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The Solubility of Phosphogypsum and Recovery of Heavy and Radioactive Elements

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KEYWORDS

Phosphogypsum, leaching, heavy elements, radioactive elements.

ABSTRACT

The essential purpose of this paper is to illustrate and inspect the leaching characteristics of Iraqi Phosphogypsum (PG). The paper presents the results of the dissolution characteristics of heavy and radioactive elements from PG, which is a by-product result from the industry of phosphate fertilizers. Leachability of heavy and radioactive elements in deionized water that has been inspected under various states of leaching, including solid/liquid ratio (10, 20 and 50 /1g/L) and temperatures (25, 45 and 85 °C), with constant other parameters such as string speed (300 rpm) and contact time (60 minutes). For the most analysis elements, the progressive release of the metals, in addition to the major elements reflects high mobility. The mobility of trace metals in PG has been generally classified into three main degrees: (1) high mobility elements such as Pb, Zn, Mn, and Cr; (2) moderate mobility elements such as Sr, V, Ba,Y,Hg, K and Ni; and (3)l ow mobility elements like Ca,Cu,Fe, and Ag. The maximum concentrations of the most of the metals were attained from a leaching state of 10/1g/L. Regarding temperature, the experimental results revealed that the PG solubility to leaching out elements increases noticeably as the applied temperature ranges from 25 to 45 °C; after this degree, the leaching efficiency decreases. Chloride had a positive and negative effect on the solubility of phosphorus. Calcium chloride had an adverse effect on solubility and observed reduced solubility with increased chloride. While the positive effect of sodium and magnesium chloride was observed, the solubility ratio increased with the increase of chlorides. However, the effect of magnesium chloride was higher compared to the sodium chloride one.

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1. INTRODUCTION

Phosphogypsum (CaSO4•2H2O) is the gypsum of chemical origin that results from producing fertilizers, whereby soils rich in phosphorus are exposed to sulfuric acid leading to phosphate fertilizers and phosphoric acid (H3PO4), according to the chemical equation below [1]. The phosphoric acid (H3PO4) production currently employed is not very efficient with respect to the generation of by-products because of each tone of the produced acid, 4.5 ton of phosphogypsum are generated, and this product by not having direct and continuous use and also by being currently stored in landfills exposed to the weather, which becomes one of the biggest environmental problems for producers of fertilizers. The destination for the phosphogypsum is urgent since the world's agricultural demand is increasing, and it is the real responsible for the emergence of this environmental problem. There are some possibilities of application of this material, typical example is the adoption in civil engineering where it can decrease the construction costs in paving roads and building houses [2,3], in agricultural uses [4] to modify and enhance the chemical and physical soil properties[5], and in treating wastewater [6]. However, all these applications are invariably challenging because phosphogypsum is classified as TENORM (Technologically Enhanced Naturally Occurring Radioactive Material), that is, a solid waste containing naturally occurring radioactive elements from the rock matrix. Phosphate fertilizers contain traces of heavy and radiation metals that are likely gathered in certain soil due to the repetitive use of the phosphate fertilizer. Radioactive and heavy metals could have considerable adverse effects on the health of people and animals. The degree of harm largely depends on the length of the exposure period; the most significant effect is associated with the most extended period. It is crucial to protect soil from being contaminated as a result of the use of phosphate fertilizer. Thus, effective and efficient techniques should be developed and adopted to exclude radioactive elements from phosphate soil. According to relevant literature, two common and recognized methods have been suggested and used to remove these harmful elements: leaching and calcination. The leaching method is quite preferred as it is more cost-effective. The calcination method requires high power consumption [7]. More than 12 million tons of phosphogypsum (PG) were accumulated as a waste by-product of phosphoric acid production at Al-Qaim fertilizers complex in western Iraq [8]. Currently, worldwide waste PG generation exceeds 100–280 Mt/y. Moreover, 14% of worldwide production reprocess, 28% dump into water bodies, and 58% are being stockpiled and may cause a huge environmental problem [9]. Phosphogypsum is mainly composed of gypsum combined by the water of hydration (0.5-2 molecules). Impurity like Al, P, F, Si, Fe, Mg, in addition to other trace elements, including rare earth element existed initially been or partition during the chemical process [10]. Naturally occurring radionuclides of U-238 and Th-232 decay series are of most concern due to their radioactivity and toxicity. Phosphogypsum also enriched by Sr and Ba. Phosphogypsum is formed from phosphate rock according to the principal reaction [11].

This study aims to find methods to recover trace elements from the Iraqi ore phosphogypsum generated as wastes by-product from Al-Qaim fertilizers complex in western Iraq. The dual-studies are beneficial to the environment and economic recovery of the heavy and radioactive elements from the ores to reduce their content. This allows for the evaluation of these elements and thus their toxicity reduces. Therefore, recovery of these valuable elements is not only a means of maximizing the mineral potential but also a means of environmental stewardship.

