Distribution and speciation of uranium in Jordan phosphate rocks and their phosphate fertilizer industry

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10/8/2019
1- Introduction

2- Objectives

3- Methods and Techniques

4- Uranium fate during different processing steps

5- Plant availability of U

6- Conclusions
Distribution of potential phosphate deposits
Lithostratigraphical sections of coquina and non-coquina areas (modified after Sofremines, 1984).
Aims of This Study

1- Determining the mode of occurrences of U in EShidiya phosphorites.

2- Determining the redistribution pathway of U during different processing steps (e.g. Crushing and Screening Processes) the beneficiation processes (e.g. Washing and Flotation) the drying processes in all beds A1, A2 and A3 and the fertilizer processes (e.g. DAP).
Aims of This Study

3- Determining the plant available toxic heavy metals like U the might be enter the soil through fertilizers produced from these phosphates.
Flow chart showing the systematic methods of Uranium investigation.

10/8/2019
Plot of the samples locations.
### Mean concentrations of major oxides (%) of phosphate from Eshidiya Mine

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<thead>
<tr>
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<td>P$_2$O$_5$</td>
<td>21.09</td>
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<tr>
<td>CaO</td>
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<td>K$_2$O</td>
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<td>TiO$_2$</td>
<td>0.11</td>
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## Mean concentrations of trace metals (ppm) of phosphate from Eshidiya Mine

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<td>4</td>
<td>3</td>
</tr>
<tr>
<td>Cu</td>
<td>4</td>
<td>5</td>
<td>3</td>
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<td>Cr</td>
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<td>Mn</td>
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<td>Ni</td>
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<td>Th</td>
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</tr>
<tr>
<td>U</td>
<td>33</td>
<td>42</td>
<td>23</td>
</tr>
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<td>V</td>
<td>87</td>
<td>87</td>
<td>63</td>
</tr>
<tr>
<td>Zn</td>
<td>52</td>
<td>61</td>
<td>48</td>
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</table>
## Average chemical analysis of U abundance in Worldwide sedimentary phosphate rocks.

<table>
<thead>
<tr>
<th>Country</th>
<th>Deposits</th>
<th>U</th>
<th>References</th>
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<tbody>
<tr>
<td>Algeria</td>
<td>Djebel Onk</td>
<td>25</td>
<td>IFDC (1997)</td>
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<td>Australia</td>
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<td>China</td>
<td>Kaiyang</td>
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<td>Abu Tartur</td>
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<td>Israel</td>
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<td>65</td>
<td>Abed et al. (2008)</td>
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<td></td>
<td>Shidiya</td>
<td>46</td>
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<tr>
<td>Eshidiya</td>
<td>$A_1$</td>
<td>33</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>$A_2$</td>
<td>42</td>
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<tr>
<td></td>
<td>$A_3$</td>
<td>23</td>
<td>This study</td>
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<tr>
<td>Peru</td>
<td>Sechura</td>
<td>72</td>
<td>IFDC; TVA</td>
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<tr>
<td>Senegal</td>
<td>Taiba</td>
<td>64</td>
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<td>Syria</td>
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<td>Tunisia</td>
<td></td>
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<td>IFDC; TVA, Altschuler (1980)</td>
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<tr>
<td>United State</td>
<td>Central Florida</td>
<td>141</td>
<td>IFDC; TVA</td>
</tr>
<tr>
<td></td>
<td>North Florida</td>
<td>81</td>
<td>IFDC; TVA; Wakefield (1980)</td>
</tr>
<tr>
<td></td>
<td>Idaho</td>
<td>107</td>
<td>IFDC; TVA; Altschuler (1980)</td>
</tr>
<tr>
<td></td>
<td>North Carolina</td>
<td>65</td>
<td>IFDC; TVA</td>
</tr>
</tbody>
</table>
A, B, C Trace element composition of Eshidiya phosphorites beds A1, A2, and A3 respectively compared with shale (after Turekian and Wedepohl 1961). D, E, and F Trace element composition of Eshidiya phosphorites beds A1, A2, and A3 respectively, compared with average global phosphorites (after Altschuler 1980).
Contour maps showing dispersion patterns of U in bed A1
Contour maps showing dispersion patterns of U in bed A2
Contour maps showing dispersion patterns of U in bed A3
### Sampling Scheme and Results for Bed A1

