Passive Metal Mining and Mine Water Treatment Using Crushed Concrete

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Abstract

Metal mining and mine water treatment using crushed concrete is passive, simple, long-term, cheap, and sustainable. It can remove >99% of dissolved "trace" metals (including cadmium, copper, iron, mercury, manganese, nickel, lead, and zinc) from water by slowly passing it through a large bed of crushed concrete particles. The water dissolves alkalinity from the concrete and the metals precipitate as hydroxides into the concrete bed. The treated filtered water discharges under gravity. When the alkalinity in the concrete bed is exhausted, the charge is excavated, the metals beneficially recovered, remaining sand and gravel recycled, and the crushed concrete is replaced.

Keywords: Hydrometallurgical mining, mine water treatment, passive treatment, concrete particles, metal impurities, sustainable water treatment

Introduction

There are over 18,000 abandoned metal mines in the Rocky Mountain cordillera in Colorado, USA (Colorado Geological Survey 2018). The majority are small, underground mines, abandoned long ago before there was any requirement for environmentally protective closure. In general the mines were operated by organizations that are long defunct, so there is no financially viable entity remaining to fund cleanup and closure now. Many of these mines have seepage coming from portals and ponds, in general metal-bearing, and frequently acidic. This seepage discharges into the pristine montane streams which form the headwaters of the major river systems of the United States, the Colorado system flowing west, the Rio Grande flowing south, and the Mississippi/Missouri system flowing east. These surface waters constitute a sensitive aquatic ecosystem that supports and contains the economically important sport fishery of the mountain west, an important source of drinking water for most of the cities of the mountain and western US, and a substantial proportion of the water used by agriculture, industry, and mining in the arid west.

There has been a continuing need for a method of dealing with the mine discharge water that is capable of being deployed and operated in the rugged terrain of the Rockies. Such a method has to meet a demanding specification: 1) be passive enough to allow unattended operation over particularly the winter months, when most of the mine sites are inaccessible; 2) inexpensive enough to be funded by the small municipalities and non-profit entities who are affected by the contamination; 3) simple enough to be installed and operated by the volunteers who form the bulk of the committed stakeholder group who are determined to solve this problem; 4) acceptable to regulatory agencies for deployment in these mountain sites without prohibitive site-specific testing and demonstration; and 5) generate no waste.

This paper describes a system that has the ability to meet that specification, and produce usable metal from it to generate revenue. Applied across the abandoned mines in the Rocky Mountains, such a system would result in substantial metal production, as well as perform an important water quality cleanup for the nation's river systems.

Metal removal from water using crushed concrete

When water containing metal impurities (in particular Al, Cd, Cu, Fe, Hg, Mn, Ni, or Zn) is brought into contact with crushed concrete and is allowed to approach chemical equilibrium, the metal impurities are removed (Schreiter et al. 1994; Johnson et al. 2000). The typical quality of the water that the author's testing has shown results from this process is largely independent of the pH and the input concentration of the trace metals in the water being processed (Tab. 1). In addition, the concrete does not add any substantial concentration of metal impurities to the flow. This behaviour provides the basis for a method to remove trace metals from water and concentrate them in the solid phase.

Metal Removal Process

The metal removal process using crushed concrete involves these six steps: 1) Water containing trace metals contacts the crushed concrete, 2) Cementitious constituents in the concrete slowly dissolve, 3) The alkalinity of the treatment water is raised, to pH in the order of 12, 4) Metal impurities in the influent water form hydroxides and precipitate, 5) The precipitates are filtered out of the water flow and retained in the concrete granular mass and 6) Water substantially free of trace metals flows out of the crushed concrete treatment bed for discharge.

