

Review

Recovering, Stabilizing, and Reusing Nitrogen and Carbon from Nutrient-Containing Liquid Waste as Ammonium Carbonate Fertilizer

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Abstract: Ammonium carbonates are a group of fertilizer materials that include ammonium bicarbonate, ammonium carbonate hydrate, and ammonium carbamate. They can be synthesized from diverse nutrient-bearing liquid waste streams but are unstable in a moist environment. While extensively utilized several decades ago, their use gradually decreased in favor of large-scale, facility-synthesized urea fertilizers. The emergence of sustainable agriculture, however, necessitates the recovery and reuse of nutrients using conventional feedstocks, such as natural gas and air-derived nitrogen, and nutrient-containing biogenic waste streams. To this extent, anaerobic digestion liquid presents a convenient source of solid nitrogen and carbon to produce solid fertilizers, since no significant chemical transformations are needed as nitrogen is already present as an ammonium ion. This review describes detailed examples of such feedstocks and the methods required to concentrate and crystallize solid ammonium carbonates. The technologies currently proposed or utilized to stabilize ammonium carbonate materials in the environment are described in detail. Finally, the agricultural efficiency of these materials as nitrogen and carbon source is also described.

Keywords: nitrogen; carbon; fertilizers; digestate; ammonium; carbonate; bicarbonate; carbamate; recovery; volatilization; stabilization

1. Introduction

The increase in the world population, estimated to reach nine billion individuals by 2050 [1–3], necessitates increasing food production. Estimates indicate that raising world agricultural production by 70% will be necessary to meet the growing food demand. However, modern agriculture is characterized by the intensive use of arable areas, which prohibits a linear increase in the land used. Thus, technological advances in agriculture, such as intelligent machinery and new soil management techniques, including pesticide and fertilizer management, have become essential [4,5]. Among these, using fertilizers is critical, with increased nutrient influx invariably needed to increase agricultural productivity while maintaining only a moderate increase in arable land use.

Nitrogen is an essential macronutrient necessary for plant growth and development. It is critical to the photosynthetic process, DNA, amino acids, protein production, and is also

essential to most plant metabolic activities. Although the atmosphere consists of ~71% nitrogen in its inert molecular form, this form is not directly available for plant assimilation [6]. This means that microorganisms present in soil need to convert atmospheric nitrogen into ammonium (NH_4^+) and nitrate (NO_3^-) ionic form to become plant-available [6].

However, direct atmospheric nitrogen fixation is insufficient to meet the plant N demand and sustain anthropogenic development. Indeed, applying synthetic N fertilizers is frequently necessary to increase crop productivity [7,8]. N fertilizers are the most produced and consumed fertilizers in the world (FAO, 2022), making high losses of fixed N to the environment inevitable. For instance, only 30–50% of the total applied nitrogen fertilizers are used by plants [9]. This inefficient N fertilizer use results in many environmental problems while increasing crop production costs [6,8,10–12]. In particular, the fate of inorganic N fertilizers after their application to soil is summarized in Figure 1. Once mineral N fertilizers, such as ammonium sulfate, urea, or ammonium nitrate, are applied, they will hydrolyze, releasing ammonium ions, which plants can take up. Ammonia can also volatilize during the soil transformation processes, affecting the environment and increasing costs to farmers [12–14]. Ammonium oxidation can further be carried out by bacteria via nitrification, producing NO_3^- , which plants can also assimilate. Nonetheless, excessive fertilizer dosages lead to nitrate leaching, which causes environmental problems, including eutrophication. A denitrification process can also happen, releasing reactive nitrogen compounds such as N_2O , which exhibit a greenhouse gas potency of around 300 times greater than that of CO_2 [12–14].

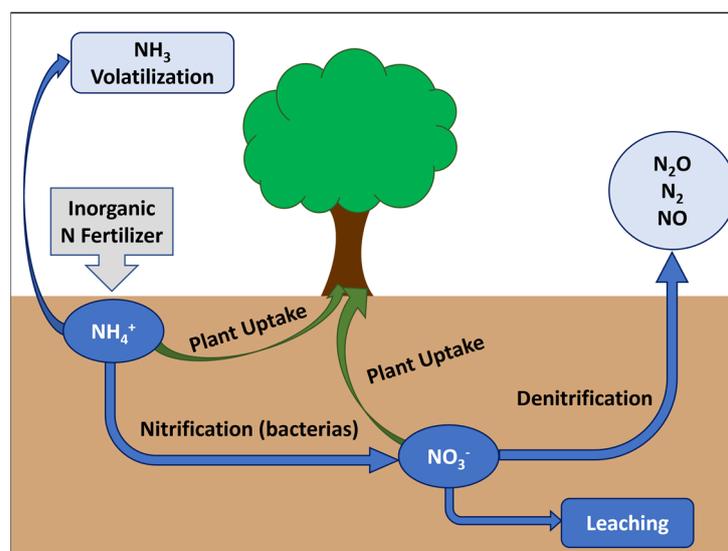


Figure 1. Inorganic nitrogen fertilizer effect after soil application.

China is currently the highest synthetic N fertilizer consumer (FAO, 2022), and urea and ammonium bicarbonate are two common sources [15,16]. From 2005 to 2020, urea represented approximately 49% of the total N fertilizer consumed in China, while ammonium bicarbonate was 17.7%. Compound fertilizers (nitrogen + potassium or phosphate, or a combination of both—NPK) represented 31.7% [16]. Although ammonium carbonate consumption was lower than urea or NPK, it was responsible for 30% of the total ammonia emissions from N fertilizers in China, as opposed to 14% of urea and 7% of NPK [16].

This higher ammonia volatilization from ammonium carbonate compounds thwarted its widespread use, decreasing its application as a fertilizer [17]. Nevertheless, it is essential to establish that the production process of ammonium carbonate has lower overall emission of greenhouse gases than that of other commonly used fertilizers. In addition, ammonium carbonate has lower cost (US\$/per unit of N) than urea, ammonium nitrate, or ammonium hydroxide [18]. This suggests that increasing the environmental stability of ammonium

carbonate materials is paramount since it would diversify nitrogen (and carbon) fertilizers while producing them from more sustainable sources.

2. Methods

The current work evaluated research studies and patents with the objective of producing a comprehensive review of the available literature regarding the use of ammonium carbonates—commonly a complex mixture of compounds mostly composed of ammonium bicarbonate—as fertilizer materials. The following topics will be systematically reviewed and discussed:

- Ammonium carbonate compound diversity and complexity: the reaction between CO_2 and NH_3 can result in a few compounds, such as ammonium carbonate and ammonium bicarbonate, depending on the conditions applied.
- Ammonium carbonate production from a more sustainable process:
 - CO_2 recovery from anthropogenic emissions.
 - Different sources and processes to produce ammonium carbonate materials from biogenic feedstock, such as liquid biomass digestion, wastewater, etc.
- Methods to increase ammonium carbonate stability to reduce nitrogen losses (formation of more stable compounds, granulation, coating, etc.).
- Ammonium carbonates as a fertilizer, focusing on its effect as a nitrogen source and, potentially, as a carbon source, highlighting the carbon path after its application on the soil.

3. Results and Discussion

3.1. Ammonium Carbonate Compounds

The significance of the interactions between the components of the ternary system ($\text{CO}_2\text{--NH}_3\text{--H}_2\text{O}$) extends to various physical sciences and is integral to several critical biological and industrial processes [19], resulting in a large complexity of the recovered and even chemically pure materials where ammonium bicarbonate salt is typically present. Figure 2 demonstrates some of the solid phases that can form within this system, referred to as ammonium carbonates [20], such as ammonium sesquicarbonate monohydrate $[(\text{NH}_4)_4(\text{H}_2(\text{CO}_3)_3\text{H}_2\text{O})]$, ammonium bicarbonate $[(\text{NH}_4)_2\text{HCO}_3]$, ammonium carbonate monohydrate $[(\text{NH}_4)_2\text{CO}_3\cdot\text{H}_2\text{O}]$, and ammonium carbamate $[\text{NH}_4\text{CO}_2\text{NH}_2]$ [19,20].

Ammonium sesquicarbonate monohydrate is a hydrous compound with a crystal structure first reported in 2003 [21]. Its orthorhombic structure consists of carbonate and bicarbonate anions, along with water molecules, linked by hydrogen bonds in chains that run parallel to the [b] axis. Ammonium tetrahedra are between the chains and bonded to four different anions, creating a 3D structure [20,21]. It is rarely identified in the ammonium carbonates utilized as fertilizers. Ammonium bicarbonate is the only compound in the ternary system to be found in nature as the teschemacherite mineral [22]. A suggested crystal structure of ammonium bicarbonate was introduced by Brooks, indicating that the CO_3^{2-} hydrogen bonds connect groups to form polymeric anions aligned in parallel to the [c] direction [23]. A more recent structure was also suggested by Pertlik, where the structure is firstly composed of lines of aligned bicarbonate anions with one of the bicarbonate oxygen atoms forming a hydrogen bond with the O-H group of the adjacent $[\text{CO}_2(\text{OH})]$ anion. The bicarbonate chains are connected along the [a] and [b] axes by ammonium tetrahedra, with each bicarbonate oxygen atom bonding with two ammonium tetrahedra [24]. Ammonium carbonate monohydrate (ACM) is rarely stable in air at a temperature above 273 K. Above 273 K, it can transform first to ammonium sesquicarbonate monohydrate, and after sufficient time, it will lose ammonia and completely transform to ammonium bicarbonate [19]. ACM's structure consists of carbonate anions, with each oxygen atom forming three hydrogen bonds with an ammonium cation. The first ammonium molecule bonds with the carbonate anions along the [a], while the second ammonium molecule forms a single hydrogen bond with a water molecule, composing the 3D structure in a layered manner [19].

