Antimony(III/V) removal from industrial wastewaters: treatment of spent catalysts formally used in the SOHIO acrylonitrile process

Richard I. Foster, Maeng-kyo Oh, Dasom Yang, Woo-Jung Shon, Kwang-Wook Kim and Keun-Young Lee

ABSTRACT

A treatment and volume reduction process for a spent uranium–antimony catalyst has been developed. Targeted removal, immobilization and disposal of the uranium component has been confirmed, thus eliminating the radiological hazard. However, significant concentrations of antimony ([Sb]/C2 = 25–50 mg L⁻¹) remain in effluent from the process, which require removal in compliance with Korean wastewater regulations. Antimony(III/V) removal via co-precipitation with iron has been considered with optimal pH, dose and kinetics being determined. The effect of selected anions – Cl⁻, SO₄²⁻ and PO₄³⁻ – have also been considered, the latter present due to a prior uranium removal step. Removal of Sb(III) from both Cl⁻ and SO₄²⁻ media and Sb(V) removal from Cl⁻ media to below release limits were found to be effective within 5 minutes at an iron dose of 8 mM (molar ratio, [Fe⁢III]/[Sb] = 20) and a target pH of 5.0. However, Sb(V) removal from SO₄²⁻ was significantly hampered requiring significantly higher iron dosages for the same removal performance. Phosphate poses significant challenges for the removal of Sb(V) due to competition between PO₄³⁻ and Sb(OH)₆⁻ species for surface binding sites, attributed to similarities in chemistries and a shared preference for an inner vs outer binding mechanism.

INTRODUCTION

Uranium–antimony catalyst

Acrylonitrile is a key chemical in the acrylic fibre used to make and manufacture a wide variety of materials (ACS 2007). The economics of acrylonitrile production were greatly improved by the development of catalysts capable of single-step selective catalytic oxidation of the raw materials (ACS 2007; Cavani et al. 2009). Development and implementation of such catalysts by the Standard Oil of Ohio company (SOHIO) paved the way for a rapid and inexpensive acrylonitrile production process which came to be known as the SOHIO process.

A variety of different catalysts have been used as part of the SOHIO process (Cavani et al. 2009). Commercially used catalysts have been based on multimetal molybdates (MMM), iron antimony oxide, uranium antimony oxide, or tellurium molybdenum oxide, with the mixed oxide dispersed in silica (Typically ≈ 50 wt%). The most commonly used catalysts nowadays are of the MMM type. Antimony is found in many of the catalyst formulations due to its role as an α-H abstraction component (Sb(III)) or as an olefin chemisorption and oxygen or nitrogen insertion component (Sb(V)) (Cavani et al. 2009).

One such catalyst, containing a uranium–antimonite active phase (U = 3–7 wt%, Sb = 15–25 wt%) on a silica support (approximately 70 vol%), had been used in Korea until 2004 (Cavani et al. 2009; Kim et al. 2018a). Since then, U-free catalysts such as Cr/Sb/O or MoVTe(Sb)NbO₅ have been used. The spent uranium-containing catalyst, classified as radioactive waste, has since been in temporary storage awaiting an appropriate treatment and disposal method. In recent years a process has been successfully demonstrated to remove the uranium component for geological disposal, thus meeting all national and international regulations for radioactive waste treatment (Kim et al. 2018a, 2018b; Foster et al. 2019; Kim et al. 2019).
uranium–antimony catalyst involves dissolution of the silica support in sodium hydroxide followed by selective precipitation of the silica and its purification with sulfuric acid. A portion of the Sb is also solubilized, along with uranium and other trace metals (e.g. iron) (Kim et al. 2018b). Hydrogen peroxide is added to the dissolved catalyst solution along with sodium carbonate for the formation of soluble uranyl peroxocarbonate (UO$_2$(O$_2$)(CO$_3$)$_2$$^-$) enabling the separation of soluble uranium species and precipitated silica. A uranium-phosphate precipitation step at pH 6.25 is then performed to remove uranium from the process effluent (Foster et al. 2019). The remaining effluent, containing between 25 and 50 mg L$^{-1}$ antimony and 50 mg L$^{-1}$ phosphate, requires final treatment before release. Final Sb and PO$_4^{3-}$ concentrations of 0.2 and 8 mg L$^{-1}$ are permitted for release in Korea (MoE 2018). Phosphate removal by co-precipitation with ferric iron has already been shown to be effective under current process conditions (Foster et al. 2019). However, the presence of antimony in the catalyst, which is subsequently found in the process effluent, is cause for concern. Korean release regulations mean a suitable method to remove antimony from the process effluent is required in order to gain regulatory approval.

Antimony chemistry

Antimony is considered toxic to the environment (Oorts et al. 1994), and is associated with cancer development (Gurmani et al. 1994). As such the environmental release of antimony and its compounds is a source of concern internationally (USEPA 1979; WHO 1996; DEFRA 2000). Such is the toxicity of Sb that permissible Sb concentrations in drinking water have been set by many of the world’s regulatory bodies including the World Health Organization which recommends Sb levels no greater than 5 μg L$^{-1}$ (5 ppb) (WHO 1996). Release limits for industrial effluents are also in force. A limit of 0.2 mg L$^{-1}$ (0.2 ppm) has recently been set by the Ministry of Environment in Korea as of 1 January 2019 (MoE 2018).

