Available online at www.sciencedirect.com
SCIENCE DIRECT®
Radiation Measurements 38 (2004) 31–36
Radiation Measurements
www.elsevier.com/locate/radmeas

The effect of sand/cement ratio on radon exhalation from cement specimens containing ^{226}Ra

S. Takriti[a,*], R. Shweikani[b], A.F. Ali[b], G. Raja[b]

[a] Department of Physics, Atomic Energy Commission of Syria, PO Box 6091, Damascus, Syria
[b] Department of Protection and Safety, Atomic Energy Commission of Syria, PO Box 6091, Damascus, Syria

Received 6 April 2003; accepted 7 July 2003

Abstract

Different ratios of Portland cement and sand were mixed with radium chloride to produce radioactive cylinder specimens. Two types of sand were used (calcite and silica). The release of radon from these samples was studied.

Results showed that radon release from the calcite–cement samples was affected by the sand ratios. It was also noticed that the release changed with the size of the sand particles. Same trends were observed from silica–cement samples. In addition, it was found that radon exhalation from calcite–cement samples were less than that of silica–cement samples. The results were explained by the creation of closed free spaces in the samples, which gave radon atoms the possibility to decay in these free spaces rather than exhalation.

Keywords: Environment radioactive; Radioactive waste; Radon exhalation; Waste disposal; Shielding solidification

1. Introduction

Every person on earth is exposed to natural radiation. The most important sources of radiation is radon gas ^{222}Rn (UNSCEAR, 1977). The concentration of radon and its short-lived daughters depend on their input rate and the rate of radon releases from the mother compounds (Murane, 1994).

The essential purpose of radioactive waste disposal is to isolate it from the human environment. The necessary isolation depends on the actual radionuclide content and the properties of the waste to be disposed. The practical degree of isolation depends on the performance of the whole disposal system (Takriti and Othman, 1997). The cementation process of radioactive wastes is safe and technically feasible (Takriti et al., 1999). The worst ecological and geochemical problem is the diffusion and exhalation of radionuclides away from where the waste products are buried (Titayva, 1991).

The release of radon (^{222}Rn) from ^{226}Ra in radioactive minerals was known since the beginning of the 20th century (Boltwood, 1970, 1980). It was observed that radon loss appeared to be related to the discordant isotopic ages found in the U–Pb system (Homes, 1948). The diffusion coefficient of radon through different thickness of cement without sand was studied (Takriti et al., 2001).

The existence of oil industries in Syria produced contaminated sites with naturally occurring radioactive materials (NORM). The presence of ^{238}U and ^{232}Th series in the oil reservoirs means that co-produced water will contain enhanced naturally occurring radioactive materials, mainly radium isotopes due to its solubility in water that allow it to be carried up with the produced oil (Shweikani and Suman, 2002). Improper disposal of this water resulted in contaminating landfills with NORM. This type of contamination with technically enhanced NORM may require remedial actions and rehabilitation measures, depending on the likelihood of exposure to the population in the affected areas and the associated risk. It was suggested to treat the contaminated soil with radium concentration over 5.2 Bq/g as a radioactive waste (Meinhold et al., 1995).

* Corresponding author. Tel.: +963-11-6111927; fax: +963-11-6112289.
E-mail address: stakriti@aec.org.sy (S. Takriti).

1350-4487/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/j.radmeas.2003.07.001

The aim of the present work was to use radon exhalation coefficient as a tool to determine the best mixture ratio of cements/sand and the effect of different sizes of sand particles to contain radium waste. As such mixtures are used for the disposal of radium wastes, the results could help to determine the best conditioning characteristics for solidifying radium waste.

2. Experimental works

Ordinary Portland cement was used in this work. The composition of this cement was reported previously (Takriti et al., 2001; Takriti and Ali, 2002). Two types of sands (calcite and silica) were chosen for this work. They exist and are used widely in cement works in Syria. The X-ray diffraction technique was used to determine the composition of these two types of sand. The following composition was determined:

$$\text{Calcite} = 95\%\ (CaCO_3) + 5\%\ (\text{Ba, Sr, Al and other oxides}).$$

$$\text{Silica} = 92\%\ (SiO_2) + 8\%\ (\text{clay}).$$

The sand samples were sieved and the following composition (results in % by wt) was found:

Sand type	Sand particle size		
	Small (45–125 μm)	Medium (125–300 μm)	Big (300–850 μm)
Calcite	31.37	23.93	44.70
Silica	8.25	75.50	15.25

The particles, which have dimension less than 45 μm and more than 850 μm, were eliminated from this study (Udden and Wentworth, 1988; Whitten and Brooko, 1997).