#### Matrix Weighs 1000 Tons

#### Crushing and Screening

- **-12.5 mm (Product)**
  - Soft Ph. Weighs (502.4 tons)
    - **Element** | **in ppm** | **in tons**
    - U | 59 | 0.03

- **+12.5 mm (Reject)**
  - Hard Ph. Weighs (497.6 tons)
    - **Element** | **in ppm** | **in tons**
    - U | 45 | 0.02

#### Beneficiation (Washing)

- **-5+1 mm reject weighs (27.7 tons)**
  - **Element** | **in ppm** | **in tons**
  - U | 61 | 0.002

- **-12.5+5 reject weighs (107.5 tons)**
  - **Element** | **in ppm** | **in tons**
  - U | 19 | 0.002

- **-1+53µ final product weighs (139 tons)**
  - **Element** | **in ppm** | **in tons**
  - U | 80 | 0.01

- **-53µ slime weighs (147.4 tons)**
  - **Element** | **in ppm** | **in tons**
  - U | 38 | 0.006
Sampling Scheme and Results for Bed A2

Matrix weighs 1000 tons

Crushing and Screening

-12.5 mm (Product)

Soft Ph. Weighs 985.4 tons

<table>
<thead>
<tr>
<th>Element</th>
<th>in ppm</th>
<th>in tons</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>54</td>
<td>0.05</td>
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</table>

Hard Ph. weighs 41.6 tons

<table>
<thead>
<tr>
<th>Element</th>
<th>in ppm</th>
<th>in tons</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>42.5</td>
<td>1.02</td>
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</table>

Ph. chert weighs 41.6 tons

<table>
<thead>
<tr>
<th>Element</th>
<th>in ppm</th>
<th>in tons</th>
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<tr>
<td>U</td>
<td>23.6</td>
<td>0.57</td>
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</table>

+12.5 mm (Reject)

+200 # coarse 881.7 tons

<table>
<thead>
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<th>in ppm</th>
<th>in tons</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>45</td>
<td>0.05</td>
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</table>

-200 # fine (dust) weighs 76.7 tons

<table>
<thead>
<tr>
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<th>in ppm</th>
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<tr>
<td>U</td>
<td>50</td>
<td>0.65</td>
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</tbody>
</table>

-4mm product weighs 844.4 tons

<table>
<thead>
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<tr>
<td>U</td>
<td>47</td>
<td>0.06</td>
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+4mm (reject) weighs 37.2 tons

<table>
<thead>
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<th>in tons</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>13.5</td>
<td>0.37</td>
</tr>
</tbody>
</table>
Sampling Scheme and Results for Bed A3

Matrix weighs 1000 tons

Crushing and Screening

-12.5 mm (Product)

+12.5 mm (Reject)

Soft Ph. weighs (615.3 tons)

H. Ph. weighs (234.4 tons)

Ph. Chert weighs (41.6 tons)

Beneficiation (washing and Flotation)

-12.5+2 mm reject weighs (253 tons)

-53# slime weighs (42.3 tons)

-1+0.053mm product (320 tons)

-2+1 mm reject weighs (48.6 tons)

-1+0.50 mm coarse weighs (200 tons)

-0.5+0.053 µm fine weighs (120 tons)

Final Product

Element | in ppm | in tons
---------|--------|--------
U        | 50     | 0.08   

Element | in ppm | in tons
---------|--------|--------
U        | 41     | 0.17   

Element | in ppm | in tons
---------|--------|--------
U        | 24     | 0.58   

Element | in ppm | in tons
---------|--------|--------
U        | 35     | 0.14   

Element | in ppm | in tons
---------|--------|--------
U        | 35     | 0.18   

Element | in ppm | in tons
---------|--------|--------
U        | 35     | 0.14   

Element | in ppm | in tons
---------|--------|--------
U        | 44     | 0.14   

10/8/2019
Matrix weighs 1000 tons

### Feed

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### Grinding

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<td>U</td>
<td>57.5</td>
<td>0.058</td>
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</tbody>
</table>

