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## Precipitation of potassium as hazenite from washing water of spent alkaline batteries

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### ABSTRACT

Hazenite ( $\text{KNaMg}_2(\text{PO}_4)_2 \times 14 \text{H}_2\text{O}$ ), a new type of struvite mineral, was precipitated from the potassium-rich washing water of spent alkaline battery black mass. Hazenite can be used as a fertilizer, which would be an additional benefit derived from the sustainable recovery of battery materials. Precipitation experiments were performed using different pH values (9.5–12), Mg:K:PO<sub>4</sub> ratios ((1.0–1.5):1:(1.0–1.5)) and temperatures (10–40 °C). Based on the results, hazenite precipitated in a wide pH range under alkaline conditions. The precipitation kinetics were fast, and the purity of the hazenite was high. Overall, hazenite can be precipitated at room temperature without the addition of excess chemicals, which minimizes the consumption of chemicals and energy.

### 1. Introduction

Phosphorus and potassium are essential nutrients for crops, animals and humans. Most of the phosphorus and potassium used are derived from mineral stones, making them non-renewable resources. Thus, other sources of phosphorus and potassium are needed to ensure the stable and sustainable development of agriculture [1].

Potassium in wastewater can be removed simultaneously with phosphorus and magnesium in alkaline conditions (pH around 11) to produce K-struvite ( $\text{KMgPO}_4 \times 6 \text{H}_2\text{O}$ ), which is a potassium analog of struvite ( $\text{NH}_4\text{MgPO}_4 \times 6 \text{H}_2\text{O}$ ) [2]. Hazenite ( $\text{KNaMg}_2(\text{PO}_4)_2 \cdot 14\text{H}_2\text{O}$ ) is a newly discovered struvite group mineral that contains two structurally distinct monovalent cations ( $\text{Na}^+$  and  $\text{K}^+$ ) [3]. The first observation of hazenite was made at the highly alkaline (pH  $\approx$  10) and saline (84–92 g/l) Lake Mono in California, where it was synthesized by biodegradable cyanobacteria. Like struvite and K-struvite, hazenite could also be suitable for fertilizer use [3,4]. In a recent study, hazenite released phosphorus slower than conventional commercial water-soluble fertilizers but faster than struvite [5]. Therefore, hazenite could be a potential phosphorus source for long-term release. Indeed, hazenite increased the biomass of sugarcane by 21% compared to commercial superphosphate in a 180-day growth experiment [6].

In this research, hazenite precipitation was studied using the washing water of spent alkaline batteries as a source of potassium, which creates an additional benefit for the sustainable recovery of battery materials. Spent alkaline batteries are hazardous waste, and the treatment of them is needed. As battery black mass is washed, a potassium-rich wastewater is produced. Here, the potassium is precipitated from the washing water as hazenite, which is a potential potassium fertilizer. This reduces the need to use primary raw materials for potassium fertilizers, since potassium is mostly recovered from mineral stones, making it a non-renewable resource. Further, the release of potassium into watercourses from wastewaters can be prevented using this precipitation procedure.

Alkaline batteries use potassium hydroxide as an electrolyte, whereas zinc-carbon batteries use ammonium chloride. When alkaline batteries are collected and crushed, a small fraction of zinc-carbon batteries often reside among the alkaline ones. Therefore, when potassium is separated from the crushed battery mass by washing with water, some ammonium also ends up in the washing water [7,8]. Currently, these potassium-rich washing waters end up in municipal wastewater treatment plants for purification. It is also possible to hydrometallurgically treat the battery mass without removing the potassium if the presence of potassium in the end solution is approved. Therefore, the

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washing phase is not always performed. However, the elevated potassium content in the zinc and manganese containing sulfate solutions could support formation of Tutton's salts [9,10]. Therefore, to produce more concentrated  $ZnSO_4$  and  $MnSO_4$  solutions, removal of the potassium from the system is needed. Precipitation experiments were performed using different pH values (9.5–12), Mg:K:PO<sub>4</sub> ratios ((1.0–1.5):1: (1.0–1.5)) and temperatures (10–40 °C). There is only a very limited number of publications related to hazenite, and this is the first in which the precipitation conditions of hazenite have been studied.

## 2. Experimental

### 2.1. Potassium-rich washing water

The washing water of spent alkaline batteries was provided by Tracegrow Oy (Kärsämäki, Finland). Tracegrow is a company that produces zinc and manganese containing trace element fertilizers from spent alkaline batteries. In this experiment, crushed and sieved alkaline black mass was dosed to a 220 l container, and water was poured among the black mass (0.8 kg water/1 kg black mass). The mixture was then mixed with a barrel mixer for about 1 h. After this, the mixing was stopped, and the black mass was left to sediment at the bottom of the barrel for one day. After this, about half of the water was transported from the surface layer with a pump to a separate container. The solution contained fine graphite, which had to be filtered away with a filter press. The result was green-shaded potassium-rich alkaline washing water (Table 1), which was then delivered to the University of Oulu. Potassium, sodium and magnesium concentrations of the washing water were measured using atomic absorption spectroscopy AAS (Varian AA240FS, Australia) and ammonium concentration was measured using an HACH HQ40d- NH<sub>4</sub>-selective electrode (Model ISENH418101, Loveland, CO, USA).

