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Relations between Radionuclides Activities before and After Leaching Processes of Different Rock Types

1A. Nada and 2Eman M. Ibrahim

1Faculty of Women for Art, Science and Education, AinShams University, Cairo, Egypt.
2Nuclear Materials Authority, Egypt.

ABSTRACT

The solid wastes, produced from leaching processes which are known as the tailings, constitute most of the original rock materials and contain most of the radioactivity emitted from 226Ra and its daughters, 222Rn, 214Pb and 214Bi. Five different rock samples were subjected to sulphuric acid leaching processes with the same parameters of solid to liquid ratio S/L, acid concentration and leaching time. After leaching process, the pregnant solution was separated from the residual and the latter was dried. The three units, named the original samples, pregnant solutions and residuals were measured radiometrically, using the hyper-pure germanium detector to determine the activity concentrations (Bq/kg) of the different radionuclides in the three units of the five samples. The results showed that the relation between the sum of activities of both pregnant solutions and residuals and originals have three categories. In the first one, the sum of the activities is 89.58% from the original (marly claysite), in the second; the sum of activities is 101.74% from the original (siltstone). In the third category; there are three grades. The first sum is 111.53% from the original (shale), the second sum is 123.36% from the original (sandy dolostone) and the third sum is 152.66% from the original (sandy dolomite) these variations depend mainly on the grain surfaces and the leaching processes. This phenomenon is varied in magnitude within the different radionuclides in each sample.

Key words: Radionuclides, Leaching, Rock Types.

Introduction

The 226Ra is the main radionuclide in the tailings after leaching process for uranium extraction and is highly active with its solid decay products. The main danger is not only during the radioactive releases during the operations of leaching processes but also for many years after cessation of operations (Metzler, 2004).

According to Swift et al., (1976), the solid tailings contain about 90% of the entire radioactivity present in the original ore and the extracted uranium accounts for the other 10%.

Noyes (1995) mentioned that the tailings from processed uranium ore contain relatively lowest concentrations of the uranium-238 decay chain; 238U, 234U, 230Th, 226Ra, 222Rn and the radioactive decay products of 222Rn; they retain about 85% of the total radioactivity of the uranium ore from which they were produced. The uranium tailings are essentially the same material as the original ore mineralization with two exceptions; a large surface area and most of the uranium has been extracted by chemical treatment. Most of the radium from the ores appears in the tailings (Lakshmanan and Ashbrook, 1978).

The physical and chemical processes used to extract uranium from ore, such as crushing and acid treatment, produce large amounts of mill tailings. In France today, approximately 50 million tons of uranium mill tailings (UMTs) are stored on the surface of specific areas. They contain 99% of the radium present in the original ore and have a much higher porosity and permeability than that of the rock from which they are derived. The average 226Ra activity value for French UMTs is between 4000 and 60,000 Bq kg⁻¹ (Ferry et al., 2002).

Uranium mill tailings contain many naturally occurring hazardous substances, both radioactive and non-radioactive, and include approximately 85% of the radioactivity present in the unprocessed uranium ore (Metzler, 2004).

Acid leaching is known to be predominant process for uranium recovery from ores, usually with sulfuric acid because of its relatively low cost (Umanskii and Klyushnikov, 2012).

(El Aassy et al., 2012) studied the behavior of most of different radionuclides in the 238U and 232Th series during the acidic leaching and they concluded that the nuclides before 226Ra in the 238U decay series are easily released in the pregnant solution than the 226Ra itself and its solid daughters (214Pb and 214Bi).

The main aim of this study is to interpret the relations between the activities of radionuclides of the original samples and the sum of activities in both pregnant solutions and residuals of the studied five samples.
2. Samples Description and Preparation:

Five samples Table 1 of different varieties were collected from the sedimentary uranium ore mineralization in Wadi (Valley) Naseib, southwestern Sinai, Egypt Fig.1. These samples represent a sedimentary rock formation which is belonging to Lower Carboniferous (Upper Visean) age. The selected samples represent different rock types and different grades of uranium with very low concentrations of thorium to achieve the aim of this study.

