

NOTE TECHNIQUE

Orano – BU Mines
DPSI/DRDI

Réf : IDF-DT-009035

Titre : Caractérisation et réactivité des résidus de traitement issus de l'exploitation des minerais d'uranium en France (Lavaugrasse, Bellezane, Ribière, Cellier). Modélisation de la mobilité à long terme de l'uranium et du radium 226 dans les résidus de traitement de Bellezane

Mots clés : Résidus de traitement, uranium, ^{226}Ra , modélisation, Bellezane, PNGMDR

Diffusion Limitée Orano

Révision n°	Date	Nature des modifications
01	06/02/2020	Première diffusion

RESUME

La division minière de la Crouzille constituait la principale zone de production d'uranium en France avec une vingtaine d'exploitations minières distinctes, une production de 27 000 tU, pour près de 15 Mt de minerai traités (teneur moyenne 1.66 ‰). Cette activité minière a généré par ailleurs 57 Mt de stériles miniers et 22 Mt de résidus de traitement. Ainsi, 1,546 Mt de résidus de traitement produits par l'usine SIMO (Société Industrielle des Minerais de l'Ouest) ont été stockés sur le site de Bellezane (BZN) de 1989 à 1993. **La mobilité à long terme du ^{226}Ra et de l'U résiduels au sein de ces résidus de traitement a été évaluée par modélisation prédictive de type transport réactif suite à des caractérisations complémentaires des eaux interstitielles et des résidus de traitement.**

Les eaux interstitielles présentent des concentrations en U et ^{226}Ra dissous respectivement de 12×10^{-6} mol/L (soit 2.8 mg/L) et 0.58 Bq/L. Les concentrations en U et ^{226}Ra résiduels mesurées dans le solide sont respectivement de 160 ppm et 25 Bq/g, en accord avec les teneurs initiales du minerai et rendements usines, soit plus de 99% du stock total, alors que la fraction mobile constitue seulement $10^{-4}\%$ du stock total. D'un point de vue composition chimique et minéralogique, ils sont principalement constitués des minéraux hérités du minerai granitique (quartz, feldspaths potassiques, plagioclases et micas) en association d'une part avec leurs produits d'altération (smectite et oxy-hydroxydes ferriques), et d'autre part coexistant avec des minéraux néoformés suite à la diagénèse rapide après neutralisation des résidus avant leur mise en place (gypse et barytine). **L'ensemble de ces minéraux constituent des pièges efficaces pour la rétention de l'U et du ^{226}Ra .** L'U est réparti d'une part dans des phases réfractaires, uraninite et coffinite micrométriques enchâssées dans des grains de quartz, et d'autre part sorbé sur la smectite et les oxy-hydroxydes ferriques. Le ^{226}Ra est quant à lui piégé principalement au sein de la barytine.

Les concentrations aqueuses en U et ^{226}Ra peuvent être décrites selon une approche thermodynamique qui permet dans un second temps d'évaluer leur mobilité à long terme par des modélisations prédictives de type transport réactif sur une période de 230 000 ans. Cette durée investiguée est nécessaire pour appréhender la faible mobilité de l'U et du ^{226}Ra . **Les résultats des simulations indiquent que la présence de pièges de rétention surcapacitaires, i.e. smectite, oxy-hydroxydes ferriques et barytine, maintiendront l'U et le ^{226}Ra à de très faibles concentrations aqueuses, inférieures à celles observées aujourd'hui. Ces résultats de modélisation confirment la rétention de ces deux radioéléments, et ce même en conditions oxydantes attendues comme favorables à leur migration. De plus, la faible perméabilité des résidus (10^{-8} m/s) entraîne dans le cas du ^{226}Ra un comportement purement contrôlé par la décroissance radioactive.**

Ce rapport d'avancement sur la réactivité à long terme des résidus de traitement alimente les études menées dans le cadre du Plan National de Gestion des Matières et Déchets Radioactifs (PNGMDR).

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ABSTRACT

The Crouzille mining division was the principal uranium production area in France with about twenty separate mining operations, representing a production of 27,000 tU, for nearly 15 Mt of ore processed (average grade 1.66 ‰). This mining activity generated in addition nearly 57 Mt of mine waste rock and 22 Mt of process tailings. 1,546,000t of mill tailings from the SIMO mill (Société Industrielle des Minerais de l'Ouest) were stored in the Bellezane site (BZN) from 1989 to 1993. **The long-term mobility of residual U and ²²⁶Ra within the tailings was assessed through the development of a 1D predictive model of reactive transport constrained by complementary characterizations of porewaters and the solid fraction of the U mill tailings.**

The porewaters taken from the core of the tailings are characterized by low concentrations of uranium (12×10^{-6} mol/L; 2.86 mg/L) and ²²⁶Ra (0.58 Bq/L). The residual U and ²²⁶Ra concentrations measured in the solid are 160 ppm and 25 Bq/g respectively, in accordance with the initial ore grades and mill yields, or more than 99% of the total stock. In terms of chemical and mineralogical composition, the tailings are mainly composed of minerals from the granitic ore (quartz, potassium feldspar, plagioclases and micas) in association with their weathering products (smectite and ferric oxyhydroxides) and with neo-formed minerals following rapid diagenesis after neutralization of the tailings before their emplacement (gypsum and barite). **All these minerals are effective traps for the retention of U and ²²⁶Ra.** The uranium is distributed partly in micrometer scale uraninite and coffinite refractory phases embedded in grains of quartz, and partly sorbed to smectite and ferric oxyhydroxides. The ²²⁶Ra on the other hand is trapped mainly within the barite.

The aqueous concentrations of U and ²²⁶Ra could be described using a thermodynamic approach so that their long-term mobility can subsequently be assessed by modeling over a 230 000 y period. Such duration was investigated in order to highlight the low mobility of U and ²²⁶Ra. **The presence of retention traps offering surplus capacity, i.e. smectite, ferric oxyhydroxides and barite, will maintain the U and the ²²⁶Ra at very low aqueous concentrations, inferior to those observed today. These results confirm the retention of the two radionuclides even under oxidizing conditions, known generally to enhance their mobility. Moreover, the low permeability of the mill tailings leads (10^{-8} m/s), in the case of ²²⁶Ra, to behavior dictated only by the radioactive decay.**

The findings of this progress report are based on multi-year studies carried out under the French National Radioactive Materials and Waste Management Plan (PNGMDR).

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1. Introduction

Cette étude pluriannuelle s'inscrit dans le cadre du Plan National de Gestion des Matières et Déchets Radioactifs. Elle concerne la problématique de la gestion à long terme des 51 Mt de résidus de traitement répartis sur 17 stockages en France. A ce jour, quatre sites de stockage de résidus font l'objet d'études toujours en cours : Bellezane (BZN), Lavaugrasse (LVG), La Ribière (RIB) et le Cellier (CEL). La stratégie d'étude développée et présentée notamment devant la Commission Nationale d'Evaluation (Descostes, 2017) est rappelée en Figure 1. Elle s'articule autour de quatre points complémentaires, alliant études historiques, caractérisations physico-chimiques et modélisations géochimiques.

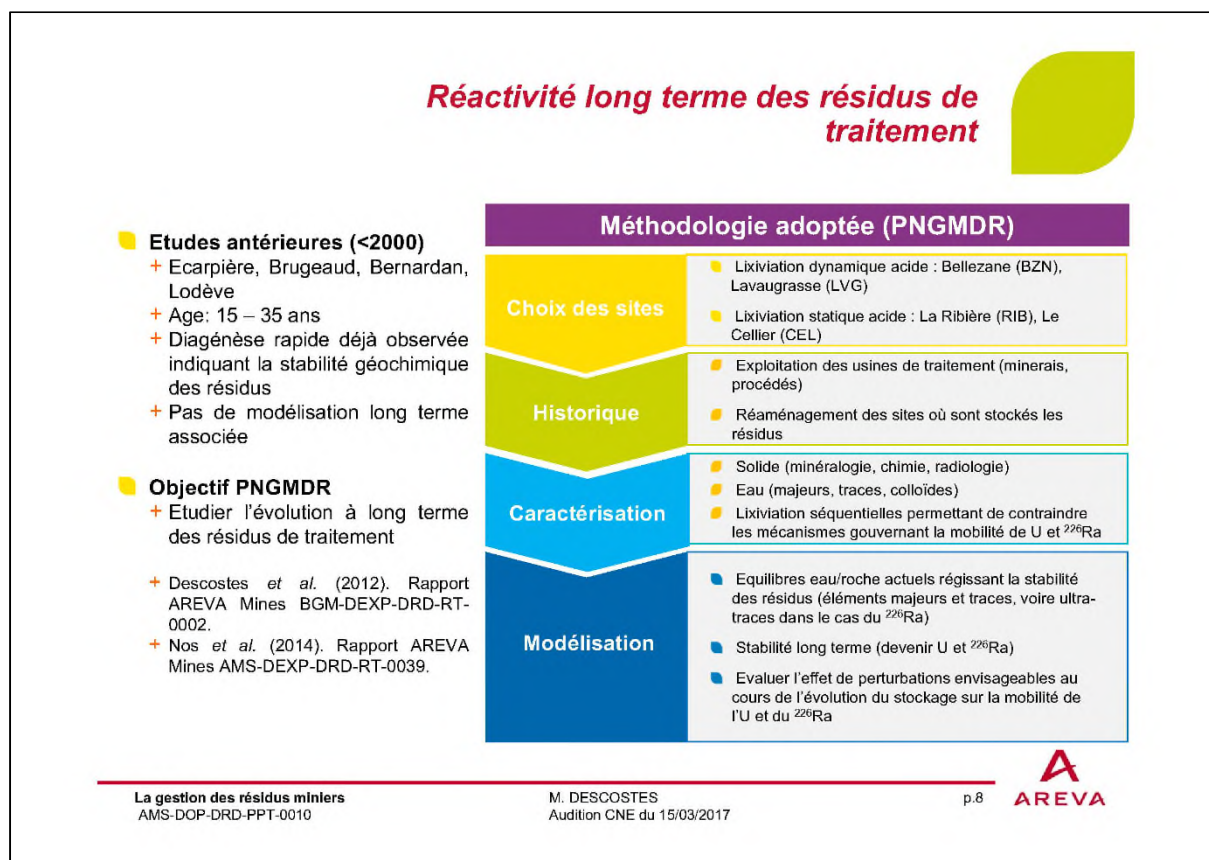


Figure 1. Stratégie d'étude développée pour l'étude de la réactivité à long terme des résidus de traitement dans le cadre du PNGMDR (Descostes, 2017).

L'ensemble des résultats acquis à ce jour a fait l'objet de plusieurs rapports d'avancement (Descostes *et al.*, 2013 ; Nos *et al.*, 2014 ; Ballini, 2018). Le présent rapport d'avancement présente plus particulièrement les modélisations concernant la stabilité à long terme des résidus de traitement du site de Bellezane, en accord avec les prescriptions de la dernière réunion bilan sur les études réalisées dans le cadre du PNGMDR (Mauroux, 2019). Ces travaux ont fait l'objet par ailleurs de valorisation et d'expertise au travers de

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communications scientifiques dans des congrès (Nos *et al.*, 2013 ; Ballini *et al.*, 2017) et une revue scientifique de rang A à comité de lecture qui est jointe à ce rapport (Ballini *et al.*, 2020 ; Cf. §7. Annexe). Le présent rapport s'articulera donc autour des chapitres suivants :

Chapitre 2 : Cette section synthétise les caractéristiques historiques sur la division minière de la Crouzille et le site de Bellezane ;

Chapitre 3 : Dans ce chapitre, les méthodes et matériels développés durant cette étude sont rappelés avec un focus sur les hypothèses de modélisation retenues pour évaluer la mobilité à long terme de l'U et du ^{226}Ra au sein des résidus de traitement ;

Chapitre 4 : Dans cette partie du rapport, deux types de modélisation ont été effectuées visant d'une part à évaluer la distribution de l'U et du ^{226}Ra dans les conditions de diagénèse aujourd'hui observées, et d'autre part, de simuler l'évolution à long terme des résidus de traitement lessivés par les eaux d'infiltration ;

Chapitre 5 : Conclusion et perspectives.

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2. Rappels historiques sur la Division minière de la Crouzille et le site de Bellezane

La division minière de la Crouzille est localisée en Haute Vienne (France), dans un périmètre de 20 km autour de la ville de Bessines-sur-Gartempe (Figure 2). Elle s'est établie dans une zone cristalline au N-O du Massif Central (Bavoux and Guiollard, 2003), caractérisée par de larges intrusions granitiques particulièrement enrichies en Uranium, mises en place entre 360 et 290 Ma, lors de l'orogénèse hercynienne. D'Ouest en Est, elle est constituée du massif de la Brême, du massif de Saint Sylvestre et du massif de la Marche (ou de Guéret) (Scaillet *et al.*, 1996).

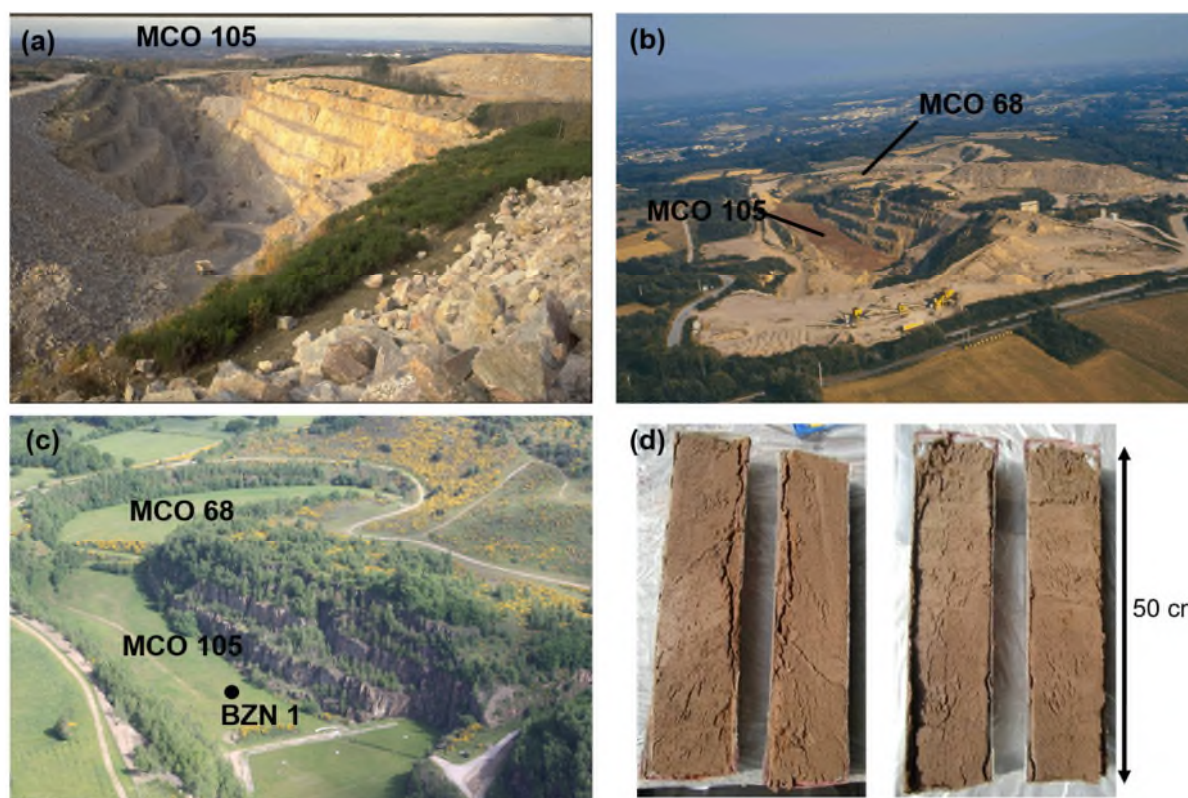


Figure 2. Site de Bellezane en exploitation (a), pendant le comblement des MCO 105 et 68 par les résidus de traitement (couleur rouge) (b), après le réaménagement (c) et photographie des carottes de résidus de traitement prélevées lors de cette étude en (d). La localisation du sondage BZN 1 dans la MCO 105 est donnée en (c). Illustrations reprises de Ballini *et al.* (2020).

La majorité des gisements exploités au sein de la division minière de la Crouzille se situe au sein du Massif de St Sylvestre et plus précisément dans le leucogranite à deux micas (biotite et muscovite) de Saint Sylvestre (318 ± 15 Ma). Sa composition chimique est rappelée plus loin en Figure 3. Dans ce massif, des filons de lamprophyres (roche magmatique filonienne microgrenue) à biotite, pyroxènes et périclites, des filons de microgranites, associés aux lamprophyres, avec phénocristaux de biotites et plagioclases, des épisyénites (granites déquartzifiés), parfois fortement minéralisées, présentes sous forme de colonnes ou d'amas sont également observés (voir Scaillet *et al.*, 1996; Kanzari *et al.*, 2017, et références incluses).

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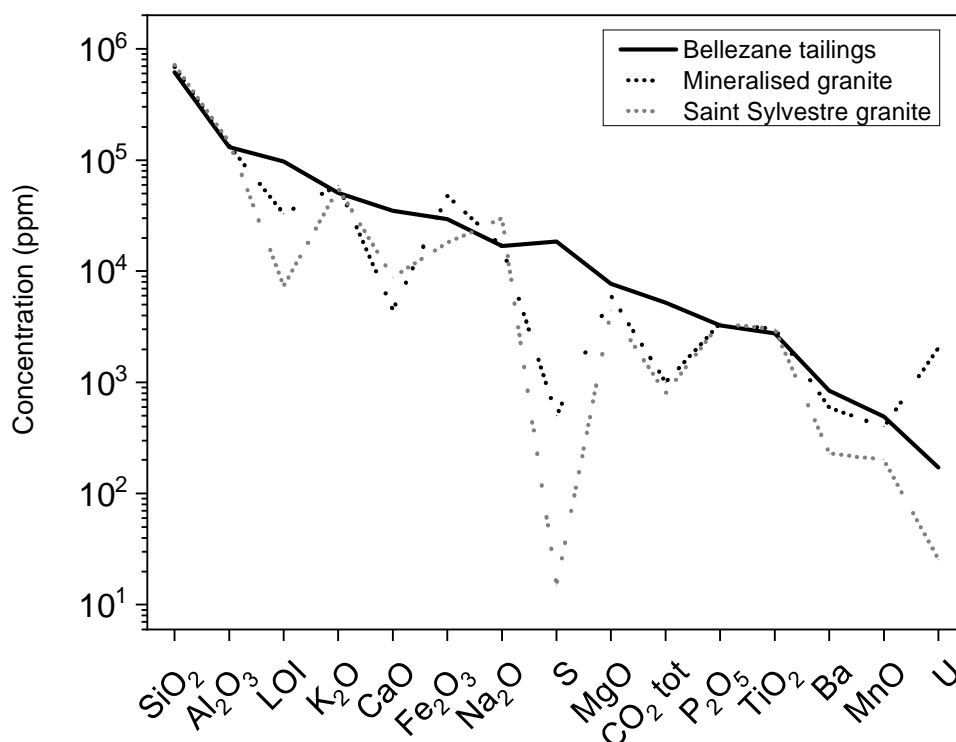


Figure 3. Concentrations élémentaires moyennes (ppm) des résidus de traitement de BZN et du granite de Saint Sylvestre minéralisé et non minéralisé (repris de Ballini *et al.*, 2020 ; données d'après Boekhout *et al.*, 2015 et Kanzari *et al.*, 2017).

La minéralisation est constituée des silicates ou des oxydes d'uranium (coffinite et uraninite) en profondeur et accompagnée par des minéraux d'altération en surface tels que les phosphates ou les oxydes hydratés d'uranium (autunite et gummite) (Barbier and Ranchin, 1969). La teneur moyenne en uranium des minerais de la division de la Crouzille était comprise entre 0,49‰ pour le secteur de secteur de Daumart, Margnac et 7‰ pour la mine d'Henriette (Figure 4 ; Paucard, 2007). La division minière de la Crouzille constituait la principale zone de production d'uranium en France avec une vingtaine d'exploitations minières distinctes, une production de 27 000 tU sous forme de diuranate d'ammonium (DUA) contenant 75% d'uranium, pour près de 15 Mt de minerai traités. Cette activité minière a généré par ailleurs 57 Mt de stériles miniers et 22 Mt de résidus de traitement (AREVA, 2004; Kanzari *et al.*, 2017).

De 1958 à 1993, le minerai de la division minière de la Crouzille (teneur moyenne de 1.66 ‰) a été traité à l'usine SIMO (Société Industrielle des Minerais de l'Ouest, rendement 95 % ; Bavoux and Guiollard, 2003) située sur la commune de Bessines-sur-Gartempe par voie acide, soit par lixiviation en tas (8 614 000 tonnes de minerai), soit par traitement dynamique (14 839 000 tonnes de minerai) en fonction de la teneur du minerai (Bavoux and Guiollard, 2003). Dans le cas de la lixiviation dynamique, le minerai était concassé puis broyé en une pulpe de granulométrie inférieure à 450 µm (Bavoux and Guiollard, 2003). La pulpe était ensuite attaquée par ajout d'acide sulfurique à 65°C en présence d'un oxydant, le chlorate

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de sodium. Après filtration, les résidus solides étaient lavés, neutralisé à la chaux (CaO) et envoyés vers un bassin de stockage. Les procédés ont très peu évolué pendant toute l'exploitation de l'usine.

