Leaching of rare earth elements and base metals from spent NiMH batteries using gluconate and its potential bio-oxidation products

Payam Rasoulnia *, Robert Barthen, Jaakko A. Puhakka, Aino-Maija Lakaniemi 1

Tampere University, Faculty of Engineering and Natural Sciences, P.O. Box 541, FI-33104 Tampere, Finland

1. Introduction

Rare earth elements (REEs) are critical materials of high economic importance with high risk of supply disruption (Barteková and Kemp, 2016). In order to overcome the environmental and supply challenges related to REEs extraction from virgin ores, recycling end-of-life products such as spent nickel-metal-hydride (NiMH) batteries is of great importance (Omodara et al., 2019), as e.g. spent NiMH batteries are important secondary sources of a variety of REEs and base metals such as Ni, Co and Mn (Innocenzi and Vegliò, 2012; Meshram et al., 2016). Together with the worldwide growth of electronic devices, the amount of spent NiMH batteries is expected to rise significantly in the coming years (Innocenzi et al., 2017; Rodrigues and Mansur, 2010). If disposed untreated, spent NiMH batteries are a hazardous waste material due to their high metal content (Innocenzi et al., 2017). However, the current physico-chemical methods for recycling spent NiMH batteries are complex, energy intensive, costly and inefficient at simultaneous recovery of base metals and REEs (Su et al., 2020; Zhang et al., 2020). Previous leaching studies on spent NiMH batteries have been focusing on the use of inorganic acids with high temperatures (Innocenzi et al., 2017; Zielinski et al., 2020), while metal leaching using organic acids under mild operational conditions can offer several advantages such as being more cost-efficient and less harmful to the environment, as well as enhancing overall dissolution through contribution of complexation promoted leaching mechanism in addition to proton mediated dissolution (Brisset et al., 2016; Lazo et al., 2017).

Heterotrophic microorganisms are capable of production of a variety of organic acids using organic carbon sources such as glucose (Hople et al., 2018; Rasoulnia et al., 2020). One example of a heterotrophic organism shown to be capable of leaching REEs from secondary metal sources such as fluid catalytic cracking (FCC) catalysts is Gluconobacter oxydans (Reed et al., 2016; Thompson et al., 2018). G. oxydans produces gluconate via oxidation of glucose using membrane-bound glucose dehydrogenase and the produced gluconate can be further oxidized to 2-ketogluconate and 5-ketogluconate during bacterial cultivation (Gupta et al., 2001; Hölscher et al., 2009). Other microorganisms such as Pseudomonas aeruginosa, Pseudomonas putida and Enterobacter intermediate have been also studied for production of gluconate and/or 2-ketogluconate and 5-ketogluconate during bacterial cultivation (Gupta et al., 2001; Hölscher et al., 2009). Other microorganisms such as Pseudomonas aeruginosa, Pseudomonas putida and Enterobacter intermediate have been also studied for production of gluconate and/or
ketogluconates for metal solubilization from various sources, however these studies did not systematically compare the leaching efficiency of the individual compounds (Hassanien et al., 2014; Hwangbo et al., 2003; McKenzie et al., 1987; Shin et al., 2015). Depending on the cultivation conditions, different ratios of gluconate and its keto-derivatives may exist in the culture supernatants of these microorganisms. Gluconate is a monocarboxylic compound and possesses five hydroxyl groups. In both 2-ketogluconate and 5-ketogluconate, one of these hydroxyl groups has been oxidized to a keto group (Fig. 1) (Nelson and Essington, 2005; Zhang et al., 2009). Furthermore, these three compounds show different acidities; gluconate, 2-ketogluconate and 5-ketogluconate have pK\textsubscript{a} values of 3.41, 2.66 (Kim et al., 2002) and 3.24 (calculated value based on ChemAxon, as experimental value is not available), respectively. As a result of the differing structural properties, metal complexation and mobilization capabilities of these organic leaching agents may also differ.

