Application of leaching tests on phosphogypsum by infiltration-percolation

H. Hassoune, M. Lahhit, A. Khalid and A. Lachehab

ABSTRACT

The phosphoric acid production obtained by attacking phosphate rock by sulphuric acid cogenerates considerable quantities of phosphogypsum. The world cogeneration is estimated about 100–280 Mt per year. In another context of sustainable development, the phosphate chemical industry develops different ways of phosphogypsum valorization, which makes its storage stack in a suitable way for its potential use as an industrial by-product. Although, this storage can cause an environmental impact largely due to the transfer of trace elements (TEs) to groundwater by leaching. It is therefore important to evaluate the impact linked to the storage in order to limit this transfer. The evaluation is usually performed through leaching tests in columns or reactor. In this work, leaching tests were performed in columns by infiltration-percolation on two filter mediums: phosphogypsum and synthetic sandy soils. The results showed that the phosphogypsum is acting as a filter, which retains and releases the TEs. Most of these TEs (Pb, Se, Ag, Zn and Cu) were highly retained in the synthetic soils surfaces and their contents in waters were considerably lower than the maximum contaminant levels (MCLs). Although As, Cd, Cr and Ni were strongly transferred to groundwater, their respective contents were higher than the MCLs.

Key words | groundwater pollution, infiltration-percolation, leaching tests, phosphogypsum, trace elements

INTRODUCTION

Phosphogypsum is an industrial by-product of the phosphate chemical industry. It is cogenerated during the phosphoric acid production with a sulfuric attack of phosphate rock by wet process (Pérez-López et al. 2010; Mousa & Hanna 2013). At present, the worldwide cogeneration of phosphogypsum is estimated about 100–280 Mt/year (Yang et al. 2009). The USA, the former USSR, China, Africa and the Middle East are considered as the main producers of phosphate rock and phosphate fertilizers (Tayibi et al. 2009). The phosphate rock is treated either by dry thermal or wet acid methods to produce phosphoric acid. The dry thermal method generates phosphorus element using an electric arc furnace. In the wet process, the raw phosphate is treated with sulfuric acid and, besides the main product which is phosphoric acid (H₃PO₄), phosphogypsum and small quantity of hydrofluoric acid are also cogenerated (Tayibi et al. 2009). The wet process is illustrated by the following simplified reaction:

\[ \text{Ca}_5\text{F(PO}_4\text{)}_3 + 5\text{H}_2\text{SO}_4 + 10\text{H}_2\text{O} \rightarrow 3\text{H}_3\text{PO}_4 + 5\text{CaSO}_4.2\text{H}_2\text{O} + \text{HF} \]

A general scheme of the processes is shown in Figure 1 (US-EPA 1993).

The wet acid process is widely used to produce phosphoric acid and calcium sulphate, mainly in dehydrate form (CaSO₄.2H₂O). This process is economic, but its disadvantage is the fact that it cogenerates a large amount of phosphogypsum which considerably exceeds the mass of the product where its amount ranges from 4.5 to 5.5 tons for every ton of phosphoric acid (Azabou et al. 2005; Canut et al. 2008). The nature and characteristics of the resulting phosphogypsum are strongly influenced by the phosphate ore composition and quality (Tayibi et al. 2009). Phosphogypsum consists primarily of calcium sulphate with small amount of silica, usually as quartz, and unreacted phosphate rocks. It also consists of toxic metals, namely, arsenic, barium, cadmium, chromium, lead, mercury, selenium and silver (Al-Hwaiti 2005). Tables 1 and 2 show the content of the main components (% weight) and some trace elements (TEs) (ppm) in different phosphogypsum sources.

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The management of phosphogypsum is an environmental problem which concerns several countries, considering the high cogenerated amount and the chemical composition of the by-product (Rutherford et al. 1994). This problem is worldwide since the phosphoric acid production is all around the world (USA, India, Jordan, Turkey, Morocco and Senegal) (Ajam et al. 2009). There are essentially three ways in which phosphogypsum can be disposed of: (i) discharging it into water body, (ii) stacking, or (iii) using it as a raw material for chemical manufacture for agricultural purposes or in construction materials (Kuryatnyk et al. 2008). These ways are constrained in some jurisdictions. For example, in the USA, stacking is the standard procedure, with limited exceptions for some types of phosphogypsum, for use, for example, in peanut farming (Canut et al. 2008). In other jurisdictions, dumping is permitted, mostly into open waters such as the Atlantic Ocean (Othman & Al-Masri 2011). The stacking procedure involves pumping the phosphogypsum slurry to the stacks that may reach several tens of meters in height and several hundred hectares in area. Once the solids settle out, pore water is channelled to a cooling pond where it is eventually recycled to the acidulation process (Murray & Lewis 1988; Luther et al. 1996; Rutherford et al. 1994).