Antimony exhibits multiple oxidation states: $-3$, $0$, $+3$ and $+5$ (Baes & Mesmer 1976). Antimony is present in the catalyst in the $+3$ oxidation state (Kim et al. 2019). In water Sb(III) (Sb(OH)$_3$) at pH 7) is stable under reducing conditions while Sb(V) (Sb(OH)$_5^-$) at pH 7) is stable under oxidizing conditions (Baes & Mesmer 1976), although it has been reported that Sb(III) and Sb(V) have been found to exist in significant quantities in oxic and anoxic waters, respectively (Filella et al. 2002). Oxidation of Sb(III) by peroxide has been previously reported (Quentel et al. 2004). The neutral Sb(OH)$_3$ species has been shown to be unreactive to H$_2$O$_2$, in the absence of catalytic trace metals, with the formation of Sb(OH)$_3^-$ required for oxidation to proceed. As Sb(OH)$_3$ exhibits a pK of 11.7, alkaline conditions are required in the presence of H$_2$O$_2$ for the oxidation of Sb(III) to proceed at any appreciable rate, an example being an Sb(III) half-life of 284 days in seawater (pH = 8.1) and 3,303 days in freshwater (pH = 7.5) (Quentel et al. 2004). Such conditions occur within the catalyst treatment process during the initial catalyst dissolution stage by way of sodium hydroxide addition and with the addition of H$_2$O$_2$. The presence of trace iron dissolved from the catalyst also offers a route for oxidation of Sb(III) to Sb(V) (Belzile et al. 2001), and via the Fenton reaction in solutions containing peroxide (Leuz et al. 2006). Trace levels of Fe(II) have been shown to be sufficient to start a chain reaction resulting in the oxidation of Sb(III) to Sb(V) by $\cdot$OH radicals before Sb(IV) reacts with O$_2$ to give Sb(V) and O$_2^-$, the latter going on to reduce Fe(III) to Fe(II), thus propagating the chain reaction. Antimony oxidation in this way occurs rapidly even under acidic conditions (>95% within 1 h and 20 s at pH 2.9 and 6.8, respectively) (Leuz et al. 2006). Thus, although not confirmed, it is likely that the chemistry of antimony in the effluent is predominated by Sb(V) and not Sb(III). At circum-neutral pH, Sb(III) is found to exist as a neutral complex, Sb(OH)$_3$, while Sb(V) is found to form a negatively charged antimony-hydroxide, Sb(OH)$_6^-$ (Figure S1, available with the online version of this paper) (Filella & May 2005). The oxidation of Sb(III) to Sb(V) and thus the presence of Sb(OH)$_6^-$ will significantly increase the concentration of soluble Sb, further complicating any treatment process.

Antimony removal

Despite the environmental and health concerns associated with antimony, there is little in the way of published research available regarding removal methods from effluents and drinking water, as noted by Guo et al. (2009). Previous Sb removal studies tend to focus on adsorption, membrane and coagulation–flocculation methods for Sb removal. In contrast the removal of arsenic, which is similar to antimony both chemically and toxicologically, has been extensively reported with over 600 references being compiled by Mohan & Pittman (2007) alone.

Precipitation and coagulation–flocculation followed by either sedimentation or filtration is commonly used as a low cost removal method for a wide range of contaminants worldwide and has been considered for antimony removal (Nakamura & Tokunaga 1996; Kang et al. 2003; Guo et al. 2009).
Commonly, aluminium, iron or calcium-based coagulants are employed. However, it has been evidenced that aluminium is ineffective for Sb removal (Kang et al. 2003; Guo et al. 2009), while the kinetics of calcium removal are prohibitively slow (Gannon & Wilson 1986).

Guo et al. (2009) investigated the removal of Sb from solution by coagulation–floculation–sedimentation with ferric chloride (FeCl₃) addition, focusing on dosage, pH and interfering ions. They found that Sb(V) removal was optimum at pH 4.5–5.5 while Sb(III) removal occurred over a much wider pH range of 4.0–10.0. Guo et al. (2009) suggested Sb removal occurs predominately through surface adsorption compared to either precipitation or co-precipitation via inclusion or occlusion mechanisms (Figure 1). They further suggested Sb adsorbed onto iron oxyhydroxides by inner-sphere complexes (ligand exchange) rather than outer-sphere (anion exchange) processes (Figure 1), a hypothesis supported by others including the attenuated total reflection infrared (ATR-IR) spectroscopic studies of McComb et al. (2007). Changes in the Sb(OH)₆⁶ spectrum and loss of OH stretching adsorptions associated with iron oxide surface hydroxyl groups imply the formation of inner-sphere Fe-O-Sb bonds under mildly acidic to neutral conditions. Inner-sphere complexation theory is further supported by EXAFS (extended X-ray absorption fine structure) analysis by Mitsunobu et al. (2010); however, they also went on to provide the first evidence of structural incorporation of Sb(V) into the iron(III) oxide structure. It is therefore likely that inner-sphere complex formation is the predominant but not sole mechanism by which Sb is removed from solution.

