

# Opportunities for Zinc Compound Recovery from Mining Influenced Water

Linda Figueroa<sup>1</sup>, Kathleen Whysner<sup>2</sup>

<sup>1</sup>Colorado School of Mines, 1500 Illinois Street, Golden, Colorado 80401, USA,

*lfiguero@mines.edu*

<sup>2</sup>Northstar Demolition and Remediation, Inc., 5150 Fox Street, Denver, Colorado 80216, USA,

*KWhysner@northstar.com*

## Abstract

The zinc value in mining influenced water (MIW) is lost when conventional alkaline water treatment process trains are employed for removal. Recovering the zinc value from MIW requires modifying the treatment sequence to produce a metal with a chemical form of value to a market/buyer. One market for zinc is the fertilizer industry, which requires feedstock that can be economically converted to zinc oxide or zinc sulfate.

This paper examines the constraints that should be considered when determining the potential value of zinc in MIW. Contaminant specifications for zinc fertilizer include limits on arsenic, cadmium, chromium, mercury and lead, metals that can co-occur with zinc in MIW. Selective recovery of zinc from MIW in the oxy-hydroxide or carbonate form has the potential to provide a usable feedstock for fertilizer manufacture. Additional processing is required of zinc feedstock to produce a salable product.

An evaluation of potential for zinc fertilizer feedstock recovery from the Nelson Tunnel drainage (Colorado, USA) is presented. The relative concentration of co-contaminants that may occur with zinc oxy-hydroxide or zinc carbonate precipitate formation is estimated. Low relative concentration of metal co-contaminants in MIW is an important factor in producing a zinc feedstock that can meet the acceptance specifications.

Key words: Mine water, resource recovery, metal sludge

## Introduction

The US exported 85% of its zinc ore production and imported refined zinc equal to 91% of US production in 2013. Thus, there is a viable market for zinc chemicals and an opportunity to reduce imports by recovery of zinc from mining influenced water (MIW). Analysis of potential metal value based on individual metal concentrations in MIW by Smith et al. (2013) suggests that metal value could offset treatment cost. A next level of analysis requires that additional details related to technical constraints should be evaluated.

## Zinc Markets

In 2013, the United States exported 670,000 Metric Tonnes (MT) of zinc and imported 713,000 MT of refined zinc. Zinc oxide and zinc sulphate were 21% of the imported refined zinc at 97,000 and 53,000 MT, respectively. In April 2016, zinc oxide prices per kg Zn were \$2.0 to \$4.4 at 93 to 99% purity; zinc sulfate monohydrate per kg Zn, \$1.5 to \$2.2 at 90 to >99% purity, at the point of shipping from China or India. The average London Metal Exchange price of zinc in April 2016 was \$1.9/kg Zn. The above costs give economic price points to target for the local production of zinc compounds in the US.

There are 4 common forms of zinc oxide/sulphate fertilizers. The chemical forms and nominal characteristics are presented in Table 1 (International Zinc Association, [www.zinc.org/crops](http://www.zinc.org/crops)).

**Table 1** Characteristics of selected zinc fertilizer forms

Zinc source	Formula	Water solubility	Soil type
Zinc sulfate heptahydrate	ZnSO <sub>4</sub> -7H <sub>2</sub> O	high	all
Zinc sulfate monohydrate	ZnSO <sub>4</sub> -H <sub>2</sub> O	high	all
Zinc oxysulfate	xZnSO <sub>4</sub> -xZnO	variable*	variable*
Zinc oxide	ZnO	low	acidic

\* depends on relative proportion of ZnSO<sub>4</sub> and ZnO

Zinc sulfate forms are the most commonly used zinc fertilizer due to high solubility and relatively low cost (Maltalvo et al. 2016). Zinc oxides have a specific niche for acidic soils and to control the rate of zinc release. Thus, details related to sulfate and oxide forms of zinc fertilizer were selected for further examination.

