Article

Transformation of Biomass Power Plant Ash into Composite Fertilizers: A Perspective to Prepare a Rain-Controlled Ammonium Ion–Releasing Composite Fertilizer

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Abstract: We have developed a convenient route to transform biomass power plant ashes (BPPA) into porous sponge-like fertilizer composites. The absence of water prevents the chemical reaction and carbon dioxide formation when concentrated sulfuric acid is mixed with BPPA and $CaCO_3$. Adding water, however, initiates the protonation reaction of carbonate ion content and starts CO_2 evolution. The key element of the method was that the BPPA and, optionally, $CaCO_3$ and/or $CaSO_4 \cdot 0.5H_2O$ were mixed with concentrated sulfuric acid to make a paste-like consistency. No gas evolution occurred at this stage; however, with the subsequent and controlled addition of water, CO_2 gas evolved and was released through the channels developed in the pastry-like material due to the internal gas pressure, but without foaming. Using a screw-containing tube reactor, the water can be introduced under pressure. Due to the pressure, the pores in the pastry-like material became smaller, and consequently, the mechanical strength of the granulated and solidified mixture became higher than that of the reaction products prepared under atmospheric pressure. The main reaction products were syngenite ($K_2Ca(SO_4)_2 \cdot H_2O$) and polyhalite ($K_2Ca_2Mg(SO_4)_4 \cdot 2H_2O$). These compounds are valuable fertilizer components in themselves, but the material's porous nature helps absorb solutions of microelement fertilizers. Surprisingly, concentrated ammonium nitrate solutions transform the syngenite content of the porous fertilizer into ammonium calcium sulfate (($NH_4)_2Ca(SO_4)_2 \cdot 2H_2O$, koktaite). Koktaite is slightly soluble in water, thus the amount of ammonium ion released on the dissolution of koktaite depends on the amount of available water. Accordingly, ammonium ion release for plants can be increased with rain or irrigation, and koktaite is undissolved and does not decompose in drought situations. The pores (holes) of this sponge-like fertilizer product can be filled with different solutions containing other fertilizer components (phosphates, zinc, etc.) to adjust the composition of the requested fertilizer compositions for particular soils and plant production. The method allows the preparation of ammonium nitrate composite fertilizers containing metallic microelements, and various solid sponge-like composite materials with adjusted amounts of slowly releasing fertilizer components like syngenite and koktaite.

Keywords: composite fertilizer; biomass power plant ash; concentrated sulfuric acid; ammonium nitrate; porosity

1. Introduction

The growing demand for energy, in conjunction with depleting mineral energy resources and the need to limit undesirable environmental changes, stimulates interest in energy production from renewable sources [1–7]. The most typical renewable energy source is agricultural biomass, but increasing the effectiveness of biomass production and

harvesting as much as possible from a given agricultural area requires intensive fertilization [2,3,8–11]. The combustion of biomass in power plants—mainly agricultural wastes such as straw and willow wood—results in a high quantity of biomass ash (BPPA), which is generally stored in dumps localized around the biomass power plants [4,12–23]. The fine powdery and alkaline BPPA contains all the plant nutrients such as potassium, phosphorus, and microelements absorbed by the biomass during the vegetation periods from the soil (except nitrogen, which decomposes into gaseous oxidation products during combustion) [8,19,24–30]. Since the soil can easily be exhausted of these components, especially during intensive agricultural activity, it is an old challenge to convert the biomass power plant ashes that formed during the combustion of agricultural wastes from an agricultural area into fertilizer [19,24–27,29–32]. The amount of nutrients (except nitrogen) missing from the soil after harvesting the biomass is practically identical to the non-volatile element content in the biomass power plant ashes [2,8]. BPPA is alkaline in nature due to its potassium carbonate content and the low availability rate of phosphorus and other compounds, which form during the combustion and are insoluble in water and weak acids in the soil. The acid treatment of these ash components can neutralize and digest the alkaline and insoluble compounds, respectively, and transform them into soluble compounds. Using nitric or sulfuric acid resulted in nitrate and sulfate compounds, important fertilizer components for plants. The main challenge of these technologies is the evolution of large amounts (up to 100–150 m^3/ton of processed ash) of carbon dioxide, which makes an acidic foam and produces a large volume of diluted fertilizer solution. The evaporation of the solution is not feasible. In order to neutralize a thousand tons of biomass power plants, it is not economical to build enormously large stainless steel reactors, which are resistant to the starting alkaline and the final acidic pH of the reaction mixture. Thus, a new solution must be developed to neutralize BPPA without the disadvantages mentioned above [19,25,28,33–36].

To solve the problem of acidic foaming, we developed a technology for the neutralization of the biomass power plant ash (BPPA), which resulted in a porous granulated composite material that contains slightly soluble syngenite ($K_2Ca(SO_4)_2 \cdot H_2O$) as one of the main components [2,8,37,38]. The method ensures the formation of hardly soluble potassium, ammonium, and sulfate ion-containing compounds. The pores of the composites formed can be filled with various micro- and macroelements-containing components, particularly special fertilizer components such as zinc for corn or sulfur for rapeseed production [8–10]. In this paper, we show the base of the special neutralization technology and the main properties, including the pore content and chemical phase compositions, of the new composite fertilizers prepared from BPPA.

2. Materials and Methods

The biomass power plant ashes, a product of willow wood combustion, were collected from the ash dump of the Biomass Power Plant of Kazincbarcika, Hungary. Chemical purity—98% sulfuric acid, calcium carbonate, ammonium nitrate, ammonium chloride, urea, potassium chloride, potassium dihydrogen phosphate, and calcium sulfate hemihydrate—were supplied by Deuton-X Ltd., Érd, Hungary.

