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REACTION PARAMETER OPTIMIZATION OF AMMONIUM SULFATE PRODUCTION FROM PHOSPHOGYPSUM

Article Highlights
- A facile approach to phosphogypsum-derived ammonium sulfate production is presented
- The application of the proposed reaction sequence on industrial potential is discussed
- An effective waste management strategy for phosphogypsum is proposed

Abstract

Phosphogypsum (PG), the by-product of wet process phosphoric acid production, has a high recycle and reuse potential within the scope of compliance with CE strategies. This study offers a straightforward, two-step solid/liquid heterogeneous reaction sequence, providing the conversion of PG to ammonium sulfate (AS). Experiments were conducted following the OFAT design matrix with 3 factors, namely solid/liquid (w/v) ratio, pH, and particle size. The highest PG to AS conversion was achieved at 54.55% by utilizing PG below 125 μm particle size in the reaction performed with 1/10 solid/liquid (w/v) ratio at pH 10. Nitrogen and sulfur content of AS samples were characterized by Dumas Method and gravimetric SO_4 (ISO 9280:1990) analysis, respectively. The elemental composition was determined by ICP-OES, the crystallographic structure was investigated by XRD analysis, and the surface morphology of the particles obtained in the reaction was examined by SEM analysis. The chemical composition of AS product obtained at these conditions was determined as 21.29 wt% nitrogen and 24.23 wt% sulfur, respectively; where theoretical nitrogen and sulfur content in AS is 21.21 wt% and 24.24 wt%, respectively. This study provides outputs that have industrial importance since it proposes a novel approach for effective waste valorization and a new insight into AS production in the current fertilizer shortage.

Keywords: ammonium sulfate; circular economy; wet conversion; phosphogypsum; resource recovery.

Recent estimations show that the global population has increased to 8.1 billion, and projections expect that the number will reach up to 8.5 billion by 2030, and 9.8 billion by 2050 [1]. A direct relation between the population and food demand has made it crucial to achieve higher yields per application in agriculture. Mineral fertilizers include the essential nitrogen (N), phosphorus (P), and potassium (K) nutrients together with trace elements specified in variable formulations, and they are extensively used to enhance yield. According to the demand for mineral fertilizer application, annual production capacity has also increased to balance the supply and demand [2,3]. Geopolitical and economic world events also affect the affordability and availability of fertilizers. The COVID-19 pandemic resulted in elevated costs of raw materials and final fertilizer products, interrupting the food production and supply balance and resulting in changes in dietary patterns. Following the Russian-Ukrainian conflict, the world this time faced a malnutrition challenge since these countries provide 24% of the global wheat demand [4,5]. In the 4 years after the emergence of the COVID-19 pandemic, it can

be said that agriculture has been mostly affected in terms of the supply-demand ratio, labor shortages in the farming systems, and relevant negative impacts on the rural economy due to price fluctuations and lack of markets [6]. Lockdowns in the major countries have disrupted the balance in the production chain as in the case of China, the world's largest urea manufacturer [7]. Apart from the food-fertilizer perspective, energy should also be discussed since fertilizer production is an energy-intensive process. COVID-19 has also had a negative impact on the energy market and oil prices, which indirectly affects the fertilizer production capacity [8]. Russia, on the other hand, is an important exporter of mineral fertilizers and apart from the pandemic, the Russia-Ukraine conflict has resulted in decreasing production trends in N, P, and K-based fertilizers [9].

Food shortage risks cause new economic and societal concerns, and it is clearly foreseen that the food supply-demand chain will face possible disturbance soon. Apart from food demand, population increase brings an increase in the industrialization capacity. These two key factors have a cumulative effect on the unsustainable resource consumption and greenhouse gas (GHGs) emission increase, resulting in irreversible environmental challenges. Global warming, global resource depletion, and industrial or municipal waste increase have resulted in crisis on environmental and societal scale [10]. These latest socio-economic and environmental issues have recalled the importance of sustainable resource utilization. In this manner, the industrial waste management approach might provide a viable route by introducing the waste generated into re-processes. Introducing the circularity of industrial wastes to serve for circular economy (CE) strategy would also maintain sustainable resource consumption.

