

## Research Article

# Nickel and Zinc Removal from Acid Mine Drainage: Roles of Sludge Surface Area and Neutralising Agents

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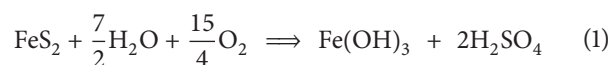
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During acid mine drainage (AMD) treatment by alkaline reagent neutralisation, Ni and Zn are partially removed via sorption to Fe and Al hydroxide precipitates. This research evaluated the effect of surface area of precipitates, formed by neutralisation of AMD using three alkalinity reagents (NaOH, Ca(OH)<sub>2</sub>, and CaCO<sub>3</sub>), on the sorption of Ni and Zn. The BET surface area of the precipitates formed by neutralisation of AMD with NaOH (173.7 m<sup>2</sup> g<sup>-1</sup>) and Ca(OH)<sub>2</sub> (168.2 m<sup>2</sup> g<sup>-1</sup>) was an order of magnitude greater than that produced by CaCO<sub>3</sub> neutralisation (16.7 m<sup>2</sup> g<sup>-1</sup>). At pH 6.5, the residual Ni concentration was 0.32 and 0.41 mg L<sup>-1</sup> for NaOH and Ca(OH)<sub>2</sub> neutralised AMD, respectively, resulting in up to 60% lower Ni concentrations than achieved by CaCO<sub>3</sub> neutralisation which had no effect on Ni removal. The residual Zn concentration was even more dependent on precipitate surface area for NaOH and Ca(OH)<sub>2</sub> neutralised AMD (0.33 and 1.02 mg L<sup>-1</sup>), which was up to 85% lower than the CaCO<sub>3</sub> neutralised AMD (2.20 mg L<sup>-1</sup>). These results suggest that the surface area of precipitated flocs and the selection of neutralising reagent critically affect the sorption of Ni and Zn during AMD neutralisation.

## 1. Introduction

Acid mine drainage (AMD) is one of the major environmental impacts of coal mines that disturb pyritic overburden on the West Coast of the South Island of New Zealand [1]. The formation of acidity associated with AMD is illustrated by



As part of AMD treatment, acidity neutralisation to pH 6–7 by alkaline reagent decreases the solubility of Fe and Al, resulting in Fe and Al hydroxide precipitation and removal by sedimentation [2, 3]. However, potentially ecotoxic metals (e.g., Ni, Zn, Cu, Pb, and Cd) require a further increase in pH (to 8 or above) to precipitate as metal hydroxides [4–6]. Incomplete removal and resultant discharge of residual metals may affect downstream freshwater fish assemblages [7].

Previous studies have reported removal of Ni and Zn during AMD neutralisation, where these metals were removed to varying degrees via coprecipitation and sorption onto Fe and Al hydroxide precipitates [8–11]. Davies et al. [10] showed a negative correlation between dissolved Zn concentration and Zn incorporation into neutralised AMD floc. Batch experiments showed that, at pH 7 and for ratios of Zn to sorbent of 1:10 to 1:100, between 70% and 90% of Zn was removed from AMD due to sorption to precipitated metal oxides [12, 13]. A similar trend was shown for Ni removal (at a similar sorbent to metal concentration ratio) where 66% of Ni was adsorbed to hydrous iron oxide at pH 7 [14].

The purpose of this paper is to investigate the importance of the surface area of floc formed during AMD neutralisation by three industrial alkaline reagents (NaOH, Ca(OH)<sub>2</sub>, and CaCO<sub>3</sub>) for Ni and Zn removal from AMD. As sorption is a solid-liquid interface process, we hypothesise that the

sorption capacity of an AMD neutralised floc is proportional to its surface area.

## 2. Experimental Methods

**2.1. Sample Collection.** The AMD used in these trials was collected from a fully oxidised stream at the Stockton Coal Mine on the West Coast of the South Island of New Zealand, and stored in 20-L plastic drums. The sample was stored for two weeks to allow full settlement of TSS before the supernatant was carefully decanted off for lab trials. The AMD had a pH of 2.6 (determined in the lab) and an acidity of  $815 \text{ mg L}^{-1} \text{ CaCO}_3$  equivalent, as determined by titration to pH 7.

**2.2. AMD Neutralisation.** The AMD neutralisation pathway was determined by titrating AMD with 5-mL increments of 0.1 M NaOH under constant mixing in a 1-L beaker. The acidity (in  $\text{mg L}^{-1} \text{ CaCO}_3$  equivalent) was determined based on the amount of NaOH required to neutralise the AMD to pH 7.