2. EXPERIMENTAL WORK

I. Materials

Phosphogypsum samples which used in this work were obtained from Iraq (Al-Qaim fertilizers complex at Al-Anbar Government). All the chemicals used have an analytical grade. Deionized water was used to prepare the solutions in the current study. Leaching has been done for bauxite of +75-150μm in leaching cell consist of 250 ml 3- neck round glass with refluxing condenser and thermometer placed on the magnetic stirrer heating mantle. The slurry in the vessel is stirred by using Teflon coated magnetic. The solution used for leaching process is kept constant (100 ml) in all leaching experiments. After each experience the ore is filtered by filtered papers, after that the residual is dried in oven at 100°C. Known weighted or known volume samples have been sent for XRF and atomic absorption analysis for ZrO2 and other. The atomic absorption spectroscopy type (nova AA 350), was used to determine the dissolved Al2O3, ZrO2 in solution of leaching and extraction process experiments at the laboratories of Ibn-Sina State Company.

II. Chemical Analysis for the Phosphogypsum sample

The samples were collected to offer a comprehensive study about phosphate, phosphogypsum, and selected trace elements, to detect the chemical composition of the ores. The XRF analysis of Phosphogypsum was done in University of Baghdad, College of Geology, The Iraqi-Germany Laboratory.

III. Mineralogical Analysis

Qualitative mineralogical analysis regarding representative sample of phosphogypsum sample taken from ore preparation step has been carried out at University of Baghdad, College of Geology, The Iraqi-Germany Laboratory. The mineralogical analysis has been achieved through the use of X-ray diffraction (XRD) (Shimadzu 7000). The X-ray diffraction was registered at 30 mA and 40 kV for a Cu-target tube.

IV. SEM Analysis

The SEM analysis involved forming an electron beam of high acceleration emitting from a LaBr6 and a tungsten source in a high vacuum. By passing the formed beam through a series of apertures and condensers, the beam is concentrated into a fine probe. As a result, this generates a raster scan over the limited area of rectangular shape. The inspection was done at Department of Production Engineering & Metallurgy, UOT. A scanning electron microscopy model was employed to examine the morphology of phosphogypsum powder

V. Atomic absorption spectroscopy

The atomic absorption spectroscopy (nova AA 350) was used to determine the dissolved some heavy and radioactive elements in the solution of the leaching process at laboratories of Ibn-Sina State Company.

VI. The leaching and solubility of phosphogypsum

Studying the solubility of calcium sulfate and the recovery of the heavy and radioactive elements were achieved for the phosphogypsum sample. The leaching behavior of Iraqi phosphogypsum was conducted deionized underwater conditions. Some variables were used, such as solid/liquid ratios and temperatures. All tests of leaching have been done for phosphogypsum powder and have a particle size -710+75µm. The pH values of phosphogypsum samples were determined by EPA method 9045D [12]. For this experiment, 20 grams of Phosphogypsum was mixed with 20 mL of the reagent water and stirred continuously for five (5) minutes; then it was allowed to stand for 1 hour. After that, the pH was measured. The pH of Phosphogypsum samples used in this study was of ~2.4, and this can attribute to the residual phosphoric, sulfuric, and hydrofluoric acids contained within the Phosphogypsum. One Phosphogypsum sample from each location was tested to determine pH. The pH of the used DI water for this experiment was 6.86, and the conductivity reached less than 0.1 µ•S/ cm. After the leaching process, the leach solution has pH ~3.3, and his value was constant in all the tested samples. The percentage of removal of the elements has been estimated depending on the following equation [14]:

$$L\ \% = [C_f / C_i] \times 100$$

Where Ci can be defined as the initial concentration in mg/kg, and Cf is defined as the final concentration in mg/kg.

VII. Effect solid/liquid ratio

To study the effect of percentage solid to liquid on the recovery of heavy and radioactive elements, three values were selected (50//1, 20\1 and 10/1 g/L) of the phosphogypsum sample in a 1.5-lit glass beaker. The mixture was shaken in a reciprocal shaker (300 rpm) at constant temperature of 85 °C, for 60 minutes. The solution was filtered with a 0.40 µm membrane filter. The remaining solid sample is taken on the filter analyzed by XRF to define concentrations of heavy and radioactive elements.

VIII. Effect temperature

To study the effect of temperatures in relation to the recovery of heavy and radioactive elements that derived from the sample of phosphogypsum, three values of temperatures (25, 45, and 85 °C) were selected. The mixture was shaken in a reciprocal shaker (300 rpm), at contact time 60 minutes, and was percentage of solid to liquid was constant (10/L) g/L.

