



Application of Full Factorial Design to Improve Phosphogypsum Conversion Process to Calcium Carbonate

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Abstract

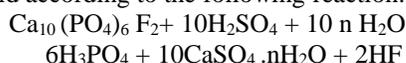
The utilization of phosphogypsum (PG) as a raw material for the production of valuable products is interesting. In this regard, the full factorial design has been performed to improve the conversion process of phosphogypsum to calcium carbonate using sodium carbonate. Four factors were taken into consideration in the experimental planning: time, solid/ liquid ratio, sodium carbonate concentration, and temperature. The analysis of variance (ANOVA) has been used to determine the main effects and interactions between the studied factors. The optimum conditions have been determined as, sodium carbonate concentration of 30 %, reaction time of 10 min and solid/ liquid ratio, g/ ml of 1:2. Under these optimum conditions, the phosphogypsum conversion to carbonate efficiency performance is 95.2 %.

Keywords: Full factorial design, optimization, phosphogypsum, calcium carbonate

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1. INTRODUCTION

Phosphogypsum (PG) is a waste material which produced as a byproduct during the commercial manufacture of phosphoric acid by the wet process [1]. In this process, concentrated phosphate rock is treated with concentrated sulfuric acid according to the following reaction:



The produced phosphogypsum can exist in one of the following forms: dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), hemihydrate ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$), or the anhydrous CaSO_4 depending on the phosphate ore, the reaction temperature, P_2O_5 concentration, free sulfate content and the quantity of water available in the reaction [2].

The produced phosphogypsum is transferred as a wet cake (approximately 20 % surface water) to open air storage known as stacks and stored in large stockpiles [3]. For every ton of phosphoric acid produced, about 5 tons of phosphogypsum are produced [4]. Worldwide, 100–280 - Mt/year PG is produced, 85% of which is stockpiled for long-term storage without further treatment [5].

Phosphogypsum is considered hazardous waste associated with the phosphoric acid production using the wet process [6]. The main environmental hazard associated with phosphogypsum stockpiles are the leaching of rain water into surface and underground water regime and the generation of airborne dust [7]. In addition, these phosphogypsum stacks occupy large areas of land and

require long-term expenditures for maintenance and monitoring [8].

Long-term storage and maintenance of phosphogypsum present economic as well as potential environmental concerns. The approach of conversion of phosphogypsum into potentially useful products is important for reducing the environmental burden and enhancing economic benefit. Therefore, this approach is considered an alternative approach to the expensive management of stockpiles [9].

In regard to achieve a sustainable and environment-friendly society, there are two main approaches were discussed in the literature for the remediation of phosphogypsum: material recycling, and chemical recycling. The first approach; has mostly been concerning with the utilization of phosphogypsum in the conditioning of alkaline soil [10] and the preparation of hardened gypsum products [11]. The second approach; is focusing in the conversion of gypsum waste into high-value elemental sulfur and calcium carbonate [7, 12].

Although phosphogypsum is utilized in many industrial processes such as cement and other construction materials, its commercial use is currently limited to small quantities where only 15 % of the PG generated is recycled in agriculture, in gypsum board and cement industries [6]. Therefore, the large-scale conversion of phosphogypsum has been an important challenge for the phosphoric acid industry, ecologists and all those concerned with disposal of waste products such as government and civil society.

One possibility for such a process is the conversion of phosphogypsum to calcium carbonate and sodium sulfate. One of these products, sodium sulfate, is utilized in manufacturers of glass and detergents, animal feeds, heat accumulators, and sponge manufacture [13-14]. The other reaction product, calcium carbonate, could be used for neutralizing acidic process water associated with the phosphate industry, for producing lime to be used in soil stabilization and acid neutralization, or for water treatment, and flue gas desulfurization [15-16].

In general, studies realized on the decomposition of phosphogypsum to calcite by using the sodium carbonate Na₂CO₃ in an aqueous solution remain very few [17-18]. In this respect, the present work aims to optimize the conversion of phosphogypsum to calcium carbonate and sodium sulfate. Therefore, the full factorial design involving 16 treatment combinations and 4 replications of the central point has been applied to investigate the effect of different factors on the phosphogypsum conversion process.

2. EXPERIMENTAL.

2.1. Materials and Apparatus.

The phosphogypsum (PG) working sample was delivered from (the wet process phosphoric acid plant) Abu-Zaabal Company for Fertilizers and Chemicals, Egypt. The phosphogypsum representative sample was washed several times to eliminate soluble impurities and suspension materials as organic matter. The washed solid PG sample was dried in electric furnace at 110 °C until complete dryness. The dried PG sample was pulverized, homogenized and sieved to homogenized particle sizes less than < 100 μm. The samples were stored under vacuum condition in a desiccator for further analysis.

The dissolution experiments were performed in a 250 ml open glass reactor of 5 cm diameter. A mechanical stirrer with 2 cm diameter Teflon-coated stirrer was used and the impeller tip speed was adjusted at 400 rpm. A temperature controlled water bath was applied to adjust the reaction temperature at desired temperature. Filtration was performed using Buchner type filter of 4.6 in. diameter. Polypropylene filter cloth of 80 mesh aperture size was used. A vacuum pump was used for filtration.

