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The Concentration of Radioactive Materials in Mine Water

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Abstract South Africa's earth crust is rich in gold and other minerals. The extraction of minerals dates back to the beginning mining. Unfortunately the mining industry left behind huge un-rehabilitated mine dumps. In the process of sorting out extracted minerals like Gold, Uranium is recovered as a by-product and also as the main product in Uranium mines. Uranium is a common element in nature that has for centuries been used as a colouring agent in decorative glass and ceramics. It is found naturally as three different isotopes: ^{238}U, ^{235}U and ^{234}U. It undergoes radioactive decay into a long series of 13 different radionuclides before finally reaching a stable state in ^{206}Pb. This study presents the radioactivity levels and the annual dose rates of the treated and fissure mine water. The samples were analysed for the gross alpha and gross beta activity using the Gas proportional counter. The gross alpha activity of 1150 and 563 and the gross beta activity of 871 and 518 were measured for the treated water and fissure water in mBq/L, respectively. The high levels of gross alpha-beta results prompted the need to perform the alpha spectroscopy radioactivity measurements for ^{238}U, ^{234}U, ^{230}Th, ^{226}Ra, ^{210}Po, ^{235}U, ^{227}Th, ^{223}Ra, ^{232}Th, ^{228}Th, ^{224}Ra nuclides in the two sets of samples, the radiation activities of treated water and fissure water of 922, 910, 40.3, 99.6, 14.1, 42.5, <MDA, <MDA, 6.69, 2.2, <MDA and 446, 454, 78.4, 31.2, <MDA, 20.5, <MDA, 0.59, 4.77, 7.61, <MDA were detected in mBq/L, respectively.
Keywords activity levels, uranium mining, gross alpha-beta

Introduction

South Africa's earth crust is rich in mineral resources especially gold and has been exporting raw materials for a number of years (Nengovhela et al. 2002). According to the SA Department of Minerals, the main raw minerals are gold, diamonds, platinum, chromium, vanadium, manganese, uranium, iron ore and coal (Annual Report 1998**)**. Majority of gold mines were concentrated in Gauteng, with only 1.4% of South Africa's land area, the tiny province contributes more than 33% to the national economy and about 10% to the GDP of the entire African continent. This province was developed with the wealth of gold found in the province which amount to 40% of the world's reserves (South Africa – Geography 2014).

Due to the high cost of deep gold mining in South Africa and the decline in world market price for gold, gold export earnings have dropped sharply by from $900 million per year to $300 million per year since 1994 (Coakley GJ 2000). These resulted in the closure of most mines in South Africa. The duty of continually monitoring the radiation levels to avoid contamination of ground water in the closed and abandoned mines rests with the South African government. To protect the public from radiation hazards in water, the Department of Water Affairs and Forestry (DWAF) has developed a framework for nuclide analysis and decision making in water.

The water from the closed and abandoned mines is continually treated before disposal to the environment. To ensure compliance to government regulations and to assess the quality and the effectiveness of water treatment plants the concentration of radionuclides in the treated and fissure water were analyzed in the current study.

Materials and Methods

The treated and fissure water samples were collected from area 1 and area 2, as depicted in fig. 1, in 3l containers. The samples were treated with acid and kept under refrigeration.

Fig. 1 *Mining activity at the border of Gauteng and North West provinces*

Sample Preparation

The samples were first filtered to remove coarse materials and suspended solids and thereafter preserved with Nitric acid (HNO_3) to ensure that the radionuclides are not adsorbed on container walls.

The samples were then screened for gross alpha\beta activity to get the first order estimate of the total activity. The volume of 50 mL of the water sample was evaporated to dryness and counted for 300 minutes on a gas proportional counter. The results were analysed using the Oxford software.

Table 1 *Gross Alpha-Beta activity concentrations of the sample in Area1 and Area2 of the mine including the minimum detectable activity concentration of the nuclide*
Table for Gross Alpha Beta concentrations

Nuclide	Concentrations of radionuclides (mBq/L)					
	Area 1			Area 2		
	Value ± Unc.		MDA	Value ± Unc.		MDA
Gross alpha	1150	130	310	563	104	290
Gross Beta	871	113	330	518	106	330

Alpha spectrometry analyses

The water samples were then analysed for selected radionuclides in the uranium and thorium decay series using alpha spectrometry.

