Re-mobilization of uranium and thorium from sediments contaminated by naturally occurring radioactive material (NORM) through leaching by acid mine drainage (AMD).

Faanhof A[1], Shongwe NS[2] and Connell, SH[2]

[1] North-West University, Private Bag X2046, Mmabatho 2735, South Africa.
[2] Department of Physics, University of Johannesburg P.O. Box 524, Auckland Park, 2006, South Africa

*Corresponding author: E-mail: shongwens@yahoo.com

Abstract. The potential re-mobilization of uranium and thorium from sediments contaminated with NORM wastes from decades of gold mining and the possible radiological environmental issues associated with the recent increase of acid mine drainage (AMD) in one of the major gold mining areas in South Africa has been studied through simple leaching experiments with simulated AMD. The K_d values of uranium and thorium predict the rapidity and reversibility between the dissolved (C_w, Bq.ℓ^{-1}) and the adsorbed (C_s, Bq.kg^{-1}) phases. In principle one would expect uranium to be more mobile than thorium and accordingly uranium may be remobilized to the liquid phase while thorium is expected to stay in the solid phase. However, uranium appears to be concentrated in the insoluble fraction of the sediments and accordingly will not be mobilized by AMD, while thorium may be homogeneously distributed (adsorbed) between the soluble and insoluble fractions of the sediments. From the K_d values it is expected that thorium contained in the soluble fraction of the sediments will quickly be adsorbed in the insoluble fraction of the sediments and accordingly will not become part of the water body.

1. Introduction

Due to excessive gold mining activities in the Witwatersrand basin heavy metals, radioactive minerals and other potentially harmful chemicals have found their way into the rivers and wetlands in the gold mining areas enhancing the radioactivity of the environment. Plants that die in the riverine system contribute to the formation of sediments, together with run-off from land and slimes-dams and through deposition of airborne dust. From a radiological point of view there are three sources of contaminants emanating from the decay chains of ^{238}U, ^{235}U and ^{232}Th. This study concentrated on uranium and thorium only. Instrumental neutron activation analysis (INAA) and inductively coupled plasma mass spectrometry (ICP-MS) were used in the analysis of the sediments and leachates.

2. AMD Formation and Nuclide Mobility

Acid mine drainage (AMD) is one of the proceeds associated with the oxidation of pyrite (iron sulphide, FeS_2) in the gold ores **[1].** AMD can basically be regarded as the ground/surface water contaminated with sulphuric acid at pH=4.

The degree of radionuclide sorption on the solid phase is quantified by the solid-liquid distribution coefficient (K_d). The K_d-values are used when assessing the overall mobility and likely residence times of the radionuclides in soils **[2].** The K_d-value (ℓ/ kg^{-1}) is based on the hypothesis of a reversible and rapid equilibrium between the dissolved (C_w, Bq.ℓ^{-1}) and the adsorbed (C_s, Bq.kg^{-1}) (solid) phases of radionuclide as shown in Equation 1:

$$\mathbf{K_d} = \frac{C_s}{C_w} \tag{1}$$

For solid sources, like ores of uranium and thorium, the mobility in the sediments depends on solubility and dissolution (leaching) **[3]**. Concentration variations are induced by local differences in sediment mineralogy and properties leading to interactions such as adsorption to clay or by physical selection processes like settling of a contaminant at the inside of a river bed due to velocity differences **[4].**

2.1 Uranium

The aqueous uranyl (VI) ion (UO_2^{2+}) is very mobile and through its mobility it can be distributed over larger areas **[5].** The adsorption of uranium is low at pH values less than 3, increases with increasing pH and reaches a plateau between pH 5 and 8 while for higher pH adsorption decreases again **[4].**Typical values for K_d (l.kg^{-1}) of uranium are 35 (sand), 400 (organic material) and 1600 (clay) in **[6]** and agrees with those in **[2].**

2.2 Thorium

In an aqueous environment thorium exists as Th (IV) and its mobility is limited by the formation of its insoluble hydroxide $Th(OH)_4$ **[4].** Thorium has a strong affinity towards suspended particles, and once mobile it will be rapidly re-adsorbed to become immobile.