Ammonium ion content was measured with potentiometry using a Radelkis (Budapest, Hungary) potentiometer and an ammonium ion–selective electrode.

Powder XRD studies were performed using a Philips Bragg-Brentano parafocusing goniometer (Amsterdam, The Netherlands). The main measurement parameters were the following: Cu Kα radiation (1.5406/1.5444 Å), the 2θ range of 4–70°, and the step size was 0.02° with 1 s interval time. The full profile technique determined the phase composition of ash and fertilizer samples, which were expressed as oxides.

The morphology of the samples was examined using a Tescan Vega Compact (Tescan Vega, Brno, Czech Republic) scanning electron microscope (SEM). The SEM images were taken with a 15 kV accelerating voltage electron beam using a secondary detector at a pressure of 10 mPa in the instrument's chamber.

The IR spectra of BPPA and the as-prepared and dried composites were recorded in an Attenuated Total Reflectance mode (ATR) with 16 scans acquired with a resolution of 4 cm^{-1} on a Bruker Alpha FT-IR (Bruker, Ettingen, Germany) instrument.

A sample of wood ash (20 g) was mixed with 10 mL of water, and the well-mixed solid was mixed with 1 mL of concentrated sulfuric acid. The mortar-like mass temperature was self-heated until the boiling point of water with some vapor formation. The volume increase of the ash–sulfuric acid mixture (swelling) was less than 50%. The sample was dried at 120 °C when a 16.5 g porous product was formed. The pH of its aqueous extract was 12, its density was 0.73 g/mL, and it absorbed 117% of water related to its weight. In the same way, but by mixing 20% (4 g) calcium carbonate powder with the wood ash, with the use of 1.5 mL of sulfuric acid, the product density was 0.37 g/mL, its water-absorbing capacity was found to be 137%, and the pH of the aqueous extract was 12. Mixing BPPA with 10% (4 g) calcium sulfate hemihydrate powder resulted in a product with d = 0.54 g/mL, 127% water absorbing capacity, and the pH of the aqueous extract was 12. As in example (A), by mixing the ash with a given amount of calcium carbonate and calcium sulfate hemihydrate and adding water/sulfuric acid to the BPPA powder, two series of composite samples were prepared. Their synthesis conditions and properties are given in Tables 1 and 2.

Table 1. Preparation and properties of the composite samples with 12 mL of water-diluted sulfuric acid from 20 g of ash.

$CaCO_3$ (g)	$CaSO_4 \cdot 5H_2O$ (g)	H_2SO_4 (g)	Bulk Density, g/mL	Mechanical Strength	Water Absorption Capacity, %
0	2	4	0.46	weak	118
0	2	8	0.87	weak	55
2	0	4	0.60	weak	99
2	0	8	0.68	weak	83
4	0	4	0.57	weak	93
4	0	8	0.78	Very weak	74

Table 2. Preparation and properties of the composite samples made with concentrated sulfuric acid from 20 g of wood ash mixed with 12 mL of water.

$CaCO_3$ (g)	$CaSO_4 \cdot 5H_2O$ (g)	H_2SO_4 (g)	Density, g/mL	Mechanical Strength	Water Absorption Capacity, %
0	2	8	0.87	medium	56
0	2	16	1.56	medium	27
2	0	16	0.60	strong	73
4	0	16	0.77	Very strong	61

In our pilot experiments, 5 kg of wood ash and 0.5 kg of calcium carbonate were mixed with 5 kg of 50% aq. sulfuric acid, and the mixture was granulated in a rotating drum. This resulted in a product with d = 0.8 g/mL, 110% water absorbing capacity, and a pH of 6 in its aqueous extract.

The neutralized fertilizer granulate (100 g) was mixed with a concentrated ammonium nitrate solution (100 g), and then the granulate was dried at 80 °C until constant weight. The samples (1 g portions) were soaked separately in water (10, 20, 50, and 100 mL). The solution samples were taken after 2 h and diluted for the measurement of ammonium ion concentrations using an ammonium ion–selective electrode.

A series of samples (100 g each) were mixed with 50 mL of saturated ammonium-*
nitrate solution and 50 mL solution of other ingredients, such as potassium dihydrogen
phosphate, [tetraamminezinc (II) sulfate], urea, or potassium chloride.