IX. Effect some chlorides (NaCl, $MgCl_2$, and $CaCl_3$) on solubility of phosphogypsum

The solubility of Phosphogypsum was studied to improve the solubility of phosphogypsum in presence of NaCl, $MgCl_2$ and $CaCl_3$ at concentrations of (0.1, 0.2, 0.3, 0.4, 0.5, 0.6 0.7, 0.8, 0.9,1 and 1.5) g/l added to one liter of DI water at different temperatures (25, 30 and 35±2 °C), and stirring speed 300 rpm for 60 minutes. The conductivity measured at every time until that they become constant, which expresses reaching saturation. A conductivity meter was used to measure the conductivity. All experiments were made at atmospheric pressure.

3. SUBMISSION PROCEDURE

I. Chemical Analysis of Phosphogypsum Samples

Table I shows the results of elements analyzed by XRF techniques. The elements abandoned in phosphogypsum samples particles size (-710 +75µm) can be classified as major elements more than 1000 ppm i.e. (S, Ca, Na, Si, Mg, P, Sr, and Ba), medium elements 100-1000 ppm, i.e. (K, Ta, Ba, and Fe) and trace elements <100 ppm, i.e. (U, Th, Cu, Ni, V, Fe, Al, Pb, Cr, La, and Zn).

TABLE I: Chemical composition of the particles size of the phosphogypsum sample as received

II. Mineralogical properties (XRD)

The mineralogical analyses of phosphogypsum were performed using XRD spectra, and their results were given in Figure 1. The previous Figure can show the main mineralogical phases of the phosphogypsum sample (calcium sulphate) with other secondary minerals such as dolomite and brucite, and from same Figure1, can be seen, the ratio of the components of the phosphogypsum ore, where percent of calcium sulphate has the most substantial proportion with a few percentages of dolomite and brucite impurities.

	symbol	Concentration %		symbol	Concentration %
١	MgO	3.536	٢٦	ZrO2	0.00014
٢	Al2O3	0.0038	٢٧	Nb2O5	0.00014
٣	SiO2	1.152	٢٨	Mo	0.00072
٤	P2O3	2.006	٢٩	Ag	0.00114
٥	SO3	46.42	٣٠	Cd	0.00020
٦	Cl	0.05028	٣١	SnO2	0.00107
٧	K2O	0.0675	٣٢	Sb2O5	0.00236
٨	CaO	36.91	٣٣	Te	0.00101
٩	TiO2	0.0082	٣٤	I	0.00159
١٠	V2O5	0.0061	٣٥	Cs	0.00040
١١	Cr2O3	0.00073	٣٦	Ba	0.02104
١٢	MnO	0.00067	٣٧	La	0.00020
١٣	Fe2O3	0.01769	٣٨	Ce	0.00020
١٤	CoO	0.00039	٣٩	Hf	0.00010
١٥	NiO	0.00185	٤٠	Ta2O5	0.01523
١٦	CuO	0.00334	٤١	WO3	0.00020
١٧	ZnO	0.00890	٤٢	Hg	0.00010
١٨	Ga	0.00005	٤٣	TiO2	0.00011
١٩	Ge	0.00005	٤٤	Pbo	0.00114
٢٠	As2O3	0.00007	٤٥	Bi	0.00010
٢١	Se	0.00005	٢٦	Th	0.00010
٢٢	Br	0.00024	٢٧	U	0.00150
٢٣	Rb2O	0.00006			
٢٤	SrO	0.6326			
٢٥	Y	0.00285			

