Pretreated magnesite as a source of low-cost magnesium for producing struvite from urine in Nepal

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HIGHLIGHTS

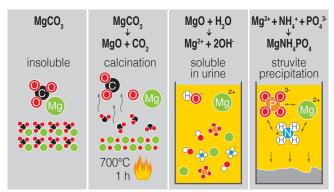
• Calcined magnesite rock can provide soluble MgO for struvite precipitation.

 \bullet Heating at 700°C for 1 h is optimal for calcination of Nepalese magnesite.

• During calcination, temperature control is crucial for the production of soluble MgO.

• MgO from calcined magnesite can be an inexpensive local magnesium source for Nepal.

GRAPHICAL ABSTRACT



ABSTRACT

Struvite is a solid phosphorus fertilizer that can be recovered easily from source-separated urine by dosing it with a soluble form of magnesium. The process is simple and low-cost, however, previous studies have shown that the cost of magnesium in low-income countries is crucial to the viability and implementation of struvite precipitation. Literature has proposed producing inexpensive magnesium locally by making magnesium oxide from magnesite. This paper aimed to investigate whether process requirements, costs, and environmental impacts would make this process viable for magnesium production in decentralized settings. Magnesite samples were calcined at temperatures between 400°C and 800°C and for durations between 0.5 h and 6 h. The release of magnesium was tested by dissolution in phosphate-depleted urine. The optimal processing conditions were at 700°C for 1 h: magnesite conversion was incomplete at lower temperatures, and the formation of large crystallites caused a decrease in solubility at higher temperatures. The narrow optimal range for magnesium production from magnesite requires reliable process control. Cost estimations for Nepal showed that using local magnesite would provide the cheapest source of magnesium and that CO_2 emissions from transport and production would be negligible compared to Nepal's overall CO_2 emissions.

KEYWORDS

Calcination; Magnesium ammonium phosphate (MAP); Magnesite; Nutrient recovery; Struvite precipitation; Urine separation

1. Introduction

In many regions around the world, wastewater treatment is inadequate, and phosphorus is discharged to the environment causing eutrophication (Corcoran et al. 2010). There is a strong push towards recovering phosphorus from waste streams instead of losing it to the environment in an uncontrolled manner. Agriculture requires phosphorus in large amounts, and the resources for synthetic phosphorus fertilizers are limited (Scholz et al. 2013). A simple way to recover phosphorus from human excreta is the precipitation of struvite (MgNH,PO, 6H,O) from sourceseparated urine, which contains about 60% of human excreted phosphorus (Larsen and Gujer, 1996; Kabdaşlı et al. 2013). The conditions for struvite precipitation are optimal in source-separated urine, firstly because nearly all the phosphorus is present in the form of phosphate, and secondly because the pH value is high due to the spontaneous urea hydrolysis that occurs during urine storage (Udert et al., 2003b). About 30% of the phosphorus precipitates in the urine storage tank itself, either as struvite or calcium phosphate (Udert et al., 2003c). The rest can be precipitated by dosing the urine with a source of magnesium.

The production of urine-derived fertilizer is especially interesting for low-income countries, where the availability of fertilizers is low and the prices are high (Sanchez and Swaminathan, 2005). Furthermore, the possibility of trading urine-based fertilizers can also serve as an incentive to promote sanitation (Koné, 2010). Struvite production from source-separated urine has received a lot of attention with regard to decentralized fertilizer production; it can be made in simple, manually operated reactors and only requires a source of magnesium reagent (Dalecha et al. 2014) Several studies have shown that struvite has a high fertilizer value (e.g. Römer, 2006; Johnston and Richards 2003; Bonvin et al. 2015). Nevertheless, the costs can be prohibitive. In a study in Nepal, the prices of magnesium sources were determined to be the main cost factor, besides urine transport. While bittern or seawater are inexpensive alternatives when close to the sea (Rubio-Rincón et al. 2014), locally available magnesite rock was identified as low-cost alternative: it is available in many regions around the world (Mindat, 2014) and is by far the most important source for magnesium oxide (MgO) production (Canterford,

1985). Etter et al. (2011) showed that chemicals such as bulk magnesium sulfate fertilizer were more expensive magnesium sources than MgO produced from magnesite. Due to its low solubility, magnesite must be pretreated before it can be used as a magnesium source to precipitate struvite. One option is to produce soluble MgO by calcination – the thermal decomposition of the mineral by burning (Canterford, 1985; Shand, 2006). MgO is a well-known struvite precipitant for use with wastewater streams (Chimenos et al. 2003; Quintana et al. 2004) as well as with source-separated urine (Lind et al. 2000; Wilsenach et al. 2007; Antonini et al. 2009). Depending on the calcination conditions, MgO of varying chemical and physical properties can be produced (Canterford, 1985).

Another option for exploiting magnesite as a source of magnesium is increasing its solubility by the addition of acid (Gunay et al. 2008), however, the high volumes of acids required and the health risks associated with strong acids prohibit their use in lowincome countries.