**Zinc Fertilizer Feedstock**

Zinc forms that have been produced by chemical treatment of MIW included: zinc carbonate, zinc hydroxide and zinc sulfide. Zinc sulfide of sufficient purity can be processed in a primary (Nyrstar, USA) or secondary zinc smelter (Horsehead Corporation, USA and Canada) to produce zinc metal. Horsehead Corp. also has the capability to produce zinc oxide from recycled zinc sources at selected facilities.

Zinc fertilizer feedstock can be zinc carbonate, zinc hydroxide or zinc sulfate. Zinc carbonate can enter the zinc sulfate fertilizer production line in the dry ZnCO<sub>3</sub> form. The use of zinc hydroxide requires roasting at 100 – 250 °C to form zinc oxide (ZnO). The use of zinc sulfide requires roasting at 700 to 1000 °C to produce ZnO and results in the formation of a sulfur dioxide (SO<sub>2</sub>) byproduct. Zinc sulfide precipitate produced by the Wellington Oro Mine Water Treatment Plant (Breckenridge, Colorado USA) is sold to Nyrstar as a feedstock. Thus, carbonate and hydroxide are the two zinc precipitate forms from MIW treatment that have the most potential for fertilizer feedstock.

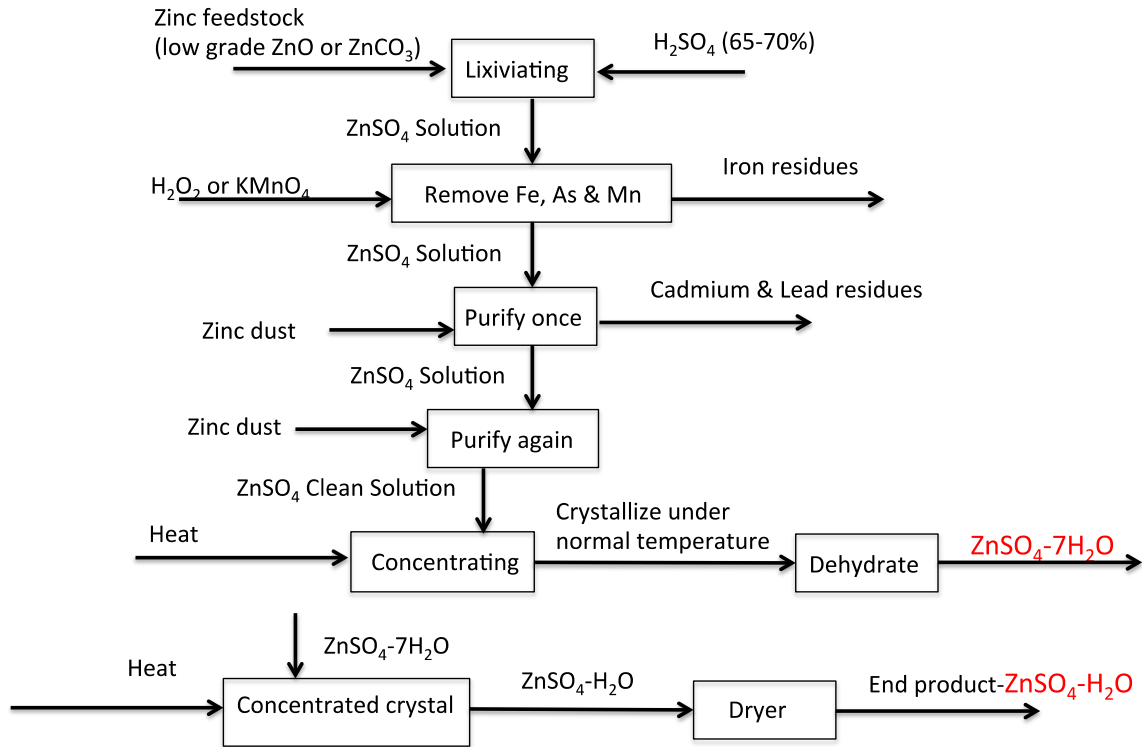
**Zinc Fertilizer**

An important consideration in using zinc precipitates from MIW treatment is the presence of trace heavy metals. In 2002, the EPA finalized regulations applied to the production of zinc fertilizer from recycled hazardous secondary materials (40 CFR Parts 261, 266, 268 and 271 [FRL-7248-3]). The rule established new product contaminant specifications. Metal contaminants potentially present in MIW sourced zinc carbonate and hydroxide precipitates are summarized in Table 2. Thus for zinc sulfate monohydrate (35% Zn by mass), arsenic content must be ≤ 10.5 ppm (by mass). The Table 2 values can be used to calculate the metal contaminant limitations for other forms of zinc fertilizer by using the relative zinc percentage of each form and the metal to zinc mass ratios derived from the EPA specifications.

**Table 2** Limits on selected metal contaminants in 35% zinc content fertilizer

Metal	ppm
Arsenic	10.5
Cadmium	49.0
Chromium	21.0
Lead	98.0
Mercury	10.5

The production of zinc sulfate fertilizer is shown in detail (Figure 1) to show the purification steps that may be required based on the grade of the zinc oxide or zinc carbonate feedstock. The cost of producing zinc sulfate from zinc oxide or zinc carbonate MIW based feedstock may be reduced if metal contaminant limits are controlled in the MIW treatment process or if the relative trace metal concentrations relative to zinc are already below the EPA specification.



