Status of naturally occurring radionuclides in copper mine wastewater in Zambia

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Abstract. For over half a century, the Zambian economy has been relying on copper and cobalt minerals from granitic rocks of the Katanga Basin. Geologically, granites tend to be good host rocks of uranium minerals. This general observation is in addition to the well-known fact that the Katanga Basin is a relatively uraniferous area. Copper mine wastewater may contain a number of alpha and beta emitters and routine control of the mine wastewater requires the measurement of mixtures of naturally occurring radionuclides. In 1993, a zero radioactivity limit value (no discharge accepted) for any radioactive material was adopted into Zambian law (Environmental and Pollution Control Act of 1993). The main objective of this study was to assess the level of naturally occurring radionuclides in mine wastewater and tailings sludge discharged to the environment from a copper mine where by-product uranium was mined and processed between 1957 and 1960. The results of this ongoing survey indicate that the radioactivity content of mine wastewater and tailings sediments exceeds the zero limit stipulated under Zambian law but are within the 'non-action level' in other countries like Poland, Portugal and South Africa. The maximum dissolved ^{226}Ra measured was 0.230 Bq/L in water discharged to surface streams and 0.176 Bq/L in the slurry discharged to tailings facilities, while ^{228}Ra was below 0.03 Bq/L in both cases. In sediments, the maximum values were 104 Bq/kg (^{226}Ra), 80.8 Bq/kg (^{228}Ra), 66.1 Bq/kg (^{224}Ra), and 1720 Bq/kg (^{40}K) discharged to tailings facilities and 56.8 Bq/kg (^{226}Ra), 47.3 Bq/kg (^{228}Ra), 56.8 Bq/kg (^{224}Ra) and 1595 Bq/kg (^{40}K) discharged to surface streams.

1. Introduction

The Zambian copper belt is one of the major mining districts of the world. The belt extends about 480 km north-west from Luanshya town in Zambia into the Katanga region of the Democratic Republic of Congo (see Fig. 1). Mining activities in Zambia started in the late 1920s. The mining industry was initially privately owned until the 1980s when the mines were consolidated into one company, the Zambia Consolidated Copper Mines (ZCCM) owned by the government of Zambia. The advent of privatization in 2000 resulted in ZCCM being privatized again, paving way for two major mining companies to come on board, Konkola Copper Mines (KCM) and Mopani Copper Mines (MCM). This study of naturally occurring radionuclides in mine wastewaters was done at Nkana mine of MCM, where uranium was once mined and processed between 1957 and 1960.

The Nkana orebody at MCM consists of mineralized beds within the sedimentary sequence of quartzite/sandstone, black shale, dolomite and argillites. The main copper ore minerals are chalcopyrite and bornite, with subordinate chalcocite and oxides occurring at the North Shaft. Minor oxide copper minerals are associated with localized leach zones. Carrolite and cobaltiferous pyrite are the major cobalt bearing minerals, with minor amounts of cattierite.

Members of the general public in Zambia usually treat exposure to ionizing radiation as a phenomenon related to nuclear power plants and/or disasters in nuclear installations. The best example is the zero radioactivity limit for radioactive materials to be discharged to the environment in terms of the Environmental Council of Zambia wastewater guidelines, compared with 'non-action' levels in other countries such as Poland, Portugal and South Africa [1, 2].

Lately, more attention is being paid to radiation exposure caused by naturally occurring radionuclides. In Zambia, investigations in this field are connected only with radon exposure in underground mines but there is also a potential external gamma radiation hazard at workplaces, as

well as a hazard to the natural environment receiving mine wastewater as the radium precipitates from the water.

FIG. 1. Map of Zambia showing the Copperbelt region

This survey of naturally occurring radionuclides in mine wastewater and sediments was done at Nkana mine of MCM, where radon gas measurements in the underground mine [3] showed that the radon levels were over 1000 Bq/m^3 [4]. It was therefore expected that the radioactivity due to radium isotopes would be enhanced. Radium is often considered to be the most important decay product of ^{238}U. Not only does it have a high 'radio toxicity' but it also decays to radon, a radioactive gas whose decay products can cause lung cancer. When ingested, radium absorption from the gastrointestinal tract into blood and soft tissue is significant, with eventual deposition in bones.