While the work of Guo et al. (2009) is without question valuable, their focus, and the focus of many others (Nakamura & Tokunaga 1996; Kang et al. 2003; Du et al. 2014; Guo et al. 2018), was predominately on drinking water treatment with low initial antimony concentrations ([Sb] < 500 μgL⁻¹), low ionic strength and either absent of anions or in the presence of low levels of organic or inorganic contaminants typically found in natural waters (Table S1, available online). In contrast, we have studied the ability to remove Sb (both Sb(III) and Sb(V)) from industrially relevant effluents. In such cases, the initial Sb concentrations far exceed recommended release limits by several orders of magnitude ([Sb] > 1 mg L⁻¹) and either

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**Figure 1** | Illustration of antimony removal mechanisms as suggested by the literature.
Cl\(^{-}\) or SO\(_4^{2-}\) are present at substantial concentrations (>0.1 M) akin to industrial effluents. The effect of phosphate on the removal of antimony has also been assessed owing to its presence within the effluent in question. By considering pH, dose, precipitation kinetics and interfering ions we have assessed the feasibility of ferric chloride addition for the removal of antimony from process effluents stemming from the treatment of a legacy spent uranium–antimony catalyst formally of the SOHIO acrylonitrile process.

The driver for this research is the recent changes to release limits in Korea for antimony-containing industrial wastewaters. The location of the site to treat the spent uranium–antimony catalyst is classified as ‘level II’ with an antimony release limit of <0.2 mg L\(^{-1}\) (0.2 ppm) newly in place as of 1 January 2019 (MoE 2018). This recent change has prompted an urgent revisit to assess removal options for Sb. Phosphate removal as part of the spent catalyst treatment process is already achieved by the addition of ferric chloride, resulting in total phosphorous levels acceptable for release (Foster et al. 2019). Co-removal of antimony and phosphate during the same step would be an ideal outcome, thus establishing required conditions for Sb removal is of the utmost importance. Understanding the fate of Sb in the process is imperative for process acceptance and regulatory approval.

**EXPERIMENTAL**

**Materials**

All materials were used as received with no further purification: sulfuric acid (H\(_2\)SO\(_4\), 98%) was obtained from Showa; antimony(III) oxide (Sb\(_2\)O\(_3\), 98%) from Kanto chemical Co. Ltd; iron(III) chloride (FeCl\(_3\), 99%) and antimony(V) oxide (Sb\(_2\)O\(_5\), 99.995%) from Sigma; and hydrochloric acid (HCl, 37%), sodium hydroxide (NaOH, 99%) and nitric acid (H\(_2\)NO\(_3\), 65%) from Merck. Ultra-pure water (18.2 M\(_2\)) prepared by a Milli-QPLUS (Millipore Co.) was used throughout.

**Real waste effluent**

A description of the spent uranium catalyst, the catalyst treatment process, and the uranium removal method have all been previously reported in full (Kim et al. 2018a, 2018b; Foster et al. 2019). Samples of the effluent produced after the uranium removal step, which included a solid–liquid filtration step to separate the precipitated uranium-phosphate from solution, were stored in 20 L plastic drums before use. The real waste effluent possesses a pH of 6.45, a high conductivity of 56.36 mS cm\(^{-1}\) and an ionic strength of 0.75 M due to the high concentration of SO\(_4^{2-}\) (0.24 M) and background sodium levels. The measured level of fine particulate material was low with solution turbidity and total suspended solids being recorded at 0.17 NTU and 0.402 mg L\(^{-1}\), respectively. The antimony and phosphorus content of the waste is found to be of the order of 25–50 mg L\(^{-1}\) and 50 mg L\(^{-1}\), respectively. A complete chemical composition is found in Table S2 (available with the online version of this paper).

**Antimony removal**

Stock solutions of Sb(III) and Sb(V) (100 mg L\(^{-1}\)) in chloride and sulfate media (1 M) were prepared by dissolving Sb\(_2\)O\(_3\) and Sb\(_2\)O\(_5\) in the respective acids and being made up with ultra-pure water. A 1 M iron stock solution was made by the dissolving FeCl\(_3\) (67.5 g) into 250 mL ultra-pure water. To assess the effect of phosphate concentration on the removal of Sb a phosphate stock solution (16.4 mM) was made by dissolving 0.6397 g of NaH\(_2\)PO\(_4\) in 250 mL ultra-pure water. Three separate sodium hydroxide solutions were made at concentrations of 5, 1 and 0.1 M.

