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ELECTROPRECIPITATION TREATMENT OF ACID MINE WASTEWATER

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Abstract—The utilization of electroprecipitation for the treatment of acid solutions associated with the non-ferrous mining industry on a laboratory scale is explored. The electrolytic couple involved in the active process includes a consumable metal anode and an inert cathode. Mechanistically, oxidation of the anode is matched by the reduction of dissolved hydrogen ion to H_2 gas resulting in a pH increase in solution. Heavy metal removal is accomplished by either precipitation of hydrous oxides or by adsorption. Reduction of the solution metal content of from 100% for Al^{3+} to 25% for Mn^{2+} is accomplished using a stainless steel rod anode; final solution pH stabilizes at a value of 4.9. Stabilization of solution pH reflects the attainment of kinetic equilibrium with respect to the rates of oxidation at the anode and diffussion of the oxidized products to the cathode where they precipitate as the hydroxide. Zinc and lead sacrificial anodes are also studied.

INTRODUCTION

Tens of millions of gallons of acid waste solutions are produced by the non-ferrous mining industry daily; state of the art treatment methodology involves neutralization of this material with lime/limestone. While the lime neutralization process can potentially achieve adequate wastewater reclamation at a minimal cost, it has important shortcomings which include: (1) the inability to remove much of the large sulfate load contained in the mining wastewaters; (2) the increase in water hardness which accompanies treatment and (3) the disposal of the waste sludge produced (Grim and Hill, 1974). In addition, the neutralization process generally requires an oxidation step to avoid the high pH required for ferrous iron precipitation. An ideal treatment process would be one in which the pH change, oxidation and subsequent metal removal process could be accomplished without degrading water quality and which would minimize the disposal problems associated with the voluminous sludge. The utilization of electrical energy to perform this function has received some attention in the past. A hybrid technology developed at Tyco Labs (1972) combines electrolytic iron oxidation at an inert anode with a subsequent increase in solution pH obtained by both hydrogen ion reduction at the cathode and limestone neutralization. While the process effectively reduces sludge volume and is potentially cost-effective, it fails to produce an effluent which does not exhibit the types of problems described in (1) and (2) above. Electrocoagulation, in which small quantities of metals are removed from dissolution of metal electrodes, has been used to remove minor amounts of copper, zinc, nickel and chromium from wastewaters (Jageliene *et al.*, 1979; Bychin *et al.*, 1978).

Electroprecipitation is similar in concept to the electrocoagulation process in that oxidation of a sacrificial anode is coupled with hydrogen ion reduction at an inert cathode but differs in the amount of metal removed from solution and in that the major metal removal mechanism is precipitation. Selitskii and Antropov (1974) were able to increase the pH of a chromium containing waste solution from 5 to 6 resulting in the co-precipitation of $Cr(OH)_3$ and $Fe(OH)_3$. In a similar experiment, Gnusin *et al.* (1978) attributed the removal of 40 ppm Zn^{2+} from simulated galvanizing plant effluents to co-precipitation of the Zn and Fe hydroxides. In this paper, the ability of the electroprecipitation process to treat acid waste solutions from the copper mining industry on a laboratory scale is studied and the process mechanism is described.

EXPERIMENTAL

Apparatus

The experimental apparatus consisted of a reaction vessel, the electrode assembly and the auxiliary power supply. The reaction vessel was a 500 ml heavy glass sampling vessel; the electrode assembly consisted of four metal rod electrodes arranged in a box configuration and supported by a rubber cork. Electrode dimensions included a rod length of 15 cm and a diameter of 1 cm; the spacing between electrodes was 2 cm along the box perimeter. Electrodes were alternatively charged, that is diagonal pairs were similarly charged, from a constant voltage d.c. source. The cork contained two holes in addition to the rod supports; one hole was located at the side of the mount and served as a port for the escape of any gas generated during the reaction process while the other was located in the center of the electrode box and served as either a sampling port or as the support of a pH probe. While polished steel rods were always used for the cathode, anode materials included steel and zinc rods and lead assay grade foil shaped into rods. To insure that the electrode surface was fresh, all anodes were polished with fine grit aluminum oxide paper prior to use. in addition, the Pb