Metal Recovery Process

When the cementitious material is exhausted, it is excavated and the metals are recovered by a four-step-process: 1) Metal hydroxides are removed from the sand and gravel host material by mechanical separation (trommel washing and gravity separation), chemical leaching (acid wash), and/or chelation (EDTA or ammonia leach), 2) Hydroxides are dissolved in acid to create high concentration pregnant liquor, 3) Metals are recovered from the pregnant liquor by electrolytic means and 4) The acid is regenerated from the barren liquor and recycled.

The solid residue from this process is barren sand and gravel, which is recycled, in general as the silicate portion of new concrete.

Metal Removal Facility Specification

The facility for removal of metal from water using crushed concrete has only two essential requirements: it must contain the crushed concrete charge, and it must allow long-term

Table 1 *Typical metal impurity removal using crushed concrete; all units in mg/L, pH without unit*

Parameter	Influent	Effluent
pH	7	11
Calcium	376	563
Magnesium	121	30
Potassium	4	11
Sodium	73	76
Silica	22	1
Chloride	3	5
Sulfate	1941	1638
Aluminum	0.12	<0.01
Cadmium	0.065	<0.005
Copper	<0.01	<0.005
Iron	94	<0.01
Lead	0.11	<0.005
Manganese	50	<0.01
Mercury	<0.001	<0.001
Nickel	0.12	<0.01
Zinc	125	<0.01

contact between the concrete charge and the water from which the metals are to be removed.

Facilities that accommodate these requirements include the following:

- Axial Trench: Concrete is placed in a sloping trench, lined or unlined; metal-containing water is introduced at one end of the trench; the metals are removed in transit; and clean water is discharged at the other end (well suited to stream beds in steep valleys).
- Upflow Trench: A perforated delivery pipe is placed in a horizontal trench, lined or unlined, the trench is filled with concrete particles, and water flows upward through the concrete, the metals removed in transit, and clean water is discharged at the top of the concrete charge (well suited to locations where space is limited, such as narrow creek valleys).
- Side-flow Trench: Concrete is placed in a horizontal trench, unlined, dug on contour across shallow metal-containing water flow; the water passes through the trench where the metals are removed; and clean water discharges on the downhill side (well suited to treatment of superficial groundwater flow in shallow hillside alluvium).
- Underground Mine Stope/Drift: Concrete is packed into or introduced through a borehole into an underground stope or drift which is in the flow pathway for metal-containing water in the mine; the metals are removed and deposited in the placed concrete; and clean water discharges from the mine (well suited to abandoned underground mines in terrain where surface facilities are difficult to locate).
- Heap: Concrete is piled on a lined area; the metal-containing water is sprinkled at slow rate onto the concrete; metals are removed in the concrete mass; and clean water is collected from the base of the heap (well suited for a fine-grained concrete charge).
- Vat: Concrete is loaded into an impervious containment vessel, the treatment water is passed slowly through the concrete charge, either upflow or downflow, metal is removed in the concrete, and clean water exits the vat (well suited to low flow, high concentration treatment water, and valuable metals like silver and gold).

Metal-containing Water Specification

The specification of the water from which metals can be removed from the influent water and concentrated in the concrete particulate bed by this method is as follows:

1. Contains dissolved metals at any concentration so far tested (for metal production, the more concentrated the better the result).
2. Is acidic through alkaline (but the system works most efficiently with acidic water).
3. Contains essentially no sediments (to avoid plugging at the influent ports of the treatment system).
4. Is substantially free of dissolved organics, including petroleum hydrocarbons and organic ligands (to avoid metals chelation, which reduces the capture of metals, and increases the concentration of metals in the discharge water, which risks not meeting relevant and applicable discharge standards).

The method works best if influent water is reduced, to minimize precipitation of (particularly) trivalent iron as hydrated ferric oxide (HFO), which may have the potential to coat or partially plug the concrete particles.

