Flotation separation of strontium via phosphate precipitation
Luong H. V. Thanh and J. C. Liu

ABSTRACT
Flotation separation of strontium (Sr) from wastewater via phosphate precipitation was investigated. While 37.33% of Sr precipitated at highly alkaline pH in the absence of PO$_4^{3-}$, it completely precipitated as Sr$_3$(PO$_4$)$_2$ at a molar ratio ([PO$_4^{3-}$]:[Sr$^{2+}$]) of 0.62 at a lower pH value. The presence of Ca$^{2+}$ hindered Sr precipitation, yet it could be overcome by increasing the PO$_4^{3-}$ dose. Sodium dodecyl sulfate (SDS) was a better collector for dispersed air flotation of Sr$_3$(PO$_4$)$_2$ than cetyl trimethyl ammonium bromide, or mixed collector systems of SDS and saponin. The highest separation efficiency of 97.5% was achieved at an SDS dose of 40 mg/L. The main mechanism in the precipitate flotation is adsorption of anionic SDS on the positively charged surface of colloidal Sr$_3$(PO$_4$)$_2$ via electrostatic interaction. SDS enhanced the aggregation of Sr$_3$(PO$_4$)$_2$ precipitates as the size increased from 1.65 to 28.0 μm, which was beneficial to separation as well.

Key words | flotation, phosphate, precipitation, strontium, water

INTRODUCTION
Due to increasing operation of nuclear power plants, nuclear research institutes and medical institutions, enormous amount of low-level radioactive wastewater containing strontium (Sr) is being generated, and it could pose risks to the environment (Inan et al. 2006; Cao et al. 2010). Moreover, Sr was also found in cathode ray tube waste (Yot & Méar 2011), or as the waste generated during the production of SrCO$_3$ (Liu et al. 2012). Sr is known as an alkaline earth metal and can be found in the Earth’s crust in the form of celestite (SrSO$_4$) and strontianite (SrCO$_3$) (Murthy & Parmer 2011). Sr is one of the most abundant elements, and its consumption has increased through recent years from 2010; in particular the 2013 consumption increased by around threefold compared to that of 2012 (US Geological Survey 2014). Considered as a radioactive waste, $^{90}$Sr may result in negative human health effects such as bone and tissue cancer, and leukemia, due to its high solubility and bio-toxicity (Liu et al. 2014). Other than radioactive isotopes, other isotopes of Sr can accumulate in plants and organisms via uptake and bioaccumulation, presenting a potential toxicity to humans, especially children, because of bone remodeling due to its high incorporation into bone (Dahl et al. 2001). Furthermore, Sr was found to be a significant contributor to the cytotoxicity of the bottom ash from a municipal solid waste incinerator (Huang et al. 2010). McPherson et al. (2014) reviewed the acute and chronic toxicity of Sr to the freshwater aquatic environment. In face of the environmental risks of Sr, it is necessary to develop treatment technologies for Sr-containing wastewater.

Studies on separation of Sr have been conducted, such as ferrocyanide precipitation (Wu et al. 2014), adsorption (Ma et al. 2011; Liu et al. 2014), ion exchange (Cho & Komarneni 2009), and electro-coagulation (Murthy & Parmer 2011). Among these techniques, chemical precipitation has been known as an easy, feasible and well-developed method (Cao et al. 2010). However, Sr at low concentrations cannot be completely precipitated in aqueous solution. The separation of fine precipitates from solution is another issue. Hence, some studies combined membrane technologies with precipitation or coagulation processes for Sr removal (Zhang et al. 2009; Cao et al. 2010). It is known that strontium phosphate (Sr$_3$(PO$_4$)$_2$) is sparingly soluble. Therefore, focusing on the separation of fine Sr precipitates, this work aims to investigate the precipitation of Sr$^{2+}$ with PO$_4^{3-}$, followed by dispersed air flotation (DiAF) separation of precipitates (Sr$_3$(PO$_4$)$_2$). The effects of pH and PO$_4^{3-}$ dose on the precipitation of Sr were examined. In addition, the interference of the calcium ion (Ca$^{2+}$) on the precipitation was examined,
because Ca$^{2+}$ forms insoluble salts in the presence of phosphate, such as hydroxyapatite (Ca$_5$(PO$_4$)$_3$(OH)). Different collectors were selected for DiAF, including sodium dodecyl sulfate (SDS), cetly trimethyl ammonium bromide (CTAB), and mixed collector systems of SDS and saponin. The effects of collector dose were investigated as well.