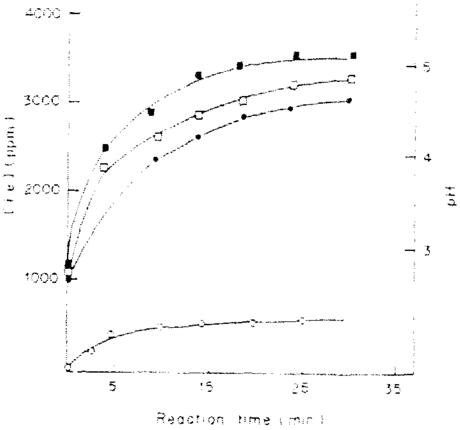

Fig. 1. Chemical changes in mixed acid solution as a function of treatment time, electroprecipitation with steel electrodes. Fe and pH. ● Fe^{2+}; ○ Fe^{3+}; ■ Fe_{total}; □ pH.

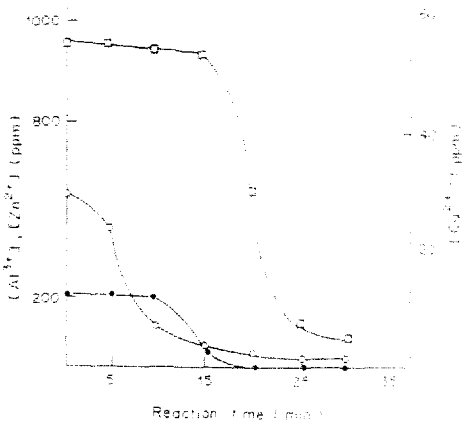

Fig. 2. Chemical changes in mixed acid solution as a function of treatment time, electroprecipitation with steel electrodes. Cu, Zn, Al. ● Cu^{2+}; ○ Al^{3+}; □ Zn^{2+}.

anodes were electropolished in a mixed perchloric acid–ethyl alcohol–ether solution as suggested by Archdale and Harrison (1972).

Solution treatment

Solutions treated by the electroprecipitation process included both equi-volume mixtures of acidic waste solutions produced at the Butte, Montana, operation of the Anaconda Mining Company and artificial waste solutions produced in the laboratory. A detailed description of the handling of the field waste solutions and the Anaconda process is given elsewhere (Jenke *et al.*, 1984). Artificial solutions containing 300 ppm Cu^{2+} or 1000 ppm Zn^{2+} were prepared by dissolution of their choride salt in 0.13 M H_2SO_4 followed by adjustment of solution phase pH to 2.5 with 6 M NaOH. An acid blank solution was pepared by adjusting the pH of a 0.13 M solution of H_2SO_4 to 2.5 in a similar manner. For the electrolysis, 350 ml of solution was used in the reactor, the electrodes were immersed into the solution to a depth of approx. 8 cm and a potential of 15 V was applied to the alternate electrode pairs. The electrolyzed solution was continuously stirred and the reaction was allowed to proceed for a pre-determined time. After this time, the treatment was stopped, the slurry pH was recorded and the solution and solid separated by filtration through 0.45 μm polycarbonate disks.

Chemical analysis

Solutions collected were immediately analyzed for trivalent iron concentration by dichromate titration, for total Fe, Cu, Zn, Mn, Mg, Pb and Al content by atomic absorption spectroscopy and, after suitable dilution, for SO_4^{2-} by ion chromatography. Precipitates collected were dried at 110°C for 24 h and digested off the inert filter media in 30 ml of a 10% HNO_3 solution at a temperature of 75°C for 1.5 h. The digestants were analyzed for their metal content by atomic absorption.

RESULTS AND DISCUSSION

Figures 1 and 2 document the change in chemical composition of the mixed acidic wastewater treated with steel sacrificial electrodes as a function of electrolysis time. After a 30 min treatment, the solution pH has increased from 2.8 to 4.7 and significant metal removal has occurred. Al and Cu removal is virtually 100% complete while approx. 90% of the zinc has been removed. Mn and Mg removal for this simulation, although not shown in these figures, is on the other of 25 and 10% respectively. Both ferrous and ferric iron concentration in solution increases during the treatment process; the similarity between the pH and iron production curves suggests that their behavior is related. In a qualitative sense, an important visual observation made during the electrolysis is the color of the precipitate formed. For electrolysis experiments in which the reaction time was 10 min or less, the precipitate formed is characterized by a red-brown color while the experiments which proceeded for longer than this time resulted in dark green precipitates. A similar change in solution chemistry is observed when the same acid solutions are treated with zinc anodes. In this case, as shown in Table 1, the final pH is somewhat higher resulting in a greater removal of Mn and Mg. Once again, the attainment of a constant pH is mirrored by the attainment of an equilibrium concentration of the anode dissolution product.