Concrete Particle Specification

The specification of concrete particles that can be effectively used in this method is as follows:

1. May be of any grainsize, although grainsizes in the 5 – 10 mm range are optimal for most systems. Granular concrete may be produced by crushing and screening recycled or new concrete, or by manufacture of agglomerated or formed concrete pellets from sand, gravel, cement and water.
2. Should be clean, that is substantially free of non-concrete materials, including bitumen, soil, vegetative matter, putrescible wastes, solvents, hydrocarbons, pesticides, poisons, pharmaceuticals, and chemicals.

3. May be made using any kind of portland cement, including Type I - General purpose; Type II – Moderate sulfate resistance; Type III - High early strength; Type IV - Low heat of hydration; Type V - High sulfate resistance; waterproof; air entraining cement; high alumina cement; and expansive cement. Other concrete materials cemented with pozzolans may also be effective, but require testing. Metal removal and water treatment time depends on cement type.

Filtration Specification

The crushed concrete particles in the facility bed filter the metal hydroxide precipitates from the treated water, resulting in the discharge being particle free. No additional filtration is required prior to discharge. This may seem surprising, as the mean particle size of the crushed concrete bed is in the order of 1 cm, which is larger than typical filtration beds. The reason the crushed concrete works as a filter is that the retention time is so long and the water velocity so slow that the metal hydroxide particles have time to settle into the interstices of the filter material and be trapped in the laminar flow regime close to the particles.

The precipitate volume is similar to the volume of cementitious material that is dissolved to create the alkalinity that drives the precipitation, with the result that there is no substantial plugging of the granular concrete metal removal medium during the process. If plugging occurs, this indicates that there has been substantial metal recovery, and the concrete particle bed is ready for metal harvesting and replacement.

Bed filtration results in the metal precipitates being captured in the treatment bed, which results in accumulation of metals in the treatment material, a form of supergene enrichment. The crushed concrete treatment bed is transformed by this process into an orebody, which is available for metal extraction when exhausted.

Effluent Water Specification

The specification of the effluent water resulting from treating metal-containing water with concrete is as follows:

1. Quality. The equilibrium quality of the effluent water (Tab. 1) is generally independent of influent water quality, except for major ions like sodium, chloride, sulfur as sulfate, and nitrogen (usually as nitrate), which pass through largely unchanged. In general, calcium is elevated by the treatment. Contact time shorter than that required to approach equilibrium results in less-complete metal production and higher concentrations of metals in the process effluent.
2. Alkalinity and pH. The effluent water is highly alkaline at equilibrium, and emerges from the treatment facility at pH of 10 to 13. Discharge of this water to most aquatic systems is beneficial, as most streams are acidic, and fish do better in hard, alkaline water due to improved gill function. However if discharge water is required to be at a lower pH, the pH can be adjusted by mixing with stream water, by contact with a vegetative bed, or by addition of acid (preferably hydrochloric acid), or by carbon dioxide treatment. The author of this paper is strongly opposed to acid treatment because it wastes resources, adds TDS (chloride or sulfate) to the environment, removes environmentally beneficial alkalinity, makes the treatment active rather than passive, and involves the handling and control of a hazardous material (concentrated hydrochloric or sulfuric acid).
3. Total Dissolved Solids. TDS is slightly reduced by the treatment, due to the increased calcium concentration being more than balanced by the removal of metals and the precipitation of magnesium carbonate (magnesite). Alkalinity increases, but does not add to TDS as it is generally hydroxide alkalinity (cement contains no carbonate, although some concrete aggregate does).
4. Sulfate. Sulfate is not present in noteworthy quantities in concrete, and as a result sulfate is not increased by the treatment. Due apparently to the elevation of the concentrations of calcium and magnesium dissolved from the cement in the concrete, sulfate is in general somewhat reduced in concentration by the treatment.

5. Toxicity. The raw effluent water is has a Whole Effluent Toxicity (WET) test survival rate for both *Ceriodaphnia dubia* (freshwater flea) and *Pimephales promelas* (fathead minnow) of about 50%. After dilution with approximately equal parts of stream water, survival rates increase to about 100% (Brown 2013).