React with sulphuric acid

### Phosphoric acid 30% weighs (950 tons)

<table>
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<tr>
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<th>in tons</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>44</td>
<td>0.05</td>
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</table>

React with Ammonia (HNO₃)

### Phosphogypsum weighs (3800 tons)

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<th>in tons</th>
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<tbody>
<tr>
<td>U</td>
<td>2</td>
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### Phosphoric acid 54% weighs (560 tons)

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</thead>
<tbody>
<tr>
<td>U</td>
<td>109</td>
<td>0.19</td>
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### DAP Fertilizer weighs (560 tons)

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<tr>
<td>U</td>
<td>126</td>
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Elements fate in bed A₁.

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<th>Beneficiation (Washing)</th>
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<td><strong>Element</strong></td>
<td><strong>Fate</strong></td>
</tr>
<tr>
<td>As</td>
<td>Feed</td>
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<tr>
<td>Cd</td>
<td>Reject</td>
</tr>
<tr>
<td>Cr</td>
<td>Even</td>
</tr>
<tr>
<td>Cu</td>
<td>Feed</td>
</tr>
<tr>
<td>Mn</td>
<td>Feed</td>
</tr>
<tr>
<td>Ni</td>
<td>~ Feed</td>
</tr>
<tr>
<td>Pb</td>
<td>Feed</td>
</tr>
<tr>
<td>U</td>
<td>~ Feed</td>
</tr>
<tr>
<td>V</td>
<td>Even</td>
</tr>
<tr>
<td>Zn</td>
<td>~ Feed</td>
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Elements fate in bed $A_2$.

<table>
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<td>V</td>
<td>Even</td>
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<td>Zn</td>
<td>Even</td>
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</table>
## Elements fate in bed A₃.

<table>
<thead>
<tr>
<th>Element</th>
<th>Crushing and Screening</th>
<th>Beneficiation (Washing and Flotation)</th>
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</thead>
<tbody>
<tr>
<td>As</td>
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<td>Feed</td>
<td>V</td>
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<tr>
<td>Zn</td>
<td>Feed</td>
<td>Zn</td>
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</table>

As fate in bed A₃:
- As: Even
- Cd: Reject
- Cr: Feed
- Cu: Feed
- Mn: Feed
- Ni: Feed
- Pb: Reject
- U: Feed
- V: Feed
- Zn: Feed
## Elements fate in phosphate fertilizer

<table>
<thead>
<tr>
<th>Phosphoric Acid 30% and Gypsum</th>
<th>Phosphoric Acid 54% and DAP</th>
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<tbody>
<tr>
<td><strong>Element</strong></td>
<td><strong>Fate</strong></td>
</tr>
<tr>
<td>As</td>
<td>Gypsum</td>
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<tr>
<td>Cd</td>
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<tr>
<td>V</td>
<td>Acid</td>
</tr>
<tr>
<td>Zn</td>
<td>Acid</td>
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### Leaching experiments from raw phosphate to DAP

<table>
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<th>Leaching agent</th>
<th>Material</th>
<th>P₂O₅</th>
<th>U</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>T %</td>
<td>cx %</td>
</tr>
<tr>
<td>0.1m EDTA pH = 4.5</td>
<td>Raw ph.</td>
<td>25.4</td>
<td>11.5</td>
</tr>
<tr>
<td></td>
<td>DAP</td>
<td>63.2</td>
<td>36.5</td>
</tr>
<tr>
<td></td>
<td>DAP/Raw ph.</td>
<td>2.5</td>
<td>3.2</td>
</tr>
<tr>
<td>1 % Citric acid pH = 2.4</td>
<td>Raw ph.</td>
<td>25.4</td>
<td>11.0</td>
</tr>
<tr>
<td></td>
<td>DAP</td>
<td>63.2</td>
<td>40.3</td>
</tr>
<tr>
<td></td>
<td>DAP/Raw ph.</td>
<td>2.5</td>
<td>3.2</td>
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</table>
Relationship between the total of heavy metals content and their metal extracted using citric acid from phosphate fertilizers.
Correlation coefficients as a measure of the degree of mobility

