

Characterization and pH Dependent Leaching Behavior of Tunisian Phosphogypsum

Raja Zmemla^{a*}, Perrine Chaurand^b, Mounir Benjdidia^c, Boubaker Elleuch^d,
Jean Yves Bottero^e

^{a,c,d}*National Engineering School of Sfax, Laboratory Water, Energy and Environment L3E, Route de Soukra
Km4.5 BP W, 3038 Sfax, Tunisia*

^{b,e}*CEREGE, UMR 6635 CNRS Aix-Marseille University, 13545 Aix-En-Provence, France*

^a*Email: zmemla@yahoo.fr*

Abstract

The current study aims to characterize and as well as to investigate the leaching behavior of Tunisian Phosphogypsum (PG). The results of the physical characterization studies showed that, as worldwide Phosphogypsum, the Tunisian PG behaves like fine silty sand with important initial water content. Relevant attention was given to the leaching behavior of the sample which was subjected to two leaching tests according EN 12457-2 (2002) at liquid to solid ratios (L/S) of 10 and 100 as well as pH stat leaching test according to the CEN/TS 14997 (2006). The progressive release of major elements as well as the metals indicates high mobility of the most analysis elements. Calcium, sulfate and phosphorus were the major elements having the highest leaching concentrations. Broadly, mobility of trace metals in PG was classified into three degrees: elements with high mobility were Sr, Zn, those with moderate mobility were As, Ba, Cd and Cr and those with low mobility were Cu, Ni, Pb, Se, V, Y and Zr. The highest concentrations of the most part of the metals were obtained from L/S 100. Based on the pH dependent leaching experiments, results show that the PG has a maximum susceptibility to leaching out metals when exposed to a strongly acidic condition (2-4). While, alkaline condition appears to be the most stable for the analyzed material. This paper offers a data base which is useful when later recycling actions are taken. Indeed, acidic conditions should be avoided in order to prevent metal leaching from PG.

Keywords: Phosphogypsum; Heavy metals; Leaching behavior; characterization; Batch leaching test.

* Corresponding author.

1. Introduction

Phosphogypsum (PG) is an industrial solid by-product formed during the production of phosphate fertilizers. It is produced by chemical processing called « wet process », when phosphate ores apatite (mainly as Fluorapatite $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$) is reacted with sulfuric acid (H_2SO_4) [1-3]. The wet process generates a large amount of PG which is filtered off and pumped as slurry to nearby ponds [4]. PG is composed mainly of calcium sulfate dehydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and partially contains impurities, as well as many trace elements, heavy metals, rare earths elements and naturally occurring radioactive materials [5-7]. Actually the worldwide production of PG is estimated to be around 280 million tons per year [8]. Only 14% of the worldwide production is reprocessed, while 28% is dumped into water bodies and 58% is being stockpiled [9]. Tunisia is the fifth important phosphate producer in the world. Five phosphate industries are responsible for the annual production of 10 million tons of Phosphogypsum [10], which is stored in stacks near the factories. A PG stockpile occupies so large land areas that cause severe pollution to the surrounding environment; in Sfax (containing 30MT of PG which occupy approx. 48 Ha up 50 meters in height) and Skhira (40 MT of PG covering approx. 112 Ha up 60 meters in height). This is a large volume which is expected to be increased in the event of exploitation of the new layers of « Sra Ouertana » in the future [11].

The management of these large quantities, which have been continuously generated, is one of the most serious problems in many countries, as well as in Tunisia. Several studies have been recommended to use Phosphogypsum as building materials [12], agricultural fertilizers [13] and as an amendment to the soil [14]. However, only a few of them were put into practice due to the absence of information about long term behavior of PG, indeed The leaching potential of Tunisian PG has received little attention. A useful tool for investigative waste and assessing the environmental soundness of the waste PH stat leaching test can be used to predict the mobility of major and trace elements in waste samples in a wide pH range [15-17].

The aim of this study is to evaluate the behavior of heavy metals present in Tunisian PG; indeed less research has been published regarding the leaching behavior of Tunisian PG and mobility of these elements. It is within this context that the present study has been undertaken aiming both at the characterization of Tunisian PG and the determination of its heavy and major leaching behavior. The main objective of this work is to gain basic information about distribution of heavy metals and its leachability as a first step previous to modulate its behavior. Physical, chemical, mineralogical, and leachable characteristics are determined in order to draw up an accomplished synopsis of studied PG. In the first section, materials and performed experimental protocol are described; then the physical characteristics and the results of leaching test are presented and analyzed according to literature.