Huang et al. (2010) investigated the removal of ammonia from wastewater, from a rare-earth element separation process, by dosing it with calcined magnesite and phosphoric acid. According to their results, calcination at 700 °C for 1.5 h was optimal for producing an efficient precipitant whilst using minimum energy input.

Sakthivel (2012) showed that analytical grade MgO dissolves completely in source-separated urine, although more slowly than MgCl₂ or MgSO₄. However, the author did not investigate MgO produced by the calcination of magnesite. In the present study, we investigated the use of calcined magnesite as a precipitant for phosphate recovery from urine. Since fully ureolyzed urine has a pH of around 9 (Udert et al. 2003a), struvite precipitates quickly after being dosed with any easily soluble source of magnesium, thus phosphate removal via struvite precipitation requires no pH adjustment. To separate the effects of struvite precipitation from the dissolution of calcined magnesite, we determined the solubility of the calcined magnesite in phosphate-depleted source-separated urine. In such a solution, the dissolved magnesium is not eliminated by struvite precipitation and the extent of magnesite dissolution can be determined by measuring the dissolved magnesium ions. Phosphate-depleted urine and neither water nor a salt solution was used, because the composition of the solution influ- ences the solubility of minerals.

By investigating the best calcination parameters for Nepalese magnesite, as well as considering any corresponding costs and carbon dioxide (CO_2) emissions, we aimed to determine whether magnesite calcination was a suitable process for low-cost struvite production in low-income countries such as Nepal. Struvite precipitation could be one way to valorize the urine collected in urine-diverting dry toilets, which have been promoted heavily in Nepal (Water Aid Nepal and Environmental and Public Health Organization (ENPHO) 2007).

2. Materials and methods

2.1. Urine

Source-separated urine was taken from the men's urine storage tank of the NoMix system in Eawag's main building, Forum Chriesbach (Goosse et al. 2009). The urine's composition is given in Table 1. For dissolution experiments, phosphate-depleted urine was generated by adding MgCl₂· $6H_2O$ (magnesium chloride hexahydrate 172,571, Merck, Darmstadt, Germany) at a molar Mg:P ratio of 1.1:1 to the urine. After dosing, the solution was mixed for 30 min using a magnetic stirrer and left to react overnight. The next day, the solution was filtered with a final pore size of 0.45 μ m (MN GF-5, Macherey-Nagel, Düren, Germany).

2.2. Magnesite rock

Magnesite rock was collected at an abandoned magnesite mine in Kharidhunga, Dolakha District, Nepal. Before the experiments, rock pieces were ground and sieved so that magnesite particle sizes ranged from 0.2 μ m to 180 μ m. The average magnesium content was 267 mg·g⁻¹, indicating the high level of purity of Nepalese magnesite. The complete composition of the magnesite sample is given in Table 2.

2.3. Calcination

In order to examine the effects of the calcination parameters on the final precipitant characteristics, magnesite rock powder was calcined in a laboratory furnace (HT 64/16, Nabertherm, Haegendorf, Switzerland) using various combinations of temperature and duration. The combinations were chosen based on the re-

Table 1: Characterization of the urine used in the experiments; standard deviations are 4% or lower.

Measurements	Unit	Ureolyzed urine
Total phosphate	[mg P·L ⁻¹]	184
Magnesium	[mg·L⁻¹]	1
Total ammonia	[g N·L ⁻¹]	2.32
Chloride	[g·L ⁻¹]	3.01
Sodium	[g·L ⁻¹]	1.72
Calcium	[mg·L ⁻¹]	16
COD	[g O₂·mg·L⁻¹]	7.7
Alkalinity	[mmol·L ⁻¹]	147
рН	[-]	8.6
El. conductivity	[mS·cm⁻¹]	24.8

Table 2: Characterization of ground magnesite used in the experiments. Mg, Fe, Ca, and Na were measured in solution after aqua regia digestion (standard deviation: < 10%); all other compounds were determined in the solid form using X-ray fluorescence (XRF).

Mg	[wt.%]	26.7	Zn	[mg·kg⁻¹]	3.4
Fe	[wt.%]	1.77	Cu	[mg·kg⁻¹]	3.1
Si	[wt.%]	1.31	V	[mg·kg⁻¹]	2.3
Ca	[wt.%]	0.3	Sn	[mg⋅kg⁻¹]	< 2.0
AI	[wt.%]	0.2	Ag	[mg⋅kg⁻¹]	< 2.0
Na	[wt.%]	0.2	Sr	[mg⋅kg⁻¹]	1.9
K	[mg⋅kg⁻¹]	374	Υ	[mg⋅kg⁻¹]	1.9
Mn	[mg⋅kg⁻¹]	290	Pb	[mg⋅kg⁻¹]	1.5
Р	[mg⋅kg⁻¹]	169	Sb	[mg⋅kg⁻¹]	1.3
CI	[mg⋅kg⁻¹]	128	Мо	[mg⋅kg⁻¹]	< 1.0
Zr	[mg⋅kg⁻¹]	119	Bi	[mg⋅kg⁻¹]	< 1.0
Ti	[mg⋅kg⁻¹]	58.8	U	[mg⋅kg⁻¹]	< 1.0
Ba	[mg·kg⁻¹]	53.7	W	[mg·kg⁻¹]	< 1.0
Cs	[mg·kg⁻¹]	39.9	Br	[mg·kg⁻¹]	0.9
S	[mg·kg⁻¹]	14.5	Cd	[mg·kg⁻¹]	0.5
Cr	[mg⋅kg⁻¹]	6.6	As	[mg⋅kg⁻¹]	0.6
Ni	[mg·kg⁻¹]	4.4	Se	[mg·kg⁻¹]	< 0.5
Со	[mg⋅kg⁻¹]	b	3.9		