### 2.2. Precipitation experiments

Potassium-rich washing water was diluted in a ratio of 1:5 before the precipitation experiments due to its abundant potassium content. 1.6 l of diluted washing water was used in each precipitation experiment. During the precipitation experiments, the effects of several parameters (pH, molar ratios and temperature) were studied (Table 2). The total precipitation time was 4 h, and samples were withdrawn after 0, 15, 30, 60, 90, 120, 180 and 240 min. All precipitation experiments were conducted in duplicate or triplicate. After the experiment, the precipitate was separated by filtration, and the solid precipitate was dried at room temperature in a desiccator for five days. In each experiment, phosphate salt ( $NaH_2PO_4 \times 2 H_2O$ ; AnalaR NORMAPUR, 99.0–102.0%, VWR Chemicals, Germany) was added to the washing water in the precipitation reactor and mixed (500 rpm) by an overhead stirrer (IKA EUROSTAR 40 digital overhead stirrer; IKA®-Werke GmbH & CO.KG, Germany) with a 2-blade impeller and stators until the salt was completely dissolved. The pH was adjusted to the desired value with 10 M NaOH (AnalaR NORMAPUR, 99.2%, VWR Chemicals, Sweden). Precipitant (solid magnesium salt,  $MgSO_4 \times 7H_2O$ , pH. Eur., 99.6%, VWR Chemicals, Belgium) was then added while stirring the solution at a constant speed (1 min 500 rpm, then 250 rpm or 50 rpm). The pH of the solution was kept constant by using 10 M NaOH and concentrated HCl (37%, EMSURE®, Merck KGaA, Germany). The effect of the ammonium ions was studied by carrying out a two-step precipitation. In the first step, the pH was set to 9 and ammonium was targeted by carrying out struvite precipitation; the pH was then raised to 11 and the potassium

**Table 1**  
Composition of the washing water.

K mg/l	NH <sub>4</sub> mg/l	Mg (mg/l)	Na (mg/l)	pH
34,500	1700	31	1220	10.8

**Table 2**  
Precipitation conditions.

Variable	Other parameters	
Effect of pH	9.5	Molar ratio
	10.0	Mg:K:PO <sub>4</sub> 1:1:1
	10.5	T = 20 °C
	11.0	t = 4 h
	11.5	
	12.0	
Effect of molar ratio Mg:K:PO <sub>4</sub>	1:1:1	T = 20 °C
	1.2:1:1	pH 11
	1.5:1:1	t = 4 h
	1:1:1.2	
	1:1:1.5	
	1.2:1:1.2	
Effect of temperature	10 °C	Molar ratio Mg:K:PO <sub>4</sub> 1:1:1
	20 °C	pH 11
	30 °C	t = 4 h
	40 °C	
Two stage precipitation	Molar ratio Mg:K:PO <sub>4</sub> 1:1:1 T = 20 °C t = 4 h stage pH 9 stage pH 11	

was precipitated as hazenite.

### 2.3. Characterization of samples

Liquid samples were filtrated through 0.45 µm filter paper. Magnesium and potassium concentrations were measured using atomic absorption spectroscopy AAS (Varian AA240FS, Australia) using standard reference solutions. Phosphate concentrations were measured using ion chromatography IC (Methrohm 761 Compact IC; Switzerland).

Solid precipitates were analyzed using X-ray diffraction (XRD). The XRD patterns were recorded by a PANalytical XPert Pro-X-ray diffractometer (Malvern Panalytical, Almelo, The Netherlands) using monochromatic CuKα1 radiation ( $\lambda = 1.5406 \text{ \AA}$ ) at 45 kV and 40 mA. Diffractograms were collected in the  $2\theta$  range of 10–85° at 0.017° intervals. The crystalline phases and structures were analyzed using HighScore Plus software (Version 4.0, PANalytical B.V., Almelo, the Netherlands).

The elemental analysis was measured using a PANalytical Axios mAX X-ray fluorescence spectrometer. The sample was fed as loose powder through Mylar film in He-atmosphere. A geostandard was used and the contribution of pure Mylar film was subtracted from the measurement results.

## 3. Results and discussion

### 3.1. Effect of ammonium on hazenite precipitation

The washing water contained ammonium ions, as described in Section 2.1. This might have affected the precipitation and purity of the precipitate. Therefore, the effect of ammonium ions was accounted for by carrying out struvite precipitation followed by hazenite precipitation (two-step precipitation). In the struvite precipitation experiments, the molar ratio of Mg:N:PO<sub>4</sub> was 1:1:1, the pH was 9 and the mixing rate was 50 rpm. The obtained filtrate was further precipitated with an Mg:K:PO<sub>4</sub> of 1:1:1, a pH of 11 and a mixing rate of 50 rpm. In addition, the hazenite was directly precipitated from the washing water (one-step precipitation) without the preceding precipitation of ammonium. In these experiments, the conditions were equal (a Mg:K:PO<sub>4</sub> of 1:1:1, a pH of 11 and a mixing rate of 50 rpm).

