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A Continuous Flow Evaluation of the Galvanic Stripping Process

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ABSTRACT

The concept of galvanically stripping cations such as Fe^{3+}, Cu^{2+}, Pb^{2+}, and Au^{3+} from organic solvents using solid metal reductants has been demonstrated on a batch test basis in a number of previous studies. In this research the first evaluation of a continuous flow system for the process was made, with Fe^{3+} removal from D2EHPA being the primary objective. The effect of operation type (separate or simultaneous stripping), the iron concentration in the organic feed, the organic flow rate, the aqueous-to-organic volume ratio (A/O), the metal reductant (pure zinc vs lead–zinc alloy), the reductant surface area and acidity of the stripping phase on the iron and zinc removal percentages, and the process rate and stoichiometry were evaluated by using continuous flow mixed reactors. The steady-state condition was reached in all the tests after about 40 minutes. In particular, the rate of iron removal was found to be greater for simultaneous than for separate galvanic stripping. A longer organic residence time produced a slightly lower rate, but increasing the aqueous-to-organic ratio augmented the overall rate. The pH of the aqueous phase controlled the iron and zinc stripping percentages, and increasing the reductant surface area increased the iron removal percent. In general, the results agreed with previous batch-type studies on galvanic stripping, and the data indicated that the galvanic stripping process rate and reactor behavior can be assessed by using mechanically agitated continuous flow mixed reactors.

Key Words. D2EHPA; Iron; Zinc; Rate; Waste

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INTRODUCTION

The presence of iron in a number of mineral and waste materials has been a recurring problem in the hydrometallurgical extraction of many nonferrous metals such as zinc, copper, and aluminum (1). One common method to control iron in zinc processing has been by precipitation as jarosite, goethite, or hematite. These processes have proven to be effective, but other environmentally acceptable methods to handle iron might be needed in the future. Galvanic stripping has been proposed as a viable alternative to remove iron from process solutions, with recovery of iron in the form of a sulfate or chloride solution (2, 3). The process has been evaluated using small-scale batch tests, and the results were sufficiently interesting to justify additional study (4).

Galvanic stripping consists of using the electrochemical reducing power of a solid metal, or alloy, to strip a more noble metal ion loaded in the organic phase. The reduced metal can then be recovered as a cemented powder deposit on the reductant or stripped by a suitable aqueous phase (2, 5). When the reduction and stripping take place in the same reactor, the process is called simultaneous stripping. In separate stripping, these steps are carried out in sequence, first reduction and then stripping in an aqueous solution. Some of the possible reactions that can take place during the galvanic stripping of iron (2, 6, 7), using zinc as reductant, where HA stands for D2EHPA [di(2-ethylhexyl) phosphoric acid], H is the hydrogen ion, and A is the anion, are given below.

Iron loading: (as ferric) aqueous phase:

$$Fe_2(SO_4)_3 + 12HA \rightarrow 2FeA_6H_3 + 3H_2SO_4 \qquad (1)$$

$$Fe_2(SO_4)_3 + 6HA + 2H_2O \rightarrow Fe_2A_6(H_2O)_2 + 3H_2SO_4 \qquad (2)$$

Iron reduction: (ferric to ferrous) organic phase:

$$Fe_2A_6(H_2O)_2 + Zn + 6HA \rightarrow Zn(A_2H)_2 + 2Fe(A_2H)_2 + 2H_2O \qquad (3)$$

$$2FeA_6H_3 + Zn \rightarrow Zn(A_2H)_2 + 2Fe(A_2H)_2 \qquad (4)$$

Iron stripping: (as ferrous) organic to aqueous phase:

$$Fe(A_2H)_2 + H_2SO_4 \rightarrow FeSO_4 + 4HA \qquad (5)$$

Although iron has been successfully separated from acid zinc sulfate solutions by utilization of galvanic stripping, the previous experimental work has mainly involved batch testing (1–5). A magnetic stirrer or a shaker had been used for agitation. A column-type reactor for the reduction/stripping has also been tested; however, the influence of the operation parameters on the galvanic process rate was not measured on a continuous basis.

The primary objective of this research was to evaluate the galvanic stripping process using a continuous flow mixed reactor. The influence of the type of operation, separate versus simultaneous stripping, the organic flow rate, the ferric ion concentration in the organic feed, the aqueous-to-organic ratio (A/O), the type of reductant (pure zinc versus Pb–zinc alloy), the acidity of the stripping phase and the reductant surface area on the iron and zinc removal percentages, and the process rate and reaction stoichiometry were determined.