sults of Huang et al. (2010), who proposed 700 °C for 1.5 h as the optimal setting. Longer heating durations were used for temperatures below 700°C, and shorter heating durations for temperatures above. Before calcination, the magnesite powder was dried for 3 h at 105 °C in a laboratory furnace (Modell UNE 200, Memmert, Schwabach, Germany). Ceramic crucibles with approximately 30 g of magnesite were calcined at each calcination setting. Since the temperature dropped during furnace opening, time measurement started as soon as the furnace temperature had returned to the set point. After the set calcination duration had passed, the crucibles were transferred directly into a desiccator to avoid moisture uptake. The difference in mass after calcination was measured as soon as samples reached ambient temperature.

2.4. Magnesium solubility

The solubility of the calcined product (hereafter called the precipitant) was determined by dissolving a certain amount of the precipitant in phosphate-depleted urine and measuring the solution's magnesium concentration. The addition of precipitant to phosphate-depleted urine was set to an arbitrary target dosage of 4 mmol Mg·L⁻¹ based on preliminary experiments of Sakthivel (2012), who showed that substantially higher dosages can be dissolved in urine. The precipitant's magnesium content was calculated based on the initial magnesium content of 26.7 wt% of magnesite and the corresponding mass loss during calcination. Due to the varying mass loss during calcination, the dose of precipitant was adjusted to reach a total magnesium concentration of 4 mmol Mg·L⁻¹. After the addition of the precipitant to phosphatedepleted urine, the solution was mixed for one hour using a magnetic stirrer, in accordance with Sakthivel (2012). During mixing, the glass beaker containing the solution was covered with Parafilm (Parafilm M, Pechiney Plastic Packaging Company, Menasha, USA) to prevent ammonia volatilization. The concentration of dissolved magnesium was measured after mixing. The addition of analytical grade MgO (magnesium oxide 105,865, Merck, Darmstadt, Germany) was also investigated for its efficacy in providing dissolved magnesium to phosphate-depleted urine.

2.5. Energy demand, CO₂ emissions, and financial costs

Energy consumption for each calcination setting was calculated using technical data for simple lime kilns typical of low-income countries (Practical Action, 2002). Total energy consumption for calcination was assumed to be the sum of the energy for heating the magnesite to its target temperature (E_{heatup}) and the transmission heat loss during heating ($E_{heatlos}$) which has to be covered by extra energy to maintain the target temperature.

$$\mathsf{E}_{\mathsf{heaturn}} = \mathsf{c}_{\mathsf{n}} \cdot \Delta \mathsf{T} \cdot \mathsf{m} \tag{1}$$

 c_p is the specific heat coefficient of magnesite (1.56 kJ·K⁻¹·kg⁻¹, Shand 2006), ΔT is the difference between ambient (20°C) and target temperatures, and m is the mass of magnesite.

$$\mathsf{E}_{\mathsf{heatloss}} = \mathsf{H}_{\mathsf{T}} \cdot \Delta \mathsf{T} \cdot \mathsf{t} \tag{2}$$

 $\rm H_{T}$ is the transmission heatloss coefficient (0.10 W·K⁻¹, cf. supplementary data for further information), ΔT is the difference between ambient and target temperatures, and t is the duration of calcination.

Diesel is assumed to be the fuel for transport and calcination. To assess the amount of diesel required for calcination, diesel's burning efficiency was assumed to be 35%, which is common for conventional shaft kilns (UN Habitat, 1993).

The annual CO₂ emissions of struvite production were calculated using the following parameters: 195 mg P·L⁻¹ for stored urine (Etter et al. 2011), 1.25 L urine·cap⁻¹·d⁻¹, and 0.31 kg CO₂·kg⁻¹ struvite (cf. Fig. 6). Nepal's carbon footprint, at 115 kg CO₂ cap⁻¹·a⁻¹, was calculated based on a countrywide CO₂ emission of 3.51 million metric tons (2009) and a population of 30.4 million (2011). Data were taken from UNdata (2014). CO₂ emissions and energy consumption caused by mining and grinding magnesite rock were not incorporated in this work due to the lack of data.