The main objective of the study was to assess the levels of naturally occurring radionuclides in mine wastewater and sediments being discharged to the environment to ascertain whether pollution is taking place in terms of Zambian law.

Previous uranium exploitation at Nkana mine and the associated radioactive tailings deposition at the Amco tailings pile were focused on a small uranium deposit exploited at the Mindola No. 4 Shaft in 1957–1960. Uranium occurred in the primary minerals pitchblende/uraninite and approximately 120 000 kg U_3O_8 was recovered from the ore with an average grade of 0.25% U_3O_8. Uranium occurs in a similar manner, but at much lower levels, in most of the copper belt mines in Zambia [5].

Investigations at gold and copper mines in Cuba [6] have indicated that ^{226} Ra concentrations range between 53 and 7216 Bq/kg in various minerals and residues. Water samples had a ^{226}Ra concentration of between 4 and 160 Bq/L. A study of NORM in the copper industry in Arizona [7] reported that groundwater from six mines had ^{226}Ra concentrations ranging from undetectable

levels to 4.81 Bq/L, ^{228}Ra from undetectable levels to 4.51Bq/L and total uranium from undetectable levels to 7.73 Bq/L.

In the United States of America, the present drinking water standard is 0.18 Bq/L for ^{226}Ra as a maximum contaminant level (MCL) and the Environmental Protection Agency has established MCLs for alpha emitters of 0.1 Bq/L for ^{226}Ra; 0.2 Bq/L for combined ^{226}Ra and ^{228}Ra and 0.6 Bq/L for gross alpha activity [8].

In Poland, wastewater from coal mines in which the content of ^{226}Ra was more than 0.7 Bq/L had to be treated as a waste material with enhanced radioactivity [9]. Unfortunately, after joining the European Community, such a requirement was cancelled due to the need for unification with European law, in terms of which there are no limitations on radium in waste water. In South Africa, there is also no limitation of radium concentration in waste water but the provisions of the Regulations of the 1993 Nuclear Energy Act applied to radioactive material in which the activity concentration of any radionuclide was 0.2 Bq/g or more [1].

This paper highlights the status of naturally occurring radionuclides in mine wastewater and sediments at one of Zambian copper mine where uranium was mined and processed. At this mine, wastewater from cobalt and copper beneficiation is discharged to surface water courses and tailings facilities. The treatment is generally restricted to sludge settlement and lime dosing.

This is the first attempt to sample and measure naturally occurring radionuclides in mine wastewater and sediments discharged to the environment in Zambia. The survey needs to be extended to other mines in Zambia to generate a complete picture of the status of NORM in uraniferous mines in Zambia.

2. Methods and instrumentation

Three sampling campaigns were conducted between September 2005 and October 2006. Sampling for both wastewater and sediments was done in the latter half of each year when production was at a maximum to meet the annual production target. In 2005, sampling was done in September and November. In 2006, sampling was done in August. Sediment sampling was not done in November 2005 due to logistical problems. The sampling sites for both wastewater and sediments were the tailings thickener feed (mine wastewater), tailings thickener overflow (after settling) to the stream and the tailings thickener underflow (sludge) to the tailings facilities. These samples were analysed for dissolved and total radionuclides at the Central Mining Institute, Laboratory of Radiometry, Katowice, Poland.

Radioactivity in copper mine wastewater is mostly from ^{226}Ra from the ^{238}U series and ^{228}Ra from the ^{232}Th series. An existing method of chemical separation of radium [10] was modified for liquid scintillation counting [11]. Radium is co-precipitated with barium in the form of sulphates and this precipitate is mixed with liquid gelling scintillator. The prepared samples were measured by a low background liquid scintillation spectrometer (Quantulus, Wallac Oy, Finland). This counter was equipped with alpha–beta separation and an anti-coincidence shield, which enabled measurements of ^{226}Ra concentration above 0.003 Bq/L to be made simultaneously with measurements of ^{228}Ra (LLD = 0.03 Bq/L) and ^{224}Ra (LLD = 0.05 Bq/L). In addition, the procedure enabled the simultaneous determination of ^{210}Pb.

