Radioactive nuclides in phosphogypsum from the lowveld region of South Africa

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We evaluated the suitability of phosphogypsum from the Lowveld region of South Africa (LSA), for the manufacturing of building materials, with reference to (1) the *National Nuclear Regulator Act 47 of 1999* and (2) the radioactivity associated risks as quantified in terms of the external and internal hazard indices, the activity concentration index and the radium equivalent. The distribution of radioactive nuclides in the LSA phosphogypsum was also examined. Analyses of 19 samples of the phosphogypsum show that phosphogypsum contains lower activity concentrations of naturally occurring radioactive nuclides of uranium and thorium and their progeny than the 500 Bq/kg limit set for regulation in South Africa. The potassium-40 (^{40}K) activity concentration was below the minimum detectable amount of 100 Bq/kg. The values obtained for external and internal hazard indices and the activity concentration index were: 2.12 ± 0.59, 3.44 ± 0.64 and 2.65 ± 0.76 respectively. The calculated radium equivalent Ra_{eq} was 513 ± 76Bq/kg. The final decision regarding phosphogypsum's suitability for use as a building material should consider scenarios of use.

Introduction

A phosphoric acid production facility has been in operation in the Lowveld region of South Africa (LSA) since the 1960s. The process of producing phosphoric acid involves the digestion of fluoro-apatite ore ($Ca_{10}(PO_4)_6F_2$) with sulfhuric acid as shown in Equation 1:

$$Ca_{10}(PO_4)_6F_2 + 10H_2SO_4 + 20H_2O \rightarrow 10CaSO_4.2H_2O + 6H_3PO_4 + 2HF \quad \text{Equation 1}$$

Each year, tons of calcium sulfate dihydrate ($CaSO_4.2H_2O$) or gypsum, or specifically phosphogypsum, is produced as a by-product. The LSA phosphogypsum is stored in waste stacks alongside the phosphoric acid factory. In a country like South Africa, that has a challenge to provide low cost or affordable housing,[1] the use of phosphogypsum to manufacture building material is an attractive option. The manufacturing of low cost prefabricated building material from gypsum has in the recent past been demonstrated by Rajkovic and Toskovic[2]. But the solubility of uranium, thorium and their daughter products that exist in apatite ores[3,4] result in these radioactive nuclides partitioning between the phosphoric acid and the phosphogypsum[5,6] during the processing of the ore. Rajkovic and Toskovic[2], Al-Jundi et al.[6] and Hussein[7] studied phosphogypsum from Serbia, Jordan and Egypt respectively. Hussein did not report on the activity concentrations of potassium-40 (^{40}K), thorium-232 (^{232}Th) and radium-226 (^{226}Ra) but the results of radioactive nuclides activities from Serbia and Jordan are given in Table 1.

Table 1: Activity concentrations (Bq/kg) of 40K, 232Th and 226Ra in phosphogypsum from other countries

Country	Number of samples	^{40}K	^{232}Th	^{226}Ra
Serbia[2]	-	8.7	8.7	439
Jordan[6]	15	40	-	376

The worldwide average activities of ^{226}Ra, ^{232}Th and ^{40}K on the earth's crust are about: 40; 40 and 400 Bq/kg, respectively.[8] Humans are therefore exposed to this naturally occurring radioactive material (NORM). If the material used for the construction of human dwellings contributes additional radioactivity to the naturally occurring radioactive material, radiation exposure increases. The presence of these radioactive nuclides impurities in the LSA phosphogypsum can limit its use as a building material.

In this study we evaluated the suitability of the LSA phosphogypsum for the manufacturing of building materials, with reference to (1) the *National Nuclear Regulator Act 47 of 1999*[9] and (2) the radioactivity associated risks as quantified in terms of the external (H_{ex}) and internal (H_i) hazard indices, the activity concentration index (I_γ) and the radium equivalent (Ra_{eq}). The effect of ore processing on the distribution of the radioactive nuclides was also examined.

