

Production of marketable multi-nutrient fertilisers from different biomass ashes and industrial by-products

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Abstract – Sewage sludge ashes (SSA) contain considerable mass fractions of phosphorus (5-10 w-% P) suitable for fertiliser production. Unfortunately, also most of the heavy metals remain in the ashes. A thermochemical process was developed for the treatment of SSA to i) remove heavy metals and ii) transform phosphates into bio-available mineral phases. The technology was already demonstrated in technical scale (capacity of 300 kg/h) and the company OUTOTEC is currently planning the first industrial plant. In order to manufacture a marketable multi-nutrient fertiliser from the thermochemically treated SSA further wastes and industrial by-products were taken into account. Ammonium sulphate occurs as a by-product of the caprolactam production and was chosen as N-carrier (21 w-% N). Straw ash was tested as potassium carrier (11-15 w-% K). Granulation campaigns were carried out with intensive mixers in lab-, medium- and technical scale. NPS- and NPKS-fertilisers were produced that were characterised by suitable particle size distributions and strength.

Keywords: sewage sludge ash, recycling fertiliser, heavy metals, thermochemical treatment, bioavailability

INTRODUCTION

Phosphorus is an essential element for all living organisms and is therefore required in huge amounts for food production. However, rock phosphate is considered as a limited resource and some scientists expect peak phosphorus even ahead of peak oil around 2030 [1]. Furthermore, phosphate rock is often highly loaded with the toxic heavy metals cadmium and uranium and is polluting our farmland in form of contaminated phosphate fertilisers. The major phosphate rock reserves are located in Africa and China whereas Western Europe is totally dependent on imports. In order to save limited resources and to become more independent of the complex phosphorus world market European scientists in particular are investigating possibilities to use phosphorus bearing waste flows for agricultural application. Of course this must be environmentally friendly and safe for the food chain. Wastewater is the most important waste flow for phosphorus recovery. In Germany, the theoretical potential in waste water is around 70,000 tons phosphorus annually. The major part (~90%) ends up in the sewage sludge and nearly half of it is utilized in agriculture or landscaping. However, the direct agricultural utilisation of sewage sludge is discussed controversially as sewage sludge is a sink for pollutants in the waste water treatment plant and contains - besides heavy metals - also a diverse array of organic pollutants. Thus, incineration of sewage sludge became more common in the last ten years and accounts already for around 53% (approx. 1.1 Mio tons) of the total sewage sludge disposal in Germany today with upward trend. A little less than half of thermal treatment takes place in mono-incineration facilities whereas a slightly larger amount is co-incinerated in cement works, power plants or incineration plants for municipal solid wastes. The ashes from co-incineration are mostly not suitable for phosphorus recovery as the phosphorus mass fraction is low due to dilution and the ashes are often highly contaminated. Thus, phosphorus is irreversibly lost for agricultural utilisation if sewage sludge is co-incinerated. In contrast, the ashes from mono-incineration facilities contain high mass fractions of phosphorus with 5-10 w-% P and are suitable for recovery purposes.

Intense research was carried out at BAM *Federal Institute for Materials Research and Testing* together with European partners within the framework of different European and national projects (EU-FP6-SUSAN, EU-FP7-SUSYPHOS, AiF-ZIM) targeting on the development of technical processes that transform sewage sludge ashes into marketable and safe fertilisers. A thermochemical process was developed for the treatment of sewage sludge ashes to i) remove heavy metals and ii) transform phosphates into bio-available mineral phases. Favorably, magnesium chloride is added to sewage sludge ash and the mixture is thermally treated in a rotary kiln at 850-1000°C for approx. 20 min. retention time. Also other chlorine donors such as CaCl₂, NaCl, Cl₂ and HCl were successfully tested. Volatile heavy metal chlorides are formed, evaporated and separated via the gas phase in this process [2-4]. At the same time bio-available magnesium and magnesium-calcium phosphates are formed [5]. The thermochemically treated ash is a suitable P-rich raw material for the production of fertilisers [6]. The technology was already demonstrated in technical scale (capacity of 300 kg/h) by the company ASH DEC Umwelt AG in Leoben, Austria. After the insolvency of ASH DEC in the year 2010 the company OUTOTEC took over the knowhow and is currently planning the first industrial plants.