Phosphoric acid is the main raw material in phosphate-based fertilizer production. Demand for mineral fertilizers also triggered the annual production capacity of phosphate-based fertilizers and as-related phosphoric acid production. Phosphogypsum (PG) management, the by-product of wet process phosphoric acid production, is a multi-fold problem solver related to the above-mentioned highlights. Being generated up to 300 million tons annually and having a relatively low recycling rate below 15%, the rest amount is stored in landfills or discharged into aquatic environments [11].

Increasing the circularity of PG for various applications would provide an efficient approach to the industrial waste storage problem, which might have adverse effects on the ecosystem in the long term together with providing multi-step sustainable resource utilization cycles [12].

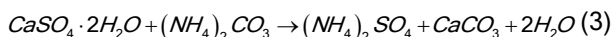## Relation between PG utilization and agriculture

PG is chemically gypsum ($CaSO_4·2H_2O$) with some impurities, having approximately 30% Ca in CaO form and 55% S in SO_4 form, making it a suitable resource for agricultural applications. Its porous structure and high water-holding capacity make the material a mitigating tool for soil degradation and soil improvement. Apart from these direct application methods, PG can also be introduced into the production cycle as raw material for organomineral fertilizer production [13]. Another utilization approach of PG is the ammono-carbonation route, in which ammonium sulfate (AS) is produced [14]. AS has nitrogen and sulfur as ammonium and sulfate forms, respectively, and provides dual nutrients to plants due to its chemical structure [15]. Application of AS can be conducted directly as a fertilizer or can be utilized as the nitrogen and/or sulfur source in the formulation of compound fertilizers. Conventional ammono-carbonation route of PG yields AS and calcium carbonate ($CaCO_3$), both products have commercial value for various industrial applications. This route also provides effective approaches to permanent CO_2 storage as stable $CaCO_3$, also known as the mineral carbonation route [16–18]. Utilization of PG as the raw material for AS production processes would provide an efficient waste management strategy. This approach would also provide a problem-solving policy for the management of PG piles on a local basis and a tool for low-cost raw materials for AS production. PG valorization in AS production processes would also provide a solution to increasing fertilizer demand. Besides, with an annual generation rate of up to 300 million tons today, PG will be provided as a continuous raw material supply for the continuity of the AS production process. The straightforward route provided by this study might offer an effective PG management strategy in developing PG-derived AS production technology. The outcomes of the study have industrial importance since it provides a novel approach for effective waste valorization. In addition, having a high potential to scale up, this study would carry a new insight into low-cost AS production in the current fertilizer shortage.

In the study on the production of ammonium sulfate from phosphogypsum due to the extreme fluctuation in ammonia prices with the COVID-19 pandemic, it was reported that the cost of producing ammonium sulfate from phosphogypsum would be more costly than the producer's production of ammonium sulfate without using phosphogypsum as a raw material [19]. The use of waste materials such as phosphogypsum as raw materials will be an important contribution to the sustainability of the circular

economy, as the amount of fixed inputs such as in-process raw materials and temperature to increase production efficiency will vary during the reaction, positively affecting the reaction efficiency. In this respect, producing ammonium sulfate from a waste material such as phosphogypsum, which is an industrially controversial waste material, will avoid its contribution to the reaction efficiency or a feasibility study that is not excessively high.
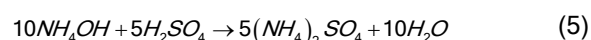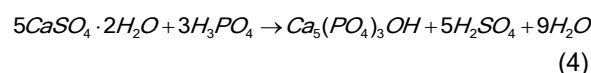
MATERIAL AND METHODS

Production of AS from PG through the ammono-carbonation route is an old-school technology. Known as the Merseburg Process in the literature, the reaction sequence is based on the reaction between anhydrous or hydrated gypsum ($CaSO_4 \cdot H_2O$) and ammonium carbonate (($NH_4)_2CO_3$), yielding AS (($NH_4)_2SO_4$) and calcium carbonate ($CaCO_3$) [20]. In case where PG is utilized, the reaction sequence is given in Eqs. (1–3) below:

$$NH_3 + H_2O \rightarrow NH_4OH \tag{1}$$

$$2NH_4OH + CO_2 \rightarrow 2(NH_4)_2CO_3 + H_2O \tag{2}$$

$$CaSO_4 \cdot 2H_2O + (NH_4)_2CO_3 \rightarrow (NH_4)_2SO_4 + CaCO_3 + 2H_2O \tag{3}$$

Merseburg Process is only available when there is a continuous CO_2 source. In this manner, this old-school technology can be a research hotspot, because it provides both CO_2 and PG consumption [21]. However, the investment and operating costs of the process hinder the real-time operation on an industrial scale and only 3% of the global AS production is through the "gypsum" route [22].