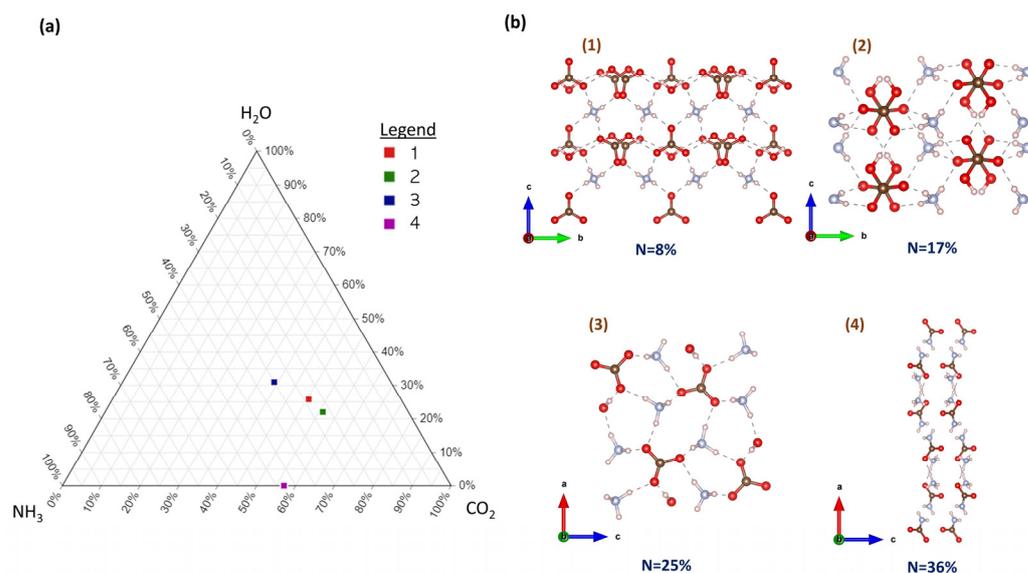


Figure 2. (a) The $(\text{CO}_2\text{-NH}_3\text{-H}_2\text{O})$ ternary system with the phases of (1) ammonium sesquicarbonate monohydrate, (2) ammonium bicarbonate, (3) ammonium carbonate monohydrate, and (4) ammonium carbamate; (b) the crystal structure of the different phases of AC mentioned in part (a), with the same order. The total theoretical nitrogen content in each material is also shown.

Furthermore, another solid phase in the ternary system is ammonium carbamate, which exists in two phases, (α) and (β). It is rarely stable beyond 273 K as it degrades and loses ammonia and carbon dioxide before transforming into ammonium bicarbonate. The thermodynamic stability of the two phases was evaluated by calculating their enthalpy in thermal conditions as a function of pressure. The α -polymorph is the stable phase at zero pressure with a lower enthalpy (difference of $399.33 \text{ J mol}^{-1}$ compared to the β -polymorph) [25]. At around 0.4 GPa, the enthalpies of the two phases intersect, and above this pressure, the β -polymorph becomes the stable phase. The enthalpy difference between the two phases continues to increase up to pressures of about 2 GPa. However, beyond this pressure, slight structural changes occur to the α -polymorph, causing the trend to reverse, and the enthalpy difference between the two phases begins to decrease [25]. The crystal structure of α -ammonium carbamate consists of carbamate ions arranged parallel to the b-axis and connected through ammonium cations [20]. It contains a hexagonal ring-like structure due to the hydrogen bonding between the centrosymmetric pairs of carbamate ions. The centrosymmetric dimer ring is not found in the crystal structure of β -ammonium carbamate as it forms two-dimensional chains connected through hydrogen bonding between carbonyl oxygens and ammonium tetrahedra [20].

3.2. Ammonium Carbonate Production and Recovery

Ammonium carbonate compounds are primarily synthesized via a chemical reaction between ammonia and carbon dioxide gas under controlled conditions [26]. Consequently, the acquisition of raw materials (ammonia and carbon dioxide) holds significant importance in the production of ammonium carbonates, with the provision of sustainable resources being crucial for ensuring the future availability of this compound. Two methods for ammonium carbonate production, each with unique advantages and challenges, are examined here. The first method involves the recovery of CO_2 from the air and flue gas, which can then be combined with ammonia to form (ACs). The second method consists of the recovery of ammonium and carbonate from liquid anaerobic digestion products of organic matter. These methods can reduce CO_2 emissions while reducing the burden associated with conventional ammonia production.

3.2.1. Ammonium Carbonate Production from CO₂ Recovery

According to the International Energy Agency, global CO₂ emissions from industrial and energy combustion processes increased by 0.9% from 2021 to 2022, reaching the highest value ever registered at 36.8 Gt, which accounts for 89% of the energy-related greenhouse gas emissions [27]. The natural processes that remove CO₂ from the atmosphere cannot reabsorb all the emissions, and the amount of carbon dioxide in the atmosphere is increasing yearly. In the 1960s, atmospheric carbon dioxide concentration grew at a rate of 0.8 ppm/year, while in the 2010s, this rate reached 2.4 ppm/year [28].

In this context, ammonium carbonate production can help to reduce CO₂ emissions in two different ways: (1) it can be produced by using carbon dioxide obtained from process emissions such as flue gas (for instance, the ammonia scrubbing process is a fascinating method for carbon dioxide sequestration, and it can have a removal efficiency of ~99%) [29]; (2) once applied as fertilizer to crops, most of the CO₂ present in AC molecules will not be released to the atmosphere, since plants can potentially assimilate it more thoroughly (due to the roots breathing or photosynthesis processes), and it will also be percolated into soil carbonates [29], as discussed in Section 3.4.2.

In one process, ammonium carbonate production can be achieved while removing CO₂ from the flue gas by ammonia scrubbing [30]. The production of ACs takes place in a scrubber, with experiments performed at room temperature, using an ammonia solution of 28% (*w/w*) and inlet CO₂ concentrations ranging from 8 to 16% (*v/v*), with a CO₂ and airflow rate of 2 L/min [30]. The results of the experiments showed that the CO₂ removal efficiency was between 95% and 98% after 60 s for all inlet concentrations, which is higher than the efficiency of monoethanolamine (MEA) scrubbing. The ammonia scrubbing capacity is 0.9 kg CO₂/mol NH₃, while the MEA scrubbing is 0.36 kg CO₂/mol MEA [30]. However, the efficiency of ammonia scrubbing decreases if the operation time exceeds 30 min, and the main product formed is ammonium bicarbonate. This process can form three products from the reaction between ammonia and CO₂: NH₂COONH₄, (NH₄)₂CO₃, and NH₄HCO₃, with the latter as the primary product in the solution and crystalline solid phase [30].

A pilot-scale process for capturing carbon dioxide using an aqueous ammonia solution leading to ammonium bicarbonate production has been reported [31]. CO₂ was extracted from the flue gas of a coal-fired power station. CO₂, SO₂, NO_x, and NH₃ were among the flue gas constituents. At temperatures below 20 °C, the ammonia/CO₂ reaction occurs, with ammonium bicarbonate precipitating as a solid product. The reaction occurs in an absorption reactor where the flue gas is in contact with an aqueous solution containing ammonium, carbonate, and bicarbonate ions. The cooling system, which includes a cooling tower and mechanical chillers, is used to cool the saturated flue gas. This method removes up to 90% of the CO₂ from the flue gas [31]. Part of the unreacted ammonia, which saturates the residual flue gas, can be returned to the process by a scrubbing process using a water wash column. The pilot plant can capture approximately 1600 kg of CO₂ per hour, equivalent to about 15,000 tonnes per year [31].

A suggested technology for ammonium carbonate production and recovery utilizes CO₂ and N₂ captured from fossil fuel-fired power plant emissions [32]. At the same time, hydrogen (H₂) can be generated through either solar photovoltaic water splitting or through natural gas (CH₄) by conducting gas reforming reactions [32]. The chemical reaction for ammonium bicarbonate production and recovery involves combining CO₂, N₂, H₂, and H₂O to create NH₄HCO₃. This technology can potentially remove up to 90% of CO₂ from flue gas, demonstrating its potential for reducing greenhouse gas emissions [32]. Additionally, the chemical reaction for ammonium bicarbonate production and recovery has a standard free energy of −86.18 kJ/mol, indicating that the reaction is naturally spontaneous [32].

3.2.2. Ammonium Carbonate Production from the Liquid Byproducts of the Anaerobic Digestion of Organic Matter

Most of the ammonia produced in the world uses the Haber–Bosch process. Although this technique has gone through several improvements over the years, e.g., the reduction of the reaction pressure, ammonia production is still responsible for consuming 2% of the total energy supply in the world [33]. It is also responsible for approximately 1.6% of total global CO₂ emissions [33]. This means that more sustainable routes are necessary to produce environmentally friendly N fertilizers. One possible option for ammonium carbonate production is the ammonia obtention from anaerobic digesters.

Anaerobic digestion is the process in which organic matter, such as animal manure, wastewater solids, crop residues, sewage sludge, and municipal solid waste, among others, is broken down by bacteria in an environment in the absence of oxygen [34–36]. This process produces biogas rich in methane (CH₄) and CO₂ (besides water vapor, H₂S, and other trace gases). It also produces a digestate, which is the residual material (liquid with suspended solids) obtained after digestion. This digestate can be used as a nutrient-rich fertilizer alone [35,36], but also has the potential to produce ammonium carbonate solid fertilizers.

Ammonia can be found in anaerobic digesters in two forms: ammonium ion (NH₄⁺) and free ammonia (NH₃) depending on the pH. These compounds are produced during anaerobic digestion due to the degradation of proteins, amino acids, urea, or nucleic acids presented in the substrate [35,37]. Ammonia can be recovered from the digestate effluent through a stripping process. Table 1 shows the literature summary regarding ammonium carbonate production from waste and the efficiency data, waste sources, and essential operating conditions.

One of the processes of ammonium carbonate production is based on various N sources from waste, such as wastewater and animal manure digestate [38]. The recovery process involves anaerobic digestion and stripping of NH₃ and dissolved CO₂ from the digestate without adding any chemicals for pH adjustment. The gaseous NH₃ is then condensed with CO₂ and water vapor at a temperature range of 35–50 °C, forming dissolved ammonium bicarbonate and ammonium carbonate in a liquid condensate. The condensate liquid is concentrated by two-stage reverse osmosis at the same temperature range, resulting in a 10-fold concentration. The concentrated liquid is then cooled to less than 35 °C, saturating the reverse osmosis and forming solid ammonium carbonate and ammonium bicarbonate. The final product yields 21.7 wt% of ammonia bicarbonate and 3.8 wt% of ammonia, with an inlet concentration of 0.1 wt% ammonia in dairy manure. Notably, there is no need for an external source of CO₂ [38].

Another production process involves using various organic waste as ammonia sources, such as crop residue, manure, organic fraction of municipal waste (OFMW), food-processing and meat-packing waste, and sewage sludge [39]. The organic substrates are subjected to anaerobic decomposition in a fermentation reactor, producing a digestate stream containing ammonia primarily in the ionized form and a biogas stream containing CO₂, methane, and other gases. Afterward, the effluent stream is subjected to carbon dioxide absorption and ammonia removal using a low-pressure system through either a packed tower or a shallow basin. This process employs a gas with low levels of CO₂ and NH₃. The pH is adjusted to 9–12 before or during the stripping process using Ca(OH)₂, Mg(OH)₂, MgO, NaOH, or KOH [39]. Before entering the stripping chamber, the stripping gas is heated. The resulting effluent, comprised of methane, NH₃, CO₂, and water vapor, is then conveyed to a precipitation chamber where the precipitation and recovery processes of ammonium bicarbonate/carbonate as products occur [39]. The precipitation chamber is kept at a temperature lower than 36 °C to ensure ammonium bicarbonate/carbonate precipitation. In parallel, a fraction of the stripping gas effluent, low in CO₂ and NH₃, is recycled as the stripping gas. The municipal anaerobic digestion facility attains 90% ammonia removal from the stripping feed, producing 6.3 kg/min of ammonium bicarbonate. The digestate contains 1160 ppm of total ammonia, while the stripping feed contains 800 ppm. The

stripped gas yields 1362.74 g/min of NH_3 , and the ammonium bicarbonate precipitation yields 6.3 kg/min. This process delivers a high energy value methane gas that is recirculated to strip the ammonia, unlike previous high-temperature stream-stripping or distillation processes [39].

