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TECHNICAL ARTICLE

Removal of Molybdenum from Mining-Impacted Water by Sorption onto Manganese-Rich Sludge

Sarah Doyle[1] · **Linda Figueroa**[1]

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Abstract

Molybdenum (Mo) concentrations in mining-impacted water can be orders of magnitude higher than health-based values for drinking water. Mo in oxidized mine waters is predominantly present as the oxyanion molybdate, which is problematic in mine water treatment because it is not removed by conventional alkaline addition treatment and requires separate Mo-specific methods. Mo removal by sorption to ferric precipitates is the typical treatment strategy. We investigated a sustainable alternative for a mine water with low-iron content and high manganese (Mn). We evaluate the potential for Mo removal by sorption onto Mn-rich sludge from a mine water treatment plant that uses lime to remove metals at pH 10. In laboratory sorption batch tests with an initial Mo concentration of 10 mg/L in a sodium chloride solution, over 90% of the Mo was removed onto the sludge at pH 6 and below (up to 34 mg Mo/g Mn). Sorption was sensitive to pH, with sharp decreases in sorption levels from pH 6 to 8. Sorption was also affected by the matrix composition of the mine water samples, apparently due to competitive sorption from other ions in the mine water. Use of site Mn for water treatment provides a more sustainable treatment approach; however, additional knowledge is required to understand the effects of site-specific complexities.

Keywords Molybdate · Adsorption · Mine water treatment · Manganese hydroxide · Manganese oxide

Introduction

Molybdenum (Mo) is an important nutrient for humans and animals but can be toxic at high concentrations (ATSDR 2020; CCME 1999). In drinking water sources, Mo levels are typically well below those of health concern (Smedley et al. 2014; WHO 2017) and regulations vary widely by jurisdiction. The U.S. Environmental Protection Agency (USEPA) has not set an enforceable standard for Mo in drinking water but has established a drinking water equivalent level of 0.2 mg/L (USEPA 2018). Canada currently has an interim guideline of 0.073 mg/L for the protection of freshwater aquatic life (CCME 1999). Water quality discharge targets are site specific.

Water affected by mining and mineralized areas can have Mo concentrations that are two orders of magnitude above these health and aquatic level guideline levels, particularly in waters affected by copper, Mo, and uranium mining. At Antamina, a copper–zinc–Mo mine in Peru, drainage from waste rock was found to contain up to 4.7 mg/L Mo from experimental waste rock piles and up to 13.9 mg/L Mo from small-scale field tests conducted in 60 L barrels (Skierszkan et al. 2016). At the Brenda mine site, a former copper-molybdenum mine in British Columbia, Canada, drainage from tailings and waste rock contains 3 mg/L Mo on average (Aubé and Stroiazzo 2000). At a former uranium ore milling site in Colorado, U.S., the groundwater contained 4.8 mg/L Mo on average (Morrison et al. 2006). Mo concentrations are typically less than 10 mg/L due to solubility controls, particularly for waters containing lead or calcium, in which Mo may precipitate as wulfenite ($PbMoO_4$) or powellite ($CaMoO_4$), respectively (Conlan 2009).

Mo chemistry is complex due to the range of oxidation states possible (2^+ to 6^+); detailed reviews of its aqueous geochemistry can be found in Smedley and Kinniburgh (2017) and Xu et al. (2013). In oxidized mine waters with a pH exceeding 4, Mo is present predominantly as the oxyanion molybdate (MoO_4^{2-}). Molybdate is problematic in mine water treatment because it is not removed by

✉ Sarah Doyle
sdoyle@mines.edu

Linda Figueroa
lfiguero@mines.edu

[1] Colorado School of Mines, Golden, CO, USA

conventional alkaline addition treatment, which removes metals from mining-impacted water by precipitation of metal hydroxides. The alkaline and oxic conditions created during conventional treatment are ideal for molybdate to remain in the aqueous phase (Smedley and Kinniburgh 2017). For stream water affected by mining, LeGendre and Runnells (1975) proposed removing Mo with ferric precipitates at low pH (3–4), although the exact mechanism of removal could not be identified (coprecipitation with ferric oxyhydroxides, adsorption, or precipitation of an iron-molybdenum compound). Ferric iron has since been used to remove Mo from mine water at the Golden Giant Mine in Ontario, Canada (Sencza 2013), Brenda mine site in British Columbia, Canada (Aubé and Stroiazzo 2000), and El Teniente mine in Chile (Aubé and Vergara 2010). Both El Teniente and Brenda mine site used an iron to Mo mass ratio of 10:1 at low pH (pH 4.5 at Brenda Mines and pH 4.7 at El Teniente).

