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Estimation of the natural radioactivity of the Albanian clays

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> …. " it happens that a man observing a phenomenon that didn't cause the surprise to the others, concentrates his attention on it and reveals that the other have not observed ….." (Leriche, 1951)

Abstract: *The paper deals with the natural radioactivity of Albanian clays used as raw materials for the construction industry (bricks, ceramics, cement, fillers etc.). The clays of Albania have already been investigated in the geological and mineralogical aspects, as well as for their physico-mechanical proprieties and reserves. Therefore, it was necessary in addition to investigate the natural radioactivity in order to complete their classification. The clays have good absorbent characteristics, especially as clays colloids.They also contain natural radioactive elements and rare elements. The gamma dose of the radiations emitted from the clays is proportional to their U, Ra, Th, and K concentration. In terms of the radiation safety, the natural radioactivity of the Albanian clays is below the recommended limits of the gama dose rate. Therefore they can be used for all kinds of public buildings. The paper also contains data on the radioactive and some other elements concentrations in soil samples.*

Key Words: *Natural Radioactivity, Albanian Clays, Raw Materials*

INTRODUCTION

Radioactive elements constitute a part of the Earth's spheres. Their composition and distribution are subject to the same natural laws as the other non-radioactive elements. Potassium (K-40) is an exception as an essential constituent of human tissues, plants and higher species animals. Many people express their concerns for any manifestation of radioactivity. The intensity of the terrestrial natural radioactivity ranges for different regions from 1 to 10 times, which represents the geological factor. The knowledge of the natural radioactivity is of first importance for the estimation of the environmental data as well as for eventual radioactive contamination during the nuclear accidents. Radionuclides like Sr-90, Zr-95, Cs-137 remain for a long time into the soils and modify the geochemical natural background (Final report, 1995). The radioactive elements are distributed everywhere and in the different concentrations in the biosphere. From the natural "risk' point of view, it is necessary to know the dose limits of public exposures. At the same time, it is necessary to measure the natural environmental radiation level provided by ground, air, water, foods, building interiors etc., for the estimation of the exposures to natural radiation sources. IAEA has published data for the doses accumulated by the human beings during their life activities. The exposures to cosmic radiation is about 0.38 mSv/year, to terrestrial radiation 0.45 mSv/year (this figure increases by nearly 20 % for brick and concrete buildings), to water, food and air 1.5 mSv/year. The exposures to X-rays diagnostics is about 0.4 mSv/year and to the other factors like color TV, air flights, nuclear power plants the exposure is about 0.1 mSv/year. Thus, in total the human being receives about 2.7 mSv/year from natural and man-made radiation sources. The dose limit for public exposure to man-made radiation sources is 1 mSv/year (International Basic Safety Standards, 1994).

From the radioactive concentration point of view, the 'normal' clays, which were used as construction materials for the residential and public buildings etc., contain some ppm U, and Th, while for K the figure is less than 4 %. In the case when the concentration of these radioactive elements in clays is higher than

10 ppm for U, 20 ppm for Th, and higher than 5 % for K, it is necessary to review the possibilities of the limitation of these clays for construction materials. The reason for this limitation comes from the high value of the exposures which create radioactive materials for the human beings. As a general rule, the total natural radioelement concentration of clays for the residential and public use should not exceeded 30 ppm Ue (uranium equivalent) . In the building industry, the most used raw materials are clays (production of bricks, tiles, ceramics, fillers etc.). Therefore we investigated 52 clay samples from different sites of Albania, including brick factories (Fig. 1 and Table 1).

This paper is dedicated to the 100th anniversary of the discovery of radioactivity by Henri Becquerel (1852-1908) who, in 1903, shared the Nobel Prize for Physics with Pierre and Marie Curie.

