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Fulfilment of EPA Discharge Requirements for ARD Using Co-Precipitation Iron Process at Neutral PH

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ABSTRACT

The dissolution of soluble metal compounds from ore and waste rock and the presence of contaminants in industrial and mining process water are a major concern for water treatment standards.

An improvement of alkaline precipitation methods to remove metals was the focus of this study. This system was based on iron co-precipitation technology, taking advantage of the beneficial characteristics of iron, such as natural coagulation, natural adsorption of heavy metals, good clarification and increased dewatering properties of solids.

Based on this iron co-precipitation technology, two different configurations were evaluated at Leviathan Mine Superfund Site (California, USA) for treatment of ARD containing the following metal concentrations (μg/L): Aluminium (107,800), Arsenic (3,240), Copper (2,150), Iron (456,430), Nickel (2,560), Cadmium (26,100), Chromium (341,000), Lead (6,200), Selenium (16,600), Zinc (538,000).

The objectives of the technology evaluation were to determine the removal efficiencies for target metals, verify reduction under discharge standards, document operating parameters, assess critical operating conditions, evaluate operational efficiency of solid separation and dewatering systems.

The treatment system was shown to be extremely effective in neutralizing acidity and reducing the concentrations of the target metals to below EPA discharge standards.

The mechanisms of this technology, combined with the characteristics of iron and operation at neutral pH, showed beneficial results that include less amount of base requirement, no requirement of final pH adjustment to fulfil discharge limits, better clarification with less settling area, and better solids dewatering.

Keywords: metal, precipitation, ARD, iron, neutral

INTRODUCTION

Conventional Alkaline precipitation

Alkaline Precipitation is an extensively used technology for removal of heavy metals. It is based on the occurrence of the following reaction:

$$M^{+2}{}_{(aq)} + 2(OH^-) \leftrightarrow M(OH)_{2\,(S)} \tag{1}$$

In this equation, the M^{2+} represents any divalent heavy metal. As it is indicated, the metal ion combines with hydroxide ion to form the insoluble metal hydroxide solid. This reaction is pH dependent; as more base is added, the reaction is driven further to the right to precipitate more of the metal complex. Conversely, as the pH is decreased, the thermodynamic equilibrium moves to the left, causing more of the metals to resolubilize. This reaction is fully reversible and results in a solubility curve (blue curve) similar to that shown in Figure 1.

The limitations of alkaline precipitation technologies result from secondary reactions which occur as more hydroxide is added. One common reaction is the combination of the metal hydroxide precipitate with additional hydroxide ion:

$$M(OH)_{2\ (s)} + OH^- \leftrightarrow M(OH)_3^-{}_{(aq)} \tag{2}$$

The metal hydroxide precipitate combines with additional hydroxide to form a soluble metal complex. Thus as the pH increases, the reaction proceeds to the right and the metal becomes more soluble. The solubility curve of this reaction (purple curve) approximately mirrors the curve of the first reaction as shown in Figure 1.