In addition to ferric iron precipitates, manganese (Mn) oxides also have the potential to remove Mo from the aqueous phase. Due to high surface area and high chemical activity, Mn oxides are well known scavengers of both metal cations and anions in the environment, with anion sorption dominating at low pH when the oxide surface has a net positive charge (Balistrieri and Chao 1990; Murray 1975; Post 1999; Smith 1999). Balistrieri and Chao (1990) compared sorption of several anions onto both amorphous iron oxyhydroxide and Mn dioxide and found that at pH 7, Mo sorption levels were about the same for the two oxides. Cui et al. (2021) and Matern and Mansfeldt (2015) also evaluated Mo sorption onto Mn oxides; at pH 7, the extent of sorption ranged from 30 to 95% depending on experimental conditions. However, these Mo sorption studies used pure laboratory-synthesized Mn oxides, which may differ in their sorption properties from Mn solids formed in mine-impacted waters.

We investigated the potential for Mo to be removed from a low-iron mine water by sorption onto Mn-rich sludge from a high-density sludge (HDS) mine water treatment plant (WTP). For this study, the effects of sorption are isolated from coprecipitation because the sorbent used in the study (sludge) had already formed at a mine WTP, where the pH of the mine water had been increased to 10 with lime, which removes metals as hydroxides. In HDS treatment systems, a fraction of the sludge from the thickener is recirculated to the reactor to promote metal precipitation. As the sludge is recirculated, newly-formed Mn hydroxide ages to form more oxidized forms, such as Mn_3O_4, MnOOH, and MnO_2 (Murray et al. 1985). This evaluation of WTP sludge as a sorbent is unique due to the amorphous characteristics of the sludge, various oxidation states of Mn solids, and presence of other precipitates. Analyses of aged sludges by Zinck et al. (1999), suggests that precipitates in the sludge may include gypsum, calcite, and hydrotalcite-like phases.

Compared to Mo treatment by ferric iron addition, removal of Mo onto Mn-rich sludge provides a more environmentally sustainable approach at sites where Mn is already present at high concentrations and/or a Mn-rich sorbent is readily available. In addition, we investigated the potential to remove Mo at circumneutral pH, thereby potentially reducing the need for pH-adjusting reagents when compared to treatment by ferric iron addition. Using on-site Mn and reducing chemical use aligns with sustainable development goal 12 of the United Nations, which aims for responsible consumption and production (United Nations 2015). Sustainable approaches like these are needed not only to reduce treatment costs, but also to reduce the carbon footprint associated with construction and transportation of equipment and chemicals to mine sites, especially for sites located in remote areas.

Materials and Methods

Water Treatment Plant Sludge

Sorption tests were conducted using sludge from an HDS mine WTP, which removes metals (primarily Mn) by raising the pH to 10 with lime. Sludge was collected from the WTP thickeners at the mine site and then sent to the Colorado School of Mines laboratory. The sludge was vacuum filtered prior to use in the sorption batch tests. The solids content of vacuum-filtered sludge was measured by drying two 6 g sludge samples at 40 °C for a total of 48 h, after which the mass was constant (change of less than 1% in 24 h). The metals content of the sludge was analyzed by microwave digesting dried sludge in nitric acid (Method 3051a from USEPA 2007), followed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis. Table 1 summarizes the properties of the vacuum-filtered sludge used in the batch sorption tests.

Table 1 Properties of vacuum-filtered sludge used in batch tests

Percent solids	Elemental content (% by mass solids)							
	Al	Ca	Fe	Mg	Mn	S	Si	Zn
54%	2.1	15	0.91	3.9	11	1.7	0.17	0.33

Values are averages of duplicates. Arsenic, cadmium, copper, selenium, and nickel were also detected, but at concentrations less than 500 ppm (content of less than 0.05% by mass of solids)

Sorption Batch Test Methods

The general method for batch sorption tests consisted of mixing vacuum-filtered sludge with 40 mL of Mo-spiked solutions. The sludge and Mo solutions were mixed in 50 mL tubes on an end-over-end mixer for 24 h, followed by analysis of the final solution. Mo-spiked solutions were prepared from both NaCl and WTP influent collected from the mine. A sample of WTP influent from the mine was analyzed by ICP-AES and ion chromatography (IC) for metals and anions, respectively. Chemical composition of the WTP influent is summarized in Table 2. All batch tests were conducted in duplicate. Additional details of batch test methods are provided in the following paragraphs.

pH Tests

Initial batch tests were conducted to evaluate the effect of pH on sorption. These tests were conducted using Mo-spiked solutions prepared from 0.1 M sodium chloride (NaCl) and WTP influent from the mine. For tests with NaCl solutions, 0.2 g of vacuum-filtered sludge was mixed with 39 mL of a mixture of 0.1 M NaCl and 0.1 M HCl (volumes of 0.1 M HCl ranged from 0 to 15 mL, with the remainder comprised of 0.1 M NaCl). For tests with WTP influent, 1 g of vacuum-filtered sludge was mixed with 33 mL of WTP influent and 6 mL of a mixture of HCl/NaCl (volumes of 1 M HCl ranged from 0.5 mL to 5 mL, with the remainder comprised of 0.1 M NaCl). The sludge and solution mixtures were allowed to equilibrate until the pH stabilized (approximately 1 h). The solutions were then spiked with 1 mL of a 400 mg/L Mo solution prepared from sodium molybdate, to achieve an initial concentration of 10 mg/L Mo. The initial pH values of the mixtures were measured and ranged from approximately 2 to 10. After mixing for 24 h, the final pH was measured, and an aliquot was filtered using a 0.45 µm filter and analyzed for Mo using spectrophotometric methods (Hach Company 2019).

