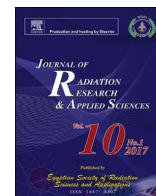


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Ammonium sulfate preparation from phosphogypsum waste

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ABSTRACT

The Egyptian phosphogypsum waste is treated using sulfuric acid prior the ammonium sulfate production. The relevant factors that would affect the removal efficiencies of some impurities are studied. The optimum conditions of the treatment are 8 M sulfuric acid solution and 1/4 solid/liquid ratio for 30 min contact time at 80 °C. Moreover, the optimum conditions of the ammonium sulfate preparation are 10 g of the suspended impure or purified phosphogypsum in 40 ml of 3% ammonium sulfate solution (as initiator), 1/4 solid/liquid ratio at pH7 at an addition of an excess ammonium carbonate, and 150 rpm stirring speed for 4.0 h contact time at 55 °C as well as the 5 mg of barium chloride is added to remove the radium in the ammonium sulfate product. Finally, the ammonium sulfate is crystallized and the chemical analysis of the product shows 20% nitrogen and 23.6% sulfur. Therefore, the purity of the obtained ammonium sulfate is 95% from the purified phosphogypsum.

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1. Introduction

Ammonium sulfate is found in the most everyday applications because of their unique chemical and physical properties. Ammonium sulfate is used in the agricultural fertilizer as a source of nitrogen and sulfur for plant nutrients (Schwenke & McMullen, 2009). Ammonium sulfate is a mixed fertilizer which contains nitrogen and sulfur nutrients (FAO, 2003; Tisdale, 2002). The ammonium sulfate provides the ideal solution that has a quick sulfate release tied in with the season-long availability of degradable sulfur (Hoefst, Sawyer, Heuvel, Schmitt, & Brinkman, 1985; Dudal, 2002).

A large amount of waste product phosphogypsum (PG) is produced during the production of wet process phosphoric acid by decomposition of phosphate rock with sulfuric acid. Phosphoric acid plants are really phosphogypsum plants because they make much more gypsum than phosphoric acid (Abu-Eishah & Abu-Jabal, 2001; Klaus, Hurth, & Hoechst, 2002; Parreira, Kobayashi, & Silvestre, 2003; UNSCEAR, 2000; Yang, Liu, Zhang, & Xiao, 2009). The

phosphogypsum is mostly disposed without any treatment, usually by dumping in large stockpiles. These are generally located in coastal areas close to phosphoric acid plants, where they occupy large land areas and cause serious environmental damage. The PG is a powdery material that is composed mainly of calcium sulfate dihydrate (>90% gypsum) and sodium fluorosilicate (Na₂SiF₆) (Berish, 1990; Kacimi, Simon-Masseron, Ghomari, & Derriche, 2006). Due to the residual phosphoric, sulfuric and hydrofluoric acids contained within the porous PG, it is considered an acidic by-product (pH < 3). The PG obtained from the filter cake usually has a free moisture content of 25–30%. The chemical composition of PG from different sources is determined where the main components (%) are CaO, sulphate, SiO₂, Al₂O₃, Fe₂O₃, P₂O₅, and F while the trace metal contents (mg/kg) of the PG are arsenic, silver, barium, cadmium, chromium, lead, mercury and selenium that elements are on the Environmental Protection Agency (EPA) list of potentially toxic elements. It can also be seen that the PG generally has high total contents of Ag, Au, Cd, Se, Sr, some lanthanides and Y (Tayibi, Choura, López, Alguacil, & López-Delgado, 2009).

With regard to the radioactivity, it is mentioned that the PG contains relatively high levels of U-series radionuclides naturally present in the phosphate rock. The most important source of PG radioactivity is reported to be radium (²²⁶Ra) (EPA, 2004; El-Didamony, Gado, Awwad, Fawzy, & Attallah, 2013; Langmuir &

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Riese, 1985; Rutherford, Dudas, & Samek, 1994; USEPA, 2002). Phosphogypsum was treated using different techniques for industrial uses and applications (Khadilkar et al., 2009; Klaus, 1974; Krempff, 1976; Manjit, 2002; Manjit, Garg, & Rehsi, 1993). Ammonium sulfate was produced from many sources whereas it was the oldest synthetic fertilizer (Blouin, Livingston, & Getsinger, 1970; Meline, Faucett, Davis, & Shirley, 1971; Reddy et al., 2011; Sharma, 1991, p. 455; Yong, Mulligan, & Fukue, 2007, p. 211).

The aim of the present study is the production of ammonium sulfate from its economic constitutions, due to the huge amounts of phosphogypsum waste currently produced annually by the phosphate industry in Egypt. The long-term storage and maintenance of the hazard material present economic as well as potential environmental concerns. This study has been found necessary to face that problem. To realize the objectives of this work, the various parameters of the impurities removal upon the phosphogypsum waste have experimentally been optimized by the sulfuric acid. Moreover, the parameters for the ammonium sulfate preparation are studied.

2. Experimental

2.1. Material

2.1.1. Phosphogypsum characteristics

The working phosphogypsum waste is a byproduct obtained from the production of wet process phosphoric acid from rock phosphate at the El Nasr Co. for Intermediate Chemicals on Fayoum City, Egypt. It is a gray colored, damp, fine-grained powder, silt or silty-sand materials. It is mainly $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ with small amounts of phosphate, sand, and clay. The studied phosphogypsum sample is completely analyzed after the complete dissolution by alkali fusion using the suitable analytical techniques.

2.1.2. Samples preparation

The phosphogypsum representative sample is prepared by grinding using a blending mill and quartering method. The separated sample by quartering is milled to -200 mesh size. The pulverized sample is then subjected to the analysis, the treatment and the preparation of ammonium sulfate using the suitable techniques.

2.2. Experimental procedures

2.2.1. Treatment procedures

The treatment process of the phosphogypsum waste is the most important method for the removal of the associated impurities which are contaminating the ammonium sulfate product. Sulfuric acid is used for the treatment of a definite amount to the studied phosphogypsum waste in 250 ml teflon beakers. In this regard, the relevant factors in the treatment are studied to minimize the most associated and harmful impurities. The studied factors will indeed upgrade the concentration of phosphogypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) to a suitable level for the required final preparation of high purity ammonium sulfate. Several treatment experiments are performed to optimize the mentioned relevant factors. In these experiments, the definite amount of impure phosphogypsum sample is progressively treated with different concentrations of sulfuric acid and the solid to aqueous phase ratio ranging from 1/2 to 1/6 for different contact times at different temperatures. In each experiment, the obtained phosphogypsum precipitate is left to settle down after which the slurry is subjected to filtration and the precipitate is thoroughly washed and dried before being directed for the preparation of ammonium sulfate. While the filtrate is analyzed using suitable methods to determine the removal of the most

impurities but fluoride ions is determined in the purified phosphogypsum for the accurate measurement.

2.2.2. Preparation procedures

Ammonium sulfate is prepared by stirring a definite amount of impure or purified phosphogypsum with a suitable amount of ammonium carbonate powder which is suspended in distilled water at different temperatures for different contact times in 250 ml teflon beakers. The reaction operating conditions such as pH of phosphogypsum slurry solution, the amount of ammonium carbonate, solid/liquid phase ratio (S/L), the amount of ammonium sulfate dissolution of phosphogypsum and contact time as well as temperature are studied. The mixture solution is then treated with a few milligrams of barium chloride saturated solution which is used as a carrier to remove the radium ions as barium-radium sulfate precipitate (Habashi, Awadalla, & Zailaf, 1986). After filtration, the ammonium sulfate solution product is obtained as filtrate while the residue is calcium carbonate and most impurities. Subsequently, the filtrate is also dried at 60°C to obtain the purified ammonium sulfate powder.

