Geochemical and Bioreactivity Assessment of Future Mining Operations at Mutanga Uranium Project, Southern Province, Zambia

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Abstract

Current concerns over global warming and fossil fuel impacts have led to an increasing demand for low CO_2 producing forms of energy, including nuclear power, resulting in increased uranium exploration activity. However, concern exists for the release of radionuclides and associated metals from such mining and therefore require continuous monitoring and adaptive management.

Low grade ore, waste rock and surface samples were collected from the Mutanga Project, a prospective uranium mine in the southern province of Zambia. Currently there are no mining activities but it is proposed that open-pit mining be initiated at two sites along with acid heap leaching and development of waste rock facilities on small seasonal feeder streams running into Lake Kariba.

Analytical techniques in accordance with appropriate British and Analytical Standards were used in this study, such as X-ray fluorescence (XRF), X-ray diffraction (XRD) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). Leachate tests were employed to assess the geochemical properties and mobility of target metals, focusing on vanadium, titanium, lead and uranium. The potential bioreactivity of airborne mineral mine dust was evaluated using a Plasmid Scission Assay (PSA), where the ability of mineral particulate matter to generate Reactive Oxygen Species (ROS) and damage plasmid DNA, over a dilution range was assessed.

The results from the 22 samples indicated very low levels of target metals were mobilised within the leachates, while the additional dilution influence from Lake Kariba would mitigate any potential impacts. The PSA analysis indicates fine dust particles could be ingested and potentially cause DNA damage, due to the high crystalline silica content within these samples. A noticeable dose effect was observed. In order to mitigate this risk, dust suppression in the mining and process facilities is recommended along with personal dust protection for mine personal involved in extraction process.

Keywords: uranium mine, mobility, bioreactivity, target metals

Introduction

The current world energy system in unsustainable, with respect to fossil fuel supply (Dittmar, 2012). Uranium provides a means of alternative fuel (nuclear energy) which is essential when faced with the current global warming issues, due to the low carbon emissions of this fuel source. Nuclear energy generates 14% of the world energy sector, with the current global demand for uranium being approximately 67000 tonnes per year. The world's current measured U-resources (5.9 million tonnes) is estimated to last about 90 years, representing a higher level of assured resources in comparison for most other minerals.

Uranium is mined similarly to other metals by techniques such as open pit, underground mining and in-situ leaching (ISL). Activity surrounding the Mutanga Uranium project is focused on extracting mineable economic orebodies from the deposits, with

the intention of mining 18.8 million tonnes of U-ore. The favoured treatment method for U-extraction is an operational method of acid heap leaching. Heap leaching occurs with low-grade deposits, where the broken ore is stacked on an impermeable surface and irrigated with an acidic solution for a period, after which the pregnant liquor is collected and treated to recover the U. This ore will be processed into uranium oxide concentrates (U_3O_8), commonly known as "Yellow Cake" and shipped to the International market for use in nuclear energy generation. Currently the project area has no known environmental liabilities as mechanised mining activities have yet to take place.

The process of extracting metals from underground ore deposits tends to generate large amounts of waste, as the metal ore of value is only a small fraction of the material being mined. This resulting waste has a large impact on the environment, as it may result in air pollution, ground deformation, water and ground contamination and water resource depletion.

This paper reviews the impact of extracting and dumping uranium mine waste rock on seasonal feeder streams, and the risks of this process on the surrounding communities and Kariba Dam in the southern province of Zambia. This involves assessing the geochemistry of the specific area, and the leaching potential and mobility of target metals focussing on uranium (U), lead (Pb), titanium (Ti) and vanadium (V), as well as determining the bioreactivity and toxicity of rock samples on receptor DNA. It is important to understand the toxicity of a material or compound by examining the degree of reactivity with regards to biological mechanisms or within physiological conditions. The bioreactivity has been assessed using particulate matter (PM), the ability of this matter to produce reactive oxygen species (ROS) and the interaction of these ROS with DNA.