The AMD was neutralised with  $\text{Ca(OH)}_2$  and  $\text{CaCO}_3$  in addition to NaOH. A 1 M NaOH stock solution was made using laboratory-grade pelletised NaOH; 1 M stock slurries of  $74 \text{ g L}^{-1} \text{ Ca(OH)}_2$  (laboratory-grade, >99.5% purity), and  $100 \text{ g L}^{-1} \text{ CaCO}_3$  (ultrafine limestone from Murchison Lime Works, >99% purity) were used and homogenised using a magnetic stirrer throughout dosing. Stock solutions/slurries of alkaline reagents were used to allow volumetric dosing of AMD (up to 18 mL of slurry per litre of AMD), simulating the slurry dosing conditions in the field at the Stockton Coal Mine.

Jar stirrers were used for neutralisation of the AMD in 1-L beakers, with different mixing regimes for different alkaline reagents. The NaOH neutralised samples were dosed with NaOH followed by a 1-min rapid mixing phase (100 rpm) and a 25-min flocculation phase (20 rpm), as neutralisation by NaOH was instantaneous. By contrast, the  $\text{Ca(OH)}_2$  and  $\text{CaCO}_3$  neutralised samples were dosed with slurry followed by a 60-min rapid mixing phase (100 rpm). In order to determine residual metal concentrations in the circum-neutral pH range, a range of alkaline reagent doses were used to neutralise AMD to between pH 6 and 7.5 for NaOH and  $\text{Ca(OH)}_2$ , and between pH 6 and 8 for  $\text{CaCO}_3$ . Neutralisation by  $\text{Ca(OH)}_2$  was essentially instantaneous, while a continued increase in pH (to a maximum pH of 8) was recorded for neutralisation using  $\text{CaCO}_3$  up to seven days after dosing. The slow dissolution kinetics of  $\text{CaCO}_3$  was also documented in earlier studies [15, 16]. In total, 21  $\text{Ca(OH)}_2$ , 15 NaOH, and 7  $\text{CaCO}_3$  neutralised samples were prepared.

At the end of the flocculation/mixing period, the beakers of neutralised AMD were allowed to settle for 2 hours. After settling, a 10 mL supernatant sample was drawn off using a syringe from 10 mm below the water surface, to avoid sampling of any floc remaining in the water column. The sample was filtered ( $0.45 \mu\text{m}$ ) into a plastic test tube and acidified (pH < 2) using 68% nitric acid before storage in a fridge at 4°C. The major cations (Na, Mg, Al, Mn, and Fe)

TABLE 1: Concentration ( $\text{mg L}^{-1}$ ) of major cations, trace elements, and anions in the acid mine drainage.

Major cations					Trace elements				Anion
Na	Mg	Al	Mn	Fe	Ca	Ni	Cu	Zn	$\text{SO}_4^{2-}$
13.1	20.7	86.0	2.6	45.9	37.7	0.75	0.91	4.42	1100

and trace elements (Ni, Cu, and Zn) were determined using an Agilent 7500cx (California, USA) Inductively Coupled Plasma Mass Spectrometry (ICP-MS) instrument, under standard hot plasma. For quality control, every tenth sample was duplicated and every twentieth was spiked, after which three blanks were run before further analysis. The instrument detection limits were determined using the three-sigma method (multiplying the standard deviation of the metal concentrations of blank samples by three). The experimental detection limits were 100 times the instrument detection limits (as samples were diluted 100x before analysis), corresponding to  $0.007 \text{ mg L}^{-1}$  and  $0.014 \text{ mg L}^{-1}$  for Ni and Zn, respectively. The Ca concentration of the AMD was determined using the EDTA titrimetric method described in the APHA standard methods textbook [17]. The sulphate concentration was determined by HACH spectrophotometer using Method 8051.

**2.3. AMD Precipitate Analysis.** After the 10 mL supernatant sample was collected, the remaining supernatant was carefully decanted, leaving only the sludge layer. The sludge from beakers of NaOH,  $\text{Ca(OH)}_2$ , and  $\text{CaCO}_3$  neutralised AMD to pH 6.5 was then poured into separate plastic containers and allowed to dewater by gravity overnight before freeze-drying. The three floc samples ( $\text{NaOH}$ ,  $\text{Ca(OH)}_2$ , and  $\text{CaCO}_3$  neutralised AMD) were analysed for BET surface area at the University of Windsor using a Quantachrome Instruments Nova 1200e Surface Area and Pore Size Analyzer (Florida, USA). Each sample was degassed under vacuum at room temperature for 24 hours prior to nitrogen gas adsorption analysis at liquid nitrogen temperatures.