The removal of potassium, magnesium and phosphate in the one- and two-step precipitation procedures is presented in Fig. 1. Similar precipitation efficiencies for potassium were observed at 54% and 56% for

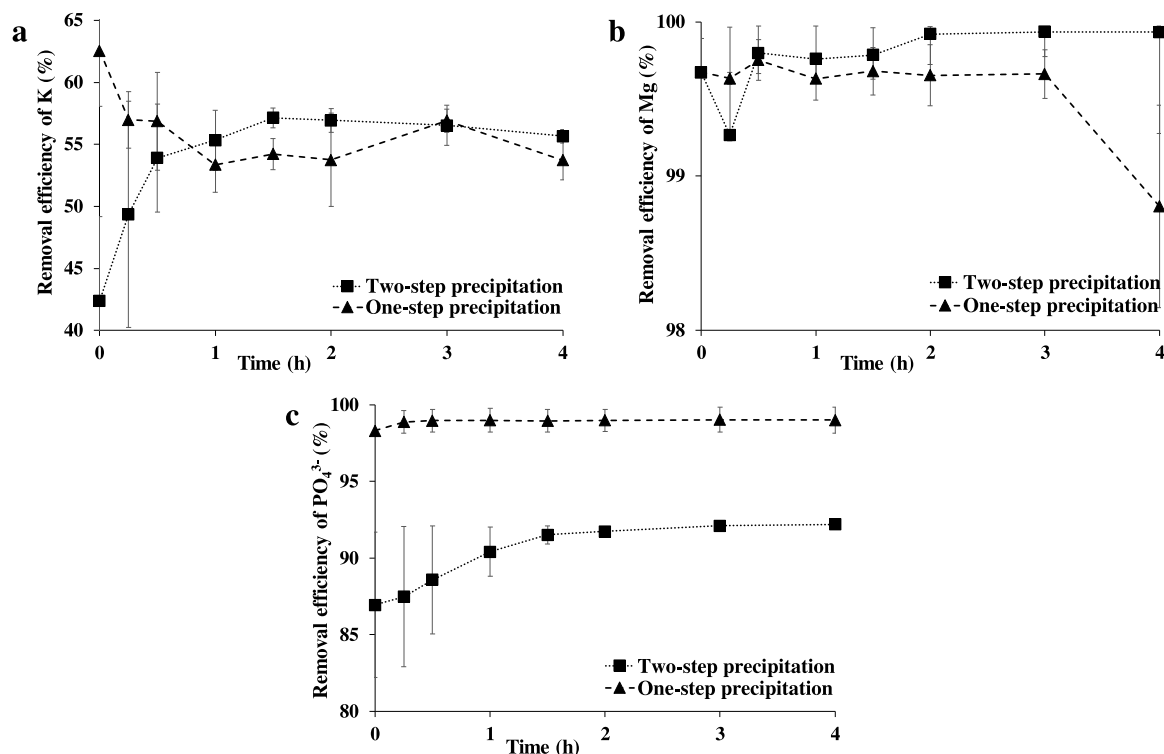


Fig. 1. Removal efficiency of potassium (a), magnesium (b), and phosphate (c) in one-step (hazenite) and two-step (struvite + hazenite) precipitations (Mg:K:PO<sub>4</sub> 1:1:1, pH 11 and 50 rpm).

the one-step and two-step precipitations, respectively; ammonium's presence in the washing water did not affect the precipitation of the potassium. This is probably because the ammonium concentration was very small (340 ppm) compared to the concentrations of potassium (6900 ppm) and sodium. Based on previous studies, a high potassium content and low ammonium content favor K-struvite formation instead of struvite formation [11,12]. Similar observations were also made in the case of phosphate (the removal efficiencies were 92% and 99% for the two-step and one-step precipitations) and magnesium (the removal efficiencies were over 98.8% for the two-step and one-step precipitations). Based on XRD analysis (not presented), the precipitates obtained from struvite precipitation contained mostly K-struvite (76–99.9%) and a little struvite (0–23.2%). Since ammonium did not influence potassium removal, direct hazenite precipitation was performed in the later stages of the research.

### 3.2. Effect of pH

The effect of pH on the precipitation of hazenite was studied in the pH range of 9.5–12 using Mg:K:PO<sub>4</sub> 1:1:1 and a mixing rate of 250 rpm. The removal efficiencies for potassium, magnesium and phosphate are presented in Fig. 2. As can be seen in Fig. 2, the pH had no effect on the precipitation efficiency. For potassium, the removal efficiency was 60%–65%. In addition, in the case of magnesium and phosphate, similar observations were made. The total removal efficiency was 98.5%–100% for magnesium and 96%–99% for phosphate. Kinetically, the precipitation was very fast at all pH values, as the reaction occurred during the first 15 min.