3. Results and Discussion

3.1. The Reaction between Sulfuric Acid and Biomass Power Plant Ash

The combustion of the willow wood in the biomass power plant furnaces resulted
in a BPPA, containing a large amount of potassium, mainly in carbonated form. The
composition of BPPA was determined and expressed as oxides as: CaO-9.4%; K_2O-39.5%;
MgO-3.5%; Na_2O-2.4%; SO_3-9.2%; CO_2-18.1%. Its chloride content is ~7.1%. The phase
relations in BPPA were determined by powder XRD (Figure 1). The main phases were
found to be $K_2Ca(CO_3)_2$ (~40%), K_2SO_4 (20%), and KCl (~15%), which were accompanied
with K_2CO_3, $Mg(OH)_2$, anhydrous, and heptahydrated Na_2CO_3 in an amount of ~5% each
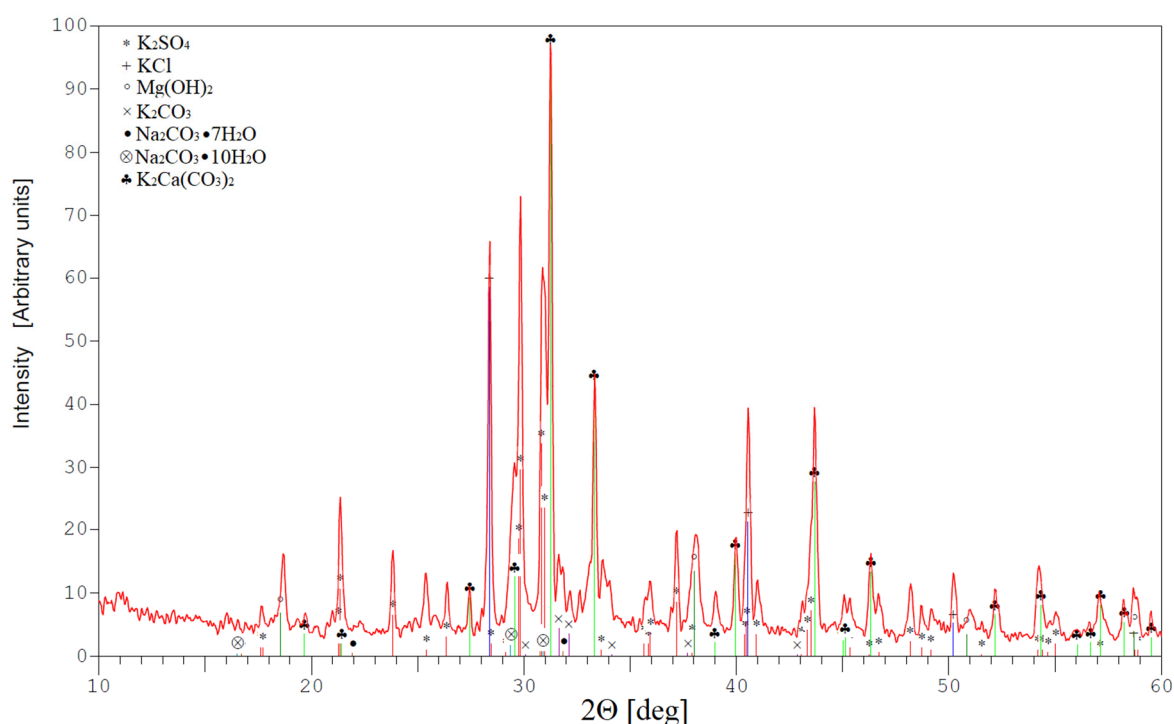(Figure 1).

Figure 1. XRD of the biomass power plant ash (BPPA) made by the combustion of willow.

The most intense band at 1409 cm^{-1} belongs to the antisymmetric stretching mode of
carbonate ion (ESI Figure S1). Due to the presence of at least three carbonate compounds
($K_2Ca(CO_3)_2$, potassium, and sodium carbonates) and the splitting of the bands due to
structural distortions in the abovementioned carbonate compounds, only a shoulder was
assigned, and the band components could not be separated. The presence of carbonate
ion is confirmed by the appearance of π (CO_3) mode at 876 cm^{-1} (ESI Figure S1) and the
antisymmetric C-O deformation mode (double degenerated) at 710 and 680 cm^{-1} [39,40].
The very intense ν_{as} mode of tetrahedral sulfate ions and silicates appear as weak bands
due to the limited amount of these components in the starting BPPA at 1120 cm^{-1} and
1047 cm^{-1}, respectively. The antisymmetric deformation mode of sulfate ions with low
intensity could also be assigned at 620 cm^{-1}.

BPPA is an excellent potassium source for fertilizer production because $K_2Ca(CO_3)_2$
and the alkaline carbonates (sodium and potassium) are expected to be transformed into
water-soluble salts with acidic (sulfates with sulfuric acid) treatment. The evolution of
carbon dioxide gas cannot be avoided during the acidic neutralization of BPPA, but in-

tensive foaming must be prevented. Since the 1 MW electric capacity produced by the biomass power plants generates ca. ~0.5–1 ton of BPPA, the estimated amount of CO_2 foam formation is above 150–300 m^3/h [2]. With our method, the carbon dioxide evolves within a high-viscosity pastry-like material, not in a diluted solution, thus the bubbles released cannot form foam due to the lack of a liquid phase. When the appropriate consistency of the reactive mass is selected, the pasta-like mass swelled instead of foaming, resulting in porous materials after solidification. Binders (e.g., calcium sulfate hemihydrate) or pore-forming materials ($CaCO_3$, whose neutralization with sulfuric acid results in a calcium sulfate binder) were also tested in various amounts to make composite materials from BPPA with various pore amounts (Tables 1 and 2).

The main challenge of the BPPA ash–sulfuric acid reaction is making a pastry-like mass from BPPA, the neutralizing agent (sulfuric acid), and binder/pore-forming materials ($CaCO_3$/$CaSO_4$) without intensive foaming. It is possible by adjusting the consistency of the reaction mixture, which consists of BPPA, the appropriate amount of concentrated or diluted sulfuric acid, and binding/pore-forming materials like $CaCO_3$ and $CaSO_4 \cdot 0.5H_2O$. The evolved CO_2 breaks a route to the surface, opening channels finished on the surface of this pastry-like material. The release of carbon dioxide through these channels can smoothly proceed without foam formation, and the inner holes that are connected to the surface via these channels make an extensive open pore system in the bulk material. After drying/solidification, the bulk density of the materials was below 1 g/mL, and due to their high open pore content, their water-absorbing capacities (aqueous solution) varied between 55% and 118%. The mechanical strength of these composites was low since they are easily grindable.

