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TECHNICAL ARTICLE

Controls on Zn Concentrations in Acidic and Neutral Mine Drainage from New Zealand's Bituminous Coal and Epithermal Mineral Deposits

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Abstract Zinc is one of the most abundant transition metals in mine water from coal mines and epithermal metal mines in New Zealand. Zinc is commonly conservative in mine drainage systems and remains soluble at concentrations that exceed guideline values for protection of aquatic ecosystems. This study presents a compilation of Zn concentrations and geochemical data from acid and neutral mine drainage sites. Geochemical modelling using PhreeqC indicates that secondary Zn minerals are unlikely to influence Zn concentrations except where Zn exceeds 100 mg/L and mine drainage $pH > 7$. Adsorption modelling using WHAM indicates that Zn is unlikely to be attenuated by adsorption onto Fe and Al precipitates that could form during neutralisation or oxidation of mine drainages, except when the ratio of precipitate to dissolved Zn is high ($\approx$100 mg/L precipitate and 0.1 mg/L Zn) and the $pH > 6$. Instead, Zn concentration is controlled by the source minerals and their rate of dissolution and dilution, rather than precipitation of secondary Zn minerals or adsorption. At some abandoned mine sites, or mineral prospects where leachate testing has been completed, Zn (±acidity) is the main chemical parameter that must be removed before discharge to the aquatic environment. Our results and interpretations constrain options for water management at future mine sites in New Zealand where Zn is present to: active treatment, passive treatment using reducing systems, or passive treatment that incorporate CaO-bearing reagents to achieve a $pH > 7$. Conventional limestone-based passive treatment systems are unlikely to remove Zn because $pH > 6$ is seldom achieved in such systems in an acceptable reaction time. Active treatment is unlikely to be possible at sites established to clean up abandoned mines sites, and therefore passive treatment should include a reducing system to remove Zn in order to meet guidelines for protection of aquatic ecosystems.

Keywords Solubility · Adsorption · Geochemical modelling

Introduction

Zinc concentrations have been measured in mine drainages from many mine environments in New Zealand and in rock leachate experiments for mine drainage prediction studies (Black and Craw 2001; Giles et al. 2010; McCauley et al. 2010; Pope et al. 2010a, and others). Zinc is one of the most abundant transition metals in mine drainage seeps and leachates from bituminous coal mines and epithermal metal mines. Sulphide minerals are the main source of Zn in mine water, especially sphalerite at epithermal metal mines and Zn impurities in pyrite at coal mines (Pope et al. 2010b; Weber et al. 2006; Weisener and Weber 2010), although leaching of Zn from other minerals (such as muscovite) is also possible. Concentrations of Zn in whole rock analysis are similar to concentrations in sulphide minerals for sub-bituminous coal measures in southern New Zealand (Black and Craw 2001). At operating sites, Zn is removed from mine drainage along with other enriched trace elements by active chemical water treatment plants. However, Zn discharges into the wider surface water environment at

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abandoned mines at concentrations that exceed background concentrations and environmental protection guideline values, sometimes by several orders of magnitude.

This study presents a compilation of data on Zn concentrations in New Zealand mine drainage environments (Fig. 1) and rock leachate experiments from a literature review, company presentations, and from company datasets. Mine drainage chemistry at bituminous coal mines has a bimodal pH, depending on the depositional environment and stratigraphy surrounding the coal measures. Acid mine drainage (AMD) from coal mines in New Zealand form where coal is mined from rocks deposited in an estuarine environment that is overlain by marine sediments. In this geological setting, the marine rocks provide SO_4(aq), diagenetic pyrite is a common Fe mineral, and mining of theses rocks allows the pyrite to oxidise, releasing acid and trace elements. Neutral mine drainage (NMD) from coal mines in New Zealand where coal was deposited in a fluvial depositional environment without overlying marine sediments. In this geological setting Fe-rich carbonates are common diagenetic minerals, sulphides are less abundant, and these rocks often release alkalinity with lower concentrations of trace elements than acid rocks after mining. Epithermal metal mines have highly variable mine drainage chemistry from different parts of the deposit because the ore zone and alteration mineralogy contains many different sulphide, carbonate, and silicate minerals, and these can be variably exposed during mining.

