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Study of the Mechanical Strength and Leaching Behavior of Phosphogypsum in a Sulfur Concrete Matrix

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Abstract: *This work suggests a treatment alternative to phosphogypsum, an industrial solid waste generated by the Tunisian Chemical Group in huge amounts, by sulfur waste from a natural gas purification plant in Tunisia, contaminated with heavy metals and mercury, used as a binder. Mixtures with different phosphogypsum contents were made at a temperature equal to 150°C and compacted at the paste phase with a pressure of 1.5 MPa. The mechanical strength and leaching behavior results were sought after a period of one month and then with an artificial ageing cycle of thermal shocks and humidity variation. The comparison between the solid PG-sulfur matrices shows that the mixture tested with 50% sulfur/50% PG had the best mechanical strength up to 40 MPa. The leaching behavior tests also proved that the mixture tested with 50% sulfur, 50% PG is most efficient, resulting in a total retention of copper, lead, cadmium and almost total retention of zinc and nickel. Artificial ageing cycles had an insignificant effect on the mechanical strength and chemical behavior of the tested matrices which proves the long term efficiency of the suggested treatment.*

Keywords: *Phosphogypsum – sulfur matrix – Chemical Fixation and Solidification artificial ageing – leachability*

I. Introduction

Phosphate rock currently accounts for over 90% of phosphoric acid (used as a fertilizer) production in the world. The processing of phosphate rock by the wet acid method generates a huge quantity of waste by-product, namely Phosphogypsum (PG). About 5 tons of PG are generated per ton of phosphoric acid production. World PG production is variously estimated to be around 100–280 Mt per year [1].

This by-product is primarily made up of gypsum in addition to phosphorus contents (1%). It is considered as a toxic residue because of its considerable contents in fluoride, metals (Zn, Cd, Hg…) [2,3]. This waste represents a hazard to the environment especially that most of it (85%) is dumped without treatment. In the Tunisian context, this problem is most prominent in the south of the country. In fact, The Tunisian Chemical Group (TCG) holds six phosphoric acid manufacturing plants settled in this area. Currently, TCG generates approximately 8 million tons of PG per year [4].

With such a huge quantity, an environmental issue arises [5]. Worldwide, only 15% of the generated PG is recycled as building materials [6], agricultural fertilizers or soil stabilization amendments and in the manufacture of Portland cement [7,8,9]. The remaining 85% is disposed of without any treatment.

The new PG waste management policies around the world aim to reduce the negative environmental impact [10] of this residue by finding better alternative uses allowing a sustainable valorization. In this regard, applications in the edification and civil engineering uses are efficient alternatives that could lead to the production of final products with good mechanical properties and very limited radionuclide content [11]. Meanwhile, its use in this field does not cope with the huge PG quantities. In addition, the performance of the issued product is by no means similar to that of traditional materials.

This work lies within the scope of a sustainable management of PG - generated by the TCG phosphoric acid manufacture plant - as it suggests a chemical fixation and solidification treatment by means of compaction under press with sulfur concrete (contaminated sulfur) emanating from British Gas Tunisia as a binder making it possible to obtain an inert matrix in which the pollutants contained in PG and sulfur are retained.

II. Materials And Methods

2.1. Waste sampling

The used PG was obtained from the open air waste stockpile of the Industrial Company of Phosphoric Acid and Fertilizers of Sfax that belongs to TCG, Tunisia.

The contaminated sulfur was obtained from the Hannibal gas purification plant of Sfax that belongs to British Gas Tunisia. With natural gas, sulfur is already in the form of H_2S and can undergo the Sulfinol process directly. During this process, a liquid rich in H_2S is obtained. The latter is transformed into elementary sulfur in

a sulfur recovery unit. H_2S is thus transformed into a solid waste. The samples were taken using a manual sample tube for extracting cylindrical samples in the open air in different locations on the waste deposits, in accordance with the French standard X 31-210 (diameter = 4 cm) [12].

2.2. Chemical composition of the used PG

The chemical composition of PG depends on the origin of the phosphate ore, of the manufacturing process, the efficiency of the plant and the age of the deposit. It is primarily made up of calcium sulfate mixed with calcium phosphate in various forms, silica and the impurities such as iron oxides, aluminum and magnesium, sulfide, organic matter, and heavy metal traces. Table 1 shows the chemical composition of the used PG.