Mineralisation On-Site

The initial identification of uranium (U) mineralisation in the Siavonga District occurred in 1957, with further exploration activities revealing the bulk uranium mineral resources are made up of three main deposits, Mutanga, Dibwe and Dibwe East, with additional smaller deposits also discovered. The Mutanga ore is a Sandstone-type deposit, which formed in permeable sandstone aquifers, below the water table at low temperatures. In these settings, oxidising groundwater flowing into the aquifer from the surface carries aqueous uranyl U^{6+} complexes which have been leached from the overlying strata, deeper into the system. When this water encounters sulphides, organic matter or hydrocarbons, the aqueous uranyl is reduced and insoluble U^{4+} is precipitate. The majority of the U found at Mutanga is contained within Uranium-Calcite-Potassium minerals of Autunite and minor Meta-Autunite, with approximately 2% of the U-bearing mineralisation comprised of brannerite and coffinite.

The uranium is sourced from surrounding Proterozoic gneisses and plutonic basement rocks, where post lithification groundwater table variations caused these U^{4+} minerals to be dissolved and transported in solution and redeposited in specific reducing environments in clay-rich zones, along fractures within siltstones and sandstones of the EGF (Anderson et al, 2017). Mineralisation takes place either by dissemination, fracture controls or mud-replacement. Disseminated U3O8 occurs as interstitial crystals of varied sizes within sandstones, conglomerates and mud- layers, balls and flakes. Sulphides such as pyrite forming beside U_3O_8 may be indicative of transitional zones where groundwater has moved through the lithology.

Methods

Samples were collected from the site for chemical analysis and were chosen based on their in-situ U concentrations to target low-grade ore (100-200ppm) and waste rock samples from different depths. Surface samples were collected from each deposit location and were chosen based on strategic positioning of the future waste rock dump at Mutanga and the leach pad at Dibwe, both from the Escarpment Grit Formation.

Several tests were carried out in accordance with relevant standards to determine the geochemical properties of the samples, including X-Ray Florescence (XRF), from which samples of chemical interest (i.e. high

U and Pb) were selected for further testing. These samples were then analysed using leachate tests, Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and X-Ray Differentiation (XRD).

To assess the bioreactivity of the samples, an invitro Plasma Scission Assay (PSA) was conducted on all surface samples, and selected core samples. This provided an indication of the quantity of target metals contained within these samples, and the effect these metals have on a plasmid DNA molecule.

Results

Each sample contained a silicon content of between 25 to 30%, with very small amounts of target metals, with rubidium and strontium being most abundant (up to 196.29ppm). Significant levels of titanium were observed in comparison to other target metals, with a wide weight percentage range within samples, from as low as 1% to 16%. The low-grade ore samples appear to have a smaller Ti content within their location, with the Mutanga more Ti-rich than Dibwe.

The lead content was very low, with trace amounts located across all samples. The Pb trend remains rather consistent, with a higher content observed at Dibwe compared to Mutanga (see Figure 1 below). There does not appear to be any relationship between the Pb and U content. Of the 22 samples collected, only four samples showed any trace of uranium, which were three of the six low grade ore samples along with a Dibwe waste rock footwall sample, where the U content is the highest obtained, at 47.63ppm.

Leaching Rates and Mobility

The target metal content leaching out of the samples is significantly low, with the most abundant elements leached out being titanium (average of 5.25ppm), potassium, silicon and aluminium. Only trace elements of vanadium, lead and uranium were recorded (average of 1.9ppb, 10.1ppb and 59.8ppb respectively). The initial compositional values were analysed against the quantities of each element found within the leachates, to provide an indication of how mobile each element is in neutral pH water.

The elements all have very low mobility rates as seen in Figure 2. The mobility averages for both vanadium and lead are slightly lower in comparison to the titanium and uranium rates. The uranium mobility average seems to be higher due to the rate of approximately 1% from a Dibwe waste rock footwall sample, while the remaining values are minor.

Mineralogy

The bulk of each sample is composed of quartz (SiO_2), a potassium-rich alkali feldspar, microcline ($KAlSi_3O_8$) and the clay mineral, kaolinite ($Al_2Si_3O_8$). None of the components observed are linked to minerals closely associated with uranium minerals.

The low-grade ore samples show a wider range of quartz compositions, with Dibwe having much lower quantities than Mutanga.

