



## A Review on Ammono-Carbonation Reactions: Focusing on the Merseburg Process

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### ABSTRACT

Various approaches for sustainable waste management to develop the most cost efficient and feasible one are of importance, and valorization of industrial wastes or by-products has been gaining attention. Due enormous amounts of generated industrial wastes promising solutions are required to overcome increasing pressure on their environmental effects. Recycling of wastes and converting them into added value provides bulk consumption. One of the mostly accumulated industrial wastes, phosphogypsum (PG) and as well as flue gas desulfurization gypsum (FGD gypsum) might perform good effectiveness in production of sulfate compounds. Ammono-carbonation reaction of any kind of gypsum (pure, PG or FGD gypsum) with ammonium carbonate known as Merseburg Process is used to produce ammonium sulfate and calcium carbonate. This study focuses on a brief review of describing the reaction sequence, thermodynamics, and mechanism, as well as operating conditions affecting gypsum conversion, product yield and purity, to evaluate the more strategic and efficient process.

## 1. Introduction

### 1.1. Focusing on the Merseburg Process

Dramatically growth in the global population resulted a continuously increasing energy and food demand, and enabled wide spread industrial applications. Industrialization caused consumption of the limited global resources (i.e. fossil fuels) in an unsustainable manner, besides the quantity of cultivated areas has been rapidly restricted. On the contrary, continuous increase in global population puts a pressure on agriculture to increase the yields and provide balanced and qualified food for the entire globe [1]. Thus, “sustainability” and “circular economy” terms have been gaining attention. Industrial wastes are generated in large amounts, most of them have promising potentials as valorizable secondary resources for food and energy industries [2]. Utilization of recyclable and re-industrialable industrial wastes might be effective for decreasing the

consumption rates of global resources, as being a second loop in the resource chain.

Recent studies about sustainable waste management have concentrated on various approaches to develop the most cost efficient and feasible ones. In this point of view, valorization of industrial wastes or by-products will be continuing gain importance because food and energy demand will continue to increase whereas the resources will be more and more limited in the near future. Due the fertilizers are the key point to achieve higher crop yields to meet the global food demand have resulted in increase in the production capacity of mineral fertilizers [3]. It is of great importance to develop or modify available processes both enabling the consumption of industrial wastes and valorizing them as fertilizer products.

Nitrogen is an indispensable element of plant nutrition directly affecting the plant growth and yield together

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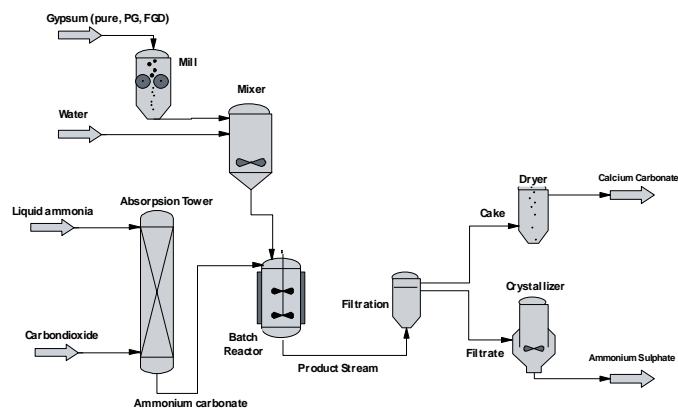
with acting in plants stress responses and host-pathogen interactions. Affecting the plants on biochemical level, sulphur, takes part in the growth, development, disease resistance and nutritional quality of crops [4,5,6,7]. Ammonium sulfate is a dual-effect nitrogenous fertilizer, composed of 21 % nitrogen and 24 % sulfur by weight in ammonium and sulfate form, respectively. It has become a well desired fertilizer product throughout the 19th century, and can be produced via a wide range of routes; the most well-known and industrially applicable one is the reaction of sulfuric acid with ammonia [8]. Besides, as-called “gypsum route” is another industrially applicable method, based on the conversion reaction between gypsum and ammonium carbonate or ammonia- carbon dioxide mixture to give ammonium sulfate and calcium carbonate. The latter route is known as the ammono-carbonation reaction of gypsum, i.e. Merseburg Process. As it was first carried out on an industrial scale in Merseburg (Germany), often referred to as the Merseburg process or the ammono-carbonation reaction of gypsum with ammonium carbonate, it is not a new process, but improvements are still in progress [9,10,11]. Merseburg process composes of absorption, conversion, filtration, and evaporative crystallization processes.  $(\text{NH}_4)_2\text{CO}_3$  is prepared via absorption of  $\text{CO}_2$  into  $\text{NH}_4\text{OH}$  solution then conversion reaction between  $(\text{NH}_4)_2\text{CO}_3$  and gypsum source (pure, PG or FGD) is performed. Reaction products are filtered to separate cake and filtrate. Cake is  $\text{CaCO}_3$  and filtrate is  $(\text{NH}_4)_2\text{SO}_4$  solution.  $(\text{NH}_4)_2\text{SO}_4$  crystals are obtained by further evaporative crystallization of the filtrate. Figure 1 shows a simplified process flow diagram for the Merseburg process. The products of Merseburg process are industrially applicable and have their individual economic value. Ammonium sulfate is a widely used nitrogenous fertilizer, and projections show that the global consumption growth around 2050 is estimated to increase by 2.5 %. Calcium carbonate is a multi-functional chemical used in various types of industries such as plastics, textiles, rubbers, adhesives, paints, cement etc. [12].