Table 1: Chemical composition of the used PG

Elements	Content (%)
CaO	41.2
SiO_2	1.2
Al_2O_3	0.1
Fe_2O_3	0.08
MgO	0.02
SO_3	50.7
Na_2O	0.6
P_2O_5	1.2
F	4.9

2.3. Chemical analysis of the used waste

Sulfur and PG samples were underwent leaching tests according to the French standard X 31-211 [13, 14] The leaching test consisted of a liquid/solid extraction of a sample via a water solution. The weighed sampling tube was set in contact with double distilled water with recourse to permanent magnetic stirring. The liquid/solid ratio was 10. After 24 hours of stirring, the obtained leachates were separated from the residue of the samples, whether through centrifugation followed by a vacuum filtration with a GF/C Whatman filter paper (medium diameter = 5 cm, pore size 0.45 µm), or through simple filtration followed by vacuum filtration. The leachates were then used for chemical analyses. The concentration of heavy metals and alkali metals was determined using the atomic absorption technique, and chloride and sulfate concentrations were measured by high-performance liquid chromatography (Waters 1515).

The same procedure was applied to a second set of samples that underwent artificial ageing.

2.4. The experimental protocol of waste treatment

The treatment of PG was realized by using contaminated sulfur as a binder. Five mixtures were tested with binder dosages ranging from 40% to 60% proportionally with the PG weight. Mixtures with different PG contents were made at a temperature equal to 150°C and compacted at the paste phase with a pressure of 1.5 MPa. The compositions of the different mixtures are shown in Table 2.

Table 2: The compositions of the tested mixtures

Mixture number	PG (% of the total content)	Contaminated sulfur (% of the total content)
M1	40	60
M2	45	55
M3	50	50
M4	55	45
M5	60	40

After having mixed the components with heat until a smooth and homogeneous paste was obtained, the mixtures of treated wastes were molded according to the Chemical Fixation and Solidification (CFS) technique with compaction at the paste phase [15]. The testing protocol, as presented in Figure 1, reveals the different steps of sample preparation and the evaluation tests of the mechanical strength and chemical behavior of the obtained solidified matrices after one month [16].