2.3. Analytical procedures

The quantitative analysis of major oxides SiO_2 , Al_2O_3 , TiO_2 and P_2O_5 in the phosphogypsum sample have been analyzed using a double beam UV–VIS recording Shimadzu UV160A spectrophotometer according to standard methods of analysis while the oxides of Na and K are determined by the flame photometric technique. The Fe_2O_3 , MgO and CaO are chemically determined by titration (Shapiro & Brannock, 1962) whereas the concentrations of the other elements have been analyzed through the inductively coupled plasma optical emission spectrometry (ICP-OES) technique. Whereas the fluoride ion is spectrophotometrically analyzed using the alizarin complexone method after distillation and it is also measured by fluoride electrode (Kandil, Gado, Cheira, Soliman, & Akl, 2016) as well as the activity of radium is obtained by gamma ray photometer. Besides that, the sulfate ions in different samples can be directly measured by the turbidimetric or gravimetric methods (Budesinsky, 1975). Finally, the nitrogen content of ammonium sulfate product is determined by using the Kjeldahl method (Goers, 1980, pp. 37–44). The thermogravimetric analysis of calcium carbonate and ammonium sulfate are obtained using the Perkin-Elmer model TGA 7 Thermogravimetric analyzer which is used to measure the weight loss of the samples.

3. Results and discussion

3.1. Characterization of phosphogypsum

The phosphogypsum basically consists of calcium sulfate dihydrate with small amounts of silica, P_2O_5 , iron, aluminum and fluoride as well as traces of radioactive materials comprises radium and uranium, also heavy metals and lanthanides as presented in Table 1. The harmful impurities in phosphogypsum sample have been affected the production of ammonium sulfate. To obtain the purified ammonium sulfate, the used phosphogypsum must be treated or purified from its impurities prior to the preparation of ammonium sulfate. The chemical analysis of phosphogypsum waste was done using suitable techniques.

3.2. Phosphogypsum treatment

The treatment is used to purify the phosphogypsum sample using sulfuric acid to increase the degree of purity of resultant product. Several series of experiments have been carried out to

Table 1
Chemical analysis of major and trace elements for phosphogypsum waste.

Constituent	Conc. (%)	Constituent	Conc. (mg/Kg)
CaO	28.31	Cr	34
SO ₃	40.45	Ni	6
SiO ₂	8.29	Cu	12
Al ₂ O ₃	0.17	Zn	25
Fe ₂ O ₃	0.31	Zr	16
MgO	0.21	Y	60
P ₂ O ₅	1.98	Ba	78
TiO ₂	0.01	Sr	888
Na ₂ O	0.29	V	25
K ₂ O	0.02	U	9
MnO	0.01	Th	1
F ⁻	0.26	Lanthanides	497
L.O.I	19.71	Ra (Activity Conc)	642 Bq/Kg

L.O.I: loss of ignition at 1000 °C.

Bq/Kg: Becquerel/Kilogram of the sample.

study the different relevant factors that would affect the removal of some impurities such as P₂O₅, Al₂O₃, Fe₂O₃ and F as well as the lanthanides from the working phosphogypsum sample. These factors involved the effects of the acid concentration, the contact time, the solid/liquid ratio and the treatment temperature. In these experiments, the phosphogypsum samples are ground to –200 mesh size.

3.2.1. Effect of acid concentration

The effect of sulfuric acid concentration upon the removal of the studied impurities from the phosphogypsum is studied at different concentrations ranging from 1 to 12 M and the other conditions are kept constant at –200 mesh size, 150 rpm stirrer speed and 1/4 solid/liquid (S/L) ratio for 60 min contact time at room temperature. From the obtained results in Fig. 1, it is obvious that the removal efficiencies of P₂O₅, Al₂O₃, Fe₂O₃, fluoride ions and lanthanides elements from the studied sample are gradually increased to 75.04, 69.17, 54.63, 77.6 and 12.49%, respectively by increasing the sulfuric acid concentration until 8 M. After which the acid concentration has ineffective upon the removal efficiencies. From the obtained result, the low removal efficiency of the lanthanides elements by increasing the sulfuric acid concentration is due to the tendency of these metal ions to form the insoluble double salts with calcium at the high sulfuric acid concentration. As well as the lanthanides are probably connected in phosphogypsum and substitute isomorphically calcium in the crystal lattice of CaSO₄ (Burnett, Schultz, & Hull,

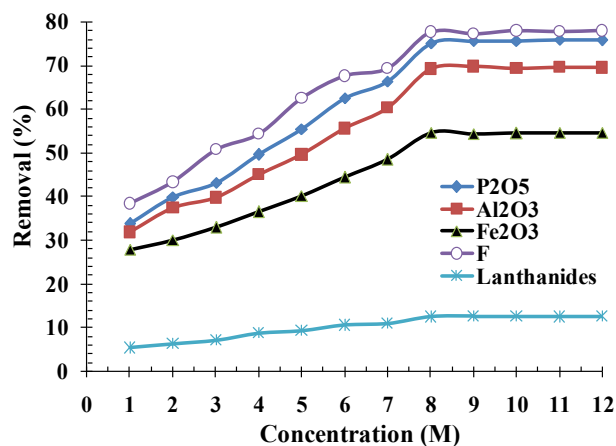


Fig. 1. Effect of sulfuric acid concentration upon removal efficiencies of some impurities from phosphogypsum waste.

1995). Finally, it is clear that the 8 M of H₂SO₄ could remove the most impurities from the studied phosphogypsum sample with acceptable efficiencies.

3.2.2. Effect of contact time

The effect of the stirring time upon the removal efficiencies of some impurities from the phosphogypsum sample using 8 M sulfuric acid is performed in the range from 10 to 60 min contact time at –200 mesh size, 150 rpm stirring speed and 1/4 solid/liquid (S/L) ratio at room temperature. From the obtained results shown in Fig. 2, it is clear that the removal efficiencies increased from 45.53, 40.51, 34.13, 67.53 and 8.59% to 75.04, 69.17, 55.51, 78.66 and 12.79% for P₂O₅, Al₂O₃, Fe₂O₃, fluoride ions and lanthanides from the phosphogypsum sample respectively with increasing the contact time from 10 to 30 min and no further increase in the removal efficiencies of impurities with more time. Therefore, the optimum contact time is 30 min which is used for further purification of phosphogypsum sample.

3.2.3. Effect of solid/liquid phase ratio

In a further trial to improve the removal efficiencies of P₂O₅, Al₂O₃, Fe₂O₃, fluoride ions and lanthanides elements from the working phosphogypsum sample, it is decided to investigate the effect of increasing the acid volume used by varying S/L ratio from 1/2 to 1/6 while the other factors are fixed. From the obtained results in Fig. 3, it is found that the removal efficiencies of P₂O₅, Al₂O₃, Fe₂O₃, fluoride ions and lanthanides elements from the phosphogypsum sample have gradually been increased from 49.73, 44.85, 38.86, 54.32, and 6.32% to 75.78, 70.32, 54.87, 77.65 and 12.51% respectively by decreasing the solid/liquid ratio until 1/4 ratio. The increase of sulfuric acid amount is usually accompanied by an increase in the removal efficiency which tends to become independent at ratios higher than 4. Thus, the best solid/liquid ratio is 1/4.

3.2.4. Effect of temperature

Temperature is a very effective parameter on the removal efficiency of the harmful metal ions from the studied phosphogypsum sample. The effect of temperature on the impurities removal efficiencies is studied in the range from 25 to 90 °C at optimum conditions determined above. From the obtained results of removal efficiencies of the study metals values which are shown in Fig. 4, it is clearly evident that increasing the temperature from 25 to 80 °C leads to increase the removal efficiencies of P₂O₅, Al₂O₃, Fe₂O₃, fluoride ions and lanthanides elements from 75.04, 68.43, 55.17, 78.66 and 12.79% to 98.67, 93.22, 80.32, 99.12 and 15.43%

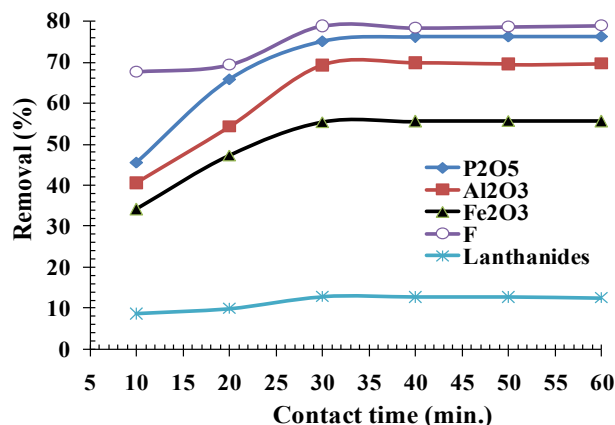


Fig. 2. Effect of contact time upon the removal efficiencies of some impurities from phosphogypsum waste.