**Figure 1** Steps in the production of zinc sulfate fertilizers from zinc oxide and zinc carbonate feedstock.

**MIW Treatment Considerations**

The cost of subsequent chemical processing by the manufacturer will be less if the amount of iron, manganese (nuisance) and arsenic, cadmium, lead (toxic) that co-precipitate with zinc are limited. The limits on iron and manganese will depend on the target product by the manufacturer. Iron and manganese are required micronutrients for plant growth. A multimicronutrient composition proposed by Bandyopadhyay et al. (2014) contained iron and manganese at relative concentrations of 333 mg Fe/g Zn and 167 mg Mn/g Zn. The co-precipitation of other metal micronutrients may have added value for some fertilizer feedstock producers or manufacturers.

The toxic metal limits for zinc fertilizer are fixed. A useful way to examine the potential concentrations of toxic metals relative to zinc from a MIW precipitation process is to assume complete co-precipitation. The equivalent of 1 ppm toxic metal for a 35% zinc material on a mg metal/g Zn basis is 0.00285 mg metal/g Zn. Thus, the standards for cadmium and lead from Table 2 can be rewritten as 0.14 mg Cd/g Zn and 0.28 mg Pb/g Zn.

Nelson Tunnel mine drainage is an attractive MIW to target for zinc recovery due to relatively low iron, manganese, cadmium and lead and no arsenic reported. A design flow of about 1000 liters per minute was used in a 2006 feasibility analysis with the following major metal constituents, Table 3.

**Table 3** Major dissolved metals in Nelson Tunnel MIW

Constituent	Concentration, mg/L
Calcium	250
Magnesium	30
Cadmium	0.5
Copper	0.2
Iron	0.2
Manganese	15
Lead	1.0
Zinc	80
Aluminum	1.5

The  $K_{sp}$  values of selected metal carbonates and hydroxides are presented (Table 4) to elucidate the potential for nuisance and toxic metals to co-precipitate with zinc. Co-contamination of the zinc precipitate with Cadmium and Lead is expected for the Nelson Tunnel MIW composition for both carbonate and hydroxide zinc precipitate forms. The  $K_{sp}$  of Cadmium and Lead relative to Zn suggest that they may co-precipitate together. Manganese and iron based on  $K_{sp}$  may co-precipitate with the zinc carbonate and copper and iron may co-precipitate with zinc hydroxide.