There are no studies in the literature on the effect of pH on hazenite precipitation. Since hazenite is naturally found in alkaline conditions (at pH 10), it will also precipitate at high pH values, like other struvite group compounds [3,4]. Generally, potassium removal efficiency increases significantly at high pH values due to the dissociation of H<sub>2</sub>PO<sub>4</sub><sup>-</sup> to HPO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup> [1,13,14]. The increased PO<sub>4</sub><sup>3-</sup> concentration increases the precipitation of potassium as phosphate compounds, such as

K-struvite and hazenite. As the pH rises above 11, the formation of magnesium hydroxide [15] could weaken the efficiency of potassium precipitation, but this was not observed in this study. If the pH drops below 11, the formation of K-struvite slows down and struvite may begin to form, with an optimum precipitation pH of 8–9 [2].

Based on the XRD analysis (Fig. 3), all main peaks were associated with hazenite regardless of the pH value, conforming the results of removal efficiencies (Fig. 2). This indicates that hazenite precipitates in a wide pH range under alkaline conditions.

### 3.3. Effect of temperature

The effect of temperature on precipitation efficiency was studied at temperatures of 10–40 °C (Fig. 4). Based on the results, temperature does not seem to have any impact on precipitation efficiency. Under the given conditions (a pH of 11, 250 rpm and a Mg:K:PO<sub>4</sub> of 1:1:1), the removal efficiencies were 60%, 99.7%–99.9% and 97.3%–99% for potassium, magnesium and phosphate, respectively, after four hours of precipitation. The precipitates obtained at different temperatures were pure hazenite (Fig. 5).

For struvite precipitation, temperature has a less significant effect than pH or molar ratio [16]. However, the solubility of struvite increases with increasing temperature until a temperature of around 35 °C [16–18]. At higher temperatures, the solubility once again decreases. Tarragó et al. (2017) reported that the optimum temperature for K-struvite formation would be 38 °C [19]. Our results indicate that hazenite precipitation is not dependent on temperatures under the 10–40 °C temperature range. Generally, lower precipitation temperatures should be preferred to avoid the high energy consumption caused by heating.

### 3.4. Effect of Mg:K:PO<sub>4</sub> ratio

The effect of molar ratios on precipitation efficiency was studied with molar ratios Mg:K:PO<sub>4</sub> (1.0–1.5):1:(1.0–1.5) (Fig. 6). The