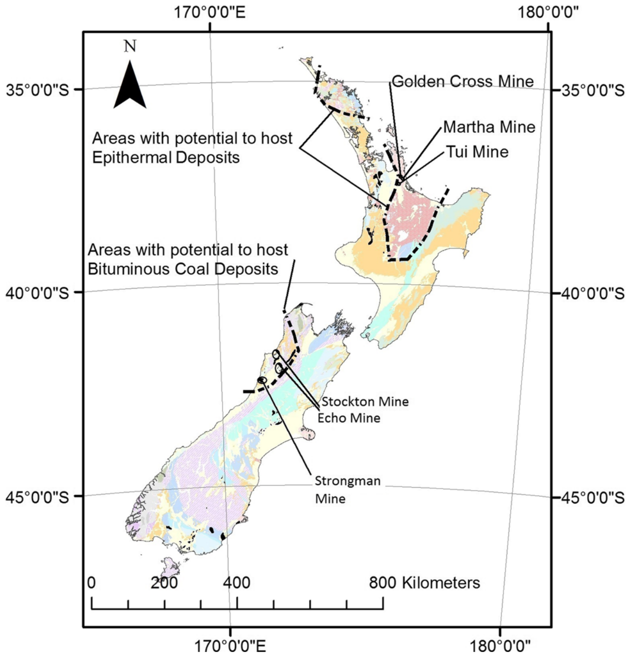

Fig. 1 Map of New Zealand showing distribution of geological formations or mine sites where Zn concentrations were measured

Our modelling indicates that minerals that might limit the concentration of Zn after release into mine drainages, such as Zn hydroxides, oxides, sulphates, or carbonates, are soluble under the conditions found in most mine drainage aqueous environments. Adsorption of Zn onto mineral surfaces occurs mostly between pH 6 and 8, depending on the ratio of sorbent to sorbate (Dzombak and Morel 1990). Therefore, at abandoned mines, elevated concentrations of Zn are likely to be partitioned into aqueous species rather than minerals or adsorbed species within and downstream of mine discharges, especially in acidic mine drainages ($pH < 6$). We interpreted data from these highly variable chemical environments with geochemical modelling, and considered the implications for remediation of historic mine sites and future development of mineral resources in New Zealand.

Methods

Mine Drainage Samples

Analyses to support this study were collected from the literature and from previous studies conducted by the authors. Details related to sample sites and related geochemical analyses are published elsewhere (Miller 1987; Pope and Weber 2013; Pope et al. 2010a, b, 2011). In general, epithermal metal deposits in New Zealand occur in the northeast of the North Island; the bituminous coal deposits occur in the west of the South Island (Fig. 1). Samples collected during this study were mostly collected as close to the source of the mine drainage seep as possible. Mine drainage samples where total aqueous concentrations are reported were collected and acidified ($pH < 2$). Samples where dissolved aqueous concentrations are reported were filtered to 0.45 μm using a disposable syringe and filter, then preserved in acid ($pH < 2$). Both total and dissolved concentrations of Zn and other components were measured by ICP-MS or ICP-OES at a commercial laboratory. The pH was measured using a field calibrated YSI multi probe; alkalinity was measured by titration.

Column Leach Tests

The laboratory-scale column leach test method adopted (Smart et al. 2002) used open Buchner funnels with a known mass (usually 1–2 kg) of crushed (−4 mm) rock, a mass-normalised distilled water weekly rinse, and a mass-normalised distilled water flush every 4 weeks. Rinse and flush volumes were scaled to match rainfall at the site where the samples were collected. Following the flush, all leachate was measured; sub-sampling and analysis varied depending on the purpose of the column test. The funnels were set up in standardised racks under heat lamps on a 12 h cycle to encourage capillary processes. Field scale column leach tests were set up in a similar manner but with ≈20 kg of crushed rock material (−10 mm) and under ambient climatic conditions. Analysis of dissolved components was completed in a similar manner to mine drainage sample analysis.

Neutralisation Experiment

Potentiometric titrations of AMD with crushed $CaCO_3$ were conducted so that sub-samples of the titre could be collected during the neutralisation process. Calcium carbonate was added to 1 L of AMD in accurately measured doses of about 0.05 g. The titre was gently stirred and the pH was recorded 2 min after the addition of the $CaCO_3$, and sub-samples were removed. Titre sub-samples were 20 mL, and were collected and filtered (0.45 μm) after every second addition of $CaCO_3$. Zinc and Fe, the major cations in these samples, were analysed at a commercial laboratory by ICP-MS.

Modelling

Aqueous speciation and mineral saturation modelling was completed using PhreeqC (Parkhurst and Appelo 1999). The saturation modelling reflects controls on Zn concentration at the time of discharge into the wider environment because samples were from the source of mine drainage seeps rather than downstream of the mines. Samples collected downstream of mines would be less useful to understand controls on Zn concentrations in mine drainage because site specific factors, such as mixing with other surface water would make interpretation difficult. All modelling was completed with a representative suite of major cation and anion chemistry so that ionic strengths and precipitation of other secondary minerals was incorporated into the modelling.