Post-Treatment Reclamation

Following complete passive metal removal to exhaustion, the concrete particulate medium will contain approximately 23 % w/w Metal Hydroxides, 47% w/w Coarse aggregate and 30% w/w Fine aggregate. It turns out that the metal hydroxides precipitated are approximately the same mass (and volume) as the hydrated cementitious materials dissolved. The exhausted crushed concrete bed can be reclaimed by closure in place. To achieve this, the supply of treatment water is turned off, and the facility is revegetated if necessary. The metals in the closed facility are not mobile, so there is no risk to the environment greater than the risk posed by any other concrete located in the environment.

However, in most applications there will be a permanent water stream requiring continuing treatment. This represents a sustainable opportunity: the spent concrete charge can be dug out and hauled to the concrete source; a new concrete charge can be backhauled from the concrete source and placed in the treatment facility; at the concrete facility the metals can be extracted from the exhausted concrete, produced, and sold; and the remaining sand and gravel can be recycled to make new concrete.

In this way the treatment cycle is closed, with recycled material as the reagent, and treated water, metals, and concrete sand and gravel as the products. And the produced metal value will offset – or in some cases exceed – the cost of the concrete needed to replace the treatment charge, thus beneficially solving a water quality challenge by reduction of toxicity (conversion of metal from dissolved to elemental form), reduction of mobility (removal of metal from the mobile water stream to the immobile solid phase), and reduction of volume (removal of metals from the environment).

Treatment Time

Concrete is almost insoluble, so the contact time that it takes for sufficient concrete to dissolve from the crushed particles to remove metal impurities needs to be in the order of 24 h for most mine waters. This time depends primarily on two factors:

1. The surface area of the concrete treatment medium. The larger the specific surface area of the concrete, the more rapid the dissolution of the alkaline constituents in the concrete. Fine-grained crushed concrete (1-10 mm) has a large specific surface area, and treats most metal-containing water in the order of an hour. Coarser-grained crushed concrete (10-25 mm) has a smaller specific surface area, and treatment takes in the order of a day. Larger grainsizes require impractically long treatment times.
2. The concentration of metal impurities in the water. The more metal constituents that are precipitated, the more dissolution of concrete is required, and the longer it takes. While the relationship is weak, a guideline is that the treatment time doubles by the time the total metal impurity concentration in the input water reaches 1 g/L, and quadruples by the time the total metal impurity concentration reaches 10 g/L.

The contact time required for metal removal is determined experimentally, by filling a 20 L (5 US gal) HDPE bucket with clean (acid etched) concrete particles of the maximum size expected to be used in the treatment facility, filling the bucket with the test water, and sampling periodically. The contact time is the time taken for the pH of the sampled water to reach 12 (or for the dissolved metal concentrations to reach required regulatory levels for discharge).

Metal Removal Capacity

The metals (M) that are removed by contact with concrete particles (Al, Cd, Cu, Fe, Hg, Mn, Ni, and Zn) are mostly divalent, and the main alkaline component of concrete is portlandite ($CaO.H_2O$), so the metal removal process can be generalized by the following characteristic equation:

$$M^{2+} + CaO.H_2O = M(OH)_2 + Ca^{2+}$$

As the most abundant metals (Fe, Mn, Zn, Cu) that are removed have molecular weights averaging around 60 g/mol, and portlandite has a molecular weight of 74 g/mol, it follows that dissolution of 1 t of alkaline concrete components will remove about 0.8 tonnes of metal from solution. Typical concrete is made by mixing 8% w/w Water, 15% w/w Cement (dry), 47% w/w Coarse aggregate and 30% w/w Fine aggregate.