Materials and method

During the production of phosphoric acid for analysis, 19 grab samples of LSA phosphogypsum were taken.

Sample preparation

The phosphogypsum was dried overnight in an oven at 80 °C. About 100 g of the dried phosphogypsum was transferred to a grinding vessel (containing stainless steel grinding balls and block) with a swing mill. Milling was performed at 960 rpm. for one min to obtain a fine powder. The process was repeated until 0.5 kg of homogeneous fine powder was generated.

Gamma analysis

A standard glass container was filled with phosphogypsum and the mass recorded. The container was closed with a lid and sealed airtight with the aid of epoxy resin. The prepared sample was allowed to stand for 3 weeks so that radon-222 (and some of its progeny) reached radioactive equilibrium with radium-226. The γ-spectrum was acquired on a high purity germanium detector calibrated for the standard glass container geometry. The detector was housed in a lead shield to reduce background radiation. Gamma spectrum analysis was performed with Genie™ 2000 Model S501 Gamma Analysis software. The weighted average activity of bismuth-214 and lead-214 was calculated and reported for radium. Thorium-228 was calculated from lead-212 and thalium-208. Radium-228 was determined from actinium-228. Potassium-40 was measured directly.

Uranium and thorium analysis by activation analysis

Aliquots of the powder were transferred into irradiation capsules. Uranium and thorium standards were prepared by transferring known amounts of these elements from certified reference solutions into capsules and evaporated to dryness. Samples and standards were sequentially transferred with a pneumatic system into an in-core position of the SAFARI-1 reactor and irradiated with neutrons for a fixed time. After irradiation, the sample was transferred to a detector to measure neutrons emitted by products formed from fission of uranium-235.

The emission of neutrons between samples and standards was compared to calculate the uranium concentration in the sample. After a prolonged period, the irradiated samples and standard were measured on a gamma detector to determine neptunium-239 and protactinium-231. These nuclides formed from the neutron activation of uranium-238 and thorium-232 respectively. By comparing the activities of the nuclides in the standards and samples, the uranium-238 and thorium-232 sample activities were calculated.

Radiation indices

From the activity concentrations of the radioactive nuclides, H_{ex}, H_{i}, I_{γ} and Ra_{eq} were calculated using the formulae in Equations 2–5 respectively. The formulae and their applications are comprehensively defined by the European Commission for Radiation Protection[8].

$$H_{ex} = \frac{C_{Ra}}{370} + \frac{C_{Th}}{258} + \frac{C_{K}}{4180} \qquad \text{Equation 2}$$

$$H_{in} = \frac{C_{Ra}}{185} + \frac{C_{Th}}{259} + \frac{C_{K}}{4810} \qquad \text{Equation 3}$$

$$I_{\gamma} = \frac{C_{Ra}}{300} + \frac{C_{Th}}{200} + \frac{C_{K}}{3000} \qquad \text{Equation 4}$$

$$Ra_{eq} = C_{Ra} + 1.43C_{Th} + 0.077C_{K} \qquad \text{Equation 5}$$

where C_{Ra}, C_{Th} and C_{K} are activities of ^{226}Ra, ^{232}Th and ^{40}K in Bq/kg, respectively.[10,11]

Results and discussion

Radionuclide concentrations in phosphogypsum

The average activity concentrations of the radioactive nuclides: uranium-238 (^{238}U), lead-210 (^{210}Pb), uranium-235 (^{235}U), radium-228 (^{228}Ra), thorium-238 (^{238}Th), ^{226}Ra, ^{232}Th and ^{40}K in the LSA phosphogypsum are presented in Table 2. According to the *National Nuclear Regulator Act, 47 of 1999,*[9] an operation or material is excluded from regulation if activity concentration of the naturally occurring radioactive nuclides of uranium, thorium and their progeny are each below 500 Bq/kg. The limit for ^{40}K is 10 000 Bq/kg.

