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ELECTROLYTIC SEPARATION AND RECOVERY IN CAUSTIC OF STEEL AND ZINC FROM GALVANIZED STEEL SCRAP

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ABSTRACT

Experiments were conducted to examine the technical and economic feasibility of a single-step process for electrochemically separating and recovering in hot caustic the components of galvanized steel. Electrochemical separation is practical because: 1. maximum anodic zinc dissolution currents yield commercially acceptable throughputs and are 1000 times greater than those for steel, 2. steel is not seriously corroded by caustic under conditions proposed and 3. the process is robust in the presence of expected aluminum, lead, cadmium and iron impurities. Stripping experiments in 5 M NaOH at 90 °C indicate that a G-90 grade (275 g Zn/m^2) of galvanized steel can be stripped in about five minutes at a current density of 200 mA/cm^2 in a cell with parallel electrodes separated 15 to 59 mm. Tests with scrap at densities of 30 and 150 lbs/ft^2 were successful at estimated current densities of about 20 mA/cm^2. Residual zinc levels on the steel are less than 0.1 wt%. A technical and economic analysis of alternative technologies for separation and recovery of the components of galvanized scrap steel suggest that none are as energy efficient or cost less to the steel industry than the single-step continuous electrolytic stripping process that is the subject of this research.

INTRODUCTION

Problem of Zinc in Scrap for Steelmaking

Half of the steel produced in the United States is derived from scrap. Zinc in the scrap charge imposes yield, nuisance, opportunity and environmental compliance cost penalties on iron and steelmaking.Since 1982, galvanized steel consumption as a percentage of total steel consumption has doubled from about 6% to almost 12%. Because of this change, the composition of the recycled ferrous scrap stream has become richer in zinc primarily from prompt scrap, such as wastage from auto-stamping plants. When today's automobiles are obsolete and recycled, the percentage of zinc-bearing scrap in the recycle stream could approach almost 20%. Although this type of scrap could be utilized in electric arc furnaces to produce certain types of steel, it cannot be utilized in integrated steelmaking nor steel and iron foundry operations. Both the integrated steel producers and the foundries require clean black scrap, and, in its absence, will utilize more pig iron and/or Direct Reduced Iron (DRI).

The Energy Perspective

The alternatives to producing steel from recycled ferrous scrap are to either 1. import raw steel, which in 1986 reached almost 20 million tons, or 2. produce raw steel from primary ores or substitutes, such as direct reduced iron (DRI). Either of these two alternatives have certain drawbacks. In the first case, imported steel increase the U.S. federal trade deficit and other macroeconomic factors such as unemployment and inflation. In the second case, the amount of energy required to produce one ton of steel from primary ore is more than twice the amount of energy required to produce one ton of steel from ferrous scrap. If the amount of steel produced from ferrous scrap in 1986 were otherwise produced from primary ores, the increased consumption of energy would have been about 820 trillion Btu's, about 1.5% of current domestic primary energy consumption.

Scrap Quantity vs. Quality

The central issue with regard to ferrous scrap is not its supply but its quality. The Institute of Scrap Recycling Industries estimates that the ferrous scrap supply that could potentially be recovered to meet demand is in excess of 500 million tons (1). More scrap appears to be recovered than is demanded in the U.S. since U.S. exports of ferrous scrap in 1989 were a record high of 12.2 million tons (2). If the scrap that is exported were instead treated to remove the zinc and provided as a substitute for pig iron, about 180 trillion Btu's per year would be conserved. A process is needed to remove the zinc before the scrap is melted to insure that recycling of galvanized scrap is not impeded.

Historical Perspective

The need for "dezincing" galvanized ferrous scrap to provide "specification-grade" scrap to the steel industry is not new. However, thermal and chemical "dezincing" concepts that have been considered prior to this investigation have not had a recovered scrap cost that could compete with the price of pig iron (3). The concept of anodically promoting the dissolution of zinc from galvanized steel scrap and simultaneously electrowinning in hot caustic appears to be technically feasible. Operating and capital cost estimates for the process indicate it is cost-effective relative to the alternatives of using pig iron or DRI and is the least costly to the steel industry compared to other processes considered (4).

Anodic dissolution of metals with cathodic deposition in the same electrolyte, i.e., one-step active-metal-dissolution/recovery, is common in electroplating practice. Tin and zinc flake pigments were produced early using this process (5). Anodically promoted detinning in caustic of tinplated scrap has been practised commercially for many years (6) and is directly analogous to the dezincing process reported on here. A Belgian patent has been granted for use of electrolytic dissolution/electrowinning to recover the components of scrap galvanized steel (7).

Also relevant, but distinct from anodic dissolution processes, are studies of recovery of zinc by electrolysis of alkaline or acid solutions derived from leaching of oxidic zinc ores (8-12) or zinc-bearing residuals such as steel making furnace dusts (13-15). These are two-step processes which put metal into solution by chemical leaching followed by electrolytic recovery using inert anodes. The predominant commercial detinning process uses chemical leaching in caustic followed by electrolytic recovery of the tin or precipitation of the stannate; this process has also been practised economically in North America and Europe for many years. Chemical detinning is not, however, practised on high-density baled scrap that is expected to comprise at least part of the feed for dezincing plants and the economics of detinning operations are favorably affected by a market price for tin that is over four times that for zinc.