2.2. Procedure.

Unless otherwise stated, 10 g of phosphogypsum sample was transferred with the proper amount of sodium carbonate solution into the reactor. After the desired reaction time, the leach slurry was immediately separated by filtration. The remaining solids were thoroughly rinsed with water, then dried over night at 105 °C and weighed. The sulfate content was determined by standard analytical procedures as described in Standard Methods for the Examination of Water and Wastewater [19]. Other elements, such as Ca and Na, were not considered as response factors because the only important parameter for phosphogypsum conversion to carbonate process evolution was considered to be the sulfate dissolution. Therefore, the reaction conversion was calculated by the following equation:

$$\text{Reaction conversion \%} = \frac{\text{Sulfate in filterate, g}}{\text{Sulfate in feed sample, g}} \times 100$$

2.3. Mineralogical Characterization.

The mineralogical composition of the phosphogypsum working sample and the formed carbonate product has been carried out using a powder X-ray diffractometer (model XD1180, Schimadzu, Japan) equipped with a copper target and a nickel filter. The elemental analyses of the samples have been performed by X-ray fluorescence (XRF) using Philips PW-2400 sequential X-ray spectrometer (Japan). The infrared (IR) spectra of the phosphogypsum and the formed carbonate product samples were carried out in the mid-infrared region from 4000 cm⁻¹ to 500 cm⁻¹ using FT-IR spectrometer (Bomen, Hartman & Braun, and model MB-157, Canada) under ambient air condition using KBr as a diluent.

2.4. Design of Experiments.

The statistical design of experiments is a systematic approach to determining the mathematical relationship between factors and responses. DoE is used to plan experiments so that the maximum amount of information can be extracted from the performed experiments. The factors in a DoE investigation are independent of each other in a statistical sense which makes it possible to evaluate the effect on the response of each factor separately (main effects). In addition, interaction effects between factors can be evaluated.

A commonly used type of DoE is full factorial design, which is used both for screening and optimization purposes. A great advantage with the full factorial design is that all main effects and interaction effects are independent of each other and therefore their effect on the response can be resolved in the evaluation. The simplest factorial is the 2ⁿ factorial design in which each variable is investigated at two levels, where each variable (X_i, i = 1– n) is investigated at minimum two levels [20, 21]. As the number of factors (n) increases, the number of runs for a complete replicate of the design also increases rapidly.

Center points are important for the DoE. The center point is usually replicated and will give information on the variation in the responses. The center points will also provide information on possible curvature in the data [22]. Curvature is detected when the average mean response at the center points is significantly greater or less than the average mean response of the factors at their low and high settings. Modeling can be performed using the first order model, defined by the equation:

$$Y = b_0 + \sum_{i=1}^n b_i x_i + \sum_{i=1}^n \sum_{j>1}^n b_{ij} x_i x_j$$

or the second order model, which is:

$$Y = b'_0 + \sum_{i=1}^n b_i x_i + \sum_{i=1}^n b_{ii} x_i^2 + \sum_{i=1}^n \sum_{j>1}^n b_{ij} x_i x_j$$

The statistical design of experiments is procedure for planning experiments so that the data obtained can be analyzed to yield valid and objective conclusions. This procedure was used to estimate the interaction between factors and decrease the number of experiments, experiments time, and process cost. To obtain a reliable statistical model, prior knowledge of the procedure is generally required [23]. The two main applications of experimental design are screening, in which the factors that influence the experiment are identified, and optimization, in which the optimal settings or conditions for an experiment can be found [24, 25].

3. RESULTS AND DISCUSSION.

3.1. Characteristics of Phosphogypsum.

The major composition of the phosphogypsum sample was analyzed by XRF. The data showed that the phosphogypsum sample is composed of (e.g., CaO, SO₃, Si, P) together with some insignificant impurities (e.g., Na, Al, Fe). The results are summarized in Table 1, which shows that the phosphogypsum is clearly dominated by CaO

(32.5%) and, SO₃ (40.6%), together with some insignificant impurities. These results are in agreement with the mineralogical compositions estimated by XRD Figure 1. The X-ray diffraction (XRD) spectrum of the phosphogypsum sample showed two main strong peaks at diffraction angles of 25.7 (d = 3.47 Å), and 31.75 (d = 3 Å). The XRD pattern of the phosphogypsum sample indicated that the sample is composed mainly of gypsum (CaSO₄·2H₂O), which can be converted to the CaCO₃ in carbonation reaction. The other weak peaks are attributed to the presence of minor phases, such as silicate, phosphate and metallic impurities, e.g. Na, Al, and Fe.

The IR spectra of the phosphogypsum sample have been measured as potassium bromide (KBr) disc Figure 2. The spectra showed O–H stretching band for water at 3439 cm⁻¹, P – H band at 2389 cm⁻¹, P – O bands at 2348 and 2238 cm⁻¹, M – H stretching band for (M) for metal at 2131 cm⁻¹, OH bending band for hydroxyl groups at 1624 cm⁻¹, Si - OH band for silicate at 801 cm⁻¹, S=O (SO₄²⁻) band for sulfate at 683 cm⁻¹, and S=O (SO₃²⁻) band for sulfite at 472 cm⁻¹.

Table (1): Chemical analysis of phosphogypsum sample.