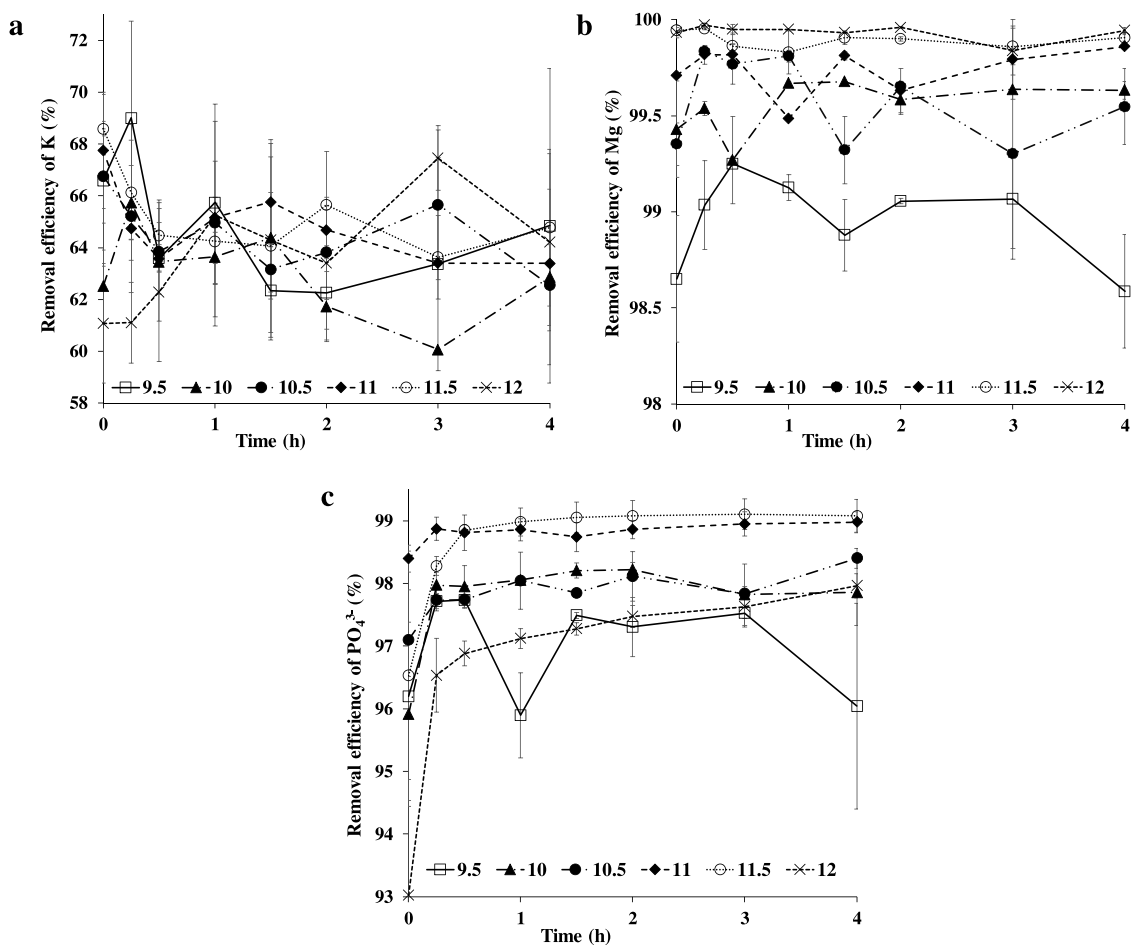


Fig. 2. Removal efficiency of potassium (a), magnesium (b), and phosphate (c) as a function of pH (Mg:K:PO<sub>4</sub> 1:1:1 and 250 rpm). Initial concentrations for K: 6900 ppm, Mg: 4750 ppm and PO<sub>4</sub><sup>3-</sup>: 17,000 ppm.

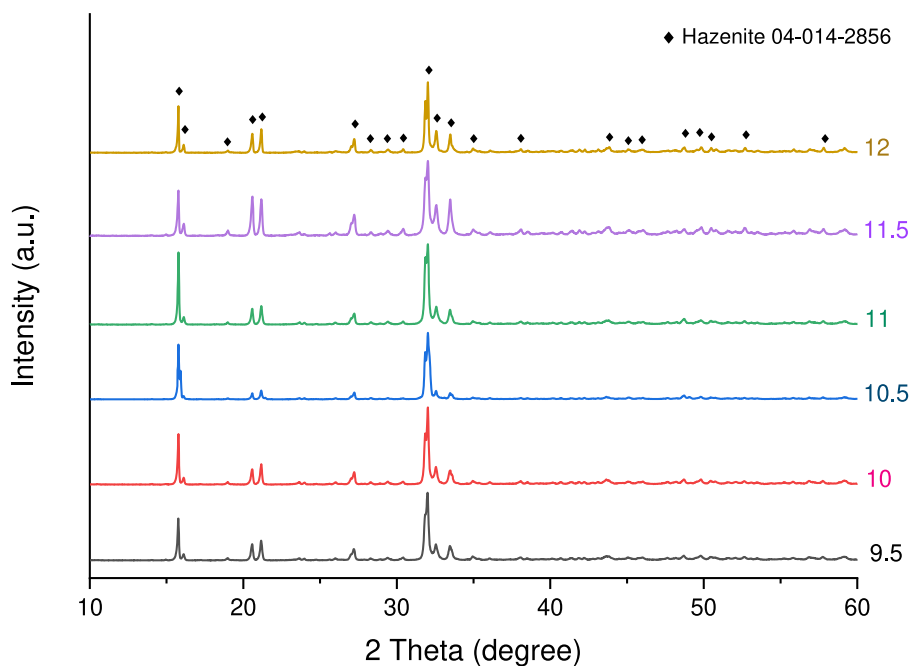


Fig. 3. XRD diffractograms of the samples precipitated at different pH values.