AS production through the reaction of PG and phosphoric acid in alkali media as a two-step sequence Eqs. (4) and (5) can also be viable [23].

$$5CaSO_4 \cdot 2H_2O + 3H_3PO_4 \rightarrow Ca_5(PO_4)_3OH + 5H_2SO_4 + 9H_2O \tag{4}$$

$$10NH_4OH + 5H_2SO_4 \rightarrow 5(NH_4)_2SO_4 + 10H_2O \tag{5}$$

PG samples used in the study were provided by a fertilizer manufacturer in Turkey. 85% H_3PO_4 (Sigma Aldrich) and 21% NH_4OH (diluted by 25% NH_4OH, Sigma Aldrich) were used as the reagents in the reaction. The above-mentioned alkali route Eqs. (4) and (5) is conducted through the preparation of PG: water suspension followed by H_3PO_4 addition for decomposition of PG and calcium phosphate (hydroxyapatite, HAp) formation (Fig. 1). Further steps include pH adjustment via aqueous NH_4OH solution to yield ($NH_4)_2SO_4$ as filtrate.
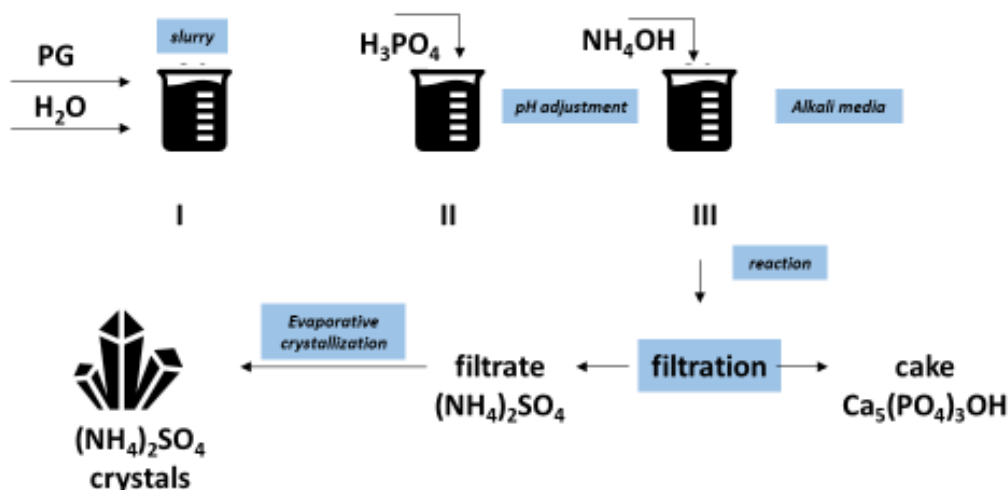

Figure 1. Simplified schematic illustration of the reaction system.

Alkali conditions also provide the precipitation of HAp particles, obtained as the cake when the reaction is terminated. Final AS crystals are obtained via further evaporative crystallization of the filtrate at 120 °C. Obtained AS crystals were oven-dried at 80 °C until constant weight was achieved. HAp particles were also oven-dried at 80 °C.

SEM analysis

SEM analysis (FEI Quanta 650) was conducted to investigate the morphological characteristics of obtained AS samples. The analysis parameters were

determined as maximum magnification 5000, WD; 9.7 mm, resolution 50 nanometers.