FLOWSHEET AND PROCESS CHEMISTRY

Flowsheet

Figure 1 is a flowsheet showing a concept for the one-step stripping of galvanized steel and recovery of zinc and steel in hot caustic. The process is simply reverse electroplating. The valued product is the stripped steel scrap, and the zinc is recovered in a relatively pure form that maintains its usefulness as a secondary material.

Galvanized scrap, baled or shredded, is made the anode in a tank filled with warm (70-90 °C) aqueous solution of sodium hydroxide. Steel plate cathodes bracket the scrap. An electrical potential is applied to the cell and, in a multistep electrode process (16-18), the zinc is anodically stripped from the scrap steel and deposited on the cathode. The minimum time for stripping the zinc from the scrap anode complies with Faraday's Law and is constrained by the maximum critical or passivation-limited current density. The critical current density depends on the cell geometry and the electrolyte chemistry and temperature. The cathodic current efficiency depends on the current density and the amount of redissolution of zinc occurring on the steel cathode.

The stripped scrap is removed from the tank and water rinsed to minimize dragout of NaOH. The washed scrap is then ready for shipment to the steel or ironmaker. Zinc deposited on the cathode is scrubbed or scraped off, settles to the bottom of the tank, and is pumped to a filter. The washed solids are sent to a zinc smelter or other converter. The liquids recovered from filtration are then returned to the stripping tank for make-up of evaporative losses. Bleed streams accommodate control of chemistry.

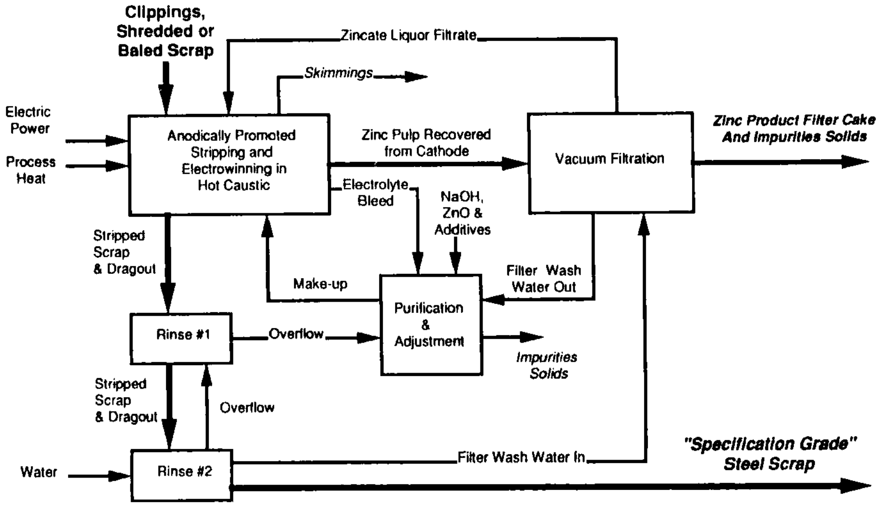

Figure 1. Process Flowsheet: Electrolytic Stripping/Recovery of Steel and Zinc in Caustic. The components of galvanized scrap are recovered as specification grade scrap steel and a metallic zinc powder.

Process Chemistry

In the stripping tank, metallic zinc on the steel is oxidized under the influence of the applied potential,

$$\mathrm{Zn}^{\circ} - 2e^{-} \quad \underset{\text{<--Cathode}}{\overset{\text{Anode--->}}{\qquad\qquad}} \quad \mathrm{Zn}^{++} ,$$

zinc hydroxide is formed,

$$\mathrm{Zn}^{++} + 2\mathrm{H}_2\mathrm{O} \quad \underset{\text{<--Cathode}}{\overset{\text{Anode--->}}{\qquad\qquad}} \quad \mathrm{Zn(OH)}_2 + 2\mathrm{H}^{+} ,$$

and, in the presence of greater than 3M NaOH (19), the divalent zincate ion is formed,

$$\mathrm{Zn(OH)}_2 + 2\mathrm{NaOH} \quad \underset{\text{<--Cathode}}{\overset{\text{Anode--->}}{\qquad\qquad}} \quad 2\mathrm{Na}^{+} + \mathrm{Zn(OH)}_4^{=} .$$

As noted, the reactions are reversed at the cathode. The overall reaction consumes only electricity. No NaOH is consumed, except for losses due to dragout and reaction with aluminum, and production of hydrogen and oxygen gases is not an intrinsic part of the process. Hydrogen is expected from corrosion of the zinc and as a side-product at the cathode; oxygen would be produced at the anode if the process is operated transpassively.