The collected samples were crushed and ground to -60 mesh and then quartered and packed in 200 ml Marinelli for 28 days before measurements.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Siltstone: Compact, dark grey to black, soft to medium hard.</td>
</tr>
<tr>
<td>2</td>
<td>Black Shale: Fissile with gypsum flakes and carbonaceous organic matter.</td>
</tr>
<tr>
<td>3</td>
<td>Marly Claystone: Compact and layered with gypsum flakes between the layers.</td>
</tr>
<tr>
<td>4</td>
<td>Sandy Dolomite: Medium hard, grey, highly ferruginous with green copper minerals and lustrous black mineral may be urano-black.</td>
</tr>
<tr>
<td>5</td>
<td>Sandy Dolostone: Mixture of sandy dolomite and fissile shale with pale yellow secondary uranium mineralization.</td>
</tr>
</tbody>
</table>

Table 1: Description of the collected samples.

Fig. 1: Geologic map of WadiNaseib area with the locations of the collect samples.
3. Experimental Technique:

The radiometrically measured samples were poured from the Marinelli and quartered till 50 g to use it for leaching experiments which were carried out by 25% \( \text{H}_2\text{SO}_4 \) with room temperature, 1:3 solid/liquid ratio and one hour stirring time.

High Purity Germanium (HP-Ge) detector, based on high resolution gamma spectrometry systems, is widely used for radioactivity analysis because of its superior energy resolution with the availability of large size crystals. Activity of many radionuclides can be determined simultaneously for any given sample, but necessitates relatively larger sample size and longer spectrum acquisition time for low level radioactivity measurement (Chinnaesakki et al., 2012).

Pregnant solutions (Bq/ℓ) and residuals (Bq/kg) were measured in addition to the original ore sample by using the HP-Ge detector. This detector has a relative efficiency of about 50% of the 3"x3" NaI(Tl) crystal efficiency, resolution of 1.90 keV and peak/Compton ratio of 69.9:1 at the 1.33 MeV gamma transition of \( ^{60}\text{Co} \). It is coupled to conventional electronics connected to a multichannel analyzer card (MCA) installed in a PC computer. The detector was shielded from the background radiation, using a 10 cm thick lead, which was internally lined with a 2 mm copper foil. The software program MAESTRO-32 was used to accumulate and analyze the data. Energy calibration of the detector was performed, using standard point sources. The system was calibrated for energy to display gamma photo-peaks between 63 and 3000 keV.

4. Analytical Technique:

In order to measure the activity of a sample, it is necessary to know the detection efficiency of the system. It is obtained by employing standard sources which have physical dimensions, chemical composition and density similar to those of the samples. With regard to the geometry, the deviation can be reduced almost to zero if standard Marinelli beakers are used for both standards and samples (Abdi et al., 2006). So, the efficiency calibration was performed by using three-well-known reference materials obtained from the International Atomic Energy Agency for U, Th and K activity measurements: RGU-1, RGTh-1 and RGK-1 (IAEA, 1987, Anjos et al., 2005, Sartandel et al., 2012).

Uranium-238 activity was determined indirectly from the gamma-rays emitted by its daughter products (\(^{234}\text{Th} \) and \(^{234m}\text{Pa} \)) whose activities are determined from the 63.3 and 1001 keV photo-peaks, respectively (Sutherland and de Jong, 1990). Uranium-235 activity was determined directly by its gamma-ray peaks; 143.8, 163.4, 185.7, and 205.3 keV (Yücel et al., 1998; Pöllänen et al., 2003; Ramebäck et al., 2010).

The specific activity of \(^{40}\text{K} \) was measured directly by its own gamma-ray at 1460.8 keV. The specific activity of \(^{226}\text{Ra} \) was measured, using the 186.1 keV from its own gamma-ray (after the subtraction of the 185.7 keV of \(^{235}\text{U} \)). The specific activity of \(^{214}\text{Pb} \) was measured using the 241.9, 295.2 keV and 351.9 keV, while that of \(^{214}\text{Bi} \) was measured using the 609.3 KeV. The specific activity of \(^{232}\text{Th} \) was measured, using the 338.4 keV and 911.2 keV from \(^{228}\text{Ac} \) and 583 keV and 2614.4 keV from \(^{208}\text{Tl} \).