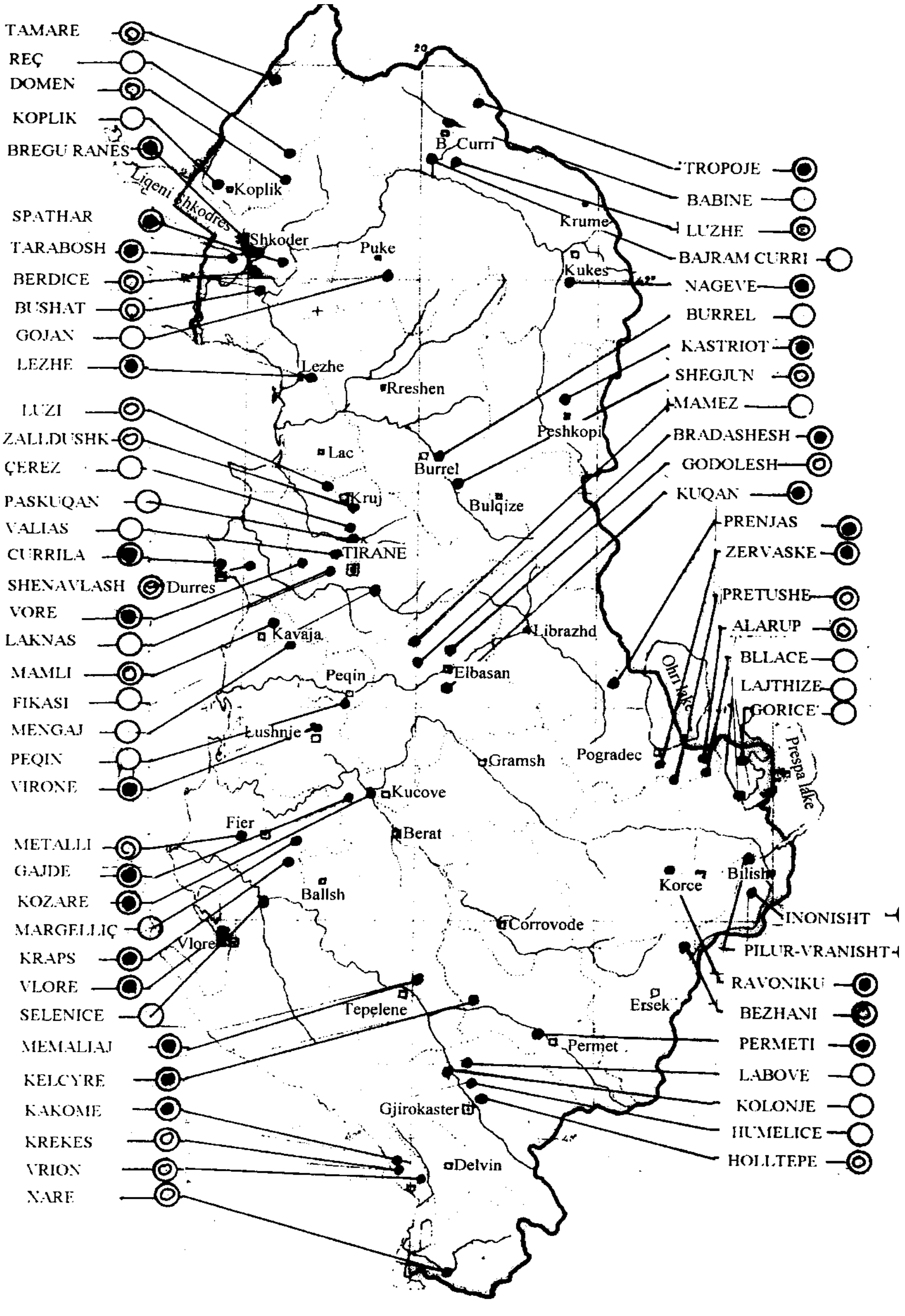

FIG. 1. Deposits and most important occurrences of the industrial clays in Albania