**MATERIALS AND METHODS**

**Solubility experiment**

Stock solution of 0.25 M Sr was prepared by dissolving Sr(NO$_3$)$_2$ (Alfa Aesar) in ultrapure water and acidified by a certain amount of 3 M HNO$_3$ (Acros). The solubility of Sr was evaluated using solutions of 1.62 mM Sr. The samples were adjusted to different pH values in the range of 8.3 to 12.5 by using 1 M NaOH (Acros) and 1 M HNO$_3$. The 40 mL samples were placed on the shaker for 3 days, and pH values were measured using a pH meter (Orion 4–Star Plus, Thermo Fisher Scientific), and filtered by 13 mm syringe with a 0.45 μm PVDF membrane (Acrodisc). Samples were then analyzed by using an inductively coupled plasma-atomic emission spectrometer (ICP-AES JY2000, Horiba Scientific) at a wavelength of 216.596 nm. All samples were triplicated and the average value was calculated.

**Precipitate flotation experiment**

For chemical precipitation, samples of simulated wastewater (1.62 mM of Sr) were prepared from the stock solution and then adjusted to a pH range of 8.5 to 12.5 using 3 M NaOH and 1 M HNO$_3$. The solution then reacted with 1.0 mM of PO$_4^{3-}$/C$_0$$_4$ for 10 min to let most of the Sr$^{2+}$ react with the PO$_4^{3-}$ before a fixed amount of collector was added, followed by stirring for 2 min using the magnetic stirrer, and was then transferred to the flotation cell. Three kinds of collector were used in this work: an anionic surfactant, SDS (Acros), a cationic surfactant, CTAB (Merck) and a non-ionic surfactant, saponin (Sigma). To evaluate the influence of ionic strength on flotation separation of Sr$_3$(PO$_4$)$_2$, various amounts of NaNO$_3$ were added. Samples from precipitation experiments were utilized for evaluating the zeta potential of Sr precipitates with and without SDS using a zeta meter (Zeta PALS, Brookhaven Instruments). Size distribution of solid colloidal Sr was measured using a small angle light scattering instrument (Mastersizer 2000, Malvern Instruments and Zeta PALS, Brookhaven Instruments). Each sample was measured three times.

**RESULTS AND DISCUSSION**

**Solubility of Sr**

Figure 1 shows that Sr at 1.62 mM was completely soluble at a pH range of 7.5 to 11.4. However, 37.33% of the Sr precipitated when the pH increased to 12.5. It is noted that only a small amount of Sr was converted into a solid at a highly alkaline pH condition. Thus, some other reagents were needed to induce precipitation of Sr. Among several potential candidates, such as carbonate (CO$_2^{3-}$), arsenate (AsO$_3^{3-}$), fluorite (F$^-$), and...
niobate (NbO\textsubscript{3})\textsuperscript{3+}, PO\textsubscript{3}\textsuperscript{4−} is the one that will form a sparingly soluble compound with Sr (K\textsubscript{sp} = 4.0 \times 10\textsuperscript{-28}) (Bjerrum et al. 1958). Hence, PO\textsubscript{3}\textsuperscript{4−} was chosen to precipitate Sr. Effects of PO\textsubscript{3}\textsuperscript{4−} dose and pH on the precipitation of Sr were investigated.