Uranium radionuclides: ^{238}U, ^{234}U and ^{235}U

The Uranium radionuclides analysed by first extracting the radionuclides from the water using the solid phase extraction followed by extraction on a cation exchange resin prior to analysis by alpha spectrometry (Benedik and Vasile 2008), (Dimova et al. 2003).
The volume of 200 mL of the sample was acidified with HNO_3 and pre-concentrated to a volume of 10 ml. The pre-concentrated sample was loaded on a pre-conditioned Truspec resin. After loading the sample on the resin, it was rinsed with diluted HNO_3 and

Hydrochloric acid (HCl). The analytes were then eluted with 15 mL of 0.1 M HCl/0.1 M Hydroflouric acid (HF) to make the first eluant.

The first eluant was then purified by loading it on a pre-conditioned cation exchange resin. After loading on this resin, it was further rinsed with 10 mL of 0.1 M HCl/0.01 M HF and then eluted with 15 mL of 2 M HCl to make the second eluant. The volume of 0.1 mL Lanthanum Oxide, 0.5 mL concentrated HF and Titanium Chloride were added to the second eluent to form a co-precipitation of Uranium with Lanthanum flouride precipitate. The precipitate was then collected by filtering the solution using a filter paper. The filtrate was then dried and analysed using an alpha spectrometer equipped with alpha spec Genie software. Extraction yield of this method was evaluated using a ^{232}**U** tracer.

Thorium radionuclides: ^{230}Th, ^{227}Th and ^{228}Th

These Thorium radionuclides were analysed by first extracting the radionuclides from the water using the solid phase extraction followed by extraction on a cation exchange resin prior to analysis by alpha spectrometry (Benedik L and Vasile M 2008), (Dimova et al. 2003).

The volume of 200ml of the sample was acidified with HNO_3 and pre-concentrated to 10 ml. The pre-concentrated sample was loaded on a pre-conditioned Truspec resin. After loading the sample on the resin, it was rinsed with diluted HNO_3 and HCl. The analytes were then eluted with 15 ml 2 M HCl to make the first eluant.

The first eluant was then purified by loading it on a pre-conditioned cation exchange resin. After loading on this resin, it was further rinsed with 10 mL of 0.1 M HCl/0.01M HF and eluted with 15 mL 2 M H_2SO_4 to make the second eluant. 0.1 mL Lanthanum Oxide and 0.5 mL concentrated HF were added to the second eluent to form a co-precipitation of Thorium with Lanthanum Flouride precipitate. The precipitate was then collected by filtering the solution using a filter paper. The filtrate was then dried and analysed using an alpha spectrometer equipped with alpha spec Genie software.

Extraction yield of this method was evaluated using a ^{229}**Th** tracer.

Radium radionuclides: 226Ra, 223Ra and 224Ra

These Radium radionuclides were extracted by adding Barium solution into a 500 mL of the water sample. The Radium radionuclides in the sample are extracted by formation of a co-precipitate with Barium Sulphate in an acidic solution. The precipitate is further enhanced by adding 0.1 M EDTA into the solution. The extract was analysed using an alpha spectrometer equipped with alpha spec Genie software. Extraction yield of this method was evaluated using a ^{133}Ba tracer.

Polonium radionuclide: 210Po

The sample of volume 200 mL was acidified with HCl and thereafter, ascorbic acid was added as a reducing agent to prevent the co-precipitation of Polonium with Iron. The silver disk was then dropped into the solution to promote the spontaneous deposition of polonium on to the surface of the silver disk. The solution was stirred for 4 hours to enhance the process (Benedik L, Vasile M 2008), (Dimova et al. 2003).

The platted disk was then removed and dried prior its analysis on an alpha spectrometer equipped with alpha spectrometer Genie software.

