sciendo

Civil and Environmental Engineering
Vol. 17, Issue 1, 45-49, DOI: 10.2478/cee-2021-0005

IDENTIFYING THE PRESENCE OF NATURAL RADIONUCLIDES IN ASHLAR SAMPLES

Elfer ARENAS[1], Jorge MARTÍNEZ[2], Mercedes Vilca GUILLEN[1], Alicia FERNANDEZ[3], Enrique FERNANDEZ[3], Luis QUINDOS[3,*]

[1] Faculty of Natural Sciences, National University San Agustín de Arequipa, Peru.
[2] Peruvian Institute of Nuclear Energy, Peru.
[3] Laboratory of Natural Radioactivity, University of Cantabria, Spain.
[*] corresponding author: quindosl@unican.es

Abstract

Humans have always been exposed to different types of natural and cosmic radiation. At present we experience 83 % natural radiation, for example from granite marbles, building materials such as concrete, brick, granite, or drywall. However, although these are potential sources of radon, they are rarely the cause of a high level of pollution in a building.Ashlar is a material of volcanic origin comprising heterogeneous and solidified detrital pyroclastic materials such as rhyolite, sand, volcanic ash and pumice, among others. Chemically, ashlar is principally composed of elements such as sodium, magnesium, calcium, iron, aluminum, sulfur, and cobalt. In order to identify the presence of these elements in the ashlar, X-ray Fluorescence studies were carried out first, using modern XRD and XRF equipment, followed by quantitative analysis using a neutron activation technique, and finally, low-level gamma spectrometry to evaluate the presence of radioactive elements.

Keywords:

Ashlar;
Characterization;
Gamma spectrometry;
Construction;
Risk.

1 Introduction

In southern Peru there are a large number of pyroclastic flow deposits covering large areas of the Western Andean strip. Due to the effect of pressure and temperature, pyroclastic flows are devitrified and welded together, becoming ashlar, a predominantly white-to-grayish colored pyroclastic rock of homogeneous granularity [1]. It has been widely used as a construction material in the city of Arequipa and its surroundings, and its resistance to compression is comparable to that of a type III brick. It does, however, have deficiencies in adhesion to the mortar used due to its great absorption capacity, which does not allow it to set properly. Chemically, ashlar is composed principally of elements such as sodium, magnesium, calcium, iron, aluminum, sulfur, and cobalt. Within the structural components of the ashlar there are believed to be radioactive substances or elements that emit radon and thoron gas (which are toxic, depending on their concentration). While the greatest presence of these gases is detected in the soil, and the rock below the foundations, the contribution of building materials is at times important [2], especially where there is a lack of ventilation [3]. For this reason, the evaluation of chemical elements in building materials that can introduce toxic substances into the building is also necessary, since the impact on the health of the inhabitants could be significant.

This paper attempts to confirm or reject these ideas, because the city of Arequipa has used this ashlar material for the construction of temples, cloisters and mansions in the past, and today it is still being used in the construction of houses in towns of lower economic standing [4].

We thus need to take the following steps:

1. Study the physical and chemical components of the ashlar via X-Fluorescence and Neutron Activation.
2. Identify the radioactive substances and elements that are found in the ashlar by gamma

2 Material and methods

As a raw material, ashlar is generally extracted from quarries, in open-pit mining, Fig. 1. Stonework is one of the oldest of all trades. The ashlar is carved by master carvers.

Fig. 1: Open-cast ashlar quarries. Photo by the authors.

The apparatus used in this research comprises: X-Ray Diffraction Equipment (DRX) and X-Ray Fluorescence Equipment (XRF) for use in research and industry, Fig. 2.

Fig. 2: XRD and XRF device.

The IPEN Neutron Activation Laboratory uses low-level gamma spectrometry to determine the specific activity of the unstable isotopes present in the samples. The sample is irradiated only to activate the non-radioactive elements. A gamma spectrometer using a Ge(Li) detector, Fig 3.

Fig. 3: Radiometry apparatus with a 70-80 % efficiency Ge detector.

The technical specifications of the instruments necessary to guarantee the quality of the measurements are described in previous work [5, 6].

3 Results and discussion

Physical properties are of great importance in the study of these samples (Table 1), most of which can be easily recognized by very simple observations, or by means of a spectroscope.

Table 1: Isotropic Physical Properties of Ashlar.