Cement and sand were mixed in different ratios with fixed amount of $^{226}RaCl_2$ to make a paste. The fluid/(cement–sand) ratio was about $\frac{1}{3}$. A cylindrical plastic mold 4.6 cm height and 4.6 cm diameter was used to form the specimens, which were left for 2 days to dry before removing the mold. The cement–sand specimens were then left for 2 weeks to solidify in air. Six groups of samples were prepared. The first group was cement only, i.e. 0% sand. The second, the third and the fourth groups were prepared with calcite sand with small, medium and big particle sizes, respectively. The fifth group was prepared with normal calcite sand (without sieving (mixed)). The sixth group was prepared using silica sand without sieving (mixed). The mixture ratios used in this work were 5, 10, 15, 20, 30, 40 and 80% as weight sand to cement. The total activity added to each sample was 250 Bq of ^{226}Ra. Duplicate cement–sand specimens were prepared for each measurement.

Radon detection was carried out in a closed glass container (volume 7 l) provided with input and output gas system circulation. Each of the prepared cement specimens was put at the bottom of the container. The active method was used to measure the increases of radon concentration in the container (Shweikani et al., 1997). This method is based on the detection of the scintillation produced when an alpha particle hits a scintillator material such as zinc sulphide (ZnS) in a closed chamber. Air containing the radon is drawn into the Lucas cell (EDA, Instruments Inc. Toronto, Canada) through a filter, which removes the daughter products, as well as any other aerosol particles and airborne contamination (Misdaq and Moustaadine, 1997). After about 3 h, the decay of each radon atom is accompanied by the simultaneous emission of three alpha particles as radon is in equilibrium with its short half-lived daughters. The scintillation produced by alpha particles was measured using a nuclear counting system (RDA-200) manufactured by EDA. Fig. 1 shows an outline of the experimental set-up.

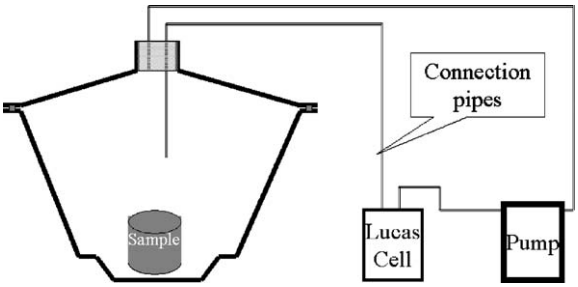

Fig. 1. Experimental set-up of radon releases.

Gamma rays emitted from ^{226}Ra, ^{214}Bi and ^{214}Pb were measured using a high purity germanium detector (Canberra). The gamma-ray counts of the 186, 609 and 351 keV peaks corresponding to ^{226}Ra, ^{214}Bi and ^{214}Pb, respectively, were taken. Background radiation was subtracted from the total counts collected over 20 min for ^{222}Rn and 30 min for ^{226}Ra, ^{214}Bi and ^{214}Pb. Therefore, all results are shown in terms of counts per minute (CPM).

3. Results and discussion

Fig. 2 shows the releases of ^{222}Rn gas from cylindrical cement–sand specimens into the containers as a function of calcite sand mixed ratios. It is clear from this figure that radon release increases with the increase of sand ratio in the samples up to about 20%, then it decreases to a value less than that of 0%.

In order to analyze the observed data, a series of theoretical and mathematical models were carried out using the principles of production, decay and diffusion kinetics of ^{222}Rn (Adda and Philibert, 1966; Crank, 1975; Misdaq and Moustaadine, 1997). The following assumptions were adopted.