The main environmental impacts related to phosphogypsum storage are: (i) atmospheric contamination resulting from floating particles such as fluoride or other toxic elements around the atmosphere; (ii) groundwater pollution with phosphogypsum cogenerated worldwide is usually disposed of in stockpiles (only 15% of the cogenerated by-product is recycled in agriculture, in gypsum board and cement industries) (Tayibi et al. 2009; El-Didamony et al. 2013).

The phosphogypsum is usually slurried with water and then pumped out of the fertilizer industrial plant to nearby settling/disposal area, using a system of pipes (Cádenas-Escudero et al. 2011). The stacking procedure involves pumping the phosphogypsum slurry to the stacks that may reach several tens of meters in height and several hundred hectares in area. Once the solids settle out, pore water is channelled to a cooling pond where it is eventually recycled to the acidulation process (Murray & Lewis 1985; Luther et al. 1993; Rutherford et al. 1995).

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**Figure 1** | Scheme of the phosphate processes.

**Table 1** | Major element composition (% weight) for different phosphogypsum sources

<table>
<thead>
<tr>
<th>Compounds</th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>SO₃</th>
<th>Na₂O</th>
<th>P₂O₅</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Morocco (Sebbahi et al. 1997)</td>
<td>30.50</td>
<td>9.50</td>
<td>2.80</td>
<td>0.90</td>
<td>0.30</td>
<td>42.90</td>
<td>–</td>
<td>0.50</td>
<td>0.15</td>
</tr>
<tr>
<td>Algeria (Kacimi et al. 2006)</td>
<td>31.18</td>
<td>0.88</td>
<td>0.10</td>
<td>0.03</td>
<td>0.06</td>
<td>40.90</td>
<td>1.32</td>
<td>0.87</td>
<td>1.20</td>
</tr>
<tr>
<td>Egypt (Taher 2007)</td>
<td>32.13</td>
<td>8.78</td>
<td>0.29</td>
<td>0.35</td>
<td>0.09</td>
<td>37.60</td>
<td>–</td>
<td>1.82</td>
<td>0.80</td>
</tr>
<tr>
<td>India (Singh &amp; Garg 2005)</td>
<td>31.09</td>
<td>0.29</td>
<td>0.54</td>
<td>–</td>
<td>1.31</td>
<td>43.21</td>
<td>0.29</td>
<td>0.47</td>
<td>0.86</td>
</tr>
<tr>
<td>Turkey (Degirmenci et al. 2007)</td>
<td>32.04</td>
<td>3.44</td>
<td>0.88</td>
<td>0.32</td>
<td>–</td>
<td>44.67</td>
<td>0.13</td>
<td>0.50</td>
<td>0.79</td>
</tr>
<tr>
<td>China (Shen et al. 2007)</td>
<td>30.79</td>
<td>1.88</td>
<td>2.10</td>
<td>–</td>
<td>0.80</td>
<td>42.56</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Tunisia (Rutherford et al. 1994)</td>
<td>31–32</td>
<td>–</td>
<td>0.10</td>
<td>0.10</td>
<td>0.40</td>
<td>46.00</td>
<td>0.30</td>
<td>1.20</td>
<td>1.20</td>
</tr>
<tr>
<td>USA (Ajam et al. 2009)</td>
<td>25–31</td>
<td>3–18</td>
<td>0.1–0.3</td>
<td>0.20</td>
<td>–</td>
<td>55–58</td>
<td>–</td>
<td>0.5–4.0</td>
<td>–</td>
</tr>
</tbody>
</table>
mobile anions, acidity, TEs; (iii) soil contamination (Rutherford et al. 1994). Several studies have investigated groundwater pollution or the potential leachability of phosphogypsum components (Rutherford et al. 1994). In landfills for the by-product disposal, a large volume of the leachates is generated by the residual process water and by the rainfall percolation through the solid material (Battistoni et al. 2006). The percolation of these leachates through subsurface soils at the phosphogypsum disposal sites constitutes a potential source of surface and groundwater contamination (Rutherford et al. 1995; Lokshin et al. 2013). The physicochemical risks related to the land-surface disposal are easy to identify, but rather more difficult to evaluate. This is mainly due to the solubility of calcium sulphate and of several minor and trace components such as fluorides, phosphates and TEs. Convective transport of these components by percolating rainwater will seriously contaminate any groundwater liable to be reached by them (Van der Heijde et al. 1990; Battistoni et al. 2006).