Density	1340 kg/m^3
Absorption, A.S.T.M. C-127-59 Standards	25.23 %
Simple compressive strength	$93.41 \cdot 10^{-4}$ kg/m^2
Elasticity modulus	$40925.93 \cdot 10^{-4}$ kg/m^2
Texture	Porous without loss of cohesion
Earthy fracture when broken	Granular or powdery
Resists the action of heat	Above 500 ^{0}C
Color	White and pink.
Apparent specific weight	2.05
Porosity	Very porous
Bad conductor of temperature	Regulator (thermostat)
Hardness	6.5 to 7 (Mohs)

The data from X-Ray Fluorescence is obtained from the electrical pulses, which pass through a pre-amplifier, an amplifier and a multichannel analyzer, responsible for sorting the energies emitted by the sample. Each peak corresponds to a certain energy. Figure 4 shows the different peaks found. For a range of energies from 0 to 20 keV, a series of peaks with different energies was observed, corresponding to the following elements: (Si, Ga, As) 1.3 %; (Sr, Rb, Pb) 2.0 %; (Mo, Pb) 1.0 %; (Th, Rb, K) 2.9 %; (Ca, Sr, Cs) 1.4 %; (Ti, V, Cr) 0.6 %; (Cr, Mn) 0.9 %; Fe-Ka1, 9.7 %; Mo-Ka1, 3.0 %; Zn-Ka1, 0.7 %; Ga-Ka1, 1.0 %; U-La2, 2.4 %; Sr-Ka1, 4.0 %; Rb-Kb1, 1.3 %; Sr-Kb1, 2.2 %; Mo-Ka1-C, 18.0 %; U-Lb1, 7.9 %; Mo-Ka1, 27.2 %; Mo-Kb1-C, 5.0 %; Mo-Kb1, 6.9 %. This initial identification of the components of the ashlar determined the development of more precise evaluation using neutron activation analysis.

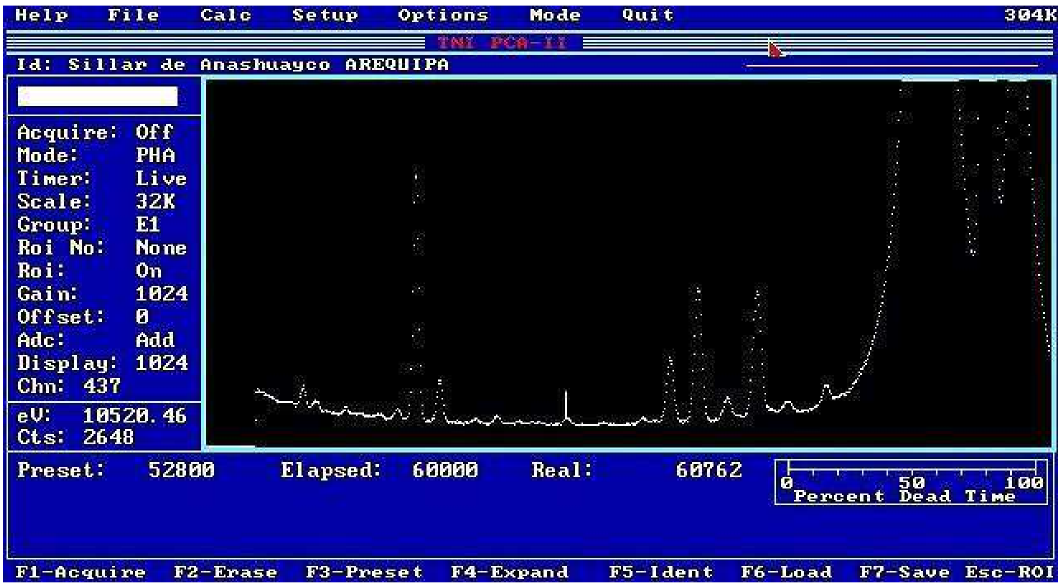

Fig. 4: I (Nº of photons emitted) as a function of E (keV). Ashlar sample (S103) M01.

Table 2 shows the results of the multi-element analysis using neutron activation for the samples of Añashuayco Ashlar Arequipa-Peru with codes S103M1 and S103M2, from a common S103 sample. For the different elements found, the homogeneity of the ashlar is very high. Also, from the toxicological point of view, the concentrations found for the different elements do not imply a corresponding health risk [7].

Table 2: Multi-element analysis in S103 samples of ground ashlar, using neutron activation analysis. The results are expressed in mg/kg.

Sample	Element	Concentration	Sample	Element	Concentration
S103-M1	As	3.30 ± 0.40	**S102-M2**	As	3.20 ± 0.40
	Ba	1270 ± 80		Ba	1280 ± 80
	Ce	83.0 ± 5.0		Ce	86.0 ± 5.0
	Co	1.60 ± 0.10		Co	1.60 ± 0.10
	Cr	1.80 ± 0.20		Cr	2.50 ± 0.30
	Cs	2.0 ± 0.10		Cs	2.0 ± 0.10
	Eu	0.70 ± 0.04		Eu	0.70 ± 0.04
	Fe	1.00 ± 0.06		Fe	1.00 ± 0.06
	Hf	5.0 ± 0.3		Hf	5.0 ± 0.3
	K	3.10 ± 0.20		K	2.70 ± 0.20
	La	43.0 ± 2.6		La	45.0 ± 2.6
	Lu	0.220 ± 0.015		Lu	0.220 ± 0.015
	Na	3.10 ± 0.20		Na	3.10 ± 0.20
	Nd	32.0 ± 2.0		Nd	31.5 ± 2.0
	U	1.30 ± 0.20		U	1.50 ± 0.20
	Th	10.0 ± 0.6		Th	10.0 ± 0.6
	Rb	110.0 ± 8.0		Rb	113.0 ± 8.0
	Sb	0.30 ± 0.03		Sb	0.30 ± 0.03
	Sc	3.00 ± 0.20		Sc	3.00 ± 0.20
	Sm	4.0 ± 0.4		Sm	4.0 ± 0.4
	Ta	0.70 ± 0.05		Ta	0.70 ± 0.05
	Tb	0.400 ± 0.025		Tb	0.400 ± 0.020
	Yb	1.40 ± 0.10		Yb	1.40 ± 0.10