MATERIALS AND METHODS

Thermochemical Treatment of Sewage Sludge Ashes

A sewage sludge ash from a large fluidized bed incineration facility in The Netherlands was used for the thermochemical experiments. The element composition of this ash internally called SSA 1 is given in Table 1.

Table 1: Composition of the sewage sludge ash SSA 1 used for the investigation. In the upper part of the table the mass fractions of main elements are given in %. Below, the mass fractions of trace elements are given in mg/kg. Furthermore, the standard deviations (SD) are given for each element.

(%)	Al	Ca	Fe	K	Mg	Mn	Na	P	S	Cl
Mass fraction	5.59	13.42	10.01	1.058	1.502	0.104	0.559	9.004	1.297	0.588
SD	0.036	0.019	0.117	0.0072	0.0146	0.0004	0.0030	0.0068	0.0092	0.0020

(mg/kg)	As	Cd	Cr	Cu	Hg	Mo	Ni	Pb	Sn	Tl	Zn
Mass fraction	34.1	6.53	145	1113	<0.07	27.8	83.2	236	48.1	<0.5	2543
SD	0.2	0.5	1.0	3.0	-	0.1	1.0	2.2	0.2	-	28

Hydrochloric acid gas (HCl 2.8 gas, Linde, Leuna, Germany), calcium chloride (CaCl₂ • 2 H₂O; extra pure, Merck, Darmstadt, Germany) and magnesium chloride (MgCl₂ • 6 H₂O; cryst., Merck, Darmstadt, Germany) were used as chlorine donors for the thermochemical experiments. Furthermore, magnesium carbonate (MgCO₃; basic heavy, Fluka, Germany) was used in combination with HCl gas as an Mg-donor (comparative trials to the utilization of MgCl₂). The experiments were carried out using a quartz glass reactor in a gas tight lab-scale rotary furnace (Carbolite HTR 11/150, Ubstadt-Weiher, Germany). For all experiments an amount of 400 g solid matter (SSA or mixture of SSA with calcium or magnesium salt) was heated to 1000°C with a rate of 20°C/min. This temperature was held for 30 min. The quartz glass reactor was continuously moved during thermal treatment (alternating rotation of 315° in both directions) and flushed with an air- or air/HCl gas flow rate of 3 L/min. Furthermore, the air gas flow was moisturized in a boiler (saturated at 50°C) before passing the reactor. The off-gas passed first a PTFE-tube for cooling and condensation of the heavy metals followed by an acidic scrubber. All experiments were carried out once and each batch was sampled and analysed twice (average values calculated from two measurements).

The elemental composition of the thermochemically treated SSAs was measured by ICP-OES (Thermo IRIS Intrepid II XSP in combination with Thermo Timberland IIS Autosampler, Thermo Fisher Scientific GmbH, Dreieich, Germany) after total digestion (HNO₃/HCl/HF) in a microwave (mikroPrepA, MLS GmbH, Leutkirch, Germany; heating with 1000W; 20 min isotherm segment at 210°C).

The P-solubility in 2% citric acid (P_{cit}) was measured by ICP-OES after extraction of 5 g sample in 500 mL 2% citric acid for 30 minutes in a rotary shaker (35-40 turns per minute) and immediate filtration through a phosphate-free filter (according to EU Directive 2003/2003 method 3.1.3). For the determination of the P-solubility in neutral ammonium citrate (P_{nac}) 3 g sample was extracted in 100 mL extractant for exactly one hour at constant temperature (65°C) and stirring (EU Directive 2003/2003 method 3.1.4). After immediate cooling to ambient temperature the suspension was quantitatively transferred into a graduated 500 mL flask with a jet of water. The flask was filled to the volume with water and mixed thoroughly. At the end the solution was filtered through a phosphate-free filter and analyzed by ICP-OES. Both extraction tests were carried out three times for each batch.