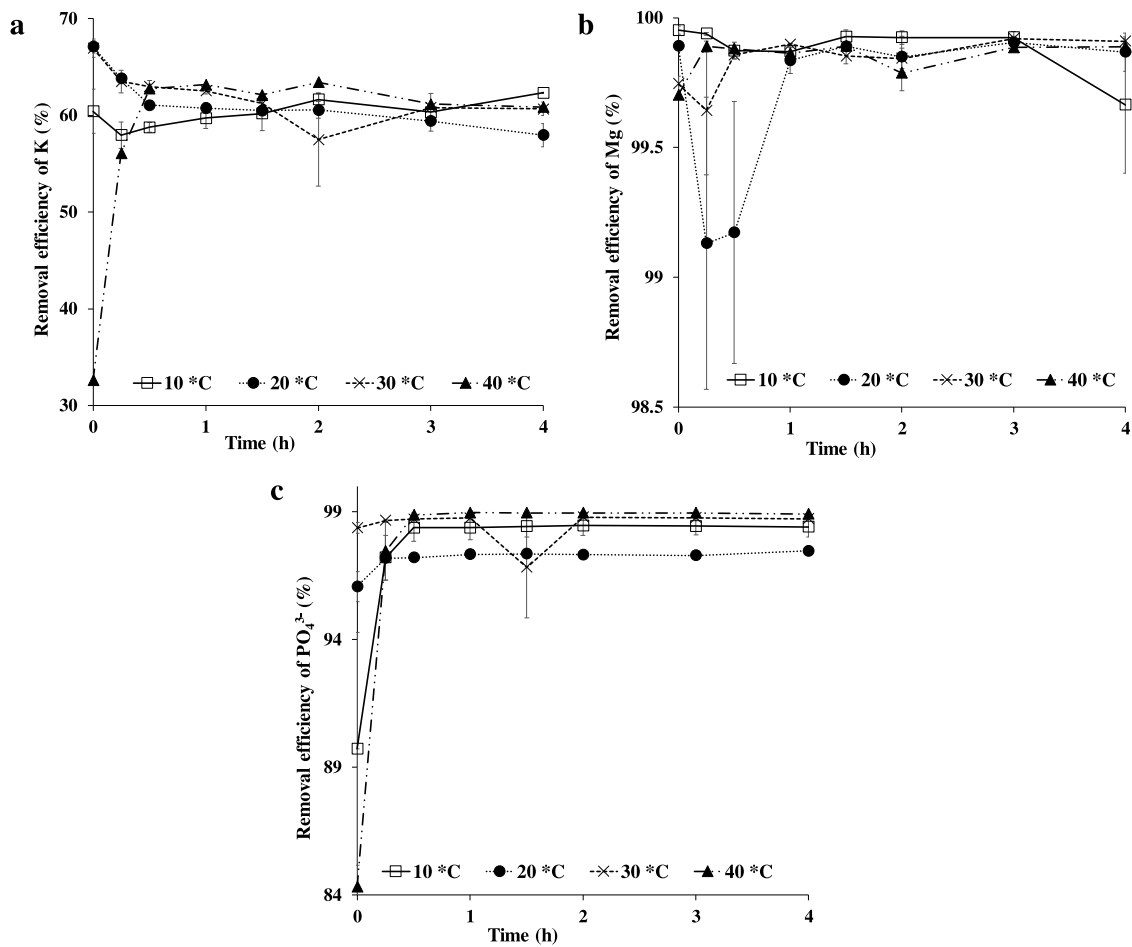


Fig. 4. The effect of temperature on the removal efficiency of potassium (a), magnesium (b) and phosphate (c) (Mg:K:PO<sub>4</sub> 1:1:1, pH 11 and 250 rpm). Initial concentrations for K: 7100 ppm, Mg: 4750 ppm and PO<sub>4</sub><sup>3-</sup>: 17,000 ppm.

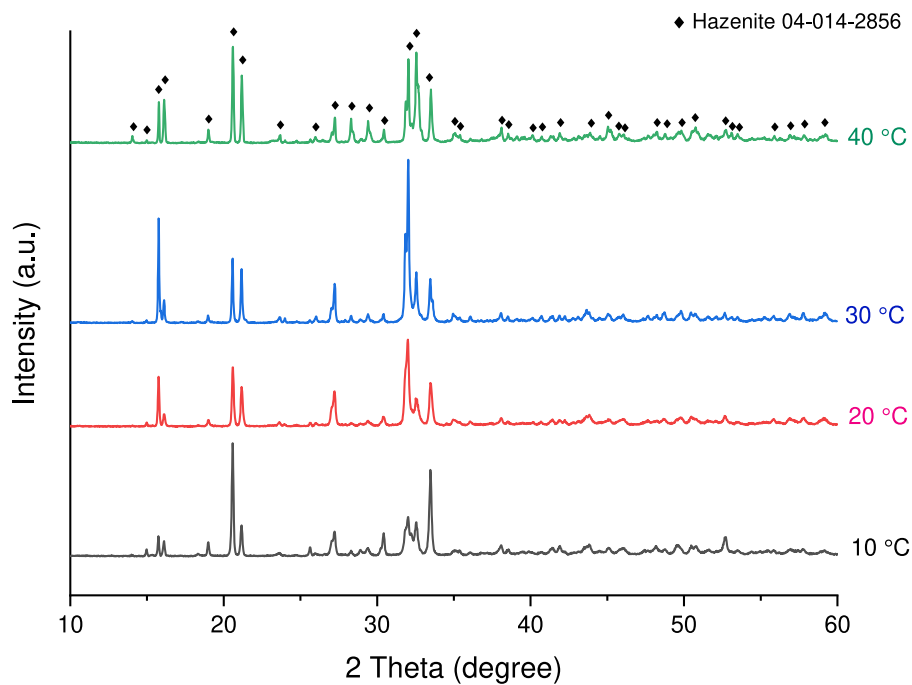


Fig. 5. XRD diffractograms of the samples precipitated at different temperatures.

