

Application of full factorial design to optimize phosphogypsum beneficiation process (P₂O₅ Reduction) by using sulfuric and nitric acid solutions

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Abstract

Inventing new ways to recycle and reuse the accumulated by-products is the most pressing and daunting challenge that face future engineers. Millions of tons of phosphogypsum (PG) is stacked worldwide every year and is progressively considered as an asset more than an environmental burden. Jordan cement industry is largely expanded in the last ten years and is considered as an opening to reuse the huge amount of Jordanian PG that is stacked every year. The impurities that PG contains hinder its use as an additive to the cement industry which is pushing towards developing a low cost and effective process to clean PG. Many researches used a number of physical, chemical and thermal methods to reduce P₂O₅ content in PG, but all of these studies are invariant, did not go deep in understanding the process of washing/leaching of P₂O₅ and is not oriented towards developing a process.

In this study, a multivariate 2⁴ full factorial methodologies is designed to study the effect of particle size, acid concentration, loading and number of washing on the P₂O₅ washing/leaching process using sulfuric and nitric acid solutions. The Factorial design analysis helped to get more insight on the relative magnitude of the main and the interaction effects. Sulfuric and nitric acid treatment results indicate clearly the importance of the number of washing on the reduction of P₂O₅ content. This emphasized the importance of renewing the driving force (adding each time a clean solution). It is found that the optimum conditions for sulfuric acid treatment are to have a loading equal to 0.15 g PG/ g solution and three washings. The optimum conditions for nitric acid treatment are estimated to be loading of 0.4 g PG/ g solution and three washings.

Keywords: Factorial design; Beneficiation; P₂O₅; Phosphogypsum.

1. Introduction

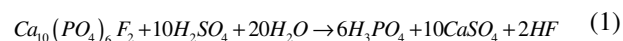
The world sailed in the new millennium with a huge burden of problems that need to be tackled. Financial crisis, global warming, climate change, wars and conflicts, food shortage, health issues, and environmental pollution are just a small portion of this big burden that the world faces. Environmental problems take the lead in this big list of challenges that humanity face nowadays and in the future. Designing an environmental friendly and sustainable products and processes is a major challenge for future engineers, in addition to the other important and pressing challenge which is alleviating the environmental effects of the accumulated by products by inventing new ways to recycle and reuse.

Jordan has limited resources and this necessitates the adoption of stringent policies to conserve consumption, prevent pollution, and recycle waste materials for better use. Jordan was one of the world's top producers of bromine, phosphate rock, and potash in 2009 [Mowafa Taib, 2011]. It also produced cement, clay, fertilizer, kaolin, limestone, pozzolanic material, refined petroleum products, silica sand, steel, and zeolitic tuff [Mowafa Taib, 2011]. Fertilizers industry, which is based on local potash and phosphates resources, is one the major pillars of the Jordanian economy. This important industry is mainly based on the production of phosphoric and

sulfuric acid. Jordan annual production of phosphoric acid (using the wet process) can be estimated to be around 500 thousand metric ton [Mowafa Taib, 2011]. In addition to these big amount of phosphoric acid, a five times this quantity is stacked every year as phosphogypsum (by product of wet phosphoric acid production process) in Aqaba, Jordan.

Many mineral production processes suffer from the generation of large amounts of mineral byproducts or wastes. Phosphogypsum is one of these mineral wastes that is accumulated in large amounts all over the world. The world production of phosphogypsum is estimated to be 100-280 million tons a year that are traditionally stacked in piles. Several impact studies for the stacking of phosphogypsum show that this practice is an economical and an ecological burden that in need to be relieved [Reijnders, 2007].

Phosphogypsum (PG) is a by product of the phosphoric acid wet production process. PG is produced by reacting phosphate rock (raw material) with sulfuric acid according to the following chemical reaction.



The phosphogypsum produced appears as dihydrate (CaSO₄·2H₂O) or hemihydrate (CaSO₄·1/2H₂O) form,

depending on the specific processing conditions. This by product is filtered from the produced phosphoric acid aqueous solution and then transferred as a wet cake (approximately 20% surface water) to open air storage known as stacks [Conklin, 1992]. Five PG tons is produced per ton of phosphoric acid. PG holding is growing at 150-200 million tons per year at present with prospect of 250 M tons per year by 2015. 5.6 to 7.0 billion tons of PG produced in lifetime of phosphoric acid industry to date [Conklin, 1992]. This huge amount accumulated over years need to be reused.

The most common practice for managing phosphogypsum is currently to stack it, which requires careful management in order to avoid unwanted environmental impacts. Stacks of PG are identified in some 52 countries, including Jordan [Hilton, 2010]. PG problem is growing over years and this by product is in need to be utilized [IFA, 2011].

1.1 Utilization of PG

Phosphogypsum has been widely tested and piloted for using it for different purposes. Plasterboard, plaster and cement are the main possibilities. Gypsum and phosphogypsum are also used in large quantities as a soil additive. Gypsum is an excellent and economic road-making material, and large quantities of phosphogypsum could be used for this purpose. PG can be used for the production of sulfuric acid and manufacture of ammonium sulphate [Chandra, 1997]. Phosphogypsum is progressively considered as an asset more than a waste, but the impurities that it contains hinders the widespread of its uses.

1.2 The need to Utilize PG in Jordanian cement Industry

In the last few years, the volume of cement industry is significantly expanded in Jordan. Jordan Lafarge Cement Factories Co. (JCFC), which had been the sole producer and distributor of cement in Jordan, had to deal with the entry of new cement producers to Jordan's cement market in 2009. State-owned Arab Company for White Cement Industry produced 130,000 metric tons per year (t/yr) of white cement. Northern Cement Co.'s plant at Muwaqar, which is located near Amman, began production in September 2009; it had an initial capacity of 1 million metric tons per year (Mt/yr). Arabian Cement Co. of Saudi Arabia moved forward with installing a new cement plant at Al Qatraneh near the city of Karak. The 2 Mt/yr-capacity started production in 2010. A second cement plant at Qatrana was being constructed by Modern Cement and Mining Co. The plant would have a production capacity of 1.2 Mt/yr of clinker and began producing Portland cement, pozzolanic cement, and sulfate-resistant cement in 2011 [Mowafa Taib, 2011]. This big expansion in cement production will increase the demand for gypsum as an additive. In addition most of the new cement factories are in the southern part of Jordan, and they are closer to the phosphogypsum stacking location in Alshidya and

Aqaba. This will be an incentive and will make it more attractive for using local PG resource in the nearby local cement industry. But the challenge that is everlasting is to invent an environmental friendly, low-cost and effective method to clean PG from its impurities to be ready for use in cement industry or other uses.