In a techno-economic assessment of ammonium bicarbonate production [40], the use of biogas slurry, which is a byproduct of the mesophilic anaerobic digestion of pig manure, was studied as a source of ammonia. Ammonia was recovered from the slurry without needing pH adjustment by vacuum membrane distillation. A polytetrafluoroethylene (PTFE) membrane was used to separate ammonia from the slurry, and the biogas mixture was circulated on one side of the membrane while being agitated and heated. A vacuum pump was used to create a vacuum on the permeate side of the membrane, with a negative pressure range of 5–20 kPa [40]. The chemical equilibrium between NH_4^+ and HCO_3^- in the slurry boundary layer was disrupted by heating, causing the decomposition of HCO_3^- into OH^- and CO_2 , which were then extracted through the membrane by the vacuum. Disrupting the chemical equilibrium accelerates the production of ammonia on the surface of the biogas slurry boundary layer, which aids in its transfer through the membrane [40]. The extracted ammonia was reacted and fixated with CO_2 obtained from biogas to produce ammonium bicarbonate. The maximum ammonia separation factor increased from 8.05 to 49.91 under optimal conditions. The profitability of ammonia recovery was $\$0.4/\text{m}^3$ of biogas slurry when no pH adjustment happened. However, if the pH was adjusted with NaOH, the ammonia recovery profit was negative ($\$-2.06/\text{m}^3$ biogas slurry) [40]. Raising the initial ammonia concentration in the biogas mixture from 0.5 to 4 g-N/L resulted in an increase in profitability from a loss of $\$0.71$ per cubic meter of biogas slurry to a gain of $\$1.88$ per cubic meter of biogas slurry. The study was based on lab experiments and the membrane lifetime was the factor that most affected profitability for a fixed initial ammonia content in the biogas slurry [40].

A recent study investigated the use of synthetic swine wastewater as a potential source of ammonia and its recovery using a flow-electrode capacitive deionization system [41]. The system was found to effectively remove NH_4^+ and HCO_3^- from the wastewater. Ammonium bicarbonate was produced and recovered through a freeze-drying method. Under optimal conditions, the ammonium bicarbonate concentration was ~ 1.61 M with a purity of 97.2% from the synthetic swine wastewater. The carbon removal rate was higher (1.01 kg C/ $\text{m}^2\cdot\text{d}$) and the energy consumption lower than other electrochemical systems (2.87 kWh/kg C) [41]. The results highlight the potential of swine wastewater as a viable source of ammonia and the effectiveness of the flow-electrode capacitive system for ion removal. The system's continuous operation and scalability make it an attractive option for future studies [41].

Moreover, a study explored the potential use of biomass liquid digestate as a source of ammonia and its recovery through a distillation process (3.3 bar). NH_3 and CO_2 were extracted with 99.9% of N effectively recovered from the liquid digestate. Ammonium bicarbonate was obtained through condensation and crystallization, with a final yield of 99.5% purity and a production rate of 309 kg/h [34] in a large-scale 30,000 kg/h digestate processing facility. The ammonium bicarbonate production from digestate gas was found to have a 25% lower global warming potential and 50% lower eutrophication potential compared to the process where the liquid digestate is directly applied to crops. A process simulation was used to obtain the data, and the distillation column parameters were found to be critical for process energy consumption. Additionally, ammonium bicarbonate production had a lower installed capital cost than $(\text{NH}_4)_2\text{SO}_4$ production by a stripping process [34].

Another ammonia source suggested for the ammonium carbonate production process is the anaerobic fermentation liquid of food waste [42]. The fermentation liquid is treated in a controlled temperature and pH reactor to recover ammonia. During this process, volatile fatty acids present in the liquid are precipitated with layered double hydroxides like hydrotalcite or anionic clays. In contrast, the NH_3 in the reactor escapes and passes

through a recovery system composed of a water bath condenser and a three-mouth flask. Once the NH₃ is recovered, it is combined with CO₂ to form ammonium bicarbonate, which is then crystallized and precipitated. The NH₃ removal efficiency achieved was 43.6% [42].

In summary, various waste sources, such as wastewater, animal manure digestate, crop residue, municipal waste, food-processing and meat-packing waste, sewage sludge, and biogas slurry, can be used as ammonia sources for ammonium carbonate production. The recovery processes involve anaerobic digestion, stripping, precipitation, and vacuum membrane distillation. The profitability of ammonia recovery and ammonium carbonate production depends on various factors such as pH adjustment, initial ammonia concentration, and membrane lifetime, as summarized in Table 1. Additionally, as reported before by patent US 7811455 B2 [39], ammonia recovery from fermentation effluent can result in an NH₃ in the stripped gas of ~720 ton/year (1362.7 g/min) and an ammonium bicarbonate production of ~3000 ton/year (6.3 kg/min) for typical flows of 1060 m³/day of liquid digestate. Most of the traditional ammonium bicarbonate fertilizer plants present in China during the 1980s used to operate on a scale of 3000–12,000 tons of NH₃/year [43]. Ultimately, fertilizer production from more sustainable sources is operating at a lower capacity than traditional technologies. However, these values can be improved using current innovations that can bring technological advances to the field, especially since the total amount of N available from diverse sources of organic waste—including animal manure, food waste, agricultural residues, forestry residues, and municipal sewage sludge, all processable in biodigesters—in the US alone approaches 10 million tons of N [44].

Table 1. Ammonium carbonate (AC) production from more sustainable sources.

Ammonia/Carbon Dioxide Sources	Ammonia Recovery	Ammonium Carbonate (AC) Production and Recovery	Concentration/Yields	Highlights
Ammonium carbonate production based on CO₂ recovery				
Commercial NH ₃ source while CO ₂ was removed from flue gas [30].		AC production takes place in the CO ₂ scrubber at room temperature. CO ₂ + air flow rate = 2 L/min. Ammonia solution = 28% (w/w). Inlet CO ₂ concentrations tested = 8, 10, 12, 14 and 16% (v/v)—obtained from a pure CO ₂ source.	After 60 s, CO ₂ removal efficiency was between 95–98% for all inlet concentrations (higher than MEA). NH ₃ scrubbing capacity = 0.9 kg CO ₂ /mol NH ₃ MEA scrubbing capacity = 0.36 kg CO ₂ /mol MEA. If operation time takes more than 30 min, the ammonia scrubbing efficiency decreases. The main product was ammonium bicarbonate as a solution and crystalline solids.	The reaction between ammonia and carbon dioxide can form: <ol style="list-style-type: none"> 1. Ammonium carbamate (NH₂COONH₄) 2. Ammonium carbonate ((NH₄)₂CO₃) 3. Ammonium bicarbonate (NH₄HCO₃)

Table 1. Cont.

Ammonia/Carbon Dioxide Sources	Ammonia Recovery	Ammonium Carbonate (AC) Production and Recovery	Concentration/Yields	Highlights
Commercial NH ₃ source while CO ₂ was scrubbed from flue gas generated by a coal-fired power plant [31].		Reaction temperature < 20 °C. Ammonia reacts with CO ₂ in an absorption reactor to form ammonium carbonate precipitating as a solid. Ammonia saturating the residual flue gas is returned to the process by scrubbing.	Up to 90% of CO ₂ is removed. Flue gas composition: CO ₂ : 9.8–12.3 (vol %) SO ₂ : 3.3–9.4 ppmv NO _x : 28–54 ppmv NH ₃ : 0.9–3.5 ppmv Flue gas temperature: 50–60 °C. This gas is cooled by using a cooling tower and mechanical chillers. The pilot plant can capture ~1600 kg CO ₂ /h (~15,000 tonnes/year).	Pilot scale process. Continuous operation.
This process utilizes N ₂ and CO ₂ produced by emission sources, such as a fossil fuel power plant or steel-making factory, to produce ammonium carbonates [32].		$2 \text{CO}_2 + \text{N}_2 + 3 \text{H}_2 + 2 \text{H}_2\text{O} \rightarrow 2 \text{NH}_4\text{HCO}_3$ CO ₂ and N ₂ were captured from the factory emissions. H ₂ could be obtained by solar photovoltaic water splitting or through natural gas reforming reactions (CH ₄).	This reaction could remove up to 90% of the CO ₂ flue gas.	The reaction: $2 \text{CO}_2 + \text{N}_2 + 3 \text{H}_2 + 2 \text{H}_2\text{O} \rightarrow 2 \text{NH}_4\text{HCO}_3$ has a standard free energy of −86.18 kJ/mol, which means it is thermodynamically spontaneous.
Ammonium carbonate production from biogenic sources				
Wastewater/ animal manure digestate [38].	Usually, the biogenic source is submitted to anaerobic digestion. Stripping is used to remove the NH ₃ and dissolved CO ₂ from the digestate.	Gaseous NH ₃ is condensed with CO ₂ and water vapor (35 < T < 50 °C), forming dissolved ammonium bicarbonate and ammonium carbonate in a liquid condensate. This liquid is concentrated by two-stage reverse osmosis (35–50 °C). It is then cooled to less than 35 °C, saturating the reverse osmosis concentrate and forming solid ammonium carbonate and ammonium bicarbonate.	0.1 wt% of ammonia at the inlet dairy manure. 21.7 wt% of ammonia bicarbonate and 3.8 wt% of ammonia at the crystallizer.	No chemicals are added to adjust pH before the stripping process. No external source of CO ₂ .

Table 1. Cont.

