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Carnallite-Derived Solid Waste as Potassium (K) and Magnesium (Mg) Source in Granulated Compound NPK Fertilizers

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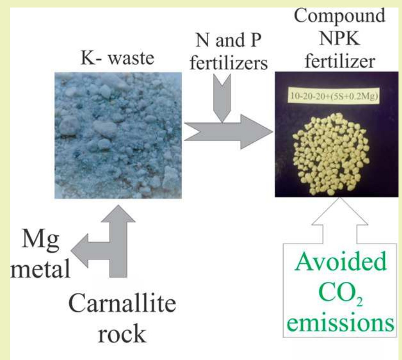
ABSTRACT: Principles of green engineering require that material inputs are renewable. To this regard, a partial or a full substitution of one of the feedstocks with the waste from other industries can minimize the environmental impacts. Potash rock is a source of a key potassium (K), but its environmental impacts, including land use and greenhouse gas emissions during the mining and beneficiations, are of concern. Carnallite rock is used to electrochemically produce elemental magnesium (Mg) and yields solid sludge waste with K_2O content of ∼43% and Mg content of 2.0%.This carnallite-derived waste is characterized physically and chemically and utilized to manufacture compound NPK fertilizers. The mesoporous waste material structure was found which facilitated the wet granulation process in spite of low 6 m^2/g measured surface area. Trace metal concentrations measured were low and did not pose significant limitations from the regulatory point of view. Several high-K_2O-content fertilizer formulations were proposed and granulated using both laboratory and industrial wet granulation in a rotary drum. Large K_2O amount from the carnallite processing waste, up to 10 times that from mined KCl, was utilized in these fertilizers. The sustainability impact of the overall process was assessed by evaluating the averted greenhouse gas (GHG) emissions when carnallite-derived waste was substituted for potash rock. It was found that up to 5000 t of CO_2/year per 100 000 t/year NPK 10-20-20 fertilizer can be avoided if waste is used rather than the potash rock.



KEYWORDS: *Carnallite, Solid waste, Magnesium, Potassium, Granulated fertilizers*

■ INTRODUCTION

Potassium (K), one of the three major plant nutrients, is derived from geological materials—minerals—via energy- and land-intensive mining processes.[1] It is typically mined from high-K-concentration water-soluble mineral ores, including pure salts, such as KCl, or other more complex minerals, such as sylvinite (KCl + NaCl).[2] Additionally and in contrast to nitrogen (N) and phosphorus (P), K fertilizers are applied at much lower rate, and less than 50% of the K removed by crops is replenished.[3] This is also due to the leaching of K, particularly in sandy soil, that contributes to the lowering of soil K content.[4] Depletion of high-quality sylvinite ores necessitates use of alternative K sources. While K is one of the most abundant nutrients in soil, only a small fraction of the minerals are soluble and available for their immediate uptake since the majority is confined within insoluble silicate materials.[1] Also, while high-K-content water-soluble fertilizers dominate the market, they are of very high cost and present significant problems in sustainably managing K soil balance for crops, especially in developing countries. For example, while K-containing rock is plentiful in the northern hemisphere, Africa is a K-rock importer which, combined with the economic deficits in most African countries, makes K a critical limiting factor for their food production.[5] In agriculture, the term *potash* refers to K fertilizers, such as potassium chloride (KCl), potassium sulfate or sulfate of potash (SOP), and potassium magnesium sulfate (SOPM) or langbeinite. Muriate of potash (MOP) is an agriculturally acceptable mix of KCl (95% pure or greater) and sodium chloride for fertilizer use.[6] Magnesium (Mg), on the other hand, is the fifth major plant nutrient[7] and a constituent of chlorophylls a and b. It is involved in many key physiological and biochemical processes related to plant growth and defense mechanisms in abiotic stress situations.[8] Recent studies have shown that two-thirds of people surveyed in developed countries received less than their minimum daily Mg requirement.[9] Mg availability in soil may become limiting under certain conditions, such as low pH or presence of competing elements, including calcium.[10] New approaches are necessary, and the recent ongoing efforts are focused on mobilizing K[11−13] and Mg[14] from insoluble rocks and minerals.

Carnallite, $KMgCl_3 \cdot 6H_2O$, is a double salt hydrate of KCl and $MgCl_2$ and a high-solubility K- and Mg-containing natural mineral. It typically is not used directly as a fertilizer since it is deliquescent and needs to be recrystallized using energy-