Table 1. Radiometric determinations: Gamma-ray spectrometer GAD-6& GSP

No.	No. Samples (Clays)	Weight (gr) Samples V = 170 cm^3	Bi-214 E_γ = 1.76 MeV	T1-208 E_γ = 2.62	K-40 E_γ = 1.46 MeV	$E_\gamma \geq$ 400KeV		$E_\gamma \geq$100KeV		Analytical Results: 1990 Geoanalyst: A. Dodona Isotopic relation		Notes
			eU	eTh	K	eUtc	eUtc	etc	eUtc	eTh/eU	eTh/K	* ≤ Limit detection
	Clays	gr	ppm	ppm	%	ppm	Bq/gr	ppm	Bq/gr			
1	Shk-01	244	6.5	44.6	1.4	30.2	0.373	36.5	0.450	6.9	32.0	
2	Shk-02	242	*	43.0	3.8	25.3	0.313	23.8	0.290	.	110.0	
3	Shk-03	233	1.0	6.0	0.8	4.8	0.059	4.8	0.059	6.0	7.5	
4	Shk-04	224	2.2	20.0	1.3	13.5	0.167	14.7	0.180	9.1	15.0	
5	Shk-05	228	2.3	19.0	0.8	12.6	0.156	13.0	0.160	8.2	23.0	
6	Shk-05/R	220	6.3	37.0	0.5	25.3	0.313	26.0	0.321	5.87	74.0	
7	Shk-06	283	*	11.5	1.9	7.7	0.095	6.6	0.082	.	6.1	
8	Shk-07	261	1.0	11.4	1.5	8.2	0.102	7.7	0.095	11.4	7.6	
9	Shk-08	232	2.9	6.4	1.2	7.3	0.090	8.3	0.103	4.8	5.3	
10	LE-09	267	8.2	0.9	1.6	6.6	0.081	6.65	0.082	9.1	0.56	
11	PU-10	234	*	~ 1	*	~1	0.012	0.5	0.006	.	.	
12	PU-11	175	*	*	*	*	.	0.6	0.007	.	.	
13	PU-12	237	*	*	*	*	.	1.3	0.016	.	.	
14	TR-13	232	1.1	3.7	1.8	4.8	0.059	7.5	0.093	3.4	2.1	
15	DR-14	249	1.1	9.0	1.4	7.0	0.086	8.1	0.100	8.2	6.4	
16	DR-15	230	1.1	5.0	1.2	4.8	0.059	7.3	0.090	4.5	4.2	
17	DR-16	230	1.1	5.2	1.2	4.5	0.061	7.2	0.089	4.7	4.3	
18	DR-17	231	1.4	1.0	1.3	3.2	0.040	6.6	0.082	.	.	
19	EL-18	245	0.1	5.1	1.8	5.35	0.066	6.6	0.082	5.1	2.8	
20	LU-19	231	1.0	4.4	1.3	4.5	0.056	6.7	0.083	4.4	3.4	
21	FR-20	220	0.9	3.6	0.6	3.3	0.041	6.6	0.082	4.0	6.0	
22	FR-21	226	1.0	1.1	0.8	2.35	0.029	5.6	0.070	1.1	1.4	
23	FR-22′	224	*	5.7	0.8	3.65	0.045	5.9	0.073	.	.	
24	FR-23′	252	1.0	5.4	1.4	5.1	0.063	6.2	0.077	5.4	3.9	
25	VL-24	246	*	5.7	1.3	4.2	0.052	6.0	0.074	.	4.4	
26	VL-25	240	0.6	3.5	1.0	3.35	0.041	5.6	0.070	.	3.5	
27	VL-26	240	1.0	9.4	1.5	7.2	0.089	8.4	0.104	9.4	6.3	
28	SR-27	53	.	.	.	.	.	9.2	0.114	.	.	
29	TP-28	261	1.5	7.5	1.6	6.9	0.085	8.5	0.105	5.0	4.7	
30	TP-29	264	0.9	7.9	1.1	6.0	0.074	6.9	0.085	8.8	7.2	
31	TP-30	217	1.7	6.2	1.2	6.0	0.074	8.2	0.101	3.6	5.2	
32	TP-31	230	1.0	6.3	1.2	5.35	0.066	5.3	0.065	6.3	5.3	
33	TP-32	205	0.5	4.2	0.8	3.4	0.042	5.1	0.063	.	5.3	
34	LB-33	230	*	8.7	*	4.4	0.054	5.6	0.069	.	.	
35	LB-34	200	1.1	5.5	*	3.9	0.048	5.2	0.064	4.4	.	
36	PG-35	266	2.5	1.8	1.1	13.6	0.168	11.4	0.141	5.1	16.4	
37	PG-36	196	2.0	11.0	0.5	8.0	0.099	9.5	0.117	5.5	.	
38	PG-37	227	1.2	20.5	1.2	12.7	0.157	13.4	0.165	17.1	17.1	
39	PG-38	160	1.0	22.0	0.8	12.8	0.158	10.0	0.124	22.0	27.0	
40	PG-39	223	1.4	12.0	0.9	8.3	0.103	9.9	0.123	8.6	13.3	
41	PG-40	40	.	.	.	.	.	13.7	0.169	.	.	
42	KO-41	258	1.3	4.8	1.2	4.9	0.061	6.4	0.079	3.7	4.0	
43	KO-42	283	3.1	14.5	2.5	12.9	0.159	14.6	0.180	4.7	5.8	
44	KO-43	203	0.8	5.8	1.4	5.1	0.063	8.8	0.102	.	4.1	
45	KO-44	118	*	7.2	1.0	4.6	0.0568	9.3	0.115	.	7.2	
46	GR-45	145	*	7.1	0.5	4.0	0.0494	5.5	0.068	.	.	
47	GR-46	246	1.6	5.4	1.2	5.5	0.068	6.44	0.0795	3.4	4.5	
48	EL-47	188	*	7.2	0.9	4.5	0.0556	8.0	0.0988	.	5.0	3 samples cements := 5-6 ppm eUtc
49	EL-48	201	*	6.0	0.7	3.7	0.0457	6.3	0.0778	.	.	
50	EL-49	42	3.8	1.4	1.7	5.0	0.061	5.9	0.0729	.	.	
51	BC-50	177	1.5	5.2	1.5	8.2	0.101	10.9	0.135	3.4	3.4	
52	BC 51-60	200	1.0	5.0	1.2	4.7	0.058	6.3	0.078	5.0	4.2	