**Effects of PO\textsubscript{3}\textsuperscript{4−} dose and pH on precipitation of Sr**

Precipitation reaction is a process that strongly depends on the concentration of reactants and pH. In precipitation of Sr, influences of both PO\textsubscript{3}\textsuperscript{4−} concentration and initial pH were investigated, and the results are shown in Figure 2. At an initial concentration of 1.62 mM, Sr effectively precipitated in the presence of PO\textsubscript{3}\textsuperscript{4−}. It was found that pH is an important parameter for precipitation of Sr with a stoichiometric amount of PO\textsubscript{3}\textsuperscript{4−}. While Sr was completely soluble at

![Figure 2](https://iwaponline.com/wst/article-pdf/75/11/2520/452939/wst075112520.pdf)

**Figure 2** | Effects of pH and molar ratio [PO\textsubscript{3}\textsuperscript{4−}]/[Sr] on precipitation of Sr\textsubscript{3}(PO\textsubscript{4})\textsubscript{2} ([Sr]\textsubscript{o}: 1.62 mM, room temperature, reaction time: 3 d).

![Figure 3](https://iwaponline.com/wst/article-pdf/75/11/2520/452939/wst075112520.pdf)

**Figure 3** | Speciation diagram of phosphate as affected by pH at 25 °C.

![Figure 4](https://iwaponline.com/wst/article-pdf/75/11/2520/452939/wst075112520.pdf)

**Figure 4** | Effect of Ca\textsuperscript{2+} (0.5 mM) on precipitation of Sr\textsubscript{3}(PO\textsubscript{4})\textsubscript{2} ([Sr]\textsubscript{o}: 1.62 mM, pH 11.5, reaction time: 60 min).

![Figure 5](https://iwaponline.com/wst/article-pdf/75/11/2520/452939/wst075112520.pdf)

**Figure 5** | Removal efficiency of Sr\textsubscript{3}(PO\textsubscript{4})\textsubscript{2} precipitates as affected by collector type ([Sr]\textsubscript{o}: 1.62 mM, pH 11.5, N\textsubscript{2} flow rate: 30 mL/min, I: 0.02 M of NaNO\textsubscript{3}).

![Figure 6](https://iwaponline.com/wst/article-pdf/75/11/2520/452939/wst075112520.pdf)

**Figure 6** | ζ potential of Sr\textsubscript{3}(PO\textsubscript{4})\textsubscript{2} precipitates as affected by SDS dose at pH 11.5.
pH 8.50, ca. 15.6% of Sr started to precipitate with PO$_3^{3-}$ at pH 8.61 at a molar ratio ([PO$_3^{3-}$]/[Sr$^{2+}$]) of 0.93. The total amount of Sr precipitated as (Sr$_3$(PO$_4$)$_2$) significantly increased to 78.2% and 99.75% of Sr when the pH increased to 9.08 and 11.43, respectively, and then slightly increased to 99.94% of Sr at pH 12.50.

Unlike pH, the PO$_3^{3-}$/CO$_4^{3-}$ dose had insignificant effects on Sr precipitation at pH 12.50 when the molar ratio ([PO$_3^{3-}$]/Sr) changed from 0.62 to 0.93. However, the effect of PO$_3^{3-}$ dose on Sr precipitation became more significant at pH 11.43.

The differences between the efficiency of Sr precipitation at a molar ratio of 0.43 and 0.62 were significant. This could be explained based on speciation of PO$_3^{3-}$ and Sr. Ma et al. (2011) indicated that ca. 100% of Sr exists in the form of cationic Sr$^{2+}$ in the pH range of 0–11, and the fraction of Sr$^{2+}$ decreases to ca. 95% and 75% when the pH increases to 11.5 and 12.5, respectively. Thus, speciation of the Sr ion mostly did not affect the precipitation of Sr and PO$_3^{3-}$ much. In terms of PO$_4^{3-}$, the speciation diagram (Figure 3) shows that PO$_4^{3-}$ constitutes 84.32% of soluble Sr.