EXPERIMENTAL

Reagents

Phosphoric acid bis(2-ethylhexyl) ester (D2EHPA), supplied by Albright & Wilson, was diluted to 30 vol% using a commercial diluent, SX-12, supplied by Phillips Mining Chemicals. SX-12 contained 22% aromatics, 42% napthenes, and 36% paraffins, and it was used as the organic phase in all tests. Water, of about the solubility level of 2 vol%, was added to the organic phase in the separate stripping tests.

A zinc neutral leach residue was dissolved in sulfuric acid to produce the solution containing the iron to be removed. The resulting leach solution, supplied by Big River Zinc Co., contained 9.2 g/L iron, 136 g/L zinc, 100 g/L sulfuric acid, and Cd, Cu, Co, Ni, As, Ge, Ca, and Sb as trace elements. This solution was contacted with the organic phase and the ferric iron was readily loaded, leaving most of the impurities in the aqueous phase.

The other aqueous phase, the stripping solution, was prepared from deionized water and analytical reagent-grade sulfuric acid, which was added until the desired pH was reached. After reduction and stripping, this by-product solution contained mostly ferrous sulfate with some zinc as the main impurity.

Special high grade (SHG) zinc ($-14+65$ mesh), 1.35 wt% lead–zinc alloy ($-14+65$ mesh), and 1.67 wt% lead–zinc alloy ($-20+60$ mesh) powders were used as reductants.

Apparatus

The experimental apparatus, shown in Fig. 1 for simultaneous galvanic stripping, consisted of a continuous flow reactor with two modifications depending on whether a magnetic or mechanical stirrer was used. Sufficient agitation was provided in both reactors to insure phase engagement and particle suspension. Flow calibrated pumps served to feed the reactor with known composition organic and aqueous phases. A third pump was connected to extract the reacting mixture. Reagent-grade nitrogen was injected into the reactor to prevent air entrainment, which might reoxidize the iron.

Temperature control was achieved during loading by immersing the flask containing the organic and aqueous phases in a thermostatic bath. Water at the desired temperature was pumped through the jacket of the reactor. Another

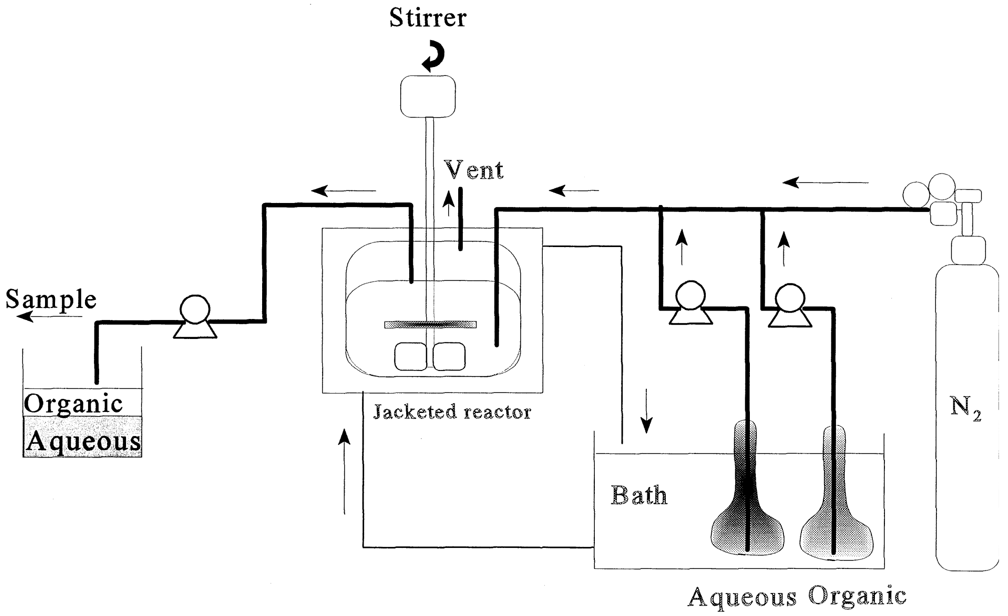

FIG. 1 Experimental apparatus for simultaneous galvanic stripping.

magnetically stirred, smaller jacketed reactor was used to strip the iron from the organic in separate stripping tests.

Peristaltic pumps served to feed organic and aqueous solutions into the reactor at fixed flow rates. The flow rates were varied in some experiments, as shown in the respective figures.