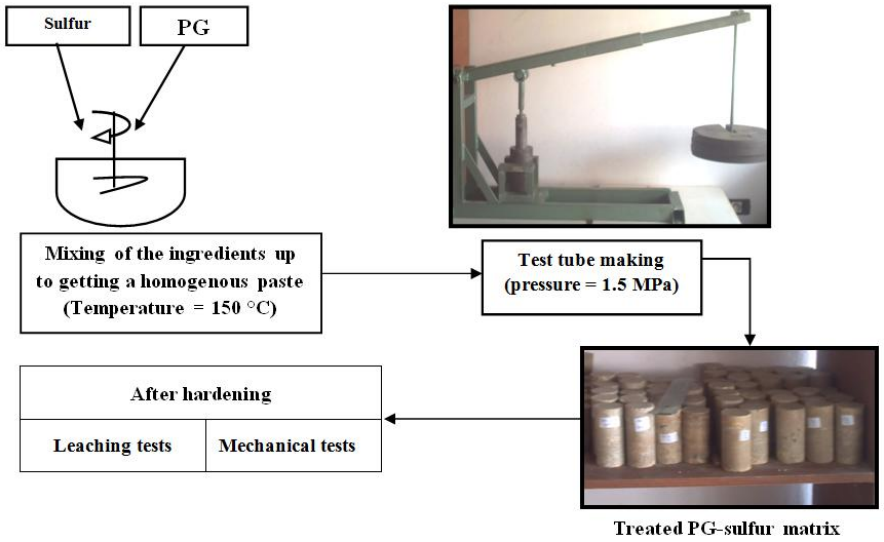


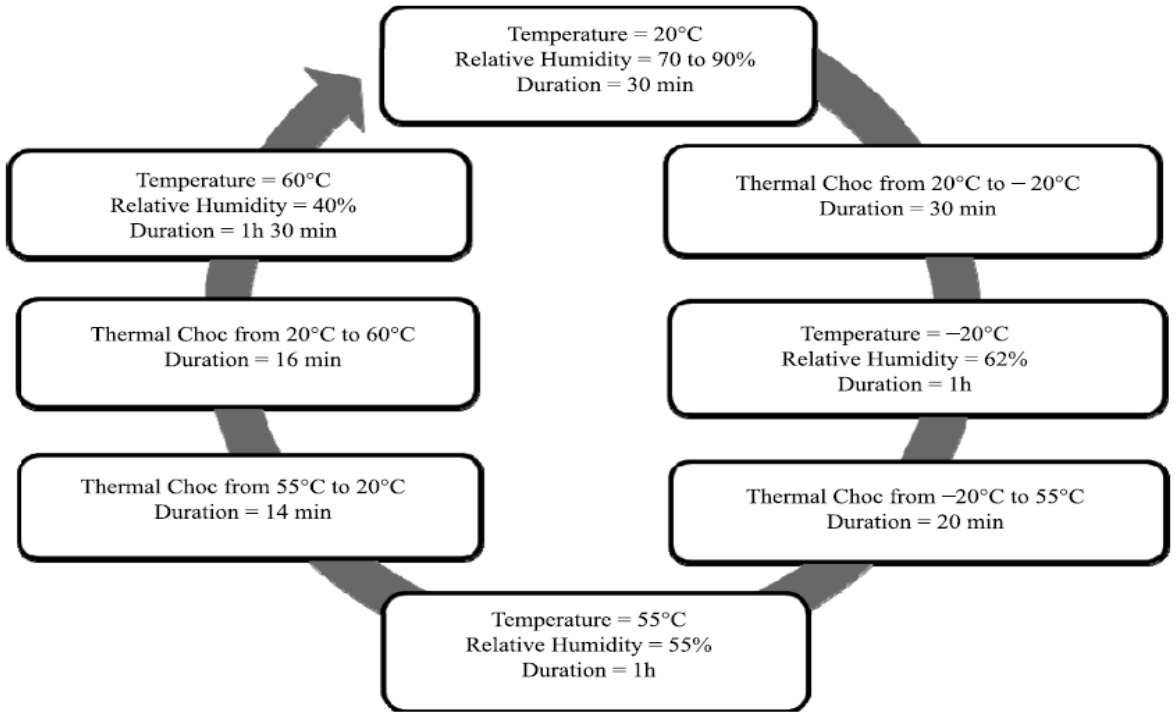
Figure 1: The sample making protocol

2.5. Evaluation measures for the suggested treatment

The chemical behavior and mechanical strength tests of the obtained treated PG-sulfur matrix were carried out to assess the proposed treatment. In addition artificial ageing cycles were applied to a set of waste matrices in order to anticipate their behavior at a longer term.

2.5.1. Artificial ageing cycles

A set of treated waste samples underwent an artificial ageing process for 100 cycles of humidity variation and thermal chocks in a manually controlled climatic chamber (Climatic Chamber freeze/thaw, 520 L, Matest C314/ZG/0001) for a period of three months. Before undergoing these artificial ageing cycles, the samples were sunk in water for 48 hours. Each artificial ageing cycle consisted of the steps summarized in Figures 2a and 2b. The temperature range and humidity variation in the climatic chamber was fixed at −20°C to 60°C and 40% to 80%, respectively. These limits were selected to be the most aggressive climatic conditions we could provide in our laboratory and which could fit the real scale. Maintaining the relative humidity between 50% and 60% is aimed, according to Young et al. [17] and to Lange et al. [18]



(a)