Constituent, %				
Component			Component	
CaO	31.58		MgO	1.96
SO ₃	40.63		K ₂ O	0.04
SiO ₂	2.76		Cl	0.03
P ₂ O ₅	0.95		TiO ₂	0.08
Fe ₂ O ₃	0.28		MnO	0.03
Na ₂ O	0.35		F	1.04
Al ₂ O ₃	0.02		L.O.I	19.4
Constituent, ppm				
U	22		REEs	356

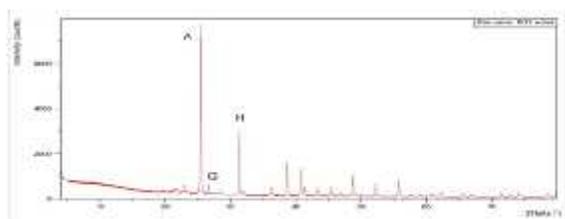


Fig (1): X-ray diffraction pattern of phosphogypsum sample.

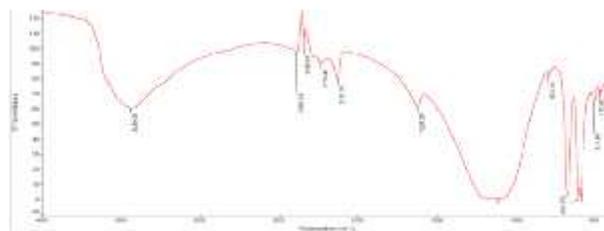


Fig (2): IR spectra of phosphogypsum sample.

Based on the above mentioned data of XRF, XRD and IR measurements, it is confirmed that the main phase composition of phosphogypsum associated with phosphoric acid produced from phosphate rock by the wet processing is calcium sulfate dihydrate, CaSO₄·2H₂O.

3.2. Statistical Analysis.

Optimization of process conditions is usually one of the most important factors to reduce the production cost. The conventional method, which involved varying one variable at a time while keeping the other variables constant is lengthy and often does not produce the effect of interaction of different variables. Laboratory scale confirmation of the products was then used to validate the feasibility of the derived optimum conditions.

The tests were performed to investigate mainly the effect of the investigated factors on the waste gypsum conversion

Table 2: The levels of experimental factors for the full factorial design.

Factors	Coded variables	Low level (-)	High level (+)	Mid-level (0)
Sodium carbonate concentration, %	A	10	30	20
Solid/ liquid ratio, g/ ml	B	2	4	3
Time, min	C	10	60	35
Temperature, °C	D	20	60	40

For 2^k factorial designs, it is assumed that the response is close to linear over the range of the factor levels. However, linearity assumption is often violated in practice. In this case, it is necessary to include one or more runs where all factors are set at their midpoint. The addition of center points to design allows the researcher to check whether the

linearity of the effects is a reasonable assumption or whether quadratic terms should be added to the model. The designed operating conditions are summarized in Table 3 showing that all factors are varied simultaneously. According to experimental plan, a total number of 16 runs and 4 replications of the center points have been designed.

to calcium carbonate. Four factors were taken into consideration in the experimental planning: sodium carbonate concentration %, (A); solid/ liquid ratio, g/ ml (B); time, min (C) and temperature, °C (D) as shown in Table 2. The experimental variables are evaluated at two levels, low (denoted as -1), high (denoted as +1, and midlevel denoted as 0), as shown in Table 2. The experiment order was randomly to avoid systematic errors. The results are analyzed with the Design Expert 10.0 software, and the main effects and interactions between factors were determined.

Table 3: Design matrix of the 2^4 full factorial designs.

Run #	Concentration		S/ L ratio		Time		Temperature		Reaction conversation, %
	A	%	B	g/ ml	C	Min	D	°C	
1	-1	10	-1	1/2	-1	10	-1	20	17.9
2	1	30	-1	1/2	-1	10	-1	20	50.9
3	-1	10	1	1/4	-1	10	-1	20	13.3
4	1	30	1	1/4	-1	10	-1	20	71.7
5	-1	10	-1	1/2	1	60	-1	20	33.8
6	1	30	-1	1/2	1	60	-1	20	60.7
7	-1	10	1	1/4	1	60	-1	20	50.1
8	1	30	1	1/4	1	60	-1	20	37.5
9	-1	10	-1	1/2	-1	10	1	60	22.5
10	1	30	-1	1/2	-1	10	1	60	95.2
11	-1	10	1	1/4	-1	10	1	60	51.8
12	1	30	1	1/4	-1	10	1	60	94.5
13	-1	10	-1	1/2	1	60	1	60	41.3
14	1	30	-1	1/2	1	60	1	60	81.3
15	-1	10	1	1/4	1	60	1	60	57.7
16	1	30	1	1/4	1	60	1	60	93.2
17	0	20	0	1/3	0	35	0	40	77.3
18	0	20	0	1/3	0	35	0	40	76.3
19	0	20	0	1/3	0	35	0	40	80.1
20	0	20	0	1/3	0	35	0	40	77.4

The effects of the experimental factors and their interactions influence the phosphogypsum conversion to carbonate are summarized in Table 4. The positive values of these effects reveal that the increase of these parameters increased leaching efficiency. Conversely, negative values of the effects decreased the response (reaction conversion %). From the obtained results it is clear that, the sodium

carbonate concentration had the greatest effect on reaction conversion %, followed by temperature, and concentration-liquid/ solid ratio-temperature-time interaction. The obtained results confirm the main advantage of the 2^k factorial design compared to the One-factor-at-a-time, where it show the effects main variable and also the effect of variables interactions.