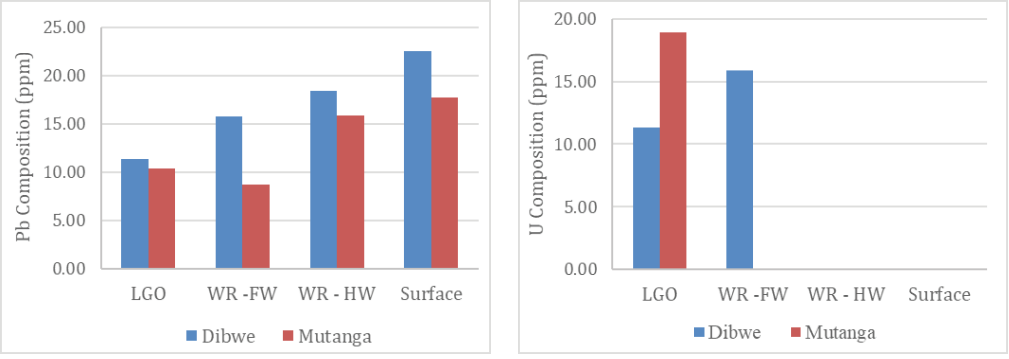

Figure 1. Lead and uranium content found in the low-grade ore (LGO), waste rock footwall (WR-FW) and hanging wall (WR-HW) and surface samples collected from the Dibwe and Mutanga site

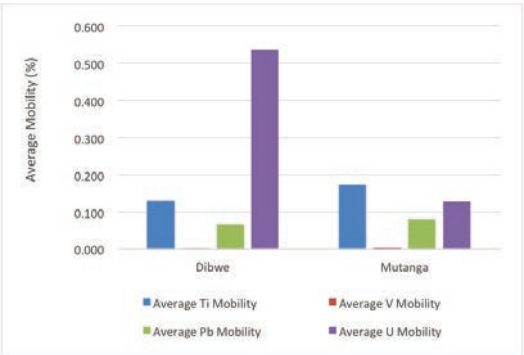

Figure 2. Mobility rates of titanium, vanadium, lead and uranium across the Dibwe and Mutanga regions

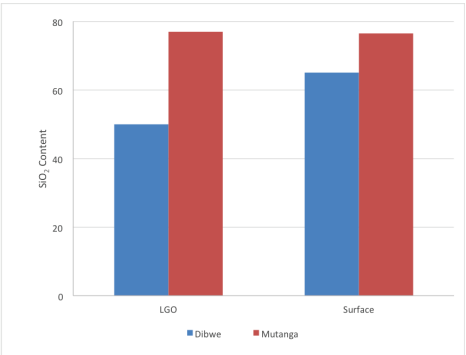

Figure 3. SiO2 content found within low-grade ore (LGO) and surface samples from Dibwe and Mutanga

After quartz, these samples are dominated by feldspar minerals, comprised of microcline and albite. Smaller amounts of clay minerals are also observed here, in the form of kaolinite and montmorillonite. The waste rock samples appear to have a more diverse range of minerals, with quartz, feldspar and clay minerals, as well as small amounts of siderite and opal. The SiO_2 trend shows the samples of Mutanga have a higher quartz content compared to those from Dibwe (Figure 3). The lowest quartz content is seen in a Dibwe low grade ore sample (50%) and waste rock hanging wall sample (57%), compared to the lowest SiO_2 content of 70% from Mutanga in both a low-grade ore and waste rock dumping surface

Bioreactivity

The impacts of the sample PM on plasmid DNA was observed at concentrations between 50 to 1000µg/ml to determine whether any bioreactivity has a dose-dependent response range. A general trend of increasing DNA damage with increasing concentration can be observed, indicating a dose effect, whereby the more concentrated the sample, the higher the observed DNA damage. The average percentage of damaged DNA across all samples is 27%, indicating overall moderate damage being done to the DNA. The oxidative potential of the PM collected from the Mutanga Project was examined using the PSA and TD20 (toxic dose causing 20% damage) values, which were calculated using linear regression. These results reinforce the trends above, showing a general minor increase in plasmid damage with increasing concentration. There is a clear correlation between the target metal content and the TD20 concentration, where samples with a higher target metal content showed a lower concentration needed to damage 20% of the DNA within the plasmid and are therefore more toxic to DNA. The relationship between the silicon content and the TD20 shows a similar trend to the one above, where the higher the silicon content within the sample, the lower the concentration of the sample needed to damage 20% of the plasmid DNA.

Discussion

The samples showed very small amounts of trace metals, such as vanadium, rubidium, strontium, lead, thorium and uranium, while the amount of titanium was slightly more significant in comparison. These low levels across the samples are however well below any significant thresholds, and therefore do not pose a significant health risk to the surrounding environment.