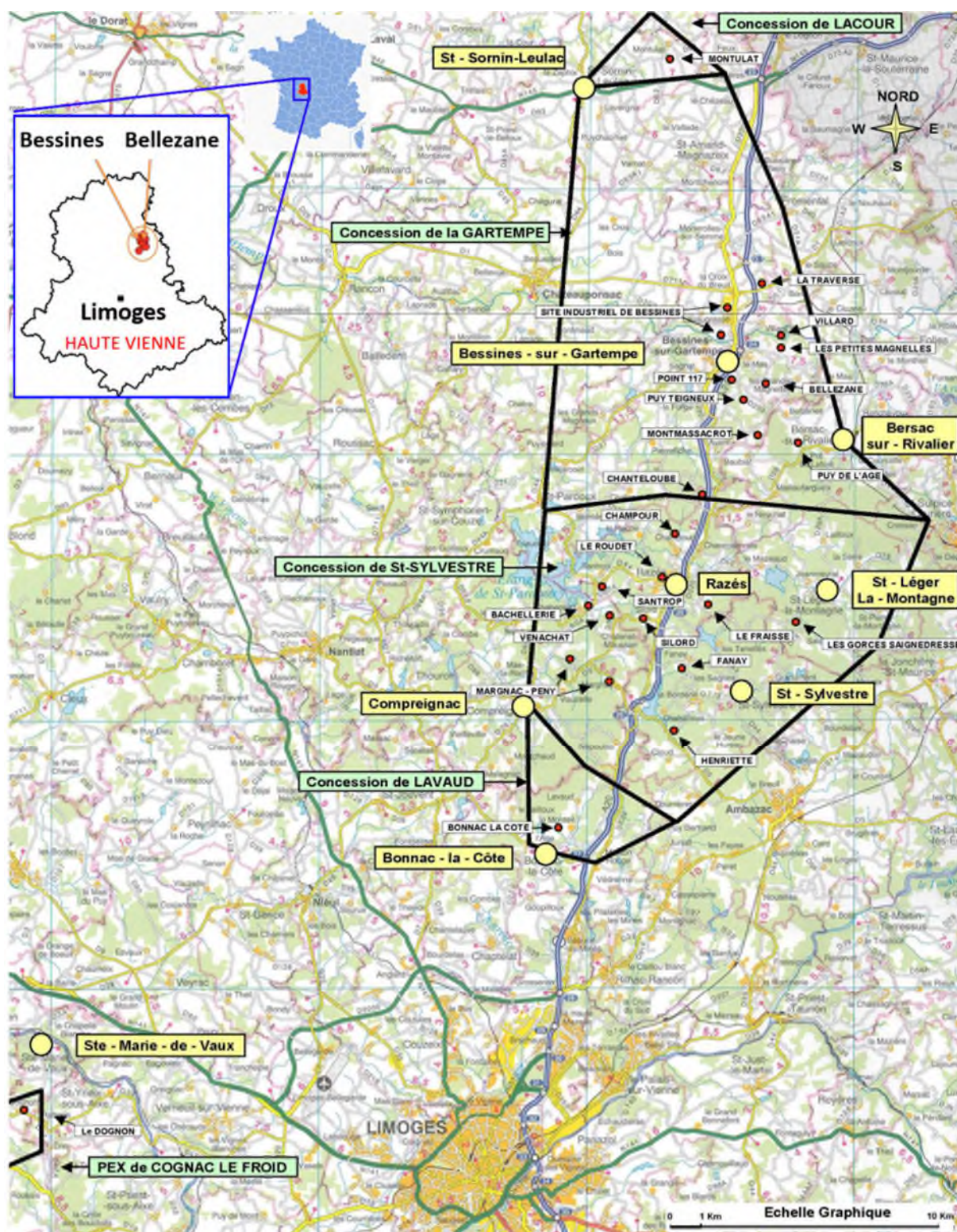


Figure 4. Localisation de la division minière de la Cruzille et de ses concessions, localisation du site de stockage de résidus de traitement de Bellezane (GEP, 2010).

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Les résidus de traitement produit l'usine SIMO ont ainsi été stockés dans le site industriel de Bessines (Lavaugrasse) de 1958 à 1978 et dans l'ancienne MCO du Brugeaud jusqu'à 1987. Ensuite, deux stockages ont été créés par élévation d'une digue périphérique sur les sites de Montmassacrot entre 1987 et 1990 et sur le site de Bellezane (BZN) de 1989 à 1993 (Figure 4). **Au total, 1 546 000t de résidus de traitement sont stockés sur le site de BZN dont 97% sont issus de traitement dynamique, se présentant sous la forme d'un sable fin argileux de granulométrie inférieure à 450 µm.**

Avant d'être un site de stockage de résidus, le site de BZN a été exploité via sept mines à ciel ouvert de différentes tailles et des travaux miniers souterrains de 1975 à 1992. Les MCO ont été partiellement comblées au fur et à mesure de l'exploitation par des stériles et des résidus de traitement, la MCO 68 de février 1989 à juillet 1990, puis la MCO 105 d'août 1990 à juillet 1993 (Figure 2). Le réaménagement final du site a eu lieu 1996, les résidus de traitement présents dans les MCO 105 et 68 ont été recouverts d'une couche de stériles servant de protection mécanique (érosion, intrusion) et radiologique (pour limiter l'émission de rayonnements et l'émanation de radon). Le stockage, ainsi que les zones remodelées de l'ensemble du site, ont été recouverts en 1998 d'une couche de terre végétale puis revégétalisés (Figure 2). Aujourd'hui, le site de BZN, composé d'un stockage de résidus et de verses à stériles, fait l'objet d'une surveillance environnementale. Les eaux d'exhaure sont rejetées, après traitement, dans le ruisseau des petites Magnelles, affluent de la Gartempe. Du point de vue hydrogéologique, des précédents travaux ont montré d'une part, que les résidus de traitement sont saturés et d'autre part, que leur perméabilité est très faible, de l'ordre de 10^{-8} à 10^{-9} m.s⁻¹ (Ledoux and Schmitt, 2010). Ceci a été confirmé notamment par la bonne corrélation entre la pression atmosphérique et le niveau piézométrique du piézomètre implanté dans les résidus (Figure 5), corrélation typique des milieux pour lesquels la perméabilité est très faible (Fatmi *et al.*, 2008). Les mouvements d'eau sont ainsi très limités au sein du stockage du fait de leur très faible perméabilité.

Les résidus de traitement stockés dans les deux MCO du site de BZN sont décrits comme ho-mogènes du point de vue granulométrique (< 450 µm), minéralogique et chimique (Somot *et al.*, 1997, 2000). En effet, les minerais en provenance des exploitations minières, traités à l'usine SIMO, présentaient des compositions chimiques et minéralogiques très proches tandis que les procédés de traitement ont peu été modifiés entre 1989 et 1993, période pendant laquelle les résidus ont été stockés sur le site de BZN.

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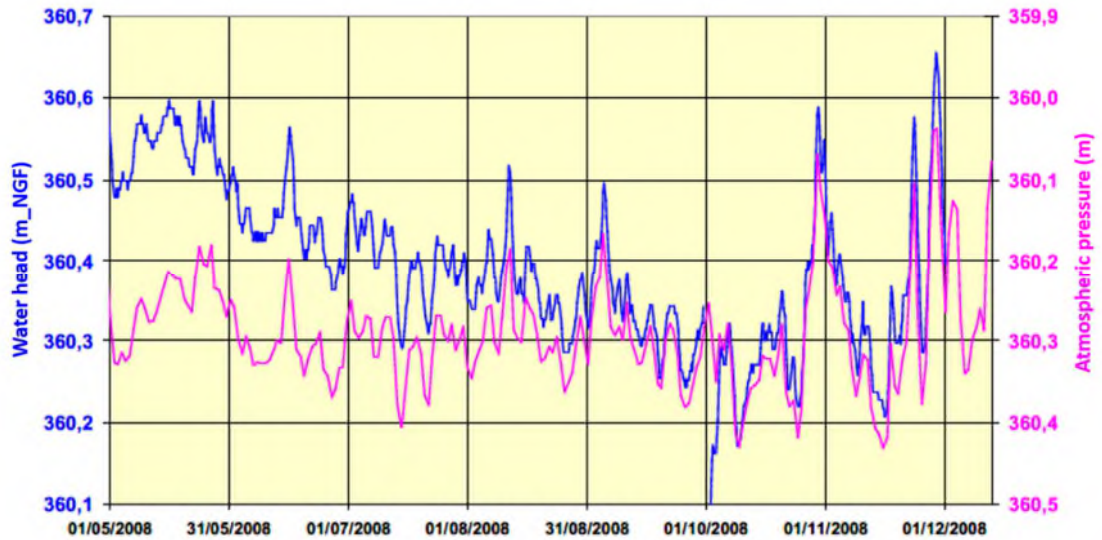


Figure 5. Corrélation entre la hauteur piézométrique mesurée au niveau de ES85 et la pression atmosphérique (Ledoux and Schmitt, 2010).

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3. Méthodes et matériels

3.1. Stratégie d'échantillonnage et méthodes de caractérisation

L'ensemble de la méthodologie développée ainsi que les diverses méthodes analytiques ont été longuement détaillées dans les précédents rapports d'avancement (Descostes *et al.* 2013 ; Nos *et al.*, 2014). Le lecteur est également renvoyé vers ces rapports ainsi que la synthèse disponible dans Ballini *et al.* (2020) pour les résultats de caractérisation. La composition des eaux interstitielles est ici reportée pour faciliter la lecture du présent rapport (Cf. Tableau 1).

Tableau 1 : Composition chimique de la solution interstitielle ES85 analysée et modélisée et de l'eau granitique (ES60 ; Ledoux and Schmitt, 2010) percolant dans la colonne de résidus de traitement (voir Ballini *et al.*, 2020 pour plus de détails). Toutes les concentrations sont exprimées en mol/L à l'exception du ²²⁶Ra qui est exprimée en Bq/L.

	ES85-Measured	ES85-Modeled	ES60
Eh (mV/SHE)			
Ionic strength			
Anions			
[Cl] _{tot}	8.5x10	8.5x10	1.8x10
tot	7.8x10	7.8x10	7.4x10
tot	1.2x10	1.2x10	
tot	4.3x10	4.3x10	2.3x10
tot	7.6x10	7.6x10	6.3x10
[Si] _{tot}	1.5x10	9.4x10	2x10
	2.5x10	2.6x10	6.6x10
Cations			
tot	8.9x10	8.9x10	2.5x10
tot	1.7x10	1.6x10	3.8x10
[Mg] _{tot}	3.3x10	3.3x10	1.4x10
tot	1.3x10	1.5x10	2.8x10
[Sr] _{tot}	3.8x10	3.8x10	
tot	1.0x10	3.8x10	2.83x10
Metals			
[Al] _{tot}	7.0x10	3.2x10	6.9x10
[Mn] _{tot}	1.0x10	1.0x10	
[Fe] _{tot}	7.9x10	7.9x10	1x10
tot			
tot	1.2x10	1.2x10	1.7x10
Elec. Bal. (% err)			

3.2. Modélisations

Deux types de modélisation ont été effectuées. Dans un premier temps, la distribution de l'U et du ²²⁶Ra a été évaluée afin de décrire les conditions de diagénèse aujourd'hui observées. Cette modélisation est effectuée en mode statique, c'est-à-dire en considérant les équilibres physico-chimiques régulant la composition chimique des eaux interstitielles au contact des résidus de traitement. Dans un second temps, la mobilité de l'U et du ²²⁶Ra a été appréhendée au travers de modélisations de type transport réactif 1D en simulant l'évolution à long terme des résidus de traitement lessivés par les eaux d'infiltration. Dans ce dernier cas,

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l'évolution de la chimie des eaux a été simulée en considérant une colonne de 25 m de résidus de traitement dans laquelle circule une eau d'infiltration de type granitique (ES-60 ; Cf. Tableau 1). L'évolution des fractions immobilisées du ^{226}Ra de l'uranium est également simulée en fonction du temps. Les durées simulées ont été jusqu'à 230 000 ans afin de mieux appréhender le rôle des différents pièges minéralogiques tels que les minéraux argileux, les hydroxydes ferriques et dans le cadre plus spécifique du ^{226}Ra , la barytine. Le détail des conditions de modélisation est fourni dans Ballini *et al.* (2020).

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4. Mobilité à long terme de l'U et du ²²⁶Ra au sein des résidus de traitement

4.1. Distribution actuelle de l'U et du ²²⁶Ra

A partir des caractérisations des eaux interstitielles et des résidus de traitement, il est possible de montrer que la majorité de l'U et du ²²⁶Ra est piégée à plus de 99% dans la fraction solide (Cf. Figure 6). Toutefois, l'étude géochimique et minéralogique des résidus seule est souvent insuffisante pour identifier les compartiments porteurs de l'U et du ²²⁶Ra au sein des résidus, et ainsi d'évaluer leur mobilité. De plus, il n'existe aucun traceur univoque de ces compartiments permettant de les identifier et quantifier facilement. Les observations microscopiques ont permis de mettre en évidence la présence de quelques minéraux réfractaires d'Uranium (uraninite et coffinite) piégés principalement au sein de quartz. Les caractérisations complémentaires par TRLFS (Time Resolved Laser Fluorescence Spectroscopy) ont permis de préciser qu'une partie de l'U est également sorbé sur la smectite (Ballini *et al.*, 2020). Cependant cette technique ne permet pas de mettre en évidence la sorption de l'U sur les HFO. Il est impossible de réaliser ce type d'analyse pour le ²²⁶Ra du fait de sa trop faible concentration élémentaire (~ 700 ppt). Sa spéciation peut être étudiée toutefois indirectement par lixiviations séquentielles. Cependant, ces expérimentations complexes peuvent présenter des biais analytiques importants. Les compartiments visés ne sont pas totalement indépendants les uns des autres et il peut exister des phénomènes de recombinaisons élémentaires au cours d'un lavage, à l'origine de résultats de rendements faussés (Bacon and Davidson, 2008). Des modélisations à l'équilibre thermodynamique ont donc été réalisées afin d'étudier la distribution de l'U et du ²²⁶Ra au sein des résidus de BZN.

La composition chimique de l'eau interstitielle mesurée dans le piézomètre montre que l'eau interstitielle des résidus de Bellezane est proche de l'équilibre avec des polymorphes du quartz (SI = 0.2), des aluminosilicates et notamment de la smectite (SI = 0.1), la calcite (SI = 0.0), la ferrihydrite (IS = -0.4) et le gypse (IS = -0.1) et légèrement sursaturée vis-à-vis de la barytine (0.5). Ceci est cohérent avec la minéralogie des résidus de traitement précédemment décrite. L'assemblage minéralogique composé de calcédoine (29 %), feldspath potassique (35 %), montmorillonite-Ca (25 %), ferrihydrite (0.6 à 1.1 % comme en fonction du modèle comme discuté au paragraphe ci-dessous), gypse (9 %), calcite (0.5 %), et barytine (0.15 %), permet de décrire la réactivité chimique du système solide-solution au sein des résidus de BZN tout au long des processus d'interaction, et de simuler la composition chimique de l'eau porale des résidus au cours du temps. Les proportions des phases minérales dans l'assemblage à l'équilibre ont été calculées à partir de la composition élémentaire des résidus. Ainsi, Si et Al sont répartis entre les argiles, la calcédoine, le feldspath potassique

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(représentant l'ensemble des feldspaths et la muscovite) et la montmorillonite-Ca (représentant l'ensemble des minéraux argileux). Mg et K sont attribués respectivement à la montmorillonite-Ca et au feldspath potassique. Na est artificiellement reporté sur les feldspaths sodiques. Fe est attribué à la ferrihydrite, tandis que S, C inorganique et Ba sont attribués respectivement au gypse, à la calcite et à la barytine. La sorption des éléments majeurs et traces (U et ^{226}Ra) sur la ferrihydrite et la montmorillonite a également été prise en compte dans la paragenèse réactive. La composition calculée de l'eau en équilibre avec l'assemblage minéralogique défini précédemment, donnée en Tableau 1 est ainsi très proche de celle de l'eau interstitielle analysée.

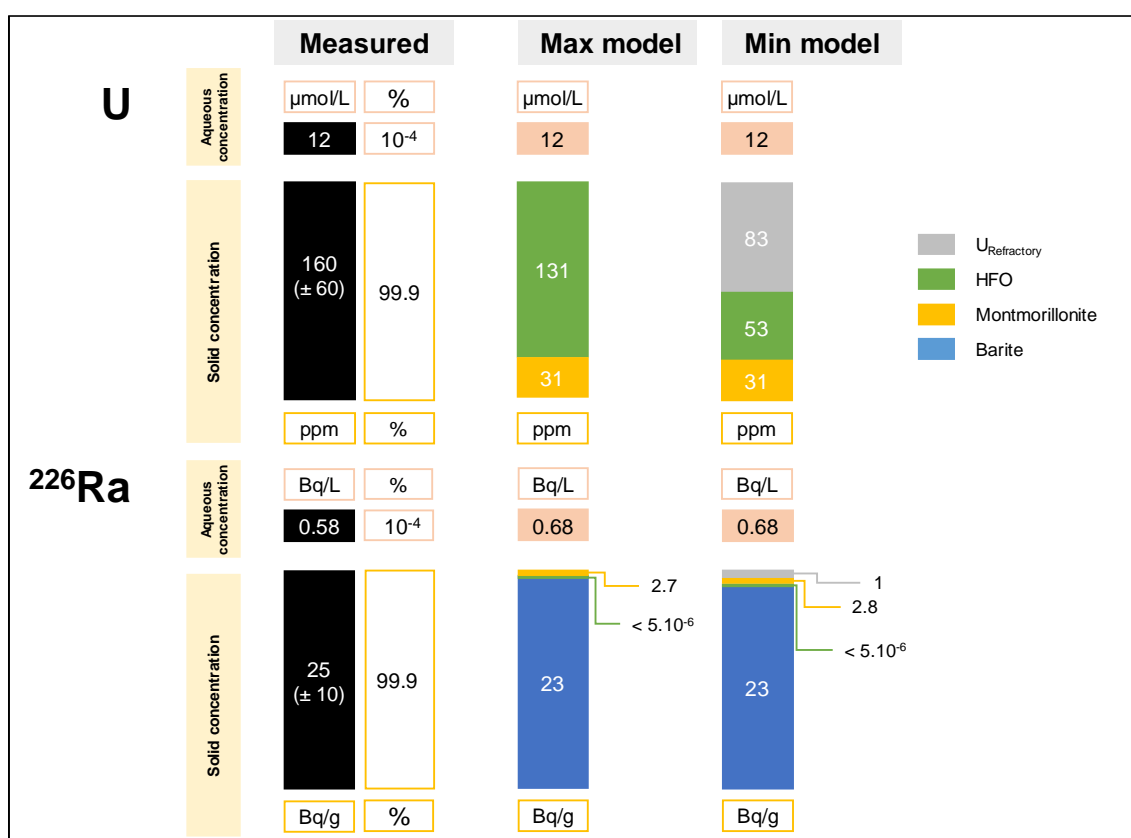


Figure 6. Distribution de l'U et du ^{226}Ra au sein des résidus de traitement selon les deux modèles développés au sein de cette étude (Min et Max). Le modèle Min considère qu'une fraction des radioéléments est piégée dans les phases héritées du minerai qui sont ici non réactives. Le modèle Max considère tous les radioéléments comme réactifs (repris de Ballini *et al.*, 2020).

La concentration moyenne en U mesurée dans le solide et de 160 ppm, dont 83 ppm (calculé avec un rendement de 95% et une teneur initiale de 1,66 ‰) peuvent être portés par des phases réfractaires fortement insolubles comme mises en avant par les précédentes caractérisations minéralogiques. Un modèle minorant (Min) prenant en compte la présence des phases réfractaires et un modèle majorant (Max) ne les considérant pas en compte sont donc présentés. La seule différence entre ces deux modèles est donc la concentration en

ferrihydrite. Pour le modèle majorant, la quantité de fer est portée exclusivement par la ferrihydrite tandis que pour le modèle minorant, le fer est réparti entre la pyrite (FeS₂) et la ferrihydrite, en respectant le bilan sur le soufre. La quantité de ferrihydrite est donc respectivement de 0.6% et de 1.1% pour le modèle majorant et le modèle minorant.

Ainsi, le calcul de spéciation effectué dans les eaux interstitielles de Bellezane indique que l'uranium en solution se trouve exclusivement sous forme hexavalente à la concentration de $1.2 \cdot 10^{-5}$ mol/L (2.9 mg/L). Du fait de la forte fugacité en CO₂ dissous, les complexes carbonatés sont majoritaires (UO₂(CO₃)₃⁴⁻ : 78.5 % ; UO₂(CO₃)₂²⁻ : 21 % ; UO₂CO₃ : 0.5 %). Les complexes ternaires calcium-uranyl-carbonates n'ont cependant pas été intégrés dans le modèle du fait de la forte incertitude sur leur constante de formation. L'analyse des indices de saturation suggère que la concentration en U n'est contrainte par aucun équilibre avec une phase minérale pure, aucune phase uranifère n'étant à l'équilibre. La sorption à la surface des minéraux argileux et des HFO a donc été envisagée pour expliquer les concentrations en U mesurées dans la fraction solide des résidus et les eaux interstitielles en accord avec les caractérisations minéralogiques et par TRLFS (Ballini *et al.*, 2020). La quantité d'U sorbé a donc été calculée en considérant une eau à équilibre avec la paragenèse minérale réactive et incluant les mécanismes de sorption. Ainsi, la concentration dans la phase solide (en équilibre avec la concentration imposée en solution de $1.2 \cdot 10^{-5}$ mol/L, soit 2.9 mg/L) est correctement reproduite (160 ppm) dont 20 à 37 % est sorbé sur les minéraux argileux et 63 à 80% est sorbé sur les HFO (Figure 6) en fonction du modèle.