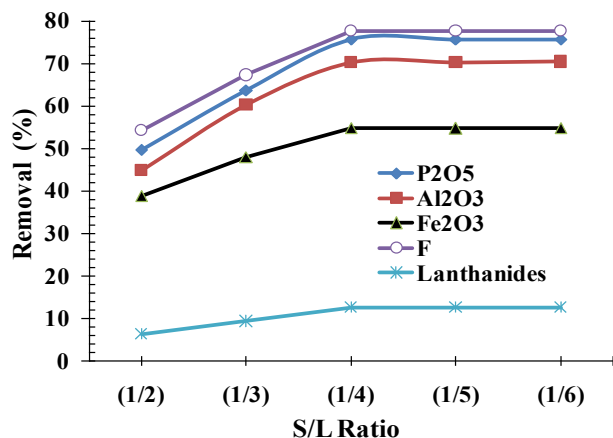


Fig. 3. Effect of solid/liquid ratio upon the removal efficiencies of some impurities from phosphogypsum sample.

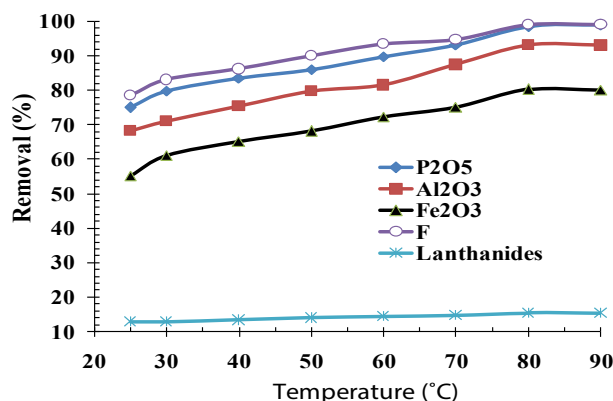


Fig. 4. Effect of temperature upon the removal efficiencies of some impurities from phosphogypsum.

respectively. This means that the increasing of the temperature favors the removal of the most impurities and may improve the removal of most harmful impurities. From the above giving, it is possible to deduce that the reaction process is endothermic and the temperature is favorable for dissolution of metal impurities from the phosphogypsum. Therefore, 80 °C is selected as the optimum temperature for the treatment process.

3.2.5. Applying the optimum conditions of treatment

From the above results, the obtained optimum conditions for the removal of the most impurities from phosphogypsum waste are obtained. The purification of the studied phosphogypsum waste by H₂SO₄ is applied by treating 1 kg of the properly ground sample (-200 mesh size) with 4 L of 8 M H₂SO₄ and 150 rpm agitating speed for 30 min contact time at 80 °C. The insoluble residue is the purified phosphogypsum using H₂SO₄ while the obtained filtrate is analyzed using suitable analytical techniques to assay 98.67% of P₂O₅, 93.22% of Al₂O₃, 80.32% of Fe₂O₃, 99.12% of fluoride ions and 15.32% of lanthanides elements which are represented as the removal efficiencies of some impurities from the phosphogypsum. The byproduct of sulfuric acid is recycled for the preparation of wet process phosphoric acid. On the other hand, the obtained treated phosphogypsum (insoluble residue) is completely analyzed and the data are obtained in the Table 2.

Table 2

Chemical composition of phosphogypsum prior and after treated with sulfuric acid.

Constituents	Concentration %	
	Impure PG	Treated PG using H ₂ SO ₄
CaO	28.31	33.81
SO ₃	40.45	48.31
SiO ₂	8.29	4.33
Al ₂ O ₃	0.17	0.03
Fe ₂ O ₃	0.31	0.02
MgO	0.21	0.005
P ₂ O ₅	1.98	0.026
F ⁻	0.26	0.002
Na ₂ O	0.29	0.002
K ₂ O	0.02	0.003
L.O.I	19.71	13.12
TREES (mg/Kg)	497 mg/kg	420 mg/kg
Ra (Activity Conc))	642 Bq/Kg	546Bq/Kg

L.O.I: loss of ignition at 1000 °C.

Bq/Kg: Becquerel/Kilogram of the sample.

3.3. Preparation of ammonium sulfate

The phosphogypsum has no fertilizing properties but when it is frequently converted to ammonium sulfate, it gains more value as a fertilizer. Normally, the conversion of phosphogypsum to ammonium sulfate is performed by the slurry phosphogypsum after purification from most impurities. The different parameters affecting the preparation processes of ammonium sulfate have been separately investigated.

3.3.1. Effect of pH

The pH of the phosphogypsum slurry is acidic due to the porosity nature of phosphogypsum where it absorbs trace amounts of sulfuric acid during the treatment process. This acidity leads to consume a small amount of ammonium carbonate; also the acidity affects the agglomeration of calcium carbonate. However, the pH of the aqueous solution is an important parameter that controlled the reaction process. The influence of pH upon the yield efficiency of ammonium sulfate product is performed at different pH values ranging from 2.5 to 9 of the suspended solution contains 10 g of impure or treated phosphogypsum individually in 40 ml distilled water (1/4) solid to liquid ratio in Teflon beaker, then adding 50 ml solution of 10% ammonium carbonate and 150 rpm stirring speed for 4.0 h at room temperature (Fig. 5). The yield of ammonium sulfate of each experiment is gravimetrically determined. From the

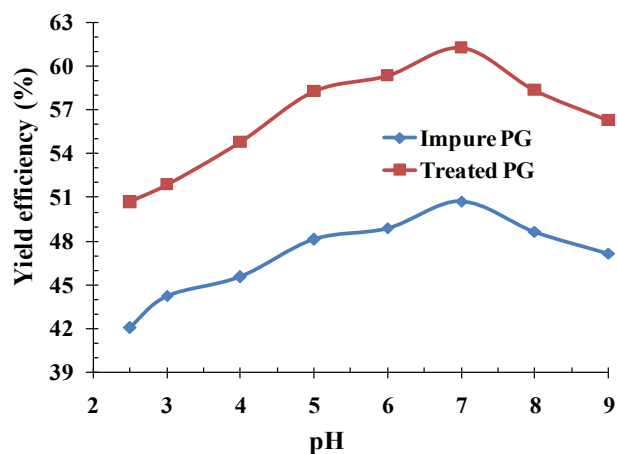
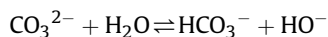


Fig. 5. Effect of pH on the yield efficiency of ammonium sulfate from impure and treated phosphogypsum.

obtained results, it is clearly evident that the yield efficiency of the ammonium sulfate product has gradually increased by increasing the pH till reaching maximum values at pH 7 and thereafter the yield efficiency has decreased with increasing the pH. Hence, the pH 7 is used for the next experiments. The reduced yield efficiency at the basic medium is due to the alkalinity which has a very undesirable effect on agglomeration of calcium carbonate as well as the presence of ammonium carbonate which displays on alkaline reaction according to the hydrolysis equation.