2.6. Analytical methods

Phosphate amounts were determined using ion chromatography (IC 881 Compact IC pro, Metrohm, Zofingen, Switzerland). Dissolved magnesium was analyzed using inductively coupled plasma-optical emission spectrometry (ICP-OES, Ciros, Spectro Analytical Instruments, Kleve, Germany). The standard deviation of all wet chemical measurements was 4% or lower.

Particle characteristics and composition were investigated using a particle size analyzer (Mastersizer 2000, Malvern Instruments, Malvern UK), an XRF spectrometer (Xepos, Spectro, Kleve, Germany), and X-ray diffractometry (XRD) (power X-ray diffractometer AXS D8 Advance, Bruker, Coventry, UK). The magnesium, iron, calcium, and sodium contents of ground magnesite were determined using ICP-OES after the samples were digested with aqua regia and microwaved. Other metals (see Table 2) were measured using XRF.

3. Results

3.1. Mass loss during calcination

In Fig. 1, the mass loss during calcination is shown for each temperature and duration setting. Mass loss varied from 1% to 50% of the initial mass. At low temperatures (400 to 500 °C), only a small amount of mass was lost during calcination, regardless of duration. At calcination temperatures equal to or higher than 700°C, mass loss was approximately 50%, independent of duration. At 600°C, mass loss varied as a function of duration: the longer the burning duration, the higher the mass loss observed. Due to the high percentage of magnesium in the magnesite (cf. Table 2), mass loss can be attributed mainly to the volatilization of CO₂ during the conversion of MgCO₃ to MgO, and can be considered as a proxy measure of MgO production.

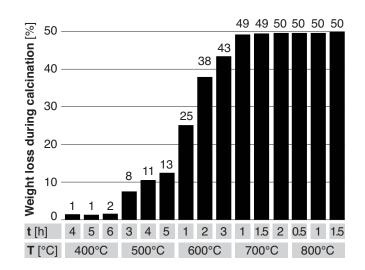


Fig. 1: Mass loss as function of calcination temperature & duration.

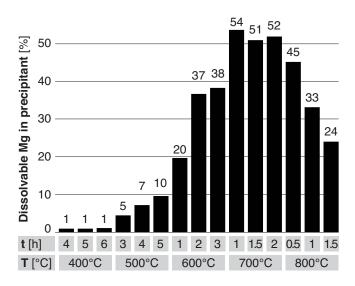


Fig. 2: Dissolvable magnesium content of the precipitant as a function of the thermal pretreatment applied.

3.2. Solubility of calcined magnesite in urine

In Fig. 2, the dissolved magnesium concentration is depicted as a percentage of the added mass of precipitant. The data show that the concentration of soluble magnesium was low and independent of duration at a calcination temperature of 400°C. For calcination temperatures between 500°C and 600°C, duration had a pronounced effect on magnesium release. It increased from 5% for 3 h at 500°C to 38% for 3 h at 600°C. The highest percentage of dissolved magnesium was observed for calcination at 700°C for 1 h: 54% of the initial precipitant mass. Longer durations and higher temperatures resulted in a decrease in magnesium solubility. After calcination at 800°C for 1.5 h, magnesium dissolution was less than half (24%) the maximum. In order to prove that MgO is completely soluble in urine when it has not been subject to the negative influences of calcination, solubility was also assessed using analytical grade MgO. In a control experiment, 59% of the added MgO dissolved into magnesium, which is very close to MgO's theoretical magnesium mass content of 60%. This result showed that no magnesium was lost due to precipitation.

3.3. Particle size distribution

The volume-weighted mean particle size of untreated magnesite was 73.6 μ m. This decreased with increasing calcination temperatures to 73.2 μ m (600°C, 1 h), 70.4 μ m (700°C, 1 h), and 68.7 μ m (800°C, 0.5 h). The longer the burning duration, the smaller the particle size. Particle size distribution measurements revealed that the magnesium released by the precipitant was not dependent on the size of the particles. The same would be valid for the specific surface area, which would increase as particle size decreased.

3.4. MgO formation during calcination

For magnesite calcined at 400°C for 4 h, follow-up XRD analysis could only detect magnesite; no pattern of MgO was found. This indicates that no MgO was present in the original magnesite powder and that calcination at 400°C for 4 h produced no MgO. Both magnesite and MgO were detected in samples calcined at 600°C. Clearly, calcination, and therefore MgO formation, was not complete at this setting. For samples calcined at temperatures of 700°C or higher, only MgO was detected.

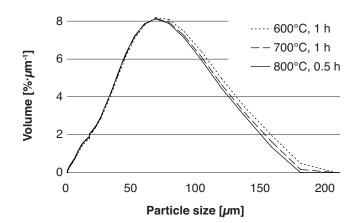


Fig. 3: Particle size distribution of magnesite treated using the following settings: 600°C, 1 h (dotted line); 700°C, 1 h (dashed line), and 800°C, 0.5 h (solid line). The trend of decreasing particle size as the temperature increased was observed for all calcination settings and was also valid for longer burning durations.