Additional Batch Tests with WTP Influent

Additional sorption batch tests were conducted using Mo-spiked solutions prepared from WTP influent to evaluate the effect of initial Mo concentration and matrix composition on sorption. Conditions for these tests are summarized in Table 3. For each test, sludge was first mixed with WTP influent and 1 M HCl. The mixture was allowed to equilibrate until the pH stabilized (approximately 1 h). The mixture was then spiked with Mo solutions to obtain the desired initial concentration (1.1, 2.6, or 10 mg/L) and the initial pH was measured. After 24 h of mixing, the final pH was measured, and an aliquot was filtered using a 0.45 µm filter. The filtrate was acidified, diluted, and analyzed for metals and sulfur using ICP-AES.

An additional test was conducted to evaluate sorption of anions from the WTP influent onto the sludge, in which 1 g of vacuum filtered sludge was mixed with 39.4 mL WTP influent and 0.6 mL 1 M HCl for 1 h. After mixing, two aliquots were collected. Both aliquots were filtered using a 0.45 µm filter, one was also diluted, and both were analyzed by IC for fluoride.

Results and Discussion

Effect of pH

Figure 1 presents results for the batch tests conducted to evaluate the effect of pH on sorption. Tests were conducted with initial Mo concentrations of 10 mg/L, and the results

Table 2 Chemical composition of WTP influent used in batch tests

pH	Sulfate[1]	F	Al	Ca	Mg	Na	K	Fe	Mn	Mo	Si	Zn
6.2	960	14	1.2	320	31	18	36	< 0.0003	10	0.13	2.0	0.20

Concentrations are mg/L, except for pH in su

[1] Sulfate concentration calculated by charge balance

Table 3 Batch test conditions

Description	Sludge mass (g)[1]	Initial solution composition			
		pH	WTP influent volume (mL)	HCl (1 M) volume (mL)	Mo solution (40,100, or 400 mg/L) volume (mL)
Low pH; low sludge mass	1	5.5	35	4	1
Low pH; high sludge mass	4	5.8	33	6	1
High pH; low sludge mass	1	6.7	38.4	0.6	1
High pH; high sludge mass	4	7.0	37.5	1.5	1