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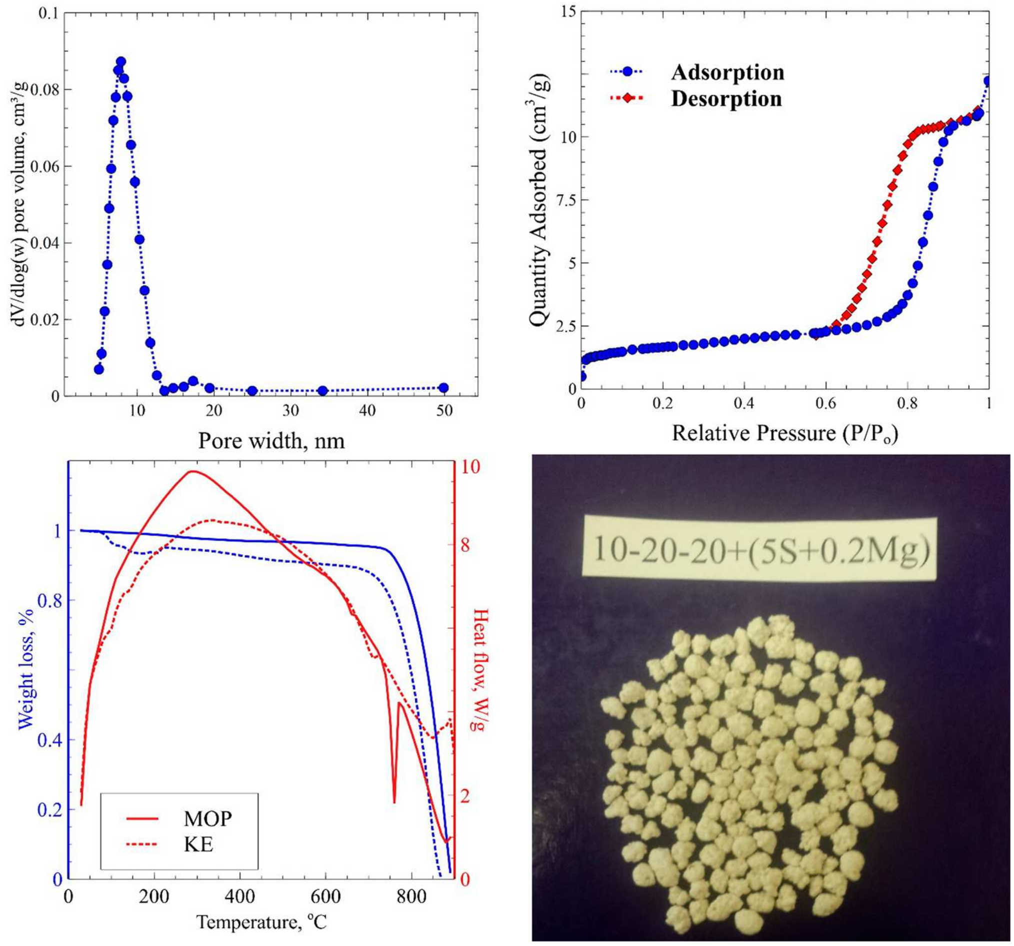

Figure 1. (top) Pore volume−width and BET adsorption/desorption isotherms for KE. (bottom) TGA/DSC analysis of KCl (MOP) and KE. The broad DSC background shape is due to instrumental thermal gradients. Optical images of granulated 10-20-20 materials containing 5% S and 0.2% Mg expressed as MgO.

intensive and expensive methods.[15] For this reason compounded with the modest K_2O content of 17%, carnallite is only a small percentage of the world's K supply. Direct production of fertilizer materials from low-grade carnallite ore, nevertheless, has been attempted using the flotation process[16] to remove any insoluble materials. Attempts reported to obtain KCl concentrate via flotation included either alkyl-morpholine or amine as a collector of carnallite decomposition products.[17] Carnallite, however, is intensely used for Mg metal electrolytic production.[18] Mg—the lightest structural material—production from carnallite was developed by Titanium Institute in Zaporozhye and VAMI in St. Petersburg, Russia. Later, this method was upgraded by Dead Sea Magnesium (DSM).[19] The initial technology included double dehydration of carnallite and electrolysis in reduction cells operating in the range of 90−180 kA. Molten carnallite was then directed to electrolytic cells operated with an electrolyte suitable for the manufacturing of elemental Mg. Spent electrolyte was recirculated with pumps to the head cell and electrolyte sludge, containing large amounts of K, was separated. NedMag Industries in The Netherlands suggested an upgraded method which enables electrolyte recovery to sludge and dehydration of carnallite in a fluidized bed in a hot HCl gas environment.[19]

This large-scale K-containing industrial waste, in principle, can be considered as a source of nutrients for fertilizer manufacturing. The chemical properties of this electrolyte sludge are complex and not fully investigated. Further, the engineering solutions that can utilize this electrolyte sludge need to be developed. In this work, we present a detailed characterization study of the carnallite-rock-derived electrolyte sludge waste. First, we determined physicochemical properties including BET for porosity and thermal analysis via TGA/DSC followed by the major nutrient and trace element analysis. Second, we obtained both laboratory- and industrial-scale granulated NPK fertilizers utilizing carnallite waste. Then, we evaluate the chemical stability of the granulated fertilizers over time. Finally, we calculated sustainability metrics of the overall K-feed substitution process from mined KCl to K-containing solid waste by assessing avoided greenhouse gas emissions.

■ EXPERIMENTAL SECTION

Instrumental Analysis. Physical characteristics of the sample were measured via nitrogen physisorption (77 K) using an ASAP 2020 instrument (Micromeritics) following degassing at 200 °C for 12 h (10 °C/min ramp). The specific surface area and the pore size distribution were calculated using the Brunauer−Emmett−Teller (BET) and Barrett−Joyner−Halenda (BJH) methods, respectively, applied to the adsorption branch. The micropore volume and external surface area were analyzed by conventional *t*-plot methods, and the total pore volume was calculated from the volume adsorbed at $P/P_0 \approx 0.99$.