The process has been examined in laboratory tests, in bench scale stripping experiments and in batch testing of up to 550 lb. scrap lots, and the results have confirmed the technical feasibility for home and prompt scrap. Residual zinc content on the scrap is less than 0.1% by weight. The process feasibility has not yet been determined for obsolete ferrous scrap.

The experimental work has been directed to addressing uncertainties in extending the concept of the one-step caustic electrolytic process to commercial operation on scrap. These include determining: 1. maximum expected rate of dissolution, 2. selectivity for zinc over steel, 3. effectiveness of zinc removal, 4. effects of variation in process conditions such as temperature, caustic concentration, zincate concentration, expected impurities and current density, 5. morphology of zinc deposits, 6. effectiveness on various types of galvanized coatings and 7. performance on actual scrap.

EXPERIMENTAL TECHNIQUES

Work was done in three areas: 1. the electrochemical behavior of zinc and steel in hot caustic was explored, 2. galvanized steel coupons were stripped, and the zinc was recovered in caustic in a bench-scale stripping cell and 3. 100 to 550 pound batches of galvanized scrap were treated using anodic dissolution in hot caustic.

Laboratory Studies

Four types of measurements were performed:

1. Potential-controlled, steady-state and cyclic voltammetry current/potential (polarization) curves were measured to determine the cathodic, anodic, and passive potential regions,
2. Galvanostatic (constant-current) passivation measurements were carried out to determine the maximum rate of metal dissolution before the onset of passivity,
3. Long diffusion path polarization measurements were made under conditions simulating scrap geometry and galvanized steel scrap from which different amounts of zinc have been stripped, and
4. Zinc deposition current efficiency was determined by measuring the volume of hydrogen evolved over time during zinc deposition under constant current.

Most polarization measurements were carried out in a cylindrical polypropylene cell (Figure 2a) positioned over a submersible magnetic stirrer or nitrogen sparger in a constant temperature bath. The electrodes and a gas feed were inserted through a large rubber stopper cover. The cell was also equipped with a reflux condenser to avoid concentration changes in the solution. Measurements were carried out at 70 and 90 °C, in 3, 5, 8, and 10 M NaOH solutions; in some tests reagent grade ZnO was added.

Normally, measurements were carried out in stagnant solution deaerated with nitrogen. A few tests were carried out with stirred and/or air saturated solution. Zinc rod test electrodes were cast from reagent grade zinc and the steel rod test electrodes were 1018 mild steel stock. The counter electrode was a platinum wire spiral. The saturated calomel reference electrode was placed in a separate compartment filled with room temperature test solution. The reference compartment was connected via a solution bridge terminating in a Teflon Luggin capillary.

For polarization and constant-current passivation measurements, the working (test) electrodes were 11/64 inch diameter metals rods, covered with heat shrinkable Teflon tubing except for a 1/8 to 1/4 inch working length with its end masked. The concentric, Pt-wire counter electrode surrounded the working electrode and the Luggin capillary was placed near the working surface.

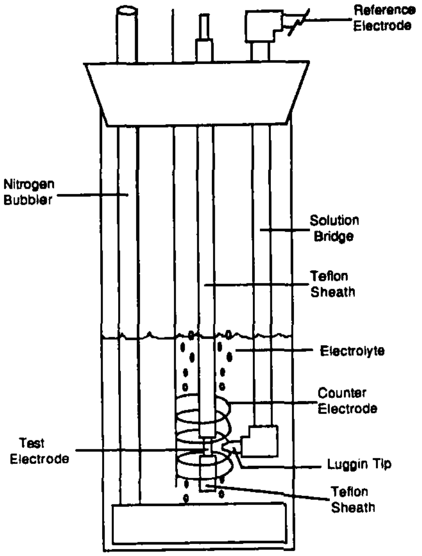

Figure 2a. Sketch of the cell for polarization measurements

Steady-state polarization curves were measured under potential control; the potential of the working electrode was controlled against the SCE and the current flowing between the working and counter electrodes was recorded. The cyclic voltammograms were also measured potentiostatically.

In the constant-current passivation measurements, a constant current was imposed between the working and the counter electrodes, and the potential between the working and reference electrodes was recorded. The passivation time was indicated by a sudden large increase of the potential.

For the long diffusion path measurements, a restrictive polyethylene insert shown as "Stripping Cell" in Figure 2b, was placed inside the measuring cell to simulate the long current path expected in baled or bundled scrap. The working electrode was a 5.5 inch long 0.25 inch diameter metal rod surrounded concentrically by a 0.75 inch i.d. plastic tube. The counter electrode and the Luggin tip connecting to the external reference electrodes were placed at the top end of the working electrode. The working electrode was prepared from steel and zinc rods held together by a hidden stud, with the zinc placed on the bottom end. Six working electrodes were prepared consisting of segmer of 100, 80, 60, 40, 20 and 0 % zinc, simulating progressive stripping the zinc from the plated scrap. A constant current was imposed betwe the working and counter electrodes, and the potential between t working and reference electrodes was recorded; a steady state w reached in a few minutes. The current values were set to give curre densities, calculated for the full length of the working electrode, 5, 10, 15, 20, 30, 40, and 50 mA/cm^2.