Table 4: Estimated Effects and Coefficients for phosphogypsum conversion.

	Term	Stdized Effect	Coefficient Estimate	Sum of Squares	% Contribution
	Constant		54.59		
Model	A-Conc.	37.07	18.54	5498.22	43.85
Model	B-S/L ratio	8.27	4.14	273.90	2.18
Model	C-Time	4.72	2.36	89.30	0.71
Model	D-Temp.	25.20	12.60	2540.16	20.26
Model	AB	-6.07	-3.04	147.62	1.18
Model	AC	-14.62	-7.31	855.56	6.82
Model	AD	10.65	5.33	453.69	3.62
Model	BC	-2.92	-1.46	34.22	0.27
Model	BD	5.95	2.98	141.61	1.13
Model	CD	-2.35	-1.17	22.09	0.18
Model	ABC	-4.93	-2.46	97.02	0.77
Model	ABD	-2.55	-1.28	26.01	0.21
Model	ACD	4.65	2.32	86.49	0.69
Model	BCD	2.85	1.42	32.49	0.26
Model	ABCD	11.30	5.65	510.76	4.07
Model	Curvature	20.74		1720.51	13.72
Error	Lack of Fit			0.000	0.000
Error	Pure Error			7.95	0.063

The four observed recoveries at the center were 77.3 %, 76.3 %, 80.1 % and 77.4 % (Table 3). The average of these four center points is 77.7 %. The average of the 16 runs for base design (Table 3) is 54.5 %. Since these two averages are not similar, it is assumed that there is a curvature present. The test for nonlinearity, however, does not tell which factor (s) contains the curvature, only that it exists [26]. Although center points can detect curvature, they don't provide

enough information to model the curvature. To model the curvature, square terms are needed, which requires adding more points to the design. In fact, since the model equation contains some interaction terms, it means that the model is, therefore, capable of representing some curvature in the response function [22]. In this regard, the regression model equation with interaction terms can be written as [27]:

$$Y = b_0 + b_1A + b_2B + b_3C + b_4D + b_{12}AB + b_{13}AC + b_{14}AD + b_{23}BC + b_{24}BD + b_{34}CD + b_{123}ABC + b_{124}ABD + b_{234}BCD + b_{1234}ABCD \dots \dots \text{(Eq1)}$$

where Y = the percentage of phosphogypsum conversion; b = model coefficients; and A, B, C, and D = dimensionless coded factors for sodium carbonate concentration, solid/

liquid ratio, reaction time, and temperature respectively. The coefficients of Equation (1) are presented in Table 4.

$$(Y) = 54.59 + 18.54 * A + 4.14 * B + 2.36 * C + 12.60 * D - 3.04 * AB - 7.31 * AC + 5.33 * AD - 1.46 * BC + 2.98 * BD - 1.17 * CD - 2.46 * ABC - 1.28 * ABD + 2.32 * ACD + 1.42 * BCD + 5.65 * ABCD \dots \dots \text{(Eq 2)}$$

The equation in terms of coded factors can be used to make predictions about the response for given levels of each factor. The coded equation is useful for identifying the

relative impact of the factors by comparing the factor coefficients. Equation (2) in terms of actual factors:

$$Y = 54.59 + 18.53 * \text{Conc.} + 4.13 * \text{S/L ratio} + 2.36 * \text{Time} + 12.60 * \text{Temp.} - 3.03 * \text{Conc.} * \text{S/L ratio} - 7.31 * \text{Conc.} * \text{Time} + 5.32 * \text{Conc.} * \text{Temp.} - 1.46 * \text{S/L ratio} * \text{Time} + 2.97 * \text{S/L ratio} * \text{Temp.} - 1.17 * \text{Time} * \text{Temp.} - 2.46 * \text{Conc.} * \text{S/L ratio} * \text{Time} - 1.27 * \text{Conc.} * \text{S/L ratio} * \text{Temp.} + 2.32 * \text{Conc.} * \text{Time} * \text{Temp.} + 1.42 * \text{S/L ratio} * \text{Time} * \text{Temp.} + 5.65 * \text{Conc.} * \text{S/L ratio} * \text{Time} * \text{Temp.} \dots \dots \text{(Eq 3)}$$

The statistical analysis of the model was performed in the form of analysis of variance (ANOVA) as shown in Table 5. This analysis included the Fisher's F-test (overall model significance), its associated probability P(F), correlation coefficient R, and determination coefficient R² that measures

the goodness of fit of regression model. The analysis also includes the Student's t-value for the estimated coefficients and associated probabilities P(t). For each variable, the quadratic models were represented as contour plots.

Table 5: Analysis of variance for phosphogypsum conversion.