The effects that bio-oxidation of gluconate to its keto-derivatives has on the leaching of either REEs or base metals from any type of metal source has not been previously studied, although this may have significant impact on the leaching efficiency. Therefore, in the present study, a set of batch leaching experiments using gluconate, 2-ketogluconate, 5-ketogluconate and their various combinations under controlled and uncontrolled pH conditions was performed to address the following research questions:

1. How do gluconate and its bio-oxidation products 2-ketogluconate and 5-ketogluconate affect REE and base metal leaching from spent NiMH batteries?
2. Do the structural differences of the different leaching agents influence their metal dissolution capability?
3. How does metal leaching capability of the different leaching agents vary with pH?
4. How do complexation and proton promoted leaching mechanisms contribute to metal dissolution under different pH conditions and what are the attainable leaching yields?

Furthermore, practical implication for developing a bioleaching process using \textit{G. oxydans} as an example microorganism with the capability of oxidizing gluconate was discussed.

### 2. Materials and methods

#### 2.1. Elemental composition of the spent NiMH battery powder

The spent NiMH battery powder was provided by AkkuSer Oy, a battery recycling company located in Finland. Prior to use in the leaching experiments, the sample was thoroughly mixed and sieved to a grain size of less than 630 \(\mu\)m. In order to determine the elemental composition, the sample was digested using aqua regia solution, composed of a 4 to 1 volume ratio of concentrated HCl and HNO\textsubscript{3}. The weight percentages of the main elements present in the spent NiMH battery were as demonstrated in Fig. 2a. Among the REEs, La (10 wt%), Ce (6 wt%) and Nd (3 wt%) were the most abundant elements (Fig. 2b). Furthermore, the sample contained 29.3 ± 3.3, 0.7 ± 0.2 and 5.0 ± 0.7 wt% of C, H and N, respectively.

#### 2.2. Leaching of spent NiMH battery

Chemical leaching of base metals and REEs from spent NiMH batteries were studied using D-gluconic acid sodium salt, 2-keto-D-gluconic acid hemicalcium salt and 5-keto-D-gluconic acid potassium salt (Sigma-Aldrich). The leaching experiments were carried out in 50 ml polypropylene tubes containing 20 ml of the solutions with 1% (wt/v) pulp density of the spent NiMH battery powder at 27 ± 1°C and 150 rpm for 14 days. In the leaching experiments without pH adjustment, individual salts and their various combinations were used at a total concentration of 60 mM (Table 1). Furthermore, the effect of pH on metal leaching using each organic leaching agent was studied by adjusting pH at three different levels of 3.0 ± 0.1, 6.0 ± 0.1 and 9.0 ± 0.1, keeping the leaching agent concentration at 60 mM (Table 1). The pH was adjusted to the target range every 2–4 days using nitric acid or sodium hydroxide. Control samples were prepared using 1% (wt/v) pulp density of the spent NiMH battery powder and ultrapure water without any of the leaching agents.

#### 2.3. Analytical methods

The pH was measured using a pH meter (3110, WTW, Germany) equipped with a Hamilton Slimtrode electrode. The concentrations of the metals in the leaching liquors were measured using inductively coupled plasma mass spectrometry (iCAP RQ ICP-MS, Thermo Scientific, USA) from samples filtered through 0.45 \(\mu\)m disposable syringe filters.
The effects of the different leaching agents on metal dissolution were further studied under controlled pH conditions using individual solutions of gluconate, 2-ketogluconate, and 5-ketogluconate and by regularly adjusting pH to target values of 3.0 ± 0.1 or 9.0 ± 0.1. At target pH of 9.0 ± 0.1, the pH of gluconate leaching solution remained almost stable at the target level, while with 2-ketogluconate and 5-ketogluconate the pH decreased to as low as 7.5 ± 0.2 and 6.3 ± 0.1, respectively (Fig. 5). When the target pH was 6.0 ± 0.1, leaching with gluconate and 2-ketogluconate resulted in similar pH changes from 6.0 ± 0.1 to 5.0 ± 0.1. At target pH of 3.0 ± 0.1, the pH varied similarly from 3.0 ± 0.2 to 5.5 ± 0.3 with gluconate and 2-ketogluconate, while equipped with a thermal conductivity detector was utilized to determine the carbon, hydrogen and nitrogen content of the spent NiMH battery sample. Helium at a flow rate of 140 ml/min was used as carrier gas. Oven and furnace temperature were 65 °C and 950 °C, respectively. Cystine was used as standard for the measurements.