The results confirm that the activity concentrations measured in the 19 LSA phosphogypsum samples are all below the regulation limits set by the *National Nuclear Regulator Act 47 of 1999*[9] for ^{238}U, ^{235}U, ^{210}Pb, ^{228}Ra, ^{226}Ra, ^{228}Th, and ^{232}Th. The activity concentration of ^{40}K in the LSA phosphogypsum was determined to be below the minimum detectable limit of 100 Bq/kg. Numerous studies have revealed that building materials contain appreciable activity concentrations of radioactive nuclides ^{226}Ra, ^{232}Th and ^{40}K. There are limited data available on the radiological safety of phosphogypsum use as a building material beyond the study by Rajkovic and Toskovic[2] and therefore to put the results obtained for LSA phosphogypsum into perspective, some of the results obtained for bricks from several countries are presented in Table 3.

Table 3: Activity concentrations (Bq/kg) of ^{40}K, ^{232}Th and ^{226}Ra in building bricks from various countries

Country	Number of samples	^{226}Ra	^{232}Th	^{40}K
Norway[12]	6	104	62	1058
Greece[13]	6	49	24	670
Australia[14]	25	41	89	681
Netherlands[15]	14	39	41	560
Egypt[16]	1	20	14	204
India[17]	1	48	52	381
Sri Lanka[18]	24	35	72	585
India[19]	Not reported	18	19	238
India[20]	Not reported	47	20	349

The average activity concentration of ^{226}Ra in the bricks listed in Table 3 range from 18 Bq/kg to 104 Bq/kg. This is lower than the average activity concentration in the LSA phosphogypsum (109 Bq/kg ± 18 Bq/kg). Similarly, the average activity concentration of ^{232}Th in the bricks ranges from 14 Bq/kg to 89 Bq/kg which is lower than the average in the LSA phosphogypsum, where ^{232}Th is 253 Bq/kg ± 160 Bq/kg. The activity concentration of ^{40}K (<100 Bq/kg) is lower in the LSA phosphogypsum

Table 2: Activity concentrations of radioactive nuclides in the phosphogypsum from the Lowveld region of South Africa

Radioactive nuclide	^{238}U	^{210}Pb	^{235}U	^{228}Ra	^{228}Th	^{226}Ra	^{232}Th	^{40}K
	Bq/kg							
Average	31	135	1	404	253	109	189	<100
Standard deviation	20	37	1	70	160	18	155	-
Number of samples	19							

compared to the range of activity concentrations reported for the bricks from other countries (204–1058 Bq/kg).

Table 4: The scenarios of use for building materials at different dose criteria

Dose criteria	0.3 mS/year	1 mS/year
Material used in bulk amounts, e.g. bricks	$I_\gamma \leq 0.5$	$I_\gamma \leq 1$
Superficial and other material with restricted use: tiles, and boards	$I_\gamma \leq 2$	$I_\gamma \leq 6$

Radiation hazard indices

The LSA phosphogypsum is rich in ^{228}Ra compared to ^{232}Th and as a result the activity concentration of the former is used in the place of the activity of the latter to calculate the hazard indices in Equations 2–4. The calculated hazard indices H_{ex}, H_{in}, I_γ and the Ra_{eq} are plotted in Figure 1. The error bars in Figure 1 represent the standard deviation of the results of the 19 LSA phosphogypsum samples. The values obtained for H_{ex}, H_{in} and I_γ are 2.12 ± 0.59, 3.44 ± 0.64 and 2.65 ± 0.76 respectively. The calculated Ra_{eq} is 513 ± 76 Bq/kg.