[1] Sludge masses are for vacuum-filtered sludge, which is 54% solids

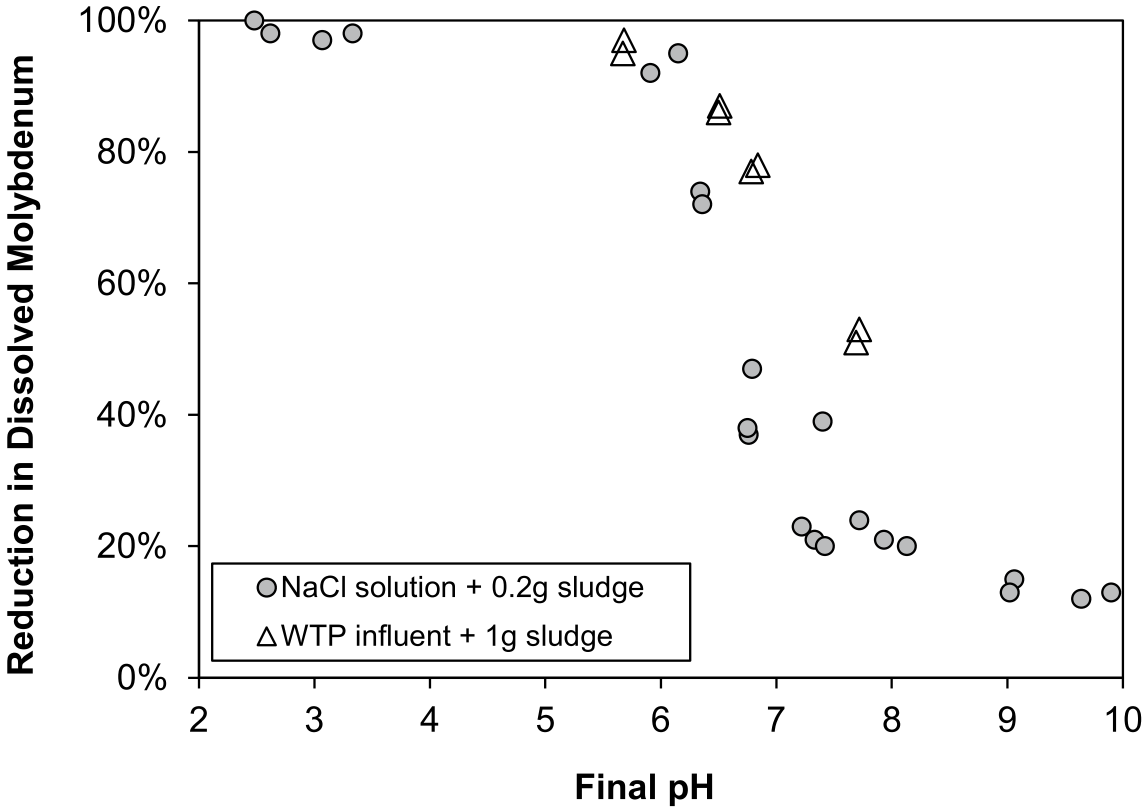

Fig. 1 Results of pH batch tests. Initial Mo concentration was 10 mg/L. NaCl solutions were mixed with 0.2 g vacuum-filtered sludge (0.11 g dried sludge). WTP influent solutions were mixed with 1 g vacuum-filtered sludge (0.54 g dried sludge)

show decreases in dissolved Mo concentrations, which are attributed to sorption of Mo onto the Mn-rich sludge from the WTP. Maximum sorption (over 90% removal of dissolved Mo) occurs in solutions with pH near 6 and below. From approximately pH 6 to pH 8, Mo sorption decreases, with approximately 20% of dissolved Mo removed from the sodium chloride solutions at pH 8. Although maximum sorption onto the WTP sludge occurs at pH less than 6, results indicate that Mo sorption still occurs to a lesser extent at neutral to alkaline pH. For example, 52% of Mo was removed from solutions of Mo-spiked WTP influent with an initial pH of 6.8 (final pH of 7.7). These results are consistent with other laboratory studies of Mo sorption onto Mn oxides. Matern and Mansfeldt (2015) found that maximum sorption occurred at pH 3 with approximately 95% of Mo sorbed, but also report 10% of Mo sorbed at pH 9. Similarly, Cui et al. (2021) observed maximum sorption at pH 4, but also report over 30% of Mo sorbed at pH 8. Balistrieri and Chao (1990) also report that over 30% of Mo was sorbed at pH near 7.5.

The observed trends with pH were expected and are typical for sorption of oxyanions on metal oxides (Smith 1999). At pH values less than the point of zero charge (PZC), the metal oxide surface has a net positive charge, which favors sorption of anions. Results from the batch tests suggest that the PZC for the Mn-rich sludge is near 7, the approximate inflection point of the sorption/pH curve (Fig. 1). This PZC is higher than values typically reported for Mn oxides/hydroxides. Kosmulski (2009) reviewed literature-reported values and found that for MnO_2, the median PZC was 4.6 with a standard deviation of 1.3, based on a review of 21 values for synthetic Mn minerals (nominally referred to as MnO_2, but often with Mn oxidation states less than 4). However, Mn solids exhibit a wide range of characteristics due to three valence states (+2, +3, +4), numerous structures, and the potential to incorporate other metal cations (Post 1999). Circumneutral PZCs have been reported by several authors, including Matern and Mansfeldt (2015; 7.3 for synthetic birnessite); Della Puppa et al. (2013; 8.3 for synthetic Mn oxide); and Kung (1989; 7 for $Mn(OH)_2$). The presence of impurities in the sludge may also change the PZC relative to studies with pure-phase Mn minerals. Adsorbed metal cations, such as zinc, may shift the PZC to a higher pH (Hohl et al. 1980; Stumm and Morgan 1996).

Sorption Mechanisms

Figure 2 shows the change in pH for tests using NaCl solutions. Increases in pH are attributed primarily to molybdate sorption onto metal oxides/hydroxides and provide further evidence for this mechanism of Mo removal. Slow dissolution reactions with the sludge may also cause pH increases; however, the effect of this was minimized during testing by equilibrating the sludge with acid prior to adding Mo solutions. Sorption of molybdate onto metal oxides, such as iron oxides, has been suggested to occur primarily through ligand exchange at low pH (Das and Hendry 2013; Davantès and Lefèvre 2015; Goldberg et al. 1998, 2008), which results in an increase in pH. Equations 1 through 3 show potential ligand exchange reactions for surface "S" for monodentate and bidentate sorption, adapted from selenium sorption reactions presented by Balistrieri and Chao (1990).

$$\mathrm{SOH} + \mathrm{MoO}_4^{2-} + \mathrm{H}^+ \rightarrow \mathrm{SMoO}_4^- + \mathrm{H}_2\mathrm{O} \quad (1)$$

$$\mathrm{SOH} + \mathrm{MoO}_4^{2-} + 2\mathrm{H}^+ \rightarrow \mathrm{SHMoO}_4 + \mathrm{H}_2\mathrm{O} \quad (2)$$

$$2\mathrm{SOH} + \mathrm{MoO}_4^{2-} + 2\mathrm{H}^+ \rightarrow \mathrm{S}_2\mathrm{MoO}_4 + 2\mathrm{H}_2\mathrm{O} \quad (3)$$