Precipitation tests were performed as follows. To a 250 mL beaker, 50 mL Sb stock solution and 50 mL ultra-pure water were added (resulting working solution: [Sb] = 50 mg L\(^{-1}\), [A] = 0.5 M (A = Cl\(^-\) or SO\(_4^{2-}\)) along with a magnetic stirrer bar. A 1 mL aliquot of the solution was removed for inductively coupled plasma mass emission spectroscopy (ICP-OES) analysis to confirm the initial Sb concentration. Under fast mixing (240 rpm) the required aliquot of FeCl\(_3\) stock solution ([Fe\(^{III}\)]\(_{initial}\) = 1 to 100 mM) was added. For those experiments in which the effect of phosphate was to be assessed, the required aliquot of NaH\(_2\)PO\(_4\) stock solution was also added at this point ([PO\(_4^{3-}\)]\(_{initial}\) = 0.04 to 4.1 mM, [PO\(_4^{3-}\)]/[Sb] = 0.1 to 10). pH change was performed by the addition of sodium hydroxide in 1 mL aliquots; 5 M was used until pH 3 with 1 M being used thereafter. The 0.1 M NaOH solution was used for fine pH adjustment. After pH control the stirrer was reduced to a slow mix (60 rpm) for 15 minutes. The resulting precipitates and supernatant were then decanted into a 250 mL PET (polyethylene terephthalate) plastic bottle and left to settle undisturbed for 60 minutes before the supernatant was sampled for ICP-OES and turbidity analysis.

**Analytical methods**

All solution samples were filtered through a 0.22 \(\mu\)m syringe filter and acidified with 5% HNO\(_3\) before being analysed via
an ICP-OES Analytikjena PQ9000 Elite. The percentage removal was calculated according to Equation (1).

$$\% \text{Removal} = \left( \frac{C_i - C_f}{C_i} \right) \times 100 \quad (1)$$

where $C_i$ and $C_f$ are the initial and final contaminant concentrations, respectively.

Solution turbidity was measured with an HI 98703 Hanna instruments turbidity meter. A blank deionized (DI) water sample was recorded at <0.1 NTU before each run. All pH measurements were conducted with an Orion Star A215 pH meter and a ROSS Ultra® pH/ATC Triode electrode (8157BNUMD; Thermo Scientific).

**RESULTS AND DISCUSSION**

**pH screening**

The addition of ferric chloride ([Fe(III)]$_{\text{initial}}$ = 10 mM) was confirmed to have a positive impact on the removal of Sb from solution regardless of pH (Figure 2), similar to previously reported results of both Kang et al. (2003) and Guo et al. (2009).

Antimony(III) removal from both chloride and sulfate media was poor below pH 4.0, failing to reach the Sb release limit of 0.2 mg L$^{-1}$ (Figure 2). In the case of chloride media a removal percentage of 65% was recorded, while removal from sulfate media was even poorer at only 15%. Above pH 4.0 the Sb(III) concentration was confirmed to fall below the release limit over the pH range 4.0–8.0 and 4.0–10.0 in chloride and sulfate media, respectively.

Antimony(V) removal from chloride media was observed to show a similar trend to that of Sb(III) (Figure 2(a)). Below pH 4.0, Sb removal failed to reach the required release limit. Between pH 4.0 and 6.0 removal of Sb(V) to concentrations below the release limit was achievable; however, this represents a narrower pH window than for Sb(III). In contrast the removal of Sb(V) from sulfate media, similar to conditions found in the process effluent, failed to reach the required release limit regardless of pH at an initial coagulant dose of 10 mM (Figure 2(d)). The greatest removal of Sb(V) was found to occur between pH 4.0 and 7.0, leading to a final concentration of 2–3 mg L$^{-1}$.

An explanation as to the observed trends can be given based on considerations of the predominant Sb species in solution across the experimental pH range (neutral species Sb(OH)$_3$ for Sb(III) and anionic species Sb(OH)$_6^-$ for Sb(V)), surface characteristics of ferric hydroxide as a function of pH, and surface complexation mechanisms. It is documented that the surface charge of ferric hydroxides decreases as pH increases (Bompoti et al. 2017), a trend illustrated by He et al. (2015) who determined surface charges of +34.5, +3.5 and −24.4 mV at a pH of 3.0, 7.0 and 10.0, respectively. Adsorption of the neutral Sb(III) species is largely unaffected by changes to the surface charge of ferric hydroxides as pH changes (Figure 2) (He et al. 2015). The trend in Sb(III) removal between Cl$^-$ and SO$_4^{2-}$ media is comparable. In the case of Sb(V) removal, as the pH increases, deprotonation of the absorbent surface occurs, forming a negatively charged surface, resulting in the repulsion of the charged Sb(OH)$_6^-$ species. In the case of Sb(V) removal from Cl$^-$ media, this leads to a reduction in percentage removal above pH 7 (Figure 2(a)). This is comparable to the results of Guo et al. (2009). Little to no effect is seen by the presence of Cl$^-$ anions on account of Sb(III) and Sb(V) showing similar levels of removal below pH 7 (Figure 2(a) and 2(c)). In contrast the removal of Sb(V) from sulfate media is hampered by competition from SO$_4^{2-}$ for surface binding sites. Sulfate is reported to bind to ferric hydroxides preferentially via a physisorption outer-sphere complexation mechanism (Equation (2)). This leads to direct competition for binding sites with Sb(OH)$_6^-$ which can also undergo outer-sphere complexation (Equation (3)). The same competition is seen between sulfate and arsenic, the latter of which is chemically similar to antimony (Hering et al. 1996). However, Sb binding is predominately governed by the stronger chemisorption inner-sphere complexation mechanism (Equation (4)). The inner-sphere mechanism is said to occur more favourably when the pH is low, where the iron oxide positive surface charge is largest (McComb et al. 2007). Consideration for the inner-sphere mechanism probably accounts for the observation that under acidic conditions greater Sb(V) removal occurs compared to alkaline conditions despite the high sulfate concentration. Such a consideration of speciation and complexation mechanisms describes both the significant reduction in Sb(V) percentage removal at higher pHs and the overall lower removal of Sb(V) from sulfate media compared to chloride media (Figure 2).