3.5. Crystallite sizes of formed MgO

XRD analysis of the samples treated at 700°C and 800°C revealed that MgO crystallite sizes increased as temperature and burning duration increased: from 152 Å at a setting of 700°C for 1 h to 262 Å at 800°C for 1.5 h. An overview of crystallite sizes is available in the supplementary data. The percentage of available magnesium in the precipitant correlates negatively with the size of the crystallites (cf. Fig. 3).

3.6. Energy consumption for calcination

The estimated energy consumption for calcination in a kiln is given in Fig. 5. The energy demand for calcination is governed by two opposite effects: reaching higher temperatures requires more energy, but lower temperatures require longer heating times and therefore more energy is needed to reach high magnesium solubility. Calcination at 700°C for 1 h showed the lowest energy consumption, at 1.3 kWh per kg soluble magnesium. Slightly more energy was needed for settings at 700 °C for 1.5h, 700°C for 2h, and 800°C for 0.5h.

3.7. Costs & CO₂ emissions for magnesite calcination in Nepal

Fig. 6 shows energy consumption, financial costs, and CO₂ emissions per kg of struvite produced. Settings with calcination temperatures below 600°C are not shown because CO₂ emissions, energy demand, and financial costs were far too high due to the low solubility of the precipitant. The data in Fig. 6 show that the setting at 700°C for 1 h had the lowest CO₂ emissions (0.31 kg CO₂·kg⁻¹ struvite), the lowest energy consumption (0.42 kWh·kg⁻¹ struvite), and the lowest costs (0.12 USD·kg⁻¹ struvite). The settings at 700°C for 1.5 h and 700°C for 2 h also showed favorable values in terms of energy, costs, and emissions. In all the settings, transportation only contributed marginally to energy consumption (around 1%) and CO₂ emissions (less than 1%). Nearly all the CO₂ was produced during calcination. The CO₂ produced by transportation was thus negligible. Furthermore, the estimated CO₂ emissions for struvite precipitation with calcined magnesite would increase Nepal's overall carbon footprint by only 0.2 %, or 0.22 kg CO2 cap-1 ·a-1 (assumptions: 0.31 kg CO2 ·kg-1 struvite, see above; 0.195 g P·L-1 for stored urine in Nepal according to Etter et al. 2011; 1.25 L_{urine}·cap⁻¹·d⁻¹ according to Udert et al. 2006; all phosphate is precipitated as struvite).

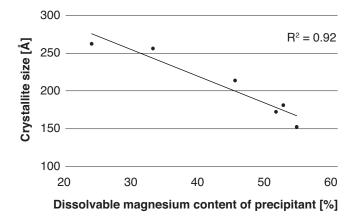


Fig. 4: Correlation between dissolvable magnesium content of precipitant and crystallite size.

4. Discussion

4.1. Factors determining magnesium solubility

Two effects determine magnesium's availability for struvite precipitation: first, the extent to which magnesite is converted to MgO, and second, the solubility of the MgO formed. Our study confirmed that 700°C is the optimal temperature of magnesite calcination to MgO. Below 600°C, magnesium solubility was low due to the incomplete conversion of magnesite to MgO. Above 700°C, practically all the magnesite was converted to MgO, but magnesium solubility was reduced. Although dissolution is a surfacecontrolled process, particle sizes and the corresponding specific surface area of the particles could not explain magnesium solubility. The reason for the lack of correlation is a change in the characteristics of the MgO crystallites. Crystallites are assemblages of small crystals that make up the structure of polycrystalline particles. Eubank (1951) showed that higher temperatures and longer burning durations result in more MgO crystal growth. However, due to the nature of surface-controlled reactivity, and in order to be highly reactive, MgO requires small crystallite size in combination with large surface area (Kimyongur and Scott, 1986). These findings are in line with the negative correlation observed between crystallite size and dissolved magnesium (cf. Fig. 4). Our study further agrees with Kimyongur and Scott (1986), as they also showed that highly soluble MgO can only be produced in a narrow band of temperature-time settings.

Huang et al. (2010) found a similar optimum setting (700°C for 1.5 h) to the present study, however, they did not observe decreasing ammonia removal rates for magnesite calcined above 700°C. The results of Huang et al. (2010) do not seem to correspond to our observation that the solubility of MgO decreases with higher treatment tempera- tures. However, the results are not directly comparable. Huang et al. (2010) did not determine directly the amount of dissolved magnesium. Furthermore, they did not determine the composition of their precipitates. Since the composition of the wastewater was very different than the composition of urine used in our study, different precipitates might have formed. Based on the molar ratios of ammonium and phosphate removal, it is very likely that the precipitates in the study of Huang et al. (2010) were not or not only struvite. Since the pH value changed strongly during the precipitation experiments (in some experiments from below 5 to above 9) and the experiments lasted for up to 6 h, it is possible that the precipitate composition changed during the experiment and also differed from experiment to experiment. In our study, the strongest pH change

was a slight increase from 8.90 to 9.02 (dissolution of magnesite treated at 700°C and for 2 h). We only assessed the formation of soluble magnesium, but previous studies have shown that dissolved magnesium will readily react to form struvite in source-separated urine (Etter et al. 2011).