In the case of calcite sand, which is mainly consisting of $CaCO_3$, as shown from X-ray diffraction results, the liquid

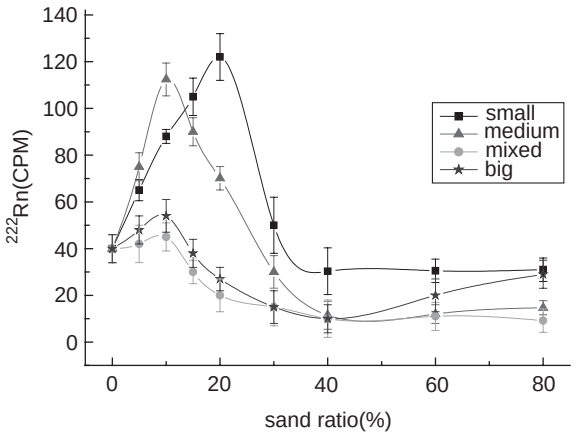

Fig. 2. Experimental radon releases from different sand size as a function of sand ratio.

radioactive radium was mixed with cement and sand. Therefore, during the solidification process, radium will be adsorbed on the sand grains (Lea, 1983). The adsorption phenomenon is due to the exchange reaction between the composition of sand and radium. The decay of radium atoms will produce ^{222}Rn, which will diffuse into the surrounded cement shield. This diffusion could be controlled by the porosity and defect existed during the solidification (Takriti et al., 2001).

It was assumed that each sand grain is covered with the radioactive cement. Fig. 3(a) illustrates a possible positioning of the surrounded sand grains in cylindrical specimens. In this case, ^{222}Rn produced from the surface of the surrounded sand grains will diffuse through a cylindrical sample. Also, there is a possibility for some of the sand grains to be accommodated in a cement shield (cluster) as presented in Fig. 3(b). This will produce an extra shield (spherical) for the emanated atoms of ^{222}Rn inside the cluster to diffuse through. However, many of the trapped ^{222}Rn atoms will decay rather than diffuse. ^{222}Rn atoms, which did not decay inside the cluster, will find a suitable path through the sample and will reach the surface by the diffusion effect. Therefore, it is possible to suggest that the process of the ^{222}Rn exhalation from each sample is a combination between diffusion through a spherical shield and then through a cylindrical shield.

$$\frac{\partial C}{\partial t} = D\,\frac{\partial^2 C}{\partial x^2}. \tag{1}$$

The diffusion process is usually following the Fick's law, where C is the radon concentration at time t; and D is the radon diffusion coefficient.

In case of sphere cluster the dimension x takes in consideration the radius r *and* Fick's law could be rewritten as

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial r^2} + \frac{2}{r}\,\frac{\partial c}{\partial r}\right). \tag{2}$$

The final solution of this equation after taking the following conditions: $t = 0 \Rightarrow c = c_0,\ r = r_0$ could be as follows:

$$c_t = c_0\left[1 + \frac{2(r_0 + a)}{\pi r_0}\sum_{n=1}^{\infty}\left\{\frac{(-1)^n}{n}\sin\left[\frac{n\pi r_0}{(r_0 + a)}\right] \times \exp\left[\frac{n^2\pi^2 D_{(1)}t}{(r_0 + a)^2}\right]\right\}\right], \tag{3}$$

where c_0 is the initial radium concentration, r_0 is the sand radius, a is the thickness of the surrounded cement shield and D_1 is the diffusion coefficient in the spherical case. When sand is added to the cement samples, there will be a probability to form spaces containing some soil grains. If we assume that there are N spaces in the samples each contains n radon atoms, and m is the number of radon atoms expected to decay inside the spaces, then the probability of the presence of radon atoms expected to decay in the free spaces N is (Takriti and Duplatre, 1988)

$$P_m = \frac{n!}{m!(n-m)!}\left(\frac{1}{N}\right)^m\left(1 - \frac{1}{N}\right)^{(n-m)}. \tag{4}$$

The n value is related to the total ^{222}Rn gas existed in the sample, which is corresponding to the distribution factor k_r. This factor represents the radioisotope distribution between sphere and cylindrical as: $n = k_r C_{(Ra)}$. Therefore, emanation quantity of ^{222}Rn gas could be calculated using the following equation:

$$^{222}\mathrm{Rn(Em)} = c_t P_m(w)^{N/n}\exp(-\lambda t), \tag{5}$$

where N, n and m have variable values corresponding to the accuracy of data fitting, λ is the radioactive decay and w is the mixed sand ratio. In reality, the ratio N/n is very important because it expresses the relationship between the free spaces and ^{222}Rn atoms confined inside as a function of distribution factor, k_r.