Outer-sphere (anion exchange) complexation mechanism:

\[ \equiv \text{FeOH} + \text{H}^+ + \text{SO}_4^{2-} \rightarrow \equiv \text{FeOH}_2^+ + \text{SO}_4^{2-} \quad (2) \]

\[ \equiv \text{FeOH} + \text{H}^+ + \text{Sb(OH)}_6^- \rightarrow \equiv \text{FeOH}_2^- + \text{Sb(OH)}_6^- \quad (3) \]
Inner-sphere (ligand exchange) complexation mechanism:

\[
\text{FeOH} + \text{Sb(OH)}_6^- \rightarrow \text{FeOSb(OH)}_5^- + \text{H}_2\text{O} \tag{4}
\]

Formed precipitates settled well across the range of pHs tested, with the exception of pH 3.0 (Figure S2(A)) (Figure S2 is available with the online version of this paper). Settling of formed particles was allowed to occur over a period of 1 hour. NTU analysis of the supernatant indicated that only a small amount of ultra-fine particles remained with measurements ranging from 0.2 to 2 NTU. While the bulk of the particles were found to settle, the release limit (NTU \(\leq 1.0\)) could not be reached consistently. Filtration would be required prior to effluent release. A significant amount of ultra-fine particles remained suspended in solution at pH 3.0 in chloride media. In contrast, under the same conditions in sulfate media, no evidence of particles was found, which probably explains the poor removal of Sb from sulfate-containing solutions at pH 3.0 of 15% (Figure 2(b)).

Dose screening

Antimony removal from Cl\(^{-}\) and SO\(_4^{2-}\) media as a function of iron dose at a target pH of 5.0 is shown in Figure 3. As seen previously, Sb(III) is easier to remove than Sb(V) from both chloride and sulfate media. Removal of both Sb(III) and Sb(V) is improved by increasing the ferric chloride dose. Antimony(III) removal from chloride media at an initial concentration of 50 ppm requires an [Fe\(^{III}\)] of \(\geq 8\) mM corresponding to [Fe\(^{III}\)]/[Sb(III)] \(\geq 20\). Antimony(III) removal from sulfate media follows the same trend. The removal of ultra-fine particles was also improved by increasing iron dose. NTU analysis shows a downward trend in measured NTU value as the iron dose increases (Figure S2(C) and S2(D)).

Antimony(V) removal is also improved by an increase in ferric chloride dose but requires higher iron dosages to achieve the same level of removal compared with Sb(III). Antimony(V) removal from sulfate media requires ferric dosages significantly higher than 8 mM (\(>40\) mM) due to
competition for binding by sulfate (Figure 3(b); Figure S3, available online).

Table 1 compares the coagulant dose used for the removal of antimony via coagulation–flocculation–sedimentation from a series of separate studies in which iron based coagulants were the primary focus. Sb(III) is consistently easier to remove, requiring a lower coagulant to Sb ratio, compared to Sb(V) regardless of target wastewater type (Kang et al. 2003; Guo et al. 2009, 2018; Du et al. 2014). Natural waters contain a range of interfering inorganic and organic components such as carbonate or humic acid. The presence of such components is known to be a detriment to Sb binding, particularly affecting Sb(V) removal as noted by Guo et al. (2009). In contrast, industrial wastewaters, where co-ions are controllable or known, the amount of coagulant can be better tailored when problematic co-contaminants are not present, thus reducing the required coagulant volumes. Although the ratio of iron to antimony is lower in our study the overall iron dose is higher than those previously reported due to higher initial Sb concentrations. The higher iron dose will lead to larger and more numerous flocs, resulting in a higher surface area per unit volume. As such, there will be more surface binding sites for antimony species to bind to, thus increasing the removal efficiency.

Removal kinetics

Kinetic profiles were obtained at fixed pH and dose (pH 5.0, 10 mM) (Figure 4). The formation of visible precipitates, identifiable by an increase in solution turbidity, occurs rapidly at pH 5.0. The rapid removal of Sb(III) from chloride and sulfate media, and Sb(V) from chloride media, to below the release limit was confirmed to occur within a few minutes of the pH adjustment. Adequate removal was found to occur within 5 minutes. While the removal of Sb(V) fails to reach the required release limit even after an hour, removal to 2–3 mg L\(^{-1}\) also occurs within minutes. A maximum removal time of 5 minutes is therefore considered optimal for the process.