Thermogravimetric analysis and differential scanning calorimetry (TGA/DSC) measurements were performed using an SDT Q600 instrument (TA Instruments). Experiments were performed from

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room temperature to 900 °C with a ramp rate of 20 °C/min in 100 mL/min N_2 flow.

Crystalline nature of all reactants and products was confirmed using powder X-ray diffraction (XRD) (Empyrean, PANalytical B.V.).

K (K_2O) concentration was determined using a flame photometer (Jenway PFP-7, Coleparmer). Chloride content was determined from the aqueous solutions using a potentiometric method with $AgNO_3$ utilizing a TitroLine Easy (SCHOTT Instruments GMBH) automatic titrator. Ca and Mg, both in solid and water-soluble forms, were determined using the AOAC 945.04 method via atomic absorption spectroscopy. Na was determined according to AOAC 974.01 using a flame photometer. Trace elements were determined using the AOAC 2006.03 method microwave digestion of the sample followed by its analysis using inductively coupled plasma−optical emission spectrometry while Hg was determined using cold-steam atomic absorption spectrometry using PerkinElmer Analyst 800 and Optima 2100 spectrometers. Insoluble impurities and moisture content were measured using gravimetry. Granulometric size distribution of the fertilizers was measured using RETSCH sieves (DIN-ISO 3310/1), with the hole size of 1.0, 2.0, 3.15, 4.0, and 5.0 mm and each size fraction determined using WPS 210/C KERN ABJ balances (precision of ±0.001 g). Granule crushing strength was determined using a dedicated instrument (IPG-2, Russia), with instrumental error of ±1.6%. For each experiment, 20 granules were utilized.

Compound NPK Fertilizer Granulation Experiments. All reagents used in granulation experiments were technical grade. In granulation experiments, ammonium sulfate (AS), diammonium phosphate (DAP), monoammonium phosphate (MAP), potassium chloride (muriate of potash)—KCl (MOP)—were used as well as sand. Carnallite-derived electrolyte waste (KE) was obtained from the magnesium metal processing industry (Avisma). The laboratory granulator described earlier was used.[20] Briefly, solid compound fertilizer granules were obtained using a lab-scale rotary drum granulator dryer with a length (L) of 0.45 m and a diameter (D) of 0.11 m. The L/D ratio was thus 4.09, similar to those typically used in granulated phosphorus fertilizer manufacturing, to maintain similar granule residence time in the drum. The granulator inclination angle was varied from 2° to 5°, whereas its rotation speed was 20 min^{-1}, similar to those used for NPK fertilizer granulation.[21] A slurry of N−P−K component particles of <0.5 mm, together with the necessary amount of moisture in the form of water, was prepared and thoroughly mixed prior to granulation and then supplied into the granulator drum. Sand was used as a filler material, and 40% of fine (1−2 mm) return material was fed into the drum together with the fresh feed at ~60 °C to yield granular materials with the measured crushing strength of 3.7−6.6 MPa with standard deviation ranging from 1.6 to 2.4 MPa averaged over 20 measurements to yield high-quality NPK 10-20-20 granulated fertilizers. Industrial-scale granulation to yield NPK 5-15-25, 5-15-30, and 4-12-32 fertilizers was performed using an "Arvi Fertis" (Marijampole, Lithuania) rotary drum granulator of identical L/D ratio and tilt angle as the laboratory-scale instrument. Here, numbers, e.g., 5-15-25, are mass concentrations of nutrients expressed as N, P_2O_5, and K_2O in the corresponding compound fertilizer, respectively.

RESULTS AND DISCUSSION

Physicochemical KE Characterization. The KE material analyzed possessed a measured BET surface area of 6 m^2/g. As shown in Figure 1, the nitrogen physisorption isotherm revealed a characteristic H2(b) hysteresis indicative of mesoporosity[22] with the pore-blocking. BJH analysis of the desorption branch of the resulting isotherms confirmed the pore body size of 7.25 nm. The total specific pore volume was 0.02 cm^3/g associated almost exclusively with mesopores. Hence, this analysis showed that KE material was predominantly mesoporous with only very small overall surface area associated with microporosity. This has implications for the granulation behavior of KE in mixture with other N, P, and K raw materials. In general, granulation poses numerous challenges due to the high-quality requirement of the formed granules in terms of content uniformity and physicochemical properties such as granule size and hardness, to name few.[23] The rotary drum granulation utilized premixed with a small amount of water resulted in *melt* granulation, e.g., wet granulation that uses a meltable binder as granulating liquid at 50−90 °C. This liquid in the present experiments was added as water to facilitate the agglomeration of powder particles with most of the raw components being water-soluble at low temperature and premelting upon exposure. The cooling of this agglomerated powder resulted in a solidification, and it was performed to avoid any organic solvents. Presence of a rather low surface area of KE of 6 m^2/g can decrease its melting propensity which would, on the other hand, be compensated by the availability of the mesopores. These mesopores (by definition 2−50 nm) can facilitate water adsorption due to the capillary condensation, as shown for other mesoporous materials[24] thus improving granulation behavior. In agreement, our granulated NPK fertilizers, both laboratory- and industrial-scale, yielded granules with high crushing strength due to the adequate melting of the KE and its incorporation into the granular structure.