The observed average value for vanadium from the site was safely below the threshold value of 130ppm, however some of the samples displayed significantly higher readings. An important example of this is seen at the Dibwe surface site, where the observed V content was 100ppm higher than the threshold value. This may therefore be an important component to consider when dealing with dust control within this area.

Table 1. Threshold vales of Ti, V, Pb and U compared to average observed vales of these elements within the Mutanga site

	Threshold Values	Average Observed Values
Titanium	1000-10000ppm[1]	4249ppm
Vanadium	Soil threshold: 130ppm[2,3]	77ppm
		Dibwe surface samples: 230ppm
Lead	20-150ppm[4]	14ppm
Uranium	23ppm (residential); 300 (industrial)[5]	6ppm

[1]Aubert & Pinta, 1977; 2Gummow et al. 2005; 3Sabbioni et al. 1996, 4Beyer, 1990, 5Canadian Council, 2007

Previous testing on the site has shown the acid-producing potential of the rock surrounding the uranium ore, and therefore should be noted. Siderite has the potential to act as a neutralising mineral, and therefore the presence of it on site suggests the possibility for the waste rock to provide local neutralisation to any acidification occurring in ground or surface water due to pyrite oxidation, only where oxygen is absent from the system (Younger, 2004). The mobility factors of titanium, vanadium, lead and uranium are very low (0.00 – 0.33%), therefore confirming that these target metals will not readily enter the surrounding environment. Ti and Pb generally tend to be immobile or have lower mobility rates compared to other metals in sedimentary environments (Gabler, 1997), and as the pH of the groundwater increases between its range of 6.5 and 9.5 the Pb mobility decreases. The low mobility rates of V and U may be caused by either unfavourable pH levels or redox conditions (Gabler, 1997).

Once these target metals are mobilised within a water source, and enter Kariba, they are diluted even further. Lake Kariba holds an incredibly large volume of water of approximately $185 \times 109m^3$ at maximum retention level. This provides a further target metal buffer, as the small concentrations of Ti, V, Pb, U and other metals reaching this lake experience a large-scale dilution factor, thereby reducing the target metal concentrations even further.

Results from the PSA testing showed a relatively moderate average of 27% DNA damage across all samples. Substantially more damage was done to plasmid DNA from surface sample in comparison to core samples, which may likely be due to the higher silicon content contained within the surface. This means that without any cellular protection, supercoiled DNA exposed to these surface samples could become linearized (no relaxed DNA was observed). These particles initiated oxidative destruction in a dose-dependent way, where DNA subjected to higher concentrations of each sample showed more damage in four of the six samples.

The target metal and TD20 relationship showed that the higher the metal content, the lower the concentration of the sample needed to destroy 20% of the DNA, and therefore provides evidence that target metals can be linked to DNA destruction. However, the target metal content within these samples was too low to be the primary cause of this plasmid damage, indicating other factors being responsible for this DNA damage. Therefore, the silicon content was considered as an influential factor, as known studies have showed a link between the inhalation of crystalline silica dust and cell damage, resulting in serious lung disease (Greaves, 2000; Chanda-Kapata *et al*, 2016). When comparing the Si content from the XRF and the TD20 values, a similar trend to the target metals was seen, where higher Si contents meant lower TD20 values, and therefore higher toxicity. This was taken further, and the silicon dioxide (SiO_2) relationship was studied. This trend showed a similar inverse relationship, providing evidence that SiO_2 has an effect on DNA damage and therefore toxicity. Overall it can be assumed that potential DNA damage can be done on the plasmid DNA, from exposure to the particulate matter from these samples, partly a result of the significant silicon dioxide content. This is likely to be the cause of most of the damage, however other elements or factors may be acting in simultaneously to damage the DNA and would therefore need to be considered.

Conclusion

The target metal content of the low-grade ore, waste rock and surface samples of Mutanga Uranium Project are too low to have a significant influence on the surrounding community. This therefore suggests the mining process and resultant dumping of mine waste rock onto seasonal feeder streams will not cause the leaching and mobility of significant quantities of these target metals into the environment. Due to the dose-dependent relationship observed, these risks are further reduced by the large dilution influence of Lake Kariba. The moderate levels of DNA damage observed is most likely the result of the silicon content within these samples, due to the low target metal content established. Previous case studies conducted on the influence of silicon dioxide on human receptors have shown a link between to fibrosis and related respiratory and lung diseases, and therefore monitoring and duct control measures should be implemented to reduce exposure to SiO_2 of workers on site.

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