The setting of the model and reaction parameters

Optimization of the reaction conditions should be designed in such an experimental strategy to investigate the degree of interactions between variables and experimental error, which have relatively high importance in the design matrix. One factor at a time (OFAT) strategy is designed to investigate the factor relation, in which the matrix was set to seek information about one individual factor per experimental trial while keeping the other factor level constant and observing the sensitivity of the reaction system to the factors [24–26]. The research hypothesis in the study Eqs. (4) and (5) provides a two-step, heterogenous solid-liquid reaction system. The stirring rate was kept constant at 750 rpm in all runs to prevent precipitation of the solid PG particles by providing a continuum in the solid-liquid interface and increasing the reaction surface area. Agitation speed also provided the elimination of mass transfer limitations by reducing diffusion resistance in the heterogenous reaction media.

Experiment runs were conducted at ambient pressure. Although temperature is an important parameter in the reaction yield, thermodynamic analysis of the reaction sequence was calculated regarding the overall reaction given below:

$$5CaSO_4 \cdot 2H_2O + 3H_3PO_4 + 10NH_4OH \rightarrow \\ Ca_5(PO_4)_3OH + 5(NH_4)_2SO_4 + 19H_2O \qquad (6)$$
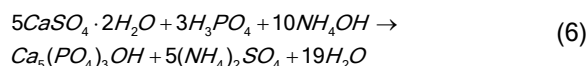
The equilibrium constant (K) of the overall reaction was calculated according to the Van't Hoff equation Eq. (7) by calculating the standard molar Gibbs energy of formation of the reactants at 25 °C (Table 1):

$$\Delta G_f \rightarrow -RT \ln(K) \qquad (7)$$

where R is the gas constant, T is temperature and K is the equilibrium constant.

Table 1. Standard Gibbs energy of formation of reactants and products at 25 °C.

	G_f (kJ/mol)			
reactants	Ref.	products		Ref.
CaSO₄·2H₂O -1795.7	[26]	Ca₅(PO₄)₃OH	-5929.7	[28]
H₃PO₄ -1119.1	[26]	(NH₄)₂SO₄	-901.7	[26]
NH₄OH -253.85	[26]	H₂O	-237.14	[26]

According to the data given in Table 1, the reaction equilibrium constant (K) was calculated to be >>1, indicating that the reaction was spontaneous-

irreversible at 25 °C. Thus, temperature was kept constant at 25 °C in experiment runs. OFAT method was applied to investigate the sensitivity of the reaction sequence based on a quantitative variance system and observed the effects upon the measurement of the output responses. Particle size, solid/liquid ratio in PG/water suspension, and pH (alkalinity strength) were chosen to be the factors, whereas AS yield was the response calculated from the conversion of PG to AS Eq. (8) obtained through evaporative crystallization of the filtrate at 120 °C. Obtained AS crystals were oven-dried at 80 °C until constant weight was achieved.

$$Conversion\ yield\,(\%) = \frac{m\left(SO_4^{2-}\right)_{filtrate}}{m\left(SO_4^{2-}\right)_{PG,initial}} \cdot 100 \qquad (8)$$

where $m(SO_4^{2-})_{filtrate}$ and $m(SO_4^{2-})_{PG,initial}$ denote the quantitative amount of SO_4^{2-} in the filtrate and PG sample, respectively.

Determination of factor ranges

Reaction runs were conducted with PG samples having two different particle sizes, sieved in a range of <10^4 µm and <125 µm to observe the rate-limiting effect of particle size.

According to Eq (4) and (5), the first step prior reaction was the preparation of PG/water suspensions to provide the aqueous reaction media. The solid/liquid (w/v) ratio was investigated at 3 levels, having a constant proportion between the edges and the medium in the determined factor range. This parameter is also directly proportional to the concentration of the filtrate obtained at the end of the reaction and as-related energy consumption during the evaporative crystallization step. Lower aqueous solubility of PG might be a rate-limiting step in the proposed two-step solid-liquid heterogeneous reaction system to provide an adequate solid surface. Although salt solutions are effective in enhancing the solubility of PG, there might be a significant chlorine contamination risk according to the chlorine content of the salt solution [29,30]. Additionally, chloride ions in the reaction media might favor the reaction to ammonium chloride formation and lower the yield of the desired product. Thus, water has been chosen to prepare the suspension before the reaction. Factor ranges were determined in such a ratio to prevent the slurry formation at a constant stirring rate according to the literature search and PG/water suspensions were prepared to have 1/5, 1/7.5, and 1/10 (w/v) ratios [31].