Variable \([\text{PO}_4^{3-}]\)

The presence of phosphate in the effluent, stemming from the use of KH\(_2\)PO\(_4\) for the formation of insoluble meta-ankoleite (KUO\(_2\)PO\(_4\).3H\(_2\)O) to facilitate the removal of uranium (Foster et al. 2019), was evaluated for its impact on Sb removal. Phosphate, itself requiring removal to below acceptable release limits, is known to impact the removal of antimony by iron precipitation due to competition for surface binding sites (Guo et al. 2009; He et al. 2015).

Removal of Sb(III) was only slightly affected by the presence of phosphate with reductions in percentage removal from a value of 99.4% to 96.2% and from 99.3% to 98.2% for chloride and sulfate media, respectively, as \(\text{[PO}_4^{3-}] / [\text{Sb(III)}] \) increased from 0.5 to 10. Such small reductions are in line with Guo et al. (2009) and He et al. (2015). However, despite the presence of phosphate only marginally
impacting the removal of Sb(III), the detrimental effect is significant enough to maintain the concentration of Sb(III) above the release limit of 0.2 mg L\(^{-1}\) (Figure 5(a)). At a \([\text{PO}_4^{3-}]/[\text{Sb(III)}] = 4\), similar to that found in the real effluent, 98.6% of Sb(III) is removed from chloride media, corresponding to a remaining concentration of 0.74 mg L\(^{-1}\). Similarly, 98.8% of Sb(III) is removed from sulfate media with a concentration of 0.64 mg L\(^{-1}\) remaining in solution (Figure 5(b)).

In contrast, the removal efficiency of Sb(V) from both chloride and sulfate media in the presence of phosphate was significantly reduced (Figure 5). As the ratio of phosphate to Sb(V) increased from 0.5 to 10 there was a decrease in removal percentage from 98.5% to 60.4% and from 82.1% to 60.6% from chloride and sulfate media, respectively. The presence of phosphate hinders the ability of Sb(V) to adsorb onto the surface of formed iron precipitates. In the presence of sulfate the effect translates to a decrease in removal percentage from 98.5% to 60.4% and from 95% to 53.9% from chloride and sulfate media, respectively. The presence of phosphate hinders the ability of Sb(V) to adsorb onto the surface of formed iron precipitates. In the presence of sulfate the effect translates to a decrease in removal percentage from 98.5% to 60.4% and from 95% to 53.9% from chloride and sulfate media, respectively.

### Table 1: Comparison of coagulant dosages used for antimony(III/V) removal in selected studies which used iron based coagulants and employed coagulation-flocculation-sedimentation techniques