Source	Sum of Squares	Df	Mean Square	F Value	p-value	
					Prob > F	
Model	10809.16	15	720.61	272.01	0.0003	significant
A-Conc.	5498.22	1	5498.22	2075.45	< 0.0001	
B-S/L ratio	273.90	1	273.90	103.39	0.0020	
C-Time	89.30	1	89.30	33.71	0.0102	
D-Temp.	2540.16	1	2540.16	958.85	< 0.0001	
AB	147.62	1	147.62	55.72	0.0050	
AC	855.56	1	855.56	322.96	0.0004	
AD	453.69	1	453.69	171.26	0.0010	
BC	34.22	1	34.22	12.92	0.0369	
BD	141.61	1	141.61	53.45	0.0053	
CD	22.09	1	22.09	8.34	0.0631	not significant
ABC	97.02	1	97.02	36.62	0.0091	
ABD	26.01	1	26.01	9.82	0.0519	not significant
ACD	86.49	1	86.49	32.65	0.0106	
BCD	32.49	1	32.49	12.26	0.0394	
ABCD	510.76	1	510.76	192.80	0.0008	
Curvature	1720.51	1	1720.51	649.45	0.0001	
Pure Error	7.95	3	2.65			
Cor Total	12537.62	19				

S = 10.57, Mean = 48.30, C.V. % = 21.89, PRESS = 1725.04, R-Sq = 92.91%, R-Sq (adj) = 88.19 %, R-Sq (Pred) = 81.78 %, Precision (Adeq) 12.72.

From the table it is clear that, the model f-value of 272.01 implicit the model was significant. There is only a 0.01% chance that a ‘model F-value’ of this magnitude would occur due to noise. The prob > F values for the models which were less than 0.05 (<0.0001) indicate model terms are significant with a confidence interval of 95%. In addition, A, B, C, D, AB, AC, AD, BC, BD, ABC, ACD, BCD, and ABCD are significant model terms while CD, ABD are not significant. The value of the adjusted determination coefficient (R²-adj) is 88.19 %, which means that only about 11.81 % only of the total variation was not explained, this proves the high significant of the model. The ‘adequate precision’ measures the signal to noise ratio. A ratio greater than 4 is desirable.

The normal probability plot was used to verify the statistically significant main and interaction effects that were included in the model [28]. Regards to the normal probability plot, Figure 3, the insignificant effects are normally distributed with mean zero and variance (σ^2) and will tend to fall along a straight line, whereas significant effects will have nonzero means and will not lie along the straight line. The results obtained in Figure 3 clear that, the main effects A, B, C and D are statistically significant. The interactions AD, BD, ACD, BCD, and ABCD are also are significant because they stray farther from the line; however the other interactions are insignificant.

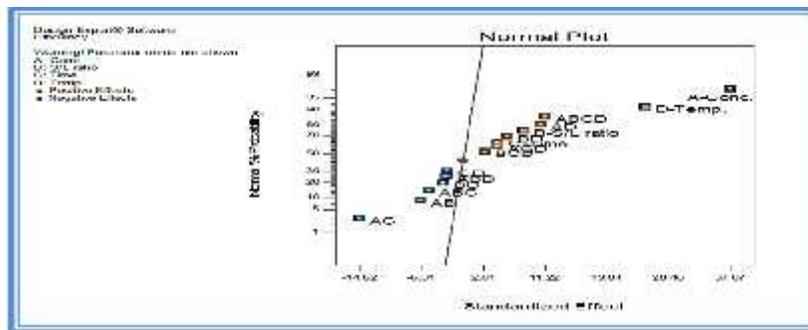


Fig (3): Normal probability plot of the standardized effects.

The same indication is given clearer in the Pareto chart of the selected effect in Figure 4. Pareto chart is a special type of bar chart where the values being plotted are arranged in descending order, therefore it helps to set the priority levels while designing the process [29]. The chart gives the factors which have a standardized effect beyond 99% confidence different factors and their interactions.

level (beyond the line at 2.77. Figure 4 shows that sodium carbonate concentration and temperature are the most significant factors in the phosphogypsum conversion to carbonate process. Also, it shows the descending order of the effects of

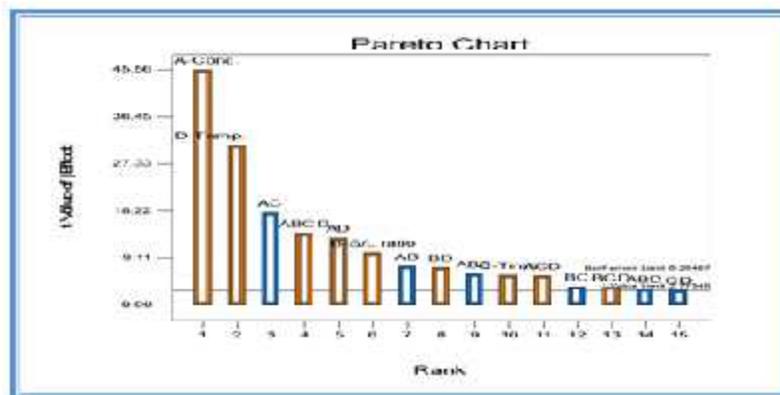


Fig (4): Pareto Chart of the Standardized Effects.

The normal plot of residuals is a graphical representation for determining if the data is distributed normally or not [22]. The normal probability plots of the residuals for the data tests the hypothesis that the residuals have a normal

distribution, where if the plot gives straight line, this means that the residuals have a normal distribution. From Figure 5, it is clear that the points were almost distributed in a line, which indicated that the model fitted moderately well.