Granulation trials

The granulation trials were carried out with the thermochemically treated SSA and different additives. Ammonium sulfate was ground in a roller mill to a fine powder and was used as N- and S-carrier for the granulation trials. An acidic ammonium sulfate solution (DOMO Caproleuna GmbH, Leuna, Germany) was used as a liquid binder and as an additional N- and S-carrier. Straw ash from a small incineration facility of the Thueringer Landesanstalt fuer Landwirtschaft (TLL) was used as a K-carrier. The granulation trials were carried out with the intensive mixers R02 (5L) and R08 (75L) from Maschinenfabrik Gustav Eirich GmbH & Co KG, Hardheim, Germany. The mixer R02 was filled with 1 kg thermochemically treated ash and 1 kg ammonium sulphate to produce an NPS-fertiliser. In a second trial, 1 kg thermochemically treated ash, 0.5 kg ammonium sulphate, and 0.5 kg straw ash were used in order to prepare a NPKS-fertiliser. The solid materials were mixed at a high impeller speed for 3 minutes. Then approx. 250-300 mL ammonium sulphate solution was added at lower impeller speed. Granulation took 10-15 minutes. The wet granules were dried on steel plates in a drying cabinet. The same procedure was used for the R08 mixer granulating 20 kg thermochemically treated ash with 20 kg ammonium sulphate and 9 L ammonium sulphate solution to produce the NPS-fertiliser and 15 kg treated ash, 15 kg ammonium sulphate, 1.5 kg straw ash and 7 L ammonium sulphate solution in order to manufacture a NPKS-fertiliser.

After drying the particle size distribution of the product was measured by classing on vibrating screens (1, 2, 3.15, 4, 5, 6.30, 7.10 mm) and weighing. The hardness was tested for those particles with the exact diameter of the mesh size of the sieves by using particles sticking in the mesh. 50 particles were collected for each diameter and measured in a self made experimental setup shown in Figure 1. The particles were inserted in a hydraulic press that was equipped with a force sensor. The signal of the force sensor was received online by a computer. The force increased until the granule broke. The braking point of the granule was characterised by a sharp decrease of the measured force. The highest force measured directly before braking was interpreted as the maximum strength (N) of the granule. The survival probability of granules was statistically analysed with the Weibull function [7].

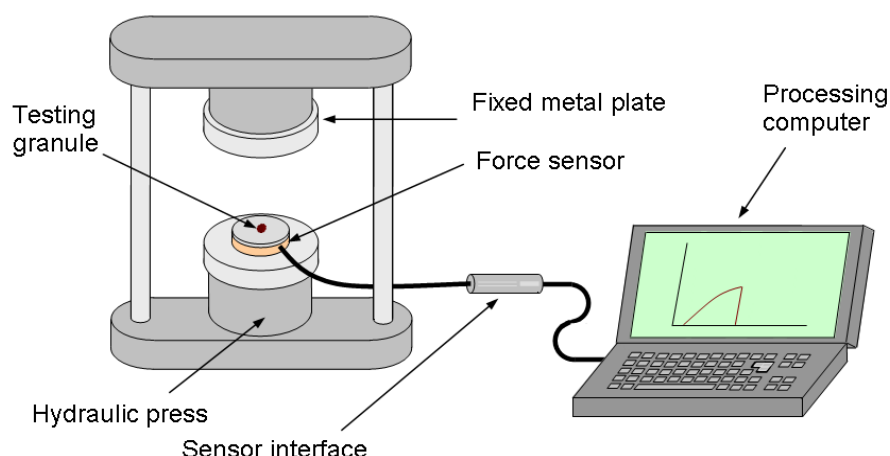


Figure 1: Experimental setup for the determination of the particle strength of fertiliser granules

RESULTS AND DISCUSSION

Thermochemical treatment of sewage sludge ashes

Figure 2 shows the heavy metal mass fractions of SSA 1 before and after thermochemical treatment with the chlorine-donors $MgCl_2$, $CaCl_2$, gaseous HCl and the combination of gaseous HCl with $MgCO_3$ as an Mg-donor. The Mg-contents of the $MgCl_2$ and the $MgCO_3$ variants were adjusted at the same level for comparison. In all experiments a total load of 150 g Cl/kg ash was adjusted.