Sediments were analyzed quantitatively using a high resolution gamma spectroscopy system equipped with an HPGe semiconductor detector. Samples of sediments were dried at 105^{o}C until reaching a stable mass. The radium isotopes were measured directly by the 186 keV energy peak (^{226}Ra) or by their progeny after equilibrium had been reached. The following gamma energies were taken into consideration and by ^{210} Pb at 295 keV and 351 keV and ^{214}Bi at 609 keV, ^{228}Ra by ^{228}Ac at 338 keV, 911 keV and ^{224}Ra by ^{212}Pb at 238 keV and 208 TI at 583 keV. The detection limit was

less than 1 Bq/kg for each radionuclide. The results are expressed in units of becquerel per kilogram dry mass and the uncertainty was quoted in terms of one standard deviation.

3. Results and discussion

The results of the analyses based on liquid scintillation spectroscopy measurements for dissolved ^{226}Ra and ^{228}Ra are given in Table 1. The measured concentrations of radium isotopes in the samples showed remarkably enhanced concentration of dissolved ^{226}Ra in the tailings discharge and little ^{228}Ra in water discharged to the stream. This was unexpected, considering the high sulphate content in the ore (chalcopyrite) with the presence of barium ions which co-precipitate with ^{226}Ra and settle out as sediment.

TABLE 1. DISSOLVED RADIONUCLIDES IN WASTEWATER

	Activity concentration (Bq/L)					
	Tailings thickener feed		Tailings thickener overflow		Tailings thickener underflow	
	^{226}Ra	^{228}Ra	^{226}Ra	^{228}Ra	^{226}Ra	^{228}Ra
September 2005	0.097 ± 0.011	0.18 ± 0.06	0.043 ± 0.007	<0.03	0.176 ± 0.019	0.08 ± 0.07
November 2005	0.115 ± 0.011	<0.03	0.041 ± 0.006	0.11 ± 0.04	0.212 ± 0.018	0.10 ± 0.03
August 2006	0.065 ± 0.010	<0.03	0.037 ± 0.005	<0.03	0.230 ± 0.021	<0.03

In sediments, enhancements of radionuclides discharged to environment are negligible as shown in Table 2. The concentrations of the radionuclides generated during beneficiation of copper and cobalt are almost the same as those in the discharge to the tailings facilities with little reduction in concentration in the discharge to the streams. This can be attributed to the alkaline nature of the mine wastewater, which does not support dissolution of ^{226}Ra. Therefore, the suspended radionuclides generated from mining activities end up in sediments at tailings facilities.

TABLE 2. NATURAL RADIONUCLIDES IN SEDIMENTS

	Activity concentration (Bq/kg)			
	^{226}Ra	^{228}Ra	^{224}Ra	^{40}K
Tailings thickener feed				
September 2005	78.4 ± 6.1	60.1 ± 3.3	54.8 ± 3.1	1621 ± 88
August 2006	80.25 ± 3.75	73.9 ± 4.6	66.1 ± 5.75	1720 ± 69
Tailings thickener underflow				
September 2005	80.6 ± 4.3	53.5 ± 3.7	50.7 ± 3.6	1424 ± 58
August 2006	104.0 ± 4.5	80.8 ± 5.1	69.8 ± 4.7	451 ± 29
Tailing Thickener Overflow				
September 2005	50.17 ± 4.3	39.7 ± 3.7	35.7 ± 3.3	81 ± 58
August 2006	56.85 ± 3.65	41.9 ± 4.5	38.6 ± 4.7	96 ± 18

The average concentrations for dissolved and suspended radionuclides in mine wastewater and sediments, respectively before and after treatment are presented on Figs 1–6.