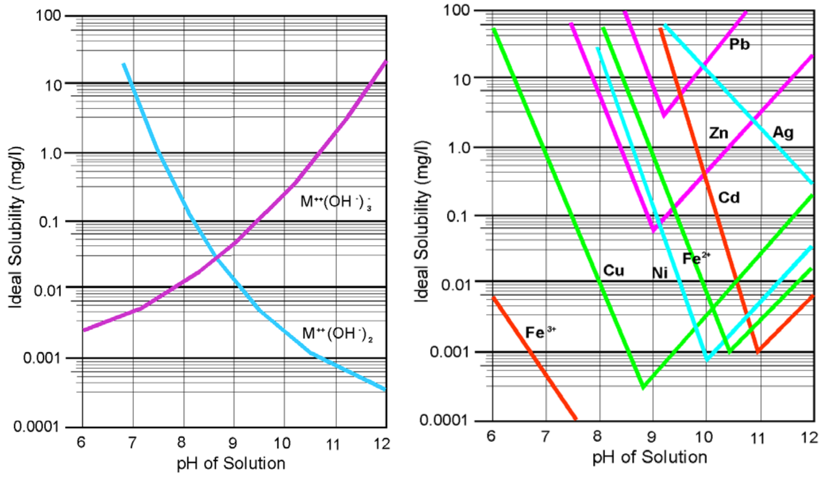

Figure 1 Solubility of metal hydroxides

By overlaying these two curves as shown in Figure 1, and then combining the effects of all the reactions which take place, the familiar V-shaped solubility curve for metal hydroxides is obtained as shown in Figure 1. The lowest point of this curve identifies the absolute lowest concentration of a particular metal which can be achieved, under ideal conditions, by alkaline precipitation technology. To obtain this concentration, pH must be maintained within a specified range to reduce the metal resolubilisation. In a wastewater stream with multiple metals, this problem becomes more challenging due to solubility dependence of metals on pH. Any operating pH is chosen to be optimal in reducing the solubility of dissolved species (Figure 1).

Iron co-precipitation process technology

Iron co-precipitation technology is based on the beneficial characteristics of iron: natural coagulation, adsorption of heavy metals onto iron solids, good clarification and increased dewatering properties solids formed.

Ferrous iron (Fe^{2+}), existing or added to water, tends to form a soluble chain-like structure in solution due to the weak ionic attractions between molecules. This close association between the heavy metals species and the iron species provides the mechanism by which the iron can be targeted to most efficiently remove the heavy metals (McPhee, n.d.).

After the soluble association is formed, base is added to control the pH and form a suspension of metal hydroxides; then, air is added to oxidize Fe (II) to Fe (III) and form crystals containing ferric ions as ferromagnetic oxides, such as Fe_3O_4, and/or oxyhydrates (or oxiyhydroxides) FeOOH, and further containing the metal ions originally in solution. Many kinds of heavy metals in the solution are substituted in the metal sites of the ferric crystal lattice to form various kinds of ferrites or of FeOOH crystal lattice. Other kinds of heavy metals are firmly adsorbed by the ferrites thus formed (Sugano, Tsuji, Kanamori, 1976).

These metals are "occluded" in the iron solids and are effectively enveloped in iron as shown in Figure 2. The occluded metals are insulated from the solution by the iron, and so are not allowed to resolubilize as solubility curves in Figure 1 would indicate. This phenomenon makes it possible to remove heavy metals from water to concentrations well below their thermodynamic solubility limits. The precipitates, ferric iron solids, can then be separated from the treated water by chemical coagulation, flocculation, and clarification processes (McPhee, n.d.).

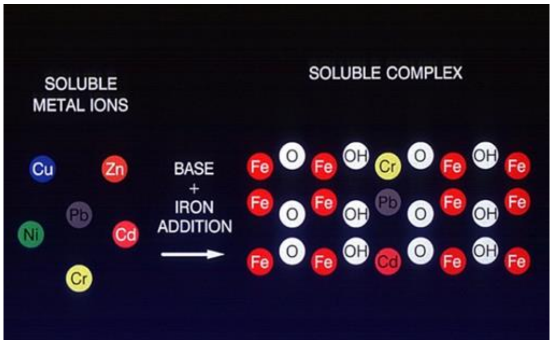

Figure 2 Soluble iron complex formation in iron co-precipitation process

Other metals which may not be removed by occlusion are adsorbed; ferric iron solids tend to adsorb heavy metals to their surface and acts as a catalyst for the oxidation of Fe(II) to Fe(III).

Process description

A treatment system based on iron co-precipitation technology was designed to treat ARD from holding ponds from an inactive underground copper mine and an open pit sulphur mines in the State of California (Siskind, 2002).