Treatment of the artificial copper and zinc solu-

Table 1. Composition of mixed acid solution during electroprecipitation with zinc anode

Treatment duration (min)	Solution composition ($mg\,l^{-1}$)						
	pH	Al	Cu	Fe	Zn	Mg	Mn
0	2.65	366	294	903	870	415	222
5	4.95	97	23	229	1480	256	133
10	5.60	4	4	139	1780	222	119
15	5.80	1	1	73	860	249	123
20	5.85	1	1	29	505	163	67
25	5.80	1	1	30	1200	109	51
30	5.80	1	1	17	1100	103	55

Table 2. Composition of artificial solutions during electroprecipitation

Treatment duration (min)	Solution composition (mg l⁻¹) Fe anode Fe	Cu	Zn	pH	Zn anode Fe	Cu	Zn	pH
(a) Cu^{2+} solution								
0	2	300	2	2.6	2	300	2	2.6
5	100	1	2	9.6	1	1	27	12.6
10	50	1	2	12.6	3	1	32	12.6
15	47	1	2	12.6	1	1	25	12.6
(b) Zn^{2+} solution								
0	3	3	1007	2.5	3	3	1007	2.5
2	840	4	2	5.2	3	1	617	5.3
4	560	5	1	6.2	2	1	287	8.4
6	120	5	1	10.2	1	1	20	12.3
10	100	5	1	12.5	1	1	23	12.3
15	50	5	1	12.5	1	1	24	12.5

tions and the acid blank indicates that the electroprecipitation process is capable of producing a relatively high solution pH when the total dissolved metal load is lower than that encountered in the industrial wastes. As shown in Tables 2 and 3, after only a treatment time of 6 min the pH of the artificial solutions has reached 12. At this pH, although the concentration of the anode decomposition product is also low, it is somewhat larger than desirable due to the formation of multi-hydroxyl complexes. Collection of the precipitate formed during the electrolysis of the acid blank allows for the identification of the form of the precipitate which can be directly traced to the anode decomposition. On the basis of its iron content, the green precipitate formed during this trial appears to be ferrous hydroxide.

Considering the removal of sulfate from the acid waste solutions, the lead sacrificial anode offers the most promise due to the low solubility of lead sulfate. Since the anode decomposition product (Pb^{2+}) does not actively compete for the hydroxide being generated at the cathode, a much higher solution pH and therefore more effective heavy metal removal should be achieved. A major difficulty encountered in the preliminary experiments performed to date is the rapid passivation of the Pb anode as a sulfur-containing coating builds up during electrolysis. As the effective anode surface becomes poisoned, electroprecipitation degrades to true solution electrolysis and heavy metal removal ends. However, the potential utility of the lead system is documented in the results of Table 4 which describes the results of one trial in which the electroprecipitation process is maintained at low potential for 5 min. Under these conditions, a significant pH change and concentration decrease of Fe, Al, Cu and SO_4^{2-} is observed.

Table 3. Results of electroprecipitation of the blank acid solution (Fe anode)

Species	Precipitate composition (weight %)	Solution composition
Fe	64.3	997.0
Cu	0.1	0.1
Al	0.3	0.1
Zn	0.1	10.0
pH		5.2

As a first approximation, the electroprecipitation process mechanism can be described as follows: as the solution is subjected to the electric potential, the anode is oxidized to an aqueous ionic form and the hydrogen ion in solution is reduced to hydrogen gas at the cathode. This results in a net increase in solution pH and subsequent precipitation of metal hydroxides as their solubility product is exceeded. This simplified mechanism is complicated in the treatment of field solutions by reaction kinetics, electrode decay, the presence of multivalent aqueous ions and compositional zonation which occurs in the solution during treatment. With respect to the discussion of electrolysis with iron anodes, three experimental observations are pertinent to describing the reaction mechanism. These observations include: (1) the apparent change in the major precipitate formed as the reaction process continues; (2) the precipitation of significant amounts of the heavy metal load of the treated solution when the bulk solution chemistry is such that the phase is undersaturated with respect to hydroxide solid phases and (3) the simultaneous leveling of both solution pH and iron concentration curves as a function of treatment time. The significance of each one of these observations is considered in greater detail below.