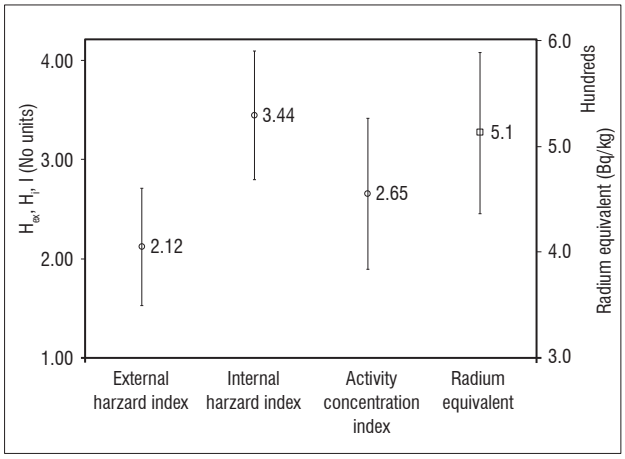

Figure 1: The calculated external (H_{ex}) and internal (H_i) hazard indices, activity concentration index (I_γ) and the radium equivalent (Ra_{eq}) in phosphogypsum from the Lowveld region of South Africa. Error lines indicate the standard deviation.

The assessment of a material's suitability for use as a building material should be based on scenarios where the material is used. The scenarios for use at different dose criteria[8] are given in Table 4. The activity concentration index,I_γ, should be evaluated against these criteria. If the I_γ is 1 or less, the material can be used as building material, without restriction, as far as radioactivity is concerned, whereas if the I_γ is above 1 and less or equal to 6, the material should be used superficially.

The Ra_{eq} as defined in Equation 5, is calculated from the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K. Equation 2 is based on the estimation that 1 Bq/kg of ^{226}Ra, 0.7 Bq/kg of ^{232}Th and 13 Bq/kg of ^{40}K generate the same γ-rays dose rate.[10,21,22] According to Mondal et al.[23] and supported by El-Taher and Makluf[24], $I_\gamma = 1$ is equivalent to the Ra_{eq} of 370 Bq/kq. The calculated Ra_{eq} of 513 ± 76 Bq/kg for LSA phosphogypsum is consistent with the activity concentration ($1 < I_\gamma < 6$).

Radioactive nuclides distribution in LSA phosphogypsum

A simplified definition of secular equilibrium is found in Zhang et al.[25] Activity of daughter radionuclides build up to that of the parent in about seven half-lives and thereafter, parent activity (A_1) is the same as the activity of its progeny (A_2). It follows therefore that at the state of secular equilibrium, the ratio of the activity of the parent to that of the daughter is 1 ($A_1/A_2 = 1$) . The secular equilibrium observed in natural ores can be disturbed by mineral processing. Al-Jundi et al.[7] showed that concentration of ^{238}U and its decay products ^{210}Pb and ^{226}Ra originating from apatite ore are partitioned during processing in such a way that ^{238}U accumulates in the phosphate fertiliser while ^{228}Ra, ^{226}Ra and ^{210}Pb accumulate in the phosphogypsum. This partitioning behaviour can be attributed to the very low aqueous solubility of radium sulfate and lead sulfate relative to that of uranium sulfate as almost all the ^{228}Ra and ^{226}Ra reported by Van der Westhuizen[26] as present in the phosphate rock is observed in the LSA phosphogypsum.

The ratios of activity concentrations in the LSA phosphogypsum for ^{238}U, ^{235}U, ^{232}Th and their progeny in the natural decay series are plotted Figure 2. The ^{226}Ra and ^{210}Pb belong to the ^{238}U natural decay series and are not in secular equilibrium in the LSA phosphogypsum. Although the linear trend of the ratio of these two radionuclides is close to unity, there is a poor correlation between their activities as shown by the regression coefficient (R^2) of 0.133. The uranium radioactive nuclide ^{238}U is also in disequilibrium with its progeny ^{226}Ra. Similarly, ^{235}U is in disequilibrium with ^{210}Pb and disequilibrium is also observed between ^{232}Th versus ^{228}Ra and ^{228}Ra versus ^{228}Th.