Combined TGA/DSC analysis of the industrial-grade KCl (MOP) and KE materials is shown in Figure 1. A sharp endothermal peak due to the melting transition at 760 °C also coincides with the mass due to the vaporization of the pure KCl salt.[25] The DSC spectrum of KE, on the other hand, exhibited two thermal effects. A small endothermal loss in the 100−150 °C region can be associated with the loss of solvent, likely water adsorbed in the pores. Another interesting feature in the DSC was measured at 650−700 °C, much lower than that of the pure KCl. Since KCl and other chlorides, such as NaCl, form a minimum melting system, the first melting temperature would follow the solidus curve. This suggests that KE contains KCl that is incorporated into a complex solid solution phase, likely with NaCl. Assuming a 660 °C melting temperature of the compound from Figure 1, the composition of said solid solution can be extrapolated to about 0.3 mol NaCl/(KCl + NaCl).[25]

Elemental analysis of the KE material is shown in Table 1. Total KCl concentration was found to vary between the batches with the measured range 67.8−69.3% by weight. Accordingly, K content of ~36% (K_2O of ~43%) was measured suggesting lower K_2O concentration than that in pure KCl of 60%. This

Table 1. Major Element Analysis in KE, wt %

element or compound	results
total KCl, %	67.8−69.3
total K, %	35.5−36.6
total NaCl, %	16.3−20.1
total Na, %	6.4−7.9
total $MgCl_2$, %	4.1−8.9
total Mg, %	1.0−2.3
Mg, water-soluble, %	0.22
$CaCl_2$, %	2.8−4.2
total Ca, %	1.1−1.4
total Cl, %	47.1−54.6
insolubles, g/100 g H_2O	0.43−0.57
insolubles, %	4.3−5.7
moisture content, %	0.2−0.5

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can have limitations in obtaining higher-K_2O compound fertilizers. Measured Na and Mg concentrations were ~7% and ~1.5%, respectively. While Na is pervasive in the carnallite rock and confirms TGA/DSC data shown in Figure 1, a presence of relatively low amounts of Mg is also notable. Only about 15% of Mg is in water-soluble form, likely incorporated into more complex siliceous materials. It will be released to the plants in a slow manner.[2,26] Similarly, a low amount of Ca was measured of ~1.2% which also could potentially be available to the plants. The majority—95%—of KE was soluble, e.g., likely in chloride form.

Further evaluation of KE usability entailed trace-element—heavy and toxic metal—analysis shown in Table 2. The concentration of Cd, Cr, Pb, Ni, As, and Hg was measured in KE and compared to those commonly found in commercial KCl used in fertilizer manufacturing. It can be seen that negligible, below regulatory limits,[27] concentrations of heavy metals were detected. In fact, concentrations of the heavy metals were very similar to those found in organic fertilizers granulated with wood chips or peat bedding[28] suggesting wide applicability of KE materials for fertilizer production.

Table 2. Comparison of Trace Element Measured in KCl (MOP) and Potassium Electrolyte Sludge Waste (KE)

	results	
parameter	KCl (MOP)	carnallite-derived potassium electrolyte sludge waste (KE)
Cd, mg/kg	<0.5	<0.5
Cr, mg/kg	1.75	4.85
Pb, mg/kg	32.7	29.8
Ni, mg/kg	8.05	11.3
As, mg/kg	<1	<1
Hg, mg/kg	n.d.[a]	n.d.

[a]n.d.: not detected.

Compound NPK Fertilizer Granulation. Granulation of NPK fertilizers using KE as one source of K_2O was first performed using the wet granulation method in a laboratory drum granulator described elsewhere.[20] The starting composition of 10-20-20 was selected since it contained a rather large K_2O mass fraction of 20% and large overall nutrient concentration. The component composition used is shown in Table 3. In particular, ammonium sulfate (AS) was used as N source also introducing sulfur which is necessary for an efficient nitrogen uptake by the plants.[20,29−31] This effectively resulted in a 10-20-20 + (5S + 0.2Mg) granulated fertilizer composition where 5S and 0.2Mg signify mass percent of sulfur and magnesium expressed in MgO. While the granulation process depends on an intricate combination of various parameters,[23] the content of water as a crystallite melting medium to initiate the crystallization process was varied in our laboratory experiments with an optimum value found to be 8−10% by weight. The resulting granules with the diameter of 2−5 mm are shown in Figure 1. Next, three compositions of NPK granulated fertilizers were proposed, namely, 5-15-25, 5-15-30, and 4-12-32, as shown in Table 3, and granulated in an industrial drum granulator. Notably, KCl (MOP) was still needed to ensure high final K_2O content, related to lower K_2O concentration in KE, as shown in Table 1. However, significant amounts of K were delivered with KE with ratio of K_2O from KE to ratio of K_2O from MOP (K_2O (KE)/K_2O (MOP) ranging from 1.14 to 9.96.