3.3.2. Effect of excess amount of ammonium carbonate

The effect of excess amount more than the stoichiometric ratio of ammonium carbonate ranging from 1 to 30% upon the yield capacity of ammonium sulfate product is studied using the suspended 10 g of the purified phosphogypsum in 40 ml distilled water at pH7 and 150 rpm stirring speed for 4.0 h at room temperature. From Fig. 6, it is revealed that increasing the excess amount more than the stoichiometric of ammonium carbonate during the equilibrium reaction with calcium sulfate that presented in phosphogypsum to form ammonium sulfate, the yield efficiency of the ammonium sulfate product has gradually increased until 55.61 and 65.80% at 10% excess of ammonium carbonate and thereafter the yield efficiency has gradually decreased for impure and treated PG. However the reaction is reversible and according to the law of mass action, the excess amount of ammonium carbonate more than the stoichiometric ratio would increase the yield of the reaction. While the yield efficiency is decreased due to the excess alkalinity of ammonium carbonate which affects the agglomeration of calcium carbonate and the formation of thin crystal particles of calcium carbonate which cover the calcium sulfate surface and the reaction is not complete. Hence, the suitable percentage excess amount of ammonium carbonate is 10% for the next experiments.

3.3.3. Effect of solid/liquid phase ratio

The influence of the amount of the phosphogypsum to the distilled water ratio (S/L) upon the product efficiency of ammonium sulfate is studied. Series of experiments are applied by varying S/L ratio from 1/2 to 1/8 while the other factors are kept constant at pH7 of the suspended phosphogypsum, the addition of 10% ammonium carbonate an excess amount more than the stoichiometric ratio in teflon beaker and 150 rpm stirring speed for 4.0 h

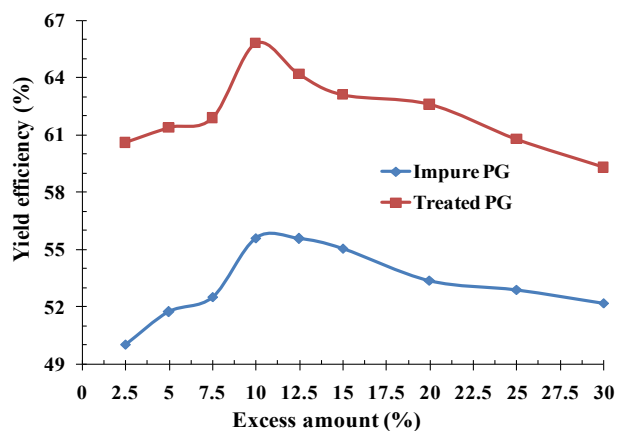


Fig. 6. Effect of $(\text{NH}_4)_2\text{CO}_3$ excess amount percent upon the yield efficiency of ammonium sulfate from impure and treated phosphogypsum.

contact time at room temperature. From the obtained data in Fig. 7, it is indicated that the yield efficiency of the ammonium sulfate product is gradually increased by decreasing the S/L till reaching a maximum value at 1/4 ratio and thereafter the yield efficiency is slightly constant with decreasing ratio of phosphogypsum to distilled water. Hence, the best ratio of the suspended phosphogypsum amount to the distilled water (S/L) is 1/4.

3.3.4. Effect of ammonium sulfate amounts on the dissolution of phosphogypsum

Since the calcium sulfate may be appreciably soluble in the ammonium sulfate solution. Prior to the addition of ammonium carbonate, the effect of ammonium sulfate amount to dissolve phosphogypsum is studied by adding different amount of ammonium sulfate (as initiator) ranging from 1 to 10% in 40 ml distilled water to suspend the phosphogypsum at pH7, 1/4 solid/liquid ratio, the addition of ammonium carbonate with 10% excess amount more than the stoichiometric ratio in teflon beaker and 150 rpm stirring speed for 4.0 h contact time at room temperature. The results in Fig. 8 reveal that the increasing the ammonium sulfate amount in the suspended solution of phosphogypsum from 1 to 3% increases the yield efficiency of the ammonium sulfate product and then with increasing the ammonium sulfate amount leads to be gradually decreased the ammonium sulfate product efficiency. However, the increasing amount of ammonium sulfate is dissolved a large amount of phosphogypsum which may be reacted with ammonium carbonate to form a very slimy calcium carbonate which coats the phosphogypsum particles and suppresses to complete the reaction with ammonium carbonate. Therefore, 3% of ammonium sulfate is the suitable concentration for the dissolution of phosphogypsum to achieve the best yield of ammonium sulfate product.

3.3.5. Effect of contact time

The influence of contact time upon the yield efficiency of ammonium sulfate product is studied in the range from 0.5 to 6.0 h while the other reaction parameters are kept constant at suspended 10 g of phosphogypsum in 40 ml 3% of ammonium sulfate solution (as initiator) at pH7, addition of ammonium carbonate with 10% excess amount more than the stoichiometric ratio in teflon beaker and 150 rpm stirring speed at room temperature. From the obtained results in Fig. 9, it is clear that the yield efficiency of ammonium sulfate product has gradually increased with increasing the contact time till reaching the maximum values at 4.0 h and remains constant after 4.0–6.0 h for the studied reaction.

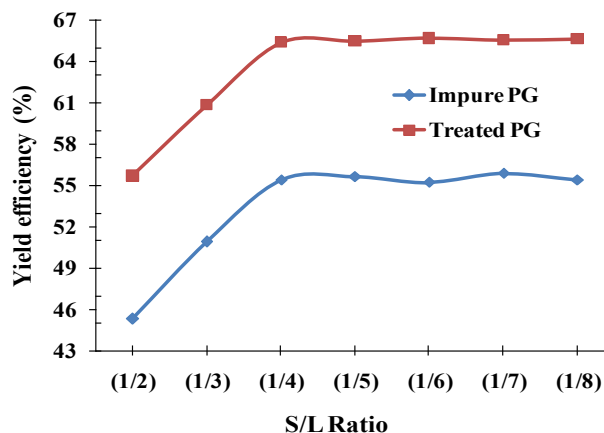


Fig. 7. Effect of the suspended phosphogypsum amount to the distilled water (S/L) ratio upon the yield efficiency of ammonium sulfate.

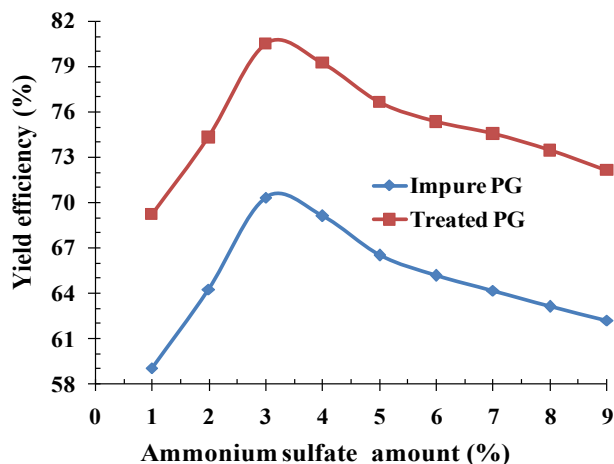


Fig. 8. Effect of the $(\text{NH}_4)_2\text{SO}_4$ amount added to phosphogypsum upon the ammonium sulfate yield efficiency.

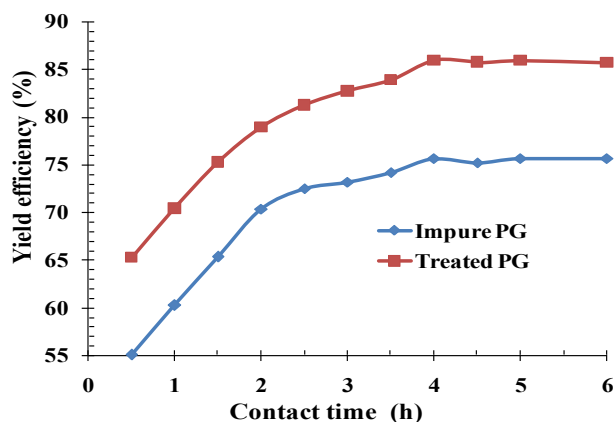


Fig. 9. Effect of the contact time upon the ammonium sulfate yield efficiency from the impure and the treated phosphogypsum.