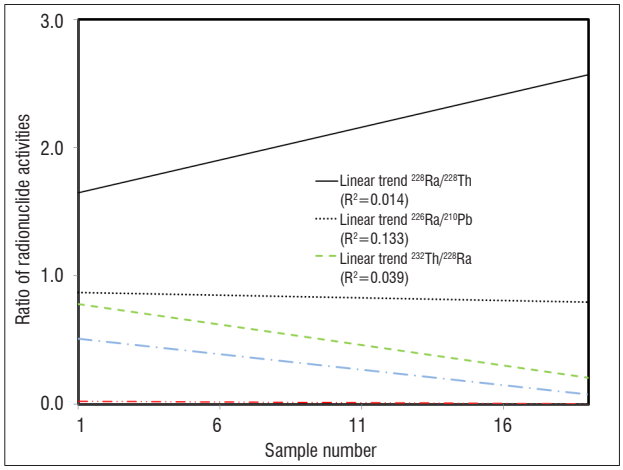

Figure 2. The ratio of activity concentrations for ^{238}U, ^{235}U, ^{232}Th and their progeny in phosphogypsum from the Lowveld region of South Africa.

The Anderson–Darling test has been shown to give appropriate empirical distribution function statistics for detecting departure from normality, even with small samples ($n \leq 25$).[27] The test was performed on a set of data to evaluate their fit to a chosen distribution pattern. For the Gaussian distribution test, the statistics are based on the squared difference between the normal and the empirical data. If the calculated *p*-value is less than a chosen alpha (one minus the confidence interval), the null hypothesis, that the data come from that distribution, is rejected. The Anderson–Darling (AD) test was performed on the radioactive nuclide activity concentration data using the Minitab® 16 statistical software to evaluate the distribution pattern of the activity concentration in the LSA phosphogypsum. The results obtained are presented in the probability plot in Figure 3.

At 95% confidence level, a *p* value of less than 0.05 indicates no deviation from the Gaussian distribution. This behaviour (normal distribution) is observed for the activity concentration of the radioactive nuclides ^{238}U ^{235}U, ^{228}Th and ^{232}Th in the LSA phosphogypsum. The contrary is observed for the ^{228}Ra and ^{226}Ra activity concentrations. The calculated *p* values are 0.318 and 0.434 respectively and the Anderson–Darling values are 0.406 and 0.350 respectively. This can be attributed to the low solubility of radium sulfate which results in accumulation in the phosphogypsum rather than the phosphoric acid.

Conclusion and recommendation

The LSA phosphogypsum contains appreciable amounts of the radioactive nuclides ^{238}U; ^{210}Pb; ^{235}U; ^{228}Ra; ^{228}Th; ^{226}Ra; ^{232}Th and below-detectable levels of ^{40}K. The average activities are below the limits set by the *National Nuclear Regulator Act 47 of 1999*.[9] The phosphogypsum is therefore excluded from regulatory control. The calculated results of