The acidity of the reaction media increases with H_3PO_4 addition. This step provides the degradation of $CaSO_4 \cdot 2H_2O$ structure and formation of calcium-phosphate structure (HAP). Further NH_4OH addition

provides the precipitation of HAP particles in alkali media, which generally occur at a slightly alkaline (pH 9–11) range [32, 33]. Thus, the pH range of the reaction runs was determined to be 9–11. NH_4OH addition favors $(NH_4)_2SO_4$ formation, being the nitrogen source of the desired product.

Table 2. OFAT design matrix for three factors.

Particle size	Solid/liquid ratio (w/v)	pH	Run #
		9	1
	1/5	10	2
		11	3
		9	4
<10^4 µm	1/7.5	10	5
		11	6
		9	7
	1/10	10	8
		11	9
		9	10
	1/5	10	11
		11	12
		9	13
<125 µm	1/7.5	10	14
		11	15
		9	16
	1/10	10	17
		11	18

Reaction runs were conducted in closed vessels according to the OFAT design (Table 2), investigating the factor-response relation per run of overall 18. Cake and filtrate were separated by filtration after the reaction was terminated, followed by the evaporative crystallization step of the filtrate to obtain AS crystals.

RESULTS AND DISCUSSION

18 runs with two replications were conducted to minimize experimental errors. The stirring rate was arranged as 750 rpm in all of the runs to create a constant solid/liquid interface between the reactants. Responses to the factors, mass conversion (%) of PG to AS, were calculated from the net AS amount obtained via the evaporative crystallization step. Table 3 gives the calculated averages of mass conversion of the replicated experiments.

According to the data given in Table 3, optimum reaction conditions in the OFAT matrix were obtained in run # 17. Figures 2 and 3 give the factor-response relation in the OFAT design matrix according to the particle size of PG used, <10^4 µm and <125 µm, respectively.

Figure 2 gives the conversion (%) of PG in specified PG/water (w/v) and pH range. 1/5 and 1/7.5 PG/water (w/v) ratio show relatively lower conversion when compared to 1/10 PG/water (w/v) ratio.

Similar to the results obtained in <10^4 µm particle-sized PG, <125 µm particle-sized PG shows the same

Table 3. Response analysis of experiment runs.

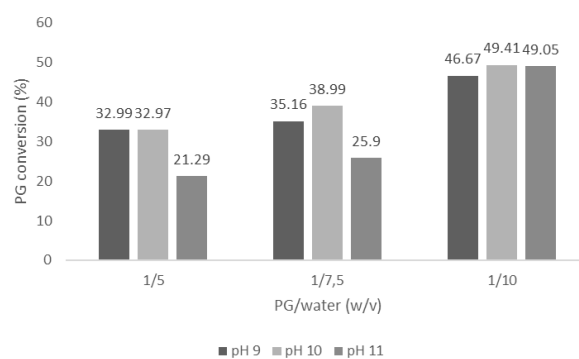| Particle size	Solid/liquid (w/v)	ratio	pH	PG conversion (%)
			9	32.99
	1/5		10	32.97
			11	21.29
			9	35.16
<10^4 µm	1/7.5		10	38.99
			11	25.90
			9	46.67
	1/10		10	49.41
			11	49.05
			9	31.25
	1/5		10	28.04
			11	28.01
			9	26.34
<125 µm	1/7.5		10	40.41
			11	36.39
			9	52.3
	1/10		10	54.55
			11	50.14

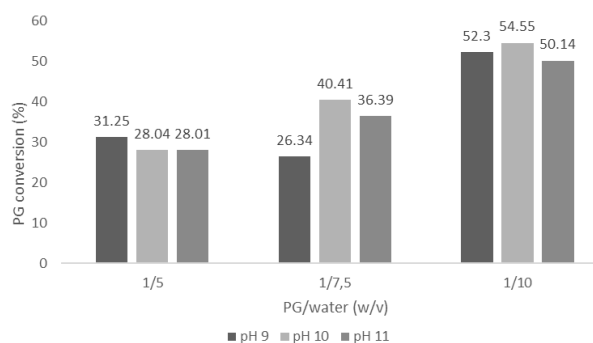*Figure 2. PG conversion (%) according to solid/liquid ratio and pH (PG particle size <10^4 µm).*

Figure 3. PG conversion (%) according to solid/liquid ratio and pH (PG particle size <125 µm).

conversion trend. A higher conversion ratio at 1/10 PG/water (w/v) ratio might be attributed to the lower aqueous solubility of PG at dense PG-water suspensions [34]. Solubility of PG at aqueous media is a driving force for the availability of SO_4^{2-} in the reaction media, which will further act as the sulfur source in the formation of AS.