**Table 4** Solubility product values for selected metal carbonates and hydroxides

Metal	Carbonates $K_{sp}$	Hydroxides $K_{sp}$
Cadmium	$CdCO_3$ $1 \times 10^{-12}$	$Cd(OH)_2$ $7.2 \times 10^{-15}$
Lead	$PbCO_3$ $7.4 \times 10^{-14}$	$Pb(OH)_2$ $1.4 \times 10^{-20}$
Zn	$ZnCO_3$ $1.5 \times 10^{-10}$ , $ZnCO_3 \cdot H_2O$ $5.4 \times 10^{-11}$	$Zn(OH)_2$ $3 \times 10^{-17}$
Copper	$CuCO_3$ $1.5 \times 10^{-4}$	$Cu(OH)_2$ $4.8 \times 10^{-20}$
Iron	$FeCO_3$ $3.1 \times 10^{-11}$	$Fe(OH)_2$ $4.9 \times 10^{-17}$ $Fe(OH)_3$ $2.8 \times 10^{-39}$
Mn	$MnCO_3$ $2.2 \times 10^{-11}$	$Mn(OH)_2$ $2 \times 10^{-13}$

The zinc precipitates will require reduction in moisture content to produce a saleable product. The zinc hydroxide form will require roasting for conversion to zinc oxide. The carbonate form would be most attractive for fertilizer feedstock as the carbonate sludge will require drying but not roasting. However, Sibrell et al. (2005) observed that aluminum and iron were removed but zinc and manganese were not in a pilot limestone treatment system with Argo Tunnel MIW (Colorado USA). Miller et al. (2013) found that the amount of zinc removed with limestone addition was a function of iron concentration in batch experiments. No zinc was removed when initial iron concentration was zero. For zinc at an initial concentration of 16 mg/L, 50% and 80% of the zinc was removed at initial iron concentrations of 48 and 480 mg/L, respectively. The relative amount of iron to zinc (6000 to 36000 mg Fe/g Zn) observed by Miller et al. (2013) are well above the micronutrient requirements of 333 mg Fe/g Zn proposed by B (2014). The zinc hydroxide form of MIW treatment sludge will have similar co-contamination issues as the carbonate form. An opportunity exists for the development of a process to selectively recover zinc from MIW in the carbonate and hydroxide forms with targeted co-contaminant levels.

The zinc precipitate derived from the Nelson Tunnel MIW will contain cadmium and lead in excess of the EPA fertilizer specification (Table 5) and thus the manufacturer will need to employ the zinc dust purification step for removal of cadmium and lead residuals (Figure 1). The MIW treatment and fertilizer manufacture could be more cost effective if a multimicronutrient fertilizer was the end goal.

**Table 5** *Estimated cadmium and lead relative to zinc mass ratios and target limits*

Constituent	Metal/Zn in precipitate	Metal/Zn limits
Cadmium	6.25 mg Cd/g Zn	≤ 0.14 mg Cd/g Zn
Lead	12.5 mg Pb/g Zn	≤ 0.28 mg Pb/g Zn

The relative concentrations of copper, iron are well below the target levels for the multimicronutrient fertilizer composition proposed by Bandyopadhyay et al. (2014) and manganese is within 15% of the target ratio. The potential zinc product yield from the Nelson Tunnel MIW is 115.2 kg Zn/d or 42 MT Zn/yr. If the manufacturer valued MIW derived zinc feedstock at \$1/kg Zn, then the annual value of the zinc product would be \$42,000/yr.

### Conclusions

The potential value of recoverable zinc from MIW will depend on the relative concentration of co-contaminants regulated by the fertilizer industry. Contaminant of concern in zinc fertilizer includes arsenic, cadmium, chromium, mercury and lead. Selective recovery of zinc from MIW in the hydroxide or carbonate form with controlled removal of co-contaminants has the potential to provide a usable feedstock for fertilizer manufacture. Evaluation of zinc recovery from the Nelson Tunnel drainage (Colorado, USA) suggests that a viable zinc feedstock can be produced.

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