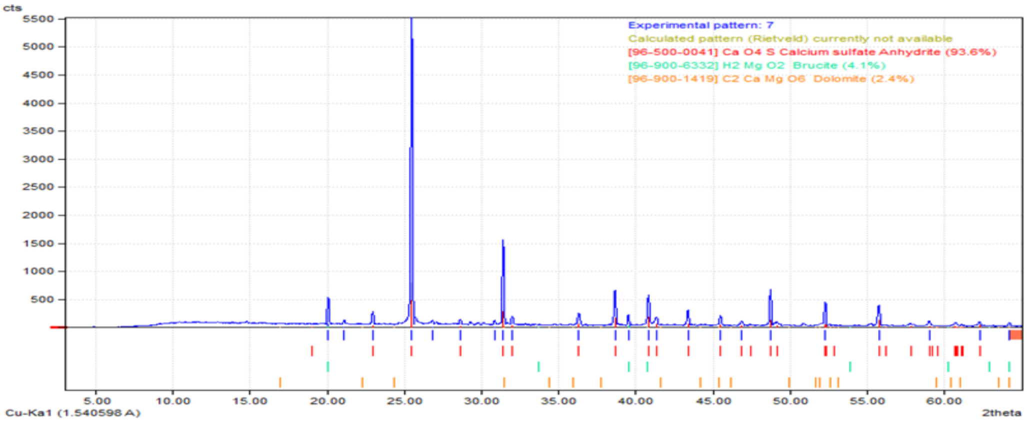

Figure 1: XRD pattern of the phosphogypsum

III. Morphological analysis SEM and EDX

An inspection was carried out by scanning electron microscopy (SEM) to inspect the morphology of selected samples of phosphogypsum (CaSO4•2H2O). Figure 2 shows different sizes of the accumulated Phosphogypsum particles. Phosphogypsum has different shapes like hexagonal, tabular and needles; also, the analysis revealed that granules of phosphogypsum are mostly with a maximum size of up to 1 mm. According to the EDS image shown in Figure 3, the recognized major elements are S, Ca, and O, which indicated gypsum [15].

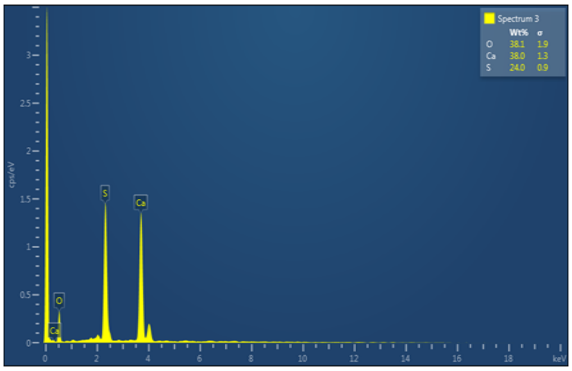

Figure 2: SEM inspection of the phosphogypsum ore

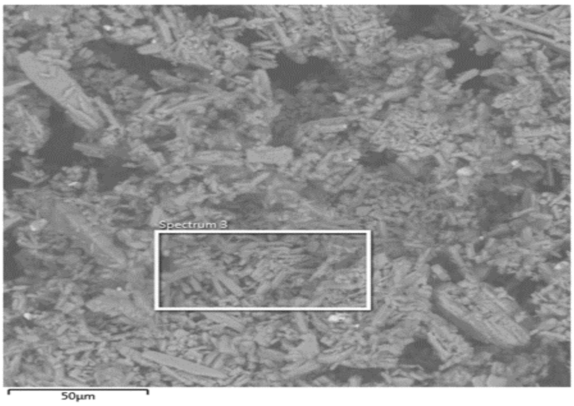

Figure 3: EDS inspection of the phosphogypsum ore

IV. Effect of Solid to Liquid ratio and temperature on leaching and solubility

A. Effect of Solid/Liquid ratio

Figure 4 states the large leached quantities of the major elements (Pb, Zn, Sr, U, Cr, and Mn) at solid/liquid ratio (S/L) equals 10/1g/L, while there is limited leaching action for the elements Sr, Cu, Fe, and Ag. According to the removal proportions, elements of Pb, Zn, Cr, and U have experienced a more leaching effect than others. Concentrations of the number of elements were dependent on the L/S ratio; when the L/S ratio was decreased, removing of the heavy and radioactive elements increased. This implies that they passed through Phosphogypsum without difficulty. Apparently, during the leaching test, there is full contact between Phosphogypsum and water. The solubility of the elements is largely influenced by the friction between solid-water and among solid particles themselves. The concentrations of the soluble heavy and radioactive elements are generally classified into two distinct groups: the first involves the elements of Ca, Cu, Fe, and Ag with removal percent less than 30%. The second group comprises the elements of Pb, Zn, and Cr, with removal percent up to 50%. In terms of percentages, the results of the removed elements are; Pb (59%), Cr (52.6%) and Zn (50.5%).

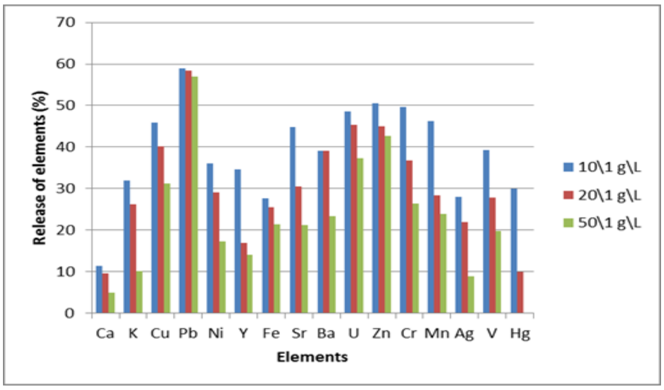

Figure 4: Effect of Solid to Liquid ratio on removed heavy and radioactive elements from Phosphogypsum by deionized water

B. Effect of temperature

For each phosphogypsum sample, the temperature was found to play a vital role in determining the removal efficiency of heavy and radioactive elements. A temperature range from 25 to 85 °C was adopted and applied to explore the influence of temperature on the removal efficiency of these harmful elements. Other boundary conditions were held constant; solid to liquid ratio is 10/1 g/L, when using magnetic stirrer at 300 rpm/min and contact time reached 30 minutes.