The precipitate chemical composition was analysed by borate fusion X-ray fluorescence spectrometry (XRF) at CRL Energy Ltd. Solid samples for XRF analysis were dried at 110°C and finely ground in a ring mill. Boric acid backed discs (40 mm diameter by 1–10 mm thick) of ground material were prepared under high pressure and analysed under vacuum. The multi-element XRF scanning procedure (Semiquant) was calibrated using Siemens standard samples containing known concentrations (ISO 17025).

## 3. Results and Discussion

**3.1. AMD Composition and Fe/Al Precipitation.** The concentrations of major cations, trace elements, and anions in the AMD are shown on Table 1, which are typical and comparable with previous studies [18, 19].

Figure 1 shows the neutralisation pathway of AMD determined by NaOH titration. Two buffer zones were clearly visible at pH ~3.3 (Fe) and pH ~4.5 (Al), which corresponded

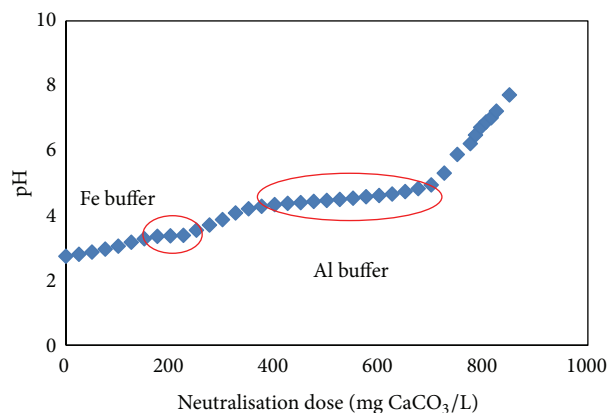
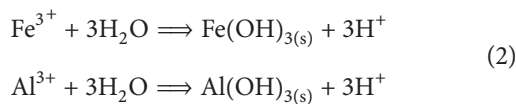


FIGURE 1: Neutralisation pathway of AMD (determined by 0.1M NaOH titration).

TABLE 2: Results of major oxide by XRF for  $\text{Ca}(\text{OH})_2$  and  $\text{CaCO}_3$  neutralised AMD precipitates.

wt. %	Alkaline reagent	
	$\text{Ca}(\text{OH})_2$	$\text{CaCO}_3$
$\text{SiO}_2$	15.4	3.5
$\text{Al}_2\text{O}_3$	30.4	15.2
$\text{Fe}_2\text{O}_3$	21.1	9.4
$\text{CaO}$	1.5	33.7
$\text{SO}_3$	4.9	3.6
$\text{Na}_2\text{O}$	0.3	0.1
LOI	29.1	34.0

to the hydrolysis of Fe and Al that resulted in the formation of metal hydroxide precipitates and the release of  $\text{H}^+$  (see (2)). These precipitates provided the solid phase for sorption of Ni and Zn. All AMD in this trial were neutralised to the pH 6–8 range, resulting in removal of 98.9%, and 99.9% of Fe and Al, respectively:



**3.2. AMD Precipitate Properties.** The flocs formed by NaOH and  $\text{Ca}(\text{OH})_2$  neutralisation of AMD had a surface area an order of magnitude ( $173.7$  and  $168.2 \text{ m}^2 \text{ g}^{-1}$ , resp.) higher than the  $\text{CaCO}_3$  neutralised floc ( $16.7 \text{ m}^2 \text{ g}^{-1}$ ). The surface areas of NaOH and  $\text{Ca}(\text{OH})_2$  neutralised AMD floc are similar to amorphous Fe and Al hydroxide precipitates formed by other treatment methods ( $85.4$  to  $135.4 \text{ m}^2 \text{ g}^{-1}$ , [11, 20]). The difference in floc structures between the alkaline reagents was visible by inspection (Figure 2). Flocs formed by NaOH and  $\text{Ca}(\text{OH})_2$  neutralisation were fluffy and amorphous in appearance, visually suggesting a low density and a high surface area, contrary to the floc formed by  $\text{CaCO}_3$  neutralisation which had a granular appearance as it contained a lot of unreacted  $\text{CaCO}_3$  particulates (Table 2).