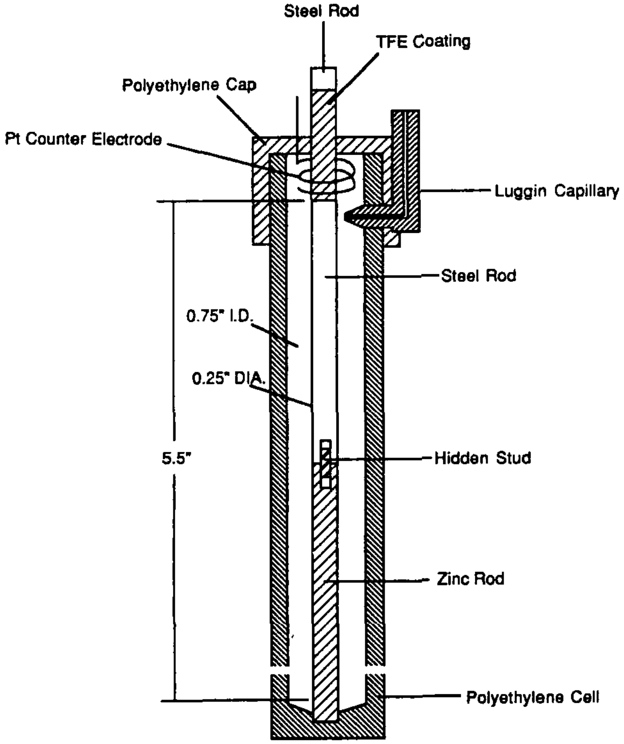

Figure 2b. Sketch of the stripping cell insert for bulk scra simulation polarization measurements

Cathodic deposition efficiency measurements were conducted using cell configured as shown in Figure 2c. The test and counter electrode were positioned in two separate compartments, the separator was poly(methylpentene) hood placed over the U-shaped test electrod assembly. This arrangement permitted the collection of the gase generated at the test electrode in an upside-down buret. The buret wa water-jacketed, and the temperature of the stagnant water was measure with a thermocouple. There was no correction made for the temperature pressure, and humidity of the evolved hydrogen. It was estimated tha the relative error resulting from this simplification is not more tha 10%. Approximately one inch long working electrode rods were connecte to the U-shaped current collector with a hidden stud, and all but small working area of this assembly was sheathed with heat shrinkable Teflon. The basic measurement conditions used in these experiments were 90 °C, and stagnant, deaerated solution containing 5 M NaOH and 0.2 M ZnO.

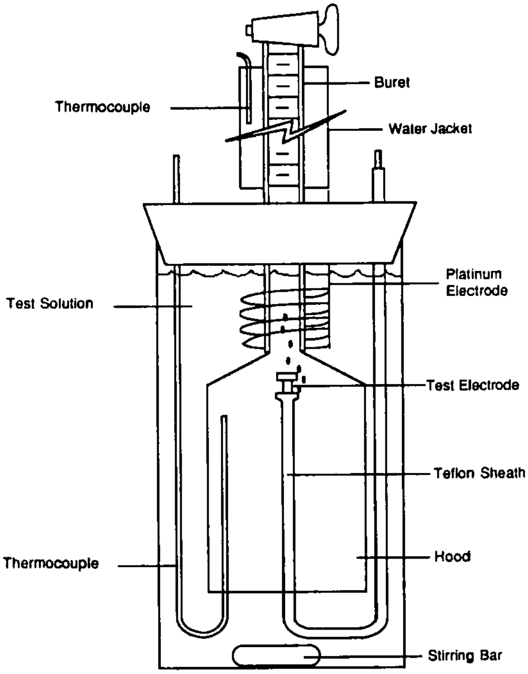

Figure 2c. Sketch of the hydrogen evolution cell

Stripping of Galvanized Steel Coupons

Electrolytic stripping of galvanized steel coupons was conducted in acid and in caustic solutions in a cell of design shown in Figure 3. The results of the acid stripping tests have been reported by Zaromb et al. (20). The cell was immersed in a 90 °C temperature bath for all tests in caustic. Solutions were 5 and 10 M NaOH with 0.1 to 0.4 M added ZnO . Stripping tests were run at various constant currents corresponding to a current density range of 40 to 380 mA/cm^2 ; cell current and voltage were recorded. Electrode current efficiencies were calculated by weighing mass loss and/or gain of the individual coupons before and after stripping and comparing to the Faradaic expectation. The exposed stripping area was 5.3 cm^2 and the electrode separation set at 15, 29 and 59 mm using cells of different lengths.

Stripping of Loose and Baled Galvanized Scrap

Electrolytic stripping tests were conducted in a 400-gallon tank containing hot caustic fitted with a pair of four-foot-wide by threefoot-deep mild steel cathodes, with a 26-inch space between them accommodate an anode basket or bales of scrap. This provided a maxin useable volume between cathodes of 26 ft^3. A 5000-A, 5-V DC pow supply was connected to the cell. Voltage and current were recorde Solution composition for the tests reported here were 5 M NaOH with C M ZnO added, and the electrolyte was maintained at approximately 70- °C. An anode basket for loose or bulk scrap was provided wi adjustable HDPE grid side panels to provide 9 to 16 inch thicknesses loose scrap. Bales of scrap were placed between the cathodes and we self-contained.