1.3 Impurities in Phosphogypsum

PG contains small amounts of many of the mineral impurities that accompany phosphate rock or produced in the phosphoric acid production process. Satish Chandra, 1997, in his book, classified the PG impurities into two groups: (1) external materials which do not react with the sulfuric acid and comes with the phosphate ore being processed, (2) materials that result from the ore processing (reaction with sulfuric acid) including excess reactants. The first group of impurities will be affected by the quality of the phosphate ore that is being processed in the phosphoric acid reactor, but the second group will be affected by the reaction and process conditions in the phosphoric acid manufacturing process [Chandra, 1997].

Also these impurities can be classified by looking at these impurities from the perspective of their ability to be water washed or their participation in later reactions when mixed as an additive to other materials (such as cement). The water solubility will determine how much these impurities will be easier to be washed by water and also will determine its effect on the properties of the mixtures, such as cement, that it is intended to be added to. Therefore, the most convenient way is to classify these impurities based on water solubility. Manjit Singh, 2003 classified phosphogypsum impurities based on the solubility in water (soluble or insoluble) and also based on its location in the phosphogypsum mixture (Present inside the PG clusters or in PG solid solution (co-crystalized)) [Chandra, 1997]. All aforementioned classifications will be helpful because each will help to look at the impurities from a different perspective that will serve in seeking an efficient, low cost and environmental friendly method to clean PG from its impurities that constraints its use.

Phosphorous and Fluor-containing compounds are the most important group of impurities that are present in phosphogypsum, in addition to organic compounds which are determined as P_2O_5 , F and "organic matter" respectively. The residues of phosphorous containing compounds are phosphoric acid, $Ca_3(PO_4)_2$, $Ca(H_2PO_4)_2$, and $CaHPO_4 \cdot 2H_2O$. The flour-containing compounds are NaF, Na_2SiF_6 , Na_2AlF_6 , Na_2FeF_6 , and CaF_2 . The organic matter in phosphogypsum is composed of aliphatic compounds of carbonic acids, amines and ketones with an average of 10-30 carbon atoms [Chandra, 1997]. The phosphorous containing compounds available in phosphogypsum from different sources are listed in Table 1.

1.4 Constraints limiting the use of PG in the manufacture of cement

The main difference between natural gypsum and phosphogypsum is the existence and the concentration of certain impurities available in each of them. Gypsum is mined from the ground and contains small amount of impurities, but PG is accompanied by many impurities that come from the phosphate ore or formed by the reaction with the sulfuric acid in the wet phosphoric acid production process. Therefore, PG is not readily available to be used for other purposes unless these impurities are reduced to the required accepted limits.

In the United States, the environmental authorities hesitate to permit PG use in view of naturally occurring radon emissions from phosphogypsum. Their suspicions have led other countries to adopt a wait-and-see attitude despite the fact that mineral phosphates, phosphate fertilizers, phosphogypsum and phosphoric acid plant effluents generally have lower radioactivities than the international limit value prescribed by the European Atomic Energy Community (EURATOM). In any case, only those materials meeting such safety requirements would be used. Pilot studies have demonstrated the very low degree of risk and it is likely that re-use of phosphogypsum will become more common in the near future [IFA 2011]. These regulations will be the constraints that will control the design of any process for cleaning PG in order to be ready for reuse.

Table 1: Phosphorous containing impurities occurring in PG

Chemical Compound	PG1**	PG1*	PG3*	PG4*
Water soluble P2O5	0.16 (17.7%)	0.36 (39.1%)	0.24 (51.1%)	0.25 (24.5%)
Co-crystalline P2O5	0.67 (74.4.7%)	0.50 (54.3%)	0.20 (42.5.7%)	0.51 (50.0%)
Water insoluble P2O5	0.07 (7.7%)	0.06 (6.5%)	0.03 (6.4%)	0.26 (24.5%)
P2O5 (total)	0.90	0.92	0.47	1.02

* Chandra, 1997, PG1= Industrial complex, Aqaba Jordan, PG2= morocco, PG3= Florida, USA, PG4= India

** This Study (Arab Phosphate Co., Industrial Complex, Aqaba, Jordan)

1.5 Treatment of PG for the use in cement industry

Reijnders, 1997, reviewed in his paper the available approaches to reduce the concentrations of minor components in phosphogypsum under the following two groups: (1) Methods based on source reduction, and (2) Methods based on separation technology. Tayibi, 2009, reviewed and classified the methods for treating phosphogypsum under two categories: (1) Methods involving chemical and physical treatment, (2) Methods involving thermal treatment [Tayibi, 2009]. Using chemical and physical treatments, researchers investigated different methods to make PG suitable for later applications, such as washing, wet

sieving, neutralization with lime, and treatment with a mixture of sulfuric acid and silica or hot aqueous ammonium sulphate solutions.