Partitioning between dissolved ionic species and adsorbed species was completed using WHAM (Tipping 1994; Tipping et al. 2002). The approach to adsorption modelling was to assume that Fe and Al dissolved in acidic or reduced mine drainages would precipitate and provide a substrate for adsorption. The sorbate: sorbent mass ratios for modelling were calculated from the measured dissolved Zn concentrations and measured total Fe and Al concentrations, assuming conversion of Fe to $Fe(OH)_3$ and Al to $Al(OH)_3$. A sensitivity analysis was completed using a range of Fe and Al concentrations with pH values measured in different types of mine drainage and no additional sorbent substrate was added. This means that the adsorption modelling reflected changes in dissolved to adsorbed Zn concentrations that can be achieved through neutralisation by hydroxide to a pH of 8, or oxidation of mine drainage without addition of other chemical reagents to increase adsorption.

Results

Bituminous Coal AMD and Column Leach Analyses

The pH was commonly between 2 and 4 in AMD from New Zealand's bituminous coal mines. Zn was typically one of the three most abundant dissolved transition metals, along with Fe and Mn, and the Al was also usually elevated. At seeps, the Zn concentration was commonly between 0.1 and 4 mg/L (Davies 2009; Davies et al. 2011b; Mackenzie 2010; Mackenzie et al. 2011; Pope et al. 2010a), although higher Zn concentrations, up to 18 mg/L, were occasionally measured (McCauley et al. 2010). The concentrations of Fe and Al was typically between 1 and 100 mg/L (Table 1). Where data was available from filtered and unfiltered samples, the Zn was typically greater than 90 % dissolved in samples from small streams (Davies 2009), and commonly close to 100 % dissolved in seep samples (Fig. 2). The fact that total Zn (unfiltered) was slightly less than dissolved Zn (filtered) in some samples reflects sampling and analytical uncertainty. Column leach data from the acid-forming coal measures samples had a range of concentrations that overlap the mine drainage seep chemistry, although the leachate sometimes had a lower pH, and higher acidity and trace element concentrations (Table 1).

Table 1 The range of Fe, Al, and Zn concentrations (mg/L) in acid mine drainage from bituminous coal mines

Mine drainage	pH		Fe		Al		Zn	
	Max	Min	Max	Min	Max	Min	Max	Min
Pope et al. (2010a, b)	5.85	2.53	105	0.86	115	0.6	4.08	0.006
McCauley et al. (2010)	3.7	2.05	1300	0.03	600	3.1	18	0.08
Davies et al. (2011a, b)	4.3	2.6	60	32	66	39	1.89	1.02
Mackenzie (2010)	3.96	2.94	3.3	0.97	55	1.1	3	0.15
Column leachate								
Pope et al. (2011), Pope and Weber (2013)	4.5	1.8	10,200	0.2	1190	2.2	99	0.4

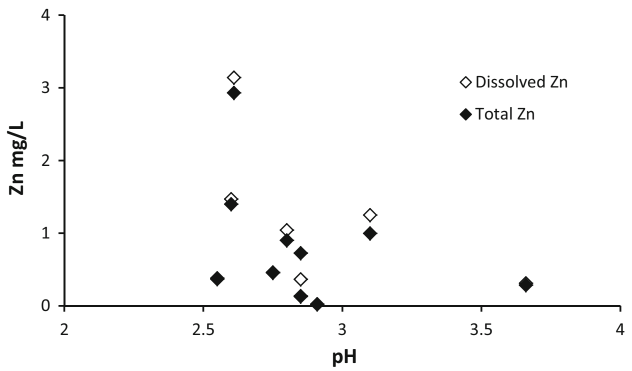

Fig. 2 Total and dissolved Zn concentrations in coal AMD seeps. Slightly elevated dissolved Zn compared to total Zn in some samples reflects analytical and sampling uncertainty

During neutralisation experiments with crushed calcium carbonate, Fe and Al concentrations decreased by more than two orders of magnitude as the pH changed from 2.8 to 6 (Supplementary Table 1) because of precipitation of Fe and Al minerals. Over this same pH range, the dissolved Zn decreased by about 40 %.

Bituminous Coal NMD and Column Leach Analyses

In NMD from coal mines, Zn was also commonly one of the three most abundant transition metals present; however, Zn concentrations were lower than in the coal AMD, with a maximum of 170 µg/L (Table 2). Iron concentrations ranged up to 12 mg/L, and reflected the presence of dissolved Fe(II). The Zn was 100 % dissolved (Fig. 3). In the NMD that contained adequate alkalinity, oxygenation caused Fe(II) oxidation and precipitation of $Fe(OH)_3$ or similar minerals, providing a substrate for adsorption of trace elements, such as Zn.