La concentration en ²²⁶Ra, présent à l'état d'ultratrace dans l'environnement ne peut être contrainte par aucune phase pure. Tout comme l'U, l'activité massique du ²²⁶Ra présent dans les phases réfractaires au traitement a été calculée et s'élève à environ 1 Bq/g. D'autres mécanismes tels que la coprécipitation du ²²⁶Ra dans la barytine, la sorption du ²²⁶Ra sur les HFO et les minéraux argileux ont donc été pris en compte afin de reproduire l'activité massique en ²²⁶Ra dans le solide. La totalité du ²²⁶Ra et du Ba présents dans le résidu solide est considérée comme associée à la solution-solide (Ba,Ra)SO₄. Les modélisations ont permis de reproduire au mieux la concentration en ²²⁶Ra à l'équilibre dans l'eau interstitielle (0.68 Bq.L contre 0,58 Bq/L ; Cf. Tableau 1). Dans ces conditions, 97,2 % du stock de ²²⁶Ra est associé à la barytine, les minéraux argileux et les HFO représentant respectivement 2.8 % et 4.10⁻⁵ %.

Ainsi, ces calculs permettent de confirmer la distribution de l'U et du ²²⁶Ra au sein des résidus de traitement avec plus de 99,9% de l'U et du ²²⁶Ra dans la fraction solide, et ce, répartis quel que soit le modèle entre les minéraux réfractaires, les minéraux argileux, les hydroxydes de fer, et dans le cas du ²²⁶Ra au sein de la barytine. Les concentrations en solution en U et ²²⁶Ra peuvent être décrites selon des équilibres

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chimiques avec les minéraux précédemment cités et ne constituent qu'un stock très faible de l'ordre de $10^{-4}\%$.

4.2. Evolution de la mobilité de U et ^{226}Ra en fonction du temps

Un modèle en transport réactif 1D permettant de simuler l'effet de la percolation d'une eau granitique au sein des résidus a été réalisé pendant 230 000 ans afin d'évaluer la réactivité à long terme de l'U et du ^{226}Ra et donc leur mobilité. Cette période, bien plus importante que dix fois la période radioactive du ^{226}Ra , permet de bien comprendre l'évolution du système géochimique dans sa globalité. L'ensemble des résultats est présenté en Figure 7.

4.2.1. Evolution du système géochimique

Les variations de composition chimique des différents compartiments (aqueux, surfaces et phases minérales) de la dernière cellule de la colonne modélisée au cours de la percolation de l'eau granitique sont présentées en Figure 7a-d.

La percolation de l'eau granitique faiblement minéralisée au sein des résidus de traitement de Bellezane induit comme attendu une diminution importante de la force ionique de l'eau interstitielle pour atteindre une force ionique du même ordre de grandeur que celle des eaux granitiques (Figure 7a). Le faciès de l'eau interstitielle, initialement sulfaté magnésien, évolue au fur et à mesure de la modification des équilibres entre la phase solide, la phase liquide, et les surfaces réactives pour se rapprocher progressivement du faciès de l'eau granitique percolante. Les principaux minéraux de la paragenèse minérale ne subissent aucune dissolution ou précipitation significative pendant la durée de la simulation (Figure 7c). Seuls le gypse puis la calcite sont dissous totalement. La dissolution du gypse et la dissolution progressive de la calcite entraînent une légère augmentation du pH passant de 6.3 à 7.2 (Figure 7b). Dans un second temps lorsque le gypse est totalement dissout (23 000 ans), le pH augmente jusqu'à 8.5 durant toute la dissolution de la calcite, soit jusqu'à 100 000 ans environ, puis se stabilise vers pH 6.6 à 150 000 ans. Cette évolution du pH est liée à la sorption préférentielle du Ca, libéré par la dissolution du gypse et de la calcite, à la surface des minéraux argileux au détriment des protons (Figure 7d). Les faibles concentrations en ions majeurs de l'eau granitique ne permettent pas une redistribution suffisamment rapide des populations cationiques sorbées au profit de H^+ , K^+ et Mg^{2+} . Ceci est également vérifié dans une moindre mesure pour le Ca sorbé sur les oxy-hydroxydes ferriques mais également pour les carbonates.

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4.2.2. Mobilité de l'uranium

La modification des équilibres chimiques induite par la percolation d'une eau granitique au sein des résidus génère une redistribution de l'U entre les différents compartiments (sorption sur les minéraux argileux, sorption sur les oxy-hydroxydes de fer, minéraux réfractaires uranifères, l'ensemble de ces minéraux ayant été mis en évidence au sein des résidus). L'évolution de cette répartition au sein de la dernière cellule de la colonne en fonction du temps est donnée en Figure 7e et f pour les deux modèles précédemment développés (modèles minorant et majorant). La partie « tot solide » représente la somme des fractions sorbées sur les minéraux argileux et les hydroxydes ferriques ainsi que l'U contenu dans les phases réfractaires lorsque celles-ci sont prises en compte (modèle minorant).

La percolation d'une eau granitique peu minéralisée et faiblement concentrée en uranium au sein des résidus de Bellezane ne permet pas le lessivage de l'uranium de la fraction solide, même si les phases uranifères réfractaires au traitement ne sont pas prises en compte (modèle minorant) alors même que les conditions sont oxydantes. Quel que soit le modèle considéré, la concentration en U dans le solide est de l'ordre de 160 ppm pendant toute la durée de la simulation et varie très faiblement (diminution de 1.8 % de la quantité d'U totale dans le solide). L'uranium est ainsi retenu alternativement sur deux pièges : la sorption sur la ferrihydrite et les minéraux argileux (Figure 7f). La sorption de l'U sur les oxy-hydroxydes de fer est prépondérante pendant toute la dissolution du gypse et de la calcite (Figure 7c). La fraction sorbée sur les oxy-hydroxydes de fer diminue ensuite parallèlement à la diminution de pH (Figure 6b) tandis que la fraction sorbée sur les minéraux argileux augmente (Figure 7f). En fonction du pH, l'évolution des fractions en U sorbé est donc anti-corrélée, l'U étant piégé alternativement sur les oxy-hydroxydes de fer et les minéraux argileux. L'augmentation de pH et l'augmentation de la concentration en calcium en solution engendrée inhibe la sorption de l'uranium sur les minéraux argileux pendant cette période.

Les concentrations à l'équilibre en U dissous diminuent significativement en plusieurs étapes en accord avec sa rétention sur les oxy-hydroxydes de fer et les minéraux argileux. Ainsi, après un peu plus de 150 ans, les concentrations atteignent $\sim 10^{-6}$ mol/L (0.2 mg/L), puis diminuent durant la phase de dissolution du gypse ($\sim 8 \cdot 10^{-8}$ mol/L jusqu'à 23 000 ans, soit 19 $\mu\text{g/L}$), et à nouveau durant la dissolution progressive de la calcite ($\sim 6 \cdot 10^{-8}$ mol/L, soit 14 $\mu\text{g/L}$, jusqu'à 100 000 ans ; Cf. Figure 7e). Lorsque toute la calcite est dissoute et que le pH est revenu à pH 6.6 (150 000 ans), la concentration en U dissout est stabilisée à 10^{-8} mol/L (2 $\mu\text{g/L}$), à savoir proche de la concentration en U de la solution de percolation.

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4.2.3. Mobilité du radium-226

La décroissance radioactive gouverne principalement l'évolution à long terme de la mobilité du ^{226}Ra . La durée de simulation ici considérée, 230 000 ans, va bien au-delà des dix périodes radioactives du ^{226}Ra . Toutefois, afin d'une part, de mieux appréhender le rôle de chacune des phases piégeant le ^{226}Ra , et d'autre part d'étudier l'influence du ^{226}Ra dans les eaux de percolation, plusieurs modélisations ont été effectuées sans tenir compte de la décroissance radioactive. Les principaux résultats sont également présentés en Figure 7g-h.

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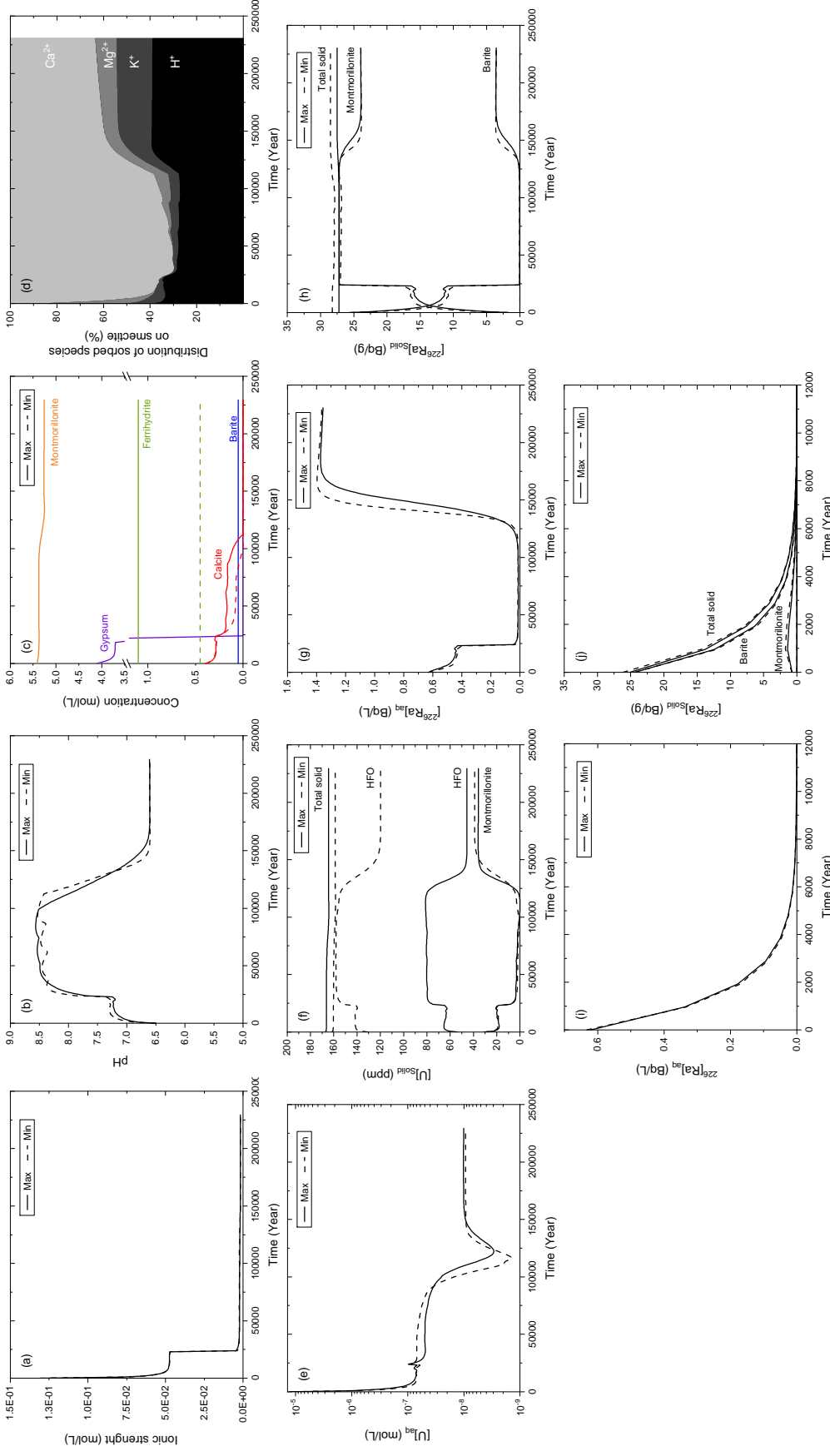


Figure 7. Modélisation à de l'évolution long terme (a) de la force ionique, (b) du pH, (c) des principaux minéraux, (d) des populations cationiques sorbées à la surface des minéraux argileux dans le cas du modèle Min (le sodium sorbé es ten quantité trop faible ici pour apparaître sur cette figure), (e) de l'uranium aqueux, (f) de l'uranium dans la fraction solide, (g) du ²²⁶Ra aqueux sans considérer la décroissance radioactive, (h) du ²²⁶Ra dans la fraction solide sans considérer la décroissance radioactive, (i) du ²²⁶Ra au sein de la fraction solide en considérant la décroissance radioactive, et (j) du ²²⁶Ra au sein de la fraction solide en considérant la décroissance radioactive (un changement d'échelle est proposé sur une durée totale de 7.5 fois la période totale de ²²⁶Ra). Le modèle Max ne considère pas la présence de phases réfractaires. Pour le modèle Min, les teneurs en U et ²²⁶Ra des phases réfractaires ont été ajoutées dans la partie tot solide sur les graphiques (f), (h) et (j).

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Quel que soit le modèle considéré (e.g. Min ou Max), le ^{226}Ra demeure toujours piégé dans le temps. En effet, la concentration élevée en SO_4 résultant de la dissolution du gypse permet à la barytine de demeurer stable. La solution solide $(\text{Ba,Ra})\text{SO}_4$ se met alors à l'équilibre avec l'eau de percolation mais la concentration aqueuse en ^{226}Ra demeure faible. En effet, le ^{226}Ra libéré de la barytine est piégé immédiatement par sorption sur les minéraux argileux (Figure 7h). Ces mécanismes de rétention complémentaires permettent de maintenir une faible concentration aqueuse en ^{226}Ra toujours inférieure à celle mesurée dans le cadre de cette étude (<0.68 Bq/L) durant 150 000 ans, soit sur une durée de l'ordre de ~ 100 périodes radioactives du ^{226}Ra (Figure 7g). Ce mécanisme est accéléré une fois que le gypse est totalement dissout (23 000 ans), les concentrations en SO_4 ne permettant plus dès lors de maintenir le complexe RaSO_4 majoritaire, qui est plus favorable au maintien de la solution solide $(\text{Ba,Ra})\text{SO}_4$ au sein de la barytine. La concentration en ^{226}Ra devient alors presque négligeable. La diminution du pH à 6.6 consécutive à la dissolution totale de la calcite et à la désorption des ions Ca^{2+} (150 000 ans), entraîne également une légère désorption du ^{226}Ra qui est à son tour coprécipité au sein de la barytine résiduelle. La concentration en ^{226}Ra augmente alors vers des valeurs proches des concentrations initiales (~ 1.4 Bq/L).

Des modélisations complémentaires ont été effectuées avec une eau de percolation ne présentant pas de ^{226}Ra . Ces modélisations fournissent les mêmes résultats que ceux présentés précédemment (voir Figure 8) indiquant que la redistribution du ^{226}Ra et en particulier que sa remise en solution après 150 000 ans est principalement gouvernée par le terme source initial que constituent ici les résidus de traitement. Sur cette base, les résultats de modélisations ont été alors corrigés de la décroissance radioactive pour chaque compartiment sondé. Les résultats sont présentés en Figure 7i et j. Comme attendu, les activités en ^{226}Ra diminuent plus rapidement, avec une distribution toujours vérifiée entre barytine et minéraux argileux et des concentrations en solution de l'ordre du bruit de fond naturel après trois périodes radioactives.

L'ensemble de ces résultats (Figure 7g-j) indique que les minéraux présentant des propriétés de rétention vis-à-vis du ^{226}Ra , présent à l'état d'ultra-trace, sont excédentaires : barytine, minéraux argileux et hydroxydes ferriques. Celui-ci est ainsi aisément piégé en fonction de l'évolution chimique du système et en particulier du pH. Lorsque la décroissance radioactive est prise en compte, l'activité massique en ^{226}Ra dans les résidus est de l'ordre de 1 Bq/g dès 5 000 ans, alors que la concentration en solution est inférieure à 0.2 Bq/L dès 1 800 ans (Figure 7i et j).

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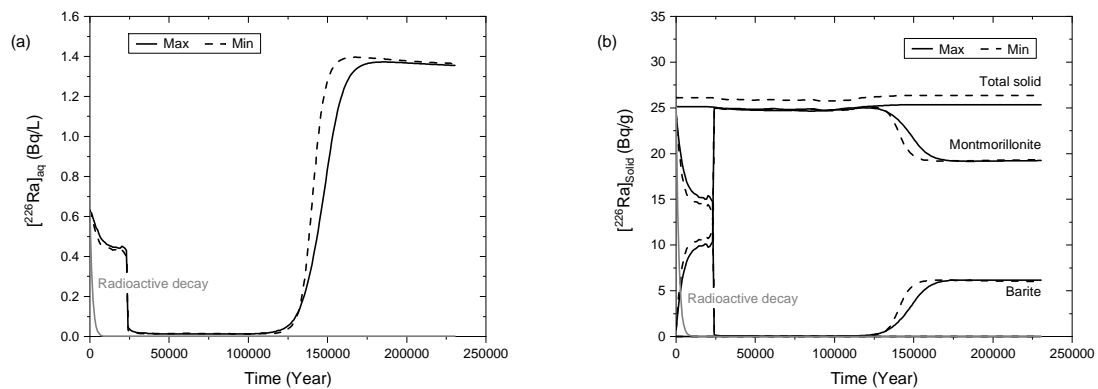


Figure 8. Evolution du ^{226}Ra aqueux en ne tenant compte de la décroissance radioactive (a), et du ^{226}Ra dans le solide en ne tenant compte de la décroissance radioactive (b) en considérant une eau de percolation sans ^{226}Ra . Les valeurs avec décroissance radioactive sont reportées en gris clair sur les deux figures.

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5. Conclusion et perspectives

Cette étude multi technique et multi scalaire des résidus de traitement de Bellezane a permis de confirmer leur stabilité chimique plus de 25 ans après leur mise en place grâce une diagénèse rapide. Ils demeurent homogènes tant d'un point de vue composition chimique, minéralogique que radiologique. En effet, les minéraux hérités du minerai (quartz, feldspaths potassiques, plagioclases et micas) sont observés en association d'une part avec leurs produits d'altération initialement présents ou néoformés (principalement des minéraux argileux tels que smectite, chlorite et kaolinite ainsi que des oxy-hydroxydes de fer), et d'autre part coexistent avec des minéraux néoformés à la suite du traitement du minerai et de neutralisation des résidus avant leur mise en place à l'instar du gypse (et dans une moindre mesure la barytine également présente dans le minerai). **L'ensemble de ces minéraux constituent des pièges efficaces quant à la rétention de l'uranium et du ²²⁶Ra en leur sein. En effet, l'uranium (160 ppm) et le ²²⁶Ra (25 Bq/g) résiduels dans la phase solide après traitement représentent plus de 99% du stock total amenant des concentrations dans les eaux interstitielles de respectivement de 12 µmol/L (2.8 mg/L) et 0.58 Bq/L pour l'U et le ²²⁶Ra.**

La réactivité chimique des résidus de traitement à long terme peut être décrite selon une approche thermodynamique incluant des équilibres de solubilité mais également de réactions de sorption et de coprécipitation dans le cas du ²²⁶Ra. **Les modélisations ainsi effectuées confirment la présence excédentaire de pièges minéralogiques (smectite, oxy-hydroxydes ferriques et barytine dans le cas spécifique du ²²⁶Ra) qui au gré de l'évolution chimique des eaux interstitielles gouvernée par la dissolution du gypse et de la calcite, maintiendront des concentrations en solution de l'U et du ²²⁶Ra toujours faibles, et ce même en conditions oxydantes, favorables normalement à la migration de l'U(VI).** De plus, la faible perméabilité des résidus de traitement stockés au sein des anciennes mines à ciel ouvert de Bellezane est à l'origine dans le cas du ²²⁶Ra d'une mobilité gouvernée principalement par la décroissance radioactive, puisque les vitesses d'écoulement estimées au sein des résidus sont de $8.10^{-8} \text{ m.s}^{-1}$.

En accord avec les discussions issues de la dernière réunion bilan sur les études réalisées dans le cadre du PNGMDR (Mauroux, 2019), l'étude de la réactivité des résidus a été étendue à la modélisation de la mobilité à long terme de l'uranium et du ²²⁶Ra depuis les sites de stockage de résidus. Il est important de préciser que les sites de stockage ne contiennent pas *sensu stricto* que les résidus de traitement mais constituent des sites plus ou moins complexes avec plusieurs termes sources potentiels supplémentaires aux résidus de

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traitement, notamment par la présence au sein de ces mêmes sites de stockage de stériles miniers, sédiments radiomarqués... Cette demande a été prise en compte depuis et passe par la définition des modèles hydrogéologiques des sites étudiés afin de greffer dans un second temps les modèles géochimiques d'évolution à long terme.

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7. **Annexe** : Ballini *et al.* (2020). A multi-scalar study of the long-term reactivity of uranium mill tailings from Bellezane site (France). Accepted in *Journal of Environmental Radioactivity*.