Recent studies show either natural ores or industrial wastes perform good effectiveness in production of sulfate compounds, and there have been several studies for the conversion of gypsum to alkaline sulfates such as  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4$ . Natural sources (i.e. olivine ( $\text{MgSiO}_4$ ), wollastonite ( $\text{CaSiO}_3$ ), serpentine ( $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ ) and industrial wastes (i.e. steel slag, calcium carbide slag, gypsum waste) studied in carbonation processes for  $\text{CO}_2$  fixation, and results show that the use of PG or flue gas desulfurization gypsum (FGD) have several advantages over other industrial wastes. Both PG and FGD have high calcium content for a high-yield  $\text{CaCO}_3$  and provide energy consumption

by eliminating extra mining operations such as crushing or grinding, since they have homogenous particle size distribution and relatively low particle size [10,11,12,13].

Carbonation process of gypsum can be performed via a wide range of alkali sources. Ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) is more widely used alkali source, first carbonated to give  $(\text{NH}_4)_2\text{CO}_3$ , followed by ammono-carbonation reaction and resulting  $(\text{NH}_4)_2\text{SO}_4$  for use in fertilizer industry and  $\text{CaCO}_3$  for various industrial applications [14,15].

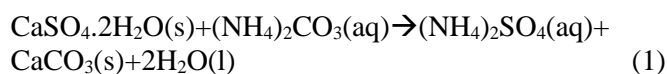
Although the first plants utilizing Merseburg Process used mined anhydrite gypsum, phosphogypsum (PG,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), and flue gas desulfurization gypsum (FGD) was began to used in the process later. Both PG and FGD are industrial by-products of wet process phosphoric acid process and coal-fired power plants, respectively. Industrial waste streams require less energy-intensive carbonation conditions that those of unmined mineral rocks, and utilization of phosphogypsum as well as  $\text{CO}_2$  consumption for the Merseburg ammono-carbonation reaction offers environmentally sustainable advantages within concepts of waste minimization and carbon capture [16, 17, 18, 19].



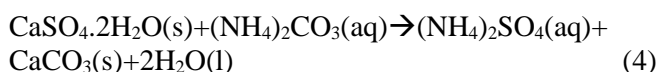
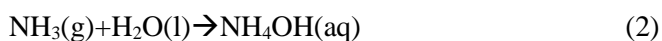
**Figure 1.** Simplified process flow diagram for Merseburg process

## 2. Reaction Sequence of Merseburg Process

Merseburg process is basically the reaction between gypsum and  $(\text{NH}_4)_2\text{CO}_3$  given below:



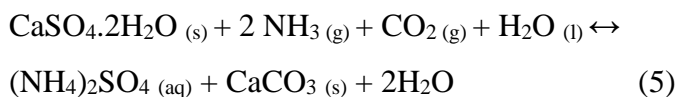
$(\text{NH}_4)_2\text{CO}_3$  is formed through the reaction of ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) and carbon dioxide ( $\text{CO}_2$ ). So, the overall reaction sequence is given in Eq. 2-4 [8].



Conversion of calcium sulfate to ammonium sulfate according to the reaction given Eq. 4, tentatively represented by a pseudo-first-order model [20]. The products solution results a combination of  $\text{CaCO}_3$  and  $(\text{NH}_4)_2\text{SO}_4$  in a slurry. Filtration process allows the separation of solid ( $\text{CaCO}_3$ ) and liquid  $(\text{NH}_4)_2\text{SO}_4$  phases. The liquid phase is then concentrated through evaporation, followed by crystallization process. Resulting ammonium sulfate crystals are used in the fertilizer industry, whereas  $\text{CaCO}_3$  is utilized in various industries [21]. Both this heterogeneous reaction sequence and the limited solubility of gypsum (G, PG, and FGD) require consideration of reactants that will react in different forms and feeding strategies, along with other reaction conditions and downstream operations.