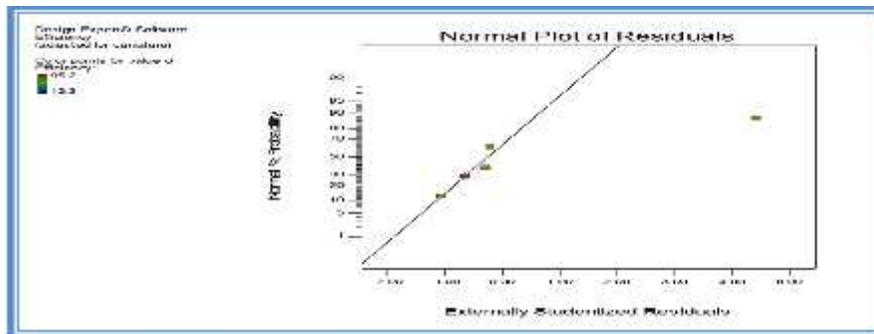


Fig (5): Normal Plot of Residuals.

The plot of residuals versus the predicted response values was presented in Figure 6. This plot tests the hypothesis of constant variance i.e., the random errors are distributed with mean zero and constant variance. From the Figure, it is

observed that there was no definite increase in residuals with predicted levels, which show that Equation (2) was in excellent agreement with the experimental data and supporting the underlying assumptions about the errors.

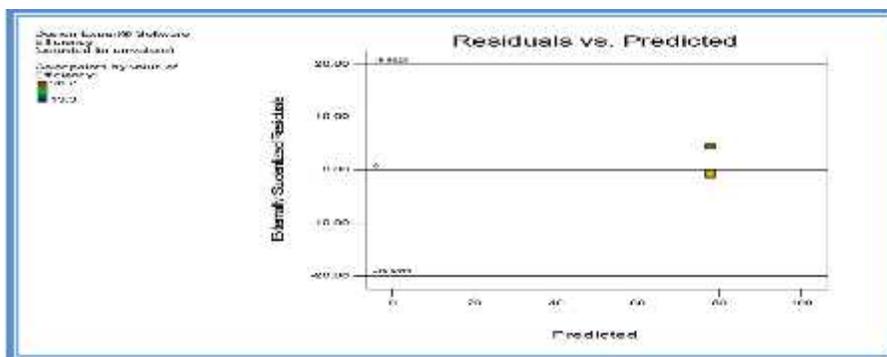


Fig (6): Plot of Residuals versus Predicted Recoveries.

The effects of the all individual factors used for the phosphogypsum conversion investigation are presented in Figure 7. Sodium carbonate concentration (A) effect plot shows that the increase in Sodium carbonate concentration is enhancing effectively the conversion of phosphogypsum to carbonate. Solid/ liquid ratio, g/ ml, (B) effect plot clarify that by increase the Solid/ liquid ratio, the phosphogypsum

conversion to carbonate is slightly increased. The same effect was observed for the reaction time (C), where the plot of time effect indicates that increase in reaction time has slightly effect on the phosphogypsum conversion to carbonate. The temperature (D) effect plot shows that, the increase in temperature is improving effectively the conversion of phosphogypsum to carbonate.

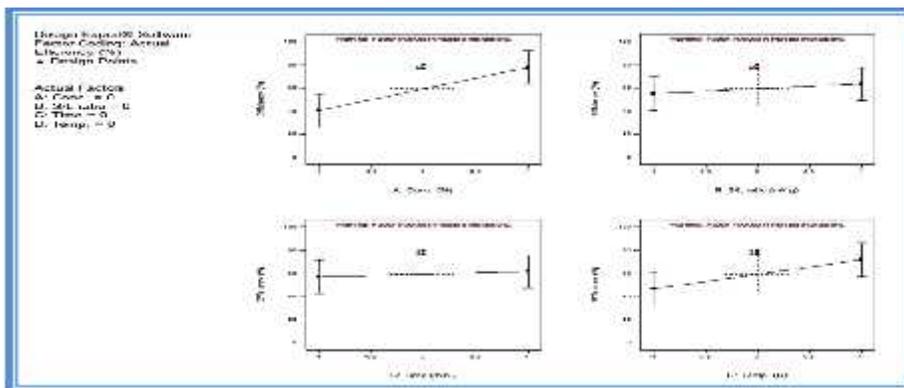


Fig (7): Main Effects Plots for phosphogypsum conversion %.

One of main advantages of factorial design procedure is the ability to show the interaction between the different factors under the investigation. The interaction effect for the phosphogypsum conversion is shown in Figure 8. Where if the lines of two factors are parallel, this means that there is

no interaction. On the contrary, when the lines are far from being parallel, the two factors do interact. From the Figure, it is clear that the two lines is intersect in all the interaction plots, which indicated that the interaction of the main effects have statistically significant.

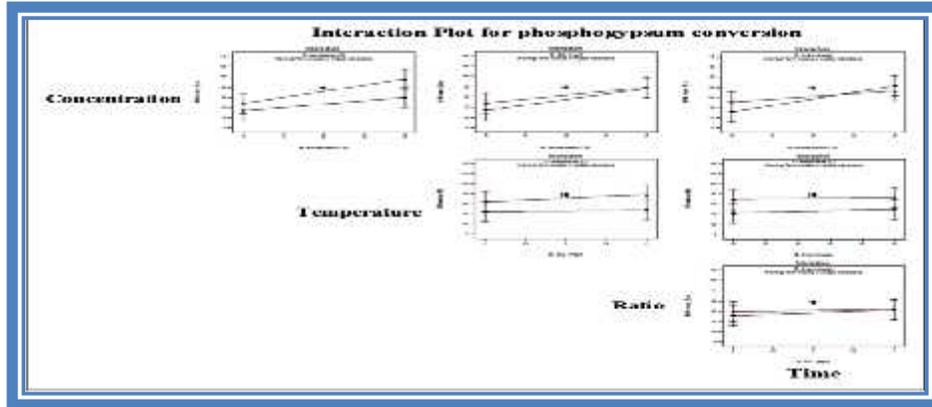


Fig (8): Interaction effect plot for phosphogypsum conversion %.