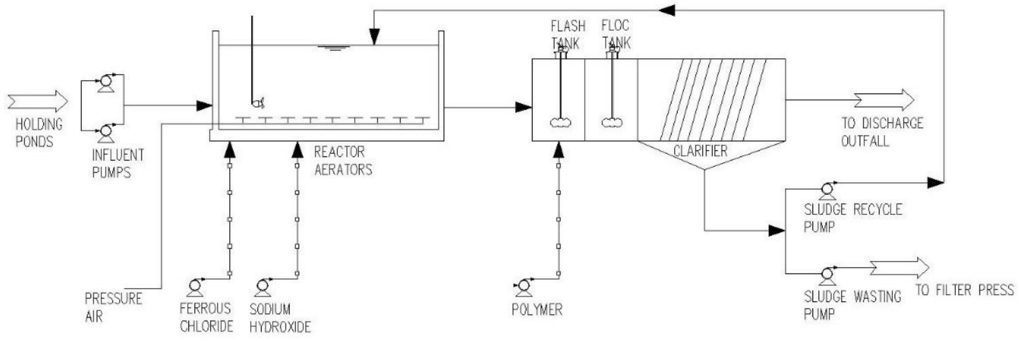

Figure 3 Co-precipitation metals treatment process flow diagram. One-stage system

The system was operated in two different modes, one-stage and two-stage. Operated as a one-stage system, the active treatment system was evaluated for its ability to treat a combined, moderate ARD flow without regard to the type of metal or concentration. Operated as a two-stage system, the active lime treatment system was evaluated for its ability to treat a high ARD flow where concentrations of arsenic were relatively high.

The treatment system for both modes involves reaction of lime with ARD (usually at a pH of 2 to 3), to raise the solution pH to 7.9 to 8.2. In one-stage mode, pH is rise to 7.8 to 8.2 in one stage. In two-stage mode the overall chemical reaction is the same as for the one-stage mode; however, metals precipitation is conducted in two steps. In stage I, the active treatment system is held at a pH of 2.8 to3.0 creating a small quantity of precipitate. In stage II, the pH is raised to 7.9 to 8.2 and the remaining metals are precipitated, creating a much larger quantity of solid waste.

The equipment for each stage consists of an aerated reaction tank (30 minutes retention time), flash and flocculation mixing tanks, plate clarifiers (settling rate of 1 m^3/m^2 h), filter press (only for first step of two-stages configuration) and a settling pond as shown in Figure 3 and Figure 4. Treatment chemicals used were lime and anionic polyacrylamide as polymer; no ferrous chloride or sulphate addition was needed due to a high concentration of iron in the ARD flow.

Ferric iron solids are present in the process as a result of the oxidation of ferrous iron, and as a result of recycle from the clarification step as shown in Figure 3 and Figure 4. The solids, due to a very high shear environment in the reaction vessel, are highly fractured resulting in a very high surface area and many active adsorption sites. The heavy metals in solution adsorb to the surface of these solids in the reactor. As ferrous iron enters the reactor with the contaminated stream, the iron preferentially precipitates, due to the autocatalytic effect, on the solids which have already formed. This layering of iron precipitate on top of adsorbed heavy metals produces results similar to those achieved by the first mechanism; the heavy metals are effectively removed from solution and are isolated from the solution so that they cannot freely follow their solubility curves as the pH varies. This reaction mechanism also results in extremely dense solids since the precipitation is occurring directly on the surface of other solids (McPhee, nd).