In case of cylinders the dimension x, from Eq. (1), takes in consideration the two dimensions: the height z and the radius r. Therefore, Fick's law could be rewritten as

$$\frac{\partial C}{\partial t} = D\left[\frac{\partial^2 C}{\partial r^2} + \frac{1}{r}\,\frac{\partial C}{\partial r} + \frac{\partial^2 C}{\partial z^2}\right]. \tag{6}$$

The final solution of this equation after taking the following conditions $t = 0 \Rightarrow c = c_0 = c\{^{222}\mathrm{Rn}_{(Em)}\}, -l \leqslant x \leqslant +l,\ 0 \leqslant r \leqslant b$, could be written as

$$^{222}\mathrm{Rn(Ex)} = \frac{8c\{^{222}\mathrm{Rn(Em)}\}}{\pi b}\sum_{n=0}^{\infty}\sum_{m=1}^{\infty}\left\{\frac{J_0(a_m b)}{(2n+1)a_m J_1(a_m b)} \times \sin\left[\pi\,\frac{(2n+1)\pi(a+b)}{2l}\right] \times \exp\left[-\left(a_m^2 + \frac{(2n+1)^2\pi^2}{4l^2}\right)D_{(2)}t\right]\right\}, \tag{7}$$

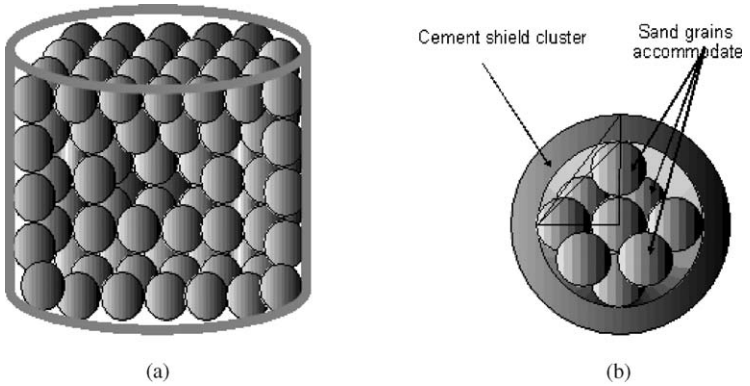

Fig. 3. Surrounded sand grains sites in the specimens (a), sand grains accommodated into one cement shield cluster (b).

Table 1
Diffusion coefficients, radon gas distribution factor and average diameter of sand tablet, obtained from fitting Eq. (7) to experimental data

Sand	Average diameter of the sand tablets (μm)	N/k_b	D_2 (cm^2/s)	D_1 (cm^2/s)
Calcite	85	70	0.287×10^{-5}	0.426×10^{-5}
	213	125	0.513×10^{-5}	0.931×10^{-5}
	326	175	0.926×10^{-5}	1.778×10^{-5}
	575	255	2.312×10^{-5}	3.503×10^{-5}
Silica	326	520	5.783×10^{-5}	9.431×10^{-5}

where c_0 is the radon releases form the cluster, b is the cylindrical radius, l is the cylindrical length and a_m is the solution of $J_0(a_m b) = 0$, where J_0 is Bessel factor (Wanger, 1952). ^{222}Rn(Ex) is the radon exhalation counts measured at equilibrium time t from the sample and ^{222}Rn(Em) is the radon emanating counting measurement at equilibrium time from the spherical cluster. While, $D_{(2)}$ is the diffusion coefficient of the ^{222}Rn gas from the cylindrical sample and a is the thickness of the cement shield.

The accuracy of results derived when fitting Eq. (7) to the experiment data was good. Therefore, our results could be explained using the above expressions. The fitted values of the diffusion coefficients $D_{(1)}$, $D_{(2)}$ (cm^2/s) and N/k_r are given in Table 1. Fig. 4 shows a comparison between the fitting lines (based on Eq. (7)) and the experimental data. While, the relationship between the diffusion coefficients, radon gas distribution factor k_r and the average diameter of the sand tablets is shown in Fig. 5.