The column leach data (Table 2) had a low range of concentrations for dissolved Fe (up to 116 µg/L) and occasionally relatively high concentrations of Zn (>1 mg/L). Zn was often the most abundant metal present in these leachates, with the exception of the alkali and alkaline earth metals.

Epithermal Metal Mine Drainage and Column Leach Analyses

In mine drainage from abandoned epithermal metal mines or upstream of water treatment at active mine sites, Zn was again commonly one of the most abundant trace metals (along with Fe, Mn, and Cu), with concentrations usually between 0.1 and 20 mg/L (Table 3; Cameron 1991; Giles et al. 2010; Peterson and Kindley 1993). Occasionally, higher Zn concentrations were measured in seeps, up to 179 mg/L (Giles et al. 2010), and concentrations up to 563 mg/L have been reported in tailings-impacted groundwater (Pang 1995).

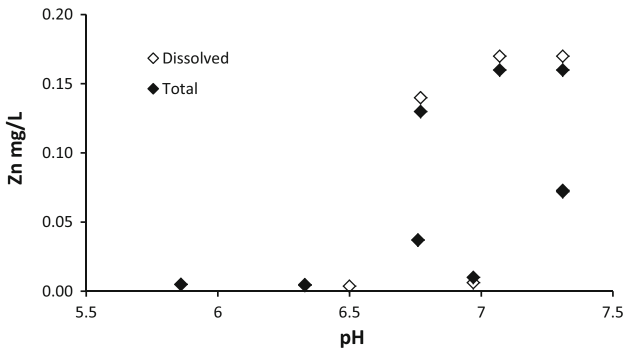

Fig. 3 Total and dissolved Zn concentrations in neutral coal mine drainage seeps

In these mine drainages, Fe was commonly present at relatively low concentrations, 0.4–10 mg/L, similar to NMD from coal mines. Leachate experiments indicate that Fe can be present at high concentrations (1100 mg/L) under acidic conditions. Commonly, leachate from epithermal mineral deposits have a lag period of NMD before acid formation occurs, as carbonate, silicate, or aluminosilicate mineral dissolution neutralises the acid produced by sulphide oxidation (Craw and Chappell 1998; Miller 1987).

Discussion

Bituminous Coal Acid Mine Drainage

The New Zealand coal AMD was undersaturated with respect to Zn minerals that could precipitate in these environments, indicating that the concentration of Zn in these systems is supply-limited (Fig. 4). Neutralisation of such drainages to pH 6–7 using limestone is achievable through fine limestone dosing (Table 2; Davies et al. 2011a) or to between 4 and 7 using limestone-based

Table 2 The range of Fe, Al, and Zn concentrations (mg/L) in neutral mine drainage from bituminous coal mines

	pH		Alkalinity as mg $CaCO_3$/L		Fe		Al		Zn	
	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min
Mine drainage	7.31	5.86	940	120	13	0.068	0.2	<	0.17	0.0037
Column leachate	8.3	4.1	75	1	0.16	0.02	0.08	0.019	1.3	0.001

Table 3 The range of Fe, Al, and Zn concentrations (mg/L) in mine drainage from epithermal gold mines

Epithermal metal mine drainage	pH		Alkalinity as mg $CaCO_3$/L		Fe		Al		Zn	
	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min
Peterson and Kindley (1993)	7	5	nd	nd	10	1	nd	nd	4	1
Cameron (1991)	7	6	nd	nd	0.2	10	nd	nd	5	0.5
Pang (1995)	7.8	6.6	nd	nd	9.75	3.97	nd	nd	25	15.5
Giles et al. (2010)	7.6	2.9	75	0	8.6	0.04	nd	nd	173	0.03
Column leachate										
Miller (1987)	6.4	7.8	nd	nd	1100	0.2	595	<	11.9	0.05

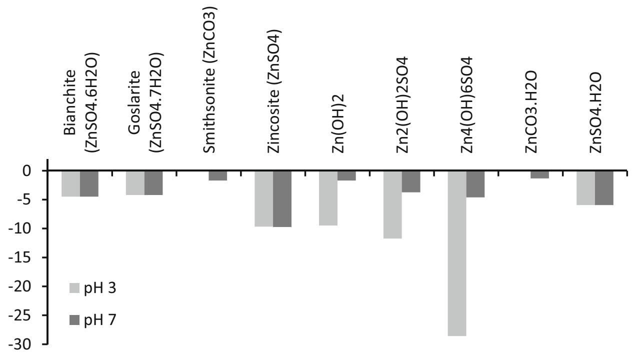

Fig. 4 Saturation of coal AMD and neutralised AMD with respect to Zn minerals, assuming maximum concentrations of 20 mg/L Zn, and 1000 mg/L SO_4. A carbonate concentration of 50 mg/L of CO_3 was introduced for modelling neutral mine drainages at pH 7; smithsonite and $ZnCO_3{\cdot}2H_2O$ were therefore only modelled at neutral pH

