Selenium recovery from kiln powder of cement manufacturing by chemical leaching and bioreduction
S. Soda, A. Hasegawa, M. Kuroda, A. Hanada, M. Yamashita and M. Ike

ABSTRACT
A novel process by using chemical leaching followed by bacterial reductive precipitation was proposed for selenium recovery from kiln powder as a byproduct of cement manufacturing. The kiln powder at a slurry concentration of 10 w/v% with 0.25 M Na₂CO₃ at 28°C produced wastewater containing about 30 mg-Se/L selenium. The wastewater was diluted four-fold and adjusted to pH 8.0 as preconditioning for bioreduction. A bacterial strain Pseudomonas stutzeri NT-I, capable of reducing selenate and selenite into insoluble elemental selenium, could recover about 90% selenium from the preconditioned wastewater containing selenium of 5 mg-Se/L when supplemented with lactate or glycerol. The selenium concentrations in the treated wastewater were low around the regulated effluent concentration of 0.1 mg-Se/L in Japan.

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Key words | biological reduction, cement manufacturing, chemical leaching, kiln powder, selenium

INTRODUCTION
The cement industry has been promoting the recycling of wastes, such as construction waste soil, coal ash, municipal waste incineration ash, and sewage sludge, as alternative raw materials and fuels (Usón et al. 2015). In the case of Japan, the unit usage of wastes and byproducts reached about 450 kg per 1,000 kg of cement in 2008 (Ministry of the Environment Government of Japan 2010). Consequently, the amount of volatile components, in particular, chlorine with an adverse effect on cement quality has increased in the kiln. Therefore, the chlorine bypass system is now equipped with the kiln-preheater for exhausting volatilized chlorine. In the treatment process by cooling the exhaust gas, the chlorine bypass dust called K (kiln) powder containing chlorine at 10–20 w/w% is generated (Sutou et al. 1999). Although K powder generates <0.1 w/w% of clinker, its generation is expected to increase with the amount of waste recycled in the cement industry.

Since it contains cement constituents such as calcium, silicon, aluminum, and iron, K powder is recyclable as a cement material after removing chlorine by washing (Ichitsubo et al. 2011a, b). However, the resulting wastewater contains toxic chemicals, such as selenium and lead in addition to chlorine. Selenium is contained in various wastes at low levels and gradually accumulated with chlorine in the kiln. A possible main form of selenium in K powder is CaSeO₃. Selenium exists in wastewater as selenium oxyanions. Although selenium is a minor metal and an essential micronutrient, it is toxic in large amounts. Selenium-containing wastewater is typically treated by coagulation of selenite (SeO₃²⁻) with ferric salt following electrochemical reduction of selenate (SeO₄²⁻) to selenite. The resulting chemical sludge containing selenium is discarded as industrial waste (Soda et al. 2012). Such physicochemical methods typically entails high costs.

A cost-effective alternative method for selenium removal from wastewater is biological reduction of soluble selenium, selenite and selenate, into elemental selenium (Se⁰) (Lenz & Lens 2009). Elemental selenium can be removed from the aqueous phase because of its insoluble characteristics (Kashiwa et al. 2000; Kagami et al. 2013). Therefore, it is desirable to recover selenium from K powder for metal resource conservation while satisfying the maximum concentration of selenium permissible in industrial wastewater (0.1 mg-Se/L in Japan).

In this study, a new treatment process by using chemical leaching followed by bacterial reductive precipitation is proposed for selenium recovery from K powder, as depicted in Figure 1. First, selenium in K powder is extracted by chemical leaching. The residue of K powder is returned to a
cement kiln. Lead leached with selenium from K powder can be easily removed from wastewater by conventional coagulation using NaSH. The resulting selenium-containing wastewater is preconditioned to adjust pH and salinity and nutrient conditions for bioreduction. Finally, selenium is recovered from the preconditioned wastewater by a selenium-reducing bacterium under aerobic conditions. This study demonstrated the feasibility of the proposed process by laboratory experiments.