The XRF analysis of the sludge samples (Table 2) showed that 21 wt.% and 30 wt.% of the  $\text{Ca}(\text{OH})_2$  neutralised AMD

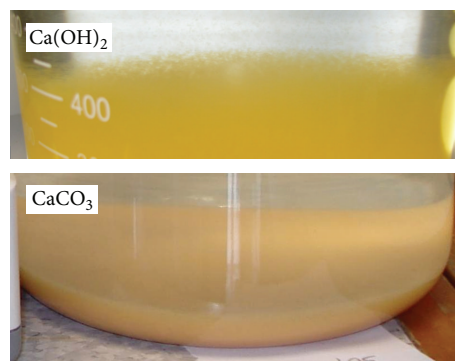


FIGURE 2: Fluffy  $\text{Ca}(\text{OH})_2$  floc compared to dense  $\text{CaCO}_3$  floc.

sludge was Fe and Al oxides, respectively, which were recognised as the active sites for metal sorption [8, 10, 11]. Only 9 wt.% and 15 wt.% of the  $\text{CaCO}_3$  neutralised AMD sludge were Fe and Al oxides, respectively, due to significant unreacted  $\text{CaCO}_3$  bulking out the sludge. Relatively high loss-on-ignition (LOI) values were reported, probably reflecting the amount of  $\text{CaCO}_3$  and physisorbed water. The NaOH neutralised sludge was assumed to be compositionally similar to the  $\text{Ca}(\text{OH})_2$  sludge as the neutralisation efficiencies for both NaOH and  $\text{Ca}(\text{OH})_2$  were close to 100%.

### 3.3. Residual Metal Concentration

**3.3.1. Ni Sorption.** Figure 3 shows that Ni concentration was lower at a given pH for NaOH and  $\text{Ca}(\text{OH})_2$  neutralised AMD compared to  $\text{CaCO}_3$  neutralised AMD. For example, at pH 6.5, Ni concentration was  $0.32$  and  $0.41 \text{ mg L}^{-1}$  for NaOH and  $\text{Ca}(\text{OH})_2$  neutralised AMD, respectively. This was up to 60% lower than the  $\text{CaCO}_3$  neutralised Ni concentration of  $0.8 \text{ mg L}^{-1}$  at the same pH. A relatively linear trend between pH and Ni concentration was shown for all three alkaline reagents in Figure 3. This was probably because the potential of Ni sorption and coprecipitation increased proportionally with increasing surface deprotonation of the AMD sludge at pH above the point of zero charge [6, 21, 22]. Over the range of pH 6 to 8, Ni concentration after  $\text{CaCO}_3$  neutralisation was approximately  $0.4 \text{ mg L}^{-1}$  higher than that of the other two alkaline reagents. Since the surface area of  $\text{CaCO}_3$  neutralised floc was an order of magnitude less per unit mass, this suggests that the greater surface area of flocs produced by NaOH and  $\text{Ca}(\text{OH})_2$  neutralised AMD increased the removal of Ni.

**3.3.2. Zn Sorption.** Figure 4 shows that the sorption of Zn (initial concentration of  $4.42 \text{ mg L}^{-1}$ ) was even more dependent than Ni on neutralisation reagent. For example, at pH 6.5, Zn concentration was  $0.33$  and  $1.02 \text{ mg L}^{-1}$  in the NaOH and  $\text{Ca}(\text{OH})_2$  neutralised AMD. This was 85% and 54% lower (for NaOH and  $\text{Ca}(\text{OH})_2$ , resp.) than Zn concentration of  $2.20 \text{ mg L}^{-1}$  in the  $\text{CaCO}_3$  neutralised AMD at the same pH. The clustering of data points at pH 6 suggests that about half of Zn removal occurred irrespective of the

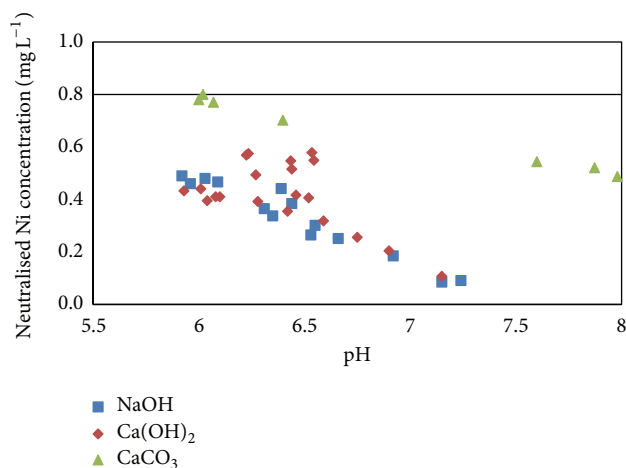


FIGURE 3: Acid mine drainage Ni concentration (initial =  $0.8 \text{ mg L}^{-1}$ ) and concentration after neutralisation by NaOH,  $\text{Ca(OH)}_2$ , and  $\text{CaCO}_3$ .