Iron and zinc concentrations in the organic and aqueous samples were quantified using a model 2501 Portaspec x-ray fluorescence portable analyzer.

Procedure

Ferric ion was loaded to the desired concentration by contacting approximately 100 mL of organic and 100 mL of the leach solution in the shaker at 40°C for 30 minutes.

Predetermined volumes of iron-loaded organic and aqueous stripping solutions were placed into the reactor and immersed in the water bath for simultaneous stripping. Once the desired temperature was reached, dry nitrogen was bubbled into the reactor for 10 minutes. For a separate galvanic stripping run, only organic was fed until the desired fluid level in the reactor was achieved. Then the reductant was added and the reaction was initiated. Nitrogen flow was decreased to a minimum, assuring that there was a positive pressure in the reactor.

In order to obtain samples from the reactor, the exit stream was diverted for a short period of time. For simultaneous galvanic stripping tests, the phases were separated and analyzed. For separate galvanic stripping tests, the organic samples were mixed for 5 minutes with an aqueous stripping solution, of known pH and A/O ratio, in another reactor under a nitrogen atmosphere, and then separated for analysis.

Steady-State Assumption

Samples were taken during each test in order to confirm that the steady state was approached. Percent iron and zinc removal from the organic was also calculated. The stoichiometric index, based on the assumption that 1 mole of zinc would reduce 2 moles of ferric to ferrous ion, was defined as the mass ratio of reductant actually consumed to reductant stoichiometrically required for iron removal. A mass balance (8) was established for each sampling time, such that the galvanic stripping process rate was estimated. The process rate for iron removal is:

$$\text{Rate} = \frac{(C_{\text{Fe}_{\text{feed}}} - C_{\text{Fe}_{\text{exit}}})F_{\text{o}}}{\nu} \qquad (6)$$

where C_{Fe} is the iron concentration in the organic (g/L), F_{o} is the organic flow rate (L/min), and ν is the reductant total surface area (cm^2) available for reaction. This parameter represents the net amount of iron stripped from the organic per unit of surface area of reductant per unit of time, which gives a rate expression of g Fe/(cm^2·min) for steady-state conditions. In galvanic stripping the rate of particle dissolution is so small that the total reductant surface area does not change significantly during one experiment, therefore steady-state conditions are assumed.

Effect of Operating Parameters

In order to investigate the effect of the operating variables on the process response, the stimulus–response technique was used. The process response variables included iron and zinc removal percentages, reaction stoichiometry, rate of the process, and exit strip pH. They were estimated on the basis of the sample analysis for each sampling time. Once a steady state was reached, one operating parameter was changed; the galvanic stripping process then responded and produced changes in the response variables until another steady state was reached. The results shown and discussed in this work mainly involve the comparison between the responses at these two steady states.

Initially, steady-state process responses for both the simultaneous and separate modes of operation are given. Then, the effects of increasing and decreasing the organic flow rate on the process responses were studied. The effects of strip pH and reductant surface area were also evaluated.

RESULTS AND DISCUSSION

Validation of Steady-State Assumption

A simultaneous stripping test was made using 40°C, 30 vol% DEHPA in SX-12, 3 g of 1.67% Pb–Zn alloy, −20+60 mesh, feed pH 1.4, A/O = 1, and magnetic stirring. The changes in iron and zinc removal, process rate, and reaction stoichiometry index with time are shown in Fig. 2. As can be seen from the figure, steady state seems to be reached at least by 60 minutes. The iron removal percentage is about 65, with almost no zinc stripped. In practice, high iron and low zinc removal are desired. The rate is 5.2×10^{-5} g Fe/cm^2·min, with a stoichiometry index of 1.5 and an exit strip pH of 2.3 at the steady-state condition. The stoichiometry index indicates the efficiency of the zinc metal in reducing ferric to ferrous iron, where the index reference value is 1 when 1 mole of zinc reduces 2 moles of ferrous ion. Based on these data, a steady state is assumed and a mass balance can be reasonably applied to evaluate the galvanic stripping process. The values shown at 60 and 90 minutes can be considered the steady state response of the system. Every run was reproduced to validate the steady-state conditions.