At initial pHs greater than 7, Mo removal was accompanied by a negligible change in pH, while tests at an initial pH exceeding 9 averaged decreases in pH (Fig. 2). At these pHs, the sorbent surface would be expected to have a net negative charge and favor adsorption of metal cations. Mo removal at high pH may be due to formation of ternary metal-anion complexes, involving co-sorption of a metal cation and molybdate ion. At alkaline pHs, studies have suggested that ternary metal-anion complexes occur as "Type A", in which the metal sorbs to the oxide surface and forms a bridge to the anion (Elzinga and Kretzschamer 2013; Yan et al. 2022; Zaman et al. 2009). The presence of impurities in the sludge may increase anion sorption capacity. Zhao et al. (2018) found that coprecipitation of zinc with MnO_2 increased the sorption capacity, affinity, and kinetics of anions (phosphate and arsenate), compared to sorption onto pure MnO_2. Equation 4 presents a proposed simplified reaction for the formation of a metal-anion complex, with zinc as an example, as adapted from studies involving other metal-anion surface complexes (Schindler and Stumm 1987; Zaman et al. 2009). Sorption of metal cations and formation of a cation-bridged ternary complex (Eq. 4) would decrease the pH and could contribute to the decreases in pH observed in several of the sorption tests conducted at alkaline pHs.

$$\mathrm{SOH} + \mathrm{MoO}_4^{2-} + \mathrm{Zn}^{2+} \rightarrow \mathrm{SOZn} - \mathrm{MoO}_4^- + \mathrm{H}^+ \quad (4)$$

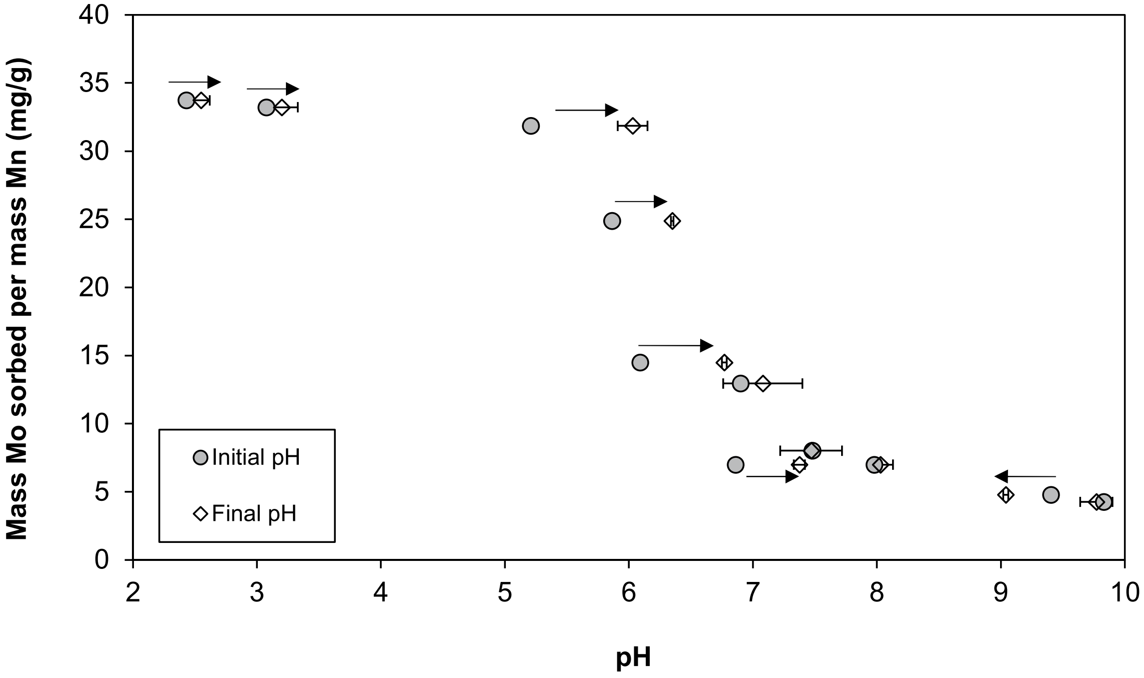

Fig. 2 Mass Mo sorbed as a function of both initial and final solution pH. Values are averages of duplicate tests. Mass sorbed is per mass of Mn in dried sludge. Arrows indicate the direction of change in pH that occurred after 24 h. Error bars indicate the range of values for final pH. Initial pH had low variability between duplicates (<=0.05 pH units) and is therefore not shown

Other Potential Mechanisms of Removal

In addition to sorption onto Mn solids, other potential mechanisms of Mo removal were evaluated, but determined to have minimal impact on Mo removal in the batch tests. Sorption onto layered double hydroxides (LDHs) was considered, as well as precipitation of powellite ($CaMoO_4$). LDHs, also referred to as hydrotalcite-like compounds, consist of layers of positively charged metal hydroxides that are charge-balanced by interlayered anions. LDHs may remove anions from solution by exchange with anions in the interlayer or by surface adsorption. Zhang and Reardon (2003) used hydrocalumite to reduce Mo concentrations in fly-ash leachate from 9.8 mg/L to less than 0.08 mg/L. Ardau et al. (2012) used a zinc-aluminum sulfate LDH to reduce Mo concentrations in synthetic solutions at neutral pH.