3. Results

3.1. Leaching of base metals and REEs under uncontrolled pH conditions

In the first part of this study, chemical leaching of spent NiMH batteries was performed without pH control using either individual solutions of gluconate, 2-ketogluconate, and 5-ketogluconate or their various combinations. Among the studied leaching agents, 5-ketogluconate resulted in the highest pH decrease from 9.7 ± 0.3 to 5.3 ± 0.2 during the 14-day leaching. With 2-ketogluconate and gluconate solutions, the pH reduced from 8.9 ± 0.2 to 7.5 ± 0.2 and from 10.2 ± 0.2 to 9.6 ± 0.2, respectively (Fig. 3a). Thus, with gluconate the pH remained higher than with the ketogluconates during the whole leaching period. The pH changes with the mixtures of the tested organic acid salts were within the ranges observed with the individual compounds (Fig. 3b). The pH of the ultrapure water controls decreased from 10.5 ± 0.2 to 10.2 ± 0.2 within 14 days (Fig. 3b). The pH of the control samples as well as the initial pH values in the leaching experiments revealed the alkaline nature of the spent NiMH batteries.

Based on the analyzed base metal and REE dissolution yields, 5-ketogluconate mobilized base metals more efficiently from the spent NiMH battery powder than the other two leaching agents, whereas gluconate resulted in higher REE extraction yields (Fig. 4a and b). After 14 days, 5-ketogluconate resulted in dissolution of 10.0% Mn, 7.0% Co, 1.0% Ni, 12.5% Cu and 5.5% Zn. The Cu leaching yields with 2-ketogluconate and gluconate were 19.5% and 8.5%, while the leaching yields of Mn, Co and Ni remained below 1.5% and 1.0%, respectively (Fig. 4a). Gluconate was the most efficient leaching agent at dissolving REEs with yields of 35.0% Y, 2.0% La, 3.0% Ce, 2.5% Pr, 3.0% Nd, 2.5% Sm, 3.5% Gd, 14.0% Er and 13.5% Yb (average total REE yield of 8.8%). The REE leaching yields with 5-ketogluconate remained below 3.0% except for Y, the yield of which was 6.5%. Similarly, REE leaching yields of less than 1.5% (except 3.5% for Y) were obtained with 2-ketogluconate (Fig. 4b).

Fig. 4c and d show the base metal and REE dissolution yields obtained with various combinations of the organic acid salts. The mixture of gluconate and 2-ketogluconate (glu-2keto), resulted in the lowest base metal leaching yields (Fig. 4c). In the case of REEs, the mixture of gluconate and 5-ketogluconate (glu-5keto) enabled a higher leaching yield compared to the other combinations (Fig. 4d). This was consistent with the obtained REE leaching yields by the individual organic acid salts: gluconate > 5-ketogluconate > 2-ketogluconate. The considerably lower REE and base metal leaching yields of ultrapure water controls confirmed that the interaction between the organic leaching agent and the metals within the spent NiMH battery were responsible for the observed chemical leaching of elements.

3.2. Leaching of base metals and REEs under controlled pH conditions

Table 1
Leaching solutions and the pH conditions used in this study.