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Figure 7 | Size distribution of Sr$_3$(PO$_4$)$_2$ precipitates; (a) in the absence of SDS; (b) at 20 mg/L of SDS.
P at pH 12.5, and sharply decreases to 43.96% and 5.10% when the pH decreases to 11.5 and 10.5 respectively. That could explain why precipitation of Sr with PO$_3^-$ was influenced by the molar ratio ([PO$_3^-$]/[Sr]) at lower pH.

**Effect of Ca$^{2+}$ ion on precipitation of Sr**

The calcium ion (Ca$^{2+}$) competes with Sr for precipitation with PO$_3^-$ due to the very low solubility product of Ca$_3$(PO$_4$)$_2$ ($K_{sp} = 2.07 \times 10^{-29}$) (Huang et al. 2010). Furthermore, Ca$^{2+}$ is also a common ion in surface water. Thus, the influence of Ca$^{2+}$ (0.5 mM) on Sr$_3$(PO$_4$)$_2$ precipitation was examined with different molar ratios ([PO$_3^-$]/[Sr]) at pH 11.5, and the results are shown in Figure 4. It is observed that the presence of 0.5 mM Ca$^{2+}$ hindered precipitation of Sr at pH 11.5 at [PO$_3^-$]/[Sr] of 0.43, and the residual concentration of Sr increased from 0.160 to 0.762 mM. However, the interference was overcome as [PO$_3^-$]/[Sr] increased to 0.93, and the residual concentration of Sr dropped to 0.098 mM.

**Effect of collector type and dose**

Precipitate flotation usually depends on hydrophobic surfaces of the precipitate that are created by adsorption of the surfactant onto the precipitate surface (Atkin et al. 2003). Three kinds of collector were used in this work, SDS, CTAB and saponin, and the results are presented in Figure 5. Removal efficiency of Sr$_3$(PO$_4$)$_2$ precipitates was 93.0% when using SDS at 20 mg/L, while only 47.3% was achieved at an identical dose of CTAB. Apparently, SDS was more effective for flotation separation of Sr$_3$(PO$_4$)$_2$ precipitate. Meanwhile, there are some studies in which combined use of mixed collectors improved flotation separation (Rao & Forsberg 1997; Penfold et al. 2002). Thus, a combination of SDS, 5 and 10 mg/L, and 5 mg/L saponin was examined in our systems. However, the results showed the mixed collector of SDS and saponin was ineffective (Figure 5). The combination of 5 mg/L of SDS and 5 mg/L of saponin removed 10.2% Sr and it increased to only 19.8% as the SDS dose increased to 10 mg/L. Similar results could be found in the previous work of Mitra et al. (2013), that removal of Cu and Zn by using saponin decreased with increasing pH solution to an alkaline condition (pH 10). The hindrance of saponin in the separation of Sr$_3$(PO$_4$)$_2$ precipitates may result from its characteristics, as saponin creates smaller and more widely dispersed bubbles that keep particles dispersed in solution (Mitra & Dungan 1997). The zeta potential of the Sr$_3$(PO$_4$)$_2$ precipitate was 19.5 mV, and it decreased slightly as the SDS dose increased (Figure 6). Thus, it could be explained that anionic SDS became adsorbed on the positively charged surfaces of Sr$_3$(PO$_4$)$_2$ precipitates via electrostatic interaction, while repulsive interaction may not favor the adsorption of cationic CTAB. The adsorption of SDS subsequently generated a hydrophobic area around the Sr$_3$(PO$_4$)$_2$ precipitates that facilitated attachment of N$_2$ bubbles, and resulted in Sr$_3$(PO$_4$)$_2$ particles’ separation from solution (Fuerstenau & Pradip 2005). It was also found that 20 mg/L of SDS induced flocculation of Sr$_3$(PO$_4$)$_2$ precipitates, whose median size increased from 1.65 μm to 28.0 μm as shown in Figure 7(a) and 7(b). It was beneficial to flotation separation as well (Nguyen et al. 2013).