The focus in this short review will be on using separation technology methods for the reduction of P₂O₅ by chemical and physical methods. The PG purification process employed by Al-Jabbari et al. (1988) consists of washing PG with water, sieving it through a 100 μm sieve, and calcining it at different temperatures (low and high). Olmez and Erdem (1989), studied the removal of impurities using several methods based on the neutralization of water-soluble impurities in PG with water and lime milk Ca(OH)₂, the removal of P₂O₅ substituted in the gypsum crystal lattice, and a calcining process. Manjit et al. (1993) tested an aqueous ammonium hydroxide solution (5–20%) to reduce phosphate and fluoride contents in PG before its use in the cement industry. Manjit et al. (1996) another purification process based on wet sieving and hydrocyclone trials were investigated. Manjit (2002) shook PG samples with 2–5% aqueous citric acid solution instead of ammonium hydroxide solution for 15–25 min at 30 C. The impurities were removed as water-soluble compounds: H₃PO₄, Na₃(C₆H₅O₇)₂, HF, H₃SiF₆, H₃AlF₆ and H₃FeF₆. The optimum aqueous citric acid solution concentration was 3–4%. Potgieter et al. (2003), studied the effect of chemical and physical treatments of PG incorporated in clinker to obtain cement with a SO₃ content of 2.3%. Two PG samples (one dried directly at 50 C and the other washed with water for 10 min and then dried at the same temperature) were subjected to different treatments using acidic and basic additions (HCl, H₂SO₄ and NH₄OH) during the washing stage. To reduce the levels of metal salts, phosphates and radioactive compounds, Klover and Somin (2004), focused their work on the use of a topochemical reaction with an unspecified agent, solubilizing phosphates and radioactive and other metal salts at temperatures between 140 and 350 °C. They claimed that the 226-Ra content of PG can be decreased by a factor of 20–50% and the P₂O₅ content by a factor of 16–28%. [Tayibi, 2009]

1.6 Private cost, tightening environmental regulations, and competition with virgin materials

Reijnders, 1997, in his literature survey, point to a very crucial issue when dealing the matter of cost in cleaning phosphogypsum from its impurities. The author stressed that the 'clean up' of mineral wastes often leads to increased private cost (the cost for the operation of a process). Lower private costs of competing production processes have led to discontinuation of processes producing phosphogypsum with reduced levels of minor components. It is used here in contradistinction to social cost (costs to society as a whole and includes costs associated with workplace intoxication and with leaching as well as costs related to the future scarcity of

resources). There are, however, cases that private cost is not increased by a 'clean up' process. There are regulatory interventions in some countries that require the application of extraction. Tightening environmental and work place regulations and higher waste disposal costs may further reduce the scope for current practices. Increased prices for competing virgin minerals may also make use of cleaner secondary minerals more attractive. [Reijnders, 1997]

1.7 Developing efficient, low cost, competitive, environmental friendly process to beneficiate PG

Based on the above literature review, it is found that

1. Jordan is having a challenge of converting PG, that is accumulated every year and threatening the environment, into a raw material for an expanding local cement industry.
2. PG has residues of contaminants that hinder its widespread reuse and there is a continuous effort from researches and industry to develop a new ways to beneficiate PG.
3. Most of the reported research is focusing on the reuse step without developing a deep understanding of the washing/leaching process.
4. Beneficiation process need to be analyzed and fully understood within the perspective of developing efficient, low cost, competitive, environmental friendly process to beneficiate PG, namely undergoing a basic research for the cleaning process within the perspective of process development.

The objective of this research is to investigate the washing/leaching beneficiation process for the reduction of P_2O_5 using two strong acid solutions. This investigation should reveal clear picture of the dynamics and the interactions between the basic components (players) in the process. This research is process oriented in terms of aiming to study the beneficiation process within the perspective of developing efficient, low cost, competitive, environmental friendly process to beneficiate PG

1.8 Process oriented research to get deeper understanding of the PG impurity leaching process

To be able to understand the leaching or washing process of impurities from PG, the process need to be analyzed to show clearly the role of the main components in achieving the cleaning of the impurity. There four main components (players) in the digestion or leaching (washing) process of PG impurities are (as illustrated in Figure 1):

1. **PG powder ($CaSO_4$):** Type of hydration of PG and its Characteristics. $CaSO_4$ constitutes 90-95% of the whole PG dry mixture.
2. **Target impurity** (P_2O_5 , F, and Radioactive elements): The impurity characteristics will play a major role in its leaching behavior.

3. **Solvent type** (usually water): Solvent used to wash or leach a specific impurity.
4. **Solute type** Solute added to the solvent to enhance the leaching/washing process of a specific impurity.

Factors affecting washing/leaching process can be grouped as (1) factors related to the four components of the washing/leaching process, and (2) factors that are related to the environmental conditions and operating and design parameters that surround and play a role in the interaction between these four components. Figure 2 shows schematically the factors these two groups of factors. This Identification of the factors affecting the washing/leaching process will be the first step in screening and optimizing these factors using factorial design methodologies in later stages.

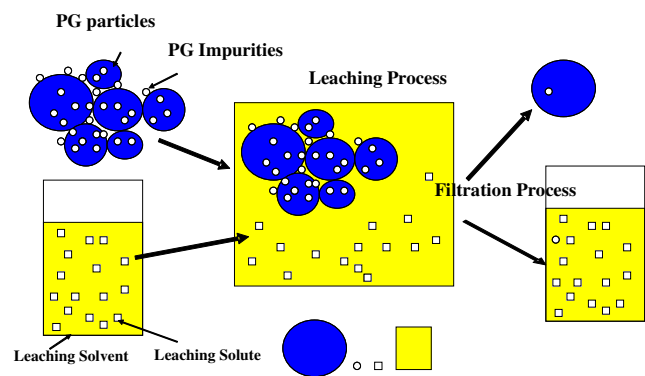


Figure 1: PG Washing/ Leaching (Digestion) Process

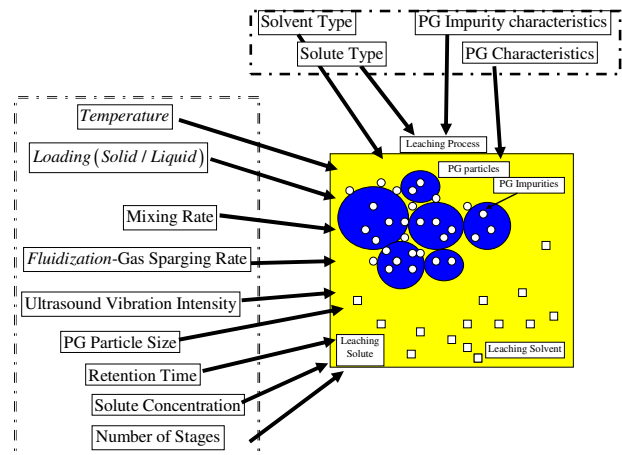


Figure 2: Process Parameters affecting the PG washing/Leaching Process

1.9 Factorial Design methodology

Experimental designs are plans for determining how one or more tests are to be run. They are used to enable the experimenter to generate a reliable conclusion to hypotheses being tested in an effective way. In selecting an appropriate test strategy, the test costs, resources available, and likely outcomes are taken into consideration when determining the test objectives.