passive treatment systems (Mackenzie 2010; Mackenzie et al. 2011; Trumm and Watts 2010; Trumm et al. 2008); however, high pH (>6) is only achieved at extended residence times. These conditions are unlikely to lead to Zn mineral precipitation from coal mine drainage, although in rare circumstances, Zn removal has been reported in these systems (Nuttall and Younger 2000). All likely minerals remain undersaturated at conditions measured to date in coal NMD (Fig. 4).

The Zn in such mine drainage is likely to be from pyrite within the coal measures, although direct analysis of Zn in the pyrite has not been completed except in the lower rank coal measures (Black and Craw 2001). Direct Ni analysis in pyrite has been completed (Weber et al. 2006) and it correlates with the Ni in the coal measures drainage (de Joux and Moore 2005). Strong correlations between Zn and Ni, independent of pH, occur in AMD from different mine sites within acid-forming coal measures (Pope et al. 2010a), suggesting that Zn and Ni have a similar source. Data from column leach experiments that produce a highly acidic leachate usually show a strong relationship between Zn and Ni, supporting a common Zn and Ni source (Supplemental Figure 1). The ratio of Zn and Ni in leachate from different rock samples varies by about an order of magnitude; however, within each sample, the ratio is consistent. The relationships between Zn and acidity, Fe, or SO_4, in these column leach datasets is weaker (Supplemental Figure 2), despite the fact that these components are also directly related to pyrite breakdown. Secondary reactions that involve H^+, Fe, and SO_4, such as feldspar dissolution and jarosite precipitation (Pope et al. 2010a), and precipitation of other secondary sulphates, are common in mine drainage environments; however, Zn concentrations are not impacted by such processes. To summarise, Zn concentrations in coal AMD is controlled by the abundance and dissolution of Zn-bearing minerals, and is based on relationships with other minerals, mainly pyrite. Precipitation of secondary minerals (e.g. jarosite) does not appear to affect Zn concentrations.

During AMD neutralisation, a variety of Fe and Al oxide, hydroxide, and hydroxyl-sulphate minerals form (Nordstrom and Alpers 1999). In New Zealand coal mine drainage, the Fe minerals are most likely to be schwertmannite ($Fe_8O_8(SO_4)OH_6$) and ferrihydrite ($Fe(OH)_3$), and the Al minerals are most likely to be basaluminite and boehmite (AlOOH) (Davies et al. 2011a; Pope and Trumm 2014). These minerals form suitable substrates for adsorption of trace elements, such as Zn.

Adsorption of trace elements onto poorly crystalline Fe and Al minerals is controlled by pH and is influenced by ionic strength, aqueous speciation, and competition for adsorption sites (Dzombak and Morel 1990; Smith 1999). The effectiveness of adsorption for Zn removal from coal mine drainage during neutralisation also depends on the ratio of sorbent (Fe and Al minerals) to sorbate (dissolved Zn), which is controlled by the mine drainage chemistry. Using the range of concentrations reported for major cations (Fe, Al, and Zn) and anions for coal AMD, modelling with WHAM indicates that it is unlikely that adsorption will effectively remove Zn except where the ratio of Fe or Al-substrate to dissolved Zn is high ($\approx$100 mg/L Fe + Al and 0.1 mg/L Zn) and the pH > 7 after neutralisation (Fig. 5). This modelling does not

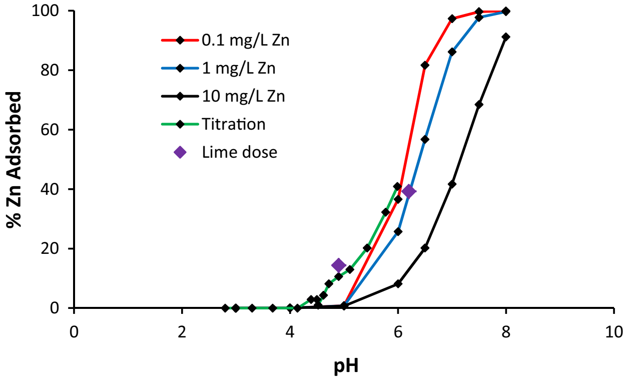

Fig. 5 Modelling of adsorption of Zn onto Fe and Al (each 50 mg/L dissolved) precipitates in coal AMD, assuming precipitation of $Fe(OH)_3$ and $Al(OH)_3$, respectively, based on titration data (Table 3) and lime dose data (Davies 2009)

integrate mineral-specific adsorption isotherms, but comparison with results from experiments indicates that this approach to modelling is appropriate. Experimental and field data representing neutralisation of coal AMD with crushed limestone indicate that the pH at which adsorption begins is about 0.5 U less than that predicted by modelling, but from pH 5 onwards, modelling matches experimental data well. Adsorption remains relatively incomplete at around 40 % after the neutralisation reaction between limestone and AMD has slowed at pH ≈ 6 (Fig. 5).