<table>
<thead>
<tr>
<th>Leaching solution (mM)</th>
<th>pH</th>
<th>Abbreviation</th>
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<tbody>
<tr>
<td>Na-gluconate (60)</td>
<td>3.0 ± 0.1</td>
<td>glu-pH3</td>
</tr>
<tr>
<td>1/2Ca – 2-ketogluconate (60)</td>
<td>3.0 ± 0.1</td>
<td>2keto-pH3</td>
</tr>
<tr>
<td>K-5-ketogluconate (60)</td>
<td>6.0 ± 0.1</td>
<td>glu-pH4</td>
</tr>
<tr>
<td>Na-gluconate (60)</td>
<td>6.0 ± 0.1</td>
<td>glu-pH6</td>
</tr>
<tr>
<td>1/2Ca – 2-ketogluconate (60)</td>
<td>6.0 ± 0.1</td>
<td>2keto-pH6</td>
</tr>
<tr>
<td>Na-gluconate (60)</td>
<td>9.0 ± 0.1</td>
<td>glu-pH9</td>
</tr>
<tr>
<td>1/2Ca – 2-ketogluconate (60)</td>
<td>9.0 ± 0.1</td>
<td>2keto-pH9</td>
</tr>
<tr>
<td>K-5-ketogluconate (60)</td>
<td>9.0 ± 0.1</td>
<td>glu-pH9</td>
</tr>
<tr>
<td>Na-gluconate (60)</td>
<td>9.0 ± 0.1</td>
<td>glu-pH9</td>
</tr>
<tr>
<td>K-5-ketogluconate (60)</td>
<td>9.0 ± 0.1</td>
<td>glu-pH9</td>
</tr>
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(CHROMAFIL® Xtra PET-45/25, Germany) and diluted 100-fold using 2% ultrapure nitric acid. Rhodium and germanium were employed as internal standards and to decrease interferences during measurements, ICP-MS analyses were conducted in kinetic energy discrimination mode. A Flash Smart elemental analyzer (Flash 2000, Thermo Scientific, USA)
with 5-ketogluconate the pH stabilized close to pH 3.0 ± 0.2 after 5 days (Fig. 5a).

At both target pH of 6.0 ± 0.1 and 9.0 ± 0.1, gluconate and 2-keto glucuronate showed no superiority over each other for base metal leaching (Fig. 6b, c). However, at target pH of 6.0 ± 0.1, 2-ketogluconate enabled higher leaching efficiencies for Cu (21.9%) and Zn (8.7%) than glucuronate and 5-ketogluconate. Leaching experiments of the spent NiMH batteries at target pH of 6.0 ± 0.1 and 9.0 ± 0.1 revealed that similar to the experiments without pH control, base metals were more efficiently dissolved using 5-ketogluconate. Moreover, comparison of the obtained dissolution yields with the different leaching agents at target pH of 6.0 ± 0.1 and 9.0 ± 0.1 revealed that the base metal leaching yields were lower under the more alkaline pH conditions. Among all the tested leaching agents at target pH of 6.0 ± 0.1 and 9.0 ± 0.1, 5-ketogluconate at target pH of 6.0 ± 0.1 enabled the highest base metal leaching yields: 10.8% Mn, 0.7% Fe, 8.5% Co, 1.0% Ni, 17.3% Cu and 5.8% Zn. Further decrease of pH to the acidic target pH of 3.0 ± 0.1 led to a considerable increase in the base metal leaching yields with all the studied leaching agents, revealing the significant role of proton promoted metal dissolution. The highest base metal leaching yields at target pH 3.0 ± 0.1 were obtained using gluconate and were: 100.0% Mn, 90.3% Fe, 89.5% Co, 58.5% Ni, 24.0% Cu and 29.3% Zn (Fig. 6a). However, the Cu leaching yield with gluconate at target pH of 3.0 ± 0.1 was lower than with both 2-ketogluconate and 5-ketogluconate. This result was in contrast to the leaching behavior of all the other elements at this pH, but the reason remains unknown.

At all studied pH conditions, gluconate showed higher REE leaching yields compared to 2-ketogluconate and 5-ketogluconate (Fig. 7a-c). The obtained REE leaching yields at target pH of 6.0 ± 0.1 were in the order of gluconate > 2-ketogluconate > 5-ketogluconate, while at target pH of
9.0 ± 0.1 the order was: gluconate > 5-ketogluconate > 2-ketogluconate. Comparison of the obtained REE leaching yields by gluconate at the different pH levels demonstrated that with decreasing pH, the leaching efficiencies were increased considerably. The average total REE leaching yields at target pH of 9.0 ± 0.1, 6.0 ± 0.1 and 3.0 ± 0.1 were 7.8%, 11.5% and 56.1% respectively. The REE and base metal leaching yields obtained with H₂O controls revealed that dissolution increased with pH decrease and confirmed the significant role of the organic
4. Discussion