Accordingly, concrete typically contains about 23% by weight of hydrated cementitious materials, like portlandite. Based on this, dissolution of the hydrated cementitious components in 1 tonne of concrete can remove up to 0.19 t of metal from water. Put another way, concrete can remove as much as 19% of its weight in metal from the water. Not all of the hydrated cementitious materials in concrete may be sufficiently soluble to participate in metal removal, even in the long term, so a good rule of thumb is that concrete can remove up to 10% of its weight in metals from the water. For most practical mine water metal extraction systems, this results in the facility requiring several thousand tonnes of crushed concrete. Testing by the author referenced above indicates that IRM has a similar metal-removal capacity (Brown 2013).

Metal Removal Facility Design

The metal removal facility must be sized to provide sufficient retention time to allow dissolution of alkaline constituents from the concrete, but may also be sized to contain more concrete if necessary to remove metals from the influent water for a specified life.

Retention time sizing

Sizing for retention time is achieved as follows:

1. Compute the volume of water that must be retained to achieve the required metal removal: *Wastewater retention volume = flow rate × retention time*
2. Compute volume of crushed concrete necessary to have a pore volume equal to the retention volume: *Concrete Retention Volume = wastewater retention volume / crushed concrete porosity (≈ 40%)*
3. Compute the mass of concrete that has the concrete retention volume: *Concrete retention mass = concrete retention volume / particle density of concrete*

Facility lifetime sizing

The expected operational lifetime of a single charge of crushed concrete in a metal removal facility designed to hold the above retention volume is computed as follows:

1. Compute the mass of metal that is available for removal from the waste water by the concrete charge: *Metal removal = mass of crushed concrete x metal removal capacity of crushed concrete (≈ 10%)*
2. Compute the rate of metal removal from the waste water: *Rate of metal removal = total mass concentration of metal × treatment flow rate*
3. Compute lifetime of concrete in facility containing the concrete retention mass: *Life of concrete retention mass = Available metal removal / Rate of metal removal*

If a greater life is required, then the concrete particle mass should be increased by the desired multiple.

How it works

As noted above, the hydrated cement that bonds concrete comprises approximately 28% by weight of the total concrete. X-ray diffraction (XRD) identified the two principal alkaline minerals in the hydrated cement in the concrete to be 6% - 12% Portlandite [$CaO.H_2O$] and 3% - 5% Ettringite [$Ca_6Al_2(SO_4)_3(OH)_{12}{\cdot}26H_2O$]. There is also very likely tricarboaluminate [$Ca_6Al_2(CO_3)_3(OH)_{12}{\cdot}26H_2O$] and an assortment of calcium aluminum silicates such as Strätlingite [$2Ca_2Al_2SiO_2(OH)_{10}{\cdot}3H_2O$] making up the balance of the 23% of the hydrated cementitious materials (Matschei 2007). Yet, these are not identifiable by XRD methods, as they appear to be amorphous. Both of the main identified minerals dissolve to release hydroxyl ions as shown by their dissolution reactions, but neither is very soluble as shown by the equilibrium constants of $\log_{10}K = -22.675$ for Portlandite and $\log_{10}K = -44.90$ for Ettringite (Allison et al. 1990; Matschei 2007).

However, at high pH the metals in the influent water form low solubility hydroxides, and they precipitate, removing the hydroxyl ions from the water, resulting in a continuing dissolution of the alkaline materials to replenish the hydroxyl ions in the solution until the metals are removed.

Conclusion

Trace metals (including cadmium, copper, iron, mercury, manganese, nickel, lead, and zinc) can be removed from metal-bearing water by passing it slowly through a large bed of crushed concrete, turning the concrete into an orebody, and reducing the trace metal concentration in the water stream to levels that allow discharge to surface or groundwater resources. The process is sustainable, as the crushed concrete metal-removal substrate is a readily available recycled material, the removed metals are filtered out of the water by the bed material, and the removed metals are recovered from the material when the treatment medium is exhausted or replaced. This metal recovery and water treatment method can be implemented by a relatively unskilled workforce at low cost at almost any location in the world.

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