Ammonia/Carbon Dioxide Sources	Ammonia Recovery	Ammonium Carbonate (AC) Production and Recovery	Concentration/Yields	Highlights
Organic substrates (manure, crop residue, food-processing and meat-packing waste, organic fraction of municipal waste, and sewage sludge) [39].	<p>The digestate stream contains ammonia primarily in its ionized form.</p> <p>In addition, a biogas stream containing CO₂, methane, and traces of other gases is produced. The digestate is subjected to carbon dioxide absorption and ammonia removal by using a low-pressure system through either a packed tower or a shallow basin. pH is adjusted (9–12) before or during the stripping process via the use of chemicals (Ca(OH)₂, Mg(OH)₂, MgO, NaOH, KOH). Stripping gas is heated before entering the stripping chamber.</p>	<p>The resulting gas effluent, mainly composed of methane, NH₃, CO₂, and water vapor, is then conveyed to a precipitation chamber where ammonium bicarbonate/carbonate precipitation and recovery processes occur.</p> <p>A fraction of the stripping gas effluent, low in CO₂ and NH₃, is recycled as the stripping gas. The precipitation chamber is kept at a temperature lower than 36 °C to ensure ammonium bicarbonate/carbonate precipitation.</p>	<p>Municipal anaerobic digestion facility:</p> <ul style="list-style-type: none"> - 90% of ammonia removal from the stripping feed. - Production of 6.3 kg/min of ammonium bicarbonate. <p>Total ammonia at the digestate = 1160 ppm. Stripping feed: total ammonia = 800 ppm. Stripped gas = 1362.74 g/min of NH₃. Ammonium bicarbonate precipitation = 6.33 kg/min.</p>	<p>Methane gas with a high BTU value is achieved through anaerobic digestion. This gas is then reused for ammonia stripping, which is an alternative to using high-temperature stream stripping or distillation methods that were previously used.</p>
Biogas slurry (obtained from a mesophilic anaerobic biogas digestion plant using pig manure as substrate) [40].	<p>Vacuum membrane distillation enabled ammonia recovery from biogas slurry without pH adjustment. A membrane of PTFE was used to separate ammonia from the biogas slurry.</p> <p>When the biogas is heated, the chemical equilibrium between NH₄⁺ and HCO₃⁻ in the slurry boundary layer is disturbed due to the decomposition of HCO₃⁻ into OH⁻ and CO₂, which will be extracted through the membrane due to the vacuum (created by a vacuum pump: 5–20 kPa). When it happens, the chemical equilibrium will be disturbed and accelerate the ammonia formation on the boundary layer of the biogas, improving its transfer through the membrane.</p>	<p>Ammonium bicarbonate can be produced by reacting the extracted ammonia with CO₂ obtained from biogas.</p>	<p>The maximum ammonia separation factor can reach 8.05 (optimal conditions). For a total ammonia recovery of 2 g-N/L and when heat is supplied by natural gas combustion, the profit is \$0.4/m³ of biogas slurry when no pH adjustment happens. If the pH is adjusted with NaOH, the ammonia recovery profit is negative: \$−2.06/m³ biogas slurry.</p> <p>If the initial ammonia content in the biogas slurry is increased from 0.5 to 4 g-N/L, the profitability increases from \$−0.71/m³ biogas slurry to \$1.88/m³ biogas slurry.</p>	<p>This study was a techno-economic evaluation based on lab experiments. The membrane lifetime is the factor that has the highest effect on profitability for a fixed initial ammonia content in the biogas slurry.</p>

Table 1. Cont.

Ammonia/Carbon Dioxide Sources	Ammonia Recovery	Ammonium Carbonate (AC) Production and Recovery	Concentration/Yields	Highlights
Synthetic swine wastewater [41].	NH_4^+ and HCO_3^- were removed from swine wastewater using a flow-electrode capacitive deionization system.	Ammonium bicarbonate was obtained via a freeze-drying method.	Ammonium bicarbonate concentration was ~1.61 M, with a purity of 97.2% from the synthetic swine wastewater, when optimal conditions were used. The carbon removal rate was 1.01 kg C/(m ² ·d), which is 2–5 times higher than other electrochemical systems. The energy consumption was 2.87 kWh/kg C, which is 25% lower than other electrochemical systems.	Swine wastewater has high concentrations of NH_4^+ and HCO_3^- . The flow-electrode capacitive system has an excellent ion removal performance, and it can have a continuous operation and be scaled up.
Biomass liquid digestate [34].	NH_3 and CO_2 were separated from the liquid digestate via a distillation process (3.3 bar) with utilization of N from the digestate of 99.9%.	Ammonium bicarbonate was obtained after its condensation. A crystallization process (12 °C to avoid ammonium bicarbonate decomposition) was used for the solid product obtention. After that, the solids were dried, with a final yield of 99.5% of pure ammonium bicarbonate at a production rate of 309 kg/h.	Compared to the process where the liquid digestate is directly applied to crops, the ammonium bicarbonate production from the digestate has a 25% lower global warming potential (GWP). Its eutrophication potential (EP) is also 50% lower.	Data were obtained by process simulation. Distillation column parameters are critical for energy consumption process. Ammonium bicarbonate production also has a lower installed capital cost than the $(\text{NH}_4)_2\text{SO}_4$ production via a stripping process.
Anaerobic fermentation liquid derived from food waste [42].	The fermentation liquid is placed in a reactor, with controlled temperature and pH, in which volatile fatty acids present on it are precipitated with layered double hydroxides (hydrotalcite or anionic clays). During this process, NH_3 in the reactor will escape and pass through a recovery system (water bath condenser and a three-mouth flask).	After NH_3 is recovered, CO_2 is introduced to react, forming ammonium bicarbonate. This material will be crystallized and then precipitated.	The NH_3 removal efficiency was 43.6%	The liquid fermentation has NH_4^+ and NH_3 in equilibrium: $\text{NH}_4^+ + \text{OH}^- \rightleftharpoons \text{NH}_3 + \text{H}_2\text{O}$ If temperature and pH were increased, the proportion of free NH_3 would be increased.

3.3. Methods to Increase Ammonium Carbonate Stability in a Moist Environment

Methods to increase the stability of ammonium carbonates and reduce nutrient losses while increasing nitrogen utilization rates in crops are of paramount importance. For instance, the nitrogen utilization rate of ammonium bicarbonate is around 25–30% and its fertilizer longevity is between 30–40 days [45]. Figure 3 summarizes the methods reported to increase ammonium bicarbonate stability and some additives applied in each method. Table 2 presents detailed information on the use of additives reported by patents and research papers. In particular, chemical methods include binding with various ionic binders, such as biochar or humic acids, and forming more stable compounds, such as $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$. Physical stabilization methods include granulation with mostly inorganic binders, while coatings include organic and mineral materials.

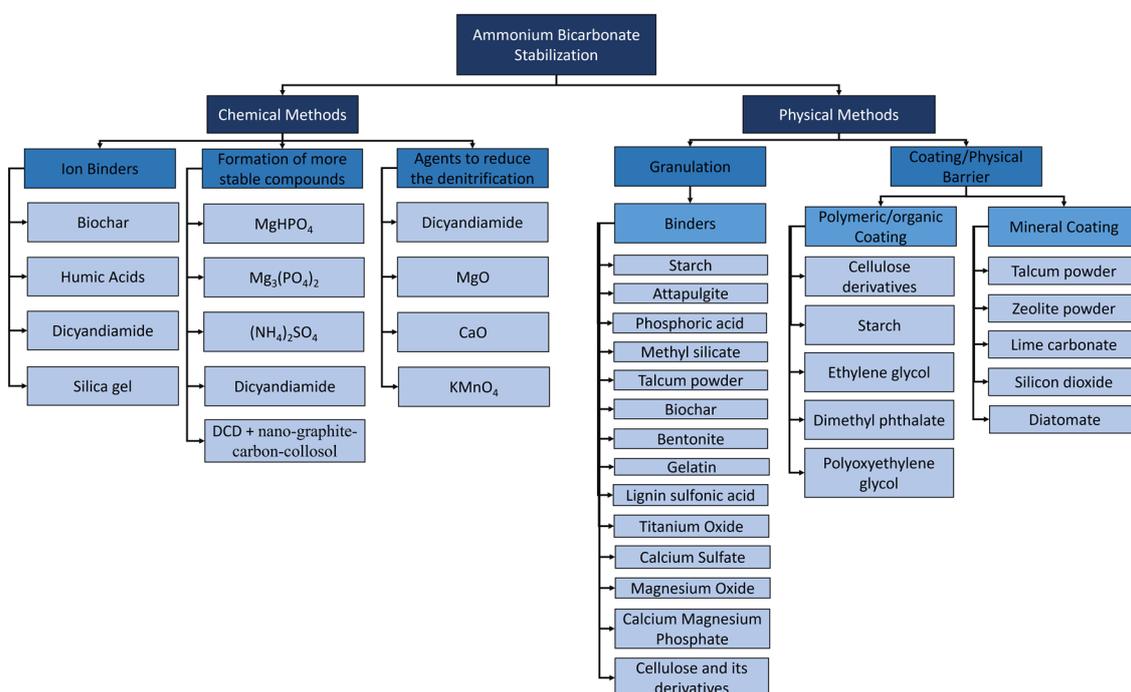


Figure 3. The main methods and additives applied to increase ammonium bicarbonate stability. Compiled from [46–56].

3.3.1. Chemical Methods

Ion Binding Compounds

Chemical methods can be applied to reduce volatilization of ammonium carbonates. Chemical agents such as biochar and silica gel can bind the NH_4^+ ion, reducing loss. This process can also provide a slow release of ammonia in soil, improving the nitrogen utilization rate [46,47]. For instance, biochar can be produced via the pyrolysis of biomass residues. The chemisorption properties of biochar are influenced by the dangling bonds found on the material after the pyrolysis process. In addition, the affinity towards NH_4^+ can be tuned by some functional groups present on its surface, such as hydroxyl and carboxyl, which can raise its cation exchange capacity to help nutrient (such as NH_4^+) retention [47]. Similarly, the addition of humic acid to ammonium bicarbonate can also result in better nitrogen utilization rates. The active groups in the humic acid can fix ammonium ions, reducing the effect of ammonia loss by volatilization by up to 26% [48]. Another material that can be used is silica gel powder since it has a large surface area, which can adsorb the ammonia released from ammonium carbonates, reducing losses [53]. Figure 4 illustrates the effect of biochar and humic acid as ion binders.