4.2. Optimal calcination conditions for Nepalese magnesite

A calcination setting of 700°C for 1 h is optimal for several reasons:

- the amount of magnesium needed for struvite precipitation is minimized, therefore reducing the consumption of valuable magnesite;
- it offers the cheapest and least energetic means of precipitant production;
- the smaller amounts of calcination residues mean the struvite is purer, thereby increasing its potential market value.

The biggest challenge in using locally calcined magnesite as a mag- nesium source in Nepal will be the calcination process itself. In kilns, burning duration and temperature are difficult to control. As shown in Fig. 5 and Fig. 6, the duration of calcination is less critical when a con- stant temperature of 700 °C can be maintained. At higher temperatures, the solubility of magnesium is reduced considerably, and energy de- mand and costs rise remarkably. Therefore, good temperature control is more important than exact calcination times.

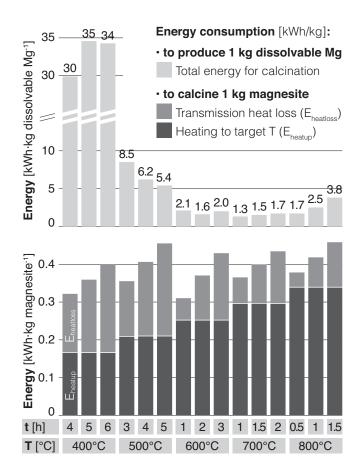


Fig. 5: Overview of energy consumption for magnesite calcination: (i) per kg magnesite, and (ii) per kg dissolvable magnesium.

4.3. Magnesium sources

Etter et al. (2011) calculated the financial costs of struvite production from urine using different sources of magnesium. They included MgO produced from locally available magnesite rock, although the costs could only be estimated because data about the calcination process were missing. Our results allow a more reliable cost estimation: while Etter et al. (2011) estimated that struvite production with locally calcined magnesite cost about USD 0.15 kg⁻¹ struvite, the costs derived from our data are even lower (USD 0.12·kg⁻¹ struvite). This confirms that in Nepal, locally produced MgO from magnesite calcination would probably be the least expensive magnesium source for struvite production using urine. In regions close to a coastline, brines containing magnesium from desalination or salt extraction plants are likely to be more promising sources. For Nepal, Etter et al. (2011) also investigated the costs of using magnesium sulfate (USD 0.47 kg-1 struvite) and bittern (USD 0.28 kg⁻¹ struvite), both imported from India.

Sakthivel et al. (2012) proposed wood ash as an inexpensive source of magnesium for struvite precipitation. However, the study showed that wood ash cannot be directly compared to other magnesium sources: low magnesium content and potentially high heavy metal content are its disadvantages.

4.4. Heavy metals

The Nepalese magnesite used in this study does contain heavy metals (cf. Table 2). Ronteltap et al. (2007) showed that heavy metals can precipitate in stored urine and can, therefore, lead to the contamination of struvite fertilizer. Among the heavy metals, cadmium comes under special focus in research and legislation due to its toxicity and mobility in the soil-plant-water system (Molina et al. 2009). However, using the optimal calcination setting of 700°C for 1 h, a worst case scenario involving processing Nepalese magnesite - where all the cadmium ends up in the struvite - leads to 1.6 mg Cd·kg⁻¹ P in the formed struvite. This value meets all the regulatory limits from the different countries listed by Molina et al. (2009), including the strict Dutch limit of 35 mg·kg⁻¹ P. Urine's contribution to the amounts of heavy metals depends on nutrition as well as on skin and lung exposure to heavy metals. Results from Ronteltap et al. (2007) showed that heavy metal concentrations in urine are generally low (e.g. Cd: 0.007 mg Cd·kg⁻¹ P), and their contribution to the heavy metal content of struvite fertilizer is negligible.

5. Conclusion

This work shows that magnesite rock is a promising source of mag- nesium for struvite precipitation using source-separated urine in Nepal. Using calcination, hard to dissolve magnesite can be converted to solu- ble MgO. However, the calcination must be maintained in a narrow range around 700°C. At this temperature, 1 h of calcination yields good magnesium solubility: 54% dissolvable magnesium in the precipi- tant compared to 59% in analytical grade MgO. Longer durations do not increase that solubility, just the costs of heating. Traditional calcination kilns are probably not suited to the job because they do not allow the necessary temperature control. If other kilns, with better process control, can be used in Nepal then MgO produced from locally available magnesite is an optimal source of magnesium for struvite production using source-separated urine.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2015.08.060.