Therefore, it is reached to equilibrium condition at 4.0 h which is considered the best reaction equilibrium contact time for further work.

3.3.6. Effect of temperature

Temperature is very effective on the preparation of ammonium sulfate. The influence of temperature on the ammonium sulfate product efficiency using 10 g of the suspended phosphogypsum in 40 ml of 3% of ammonium sulfate solution (as initiator), 1/4 (S/L) ratio at pH7 is investigated in the range from 25 to 80 °C while the other reaction parameters are kept constant by the addition of ammonium carbonate with 10% excess amount more than the stoichiometric ratio in teflon beaker and 150 rpm stirring speed for 4.0 h contact time. The obtained data in Fig. 10 indicate that the ammonium sulfate product efficiency has gradually increased with increasing the temperature till reaching the maximum values of 84.22 and 95.12% for impure and treated PG at 55 °C and the rate of reaction is decreased with increasing the temperature from 55 to 80 °C. The increase in the formation of ammonium sulfate with temperature increased until 55 °C which may be either attributed to the increase in the number of active ions available in the reaction solution due to the particles are gained energy and quickly moved, therefore it has more chance for collisions of reactant particles at a short period time. The rate of ammonium sulfate formation is

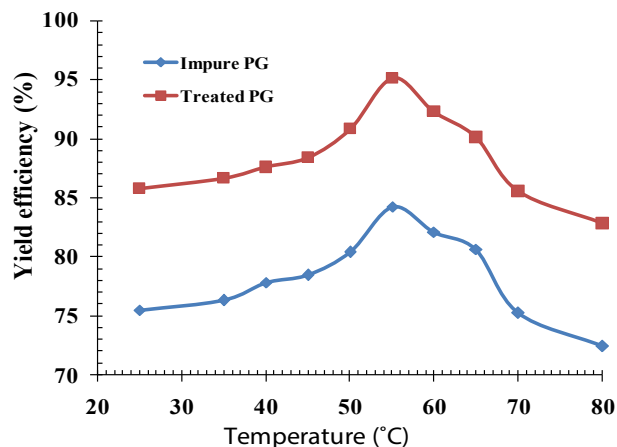


Fig. 10. Effect of temperature on the ammonium sulfate yield efficiency from the impure and the treated phosphogypsum.

decreased with increasing the temperature from 55 to 80 °C due to the breaking of ammonium carbonate and liberation of ammonia from the reaction medium. Therefore, the best of reaction rate at 55 °C.

3.3.7. Effect of radium removal

The radioactive impurity of phosphogypsum is especially radium which is derived from the uranium-rich phosphate rock. Phosphogypsum may be radiochemically converted to another form without the associated radionuclides in a cost effective manner. To assess of radium behavior on the impure and the treated phosphogypsum by sulfuric acid when they react with ammonium carbonate to form ammonium sulfate and calcium carbonate, the activity concentration of radium is determined using high-resolution gamma spectrometry (Table 3). The results indicate that the radium associated with phosphogypsum is almost found exclusively in the byproduct calcium carbonate but the activity concentration of radium may be extremely low in ammonium sulfate. However, the ^{226}Ra originally contained in phosphogypsum will be quantitatively transferred to calcium carbonate. To estimate the final activity of radium in the calcium carbonate by accounting for the differences in molecular weights between the two phases (mol. Wt. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} = 175$, and mol. Wt. $\text{CaCO}_3 = 100$). Thus, assuming that the pure phases are used, therefore, a quantitative transfer of radium from dihydrate gypsum to calcium carbonate will result in the carbonate phase being 1.75 times more concentrated in ^{226}Ra than the gypsum. It should be emphasized, however, that the actual materials in question are not pure. Typical phosphogypsum samples contain 5–15% impurities in the form of silica sand, organic material, and other components. From the results, it is noted that CaCO_3 resulted from impure phosphogypsum is more contaminated than the calcium carbonate obtained from purified

Table 3

Radium activity concentration of the obtained ammonium sulfate from the impure and the treated phosphogypsum using barium chloride.

Constituents	Activity of ^{226}Ra (Bq/Kg)	
	Impure PG	Treated PG
Phosphogypsum	642	546
$(\text{NH}_4)_2\text{SO}_4$ without BaCl_2	35	22
$(\text{NH}_4)_2\text{SO}_4$ with 5 mg BaCl_2	0	0
CaCO_3	895	793

Bq/Kg; Becquerel/Kilogram of the sample.

phosphogypsum with sulfuric acid.

To study the complete removal of the trace amount of radium from the obtained ammonium sulfate products, which are produced from the impure or the treated phosphogypsum using 10 g of the suspended phosphogypsum in 40 ml of 3% ammonium sulfate solution (as initiator), 1/4 solid/liquid ratio at pH7, addition of ammonium carbonate with 10% excess amount more than the stoichiometric ratio in teflon beaker, 150 rpm stirring speed and after 3.0 h subsequently addition of barium chloride amount ranging from 1 to 10 mg and then permitted the reaction is complete up to 4.0 h contact time at 55 °C. The addition of barium chloride to the reaction mixture in order to transfer the trace amount of radium on calcium carbonate due to the formation of a precipitated double salt of radium-barium carbonate whereas barium is acted as a carrier of radium from its solutions where barium is similar to radium in the chemical properties. Calcium carbonate residue is removed by filtration whereas the filtrate solution is ammonium sulfate which is dried and crystallized to obtain a solid crystal of ammonium sulfate which is introduced to determine the activity concentration of radium in solid ammonium sulfate. From the obtained results it can be seen that there is not any activity concentration of radium in the ammonium sulfate product above the addition of 5 mg of barium chloride. Accordingly, 0.25 g of barium chloride is added to 0.5 Kg of impure or purified phosphogypsum to remove all radium ions from ammonium sulfate product.

3.4. Purity of calcium carbonate byproduct

The effects of the impure and the treated phosphogypsum upon the calcium carbonate byproduct efficiency (purity of byproduct) are really applied using 10 g of the suspended impure or treated phosphogypsum in 40 ml of 3% ammonium sulfate solution (as initiator), 1/4 solid/liquid ratio at pH7 while the other reaction parameters are kept constant at an addition of ammonium carbonate with 10% excess amount more than the stoichiometric ratio in teflon beaker and 150 rpm stirring speed for 4.0 h contact time at 55 °C. The obtained calcium carbonate byproduct from the two experiments are dried in air and then analyzed by a titrimetric method using ethylene diamine tetraacetic acid (EDTA) and thermogravimetric analysis (TGA) to determine the yield efficiency of calcium carbonate. Thermogravimetric analysis (TGA) is conducted under heating from room temperature to 995 °C at 10 °C/min in a nitrogen atmosphere with a nitrogen flow rate of 20 ml/min. The weight loss profile is used for preliminary estimates of purity and composition of calcium carbonate. From the TGA data shown in Figs. 11 and 12 and the analytical results indicated that the recoveries of calcium carbonate are attained at 68.18 and 89.31% for the impure and the treated phosphogypsum respectively. The TGA curves show a weight loss occurring between 600 °C and 770 °C. These are attributed to the evolution of carbon dioxide from the decomposition of calcium carbonate. To evaluate the purity of calcium carbonate, suppose the purity of the obtained calcium carbonate byproduct is 100% during the complete stoichiometric reaction of the purified reactants, thus, the evolved amount of CO₂ is attained 44%. Using TGA data, the evaluation the yield efficiency or purity of CaCO₃ is obtained for the impure and purified phosphogypsum. And therefore, the amount of ammonium sulfate can be determined which it is conjugated with the CaCO₃. Accordingly, the best yield of ammonium sulfate is also confirmed using the above data. The byproduct, calcium carbonate, may be used for neutralizing acidic process water associated with the phosphate industry, or calcined to drive off the CO₂ which could be recycled for the production of the ammonium carbonate needed in the production of ammonium sulfate.