Figure 5 show the removal efficiencies for the solid and radioactive elements based on the experimental results. It is quite clear that when the temperature ranges from 25 to 45 °C, the eliminating efficiencies of the following elements increase as well: Ca,K,Cu,Pb,Ni,Y,Fe,Sr,Ba,U,Zn,Cr,Mn,Ag,V and Hg. Speaking in numbers, the percentages of efficiencies rose from 32.73, 0.0508, 0.00181, 0.00059, 0.00182, 0.00282, 0.0287, 0.349, 0.0183, 0.00077, 0.0044, 0.0009, 0.00036, 0.00082, 0.0037 and 0.00007% to 30.55, 0.0331, 0.00103, 0.00041, 0.00123, 0.0013, 0.0113, 0.0153, 0.0183, 0.00071, 0.0021, 0.00051, 0.00013, 0.00063, 0.0022 and 0.00005, respectively. In contrast, they decreased with increasing leaching temperature, until reach to 34.8, 0.0431, 0.00125, 0.00105, 0.00147, 0.00247, 0.0134, 0.0288, 0.0288, 0.00105, 0.0034, 0.00087, 0.00046, 0.00094, 0.004 and 0.0001%, respectively.

The characteristic of phosphogypsum is to some extent, water-soluble, and unlike the majority of other salts. It displays reversing solubility because it is considered less solvable at higher temperatures [16, 17]. From the obtained results, it can be seen that below ~25 °C, gypsum is with the minimum solubility, and thus it represents the greatest thermodynamically stable phase. As the temperature rises, the solubility increases to 45 degrees and then decreases. Such behavior can be attributed to the point that gypsum exhibits anhydrite conditions at temperature values of nearly 40±2 °C. Moreover, gypsum exhibits hemihydrate conditions when the temperature is about 99±2 °C. For temperature values between 40±2 °C and 99±2 °C, gypsum is appraised as metastable [18, 19]. As a consequence, the removal efficiency of radioactive and solid elements continues rising as temperature rises but up to a defined limit. The preceding results imply the endothermic nature of the reaction process; in addition, 45 °C is the most preferred temperature for the solubility of the metal with negative environmental impacts from the phosphogypsum. Finally, the optimum temperature for such metal treatment is 45°C.

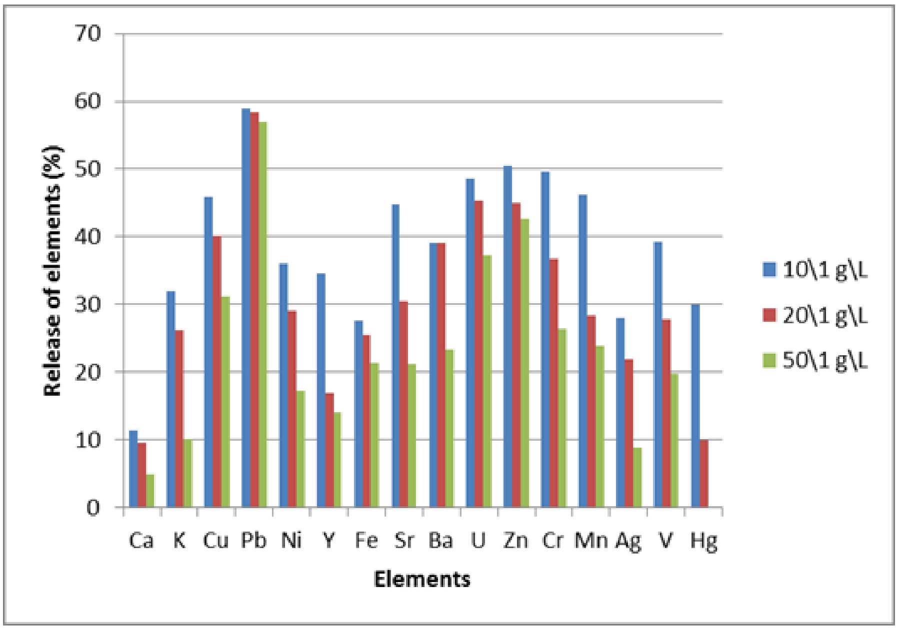

Figure 5: Effect of Temperatures on removed heavy and radioactive elements from Phosphogypsum by deionized water.