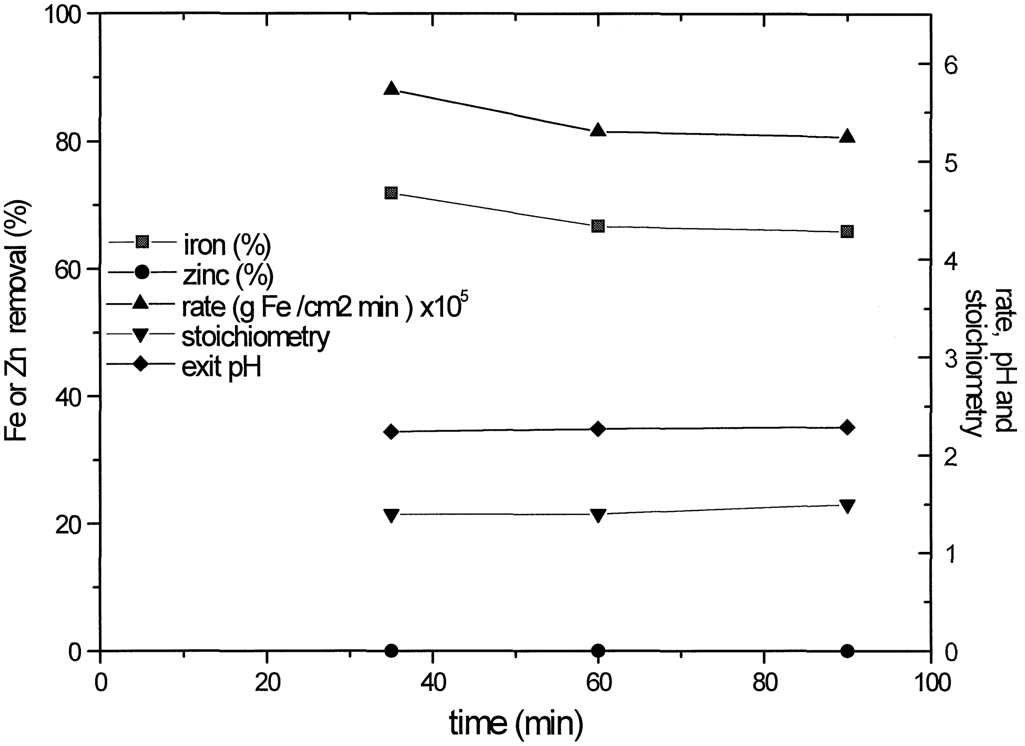

FIG. 2 Effect of time on the simultaneous galvanic stripping process variables.

Simultaneous or Separate Stripping

Another galvanic stripping test was carried out under conditions similar to those listed previously, but using the separate stripping mode. The steady-state iron removal reached only about 43%, and there are probably several reasons why the recovery is lower. First, the simultaneous process is simpler to operate than the separate process on a small scale, particularly with regard to phase separation and air entrainment or reoxidation. Due to a greater number of handling steps involving the organic phase, air exposure during transference and stripping is more likely with reoxidation of iron. The apparent improved performance of simultaneous over separate stripping was also experienced in batch experiments (3–5). Even though these results are typical, the operating conditions can usually be manipulated in both processes to attain the same percent iron removal. However, separate stripping has one major advantage in that the removal of iron into the aqueous phase can be controlled independently of the reduction step, with obvious benefits for controlling the stripping of zinc.

Zinc removal was not significantly affected by the mode of operation, probably because it is controlled by the pH of the system. The aqueous strip phase had an initial pH of 1.4 and the exit pH values were in the 2.2 to 2.3 range in both tests. A higher iron removal rate was obtained by simultaneous stripping than with separate stripping. This might be due to the presence of the aqueous phase which is in constant contact with the organic phase during simultaneous stripping. Conversely, in separate stripping the aqueous and organic phases are contacted once and there is a changing pH value for the aqueous solution during stripping.

Effect of Organic Iron Concentration and Flow Rate

Another test was made to determine the effects of iron concentration in the organic feed and the organic residence time. The test was carried out at 40°C, using 30 vol% DEHPA in SX-12, mechanically agitated at 1400 rpm, with 10 g of 1.67% Pb–Zn alloy ($-20+60$ mesh) as reductant, and $A/O = 1$, using simultaneous stripping. The effect of time, iron concentration, and organic flow rate on the process variables is illustrated in Fig. 3.