### METHODS

As shown in Figure 2, the leaching tests of phosphogypsum by infiltration-percolation were performed on two cylindrical columns. The first column (4) used is transparent glass of 9.8 cm in diameter and 53.5 cm in height. It was filled with a filter medium 1 (5) consisting of a mass of phosphogypsum. The glass beads were deposited on phosphogypsum surface so as to improve the flow distribution at the inlet of the column. The second column (6) used is transparent polypropylene of 10.9 cm in diameter and 40.4 cm in height. It was filled with a filter medium 2 (9) that consists of two different synthetic sandy soils (anthracite sand and sea sand) deposited on a layer of gravel used as a leachate drainage system. This column is equipped with a scour protection system deposited on the surface of the filter medium 2 in order to limit the migration of fine particles. The leachate 2 was recovered by collecting tank (11).

#### Reagents and raw materials

Samples of phosphogypsum were collected from phosphoric filter rotary separating acid phosphogypsum. The synthetic soils consist of sand layers (anthracite and sea sand) and gravel. Sand was washed for the removal of suspended solids, while the gravel was crushed to obtain desired particle sizes (5/6.7 mm and 3.15/5 mm).

#### Standard leaching test

The phosphogypsum sample was introduced into the first column by layers of 2 to 3 cm, which was statically compacted with a pestle. The distilled water used as the leaching agent was injected into the column by using a peristaltic pump which maintains a constant flow. The leachate 1 was generated downstream the filter medium 1 resulting from the contact between phosphogypsum and the leachant agent. Then, the sand was placed in the second column. The corresponding bed height was about 20 cm. It was introduced by layers of 4 to 6 cm. The assembly was water soaked without disturbing the surface, avoiding segregation between grains of different sizes. After infiltration-percolation of the leachate 1 through the synthetic soil, the leachate 2 was recovered downstream the synthetic soil, the leachate 2 was recovered downstream the filter medium 2.

#### RESULTS AND DISCUSSION

Phosphogypsum waste was continuously rinsed by rainwater during winter. The range of rain pH was generally neutral to slightly acid. This rainwater causes the transfer of TEs from the stored phosphogypsum to groundwater by dissolution (Al-Masri et al. 2004). This work was conducted...
to evaluate the TEs quantity dissolved by rainwater using column leaching tests with distilled water as leaching agent. The contents of TEs dissolved in the leachates (Pb, Se, Cd, Cr, Ni, As, Zn, Cu and Ag) of both phosphogypsum and synthetic sandy soils were determined by Inductively Coupled Plasma Mass Spectrometer (ICP-MS) (ISO 11885:1996). The elements were selected based on their concentrations and on their environmental sensitivity. The volume of distilled water used was always 1 liter at each leaching test experiment.

**Column leaching tests**

**Leaching of TEs from different heights of phosphogypsum**

Three leaching experiments were investigated with three different heights of phosphogypsum (H₁, H₂ and H₃). The height 1 (H₁ = 15 cm) was attributed to the first phosphogypsum mass used in the first leaching test. The height 2 (H₂ = 50 cm) was used in the second leaching test. It was attributed to the sum of the first mass previously leached and a new mass deposited on this latter (H₁ + 15 cm), while the height 3 (H₃ = 45) which was used in the third leaching test, was attributed to the sum of the first two phosphogypsum masses previously leached and a new mass deposited on these latters (H₁ + H₂ + 15 cm). Figure 3 shows the effect of phosphogypsum height on the TEs quantity dissolved during leaching experiments.