Table 3. Composition of Laboratory (10-20-20) and Industrial (5-15-25, 5-15-30, and 4-12-32) Rotary-Drum-Obtained Compound NPK Fertilizers in kg/t Product[a]

	10-20-20[b]	5-15-25[c]	5-15-30[c]	4-12-32[c]
AS	145	0.0	0.0	0.0
DAP	320	208.3	208.3	166.6
MAP	90	104.2	104.2	83.4
KCl (MOP)	160	40.5	123.1	88.4
KE	250	550.0	550.0	650.0
K_2O (KE)/K_2O (MOP)	1.14	9.96	3.28	5.39
Filler (sand)	35	97.0	14.4	11.6

[a]AS: ammonium sulfate; DAP: diammonium phosphate; MAP: monoammonium phosphate; MOP: muriate of potassium; and KE: potassium-containing electrolyte solid waste. [b]Laboratory rotary drum granulator.[20] [c]Industrial rotary drum granulator.

Stable NPK granules were stored at room temperature (23 °C) and a relative humidity of 50%. It is known that chemical reactions within the granule continue proceeding long after the granulation during the *curing*.[32] The reactive products formed can significantly affect the long-term storage properties of the granules, such as caking. The formation of ammonium chloride (NH_4Cl) has been reported to be a major cause of the granule caking in compound fertilizer due to the ammonium chloride forming crystal bridges between the adjacent particles.[33] However, NH_4Cl can serve as a convenient means of describing reactivity of chloride salts within KE. We performed XRD analysis of all granular fertilizer materials 60 days after their granulation. These are shown in Figure 2 together with the corresponding XRD patterns of their parent materials. While the resulting XRD patterns are complex, comparison with the parent materials allowed identifying the main solid-state reaction products. In particular and in all cases, two new crystalline phases were identified in the granulated materials, namely, (○) NH_4Cl[34] and (●) KH_2PO_4.[35] These are likely to form via solid-state reactions (1−2) with phosphate fertilizer components via[20]

$$(NH_4)_2HPO_4 + 2KCl \rightarrow 2NH_4Cl + K_2HPO_4 \quad (1)$$

$$2(NH_4)_2HPO_4 + KCl \rightarrow (NH_4)K(H_2PO_4)_2 + 2NH_4Cl \quad (2)$$

Importantly, these data suggest that K is mobilized from the KE in a similar fashion as in KCl[20] allowing KE to be utilized as an equivalently effective K source. Thus, since K is involved in solid-state reactions forming water-soluble compounds, it will be equally available to the plants.

Sustainability Metrics of Substituting Potash Rock with KE. We begin the sustainability metrics assessment by evaluating the potential gaseous greenhouse gas emission waste that can be avoided when KE is used as K source for fertilizer production. We utilize these metrics[36] according to the principles of green chemistry as it entails prevention of greenhouse emissions rather than treatment of their effects.[37] The system boundary was defined as shown in Figure 3. In particular, raw K_2O material from potash rock was substituted for that coming from the waste electrolyte. N and P_2O_5 mineral fertilizers needed to produce NPK will maintain the same raw materials and energy feed as well as greenhouse gas (GHG) emissions which will not require adjustments. Hence, only diesel fuel and natural gas, as well as the corresponding material

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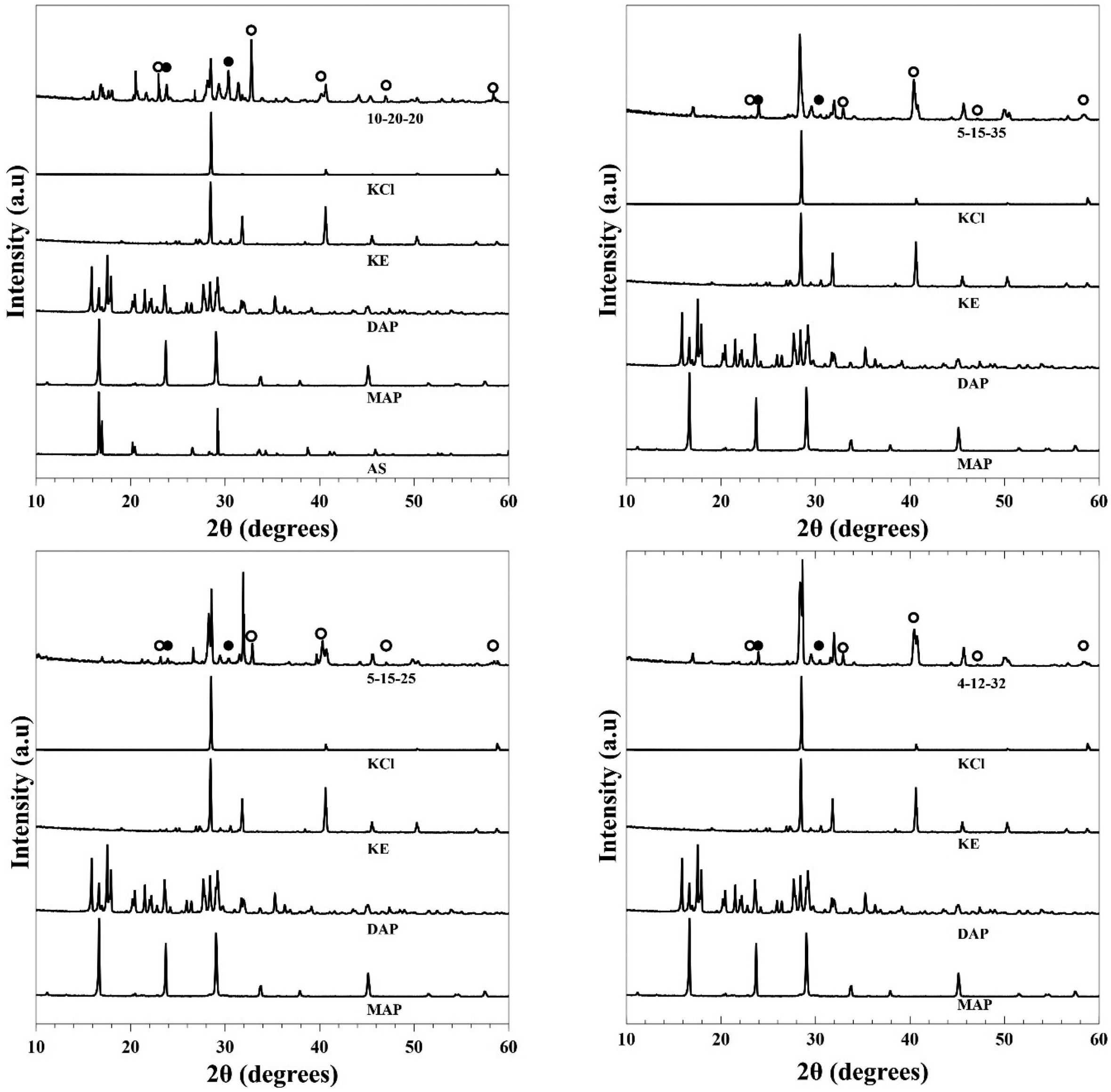