RADIOMETRIC MEASUREMENTS AND RESULTS

The geological and mineralogical aspects of clays in Albania are presented by Burri (1985). The main constituents of clays are SiO_2 (30-60 %), Al_2O_3 (10-35 %), Fe_2O_3, MgO, Na_2O, CaO etc. Clays are composed of different hydrous alumosilicates, biquartz-feldspars, iron and aluminum oxides and hydroxides, which are the rockforming minerals. Among these the high absorbing clay colloids are present.

Due to their natural rock composition and absorbing features, these clays contain numerous rare elements. Besides the most important natural radioactive elements such as U, Th, K, Ra, Rn, clays must have in their composition radioactive isotopes of rare elements such as Rb-87, Sm-152, Lu-76, Re-187 etc. The main irradiator of clays is U-238 (in equilibrium) with 0.33 mCi/g specific activity. 1 g U-238 emanates $3.3.10^4$ gamma-quantum/sec and $8.4.10^3$ beta particles/sec. The specific radioactivity of Th-232 (in equilibrium) is 0.11 mCi/gr. Thus, 1 g. Th-232 emanates $1,7.10^4$ gamma-quantum/sec and $1,5.10^3$ particle-beta/sec. K-40 is gamma and beta irradiator. In one disintegration, it radiates 0.11 gamma-quantum and 0.89 beta particle. So, 1 g. Potassium (K-40 = 0.0118 % K) emanates 3.3 gamma-quantum/sec and 27.5 beta particle/sec (Thereska, 1980). The number of natural radioactive elements is nine, but in terms of the radiation intensity, only three of them (U, Th, K) are important and therefore the radiometric and gammaspectrometric analyses are made for these elements.

The GAD-6 type gamma-spectrometer with 4 channels (one integral and three differentials) is used to determine the concentrations of radioelements eUtc, eU, eTh in ppm and K in % . The clay sample is milled about 100 mesh and placed in a "marineli" type container 170 cm^3, which is hermetically closed to prevent the emanation escape. This makes it possible to use 4π geometry of sample-detector measurement.

