Uranium Series Disequilibrium in Abu-Tartor Phosphate Ore Beneficiation

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Abstract: Beneficiation processes (crushing, screening, washing, magnetic separation and wet screening) of run-of-mine (ROM) phosphate ore aim at escalate the phosphorus content. It starts with the ROM and ends with the ore concentrate, and different rejects. Representative samples of ROM, concentrate, and rejects e.g., wet screening, magnetic separation, slime, clay rock and dolomite rock rejects were collected. Uranium-238 series radionuclides (^{238}U, ^{226}Ra and ^{210}Pb), ^{228}Ra, and ^{40}K, and elemental U, Th and K were measured using gamma-ray spectrometer and ICP-MS analytical techniques, respectively. Uranium concentration and ^{238}U series disequilibrium were discussed in relation with the beneficiation physicochemical processes.

Keywords: Uranium series, Phosphate ore, Beneficiation, Gamma-ray spectrometer, ICP-MS.

1 Introduction

Phosphate ores are normally in the form of calcium phosphates $Ca_3(PO_4)_2$ (phosphorites), which are very old marine deposits associated with fossils. This form of phosphate ore represents about 85% of the world-wide production. The materials are often calcined by heating to 950 ºC before dispatch in order to decompose calcium carbonate and organic matter. The second type of phosphate ore is apatite $Ca_5[(PO_4)_3(F)]$ of igneous origin. Economically interesting phosphate deposits contain between 4 and 38 % P_2O_5. The world's most important phosphate mining nations are China, Morocco, USA, Russia and Jordan [1,2].

Phosphate rocks are used extensively, mainly as a source of phosphorus for fertilizers and secondarily for phosphoric acid and other specialty chemicals. Sedimentary phosphate ores tend to have high concentrations of uranium, whereas magmatic ores, such

as apatite, do not. The range of U concentrations in phosphate ores range from 25 to150 ppm and reach as high as 600 ppm in some ore [3,4]. Uranium-238 is generally found in radioactive equilibrium with some of its decay products, such as ^{226}Ra. The activity concentrations of ^{232}Th and ^{40}K in sedimentary phosphate rocks are much lower than those of ^{238}U, and comparable to those normally observed in soil [5].

Beneficiation processes (crushing, screening, washing, magnetic separation and wet screening) of the run-of-mine (ROM) phosphate ore aim at escalating the phosphorus (P_2O_5%) content from 24 to 31% in case of Abu-Tartor's ore beneficia [1,6,7]. This study aim at shed more light on the behaviour of uranium and uranium series disequilibrium in Abu-Tartor phosphate ore beneficiation processes.

Beneficiation processes

The beneficiation processes (BP) of Abu-Tartor phosphate ore were shown in Fig 1 where the ROM ore is screened at 60 mm where the oversize particles were crushed in a rotary crusher and screened again. The clay and dolomite were picked up manually from the oversize ore (> 60 mm) that discarded due to its high impurities. The fraction below 60 mm is scrubbed in drum scrubber to disintegrate the ore. The scrubbed product is then screened on 2 mm screen. The fraction below 2 mm is subjected to classification using a group of hydro- cyclones to separate the clay fraction below 0.080 mm. The latter is discharged to the main thickener of the plant as slimes. The de-slimed product (< 2.0 & > 0.080 mm) is then subjected to a second stage of washing in attrition scrubbers.

The product of the latter is further classified using a hydro-separator, at about 0.2 mm, into coarse and fine fractions. The coarse fraction is filtrated and dried to ~1.5% moisture. In the meantime, the fine fraction (< 0.2 mm) of the hydro-separator is discharged to a group of hydro-cyclones for

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further classification to separate the slimes below 0.080 mm. The underflow of the hydro-cyclones (< 0.2, > 0.080 mm) is then discharged to a high-intensity magnetic separator to separate the ankerite (ferrogenated dolomite) impurities as a magnetic product. The nonmagnetic fraction (fine concentrate) is then subjected to filtration and drying. Both coarse and fine concentrates are blended to produce a final concentrate assaying ~30% P_2O_5 and 0.55% MgO. Table 1 shows the chemical analysis of the produced concentrate phosphate ore [1].
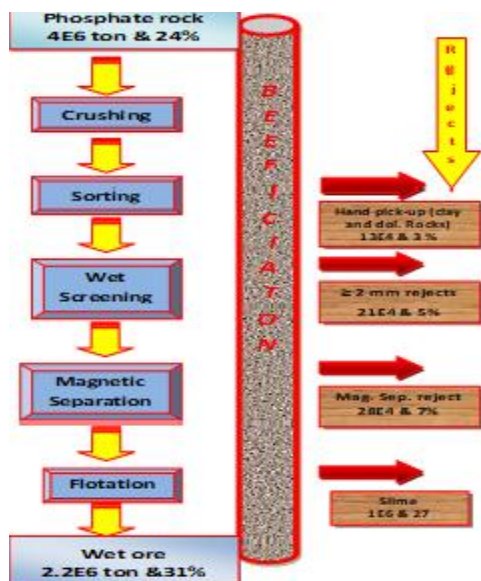