<table>
<thead>
<tr>
<th>Ranges (r)</th>
<th>Degree of Mobility</th>
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<tbody>
<tr>
<td>0.01-0.30</td>
<td>low mobility (L. M)</td>
</tr>
<tr>
<td>0.30-0.59</td>
<td>Intermediate (I. M)</td>
</tr>
<tr>
<td>0.60-1.00</td>
<td>high mobility (H. M)</td>
</tr>
<tr>
<td>Element</td>
<td>Techniques</td>
</tr>
<tr>
<td>---------</td>
<td>------------</td>
</tr>
<tr>
<td>P&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;</td>
<td>EDTA</td>
</tr>
<tr>
<td>Citric acid</td>
<td>0.99</td>
</tr>
<tr>
<td>Cd</td>
<td>EDTA</td>
</tr>
<tr>
<td>Citric acid</td>
<td>0.98</td>
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<tr>
<td>Zn</td>
<td>EDTA</td>
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<tr>
<td>Citric acid</td>
<td>0.98</td>
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<tr>
<td>Cu</td>
<td>EDTA</td>
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<tr>
<td>Citric acid</td>
<td>0.94</td>
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<tr>
<td>Cr</td>
<td>EDTA</td>
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<tr>
<td>Citric acid</td>
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<tr>
<td>Pb</td>
<td>EDTA</td>
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<td>EDTA</td>
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<td>Citric acid</td>
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</table>

Abbreviation: L.M. = low mobility, H.M. = high mobility and I.M. = intermediate mobility

10/8/2019
CONCLUSIONS
AND
RECOMMENDATIONS
CONCLUSIONS

I

Geochemical findings
III Geochemical findings:

1- Based on the $\text{P}_2\text{O}_5$, CaO and fluorine contents the dominant Eshidiya phosphorite mineral phase is francolite.
CONCLUSIONS

III Geochemical findings:

2- U is accommodated in the francolite mineral phase

3- U is enriched in the raw phosphates when compared with their abundances in shale, while they depleted when compared with average global phosphorites.
II

Redistribution and mobility findings
1. Uranium fates during crushing and screening process of the three phosphatic beds are variable, whereas during beneficiation and drying they exhibit some consistency.
2. U redistribution pathways during the phosphate processing steps were determined in the feed and in the final product. During crushing and screening process, U measured elements got enriched in the feed bed A1 and A3, whereas U got enriched in the reject bed A2. During beneficiation process, most U elements got enriched in the final product of three beds A1, A2 and A3.
3- Uranium (ppm) fate during crushing and screening and beneficiation processes allow drawing the following conclusions:

<table>
<thead>
<tr>
<th>Final product</th>
<th>Hard Phosphate</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>80</td>
</tr>
<tr>
<td>A2</td>
<td>47</td>
</tr>
<tr>
<td>A3</td>
<td>44</td>
</tr>
</tbody>
</table>
4. Uranium redistribution pathways during the phosphate fertilizer processing steps were determined in the feed and in the final product. U measured elements got enriched in the phosphoric acid (30%), phosphoric acid (54%) and DAP product. It was found that 93% of the U is partitioned in the phosphoric acid while the remainder is precipitated with PG waste materials.
5- Uranium (ppm) fate during phosphate fertilizer allow drawing the following conclusions:

<table>
<thead>
<tr>
<th>Product</th>
<th>U (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphoric acid (30%)</td>
<td>44</td>
</tr>
<tr>
<td>Phosphoric acid (54%)</td>
<td>109</td>
</tr>
<tr>
<td>DAP</td>
<td>126</td>
</tr>
<tr>
<td>Phosphogypsum</td>
<td>2</td>
</tr>
</tbody>
</table>
6. The assessment of the availability (mobility) of U elements from DAP to plant through soil using Citric Acid techniques allow drawing the following conclusions:

a- Based on citric acid, U elements with exhibit high mobility in acidic soils (pH ≥ 2.4)

b- The mobility of U elements will decrease strongly in alkaline soils (pH ≥ 7).
7. The assessment of the variability of toxic elements to plants using Citric Acid leaching techniques allowed to show the following conclusion: U is going to be available for plants even in acidic soils, and will be available upon direct application of phosphate to soils as well.
THANK YOU FOR YOUR ATTENTION