### 2.1. Thermodynamics and Mechanism of Overall Reaction focusing on the Merseburg Process

The overall reaction written as the combination of Eq. 2 and 4 given below:



Enthalpy and Gibbs energy of overall reaction (Eq. 5) at different temperatures are given in Table 1.

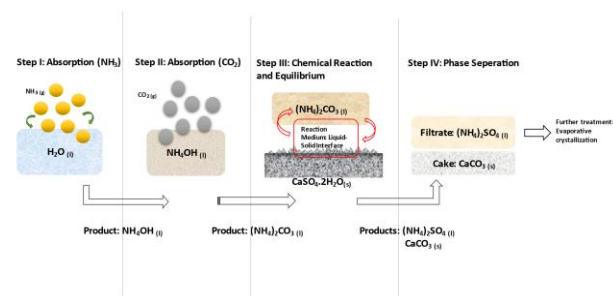
**Table 1.** Enthalpy and Gibbs energy of overall reaction [22]

T (°C)	$\Delta H$ (kJ.mol <sup>-1</sup> )	$\Delta G$ (kJ.mol <sup>-1</sup> )
0	-178.3	-51.8
20	-178.5	-42.5
40	-178.8	-33.3
60	-179	-24

The overall reaction is exothermic, increase in the operating temperature triggers decomposition of  $(\text{NH}_4)_2\text{CO}_3$ , whereas low temperatures enables the precipitation of different types of salts besides  $(\text{NH}_4)_2\text{SO}_4$  [23]. According to Table 1, Gibbs energy of the overall reaction is negative at ambient temperatures i.e. the reaction spontaneously undergoes, however it tends to increase at higher temperatures. There is also a possibility of the formation of some side

products such as  $\text{NH}_2\text{COONH}$  and  $(\text{NH}_4)_2\text{CO}_3 \cdot 2\text{NH}_4\text{HCO}_3$ , affecting the conversion yield at higher temperatures. So, the optimum temperature range of the overall reaction should be below 60 °C [22].

Kinetics of the reaction between gypsum and  $(\text{NH}_4)_2\text{CO}_3$  can be defined as a multiphase model, since there is a suspension of gypsum and water; and a mixture of gases i.e.  $\text{NH}_3$  and  $\text{CO}_2$ . The system can be defined as the reactive crystallization of gypsum in a ternary gas ( $\text{CO}_2$ )- liquid ( $\text{NH}_4\text{OH}$ )- solid (PG) system. Kinetic mechanism of the three phase- reaction system can be explained as the mass transfer from gas ( $\text{NH}_3$ ) to liquid ( $\text{H}_2\text{O}$ ) phase in the first step. The mechanism is followed by the chemical reaction to give  $(\text{NH}_4)_2\text{CO}_3$  solution in liquid phase. Third step is the transport of  $(\text{NH}_4)_2\text{CO}_3$  to liquid- solid (gypsum) interface. After the conversion reaction,  $(\text{NH}_4)_2\text{SO}_4$  forms in the liquid phase, and  $(\text{NH}_4)_2\text{CO}_3$  is diffused through the solid product,  $\text{CaCO}_3$ . Also, conversion reaction undergoes on the surface of unreacted  $\text{CaSO}_4$  [20].



**Figure 2.** Schematic illustration of the reaction mechanism

Simultaneous ongoing sub-processes makes multiphase reactive crystallization process a complex phenomenon. However, possible mechanism can be detailed as the absorption of gaseous  $\text{NH}_3$  to aqueous phase, further ionization of  $\text{NH}_4\text{OH}$ . Subsequently, gaseous  $\text{CO}_2$  diffuses into ionized  $\text{NH}_4\text{OH}$  solution and forms  $\text{HCO}_3^-$  ions. Reaction of  $\text{HCO}_3^-$  and  $\text{OH}^-$  ions forms  $\text{CO}_3^{2-}$  ions, further reacts with  $\text{NH}_4^+$  ions and results  $(\text{NH}_4)_2\text{CO}_3$ . Dissolution of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) results in a fast substitution reaction which formation of  $(\text{NH}_4)_2\text{SO}_4$  between  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  ions and simultaneously formation of  $\text{CaCO}_3$  between  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$ . While  $(\text{NH}_4)_2\text{SO}_4$  remains in the aqueous phase, and its crystals obtained by further evaporative crystallization process,  $\text{CaCO}_3$  subsequently crystallizes (Figure 2).