Figure 2. XRD patterns obtained of granulated aged 10-20-20, 5-15-25, 5-15-30, and 4-12-32 fertilizers and their parent compounds. New crystalline compounds arising from the solid-state reaction during curing were marked as (○) NH_4Cl and (●) KH_2PO_4.

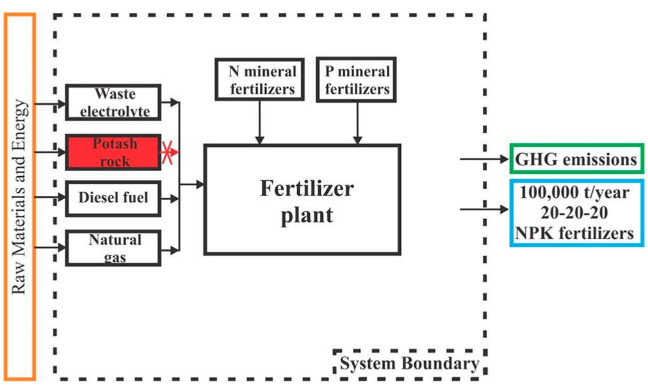

Figure 3. System boundaries used for the sustainability analysis of potash-rock substitution with KE.

that averted GHG emissions, were accounted as inputs and outputs of the system. This boundary condition does not account for the GHG emissions due to the upstream of Mg metal production, e.g., carnallite-rock mining and its processing, as KE results as a waste from that process.

In principle, K_2O involves extensive mining operations with potash rock as the solid K_2O input and gasoline, diesel, and electricity as energy inputs. Waste rock is generated and disposed of in the result of potash-rock beneficiation, and the recovery ratio of potash is 21.5%.[6,38] During potash processing and recovery, electrostatic dust precipitators are used to minimize dust emissions to the environment. However, the energy requirement for mining and beneficiation is significant and will serve as a basis of our sustainability analysis. Reported values during mining for truck processing were 16 200 BTU/t of rock while electricity for the equipment was estimated 28 300 BTU/t of rock, as reported in Table 4. Similarly, for potash-rock beneficiation, electricity consumption was estimated to be 44 400 BTU/t of rock.[38] We converted the energy used for these operations (but now averted) into t of CO_2 emitted using known emission factors of this greenhouse gas for diesel (73.16 kg CO_2/million BTU) and natural gas (53.07 kg CO_2/million BTU).[39] The calculations shown in Table 4

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Table 4. Avoided GHG (CO_2) Emissions by Utilizing K_2O-Containing Industrial Waste for 100 000 t/year NPK 10-20-20 Production[a]

potash-rock-to-K_2O operation	energy consumption method	energy consumption, BTU/t rock	avoided GHG emissions, kg CO_2/t rock	avoided GHG emissions, kg CO_2/t K_2O	avoided GHG emissions, ton CO_2 for 100 000 t/year NPK 10–20–20
mining	trucks (diesel fuel)	16 200	1.2	5.6	113
	electricity (natural gas)	28 300	1.5	7.2	143
beneficiation	electricity (natural gas)	44 400	2.4	11.2	224
total					480

[a]Assumptions: recovery ratio of potash is 21.5%.[6,38] Diesel emits 73.16 kg CO_2/million BTU and natural gas 53.07 kg CO_2/million BTU.[39]

suggest that, for a typical NPK fertilizer plant producing NPK 10-20-20 at 100 000 t/year, 480 t of CO_2 are avoided when using K_2O-containing industrial waste. This likely can be regarded as the lower value as varying estimates of energy consumption for potash mining and beneficiation can be found in the literature ranging up to 4 million BTU/t K_2O.[38] In this case, the avoided CO_2 emissions due to the use of the recycled KE waste can be estimated to reach ~5000 t of CO_2 per year per 100 000 t/year NPK 10-20-20 fertilizer.