As can be seen in the figure, the first steady state prevailed between 40 and 60 minutes, the second was partially reached between 100 and 120 minutes, with the third occurring after 180 minutes. As the iron concentration was step increased about four times, iron removal remained high (about 97%), zinc removal was erratic, the rate increased almost four times, and the stoichiometry index improved to 1.0. The rate increase was approximately proportional to the iron concentration, suggesting a first-order relationship on the feed iron concentration assuming sufficient reductant is present. Note that the zinc con-

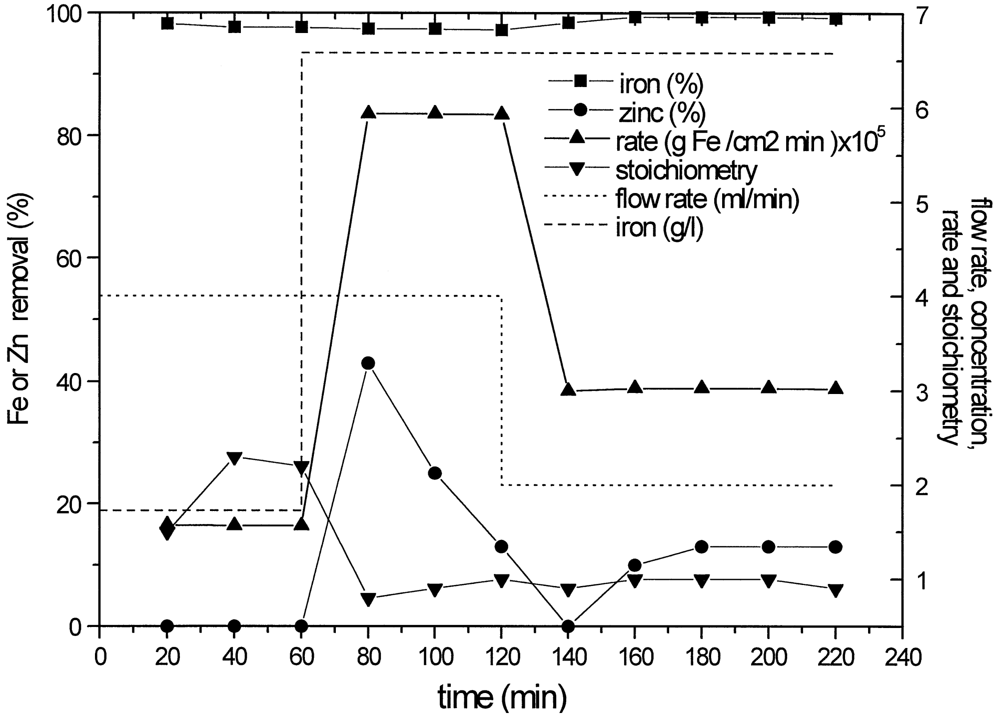

FIG. 3 The effect of time, iron concentration in the organic feed, and residence time on the simultaneous galvanic stripping process variables.

tent in this run was nearly three times greater than the amount used in the previous test. The zinc stripping changes were most probably due to the wide range of pH values used.

Comparison of the second to third steady state shows the effect of increasing the reactor residence time. As illustrated in Fig. 3, percent iron removal continues to be very high, zinc removal remained low, the rate decreased by about half, and the stoichiometry index remained almost constant. The most significant change was the decrease in the process rate, which is caused by a lower amount of iron available for reduction and stripping.

The effect of a decreasing step change in the flow rate, or increasing the organic phase residence time, on the separate galvanic stripping process was also investigated. It was found that iron removal again remained constant and the zinc removal percentage did not change, which indicates that the removal of these elements is not strongly controlled by the reaction residence time. The separate stripping process rate decreases to half its value with decreasing organic flow rate. This is expected if it were assumed that the rate is a first-order process with ferric ion concentration. The reaction stoichiometry index improved only slightly. Overall, the ferric ion concentration in the organic phase does appear to have an important effect on the process response variables and reaction efficiency. Overall, the results indicate that high zinc metal reductant loading with a shorter residence time are desirable for optimum efficiency.

Effect of A/O Ratio

The effect of decreasing the organic flow rate on the simultaneous galvanic stripping response variables was also evaluated. An experiment was made using simultaneous stripping at 40°C, 15 g 1.67% Pb–Zn alloy (−20+65 mesh) as reductant, 30 vol% DEHPA in SX-12, mechanical agitation, strip pH 1.4, with an A/O of 1 or 2. In the simultaneous mode, increasing the organic residence time and/or the A/O ratio increased iron removal but zinc stripping did not change. This increment could be the result of a higher stripping power in the reactor due to the greater volume of the aqueous phase and the maintenance of a lower pH in the strip solution. However, the rate decreased 40%, probably due to the 20% lower ferric ion concentration which resulted from the dilution. The reaction stoichiometry continued at a reasonably low level of 1.8.