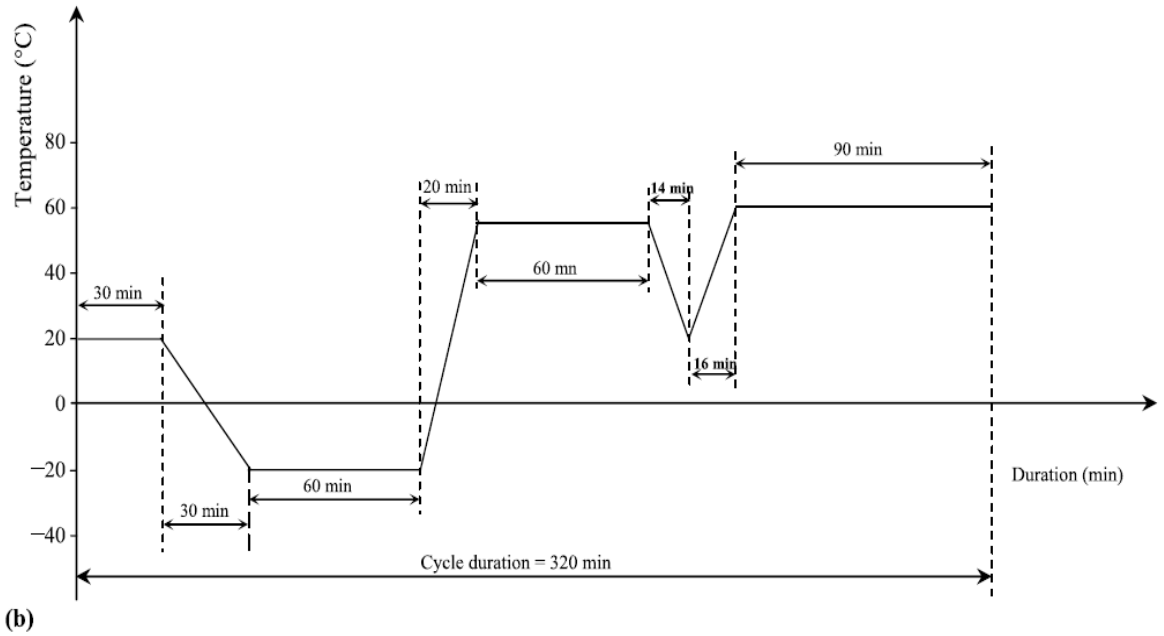


Figure 2: Artificial Ageing Cycles

2.5.2. Evaluation of the leaching behavior of treated PG-sulfur matrix before and after artificial ageing

Leaching tests were applied to the treated PG-sulfur matrix according to the French standard X 31-211[14]. The leachates obtained after a 24 hour test were then used for chemical analyses. The atomic absorption technique was adopted to evaluate the concentration of heavy and alkali metals, and chloride and sulfate concentrations were measured by high-performance liquid chromatography (Waters 1515).

The same procedure was applied to a second set of samples that underwent the artificial ageing cycles described above.

2.5.3. Mechanical strength tests of treated PG-sulfur matrix before and after artificial ageing

Mechanical properties are based on compression test results. The tests of mechanical strength reveal the degree of firmness of the treated PG samples. The evolution of the mechanical strength of the treated PG-sulfur matrix was examined according to the dosage of sulfur. The mechanical strength of the samples was measured according to the French standard P18-406 [19] with a press machine (Mod. E160P106, Matest, Treviolo, Italy). The same procedure was applied to the second set of samples that underwent artificial ageing.

III. Results And Discussion

3.1 The chemical characterization tests on untreated wastes

The chemical analyses of samples of the untreated PG confirm the existence of heavy metals in significant quantities in this waste. Table 3 presents the concentrations of principal impurities present in the studied PG. It clearly proves that PG contains significant heavy metal concentrations primarily Cadmium, Mercury and Zinc [20].

Table 3: Pollutants present in the studied PG

Element	NT 106-002 (mg/l)	Content (mg/l)
Cd	0.005	40
Cl	600	0.025
Co	0.1	8
Cr	2	20
Cu	0.5	6 -11.5
Hg	0.001	14
Mn	0.5	6
Mo	0.5	5
Ni	0.2	15
Pb	0.1	5
Ti	0.001	2
Zn	5	315

The chemical analyses were carried out on the samples of contaminated sulfur according to the same standard. Contaminated sulfur shows a very significant sulfur concentration and the presence of certain toxic elements primarily mercury and iron, higher than the fixed limits stipulated by the Tunisian standard for liquid discharge, NT 106-002 [21]. Table 4 shows the chemical characteristics of the used sulfur.

Table 4: Chemical characterization of the used sulfur

Elements	NT 106-002 (mg/l)	Content (mg/l)
sulphur		93.4
Mercury	0.001	1.58
Iron	2	2.13
Sodium	300	0.08
Sulphates	600	0.02
Chlorides	600	0.21
Potassium	50	1.00

3.2. Leaching behavior of the chemical pollutants in the treated PG-sulfur matrix

In order to check the behavior of the pollutants in the solid matrix and to determine the most effective mixture, the same elements detected in non treated PG were determined in the treated PG-sulfur matrix leachate before ageing. The obtained results are illustrated in table 5.

Table 5: heavy metal concentrations in the leachate of the treated PG-sulfur matrix before ageing

	Zn (µg/l)	**Cu** (µg/l)	**Pb** (µg/l)	**Cd** (µg/l)	**Ni** (µg(l)
Leachate M1	25	ND(<5µg/l)	ND(<5µg/l)	ND(<5µg/l)	47
Leachate M2	27	ND(<5µg/l)	ND(<5µg/l)	ND(<5µg/l)	75
Leachate M3	42	ND(<5µg/l)	ND(<5µg/l)	ND(<5µg/l)	9
Leachate M4	60	ND(<5µg/l)	ND(<5µg/l)	ND(<5µg/l)	12
Leachate M5	57	ND(<5µg/l)	ND(<5µg/l)	ND(<5µg/l)	8
NT 106-002	5000	500	100	5	200