Table 2 *Activity concentrations of nuclides in Area1 and Area2 of the mine including the minimum detectable activity concentration of the nuclide*

Nuclide	Concentrations of radionuclides (mBq/L)			
	Area1		Area2	
	Value ± Unc.	MDA	Value ± Unc.	MDA
^{238}U	922 ± 29	2.4	446 ± 22	3.1
^{234}U	910 ± 29	2.4	454 ± 23	3.1
^{230}Th	40.3 ± 7.7	27	78.4 ± 13.6	29
^{226}Ra	99.6 ± 5.4	2.7	31.2 ± 3.1	2.2
^{210}Pb	Not analysed		Not analysed	
^{210}Po	14.1 ± 4.2	10	<MDA	51
^{235}U	42.5 ± 1.3	0.11	20.5 ± 1	0.14
^{227}Th	<MDA		<MDA	8.4
^{223}Ra	<MDA		<MDA	1.7
^{232}Th	6.69 ± 2.11	4.3	4.77 ± 1.89	4.4
^{228}Th	<MDA	4.2	7.61 ± 2.11	1.6
^{224}Ra	<MDA	8.1	<MDA	4.6

Observation and discussion

The analysis was performed in a SANAS ISO 17025 accredited laboratory (T0111). Only the accredited methods were used for the analysis of samples in question.

The analyses confirms that samples are NORMs since:

- the equilibrium ratio of **^{238}U** to **^{234}U** is closer to one, and
- the equilibrium ratio of **^{238}U** to **^{235}U** is 21.75 which is a common occurrence of Uranium radionuclides in nature.

The results confirm that the samples were sourced from two different shafts because the measured radioactivity of the treated water (after treatment) is higher than the activity of fissure water (before treatment).That is, if we assume that the treatment was effectively removing the radionuclides in the water, the treated water should have had a lower activity than the fissure water.

The activity of ^{210}Po (fissure water only), ^{227}Th, ^{223}Ra and ^{228}Th (treated underground only) and ^{224}Ra in these results are below the minimum detectable activity (MDA).

Dose rate calculations

Exposure of the members of the public to the ionizing radiation emanating from this sample was measured. A conservative approach was used to calculate the annual dose rate of these samples via the drinking water exposure pathway. The annual radiation dose from any given radionuclide and for any given age group is expressed as Regulatory **G**uide-002:

Annual dose=Activity concentration×*Annual consumption*×*Dose Conversion factor*

In units of [*mSv*/*a*]=[*mBq*/*l*]×[*l*/*a*]×[*mSv*/*Bq*]

where the activity concentration was measured**,** the annual consumption rates of different age groups and dose conversion factors as reported by the IAEA Safety Series 112 (1996). The dose rates were calculated according to the guidelines specified in National Nuclear Licensing Regulatory Guide-002 (RG 002).

Table 3 *Dose rates calculations due to the activity concentrations of nuclides in Area1 and Area2 of the mine*

	Age group					
	<1a	1-2a	2-7a	7-12a	12-17a	>17a
Sample	Dose rates (μSv/a)					
Area 1	420	150	110	110	220	120
Area 2	430	150	100	95	160	97

Conclusions

The annual dose rate for all age groups varies from 95 to 430 μSv/a. According to NNR Regulatory Guide 002, the dose rates constraints applicable for members of the public within the exposed population is 250 μSv/a (DWAF Report 1999). From table 3 above it is clear that this level has only been exceeded for babies (<1 age group), but it is below limit for all other age groups. Therefore, these water samples are not suitable for consumption by babies. The disposal of the treated and fissure water must be done in consultation with NNR.

Dose limits to members of the public relate to the combined effect of all exposures from human activities. It is common practise to place a dose constraint on releases from individual facilities. Such a constraint is normally set at some fraction of the dose limit of 1 mSv/a, commonly of the order of 0.25 mSv/a that is allowing for the combined dose from up to four separate facilities on a single individual not exceeding the 1 mSv/a limit.

Although this approach is intended for new rather than existing operations, it may have some relevance to water systems in gold mining areas in that it embodies the concept of allowing for doses from other sources of exposure without causing the 1 mSv/a dose limit to be exceeded. The reference value of 0.25 mSv/a is the dose limit already imposed by the NNR on individual mines in the Mooi river catchment (DWAF Report 1999).

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