A multi-scalar study of the long-term reactivity of uranium mill tailings from Bellezane site (France).

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Abstract

The mill tailings from uranium mines constitute very low-level, long-lived, radioactive process waste. Their long-term management therefore requires a good understanding of the geochemical mechanisms regulating the mobility of residual U and ²²⁶Ra. This article presents the results of the detailed characterization of the tailings resulting from the dynamic leaching processes used on the ore of the La Crouzille mining division and stored at the Bellezane site (Haute-Vienne, France) for over 25 years. A multi-scalar and multidisciplinary approach was developed based on a study of the site's history, on the chemical, radiological and mineralogical characterizations of the solid fraction of the tailings, and on porewater analyses. These were supplemented by thermodynamic equilibrium models to predict the long-term mobility of U and ²²⁶Ra. Weakly acidic (pH = 6.35) and oxidizing (Eh = 138 mV/SHE) porewaters had a sulfated-magnesian facies ([SO₄]_{tot} = 43 mmol/L; [Mg]_{tot} = 33 mmol/L) with an accessory calcium bicarbonate component (TIC = 25 mmol/L; [Ca]_{tot} = 13 mmol/L) and dissolved concentrations of uranium and ²²⁶Ra of 12x10⁻⁶ mol/L and 0.58 Bq/L respectively. Ultra-filtration at 10 kDa indicated the absence of colloidal phases. The characterization of the tailings confirmed their homogeneity from a radiological, chemical and mineralogical point of view. The residual U and ²²⁶Ra concentrations measured in the solid were 160 ppm and 25 Bq/g respectively, in accordance with the initial ore grades and mill yields, or more than 99% of the total stock. In terms of chemical and mineralogical composition, the tailings were mainly composed of minerals from the granitic ore (quartz, potassium feldspar, plagioclases and micas) in association with their weathering products (smectite and ferric oxyhydroxides) and with neo-formed minerals following rapid diagenesis after neutralization of the tailings before their emplacement (gypsum and barite). All these minerals are effective traps for the retention of U and ²²⁶Ra. The uranium is distributed partly in micrometer scale uraninite and coffinite refractory phases embedded in grains of quartz, and partly sorbed to smectite and ferric oxyhydroxides. The ²²⁶Ra on the other hand is trapped mainly within the barite. The aqueous concentrations of U and ²²⁶Ra could be described using a thermodynamic approach so that their long-term mobility can subsequently be assessed by modeling. The paragenesis of the tailings could be seen to be stable over time with the exception of neo-formed gypsum and calcite, which will gradually dissolve. The presence of retention traps offering surplus capacity, *i.e.* smectite, ferric oxyhydroxides and barite, will maintain the U and the ²²⁶Ra at very low aqueous concentrations, even under oxidizing conditions. Moreover, the low permeability of the mill tailings leads, in the case of ²²⁶Ra, to behavior dictated only by the radioactive decay.

Highlights

- U mill tailings from Bellezane (France) were studied 25y after their deposition
- U and ²²⁶Ra are immobile through retention process
- U mobility is constrained by sorption onto smectite and ferrihydrite
- ²²⁶Ra mobility is governed by coprecipitation into barite and radioactive decay

Keywords

Uranium, mill tailings, ²²⁶Ra, geochemical modeling, reactivity, retention

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1. Introduction

Uranium mining took place in France throughout the second half of the twentieth century (1948-2001) with some 250 mining sites of varying sizes being operated. This yielded aggregate production of 76,000 tU at the national level, roughly the equivalent of a year's worldwide output today (WNA, 2019). At the same time, this activity generated nearly 160 Mt of mine waste rock and 52 Mt of mill tailings (AREVA, 2004).

During this period, the uranium mines were operated by conventional techniques, either as open-pit mines or underground mine workings. The ore was then milled either by heap leaching at the mining sites, or by dynamic leaching in eight processing plants or mills. The milling processes used were generally the same from case to case, consisting, after crushing the ore, in an acid extraction process in a sulfuric and oxidizing medium, involving a series of physico-chemical processes (mainly dissolution, oxidation, filtration, extraction, and concentration), leading to the formation of "yellowcake" on the one hand, and to the production of mill tailings on the other. The latter therefore corresponded to the fraction of the rock rejected after extracting most of the uranium through chemical processes. These mill tailings were then stored near the ore processing plants, as is the case for mines operating today overseas (see for instance Déjeant et al. (2016) for Niger and Robertson et al. (2019) for Canada).

Today, 17 storage facilities for mill tailings (referred to as Tailings Management Facilities or TMFs) are spread over 16 sites in France, generally located close to former production sites. Remediated in accordance with regulations on ICPE-classified environmentally regulated sites (ICPE - Installations Classées pour la Protection de l'Environnement), these TMFs are subject to environmental monitoring. Each TMF has a surface area of between one and a few dozen hectares. Depending on the mining method used, these sites may hold between a few thousand and several million tons of dynamic, static or combined process tailings (AREVA, 2004). This contrasts with current uranium extraction methods, as nearly 50% of the world's uranium production is now produced by *In Situ Recovery*, without production of mill tailings (WNA, 2019). The configuration chosen for these TMFs was determined according to the topography of each mining site. For example, the tailings could be stored "in-pit" by filling in the open pits of mined-out surface deposits, with or without a tailings dyke, or else in a thalweg dammed with a dyke. They are capped with a vegetated solid cover or water layer (see for example Chautard et al. (2017) for France and Robertson et al. (2019) for Canada). Finally, where tailings from dynamic leaching processes were cycloned, the coarser fraction was used to backfill old underground workings or to create dams, while the finer fraction was stored in tailings piles.

From a mineralogical and geochemical point of view, process tailings can be considered as milled ore that has undergone oxidative dissolution through a sulfuric medium and has a low residual uranium content. Chemical composition can sometimes be more complex because it depends on the nature of the ore undergoing the mill process, the mining process used, and the operating history of the TMF. The vast majority of the stored materials therefore consist of ore tailings, but may also contain a marginal proportion of slurry from water treatment stations. Indeed, there are three main elements of concern (or EOCs) - both from a chemical and radiological standpoint - generally associated with tailings: residual U, radon (^{222}Rn) and radium (^{226}Ra). Despite the high extraction yields achieved by the mills, the residual U is generally present in the tailings on average at concentrations in the order of 5 to 25% of that of the ore processed, i.e. in the order of 100 ppm, and may therefore present chemical toxicity in aqueous form. In addition, the mill tailings also contain the other non-extracted radionuclides belonging to the two families of natural uranium (^{238}U and ^{235}U) including radon (^{222}Rn) and radium (^{226}Ra). The installation of a solid cover or a water layer limits the migration of radon in gaseous form. With its half-life (~1600 years) and high specific activity (3.66×10^{10} Bq.g $^{-1}$), radium 226 is one of the main

EOCs in the tailings solids. The tailings thus constitute very low-level, long-lived, radioactive process waste.

Numerous studies have been conducted on the reactivity of U mill tailings (Fernandes et al., 1996; Abdelouas et al., 1998; Donahue et al., 2000; Martin et al., 2003; Moldovan et al., 2003; Landa, 2004; Scheinost et al., 2006; Essilfie-Dughan et al., 2010; Déjeant et al., 2014; Yan and Luo, 2015; Chautard et al., 2017; Liu et al., 2017). However, these studies are mostly specific to the sites considered and to the associated ores and processes. Indeed, apart from the uranium and radium, the reactivity of certain metals such as Mo, Ni, Se or As, which are sometimes present in significant quantities in the ore and are still present in the tailings, mean that these are also EOCs, distinct from those belonging to the ^{238}U radioactive decay chain.

Previous characterization work on ore tailings stored in France showed that they consist mainly of minerals inherited from the original ore, as well as a smaller fraction of minerals (gypsum, clay minerals, metal hydroxides) that have been neo-formed during rapid diagenesis after deposition (Somot et al., 1997, 2000; Nos et al., 2013; Ballini et al., 2017; Lestini et al., 2019). Consequently, mill tailings constitute a highly anthropized and complex reactive system for investigation, wherein diagenesis and weathering phenomena are observed.

More generally, the mobility of uranium and radium in the environment has been the subject of considerable scientific research (see Langmuir (1978) and Langmuir and Riese (1985)). Uranium has a complex chemistry mainly governed in the natural environment by redox and pH conditions. Insoluble under reducing conditions, it has higher mobility in an oxidizing environment, exacerbated under acid or alkaline conditions. Additionally, the presence of inorganic (carbonate, sulfate, phosphate, silicate, etc.) or organic complexing agents can also increase the solubility of uranium and hence its mobility in the environment. However, due to its concentration at trace level in the natural environment (in the order of a few ppm), the mobility of uranium, even in hexavalent form, is strongly affected by sorption reactions at the surface of clay minerals (Catalano and Brown Jr, 2005; Schlegel and Descostes, 2009; Bachmaf and Merkel, 2011; Tayal et al., 2019) or metal hydroxides (Ames et al., 1983a; Waite et al., 1994; Walter et al., 2003) frequently encountered in mining environments. Uranium can also in some cases be sorbed to organic matter (Cumberland et al., 2016; Bordelet et al., 2018), or else form very poorly soluble phosphate minerals (Murakami et al., 1997; Cretaz et al., 2013). Due to its very low elemental concentration ($1 \text{ Bq/L} \sim 1.21 \times 10^{-13} \text{ mol/L} \sim 27.3 \text{ pg/L}$), ^{226}Ra is regarded as an ultra-trace element with a fairly simple aqueous speciation (Molinari and Snodgrass, 1990). The geochemistry of ^{226}Ra in the natural environment is exclusively governed by interface reactions such as sorption on clay minerals (Ames et al., 1983b; Tachi et al., 2001; Reinoso-Maset and Ly, 2016; Robin et al., 2017), metal oxides and oxyhydroxides (Ames et al., 1983b; Nirdosh et al., 1984; Sajih et al., 2014), carbonates (Jones et al., 2011), organic matter (Bordelet et al. (2018) and references included), but also co-precipitation within sulfate-bearing minerals (Zhu, 2004; Curti et al., 2010; Zhang et al., 2014; Brandt et al., 2015; Lestini et al., 2019) such as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), celestine (SrSO_4) and barite (BaSO_4). Unfortunately, it is still difficult to directly access the location of ^{226}Ra at the mineral scale, although recent work focusing on alpha autoradiography points to some promising possibilities with observations at the micrometer scale (Sardini et al., 2016; Angileri et al., 2018). Often the only approach put forward for identifying the ^{226}Ra carrier phases is the use of sequential leaching, a method which frequently leads to interpretation bias (Bacon and Davidson, 2008).

This article presents the results of the long-term reactivity study on dynamic process tailings resulting from the milling of ore at the La Crouzille mining division and stored at the Bellezane site (Haute-Vienne, France). To conduct this study, a multi-scalar and multidisciplinary approach had been devised. This had been based on an investigation of the site's history, allowing an understanding of the composition of the tailings storage on a macroscopic scale,

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on chemical, radiological and mineralogical characterizations of the solid fraction of the U mill tailings, and on porewater analyses. These data were complemented by thermodynamic equilibrium modeling to better understand the water-rock interactions, which in a second step allowed the long-term mobility of U and ^{226}Ra to be assessed through the development of a 1D predictive model of reactive transport. This study therefore presents unique findings in relation to the characterization and understanding of the long-term geochemical evolution of U mill tailings some 25 years after their emplacement. The findings were based on multi-year studies (Descostes et al., 2013; Nos et al., 2014; Ballini, 2017) carried out under the French National Radioactive Materials and Waste Management Plan (PNGMDR ; ASN, 2019).

2. La Crouzille Mining Division and the Bellezane site

The mining division of La Crouzille is located in Haute Vienne (France), within a 20 km radius of the town of Bessines-sur-Gartempe (Figure SI-1). This is a crystalline zone in the northwestern part of the Massif Central (Bavoux and Guillard, 2003), characterized by large granitic intrusions, particularly rich in uranium, and that were formed between 360 and 290 m.y. ago during the Hercynian orogenesis. From west to east, the mining division comprises the Brême massif, the St-Sylvestre massif and the Marche (or Guéret) massif (Scaillet et al., 1996).

Most of the deposits developed within the La Crouzille mining division are concentrated in the St-Sylvestre massif and more precisely in the two-mica (biotite and muscovite) St-Sylvestre leucogranite (formed 318 ± 15 m.y. ago). Its chemical composition is shown below in Figure 1. In this massif, veins of lamprophyres (vein-type microgranular magmatic rock) with biotite, pyroxenes and peridots, microgranite veins, with biotite and plagioclase phenocrysts, and episyenites (de-quartzified granites), sometimes highly mineralized, present as columns or clusters, are also observed (Scaillet et al. (1996) and Kanzari et al. (2017) and references included).

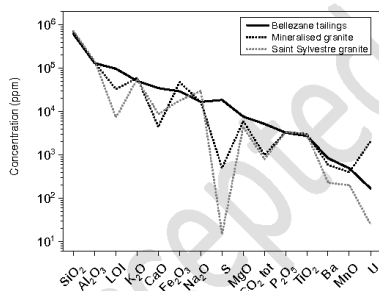


Figure 1. Mean elemental concentrations (ppm) of BZN tailings compared to mineralized and non-mineralized St-Sylvestre granite (data according to Boekhout et al. (2015) and Kanzari et al. (2017)).

Mineralization consists of silicates or uranium oxides (coffinite and uraninite) at depth and accompanied by surficial weathering minerals such as phosphates or hydrated uranium oxides (autunite and gummite) (Barbier and Ranchin, 1969). The mean uranium content of the ores in the La Crouzille division ranged from 0.49‰ in the Daumart-Margnac sector and 7‰ for the Henriette mine (Figure SI-1) (Paucard, 2007).

The Crouzille mining division was the principal uranium production area in France with about twenty separate mining operations, representing a production of 27,000 tU in the form of ammonium diuranate (ADU) containing 75% uranium, for nearly 15 Mt of ore processed. This mining activity generated in addition nearly 57 Mt of mine waste rock and 22 Mt of process tailings (AREVA, 2004; Kanzari et al., 2017).

Between 1958 and 1993, the ore from the La Crouzille mining division (average grade 1.66 ‰) was processed by the SIMO mill (Société Industrielle des Minerais de l'Ouest, 95% yield (Bavoux and

Guillard, 2003)) at Bessines-sur-Gartempe by an acid extraction process, which was either heap leaching (8,614,000 tons of ore) or dynamic leaching (14,839,000 tons of ore) depending on the ore grade (Bavoux and Guillard, 2003). In the case of dynamic leaching, the ore was crushed and then ground to a pulp with a granulometry of under $450 \mu\text{m}$ (Bavoux and Guillard, 2003). The pulp was then treated by adding sulfuric acid at 65°C in the presence of sodium chlorate as an oxidizing agent. After filtration, the solid waste was washed, neutralized with lime (CaO) and transferred to a storage pond. The processes changed very little during the entire operation of the mill.

The process tailings produced by the SIMO mill were stored at the Bessines industrial site (Lavaugrasse) from 1958 to 1978 and in the former open-pit mine of Brugeaud until 1987. Subsequently, two tailings management facilities (TMFs) were created with the erection of peripheral dams at the Montmassacrot site (between 1987 and 1990) and at the Bellezane site (BZN) (between 1989 and 1993) (Figure SI-1). In total, 1,546,000 t of mill tailings are stored at the BZN site, 97% of which are the product of dynamic leaching and take the form of fine clayey sand with a particle size of under $450 \mu\text{m}$.

Before becoming a tailings disposal site, the BZN site was an active mining site between 1975 and 1992 with seven open-pit mines of various sizes as well as underground workings. The open-pit workings were partially backfilled as mining progressed with both waste rock and mill tailings. In the case of pit MCO 68, this was from February 1989 to July 1990, and then for pit MCO 105 from August 1990 to July 1993 (Figure 1). The final remediation of the site took place in 1996, when the process tailings in MCO 105 and MCO 68 were covered over with a layer of waste rock both for mechanical protection (against erosion, intrusion) and for radiological protection (to limit radiation emissions and radon migration). The storage facility, as well as the remediated areas of the entire site, were covered over in 1998 with a layer of topsoil and then revegetated (Figure 2). Today, the BZN site, consisting of a TMF and waste rock disposal site, is subject to environmental monitoring. Drainage water is discharged, after treatment, into a stream (Les petites Magnelles), a tributary of the river Gartempe.

From a hydrogeological point of view, previous work in this area showed that the process tailings are saturated and that their permeability is very low, in the range of 10^{-9} to $10^{-6} \text{ m}\cdot\text{s}^{-1}$ (Ledoux and Schmitt, 2010). This was confirmed notably by the strong correlation between atmospheric pressure and the piezometric level of the piezometer implanted in the tailings (Figure SI-2), such a correlation being typical of media with very low permeability (Fatmi et al., 2008). Water movements are therefore very limited within the TMF.

The mill tailings stored in the two open-pit mines at the BZN site were described as homogeneous in terms of particle size ($< 450 \mu\text{m}$), mineralogy and chemistry (Somot et al., 1997, 2000). In fact, the ores from the two mining operations, processed at the SIMO mill, had very similar chemical and mineralogical compositions, while the mill processes were not significantly modified between 1989 and 1993, during which period the tailings were stored at the BZN site.

3. Methods and materials

3.1. Core drilling and sampling strategy for solids

A sonic percussion borehole was drilled in April 2011 in the downstream part of the MCO 105 pit for the BZN 1 survey. Tailings samples were collected over the entire height of the storage, with a recovery rate of $\sim 80\%$. The sampling was carried out in 1.5 m long runs on average, which were dry-subdivided into sections of 30 to 50 cm in length. Drilling, cutting and sampling techniques were chosen to avoid water inflows and preserve the sediment structure.

The samples are composed of brown and ochre fine-grain tailings, with locally darker brown and black layers and a high degree of homogeneity of facies. Dose rate measurements using a CANBERRA INSPECTOR 1000 (LaBr) radiometric probe approximately every 25 cm showed slight variability with depth,

with values ranging from 0.4 to 0.7 $\mu\text{Sv/h}$ for the first samples taken from 0 to 7.5 m deep (mine waste rock used as solid cover) and higher values ranging from 1.3 to 4.1 $\mu\text{Sv/h}$ for at higher depth (process tailings in the strict sense). After observing the facies and analyzing the dose rate of each section, thirteen of core samples were selected at regular two-meter intervals to be representative of the entire height of the tailings storage (Figure 3). Two sections

exhibiting a radiometric peak and one section corresponding to a radiometric drop were also selected. Each section was divided longitudinally into two equal parts for dose rate measurement and lithological observations. A total of 16 sections were sampled for chemical analysis, and for mineralogical and radiological characterization (Figure SI-3 and Table SI-1).

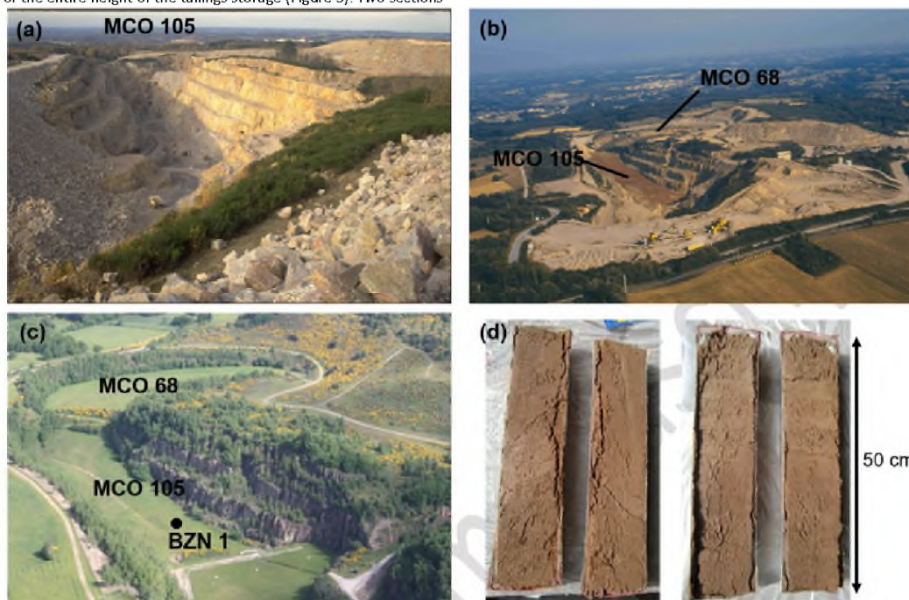


Figure 2. Bellezane site in (a) operation, (b) during backfilling of pits MCO 105 and 68 with tailings (red color), and (c) after remediation (d). Tailings core collected during this study (d). The location of the BZN 1 borehole in the MCO 105 pit is given in (c).

3.2. Analysis of the solid samples

Samples were characterized using different complementary analytical techniques. Considering the chemical, mineralogical and granulometric homogeneity of the samples, these characterizations were performed in some cases on a reduced number of samples.

3.2.1. Particle size distribution

Only one specimen (BZN_1_13.25-14.75m_2T) was used for particle size characterization. This sample was selected on account of its relatively high U content (240 ppm) and is deemed to be representative of all the samples taken. The characterizations were performed by dry sieving on a total mass of 630 g, to avoid the dissolution of soluble minerals such as gypsum and to avoid altering the chemical composition distribution within each grading category. The sieving thresholds applied were: 2 mm, 400 μm , 250 μm , 100 μm and 40 μm . Once separated, the different grading families were weighed and then subjected to chemical and radiological analyses.