3.5. Crystallization of high purity ammonium sulfate

The highly purified ammonium sulfate fertilizer is obtained by applying the obtained optimum conditions for the removal of the most impurities in the used phosphogypsum using sulfuric acid and also applying the optimum condition of the ammonium sulfate preparation. The purification of the studied phosphogypsum by H₂SO₄ is obtained by treatment 1 Kg of the properly ground sample (–200 mesh size) with 4 L of 8 M H₂SO₄ and 150 rpm agitating speed for 30 min contact time at 80 °C. The obtained precipitate is the highly purified phosphogypsum which is used to obtain the highly purified ammonium sulfate fertilizer, the preparation of ammonium sulfate process is applied using suspended 500 g purified phosphogypsum which is contained 410.6 g calcium sulfate in 2 L of 3% ammonium sulfate solution (as initiator), 1/4 solid/liquid ratio at pH7, the slurry is reacted with ammonium carbonate with 10% excess amount more than the stoichiometric ratio (3.18.8 g of (NH₄)₂CO₃) in the reactor at 150 rpm stirring speed and after passed 3.0 h on the reaction, it is subsequently added 250 mg of barium chloride to remove radium from the solution and the reaction is permitted to complete up to 4.0 h contact time at 55 °C. The slurry is subjected to precipitate and then filter the solution. The ammonium sulfate filtrate solution is subjected to concentrate to a suitable volume at a constant temperature. The residual concentrate is kept at room temperature to form ammonium sulfate crystals. The condensation and crystallization steps are repeated until no more crystal could be produced. The combined product was dried under ambient air before determining the total weight. The obtained weight of the dried ammonium sulfate is 378.5 g. The purity of ammonium sulfate is determined by measuring the melting point which is attained 238 °C whereas the melting point for the standard ammonium sulfate is 240 °C and the chemical analysis for the nitrogen and sulfur are attained 20 and 23.6% respectively using the Kjeldahl method for nitrogen content and gravimetric determination of sulfur content. From the obtained data of TGA curve is shown in Fig. 13, the total decomposition of the ammonium sulfate product is achieved at a maximum weight loss at 422.5 °C. The obtained ammonium sulfate product has a 94.39% purity that is close to the practical yield efficiency (95%). Besides, the studied ammonium sulfate product is really contained 20% nitrogen while the ammonium sulfate produced from Suez Company for Fertilizer Production (SCFP) is contained 20.6% nitrogen and taking into account the production of SCFP, ammonium sulfate is made by the direct method which is comprised the reaction between ammonia and sulfuric acid. The formulated flow sheet for the highly purified ammonium sulfate production from phosphogypsum sample is presented in Fig. 14.

4. Conclusion

The highly purified ammonium sulfate fertilizer is obtained by applying the obtained optimum conditions for the removal of the most impurities in the used phosphogypsum using sulfuric acid and also applying the optimum condition of the ammonium sulfate preparation. The purification of the studied phosphogypsum by H₂SO₄ is obtained by treating 1 Kg of the properly ground sample (–200 mesh size) with 4 L of 8 M H₂SO₄ and 150 rpm agitating speed for 30 min contact time at 80 °C. The obtained precipitate is the highly purified phosphogypsum which is used to obtain the highly purified ammonium sulfate fertilizer, the preparation of ammonium sulfate process is applied using the suspended of 500 g purified phosphogypsum which is contained 410.6 g calcium sulfate in 2 L of 3% ammonium sulfate solution (as initiator), 1/4 solid/liquid ratio at pH7, the slurry is reacted with ammonium carbonate with 10% excess amount more than the stoichiometric ratio

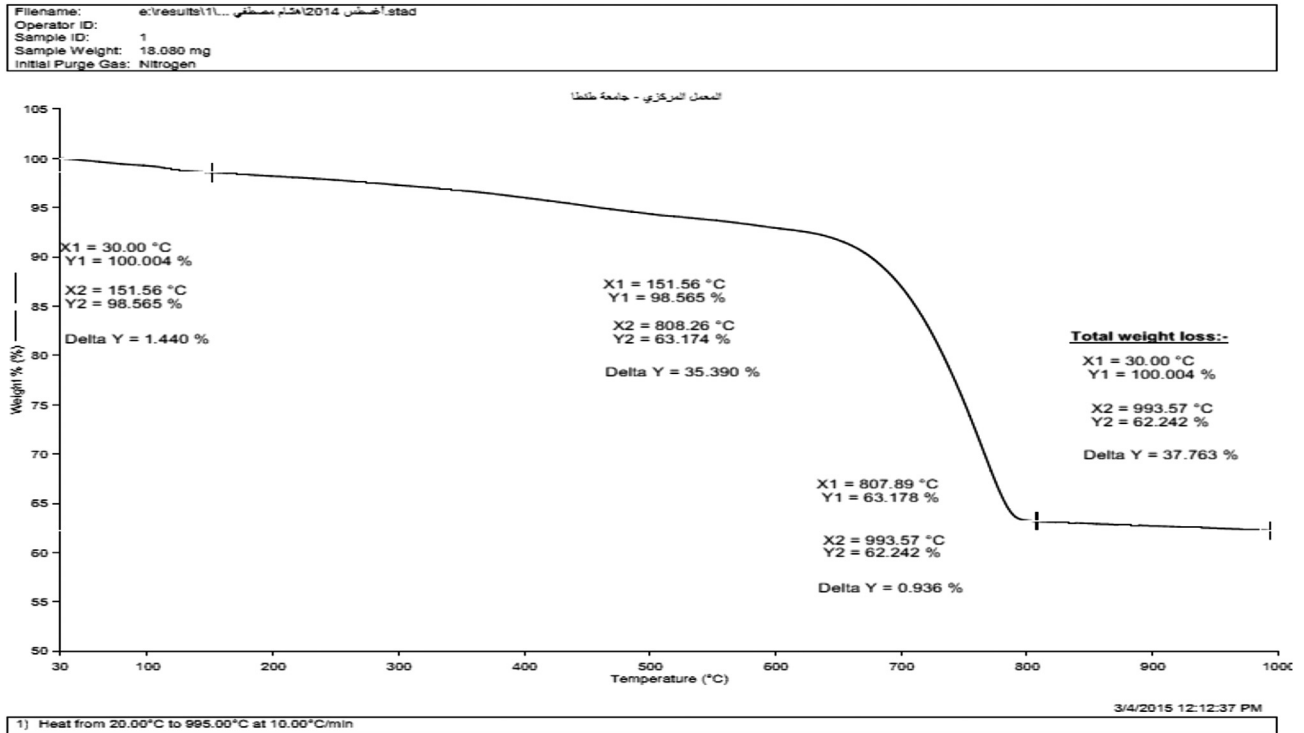


Fig. 11. TGA results of weight loss for the obtained CaCO_3 solid byproduct from the impure PG at a heating rate of $10^\circ\text{C}/\text{min}$ in nitrogen atmosphere.