Neutral Bituminous Coal Mine Drainage

The Zn concentrations in NMD was undersaturated with respect to Zn minerals throughout the range of pH and Zn concentrations measured (Fig. 6), and therefore its concentration in these NMD is limited by the abundance of Zn-bearing minerals and their dissolution rates rather than precipitation of secondary Zn minerals.

The source of Zn in the coal measures that produce NMD has been less studied than in AMD. However, in weakly acid to circumneutral column leach data, there are relationships between Zn and Ni that indicates a common source for Ni and Zn similarly to AMD, and, despite the neutral conditions, the source could be the pyrite that is present in these coal measures rocks, though less abundant than in acid-forming rocks. In these conditions, pyrite oxidation and breakdown could still take place; however, the acidity generated would be neutralised by the carbonate minerals that are common in these rock types.

In NMD that contain dissolved Fe(II), oxygenation will cause oxidation to Fe(III) and precipitation of $Fe(OH)_3$. The effectiveness of this substrate to adsorb Zn in the mine drainage and column leach experiments depends on the pH and abundance of Fe (Fig. 7). At $pH > 7.5$ and with a ratio of 10 mg/L Fe to 0.01 mg/L Zn modelling indicates that over 90 % of Zn will be adsorbed. However, under the other scenarios modelled, less than 50 % of the Zn is likely to be adsorbed, even if all the dissolved Fe precipitates.

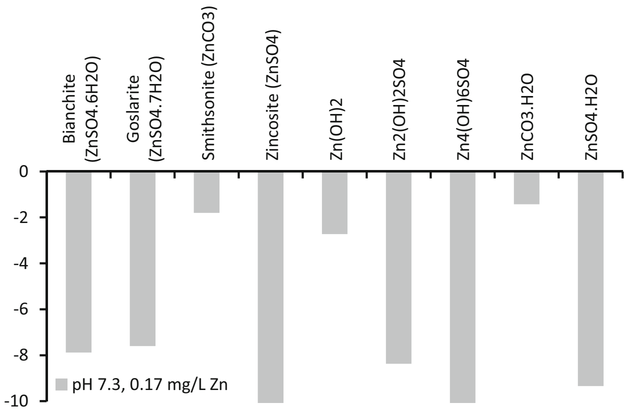

Fig. 6 Saturation of coal neutral mine drainages with respect to Zn minerals with 50 mg/L CO_3

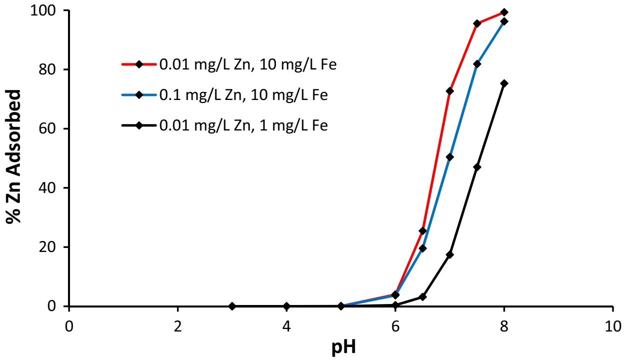

Fig. 7 Modelling of adsorption of Zn onto Fe precipitates, assuming $Fe(OH)_3$ precipitated as the mine water was oxygenated and Fe(II) oxidised

Epithermal Metal Mine Drainage

The concentration of Zn in mine drainages from epithermal deposits can be saturated with respect to carbonate minerals (smithsonite, $ZnCO_3$ and $ZnCO_3{\cdot}2H_2O$), and hydroxide minerals ($ZnOH_2$), and close to saturated with respect to hydroxi-sulphate ($Zn_4(OH)_6SO_4$) minerals (Fig. 8). This means that the high Zn levels in these mine drainages could be controlled by secondary minerals that precipitate as sphalerite breaks down during formation of mine drainages, or possibly by smithsonite, if this is a source for Zn in the ore/alteration mineral assemblage of these deposits.