This study revealed the potential impacts of bio-oxidation of gluconate to its keto derivatives on REE and base metal leaching from spent NiMH batteries. Gluconate at target pH of 3.0 ± 0.1 resulted in the highest overall REE and base metal leaching yields. While the use of gluconate resulted in higher REE leaching yields than its keto-derivatives under all the studied pH conditions, use of 5-ketogluconate enabled higher base metal leaching than gluconate and 2-ketogluconate at target pH 6.0 ± 0.1 and above. Depending on pH and type of the organic leaching agents, the REE and base metal leaching behaviors differed. Thus, practical implication of this phenomenon was evaluated for a situation where bioleaching would be conducted using a microorganism with the capability of producing and further oxidizing gluconate, e.g. *G. oxydans*.

4.1. Effect of the leaching pH

The lower the pKₐ value of the acid, the stronger the acid is (Qin et al., 2018). The observed initial pH of the respective leaching solutions which contained the same concentration of the organic acid and the spent NiMH battery material are consistent with the pKₐ values of the leaching agents. The initial pH of spent NiMH battery containing solutions of gluconate, 2-ketogluconate and 5-ketogluconate were 10.2 ± 0.2, 8.9 ± 0.2 and 9.8 ± 0.3 respectively (Fig. 3a), while the pKₐ values of gluconate, 2-ketogluconate and 5-ketogluconate are 3.41, 2.66 (Kim et al., 2002) and 3.24 (calculated value based on ChemAxon, as experimental value is not available), respectively. During leaching without pH control, the pH of the solution containing gluconate with a higher pKₐ value, remained higher than the pH of solutions containing its keto-derivatives. In case of 2-ketogluconate and 5-ketogluconate, unlike the initial pH values, the final pH did not correspond with the pKₐ values, as leaching with 5-ketogluconate, despite having a higher pKₐ, resulted in a lower final pH compared to 2-ketogluconate. This indicates that the final pH of the solution results not only from the properties of the applied leaching agent but also the elements dissolved from the leached material.

The leaching pH also affects the dominating leaching mechanism (Rasoulnia et al., 2020). Metal dissolution by organic molecules may proceed via complexolysis or acidolysis (Glombitza and Reichel, 2013; Rasoulnia et al., 2020). Both leaching mechanisms are competing reactions and a deprotonated molecule may interact differently with the metal than when the metal still has to displace the proton from the carboxylic group. Leaching under controlled pH conditions, enabled to assess the contribution of complexion and protonation promoted leaching mechanisms. Leaching at target pH of 6.0 ± 0.1 and 9.0 ± 0.1 enabled comparison of complexion-based leaching with the three organic leaching agents, as these pH values were higher than the pKₐ values of the leaching agents. Leaching at target pH of 3.0 ± 0.1, which is in the same range as the pKₐ values of the applied organic acids, enabled to evaluate the contribution of protonation of the organic acids to metal dissolution. The leaching results from the H₂O controls (Figs. 6d and 7d) clearly demonstrate the pH effect in leaching and show that acidolysis at target pH of 3.0 ± 0.1 is an important mechanism in NiMH battery dissolution, while at target pH values of 6.0 ± 0.1 and 9.0 ± 0.1 proton concentration seems to be too low to promote the dissolution of large amount of metals within the investigated time period.

4.2. The roles of organic acids in metal dissolution

While leaching with H₂O showed some dissolution at target pH 3.0 ± 0.1 and barely any dissolution at target pH values of 6.0 ± 0.1 and 9.0 ± 0.1, the addition of any of the three studied organic leaching agents led to a distinct increase in both base metal and REE leaching at all investigated pH values. This indicated a strong contribution of
complexation to the overall dissolution. However, the dominant mechanism (proton or complexation driven mechanism) depends on the type of leaching agent, the metal bearing source, pH and the target element (Rasoulnia et al., 2020). For a schematic representation of general processes during organic acid mediated REE leaching please see Rasoulnia et al. (2020). While interactions of nitrate (added for pH adjustment) with the battery powder cannot be ruled out completely, it is doubtful that nitrate contributed greatly to the dissolution as nitrate, unlike gluconate, forms only weak complexes with the metals (e.g., $\text{REE}^{3+} + \text{NO}_3^{-} \rightarrow \text{REE(NO}_3)_2^{2+}$ $\log K = 0.6 \pm 0.8$ vs $\text{REE}^{3+} + 2 (\text{C}_6\text{H}_5\text{O}_2)^{-} \rightarrow \text{REE(C}_6\text{H}_5\text{O}_2)_2^{2-}$ $\log K = 4.25 \pm 4.78$) (Martell and Smith, 1977; Smith and Martell, 1976). For a review see Rasoulnia et al. (2020).