V. Effect of some chlorides on the solubility of phosphogypsum

A. Effect of NaCl concentration and temperature on the solubility of phosphogypsum

The solubility behaviour of phosphogypsum in sodium chloride solutions was examined with a range of concentrations from 0.1 to 1.5 g/L and at three distinct temperatures 25, 30, and 35 oC. Figure 6 describes the experimental data of the measured solubility. According to this Figure, as the concentration of NaCl goes up the solubility of phosphogypsum goes up to a specific value too and then gradually goes down. Regardless of the variation in temperature, the measured maximum amount of the solubility is approximately 0.7 g/L. These findings are quite similar to those noticed in other previous relevant studies [20]. For all the examined concentrations, the solubility of Phosphogypsum is positively associated with temperature values; this implies that as the temperature increases the Phosphogypsum solubility increases in aqueous NaCl solutions too. These results are in agreement with [21, 22].

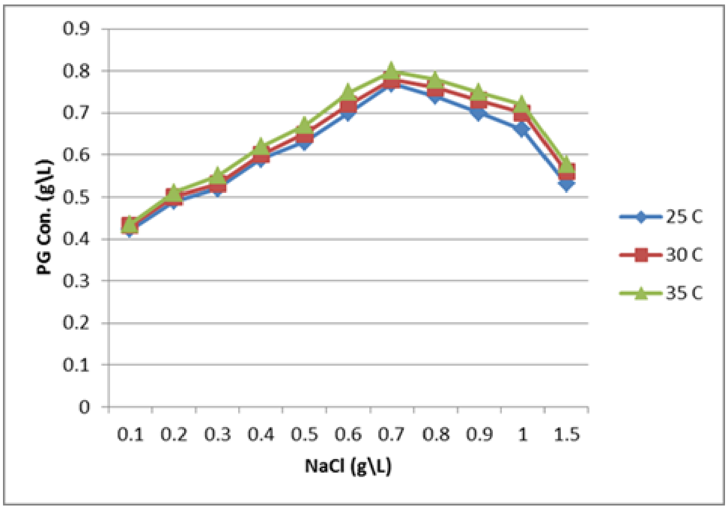

Figure 6: Solubility of phosphogypsum in aqueous solutions of NaCl

B. Effect of $MgCl_2$ concentration and temperature on solubility of phosphogypsum

Similarly, Figure 7 show the experimental results of the $CaSO_4 \cdot 2H_2O$ solubility in magnesium chloride solutions at temperatures range between 25 $^{\circ}$C and 35 $^{\circ}$C. The range of magnesium chloride concentration adopted for the examination from 0.1 to 1.5 g/L. It was apparent that the results proved that phosphogypsum becomes more soluble until $MgCl_2$ reaches 0.9 g/L (see Figure 4). The data show that the solubility of phosphogypsum was augmented with the magnesium cation at levels up in comparison with its dissolution in water. The increase of insolubility is due to the relation between magnesium cation and the partial sulphate ion in the form of stable $MgSO_4$ ion pairs. Several relevant studies have highlighted this relation between $MgCl_2$ concentration and the PG solubility [23, 24].

The maximum values of the solubility can be seen as in Figure 5, 1.05 g/L, 1.13 g/L and 1.15 g/L for 25, 30 and 35 °C, respectively. It is worthwhile highlighting that these concentrations are more prominent than those found in the case of NaCl solutions for the same corresponding temperature degrees. This implies the impact of magnesium chloride on PG solubility which relatively more similar to the impact of sodium chloride. Nevertheless, keeping the increase of magnesium chloride after a certain value will lead to a minor reduction in the Phosphogypsum solubility. Likewise, the temperature and dissolution of phosphogypsum in $MgCl_2$ are positively proportional. These results agree with the findings of [22].

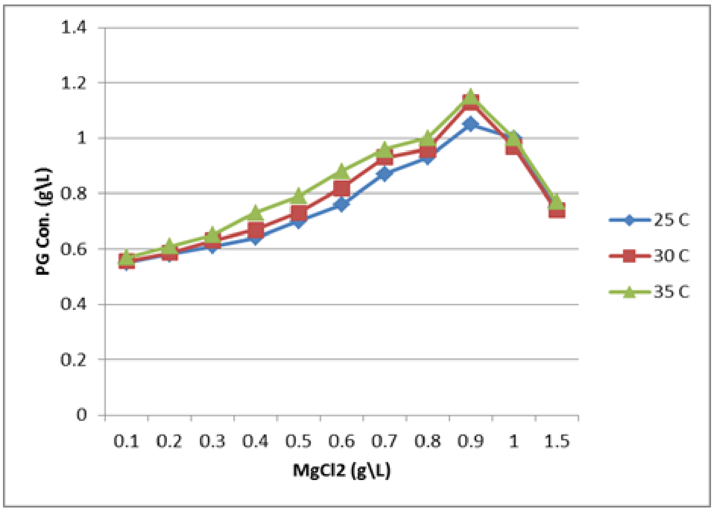

Figure 7: Solubility of phosphogypsum in aqueous solutions of $MgCl_2$.