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The gamma-spectrometric measurements are considered difficult because they are affected by numerous factors such as physical, geometrical etc. The necessary analytical accuracy is obtained through a special experimental technical-methodical scheme. It also provides the necessary efficiency and accuracy of the U, Th, K measurements (Dodona, 1988). The U determination is made possible through the radioisotope of its row Bi-214, (Eg = 1.760 MeV). Thorium is determined through the radioisotope of T1-208 (Eg = 2.62 MeV), while the potassium is analyzed through K-40 (Eg = 1.46 MeV) in accordance with the respective gammaspectrometer channels. The total equivalent value of the radioelements which is given in eUTC value is determined by the integral measurements with a threshold energy of 400 and 100 KeV (Dodona and Tashko, 1993).

Table 2. Element concentration mg/kg (ppm)
Laboratory: XRF Laboratory (IFB)& Radiometric Laboratory (CGGE), Tirana
Analys Date: February 1996; Soil samples

	G95/1	G95/3	G95/8	G95/12
eU (GAD-6)	2.02	0.48*	0.73	*
eTh-II-	6.19	2.51	2.0	2.0
K% -II-	1.46	0.59	0.99	0.73
eU_{TC} (400 KeV)-II-	6.58	2.32	2.72	1.8
eU_{TC} (100 KeV)	7.82	2.9	4.57	3.72
Mg % (XRF)	3.98*	8.228	4.862	6.402
Al %	8.514	6.05	6.699	4.466
Si %	29.381	24.013	25.817	26.356
K %	1.76	0.689	0.831	0.64
Ca %	0.469	1.573	3.311	1.727
Ti %	0.622	0.31	0.297	0.279
V %	127.6	119.9	147.4	82.5*
Cr	789.8	2296.8	682.0	5241.5
Mn	1425.6	1710.5	1035.1	1543.3
Fe %	5.28	6.138	5.269	7.117
Ni	350.9	1416.8	313.5	1839.2
Cu	57.2	67.1	110.0	47.3
Zn	94.6	85.8	99.0	80.3
Ga	18.7	12.1	12.1	8.8*
As	**	**	**	**
Br	9.9*	4.4*	3.3*	3.3*
Rb	84.7	36.3	38.5	31.9
Sr	44.0	44.0	104.5	42.9
Y	42.9	17.6	14.3	14.3
Zr	194.7	68.2	71.5	113.3
Pb	36.3	46.2	24.2	19.8*
Cs	9.9*	**	**	**
Ba	332.2	129.8	254.1	149.6
La	47.3	15.4*	**	13.2*
Ce	67.1	24.2	26.4	26.4
Pr	14.3*	**	**	**
Nd	47.3	13.2	13.2	14.3*