■ CONCLUSIONS

Potash rock is a source of a key nutrient K, but its environmental impacts are of concern for sustainable food development. Carnallite-rock processing to extract elemental Mg allows for its natural concentration where K_2O content increases from 17% to ~43%. This carnallite-derived waste was characterized physically and chemically and used to manufacture compound NPK fertilizers. The mesoporous material structure was found and likely facilitated the wet granulation process in spite of the low 6 m^2/g measured surface area. Waste material was found to contain significant secondary nutrients, such as Mg and Ca, as well as Na. Mg was mostly contained in low-solubility minerals. Trace metal concentrations were low and did not pose significant limitations from the regulatory point of view. Several high-K_2O-content fertilizer formulations were proposed and granulated using laboratory and industrial wet granulation in a rotary drum. High KE content with K_2O (KE)/K_2O (MOP) ranging from 1.14 to 9.96 was utilized in obtaining these fertilizers. The sustainability impact of the overall process was assessed by evaluating the averted GHG emissions when KE is substituted for potash rock. It was found that up to 5000 t of CO_2 per 100,000 t of NPK 10-20-20 fertilizer can be avoided if KE waste is used rather than the potash rock excavated.

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■ REFERENCES

(1) Manning, D. A. C. Mineral sources of potassium for plant nutrition. A review. *Agron. Sustainable Dev.* **2010**, *30* (2), 281–294.

(2) Van Straaten, P. Farming with rocks and minerals: challenges and opportunities. *An. Acad. Bras. Cienc.* **2006**, *78* (4), 731–747.

(3) Li, T.; Wang, H.; Wang, J.; Zhou, Z.; Zhou, J. Exploring the potential of phyllosilicate minerals as potassium fertilizers using sodium tetraphenylboron and intensive cropping with perennial ryegrass. *Sci. Rep.* **2015**, *5* (1), 9249.

(4) Römheld, V.; Kirkby, E. A. Research on potassium in agriculture: needs and prospects. *Plant Soil* **2010**, *335* (1), 155–180.

(5) Sardans, J.; Penuela, J. Potassium: a neglected nutrient in global change. *Glob. Ecol. Biogeogr.* **2015**, *24* (3), 261–275.

(6) USGS; *Mineral Commodity Summaries*; U.S. Geological Survey; 2017.

(7) Jacob, A. *Magnesium, the Fifth Major Plant Nutrient*; Staples Press Ltd., 1958.

(8) Cakmak, I. Magnesium in crop production, food quality and human health. *Plant Soil* **2013**, *368* (1), 1–4.

(9) Guo, W.; Nazim, H.; Liang, Z.; Yang, D. Magnesium deficiency in plants: An urgent problem. *Crop J.* **2016**, *4* (2), 83–91.

(10) Christenson, D. R.; White, R. P.; Doll, E. C. Yields and Magnesium Uptake by Plants as Affected by Soil pH and Calcium Levels1. *Agron. J.* **1973**, *65*, 205–206.

(11) Ciceri, D.; de Oliveira, M.; Allanore, A. Potassium fertilizer via hydrothermal alteration of K-feldspar ore. *Green Chem.* **2017**, *19* (21), 5187–5202.

(12) Zhong, Y.; Gao, J.; Chen, P.; Guo, Z. Recovery of Potassium from K-Feldspar by Thermal Decomposition with Flue Gas Desulfurization Gypsum and CaCO3: Analysis of Mechanism and Kinetics. *Energy Fuels* **2017**, *31* (1), 699–707.

(13) Zhou, J.-F.; Liu, C.-C.; Ma, J.-Y.; Qin, Y.-H.; Wu, Z.-K.; Yang, L.; Wang, T.-L.; Wang, W.-G.; Wang, C.-W. Intensification of potassium leaching from phosphorus-potassium associated ore with lauryl alcohol. *Sep. Purif. Technol.* **2018**, *191*, 1–7.

(14) Baltrusaitis, J.; Sviklas, A. M. A. M. From Insoluble Minerals to Liquid Fertilizers: Magnesite as a Source of Magnesium (Mg) Nutrient. *ACS Sustainable Chem. Eng.* **2016**, *4* (10), 5404–5408.

(15) UN Industrial Development Organization, I. F. D. C. *Fertilizer Manual.*, 3rd ed.; Kluwer Academic, 1998.

(16) Foot, D. G.; Huiatt, J. L. Evaluation of Methods for Recovering Potash From Carnalite Ore. *Bur. Mines Rep. Investig.* **1984**, 8846.

(17) Wang, X.; Miller, J. D.; Cheng, F.; Cheng, H. Potash flotation practice for carnallite resources in the Qinghai Province, PRC. *Miner. Eng.* **2014**, *66*, 33–39.