Results and Discussions

The \( \gamma \)-activity of the radionuclides \((^{238}\text{U}, \ 235\text{U}, \ 226\text{Ra}, \ 214\text{Pb}, \ 214\text{Bi}, \ 232\text{Th} \) and \(^{40}\text{K} \)) were measured for the original samples (Bq/kg), pregnant solutions (Bq/ℓ) and residuals (Bq/kg). The activities of the pregnant solutions were recalculated in order to be in homogenous during summation with equivalents of residuals. The percents of activities of different radionuclides for both pregnant solutions and residuals relative to that of original samples were calculated and tabulated in Tables 2, 3, 4, 5 and 6 for different rock samples.

<table>
<thead>
<tr>
<th>Radiouclide</th>
<th>Original (Bq/kg)</th>
<th>Pregnant Solution (%)</th>
<th>Residual (%)</th>
<th>Summation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^{238}\text{U} )</td>
<td>5373.61 ± 63.14</td>
<td>33.39</td>
<td>74.93</td>
<td>108.32</td>
</tr>
<tr>
<td>( ^{235}\text{U} )</td>
<td>6824.37 ± 18.01</td>
<td>2.64</td>
<td>85.93</td>
<td>88.57</td>
</tr>
<tr>
<td>( ^{226}\text{Ra} )</td>
<td>4985.13 ± 6.01</td>
<td>0.76</td>
<td>108.24</td>
<td>109.01</td>
</tr>
<tr>
<td>( ^{214}\text{Pb} )</td>
<td>5011.71 ± 5.62</td>
<td>0.73</td>
<td>104.57</td>
<td>105.31</td>
</tr>
<tr>
<td>( ^{214}\text{Bi} )</td>
<td>244.74 ± 18.01</td>
<td>33.69</td>
<td>73.00</td>
<td>106.69</td>
</tr>
<tr>
<td>( ^{232}\text{Th} )</td>
<td>49.87 ± 2.02</td>
<td>5.49</td>
<td>92.69</td>
<td>98.18</td>
</tr>
<tr>
<td>( ^{40}\text{K} )</td>
<td>315.00 ± 6.12</td>
<td>0.97</td>
<td>99.01</td>
<td>99.99</td>
</tr>
<tr>
<td>Total (Bq/kg)</td>
<td>22804.43 ± 103.60</td>
<td>2137.46</td>
<td>21064.01</td>
<td>21201.52</td>
</tr>
<tr>
<td>%</td>
<td>9.37</td>
<td>92.37</td>
<td>101.74</td>
<td></td>
</tr>
</tbody>
</table>
Table 3: Gamma radio activities for different radionuclides in pregnant solution and residual in percent of Black Shale sample no.2.

<table>
<thead>
<tr>
<th>Radiouclide</th>
<th>Original (Bq/kg)</th>
<th>Pregnant Solution (%)</th>
<th>Residual (%)</th>
<th>Summation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U-238</td>
<td>5843.17 ± 61.64</td>
<td>30.03</td>
<td>80.40</td>
<td>110.43</td>
</tr>
<tr>
<td>Ra-226</td>
<td>6297.07 ± 14.34</td>
<td>8.31</td>
<td>91.69</td>
<td>100.00</td>
</tr>
<tr>
<td>Pb-214</td>
<td>4975.98 ± 33.09</td>
<td>3.45</td>
<td>96.55</td>
<td>100.00</td>
</tr>
<tr>
<td>Bi-214</td>
<td>267 95 ± 5.44</td>
<td>9.25</td>
<td>90.75</td>
<td>100.00</td>
</tr>
<tr>
<td>Tb-232</td>
<td>35.80 ± 1.27</td>
<td>5.14</td>
<td>94.86</td>
<td>100.00</td>
</tr>
<tr>
<td>K-40</td>
<td>213.77 ± 5.11</td>
<td>1.73</td>
<td>98.27</td>
<td>100.00</td>
</tr>
<tr>
<td>Total (Bq/kg)</td>
<td>22525.42 ± 128.53</td>
<td>2601.81</td>
<td>22519.93</td>
<td>25121.73</td>
</tr>
<tr>
<td>%</td>
<td>11.55</td>
<td>99.98</td>
<td>111.53</td>
<td></td>
</tr>
</tbody>
</table>

From these tables, it can be noticed that the relations between the total activities of radionuclides in original samples and the sum of them in the pregnant solutions and residuals are different from one sample to another especially in the nuclides of $^{238}$U decay series. These differences can be categorized in three groups:

1. The sum of activities of the measured radionuclides in pregnant solution and residual (121567.14 Bq/kg) is lower (89.59%) than that of the same radionuclides in the original sample (135696.55 Bq/kg) for the marlyclaystone sample in Table 4 and Fig.2.