Table 1 provides some of the adsorption coefficients of NORM nuclides to a number of matrices.

Table 1. Partition coefficient, K_d of some of the NORM nuclides of interest in soils (ℓ.kg^{-1}) **[2].**

Nuclide	Sand	Loam	Clay	Organic
Ac	450	1500	7400	5400
Bi	120	400	670	1500
Pa	540	1800	2700	6600
Pb	270	16000	540	22000
Po	150	400	2700	6600
Ra	490	36000	9000	2400
Th	3000	3300	5400	89000
U	33	12	1500	400

3. Materials and Methods

3.1 Study location/area

Figure 1. Locality of Wonderfonteinspruit catchment.

The measurements were conducted on twenty-one (21) selected samples from a batch of 250 samples collected in a previous study on the Mooi-river sediments from the Wonderfontein catchment. The samples selected were distributed through the catchment area. Samples with high uranium and thorium concentrations were selected to ensure adequate sensitivity of the analysis techniques applied. The leaching experiments were done at the Radioanalytical laboratories of Necsa. INAA was also done at Necsa, while the ICP-MS analyses were partly done at Necsa as well as at the University of Johannesburg.

3.2 Summary of the experimental design

The chosen sediment samples were analyzed prior to leaching both by ICP-MS and INAA. Thereafter, a 25 gram portion of the sediments were leached in 150 mℓ of a diluted sulphuric acid (pH=4) for 24 hours using a magnetic stirrer, stirring at such a speed that sediments were equally distributed along the water column, simulating the potential remobilization of naturally occurring radionuclides after heavy flooding of the catchment area with the AMD contaminated water. At the end of 24 hour leaching it was assumed that a near constant K_d value resulted for the dissolved elements in each sample. The samples were filtered and the leachates were stored in polyethylene bottles for analysis by ICP-MS. The leached sediments were washed three times with distilled water to remove any remaining acid and analyzed for uranium and thorium using both INAA and ICP-MS.

4. Results and Discussion

4.1 *Quality control*

In a previous study **[8]** the same sediments were analysed for a suite of toxic elements including uranium and thorium. These data were used to assure some quality control on the current results. The two sets of data indicate that the uranium and thorium concentration ratios are close to 1 (1.12 ± 0.29 for uranium and 1.24 ± 0.25 for thorium) for most samples except for one, which gives an indication that "hot" particles can lead to substantial discrepancies and that the samples are not entirely homogeneous at the mass of 300 mg as used for INAA.

4.2 Uranium and thorium leaching from the sediments

The average concentrations of uranium and thorium in the sediments before and after leaching with AMD based on INAA results are given in table 2.

Table 2. Uranium and thorium leaching as observed through INAA.

Sediment mass (g)			**Uranium mass (mg)**			**Thorium mass (mg)**		
Prior to	After	Loss (%)	Prior to	After	Loss (%)	Prior to	After	Loss (%)
25.0	20.22	19.1	3.25±0.11	3.28±0.15	-0.88	0.289±0.08	0.235±0.08	18.8

It can be seen from table 2 that after doing mass corrections there is on average no decrease in the uranium mass. This is confirmed by the low uranium content of the leachates as shown in table 3. In general the simulated AMD has apparently not leached U from the sediments into the leachate. The U recovered in the leachate from table 3 is $9.01\mu g$. This indicates the insolubility of the uranium containing mineral as shown by a K_d value for U (see table 1), and accordingly to the conclusion that uranium is adsorbed to insoluble clay particles and/or part of insoluble particles originating from effluents from the mining industries released to the surface water and/or run-off or wind-blown residues from tailings dams.

The AMD modelling indicates that potential remobilization of uranium nuclides after heavy flooding of the catchment area in real life samples may not exist.