**MATERIALS AND METHODS**

**K powder**

K powder used in this study was sampled at the Kumagaya Plant of Taiheiyo Cement Corporation. Elements in the K powder sample are shown in Table 1. Reportedly, K powder was mainly composed of Na$_2$SO$_4$, K$_2$SO$_4$, KCl, CaSO$_4$, CaO, SiO$_2$, 2CaO-SiO$_2$, 2CaO-Al$_2$O$_3$-SiO$_2$, 2CaO-Fe$_2$O$_3$, CaMg(CO$_3$)$_2$, Pb$_{10}$(SiO$_4$)$_3$(SO$_4$)$_3$Cl$_2$ and KCl$_2$-2PbCl$_2$ and its median size was about 12 μm (Ichitsubo et al. 2011a, b). Selenium, rubidium, cadmium, zinc, cesium, and titanium were also contained in the K powder sample.

**Table 1 | Elements in K powder used in this study (mg/kg)**

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>1.7 × 10$^5$</td>
</tr>
<tr>
<td>Ca</td>
<td>1.1 × 10$^2$</td>
</tr>
<tr>
<td>Pb</td>
<td>4.3 × 10$^4$</td>
</tr>
<tr>
<td>Na</td>
<td>1.0 × 10$^4$</td>
</tr>
<tr>
<td>Al</td>
<td>8.8 × 10$^3$</td>
</tr>
<tr>
<td>Rb</td>
<td>3.6 × 10$^3$</td>
</tr>
<tr>
<td>Cd</td>
<td>2.4 × 10$^3$</td>
</tr>
<tr>
<td>Zn</td>
<td>1.8 × 10$^3$</td>
</tr>
<tr>
<td>Cs</td>
<td>1.6 × 10$^3$</td>
</tr>
<tr>
<td>Ti</td>
<td>4.3 × 10$^2$</td>
</tr>
<tr>
<td>Se</td>
<td>3.7 × 10$^2$</td>
</tr>
<tr>
<td>Sr</td>
<td>1.8 × 10$^2$</td>
</tr>
<tr>
<td>Cu</td>
<td>1.1 × 10$^2$</td>
</tr>
<tr>
<td>Sr</td>
<td>1.8 × 10$^2$</td>
</tr>
<tr>
<td>Ba</td>
<td>1.7 × 10$^2$</td>
</tr>
<tr>
<td>Fe</td>
<td>1.2 × 10$^2$</td>
</tr>
<tr>
<td>Mn</td>
<td>1.9 × 10$^2$</td>
</tr>
<tr>
<td>V</td>
<td>1.5 × 10$^2$</td>
</tr>
</tbody>
</table>

**Chemical leaching of K powder**

For chemical leaching, 10 g of K powder was added to 100 mL of leaching solutions (10 w/v% slurry) and stirred at 28°C and 100 rpm for 24 hours. Solutions with 0.25 M or 0.75 M NaOH, Na$_2$CO$_3$, K$_2$HPO$_4$, sodium citrate, or tap water were used for leaching. After one-day leaching, the solutions were filtered through a glass fiber filter (pore...
size 0.6 μm). The residue of K powder was weighed after drying at 105 °C.

Bacterial strain

_Pseudomonas stutzeri_ NT-I isolated from drainage of a selenium-refining plant, was used as a selenium-reducing bacterium. Even in aerobic culture conditions, _P. stutzeri_ NT-I reduces selenate into elemental selenium via selenite (Kuroda et al. 2011).

Preconditioning and biological treatment of wastewater

The wastewater (leachate) was diluted four-fold by a basal salt medium (K2HPO4 1.0 g/L, (NH4)2SO4 1.0 g/L, MgSO4·7H2O 0.2 g/L, FeCl3 0.01 g/L, NaCl 0.05 g/L, and CaCl2 0.01 g/L) and then adjusted to pH 8.0 by using 30% NaOH solution. The carbon source, lactate, corn steep liquor (CSL), or glycerol were then added to the wastewater at 1,300 mg-C/L, 4,000 mg/L, or 1,500 mg-C/L, respectively. CSL contained soluble and insoluble fractions, which are supposed to be cheaply-available as industrial wastes. Cells of _P. stutzeri_ NT-I was inoculated to 100 mL of the preconditioned wastewater in a 300-mL flask at 1.8 × 10^9 cells/L. The flasks were aerobically incubated on a rotary shaker at 120 rpm and 28 °C for 48 hours. The experiments were done in triplicate.