2. Materials and methods

2.1. Material

PG sample was collected from a phosphoric Tunisian plant: Industrial society of phosphoric acid and fertilizers of Skhira, situated in the Gulf of Gabes in south-eastern Tunisia ($34^{\circ}20'50''\text{N}$; $10^{\circ}08'50''\text{E}$) as shown in Figure 1. Around 20 kg of PG were collected from each sampling point. Later on, material is homogenized and

stored in plastic bags.

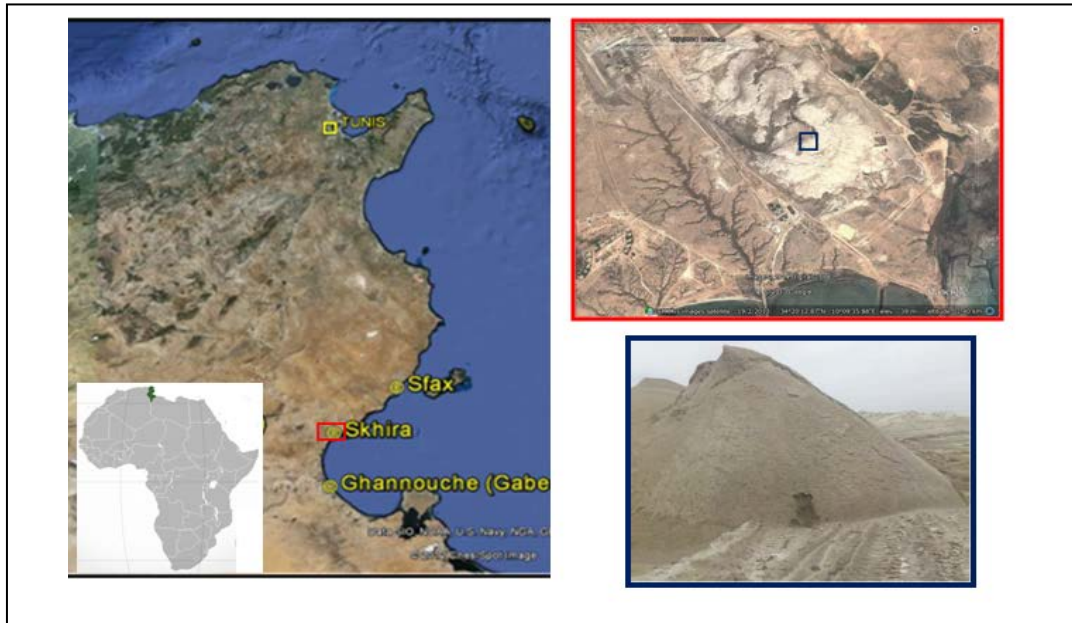


Figure 2: Location of the PG pile, with sampling point indicated

2.2. Experimental program

- Physical characterization

Physical characterization of Tunisian PG includes the determination of classical soil properties as water content NF P94-050, grain size distribution using the dry sieving method NF P94-056, bulk density NF P94-060, real density NF P94-061. To add more information, particle size analysis was determined also by laser granulometry in wet suspensions with water saturated of gypsum NF ISO13320-1. Furthermore, morphology and microstructures of PG were performed by scanning electron Microscopy, SEM (SU 8010 Hitachi) at 30 kV.

- Chemical and mineralogical characterization

The chemical composition of PG major and trace elements was determined by ICP-AES (Jobin-Yvon Horiba Ultima-C2000), after either acid digestion by HNO₃ and H₂O₂, alkaline hydrolysis by LiBO₂ or microwave assisted digestion in HF/HNO₃/HCL. The major mineral phases of the PG were identified using X ray powder method with bruker diffractometer (X'Pert Pro MPD Panalytical) with Co K α radiation (λ 1.79 Å) and running at 35 kV and 40 mA, the total counting time during XRD measurements was 10h . The international Center of diffraction Data PDF-2 database and the X'Pert High score plus software Panalytical were used to identify the mineral phases from the obtained X- ray diffraction XRD patterns.