With decreasing pH and increasing protonation of the organic leaching agents, complexation promoted dissolution is suppressed (Purrer and Stumm, 1986). However, the relative contribution of complexation and acidolysis to the overall dissolution process is different for each leaching agent. When gluconate and 2-ketogluconate were used, base metal and REE leaching yields increased when pH was decreased, while in the case of 5-ketogluconate, REE leaching yields were lower at pH 6.0 $\pm$ 0.1 than at 9.0 $\pm$ 0.1. This may indicate that for 5-ketogluconate, the dissolution enhancement due to higher proton availability caused by pH reduction from 9.0 $\pm$ 0.1 to 6.0 $\pm$ 0.1 did not compensate for the reduced contribution of complexation to REE dissolution. A further decrease of pH to 3.0 $\pm$ 0.1 led to the highest REE and base metal leaching yields for all the studied leaching agents, indicating an increasing contribution of proton promoted dissolution.

Leaching experiments at controlled target pH of 6.0 $\pm$ 0.1 and 9.0 $\pm$ 0.1 as well as those without pH control consistently showed that gluconate was more efficient in dissolving REEs, while 5-ketogluconate was more effective in leaching of the base metals. The higher REE leaching yields obtained with gluconate compared to the ketogluconates, despite having a higher pH, indicate that gluconate is more effective in forming stable complexes with REEs. The stability of metal complexes depends on the chemical structure of the ligand and its interaction with the metal ions (Ilyas and Lee, 2014; Shin et al., 2015). The stability of the complex increases with the denticity of the ligand (Janiak et al., 2012). Gluconate is comprised of one carboxylic group and five hydroxyl groups which can contribute to complexation. In 2-ketogluconate and 5-ketogluconate, one hydroxyl group is replaced by a keto group at the C2- and C5-position, respectively. It has been shown that in addition to the carboxylate group (COO$^-$), the C2-OH and C3-OH binding sites of gluconate interact with the REE ions (Giroux et al., 2000; Kutus et al., 2017; Taga et al., 1978; Zhang et al., 2007). Due to the involvement of the C2-OH group in complexation, it can be suspected that complexation behavior changes when this group is replaced by the keto group in 2-ketogluconate. In fact, it has been shown that metal coordination by the hydroxyl group is stronger than by the keto group (Yang et al., 2018). Furthermore, it has been demonstrated that the keto group in 2-ketogluconate positioned at C2 is not involved in complexation of trivalent metal ions of Al$^{3+}$ and Fe$^{3+}$ (Essington et al., 2005) and this might be relevant for REE complexation as well. In the structure of 5-ketogluconate, however, the carboxyl group is positioned at C5 and thus the C2-OH functional group is available for metal ion interactions as it is the case in gluconate. Therefore, it can be assumed that 5-ketogluconate shows higher complexation capability than 2-ketogluconate, similarly to gluconate. However, to the best of our knowledge, there is no research available discussing the interactions of 5-ketogluconate with metals. It can be postulated that both complexation and proton driven process contribute to metal leaching from NiMH batteries using gluconate and its oxidation products. While at target pH of 3.0 $\pm$ 0.1 both mechanisms contribute, metal complexation seems to be the main driver for dissolution at target pH of 6.0 $\pm$ 0.1 and 9.0 $\pm$ 0.1. As complexation becomes more relevant in the dissolution process, the molecular structures of the leaching agents become more important resulting in higher leaching yields of gluconate and 5-keto-gluconate compared to 2-ketogluconate.