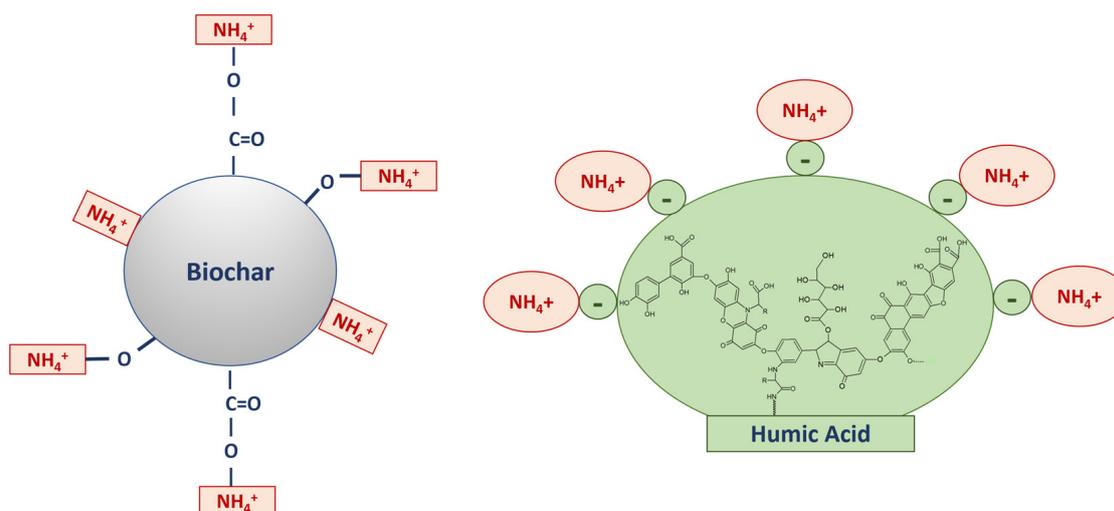


Figure 4. Ion binder–ammonium ion interactions are used to stabilize ammonium carbonate materials. Compiled from [47,48].

Formation of More Stable Compounds

The reaction of ammonium carbonates with other compounds can also be applied, resulting in a more stable material [46,50]. For instance, ammonium bicarbonate can be mechanochemically treated in a pug mill with magnesium hydrogen phosphate, resulting in a more stable compound. The ammonia released spontaneously by the ammonium bicarbonate will react with MgHPO_4 , forming $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ [50]. Besides reducing ammonia losses by slowing its release and providing nitrogen to plants, this more stable compound can also provide more essential nutrients, such as magnesium and phosphorus [50]. A similar mechanochemical treatment was successfully applied to urea by milling with metal salts, resulting in a more stable fertilizer [57,58]. The addition of ammonium sulfate before ammonium bicarbonate precipitation during its production process can also result in a product with increased stability, in comparison to only ammonium bicarbonate. The resulting ammonium bicarbonate: $(\text{NH}_4)_2\text{SO}_4$ complex reduced product volatilization during its storage, increasing its shelf life [51].

Dicyandiamide (DCD), a well-reported nitrification inhibitor, can also be used as an additive to improve the ammonium bicarbonate effect as a fertilizer [59]. This organic compound is added during the ammonium bicarbonate production process at a concentration of less than 1%. Both DCD and ammonium bicarbonate were crystallized together, forming a proposed cocrystal (with a rod shape or cuboidal crystal structure) [52], although a crystal structure was not readily available. This cocrystal presents higher thermal stability than ammonium bicarbonate and will result in durable efficacious ammonium bicarbonate [59]. Instead of co-crystallization, the admixing of both compounds can also be done. DCD's structure has primary and secondary amino groups. These groups can adsorb free ammonium by hydrogen bonding [45]. In comparison with regular NH_4HCO_3 , the application of the compound ammonium bicarbonate:DCD was found to reduce ammonia volatilization losses by 53% and increase fertilizer availability from 35–45 days to 90–110 days. This resulted in a 20–30% savings of the amount of applied fertilizer and ended up increasing the crop yield by over 10% when the same level of ammonium bicarbonate was used [59]. In addition, DCD can reduce the ammonium carbonate nitrification process, which means that a lower amount of ammonium will be transformed into NO_3^- ions. Although ammonia losses by volatilization are an issue for ammonium carbonates, the release of NO_3^- has a more harmful effect on the environment than ammonium due to NO_3^- mobility, and DCD addition can decrease NO_3^- production/release. In this context, when compared with regular ammonium bicarbonate, the ammonium bicarbonate:DCD can reduce N_2O emissions

from maize fields by 74% [60]. Figure 5 reports the additives previously discussed along with their effects on increasing ammonium bicarbonate stability.

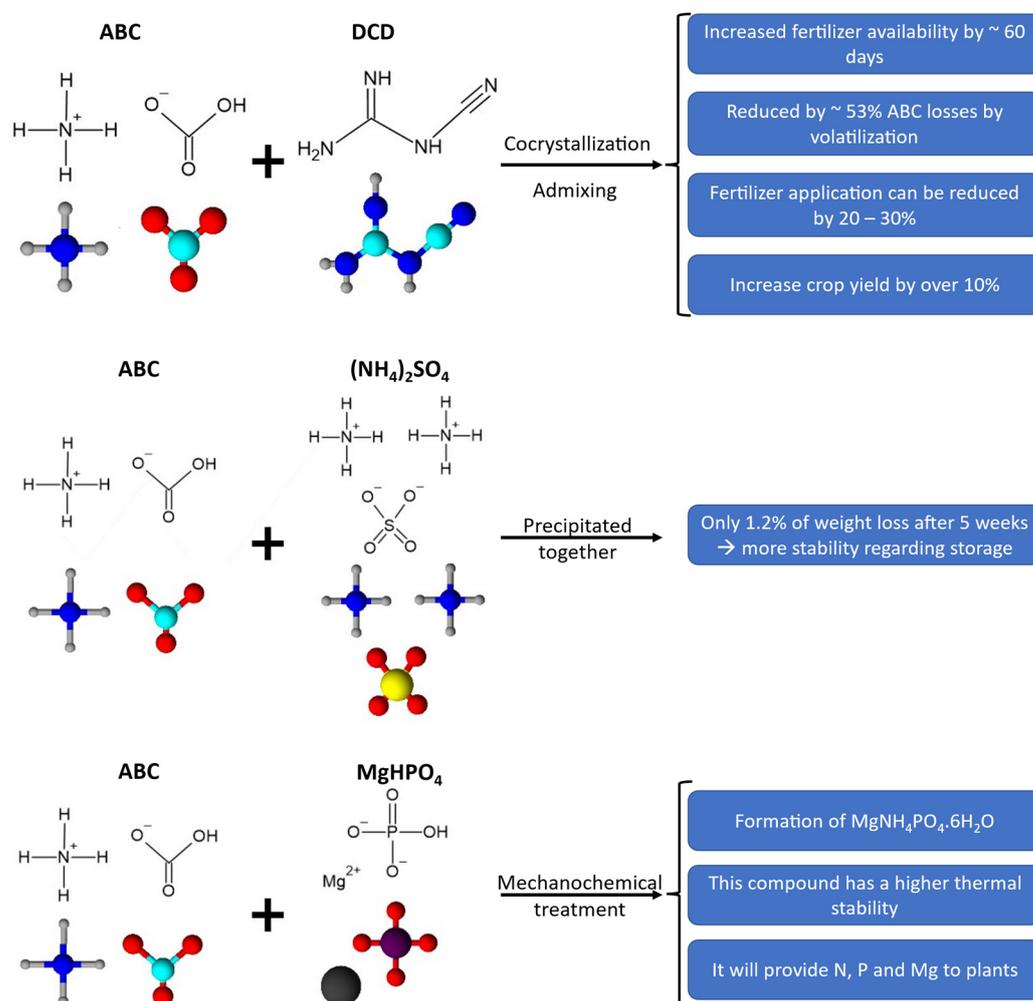


Figure 5. Ammonium bicarbonate reactions with other substances to form more stable compounds. Compiled from [50–52,59].

The production of a NH_4HCO_3 :DCD:carbon nanomaterial composite has also been reported, in which the carbon nanomaterial is nano-graphite-carbon-collosol [45]. Besides the DCD positive effects, adding the nano-carbon during the ammonium bicarbonate production process can reduce the water content of ammonium bicarbonate. This results in a more compact and ordered structure, which increases the water and thermal stability of ammonium bicarbonate [45]. Field experiments showed that the N_2O emissions could be reduced by 70% compared to ammonium bicarbonate application without DCD [45]. Additionally, it can increase fertilizer persistence in soil over time.

Although not reported for fertilizer applications, ammonium carbonates could react with some compounds, such as manganese sulfate and phosphorus chlorides. For instance, reactions between ammonium bicarbonate and phosphorus pentachloride (PCl_5) or phosphorus oxychloride (POCl_3) have also been reported [61]. These reactions can be carried out at room temperature and will produce ammonium pyrophosphate ($(\text{NH}_4)_4\text{P}_2\text{O}_7$). Ammonium pyrophosphate and orthophosphate are effective P fertilizers for corn (*Zea mays* L.) grown in cool (16°C) soil [62]. When benzene is used during the reaction between ammonium bicarbonate and PCl_5 , diammonium phosphate, a conventional N-P fertilizer, is formed [61]. The formation of these compounds is illustrated in Figure 6.

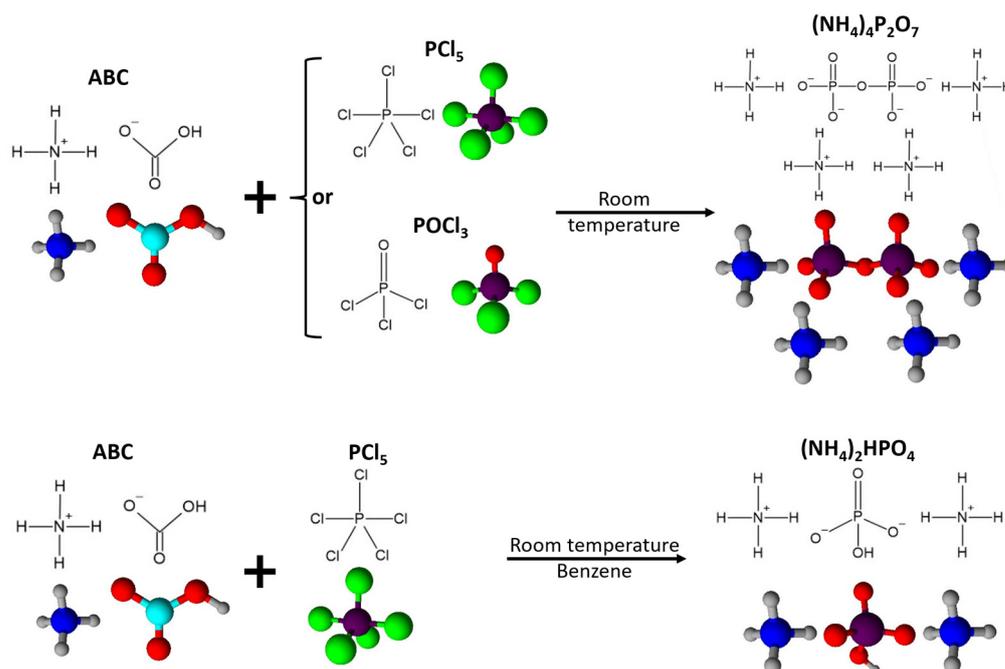


Figure 6. Alternative routes for ammonium bicarbonate conversion into N-P fertilizers. Compiled from [61].