- Leaching procedure and conditions

PG was subjected to a pH static experiment according to European standard CEN/TS 14997 (2006) [18].The pH

dependence leaching test with continuous pH control can be useful for simulating different scenarios including in particular the worst-case scenarios. The pH-static experiments were conducted under ambient conditions for 48 h at a liquid-to-solid (L/S) ratio of 10. Values were selected within the wide pH range from 3 to 11 (3, 4, 5, 6, 8, 9, 10, and 11); including experiment under natural pH (i. e., without addition). The leachants were prepared by adding sodium hydroxide (NaOH) solution to deionized water. In addition, a 24-h leaching test in deionised water at a L/S ratio of 10 and 100 according to European standard EN 12457-2 (2002) [19] was performed to assess the hazardous properties of the studied PG according to EU legislation (EU, 1999; EU, 2003) [20]. All the experiments were performed in duplicate.

3. Results and discussion

3.1. Physical characterization

The basic data of Physical properties of PG are summarized in Table 1. Results allow to conclude that the PG was characterized by a high water content (6.5%) higher than natural gypsum (approx 1-2%). The bulk (apparent) density was 0.85 g/cm³. The absolute (real) density of PG is in the same range and comparable to that of natural gypsum (2.3 g/cm³), the real density is a parameter that depends mainly on the mineralogical composition of the material. Based on the results, it can be concluded that PG is a light material compared to natural sand (approx 2.6g/cm³); also it is characterized by high initial water content. These results are similar to those reported in other studies [21].

Table 1: Physical properties of Phosphogypsum

Water content (%)	6.5
Bulk density (g/cm ³)	0.85
Real density (g/cm ³)	2.33
Particle size D<80µm	65
Laser distribution D50 µm	40-250

The main granulometric results obtained are compiled also in Table 1. It is clear that PG was composed of a very fine material. Indeed 65 % of a PG fraction under 80µm. Laser granulometric was used to better understand the particular distribution of PG.

Figure 2 shows the percentage of particles size of PG sample, by volume, the granulometric curve of PG denotes t two populations of the particles with large size range; the first population has a significant particle number of around 40µm of diameter, is the greatest fraction, the second population has a particle number above 400µm. The grain size distribution of the samples was found to be very similar and consistent with the data in the literature [22].

Microstructural of samples was shown in Figure3. PG particles are regular in form and small in size, which confirms the results obtained by the laser granulometry analysis. PG has a clear crystalline structure, a crystals

exhibited shapes in the form of a tabular structure associated with crystals in needle. The morphology of PG is characterized by the abundance of needle crystals, which illustrates the fact that PG is submitted to several physical processes of erosion and dissolution [23].