In the case of silica sand, the releases of ^{222}Rn gas from samples followed the same phenomenon, but radon exhalation was more than that released in the case of calcite sand. This observation could be explained by the non-adsorption effect on this kind of sand because the sand composition

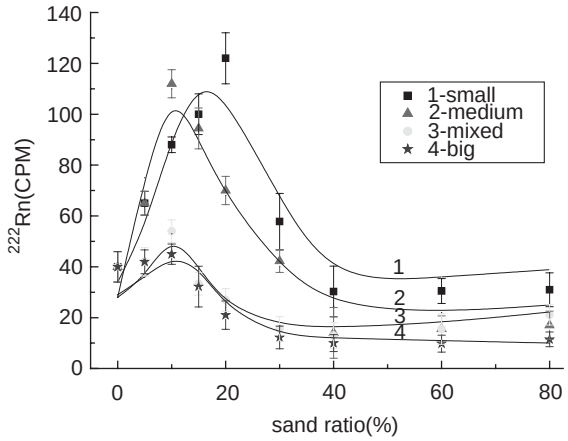

Fig. 4. Fitting curve for different sand size as a function of sand ratio.

is different (as shown from the X-ray diffraction measurements). On the other hand, the rate of emanating radon will be higher (Rayski and Suarez, 1988). Fig. 6 illustrated the difference on the releases of ^{222}Rn gas from both sand samples (calcite and silica). Therefore, with increases of sand ratio small quantity of the sand gathered in the cluster and the probability of the radon decay would be less than in the calcite case.

4. Conclusion

In order to reduce the exhalation of ^{222}Rn into the environment, liquid containing ^{226}Ra could be solidified with sand–cement. It was noticed that the best ratio of sand to cement is around 40%. The solidification process may create some defects in the samples. As a result, radon emanation will increase. Increasing the sand ratio will create more pores spaces. This will allow the produced ^{222}Rn to diffuse

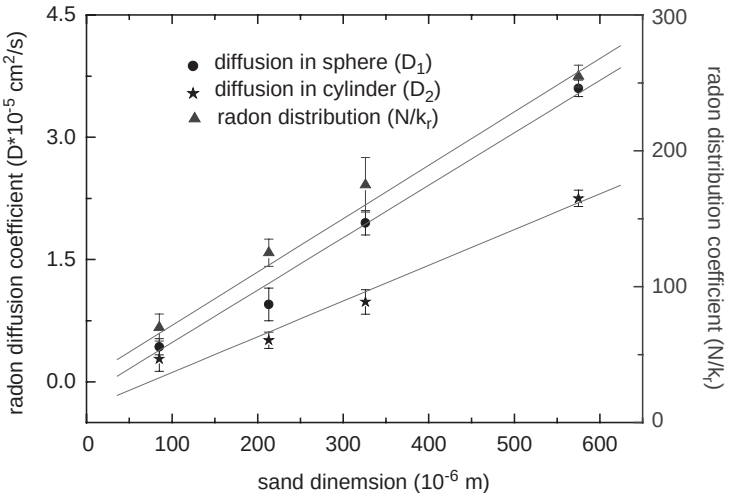

Fig. 5. Relationship between radon diffusion, distribution and sand dimension.

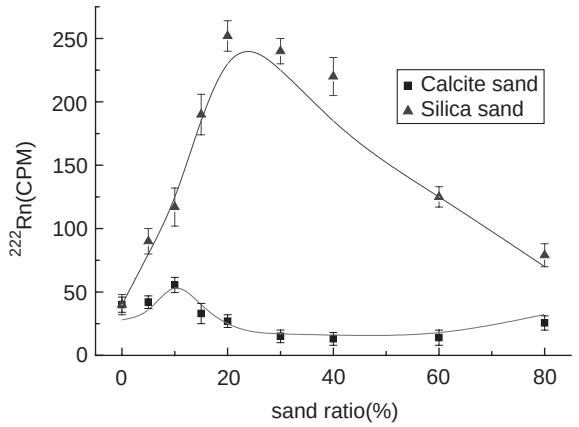

Fig. 6. Comparison between calcite and silica sand on radon releases as a function of sand ratio.

easily and exhale rapidly from the sample. Further increasing in sand ratio will lead some sand grains to gather inside a cement shield, forming a cluster. Same radon atoms trapped in the cluster will decay before getting a chance to exhale. This is especially true for the high sand ratio where more free spaces were created and gave a high probability for ^{222}Rn to decay inside. In this case, the radioactivity of ^{222}Rn emanated from the cluster was low.