3.3.2. Physical Methods Granulation

Physical methods can also be applied to increase ammonium carbonate stability. For instance, granulation can help reduce the specific surface area of the fertilizer compared to its powder form, and this compound will be subjected to a lower volatilization loss [63]. Inter-particle bonds between the molecules need to be formed to promote granulation. If these bonds are not formed, or if they are weak, the granule can collapse, and dust will be formed [64]. Additives can be added to increase the granule strength, promoting inter-particle bonds [64]. Patents report the utilization of starch, attapulgite, phosphoric acid, methyl silicate, talcum powder, etc., as ammonium carbonate additives for granulation [53]. The granulation of ammonium bicarbonate in the presence of binders such as phosphoric acid or magnesium compounds reduces nitrogen losses by 60–84.8% compared with commercial ammonium bicarbonate. In addition, corn production increased by 8.7% with these granules compared with commercial fertilizer [53].

Besides increasing the granule strength, the additives can also improve the fertilization properties. For instance, if a magnesium compound (magnesium oxide or hydroxide) is used in the presence of phosphoric acid, an ammonium magnesium phosphate salt can be formed, increasing the fertilizer's hardness and slowing down the ammonia release, in comparison with regular ammonium bicarbonate [53]. Attapulgite is a binder agent with a very strong absorptivity, which can delay ammonium release [53]. Additionally, oxidizing agents such as MgO, CaO, or KMnO₄ can be added to the formulation. These compounds control the nitrate reduction process, decreasing the denitrification process.

Coatings

Coating is another method that can increase ammonium carbonate's stability under variable conditions during its storage and after its application. Developing an N-coated fertilizer aims to slow down and control nutrient release. It can provide nutrient release kinetics that more closely matches the plants' N requirements, significantly reducing losses [10]. The coating can be obtained using natural or synthetic materials. Once the coated product is applied to soil, water penetrates the membrane through its pores. The release starts when the water reaches the fertilizer core, solubilizing it [65,66]. Another

means of nutrient release is by coating disintegration (by chemical, biological, and physical actions), releasing the encapsulated nutrient [10]; however, this process can speed up fertilizer release, affecting the controlled release process [66,67]. The coating effect over the ammonium bicarbonate fertilizer and an illustration of how the fertilizer release rate of a powder, granule, and coated granule should look is shown in Figure 7.

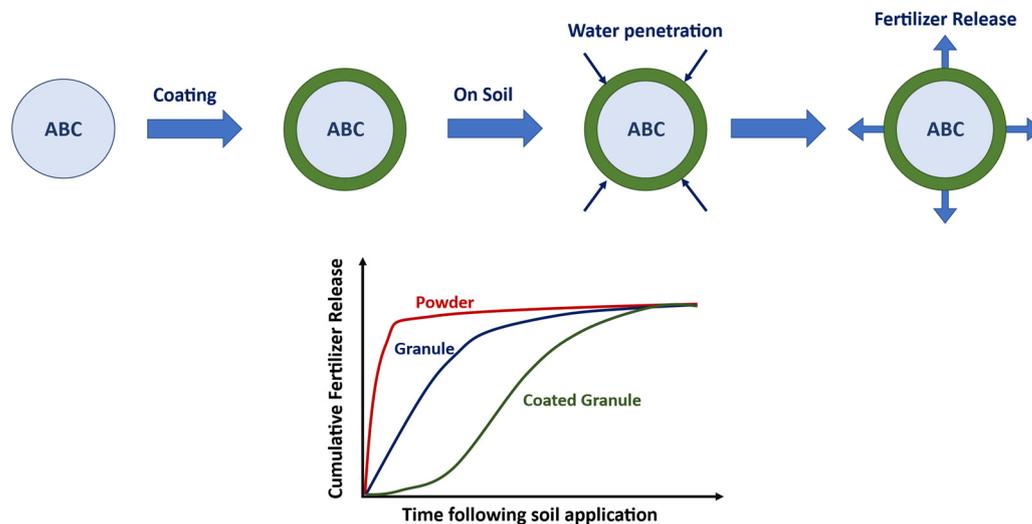


Figure 7. Schematic representation of coatings affecting nutrient release from ammonium bicarbonate fertilizers.

For ammonium bicarbonate, a patent was identified that uses polymers, such as starch and microcrystalline cellulose, as coatings [68]. Mineral membranes, such as talcum powder, zeolite powder, lime carbonate, silicon dioxide, and softening agents (polyoxyethylene glycol, propylene glycol, ethylene glycol and dimethyl phthalate), have also been investigated. Using a mineral membrane can help overcome adhesion issues during the coating process, and it can also help control pore size, affecting the fertilizer dissolution rate. A softening agent can increase the plasticity and toughness of the coating film [68]. For instance, a coating with increased plasticity applied postponed the fertilizer discharge by 20–60 days and the coating wall provided a controlled release of the fertilizer, increasing the utilization rate by 60% [68].

Figure 8 summarizes the effect of some stabilization methods on the reduction of ammonia volatilization from ammonium carbonate materials. Both the material granulation or the ammonium bicarbonate admixed with DCD and a nanocarbon material resulted in a loss reduction of ~70% compared to only ammonium bicarbonate without a stabilization method.

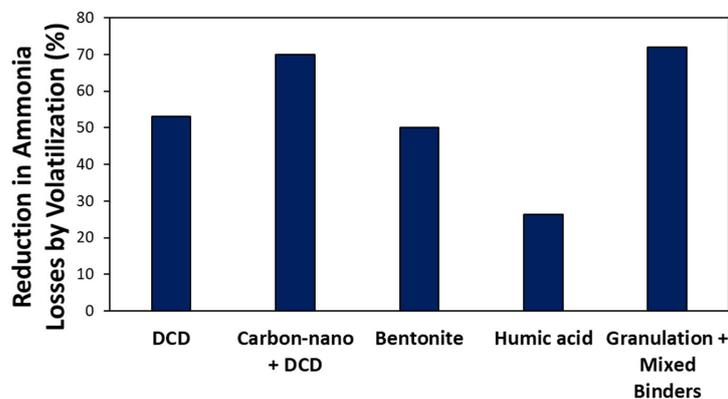


Figure 8. Effect of some methods on ammonia loss reduction from granulated ammonium bicarbonate fertilizer materials. Compiled from [45,46,48,53,59].

Table 2. Summarized studies to increase ammonium bicarbonate stability.

Study Main Objective	Additive/Stabilization Method	Effect and General Comments	Reference
Production of fertilizers containing ammonium bicarbonate and at least one inexpensive and non-toxic additive for binding NH ₃ and CO ₂ to reduce losses	One or a combination of <ul style="list-style-type: none"> - Biochar - Cellulose derivative - Non-oxidizing inorganic salt (e.g., Mg₃(PO₄)₂, Mg₂SiO₄, CaCO₃, Ca(HCO₃)₂, or Ca₃(PO₄)₂) - Bentonite - Oxidizing agent (e.g., MgO, CaO, or KMnO₄) - Granulation (compacting agents: gelatin, TiO₂, lignin sulfonic acid) - Coating (Olivine, Mg₂SiO₄, Ca₃(PO₄)₂, Mg₃(PO₄)₂) 	<ul style="list-style-type: none"> - Biochar: It can absorb CO₂ and NH₃ due to the presence of functional groups and dangling bonds on its surface. Its addition to ammonium carbonates will increase the product’s shelf life. - Cellulose derivative: it will coat ammonium bicarbonate, preventing its hydrolysis. Improves NH₄HCO₃ shelf life. Concentration: 1–10% (<i>w/w</i>) in total fertilizer weight. - Non-oxidizing inorganic salts can bind CO₂ and NH₃, slowing their releases. In addition, using magnesium or calcium compounds can prevent the release of CO₂ into the atmosphere. Its concentration should be between 5–20% (<i>w/w</i>). <p>Bentonite can reduce ammonia losses from 62% to 34% when added to ammonium carbonates. In general, the fertilizer is pressed into compact pellets to increase fertilizer stability. Its concentration should be between 5–20% (<i>w/w</i>) in the final fertilizer. Oxidizing agents such as MgO, CaO, or KMnO₄ can counteract the reduction of nitrate (reducing the denitrification process). Their concentration should be between 1–10% (<i>w/w</i>) in the final fertilizer.</p> <ul style="list-style-type: none"> - Fertilizers in the form of pellets and granules are preferred since they will increase fertilizer stability and no dust will be formed during its application on soil. 	[46]
Production of a fertilizer containing ammonium carbonates and ammonium sulfate, resulting in a product with better stability	Ammonium sulfate ((NH ₄) ₂ SO ₄)	<ul style="list-style-type: none"> - A saturated ammonium sulfate solution is added and mixed with ACs. This mixture is then precipitated, resulting in a more stable compound than ammonium bicarbonate. - Final composition: 35% ammonium bicarbonate and 65% ammonium sulfate. - After 5 weeks of storage, the fertilizer presented the same appearance and no appreciable loss in weight occurred (only 1.3% loss). 	[51]

Table 2. Cont.

Study Main Objective	Additive/Stabilization Method	Effect and General Comments	Reference
Increase ammonium bicarbonate stability via its reaction with $MgHPO_4$	Magnesium hydrogen phosphate ($MgHPO_4$)	<ul style="list-style-type: none"> - NH_4HCO_3 and $MgHPO_4$ are milled together at room temperature and then conditioned. The $MgHPO_4$ should be added in a proportion of not below 5% compared to ammonium bicarbonate. - $MgHPO_4$ combines with the ammonia released by the spontaneous decomposition of the ammonium carbonates, forming $MgNH_4PO_4 \cdot 6H_2O$. - The individual crystals of NH_4HCO_3 will present a coating layer of magnesium ammonium phosphate, which has a double effect: (1) it will make the mixture freely flow (preventing cake); and (2) it will inhibit the decomposition of ammonium carbonates. 	[50]
Production of a fertilizer containing humic acids and ammonium bicarbonate	Humic acid	<ul style="list-style-type: none"> - Ammonium bicarbonate is produced in the presence of humic acid and in the following composition range: 0.15–0.60% (wt) of humic acid and 99.4–99.85% (wt) of ammonium bicarbonate. The active groups in the humic acid can fix ammonium ions, reducing the effect of ammonia loss by volatilization by 26.3%, and improving the utilization rate of the fertilizer. 	[48]
Production of granular nitrogen fertilizer with ammonium bicarbonate	Granulation Binders: <ul style="list-style-type: none"> - Phosphoric acid - Magnesium compound (salts, oxide, or hydroxide) - Attapulgate - Methyl silicate - Talcum powder - Silica gel 	<ul style="list-style-type: none"> - Composition: - 75–92% Ammonium bicarbonate. - 3–22% Urea. - 2–22% Binder. - Materials were mixed in a pan mixer and granulated in a pair roller (2–5 mm diameter). - When the Mg compound is used with phosphoric acid, it can form ammonium–phosphate–magnesium salts. These compounds will increase the material’s hardness and also reduce the ammonia volatilization. - Attapulgate is a binder agent with a very strong absorptivity. - Methyl silicate can reduce the moisture adsorption of the fertilizer. - Talcum powder can favor the granulation process by making the granules release from the roll easier. 	[53]

Table 2. Cont.