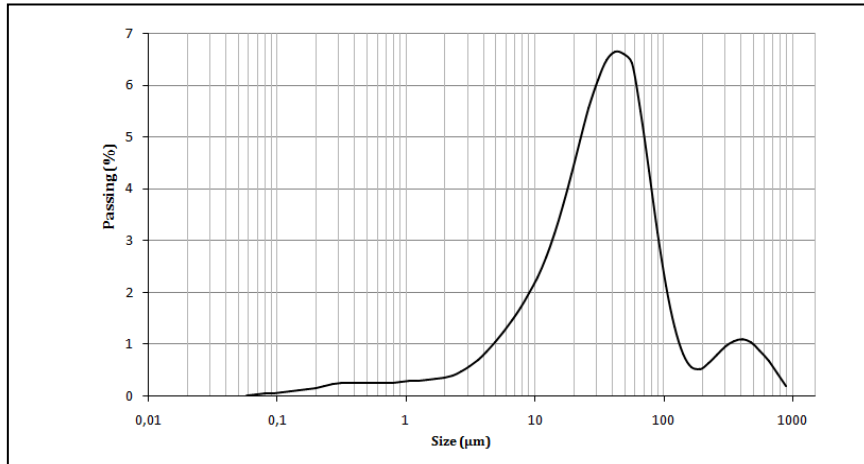


Figure 2: Particle- size distribution of PG

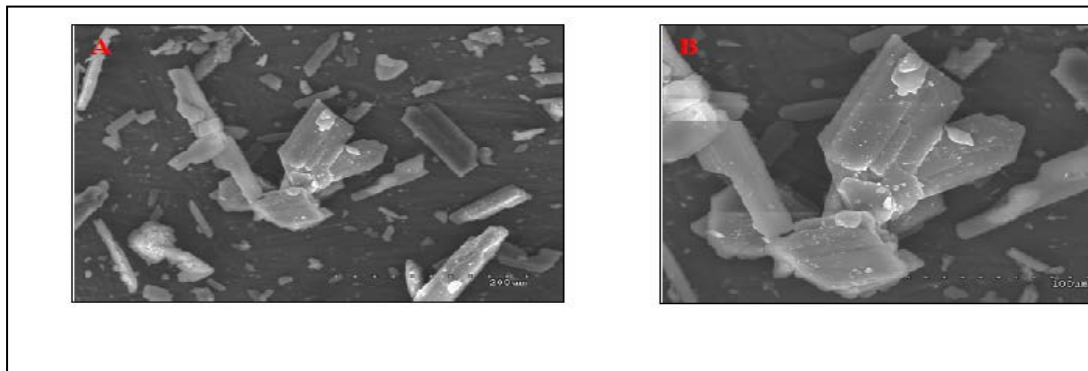


Figure 3: SEM images of PG sample (A: x250; B: X500)

3.2. Chemical and Mineralogical composition

- Major and trace elements distribution

Chemical composition of the PG is shown in Table 2. This provides also a comparison of those components in PG (max-min) from literature [24]. Data on the major content as oxides indicate that PG is mainly composed of CaO and SO₃, indeed their mass is approximately close to 80% of the total weight. There is also appreciated quantity of SiO₂, P₂O₅ and Al₂O₃ and a lesser extent of Fe₂O₃, K₂O, MgO and TiO₂. Compared to literature values, major elements were present the same order of concentrations of other PG reported in the literature. Analyses also show a higher content of organic material (19.691%) by the weight. Concerning the trace elements (expressed in ppm), results show that the most abundant concentrations in the PG are: Sr, Cs, Zn, Cu, Y, Ni, Ba, As and Cd, in order of abundance. The lowest concentration values observed were for Cr, Pb, Zr, V, Se and Hg. The amount of the selected elements has a similar concentration to those reported by authors in PG

obtained from sedimentary phosphate rock, except the concentrations of Zn and Sr, which exceeded maximum concentrations reported in the literature ranges.

Table 2: Major and trace element concentrations in PG sample

		Literature	Trace elements	Literature
Free water (%)	12.19	-	As	21
Organic material MO (%)	19.691	-	Ba	29.33
Loss on ignition (LOI-MO) (%)	1.158	-	Cd	12.23
Major elements			Cr	6.12
Al ₂ O ₃	0.649	0.05-0.60	Cs	186.56
CaO	38.785	27.8-34	Cu	69.08
Fe ₂ O ₃	0.05	0.01-0.25	Hg	0.03
K ₂ O	0.02	-	Ni	34.82
MgO	0.01	0.01-0.54	Pb	6.67
MnO	<LD	-	Se	4.95
Na ₂ O	0.686	0.12-10	Sr	1485
P ₂ O ₅	1.245	0.05-1.42	V	2.44
SiO ₂	2.31	0.5-6	Y	64.98
TiO ₂	0.030	26-470	Zn	123.2
SO ₃	41.738	39.6-47.1	Zr	5.67

• . Mineralogical characterization

The X- ray diffraction pattern of PG samples are presented in Figure 4. The diffraction lines are attributed to the calcium sulfate dihydrate (CaSO₄ 2H₂O) that represents the dominant phase. Secondary crystalline phases are also detected, which are Brushite (CaHPO₄.2H₂O) and Quartz (SiO₂); such composition is in good consistence with its major chemical constituents as reported in Table 2. Obtained results are also coherent with previous studies [25].

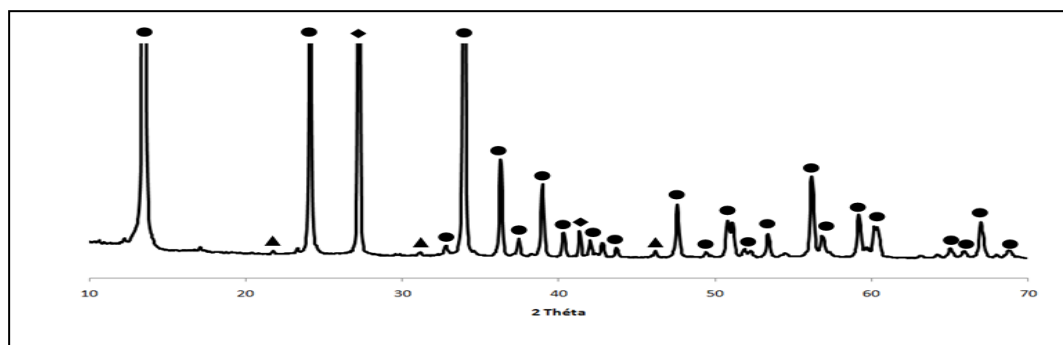


Figure 4: XRD patterns of PG (Gypsum ● Brushite ◆ Quartz ▲)

