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RADIOACTIVITY MEASUREMENTS OF ZIRCONIA POWDERS

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ABSTRACT

Partially Stabilized Zirconia (PSZ) ceramics are proposed as an alternative material to the A12O3 components now used in prosthetic devices, for their better toughness and wear resistance compared to the Alumina ones. Due to the fact that to Zirconium may be associated a low content of actinides, it is worthwhile to assess the total radioactivity of PSZ materials to be used in biomedical applications. Measurements were performed on four PSZ samples, two coming from the market and two manufactured by Gel Supported Precipitation (GSP) process by TEMAV SpA. Natural radioactivity of bone was measured and results are reported for comparison. Measurements were performed by HPGe detectors, coincidence connected with a NaI (30.5 x 30.5) cm Compton suppressor, thus enhancing sensitivity to 5x10-4Bq.

INTRODUCTION

Hearth crust is relatively rich in Zirconium, as it ranks as eleventh in abundance scale, that is more than common metals as Copper, Lead, Nickel, Zinc. Zirconium minerals of industrial interest are the Zircon (ZrSiO2) found in Madagascar, Brazil and in Florida, Australia and South Africa beach sands, and the Badelleyte, (ZrO2) extracted from the Mountain Plateau in Brazil.

It is well known that some Zirconium ores may contain radioactive isotopes, and this fact originated, in a society more and more concerned with environmental questions, attention about possible harmful radioactivity levels of Zirconia items, like for instance, X-Ray contrast media for bone cements [1].

Radioactivity of Zirconium is mainly due to the presence of isotopes coming as decay products from natural Uranium and Thorium associated to Zirconium bearing ores.

Zirconia ceramic precursor today present on the market are mainly made for refractory use, as furnace liners, for the manufacture of high-temperature structural components, for protective coatings on alloys. All of these applications do not need much attention to the small radioactivity levels linked to the material, but it is worthwhile a careful assessment of this quantity when the material has to be used within the human body, as for the manufacture of prosthetic devices.

MATERIALS AND METHOD

Materials

The gamma radioactivity of four PSZ powder samples, two coming from the market (samples A and B), two manufactured by TEMAV SpA by GSP process (samples C and D) as well as the gamma radioactivity of human bone were measured (See Table 1). Sample geometry was a cylinder 50 mm in diameter, 15 mm high.

TABLE 1
PSZ samples characteristic

Sample	A	B	C	D
Composition	Y-PSZ	Y-PSZ	Y-PSZ	Ca-PSZ
Manufacturer	Tosoh	Dyn.Nobel	TEMAV	TEMAV

Human bone specimens from surgeries were calcinated at 900 C for 8h and reduced to powder in a planetary ball mill using agate jars.

Method

Gamma countings were performed by lead shielded Ge (Hp) detector (ORTEC), with FWHM 1.68 KeV and efficiency of 29% at 1332 KeV, coincidence connected with a NaI (30.5 x 30.5)cm Compton suppressor enhacing sensitivity to $5x10^{-4}$ Bq, coupled with a ORTEC PHA/MCA system. After correction of spectra for low energy gamma rays self absorption, background subtraction and multiplet deconvolution, total activities were evaluated by direct comparison with multipeak aqueous solution with the same geometry of the samples, to calibrate the energy and efficiency scales of the measuring system to absolute units. Calculations were performed by ORTEC Maestro II standard software package.

RESULTS

The measured total specific gamma activities are summarized in Table 2, the main identified radionuclides contents is reported in Table 3.

TABLE 2
Experimental results (Bq/Kg)

A	B	C	D	Bone
70±12	7240±210	1220±140	1160±140	85±15

TABLE 3
Main radionuclides contents in the samples (Bq/Kg)

	A	B	C	D	Bone
210 Pb	-	428	69	83	-
212 Pb	-	505	75	35	-
214 Pb	7	764	295	115	5
212 Bi	-	556	114	95	-
214 Bi	7	674	258	115	5
219 Rn	-	107	36	57	-
223 Ra	-	96	29	49	-
224 Ra	-	482	69	83	-
226 Ra	-	1221	-	164	-
227 Th	-	102	31	56	-
228 Th	-	245	151	223	-
230 Th	-	1327	-	-	-
234 Th	-	319	-	-	-
235 U	1	27	-	-	-
208 Tl	-	154	23	8	-
228 At	-	429	96	69	13
40 K	52	-	43	104	60

DISCUSSION

Measurements reported deals only with gamma activities; alpha emitters are below the detection limit of our system (~5 Count/h), while Beta activity was negligible (~4 Bq) due to the limited range in ZrO_2. Total gamma activity from Table 2, must be rescaled to the actual mass of a 28mm dia. ceramic THP sphere, i.e. 50 g, and put in comparison with the total mass of the mineral part of human skeleton (4 Kg) and of whole body radioactivity, as reported in Table 4.

TABLE 4
Radioactivity data comparison (Bq)

PSZ sphere	Whole human body	Skeleton
3.5 - 360	3700	340

Resulting whole body doses from the above sources are reported in Table 5 in comparison with other sources.

TABLE 5
Whole body doses (μSv/anno)

PSZ sphere	inner body sources	full skeleton	natural background	medical doses
2-1070	125	12	1800	800

Natural source of external irradiation are cosmic rays. (In Italy at sea level the whole body dose is 0.5 mSv/year).

A second source of external irradiation comes from the natural abundance of radionuclides in the rocks and in the ground and buildings. In Italy the whole body dose is 0.5 mSv/year in the Aosta district in the Alps, and 2 mSv/year in the Viterbo district, near Roma.

Diagnostic radiology dose (X-rays) on Italy's population is 0.8 mSv/year on bone marrow and 0.5 mSv/year on gonads. As majority of bone marrow is deeply inside the human body, this dose has to be accounted as whole body irradiation.

In conclusion, the average external irradiation in Italy accounts about 1.8 mSv/year (180 mrem/year), 0.9 mSv/year due to natural background (cosmic rays, ground radiations), 0.8 mSv/year due to medical diagnostic and the balance due to technological sources of radiations.

CONCLUSIONS

The examined zirconia powders show a wide range of total specific radioactivity values, and a qualitative difference in gamma spectrum of contained radioactive isotopes. As shown in table 3, in some cases (sample A) only 40-K, 214-Pb and 214-Bi are present, while in other samples (sample B) all decay products from 235-U, 238-U and 232-Th are present in not negligible amounts.

From these data the following conclusions can be drawn:
i) zirconia can contain a wide variety of gamma emitting isotopes . The associated radioactivity level highly depends from the source of minerals used in preparation, and from the purification level of the chemical precursors of the oxide;
ii) to lower the radioactivity levels of PSZ up to negligible levels is mandatory for materials selected for prosthetic applications. This implies the need of performing accurate radioactivity measurements for the selection of chemical precursors to be used in the preparation of ceramic powders;
iii) the quality and the intensity of gamma spectra are an useful tool for the determination of the chemical purity level of materials. Our work is in progress to characterize potentially toxic elements in Zirconia and to evaluate their correlations with the identified radionuclides.

REFERENCES

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