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Chemical distribution of hazardous natural radionuclides during monazite mineral processing

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ABSTRACT

It is very important to calculate the radioactivity concentration for low-grade monazite ore (50%) and different other materials produced as results of chemical processing stages to avoid the risk to workers. Chemical processing of low-grade monazite pass through different stages, washing by hydrochloric acid and digested with sulfuric acid and influence of pH on the precipitation of rare earth elements has been studied. The radioactivity concentrations of ^{238}U(^{226}Ra) and ^{232}Th as well as ^{40}K were calculated in crude low-grade ore and found to be 54,435 ± 3138, 442,105 ± 29,200 and 5841 ± 345 Bq/kg, respectively. These values are greatly higher than the exempt levels 25 Bq/kg. After chemical digestion of the ore, the results demonstrated that un-reacted material contains significant radioactivity reached to approximately 8, 13 and 23% for ^{238}U, ^{232}Th and ^{40}K, respectively. The results show that 60% of ^{232}Th are located in the digested white slurry with small portions of ^{238}U and ^{40}K. Most of ^{238}U radioactivity is extracted in the green phosphoric acid which produced from conversion of P_2O_5 by H_2SO_4 into phosphoric acid. The average values of the Ra_{eq} for monazite ore, un-reacted black precipitate, white precipitate, brown precipitate and crystalline material samples were calculated and found to be 687,095 ± 44,921, 85,068 ± 5339, 388,381 ± 22,088, 313,046 ± 17,923 and 4531 ± 338 Bq/kg, respectively. The calculated values of Ra_{eq} are higher than the average world value (it must be less than 370 Bq/kg). Finally the external hazardous, internal hazardous and $I_{\gamma r}$ must be less than unity. This means that specific radiation protection program must be applied and implemented during monazite processing.

1. Introduction

Human beings have always been exposed to natural radiation, which is mainly due to the activity concentration of primordial radionuclides ^{238}U(^{226}Ra) series, ^{232}Th series and ^{40}K that present in the earth's crust, in building materials, air, water, foods and the human body itself (UNSCEAR, 2000). As these radionuclides are not uniformly distributed, the knowledge of their distribution in soil, sand and rock play an important role in radiation protection and measurement (Santos et al., 2008). Radioactive elements can be found in earth crust and mantle in different quantities, depending on the rocks and minerals present in a particular region. The major naturally occurring radionuclides are ^{40}K and the long lived parents of two of the naturally occurring radioactive series, namely, ^{238}U, ^{232}Th including their progenies such as ^{226}Ra and ^{228}Ra. It is not the individual minerals that are important, but their host rocks that will determine the quantities of the radioactive elements present. Furthermore, minerals containing uranium and thorium as essential constituents are found only as trace minerals in common rocks or as minerals in primary or secondary mineral deposits (Van Schumus, 1995; Eisenbud and Gessel, 1997).

The presence of natural radionuclides from the thorium and uranium series in beach sands is a well recognized fact. Most coastal areas have long been known for their unusually high levels of natural radioactivity, caused by deposits of monazite-bearing sands (Anjos et al., 2007). Potassium, on the other hand, is abundant in light minerals such as quartz and feldspars which are part of the source rocks. It is not expected any significant enrichment or depletion of potassium during the sediment transport process, thus this element works as a radioactive label of the source rock (Anjos et al., 2007). The study of the distribution of primordial radionuclides allows the understanding of the radiological implication of these elements due to the γ-ray exposure of the body and irradiation of lung tissue from inhalation of radon and its daughters (Alam et al., 1999; Singh et al., 2005). In particular, it also is

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important to assess the radiation hazards arising due to the use of soil or sand samples in the construction of dwellings (UNSCEAR, 1993). In certain beaches of Brazil there are areas well-known for their high background radiation. These areas are directly connected with the occurrence of heavy-mineral deposits.

The processing of ores and other raw materials containing small but measurable amounts of natural radionuclides by the industry may enhance the concentration of those radionuclides and, consequently, may cause radiological problems in workplaces and in the nearby environment. This is the case of plants that process beach sands for the production of monazite or zircon sands which are widely used in the manufacture industry. Concentration of radioactive materials (forming the so-called TEN0RM) in the mineral industry occurs during the mineral processing. Once formed, those materials can be detrimental to the workers as radiation doses to individuals working in the industry can be significant. Radiation doses due to the presence of TENORM can be derived from external radiation and from internal exposures, the later being caused by inhalation of radionuclides attached to aerosols and dust particles or by inhalation of radon and its short lived daughters (Righi et al., 2006; Van Der Steen and Van Weers, 2004). The radioactivity level is not the most important parameter for defining the quality of mineral products, but it plays a role in the economics of the mineral sand production, as high uranium and thorium contents may affect negatively the price of the monazite or zircon produced.

Many efforts has been expended by several research groups to develop an effective process for recovering thorium, rare earth elements and uranium from monazite sands. Moreover because of its demand of rare is highly increased recently, the production of rare earth elements for commercial uses have already reached to the large magnitude (Gupta and Mukherjee, 1990). The recovery of the rare earth elements (REEs) and the associated thorium and uranium from monazite concentrate is actually accomplished by a variety of methods after its breakdown with either sulfuric acid or sodium hydroxide (Gupta and Mukherjee, 1990).