Fig. 1: Abu-Tartor phosphate ore beneficiation processes.

2 Experimental Works

2.1 Sampling and Samples Preparation

Phosphate ore and beneficiation rejects [ROM ore, concentrate ore (CO), primary rejects (clay- Cl and dolomite- Dol rocks), wet screening-WS rejects (> 2 mm), magnetic separation- Ms rejects and slime- Sl] samples were collected from Abu-Tartor phosphate mine. All samples (except the ROM ore sample) were collected from the beneficiation plant. Samples were dried at 110 ^{0}C, mechanically crushed, mixed and sieved through a 2 mm mesh [8].

2.2 Analytical Methods

2.2.1 Gamma-Spectrometric Analysis

Portions of the prepared samples were transferred to cylinder polyethylene containers of 100 ml volume. Activity concentration in Bq/kg of ^{238}U, ^{226}Ra, ^{210}Pb, ^{235}U, ^{228}Ra and ^{40}K were measured using gamma-spectrometry based on hyper-pure germanium detectors ray determinations were performed, at Karlsruhe institute of technology (previously, Karlsruhe research center), with a coaxial hyper-pure Ge detector, Canberra extended range (XtRa) type, mounted with a carbon window of 0.5 mm thickness, relative efficiency of 40%, and FWHM of 0.95 keV at the 122 keV line of ^{57}Co and 1.9 keV at the 1332 keV line of ^{60}Co. The gamma transmissions used for activity calculations are 46.4 keV for the ^{210}Pb, 1001.4 keV (^{234}Pa) for the ^{238}U and 143.77 keV for the ^{235}U, 351.9 (^{214}Pb), 609.3, 1120.3 and 1764.5 keV (^{214}Bi) for the ^{226}Ra, 338.4, 911.1 and 968.9 keV (^{228}Ac) for ^{228}Ra, and 1460.7 keV for ^{40}K. The count rate of 185 keV energy line was corrected for the 186 keV energy line of ^{226}Ra contribution [9]. The gamma spectrometer was calibrated using multi-elements standard source in the same geometry as the samples that contain ^{109}Cd, ^{57}Co, ^{113}Sn, ^{137}Cs, ^{88}Y, ^{60}Co and ^{40}K [10].

A quality control program was applied to ensure the reliability of the results and include participating in international inter-comparison exercises, and regular measurements of reference samples of different matrixes. Repeated measurements of duplicate samples showed that results were reproducible. Results of some quality control measurements were given in Table 2.

2.2.2 Inductively Coupled Plasma-mass Spectrometry, ICP-MS;

Sample aliquots were treated with aqua ragia and other aliquots were treated with four mineral acids (HNO_3, HCl, HF and H_2SO_4) to extract the leachable and total portions, respectively, of U, Th and K. The U, Th and K were analyzed in adjusted solutions

using a Perkin-Elmer Elan 9000 ICP-MS system at ALS-Chemex laboratory - Canada. All samples were analyzed twice and only the average concentration were considered in this study.

Table 1: Chemical analysis of Abu-Tartor concentrate [1].

Analysis	%	Analysis	%
P_2O_5	31.0	CO_2	3.6
MgO	0.55	Al_2O_3	0.25
Fe_2O_3	2.9	Na_2O+K_2O	0.95
Organic carbon	0.5	Cl	0.025-0.035
SiO_2	3.2		

Table 2: Specific activity (Bq/kg dry weight) of ^{210}Pb, in reference samples, reference values and measured values.