Biomass power plant ash (BPPA) and other carbonates such as $CaCO_3$ do not react directly with concentrated sulfuric acid when mixed due to the lack of protic processes without water [2]. Adding the appropriate amount of water results in the dilution of sulfuric acid, which initiates carbonate ion protonation and carbonic acid formation and subsequent decomposition with carbon dioxide evolution. In practice, it means that the dry ash (and its mixture with $CaCO_3$ and/or $CaSO_4 \cdot 0.5H_2O$) can be mixed with concentrated sulfuric acid, and this pastry-like mixture can be filled into a screw reactor without any chemical reaction. The addition of water under pressure, however, initiates the reaction between the liberated protons and carbonate ions, and CO_2 evolution creates a large volume of pores in the pastry-like mass.

At the open end of the screw reactor, the pressure is equalized to atmospheric pressure, thus the gaseous components (CO_2 and the evaporated H_2O due to the reaction heat and dilution heat of the sulfuric acid) located in the closed gas/steam pores break out channels within the pastry-like material toward the surface and are released without foaming (Figure 2). In this way, mechanically strong composite materials (Table 2) can be produced, which may be granulated immediately at the end of the screw reactor before solidification. Good mechanical strength may be attributed to the pressure used during the synthesis because a lower volume of pores is formed than at atmospheric pressure. Consequently, the number/size of open pores and water (liquid) absorbing capacities are also lower than in the samples of the atmospheric pressure synthesis (Tables 1 and 2). A screw reactor developed to neutralize BPPA with concentrated sulfuric acid with the addition of water under pressure (to prevent foaming and swelling) is shown in Figure 2.

The depressurizing process at the end of the pipe reactor may be followed by granulation drying or grinding, resulting in pore-containing composite materials [2,31]. Depending on demands determined by the soil and plant, these pores can be filled with various liquids, e.g., acids, bases, fertilizer solutions, microelement-containing solutions, and others.
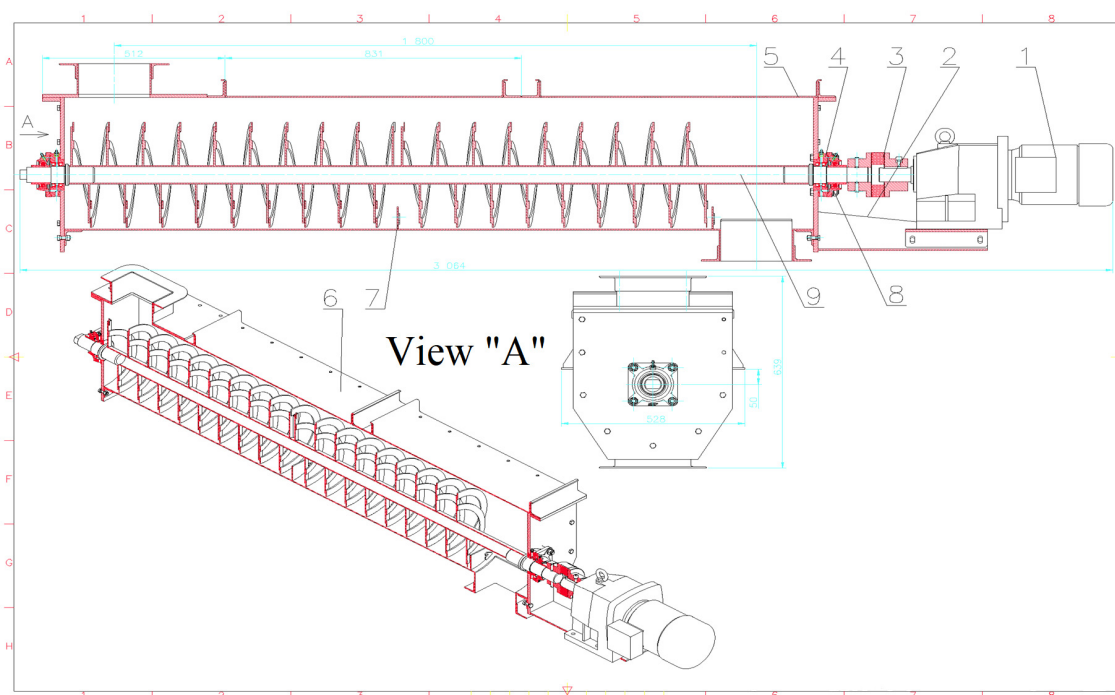
Figure 2. A screw-supplied tube reactor to neutralize biomass power plant ash with sulfuric acid. Annotations: 1—Motor; 2—Console; 3—Clutch; 4—Sealing; 5—Trough; 6—Lid; 7—Insert; 8—Bearing; 9—Axle.

3.2. The Phase Composition of the Biomass Power Plant Ash and Sulfuric Acid Reaction Product and Its Transformations with Concentrated Ammonium Nitrate Solutions

The $K_2Ca(CO_3)_2$ content of the biomass power plant ash (BPPA) readily reacts with diluted H_2SO_4, but not the expected K_2SO_4 and $CaSO_4$ but their double salts, $K_2Ca(SO_4)_2 \cdot H_2O$ (syngenite) [37,38], and due to the presence of $Mg(OH)_2$, $K_2Ca_2Mg(SO_4)_4 \cdot 2H_2O$ (polyhalite) was formed (Figure 3).