Table 4. Treatment of mixed acid solution with Pb anode

	Concentration (mg l⁻¹) Fe	Al	Cu	Zn	Mn	Mg	Pb	SO_4^{2-}	pH
Original solution	900	370	290	870	220	415	1	4500	2.65
After 5 min treatment	700	150	120	750	205	403	10	3600	3.85

Both qualitatively in terms of precipitate color and quantitatively in terms of iron stoichiometry, a change in the oxidation state of the major precipitate formed in the electrolyzed solution is occurring. At short treatment times of 10 min or less the iron in the precipitate is dominated by its trivalent state while after this time iron precipitates solely as its ferrous form. This change in oxidation state is also related to the trend in pH change observed in that the oxidation state change and the pH leveling occur at nearly the same time. Mechanistically, the relationship between the relative concentrations of dissolved ferric and ferrous iron, total amount of iron oxidized, current efficiency and solution pH is not presently known.

The second observation concerning the formation of the heavy metal precipitate is also documented by Jageline *et al.* (1979) when they report that the pH of precipitation of Cu, Zn, Ni and Cr during electrocoagulation is lower than that required for precipitation if the hydroxide source is an alkali salt. The fact that these species do precipitate as the hydroxide is confirmed by the stoichiometry of the solid and by the absence of counterions other than hydroxide in the material. Indirectly, it is suggested that absorption is the only other potential mechanism for metal removal and this process cannot account for the magnitude of the change noted. Under the experimental conditions noted, the absolute mass of the precipitate formed coupled with the low adsorption capacity of especially the ferrous hydroxide implies that heavy metal removal by adsorption is minimal. When one considers that the pH of the solution near the zone of active hydrogen reduction is somewhat higher than that of the bulk solution and that the heavy metals will tend to migrate towards this zone of higher pH, it is possible to explain the precipitation process. While the actual spatial distribution of the pH zone around the cathode is difficult to characterize under the experimental conditions used, a pH difference of as much as two units was observed in the immediate vacinity of the cathode. Eventually then, the metal ion will find itself in a pH environment in which its hydroxide precipitate is stable. However, as the precipitate leaves the zone of higher pH the thermodynamic stability is not maintained and dissolution is expected. The two factors that contribute to the stability of the metal precipitation are the kinetic constraints on the redissolution process and the iron precipitate coating on the hydroxides of the other heavy metals. It is suggested that the relatively small amount of the thermodynamically unstable heavy metal precipitate is essentially shielded from the solution by the large excess of the stable iron precipitate produced.

CONCLUSIONS

Electroprecipitation has demonstrated on a laboratory scale the ability to effectively remove heavy metals from artificial and industrial acid waste solutions. Sacrificial oxidation of a metallic anode is coupled with hydrogen ion reduction at the cathode to produce an increase in solution pH which results in the precipitation of heavy metal hydroxides. When anodes, whose decomposition product forms a relatively insoluble hydroxide are used (Fe and Zn), ultimate solution pH and, therefore, metal removal efficiency is related to the attainment of a steady state condition with respect to the rates of anode dissolution and migration towards the zone of active precipitation. Although the bulk solution pH is too low for the solid metal hydroxides to be thermodynamically stable, the metals do precipitate within the proposed local zones of high pH which surround the cathode. Such precipitates are kinetically stabilized by the large excess of precipitate formed from the anode decomposition product. While the use of a Pb sacrificial anode is potentially attractive due to the potential to both remove SO_4^{2-} from solution and the resulting higher solution pH, the electrode is quickly poisoned as its surface is coated by a lead sulfate phase.

The laboratory simulations provide an experimental basis upon which the potential of the electroprecipitation process to address the shortcomings noted earlier, in the lime/limestone neutralization process can be judged. For especially the lead anodes, problems (1) and (2) (reduction of the sulfate load and increased water hardness) are effectively eliminated by the proposed process. While the utilization of other electrode materials will not produce such a large decrease in the sulfate load, their use will not produce as large an increase in water hardness as does lime addition. In the case of the steel anodes, the increase in water hardness can be eliminated by removal of the decomposition product (Fe^{2+}) by prior or subsequent oxidation. Although this research does not directly address the third problem (that of sludge disposal) it is our opinion that the electroprecipitation process will produce a solid product which is more amenable to reclamation than disposal.

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