NH_4OH addition has critical importance in ther

reaction sequence since it is the nitrogen source of the desired AS product. pH and NH_4OH addition are related to each other, and the lowest conversions were obtained for pH 9 condition sets. Reactions conducted at pH 10 and 11 showed similar conversion (%) at a 1/10 PG/water (w/v) ratio, however, the highest conversion yields were obtained at pH 10 condition. Higher conversion with lower raw material input might favor the economic feasibility of the reaction sequence in case of scaling up. A decrease in the particle size has increased the conversion yield of PG. Variations in the particle size might have acted as a rate-limiting step during the reaction [35]. $<10^4$ µm particle-sized PG might have a variable particle size distribution when compared to <125 µm particle size range and lower particle size has increased the surface area during the reaction.

According to the factor-response analysis, the optimum reaction conditions for the proposed reaction sequence were determined as in the case of run #17, where the PG/water ratio was 1/10 (w/v), pH 10 with PG having <125 µm particle size. Experimental studies revealed that a higher conversion yield was obtained as the particle size of the PG sample decreased. This phenomenon can be attributed to the increase in the reaction rate due to the increased surface area as the particle size of the reactant decreases. 54.55% mass conversion was obtained at the determined optimum conditions. However, stoichiometric conversion (Eq. 6) was calculated as 76.74%. When compared to stoichiometric data, the 54.55% conversion efficiency of PG can be considered relatively low. Reaction modifications such as excess NH_4OH utilization, incorporating AS in the reaction media as the seed product, or observing the catalytic effect of H_2SO_4 on the probable ongoing side reaction between NH_4OH can be employed to increase the conversion efficiency. H_2SO_4 can also be utilized as a crystallization aid after phase separation by directly introducing it to the filtrate in the evaporative crystallization step [36].

Chemical composition verification of obtained AS in the optimum conditions was conducted via Dumas and ISO 9280:1990 methods to measure nitrogen and sulfate content, respectively. Ammonium sulfate theoretically has 27.27 wt% of NH_4, which is attributed to 21.21 wt% of nitrogen. According to Dumas method, synthesized AS product had 21.29 wt% nitrogen. Sulfate content in theoretical AS is 72.72 wt%, whereas sulfur content is calculated as 24.24 wt%. According to ISO 9280:1990 analysis, the AS sample had 72.69 wt% sulfate, which is calculated as 24.23 wt% sulfur. Chemical composition analysis results revealed that the nitrogen and sulfur content of obtained AS samples comply with theoretical grades in AS.

The elemental composition of AS samples obtained at the optimum conditions was investigated by the ICP-OES analysis (Table 4) in comparison with the analytical grade AS (Sigma Aldrich).

Table 4. ICP-OES analysis results of AS.

Sample	Elemental Composition (ppm)			
	Al	Cd	Cu	Mn
Reference AS Sigma Aldrich	1,533	(-)	(-)	0,0197
AS obtained at <125 µm PG, s/l 1/10 (w/v), pH 10	1,429	0,143	1,404	(-)

Cr, Ni, and Pb were not detected in both reference and obtained AS samples. The Al content in the obtained AS sample was lower than the reference, at 1.429 and 1.533 ppm, respectively. Cd and Cu were not observed in the reference material; however, 0.143 and 1.404 ppm Cd and Cu were analyzed in the obtained AS sample, respectively. Contrary to Cd and Cu, the Mn content was analyzed in the reference AS sample as 0.0197 ppm and was not analyzed in the synthesized AS sample. According to ICP-OES results, the synthesized AS sample has a low impurity content, indicating that PG-based impurity transition occurs to the solid phase, and the AS sample obtained through evaporative crystallization of the filtrate has relatively low impurity content. ICP-OES results of PG used in the reaction and HAp particle obtained in the optimum reaction conditions are given in Table 5.