On the other hand, further investigations are needed to elucidate clearly the suggested mechanism of the increased emanation of ^{222}Rn gas which passed through many events. The homogeneity of the paste and the solidification time, which determined the distribution of water molecules, may be an important factor.

Acknowledgements

The authors would like to thank Professor I. Othman, Director General of A.E.C.S., for his helps.

References

Adda, Y., Philibert, Y.J., 1966. La Diffusion dans les Solides, T. 1-2. Presses Universitaires de France, Paris.

Boltwood, B.B., 1970. On the ultimate disintegration products radioactive elements, P. 2. The disintegration products of uranium. Am. J. Sci. 23 (134), 77–88.

Boltwood, B.B., 1980. Radioactivity of uranium minerals. Am. J. Sci. 25 (148), 269–298.

Crank, J., 1975. The Mathematics of Diffusion, 2nd Edition. Clarendon Press, Oxford (Chapter 3–4).

Homes, A., 1948. The oldest known minerals and rocks. Edinburgh Geol. Soc. Bull. 14 (2), 435–441.

Lea, F.M., 1983. The Chemistry of Cement and Concrete, 3rd Edition. Edward Arnold Publisher Ltd, London.

Meinhold, A.F., Holtzman, S., Hamilton, L.D., 1995. Health risk assessment for radium discharged offshore in produced water. SPE 29728, pp. 357–372.

Misdaq, M.A., Moustaadine, H., 1997. A new method for determining the radon emanation coefficients and radon production rates. J. Radioanal. Nucl. Chem. 218 (1), 9–12.

Murane, D.M., 1994. Model standard and techniques for control of radon in new buildings. Radiat. Prot. Dosim. 56, 5–7.

Rayski, B.M., Suarez, A.A., 1988. Evaluation of homogeneity of radioactive waste forms: statistical criteria. Nucl. Chem. Waste Manage. 8, 235–241.

Shweikani, R., Suman, H., 2002. Regulatory control in the rehabilition of contaminated sites in Syria. International Conference on Safe Decommissioning for Nuclear Activities, 14–18 October, Berlin, Germany, CN-93(7–14).

Shweikani, R., Al-Bataina, B., Durrani, S.A., 1997. Thoron and radon diffusion through different types of filter. Radiat. Meas. 28, 641–646.

Takriti, S., Ali, A.F., 2002. Initial distribution of ^{137}Cs in cement specimens and the effect of leaching. J. Radioactive Waste Manage. Environ. Restoration 22/4, 1126–1136.

Takriti, S., Duplatre, G., 1988. Thermal decomposition of KIO_4 and $NaIO_4$ in relation to solid state isotopic exchange reactions. J. Chem. Soc. Faraday Trans. I 84 (4), 2831–2841.

Takriti, S., Othman, I., 1997. Diffusion coefficients of ^{90}Sr and ^{137}Cs in Syria rocks and the dependence on pH. Appl. Radiat. Isot. 48 (8), 1157–1160.

Takriti, S., Kheitou, M., Ali, A.F., 1999. Migration study of radioisotopes incorporated in cement. Appl. Radiat. Isot. 50, 401–406.

Takriti, S., Shweikani, R., Ali, A.F., Hushari, M., Kheitou, M., 2001. Diffusion of radon through varying thickness of cement used for disposal of radioactive waste. Appl. Radiat. Isot. 55, 115–116.

Titayva, N.A., 1991. Geochemistry of Natural Radionuclides in Hypergenesis Zone: The Problems of Radiochemistry and Cosmology. Nauka, Moscow.

Udden, J.A., Wentworth, C.K., 1988. Sedimentry Petrology. Alden Press, Oxford.

UNSCEAR, 1977. Source and effects of ionizing radiation. United Nations Scientific Committee on the Effect of Atomic Radiation, New York, United Nations.

Wanger, C., 1952. Diffusion in Solids, Liquids and Gases. Academic Press, Paris, pp. 68–75.

Whitten, D.G.A., Brooko, J.R.U., 1997. The Penguin Dictionary of Geology. Penguin Books Ltd., Middlesex, UK.