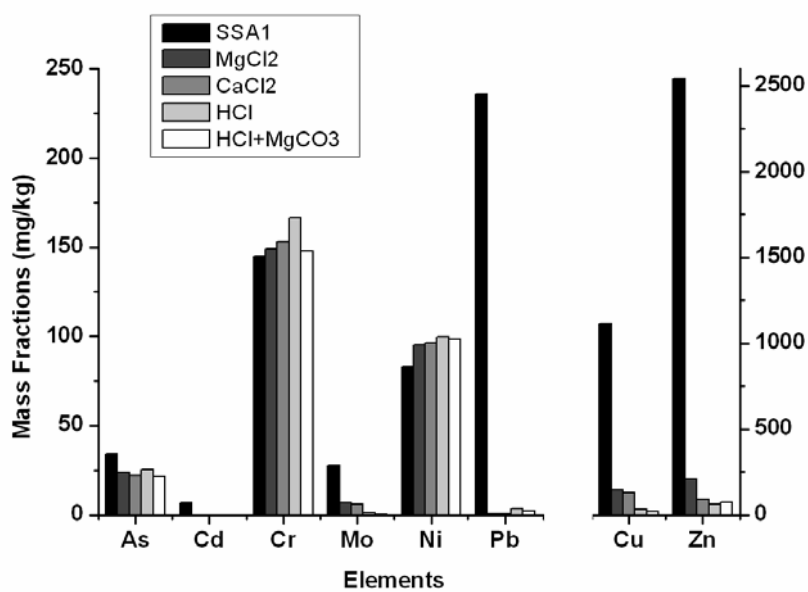


Figure 2: Mass fractions of As and some heavy metals before (SSA 1) and after thermochemical treatment of SSA 1 with different Cl-donors (const. parameters: Cl-load 150 g Cl/kg SSA, 30 min retention time, 1000°C)

The comparison shows that the heavy metal elimination was almost independent of the chlorine-donor used and the additive $MgCO_3$ had no effect on heavy metals removal with HCl as Cl-donor. Cd, Mo, Pb, Cu and Zn were effectively removed with efficiencies >90%. As, Cr and Ni were not removed as already observed in former investigations. This result is in accordance with thermodynamic calculations [2]. Generally, the mass fractions of As, Cr and Ni present in different sewage sludge ashes are already below the limit values of fertiliser ordinances of different European countries. If a removal of these elements is required to meet a lower limit value higher Cl-concentrations would have to be adjusted.

The plant-availability of phosphorus was significantly different due to the particular formed mineral P-phases. In a previous paper [5] SSA 1 (raw material) and SSA 1 thermochemically treated at different temperatures with $MgCl_2$ or $CaCl_2$ were analyzed by XRD in order to determine the P-bearing mineral phases. The raw ash SSA 1 contained whitlockite ($Ca_3(PO_4)_2$) and aluminum phosphate ($AlPO_4$) as the two major P-bearing mineral phases; a result that was also found for 10 further SSAs stemming from different European sewage sludge incineration plants. After thermochemical treatment of SSA 1 with $CaCl_2$ at 1000°C for 30 min, chlorapatite ($Ca_5(PO_4)_3Cl$) was detected as the single P-phase. By utilization of $MgCl_2$ as Cl-donor additionally farringtonite ($Mg_3(PO_4)_2$) was formed and was the dominant P-bearing mineral phase in the treated ash. In both cases $AlPO_4$ and $Ca_3(PO_4)_2$ were completely destroyed during thermochemical treatment and alkaline earth metal phosphates were formed. In contrast, during thermal treatment with HCl-gas only a small fraction of $AlPO_4$ was transformed into calcium phosphates and the main $AlPO_4$ -fraction remained in the treated ash. Whitlockite was transformed into chlorapatite which was a major P-bearing mineral phase together with $AlPO_4$. The formation of the different P-bearing mineral phases significantly affects the P-bioavailability [8]. Table 2 shows the P_{cit} and P_{nac} solubilities of SSA1 treated with the different Cl-

donors and the HCl+MgCO₃ variant. The MgCl₂-variant showed the best P-solubilities (Pnac and Pcit) of the thermochemically treated SSAs due to the formation of Mg₃(PO₄)₂. In contrast, the CaCl₂- and the HCl-treatment showed the worst P-solubilities (Pnac and Pcit) of the treated SSAs which was due to the compounds present: chlorapatite in the case of CaCl₂-treatment and chlorapatite and aluminium phosphate in the case of HCl-treatment. The addition of MgCO₃ to the SSA before thermochemical treatment with gaseous HCl had obviously a positive effect on the P-solubility (Pnac and Pcit) which was near to those of the MgCl₂ variant. Thus, heavy metal removal with HCl gas can be combined with the formation of plant-available magnesium phosphates by addition of MgCO₃.