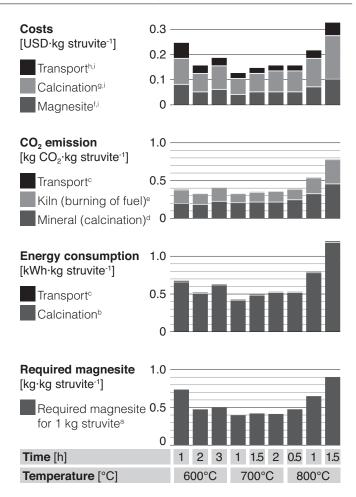


Fig. 6: Overview of costs, CO_2 emissions, energy consumption, and magnesite required per 1 kg of struvite for calcination temperatures of 600°C and above. Exact values are given in the supplementary information.

^aSafety factor for struvite formation: molar ratio Mg:P of 1.1:1. ^bBurning efficiency 35% (UN Habitat, 1993).

^c4.5 km·L⁻¹ average fuel efficiency for trucks in Nepal (Malla, 1993). ^dCO_a emissions based on mass loss during calcination.

°0.83 kg·L⁻¹ diesel, 44 MJ·kg⁻¹ diesel, 2.62 kg CO²·L⁻¹ diesel.

¹26.7 % magnesium content, 32 NPR·kg⁻¹ Mg (Etter et al. 2011).

^{*g}70 NPR·L⁻¹ diesel (Etter et al. 2011), 60 % of total costs for fuel (UN Habitat, 1993).*</sup>

^h0.1 NPR·km¹·kg⁻¹ (Ministry of Local Development of the Government of Nepal, 2010), 80 km transportation distance Kharidhunga-Kathmandu (Etter et al. 2011).

Exchange rate October 22, 2008: NPR 78.64 for USD 1 (Federal Reserve Bank of New York, 2014).

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6 References

Antonini, S., Paris, S., Clemens, J., 2009. Decentralised water treatment systems in the Mekong Delta. SANSED — PROJECT, Final Report. In: Arnold, U., Gresens, F. (Eds.), INRES-Plant Nutrition. University of Bonn, Germany, pp. 49–55.

Bonvin, C., Etter, B., Udert, K.M., Frossard, E., Nanzer, S., Tamburini, F., Oberson, A., 2015. Plant uptake of phosphorus and nitrogen recycled from synthetic sourceseparated urine. Ambio 44 (Suppl. 2), S217–S227.

Canterford, J.H., 1985. Magnesia — an important industrial mineral: a review of processing options and uses. Miner. Process. Extr. Metall. Rev. 2 (1–2), 57–104.

Chimenos, J.M., Fernandez, A.I., Villalba, G., Segarra, M., Urruticoechea, A., Artaza, B., Espiell, F., 2003. Removal of ammonium and phosphates from wastewater resulting from the process of cochineal extraction using MgO-containing by-product. Water Res. 37 (7), 1601–1607.

Corcoran, E., Nellemann, C., Baker, E., Bos, R., Osborn, D., Savelli, H., 2010. Sick water? The central role of wastewater management in sustainable development. A rapid response assessment. United Nations Environmental Programme, UN-HABITAT, GRID-Arendal.

Dalecha, T., Assefa, E., Krasteva, K., Meinhold, K., 2014. Struvite production from source separated urine: Application and economic feasibility in Arba Minch, Ethiopia. Sus- tainable Sanitation Practice 19, 16–22.

Etter, B., Tilley, E., Khadka, R., Udert, K.M., 2011. Low-cost struvite production using source-separated urine in Nepal. Water Res. 45 (2), 852–862.

Eubank, W.R., 1951. Calcination studies on magnesium oxides. J. Am. Chem. Soc. 34 (8), 225–229.

Federal Reserve Bank of New York, 2014. Foreign exchange rates historical search. http:// www.ny.frb.org/markets/fxrates/historical/home.cfm. Accessed in December 2014.

Goosse, P., Steiner, M., Udert, K.M., Neuenschwander, W., 2009. NoMix-Toilettensystem: Erste Monitoringergebnisse im Forum Chriesbach — NoMix toilet system: first monitoring results from the Chriesbach Forum. pp. 567–574.

Gunay, A., Karadag, D., Tosun, I., Ozturk, M., 2008. Use of magnesite as a magnesium source for ammonium removal from leachate. J. Hazard. Mater. 156 (1–3), 619–623.

Huang, H.M., Xiao, X.M., Yang, L.P., Yan, B., 2010. Removal of ammonium as struvite using magnesite as a source of magnesium ions. Water Pract. Technol. 5(1).

Johnston, A.E., Richards, I.R., 2003. Effectiveness of different precipitated phosphates as phosphorus sources for plants. Soil Use Manag. 19 (1), 45–49.

Kabdaşlı, I., Tünay, O., Udert, K.M., 2013. Transfer into the solid phase. In: Larsen, T.A., Udert, K.M., Lienert, J. (Eds.), Source Separation and Decentralization for Wastewater Management. IWA Publishing, London, UK, pp. 351–362.