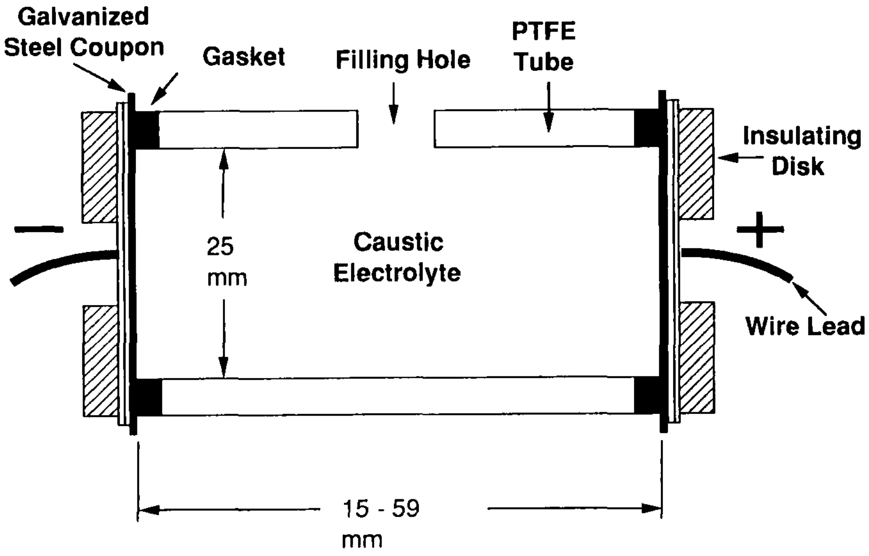

Figure 3. Electrolytic cell for stripping galvanized steel coupons : caustic at 90 °C.

EXPERIMENTAL RESULTS

Laboratory Results

Steady-state polarization curves. An example of the steady-stat polarization curves is shown in Figure 4. As the zinc is polarize positively from its rest potential, first there is an active anodi dissolution with rapidly increasing current density until passivatic sets in and the current decreases to almost zero. The multiple peaks i the active region are characteristic of zinc in alkaline solutions (21) they are caused by complex, multiple-layer passive film formation. A potentials positive relative to -1.2 V, the anodic dissolution continue in the passive region. In this region, the current must pass through highly resistive passive film; therefore, considerable curren densities, at 100% current efficiency, can be obtained in this potentia range, but at a relatively high energy cost. At potentials positive t +1.5 V, the current sharply increases as transpassive oxygen evolutio begins. In this potential range, the current efficiency of the anodic zinc dissolution is low, as the zinc dissolution proceeds with about the same low rate as during the passive dissolution. The polarization curve for steel is qualitatively similar, but at three orders of magnitude less dissolution current.

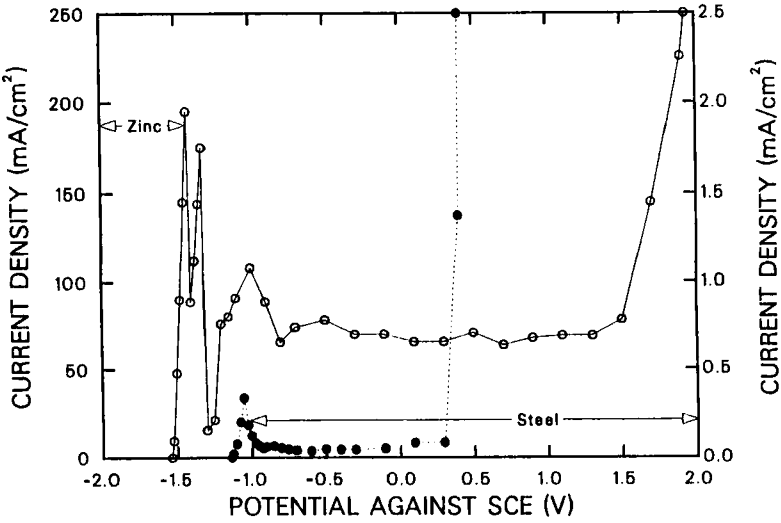

Figure 4.. Steady-state polarization curves of zinc and steel in 5 M NaOH with 0.2 M ZnO at 90 °C. Nitrogen saturated solution.

Cyclic voltammetry polarization curves. Additional details are revealed in Figure 5 in a polarization curve measured with cyclic voltammetry. Starting at the rest potential of zinc (-1.6 V) and proceeding clockwise, a positive current peak is shown (solid curve) indicating the active dissolution of zinc. Passivation begins at about -1.25 V; the current first decreases due to passivation, then it slightly increases as the increasing potential drives the current through the passive film. The reverse scan (dotted line) begins at -0.4 V. The passive dissolution continues, with some hysteresis, until about -1.0 V, where the current becomes unstable due to the periodic breakdown and reformation of the passive film. These oscillations are not shown in the Figure. At about -1.3V the current becomes stable again and follows the course of the positive scan with some hysteresis. Deposition of zinc begins at around -1.5 V, and it peaks at -1.8 V. Oxygen evolution will occur at potentials more positive and hydrogen evolution at potentials more negative than those covered by this scan.