Dr. Douglas Montgomery states that all experiments are considered as Design of Experiments, but with variation in the quality of planning that some experiments have (Montgomery, 1991). Test strategies are widespread over wide spectrum. They range from trial-and-error testing through one- factor or variable-at-a-time testing (OVAAT) to what is more commonly considered Design of Experiments (DOE). Experimental Design (ED) is implemented through a pre-planned test arrays and statistical analysis techniques capable of distinguishing between main effects, interaction effects, and experimental error. While there are appropriate situations for any type of test strategy, only DOE allows measurement of interaction effects needed to obtain high levels of complex process understanding.

The study of input variables that is controlling the performance of a process based on the univariate procedure is tedious and time-consuming. The main disadvantage of this procedure is the difficulty of determining the global optimum conditions. Part of this difficulty is due to neglecting of interactions among all parameters. More importantly, varying the level of input parameters in univariate procedure would result in different local optimum conditions.

2. Experimental

2.1 Raw Materials

Phosphogypsum samples were collected from Arab Phosphate Co. /Industrial Complex, Aqaba, Jordan. The samples were produced by the dihydrate process. This sample was analyzed for chemical constituents and compared with the composition of PG from other sources as listed in Table 2

2.2 Chemicals

1. Reagent grade sulfuric Acid
2. Reagent grade nitric Acid
3. Local Tap water.

2.3 Batch purification of phosphogypsum

The Phosphogypsum samples were thoroughly shaken with aqueous Acid solution in a mechanical shaker for 30 minutes at 25 °C, filtered through a Buckner funnel and then dried for 1 hr in an oven at 60 °C. Batch purification experiments were conducted in 50 ml polyethylene bottles.

3. Results and Discussion

3.1 Screen analysis

The crystallization or precipitation process of PG during the reaction of phosphate ore with sulfuric acid (the reaction of wet phosphoric acid manufacturing process) result in a wide spectrum of grain sizes that are mostly fine (less than 75 μm). A number of samples of PG samples were dried in the oven at 60 °C for one hour

and then screened as shown in Figure 3 . This screen analysis shows that more than 80% of PG samples are less than 75 μm .

Table 2: Chemical compositions of Jordanian phosphogypsum in comparison to other sources

Chemical Compound	PG1*	PG2**	PG3**	PG4**
H ₂ O	20	19.5	20.0	18.0
SO ₂	47.6	43.2	44.0	43.6
CaO	32.60	32.2	31.0	32.0
MgO	0.01	0.01	--	0.40
Al ₂ O ₃ + Fe ₂ O ₃	0.173	0.27	0.14	1.82
SiO ₂	1.46	1.51	2.40	1.64
Na ₂ O	0.15	0.47	0.18	0.36
P ₂ O ₅ (total)	1.07	1.01	0.78	1.03
F (total)	0.61	1.67	0.57	0.76
Organic Matter	0.14	0.08	0.24	0.26

* In this study PG1= Arab Phosphate Co., Industrial complex, Aqaba Jordan

** Chandra, 1997, PG2= morocco, PG3= Florida, USA, PG4= India

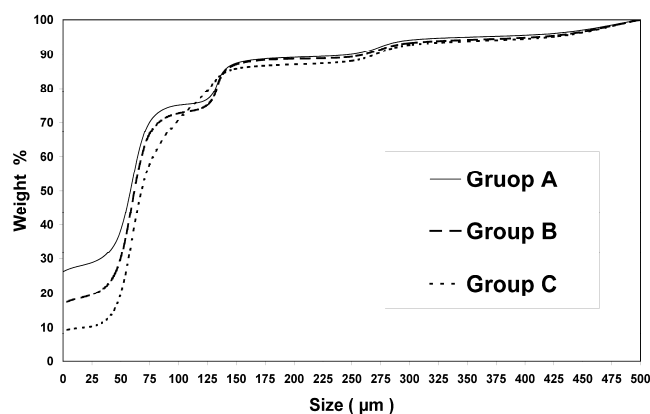


Figure 3: Screen analysis for three different samples of Jordanian PG, Arab Phosphate Co., Chemical Complex, Aqaba, Jordan

3.2 Experimental factorial design

Particle size (X_1), acid concentration (X_2), loading (S/L ratio) (X_3) and Number of Washings (X_4) were chosen as independent input variables and the amount of ion P₂O₅% concentration as dependent output response variable. Since the factorial design involves four independent variables at two levels (low designated as - and high designated as +), 2⁴ full-factorial design with five center points (designated as 0) has been applied. To quantify the variability in the collected data, the center point run was repeated five times. **Table 3** and **Table 4** show the complete design matrix of experiments and the results obtained for P₂O₅% concentration using sulfuric and nitric acidic solution respectively.

3.3 Factorial Design Analysis for P₂O₅ reduction in PG

The study of the input variables that affect a process based on a univariate procedure is tedious and time-consuming. The main disadvantage of one variable at a

time (OVAAT) methodology is the difficulty of determining the global optimum conditions. Part of this difficulty is due to neglecting interactions among all parameters. More importantly, varying the level of input parameters in a univariate procedure would result in different local optimum conditions. To overcome these difficulties and disadvantages, an effective full factorial experimental design methodology was used to investigate the effects and interactions of some input parameters on the P_2O_5 leaching/washing process.