There are various parameters affecting the ammono-carbonation reaction efficiency such as the chemical composition, particle size and particle size distribution

of PG used,  $(\text{NH}_4)_2\text{CO}_3$  solution concentration, mass ratio of solid:liquid (PG: $(\text{NH}_4)_2\text{CO}_3$ ) and their feed strategy and reaction temperature. Downstream processes, including filtration to effectively separate reaction products with solid  $\text{CaCO}_3$  and liquid  $(\text{NH}_4)_2\text{SO}_4$  phases, evaporation of the liquid phase followed by crystallization to obtain the crystalline  $(\text{NH}_4)_2\text{SO}_4$  product, also affect the overall process efficiency.

Excess  $(\text{NH}_4)_2\text{CO}_3$  input is preferable in order to prevent different side reactions of gypsum [23]. Solution concentration as well as the solid:liquid ratio is more important parameter on the overall conversion, since decrease in the solid:liquid ratio has a diluting effect because larger volumes of solution increase the solubility of Ca, so the carbonation efficiency tends to increase [17]. When pure gypsum ( $\text{CaSO}_4$ ) is used in the process, the equilibrium conversion of  $\text{CaSO}_4$  can reach up to 99.97 %; whereas PG shows a lower conversion efficiency around 97 %. However, when hemihydrate gypsum is used, the equilibrium conversion is observed up to 99 % [24]. Although impurities in the PG structure have a lowering effect on the equilibrium conversion, crystal water might also have an effect on the lower conversion efficiency in the case of PG utilization in the ammono-carbonation reaction. However, the overall performance of PG is still considerable, and necessity of pre-purification treatments is of economic issue. On the other hand, in some cases, liquid phase is neutralized with  $\text{H}_2\text{SO}_4$  in order to increase the yield of  $(\text{NH}_4)_2\text{SO}_4$  crystals. Basically,  $\text{H}_2\text{SO}_4$  is reacted with unconverted  $\text{NH}_4\text{OH}$  to give  $\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{SO}_4$ , favoring the overall yield of  $(\text{NH}_4)_2\text{SO}_4$  crystals. Gypsum, PG or FGD are slightly soluble in aqueous media, and insoluble particles in the heterogenous reaction medium might act as rate limiting steps, affecting the overall rate of the reaction. Thus, particle size and particle size distribution are one of the important parameters to be considered, and effective stirring rate is also required to prevent undesired precipitations. Both gypsum sources (pure, PG or FGD) and  $(\text{NH}_4)_2\text{CO}_3$  are instantly solid materials. Solid-solid phases are indispensable to react, and it is crucial to feed these inputs as in slurry forms, providing appropriate reaction medium. Equilibrium constant of the ammono-carbonation reaction is high (4280 at 25 °C) when pure gypsum is used (Burnett et al., 1996) [24]. High equilibrium constant shows that the reaction spontaneously undergoes, and temperature has insignificant effect on reaction rate. However, to prevent the formation of undesired salts and to satisfy the process economy ambient temperature is preferred as operating temperature.

## 2.2. Studies on The Merseburg Process

There have been various kinetic studies in the Merseburg Process in order to obtain the optimum reaction parameters and modification studies in order to obtain higher conversion yields together with to lower the process's operational costs and make it economically feasible [25]. This study provides brief summaries of the theoretical studies on the Merseburg Process, and discusses the operating conditions and the kinetic parameters which favors the rate of the reaction to achieve higher gypsum conversion yields. Not only pure gypsum studies, but also PG or FGD studies are also discussed, providing a promising approach for the valorization of these industrial wastes as a secondary resource for  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{CaCO}_3$  production.

Blouin et al. reported the optimum temperature range of the reaction between 50-60 °C, having a 95-98 % conversion after 2 hours reaction period [26]. Elkanzi and Chalabi investigated the kinetics of the reaction. They performed the reaction between 10-20 °C temperature range with the input suspension having a 5 wt % PG content, and reaction conducted at vigorous stirring. According to the experimental data, they offered a pseudo first order kinetic model with an activation energy of 72  $\text{kJ}\cdot\text{mol}^{-1}$  [20].