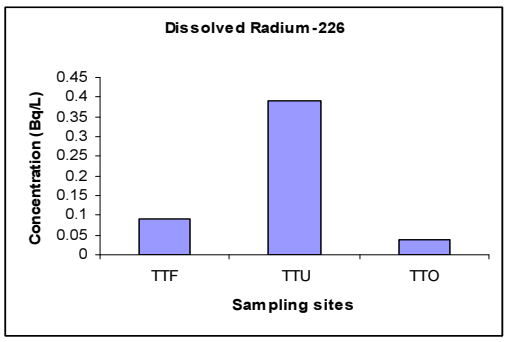

FIG.1. Dissolved ^{226}Ra in wastewater

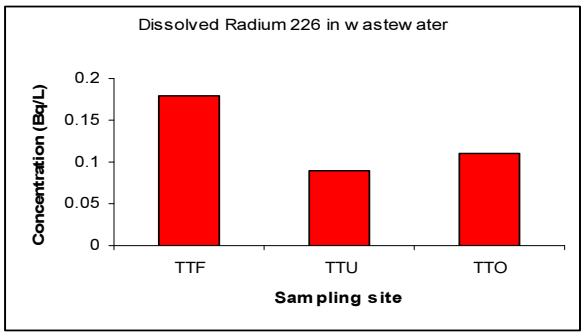

FIG. 2. Dissolved ^{228}Ra in wastewater

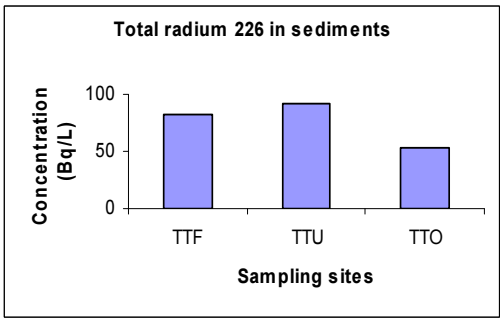

FIG.3. Total ^{226}Ra in sediments

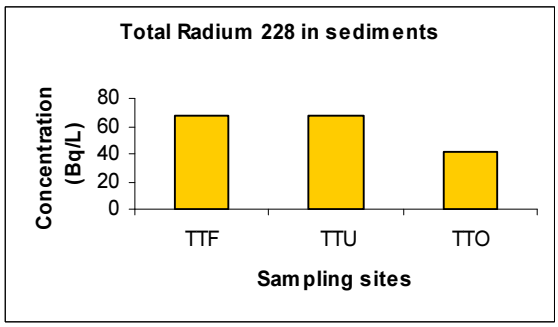

FIG.4. Total ^{228}Ra in sediments

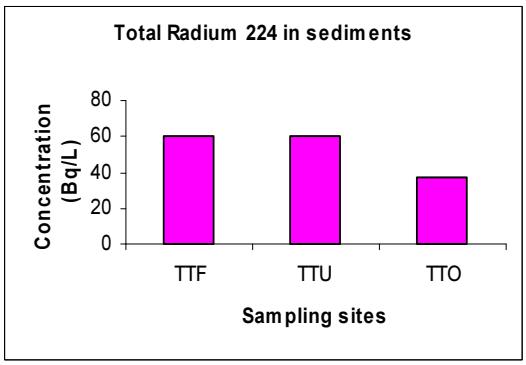

FIG. 5. Total ^{224}Ra in sediments

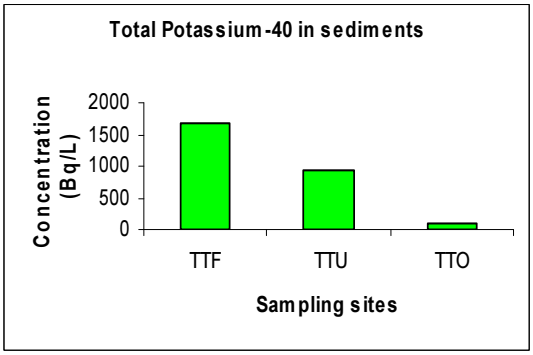

FIG. 6. Total ^{40}K in sediments

Note to Figs 1–6: TTF: Tailings thickener feed (mine wastewater)
TTU: Tailings thickener underflow (to tailing facilities)
TTO: Tailings thickener overflow (to the stream)

4. Conclusions

From the preliminary survey with a limited number of sample measurements, it can be concluded that the current treatment strategy of lime dosing and sludge settling enhances dissolved ^{226}Ra concentration in the tailings thickener underflow discharged to the tailing facilities and little is discharged to the streams. It can also be concluded that this treatment strategy has little or no effect on the suspended radionuclides in the sediments — almost all the radioactivity associated with copper and cobalt beneficiation ends up in the tailings facilities. Therefore, under Zambian law of zero limit for radionuclides discharge into the environment, pollution in the form of naturally occurring radionuclides can be said to be taking place.

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