$$K_2Ca(CO_3)_2 + 2H_2SO_4 = K_2Ca(SO_4)_2 \cdot H_2O + H_2O + 2CO_2$$

The reaction heat evaporated a part of the water, forming a pre-dried mass (Figure 3). The reaction mixture called porous base fertilizer (PBF) consisted of syngenite (~30%), polyhalite (~55%), and potassium chloride (~5%). The concentrated sulfuric acid reacted with potassium chloride and magnesium hydroxide with hydrochloric acid and magnesium sulfate formation, which immediately reacted with potassium (sodium) carbonates and potassium sulfate/calcium sulfate with K(Na)Cl and polyhalite formation, respectively. The aqueous extract of PBF is acidic, the composition is offered for basic soils. However, the excess sulfuric acid content of the pre-dried PBF sample can easily be neutralized by adding further calcium carbonate powder before final drying and granulation. This reaction led to the decomposition of polyhalite, and the resulting composite Ca-PBF consisting of ~30% syngenite, 10% potassium sulfate, 5% KCl, and 50% calcium carbonate, the pH of its aqueous extract is 6. The product can be granulated in its semi-dry form with conventional technology [8,31].

The IR spectra of a sulfuric acid-treated and calcium carbonate neutralized composite sample can be seen in Figure 4(b). According to the phase analysis results, the residual carbonate bands ($CaCO_3$ was used in excess to neutralize the excess of sulfuric acid) appear with low intensity at 1400 and 874 cm^{-1}. The carbonate compounds of ash were transformed into sulfate compounds, gypsum, syngenite, and polyhalite. The presence of syngenite and polyhalite could be assigned by the appearance of the antisymmetric S-O deformation bands of syngenite (F2) at 655 and 645 cm^{-1} and at 618 cm^{-1} as a shoulder,

respectively. The symmetric S-O deformation mode at 639 cm^{-1} might belong to both syngenite and polyhalite, and there is no presence in the spectra of gypsum [41]. The symmetric stretching mode at 982 cm^{-1} is a characteristic for gypsum, whereas the other weak peak at 1000 cm^{-1} belongs to the symmetric S-O stretching mode of polyhalite. The symmetric/antisymmetric O-H bands of water in the hydrated compounds appear at 3300 and 3380 cm^{-1}, and the scissoring mode at 1630 cm^{-1} and 1680 cm^{-1}, which show that various hydrated phases are present.
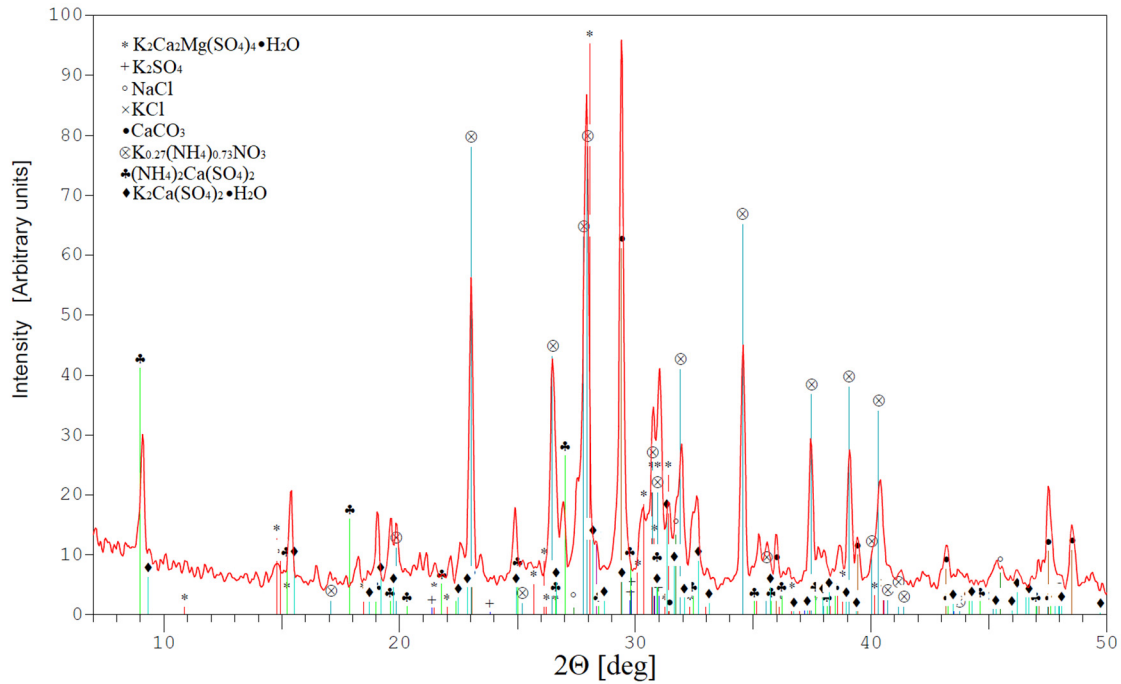
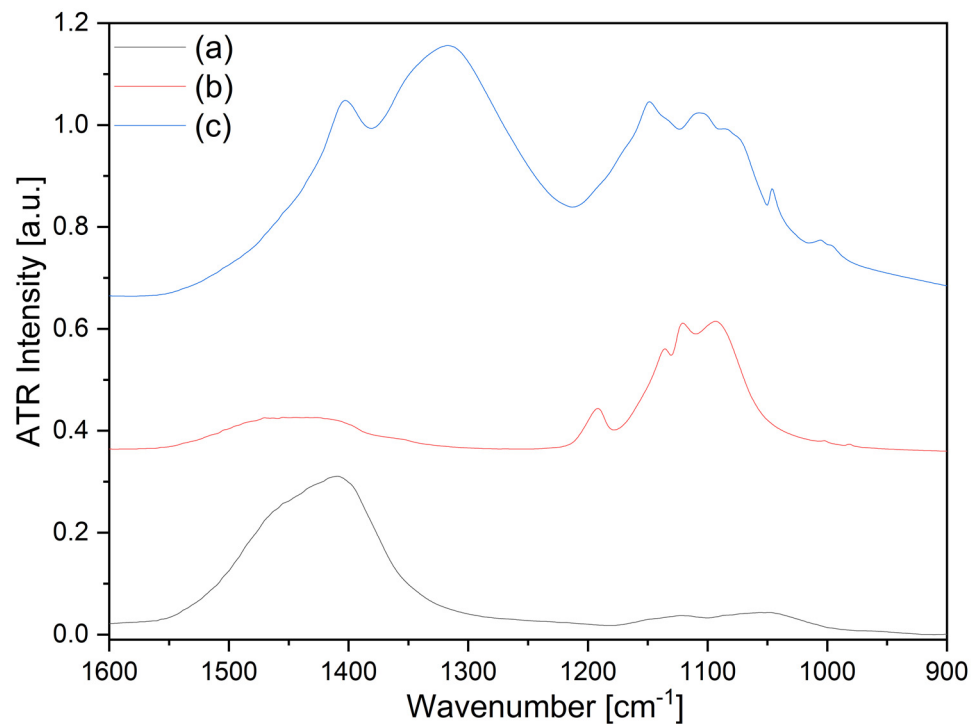**Figure 3.** The XRD of NPG made from PBF and a concentrated ammonium nitrate solution.