Chou et al. evaluated the technical feasibility of FGD- $(\text{NH}_4)_2\text{CO}_3$  reaction for  $(\text{NH}_4)_2\text{SO}_4$  production. They performed the reaction at different temperatures and residence times to determine the optimum conditions for higher conversion and higher-quality reaction products by using FGD solid by-product samples collected from two different power plants. The reaction was conducted at the temperatures 60, 70 and 80 °C with 4 and 6 hours residence times, respectively. Synthesized  $(\text{NH}_4)_2\text{SO}_4$  had up to 99% quality, and up to 85% FGD gypsum conversion was achieved at relatively mild conditions. Optimum reaction conditions were reported as 60 °C temperature and 4 hours residence time [27].

Abbas performed the ammono-carbonation reaction at 44 °C constant temperature in order to prevent the decomposition of  $(\text{NH}_4)_2\text{CO}_3$  at higher temperatures and avoid the precipitation of different types of salts at lower temperatures. Carbonation reaction was performed by bubbling  $\text{CO}_2$  gas with a flow rate of 70 L/h into 24%  $\text{NH}_3$  solution, during an optimized period of 1 hour. Ammonia carbonation is an exothermic reaction and the temperature was kept constant at 44 °C by cooling. Once  $(\text{NH}_4)_2\text{CO}_3$  solution was prepared, it was then reacted with PG with an excess amount of 120% and a ratio of 400 ml  $(\text{NH}_4)_2\text{CO}_3$  solution to 192 g PG at 23 °C. Optimum reaction time was obtained as 4 hours for increased conversion [23].

Vlasjan et al. performed experimental studies on the dissolution of  $\text{CaCO}_3$  by PG conversion with

$(\text{NH}_4)_2\text{CO}_3$ . 250 g of PG sample having 20% moisture content was firstly grinded for a homogenous particle size, followed by introduced with 450 ml of 30%  $(\text{NH}_4)_2\text{CO}_3$  solution. The reaction was conducted in an intermittent fed of PG to batch system during 2 hours period at a constant temperature of 50 °C. Suspension was than vacuum-filtered, and the volume and concentration of  $(\text{NH}_4)_2\text{SO}_4$  was measured together with the amount of precipitated  $\text{CaCO}_3$ . Authors claim that the  $(\text{NH}_4)_2\text{SO}_4$  satisfies the criteria for utilizing as a fertilizer product, whereas  $\text{CaCO}_3$  does not require the quality standards for being used as a pure raw material, because it contains an amount of rare earth elements (REEs). The crystal lattice of  $\text{CaCO}_3$  is mainly polluted by strontium, lanthanum, cerium, iron, aluminum, titanium, zinc, and others [25].

Mattila and Zevenhoven performed a thermodynamic modelling study by using Gibbs energy minimization software Outotec HSC Chemistry 8.0.3 together with an experimental study as a function of reactant concentration and temperature for verification of the model. Thermodynamic modelling was realized with a base 100 g/L PG introduced in a total volume of 200 ml water at ambient temperature and conversion calculations at 20, 45 and 80 °C. Initial concentrations of  $\text{NH}_3$  and  $\text{CO}_2$  were modeled as <3.5 mol  $\text{NH}_3$ /mol PG and <2 mol  $\text{CO}_2$ /mol PG, respectively. Verification of thermodynamic modelling was performed by two different approaches. Experimental studies by investigating the reaction temperature, pH and initial  $\text{NH}_3$  and  $\text{CO}_2$  concentrations were used in the first approach. In this way, pre-determined amounts of PG, pre-dissolved  $\text{NH}_3$  were introduced in a batch reactor of 200 ml with a magnetic stirrer equipment, while  $\text{CO}_2$  gas was bubbled at atmospheric pressure. As reaction undergoes,  $\text{NH}_3$  was consumed throughout the system and leading a decrease in the pH. Second approach was to perform the carbonation reaction at constant pH. PG-water suspension (200 ml) and 25 %  $\text{NH}_3$  solution (100 ml) was gradually added during the reaction. This approach provided a constant and non-acidic reaction medium, providing the precipitated  $\text{CaCO}_3$  from re-dissolving.  $\text{CO}_2$  flow during all experiments kept constant, and ranged from 0.07- 0.16 L/min. After reaction was performed, products were filtered. The cake was dried at 105 °C and further characterized by SEM and XRF. The filtrate involved dissolved  $(\text{NH}_4)_2\text{SO}_4$  crystals with a concentration of 0.6 mol/L. Since  $(\text{NH}_4)_2\text{SO}_4$  has a solubility of 5.8 mol/L at 25 °C approximately 90% of water in the filtrate was removed to obtain the supersaturation point leading to crystallization by evaporative crystallization. Authors also performed experimental testing of a reverse osmosis membrane cartridge. The cartridge was used to pre-concentrate the liquid phase before crystallization, resulting a reduction of the steam consumption during

evaporative crystallization and providing energy efficiency throughout the entire process, providing promising results when compared to evaporative crystallization process [28].