(18) Shekhovtsov, G.; Shchegolev, V.; Devyatkin, V.; Tatakin, A.; Zabelin, I. Magnesium Electrolytic Production Process. In *Essential Readings in Magnesium Technology*; Mathaudhu, S. N., Luo, A. A.,

DOI: 10.1021/acssuschemeng.8b01773
ACS Sustainable Chem. Eng. 2018, 6, 9427–9433

Neelameggham, N. R., Nyberg, E. A., Sillekens, W. H., Eds.; Springer International Publishing: Cham, 2016; pp 97−100.
(19) Holywell, G. C. Magnesium: The first quarter millennium. *JOM* **2005**, *57* (7), 26−33.
(20) Baltrusaitis, J.; Sviklas, A. M. A. M.; Galeckiene, J. Liquid and Solid Compound Granulated Diurea Sulfate-Based Fertilizers for Sustainable Sulfur Source. *ACS Sustainable Chem. Eng.* **2014**, *2* (10), 2477−2487.
(21) Salman, A. D.; Hounslow, M. J.; Seville, J. P. K.; Eds. Granulation. In *Handb. Powder Technol.*; Elsevier B.V., 2007.
(22) Thommes, M.; Kaneko, K.; Neimark, A. V.; Olivier, J. P.; Rodriguez-Reinoso, F.; Rouquerol, J.; Sing, K. S. W. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). *Pure Appl. Chem.* **2015**, *87* (9−10), 1051.
(23) Shanmugam, S. Granulation techniques and technologies: recent progresses. *BioImpacts* **2015**, *5* (1), 55−63.
(24) Oh, J. S.; Shim, W. G.; Lee, J. W.; Kim, J. H.; Moon, H.; Seo, G. Adsorption Equilibrium of Water Vapor on Mesoporous Materials. *J. Chem. Eng. Data* **2003**, *48* (6), 1458−1462.
(25) Broström, M.; Enestam, S.; Backman, R.; Mäkelä, K. Condensation in the KCl−NaCl system. *Fuel Process. Technol.* **2013**, *105*, 142−148.
(26) Beerling, D. J.; Leake, J. R.; Long, S. P.; Scholes, J. D.; Ton, J.; Nelson, P. N.; Bird, M.; Kantzas, E.; Taylor, L. L.; Sarkar, B.; et al. Farming with crops and rocks to address global climate, food and soil security. *Nat. Plants* **2018**, *4*, 138.
(27) US EPA. *Clean Water Act 40 CFR 503, Sludge Rule*; Washington DC, 1993.
(28) Mazeika, R.; Staugaitis, G.; Baltrusaitis, J. Engineered pelletized organo-mineral fertilizers (OMF) from poultry manure, diammonium phosphate and potassium chloride. *ACS Sustainable Chem. Eng.* **2016**, *4* (4), 2279−2285.
(29) Salvagiotti, F.; Castellarín, J. M.; Miralles, D. J.; Pedrol, H. M. Sulfur fertilization improves nitrogen use efficiency in wheat by increasing nitrogen uptake. *F. Crop. Res.* **2009**, *113* (2), 170−177.
(30) Bologna-Campbell, I.; Franco, H. C. J.; Vitti, A. C.; Faroni, C. E.; Costa, M. C. G.; Trivelin, P. C. O. Impact of Nitrogen and Sulphur Fertilisers on Yield and Quality of Sugarcane Plant Crop. *Sugar Tech* **2013**, *15* (4), 424−428.
(31) De Bona, F. D.; Fedoseyenko, D.; von Wirén, N.; Monteiro, F. A.; Bona, F. D. De; Fedoseyenko, D.; von Wirén, N.; Monteiro, F. A. Nitrogen utilization by sulfur-deficient barley plants depends on the nitrogen form. *Environ. Exp. Bot.* **2011**, *74*, 237−244.
(32) Cekinski, E.; Thomassin, J. H. Influence of calcium sulfate crystal size on the curing time of single superphosphate. *Nutr. Cycling Agroecosyst.* **1996**, *46* (1), 23−28.
(33) Walker, G. M.; Magee, T. R. A.; Holland, C. R.; Ahmad, M. N.; Fox, J. N.; Moffatt, N. A.; Kells, A. G. Caking Processes in Granular NPK Fertilizer. *Ind. Eng. Chem. Res.* **1998**, *37* (2), 435−438.
(34) Sirdeshmukh, D. B.; Deshpande, V. T. X-ray measurement of the thermal expansion of ammonium chloride. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1970**, *26* (2), 295−295.
(35) Frazer, B. C.; Pepinsky, R. X-ray analysis of the ferroelectric transition in KH 2 PO 4. *Acta Crystallogr.* **1953**, *6* (3), 273−285.
(36) Allen, D. T.; Hwang, B.-J.; Licence, P.; Pradeep, T.; Subramaniam, B. Advancing the Use of Sustainability Metrics. *ACS Sustainable Chem. Eng.* **2015**, *3* (10), 2359−2360.
(37) Anastas, P. T.; Zimmerman, J. B. Peer Reviewed: Design Through the 12 Principles of Green Engineering. *Environ. Sci. Technol.* **2003**, *37* (5), 94A−101A.
(38) BCS, Inc. *ITP Mining: Energy and Environmental Profile of the U.S. Mining Industry*; 2002.
(39) U.S. Energy Information Administration Frequently Asked Questions. https://www.eia.gov/tools/faqs/faq.php?id=73&t=11.

DOI: 10.1021/acssuschemeng.8b01773
ACS Sustainable Chem. Eng. 2018, 6, 9427−9433