The experimental results and the predicted results for phosphogypsum conversion to carbonate process were presented graphically in Figure 9. From the Figure, it is clear that there is a good agreement between experimental results and those predicted by the model.

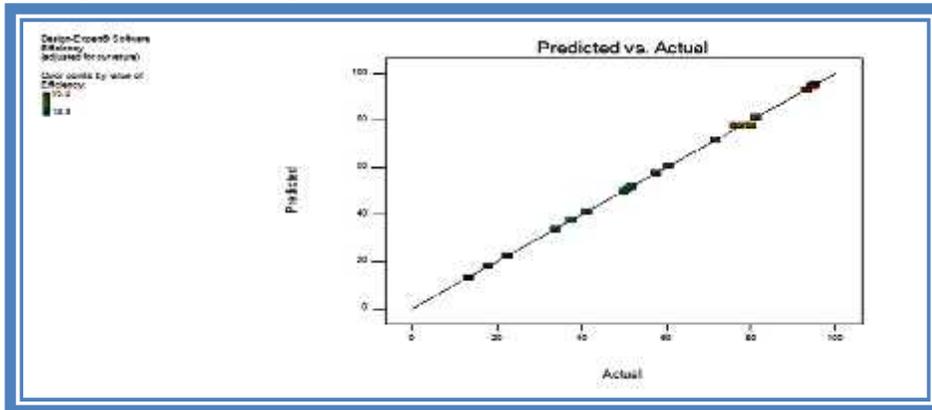


Fig (9): Scatter diagram of experimental values versus predicted values by Equations (2).

Based on the experimental results and the fitting model analysis, the optimized contours and response surface between the sodium carbonate concentration and the reaction temperature for the phosphogypsum conversion optimization scheme are shown in Figure 10, under the conditions that the reaction time is 10 min, and the solid/ liquid ratio was 2/1.

Figure 10 represents 3D plot for the interaction between input parameters. Figure 10 shows a significant curvature in the phosphogypsum conversion with sodium carbonate concentration and reaction temperature. The optimum conditions were found with 30 % sodium carbonate concentration and 60 °C reaction temperature.

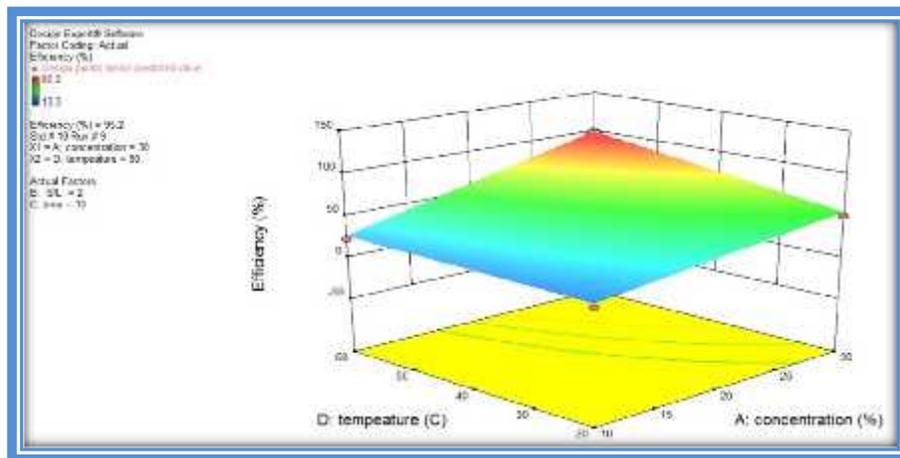


Fig (10): 3D Plots of phosphogypsum conversion.

According to the statistical modeling performed, the optimal conditions for phosphogypsum conversion to carbonate using sodium carbonate were: sodium carbonate concentration 30 %, solid/ liquid ratio, g/ ml, 2/1, reaction temperature 60 °C, and stirring time of 10 min. Regards to these optimal conditions, about 95.2 % of phosphogypsum was successfully converted to calcium carbonate.

The validation of the model was achieved by performing additional experiments under the predicted optimal conditions. The two experiments yielded an average waste gypsum conversion of 94.7 %, which clear that there is an agreement between the predicted and experimental results confirmed the experimental adequacy of the model and the existence of the optimal conditions. This means that, the model developed was considered to be accurate and reliable for phosphogypsum conversion to carbonate using sodium carbonate.

3.3 Characterization of the Produced Solid.

Based on the aforementioned investigations, a process for phosphogypsum conversion to carbonate using sodium carbonate was developed under the obtained optimal conditions. The produced solid (calcium carbonate) was filtered, rinsed with water and dried at 105 °C. The characterization of the produced calcium carbonate, and

sodium sulfate have been achieved using XRF, XRD and FT-IR.