Kimyongur, N., Scott, P.W., 1986. Calcined natural magnesite — influence of time and temperature on the transformation and resulting industrial properties. Mater. Sci. Forum Vol. 7, 83–90.

Koné, D., 2010. Making urban excreta and wastewater management contribute to cities' economic development: a paradigm shift. Water Policy 12 (4), 602–610.

Larsen, T.A., Gujer, W., 1996. Separate management of anthropogenic nutrient solutions (human urine). Water Sci. Technol. 34 (3–4), 87–94.

Lind, B.B., Ban, Z., Byden, S., 2000. Nutrient recovery from human urine by struvite crystallization with ammonia adsorption on zeolite and wollastonite. Bioresour. Technol. 73 (2), 169–174.

Malla, S., 1993. Urban energy use and environmental management: case of Kathmandu valley. Master's thesis Asian Institute of Technology, Bangkok, Thailand.

Mindat, 2014. Mineral and locality database. http://www.mindat.org/show. php?id=2482&ld=1#themap. Accessed in December 2014.

Ministry of Local Development of the Government of Nepal, 2010. District technical office khotang: annual road maintenance plan. Khotang, Nepal.

Molina, M., Aburto, F., Calderon, R., Cazanga, M., Escudey, M., 2009. Trace element com- position of selected fertilizers used in Chile: phosphorus fertilizers as a source of long-term soil contamination. Soil Sediment Contam. 18 (4), 497–511.

Practical Action, 2002. Lime kiln designs: small-to-medium scale oil fired lime kilns. The Schumacher Centre for technology and development. Warwickshire, UK.

Quintana, M., Colmenareio, M.F., Barrera, J., Garcia, G., Garcia, E., Bustos, A., 2004. Use of a byproduct of magnesium oxide production to precipitate phosphorus and nitrogen as struvite from wastewater treatment liquors. J. Agric. Food Chem. 52 (2), 294–299.

Römer, W., 2006. Plant availability of P from recycling products and phosphate fertilizers in a growth-chamber trial with rye seedlings. J. Plant Nutr. Soil Sci. 169 (6), 826–832.

Ronteltap, M., Maurer, M., Gujer, W., 2007. The behaviour of pharmaceuticals and heavy metals during struvite precipitation in urine. Water Res. 41 (9), 1859–1868. Rubio-Rincón, F.J., Lopez-Vazquez, C.M., Ronteltap, M., Brdjanovic, D., 2014. Seawater for phosphorus recovery from urine. Desalination 348 (0), 49–56.

Sakthivel, S.R., 2012. Design and development of waterless urinal systems and nutrient recovery processes from stored urine PhD Dissertation Indian Institute of Technology Delhi (IITD), New Delhi, India.

Sakthivel, S.R., Tilley, E., Udert, K.M., 2012. Wood ash as a magnesium source for phosphorus recovery from source-separated urine. Sci. Total Environ. 419, 68–75.

Sanchez, P.A., Swaminathan, M.S., 2005. Hunger in Africa: the link between unhealthy people and unhealthy soils. Lancet 365 (9457), 442–444.

Scholz, R.W., Ulrich, A.E., Eilitta, M., Roy, A., 2013. Sustainable use of phosphorus: a finite resource. Sci. Total Environ. 461, 799–803.

Shand, M.A., 2006. The chemistry and technology of magnesia. John Wiley & Sons, Inc., Hoboken, USA.

Udert, K.M., Larsen, T.A., Gujer, W., 2003a. Biologically induced precipitation in urine-collecting systems. Water Sci. Technol. Water Supply 3 (3), 71–78.

Udert, K.M., Larsen, T.A., Gujer, W., 2003b. Estimating the precipitation potential in urine-collecting systems. Water Res. 37 (11), 2667–2677.

Udert, K.M., Larsen, T.A., Biebow, M., Gujer, W., 2003c. Urea hydrolysis and precipitation dynamics in a urine-collecting system. Water Res. 37 (11), 2571–2582.

Udert, K.M., Larsen, T.A., Gujer, W., 2006. Fate of major compounds in sourceseparated urine. Water Sci. Technol. 54 (11–12), 413–420.

UN Habitat, 1993. Vertical shaft lime kiln technology. United Nations Centre for Human Settlements (Habitat), Nairobi, Kenya.

UNdata, 2014. United nations data retrieval system. http://data.un.org/CountryProfile.aspx?crName=Nepal. Accessed in December 2014.

Water Aid Nepal and Environmental and Public Health Organization (ENPHO), 2007o. Assessment of urine diverting EcoSan toilets in Nepal. ENPHO, Kathmandu, Nepal.

Wilsenach, J.A., Schuurbiers, C.A.H., van Loosdrecht, M.C.M., 2007. Phosphate and potassium recovery from source separated urine through struvite precipitation. Water Res. 41 (2), 458–466.