In the present work, the radiological assessments of the primordial radionuclides as well as ^{40}K for low grade monazite ore before and after processing have been studied. Also the different radiation hazardous parameters were determined to evaluate the risk of radiation on operational and/or workers in processing stages.

2. Experimental

2.1. Materials and method

2.1.1. Raw materials and chemical reagent

In the present work, low grad monazite sand (50%) was supplied by nuclear material authority, Egypt. Concentrated sulfuric, hydrochloric acids, and sodium hydroxide were used in digestion and leaching processes. All these chemicals and analytical reagents were of analytical reagent grade and were used without further purification.

2.1.2. Decomposition procedure

The washed low-grade monazite (500 g) was digested by mixing with 1.4 L H_2SO_4 (sp. gr. 1.84) and heated for 3 h at 483–493 K (210–220 °C) continuous stirring mechanically. When the mixture becomes pasty the decomposed mixture or sulfate paste (slurry) was directly placed in 2 L cold water and left for about 24 h (it must be stand overnight). Two different precipitates were formed in two layers, black residue and white precipitate and the above of these layers is green solution. Diagram in Fig. 1 shows the complete proposed process flow-sheet for digestion of low-grade monazite ore.

2.2. Gamma-spectroscopic system

The natural radionuclides present in different samples and the radioactivity concentration were identified using non destructive nuclear spectroscopic technique. It has been performed by γ-spectroscopic system consists of High Purity Germanium detector (HPGe) model GR3019 Canberra with serial number 6419 is a cylindrical crystal with 7.6 cm diameter and 11.3 cm length with 512 cm^3 active volume. Relative efficiency of the detector is 30% with resolution of 1.9 keV at the γ-energy line 1332.5 keV, linear amplifier model TC 2002CSL, multichannel analyzer MCA 16384 channel and Genie 2000 software. The detector is surrounding by cylindrical lead shield 12.5 cm thickness with movable cover, while the inner part of shield lined by cadmium copper sheets to attenuate X-ray stimulated in the lead shield.

Energy calibration was performed using certified several sealed point sources (Amersham, England) of known gamma-energy lines, namely, 661.67 keV for ^{137}Cs, 1173.4 and 1332.5 keV for ^{60}Co and 81.9, 282.9, 302.9 and 356.1 keV for ^{133}Ba. Efficiency calibration of the detector was done using certified reference materials IAEA-314 from the International Atomic Energy Agency, Vienna, Austria (Stracchnov et al., 1991). This certified reference materials contain known activity concentration for radionuclides, (^{238}U, ^{232}Th and ^{226}Ra) which covering the energy range of natural radioactivity. The geometry for all samples during gamma ray measurements was identical.

2.3. Radioactivity levels and radiation hazardous parameters determination

2.3.1. Radioactivity levels determination

The radioactivity concentrations of the parent radionuclide can be determined in test samples through the quantitative analysis of any daughter radionuclide under secular equilibrium condition. ^{226}Ra belongs to the ^{238}U-series has decayed to radioactive noble gas of ^{222}Rn (3.82 d). The decay of radon produces airborne radioactive isotopes of Po, Bi and Pb. ^{226}Ra reaches radioactive equilibrium with all its daughter products to ^{210}Pb in several weeks i.e., seven half-life of ^{222}Rn (3.82 d). Therefore, each packed sample was sealed and stored for 30 days to reach secular equilibrium between ^{226}Ra and its daughters. The radioactivity concentration of ^{238}U was determined depending on the gamma rays emitted from daughter radionuclides decayed ^{234}Th (63.3 and 92.6 kev) and ^{226}Ra (186.2 kev) and their decay products ^{214}Pb (351.9 keV) and ^{214}Bi (609.3 and 1764.5 keV (Uosif et al., 2008), at the secular equilibrium test samples. Also, the activity concentration of ^{232}Th was determined from the average concentrations of its daughters ^{212}Pb (238.6 keV), ^{228}Ac (911.1 keV) and in ^{208}Tl (583.1 and 2614.7). The radioactivity concentration A in Bq/kg in the scale samples was calculated from following Eq. (1):

$$\mathbf{A_i} = \frac{(\mathbf{C/S})_{\mathbf{measured}}}{\boldsymbol{\varepsilon_i} * \mathbf{I_i} * \mathbf{W}} \quad (1)$$

where $(C/S)_{measured}$, I_i, ε_i and W are the net counts per second measured under specified energy, the abundance of the specific gamma-ray line i, the photo peak detection efficiency for the same gamma-ray line and the sample white in Kg.

2.3.2. Absorbed dose rate determination

Conversion factors to transform specific radioactivity levels C_K, C_U and C_{Th} of ^{40}K, ^{226}Ra and ^{232}Th respectively, and the absorbed dose rate at 1 m above the ground (in nGy/h) by (Bq/kg) are