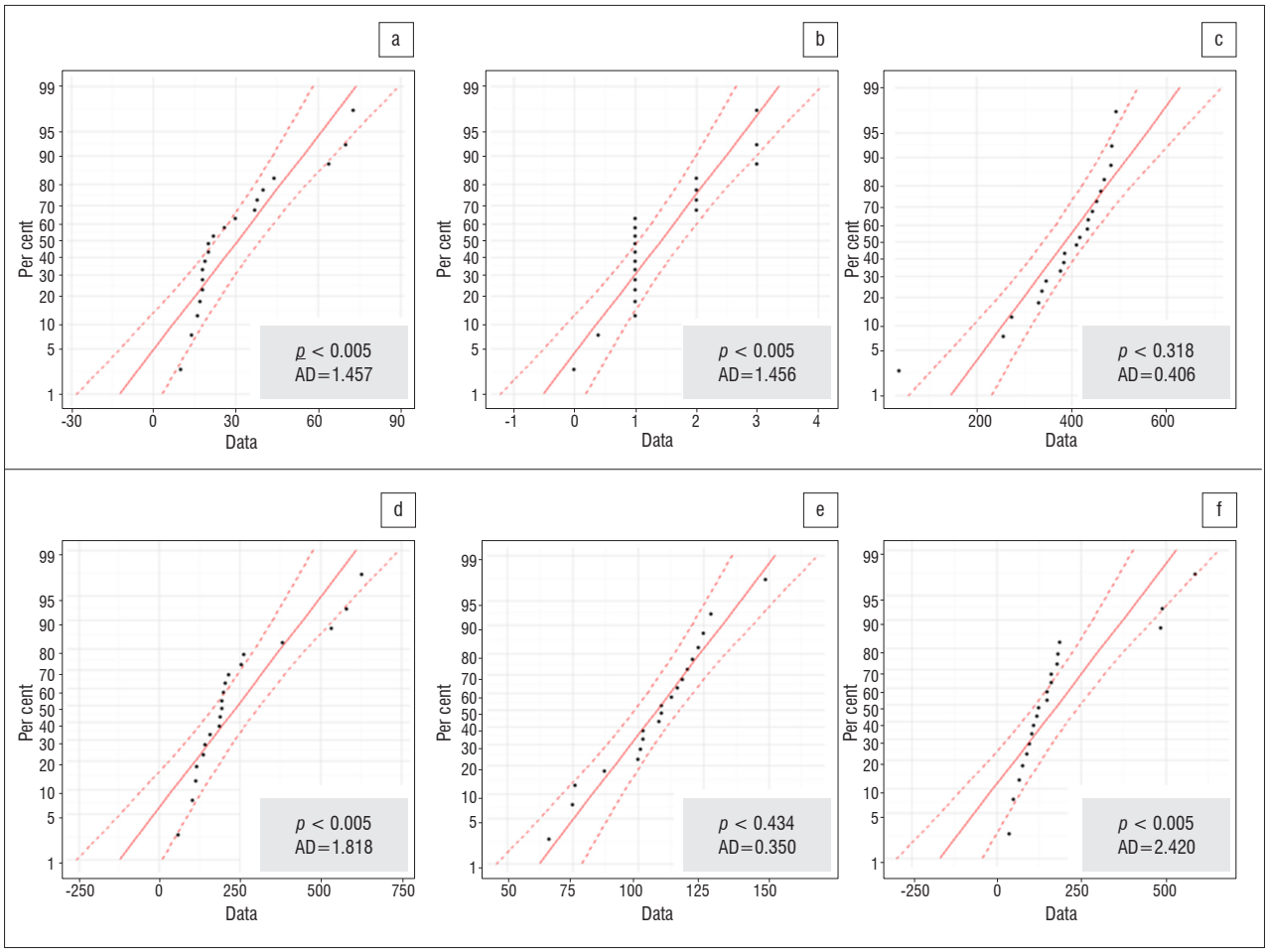

Figure 3: Probability distribution for the activity concentration of (a) ^{238}U, (b) ^{235}U, (c) ^{228}Ra, (d) ^{228}Th, (e) ^{226}Ra and (f) ^{232}Th. In all figures, the data on *x*-axis are the activity concentrations in Bq/kg. The Anderson–Darling (AD) statistic for each radioactive nuclide is displayed on each figure.

hazard indices: H_{ex}, H_{in}, I_{γ} and Ra_{eq} indicate that the LSA phosphogypsum can be utilised as building material if used superficially or with restriction. A final decision on the usability of the material can be made when the scenario of use is known and a more representative sample of the aged bulk material is analysed. The radioactive nuclides and their progenies are not in secular equilibrium in the LSA phosphogypsum and the distribution ^{238}U, ^{235}U, ^{232}Th and ^{228}Th deviates from Gaussian.

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Authors' contributions

D.G.B. and W.B. were the project leaders, F.L. was responsible for sampling and arranging for analysis. X.M. handled the arrangement for sample analysis, performed the calculations and wrote the manuscript.

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