C. Effect of CaCl2 concentration and temperature on the solubility of phosphogypsum

The last experiment was devoted for studying the behaviour of solubility of phosphogypsum (CaSO4•2H2O) in the solution of calcium chloride. The experiment was conducted at temperatures of 25, 30 and 35 °C and for CaCl2 concentrations ranges between 0.1 and 1.5 g/L. Figure 8 depicts the dissolution results. According to this Figure, the amount of PG solubility shrinkages as the CaCl2 concentration goes up. Furthermore, for low concentrations, CaSO4.2H2O becomes very insoluble, and then the solubility keeps declining just about linearly as the CaCl2 quantity goes beyond 0.5 g/L. The possible explanation for this case is the impact of the common ion [23]. Additionally, Figure 6 indicates that as temperature degrees rise, the dissolution rate of CaSO4•2H2O rises as well even though this effect is partial. The previous work conducted by [25] agrees quite to these findings.

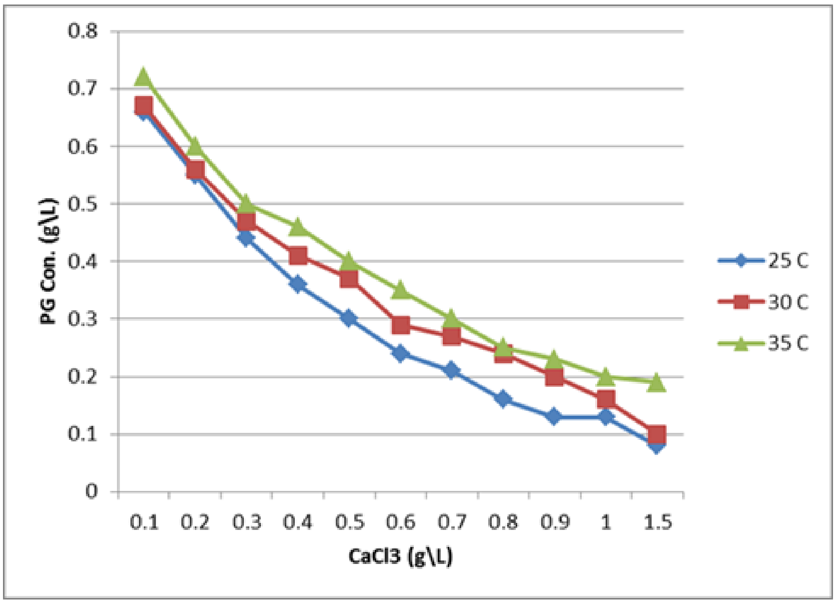

Figure 8: Solubility of phosphogypsum in aqueous solutions of $CaCl_3$.

4. CONCLUSIONS

i-Using deionized water can be a successful medium in the leaching process to recover elements from the phosphogypsum sample.

ii- The main mineralogical phase of the phosphogypsum sample is calcium sulfate with other secondary minerals such as dolomite and brucite.

iii-The solid to liquid ratio has a significant impact on the leaching efficiency, where the efficiency of leaching increases with the low ratio of solid to liquid.

iv-The leaching efficiency of the elements increases when the temperature increases to 45 **°C** and will decrease later on once again when it reaches to that degree.

v-The addition of some chlorides affect the solubility of phosphogypsum, observed both sodium chloride and magnesium chloride have a positive effect on solubility. Increasing the proportion of these chlorides leads to increase the solubility of phosphogypsum. On the other hand, the solubility decreases with increasing the concentration of calcium chloride.

5. REFERENCES

[1] F.R. Gennari, I. Garcia, N. H. Medina, M. A. G. Silveira"Phosphogypsum Analysis: Total Content And Extractable Element Concentration" International Nuclear Atlantic Conference, 24-28, 2011.

[2] M., Canut "Viability study for the substitution of gypsum by phosphogysum as a building material "Belo Horizonte, Universidade Federal de Minas Gerais, 2006.

[3] C. A. Gregory, D. Saylak, W. B. Ledbetter, "The use of by-product phosphogypsum for road bases and subbases", Transportation Research Record, 998, pp 47-52, 1984.

[4] Florida Institute of Phosphate Research – FIRP, "The economic benefit of phosphogysum use in agriculture in the Southeastern United States". Bartow, FIPR Publication, 01, pp124-119, 1996.