Table 3: Experimental design matrix and results for P_2O_5 wt% in treated PG samples using Sulfuric Acid

Run	Independent variables (levels)				P_2O_5 %
	X1	X2	X3	X4	
1	125 (-1)	0.5 (-1)	0.05 (-1)	1 (-1)	0.417
2	500 (+1)	0.5 (-1)	0.05 (-1)	1 (-1)	0.711
3	125 (-1)	1.5 (+1)	0.05 (-1)	1 (-1)	0.489
4	500 (+1)	1.5 (+1)	0.05 (-1)	1 (-1)	0.501
5	125 (-1)	0.5 (-1)	0.15 (+1)	1 (-1)	0.392
6	500 (+1)	0.5 (-1)	0.15 (+1)	1 (-1)	0.644
7	125 (-1)	1.5 (+1)	0.15 (+1)	1 (-1)	0.394
8	500 (+1)	1.5 (+1)	0.15 (+1)	1 (-1)	0.515
9	125 (-1)	0.5 (-1)	0.05 (-1)	5 (+1)	0.380
10	500 (+1)	0.5 (-1)	0.05 (-1)	5 (+1)	0.107
11	125 (-1)	1.5 (+1)	0.05 (-1)	5 (+1)	0.263
12	500 (+1)	1.5 (+1)	0.05 (-1)	5 (+1)	0.034
13	125 (-1)	0.5 (-1)	0.15 (+1)	5 (+1)	0.323
14	500 (+1)	0.5 (-1)	0.15 (+1)	5 (+1)	0.505
15	125 (-1)	1.5 (+1)	0.15 (+1)	5 (+1)	0.247
16	500 (+1)	1.5 (+1)	0.15 (+1)	5 (+1)	0.353
17	250 (0)	1 (0)	0.1 (0)	3 (0)	0.275
18	250 (0)	1 (0)	0.1 (0)	3 (0)	0.287
19	250 (0)	1 (0)	0.1 (0)	3 (0)	0.273
20	250 (0)	1 (0)	0.1 (0)	3 (0)	0.260
21	250 (0)	1 (0)	0.1 (0)	3 (0)	0.276

X1= Size (micrometer), X2= Acid Concentration (Wt %), X3=gram of PG/ gram solution, X4= number of washings, P_2O_5 %= Wt% (g P_2O_5 /g Solid Sample)

Table 4: Experimental design matrix and results for P_2O_5 wt% in treated PG samples using Nitric Acid

Run	Independent Variables (levels)				P_2O_5 %
	X1	X2	X3	X4	
1	125 (-1)	1 (-1)	0.2 (-1)	1 (-1)	0.755
2	500 (+1)	1 (-1)	0.2 (-1)	1 (-1)	0.962
3	125 (-1)	5 (+1)	0.2 (-1)	1 (-1)	0.716
4	500 (+1)	5 (+1)	0.2 (-1)	1 (-1)	0.613
5	125 (-1)	1 (-1)	0.6 (+1)	1 (-1)	1.190
6	500 (+1)	1 (-1)	0.6 (+1)	1 (-1)	1.240
7	125 (-1)	5 (+1)	0.6 (+1)	1 (-1)	1.180
8	500 (+1)	5 (+1)	0.6 (+1)	1 (-1)	1.060
9	125 (-1)	1 (-1)	0.2 (-1)	5 (+1)	0.145
10	500 (+1)	1 (-1)	0.2 (-1)	5 (+1)	0.144
11	125 (-1)	5 (+1)	0.2 (-1)	5 (+1)	0.139
12	500 (+1)	5 (+1)	0.2 (-1)	5 (+1)	0.118
13	125 (-1)	1 (-1)	0.6 (+1)	5 (+1)	0.333
14	500 (+1)	1 (-1)	0.6 (+1)	5 (+1)	0.550
15	125 (-1)	5 (+1)	0.6 (+1)	5 (+1)	0.293
16	500 (+1)	5 (+1)	0.6 (+1)	5 (+1)	0.137
17	250 (0)	3 (0)	0.4 (0)	3 (0)	0.274
18	250 (0)	3 (0)	0.4 (0)	3 (0)	0.255
19	250 (0)	3 (0)	0.4 (0)	3 (0)	0.266
20	250 (0)	3 (0)	0.4 (0)	3 (0)	0.256
21	250 (0)	3 (0)	0.4 (0)	3 (0)	0.291

X1= Size (micrometer), X2=Acid Concentration (Wt %), X3=gram of PG/ gram solution, X4=Number of washings, P_2O_5 %= Wt% (g P_2O_5 /g Solid Sample)

The most important input parameters that affect the P_2O_5 leaching/washing process are the PG particle size,

acid concentration, loading (mass of PG/mass of solution) and number of washings. As a part of applying full factorial design experimental methodology, P_2O_5 percentage is chosen as the response output variable, and PG particle size (X_1), acid concentration (X_2), loading (mass of PG/mass of solution) (X_3) and number of washings of the solution (X_4) as the input parameters. These choices enabled us to determine the main effects, and the cross parameters interaction effects. These effects are regressed by a linear model with coefficients of statistical significance indicated by the probability (p-value) and the standard deviation. Based on this methodology, a full 2^4 experimental factorial design was constructed (Table 3 and Table 4) and statistically analyzed (Table 5 and Table 6) for the treatment of P_2O_5 by sulfuric and nitric acid solution, respectively.

Table 5: Full 2^4 factorial design for P_2O_5 wt% in treated PG samples using Sulfuric Acid

Term	Effect	Coefficient	SE Coeff.	T	P
Constant		0.3922	0.002407	162.93	0
X1	0.0581	0.0291	0.002407	12.07	0
X2	-0.0854	-0.0427	0.002407	-17.73	0
X3	0.0589	0.0294	0.002407	12.23	0
X4	-0.2314	-0.1157	0.002407	-48.06	0
X1×X2	-0.0556	-0.0278	0.002407	-11.55	0
X1×X3	0.1071	0.0536	0.002407	22.25	0
X1×X4	-0.1116	-0.0558	0.002407	-23.19	0
X2×X3	-0.0034	-0.0017	0.002407	-0.7	0.522
X2×X4	-0.0191	-0.0096	0.002407	-3.97	0.017
X3×X4	0.1021	0.0511	0.002407	21.21	0
X1×X2×X3	0.0039	0.0019	0.002407	0.8	0.466
X1×X2×X4	0.0476	0.0238	0.002407	9.89	0.001
X1×X3×X4	0.0904	0.0452	0.002407	18.77	0
X2×X3×X4	-0.0061	-0.0031	0.002407	-1.27	0.272
X1×X2×X3×X4	-0.0339	-0.0169	0.002407	-7.04	0.002

X1= Size (micrometer), X2=Acid Concentration (Wt %), X3=gram of PG/ gram solution, X4=Number of washings, P_2O_5 %= Wt% (g P_2O_5 /g Solid Sample)

3.3.1 P_2O_5 reduction using sulfuric Acid

Full ANOVA analysis is applied to the 2^4 full factorial design of P_2O_5 reduction by sulfuric acid solution, as shown in Table 5. The ANOVA analysis results are plotted in the form of Pareto plot to show the significance of each calculated effects (Figure 4).