<table>
<thead>
<tr>
<th>Antimony oxidation state</th>
<th>Initial [Sb] (mg L(^{-1}))</th>
<th>Coagulant*</th>
<th>Iron dose (mg L(^{-1}))</th>
<th>[Fe]/[Sb] mole ratio</th>
<th>Optimal pH</th>
<th>Percentage removal</th>
<th>Final [Sb] (μg L(^{-1}))</th>
<th>Target wastewater type</th>
<th>Major solution matrixb</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>0.010</td>
<td>FC</td>
<td>30</td>
<td>6.543</td>
<td>4.0-5.5</td>
<td>80-90%</td>
<td>1–2</td>
<td>Natural aquatic environment</td>
<td>Dechlorination tap water (North Kyushu district, Japan)</td>
<td>Nakamura &amp; Tokunaga (1996)</td>
</tr>
<tr>
<td>V</td>
<td>0.250</td>
<td>FC</td>
<td>200</td>
<td>1.745</td>
<td>4.0-5.5</td>
<td>80-90%</td>
<td>50–25</td>
<td>Natural reservoir and river waters</td>
<td>Filtered Kim Reservoir water (Okinawa, Japan)</td>
<td>Kang et al. (2005)</td>
</tr>
<tr>
<td>III</td>
<td>0.040</td>
<td>FC</td>
<td>6</td>
<td>338</td>
<td>5.0</td>
<td>95%</td>
<td>2</td>
<td>Natural river water</td>
<td>Synthetic natural water</td>
<td>Spiked DI water:</td>
</tr>
<tr>
<td>V</td>
<td>0.006</td>
<td>FC</td>
<td>21</td>
<td>7,524</td>
<td>5.0</td>
<td>92%</td>
<td>0.48</td>
<td>Synthetic natural water</td>
<td>Spiked DI water:</td>
<td>Guo et al. (2018)</td>
</tr>
<tr>
<td>III</td>
<td>0.050</td>
<td>FC</td>
<td>22</td>
<td>974</td>
<td>6.0</td>
<td>&gt;98%</td>
<td>0.7</td>
<td>Natural reservoir and river waters</td>
<td>Filtered Kim Reservoir water (Okinawa, Japan)</td>
<td>Kang et al. (2005)</td>
</tr>
<tr>
<td>V</td>
<td>0.050</td>
<td>FC</td>
<td>34</td>
<td>1,460</td>
<td>6.0</td>
<td>&gt;98%</td>
<td>0.7</td>
<td>Synthetic natural water</td>
<td>Spiked DI water:</td>
<td>Guo et al. (2009)</td>
</tr>
<tr>
<td>III</td>
<td>0.150</td>
<td>FC</td>
<td>22</td>
<td>325</td>
<td>6.0</td>
<td>94-96%</td>
<td>2.2</td>
<td>Natural river water</td>
<td>Synthetic natural water</td>
<td>Spiked DI water:</td>
</tr>
<tr>
<td>III</td>
<td>0.250</td>
<td>PFS</td>
<td>4</td>
<td>39</td>
<td>4.0–6.0</td>
<td>99–100%</td>
<td>&lt;2.5</td>
<td>Synthetic natural water</td>
<td>Spiked DI water:</td>
<td>Guo et al. (2018)</td>
</tr>
<tr>
<td>V</td>
<td>0.250</td>
<td>PFS</td>
<td>22</td>
<td>195</td>
<td>4.0–6.0</td>
<td>&gt;95%</td>
<td>&lt;12.5</td>
<td>Synthetic natural water</td>
<td>Spiked DI water:</td>
<td>Guo et al. (2018)</td>
</tr>
<tr>
<td>V</td>
<td>0.500</td>
<td>PFS/FS(^c)</td>
<td>42</td>
<td>183</td>
<td>5.0–6.0</td>
<td>79.90%</td>
<td>101</td>
<td>Simulated textile wastewater</td>
<td>Spiked DI water:</td>
<td>Liu et al. (2019)</td>
</tr>
<tr>
<td>V</td>
<td>0.500</td>
<td>PFS/FS(^c)</td>
<td>42</td>
<td>183</td>
<td>5.0–6.0</td>
<td>82.60%</td>
<td>87</td>
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<td>Spiked DI water:</td>
<td>Liu et al. (2019)</td>
</tr>
<tr>
<td>V</td>
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<td>PFS/FS(^c)</td>
<td>42</td>
<td>183</td>
<td>5.0–6.0</td>
<td>77.60%</td>
<td>112</td>
<td>Simulated textile wastewater</td>
<td>Spiked DI water:</td>
<td>Liu et al. (2019)</td>
</tr>
<tr>
<td>III</td>
<td>50.000</td>
<td>FC</td>
<td>446</td>
<td>20</td>
<td>5.0</td>
<td>99.60%</td>
<td>200</td>
<td>Simulated industrial wastewater</td>
<td>[Cl(^-)] = 0.5 M</td>
<td>This study</td>
</tr>
<tr>
<td>III</td>
<td>50.000</td>
<td>FC</td>
<td>460</td>
<td>20</td>
<td>5.0</td>
<td>99.60%</td>
<td>200</td>
<td>Simulated industrial wastewater</td>
<td>[SO(_4^{2-})] = 0.5 M</td>
<td>This study</td>
</tr>
<tr>
<td>V</td>
<td>50.000</td>
<td>FC</td>
<td>474</td>
<td>21</td>
<td>5.0</td>
<td>99.60%</td>
<td>200</td>
<td>Simulated industrial wastewater</td>
<td>[Cl(^-)] = 0.5 M</td>
<td>This study</td>
</tr>
<tr>
<td>V</td>
<td>50.000</td>
<td>FC</td>
<td>2,232</td>
<td>97</td>
<td>5.0</td>
<td>99.60%</td>
<td>200</td>
<td>Simulated industrial wastewater</td>
<td>[SO(_4^{2-})] = 0.5 M</td>
<td>This study</td>
</tr>
<tr>
<td>V</td>
<td>33.000</td>
<td>FC</td>
<td>4,464</td>
<td>295</td>
<td>5.0</td>
<td>99.40%</td>
<td>200</td>
<td>Real industrial wastewater</td>
<td>[PO(_4^{3-})] = 0.25 M; [PO(_4^{3-})] = 51 mg L(^{-1})</td>
<td>This study</td>
</tr>
</tbody>
</table>


1. Complete description of solution matrices found in Table S1 (available with the online version of this paper).

2. Achieved by coagulation-flocculation- ultrafiltration.

3. Coagulation PFS/FS.

4. Aerated PFS/FS.
particularly significant as phosphate raises the antimony concentration above the required release limit.

A likely explanation for the significant difference in Sb(V) removal with and without the addition of phosphate is due to both elements existing in group 15 of the periodic table and possessing similar chemistries. As with sulfate, phosphate forms anionic species in solution, with H2PO4-/CO being the dominant species at pH 5.0 (He et al. 2018). However, unlike sulfate which binds via an outer-sphere mechanism, phosphate adsorption is considered to proceed via an inner-sphere surface complexation mechanism (Equation (5)) (Kim et al. 2011), similar to Sb, and so not only does phosphate compete for the same adsorption sites as Sb(V) but it does so through the same mechanism. The formation of strong inner-sphere complexes between phosphate and ferric hydroxide results in a significant decrease of Sb(V) removal from both Cl⁻ and SO₄²⁻ media. The formation of insoluble iron-phosphate complexes may also affect both Sb(III) and Sb(V) removal by changing the physicochemical characteristics of the formed iron precipitates and their surfaces (Pierri et al. 2000).