Table 5. ICP-OES analysis results of PG and HAp.

Sample	Elemental Composition (ppm)					
	Cd	Cr	Cu	Mn	Ni	Pb
PG [36]	1,56	6,27	9,55	15,7	17,16	3,68
HAp [37]	1,468	6,059	NA	3,429	0,3	3,552
*Not Applicable						

Table 5 indicates that the major amount of the impurities that originated in PG remained in the solid phase after the conversion reaction. Considering 54.55% PG conversion to AS, the solid phase can be evaluated as a Ca-rich precipitate with impurities on ppm level.
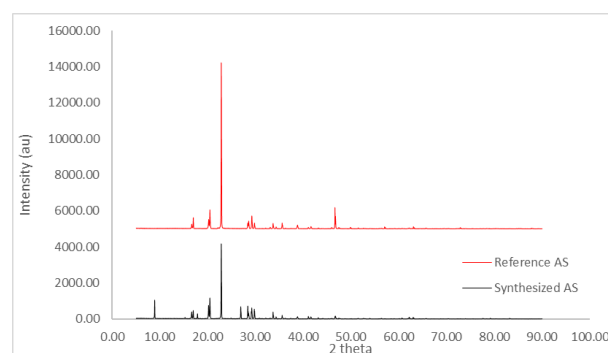

Figure 4. XRD patterns of reference and synthesized AS samples.

Figure 4 was provided as including the XRD pattern of JCPDS standard as a small figure in the upper section, indicating that the crystallographic structure of both samples shows high consistency. Relatively lower intensities of the characteristic peaks of synthesized AS samples are attributed to the impurities in the sample.

The preliminary analysis shows that the obtained crystal product meets the chemical content requirements of AS, but further characterization analysis should be employed. However, the problem is that HAp obtained as a by-product in the production of ammonium sulfate from phosphogypsum cannot be utilized in the agricultural industry [38,39], except for the impurities such as cadmium it contains. It is directly related to the problem of dissolution rate in water and soil.

HAp obtained in the synthesis route can be evaluated through various routes. Owing to the calcium and phosphorus in its chemical composition, HAp particles can be used in agriculture as an alternative phosphorus fertilizer with calcium nutrients. Besides, micronutrient impregnation might also help to widen the fertilizer formulation for specific applications such as nutrient demand for a particular plant growth or deficient nutrient content in the soil where fertilizer is applied. HAp can also be functionalized as a slow-release fertilizer, providing nutrient release in a prolonged time rather than burst release after application [40,41]. HAp particles can also be evaluated as a substitute for bone ash in the ceramics industry; however, there is a lack of literature in this field [42].

According to SEM analysis (Figures 5 and 6), important results were obtained about the transition to crystal structure and the surface properties of different by-products formed depending on the conversion rate.
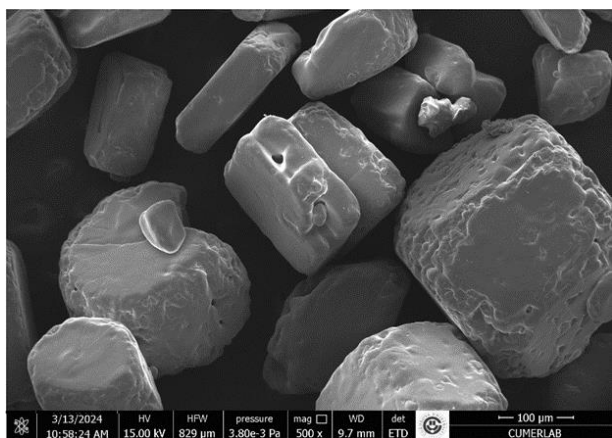

Figure 5. Surface morphology of ammonium sulfate obtained as a result of the experimental process.