At the height 1, the contents of Cd and Cr were strongly transferred to the phosphogypsum leachate compared to their contents in the leachate at the height 2. They ranged from 1.558 to 0.397 ppm for Cd and 0.539 to 0.111 ppm for Cr. At height 3, the TEs contents were found to be increased in the phosphogypsum leachate. They ranged from 0.397 to 1.155 ppm for Cd and 0.111 to 0.408 ppm for Cr. However, As, Ba, Pb and Se possessed slightly high contents at the height 1 compared to the height 2, their contents were found slightly increased in the leachate at the height 3. The increase and the decrease of the TEs quantity in the leachate, proved that the phosphogypsum released TEs by dissolution during the first leaching experiment with the height 1, which means that the phosphogypsum
was prepared to retain in its empty seats the TEs dissolved from the new phosphogypsum mass during the second leaching experiment with the height 2.

**Consecutive leaching experiments of TEs from phosphogypsum**

The TEs quantity dissolved by rainwater can be evaluated using consecutive leaching experiments, which consists of carrying out a defined number of leaching experiments (Nth leaching) on the same sample of phosphogypsum. In the present study, a fixed height of phosphogypsum (H = 15 cm) was subjected to four consecutive leaching tests, giving rise to four extracts of leachates (L1, L1’, L1” and L1’’) as function to the volume of the leaching agent (1 L of the leaching agent for each leaching test). The results of the consecutive leaching effect on the TEs quantity dissolved are shown in Figure 4. The pH value of the four leachates resulted from consecutive leaching were analyzed (Table 3).

According to the results, the contents of all TEs decreased in the second leaching and stabilized in the fourth leaching for As, Cd, Cr, Ag, Pb and Ba in a range varying from 0 to 0.014 ppm. This is due the fact that phosphogypsum has reached its maximum capacity of the release of TEs during the four consecutive leaching by distilled water.
The pH value of the leachates increased as a function to the consecutive leaching tests applied on a fixed height of phosphogypsum. This can be explained by the neutralization of phosphogypsum during the washing process by distilled water.

**Phosphogypsum compaction effect on leaching behavior**

To study the effect of compaction on the quantity release of TEs, two representative materials were used for leaching tests: compacted and uncompacted phosphogypsum. Figure 5 shows the results of the compaction effect on leaching behavior.

![Figure 5](image_url)

**Table 3** | The effect of consecutive leaching on the pH of phosphogypsum leachates

<table>
<thead>
<tr>
<th>Leachate</th>
<th>L₁</th>
<th>L’₁</th>
<th>L”₁</th>
<th>L’’₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>1.85</td>
<td>2.00</td>
<td>2.10</td>
<td>2.30</td>
</tr>
</tbody>
</table>

A comparison of the leaching data related to the TEs quantity revealed similar results for both studied materials, except for the case of Cd (less than 5% variance). According to the results, compaction condition had no significant effect on the leaching behavior of phosphogypsum.

**Columns infiltration-percolation tests**

Dynamic leaching tests is the process by which the leaching medium is continuously fed to a column containing the tested waste, simulating the leaching behavior of the waste material in short, medium and long term release close to real environmental conditions (Tsiridis et al. 2015). Because the exact reproduction of real scenarios is extremely expensive, laboratory tests were performed in conditions that closely mimicked the actual situation. In this experiment, a distilled water infiltrated through both filter mediums (phosphogypsum and synthetic sandy soils) which gave rise to two different leachates (L₁ and L₂), respectively. Tables 4 and 5 describe the input and output of TEs quantity dissolved in both leachates through two sand natures (anthracite and sea sand, respectively). The quantities of pollutants dissolved in both leachates were measured and the values of the output leachate (L₂) were compared with maximum contaminant levels (MCLs). The pH values of the leachates are shown in Table 6.

The results showed that phosphogypsum leachate has a low pH value (pH < 2). This acidity is resulted from residual acids contained in phosphogypsum pores after acidulation and filtration (sulfuric, phosphoric and fluoridric acids). The pH value of the output leachate (L₂) increased during infiltration-percolation test. This is due to the fact that acidic seepage waters may be buffered by alkaline components of the synthetic sandy soils.