3.3. Leaching behavior

- Batch leaching test : Effect of L/S ratio

The leaching behavior of Tunisian PG was conducted under strong acidic condition of the natural pH range between 2.3 and 2.5 for L/S 10 and L/S 100, respectively. A strong acid condition is due to the presence of free acid such H₂SO₄, HF, H₃PO₄ and H₂SiF₆. Obtained results were expressed in terms of the cumulative mass released (mg/kg) as well as in terms of the total fraction release (TFR %). Further, the leachate concentrations of the parameters of environmental concern were compared to the requirements of the EU landfill directive of wastes, where criteria for wastes intended for landfill are given.

As can be noted from Table 3, the amount of the major elements (Si, P, S, Mg, Ca, and K) released highly under liquid to solid ratio L/S 100, except the following elements (Al, Fe and Ti) which seems to be limited. Based on the values of the cumulative mass released, results show that the following elements (Ca, P, S, and Si) leached out higher than other elements.

Table 3: Release of major elements

	L/S 10		L/S 100	
	C (mg/kg)	TFR%	C (mg/kg)	TFR%
Al	5.64	0.07	46.5	0.7
Ca	5764	1.48	57817.13	14.9
Fe	91.6	11.4	16.29	3.25
K	34.39	17.8	28.10	14.05
Mg	49.3	16.3	70.24	70.5
P	410.72	3.29	1074.16	41.3
S	7286.93	1.74	61265.71	14.67
Si	3336.15	14.4	3395.12	14.69
Ti	0.53	0.17	1.6	0.5

Concerning trace elements, the results are given in Table 4. Heavy metals contained in PG were greatly released in a considerable content. Concentrations of amount of elements were dependent on L/S ratio, when the L/S ratio was increased, the heavy metal concentrations increased as well; indicating that they leached easily from PG. In fact, in the batch leaching test, PG and water contacted completely and friction between solid particles and solid-water particles accelerated the dissolubility of the element contents.

Cd, Sr and Zn have the highest concentration values which released from the PG sample than other elements. Based on leaching results under L/S100 ratio , concentrations of trace elements in leach solutions can be broadly grouped into two categories: the first one is composed of (Cu, Ni) which FTR% was below to 10%, the second

category is composed of the following elements (As, Ba, Cr, Cd, Se, Sr, and Zn) which FTR % up to 20%.

Results are also expressed in terms of the cumulative mass release values (mg/kg); shows that Sr (582.13 mg/kg) and Zn (58.39mg/kg), Cd (5.3 mg/kg) and Cr (9.4 mg/kg) have high concentrations.

The results show that releases of these trace elements were all exceeded the non hazardous material limit value, that's why it should be carefully monitored.

Results also show that the leaching of Zn was independent of the L/S ratio at high value, indeed, a high initial leaching at both low (51.4 mg/kg) and high (58.39 mg/kg) L/S ratio.

Generally, the cumulative release concentrations of all elements increase by L/S ratio increasing, indicating that metals would possibly leach in greater amounts if exposed for longer durations.

Indeed, the higher L/S ratio corresponded to longer durations and replicated conditions to observe long term leaching behavior of trace elements. Concentrations increased continuously with L/S ratio, which is a typical behavior of dissolution of the solid phase under acidic conditions which indicated that surface dissolution of the metals is still the prevailing mechanism for leaching [26]

Table 4: Release of trace elements

	L/S 10		L/S 100		Criteria EU landfill		
	C (mg/kg)	TFR%	C (mg/kg)	TFR%	Inert	Nn Haz	Haz
As	2.8	13.3	5.3	19.8	0.5	2	25
Ba	12.7	43.3	16.1	53.9	20	100	300
Cd	1.29	5.23	5.3	43.3	0.04	1	5
Cr	3.12	17.33	9.4	23.64	0.5	10	70
Cu	2.5	0.5	3.18	7.18	2	50	100
Ni	1.3	2.26	2.23	9.27	0.4	10	40
Pb	0.69	10.3	1.57	23.55	0.5	10	50
Se	0.9	20.5	1.42	32.17	0.1	0.5	7
Sr	114	7.7	582.13	39.2	-	-	-
Zn	51.4	41.8	58.39	47.47	4	50	200

- Solid residue analyses

Solid residue was dried and then analyzed by SEM/DRX to detect morphological alterations, and to make a qualitative comparison of the effects caused by water erosion.