LDHs may be present in the sludge collected at the mine site and used in this study, thereby providing additional capacity to remove Mo from solution. Chemical speciation of the WTP influent (Table 2) indicates that hydrotalcite ($Mg_4Al_2(OH)_{14}.3H_2O$) is oversaturated at pHs greater than 8, when using a solubility constant of $\log K_{sp}$ 73.74, as defined by Atkins et al. (1992) in the ThermoChimie thermodynamic database (ThermoChimie Partners 2018). Hydrotalcite-like compounds also were found to potentially exist in sludge formed by lime treatment in a study of sludge aging (Zinck et al. 1999). The major phase found in most of their aged sludge samples was a non-homogeneous, poorly crystalline Ca–Mg–Fe sulfate hydroxide hydrate, which the authors presume to be a member of the hydrotalcite group. LDHs have also been reported as secondary minerals in net-alkaline mine drainage at the Baccu Locci mine in Sardinia, specifically zinc-copper–aluminum sulfate LDHs (Ardau et al. 2011).

The potential presence of LDHs in the sludge is estimated to contribute to less than 10% of the Mo removed at neutral to alkaline pHs. Zhang and Reardon (2003) report approximately 0.4 mg Mo removed per gram of hydrocalumite. Assuming WTP sludge is up to 10% hydrotalcite by mass (based on aluminum content), and similar sorption affinities to hydrocalumite, estimated Mo removal onto hydrotalcite would be approximately 0.04 mg Mo/g dried sludge. For comparison, tests in this study have Mo removal rates of 0.4 to 0.8 mg Mo/g dried sludge at neutral to alkaline pH.

Precipitation of powellite ($CaMoO_4$) was also evaluated as a potential mechanism of Mo removal in the batch tests. Initial batch test solutions are oversaturated with respect to powellite, with saturation indices ranging from 0.3 to 1.3 for initial solutions with 320 mg/L calcium and Mo concentrations from 1.1 to 10 mg/L, respectively, when using a $\log K_{sp}$ of − 8.05 for powellite (Essington 1990). In a study by Conlan et al. (2012), waste rock from Antamina was found to contain a secondary mineral phase with a transitional composition close to powellite. However, Conlan et al. (2012) also found that powellite formation was kinetically limited in laboratory batch tests. In tests using high initial concentrations of 600 mg/L calcium and 200 mg/L Mo, they fit their early-time data using a second-order rate constant of 1.4×10^{-3} L/(mol•d) for powellite precipitation and $\log K_{sp}$ of − 8.05 from Essington (1990). However, as conditions approached equilibrium, precipitation was overpredicted and a revised $\log K_{sp}$ of − 6.40 was used to fit the data. For the 24 h batch tests described here, initial Mo concentrations are low relative to Conlan et al. (2012) and solutions are near equilibrium with respect to powellite. Powellite precipitation would therefore be expected to be kinetically limited. Furthermore, initial batch test solutions are undersaturated if the revised $\log K_{sp}$ of − 6.40 is used to predict equilibrium conditions, with saturation indices ranging from − 1.3 to − 0.3, suggesting that precipitation of powellite would not occur.

Degree of Sorption

Figure 3 shows the mass of Mo sorbed as a function of end-of-test Mo concentration for tests using solutions prepared from WTP influent. Initial Mo concentrations ranged from 1.1 to 10 mg/L Mo, which was selected to target the concentration range most likely encountered in mining-affected waters requiring Mo treatment. For an end-test-concentration of 0.3 mg/L, a reasonable target for water treatment, Mo sorption is 6.7 mg Mo/g Mn for tests with an initial pH of 5.5 (final pH of 6). Sorption is reduced to 0.4 mg Mo/g Mn for tests with an initial pH of 6.7 (final pH of 7.8). Balistrieri and Chao (1990) and Cui et al. (2021) found similar levels of Mo sorption in batch tests with Mn oxides prepared in the lab. In kinetic sorption tests, data from Cui et al. (2021) show sorption of approximately 3 mg Mo/g Mn and 1 mg Mo/g Mn after 24 h in tests with initial concentrations of 1 mg/L Mo and initial pH values of 6 and 8, respectively. Balistrieri and Chao (1990) report approximately 70% removal of Mo by sorption at pH 7.2 for a solution with an initial concentration of 1 mg/L and 100 mg/L MnO_2 (sorption of 11 mg Mo/g Mn). These two studies used MnO_2 solids formed in the laboratory from permanganate solutions, which allowed for formation of relatively pure-phase minerals. In contrast, the sorbent in our study was WTP sludge with a high Mn content of approximately 11% by mass and containing numerous trace metals (See Table 1). The similar degrees of sorption, as measured in mg Mo/g Mn, suggest that impurities in the sorbent do not significantly affect the sorption properties and pure phase MnO_2 minerals are not needed for Mo sorption to occur.