3.2.2. Elemental and radiological compositions

The samples were previously ground in an agate bowl. After being fused with LiBO_2 and dissolved in acid solution. Major and trace elements concentrations were determined by ICP-OES (Thermo Elemental IRIS radial) and ICP-MS (Perkin-Elmer Elan 6000), respectively. Loss of ignition (LOI) measurements were complementary performed. Analytical uncertainties range from 1 to 15% for ICP-OES and from 5 to 15% for ICP-MS. Total CO_2 (uncertainty < 5%), C_{org} (uncertainty < 20%) and S (uncertainty < 2%) concentrations were determined with a Leco SC 144DR apparatus by calcining the sample under oxygen stream at 1400°C in the presence or not of an oxidant (iron phosphate). For C_{org} , the

measurement was carried out after elimination of the carbonates with HCl. The total inorganic carbon (TIC) content was calculated from the difference between the total CO_2 and C_{org} concentrations.

The ^{238}U , ^{234}Th and ^{226}Ra concentrations were also determined on the previously ground samples, after a one-month waiting period so that daughters ^{214}Pb and ^{214}Bi would be in equilibrium with their parent. The measurements were made by gamma-ray spectrometry according to the NF ISO 18589-3 standard (apparatus comprising Canberra COAX type N type EGC 35-195-R, Canberra BEGe type BE5030P and DSG type NGC 4021).

3.2.3. Mineralogy

As the BZN samples were already relatively fine, no grinding was necessary prior to characterization by X-ray diffraction. The characterizations were performed in parallel with a Bruker D8 diffractometer (CREGU, Nancy) and an X'Pert Pro Panalytical (IMPMC-UPMC, Paris), both with Cobalt anode. Two types of samples were analyzed: on the one hand, non-oriented bulk rock powders used to determine the predominantly present mineral phases and, on the other hand, fractions < 2 μm collected by wet granulometric separation on bulk samples, in the form of oriented deposits to more accurately determine the presence of clay minerals. These oriented preparations were then treated with ethylene glycol and heated to 550°C for 3 hours.

Seven tailings samples were studied using a scanning electron microscope (SEM) on a thin section and/or in powder form. The observations were made on a Hitachi FEG S4800 device coupled with a wavelength dispersion spectrometer (WDS). For thin sections, a JEOL JSM7600F scanning electron microscope was also used.

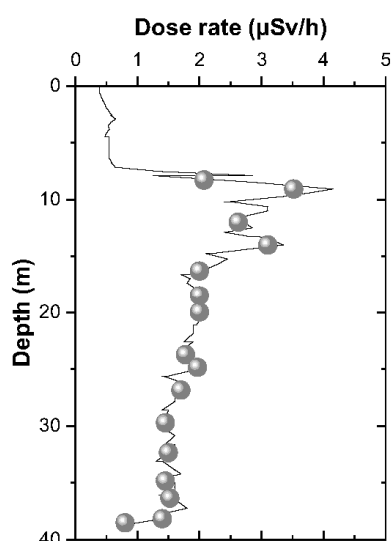


Figure 3. Dose rate measured on core as a function of depth. The grey dots represent the samples that have undergone full characterization.

Uranium (VI) carrier phases were identified directly on samples fixed in resin used to make the thin sections using time-resolved laser-induced fluorescence spectrometry (TRLFS) (Vercouter et al., 2017). A sorbed U-doped montmorillonite was used as U(VI) reference compound already studied by Tayal et al. (2019). Measurements were made using an arrangement featuring a 266 nm nanosecond excitation laser and collection of luminescence emission through an optical fiber connected to a monochromator and an intensified CCD camera (Othmane et al., 2016).

3.3. Porewater chemistry

The porewater from the process tailings was sampled in July 2013 in piezometer ES85 capturing the core of the storage located near the BZN 1 borehole using a WATERRA pump. A complete purge of the piezometer was performed the day before the sampling. A second (partial) purge was carried out just before sampling, until the physico-chemical parameters were stabilized. The physico-chemical parameters were measured online using a HORIBA probe (model W-22XD) for pH, redox potential and temperature, a WTW TetraCon 325 electrode for conductivity and a WTW FDO 925 electrode for dissolved oxygen. All the probes were pre-calibrated.

On site, immediately after sampling, the samples were filtered through a 0.2 µm pore-size filter. The samples were also immediately ultrafiltered through 10 kDa using BIOMAX membranes for analysis of anions, organic carbon (C_{org}), major cations, metals, U and ²²⁶Ra to verify the presence of colloids. All samples were acidified for conservation (HNO₃ pH 2) except for the anion and C_{org} fractions. The alkalinity was also measured by titration with sulfuric acid immediately after field filtration allowing the total inorganic carbon concentration (TIC) to be recalculated. The samples were then analyzed for anions by ion chromatography (DIONEX ICS 5000 - DX 500, standard NF EN ISO 10304-1), the sulfate and phosphate ions being determined by photometry (ThermoFisher AQUAKEM 250 sequential analyzer, NF T 90-040 and NF EN ISO 6878 standards). The concentrations of the major cations (Na, K, Ca, Mg) were determined by flame atomic absorption (AGILENT AA240, standards NF T90-020 and NF EN 7980). Si and trace elements (Al, As, Ba, Cu, Fe, Mn, Mo, Sc, Se, Sr, V) were assayed by ICP-AES (VARIAN 720ES, standards NF EN ISO 11885 and 2 N) but also by ICP-MS (THERMO ELECTRON X7, standard ISO

17294-2) for rare earth elements (Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Y, Yb) and U. Dissolved total organic carbon was quantified on a Shimadzu TOC VCPN analyzer (standard 79 N). Lastly, aqueous ²²⁶Ra activities were determined by gamma-ray spectrometry after a one-month waiting period (see Section 3.2.2 Elemental and radiological compositions).

3.4. Reactive transport modeling

Modeling was carried out using Phreeqc software (Parkurst and Appelo, 1999) to describe the speciation and distribution of U and ²²⁶Ra in the porewater and tailings system in thermodynamic equilibrium, and to evaluate U and ²²⁶Ra concentrations over the mid-term and long-term using predictive calculations according to a 1D model for reactive transport.

The thermodynamic database used for the construction of the geochemical models was the LLNL database (llnl.dat 4023 2010-02-09) for Phreeqc. The ionic strength correction model used was the extended Debye-Huckel model, considered sufficiently accurate to predict the activities of aqueous species up to ionic forces of 0.3 to 1 molal (Bethke, 2007). Sorption of major elements and Ba onto ferrihydrite (HFO) was taken into account via the surface complexation model of Dzombak and Morel (1990) and the constants already incorporated in the LLNL database. Sorption of U and ²²⁶Ra and carbonates onto ferrihydrite was implemented in the database considering surface complexation data from Mahoney et al. (2009) and Sajih et al. (2014). Cation exchange reactions on montmorillonite of the major cations, uranium and radium 226 were incorporated considering a multi-site ion exchange model (Reinoso-Maset et al., 2012a, 2012b; Reinoso-Maset and Ly, 2014, 2016). The sorption constants used are indicated in Tables SI-2 and SI-3. The incorporation of ²²⁶Ra into a solid solution (Ba,Ra)SO₄ was considered using the concentrations of ²²⁶Ra, Ba and SO₄²⁻ measured in the tailings porewater and the total contents of Ba and Ra in the tailings. The solid/solution distribution coefficient (D) for Ra, under thermodynamic equilibrium conditions is expressed as follows:

$$D = \frac{\frac{[Ra]_{solid}}{[Ba]_{solid}}}{\frac{[Ra]_{solution}}{[Ba]_{solution}}} = \frac{f_{BaSO_4} \gamma_{Ra} K_{BaSO_4}^0}{f_{RaSO_4} \gamma_{Ba} K_{RaSO_4}^0} \quad (1)$$

$K_{BaSO_4}^0$ and $K_{RaSO_4}^0$ are the respective solubility constants of BaSO₄ and RaSO₄, γ and f respectively representing the activity coefficients of Ba, Ra in the aqueous solution and in the solid solution. Assuming a regular, diluted solid solution, the activity coefficients in the solid solution are defined as follows: $\ln f_{BaSO_4} = 0$ and $\ln f_{RaSO_4} = a_0$, a_0 being a parameter reflecting the deviation from ideality (Curti et al., 2010). A solid-solution model was therefore implemented, with a Guggenheim mean parameter a_0 of 1.27 in agreement with values reported in Brandt et al. (2015) and Vinograd et al. (2013) (e.g. $a_0 = 1.0 \pm 0.4$). The molar fraction in the solid solution was calculated and led to a molar fraction of ²²⁶Ra in the solid solution of 4.6×10^{-2} . This results in a distribution coefficient of 0.21 in agreement with values already reported in Lestini et al. (2019).

The geometry of the 1D transport model amounted to a column of 25 cells 1 m high, representing a vertical section (height 25 m) of the process tailings in the open-pit mine MCO 105 under saturated conditions. The initial conditions of the water-tailings system are described in Section 5.1 and correspond to the steady state of the pore solutions with the mineral paragenesis observed in the tailings. The transport parameters were taken from Ledoux et Schmitt (2010), namely a porosity of 0.33, a permeability of 5×10^{-8} m.s⁻¹ (high assumption) and a hydraulic load gradient of 0.16, which means a low flow velocity in the tailings of 8×10^{-8} m.s⁻¹. It therefore requires 99 years to pass through the 25 m of tailings. In this simplified configuration, the phenomena of dispersion and molecular diffusion had been disregarded, only the advective transport of the solutions being taken into account. Water percolates from the top to the bottom of the column. The composition of the percolating solution (Table 1) is based on analyses of samples taken in 2008 from the superficial granitic aquifer (ES60; Ledoux and Schmitt (2010)). The water is weakly mineralized, containing sodium bicarbonate, of low ionic strength

($I = 1.69 \cdot 10^{-3}$ mol/L), slightly acidic (pH = 6.31) and oxidizing (Eh = 319 mV/SHE). It is close to the solubility equilibrium for some aluminosilicates, including smectites, feldspars and muscovite, quartz polymorphs, aluminum hydroxides, ferrihydrite, and barite and therefore with the initial mineral assemblage used in the model (see Section 5.1 Current distribution of U and ^{226}Ra). Lastly,

it is under-saturated with respect to all uranium-carrying phases with a uranium concentration (1.7×10^{-8} mol/L) three orders of magnitude lower than that of the tailings porewater (1.19×10^{-5} mol/L). In addition, the ^{226}Ra specific activity is 0.2 Bq/L, which represents one third of the specific activity measured in the tailings.

Table 1. Chemical composition of the ESBS porewater solution (measured and modeled) and the granitic water (ES60; from Ledoux and Schmitt, 2010) percolating in the tailings column. All the concentrations are given in mol/L, except ^{226}Ra concentration in Bq/L.

	ESBS-Measured	ESBS-Modeled	ES60
pH	6.35	6.49	6.31
Eh (mV/SHE)	138	185	319
T (°C)	12	12	13.8
Ionic strength	0.13	0.13	$1.69 \cdot 10^{-2}$
Anions			
$[\text{Cl}]_{\text{tot}}$	$8.5 \cdot 10^{-3}$	$8.5 \cdot 10^{-3}$	$1.8 \cdot 10^{-4}$
$[\text{F}]_{\text{tot}}$	$7.8 \cdot 10^{-4}$	$7.8 \cdot 10^{-4}$	$7.4 \cdot 10^{-5}$
$[\text{NO}_3]_{\text{tot}}$	$1.2 \cdot 10^{-3}$	$1.2 \cdot 10^{-3}$	
$[\text{SO}_4]_{\text{tot}}$	$4.3 \cdot 10^{-2}$	$4.3 \cdot 10^{-2}$	$2.3 \cdot 10^{-4}$
$[\text{PO}_4]_{\text{tot}}$	$7.6 \cdot 10^{-8}$	$7.6 \cdot 10^{-8}$	$6.3 \cdot 10^{-7}$
$[\text{Si}]_{\text{tot}}$	$1.5 \cdot 10^{-4}$	$9.4 \cdot 10^{-5}$	$2 \cdot 10^{-4}$
TIC	$2.5 \cdot 10^{-2}$	$2.6 \cdot 10^{-2}$	$6.6 \cdot 10^{-4}$
Cations			
$[\text{Na}]_{\text{tot}}$	$8.9 \cdot 10^{-3}$	$8.9 \cdot 10^{-3}$	$2.5 \cdot 10^{-4}$
$[\text{K}]_{\text{tot}}$	$1.7 \cdot 10^{-3}$	$1.6 \cdot 10^{-3}$	$3.8 \cdot 10^{-5}$
$[\text{Mg}]_{\text{tot}}$	$3.3 \cdot 10^{-2}$	$3.3 \cdot 10^{-2}$	$1.4 \cdot 10^{-4}$
$[\text{Ca}]_{\text{tot}}$	$1.3 \cdot 10^{-2}$	$1.5 \cdot 10^{-2}$	$2.8 \cdot 10^{-4}$
$[\text{S}]_{\text{tot}}$	$3.8 \cdot 10^{-6}$	$3.8 \cdot 10^{-6}$	
$[\text{Ba}]_{\text{tot}}$	$1.0 \cdot 10^{-7}$	$3.8 \cdot 10^{-8}$	$2.8 \cdot 10^{-7}$
Metals			
$[\text{Al}]_{\text{tot}}$	$7.0 \cdot 10^{-6}$	$3.2 \cdot 10^{-6}$	$6.9 \cdot 10^{-7}$
$[\text{Mn}]_{\text{tot}}$	$1.0 \cdot 10^{-3}$	$1.0 \cdot 10^{-3}$	
$[\text{Fe}]_{\text{tot}}$	$7.9 \cdot 10^{-3}$	$7.9 \cdot 10^{-3}$	$1 \cdot 10^{-6}$
$[\text{}^{226}\text{Ra}]_{\text{tot}}$	0.58	0.68	0.2
$[\text{U}]_{\text{tot}}$	$1.2 \cdot 10^{-5}$	$1.2 \cdot 10^{-5}$	$1.7 \cdot 10^{-8}$
Elec. Bal. [% err]	6.24%	6.06%	6.83%

The modeling was carried out over a total period of 230,000 years in order to better assess the long-term reactivity of the tailings and in particular the processes at the interfaces regulating the aqueous concentrations of U and ^{226}Ra . This time span is naturally longer than 16,000 years, i.e. 10 times the radioactive half-life of ^{226}Ra . A correction for the radioactive decay of ^{226}Ra was performed retrospectively. Finally, production of ^{226}Ra from the residual stock of U in the tailings was not considered.

4. Geochemical and mineralogical characterization of the mill tailings

4.1. Composition of the porewaters

The waters taken from the core of the tailings were weakly acidic (pH = 6.35), weakly oxidizing (Eh = 138 mV/SHE) and exhibited high ionic strength (0.13 mol/L; electrical conductivity = 7630 mS/cm). The analyses displayed a satisfactory ionic balance of 6.2 and 5.8% respectively for the fraction filtered at 0.2 μm and 10 kDa, allowing these results to be exploited (Table 1). These waters had a sulfated-magnesian facies ($[\text{SO}_4]_{\text{tot}} = 43$ mmol/L; $[\text{Mg}]_{\text{tot}} = 33$ mmol/L) with a calcium bicarbonate component (TIC = 25 mmol/L; $[\text{Ca}]_{\text{tot}} = 13$ mmol/L). In addition to chloride ions (8.5 mmol/L) and sodium ions (8.9 mmol/L), iron and manganese were also observed at significant concentrations (7.9 mmol/L and 1 mmol/L respectively). The concentrations of uranium and ^{226}Ra were $12 \cdot 10^{-6}$ mol/L and $7 \cdot 10^{-14}$ mol/L (0.58 Bq/L) respectively.

Figure SI 4 shows the concentration ratio of both 0.2 μm and 10 kDa fraction for each EOC. Concentration ratios close to 1 (taking into account the measurement uncertainty) indicate an absence of colloidal phases in the sample. Examination of the ratios between the two fractions also shows that uranium and ^{226}Ra are mainly present in dissolved form. In the case of ^{226}Ra , the large variation in the ratio is due to the uncertainty of the measurement of this element (40%), which nevertheless remains at low concentration. However, exceptions are observed for nitrates ($\sim 10^{-6}$ - 10^{-5} mol/L) and copper ($\sim 10^{-9}$ - 10^{-8} mol/L) due to the cleaning protocol of the ultrafiltration device (successive rinses with HNO_3 , distilled water, basic solution to remove organic matter, distilled water) and to the pollution from the ultrafiltration system, respectively.

Nonetheless, both elements concentration in each fraction remain at trace level.

4.2. Mill tailings

4.2.1. Chemical composition

The chemical composition of the mill tailings was very homogeneous over all the samples taken as shown in Figure 4. The samples were mainly composed of Si, Al, K, Ca, Fe, S, Na and Mg in accordance with the initial composition of the ore. The average element contents measured are given in Table SI-4, as well as the minimum and maximum levels. Levels of P, Ti and Mn were an order of magnitude lower (less than 1%, by weight of oxide). The total CO_2 contents were also fairly low in the order of 0.5%. C_{org} contents were also quite low (0.28%), reflecting TIC (Total Inorganic Carbon) contents in the order of 0.22%. Concentrations of trace elements are available in Supplementary Information (Table SI-4).

The average concentrations measured are quite close to those measured within the mineralized or non-mineralized granites of the Saint-Sylvestre Massif, as shown in Figure 1. The only differences are in the measured concentrations of S, Ca, TIC and LOI, which are much lower in the reference and mineralized granites than in the tailings (CaO: 0.9-0.5% vs. 3.4-3.3%; S: 0.0015-0.05% vs. 1.8-1.5%; TIC: ~ 0.03 -0.1% vs. 0.22-0.6%; LOI: ~ 0.7 -3.3% vs. 9.5-8.2%).

Ca and S concentrations are consistent with the presence of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and to a lesser extent of calcite, in agreement with the mineralogical characterizations presented below. This is illustrated in Figure 5a, where S and TIC concentrations are indicated as a function of Ca content (expressed in mol/100g). A good correlation is observed between S and Ca contents, with a S/Ca molar ratio slightly below 1, i.e. slightly below the S/Ca molar ratio in gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). On the other hand, the molar ratio (S+TIC)/Ca is very close to 1, this excess of Ca being interpreted by the distribution of Ca within other phases such as carbonated minerals (calcite). Additionally, the good correlation LOI/S evidenced the presence of gypsum (see Figure 5b). Indeed, this mineral is strongly hydrated and can therefore be first approximated using the simple parameter of LOI. Sulfur is also

present as sulfides, but in much smaller proportions (see Section 4.2.4 Mineralogical characterization).

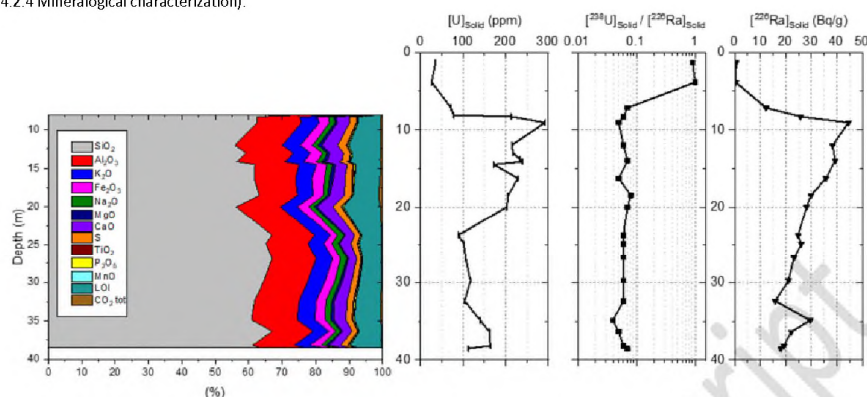


Figure 4. Elemental chemical composition of BZN tailings, $[U]_{\text{Solid}}$, $[^{238}\text{U}]_{\text{Solid}}/[^{226}\text{Ra}]_{\text{Solid}}$ mass activity ratio and $[^{226}\text{Ra}]_{\text{Solid}}$ as a function of depth.

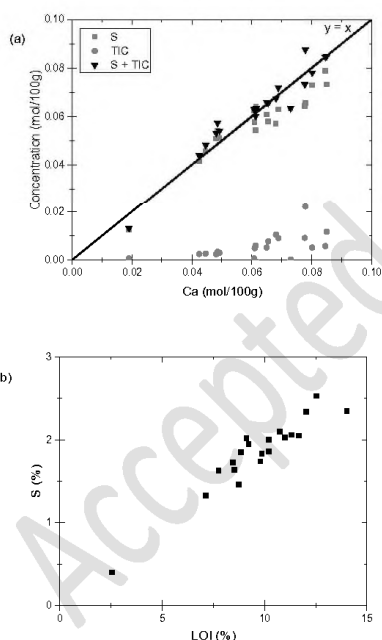


Figure 5. Molar concentrations of S and TIC as a function of molar concentrations of Ca (a). Elemental correlation in S and loss on ignition (LOI) in samples (b).