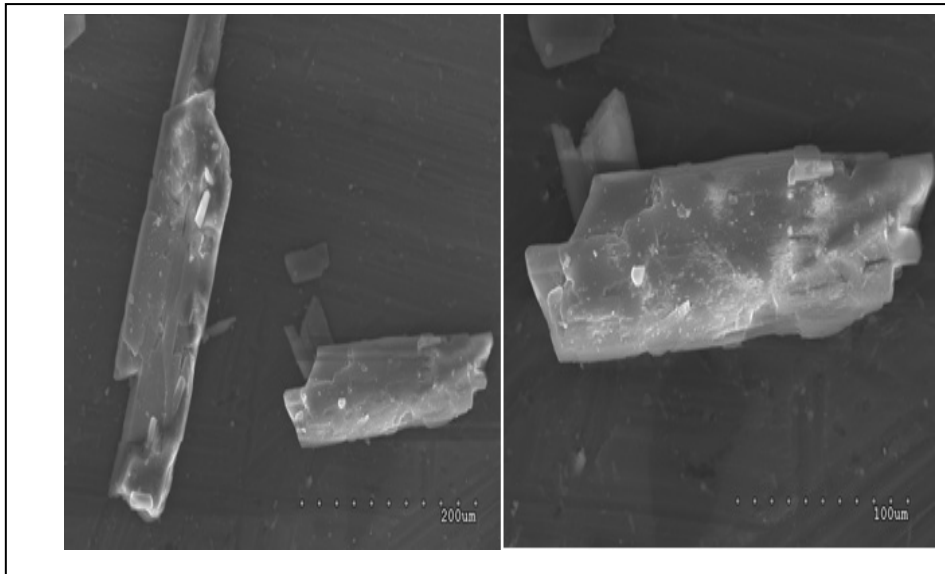


Figure 5: SEM images of PG after leaching tests

Figure.5 shows morphologies of PG after leaching; it can be seen that the same microstructure of the particles which is tabular form. However, the surface particles of PG were almost alliterated after leaching; this is a result of water erosion of the particles and the chemical dissolution of the elements. As evident from Figure 6, the same main mineral phases were identified in the PG sample also found in leached sample. A mineralogical stability of PG was observed after the leaching test. It is clear that strong peaks of the sample remained stable after leaching.