Main effects

The significance of model coefficients are determined based on the value of probability p. Results presented in Table 5 show that PG particle size (X_1), acid concentration (X_2), and Loading (mass of PG/mass of solution) (X_3) and number of washings of the solution (X_4) were significant within the 95% confidence interval ($p \leq 0.05$). But the relative amount the number of washings effect (X_4) is more than three times the magnitude of the other main effects. This shows the

relative importance of renewing the driving force for the leaching/washing process in enhancing the effectiveness of P_2O_5 reduction as shown in the main effects plots (Figure 5).

The main effect plots (Figure 5) shows a behavior for the main input parameters that in agreement with our expectation and our common sense. PG particle size (X_1) effect plot shows that the increase PG particle size is lowering the ability of the solution to wash P_2O_5 . This behavior is due to mass transfer limitations that get to the picture as the size of the PG particle get larger in size (Figure 5).

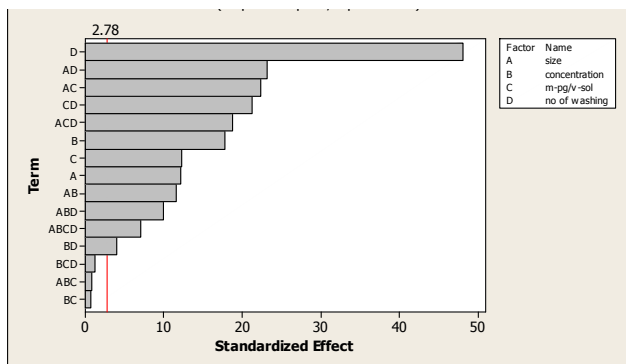


Figure 4: Puerto chart for sulfuric acid treatment 2^4 full factorial design experiments

Acid concentration (X_2) effect plot shows that the increase in sulfuric acid concentration is enhancing the ability of the solution to wash P_2O_5 more effectively. This behavior is due to the ability of sulfuric acid to react with the remains of unreacted phosphate ore and with the other phosphatic impurities by convert them into a soluble and washable form in aqueous acidic solution (Figure 5).

Loading (mass of PG/mass of solution) (X_3) effect plot shows that the increase in PG loading of sulfuric acid solution is lowering the ability of the solution to wash P_2O_5 . This behavior is a result of adding more PG load per kg of acidic solution, namely adding more impurities duty to be cleaned, and normally result in weakening the acidic solution ability to clean these impurities (Figure 5).

The number of washings of the solution (X_4) effect plot shows that increasing the number of washings has the most pronounced effect on enhancing the washing/leaching P_2O_5 process. Also as mentioned before, the relative amount of this effect is more than threefold the other three main effects. This reveals the importance of renewing the driving force for the leaching washing process in enhancing P_2O_5 reduction process as shown in the main effects plots (Figure 5).

Interaction effects

One of main advantages of factorial design methodologies is their ability to reveal the interaction between the input parameters under study. The focus in this study will be on the two factor interactions. The

higher level of interactions (three and four factor interaction) is neglected because it has less practical implications.

The two factor interaction plots for the study of P_2O_5 reduction by sulfuric acid solution is shown in Figure 6. These plots (Figure 6) shows that the PG particle size (X_1) has a significant interaction with acid concentration (X_2), loading (mass of PG/mass of solution) (X_3) and number of washings (X_4) within the 95% confidence interval ($p \leq 0.05$). The loading (X_3) also has a significant interaction with number of washings (X_4). But on the contrary, acid concentration has no significant interaction with the loading (X_3) and the number of washings (X_4). These interaction results show that most of the input parameters are mutually interacted. Such interactions would not be revealed if experiments were carried out using univariate procedure.

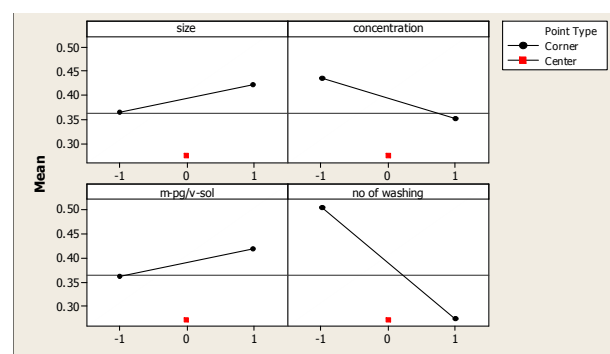


Figure 5: Main effect plots for sulfuric acid treatment 2^4 full factorial design experiment

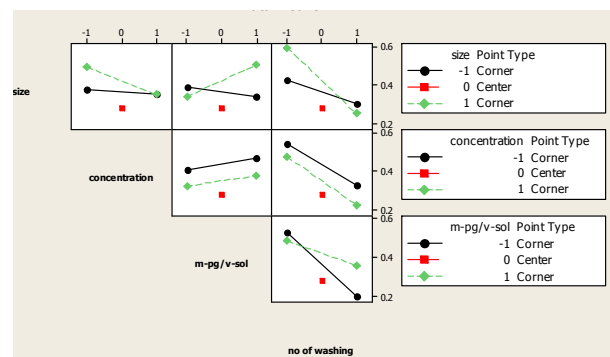


Figure 6: Interaction effects for sulfuric acid treatment 2^4 full factorial design experiment