Figure 4. IR spectra of BPPA (a); sulfuric acid-treated/calcium carbonate neutralized (b) and ammonium nitrate solution absorbed (c) composites in the 900 and 1600 cm^{-1} region.

The large number of open pores in PBF and Ca-PBF can absorb water (or aqueous solutions) like a sponge and keep it in their pores (holes), increasing the water-retaining capacity of the soil. The morphology of a dried sample can be seen in Figure 5.
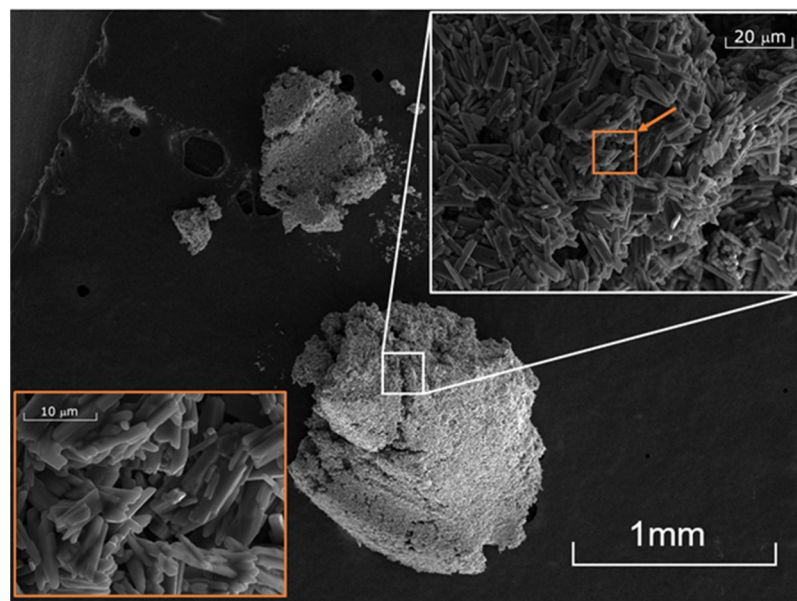

Figure 5. The morphology of a sulfuric acid-treated and $CaCO_3$-neutralized BPPS sample.

The composite consists of crystalline plates, which make hole-like pores. These pores are big holes in reality, which can give some "sponge property" for the sample, but the crystalline nature of components does not leave to evolve large surface volume micro or mesopores. Thus, these materials are more rather absorbent than adsorbents. Therefore, the BET surface area measurements were neglected because the surface area change of BPPA samples (10–1000 m^2/g) [42] may be attributed to the presence and amount of accompanying carbon-like phases.

An environmental protection aspect is that no liquid or solid wastes form at all; all the components used are built into the product. Due to the porosity (50–120%) of PBF and Ca-PBF granulates, not only water but other aqueous solutions—like fertilizer solutions or intermittent products of fertilizer production (e.g., concentrated ammonium nitrate solution from the neutralization process of nitric acid with ammonia [9,43–45])—can also be absorbed in these pores.

It opens an excellent new perspective, namely absorbing different kinds of nitrogen compounds or other fertilizers, including microelements such as zinc, insecticides, or any compounds that are preferred to be injected into the soils. The most common nitrogen fertilizer is solid ammonium nitrate prepared by melt-prilling; however, it is not possible to add zinc or other metal oxides into the melted ammonium nitrate due to the risk of explosion. Our method of preparing BPPA-based porous fertilizer and ammonium nitrate solutions allows us to incorporate other metal compounds (salts) into the ammonium nitrate solutions in the required ratio without risk.