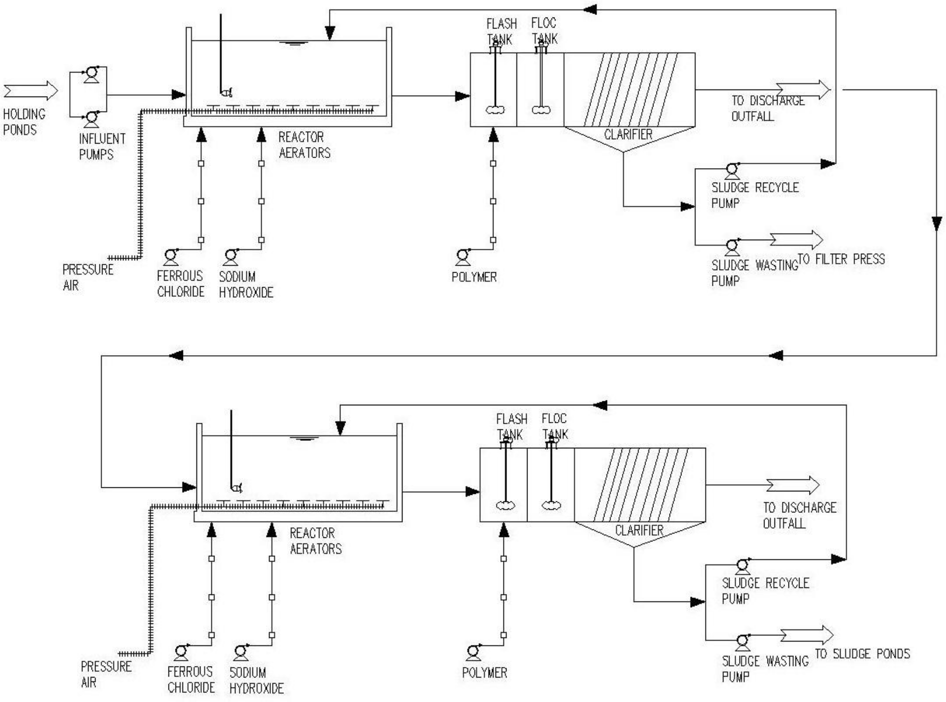

Figure 4 Co-precipitation metals treatment process flow diagram. Two-stage system

The principal objectives of the technology evaluations carried out by EPA (Bates, 2006) were: ability to neutralize acidity, determine removal efficiencies of ten metals (Al, As, Cu, Fe, Ni, Cd, Cr, Pb, Se and Zn) , determine the concentrations of the primary and secondary metals in effluent are below EPA-mandated discharge standards, document operating parameters, optimize system performance, monitor chemical composition of ARD as it passes through the treatment system, operational performance of solids separation systems, document solids transfer, dewatering, and disposal operations.

RESULTS AND DISCUSSION

The study was carried out over a two-year period. A total volume of 83,600 m^3 of ARD was treated with both systems, 93% of this volume with the two-stage system, 7% with the one-stage configuration. Three tables summarizing the outcomes are provided in Table 1 – 3.

Table 1 and 2 show the results of influent, effluent concentrations and removal efficiencies for the considered metals. This included one-stage and two-stage operations. Table 3 shows the amounts of waste generated during the evaluation and its composition.

Table 1 Active lime treatment system removal efficiencies: two-stage operation in 2002 and 2003

Target metal	Avg. influent conc. (µg/L)	Std. Dev.	Avg. effluent conc. (µg/L)	Std. Dev.	Exceeds discharge standards (Y/N)	Avg. removal efficiency (%)	Range of removal efficiencies (%)
Aluminium	381,000	48,792	1,118	782.00	N	99.70	99.20 to 99.90
Arsenic	2,239	866.00	8.60	1.90	N	99.60	99.20 to 99.80
Copper	2.383	276.00	8.00	2.50	N	99.70	99.40 to 99.80
Iron	461,615	100,251	44.90	66.20	N	100.00	99.90 to 100.00
Nickel	7,024	834.00	34.20	15.40	N	99.50	99.20 to 99.90
Cadmium	54.40	6.10	0.70	0.28	N	98.70	99.20 to 99.90
Chromium	877.00	173.00	5.70	12.20	N	99.30	93.80 to 99.90
Lead	7.60	3.60	2.00	1.10	N	78.30	69.20 to 86.70
Selenium	4.30	3.90	3.80	1.50	N	Not Calculated	Not Calculated
Zinc	1,469	176.00	19.30	8.90	N	98.70	97.40 to 99.40