The results showed high retention of Cd, Cr, Pb, Se and Cu in the sea sand surfaces (% retention > 50%) compared to the anthracite sand, but the quantities of some TEs (Cd and Cr) in the leachate 2 were extremely high compared to MCLs. However, contents of Pb and Se were always under the MCLs. The

![Table 4](image_url)

<table>
<thead>
<tr>
<th>TE (mg/L)</th>
<th>As</th>
<th>Cd</th>
<th>Cr</th>
<th>Pb</th>
<th>Se</th>
<th>Ag</th>
<th>Zn</th>
<th>Cu</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leachate 1</td>
<td>0.074</td>
<td>1.558</td>
<td>0.539</td>
<td>0.021</td>
<td>0.017</td>
<td>0.005</td>
<td>1.143</td>
<td>0.496</td>
<td>0.125</td>
</tr>
<tr>
<td>Leachate 2</td>
<td>0.062</td>
<td>1.285</td>
<td>0.415</td>
<td>0.019</td>
<td>0.010</td>
<td>–</td>
<td>0.931</td>
<td>0.400</td>
<td>0.018</td>
</tr>
<tr>
<td>Retention (%)</td>
<td>16.216</td>
<td>17.522</td>
<td>23.005</td>
<td>9.524</td>
<td>41.176</td>
<td>100.000</td>
<td>18.548</td>
<td>19.355</td>
<td>85.600</td>
</tr>
<tr>
<td>MCLs for drinking water quality</td>
<td>0.050</td>
<td>0.005</td>
<td>0.050</td>
<td>0.050</td>
<td>0.010</td>
<td>0.010</td>
<td>5.000</td>
<td>1.000</td>
<td>0.050</td>
</tr>
</tbody>
</table>
element of Ni was highly retained in the anthracite sand surfaces (85.6%), but its content in the leachate 2 exceeded significantly MCLs. Both synthetic sandy soils retained almost totally the element of Ag due to its very low content in the input leachate (0.005 mg kg⁻¹). The most important factor influencing TEs is soil reaction. If pH value is low, TEs like Cd, Cr, Pb, Zn, and Ni have maximum mobility (Barančíková et al. 2013). For example, the potential transfer of Cd to the leachate 2 was due to its high mobility in soil acid conditions and the absence of organic matter which has a strong affinity to Cd. The high retention of Pb, Zn and Cu in the sea sand surfaces was due to their sorption into mineral soil phases (Kassir et al. 2012).

CONCLUSIONS

The storage of phosphogypsum has a negative impact on the environment by air, soil and water. Air pollution results from the fly-off of toxic dust during dry periods. Soil contamination is primarily due to TEs accumulation phenomenon by sorption mechanisms with components of the soil, while water contamination is due to the TEs transfer phenomenon into groundwater by leaching. In this work, we are particularly focused on the impact related to the transfer of TEs to groundwater by leaching tests of phosphogypsum. These tests were carried out by infiltration-percolation of the leach solution on two filter mediums: phosphogypsum and the synthetic sandy soils (anthracite sand, sea sand). The effects of the operational parameters on phosphogypsum leaching by infiltration-percolation were investigated to determine on one hand, the phosphogypsum behavior during leaching by infiltration-percolation and, on the other hand, the potential of transfer of TEs to the leachate 2 through the synthetic sandy soils. Based on the results of the experimental tests, the following conclusions could be drawn:

1. The increase and decrease of TEs quantity in the leachate 1 during the variation of the height parameter show that the phosphogypsum is acting as a filter, which can both retain and release TEs during leaching by infiltration-percolation.

2. The increase of pH value of the leachate 1 as a function to the continuous leaching can be explained by the neutralization of phosphogypsum during washing process by distilled water.

3. The compaction condition of phosphogypsum had no significant effect on the leaching behavior of phosphogypsum.

4. The increase of pH value of the leachate 2 during infiltration-percolation through the synthetic sandy soils is due to the fact that acidic seepage waters may be buffered by alkaline components of the synthetic sandy soils.

5. Pb, Se, Ag, Zn and Cu were highly retained in synthetic sandy soils and their contents in the leachate 2 were largely lower than the MCLs. Although As, Cd, Cr and Ni were strongly transferred to the leachate 2, their respective contents were higher than the MCLs.

Therefore, further studies are needed to evaluate potential effects on health from groundwater containing TEs. Furthermore, research on the soil quality should be conducted to reduce the mobility of such toxic elements in soil by several processes of natural attenuation during infiltration of phosphogypsum leachates through the soil.

REFERENCES