The voltammogram of the steel shows similar features (note the different current scale). The rest potential is around -1.15 V, at more positive potentials the steel actively dissolves, and subsequently it passivates (the small peak at -1.1 V is the oxidation of hydrogen which was produced in a previous scan). Transpassive oxygen evolution (not shown) will occur at around +0.3 V. During the reverse scan iron oxide is reduced, peaking at -1.25 V, then hydrogen evolution starts around -1.3 V.

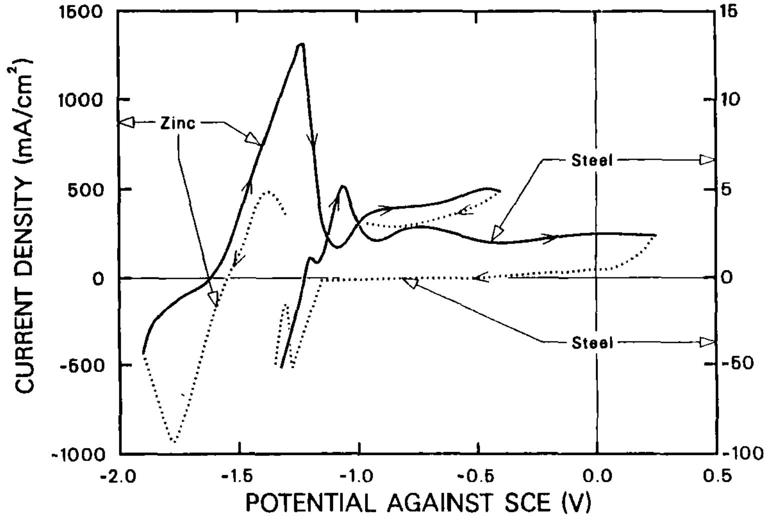

Figure 5. Cyclic voltammetry polarization curves of zinc and steel in 8 M NaOH at 90 °C. 100 mV/sec scan rate, nitrogen saturated stagnant solution.

Air saturation and stirring. The polarization curves reported here were measured in nitrogen saturated, stagnant solutions. A few tests were also carried out with stirred and/or air-saturated solutions. Saturating the solution with air did not produce any difference. Stirring the solution with a magnetic stirrer produced a negligible effect on the steel but increased the dissolution current of zinc by about 30%. Sparging with nitrogen increased maximum zinc dissolution currents by a factor of three. The zinc stripping process will be operated on bulk scrap, whether in containers or self-contained as bales, under very nearly stagnant solutions, especially inside the body of baled scrap, therefore all further tests were carried out in stagnant solutions.

The main information gained from polarization experiments is the potential range where active dissolution of the zinc can be carried out without passivation and without steel dissolution. This potential window, about 0.4-0.5 V positive to the zinc rest potential, was not greatly affected by either temperature or NaOH and ZnO concentrations. The stripping process may be operated at more positive potentials, but at an energy penalty and with some iron dissolution; however, the latter will typically occur at a rate that is about 1000 times slower than the zinc dissolution rate.

Constant-current passivation measurements. In these measurements, a constant current is imposed on the zinc electrode and the passivation time, indicated by a sudden increase of the potential, is observed. In basic solutions, zinc passivation is known to occur with a dissolution-precipitation mechanism, that is, zinc first dissolves to produce a soluble species, and a passive film precipitates only when the solubility limit is exceeded. Two opposing processes are operating: (a) the anodic dissolution increasing the zincate concentration at the surface and (b) the mass transport removing zincate from the surface. The result is that the passivation time will be a function of the current density in constant-current passivation, and the current will be a function of the scan rate in potentiostatic cyclic voltammetry. That is, at high current densities passivation will be fast, while at low current densities it will take a longer (even infinite) time. For this mechanism, the results can be expressed in the form of $(i - i_c)t^{0.5} = k$ if the mass transport occurs only by diffusion. Therefore, the results can be expressed with an i versus $t^{-0.5}$ plot, where the intercept i_c, gives the critical current density below which passivation does not occur, and k is the slope of the line.

Zinc passivation experiments were carried out in 3, 5, 8 and 10 M NaOH at 70 and 90°C, in 5 M NaOH solutions containing 0.15, 0.30, 0.45 and 0.60 M ZnO at 70 °C. Also additive effects were measured in 5 M NaOH containing 0.2 M ZnO at 90°C. A representative i versus $t^{-0.5}$ plot is shown in Figure 6. The i_c values are dependent on the solution composition and temperature and are plotted as a function of NaOH concentration in Figure 7. Figure 8 shows the effect of ZnO concentration on critical current density. The values of i_c increase with temperature; initially, i_c increases with NaOH concentration, but after a broad maximum declines in 10 M NaOH. Critical current density decreases with increasing ZnO content of the solution. These trends are in agreement with the known behavior of zinc in KOH solutions and with the expected trends from a dissolution-precipitation mechanism (16,21).