Study Main Objective	Additive/Stabilization Method	Effect and General Comments	Reference
Production of an ammonium bicarbonate fertilizer with a longer efficiency time	Dicyandiamide—DCD ($N_4H_4C_2$)	<ul style="list-style-type: none"> - Silica gel has a high surface area, and it can adsorb the ammonia discharged from ammonium carbonates, reducing losses. - Ammonia losses by volatilization in comparison with regular ammonium bicarbonate can be reduced by 60–84.8%. When applied on crops, it can increase corn production by 8.7% in comparison with commercial NH_4HCO_3. 	
		<ul style="list-style-type: none"> - DCD can be added during the ammonium bicarbonate production process (proposed co-crystallization) or it can be admixed with ammonium bicarbonate after its production. - DCD addition: it reduces NH_4 volatilization loss by inhibiting the oxidation of NH_4^+ to NO_2^-. - The additive amount must be <1% and >0.3 wt%. - Improves storage rates of soil ammonia-state nitrogen by up to 37%. - Improves the efficiency period of ammonium bicarbonate on soil from 35 to more than 65 days. - Improves the nitrogen utilization rate by 25 to 30%. 	[52]
Production of a durable and efficacious ammonium bicarbonate fertilizer	Dicyandiamide—DCD ($N_4H_4C_2$)	<ul style="list-style-type: none"> - DCD is added to ammonium bicarbonate by proposed co-crystallization or admixing and will act as an ammonia-stabilizing agent. - Reduced the direct volatilization loss of ammonium bicarbonate by 53%. - Increased the fertilizer availability period from 35–45 days to 90–110 days. - Saving the amount of fertilizer to be applied by 20–30%. - Increased the crop yield by over 10%. 	[59]

Table 2. Cont.

Study Main Objective	Additive/Stabilization Method	Effect and General Comments	Reference
Evaluation of the N ₂ O emissions from ammonium bicarbonate and the more stable fertilizer ammonium bicarbonate:DCD	Dicyandiamide—DCD (N ₄ H ₄ C ₂)	<ul style="list-style-type: none"> - Commercial NH₄HCO₃:DCD was obtained by the cocrystallization of these materials. - Laboratory tests showed that NH₄HCO₃:DCD reduced the N₂O emissions in meadow brown soil by 80%, in comparison with commercial ammonium bicarbonate, at a moisture of 12% and by 40% at a moisture of 22%. - NH₄HCO₃:DCD decreased the N₂O emissions by 74% in maize fields. It also increased maize yield by 13.6% in comparison with commercial ammonium bicarbonate. 	[60]
Production of a controlled-release fertilizer	<p>Granulation Nitrification inhibitor</p> <ul style="list-style-type: none"> - Dicyandiamide (DCD) - 4-dimethyl phosphoric acid pyrazoles (DMPP) <p>Coating</p> <ul style="list-style-type: none"> - Polymers (starch and microcrystalline cellulose) - Mineral membranes (talcum, zeolite, lime carbonate, silicon dioxide, diatomite) <p>Softening agents</p> <ul style="list-style-type: none"> - Polyoxyethylene glycol - Ethylene glycol - Propylene glycol - Dimethyl phthalate 	<ul style="list-style-type: none"> - The coating is performed in a fluidized bed by a spray-coating technique, and it resulted in a controlled release fertilizer. - The mineral membrane can help overcome the adhesion phenomenon during the coating process. It can also help to control the pore size, which will impact the fertilizer dissolution rate. - The softening agents can increase the coating film's plasticity and hardness. - This method can postpone the fertilizer discharge by 20–60 days and it can increase the N utilization rate by up to 60%. - The nitrification inhibitors can reduce nitrogen losses and improve the nitrogen utilization rate. 	[68]
Production of a fertilizer made of ammonium bicarbonate and biochar	Biochar from peanut hulls	<ul style="list-style-type: none"> - Biochar is placed inside a gas-phase ammonium bicarbonate production reactor (gas-phase ammonia-scrubbing CO₂ solidifying process). - The biochar particles will act as nucleation sites for the formation of solid NH₄HCO₃ crystals. - The binding affinity of the biochar for ammonium bicarbonate is a result of the biochar surface functional groups (e.g., carboxyl and hydroxyl groups) and some dangling bonds (resulting from the biomass pyrolysis thermochemical process). - Biochar has a pH of ~9.8. Ammonium bicarbonate addition can help to neutralize the material's pH to ~7.9, which could favor this fertilizer usage in different soil conditions. 	[47]

Table 2. Cont.

Study Main Objective	Additive/Stabilization Method	Effect and General Comments	Reference
Production of a long-effective ammonium bicarbonate composite fertilizer	Granulated material Composite materials: - NH_4HCO_3 - Monoammonium phosphate or diammonium phosphate - KCl or K_2SO_4 - DCD: 0.3–1% - Humic acid: 10–20% - Anticaking agent (magnesia): 2–5% - Binding agent (wilkinsonite or attapulgite): 2–3%	<ul style="list-style-type: none"> - Nitrogen: 11–17% (<i>w/w</i>) - Phosphorus: 4–6% (<i>w/w</i>) - Potassium: 4–6% (<i>w/w</i>) - Carbon: 11–17% (<i>w/w</i>) - Humic acid can improve soil nutrition. - The anticaking and binding agents and the P-source and K-source are added and mixed with NH_4HCO_3-DCD. After that, the material is pressed using a pair roller, forming particles with diameters between 4–6 mm. - Effect on plants: increased by 10.6% the tomato production and by 15.4% the cucumber production in comparison with common ammonium bicarbonate. 	[54]
Production of a multi-element granular fertilizer	Granulation Additives (2–30%) - Calcium sulfate, calcium magnesium phosphate, magnesium oxide, zeolite, talcum, sulfur, or wilkinsonite	<ul style="list-style-type: none"> - The direct granulation of NH_4HCO_3 is difficult due to the high amount of water that this compound has (3–6.5%). To granulate it, the amount of water should be lower than 1%. - All components are mixed using a mixing machine, and then the final product is granulated. - The final product will have lower water content and lower volatility. 	[55]
Production of an ammonium carbonate fertilizer that has bentonite as a filler	Bentonite	<ul style="list-style-type: none"> - Bentonite is a strong water absorbent; has a strong adsorptivity (has negative charges); has a strong cation exchange capacity. - Bentonite can adsorb ammonium ions and it can also reduce the caking tendency of ammonium carbonates. - Bentonite also has trace elements, such as K, Na, Ca, and P, which can improve plant nutrition. - Ammonium carbonate:bentonite ratios = 1.5–4:1. 	[56]

3.4. Ammonium Carbonates as a Fertilizer Material

3.4.1. Ammonium Carbonates as N Source

Although ammonium carbonate presents significant losses due to NH_3 volatilization, different strategies are reported in the literature to retain it in soil and improve plant nitrogen availability. The first practical route described is the application of ammonium carbonates via deep placement in soil. This strategy allows ammonium nitrogen to be absorbed through cation exchange complexes in the soil, reducing the amount of ammonium that rises to the surface due to diffusion [69]. Xu et al. [69] showed that placing ammonium bicarbonate deep into the soil from direct seeding of rice (DSR) fields resulted in a low ammonium concentration in surface water or soil solution, which reduced the NH_3 volatilization rate. The authors showed that fertilizer applied through surface broadcasting

had an NH_3 volatilization rate of 35.8 kg-N/ha, corresponding to 59% of total applied nitrogen. In comparison, the ammonium carbonate placement at a depth of 5 cm reduced the volatilization to 27.1 kg-N/ha from the total 60 kg-N/ha applied, equivalent to 45% of the total applied nitrogen [69]. Table 3 shows the main crops, N fertilization rates, and the effects observed from ammonium bicarbonate use as fertilizer. Likewise, Pan et al. [70] compared two types of nitrogen fertilization from a commercially available fertilizer (CF, with a total N content of 15% and a P_2O_5 content of 15%) and ammonium bicarbonate in two rice crops (Tianyou 998 and Yuxiangyouzhan). Fertilizers were evaluated in two conditions: (i) manually released and (ii) mechanically placed 10 cm deep in the soil. The authors observed that ammonium bicarbonate mechanically placed 10 cm deep in the soil showed an increase in nitrogen use efficiency (NUE) and grain yield and an improved nitrogen recovery efficiency (NRE) of 32–50% and 21–32% for Tianyou 998 and Yuxiangyouzhan, respectively. Moreover, agronomic nitrogen efficiency (NAE) increased by 32–50% and 19–38% for Tianyou 998 and Yuxiangyouzhan, respectively [70].

Stainless steel-box experiments conducted in South China also demonstrated that it is possible to improve grain yield, nitrogen use efficiency, and root characteristics in direct-seeded rice (DSR) [71]. The authors revealed that adequate nitrogen management could improve nutrient uptake. Moreover, ammonium bicarbonate fertilizer combined with deep placement significantly increased grain yields (72%) and nitrogen agronomic efficiency (165%) compared to the control. This effect also impacted rice root growth, leading to thicker root diameter formation and the highest root length and surface area [71].

Ammonium bicarbonate application also can impact the remediation of polluted soils, such as cadmium (Cd). Usually, some synthetic chelators are used to remove potentially toxic metals, such as ethylenediaminetetraacetic acid, ethylene-glycol-bis(oxyethylenitrilo)-tetraacetic acid, and [S, S]-ethylenediaminedisuccinic acid [72]. However, these chelators can have negative effects on the environment, such as elevated toxicity to soil microorganisms and the potential risk of the chelator leaching into the groundwater. On the other hand, phytoextraction is an alternative for the remediation of potentially toxic metals. Phytoextraction is a technique that uses hyperaccumulating plants to absorb contaminants, which are absorbed by the roots and accumulated in the leaves. Thus, biomass production has a direct impact on nutrient absorption capacity (phytoextraction) [72–74], since soil corrections can facilitate both plant biomass production and metal absorption. Moreover, ammonium bicarbonate application can be a promising way to increase the hyperaccumulator capacity to remove metals from polluted soil.