2. The sum of activities of the measured radionuclides in the pregnant solution and residual (23201.53 Bq/kg) is nearly (101.74%) equal to the total activities in the original (22804.43 Bq/kg) as shown in the siltstone sample Table 2 and Fig.2.

3. The sum of activities of the measured radionuclides in the pregnant solution and residual (25121.73 Bq/kg) is higher (111.53%) than the total activities of the originals as in the shale sample (22525.42 Bq/kg) Table 3 and Fig.2, for sandy dolostone sample the sum of activities of the measured radionuclides in pregnant solution and residual (76632.03 Bq/kg) is higher (123.6%) than that of the original sample (62122.87 Bq/kg) Table 6 and Fig.2. This case is also noticed in the work of (Carvalho and Oliveira 2007) in uranium mining areas of Portugal.

From the previously mentioned results, it can be concluded that the type of sample plays its role in these variations between the activity concentrations of the original and the sum of pregnant solutions and residuals. In the first group there is an attenuation of the gamma activities during the leaching process, while in the second
case in which the sum is nearly equal to original as seen for the siltstone there is no attenuation noticed. In the third case, the leaching process by using acid solution may have led to clean the grain surfaces and permit the gamma activities of the inner grains in the residuals to be detected and measured this depends on the lithological type of the sample.

![Graph showing activity concentration (Bq/kg) of different radionuclides in the original samples and the sum of pregnant solutions and residuals.](image)

**Fig. 2:** Relation between the activity concentration (Bq/kg) of different radionuclides in the original samples and the sum of pregnant solutions and residuals.

![Activity concentrations in percent of different radionuclides in the residuals relative to original samples.](image)

**Fig. 3:** Activity concentrations in percent of different radionuclides in the residuals relative to original samples.

The behavior of each radionuclide in the five samples showed that the $^{214}$Pb and $^{214}$Bi activity concentrations are higher in the residual than that in the original for the all samples except that of the marlyclaystone Fig.3. The other abnormality is shown in the $^{226}$Ra in which the activity concentration of the residual is higher than that in the original in two samples (sandy dolomite and sandy dolostone) and nearly equal in one sample (black shale) and lower in the residual than that of the original in two samples (siltstone and marlyclaystone). This may depend on the acid used and the lithological type of the sample used. The results of (Fernands et al., 2006) for the uranium mining site of Caetite, Brazil, showed that the $^{226}$Ra activity concentration (Bq/kg) represents (104%) from that in the ore sample.
For $^{232}$Th the sum of the activity concentration in the pregnant solution and residual compared to the original samples ranged between (28.20%) for S4 sandy dolomite which contains high organic carbon content which makes complexes with thorium to (110.04%) in S2 black shale and for $^{40}$K it ranged between (86.39%) in S3 marly claystone to (100.44%) in S4 Fig. 4.

![Graphs showing activity concentrations in percent of different radionuclides for the sum relative to original samples.](image)

**Fig. 4:** Activity concentrations in percent of different radionuclides for the sum relative to original samples.

**Conclusions:**

The results showed that the sum of activities of both pregnant solutions and residuals in four samples are higher than that of the originals. One sample (marly claystone) only showed lower summation than the original. This phenomenon is varied in magnitude within the different radionuclides. The type of sample plays its role in these variations. Sometimes, there is an attenuation of the gamma activities during the leaching process, while in the second case, which is the logic result, there is no attenuation or other causes for increasing the measured activities. In the third case, the leaching process by using acid solutions may have led to clean the grain surface and permit the gamma activities of the inner grains to be measured which means that the treatment of samples before measurements may be needed.

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**References**