In one-stage operation, the resulting solid waste stream exhibited hazardous waste characteristics due to high arsenic and nickel concentrations, and must be disposed of in an off-site treatment, storage and disposal (TDS) facility. In step I of two-stage operation, a small quantity of precipitate containing high arsenic concentrations is produced, which when dewatered, exhibits hazardous waste characteristics and requires off-site disposal in a TDS facility. In step II, a much larger quantity of solid waste is generated; however, arsenic concentrations are low enough that the step II solid waste is not classified as a hazardous waste and can be disposed of on site

Table 2 Active lime treatment system removal efficiencies: one-stage operation in 2003

Target metal	Avg. influent conc. (μg/L)	Std. Dev.	Avg. effluent conc. (μ/L)	Std. Dev.	Exceeds discharge standards (Y/N)	Avg. removal efficiency (%)	Range of removal efficiencies (%)
Aluminium	107,800	6,734	633.00	284.00	N	99.50	99.00 to 99.80
Arsenic	3,236	252.00	6.30	3.50	N	99.80	99.70 to 99.90
Copper	2,152	46.40	3.10	1.50	N	99.40	99.00 to 99.70
Iron	456,429	49,430	176.00	130.00	N	100.00	99.90 to 100.00
Nickel	2,560	128.00	46.80	34.70	N	97.90	95.70 to 99.30
Cadmium	26.10	14.10	0.20	0.03	N	99.10	98.40 to 99.70
Chromium	341.00	129.00	3.00	3.80	N	99.00	95.60 to 99.80
Lead	6.20	3.60	1.60	1.30	N	74.60	48.30 to 89.80
Selenium	16.60	13.60	2.10	0.43	N	93.10	91.00 to 94.40
Zinc	538.00	28.90	5.60	3.60	N	98.80	97.70 to 99.60

Table 3 Determination of hazardous waste characteristics of solid waste streams at Leviathan mine

Mode of Operation	Operational year	Solid waste stream evaluated	Total solid waste generated (DryTons)	TCLP	Waste handling requirement
Biphasic	2002	Phase I Filter cake	22.70	Pass	Off-site TSD facility
Biphasic	2002	Phase II Pit clarifier Sludge	118.00	Pass	On-site disposal
Biphasic	2003	Phase I Filter cake	21.10	Pass	Off-site TSD facility
Biphasic	2003	Phase II Pit clarifier Sludge	93.60	Pass	On-site disposal
Monophasic	2002	Filter cake	20.40	Pass	Off-site TSD facility

CONCLUSION

Both treatment systems were shown to be extremely effective at reducing metal concentrations of the ten target metals in the ARD flows to below EPA-mandated discharge standards. In general, removal efficiencies for the ten target metals exceeded ninety percent at a maximum pH value of 8.2.

In addition, the active two-stages treatment system was shown to be very effective at separating arsenic from ARD prior to precipitation of other metals, subsequently reducing the total volume of hazardous solid waste produced. Solids generated in stage II of two-stage configuration pass the EPA Toxicity Characteristic Leaching Procedure TCLP 1311, and the solids were allowed to be disposed of in a municipal landfill or on-site, with a reduction in the cost of disposal from about 500 US$ per metric ton to as less as 20 US$ per metric ton.

In Table 4, a process and cost comparison is shown between the iron co-precipitation technology and High Density Sludge (HDS) technology, a common technology applied to treat ARD.

Table 4 Process comparison. Iron co-precipitation vs. HDS

Technology	Reactor TSS(mg/L)	Reactor HRT(min)	Process pH	Minimum Process No. steps
Iron Co-precipitation	500-3,000	20-30	6-8.2	1
HDS	10,000-25,000	30-60	6-11	2

Regarding capital cost comparison between Iron co-precipitation and HDS, for a regular metal-removal system for ARD, an HDS system will need 2 series-reactors and an sludge conditioning step where the lime or base is added to a sludge conditioning reactor prior to being returned to the primary reactor; on the other hand, an iron-co-precipitation system can be implemented in only 1 reactor step. Regarding expenditure costs, in a HDS system is needed to maintain a higher pH than in iron co-precipitation, with an increase in base consumption. It is important to remark the importance of running pilot test to ensure treatment characteristics in order to develop a complete installation.

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