4.3. Practical implications for bioleaching of REEs and base metals using *Gluconobacter oxydans*

In order to develop a heterotrophic bioleaching process utilizing *G. oxydans*, optimization of both biolixiviant production and the leaching step is required. *G. oxydans* produces gluconate via oxidation of glucose and the produced gluconate can be further oxidized to 2-ketogluconate and 5-ketogluconate (Höltcher et al., 2009). As gluconate and its bio-oxidation products 2-ketogluconate and 5-ketogluconate showed different base metal and REE dissolution properties, it is important to recognize the growth conditions which promote production of the desirable leaching agents depending on the target elements for the leaching. Based on our results, under acidic pH conditions, gluconate is the most efficient leaching agent enabling highest dissolution of both base metals and REEs. Under neutral and alkaline pH conditions, gluconate and 5-ketogluconate are the desirable leaching agents for dissolution of REEs and base metals, respectively.

It has been shown that the rate of ketogluconate production is strongly dependent on glucose concentration, pH and the applied buffering agent (Beschkov et al., 1995). When glucose concentration falls below the critical value of 15 mM, the production of ketogluconates has been shown to start (Beschkov et al., 1995; Weenk et al., 1984). The applied pH controlling agent also plays a decisive role in gluconate conversion to the ketogluconates. For example, utilization of CaCO$_3$ as buffer leads to accumulation of 5-ketogluconate due to the low solubility of calcium-5-ketogluconate which shifts the reaction equilibrium toward keto-acid production (Beschkov et al., 1995). In addition to the cultivation factors, enhanced production of the desired leaching agent is possible via use of genetically modified microorganisms. For example, selective production of 5-ketogluconate has been obtained by using a genetically engineered *G. oxydans* strain, in which 2-ketogluconate forming membrane-bound gluconate-2-dehydrogenase is inactivated and the gene coding for the enzyme producing 5-ketogluconate is overexpressed (Merfort et al., 2006). While the crucial role of glucose concentration and CaCO$_3$ addition to the medium in promotion of production of ketogluconates has been confirmed, there is no consensus for the pH effect and its optimum range (Beschkov et al., 1995; Elfari et al., 2005; Gupta et al., 2001; Weenk et al., 1984). Nevertheless, some studies have reported that pH of 5.0–5.5 favors oxidation of gluconate especially to 5-ketogluconate (Elfari et al., 2005; Weenk et al., 1984). As the optimum pH range for production of the desired leaching agent and metal dissolution might differ, specifying pH in one-step bioleaching, where bacterial growth and metal leaching phases are concurrent, is challenging. In order to overcome this issue, it is recommended to use spent-medium bioleaching process where the biolixiviant production and metal leaching are carried out separately.

High simultaneous leaching of base metals and REEs could be achieved with gluconate at target pH of 3.0 $\pm$ 0.1, whereas potential for selective leaching of base metals over REEs was demonstrated at target pH of 6.0 $\pm$ 0.1 with 5-ketogluconate. Thus, a possible approach for selective leaching of REEs and base metals could be application of a two-stage leaching procedure, where in the first stage the base metals are predominantly leached using 5-ketogluconate at pH 6.0 $\pm$ 0.1 followed by the next stage where REEs are leached using gluconate at acidic pH range. Two separate leaching steps would increase the capital and operating costs of the leaching, but could lead to lower-cost post-leaching metal recovery, as up to 60% of the overall metal production costs are associated with the down-stream separation processes (Thompson et al., 2018).

5. Conclusions

This study revealed that due to their structural differences, gluconate and its bio-oxidation products 2-ketogluconate and 5-ketogluconate show different REE and base metal leaching capabilities. The relative contribution of complexolysis and acidolysis to the overall dissolution
process is different for each leaching agent. Gluconate enables higher REE leaching yields than 2-ketogluconate and 5-ketogluconate under all the studied pH conditions, while 5-ketogluconate leaches more base from the REE leaching solutions in the pH range of 2–8. Dalt. Trans. 46, 6049–6058. https://doi.org/10.1039/c7fd00909g.