These enrichments in Ca, S and TIC are due to the initial presence of a neutralizing limewash slurry in the process tailings. The additional calcium reacts with the residual sulfur from the sulfuric acid leach to form gypsum (hydrated mineral) which is consistent with the high Ca, S and LOI levels and mineralogical observations. The addition of lime has also resulted, by increasing the pH, in the formation of carbonate precipitates in the slurries, by reacting with CO_2 from the air, a source of carbon.

All the results of the chemical and radiological characterizations are presented in the form of an element correlation matrix in Supplementary Information (Table SI-5). The correlation coefficients calculated confirm the presence of two fractions: the first enriched in Si and Na ($R_{\text{SiO}_2\text{-Na}_2\text{O}} = 0.74$) corresponding to the residual ore, and a second enriched in Ca ($R_{\text{SiO}_2\text{-CaO}} = -0.92$), Mg ($R_{\text{SiO}_2\text{-MgO}} = -0.83$), Fe ($R_{\text{SiO}_2\text{-Fe}_2\text{O}_3} = -0.93$), S ($R_{\text{SiO}_2\text{-S}} = -0.90$) and water content ($R_{\text{SiO}_2\text{-H}_2\text{O}} = -0.92$) and LOI ($R_{\text{SiO}_2\text{-LOI}} = -0.94$) which is interpreted as tracing the presence of neo-formed minerals including gypsum ($R_{\text{S-CaO}} = 0.94$, $R_{\text{S-H}_2\text{O}} = 0.87$, $R_{\text{S-LOI}} = 0.92$).

The other main correlations highlighted concern REE-type trace elements with Zr, H and P_2O_5 consistent with the presence of accessory heavy minerals such as zircon, titanium oxide and monazite (see Section 4.2.4 Mineralogical characterization).

4.2.2. U and ^{226}Ra contents

The U and ^{226}Ra concentrations measured were relatively constant for all the mill tailings samples (see Table SI-4) with mean values of 169 ± 61 ppm and 23 ± 15 Bq/g respectively. The significantly higher concentrations of U (292.4 and 239.3 ppm) were found at the highest dose rate values (at a depth of 9 and 14 m; see Figure 3). The measured values are consistent with the yields (90-95%) and average U content of the ore milled at the SIMO plant (1.66%). Furthermore, the ^{226}Ra activities measured are also of the same order of magnitude as those expected for an ore with an average grade of 1.66% at secular equilibrium before processing in the mill (20.7 Bq/g). An examination of the profiles of the $[^{238}\text{U}]/[^{226}\text{Ra}]$ activity ratio, calculated from the $^{234\text{Th}}$ activity measurements (assimilated to ^{238}U activity), can be interpreted in terms of U extraction efficiency, but may also illustrate the presence of unprocessed ores and/or differential migration of the U and ^{226}Ra (Figure 4). As the U was extracted during mining operations, the observed $[^{238}\text{U}]/[^{226}\text{Ra}]$ ratio is logically low. The two most superficial samples (at depths of about 1 and 4 m) were close to radioactive equilibrium ($[^{238}\text{U}]/[^{226}\text{Ra}] \sim 1$ with U concentrations less than or equal to 30 ppm). Then, below 7 m in depth, the activity ratio was low and fluctuated little, ranging from 0.04 to 0.08. The cover over the tailings repository consists of mine waste rock whose $[^{238}\text{U}]/[^{226}\text{Ra}]$ activity ratio is close to equilibrium, and therefore higher than that of the process tailings. The low and homogeneous $[^{238}\text{U}]/[^{226}\text{Ra}]$ values observed in the tailings confirm respectively that the extraction of U during the mill process was effective and that in principle there was no differential migration of U and ^{226}Ra .

The element correlation matrix (Table SI-6) also provides some insight into the distribution of ^{226}Ra and U. Indeed, ^{226}Ra concentrations were positively correlated with those of U ($R_{^{226}\text{Ra-U}}$).

= 0.80), which is consistent with a fraction of ^{226}Ra associated with refractory uranium minerals (see Section 4.2.4 Mineralogical characterization). However, the difference in concentrations between ^{226}Ra and the other chemical elements analyzed does not allow for clear identification of reliable elemental correlations. Thus, considering Ba and Fe, which are in principle the chemical elements tracing the carrier phases at the origin of ^{226}Ra retention (barite, ferric oxyhydroxides), no correlation was found ($R_{226\text{Ra-Ba}} = 0.11$ and $R_{226\text{Ra-Fe2O3}} = 0.51$), except with Mn ($R_{226\text{Ra-MnO}} = 0.76$). U concentrations on the other hand were correlated with those of Fe ($R_{\text{U-Fe2O3}} = 0.75$), As ($R_{\text{U-As}} = 0.80$) Mn ($R_{\text{U-MnO}} = 0.81$) and to a lesser extent with those of Ca ($R_{\text{U-CaO}} = 0.70$) and S ($R_{\text{U-S}} = 0.68$). They were also anticorrelated to Si ($R_{\text{U-SiO2}} = -0.69$) and Na ($R_{\text{U-Na2O}} = -0.61$) concentrations. The observed correlations between the concentrations of Mn, U and ^{226}Ra reflect the high affinity of these elements with respect to ferric oxyhydroxides ($R_{\text{Fe2O3-MnO}} = 0.76$ and $R_{\text{Fe2O3-As}} = 0.91$). Thus, Mn would indicate the presence of ferric oxyhydroxides known for their retention properties for both As and Mn (Dzombak and Morel, 1990; Root et al., 2007).

These elemental correlations do not strictly allow to identify the U and ^{226}Ra bearing minerals, as the volumes analyzed are too large to differentiate minerals unambiguously. It is more reasonable to attempt to associate U and ^{226}Ra with the two previously identified fractions, that is, on the one hand, the inherited fraction of the ore (predominantly SiO_2 and Na_2O) and, on the other hand, the neo-formed fraction (enriched in CaO , S , Fe_2O_3). In this manner, ^{226}Ra appears to be preferentially in the neo-formed fraction while uranium, as confirmed by the results of the particle size characterization, appears to be in both fractions.

4.2.3. Chemical composition of each particle size fraction

The majority of the particles had a size less than or equal to 400 μm (91% by mass) as shown in Figure S1-5. This result is consistent with the nature of dynamic process tailings, which are mainly composed of fine sands and fines (term used here to include silt and clay grades). This result should be considered as indicative because only one particle size analysis was conducted. Nevertheless, the study of the chemical composition of each granulometric class points to an enrichment of the smallest particle fractions with respect to LOI and Ca, S, Fe contents (LOI: from 12.7 to 17.4%; CaO: from 1.83 to 6.60%; S: from 0.65 to 3.48%; Fe_2O_3 : from 2.67 to 4.64%) associated with a decrease in Si, Na and K contents (SiO_2 : from 64.6 to 48.5%; Na_2O : from 1.57 to 1.24%; K_2O : from 6.72 to 4.70%), as observed in the overall analysis. The enrichments observed in TiO_2 and P_2O_5 are interpreted as a small increase in heavy minerals such as titanium oxides and monazite. Elemental enrichment was also visible for Ba (from 781 to 1190 ppm) as well as ^{226}Ra (from 15.7 to 65.8 Bq/g). Uranium concentration was higher in the 2000 μm fraction and to a lesser extent in the finest fraction. This results in a decrease in the $^{238}\text{U}/^{226}\text{Ra}$ activity ratio in the finest particle size fractions (from 0.29 to 0.05). These results are interpreted as a concentration of ^{226}Ra mainly associated with barite type neo-formed or inherited reactive phases found in the finest fraction of the tailings dominated by gypsum while uranium is distributed within both fractions (inherited and neo-formed).

4.2.4. Mineralogical characterizations

Characterization by X-ray diffraction (XRD) confirmed the homogeneity of the set of samples which was consistent with the chemical characterizations. Representative diffractograms on total rock and fine fraction are presented in Figure 6. They underlined the presence principally of the minerals constituting the ore, namely quartz, potassium feldspar, plagioclases and micas, but also of the phases due to weathering of the ore (smectite, chlorite and kaolinite) and inherited from the milling process, such as gypsum. Iron oxides were observed in smaller quantities. Gypsum was not observed in the fraction below 2 μm . This is explained by the dissolution of this highly soluble mineral during the extraction of the fine fraction by wet process. The XRD did not detect any U-carrier phase.

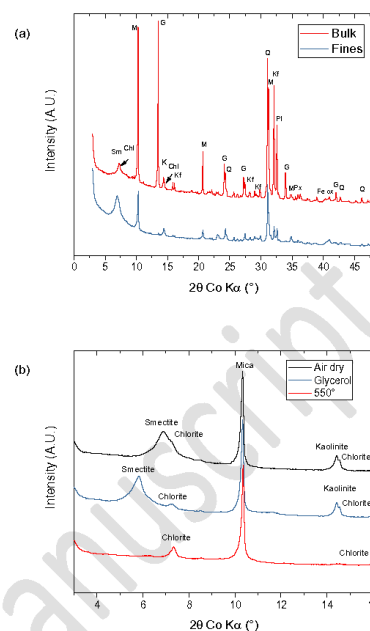


Figure 6. (a) Comparisons of X ray diffraction patterns of the bulk and the clay fraction (<math><2 \mu\text{m}</math>) and (b) clay mineralogy on oriented air-dried, glycolated and heated or tailing sample BZN_1_15_25-14./sm_31. Abbreviations: sm: smectite, Chl: Chlorite, G: Gypsum, K: Kaolinite, M: Mica, Q: Quartz, Kf: K-feldspar, Pl: Plagioclase, Fe ox: Fe oxide, Px: Pyroxene.

Elemental and micromorphological observations using SEM (Figure 7) confirmed the results of the XRD characterizations. They highlighted the presence of the St-Sylvestre granite primary minerals, but also a fairly rapid diagenesis at the scale of the storage duration of the mill tailings. This was evidenced by the observation of weathering phases of inherited minerals such as the iron oxyhydroxides which had been neo-formed mainly within phyllosilicates (Figure 7). The accessory minerals were also visible at this scale of observation, namely zircons, barite, monazites and apatite-type rare earth phosphates. Occurrences of barite in the presence of neo-formed gypsum are neo-formed barite resulting from the neutralization slurries. This neo-formed barite coexists with inherited barites since the reference and the mineralized St-Sylvestre granites already contain significant levels of Ba in the form of barite (110 and 591 ppm respectively in the granites versus 839 ppm in the tailings samples) (Barbier and Ranchin, 1969).

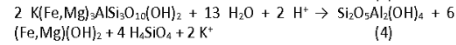
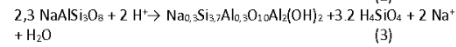
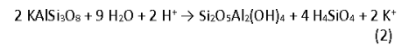
The uranium carrier phases were mainly either of the uraninite or coffinite type, generally at the micrometer scale, preserved within resistant minerals (quartz) or accessory minerals such as phosphates and zircons. These were inherited phases that had withstood the milling process. Their dimensions were smaller than the release mesh produced by grinding at 450 μm . Micromorphological analysis also indicated that sulfide-type minerals were generally not accessible to fluids.

4.2.5. Evidence of the reactivity of clay minerals

The mineralogical and elemental characterizations by XRD revealed the presence both of minerals inherited from the mineralized granites, and of sulfated, oxyhydroxide-type and also clayey neo-formed phases (in particular kaolinite and smectite). In this section, a focus is proposed on the neo-formation of clay minerals and their important U and ^{226}Ra retention properties (Schlegel and Descostes, 2009; Reinoso-Maset et al., 2012;

Reinoso-Maset and Ly, 2014, 2016; Robin et al., 2017; Tayal et al., 2019).

The use of ternary diagrams makes it possible to highlight the weathering of feldspars (and micas) as well as the formation of kaolinite and smectite type clays and oxides using only the elemental concentrations determined in the solid samples. The poles $Al_2O_3 - (CaO+Na_2O) - K_2O$ commonly used (Nesbitt and Young, 1984) could not be used because of the presence of gypsum in the samples. For this reason, results were plotted in Figure 8 on a $(K_2O+Na_2O) - ([Al_2O_3 - (Na_2O+K_2O)]/2) - ([Fe_2O_3+MgO+MnO]/3)$ diagram allowing for the consideration of an alkaline pole (representing feldspars) - $(Na,K)AlSi_3O_8$, an aluminous pole (representative of kaolinite - $Si_2O_5Al_2(OH)_4$) and finally a ferromagnesian pole (representative of micas - $K(Fe,Mg)_3AlSi_3O_{10}(OH)_2$). As a reminder, the weathering of feldspars and micas results in a depletion of alkaline elements (K and Na) and the formation of kaolinite and to a lesser extent smectite, schematically summarized below according to the respective balanced equations:



The data from the BZN tailings samples exhibited limited scatter, consistent with their homogeneity (Figure 8). Other analyses from samples from the St-Sylvestre massif are also documented (Boekhout et al., 2015; Kanzari et al., 2017). This is a non-weathered granite, an episyenite considered representative of the mineralizations, and a granitic waste rock subjected to varying stages of weathering since its first emplacement. In particular, the mineralogical and petrographic observations on these latter, more weathered samples, indicated the presence of smectite and kaolinite. The dots representing the tailings align well with the weathering profile ranging from the sound granites to the most weathered mine waste rock. They confirm the presence of clay minerals in greater quantities in the process tailings than in the ore.

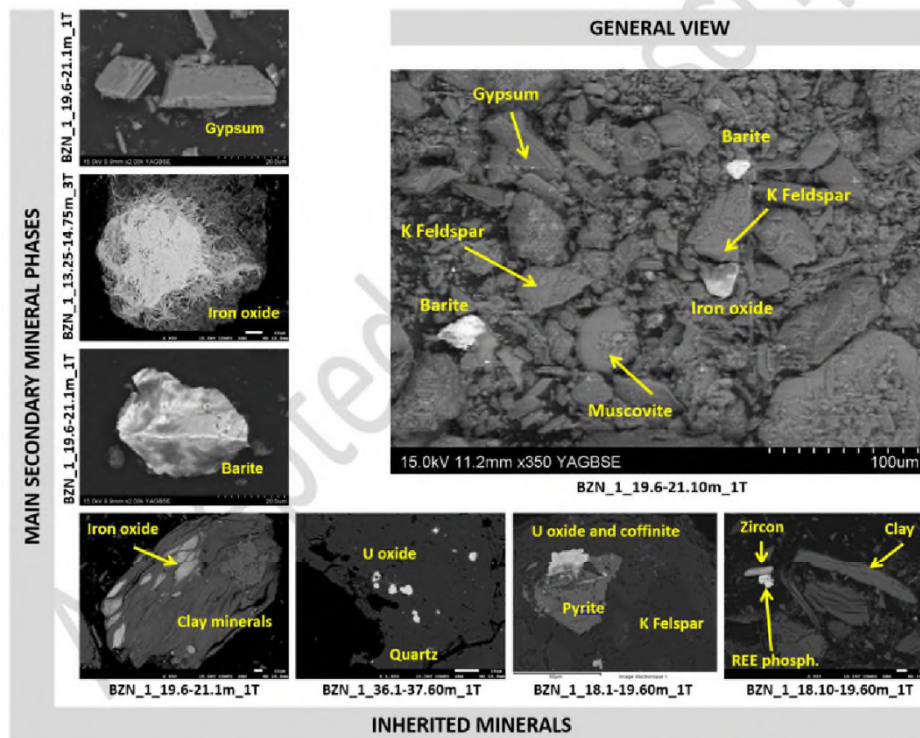


Figure 7. SEM images of Bellezeane tailings. In the center, an overall view completed by details of inherited phases and secondary phases (inherited and/or neo-formed) on powder or thin sections. Phases were identified by SEM-EDX (EDX spectra not shown).

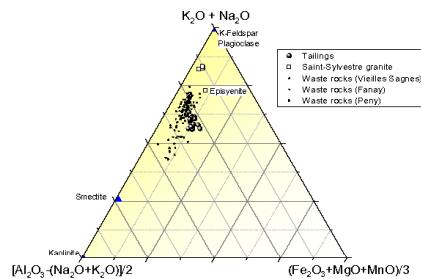


Figure 8. Ternary diagram $(K_2O+Na_2O) - [(Al_2O_3-(Na_2O+K_2O))/2] - [(Fe_2O_3+MgO+MnO)/3]$ showing the weathering of feldspars to clay minerals in BZN samples. Additional data from Boekhout et al. (2015) and Kanzari et al. (2017) for waste rocks are also plotted.

The interpretation of the chemistry data led to consideration of the U within the minerals inherited from the ore, here in the form of uranium oxides and coffinite, but also within neo-formed minerals. As no uranium-carrying mineral phase was clearly identified, the presence of uranium sorbed to the surface of the smectite was investigated by TRIFS, a technique that can only detect the environments of U (VI). The superposition of the experimental spectra of the BZN_1_13.25-14.75m_2T sample with that acquired on the U-doped reference smectite confirmed the presence of U also sorbed to the surface of the smectite (Figure 9). Uranium also has a high affinity for ferric oxyhydroxides. However, these phases could not be investigated because iron is known to inhibit U(VI) fluorescence.

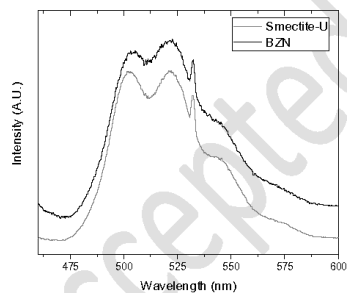


Figure 9. TRIFS spectra of a BZN sample (BZN_1_13.25-14.75m_2T) and a smectite doped with sorbed uranium.

5. Long-term Mobility of U and ^{226}Ra in Mill Tailings

Two types of modeling were performed. Firstly, the distribution of U and ^{226}Ra was investigated in order to describe the diagenesis conditions observed today. This modeling was carried out in static mode, i.e. by considering the physico-chemical equilibria (saturation indexes, SI) regulating the chemical composition of the porewaters in contact with the tailings. In a second step, the mobility of the U and ^{226}Ra was assessed using 1D reactive transport models simulating the long-term evolution of the tailings under leaching by inflow-water.

5.1. Current distribution of U and ^{226}Ra

On the basis of the characterizations of the porewaters and tailings, it was shown that the majority (more than 99%) of the U and ^{226}Ra was trapped in the solid fraction (Figure 10). However,

the geochemical and mineralogical study of tailings alone was often insufficient to identify the compartments carrying U and ^{226}Ra within the tailings, and thus to assess their mobility. Moreover, there was no unambiguous marker for these compartments that would allow them to be easily identified and quantified. Microscopic observations revealed the presence of some resistant uranium minerals (uraninite and coffinite) trapped mainly within quartz. The additional characterizations by TRIFS allowed us to determine that a part of the U is also sorbed to the smectite. However, this technique did not allow the sorption of U to the HFOs to be evidenced. It was impossible to perform this type of analysis for ^{226}Ra because of its low elemental concentration (~700 ppt). However, its speciation can be studied indirectly by sequential leaching. These complex experiments are subject to significant analytical bias. The compartments targeted are not completely independent of each other and there may be elemental recombination phenomena during a wash, leading to distortion in yield results (Bacon and Davidson, 2008). Therefore, thermodynamic equilibrium modeling was performed to study the distribution of U and ^{226}Ra in the BZN tailings.

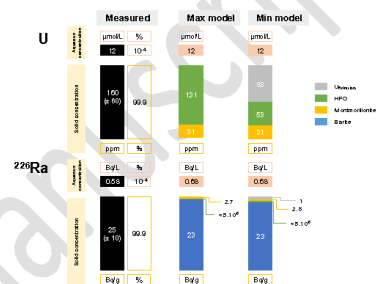


Figure 10. Distribution of U and ^{226}Ra within the mill tailings and according to the Min and Max models developed in this study. The Min model considers that a fraction of the radioelement is trapped in phases inherited from the ore that are considered non-reactive. The Max model considers all the radioelements as reactive.

The chemical composition of the porewater measured in the piezometer showed that the BZN tailings porewater was close to equilibrium with quartz polymorphs (SI = 0.2), aluminosilicates and especially smectite (SI = 0.1), calcite (SI = 0.0), ferrihydrite (SI = -0.4) and gypsum (SI = -0.1), and slightly supersaturated with barite (0.5). This is consistent with the mineralogy of the tailings previously described. The mineral assemblage composed of chalcedony (29%), potassium feldspar (35%), Ca-montmorillonite (25%), ferrihydrite (0.6 to 1.1% as per model discussed in the paragraph below), gypsum (9%), calcite (0.5%), and barite (0.15%), was used to describe the chemical reactivity of the solid-solution system within the BZN tailings throughout the interaction processes, and to simulate the chemical composition of the tailings porewater over time. The proportions of the mineral phases in the equilibrium assemblage were calculated from the elemental composition of the tailings. Thus, Si and Al were divided between clays, chalcedony, potassium feldspar (representing all the feldspars and muscovite) and the Ca-montmorillonite (representing all the clay minerals). Mg and K were attributed to the Ca-montmorillonite and potassium feldspar respectively. Na was artificially transferred to the sodium feldspars. Fe was attributed to ferrihydrite, while S, Inorganic C and Ba were attributed to gypsum, calcite and barite respectively. Sorption of major elements and traces (U and ^{226}Ra) to the ferrihydrite and montmorillonite had also been taken into account in the reactive paragenesis. Thus, the calculated composition of the water in equilibrium with this mineralogical assemblage, given in Figure SI-6 and Table 1 was very close to that of the porewater analyzed.