The effects of SDS dose on flotation separation were examined, and the results are shown in Figure 8. When in the absence of SDS, 33.5% Sr$_3$(PO$_4$)$_2$ precipitates were removed. It was observed that ca. 69.8% of Sr was removed from solution with a small amount of SDS (10 mg/L) and the yield remarkably increased to 93.0% when the SDS concentration rose to 20 mg/L, then slightly improved to 94.25 and 97.5% at an SDS dose of 30 and 40 mg/L, respectively.

**Effect of ionic strength**

Effects of ionic strength on the Sr$_3$(PO$_4$)$_2$ precipitates’ flotation separation were examined by varying the NaNO$_3$ concentration rose to 20 mg/L, then slightly improved to 94.25 and 97.5% at an SDS dose of 30 and 40 mg/L, respectively.

### Table 1 | Effect of ionic strength on removal of Sr$_3$(PO$_4$)$_2$ precipitate at pH 11.5

<table>
<thead>
<tr>
<th>NaNO$_3$ (mM)</th>
<th>Removal efficiency (%)</th>
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<tbody>
<tr>
<td>0.02</td>
<td>93.0 ± 0.8</td>
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<tr>
<td>0.2</td>
<td>86.4 ± 0.3</td>
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![Image](https://iwaponline.com/wst/article-pdf/75/11/2520/452939/wst075112520.pdf)
concentration. Experimental results revealed that the separation efficiency of Sr decreased from 93.0% to 86.4% when the NaNO₃ concentration increased from 0.02 M to 0.2 M (Table 1). It could be explained that the electrostatic interactions were screened under higher electrolyte concentration, which led to reduced adsorption of SDS onto the Sr₃(PO₄)₂ precipitate surface (Huang & Liu 1993; Micheau et al. 2015). It confirmed that the main interaction in the flotation separation of Sr₃(PO₄)₂ precipitate at pH 11.5 was electrostatic interaction. As an effective collector for flotation separation of Sr₃(PO₄)₂ precipitates, SDS made Sr₃(PO₄)₂ surfaces hydrophobic and induced flocculation, both contributed to flotation separation. The reaction mechanisms are illustrated in Figure 9, in which Sr was first reacted with PO₃⁻ and formed Sr₃(PO₄)₂ precipitates, SDS became adsorbed via electrostatic interactions, and facilitated flotation separation of Sr₃(PO₄)₂.

CONCLUSIONS

The flotation separation of Sr via phosphate precipitation as Sr₃(PO₄)₂ was studied and the major findings are summarized as follows:

1. Both pH and molar ratio ([PO₃⁻]:[Sr²⁺]) affected the precipitation reaction of Sr₃(PO₄)₂. At a molar ratio ([PO₃⁻]:[Sr²⁺]) of 0.93, a significant amount (>99.75%) of Sr precipitated at pH > 11.43. Hindrance of the Ca²⁺ ion on the precipitate of Sr was observed but it could be overcome by increasing the PO₄³⁻ dose.

2. SDS was an effective collector for flotation separation of Sr₃(PO₄)₂ precipitates compared with CTAB or mixed collector systems of SDS and saponin. Approximately 93% of Sr was separated at 20 mg/L of SDS and it increased to 97.5% at 40 mg/L of SDS.

3. The main mechanisms in the flotation separation of Sr₃(PO₄)₂ precipitates was the adsorption of anionic SDS on the positively charged surface of colloidal Sr₃(PO₄)₂ via electrostatic interaction. SDS also induced flocculation of Sr₃(PO₄)₂ precipitates, which was beneficial for flotation separation as well.

REFERENCES


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