Effect of Reductant Surface Area

The effect on simultaneous galvanic stripping of increasing the reductant surface area from 21 to 105 cm^2 is shown in Fig. 4. This test was carried out

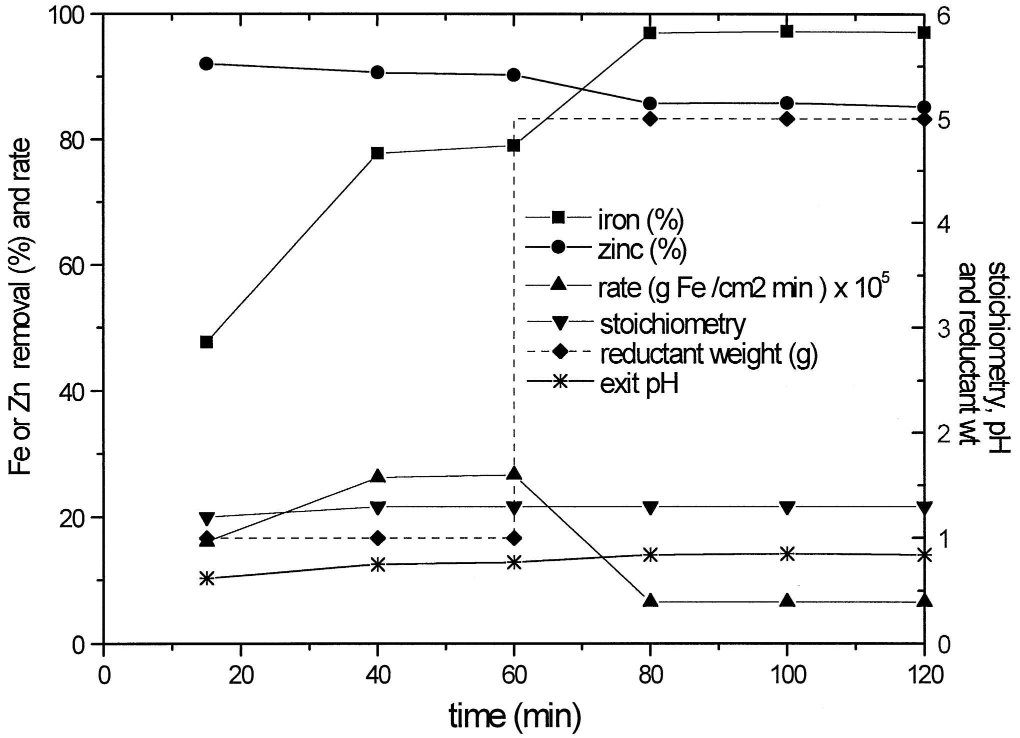

FIG. 4 Effect of reductant surface area and operation time on the simultaneous galvanic stripping process variables.

at 40°C, 30 vol% DEHPA in SX-12 as the organic phase loaded with iron, using 1.67% Pb–zinc alloy ($-20+60$ mesh), mechanical agitation, and $A/O = 1$. Again, it is seen that two steady states were reached at 40 minutes and after 80 minutes. Iron removal was increased from 75 to 98% by increasing the surface area. This result agreed with batch testing results (4), where it was found that surface area is a strong factor in the reaction and probably obeys first-order kinetics. Moreover, iron recovery has been increased in previous batch experiments by adding more reductant (4). This suggests that iron reduction is strongly surface-area-dependent. Zinc removal did not change substantially. The steady-state rate decreased from 2.6×10^{-4} to 6×10^{-5} g Fe/cm^2·min when the reductant surface area was increased. Moreover, in another test with similar conditions, 10 g of same reductant gave a rate of 4.5×10^{-5} g Fe/(cm^2·min), probably attributable to the apparent excess of reducing agent.

CONCLUSIONS

Based on the results presented, it is clear that a continuous fluid flow mixed reactor can be used to determine the effects of some of the operating parameters used in the galvanic stripping process. The results show that it is possible to operate a continuous reactor in either the separate or simultaneous galvanic stripping mode. Operating with separate stripping seemed easier to control than simultaneous stripping, but similar results can be achieved using either mode. The process rate appeared to be proportional to the iron concentration in the organic feed and to the surface area of the metal reductant. Galvanic stripping is sensitive to changes in organic flow rate; therefore, this could be a useful parameter to control the operation. The pH of the aqueous strip is very important to maximize iron and minimize zinc removal. The reaction stoichiometry was less affected than initially indicated by batch test results and was considered to be acceptable in terms of zinc metal usage. Overall, the results were very promising. The next major step is to obtain a complete material balance on the primary impurities from a long-term run on the continuous flow system.

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