al* Fe Valence	6	690.7	115.1	1.833	0.112453
Error	48	3014.5	62.8		
Total	71	51348.8			

*DF = Degree of freedom; ** p significant value<0.05

Table A.15. Tukey between ammonium fluoride extraction and treatments

Treatment	Tukey	Treatment	Tukey	Treatment	Tukey
T4C	a	3T1A	cd	2T2B	defgh
T4B	a	2T2C	cde	3T3A	efgh
T4A	ab	2T3B	cde	2T1C	fgh
3T2B	bc	3T1C	cde	2T1B	fgh
2T3C	bc	3T3C	cdef	2T2A	gh
3T2C	bcd	2T3A	cdefg	2T1A	h
3T2A	bcd	3T1B	cdefgh		
		3T3B	cdefgh		