Sample	Reference value	Confidence range	Measured value
IAEA-384, Sediment	23.5	(22.2 - 24.2)	23.5 ± 1.3
IAEA-326, Soil	52.5	(47.9 - 57.1)	49.6 ± 3.9
IAEA-327, Soil	58.8	(53.9 - 63.7)	57.5 ± 4.4
IAEA-RGU	4914	(4844 – 4984)	5009 ± 187

3 Results and Discussion

Activity concentration (BqKg^{-1}) of ^{238}U, ^{226}Ra, ^{210}Pb, ^{235}U, ^{228}Ra and ^{40}K was given in table 3. The activity concentration of ^{238}U series radionuclides in ROM ore, concentrate and other beneficiation rejects shows a distinct degree of variation as a result of subjecting to both physical (e.g., crushing, dry screening and magnetic separation) as well as chemical (e.g., wet screening, leaching, dissolution and adsorption/absorption) processes. For ^{238}U, its concentration appears disturbed during the beneficiation processes, i.e. it was leached from ore during mining and beneficiation procedures where its activity levels in ROM ore and concentrate were 356 and 298 Bq kg^{-1}, respectively. The possible explanation could be that uranium was removed as soluble U, i.e. 6+ oxidation state of uranium, particularly during wet screening and/or it was partially removed by adsorption on iron and manganese oxides. The oxidized 6+ uranium (uranyl) ion complexes with carbonate, phosphate or sulphate ions and it is easily transported in hydrological cycle. Uranium in solid phase may be found as an adsorbed or co-precipitated constituent in Fe and Mn oxy-hydroxides and organic materials [11]. This could also explain the comparatively elevated concentration of U in magnetic rejects containing elevated concentration of iron and other ferromagnetic components. It is worth noting that, except for ^{40}K, the concentration of most NOR is comparatively high in magnetic rejects. For ^{226}Ra, concentration was mildly increased in concentrate where Ra is only moderately soluble in natural water and insoluble, particularly in the presence of sulphate ions [12]. This variation could be explained by the separation of non-phosphatic materials (e.g., clay and dolomite) that had a relatively low ^{226}Ra concentration during beneficiation. For ^{210}Pb, its concentration did not demonstrate significant changes in concentrate compared to ROM ore. Concentrations of ^{232}Th series radionuclides and ^{40}K in sedimentary phosphate ore are comparable to those found normally in soil [5,13]. Most NORs activity concentrations, except that for ^{40}K, in magnetic separation rejects, table 3, were relatively higher than that in other rejects (2mm and slim), as stated earlier, which could be due to their adsorption on iron and manganese oxides. The activity concentration of NORs in clay and dolomite were within their average activity concentration in sedimentary

rock and soils [14].

Concentrations of U (mg kg^{-1}), Th (mg kg^{-1}) and K (%) using ICP-MS technique and two different sample dissolution methods, i.e. one using aqua ragia and the other using four mineral acids (NHO$_3$, HF, HCl and H$_2$SO$_4$), as well as calculated activity concentration, Bq/kg, of ^{238}U, ^{232}Th and ^{40}K. For, and their ratios were given in table 4. In this section, the concentrations of U, Th and K in different samples were compared to highlight the effect of dissolution protocol. One protocol (A) is defined as near total sample dissolution using four mineral acids and the other protocol (B) is defined as leachable sample dissolution using aqua ragia. For U, its concentration in concentrate ore is greater than its concentration in the ore. Its concentration in magnetic separate reject is comparable to that of the ROM and the concentrate ores. Its concentrations in 2 mm and slime reject samples are comparable to and less than those of the other samples except for the clay and dolomite samples. The concentration ratios of (A/B) for U were less than unity and ranged from 0.83 to 0.93. For clay sample the ratio was 1.23. This could be clarified, firstly, becasue of the adequate ability of aqua ragia for dissolving most base element sulphates, sulphides, oxides and carbonates [15] and secondly because of the different behavior of uranium ion according to its oxidation state (4+ or 6+). Due to the similarity in ionic size between U^{4+} (0.99 A) and Ca (0.89A), the tetravalent uranium can readily enter the apatite structure. While the uranyl (U^{6+}) is much larger, it can only be fixed in the exterior part of the structure by various adsorption processes. The presence of tetravalent uranium implies strongly reducing organic mud in which apatite is formed. Hexavalent uranium exists under more oxidizing post-sedimentary conditions that occur generally during emergence [16].

The results indicate low U content compared to the typical activity concentration of ^{238}U in sedimentary phosphate deposits [5]. El-arabi and Khalifa, reported that the uranium content in the same mine ore was ranged from 16 to 199 mg kg^{-1} with an average of 107 mg kg^{-1} [17].