Fitting into a model

The model presented by Eqn. (2) was fitted to the experimental data shown in Table 5. Based on the above discussion, the insignificant coefficients and their terms were deleted from the general fitting model (Eqn. 2). This results in the following refined fitting model for the studied system in term of coded parameters.

$$P_2O_5 \% (\text{Sulphuric Acid treatment}) = 0.3922 + 0.0581X_1 - 0.0854X_2 + 0.0589X_3 - 0.2314X_4 - 0.0556X_1X_2 + 0.1071X_1X_3 - 0.1116X_1X_4 - 0.0191X_2X_4 + 0.1021X_3X_4 \quad (2)$$

The strong interaction between input parameters shows a significant curvature in the P_2O_5 3D plot with

loading and number of washing. This optimum conditions can be estimated to be at the center point of loading and number of washings (loading = 0.15 g pg/ g sol, number of washing= 3)

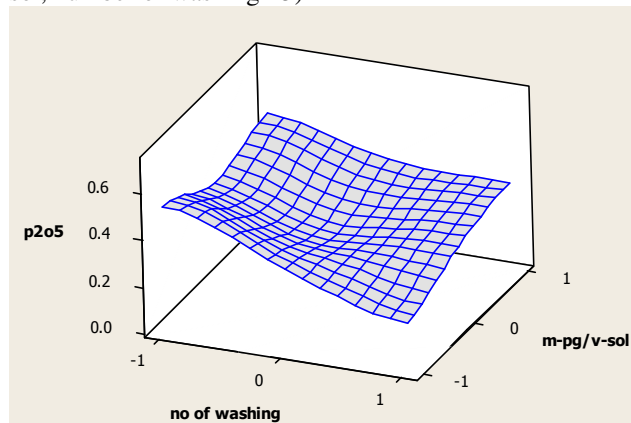


Figure 7: 3D plot for sulfuric acid treatment 2^4 full factorial design experiment

Table 6: Full 2^4 factorial design for P₂O₅ wt% in treated PG samples using Nitric Acid

Term	Effect	Coefficient	SE Coef	T	P
Constant		0.5984	0.003711	161.28	0
X1	0.0091	0.0046	0.003711	1.23	0.286
X2	-0.1329	-0.0664	0.003711	-17.9	0
X3	0.2989	0.1494	0.003711	40.27	0
X4	-0.7321	-0.3661	0.003711	-98.65	0
X1×X2	-0.1091	-0.0546	0.003711	-14.7	0
X1×X3	-0.0114	-0.0057	0.003711	-1.53	0.2
X1×X4	0.0006	0.0003	0.003711	0.08	0.937
X2×X3	-0.0279	-0.0139	0.003711	-3.76	0.02
X2×X4	0.0116	0.0058	0.003711	1.57	0.192
X3×X4	-0.1071	-0.0536	0.003711	-14.43	0
X1×X2×X3	-0.0266	-0.0133	0.003711	-3.59	0.023
X1×X2×X4	0.0109	0.0054	0.003711	1.47	0.217
X1×X3×X4	0.0321	0.0161	0.003711	4.33	0.012
X2×X3×X4	-0.0774	-0.0387	0.003711	-10.43	0
X1×X2×X3×X4	-0.0616	-0.0308	0.003711	-8.3	0.001

X1= Size (micrometer), X2=Acid Concentration (Wt %), X3=gram of PG/ gram solution, X4=Number of washings, P₂O₅ %= Wt% (g P₂O₅/g Solid Sample)

3.3.2 P₂O₅ reduction using Nitric Acid

Full ANOVA analysis using Minitab 15 statistical software is also accomplished to the 2^4 full factorial design of P₂O₅ reduction using nitric acid solution (results listed in Table 6). The ANOVA analysis results are plotted in the form of Pareto plots to show the significance of each of the main and the interaction effects (Figure 8).

Main effects

The significance of model coefficients are determined based on the value of probability p. Results

presented in Table 6 and plotted in Figure 9 show that acid concentration (X₂), loading (mass of PG/mass of solution) (X₃) and number of washings (X₄) were significant within the 95% confidence interval (p<0.05). But, the nitric acid treatment data shows that PG particle size (X₁) has no significant effect on the reduction of P₂O₅. In a similar behavior to the sulfuric acid treatment, the relative amount of the effect of the number of washings (X₄) is significantly higher than the magnitude of other main effects. This confirms the importance of renewing the driving force for the washing/leaching process of P₂O₅ as shown in the main effects plots (Figure 9).

The main effect plots of the nitric acid treatment factorial design experiments (Figure 9) shows a similar behavior to the sulfuric acid treatment factorial design experiments except for PG particle size (X₁). Acid concentration (X₂) effect plot shows that the increase sulfuric acid concentration is enhancing the ability of the solution to wash P₂O₅. This behavior is confirming the ability of nitric acid to react with the remains of unreacted phosphate ore and also reacting with the other phosphatic impurities by convert them into a soluble and washable form in aqueous acidic solution (Figure 9).

Loading (mass of PG/mass of solution) (X₃) effect plot shows also that the increase nitric acid loading is lowering the ability of the solution to wash P₂O₅ (Figure 9).

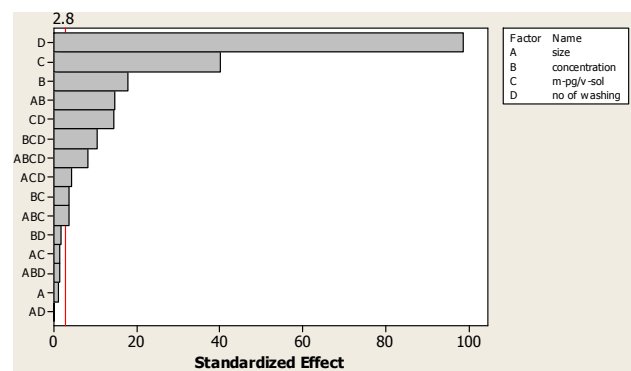


Figure 8: Pareto plot for Nitric acid treatment 2^4 full factorial design experiment

The number of washings of the solution (X₄) effect plot shows that increasing the number of washings has the most pronounced effect on enhancing the washing/leaching P₂O₅ process. Also as mentioned before, the relative amount of the effect of the number of washings of the solution (X₄) is more than triple the other three main effects. This reveals the importance of renewing the driving force for the leaching washing process in enhancing the washing/leaching process of P₂O₅ as shown in the main effects plots (Figure 9).