Analytical procedures

Water samples (1 mL) were centrifuged (21,900 × g, 4 °C, 10 min) and filtered through a cellulose acetate membrane filter (pore size 0.2 μm) for removing the cells and elemental selenium (Kagami et al. 2015). Total selenium and selenite concentrations in the water samples were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) (SPS7800, SII NanoTechnology, Chiba or ICP-8100, Shimadzu, Kyoto) with and without pretreatment, respectively. As the pretreatment for total selenium measurement, selenate in the samples was reduced to selenite. A 50 mL aliquot of the filtrate of the water sample was mixed with 5.0 mL of tap water and 0.1 mL of 5.0 w/v% KMnO4 solution. The mixture was then boiled for 10 min. at 100 °C. After cooling down at room temperature, the mixture was messed up to 50.0 mL with ultrapure water, filtered through the glass fiber filter, and served for total selenium measurement. Electric conductivity and salinity were measured by using a probe (CDC401-01, Hach, Colorado) and a salinometer (SK-5S, Sato Keiryoki, Tokyo), respectively. Dissolved organic carbon (DOC) was measured by using a total organic carbon (TOC) analyzer (TOC-5000A, Shimadzu).

RESULTS AND DISCUSSION

Chemical leaching of selenium from K powder

Results of selenium extraction from K powder by various leaching solutions are summarized in Table 2. Chloride was completely leached from K powder in all conditions (data not shown). Tap water solubilized 54% weight of K powder but extracted only 5% of selenium. However, the selenium concentration in the tap-water leachate (2 mg-Se/L) was higher than the effluent standard in Japan (0.1 mg-Se/L). In a preliminary experiment, tap-water at 60 °C leached only 7.7% selenium from K powder, indicating low extractability of selenium in K powder without leaching agents. These results suggest that if the selenium concentration in leachate exceed the effluent standard in any case, it is a reasonable way to extract and recover selenium fully from K powder.

Selection of a suitable leaching chemical is important for achieving effective selenium extraction from K powder. Desirable leaching chemicals should extract selectively selenium, whereas other chemicals except chloride should remain in K powder. High extraction of selenium from K powder over 86% was successfully obtained by the Na2CO3 solution and the K2HPO4 solution.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Final pH</th>
<th>Se, mg/L (extraction, %)</th>
<th>Salinity, %</th>
<th>Residue, g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tap water</td>
<td>12.3</td>
<td>2 (5)</td>
<td>4.4</td>
<td>4.5</td>
</tr>
<tr>
<td>0.25 M NaOH</td>
<td>13.1</td>
<td>14 (37)</td>
<td>4.8</td>
<td>4.6</td>
</tr>
<tr>
<td>0.75 M NaOH</td>
<td>13.2</td>
<td>36 (97)</td>
<td>12.3</td>
<td>4.5</td>
</tr>
<tr>
<td>0.25 M Na2CO3</td>
<td>13.2</td>
<td>32 (87)</td>
<td>7.5</td>
<td>5.4</td>
</tr>
<tr>
<td>0.75 M Na2CO3</td>
<td>13.0</td>
<td>39 (100)</td>
<td>13.2</td>
<td>6.1</td>
</tr>
<tr>
<td>0.25 M K2HPO4</td>
<td>13.3</td>
<td>42 (100)</td>
<td>6.4</td>
<td>7.0</td>
</tr>
<tr>
<td>0.75 M K2HPO4</td>
<td>11.4</td>
<td>52 (86)</td>
<td>8.4</td>
<td>9.0</td>
</tr>
<tr>
<td>0.25 M sodium citrate</td>
<td>12.9</td>
<td>22 (60)</td>
<td>6.0</td>
<td>4.3</td>
</tr>
<tr>
<td>0.75 M sodium citrate</td>
<td>12.8</td>
<td>26 (71)</td>
<td>8.8</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Extraction condition: 10.0 g of K powder in 100 mL solution at 28 °C for 24 hours.
solution at 28 °C. A possible main form of selenium in K powder is CaSeO₃. Selenium oxyanions combined with cations such as calcium and sodium in K powder were possibly exchanged with carbonate and phosphate. Those leaching chemicals can effectively extract selenium from soil (Sharmasarkar & Vance 1997; Lim & Goh 2005) and ash (Soda et al. 2013). The resulting wastewater contained soluble selenium of >30 mg-Se/L. Selenite in total selenium was almost 100% in leachate obtained by tap water, the NaOH solution, and the Na₂CO₃ solution and >92% in leachate obtained by the K₂HPO₄ solution and the sodium citrate solution. Although citrate as a chelating agent also leached a large amount of chemicals from K powder, the selenium extraction was not so high (<71%). Although the K₂HPO₄ solution effectively leached selenium from K powder, large amounts of the K powder residue suggest phosphate was partly precipitated during the leaching process. If phosphorus enters the clinker minerals, it negatively affects the phase composition clinker, and thus the quality of cement (Lin et al. 2011). Moreover, the price of phosphorus as an important resource has increased (Scholz et al. 2013). Thus, considering the chemical cost, Na₂CO₃ was selected as a suitable chemical for leaching selenium from K powder. In additional experiments, the required concentration of Na₂CO₃ for selenium extraction from K powder (slurry concentration at 10 w/v%, 28 °C) was confirmed to be 0.2–0.25 M (data not shown). However, the high salinity and high pH values of the resulting wastewater indicate the necessity of dilution and neutralization as preconditioning for bioreduction of selenium.