Azdarpour et al. studied the effect of  $\text{CO}_2$  pressure, reaction temperature, particle size, and  $\text{NH}_4\text{OH}$  concentration on  $\text{CaCO}_3$  purity. Conversion reaction was performed in a 100 ml high temperature- high pressure autoclave reactor. They investigated the inlet ammonia solution concentration (0.1-5 M), reaction pressure (up to 70 bar), reaction temperature (up to 400 °C) and gypsum particle size (45, 100, 200 and 400  $\mu\text{m}$ ). Gypsum source used in the experiments was FGD gypsum. They first prepared a slurry by introducing  $\text{NH}_4\text{OH}$  solution into FGD gypsum. The slurry was then taken into the autoclave reactor, with a  $\text{CO}_2$  feed in pre-determined temperature and pressure. Reaction time was determined as 1 hour. They reported that the increase in the reaction temperature and pressure favors the purity of  $\text{CaCO}_3$  product. Smaller particle size of gypsum and increased ammonia solution also enhanced the purity of  $\text{CaCO}_3$  [29].

Danielik et al. performed quantitative evaluation of the rate of the gypsum conversion reaction by investigating the four different parameters which were the initial rate of the reaction, half time of the reaction, conversion after a certain time and maximum conversion achieved by using two different analyzing procedure. Ammono-carbonation reaction of gypsum was conducted in a glass beaker, starting with 0.8 M, 250 ml of  $(\text{NH}_4)_2\text{CO}_3$  solution and stoichiometric equivalent of 34.4 g gypsum suspension as the reactants. First procedure was based on the determination of unreacted ammonium carbonate. Once reaction started, liquid samples was taken from the reaction medium at 25 minutes intervals and centrifuged. 5 ml of liquid sample was taken from centrifuge tube, neutralized with 10 ml HCL, and back titrated with NaOH solution to obtain the unconverted  $(\text{NH}_4)_2\text{CO}_3$  amount. Second procedure was based on the determination of sulfates generated during the reaction. 25 g of gypsum sample was dried at 60 °C for 48 h, dispersed in 50 ml deionized water. 30 %  $(\text{NH}_4)_2\text{CO}_3$  solution was added in 10% excess to the stoichiometry. After reaction completed then suspension was filtered. Filtrate was than precipitated with  $\text{BaCl}_2$  in acidic medium as  $\text{BaSO}_4$ . There was a possibility of the precipitation of  $\text{BaCO}_3$ , further decomposed by HCL. Remaining  $\text{BaSO}_4$  samples were gravimetrically evaluated. Throughout these two different analyzing procedures, initial rate of the reaction was determined by extrapolation of the conversion curve. However, this calculation was affected by the disintegration of agglomerates and the moisture of the solid sample. Half time of the reaction was calculated by the conversion curve, a more reliable data than the initial rate of the

reaction. Conversion after a time interval was chosen as 25 minutes, and data showed that this evaluation was the most reliable data for the determination of the rate of the reaction. Maximum conversion was reached after 2 hours. Results showed that flue gas desulphurization gypsum (FGD) was more reactive than pure gypsum. Analyzing procedure 2 showed a higher conversion, probably due to the co-precipitation of  $\text{BaCO}_3$  together with  $\text{BaSO}_4$  [22].

Msila et al. performed a modified reaction by omitting a  $\text{CO}_2$  scrubber to lower the overall cost of the process and evaluated the technical feasibility of this modification. They prepared the  $\text{NH}_4\text{OH}$  solution by diluting a commercial 30% solution to 17%. Reactions were performed at ambient (atmospheric) pressure and 343 K (70 °C) in a bench-scale reactor fitted with a mechanical stirrer and thermocouple to provide stirring and temperature control throughout the reaction, respectively.  $\text{CO}_2$  flow rate was  $10 \text{ dm}^3 \cdot \text{min}^{-1}$ . Different reaction sets at the reaction time of 2, 3, 4, 5 and 7 hours were performed then reaction mixture was filtered.  $\text{H}_2\text{SO}_4$  was used to neutralize the filtrate, further heated for evaporative crystallization to obtain  $(\text{NH}_4)_2\text{SO}_4$  crystals. Introducing a  $\text{CO}_2$  scrubber has an effect on the reactor temperature and the pH, and the results proved that the modification was technically feasible [30].