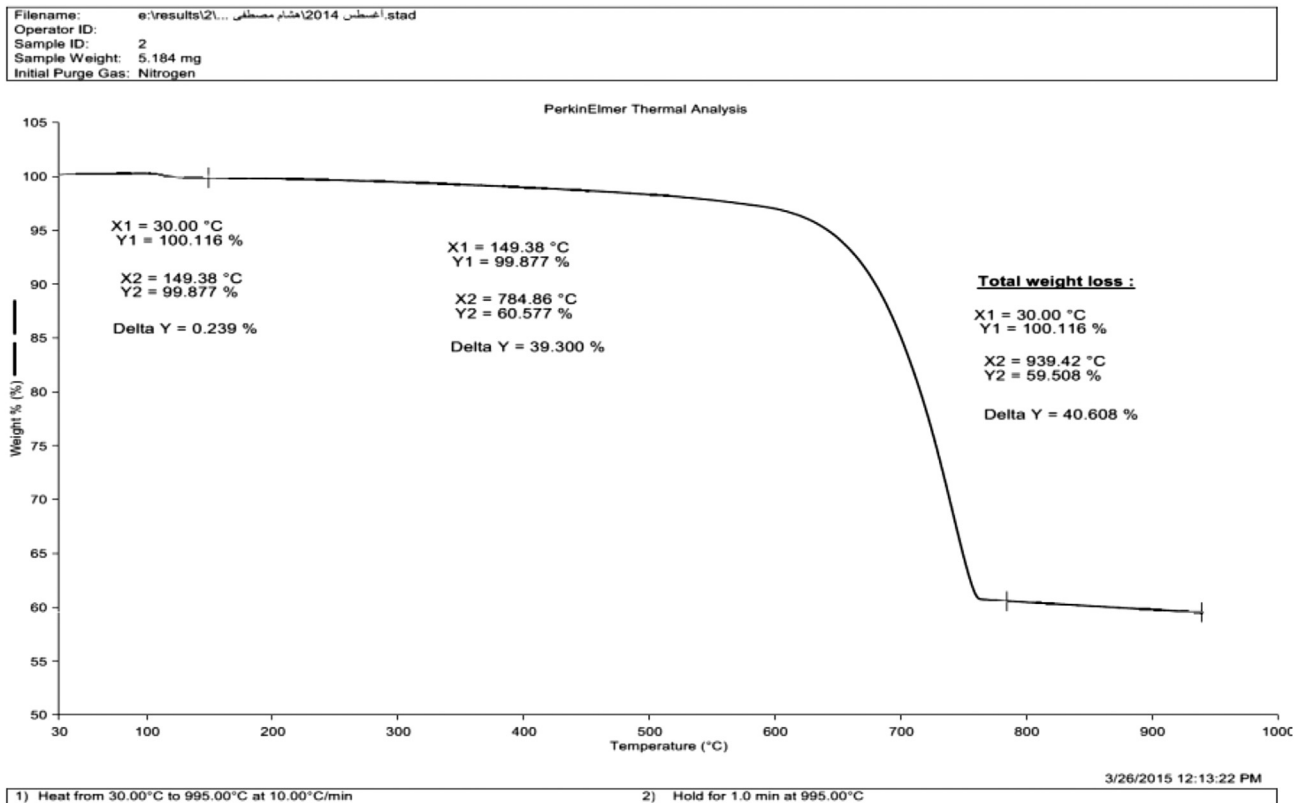


Fig. 12. TGA results of weight loss for the obtained CaCO_3 solid byproduct from the treated PG at a heating rate of $10^\circ\text{C}/\text{min}$ in nitrogen atmosphere.

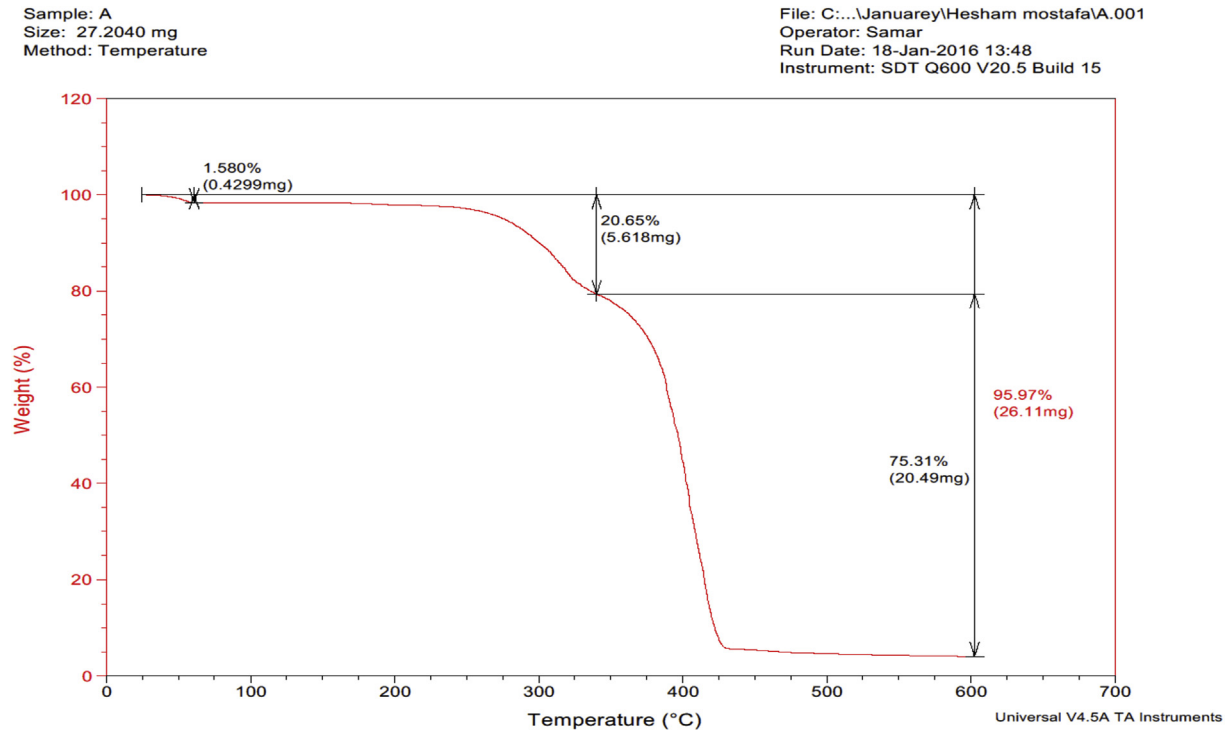


Fig. 13. TGA results of weight loss for the $(\text{NH}_4)_2\text{SO}_4$ solid obtained from the treated phosphogypsum at a heating rate of $10^\circ\text{C}/\text{min}$ in nitrogen atmosphere.

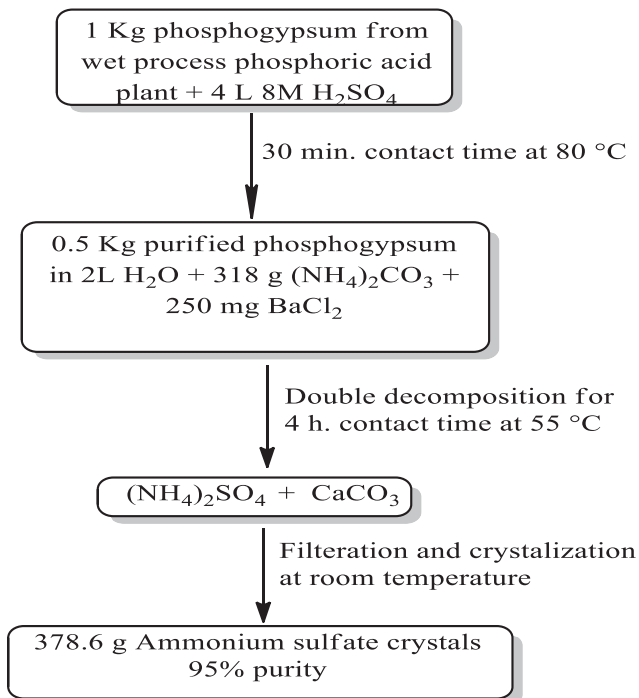


Fig. 14. Formulated flowsheet for the production of highly purified ammonium sulfate fertilizer from phosphogypsum sample.

(3.18.8 g of $(\text{NH}_4)_2\text{CO}_3$) in the reactor at 150 rpm stirring speed and after passed 3.0 h on the reaction, it is subsequently added 250 mg of barium chloride to remove radium from the solution and the reaction is permitted to complete up to 4.0 h contact time at 55°C . The slurry is subjected to precipitate and then filter the solution.