Most reported analyses for these mine drainages have circumneutral pH and relatively low concentrations of Fe. Therefore, Zn adsorption during precipitation of secondary

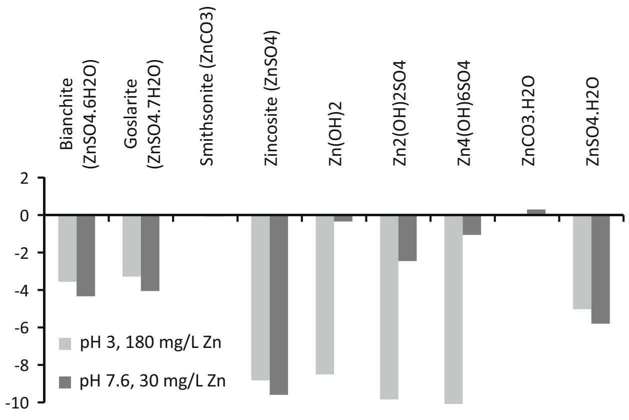

Fig. 8 Saturation acid and neutral gold mine drainages with respect to Zn minerals. Carbonate concentration of 50 mg/L CO_3 was introduced for modelling neutral mine drainages; smithsonite and $ZnCO_3 \cdot 2H_2O$ are therefore only modelled at neutral pH

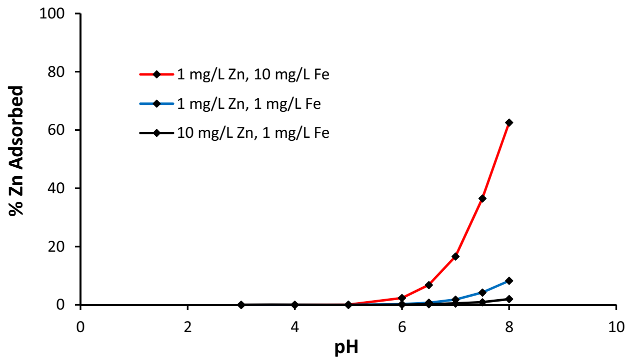

Fig. 9 Modelling of adsorption of Zn onto Fe precipitates assuming $Fe(OH)_3$ precipitates either through oxygenation and oxidation of Fe(II) or neutralisation

Fe(III) minerals is unlikely to significantly decrease the dissolved Zn (Fig. 9). If acidic conditions are generated, such as those predicted by the leaching experiments, and Fe concentrations are high enough, adsorption could influence Zn concentrations as the AMD is neutralised. However, this iron-rich AMD chemistry, although possible based on leaching experiments, has not been observed in the field.

Guideline Values for Zn Concentrations in Water

Concentrations of Zn in most freshwater usually does not naturally exceed 0.01 mg/L (ANZECC 2000); however, its concentration in mine drainage almost always exceeds this value, commonly by 1–2 orders of magnitude, and by up to more than four orders of magnitude at epithermal metal mine sites. Guideline values (Supplemental Table 2) for water use (drinking, irrigation, etc.) range between 1.5 and 20 mg/L because Zn is an essential micro-nutrient for plants and animals, and has minimal toxic effects (ANZECC 2000; MOH 2005) for these organisms. However, guideline values for protection of aquatic ecosystems are much lower, between 2.4 and 31 µg/L, with scope to adjust these values depending on site-specific water chemistry, because some aquatic organisms are sensitive to elevated Zn concentrations.

Guideline values for Zn in water spans almost five orders of magnitude, which complicates decision making for discharging Zn to the environment. For example, leakage of livestock drinking water with 20 mg/L could significantly contaminate the surrounding freshwater environment. Zinc concentrations produced by mineral resource developments in areas where agriculture occurs is unlikely to cause concern. However, the Zn present in mine drainage will require planning, management, and likely active treatment in all resource developments within areas that have pristine water quality. It is possible that acceptable protection of the ecosystem can be achieved with discharges that exceed the current guideline values; however, this would require site-specific ecological toxicity testing.

Implications

Elevated Zn concentrations in AMD with a $pH < 5$ are not controlled by mineral precipitation reactions or attenuated by adsorption onto minerals that precipitate during mine drainage evolution. Therefore, the concentration of Zn will accumulate in AMD at $pH < 5$ and will be controlled by the abundance and dissolution rate of Zn-bearing minerals. In the downstream environment, dilution is likely to be the most important factor unless there is an abundant substrate for adsorption. Water recycling or reuse will likely increase Zn concentrations in mine impacted water, and saturation with respect to Zn minerals will only occur at Zn concentrations exceeding 100 mg/L.