Lu et al. investigated the effect of temperature, reaction time and  $\text{CO}_2$  inlet flow rate on the particle size distribution of formed  $\text{CaCO}_3$  particles. PG: deionized water slurries having 1:9 to 1:7 weight ratios were reacted with the  $\text{NH}_4\text{OH}$  according to the molar ratio of  $\text{NH}_3:\text{SO}_4$  (gypsum) varying between 2.3 to 2.5.  $\text{CO}_2$  gas was bubbled into the reactor, and supernatant of the slurry was decanted in pre-determined time intervals for and analyzed the  $\text{SO}_4$  concentration in order to investigate the conversion of PG. Analysis of  $\text{SO}_4$  concentration was realized by visible spectrophotometer in the presence of  $\text{BaCrO}_4$  solution. Reaction time was determined by pH monitoring, and terminated once pH was below 8. Reactor output was filtered and dried, obtained  $\text{CaCO}_3$  was characterized in order to comment on the effects of the varied parameters. Authors concluded that the temperature and  $\text{CO}_2$  flow rate significantly effects the particle size distribution of  $\text{CaCO}_3$ . Increase in reaction temperature and decrease in the  $\text{CO}_2$  flow rate resulted relatively smaller particle size in  $\text{CaCO}_3$ . By adjusting the reaction temperature between 30-40 °C and  $\text{CO}_2$  flow rate between 138-251 ml/min yields  $\text{CaCO}_3$  with an average particle diameter of 86-104 nm [31].

Kandil et al. synthesized the PG-derived ammonium sulfate by using the PG samples pre-treated with sulfuric acid to remove impurities and increase the reaction yield. They optimized the operating conditions of both pre-treatment and reaction processes. For pre-treatment

process, the optimum conditions were reported as the concentration of sulfuric acid to be 8 M, solid: liquid ratio 1:4, time 30 minutes and temperature 80 °C. Reaction was performed directly by using  $(\text{NH}_4)_2\text{CO}_3$  and PG in a 250 ml teflon beaker, without  $\text{NH}_4\text{OH}$  preparation and  $\text{CO}_2$  bubbling procedures. The effects of  $(\text{NH}_4)_2\text{CO}_3$  amount, pH of PG slurry, solid: liquid ratios both PG and  $(\text{NH}_4)_2\text{CO}_3$  suspensions and temperature were studied. After reaction was terminated, they separated filtrate and cake. Filtrate was dried at 60 °C to obtain  $(\text{NH}_4)_2\text{SO}_4$  powder. Pre-treatment of PG favored the purity of obtained  $(\text{NH}_4)_2\text{SO}_4$  powder. Optimum reaction conditions were determined the initial slurry composition as 500 g PG in 2 L 3%  $(\text{NH}_4)_2\text{SO}_4$  solution (solid: liquid ratio 1:4), with 10 % excess  $(\text{NH}_4)_2\text{CO}_3$  suspension at pH:7 and temperature 55 °C. Presence of  $(\text{NH}_4)_2\text{SO}_4$  in the reaction media is a crucial step, favoring the nucleation and subsequent crystal growth of  $(\text{NH}_4)_2\text{SO}_4$  product. Purity of obtained  $(\text{NH}_4)_2\text{SO}_4$  powder was determined as 95% [32].

Idboufrade et al. proposed an efficient method which allows the valorization of the Moroccan phosphogypsum waste (MPG) by converting it to potassium sulfate ( $\text{K}_2\text{SO}_4$ ), portlandite ( $\text{Ca}(\text{OH})_2$ ) and calcium carbonate ( $\text{CaCO}_3$ ). Experiments were conducted in a glass jacketed 500 mL reactor equipped with auxiliary ports to monitor pH, electrical conductivity, temperature. The effects of the reaction conditions which were portlandite ( $\text{Ca}(\text{OH})_2$ ) concentration, molar ratio of  $\text{OH}^-/\text{Ca}^{2+}$ ,  $\text{CO}_2$  flow rate and temperature on mineral carbonation of MPG in aqueous solutions were investigated. They concluded that the molar ratio studied between  $2 \leq n(\text{OH}^-)/n(\text{Ca}^{2+}) \leq 4$  had a significant effect on the conversion. Besides the purity of reactants (synthetic gypsum and MPG); reaction time and yield was also studied. Products were characterized by XRD, XRF, FTIR, SEM/EDX, pH, and EC methods, concluded that PG can be a promising candidate as a substitute to gypsum in mineral-carbonation reaction [33].