The mean U concentration measured in the solid was 160 ppm, of which 83 ppm (calculated with a yield of 95% and an initial content of 1.66‰) could be borne by highly insoluble resistant

phases as highlighted by the preceding mineralogical characterizations. Therefore, a low model (Min) taking into account the presence of resistant phases and a high model (Max) not taking them into account were presented. The only difference between these two models was the concentration of ferrihydrite. For the high model, the quantity of iron was carried exclusively by ferrihydrite while for the low model, the iron was distributed between pyrite (FeS_2) and ferrihydrite, respecting the sulfur balance. The quantity of ferrihydrite was 0.6% for the high model and 1.1% for the low model.

Thus, the speciation calculation carried out in the BZN porewaters indicated that uranium in solution was found exclusively in hexavalent form at a concentration of 1.2×10^{-5} mol/L. Due to the high fugacity of CO_2 , carbonate complexes were in the majority ($\text{UO}_2(\text{CO}_3)_3^{4-}$: 78.5 % ; $\text{UO}_2(\text{CO}_3)_2^{2-}$: 21 % ; UO_2CO_3 : 0.5 %). However, calcium-uranyl-carbonate ternary complexes were not included in the model due to the high degree of uncertainty about their formation constant. Analysis of the saturation indices suggested that the U concentration was not constrained by any equilibrium with a pure mineral phase, as no uranium phase was in equilibrium. Therefore, surface sorption of clay minerals and HFOs was considered to explain the U concentrations measured in the solid fraction of the tailings and the porewaters in accordance with the mineralogical and TRIFS characterization. The amount of sorbed U was calculated by considering water in equilibrium with reactive mineral paragenesis and including the sorption mechanisms. In this way, the concentration in the solid phase (in equilibrium with the imposed concentration in solution of 1.2×10^{-5} mol/L) was correctly reproduced (160 ppm), of which 20 to 37% was sorbed to the clay minerals and 63 to 80% was sorbed to the HFOs (Figure 10) according to the model.

As with the U, the specific activity of the ^{226}Ra present in the process-resistant phases was calculated and was approximately 1 Bq/g. The concentration in ^{226}Ra , present at ultra-trace concentration in the environment, could not be constrained by the solubility of a pure ^{226}Ra phase. Therefore, other mechanisms such as the co-precipitation of ^{226}Ra in barite, sorption of ^{226}Ra to HFOs and clay minerals were taken into account in order to reproduce the ^{226}Ra specific activity in the solid. All of the ^{226}Ra and Ba present in the solid tailings were considered to be associated with the solid solution $(\text{Ba,Ra})\text{SO}_4$. Under these conditions, estimation of the ^{226}Ra concentration in porewater gave 0.68 Bq/L (Table 1) while over 97.2% of the ^{226}Ra stock was associated with the solid solution of $(\text{Ba,Ra})\text{SO}_4$, with clay minerals and HFOs respectively accounting for 2.8 % and 4.10^{-5} % (Figure 10). Finally, the concentration of SO_4 imposed by the solubility balance of gypsum explained the predominance of ^{226}Ra in the form of the aqueous complex RaSO_4 . The latter therefore promoted equilibrium with the solid solution $(\text{Ba,Ra})\text{SO}_4$.

These calculations confirmed the distribution of U and ^{226}Ra in the mill tailings, with over 99.9% of the U and the ^{226}Ra in the solid fraction, divided regardless of the model between the resistant minerals, the clay minerals, iron hydroxides, and, in the case of ^{226}Ra , in the barite. The concentrations of U and ^{226}Ra in solution, reproduced according to the chemical equilibria with the minerals mentioned above, constituted a very small stock in the order of 10^{-4} %.

5.2. Evolution of U and ^{226}Ra distribution over time

A 1D reactive transport model to simulate the effect of percolation of granitic water within the tailings was run over a period of 230,000 years to evaluate the long-term reactivity of the U and ^{226}Ra and thus their mobility.

5.2.1. Evolution of the geochemical system

The variations in the chemical composition of the different compartments (aqueous, surfaces and mineral phases) of the last cell of the column modeled during the percolation of the granitic water are presented in Figure 11.

The percolation of weakly mineralized granitic water within the Bellezane mill tailings led, as expected, to a significant decrease in the ionic strength of the porewater, down to an ionic strength of

the same order of magnitude as that of the granitic waters (Figure 11a). The facies of the porewater, initially sulfated-magnesian, evolved as the equilibrium between the solid phase, the liquid phase, and the reactive surfaces changed and gradually converged with the facies of the percolating granitic water. The principal minerals from the mineral paragenesis did not undergo any significant dissolution or precipitation during the simulation period (Figure 11c). Only the gypsum and then the calcite were fully dissolved. The dissolution of the gypsum and the progressive dissolution of calcite led to a slight increase in pH from 6.3 to 7.2 (Figure 11b). In a second step, when the gypsum was completely dissolved (23,000 years), the pH increased to 8.5 for the entire calcite dissolution period, i.e. up to about 100,000 years, then reduced to a pH of around 6.6 at 150,000 years. This last decrease in pH was related to cation exchange reactions on the surface of clay minerals and more particularly to the preferential desorption of Ca, resulting from the dissolution of the gypsum and calcite, to the detriment of protons (Figure 11d). Finally, this slow decrease in pH was explained by the low concentrations of major ions in granitic water, not allowing sufficiently rapid redistribution of the initially sorbed cation populations in favor of H^+ , K^+ and Mg^{2+} . This was also verified to a lesser extent for the Ca sorbed to the ferric oxyhydroxides and also for the carbonates.

5.2.2. Uranium mobility

The modification of the chemical equilibria resulting from the percolation of granitic water within the tailings generated a redistribution of U between the different compartments (sorption to clay minerals, sorption to iron oxyhydroxides, resistant uranium-bearing minerals, all of these minerals having been evidenced within the tailings). The evolution of this distribution within the last cell of the column over time is given in Figure 11e and f for the two models previously discussed (low model and high model). The "total solid" part represents the sum of the fractions sorbed to the clay minerals and ferric hydroxides as well as the U contained in the resistant phases when these are taken into account (Min model).

Percolation of weakly mineralized granitic water with low uranium concentration within the BZN tailings was not sufficient to leach the uranium from the solid fraction, even if the uranium-bearing phases that were resistant to the process were not taken into account (low model), and despite the prevailing oxidizing conditions. Irrespective of the model considered, the U concentration in the solid was in the order of 160 ppm throughout the simulation period and varied only slightly (1.8% decrease in the total amount of U in the solid). The uranium was thus sequestered alternatively by two traps: sorption to ferrihydrite and sorption to clay minerals (Figure 11f). U sorption to iron oxyhydroxides was predominant throughout the dissolution of gypsum and calcite (Figure 11c). The fraction sorbed to the iron oxyhydroxides then decreased as the pH decreased (Figure 11b) while the fraction sorbed to the clay minerals increased (Figure 11f). Therefore, as a function of pH, the evolution of the sorbed U fractions was anti-correlated, the U being trapped alternatively on the iron oxyhydroxides and clay minerals. The increase in pH and the increase in the concentration of calcium in solution generated inhibited the sorption of uranium to clay minerals during this period.

Dissolved U equilibrium concentrations decreased significantly in several stages in accordance with its retention on the iron oxyhydroxides and clay minerals. Thus, after a little over 150 years, concentrations reached $\sim 10^{-6}$ mol/L, then decreased during the gypsum dissolution phase ($\sim 8 \times 10^{-8}$ mol/L up to 23,000 years), and again during the progressive dissolution of the calcite ($\sim 6 \times 10^{-8}$ mol/L up to 100,000 years; Figure 11e). When all the calcite was dissolved and the pH was returned to pH 6.6 (150,000 years), the dissolved U concentration was stabilized at 10^{-8} mol/L, which is close to the U concentration of the percolation solution.

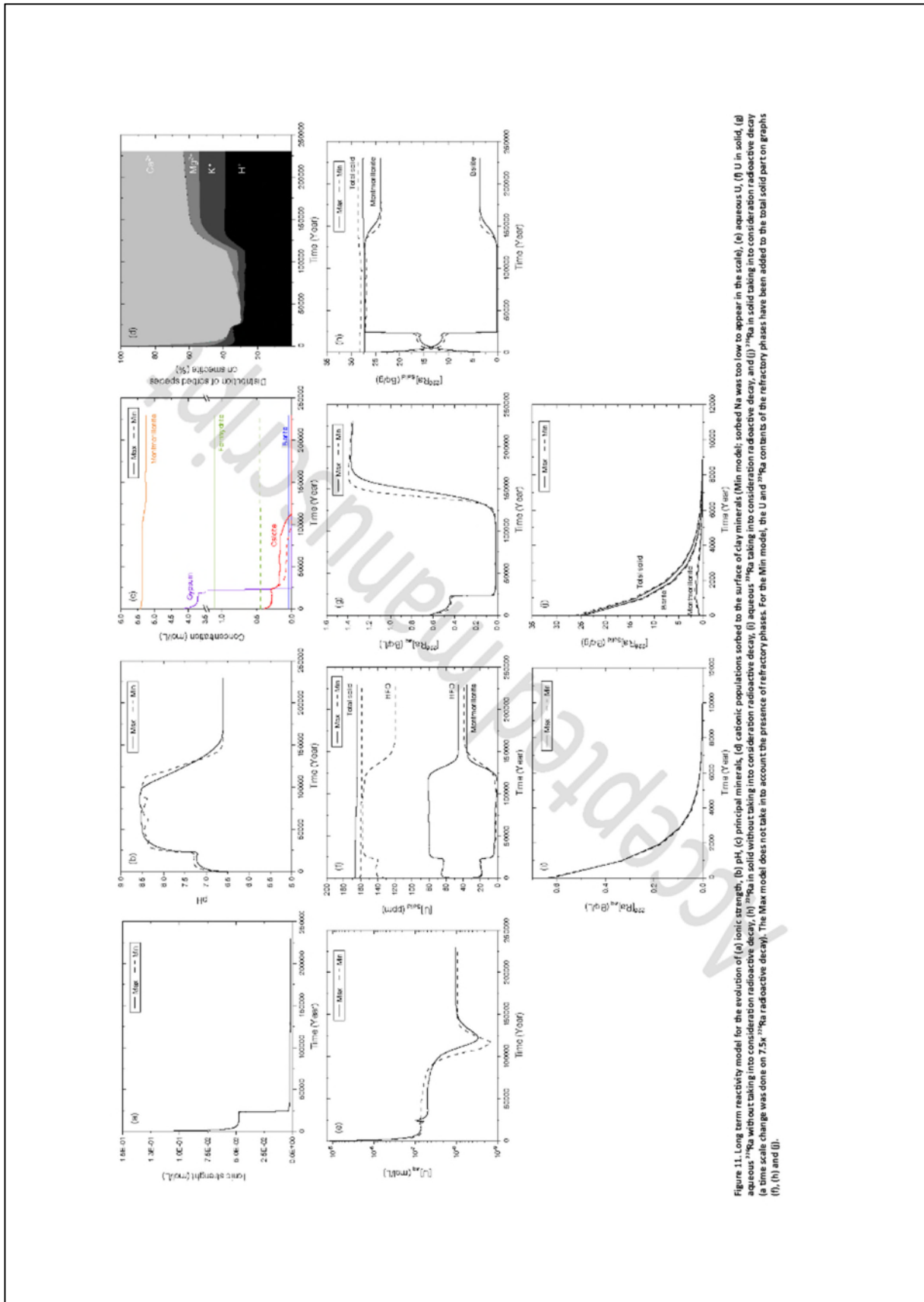


Figure 11. Long term reactivity model for the evolution of (a) ionic strength, (b) pH, (c) principal minerals, (d) cationic populations sorbed to the surface of clay minerals (Min model), sorbed Na was too low to appear in the scale), (e) aqueous U, (f) U in solid, (g) aqueous ²²⁶Ra without taking into consideration radioactive decay, (h) ²²⁶Ra in solid without taking into consideration radioactive decay, (i) ²²⁶Ra in solid taking into consideration radioactive decay (a time scale change was done on 7.5x ²²⁶Ra radioactive decay). The Max model does not take into account the presence of refractory phases. The Max model does not take into account the presence of refractory phases. For the Min model, the U and ²²⁶Ra contents of the refractory phases have been added to the total solid part on graphs (f), (h) and (j).

5.2.3. Radium 226 mobility

Radioactive decay mainly governs the long-term evolution of ^{226}Ra mobility. The simulation period considered here, 230,000 years, goes well beyond ten radioactive periods of ^{226}Ra . However, in order to better understand the role of each of the phases of ^{226}Ra sequestration, and to study the influence of ^{226}Ra in the percolation waters, several models were performed without taking into account the radioactive decay. The main results are also presented in Figures 11g and h.

Whichever model is considered (e.g. Min model or Max model), the ^{226}Ra always remained sequestered over time. Indeed, the high sulfate concentration resulting from the dissolution of gypsum allowed the non dissolution of barite. However, the solid solution $(\text{Ba,Ra})\text{SO}_4$ entered equilibrium with the percolation water, showing a low level of ^{226}Ra activity. This therefore explained the decrease in the specific activity of the ^{226}Ra within the barite, in favor of sorption to the clay minerals (Figure 11h). Therefore, these retention mechanisms maintained a low aqueous concentration of ^{226}Ra , systematically below that measured in this study ($< 0.68 \text{ Bq/L}$) during 150,000 years (~ 100 radioactive decay); see Figure 11g for modeling results.

This mechanism was accelerated once the gypsum was completely dissolved (23,000 years), with SO_4 concentrations no longer allowing the RaSO_4 complex to be predominant and more conducive to the establishment of the solid solution $(\text{Ba,Ra})\text{SO}_4$. The aqueous concentration of ^{226}Ra became almost negligible. The decrease in pH to 6.6 after the complete dissolution of the calcite and the desorption of Ca^{2+} ions (150,000 years), also led to a slight desorption of ^{226}Ra which was in turn co-precipitated within the residual barite. The solid solution $(\text{Ba,Ra})\text{SO}_4$ again constrained the ^{226}Ra solution concentration, which then increased to values close to the concentrations initially observed ($\sim 1.4 \text{ Bq/L}$).

Additional modeling was performed with percolation water not containing ^{226}Ra . These models yielded the same results as those presented above (see Figure S1-7) indicating that the redistribution of ^{226}Ra and in particular its re-dissolution after 150,000 years was mainly governed by the initial source term here consisting of the mill tailings.

On this basis, the results of the modeling were then corrected for the radioactive decay for each compartment investigated (Figure 11i and j). As expected, ^{226}Ra activities decreased more rapidly, with a consistently verified distribution between barite and clay minerals and concentrations in solution in the order of natural background noise after three radioactive periods.

All these results (Figures 11g - 11j) indicated that the minerals with retention properties with respect to ^{226}Ra , present in the ultra-trace concentration, were in surplus: barite, clay minerals and ferric hydroxides. The ^{226}Ra was easily trapped as a function of the chemical evolution of the system and in particular the pH. When radioactive decay was taken into account, the specific activity of ^{226}Ra in the tailings was in the order of 1 Bq/g from 5,000 years onwards, while the concentration in solution was less than 0.2 Bq/L from 1,800 years onwards (Figures 11i and 11j).

Conclusions

This multi-technical and multi-scalar study of the Bellezane mill tailings confirmed their chemical stability more than 25 years after emplacement thanks to rapid diagenesis. They remained homogeneous from the point of view of chemical, mineralogical and radiological composition. Indeed, the minerals inherited from the ore (quartz, potassic feldspar, plagioclases and micas) were observed in association with their initially present or neo-formed weathering products (mainly clay minerals such as smectite, chlorite and kaolinite as well as iron oxyhydroxides), and coexisting with neo-formed minerals following milling of the ore and neutralization of the tailings before their emplacement, such as in the case of gypsum (and to a lesser extent barite also present in the ore). All these minerals are effective traps for retention of U and ^{226}Ra . The residual uranium (160 ppm) and ^{226}Ra (25 Bq/g) in the solid phase after treatment represented in fact more than 99% of

the total stock leading to concentrations in the porewaters of $12 \mu\text{mol/L}$ and 0.58 Bq/L respectively for U and ^{226}Ra .

The long-term chemical reactivity of mill tailings could be described using a thermodynamic approach including solubility equilibria and also sorption and coprecipitation reactions in the case of ^{226}Ra . The modeling carried out in this study confirmed the surplus presence of mineralogical traps (smectite, ferric oxyhydroxides and barite in the specific case of ^{226}Ra) which, as the porewater chemistry evolves under the dissolution of gypsum and calcite, will maintain the concentrations of U and ^{226}Ra in solution at low levels, even under oxidizing conditions, normally favorable to the migration of U(VI). In addition, the low permeability of the mill tailings stored within the former Bellezane open-pit mines led to mobility, in the case of the ^{226}Ra , being governed mainly by radioactive decay, since the estimated flow rates within the tailings are in the region of $8 \cdot 10^{-9} \text{ m s}^{-1}$.

These results will in the future be complemented by more detailed characterization of the tailings, in particular by X-ray absorption spectroscopy and alpha autoradiography coupled with sequential leaching experimentation.

Acknowledgements

The authors would like to thank ORANO Mining's AMF department (Bessines sur Gartempe, France) for providing access to the Bellezane site and for their assistance in carrying out all the sampling work. Thanks also to Martine Gérard of IMPMC for her valuable expertise in the characterization of clay minerals.

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Supplementary Information: A multi-scalar study of the long-term reactivity of uranium mill tailings from Bellezane site (France).

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Accepted manuscript

Modélisation de la mobilité à long terme de l'uranium et du radium 226 dans les résidus de traitement de Bellezane	02/02/2020	Page : 43/50
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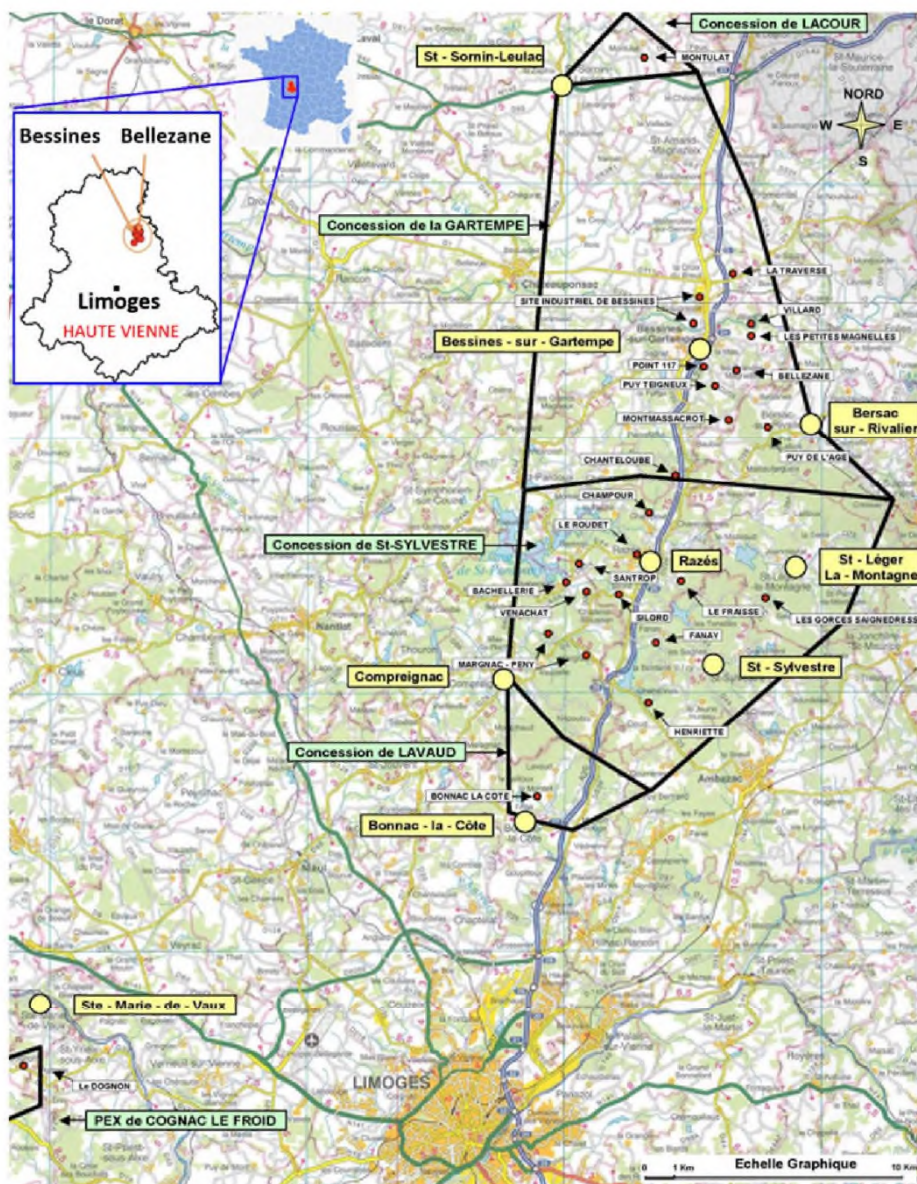


Figure SI-1. Location of the La Cruzille mining division, its mining operations, and the Bellezane Tailings Management Facility (GEP, 2010).