Zn concentrations in NMD with $pH > 5$ (based on experimental data) or $pH > 6$ (based on modelling) could be attenuated by adsorption onto Fe and Al mineral precipitates. However, this is only likely to be significant where Zn levels are relatively low (<1 mg/L) and the amount of adsorbing minerals is relatively high (>10 mg/L). The only mine drainages in this study that typically have concentrations of Fe and Al that could form precipitates with concentrations >10 mg/L are coal AMD. These will always require neutralisation in order to precipitate the Fe and Al minerals, and if the neutralisation is completed with limestone, reactions become slow at $pH > 6$, and so adsorption, which requires a $pH > 7$, is unlikely to go to completion.

In NMD (epithermal or coal), dissolved Fe(II) can be present that will form Fe-hydroxide precipitates on oxidation. However the Fe concentration is generally low (<10 mg/L), and therefore adsorption will only be significant if Zn concentrations are also low (<0.1 mg/L). This is unlikely at epithermal metal deposits where Zn concentrations are typically >1 mg/L.

Zinc's conservative behaviour means that limestone-based neutralisation of AMD is unlikely to reliably treat Zn, and alternative strategies must be adopted. Options include either active treatment, where sorbent phases are added and pH is increased to promote effective adsorption, or passive treatment by systems that promote sulphate reduction and precipitation of Zn-sulphide, or trapping of Zn within other sulphide minerals. Successful Zn removal has been observed in sulphate-reducing passive treatment systems constructed to treat AMD from coal mines in New Zealand (McCauley et al. 2009; Trumm et al. 2008; Uster et al. 2015). Oxidising passive treatment systems that use CaO-bearing waste materials (steel slag or cement kiln dust) to raise $pH > 7$ could also effectively remove Zn.

The conservative behaviour of Zn in the mine drainage forming environment means that precipitation is unlikely to occur downstream. Downstream processes that might attenuate Zn in otherwise untreated mine drainage discharges will be site specific and are limited to dilution and adsorption. Adsorption substrates can be more abundant in the wider environment, depending on the surrounding geology and geochemistry, and include Fe and Al oxy-hydroxide, clays, and organic particles.

The guideline values for Zn discharging into aquatic ecosystems are low (2.4–31 μg/L), while guideline values for use of water containing Zn are high (1–20 mg/L). In general, this means that consenting for either coal or epithermal gold mines will require careful planning for Zn, either with an active treatment system, an accepted risk to ecology, or possibly discharge of mine water to irrigation storage or the town water supply (assuming that the water does not elevated concentrations of other regulated components).

Summary and Conclusion

Zn concentrations are elevated in both AMD and NMD from coal mines, up to 18 and 0.17 mg/L, respectively. Most of the Zn is likely to be from pyrite in the coal measures because Zn concentrations are strongly related to Ni concentrations, and Ni has been positively identified in the pyrite. In coal mine drainage, the Zn concentration is controlled by the abundance and dissolution of Zn-bearing minerals rather than by secondary minerals or adsorption. Zn concentrations in epithermal metal mine AMD and NMD can be much higher, up to 179 mg/L in seeps and >500 mg/L in pore waters. At epithermal deposits, the Zn is sourced from sphalerite, which is an abundant ore and alternation mineral.

The Zn concentration in AMD and NMD is not controlled by precipitation of Zn minerals, except in rare cases at epithermal metal mines where carbonates, hydroxides, and hydroxy-sulphates are at or close to saturation. This means that Zn accumulates, and if the water on a mine site is recirculated, Zn concentrations are likely to increase with time. Attenuation of Zn by adsorption is only likely at $pH > 5$, based on experimental data or $pH > 6$, based on modelling. Adsorption is only likely to go to completion or exceed 90 % adsorbed where the $pH > 7$ and the ratio of adsorbing minerals, Fe and Al oxy-hydroxides or hydroxyl-sulphates to Zn is high ($\approx$100 mg/L precipitate and 0.1 mg/L Zn). This means that the Zn concentration in mine drainages is primarily controlled by sulphide dissolution rates.

This study has implications for mine drainage treatment because limestone-based passive treatment systems usually only produce a pH of $\approx$6 in an acceptable reaction time; Zn removal is not effective at this pH. In addition, adsorption of Zn to precipitates is unlikely to be complete under these conditions. Therefore, effective removal options for Zn include active treatment, anoxic (sulphate-reducing) passive treatment, or less common passive treatment technology that incorporates a CaO-bearing waste to achieve a $pH > 7$.

Guideline values for Zn in irrigation, stock water, or water for human consumption are high (1–20 mg/L) and guideline values for Zn concentrations to protect aquatic ecosystems are low (2.4–31 μg/L). Therefore, the implications and importance of Zn treatment and management depends highly on the environment into which the mine discharges the water. In a farmland setting, the discharge could have elevated Zn and be quite acceptable, but in a pristine environment, even low concentrations could cause environmental impact.

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