During the ammonium sulfate formation reaction,

a significant difference in the crystal structure stands out depending on the conversion rate, but with the formation of HAp, it has been observed that rod-like molecules develop in a way that creates deformation in the crystal structure.
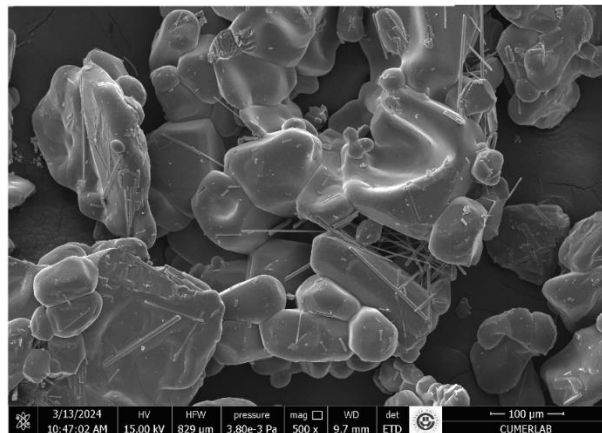

Figure 6. By-products such as HAp formed during the experimental process depending on the conversion rate of ammonium sulfate and their effects on the crystal structure.

According to Figure 6, effective phase separation might reduce reaction residues in the AS sample.

CONCLUSION

The two-step, heterogeneous solid/liquid reaction sequence provided by this study offers the conversion of PG to AS and calcium phosphate, namely hydroxyapatite. OFAT design matrix with three factors, solid/liquid ratio, pH, and particle size, was utilized to investigate the PG conversion (%) as the response. 18 experiment runs with two replicates were performed and the highest PG conversion was achieved at 54.55% in a reaction conducted with a solid/liquid ratio (w/v) of 1/10, pH 10, and PG with the particle size of <125 µm. Obtained solid sample in these reaction conditions had 21.29 wt% nitrogen and 24.23 wt% sulfur, meeting the nitrogen and sulfur content requirement of AS. A dilute suspension system favors PG solubility and provides an adequate solid/liquid interface, and a decrease in particle size also enhances the solid interface. These parameters might adversely affect the economic feasibility of the proposed sequence in terms of scaling up due to the high amount of process water consumption. Detailed research on the development of the study might enhance the industrial applicability of the proposed synthesis route. In case of scaling up, this study might provide local investments where PG piles are stored, where an effective recycle route for PG and low-cost production of AS are conducted.

ACKNOWLEDGMENT

NOMENCLATURE

PG	Phosphogypsum
AS	Ammonium sulfate
HAp	Hydroxyapatite
OFAT	One factor at a time
CE	Circular Economy
GHG	Greenhouse Gas
XRD	X-Ray Diffraction Spectroscopy
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectroscopy

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OPTIMIZACIJA REAKCIONIH PARAMETARA PROIZVODNJE AMONIJUM-SULFATA IZ FOSFOGIPSA

Fosfogips (PG), nusproizvod proizvodnje fosforne kiseline u vlažnom procesu, ima visok potencijal recikliranja i ponovne upotrebe u okviru usaglašenosti sa strategijama cirkularne ekonomije. Ova studija nudi jednostavnu, dvostepenu heterogenu čvrsto/tečno reakciju kojom se PG konvertuje u amonijum-sulfat (AS). Eksperimenti su sprovedeni prema dizajnu OFAT matrice sa 3 faktora - odnos čvrsto/tečno, pH i veličina čestica. Najveća konverzija PG u AS od 54,55% postignuta je korišćenjem PG čestica manjih od 125 μm u reakciji izvedenoj sa odnos čvrsto/tečno 1/10 pri pH 10. Sadržaj azota i sumpora u AS uzorcima je određen Dumasovom metoda i gravimetrijski kao sulfat (ISO 9280:1990)a, redom. Elementarni sastav je određen ICP-OES, kristalografska struktura je ispitana KSRD analizom, a površinska morfologija čestica dobijenih u reakciji SEM analizom. Hemijski sastav AS proizvoda dobijenog u ovim uslovima je 21,29 tež% azota i 24,23 tež% sumpora, redom; teorijski sadržaj azota i sumpora u AS je 21,21 tež% i 24,24 tež%. Ova studija pruža rezultate koji imaju industrijski značaj jer predlaže novi pristup za efektivnu valorizaciju otpada i novi uvid u proizvodnju AS u trenutnoj nestašici đubriva.

Ključne reči: amonijum sulfat; cirkularna ekonomija; mokra konverzija; fosfogips; iskorišćenje resursa.

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