**Biological reduction of selenium in wastewater**

For biological reduction experiments, another batch of the K powder sample was washed by 0.2 M Na₂CO₃ solution. Leachate contained selenium at 29 mg/L, zinc at 6.7 mg/L, calcium at 110 mg/L, and lead at 900 mg/L with conductivity of 140 mS/cm (equivalent to 9.0% NaCl). Although anaerobic sludge can be used for selenite removal from wastewater, its characteristics depend on the bacterial composition and activity (Soda et al. 2011). Therefore, *P. stutzeri* NT-I was used as a model selenium-reducing bacterium. Even in aerobic culture conditions, *P. stutzeri* NT-I reduces selenite into elemental selenium via selenite. *Pseudomonas stutzeri* NT-I reduces selenite at a similar specific reduction rate at pH 6–9, whereas it reduces selenate at pH 7–9 with a maximum rate at pH 8.0 (Kuroda et al. 2011). The bacterial reduction of selenium is inhibited by high salinity over 10 g/L NaCl (Kuroda et al. 2011). Therefore, the leachate was diluted 4-fold and then adjusted to pH 8.0 as preconditioning. The preconditioned wastewater contained soluble selenium at 5 mg-Se/L, indicating about 30% of selenium was precipitated by pH neutralization. The conductivity of the preconditioned wastewater supplemented with lactate, CSL, and glycerol was 30.2 mS/cm, 29.2 mS/cm, and 28.8 mS/cm, respectively.

Figure 2 portrays the removal of soluble selenium by *P. stutzeri* NT-I in the preconditioned wastewater under aerobic conditions. Selection of a suitable and cheap-available carbon source for the bacterium is important for achieving effective selenium removal. Although its initial concentration was low, CSL was not effective for selenium

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**Figure 2**  | Effects of carbon source on removal of selenium from wastewater by *P. stutzeri* NT-I. Concentrations of soluble selenium (a) and DOC (b) are shown. As preconditioning, wastewater produced by leaching of K powder was diluted four-fold and adjusted at pH 8.0 and supplemented with lactate, CSL, or glycerol (n = 3).
removal by *P. stutzeri* NT-I. On the other hand, removal of soluble selenium was successfully achieved >90% in the preconditioned wastewater supplemented with lactate and glycerol. Although, there was little change of color in the wastewater after 24 hours, collected particles by centrifugation from the treated wastewater showed a slight red coloration, indicating formation of elemental selenium as shown in Figure 3. The selenium concentrations in wastewater supplemented with lactate and glycerol finally decreased to 0.4–0.6 mg-Se/L. In a preliminary experiment, the soluble selenium concentration remained constant in wastewater without the bacterial cells (data not shown). Those results indicate that the bacterium reduced selenite in the preconditioned wastewater into insoluble elemental selenium. Remaining selenium in wastewater might be methylated selenium as minor components, in addition to selenate and selenite. *Pseudomonas stutzeri* NT-I can reduce selenate into elemental selenium under low dissolved oxygen concentrations and remove methylated selenium from water into air by vigorous aeration (Kagami et al. 2013). Another possible minor component in treated water was nanoscale elemental selenium which could not be removed by centrifugation and filtration.