Ammonium nitrate solution is prepared in an exothermic reaction of ~65% nitric acid with ammonia gas when a concentrated aqueous solution of NH_4NO_3 forms [43–45]. Evaporation of this solution at high temperatures leads to the melting of ammonium nitrate, which is prilled in the next manufacturing step. Contacting concentrated NH_4NO_3 solution from N-fertilizer production with the PBF prepared in the reaction of sulfuric acid and $CaCO_3/CaSO_4$ with BPPA resulted in a new nitrogen-containing porous composite granulate (NPG). The residual water content of NH_4NO_3 solution from N-fertilizer production absorbed by PBF can be removed from NPG without melting and prilling of NH_4NO_3 content. It means that metal compounds (e.g., zinc salts for specific corn fertilizers) [19],

which catalyze the decomposition of ammonium nitrate in the melt (explosion) and, due to this, must not be used in the conventional prilling technology, can be used in our method as additives in NPG production without any risk.

The powder XRD of the solid product (NPG) made by absorbing concentrated NH_4NO_3 solution onto the Ca-PBF showed that the concentrated NH_4NO_3 solutions not only fill the pores of the granules and form NPG but react with some components of Ca-PBF, e.g., syngenite forms ammonium calcium sulfate (koktaite, $(NH_4)_2Ca(SO_4)\cdot2H_2O$) [46,47]. Koktaite is a slow-releasing fertilizer compound [11,48–51], or because of the similar size of the potassium and ammonium ions, the mixed solution of potassium and ammonium nitrate was also formed.

The reaction of the ash–sulfuric acid reaction product and concentrated aq. ammonium nitrate solution at room temperature resulted in a wet solid (NPG), which was dried and studied by powder XRD (Figure 3). The powder XRD showed that a part of syngenite is reacted with ammonium nitrate and transformed into koktaite, and KNO_3 or $K_{0.27}(NH_4)_{0.73}NO_3$ formed as a by-product.

$$K_2Ca(SO_4)_2\cdot H_2O + 2NH_4NO_3 = (NH_4)_2Ca(SO_4)_2\cdot H_2O + 2KNO_3$$
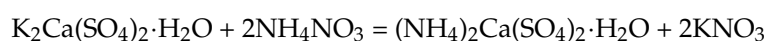
The IR spectrum of the composite sample made from the sulfuric acid treated and calcium carbonate neutralized BPPA shows some obvious differences compared to the sample without absorption of ammonium nitrate. First of all, the symmetric and antisymmetric N-H stretching modes appear at around 3000 and 3200 cm^{-1}, which shows that at least two different ammonium ion-containing materials are present in the sample. These are koktaite and ammonium nitrate (potassium ammonium nitrate solid solution according to the PXRD results). The presence of ammonium ions is also confirmed by the appearance of overtone bands in the region of ~2800 cm^{-1} [52]. The symmetric and antisymmetric N-H deformation bands appear at 1619 cm^{-1} and 1404 cm^{-1}, respectively. The strong band at 1310 cm^{-1} belongs to ν_{as} (N-O) in nitrates, and the new band at 827 cm^{-1} belongs to π (NO_3)). The two new bands at 673 cm^{-1} and 714 cm^{-1} might belong to two kinds of nitrate ions (δ_{as} (N-O)), which might be in hydrogen-bound (ammonium nitrate) and non-hydrogen bound (potassium nitrate) environments, respectively.

The shape of the ν_{as} (S-O) bands of sulfate ion changed due to the koktaite formation from syngenite. Five components of the sulfate band can be identified, so at least two kinds of sulfate compounds (two coinciding triplet (F2) bands might result in less than six bands) were present in the sample. The transformation of BPPA into syngenite and polyhalite-containing composites, then this composite into ammonium nitrate/koktaite-containing composites, is shown in Figure 4. The morphology of the ammonium nitrate solution-treated sample prepared from BPPA with sulfuric acid/calcium carbonate treatment is given in Figure 6.

The SEM picture shows that the studied material has a crystalline nature, and the shape of the crystals is plate-like. The reaction between the ammonium nitrate solution probably a solid–liquid reaction (syngenite/ammonium nitrate solution, a kind of ion exchange), when the surface layer of the potassium calcium sulfate crystals is reacted and enriched in (ammonium) nitrogen.

The koktaite and syngenite are sparingly soluble in water. Thus, the ammonium ion released from syngenite in the presence of water depends on the amount of water that dissolves the koktaite and the dissolved calcium and sulfate concentrations. The gradual dissolution of ammonium ions was measured with a potentiometric method using ammonium ion selective electrodes, and the ammonium ion dissolution was found to be proportional to the amount of water added to the same amount of fertilizer (Figure 7). It shows the possibility of preparing fertilizer formulations having rain-controlled ammonium ion release. If the total amount of the ammonium ions are liberated, the decomposition by soil bacteria starts even in dry conditions when the plants can absorb that only partially. In rainy conditions, when the plants can absorb water and ammonium ions, the ammonium ion can mainly be utilized by the plant because when the plant absorbs the ammonium

ion from the soil, a part of the solid koktaite is dissolved and supplies a new portion of ammonium ion for the plants.
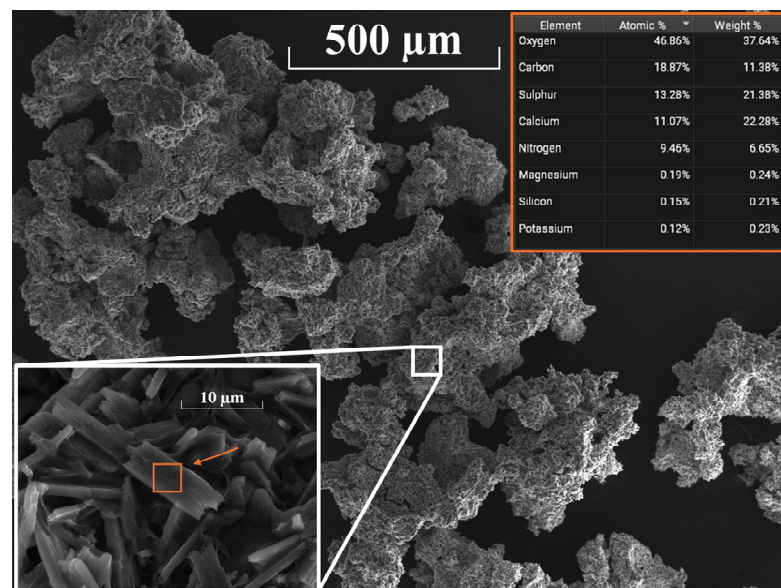