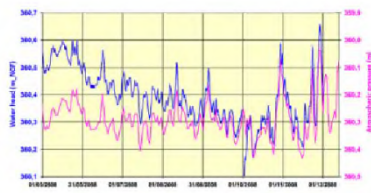


Figure SI-2. Correlation between the piezometric height measured at ES85 and atmospheric pressure (Ledoux and Schmitt, 2010).

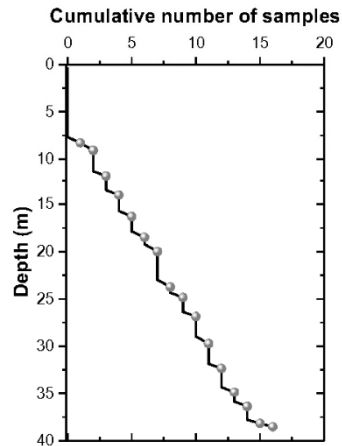


Figure SI-3. Cumulative number of samples as a function of depth. The grey dots represent the samples that have undergone full characterization.

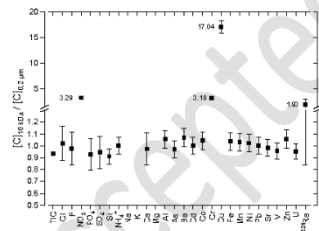


Figure SI-4. Ratios of concentrations measured in the porewater fraction filtered at 10 kDa and 0.2 μm , sampled in piezometer ES85.

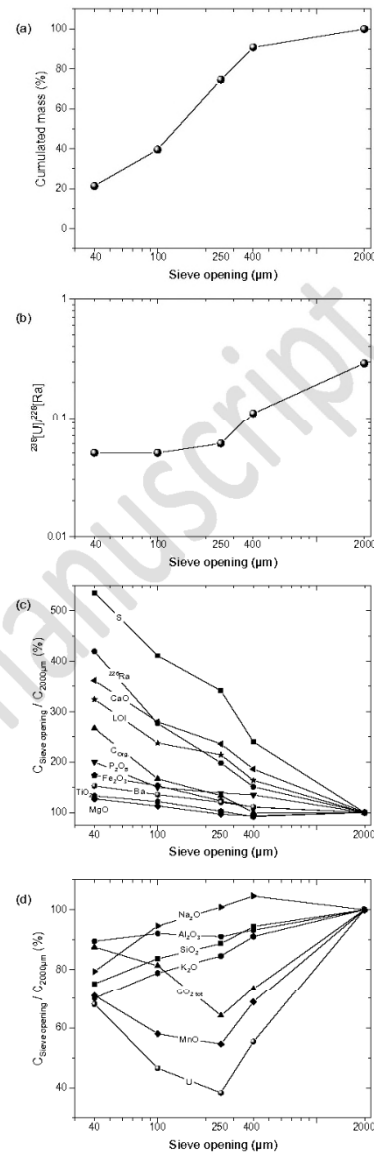


Figure SI-5. Particle size distribution (a), $[^{238}\text{U}]/[^{226}\text{Ra}]$ mass activity ratio (b), major (c) and trace (d) element concentrations in each of the particle size fractions of sample BZN_1_13.25-14.75m_2T. The concentrations of major and trace elements in each particle size fraction are normalized with those measured in the 2000 μm fraction.

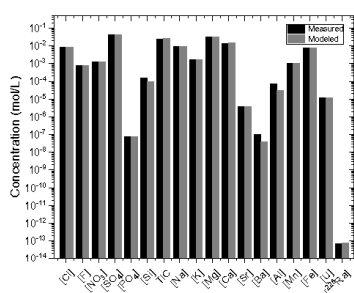


Figure SI-6. Comparison between measured and modeled ES85 porewater concentrations.

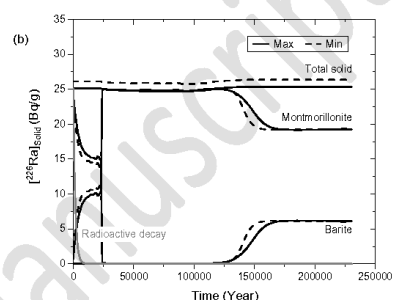
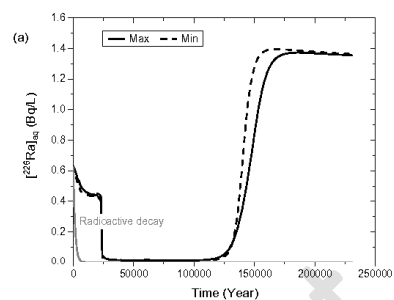


Figure SI 7. Evolution of aqueous ^{226}Ra without taking into account the radioactive decay (a), and ^{226}Ra in the solid without taking into account the radioactive decay (b) and considering a percolation water without ^{226}Ra . Values with radioactive decay are shown in light grey on both figures.

TableSI-1. Summary of the characterization analyses carried out for all the samples studied.

Sample name	Mean depth (m)	Chemistry	Radiological characterization	Mineralogical characterization	Particle-size distribution	TRLFS
BZN 1_Carotte 1	1.30		X			
BZN 1_Carotte 3	3.85		X			
BZN 1_Carotte 5	7.15		X			
BZN 1_7.90-10.25m_1T	8.30	X	X	X		
BZN 1_7.90-10.25m_2T	9.10	X	X	X		
BZN 1_11.75-13.25m_1T	12.00	X	X	X		X
BZN 1_13.25-14.75m_1T	13.50	X	X	X		
BZN 1_13.25-14.75m_2T	14.00	X	X	X	X	
BZN 1_13.25-14.75m_3T	14.50	X	X	X		
BZN 1_14.75-16.60m_3T	16.30	X	X	X		
BZN 1_18.10-19.60m_1T	18.50	X	X	X		
BZN 1_19.60-21.10m_1T	20.00	X	X	X		
BZN 1_22.60-24.10m_2T	23.70	X	X	X		
BZN 1_24.10-25.60m_2T	24.90	X	X	X		
BZN 1_25.60-27.10m_3T	26.90	X	X	X		
BZN 1_28.60-30.10m_2T	29.70	X	X	X		
BZN 1_31.60-33.10m_2T	32.40	X	X	X		
BZN 1_34.60-36.10m_1T	34.90	X	X	X		
BZN 1_36.10-37.60m_1T	36.40	X	X	X		
BZN 1_37.60-38.70m_2T	38.20	X	X	X		
BZN 1_37.60-38.70m_3T	38.50	X	X	X		

Table SI-2. Sorption constants of U, ^{226}Ra and CO_3^{2-} on ferrihydrite added to the PHREEQC database (_w and _s stands for weak and strong binding sites respectively).

		Lg k	Reference
^{226}Ra	$\text{HFO_sOH} + \text{Ra}^{2+} = \text{HFO_sOHRa}^{2+}$	6.66	Sajih et al. 2014
	$\text{HFO_wOH} + \text{Ra}^{2+} = \text{HFO_wORa}^{2+} + \text{H}^+$	-5.67	
U	$\text{HFO_sOH} + \text{UO}_2^{2+} = \text{HFO_sOUO}_2^{2+} + \text{H}^+$	3.73	Mahoney et al. 2019
	$\text{HFO_wOH} + \text{UO}_2^{2+} = \text{HFO_wOUO}_2^{2+} + \text{H}^+$	2.53	
	$\text{HFO_wOH} + \text{UO}_2^{2+} + \text{CO}_3^{2-} = \text{HFO_wOUO}_2\text{CO}_3 + \text{H}^+$	9.03	
	$\text{HFO_wOH} + \text{UO}_2^{2+} + 2 \text{CO}_3^{2-} = \text{HFO_wOUO}_2(\text{CO}_3)_2 + \text{H}^+$	15.28	
	$\text{HFO_wOH} + \text{UO}_2^{2+} + \text{H}_2\text{O} = \text{HFO_wOUO}_2\text{OH} + 2 \text{H}^+$	-5.11	
	$\text{HFO_wOH} + \text{CO}_3^{2-} + \text{H}^+ = \text{HFO_wOCO}_3 + \text{H}_2\text{O}$	12.78	
CO_3^{2-}	$\text{HFO_wOH} + \text{CO}_3^{2-} + 2 \text{H}^+ = \text{HFO_wOCO}_3\text{H} + \text{H}_2\text{O}$	20.37	Mahoney et al. 2019

Table SI-3. Site concentration and selectivity coefficients of cation exchange reactions for montmorillonite added to the PHREEQC database (Gaines-Thomas convention) (Reinoso-Maset et al., 2012a and 2012b).

	Site				
	>X1	>X2	>X3	>X4	>X5
	Site concentration (mmol/g clay)				
	6.20×10^{-4}	1.50×10^{-1}	1.40×10^{-1}	1.50×10^{-1}	4.10×10^{-4}
	Selectivity coefficient				
H^+/Na^+	-2.2	-12.5	-12.5	-12.5	
H^+/K^+	0.75	-1.4	-4.4	-7.2	7.3
$2\text{H}^+/\text{Ca}^{2+}$	0.1	-2.5	-11.5	-17.5	
$2\text{H}^+/\text{Mg}^{2+}$	0.1	-2.5	-11.5	-17.5	
$2\text{H}^+/\text{UO}_2^{2+}$		-0.475	-3.44		
$2\text{H}^+/\text{Ra}^{2+}$		-2.37	-6.55	-10.17	

Table SI-4. Mean (C_{mean}), minimum (C_{min}) and maximum (C_{max}) elemental levels measured in BZN samples. Mean values are accompanied by the standard deviations. C_{org} and LOI denote organic C content and loss on ignition respectively.

	C_{mean}	C_{min}	C_{max}
<i>Major elements(%)</i>			
SiO_2	61.9 ± 4.4	55.4	73.2
Al_2O_3	13.1 ± 0.8	11.2	14.5
K_2O	5.04 ± 0.27	4.61	5.57
CaO	3.48 ± 0.93	1.07	4.77
Fe_2O_3	2.94 ± 0.61	1.50	3.76
Na_2O	1.68 ± 0.29	1.26	2.61
S total	1.85 ± 0.45	0.40	2.53
MgO	0.77 ± 0.26	0.32	1.19
P_2O_5	0.33 ± 0.05	0.24	0.42
TiO_2	0.27 ± 0.07	0.16	0.46
MnO	0.05 ± 0.02	0.03	0.09
$\text{CO}_2 \text{ total}$	0.52 ± 0.25	0.24	1.23
C_{org}	0.08 ± 0.04	0.03	0.20
LOI	9.69 ± 2.39	2.56	14.02
<i>Traces (ppm)</i>			
Ba	839 ± 609	294.9	2502
U	169 ± 61	77.7	292.4
	^{226}Ra (Bq/g)		
^{226}Ra	23 ± 15	0.3	44.5

Table SI-5. Trace-level element concentrations measured in mill tailings samples (D. L. stands for detection limit).

	BZN / 7.9-10.25m / 1T A	BZN / 7.9-10.25m / 1T B	BZN / 7.9-10.25m / 2T	BZN / 11.75-13.26m / 1T	BZN / 13.26-14.75m / 1T	BZN / 13.26-14.75m / 2T A	BZN / 13.26-14.75m / 2T B	BZN / 13.26-14.75m / 3T	BZN / 14.75-16.60m / 3T	BZN / 18.10-19.60m / 1T	BZN / 19.60-21.10m / 1T	BZN / 22.60-24.10m / 2T	BZN / 24.10-25.60m / 2T	BZN / 25.60-27.10m / 3T	BZN / 28.60-30.10m / 2T	BZN / 31.60-33.10m / 2T	BZN / 34.60-36.10m / 1T	BZN / 36.10-37.60m / 1T	BZN / 37.60-38.70m / 2T	BZN / 37.60-38.70m / 3T
As	42.32	143.50	146.60	146.40	146.00	176.70	172.80	91.26	147.20	156.30	173.30	78.71	89.70	80.31	111.90	107.30	136.50	86.91	154.00	110.40
Ba	294.90	530.90	848.70	1026.00	508.20	539.00	1062.00	987.10	2463.00	389.20	961.50	399.70	317.50	505.00	711.70	697.40	750.80	532.10	2502.00	752.60
Be	16.53	24.65	19.20	22.38	20.40	22.71	22.28	17.50	18.13	18.21	22.42	19.07	20.72	20.73	19.48	18.80	19.76	19.42	19.34	17.14
Bi	3.17	10.60	7.85	3.15	3.49	3.40	2.97	3.52	4.02	9.45	3.06	5.74	6.06	4.49	3.88	2.98	2.41	5.89	3.89	3.14
Cd	0.94	2.89	2.34	0.37	0.25	0.68	0.29	0.24	0.26	3.78	0.29	0.23	0.31	0.19	0.28	0.35	0.21	0.44	0.19	0.29
Ce	39.62	54.58	57.86	77.08	63.74	56.87	81.00	77.99	90.90	43.61	67.72	49.30	52.47	54.69	61.96	69.74	70.16	53.80	75.07	65.74
Co	5.84	10.77	10.82	5.77	3.38	4.53	5.32	6.86	9.60	14.69	5.03	4.88	4.58	3.81	5.64	5.55	4.83	5.25	8.09	4.83
Cr	21.04	23.91	19.63	37.90	17.84	18.38	41.28	55.17	74.01	24.00	36.35	20.02	17.76	14.99	39.36	42.68	49.87	24.23	59.48	30.81
Cs	25.58	31.99	28.47	31.73	37.69	37.82	31.92	30.84	29.20	21.27	34.09	28.34	28.41	26.77	43.35	33.85	39.18	30.38	42.55	30.79
Cu	169.70	238.10	221.80	19.34	22.13	51.40	18.14	24.62	45.83	335.60	19.50	51.77	45.66	41.23	36.78	26.83	22.93	46.31	42.34	23.38
Dy	1.68	2.86	2.97	3.06	2.78	2.99	3.19	3.31	4.53	2.80	2.96	2.20	2.57	2.21	3.10	3.59	3.32	2.20	4.32	2.96
Eu	0.61	1.02	1.02	1.09	0.98	1.15	1.16	1.22	1.83	0.96	1.06	0.77	0.97	0.78	1.18	1.38	1.32	0.77	1.78	1.09
Eu	0.45	0.83	0.77	0.91	0.66	0.69	0.95	1.06	1.51	0.79	0.90	0.49	0.53	0.46	0.85	0.94	0.91	0.56	1.18	0.75
Ga	21.81	25.21	26.10	27.63	27.76	28.02	28.21	24.07	22.32	21.46	25.90	24.94	24.28	25.65	26.54	25.87	25.79	25.13	25.03	26.01
Gd	2.65	4.63	4.84	5.29	4.62	4.74	5.32	5.27	6.34	4.29	4.89	3.48	4.00	3.64	4.55	5.34	5.51	3.52	5.91	4.72
Ge	1.72	2.75	2.77	2.83	3.08	2.92	2.93	2.28	2.28	2.31	2.81	2.01	2.00	2.28	2.43	2.27	2.50	2.01	2.71	2.64
Hf	2.30	3.19	3.36	4.33	3.49	3.37	4.52	4.88	5.81	2.58	3.97	2.85	2.88	3.39	4.08	4.45	3.86	3.04	4.92	4.23
Ho	0.25	0.43	0.44	0.46	0.41	0.48	0.48	0.50	0.72	0.41	0.45	0.33	0.39	0.33	0.48	0.56	0.55	0.32	0.71	0.45
In	0.09	0.15	0.16	0.12	0.12	0.13	0.12	0.11	0.11	0.17	0.13	0.14	0.14	0.14	0.12	0.14	0.12	0.16	0.12	0.11
La	18.79	26.00	27.05	36.83	30.40	27.30	40.28	39.33	51.29	20.26	33.22	22.72	23.95	25.70	32.45	34.64	34.13	25.42	42.30	32.05
Lu	0.08	0.12	0.11	0.12	0.12	0.13	0.13	0.14	0.23	0.11	0.13	0.09	0.11	0.09	0.14	0.16	0.15	0.09	0.22	0.13
Mo	0.65	0.59	0.69	0.85	0.87	0.87	0.96	0.70	1.35	0.94	0.93	0.83	0.50	0.53	0.57	0.65	0.76	0.87	1.41	0.59
Nb	10.66	13.06	13.40	16.05	14.47	14.74	16.37	16.40	17.39	10.46	14.92	15.17	15.76	16.33	16.00	16.29	14.88	15.16	17.31	15.91
Nd	18.14	26.08	27.87	36.64	30.16	27.37	37.88	36.81	43.17	21.86	32.47	24.07	25.34	26.06	29.48	33.72	33.86	26.34	35.67	31.45
Ni	18.09	12.21	9.68	15.22	7.95	8.33	14.83	19.92	27.10	13.59	13.23	10.18	9.62	8.14	13.35	15.53	12.99	9.95	20.56	11.15
Pb	109.35	335.51	310.21	120.50	131.97	194.88	120.56	90.61	124.11	421.95	115.88	72.42	71.92	72.79	106.93	109.69	78.38	106.83	109.42	109.96
Pr	4.59	6.45	6.80	8.96	7.46	6.67	9.39	8.97	10.44	5.21	7.81	5.81	6.10	6.41	7.23	8.13	8.20	6.40	8.64	7.53
Rb	379.60	381.90	391.00	398.00	396.70	399.10	416.10	377.80	340.40	336.70	379.40	430.40	440.10	446.80	412.50	401.70	402.30	450.10	390.30	413.50
Sc	< D. L.	< D. L.	< D. L.	< D. L.	< D. L.	< D. L.	< D. L.	< D. L.	< D. L.	< D. L.	< D. L.	< D. L.	< D. L.	< D. L.	< D. L.	< D. L.	< D. L.	< D. L.	< D. L.	< D. L.
Sb	1.10	4.19	4.17	3.17	3.30	3.17	3.24	2.13	5.97	4.12	2.76	1.56	1.49	1.68	2.35	2.31	1.93	2.43	5.93	2.56
Sm	3.85	5.89	6.23	7.61	6.48	5.99	7.61	7.58	8.70	5.33	6.81	5.23	5.63	5.62	6.37	7.31	7.46	5.49	7.75	6.65
Sn	20.05	20.02	16.76	15.85	23.17	19.95	16.47	16.96	16.21	15.95	25.06	24.40	24.67	23.21	24.43	21.03	21.45	24.38	23.29	18.25
Sr	79.16	96.11	103.50	151.30	105.80	109.70	158.50	181.30	271.60	78.33	151.00	72.80	73.86	75.72	132.80	138.00	125.40	82.83	205.50	127.20
Ta	2.38	2.97	2.73	2.66	2.88	3.00	2.67	2.70	2.72	2.11	2.80	3.69	4.03	3.61	3.13	3.12	2.99	3.64	3.12	2.77
Tb	0.36	0.63	0.66	0.69	0.61	0.64	0.71	0.70	0.90	0.60	0.65	0.49	0.55	0.48	0.65	0.75	0.75	0.48	0.86	0.65
Th	14.10	17.03	19.48	22.78	20.98	19.22	23.47	21.16	19.74	14.76	19.14	18.63	20.33	21.58	18.11	22.23	22.62	19.28	19.24	22.86
Tm	0.08	0.13	0.13	0.14	0.13	0.15	0.15	0.16	0.26	0.13	0.14	0.11	0.13	0.11	0.16	0.18	0.18	0.10	0.25	0.14
U	77.65	212.50	292.40	214.30	217.10	233.20	239.30	171.70	228.40	205.90	202.70	88.83	101.30	106.10	116.90	103.70	140.10	161.70	163.90	111.90
V	12.71	37.09	30.23	28.02	16.53	21.39	28.78	30.98	39.68	35.83	24.93	16.87	15.96	17.11	23.51	23.62	23.17	15.38	30.75	20.74
W	402.40	47.91	20.17	18.53	14.91	20.05	17.54	19.60	37.12	50.02	18.17	14.32	24.52	24.13	23.53	18.22	13.17	18.78	32.36	14.32
Y	8.12	14.44	14.85	14.20	13.40	16.81	14.90	15.40	21.58	14.16	13.91	10.16	12.61	10.15	14.88	17.64	17.14	9.90	22.53	13.87
Yb	0.55	0.83	0.82	0.90	0.82	0.95	0.95	1.01	1.63	0.80	0.87	0.66	0.84	0.67	0.98	1.11	1.06	0.65	1.56	0.88
Zn	273.00	514.10	397.90	107.90	92.04	169.00	102.80	77.51	84.43	577.00	89.47	80.26	79.37	73.36	86.52	123.10	75.55	105.40	77.83	102.90
Zr	79.63	113.00	115.30	156.60	120.10	114.30	161.30	180.00	221.00	91.85	143.80	95.01	94.98	112.60	145.10	157.20	137.30	104.70	180.90	148.70

Table S1-6. Elemental correlations calculated from the chemical and radiological characterizations of the mill tailings.

Table with 30 columns (As, Ba, Be, Bi, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Gd, Ge, Hf, Ho, In, La, Lu, Mo, Nb, Nd, Ni, Pb, Pr, Rb, Sb, Sm, Sn, Sr) and rows for various elements including As, Ba, Be, Bi, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Gd, Ge, Hf, Ho, In, La, Lu, Mo, Nb, Nd, Ni, Pb, Pr, Rb, Sb, Sm, Sn, Sr, Th, U, V, W, Y, Yb, Zr, and Totals. The cells contain numerical correlation coefficients.

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