≡FeOH + H₂PO₄⁻ → ≡FeOP(H)O₃⁻ + H₂O

(5)

Phosphate concentrations were also measured to ensure satisfactory removal occurred (Figure 5(c) and 5(d)). A release limit of 8 mg L⁻¹ is imposed for industrial wastewaters in Korea (MoE 2018). Removal of phosphate occurred to below the release limit at [PO₄³⁻]/[Sb] ≤ 9 corresponding to an initial phosphate concentration of 125 ppm, a concentration almost three times higher than what is found in the actual effluent (Foster et al. 2019). Phosphate removal appears unaffected by the presence of antimony in either oxidation state from sulfate media with only a minor difference in removal efficiency between Sb(III) and Sb(V) in chloride media. It can therefore be said with some confidence that, under the current process conditions, phosphate removal should pose no issue, with the extent of removal being directly related to the phosphate to iron ratio.

**Real waste tests**

As part of process verification, pilot plant trials for the treatment of the uranium-containing effluent were performed (Foster et al. (submitted)). These generated antimony-laden effluents high in phosphate for which antimony removal via ferric chloride dosing could be trialled (Table S2). A range of iron dosages were tested. Figure 6 shows the concentrations of phosphate and antimony remaining in the real effluent as a function of iron concentration. For comparison, the concentration of Sb(V) remaining in solution as a function of iron dose in sulfate media from laboratory tests is also shown.

Phosphate removal to below the release limit was confirmed at iron dosages ≤5 mM. This is in line with previous reported results (Foster et al. 2019). The removal of antimony was found to require significant iron dosages, only reaching the release limit at [Fe(III)] ≥ 80 mM ([Fe(III)]/[Sb] = 295) (Table 1). Comparing this result to earlier laboratory tests shows a clear similarity to the experimental conditions in which antimony is present in the +5 oxidation state. The difference in required iron dose to reach the targeted release limit for Sb between the laboratory and pilot plant tests is attributed to the presence of phosphate. It is
therefore likely that Sb(V) predominates in the real effluent and its removal is significantly affected by the presence of phosphate for reasons previously discussed. However, it should be noted that the effect of other contaminants, such as Mo or Si, cannot be ruled out at this point. Competition for binding sites by the molybdate anion, MoO$_4$$^-$$^2$, may be of particular prevalence and warrants further investigation.

**CONCLUSIONS**

Iron dosing followed by pH adjustment has been shown to be effective for the removal of antimony from wastewaters at initial concentrations akin to industrial processes via precipitation–coagulation–flocculation. Of the two oxidation states exhibited by antimony in solution, the removal of Sb(III) is significantly easier than Sb(V) owing to the formation of the charged Sb(OH)$_6$$^-$$^2$ species. Further, it has been shown that removal of Sb(V) from chloride media is easier than from sulfate media owing to competition for surface binding sites between Sb(OH)$_6$$^-$$^2$ and SO$_4$$^-$$^2$.  

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**Figure 5** Concentration of antimony remaining in solution as a function of phosphate concentration at optimal iron dose and pH: (a) from chloride media [Cl$^-$$^=0.5$ M; (b) from sulfate media [SO$_4$$^-$$^2$$^=0.5$ M. Corresponding concentrations of phosphate remaining in solution as a function of phosphate concentration at optimal iron dose and pH: (c) from chloride media [Cl$^-$$^=0.5$ M; (d) from sulfate media [SO$_4$$^-$$^2$$^=0.5$ M.

**Figure 6** Concentration of antimony and phosphate remaining in the real waste effluent as a function of iron dose.
species. A similar but more pronounced effect is also seen upon the addition of phosphate to solution, even in chloride media, due to Sb(OH)$_6$ and PO$_4^{3-}$ possessing a shared preference for inner-sphere binding. Real waste tests confirmed that antimony can be removed from solution but would require significant iron dosages and generate significant quantities of floc. The assumption that Sb(III) present in the original catalyst is oxidized to Sb(V) due to the oxic conditions of the treatment process seems to be supported based on a comparison of results from the laboratory and real waste tests. Under test conditions used there appears to be no issue with the removal of residual phosphate from the effluent to below the required release limit.

Based on the results obtained in this study, the removal of antimony from industrial effluents via iron precipitation–coagulation–flocculation is possible, and viable under most conditions such as chloride media, 3+ oxidation state or in the absence of phosphate. However, owing to the large dosages of iron required and subsequent large floc volumes generated, the removal of Sb(V) from phosphate-containing sulfate media, such as those generated during the treatment of the uranium–antimony catalyst, via iron precipitation–coagulation–flocculation is not recommended. An alternative approach, such as ion exchange, tailored adsorbents (e.g. nano zero valent iron) or membrane separation techniques, may offer a more viable solution to the problem at hand.

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COMPETING FINANCIAL INTERESTS

The authors declare no competing financial interests.

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