Element	Atomic %	Weight %
Oxygen	46.86%	37.64%
Carbon	18.87%	11.38%
Sulphur	13.28%	21.38%
Calcium	11.07%	22.28%
Nitrogen	9.46%	6.65%
Magnesium	0.19%	0.24%
Silicon	0.15%	0.21%
Potassium	0.12%	0.23%

Figure 6. The morphology of the ammonium nitrate solution-treated sample prepared from BPPA with sulfuric acid/calcium carbonate treatment. EDS measurements were performed from the area that is annotated with orange square.
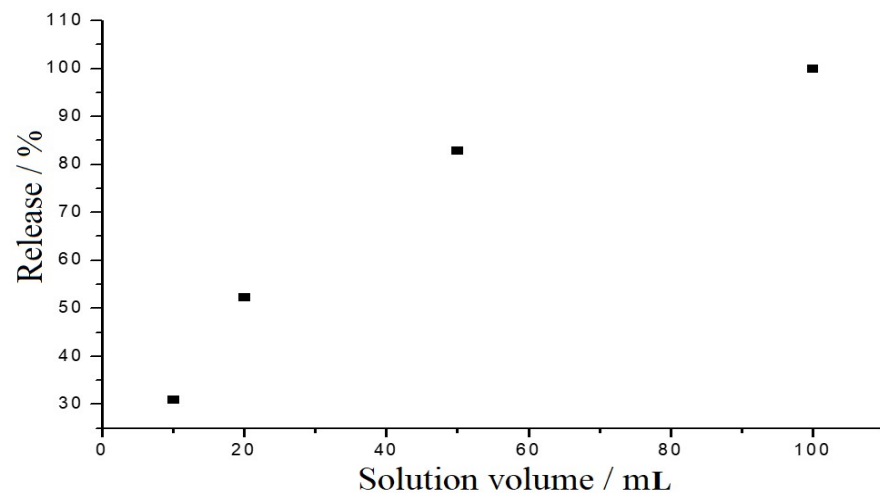

Figure 7. The dependence of ammonium ion release from NPG fertilizer as a function of water amount (rain or irrigation).

Since the equilibrium ammonium ion concentration is closely constant due to the solubility product of koktaite, the amount of water (rain or irrigation) can control the amount of the released ammonium ion. During a drought period, when there is a lack of water, the plants cannot absorb ammonium ions from the soil, no koktaite is dissolved, and no ammonium ions are released, which would be decomposed by soil bacteria. Other ammonium salts, potassium dihydrogen phosphate, and urea as fertilizers were also tested. These materials can be taken up as solutions without important alteration of the syngenite and other components of PBF composites.

The acidic treatment of BPPA ensures a complete digestion of ash components into their water-soluble forms. The formation of syngenite and that subsequent reaction with an ammonium nitrate result in slow-releasing and watering-controlled ammonium ion-releasing composite fertilizers. Other additives, such as microelement components, can

also be added to the NPG fertilizer without the risk of explosion. These fertilizers are essential in reaching high yields of plants for combustion with fast metabolisms, such as sweet sorghum/corn stalk, willow, or energy grass. The sulfur deficiency of the soils for extreme sulfur-demanding plants such as rape can also be satisfied [10].

4. Conclusions

1. The biomass power plant ash, which contained mainly carbonate components, was mixed with concentrated sulfuric acid without any chemical reaction. The protonation-driven carbonic acid evolution was available by controlled adding of water, optionally under pressure, to form a paste-like consistency material containing carbon dioxide bubbles without foam formation. The dwelled paste-like material releases carbon dioxide during drying or depressurizing when a strongly porous solid material is formed.

2. The reaction products of ash and sulfuric acid in the reaction route described in point 1 were mainly syngenite and polyhalite. These are valuable, slow-releasing, slightly soluble fertilizer materials. The phase identities were assigned by IR and PXRD, and SEM results of the product were also given.

3. The sponge-like solid composites formed in the reaction route described in point 1 may be reacted with concentrated ammonium nitrate solution (a cheap intermediate of crystalline ammonium nitrate fertilizer production), which ensures a safe possibility of adding various metal-containing additives, which cannot be performed in the usual ammonium nitrate melt technologies.

4. The ammonium nitrate solution reacts with the syngenite content of the composite prepared in the reaction route described in point 1 when ammonium calcium sulfate was formed, which is an excellent slow-releasing ammonium-ion source for soils. It is slightly soluble, so the water content (irrigation, rain) controls its dissolution. The reaction is probably a solid–liquid interaction when the solid syngenite acts as an ion exchanger, and a surface ammonium ion-enriched koktaite formation was found. The phase identities were also assigned by IR and PXRD, and SEM results of the product were also given.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/jcs8090336/s1, ESI Figure S1: IR spectra of BPPA (a), sulfuric acid-treated/calcium carbonate neutralized (b) and ammonium nitrate solution absorbed (c) composites.

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