Although lactate is a suitable carbon source for *P. stutzeri* NT-I (Kuroda et al. 2011), utilization of glycerol as a byproduct of biodiesel production is preferable for the sustainable process for selenium recovery. The DOC concentration in wastewater supplemented with glycerol still remained high at about 850 mg-C/L (Figure 2), suggesting that glycerol as the carbon and energy source was not the rate-limiting factor on the bioreduction of selenium. It is important to elucidate effects of coexisting substances in actual crude glycerol, such as methanol and fatty acids (Thompson & He 2006), on the bacterium. Moreover, effects of chemicals leached from K powder should be elucidated because copper, cadmium, and arsenic are inhibitory against *P. stutzeri* NT-I (Soda et al. 2012). Pre- and post-treatment of wastewater will be needed for removing organic and inorganic residues.

The bacterial cells formed flocs in wastewater supplemented with lactate and glycerol (Figure 3). Reportedly, a *Pseudomonas* strain grown on glycerol can produce an extracellular polysaccharide with the flocculating activity (Freitas et al. 2009). This bacterium can be attached or flocculated on biomass carriers such as acrylic fringe and granules in bioreactors for avoiding the cells from washout. The bioreactors should be operated under non-sterile condition for practical uses. It was reported that *P. stutzeri* NT-I survived for more than 25 days in a pilot-scale bioreactor equipped with acrylic fringe (Soda et al. 2012). With further research on the design and operation of bioreactors for selenium removal, the regulated effluent concentration of 0.1 mg-Se/L in Japan will be achieved by the proposed process.

Biological treatment processes have been reported, targeting wastewater containing low concentrations of soluble selenium, up to 0.65–0.8 mg-Se/L (Lenz & Lens 2009). Only a few attempts have been made to develop biological treatment processes (Soda et al. 2011, 2012, 2013) which are applicable to the high concentrations of soluble selenium contained in industrial wastewater such as the one used in this study. The biological treatment process for wastewater containing selenium at high concentrations has an advantage over the physicochemical treatment: selenium accumulated in bio-sludge would be recyclable as a minor metal by incinerating the bio-sludge in a
selenium-refining kiln (Soda et al. 2011). Further studies on the post-treatment of the selenium-containing sludge will be needed because P. stutzeri NT-I can volatile biogenic elemental selenium into dimethylselenide and dimethylselenide in prolonged cultivation. After temporal accumulation in the aqueous phase, the volatile selenium can be transferred into the gaseous phase and trapped in nitric acid solution (Kagami et al., 2015). The results obtained in this study demonstrated feasibility of the new treatment process by using chemical leaching followed by bacterial reductive precipitation for selenium recovery from K powder (Figure 1). Implementing the proposed process to cement plants can be expected to promote recycling of K powder as a cement material.

CONCLUSIONS

A novel process by using chemical leaching followed by bacterial reductive precipitation was proposed for selenium recovery from K powder as a byproduct of cement manufacturing. Selenium can be extracted from K powder at the slurry concentration of 10 w/v% with 0.2 M Na2CO3 solution at 28 °C. The resulting wastewater should be diluted four-fold and adjusted to pH 8.0 as preconditioning for biological reduction. P. stutzeri NT-I could reduce about 90% selenium at about 5 mg Se/L from the preconditioned wastewater supplemented with glycerol. The proposed process will promote further recycling of wastes as alternative raw materials and fuels in cement manufacturing.

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