The chemical composition of the produced calcium carbonate was identified using XRF as shown in Table 6. From the table, it is clear that the produced solid consisted mainly of calcium carbonate with low contents of SO₃, SiO₂, and P₂O₅ as well as traces of some insignificant impurities such as; Na, Al, Fe. In addition, several impurities that are present in the phosphogypsum, including uranium and rare earth elements, transfer to the produced calcium carbonate.

The X-ray diffraction (XRD) spectrum of the produced calcium carbonate showed one phase (Figure 11). The identification of the obtained peaks clarify that the obtained solid is mainly composed of calcium carbonate CaCO₃. The other weak peaks are attributed to the existing of impurities, such as unreacted phosphogypsum, silicate, phosphate and metallic impurities, e.g. Na, Al, and Fe.

The FT-IR analyses were performed to support the XRF and XRD data. Figure 12 represents the FT-IR of the produced calcium carbonate. The obtained spectra showed O–H stretching band for water at 3439 cm⁻¹, C=O (CO₃²⁻) bands characterized to CaCO₃ compound at 1443, 872 and 701 cm⁻¹, P – H band at 2506 cm⁻¹, and Si - O stretching band at 1107 cm⁻¹.

Table (6): Chemical analysis of the produced calcium carbonate.

Constituent, %			
Component		Component	
CaO	44.22	Inorganic C	48.5
SO ₃	3.37	MgO	0.02
SiO ₂	0.99	K ₂ O	0.02
P ₂ O ₅	1.57	Al ₂ O ₃	0.14
Fe ₂ O ₃	0.19	TiO ₂	0.03
Na ₂ O	0.42	MnO	0.02
Constituent, ppm			
U	29	REEs	384

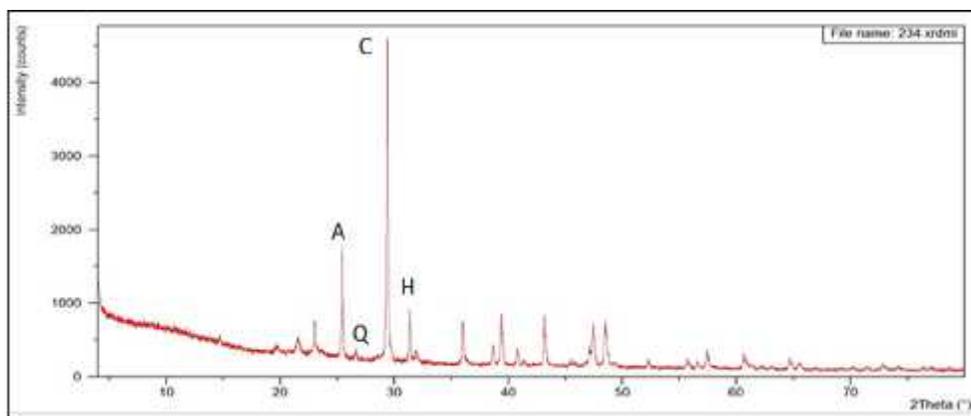


Fig (11): X-ray diffraction pattern of the produced calcium carbonate.

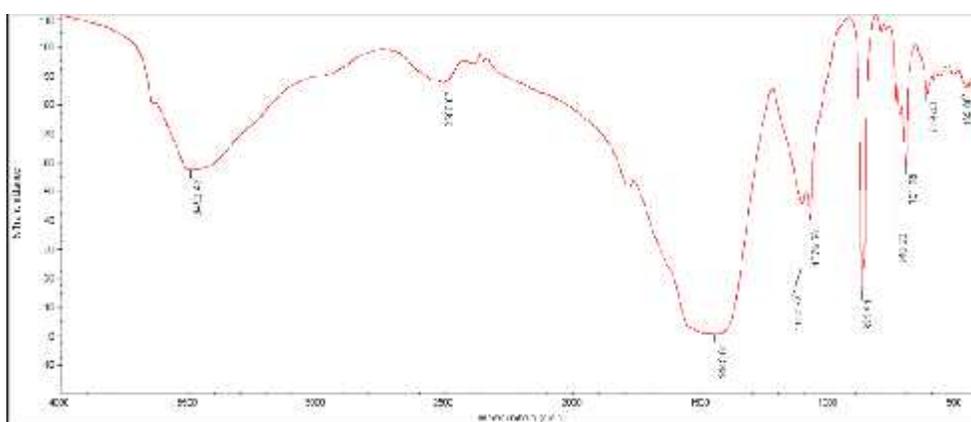


Fig (12): IR spectra of the produced calcium carbonate.

4. Conclusion.

The conversion of phosphogypsum to carbonate by sodium carbonate has been investigated using the full factorial design methodology. The phosphogypsum sample was characterized in terms of spectroscopic analysis (X-ray diffraction, X-ray fluorescence, and IR spectra). The studied factors were sodium carbonate concentration, solid/ liquid ratio, time, and temperature. The obtained results were statistically analyzed by using analysis of variances (ANOVA) to determine the main effects and interactions

between the investigated factors. The obtained results indicate that, both sodium carbonate concentration and temperature are effectively enhance the phosphogypsum conversion, while both of time and solid/ liquid ratio has slightly effect on the conversion efficiency. 95.2 % of the phosphogypsum successfully converted to calcium carbonate under the following optimum conditions; sodium carbonate concentration of 30 %, time of 10 min, temperature 60 °C, and solid/ liquid ratio of 2:1.

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