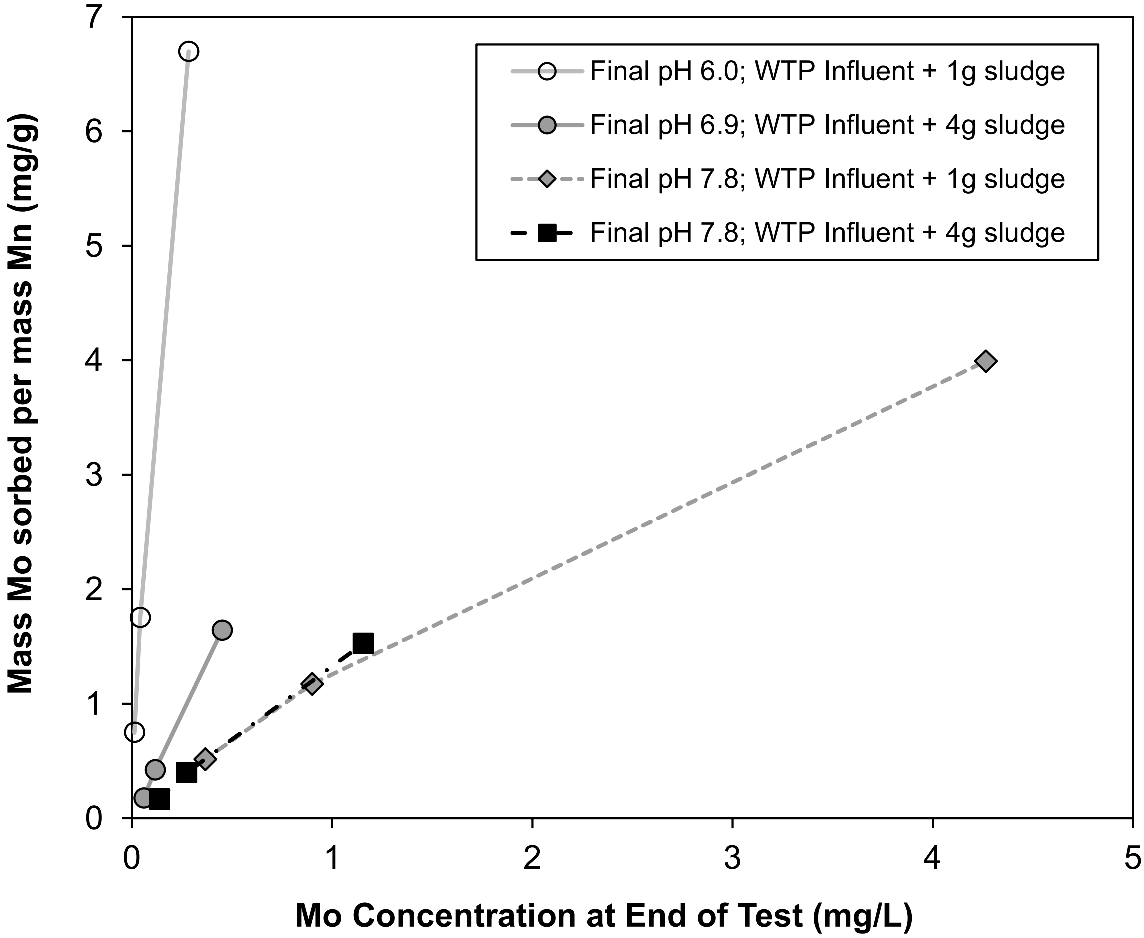

Fig. 3 Mo sorption as a function of end-of-test Mo concentration for tests using WTP influent. WTP influent was mixed with either 1 g or 4 g of vacuum-filtered sludge (dried sludge mass of 0.54 g or 2.2 g, respectively). Values shown are average of duplicate tests

Matrix Effects

In tests using WTP influent, Mo sorption was less than in the pH sorption tests using sodium chloride solutions. For tests with a final pH near 6 and initial Mo concentration of 10 mg/L, Mo sorption averaged 28 mg Mo/g Mn in tests using sodium chloride solutions, compared to 7 mg Mo/g Mn in tests using WTP influent. Similarly, for a final pH near 7.8, Mo sorption averaged 8.3 mg Mo/g Mn for sodium chloride solutions, compared to 3.8 mg Mo/g Mn for WTP influent. Lower levels of Mo sorption in solutions prepared from WTP influent are attributed to competitive sorption from other anions in WTP influent. To evaluate which anions are sorbing to the sludge, the chemical composition of WTP influent was compared before and after mixing with acidified sludge (1 g vacuum-filtered sludge mixed with 39.4 mL WTP influent and 0.6 mL 1 M HCl for 1 h). Fluoride concentrations were reduced from 14 mg/L to an average of 8.4 mg/L (± 0.5 mg/L) when the WTP influent was mixed with sludge, suggesting sorption of fluoride onto the sludge. Lower levels of sorption with WTP influent compared to sodium chloride solutions are therefore attributed, at least in part, to the presence of fluoride in the WTP influent. Concentrations of phosphate, arsenate, and selenate are low in the WTP influent (<0.04 mg/L) and were therefore expected to have a negligible effect on molybdate sorption. The effects of both sulfate and silicate could not be evaluated because sulfur and silicon concentrations increased during the batch tests. Sulfate concentrations in the WTP influent are high (≈1000 mg/L); however, Matern and Mansfeldt (2015) observed that sulfate enhanced Mo adsorption to Mn dioxides.