For instance, Wei et al. [71] evaluated the effects of different N-containing chemicals (including NH_4HCO_3) on Cd hyperaccumulating properties of *Rorippa globosa*. The authors used ammonium nitrate, ammonium chloride, ammonium thiocyanate, monoammonium or diammonium phosphate, ammonium sulfate, ammonium persulphate, and urea. This study showed that the ammonium bicarbonate addition caused the highest increase in Cd concentrations in roots compared to the other N-containing products, and 56% higher compared to the control. Moreover, Cd accumulation capacity using ammonium bicarbonate was the highest compared to the other fertilizers, as well as demonstrating 8.6- and 10.6-fold increases in shoots and roots compared to the control. The ammonium bicarbonate also showed a high increase in both root and shoot biomasses of *R. globosa*, by 5.8- and 7.4-fold, compared to the control [72].

Table 3. The main crops, fertilizer doses, and effects observed from ammonium bicarbonate application as fertilizer.

Crop	Fertilizer Dosage	Effect	Reference
Rice (Japonica rice)	60 kg-N/ha	Deep placement reduced the NH ₃ volatilization rates from ammonium bicarbonate.	[69]
Rice (Tianyou 998)	120 kg-N/ha	Ammonium bicarbonate placed mechanically at 10 cm of soil depth allowed improved nitrogen recovery efficiency (32–50%), agronomic nitrogen efficiency (32–50%), and increased nitrogen use efficiency and grain yield.	[70]
Rice (Yuxiangyouzhan)	120 kg-N/ha	Ammonium bicarbonate placed mechanically at 10 cm of soil depth allowed enhanced nitrogen recovery efficiency (21–32%) and agronomic nitrogen efficiency (19–38%).	[70]
Rice (<i>Oryza sativa</i> L.)	195 kg-N/ha	Ammonium bicarbonate combined with compound fertilizer accelerated straw decomposition, promoted the early growth of tillers and roots, as well as improved the leaf area index, dry matter accumulation, and N use efficiency.	[75]
Rice	150 kg-N/ha	Deep placement of ammonium bicarbonate fertilizer significantly increased grain yields (72%) and nitrogen agronomic efficiency (165%) compared to the control.	[71]
<i>Solanum nigrum</i> L.	50–800 mg-N/kg soil	The increasing ammonium bicarbonate concentrations improved Cd phytoaccumulation capacity in <i>S. nigrum</i> shoots.	[73]
<i>R. globosa</i>	40 mg-N/kg soil	Ammonium bicarbonate had a positive effect on Cd uptake, and a high increase in biomass yield resulted in a high Cd accumulation capacity.	[72]

3.4.2. Ammonium Carbonate Effect on the C Cycle

An intriguing idea is to utilize ammonium carbonate not only as nitrogen but also as a carbon source for the soil, thus potentially using it as a vehicle towards cyclic carbon use. Once ammonium carbonate materials are applied to the soil, they dissociate into NH₄⁺ and HCO₃⁻, and both ions will affect carbon dioxide sequestration [76]. As stated before, ammonium ions are a nitrogen source for plants, which will enhance the photosynthesis process and, consecutively, increase the CO₂ capture from the atmosphere, forming, then, organic carbon, which will contribute to reducing the carbon dioxide concentration in the atmosphere [76]. Eventually, this biomass can be used as a fuel (releasing CO₂) or it can become organic matter in the soil, which means that eventually this carbon will come back into the atmosphere via biomass decomposition. Carbon storage via this process is called “short-term carbon storage” [76]. The bicarbonate ions in ammonium carbonate molecules will react with free alkali ions, precipitating salts into the soil or groundwater. This reaction happens since HCO₃⁻ is a weak acidic ion and can form CaCO₃ and MgCO₃, which are environmentally benign insoluble salts. Since these salts are very stable, this process is called “long-term CO₂ storage” [29,76]. Figure 9 summarizes the short- and long-term carbon storage process.

To better evaluate and understand the path of the carbon present in the NH₄HCO₃ molecule after its application, a ¹⁴C-tagged isotope was used to produce ammonium bicarbonate [29,76]. When applied in the soil during wheat production, the authors found that alkaline soils presented the highest carbon capture from NH₄HCO₃ (up to 75%), followed by neutral soil (~47%) and then acidic (~40%). This difference can be explained by the fact that in weak alkaline conditions, the HCO₃⁻ ions can be more easily percolated with Ca²⁺ and Mg²⁺ ions [29,76]. In acidic environments, carbonated materials are not stable [77]. Consequently, C losses to air are higher in acidic soils (~50%) than in alkaline soils (~25%) [29,76]. Additionally, approximately 10% of the carbon provided by ammonium bicarbonate was assimilated by wheat through the photosynthesis or root breathing

processes, and plants grown in neutral pH tend to store more C. It was also reported that the soil pH can also affect the amount of carbon dioxide released back into the atmosphere. For instance, acid soils can release more carbon (~52%) than neutral (~45%) and alkaline soils (~20%) [29,76].

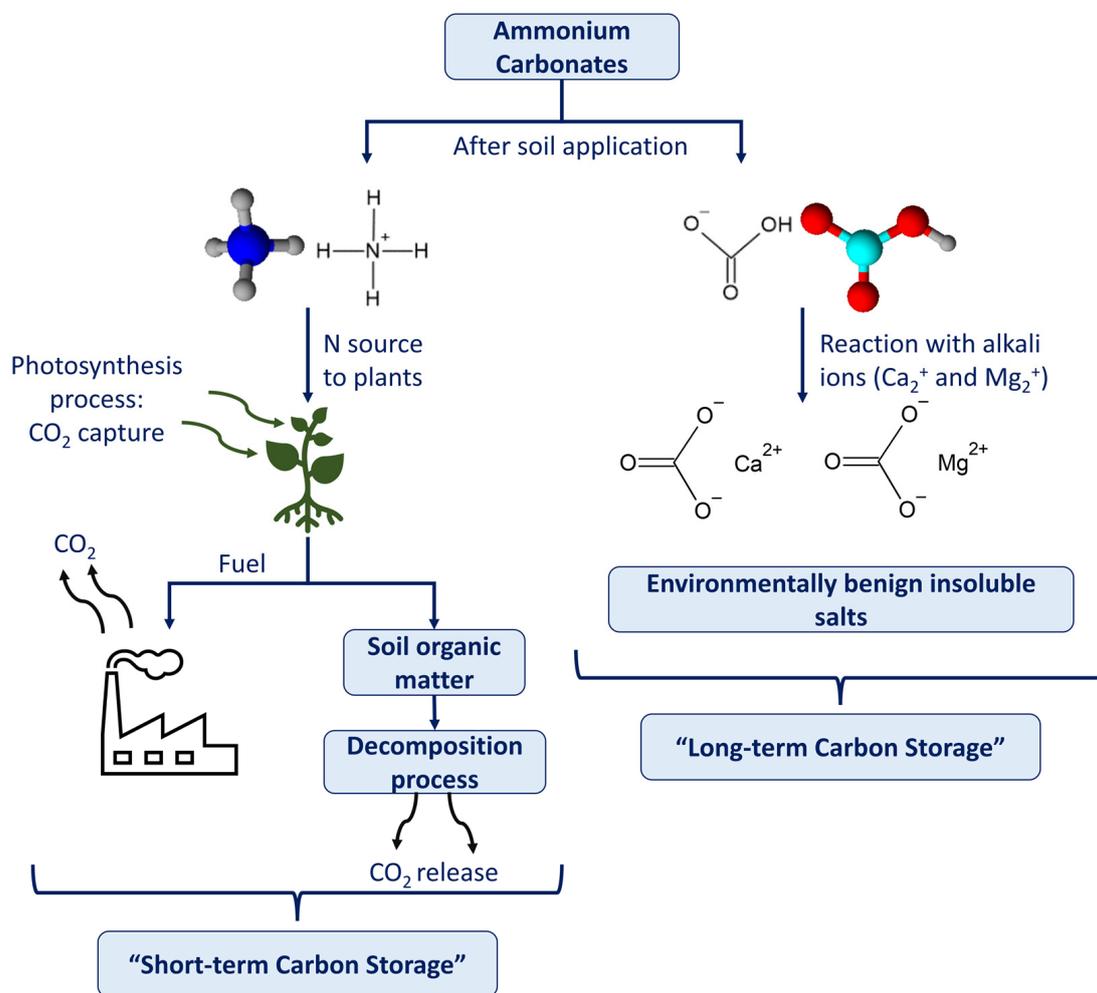


Figure 9. Ammonium carbonate effect on carbon dioxide sequestration. Compiled from [29,76].

A field experiment with spring wheat in China was conducted to evaluate the effect of soil CO_2 concentration on plant growth [78]. NH_4NO_3 and NH_4HCO_3 were used as fertilizers, with the same nitrogen fertilization level of $\sim 88 \text{ kg-N h/m}^2$, and the results showed that ammonium bicarbonate addition increased the soil CO_2 concentration in $14.5 \text{ } \mu\text{mol/mol}$ in comparison with ammonium nitrate. This higher carbon dioxide content in soil resulted in higher grain yield, since fertilization with NH_4NO_3 increased the yield compared to the control (no fertilization) by 148%. In comparison, the ammonium bicarbonate addition resulted in a 163% improvement [78]. Additionally, it is important to highlight that the power consumption per unit of nitrogen during production of ammonium carbonate compounds is approximately two times lower than the production of ammonium nitrate [79]. Additionally, although not carried out with ammonium carbonate compounds, these studies suggest that increasing the rhizosphere carbon dioxide concentration is responsible for an increase in the N assimilation by plants, producing organic and amino acids [80,81].

4. Conclusions

Ammonium carbonate compounds can be recovered from flue gas using an external NH_3 source and from biogenic waste digestion liquid byproduct to recover both C and N.

While the complexity of the resulting solid precipitate is high, most of the reported instances recognized ammonium bicarbonate as comprising the chief portion of the product. As such, ammonium carbonate materials in general and ammonium bicarbonate in particular can act as helpful platform molecules to recover, store, and recycle both major nutrients, C and N, back into the environment. Thus, the proposed utility of recovered ammonium (bi)carbonate is manifold but can only be implemented if it can be sufficiently stabilized in the environment, so its intrinsic reactivity is overcome. An extensive database of chemical and physical ammonium carbonate stabilization methods already exists to suggest that the inherent instability can be overcome, and nutrients can be released efficiently. Further needs exist relating to the obtaining of integral multi-nutrient ammonium carbonate materials that can disrupt the existing conventional N-P-K fertilizer production network, thus potentially increasing overall fertilizer use sustainability. This includes novel ammonium (bi)carbonate processing routes and formulations, scale-up procedures, and pot and field trials to measure the resulting yields and nutrient utilization efficiencies to evaluate global impacts. Corresponding process designs incorporating green electricity and the resulting life cycle analyses of these novel materials need to be performed.

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