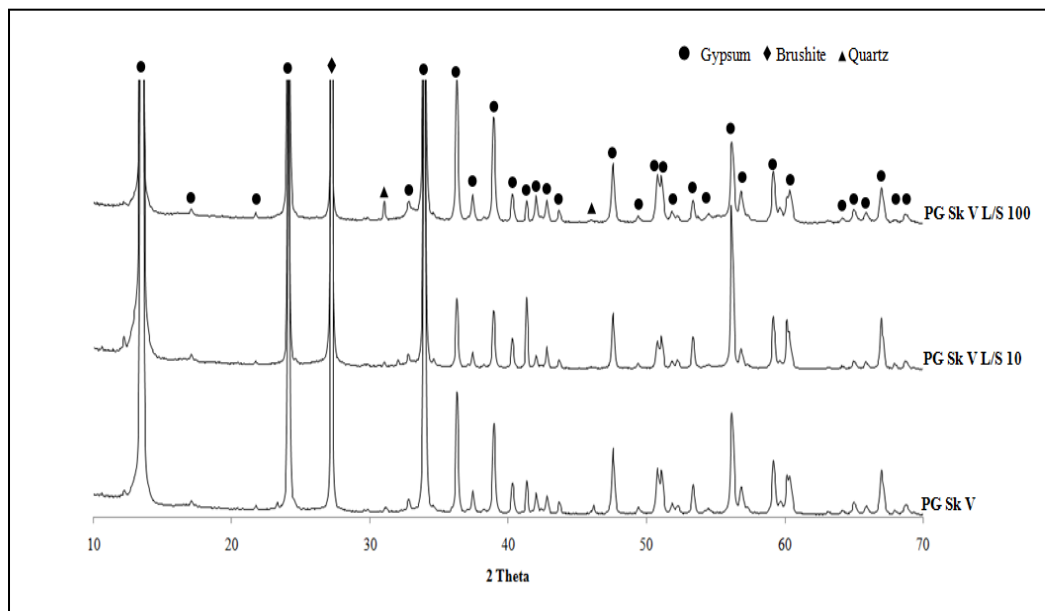


Figure 6: XRD patterns of leached residue

- Effect of pH

The pH dependent leaching tests were further conducted to reproduce different environmental conditions which affect the leaching behavior of trace metals from PG. Indeed, pH is one of the main parameters that determine heavy metal mobility in materials.

Several studies showed that the concentration of the contaminants released can change depending on pH [27-29]. The obtained results are presented in Figure 7.

Focus on the leaching behavior of trace elements under the “native” pH, which about 2.3, trace elements may be mobilized from PG in important quantities which exceed highly the values of the European limit, especially for the Zn (300 mg/kg), Cr (11.19 mg/kg), Se (4.05 mg/kg), As (3.7 mg/kg), Ni (1.2 mg/kg); Low pH related extreme scenarios which may occur on the dumping sites; several studies representing the distributions of major and trace elements in surrounding of stockpiles of PG found to be in agreement with our results. [30-33].

Further information on heavy metal leachability was obtained from the metal release during a pHstat test; only the most important contaminants are discussed through this test.

The leaching behavior of PG as a function of the pH can be derived also from Figure 7. The leached concentrations of the trace elements showed strong pH dependence. Based on the shape of the curves, three groups can be distinguished.

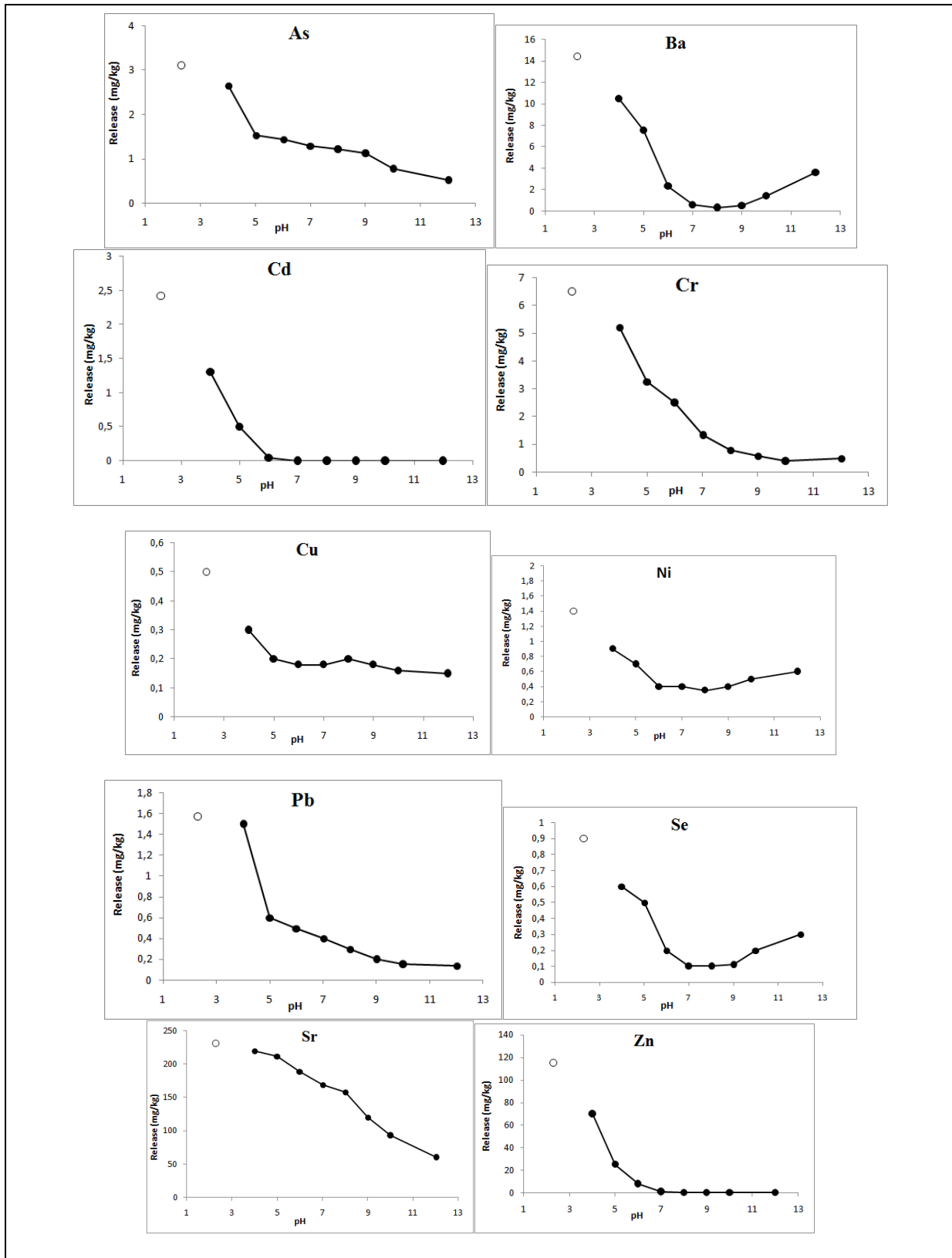
The first group of the elements includes Zinc and Cd, the leaching trend of the two elements was very similar, highest concentrations released at pH 2- 4, followed by a rapid decrease with increasing pH, their concentrations decreased significantly with increasing of pH to almost non-detect levels and can be attributed to metal precipitation as hydroxides.