Table 2: P-solubilities in 2% citric acid (Pcit) and neutral ammonium citrate (Pnac) (±SD; n=3) of SSA 1 after thermochemical treatment with different chlorine-donors (150 g Cl/kg SSA, 30 min treatment at 1000°C). The Mg-content of the variant HCl+MgCO₃ was adjusted at the same level as the MgCl₂-variant

chlorine donor (150 g Cl/kg SSA)	SSA 1	MgCl ₂	CaCl ₂	HCl	MgCO ₃ /HCl
Pcit (%)	43 ±1.7	71 ±2.0	64 ±1.8	53 ±1.7	71 ±2.1
Pnac (%)	10 ±0.7	22 ±1.0	3 ±0.2	6 ±0.3	15 ±0.5

Granulation of ash based multi nutrient fertilisers in small scale (Eirich® R02)

Generally, the granulation of thermochemically treated sewage sludge ashes with ammonium sulphate by products of the caprolactam production worked very well. Suitable granules were also produced in combination with straw ash as a potassium carrier. Photos of granules produced in the intensive mixer Eirich® R02 are shown in Figure 3. The products were spherical granules with smaller particles attached (coarse surface). An example for the particle size distribution of a typical granulation trial is shown in Figure 4. The largest mass fraction was found in the particle size fraction 2-3.15 mm. The particles 2-4 mm made around 63% of the total mass. Assuming that particles 1-6.3 mm are suitable for fertiliser application a product output of approx. 86% was achieved. The fraction < 1mm made 6% of the total mass and would be recharged into the mixer to the new batch. The oversized grain > 6.3 mm made 7.5% of the total mass and would possibly be crushed and added to the product (of course with lower quality concerning the shape which is not spherical in this case).

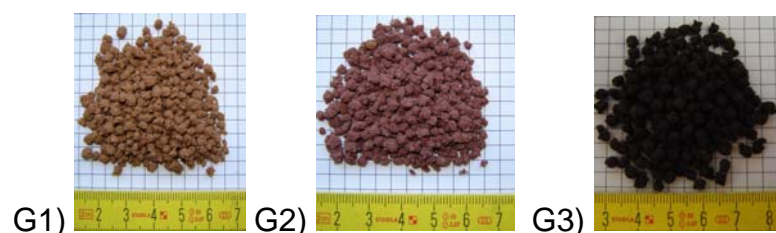


Figure 3: Ash based fertiliser granules (fraction 1- 3 mm) prepared with an Eirich® R02 intensive mixer:

- G1) SSA 1 treated with MgCl₂ and granulated with (NH₄)₂SO₂ and (NH₄)₂SO₂ solution,
- G2) SSA 1 treated with CaCl₂ and granulated with (NH₄)₂SO₂ and (NH₄)₂SO₂ solution,
- G3) SSA 1 treated with MgCl₂ and granulated with (NH₄)₂SO₂, straw ash and (NH₄)₂SO₂ solution

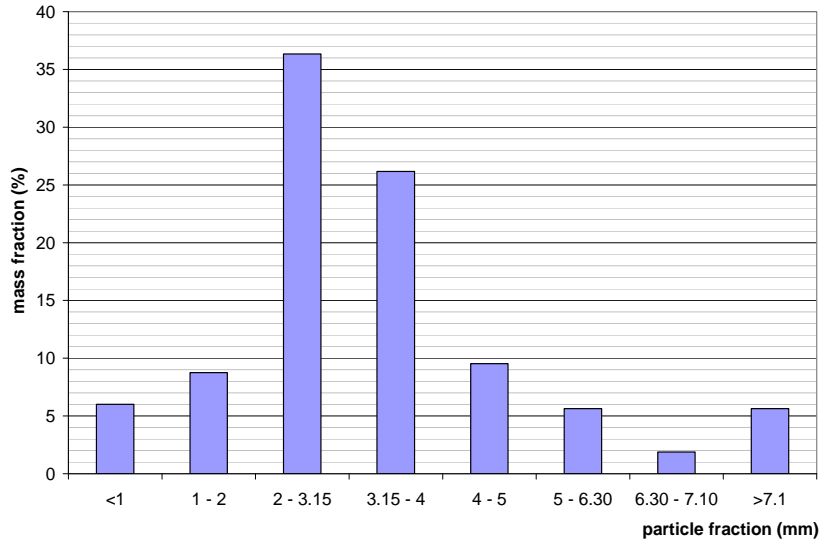


Figure 4: Particle size distribution of a granulation trial: 1 kg SSA 1 thermochemically treated with $MgCl_2$ + 1kg ammonium sulphate (milled) + 300 mL ammonium sulphate solution. 3 minutes mixing at high speed and 15 min granulation at low impeller speed