According to literature data, higher conversions on the ammono-carbonation reaction of gypsum can be achieved below 60 °C, since the overall reaction is exothermic, increase in the operating temperature triggers decomposition of  $(\text{NH}_4)_2\text{CO}_3$ . Excess  $(\text{NH}_4)_2\text{CO}_3$  to the stoichiometry is preferred in order to prevent different side reactions of gypsum and increase the conversion yield. Any type of gypsum, i.e. pure, by-product of phosphoric acid production process (PG), flue gas desulfurization gypsum (FGD gypsum) show similar conversion yields, this is advantageous in terms of industrial waste beneficiation. However, pre-purification treatments are of economic issue.

#### 4. Conclusion

Gypsum (PG or FGD) as an industrial waste is one of the major environmental problems due to its large amount of occurrence and impurities in it. On the other hand, its potential to be used as a raw material in many production processes due to its high calcium and sulfate content is remarkable. By using this industrial waste as a secondary raw material, sustainable waste management will be achieved in a way that will also reduce the greenhouse gas emissions, while low-cost raw material supply will be possible. Although various production methods have been developed for the valorization of this waste, due using CO<sub>2</sub> together with the gypsum as process input is one of the most important advantages of the Merseburg process mentioned in this study due to its reducer effect on greenhouse gas emissions. Also, by using the Merseburg process, an ammonio-carbonation reaction, industrially valuable products which are ammonium sulfate directly utilized as fertilizer and calcium carbonate widely used at various sectors are produced. In general, this brief review provides the applications and improvements to obtain high PG or FGD conversion (>95% for PG and >85% for FGD), product purity (>99%) and process economy for Merseburg process which has promising route for CO<sub>2</sub> sequestration but has still limited applications in industry.

Due to the heterogeneous reaction system, it is inevitable that the improvements in the Merseburg process, realized by physical and chemical processes, should be handled separately in three main stages: preparation of the inputs, reaction of the inputs and separation of the reaction products. In the first stage, the pretreatment of phosphogypsum with suitable solvents will increase the purity of the reaction products, but both new waste generation and additional cost should be considered for purification process. Improvements in the conditions of the second step, the reaction, are more diverse and more effective on conversion and product purity. These conditions are mainly the feed type of the inputs, the input concentrations and ratio, the reaction temperature, and the pH. It has been determined that the feeding of carbon dioxide to the reactor in the form of bubbles (omitting the CO<sub>2</sub> scrubber) and intermittent feeding of phosphogypsum will both reduce the process cost and increase the input conversion. The reasons for these practices can be explained as follows; The absorption of carbon dioxide with ammonia solution to give ammonium carbonate will lead to an increase in temperature and the conversion to ammonium carbonate will be reduced if not carried out under refrigerated conditions. On the other hand, due to both the limited solubility of phosphogypsum and the heterogeneity of the reaction, conversion of the reactants can be controlled by solid:liquid ratio and intermittent batch

solids feeding. It can be stated that the acceptable input conversion and the product purity by Merseburg process can be carried out under mild conditions (20-80 °C and atmospheric pressure) which is important in terms of process economy. However, due to the exothermic nature of the overall reaction, the reaction temperature should be kept constant at 20-40 °C, considering that the increased temperature also favors the precipitation of different salts. The constant temperature at which the reaction being performed will affect the reaction time, lower temperature will require longer reaction time. Whether the ammonia carbonation reaction involves the absorption of carbon dioxide into ammonia solution or is carried out directly with ammonium carbonate solution, it is recommended to use more than stoichiometric ammonium carbonate (around 10%). Furthermore, being ammonium sulfate in the reaction mixture about 3% as initiator or using sulfuric acid favor crystallization of it. The final step, the separation of reaction products, is related to the reaction conditions. When the pH of the reaction mixture is greater than 8, it will be easier for calcium carbonate to precipitate and separate from the reaction mixture. In addition, decrease in the solid:liquid ratio in the reaction mixture will result in a more dilute reaction mixture, which will adversely affect the evaporative crystallization of ammonium sulfate crystals. To improve this situation, the researchers suggested the use of reverse osmosis membranes to reduce the energy requirement in evaporative crystallization by concentrating the ammonium sulfate solution.

As a result, the operating conditions of the Merseburg process, which is a critical process in which the sustainable management of phosphogypsum or FGD can be realized with carbon dioxide capture, must be optimized, and controlled for maximum input conversion and product purity as well as minimum cost.

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