The observed critical current densities range from 60 to 320 mA/cm^2. The removal of a one mil thick zinc coating requires 15 mA-h/cm^2 charge, therefore the stripping time will be in the range of 2.8 to 15 minutes for each mil of coating. These current densities can easily be achieved with a few tenths of a volt polarization of the anode. Even at the lowest current densities observed here, anodic stripping times are about a factor ten less compared to the several hours that would otherwise be required in a two-stage leach and electrolytic recovery process.

Some anions, notably chloride, fluoride, and sulfate, are known to break down passive oxide films (22). The addition of these anions to the solution may increase the achievable maximum stripping current, but possibly at the price of increased steel dissolution. Potentiostatic polarization measurements were carried out with zinc electrodes using 0.1 M and 1.0 M NaCl, 0.75 M Na_2SO_4, 0.025, 0.050 and 0.075 M NaF in 5 M NaOH at 90°C. The additives produced no beneficial effects. The active/passive potential ranges were not affected, and the active dissolution current density of the zinc remained unchanged or decreased

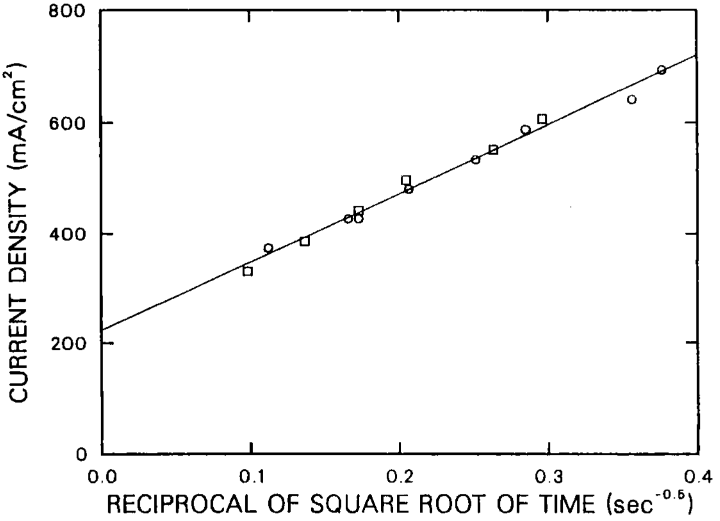

Figure 6. Constant current passivation of zinc in 5 M NaOH with 0.2 M ZnO at 90 °C. Nitrogen saturated stagnant solution.

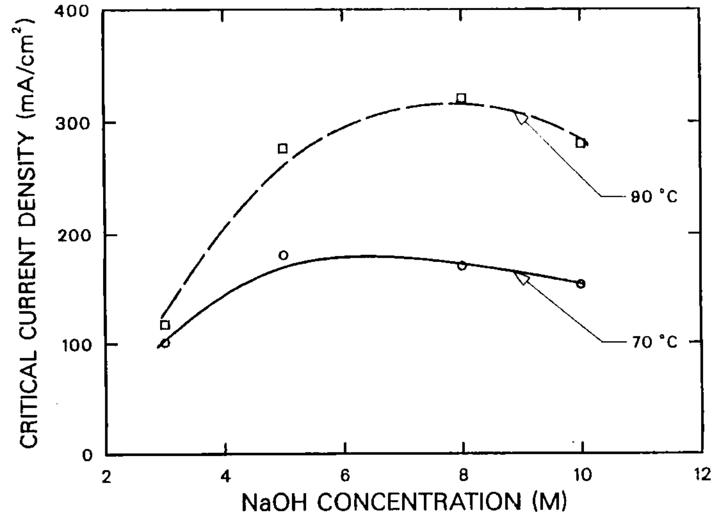

Figure 7. Critical current density of zinc passivation as a function of NaOH concentration and temperature.

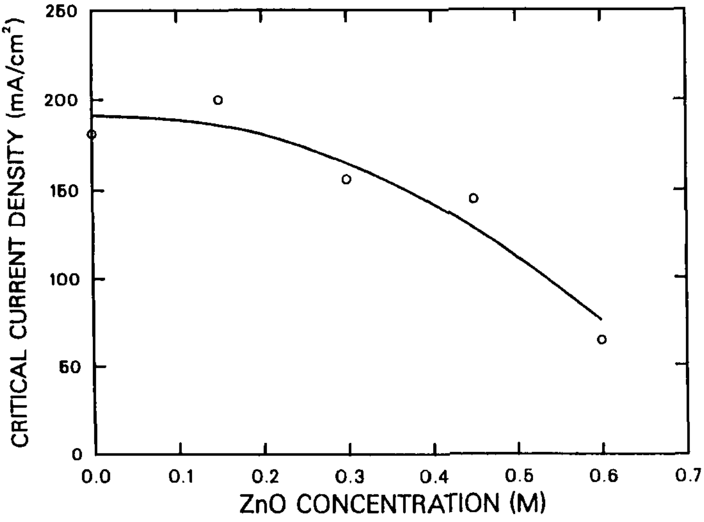

Figure 8. Critical current density as a function of ZnO concentration in 5 M NaOH at 70 °C.

somewhat. The steel dissolution current seemed unaffected. The decrease of the zinc dissolution current was probably caused by the additives tying up water molecules in their hydration shells, thereby causing earlier precipitation of the ZnO. Most of the changes observed were within experimental error.