The strong positive correlation between P$_2$O$_5$ % and U reflects the fixation of uranyl ion and the formation of secondary uranium phosphate minerals. The variation of uranium contents relative to P$_2$O$_5$ is also ascribed to either temporal or aerial variations in seawater uranium content at deposition or variation in sedimentation rate. When

sedimentation is slow, each crystal of phosphate ore is in contact with seawater for a longer time and may adsorb more uranium [17].

Activity concentration ratios of $^{226}Ra/^{238}U$, $^{210}Pb/^{226}Ra$, $^{228}Ra/^{232}Th$, $^{226}Ra/^{228}Ra$ and $^{232}Th/^{238}U$ were given in table 5. Enrichment factor in concentrate as well as beneficiation processes by-products were given in table-4.

The variation percentages of activity concentration in different samples relative to ROM ore sample were given in table 4 and calculated using the following equation [18]:

$\Delta \% = (C - C') \times 100/C$ Where

C   is activity concentration in the sample
C'   is activity concentration in ROM ore

The positive and negative values mean increasing and decreasing the concentration of the radionuclide relatively to that of ore sample, respectively. The calculated enrichment factors of ^{238}U, ^{235}U, ^{226}Ra, ^{210}Pb, ^{228}Ra, ^{232}Th and ^{40}K in Abu-Tartor phosphate ore beneficiation samples (concentrate, > 2mm, magnetic separation, slime, dolomite and clay were given in Table 6.

Table 3: Activity concentration of ^{238}U, ^{235}U, ^{226}Ra, ^{210}Pb, ^{228}Ra and ^{40}K in Abu-Tartor phosphate ore beneficiation samples (run of mine- ROM, concentrate, > 2mm, magnetic separation, slime, dolomite and clay)

		$^{238}U \pm E$		$^{235}U \pm E$		$^{226}Ra \pm E$		$^{210}Pb \pm E$		$^{210}Pb (A) \pm E$		$^{228}Ra \pm E$		$^{40}K \pm E$	
1	Ore	356	± 19	14	± 7	316	± 10	279	± 56	396	± 37	29	± 4	46	± 8
2	Conc.	298	± 17	17	± 6	353	± 7	251	± 15	356	± 32	33	± 3	34	± 15
3	2 mm	196	± 9	17	± 3	234	± 4	154	± 7	237	± 11	24	± 2	76	± 11
4	Mag.	315	± 31	30	± 6	311	± 6	202	± 14	340	± 18	35	± 3	18	± 4
	slime	209	± 9	15	± 6	230	± 6	173	± 17	249	± 12	34	± 3	39	± 11
6	Dol.	67	± 5	6	± 1	73	± 2	65	± 5	85	± 4	18	± 1	329	± 21
7	Clay	38	± 5	< 11		47	± 1.5	35	± 4	37	± 2	30	± 1.8	290	± 20

Table 4 (a-b): Activity concentration (Bq/kg) of 238U, 232Th and 40K based on the elemental analysis of U, Th and K using ICP-MS in Abu-Tartor phosphate ore beneficiation samples (run of min- ROM, concentrate, > 2mm, magnetic separation, slime, dolomite and clay)

(a)

		$^{238}U^{\#} \pm E^{\&}$		$^{232}Th^{\#} \pm E$	
		A	B	A	B
1	Ore	320 (26)* ± 18	348 (28) ± 19	32 (8)* ± 6	32 (8) ± 6
2	Conc.	339 (27) ± 18	394 (31) ± 20	37 (9) ± 6	32 (8) ± 6
3	2 mm	226 (18) ± 15	251 (20) ± 16	25 (6) ± 5	24 (6) ± 5
4	Mag.	313 (25) ± 18	379 (30) ± 19	40 (10) ± 6	34 (8) ± 6
5	slime	228 (18) ± 15	275 (22) ± 16	34 (8) ± 6	31 (8) ± 6
6	Dol.	76 (6) ± 99	82 (6) ± 9	16 (4) ± 4	17 (4) ± 4
7	Clay	58 (5) ± 88	47(4) ± 7	27 (7) ± 5	32 (8) ± 6

(b)