* - Conc. is close to Min. Det. Limit;
* - Conc. is below Min. Det. Limit

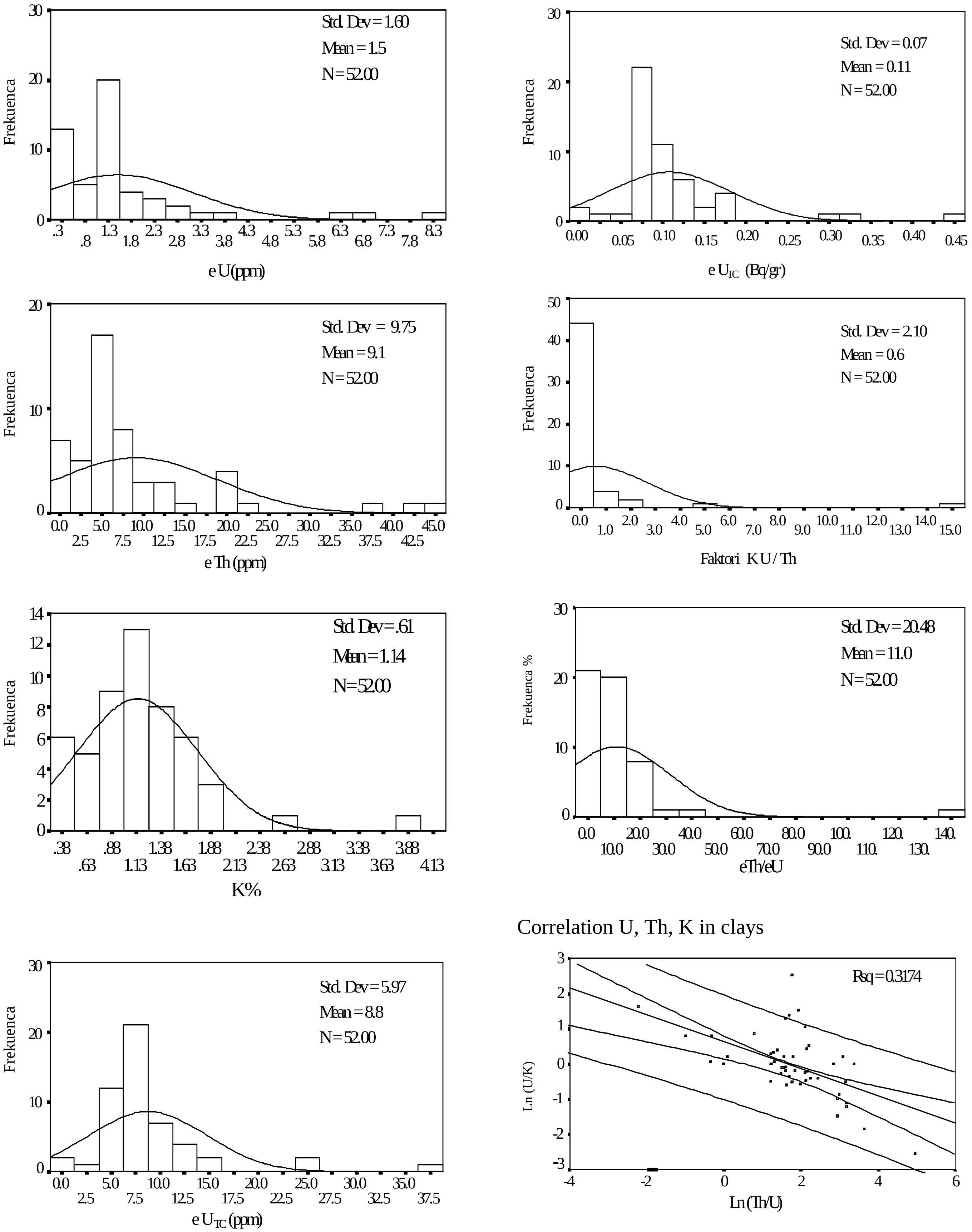
Correlation U, Th, K in clays

FIG. 2. Histograms of natural radioelements in clays of Albania

Table 1 presents the results of the radiometric analyses of radioelements in the clay samples. The analyses were carried out with the gamma-spectrometer. The measurements show contrasts in the radioelement concentrations for different samples through the values of eUtc, as well as for particular radioelements. The results obtained are presented through respective histograms as well as through the correlations between U, Th, K (Fig. 2). The maximum concentration values are for eTh (up to 45 ppm), eU (up to 6.5 ppm) and K (up to 3.8 %) respectively . The relative low value for the U concentration, brings about low emanation of Rn-222, which becomes a positive factor for the radiation protection in the dwellings. To fulfill the environmental picture of the grounds on which the dwellings are constructed, in Table 2 results from analyses of some representative soil samples collected in several areas are presented. Figure 1 represents the most important deposits for the industrial clays in Albania, where the sampling was done.

CONCLUSIONS AND RECOMMENDATIONS

The results obtained show that the concentration of radioelements in clays and soil are within the values accepted as "normal". The value of the 30 ppm for eU_{TC} which is considered as upper concentration level (30 ppm eU_{TC} = 0.37 Bq/gr) (Smirnov, 1984), which has not been overcome for the majority of clay samples under measurements, besides sample Shk.- 01 (Tamare), which has a concentration of eU_{TC} = 30.5 ppm = 0.38 Bq/gr. In spite of the relative high concentration value, being a thorium carrier clay (45 ppm eTh), this clay represents the absence of radon emanation. Nevertheless this clay is not recommended for residental building constructions. The use of the cornerstones is not recommended either with natural radioelements concentrations of 20 ppm U, 40 ppm Th and 2% K, because the total concentrations of 0.52 Bq/gr and therefore exceed the upper concentration level.

The results achieved by this study will contribute to a proper and adequate use of the construction materials and their industrial products such as bricks, cement, stones, sands, filler etc., in connection with effective economic and "public health " costs.

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