From table 2 one can see that on average the thorium content in the sediments decreased by about 18.8%. This coincides well with the observed average relative reduction of the mass of the sediments upon leaching with the simulated AMD of 19.1%. Accordingly, in spite of the high K_d values for thorium for a majority of materials one may come to the conclusion that thorium also forms part of the soluble fraction of the sediments and as such may be partly remobilized by AMD. However, looking at the ICP-MS results in table 3 one observes almost no thorium recovery in the leachate.

From this one can conclude that part of the thorium that was remobilized as a result of dissolution of the soluble part of the sediments did not remain in the leachate but was again strongly adsorbed to most likely the wall of the containers the leachate was stored in or to the filter used in the filtration process. This is a strong indication that thorium once remobilized will be rapidly re-adsorbed to the residual sediments and that potential remobilization of thorium after heavy flooding of the catchment area in real life samples may not exist.

Table 3. Uranium and thorium concentrations in the leachates by ICP-MS.

Sediment mass (g)			Uranium mass (mg)			Thorium mass (mg)		
Prior to	After	Loss (%)	Prior to	Leachate	Loss (%)	Prior to	Leachate	Loss (%)
25.0	20.22	19.1	3.246±0.11	0.009	0.288	0.289±0.08	9.2×10^{-6}	0.003

5. Conclusion

The current study suggests that at a pH of 4, uranium is not readily desorbed being part of the insoluble matrix when exposed to acid mine drainage, while thorium will be initially remobilized as part of the soluble fraction of the sediments, but will most likely be re-adsorbed to the remaining sediments. Actual samples in the catchment areas influenced by AMD should be collected to confirm our results.

The potential remobilization of other nuclides from the NORM-series nuclides should also be investigated in follow-up work.

Acknowledgements

The author would like to acknowledge the National Research Foundation, Necsa and the University of Johannesburg for financial support. We are also grateful to the staff at SPECTRAU at the University of Johannesburg.

References

[1] Diale PP, Mkhize SL, Muzenda E and Zimba J 2011 The sequestration of heavy metals contaminating the Wonderfonteinspruit catchment area using natural zeolite. *WASET* **74:**766—72.

[2] International Atomic Energy Agency (IAEA) 2010 *Handbook of Parameter Values for the Prediction of Radionuclide Transfer in Terrestrial and Freshwater Environments.* Technical Reports Series No. 472.

[3] Battacharyya, DK 1998 Issues in the disposal of waste containing NORM. *Appl. Radiat & Isot* **49**:215—26.

[4] van der Graaf ER, Koomans RL, Limburg J and Vries K 2007 In situ radiometric mapping as a proxy of sediment contamination: Assessment of the underlying geochemical and physical principles. *J. Appl. Radiat and Isot* **65**:619—633.

[5] International Atomic Energy Agency (IAEA) 1997 *Environmental Impact Assessment for Uranium Mine, Mill and In situ Leach Projects*, IAEA – TECDOC-979, Vienna.

[6] Environmental Protection Agency (EPA) 1999 *Understanding Variation in Partition Coefficients, K_d, values for Cadmium, cesium, Chromium, Lead, Plutonium, Radon, Strontium, Thorium, Tritium (3H) and Uranium.* EPA Report 402-R-99-004B, United States. EPA, Office of Air and Radiation, USA.

[7] International Atomic Energy Agency 2007 Modeling the transfer of Radionuclides from Naturally Occurring Radioactive Material. Report of the NORM Working Group of (Environmental Modeling for Radiation Safety) Theme 3.

[8] Ramatlhape II 2009 *Analysis of Naturally Occurring Radioactive Material and Radio-cesium in sediments from the Wonderfonteinspruit Catchment Area in the North-West Province and Mosses from Minsk Using Gamma Spectroscopy and Gas Flow Proportional Counting.* Dissertation, Radiation Science & Technology, Northwest University.