Balistrieri and Chao (1990) evaluated the effect of competitive anions (fluoride, molybdate, sulfate, phosphate) on selenite sorption onto both iron and Mn oxides. They found that when equimolar anion concentrations were tested at pH 7, the sorption affinity on Mn oxide was highest for molybdate, followed by phosphate, and silicate. Sulfate and fluoride were found to not influence selenite adsorption on the oxides, except at the highest anion to selenite ratios studied (100,000 times higher molar concentrations). Results from our study suggest that fluoride sorption may be more significant in competing with molybdate for sorption sites. In one hour of mixing with the sludge, fluoride sorption was 0.21 mmol F/g Mn, which is a similar magnitude to the highest 24 h Mo sorption in this study (0.34 mmol Mo/g Mn). These results suggest that fluoride has the potential to occupy a large fraction of the available anion sorption sites. Sorption competition from fluoride is also an important consideration for molybdate treatment because fluorine is often present (commonly > 1%) in porphyry Mo deposits (Ludington and Plumlee 2009).

Implications for Treatment

Results of laboratory batch tests support alternative approaches for Mo removal onto Mn-rich sludge and the feasibility of the approaches depends on site-specific characteristics, including Mn-to-Mo ratios during treatment and the required post-treatment concentration. The highest extent of Mo removal would require that the pH 10 sludge from the initial stage of treatment be acidified to pH 5.5 for use as a sorbent for Mo in a second treatment stage. At an initial pH of 5.5, Mo removal in batch tests was above 90%, with sorption of 32 mg Mo/g Mn (Figs. 1 and 2). In the absence of competing ions, an influent Mo concentration of 2 mg/L could be treated to 0.2 mg/L (the USEPA drinking water standard for Mo; USEPA 2018) in the presence of 0.5 g/L sludge (56 mg/L Mn). If lower Mo removal rates are sufficient to meet treatment objectives, then sludge could be acidified to circumneutral for use as a sorbent in second stage treatment.

Additional research is recommended prior to pilot testing. Previous sorption studies have shown that Mo sorption onto Mn oxides is initially fast (minutes) and decreases over time (Matern and Mansfeldt 2015; Zhao et al. 2009); however, additional kinetic tests would be needed to determine process hydraulic residence times for using WTP sludge. Additional laboratory testing is also recommended to evaluate simultaneous removal Mo and Mn at neutral to acidic pHs, which may allow for Mo removal through both sorption and coprecipitation. At neutral pH, Aguiar et al. (2013) demonstrated that Mn oxide residue from zinc electrowinning could be used as a catalyst to reduce Mn concentrations in mine water from approximately 100 mg/L to less than 1 mg/L. The addition of Mn oxide would also be beneficial for Mo removal, as it would provide additional sorption sites. Permanganate could also be used to simultaneously remove Mn and Mo and would also provide additional Mn for sorption. Freitas et al. (2013) demonstrated that potassium permanganate removed Mn from mine waters at pHs ranging from 3 to 7. Their work suggests that the treatment pH could be optimized for Mo sorption.

Summary

Manganese-rich sludge from a mine water treatment plant was used to remove Mo from solution, with sorption levels up to 34 mg Mo/g Mn. Sorption was found to strongly depend on pH, with highest Mo removal (over 90%) found in tests with final pH values from 3 to 6, and then decreasing above pH 6. Mo sorption onto the sludge, as measured in Mo mass sorbed per mass of Mn, was similar in magnitude to sorption reported in studies using laboratory-synthesized MnO_2 (Balistrieri and Chao 1990; Cui et al. 2021). Our results demonstrated that pure-phase MnO_2 is not necessary for sorption. Mo sorption occurred on non-crystalline solids with a large content of impurities and Mn likely in a range of oxidation states. This result may lead to more opportunities to remove Mo by sorption by broadening the range of applicable sorbents that may be used to remove Mo from mining-affected water.

The results of this study underscore the importance of using site-specific, rather than synthetic or laboratory-generated materials to evaluate treatment feasibility. Unique characteristics of site materials and water composition may act to either enhance or decrease treatment effectiveness. In this study, impurities in the sludge did not reduce Mo sorption relative to pure-phase Mn oxides, and the composition of the mine water reduced Mo sorption relative to a salt solution. In practice, other factors may also affect Mo removal. This study used pre-formed sludge; however, in-situ formation of MnO_2 would likely remove more Mo through coprecipitation. In addition, microbial and catalytic factors would influence the in-situ formation of MnO_2. Use of site Mn for water treatment provides a more sustainable treatment approach; however, additional knowledge is required to understand the effects of site-specific complexities.

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