Two comparative results of hardness tests are shown exemplarily in Figure 5. Particles with the diameters 2, 3 and 4 mm from granulation trials with $MgCl_2$ - and $CaCl_2$ -treated ash were tested (granules shown in Figure 3). It can be clearly seen that larger particles are more stable than smaller ones. The granules of the $MgCl_2$ -variant were harder than those of the $CaCl_2$ -variant. The lower limit that was defined in discussion with different fertiliser manufacturers was 20 N. Granules that can resist a force >20 N were expected to be suitable for typical fertiliser handling including transport, storage and spreading. This target can be definitely achieved with the proposed method of granulation.

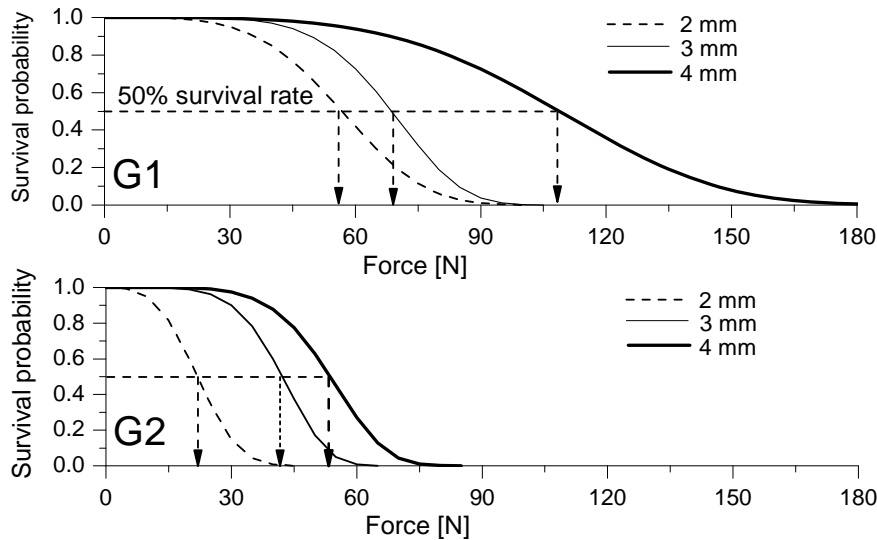


Figure 5: Survival probability of granules G1 (SSA1 treated with $MgCl_2$) and G2 (SSA1 treated with $CaCl_2$) depending on the force applied in a press expressed as a Weibull diagram. The survival probabilities are shown for three particle sizes each

Upscaling of the granulation trials

Based on the results with the small scale mixer Eirich® R02 a trials series with the larger mixer Eirich® R08 was carried out. Due to the larger amounts required for those trials thermochemically treated sewage sludge ash from the ASHDEC Umwelt AG pilot trials were used. The P-content of this

thermochemically treated ash was adjusted with triple super phosphate to a P_2O_5 -mass fraction of approx. 26%. The results achieved with the large mixer were comparable to those of the small-scale trials. The product output was in all cases above 80% and the hardness of the particles above 30 N. The composition of the NPS-fertiliser was: 11% N, 16% P_2O_5 and 13.6 % S. The composition of the NPKS-fertiliser produced under addition of straw ash was: 10% N, 14.4% P_2O_5 , 1.8% K_2O and 13.4% S. In a first industrial-scale trial approx. 7 tons of the ash based NPS-fertiliser was successfully produced in a 250 L mixer by an industrial partner.

CONCLUSIONS

Sewage sludge ashes are suitable raw materials for fertiliser production. Heavy metals must be removed and the bio-availability of phosphorus must be improved before agricultural application. This target can be achieved with a new thermochemical treatment which is intended to be applied in industrial scale in the near future. The thermochemically treated ash can be manufactured to an applicable multi-nutrient fertiliser by granulation with further nutrient carriers. A promising approach is the utilisation of solid and liquid ammonium sulfate by-products from the caprolactam production to produce NPS-fertilisers. Straw ash is a suitable potassium carrier that could be used to produce NPKS-fertilisers. Fertiliser granules were produced in small and industrial scale using Eirich® intensive mixers. The particle size distribution, the strength of the granules and the product output were promising. The described technologies could contribute to a sound way of nutrient recycling in order to save natural resources.

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