(ND: non detected)

The content of all the heavy metals detected in the leachate of the solidified matrix of PG treated with contaminated sulfur are less than those found on the untreated PG leachate. All the values are lower than the limits fixed by the Tunisian standard for liquid discharge, NT 106-002 [22]. The tests also prove that all mixtures result in a total retention of copper, lead, cadmium and almost total retention of zinc and nickel.
Similar results were obtained from the leaching tests after ageing. In fact the artificial cycles had no effect on the matrix. This proves that the use of contaminated sulfur as a binder enhances the leaching behavior of the matrix, by reducing the solubility and fixing the pollutants, which inhibits their release out to the environment.

3.3. Evaluation of the mechanical properties of treated PG

Mechanical strength tests of treated PG inform about the strength and the cohesion of the matrix. The evolution of strength according to time (1, 20, 40 and 60 days) and according to sulfur dosages is presented in figure 3.

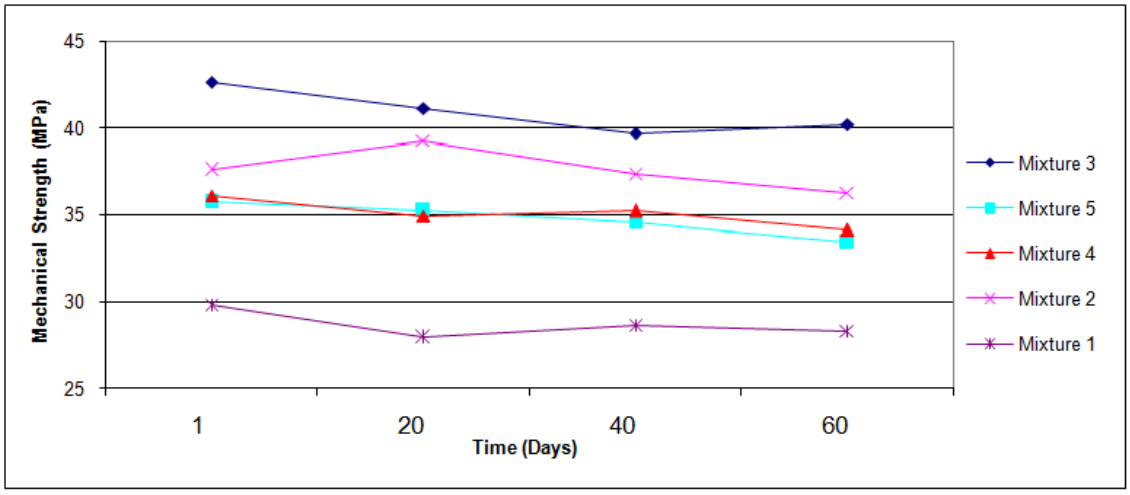


Figure 3: Evolution of the mechanical strength of PG treated according to time

Figure 3 reveals that low sulfur dosages (less than 50%) do not yield an appropriate mechanical resistance of the matrix and that the optimal sulfur dosage as a binder for mechanical strength is 50%. In fact, it was also found that high dosages in sulfur as shown in figure 3 decrease the resistance. A 60% sulfur content led to a minimum strength and this might be due to the fragility of sulfur. Results also prove that the mechanical strength was almost the same after 20, 40 and 60 days. We can thus claim that time has no influence on the mechanical strength of the sample tubes of treated PG according to sulfur dosages.

Similarly with the leaching behavior, the mechanical behavior test results after ageing were the same before and after ageing; which proves that artificial ageing has no effect on the strength of the obtained matrix; which favors the use of contaminated sulfur as a binder for the enhancement of the mechanical properties. These results pave the way to a multitude of uses in different domains of the obtained solidified material.

IV. Conclusion

The target of this work was to provide a sustainable treatment of PG by the chemical fixation and solidification technique. Sulfur emanating from a natural gas purification plant contaminated with heavy metals and mercury was used as a binder. Results of the leachability and mechanical strength assessment of different sulfur/PG mixtures prove that this treatment provides an almost inert solid matrix where pollutants emanating from PG and sulfur are retained with a high mechanical strength up to 40 MPa.

The results obtained in this work are promising and showed that solidification with contaminated sulfur as a binder could be a suitable option for the management of PG. The artificial ageing tests also proved a high performance at a longer term. The obtained treated PG by manufactured monolithic blocks could have different applications in the edification and civil engineering uses once long term behavior is assessed in a real scale context.

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