The gamma spectrometry technique was used to evaluate the radioactive elements present in an ashlar sample. The specific activity, together with its uncertainty, is then calculated, allowing the radioactive chains present in the ashlar sample, and the state of equilibrium found, to be identified. The results obtained for the most important radionuclides are set out below in Table 3.

Table 3: Values obtained from specific activity, for ashlar sample S103.

Radioisótopo	Energía (keV)	P_gamma	Eficiencia	Área	U_area	Act_esp (Bq/Kg)	U_act_esp (k=2)	observaciones
Ra-226	185,6	0,0329	0,04617	1990	83	26,6	2,5	U-238
Pb-212	238,59	0,429	0,04229	34381	199	38,5	1,6	Th-232
Tl-208	277,31	0,0679	0,03918	1470	65	11,2	1,1	Th-232
Pb-214	295,2	0,191	0,03783	4968	199	14,0	1,2	U-238
Pb-214	351,92	0,37	0,03402	8744	108	14,1	0,7	U-238
Tl-208	583,1	0,841	0,02466	12689	120	12,4	0,5	Th-232
Bi-214	609,29	0,449	0,0240	6826	93	12,9	0,6	U-238
Tl-208	860,41	0,14	0,01954	1602	50	11,9	0,9	Th-232
Ac-228	911	0,25	0,01891	9085	101	39,0	2	Th-232
K-40	1460,83	0,107	0,01428	73445	272	975	40	

The data analysis in Table 3 shows the presence of U-238 and Th-232 as its decay products, but in general with a low mass activity concentration, which is a little higher for Th-232 than for U-238. Cs-137 does not appear in the Table because the values found are below the minimum detectable amount, with a value of 1.0 Bq/kg on average. Pb-214 and Bi-214, daughters of U-238, reach a secular balance, where the ratio between their activities is close to 1. There is no equilibrium with the other members of the chain because of the release of radon gas. A similar result is found for the Pb-212 and Bi-212 isotopes, which come from Th-232. They reach equilibrium, but as in the case of the U chain, this is also broken, due to the release of thoron gas. The activity of K-40 has a higher value than the global average of 500 Bq/kg [8].

In conclusion, the activity concentrations of the building material studied suggest that it is radiologically suitable, and radon and thoron emanation is expected to be low. Given these values, a study will be carried out to measure the concentration of radon gas in the premises, to determine the rate of radon exhalation, or the dose to which people who frequent these places are exposed. The chemical elements present in the ashlar have concentrations below the recommendations of the international health authorities.

References

[1] GUZMÁN, R. - DE LA VERA, P. - RÍOS, G. - BUSTAMANTE, A. - CAPEL, F. Y. - BOLMARO, R.: Caracterización y Agentes de la Alteración del Sillar como Base de Estudio para la Preservación de los Monumentos Históricos de la Ciudad de Arequipa. Acta Microscópica, Vol. 16, No. 1-2, 2007.
[2] EPA 402/K12/002: A citizen´s Guide to radon. Environmental Protection Agerncy, 2016.
[3] OMS, Organización Mundial de la Salud., El Radón: Un problema de salud publica. Geneve, 2009.
[4] SALAS, A. G. - VATIN-PÉRIGNON, N. – POUPEAU, G.: El sillar de Arequipa (Perú): características de los depósitos de flujos piroclásticos de la quebrada Añashuayco. Symposium Internacional Géodynamique Andine: résumés des communications. París, ORSTOM, 1990, Colloques et Séminaires. Symposium International Géodynamique Andine, 1990/05/15-17, Grenoble, 1990, pp. 333-335.
[5] FUENTE MERINO, I: Puesta a punto de un equipo de fluorescencia de rayos X portatil con fuenes radiactivas. Aplicaciones Ambientales. PhD. University of Cantabria, 2015.
[6] CLEMENTE JUL, M.C.: Aplicaciones de la espectrometría gamma de bajas energías al análisis de activación neutrónica con detectores de Ge(Li). PhD. University Complutense, 2015
[7] AGENCY FOR TOXIC SUBSTANCES AND DISEASE REGISTRY, www.atsdr.cdc.gov, 2020.
[8] DURUSAOY, A. - YILDIRIM, M.: Determination of radioactivity concentrations in soil samples and dose assessment from Rize Province, Turkey. Journal of Radiation Research and Applied Sciences, Vol. 10, Iss. 4, 2017, pp. 348-352.