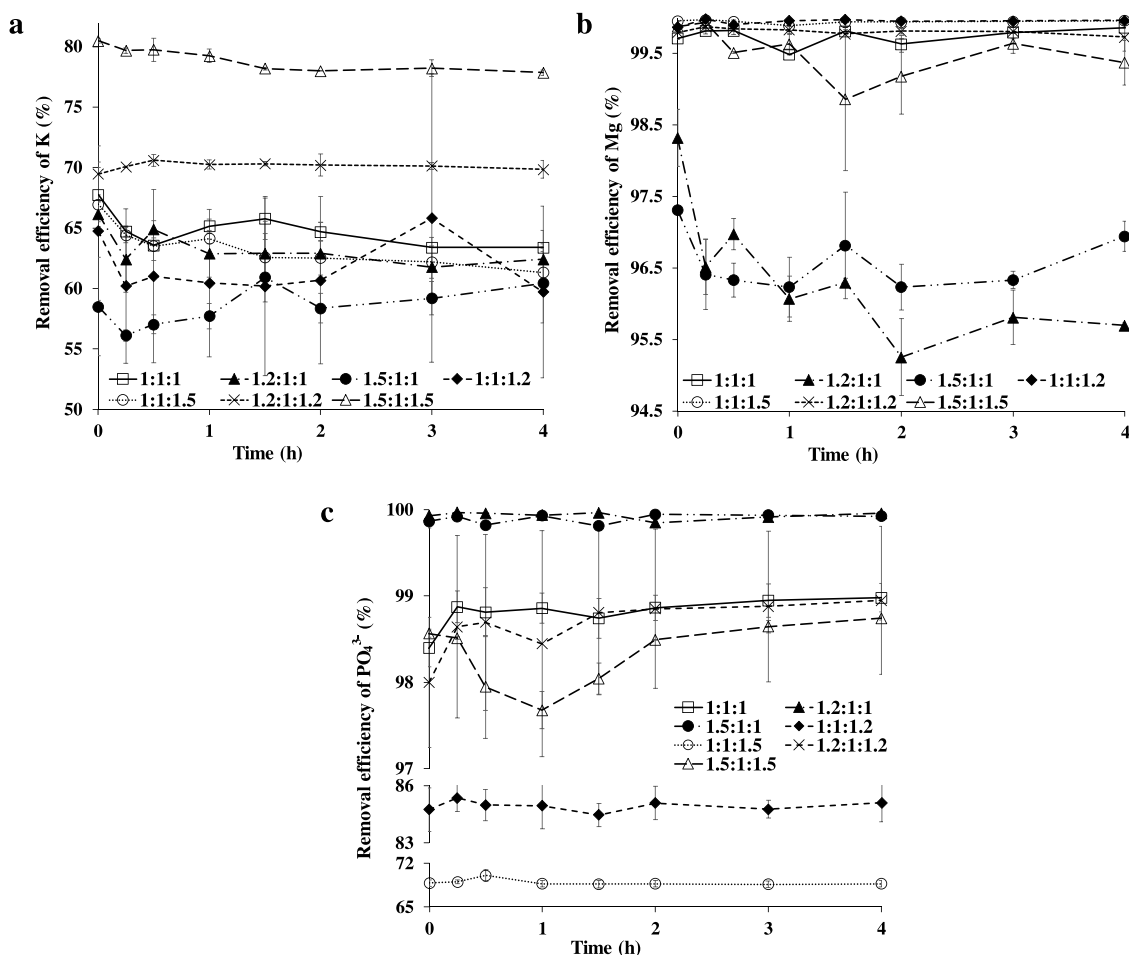


Fig. 6. Removal efficiency of potassium (a), magnesium (b) and phosphate (c) with different molar ratios Mg:K:PO<sub>4</sub> (250 rpm and pH 11).

potassium precipitation efficiency increased from 63.4% to 78% when the molar ratio of Mg:K:PO<sub>4</sub> changed from 1:1:1 to 1.5:1:1.5. Thus, the more magnesium and phosphate salts were added to the washing water, the more potassium was removed. However, if there was an excess of only one component (magnesium or phosphate), it did not improve the removal of potassium from the washing water.

The excess of phosphate or magnesium and phosphate had little effect on the magnesium removal rate, as it was over 99% (Fig. 6a). When excess magnesium was present, 95.7% (Mg:K:PO<sub>4</sub> = 1.2:1:1) and 96.9% (Mg:K:PO<sub>4</sub> = 1.5:1:1) of the magnesium were removed. Phosphate removal efficiencies (see Fig. 6c) were similar when the precipitations were performed with a 1:1:1 molar ratio of Mg:K:PO<sub>4</sub> and a simultaneous excess of magnesium or phosphate and magnesium. In all these precipitates, more than 98.5% of the phosphate was removed. When magnesium was present in excess, the percentage of phosphate removal was slightly (about 1%) higher than with Mg:K:PO<sub>4</sub> molar ratios of 1:1:1, 1.2:1:1.2 or 1.5:1:1.5. Thus, excess magnesium slightly increased the removal of phosphate from the washing water. At molar ratios of Mg:K:PO<sub>4</sub> of 1:1:1.2 and 1:1:1.5, about 85% and 69% of the phosphate were removed, respectively. The amount of phosphate added in excess remained in the washing water and did not precipitate.

Theoretically, potassium should be removed completely from washing water when the Mg:K:PO<sub>4</sub> molar ratio is 1:1:1. Xu et al. (2011) studied the removal of potassium and phosphate as K-struvite from synthetic urine and found that the concomitant excess of magnesium and phosphate increased the removal of potassium [13]. However, an excess of magnesium and phosphate that is too high can cause the precipitation of Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>. Excess phosphate (without excess Mg) leads to residual phosphate in the filtrate.

Gao et al. (2018) also studied synthetic urine and concluded that excess magnesium increased phosphate removal [14]. However, these results contradict the results of Xu et al. (2011), in which excess magnesium reduced potassium removal, increased the amount of precipitate and decreased its purity [13]. They also found that excess phosphate decreased phosphate removal efficiency but slightly increased potassium removal efficiency. However, excess phosphate did not play a major role in the amount or purity of the K-struvite formed. The simultaneous excess of phosphate and magnesium increased the phosphate's and potassium's removal efficiencies. The highest potassium removal efficiency (78.1%) was achieved with a Mg:K:PO<sub>4</sub> molar ratio of 1.8:1:1.8 when the pH of the solution was 11. However, in their study the simultaneous excess of phosphate and magnesium increased the precipitate formed but decreased its purity due to the formation of trimagnesium phosphate.