Interaction effects

The interaction focus in this study will be on the two factor interaction effects and not on the higher lever of interaction (three and four factor interaction) that is

neglected due to its less practical implications. The two factor interaction plots for the study of P_2O_5 reduction by nitric acid solution is shown in Figure 10. The interaction plots in general shows less pronounced effects than that of sulfuric acid system. The two factor interaction plots (Figure 10) shows that the PG particle size (X_1) has a significant interaction with acid concentration (X_2). Nitric acid concentration (X_2) shows also a significant interaction effect with loading (X_3). These interaction results show that most of the input parameters are not mutually interacted.

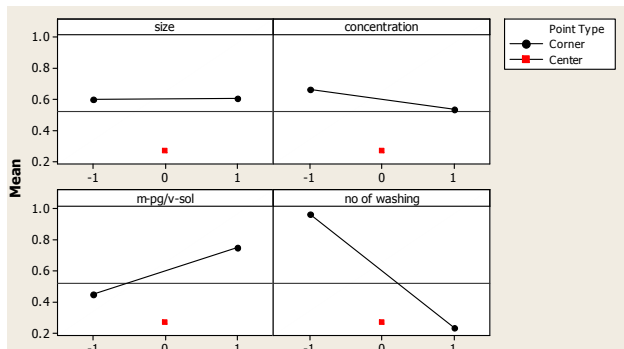


Figure 9: Main effect plots for Nitric acid treatment 2^4 full factorial design experiment

Fitting into a model

The model presented by Eqn. (2) was fitted to the experimental data shown in Table 6. Based on the above discussion, the insignificant coefficients and their terms were deleted from the general fitting model (Eqn. 2). This results in the following refined fitting model for the nitric acid treatment systems in term of coded parameters.

$$P_2O_5\% \text{ (Nitric Acid treatment)} = 0.5984 - 0.1329X_2 + 0.2989X_3 - 0.7321X_4 - 0.1091X_1X_2 - 0.1071X_3X_4 \quad (3)$$

The mild behavior of the interaction between input parameters shows a significant curvature in the P_2O_5 3D plot with Loading and number of washing shown in Figure 11. This optimum conditions can be estimated to be at the center point of loading and number of washings (loading = 0.4 g pg/ g sol, number of washing= 3)

4. Conclusion

Future engineers is facing a pressing and daunting challenge to alleviate the environmental effects of the accumulated by products by inventing new ways to recycle and reuse. Millions of tons of PG is stacked in the environment every year and is progressively considered as an asset more than an environmental burden. Jordan cement industry is largely expanded in the last ten years and is considered as an opening to reuse the huge amount of Jordanian PG that is stacked every year. The impurities that PG contains hinder its use as an additive to the cement industry which is pushing towards

developing a low cost and effect process to clean PG in order to be ready as a cement additive. Many researches used a number of physical, chemical and thermal methods to reduce P_2O_5 content in PG, but all of these studies are univariate and did not go deep in understanding the process of washing/leaching of P_2O_5 .

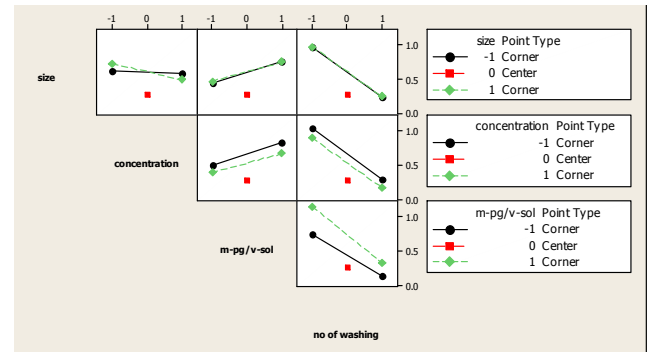


Figure 10: Interaction plot for Nitric acid treatment 2^4 full factorial design experiment

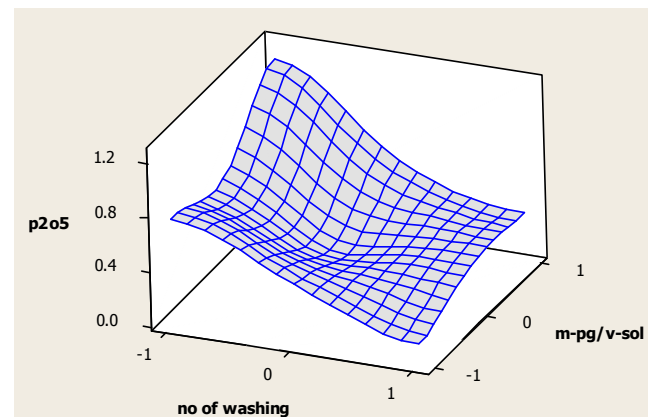


Figure 11: 3d plot for Nitric acid treatment 2^4 full factorial design experiment

In this study, a 2^4 full factorial methodology is designed to study the effect of particle size, acid concentration, loading and number of washing on P_2O_5 reduction using sulfuric and nitric acid solutions. Factorial design analysis helped us to get more insight on the significance of the main effects and revealed the interaction effects between the input parameters.

Sulfuric and nitric acid treatment results indicate clearly the importance of the number of washing on the reduction of P_2O_5 content. This emphasized the importance of renewing the driving force on the washing leaching P_2O_5 reduction process.

In this research it is tried to mimic what we already happened in real process by sending the solids to the next washing step without rinsing, because rinsing is considered as an extra step in terms of subjecting the samples to renewed driving force.

It is found that the optimum conditions for Sulfuric acid treatment is estimated to be of loading equal to 0.15 g PG/ g sol and three washings. The

optimum conditions for nitric acid treatment are estimated to be loading of 0.4 g PG/ g sol and three washings.

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