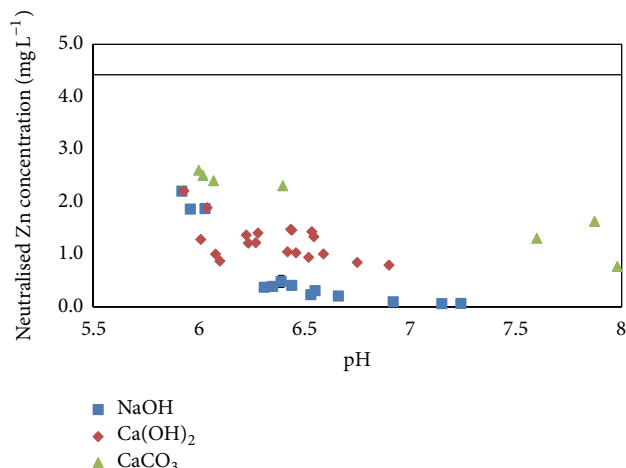


FIGURE 4: Acid mine drainage Zn concentration (initial =  $4.42 \text{ mg L}^{-1}$ ) and concentration after neutralisation by NaOH,  $\text{Ca(OH)}_2$ , and  $\text{CaCO}_3$ .

neutralisation reagent used. Between pH 6 and 6.5, the data diverged with a residual Zn concentration hierarchy of NaOH neutralised <  $\text{Ca(OH)}_2$  neutralised <  $\text{CaCO}_3$  neutralised. This may correspond to the saturation of the limited sorption sites on  $\text{CaCO}_3$  neutralised precipitates, while the greater surface area of NaOH and  $\text{Ca(OH)}_2$  precipitates allowed Zn sorption and coprecipitation to continue [8, 21].

**3.3.3. Calcium Competition.** The difference in Zn removal from NaOH and  $\text{Ca(OH)}_2$  neutralised AMD at a given pH may also result from the effect of background cations. Neutralisation of AMD using NaOH and  $\text{Ca(OH)}_2$  was found to result in the release of significant quantities of Na and Ca ( $\sim 400 \text{ mg L}^{-1}$ ), respectively. Dissolved Ca complexation with hydroxyl groups was potentially significant given the elevated Ca concentrations after neutralisation [23]. Thus, competition for binding sites on AMD precipitates from Ca may be responsible for the reduction in Zn removal when comparing NaOH and  $\text{Ca(OH)}_2$  neutralisation systems (Figure 4). In the case of  $\text{CaCO}_3$  neutralisation, the combination of low precipitate surface area and Ca competition for sorption sites led to significantly lower sorption of Ni and Zn.

There was a minor difference in NaOH and  $\text{Ca(OH)}_2$  neutralised AMD Ni concentrations, which suggests Ca competition does not affect Ni removal. This may be due to the relatively low Ni concentration in AMD, and the relatively low tendency for Ni to adsorb onto the precipitates rendering Ca competition for binding sites negligible.

## 4. Conclusions

The removal of Ni and Zn by sorption onto AMD precipitates is influenced by the surface area of floc formed during neutralisation. Neutralisation of AMD by NaOH and  $\text{Ca(OH)}_2$  produces large fluffy floc, with surface areas, an order of magnitude greater than floc formed by  $\text{CaCO}_3$  neutralisation. As a result, significantly more Ni and Zn were sorbed and

coprecipitated on the NaOH and  $\text{Ca(OH)}_2$  floc. Moreover, competition for sorption sites from the Ca released during  $\text{Ca(OH)}_2$  dissociation appears to reduce the removal of Zn when compared to NaOH neutralised AMD. These results account for the lower Ni and Zn concentrations in water discharged from treatment systems using NaOH or  $\text{Ca(OH)}_2$  as opposed to  $\text{CaCO}_3$ , which is an important consideration when selecting alkaline reagents for AMD treatment.

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