The XRD patterns of precipitates at different molar ratios are shown in Fig. 7. All the main spikes were associated with hazenite. The precipitates formed with different molar ratios Mg:K:PO<sub>4</sub> were also characterized using XRF (Table 3). The precipitates were nearly pure hazenite, excluding the experiment with excess Mg (molar ratio 1.5:1:1), where unreacted MgSO<sub>4</sub> was also present. This explains the higher-than-expected Mg removal observed using this molar ratio.

#### 4. Conclusions

Crushed and sieved alkaline battery black mass was washed with water, and this filtered washing water containing potassium and ammonium was treated by removing potassium using phosphate and magnesium salts. The precipitation efficiencies for potassium were

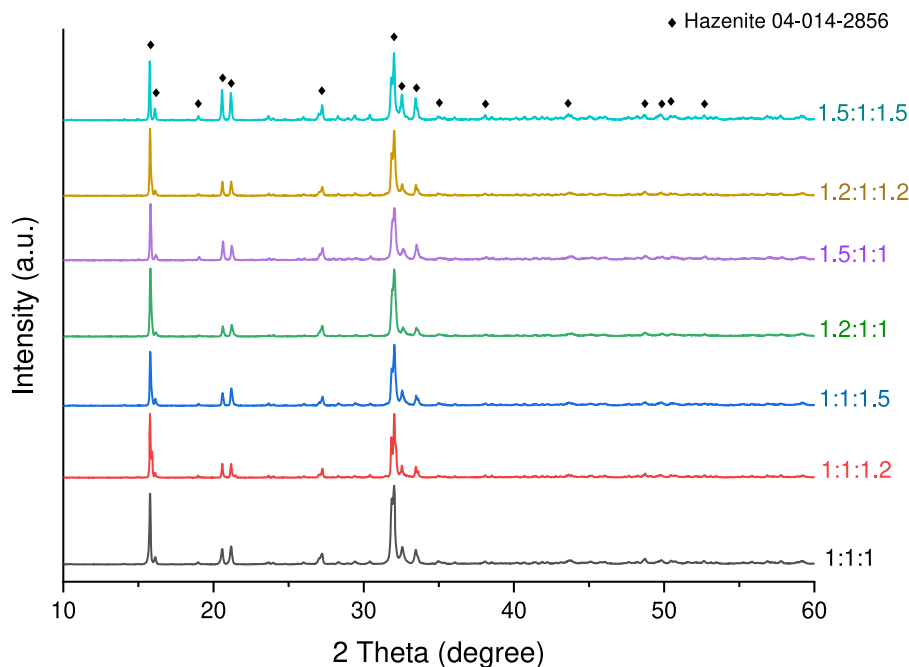


Fig. 7. XRD diffractograms of the samples precipitated at different molar ratios of Mg:K: PO<sub>4</sub>.

Table 3

Composition of the precipitates at different molar ratios measured with XRF.

Molar ratio Mg:K: PO <sub>4</sub>	Hazenite (%)	Na <sub>2</sub> O (%)	MgO (%)	P <sub>2</sub> O <sub>5</sub> (%)	SO <sub>3</sub> (%)	Cl (%)	CaO (%)
1:1:1	98.483	0.00	0.00	0.40	0.73	0.14	0.19
1.2:1:1	98.391	0.00	0.02	0.29	0.88	0.11	0.20
1.5:1:1	89.528	0.56	4.32	0.38	4.49	0.44	0.19
1:1:1.2	98.606	0.00	0.00	0.64	0.40	0.08	0.19
1:1:1.5	98.635	0.00	0.00	0.51	0.50	0.09	0.18
1.2:1:1.2	98.174	0.00	0.00	0.80	0.65	0.09	0.21
1.5:1:1.5	96.069	0.54	0.08	2.17	0.77	0.10	0.21

typically 60–65%, and hazenite was formed. The simultaneous excess of magnesium and phosphate increased the potassium removal efficiency to 78%. When precipitation was performed at different pH values, there was no difference in potassium removal efficiencies. Further, an excess of magnesium or phosphate or different temperatures did not affect the potassium removal rate. Thus, it can be concluded that hazenite precipitates over a wide pH range, but if the pH is alkaline, it does not require excess magnesium or phosphate or heating during precipitation. In addition, the precipitation is kinetically fast, and short reaction times are enough. There was no need to remove ammonium ions from the washing water prior to hazenite precipitation, as ammonium did not inhibit hazenite formation. Even though, the excess amount of magnesium and phosphate improved the removal efficiency of potassium, the optimal conditions for the precipitation of hazenite from washing water would be room temperature at pH 9.5, without the addition of excess magnesium or phosphate. This would mean that the consumption of chemicals and energy would be minimized. Hazenite can be used as a fertilizer, but it is a relatively new compound that has not been studied in depth. Therefore, more research is needed on hazenite precipitation and its use as a fertilizer.

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#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

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