[5] P. R Ernani, M. S. Ribeiro, C. Bayer, "Chemical modifications in acid soils caused by addition of gypsum or limestone," Sci. Agric., 58: pp 825-831, 2001.

[6] P. A. Bellingieri, E.G. Bertin, L. Z. Mays, "Effects of the application of sewage, slags and limestone in the chemical properties of a soil cultivated with corn," Scientifica, 31 pp 81-89, 2003.

[7] J. Keith Syers, "Progress in the development of decimation of phosphorus fertilizers. In: Conference Fertilizer in Focus, "Fertilizer Industry Federation of Australia, Inc., pp. 28–29. 2001.

[8] JICA (Japan International Cooperation Agency), "Preliminary feasibility study report on mining and industrial sector in Mid-Western," Iraq, 2010.

[9] M. Al-Hwaiti, K. Ibrahim, M. Harrara, "Removal of heavy metals from waste phosphogypsum materials using polyethylene glycol and polyvinyl alcohol polymers," Arabian Journal of Chemistry, 2015.

[10] M.S. Al-Masri, Y. Amin, S. Ibrahim, F. Al-Bich, "Distribution of some trace metals in Syrian phosphogypsum," Applied Geochemistry, Vol. 19, pp. 747–753, 2004.

[11] N M. Alkheder, Y.J., Kher A. Alkhateb, and A. Kodlaa, "Treatment of Syrian phosphogypsum using acids and bases," Chemistry and Materials Research, Vol. 8 No.9, 2016.

[12] A. Smith and B. Wrench, "Aspects of environmental control of phosphogypsum waste disposal. " Proc., Reg. Conf. for Africa on Soil Mechanics and Foundation Engineering, 487-490, 1984.

[13] M. Abd El-Mottaleb, M. F. Cheira, A. H. Gamal , A. S. Ahmed, " Leaching of Rare Earth Elements from Egyptian Western Desert Phosphate Rocks using HCl," Chemistry of Advanced Materials Vol.1,No.1 ,pp33-40,2016.

[14] K. Grabas, A. Pawełczy, W. Stre, E. Szełe, S. Stre, " Study on the Properties of Waste Apatite Phosphogypsum as a Raw Material of Prospective Applications," Waste and Biomass Valorization,2018.

[15] A. T. Hoang, H. M. Ang, A. L. Rohl, "Effects of temperature on the scaling of calcium sulphate in pipes," Powder Technology, 179, pp 31–37, 2007.

[16] E. Bock, "On the solubility of anhydrous calcium sulphate and of gypsum in concentrated solutions of sodium chloride at 25 °C, 30 °C, 40 °C, and 50 °C, " Canadian Journal of Chemistry. Vol. 39, No.9, pp. 1746–1751, 1961.

[17] G. Azimi, V.G. Papangelakis, J.E. Dutrizac, "Development of an MSE-based chemical model for the solubility of calcium sulfate in mixed chloride–sulfate solutions," Fluid Phase Equilib., 266, pp172-186, 2008.

[18] G. Azimi, V.G Papangelakis., "Mechanism and kinetics of gypsum-anhydrite transformation in aqueous electrolyte solutions," Hydrometallurgy 108, pp 122-129,2011.

[19] W. L. Marshall, R. Slusher, "Thermodynamics of calcium sulfate dehydrate in aqueous sodium chloride solutions," 0−110°. J. Phys. Chem., 70, pp. 4015−4027, 1966.

[20] J. Sun, L. Wangand, Y.Guomin, " Effects of Na, Ca, Mg, and Al Chloride Salts on Dissolution and Phase Stability of Calcium Sulfate Dihydrate in Aqueous Solutions at 278.15 K to 308.15 K," Journal of Chemical & Engineering Data, 2015.

[21] X. W., Wei He, B. Guan, Z. Wu, "Solubility of Calcium Sulfate Dihydrate in Ca-Mg-K Chloride Salt Solution in the Range of (348.15 to 371.15) K," J. Chem. Eng. Data, 55, pp. 2100–2107, 2015.

[22] X.Wu, K. Wang, Z. Xiong, X.i Ye, "Solubility of α-calcium sulfate hemihydrate in Ca−Mg−K chloride salt solution at (353.0 to 371.0) K," J. Chem. Eng. Data, 58, pp. 48−54, 2013.

[23] K. S. Johnson, “A Comment on MgSO4 Ion association in seawater by Fisher, Gieskes and Hsu. Mar, “Chemical., Vol.11, and pp. 285−286, 1982.

[24] Li Zhibao, P. G. Demopoulos, “Solubility of CaSO4 Phases in Aqueous HCl + CaCl2 Solutions from283 K to 353 K,” J. Chem. Eng. Data, 50, pp 1971-1982, 2005.