		$^{40}K^{\#} \pm E$		Ratio$^{\$}$		
		A	B	U	Th	K
1	Ore	34 (0.11)$^{+}$ ± 6	31 (0.10) ± 6	0.92	1.0	1.1
2	Conc.	23 (0.08) ± 5	25 (0.08) ± 5	0.86	1.2	0.92
3	2 mm	85 (0.27) ± 9	83 (0.27) ± 9	0.90	1.0	1.0
4	Mag.	22 (0.07) ± 5	23 (0.08) ± 5	0.83	1.2	0.96
5	slime	31 (0.10) ± 6	31 (0.10) ± 6	0.83	1.1	1.0
6	Dol.	236 (0.76) ± 15	149 (0.48) ± 12	0.93	0.94	1.6
7	Clay	263 (0.84) ± 16	102 (0.33) ± 10	1.23	0.84	2.3

$^{\&}$ Standard deviation $^{\#}$ Bq kg^{-1} A: four acid sample dissolution   B: Aqua ragia sample dissolution $^{\$}$A/B ratio   * (mg.kg^{-1}) $^{+}$ (%)

Table 5: Activity concentration ratio of $^{238}U/^{226}Ra$, $^{210}Pb/^{226}Ra$, $^{210}Pb/^{238}U$, $^{228}Ra/^{232}Th$, $^{226}Ra/^{228}Ra$ and $^{232}Th/^{238}U$ in Abu-Tartor phosphate ore beneficiation samples (run of min- ROM, concentrate, > 2mm, magnetic separation, slime, dolomite and clay).

		$^{238}U/$ ^{226}Ra	$^{210}Pb/$ ^{226}Ra	$^{210}Pb/$ ^{238}U	$^{234}U/$ ^{238}U	$^{228}Ra/$ ^{232}Th	$^{226}Ra/$ ^{228}Ra	$^{232}Th/$ ^{238}U
1	Ore	0.89	1.26	1.11	1.01	0.90	11	0.102
2	Conc.	1.18	1.01	1.19	0.96	1.02	11	0.095
3	2 mm	1.19	1.01	1.21	0.94	1.02	10	0.106
4	Mag	0.99	1.10	1.08	0.91	1.01	9	0.110
5	slime	1.10	1.08	1.19	0.94	1.08	7	0.137
6	Dol.	1.09	1.17	1.28	0.98	1.06	4	0.220
7	Clay	1.25	0.77	0.97	1.07	0.92	1.6	0.550

Table 6: Activity concentration enrichment factor of ^{238}U, ^{235}U, ^{226}Ra, ^{210}Pb, ^{228}Ra, ^{232}Th and ^{40}K in Abu-Tartor phosphate ore beneficiation samples (concentrate, > 2mm, magnetic separation, slime, dolomite and clay)

		U-238	U-235	Ra-226	Pb-210	Pb-210(A)	Ra-228	Th-232	K-40
1	Ore	356	14	316	279	396	29	32	46
		Δ %*							
2	Conc.	-16	22	12	-10	-10	12	-1.3	-27
3	2 mm	-45	18	-26	-45	-33	-17	-25	65
4	Mag	-12	110	-2	-28	43	18	43	-62
5	slime	-41	8	-27	-38	-27	15	-9	-15
6	Dol	-81	-60	-77	-77	-66	-40	-47	616
7	Clay	-89		-85	-88	-57	1	93	531

*Δ % = (C –C') x 100/C   C is activity concentration in the sample C'   is activity concentration in ROM ore.

4 Conclusions

Both radium and lead concentrations were decreased in almost all samples (except wet ore sample) that could be explained due to the chemical properties of both elements and the radiological features of P rock and different rejects, Both leachable and total uranium concentrations were increased in wet ore and decreased in other rejects. Concentration of uranium-238 and its decay products tend to be elevated in phosphate deposits of sedimentary origin. Also, uranium concentration increased with increasing P_2O_5 content, Although the concentrations of both ^{232}Th series and ^{40}K in P rock are much lower than that of ^{238}U series. Leachable ^{232}Th concentration was enhanced (+10%) in wet ore while its total concentration did not change, i.e. Th compounds were adsorbed on the wet ore particles surface, Although clay particles have high adsorption affinity due to their large surface area and surface charge, their Th concentration % were not enhanced. While K concentrations were enhanced for clay, dolomite and > 2 mm rejects. That could be explained due to the difference in their solubility during PB and Uranium-238 series and its decay products show decreasing in their concentrations (not more than 40%) in all reject except hand pick-up reject (Clay and dolomite).

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