The byproduct, calcium carbonate residue, may be used for neutralizing acidic process water associated with the phosphate industry, or calcined to drive off the CO_2 which could be recycled for the production of the ammonium carbonate needed in the production of ammonium sulfate. Moreover, the ammonium sulfate solution is subjected to concentrate to a suitable volume in a constant temperature water bath. The residual concentrate is kept at room temperature to form ammonium sulfate crystals. The obtained weight of the dried ammonium sulfate is 378.5 g. The purity of ammonium sulfate is determined by measuring the melting point which is attained 238°C whereas melting point for the standard ammonium sulfate is 240°C and chemical analysis for the nitrogen and sulfur are attained 20 and 23.6% respectively. The obtained ammonium sulfate product has a percent of purity equals 95%. The flow sheet for the highly purified ammonium sulfate production from phosphogypsum sample is constructed.

References

- Abu-Eishah, S. I., & Abu-Jabal, N. M. (2001). Parametric study on the production of phosphoric acid by the dihydrate process. *Chemical Engineering Journal*, 81(1–3), 231–250.
- Berish, C. W. (1990). Potential environmental hazards of phosphogypsum storage in central Florida. In *Proceedings of the third international symposium on phosphogypsum, Orlando, FL* (pp. 1–29). FIPR Pub. No. 01060083, 2.
- Blouin, G. M., Livingston, O. W., & Getsinger, J. G. (1970). Bench-scale studies of sulfate recycle nitric phosphate process. *Journal of Agricultural and Food Chemistry*, 18(2), 313–318.
- Budesinsky, B. W. (1975). Determination of sulfate in waters. *Microchemical Journal*, 20(3), 360–362.
- Burnett, W. C., Schultz, M., & Hull, C. (1995). *Behavior of radionuclides during ammonocarbonation of phosphogypsum*. Final Repot. Florida 32306, USA: Florida State University Tallahassee, 29p.
- Dudal, R. (2002). Forty years of soil fertility work in sub-Saharan Africa. In B. Vanlauwe, et al. (Eds.), *Integrated plant nutrient management in sub-Saharan Africa: From concept to practice*. Wallingford: CAB International.
- El-Didamony, H., Gado, H. S., Awwad, N. S., Fawzy, M. M., & Attallah, M. F. (2013). Treatment of phosphogypsum waste produced from phosphate ore processing. *Journal of Hazardous Materials*, 244–245, 596–602.
- EPA. (2004). Understanding variation in partition coefficient, K_d , values. In *Review of*

- geochemistry and available K_d values for americium, arsenic, curium, iodine, neptunium, radium, and technetium (Vol. 3).
- FAO. (2003). Towards sustainable agriculture and rural development in the Ethiopian highlands. In D. Alemneh, Z. Gete, A. Solomon, & L. Mekonnen (Eds.), *Proceedings of the technical workshop on improving the natural resources base and rural well-being, 25–27 November 2003, Bahir Dar, Ethiopia*. Environment and Natural Resources Working Paper No. 17.
- Goers, W. E. (1980). Nissan hemi phosphogypsum, phosphogypsum. In *Proceedings of the international symposium on phosphogypsum utilization and/or disposal of phosphogypsum potential barriers to utilization, Lake Buena Vista*. The Florida Institute of Phosphate Research.
- Habashi, F., Awadalla, F. T., & Zailaf, M. (1986). The recovery of uranium and the lanthanides from phosphate rock. *Journal of Chemical Technology and Biotechnology*, 36, 259–267.
- Hoefl, R. G., Sawyer, J. E., Heuvel, R. M. V., Schmitt, M. K., & Brinkman, G. S. (1985). Corn response to sulfur on Illinois soils. *Journal of Fertilizer*, 295–304.
- Kacimi, L., Simon-Masseron, A., Ghomari, A., & Derriche, Z. (2006). Reduction of clinkerization temperature by using phosphogypsum. *Journal of Hazardous Materials*, 137(1), 129–137.
- Kandil, A. T., Gado, H. S., Cheira, M. F., Soliman, M. H., & Akl, H. M. H. (2016). Potentiality of fluoride determination from Egyptian phosphogypsum using an ion selective electrode. *IOSR Journal of Applied Chemistry*, 9(4), 1–11.
- Khadilkar, S. A., Karandikar, M. V., Anikode, P. R., Lele, P. G., Vaity, R. S., Pathak, A. K., 2009. Method of intertising impurities in phosphogypsum. US Patent. 20090291037.
- Klaus, G., 1974. Processes for the treatment of crude calcium sulfate to render it suitable for conversion to plaster of Paris. US Patent, 3847766.
- Klaus, S., Hurth, G., & Hoechst, A. (2002). *Ullmann's encyclopedia of industrial chemistry*. Germany: Wiley-VCH Verlag.
- Krempff, R., 1976. Method for the treatment of phosphogypsum. US Patent, 3951675.
- Langmuir, D., & Riese, A. C. (1985). The thermodynamic properties of radium. *Geochemica et Cosmochimica Acta*, 49, 1593–1601.
- Manjit, S. (2002). Treating waste phosphogypsum for cement and plaster manufacture. *Cement and Concrete Research*, 32(7), 1033–1038.
- Manjit, S., Garg, M., & Rehsi, S. S. (1993). Purifying phosphogypsum for cement manufacture. *Construction and Building Materials*, 7(1), 3–7.
- Meline, R. S., Faucett, H. L., Davis, C. H., & Shirley, A. R., Jr. (1971). Pilot-plant development of the sulfate recycle nitric phosphate process. *Industrial & Engineering Chemistry Process Design and Development*, 10(2), 257–264.
- Parreira, A. B., Kobayashi, A. R. K., & Silvestre, O. B. (2003). Influence of Portland cement type on unconfined compressive strength and linear expansion of cement-stabilized phosphogypsum. *Journal of Environmental Engineering*, 129, 956–960.
- Reddy, K. S., Naidu, M. V. S., Vani, P. M., Padmaja, D., Kavitha, P., & Prasad, P. R. K. (2011). *Manures, fertilizers and agricultural chemicals*. Course No.: SSAC 321. Tirupati-517 502: Department of Soil Science and Agril. Chemistry S.V.Agricultural College.
- Rutherford, P. M., Dudas, M. J., & Samek, R. A. (1994). Environmental impacts of phosphogypsum. *The Science of the Total Environment*, 149(1–2), 1–38.
- Schwenke, G., & McMullen, G. (2009). Nitrogen volatilization from northern cropping soils. In *GRDC advisors update - Dubbo*, 6.
- Shapiro, L., & Brannock, W. W. (1962). *Rapid analysis of silicate, carbonate, and phosphate rocks*. U.S. Geol. Surv. Bull. 1144. A, 56.
- Sharma, B. K. (1991). *Industrial chemistry*. Krishna Prakashan Media (P) Ltd., p. 455.
- Tayibi, H., Choura, M., López, F. A., Alguacil, F. J., & López-Delgado, A. (2009). Environmental impact and management of phosphogypsum. *Journal of Environmental Management*, 90, 2377–2386.
- Tisdale, S. L. (2002). *Sulfur in forage quality and ruminant nutrition*. 1140 Connecticut Avenue NW, Suite 612, Washington DC 20036, USA: The Sulphur Institute. Technical Bulletin Number 22, 11.
- UNSCEAR. (2000). *United nations scientific committee on the effect of atomic radiation, exposure from natural radiation sources*. New York: United Nations.
- USEPA. (2002). *U.S. Environmental protection agency, national emission standards for hazardous air pollutants* (Subpart R).
- Yang, J., Liu, W., Zhang, L., & Xiao, B. (2009). Preparation of load-bearing building materials from autoclaved phosphogypsum. *Construction and Building Materials*, 23, 687–693.
- Yong, R. N., Mulligan, C. N., & Fukue, M. (2007). *Geoenvironmental sustainability*. CRC press, Tylor & Francis Group. p. 211.