The second group consists of the elements (As, Pb, Cu and Sr), which showed comparable trends, a decreasing with increasing of pH values, but they leach out a non negligible quantity under alkaline conditions 0.4 mg/kg As, 0.5 mg/kg Pb 1mg/kg Cu and 50 mg/kg Sr. it should be noted that leachability of these elements is much more important under strongly acidic conditions compared to highly alkaline ones.

The third group composed of Ba, Se and Ni, they demonstrated a U- shaped curve, a maximum concentration of leached contaminants occurs at strongly acidic conditions (pH- 2-4), significantly decreasing towards natural pH (6-7) and slightly increasing at highly alkaline conditions with less important leached quantity.

Comparing results of tests done for PG, it is clear that important leachability of the PG is observed at the pH range 2-4 and above all at the native pH (2.3).

PG shows a maximum susceptibility to leaching out metals when exposed to a strong acidic condition, this point is significant for environmental considerations, the pH dependent leaching tests were further conducted to reproduce different environmental conditions which affect the leaching behavior of element content of PG; consequently, acidic conditions should be avoided in order to prevent metal leaching from PG.



—●— pHstat test ○ native pH

Figure 7: Effect of pH on the release of trace elements from PG

4. Conclusions

Characterization of PG is done to examine its physical, chemical, mineralogical properties as well as its major and trace leaching behaviour. From the above studies following conclusions can be drawn:

- (1) As worldwide Phosphogypsum, Tunisian PG is classified as silty sand with high water content; PG included a significant amount of fines 65% by weight with a typical diameter (D50) of 40 μm .
- (2) Chemical and mineralogical results show that the trends have broadly similar trace element concentrations as the average worldwide PG values except to Zn and Sr which more enhanced in studied sample.
- (3) The Tunisian PG was examined for leaching of heavy and major elements using a standard leaching test the parameters which affect leaching are liquid to solid L/S ratio and pH; leaching experiments provide useful information on the behavior of major/minor elements. The initial pH values of leachates were observed in the range of 2.3. Calcium, sulfate and phosphorus were the major elements having the highest leaching concentrations in all samples. Concerning trace elements, The degree of mobility as reflected by the fraction of total release was found to follow the order Sr>Zn>Ba>As>Cd>Cr>Ni>Cu>Se>Y>V>Pb>Zr. Higher concentrations of several elements of potential environmental significance are found in leachates giving evidence that special attention should be taken in the case of later valorization.
- (4) Considering the results obtained from pH-dependent leaching experiments, in general, the leaching of PG trends increase at low pH, maximum leached concentration showed at pH 2-4. Indeed, PG shows a maximum susceptibility to leaching out metals when exposed to a strongly acidic condition, whereas, alkaline condition appear to be the most stable for the analyzed material. In fact, the results show a higher immobilization of the heavy metals.

The findings of this study promote the quantitative consideration of environmental impacts of long-term leaching of Tunisian PG and it can serve as guidance in different waste management scenarios to control leaching behavior of PG when later recycling actions are taken.

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