KOH vs NaOH. In alkaline zinc batteries, KOH electrolyte is used rather than NaOH because of its higher conductivity. The higher conductivity is usually associated with higher diffusivity, which, in turn, is expected to increase the active dissolution current density. Potentiostatic and galvanostatic polarization and galvanostatic passivation experiments were carried out with 5 M KOH solutions containing 0.2 M ZnO. The constant-current passivation experiment yielded a critical current density of 160 mA/cm^2. Comparison of these data with those taken with NaOH electrolyte shows that the substitution of NaOH with KOH did not have any significant beneficial effect. On the contrary, a slight decrease in the active dissolution current was found.

Long diffusion path polarization measurements. The purpose of these measurements was to test if a simple potential measurement with the reference electrode (or Luggin capillary) placed at the surface of a bundle of scrap could determine the depth of stripping potential into the bundle. Constant-current polarization measurements were made under conditions simulating scrap geometry and galvanized steel scrap from which different amounts of zinc have been stripped (see Figure 2b). The measurements were carried out at only one condition: 5 M NaOH and 70 °C, with the results presented in Figure 8. The end-point detection technique seems to work at low current densities. The electrode potential is a monotonous and well behaved function of the current density up to about 20 mA/cm^2 . At higher current densities, the potentials are bunched too closely together at the steel potential to be of value as an end-point indication.

These test results demonstrate the difficulties involved in stripping the zinc from bundled scrap. The current will have to penetrate deep into the bundle through long narrow solution paths to reach all the zinc on the surface of the scrap. The current distribution will be strongly nonuniform and will change with time. At first, all the current will be concentrated close to the surface of the bundle, stripping zinc only. As the zinc is removed, the current will be thrown further into the bundle, but that requires a fairly large potential to drive the current through the narrow, highly resistive solution channels (note the large polarizations in Figure 9), thereby inducing the dissolution of the steel close to the surface of the bundle and, if the potential becomes sufficiently positive, also the anodic production of oxygen. The steel dissolution current will be orders of magnitude smaller than that of the zinc, and it will probably cause only a small current inefficiency at the anode. The metals dissolved will likely precipitate as oxides/hydroxides. However, if these compounds are even slightly soluble, they may cause hydrogen evolution and loss of cathodic current efficiency if the impurity metal(s) have a lower hydrogen overpotential than zinc. Oxygen evolution can cause considerable current efficiency loss at the anode.

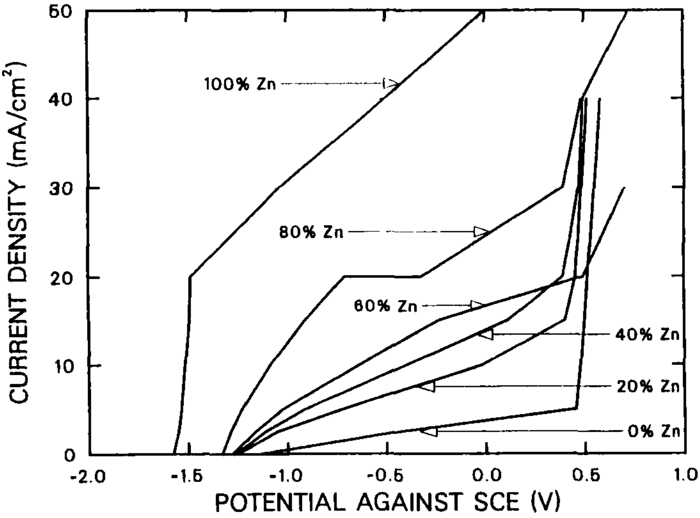

Figure 9. End-point detection of zinc stripping in 5 M NaOH with 0.2 M ZnO at 70 °C. Nitrogen saturated stagnant solution. Working electrode potential as a function of percent stripping and current density.

<u>Cathodic efficiency measurements</u>. The purpose of the hydrogen evolution experiments was to investigate the effect of some cationic impurities on the current efficiency and morphology of zinc deposition.

The current efficiency and morphology of zinc deposition from alkaline solutions is known to be affected by impurities in the solution. The effect of some impurities expected to be present in the process was investigated with the cell shown in Figure 2c. The morphology of the deposition was visually examined. Experiments were carried out with and without stirring (by the magnetic stirrer). No quantitative stirring rate can be given, but the rate was kept constant for all experiments. The current density was varied between 25 and 150 mA/cm^2, and the maximum plating time was adjusted to avoid the depletion of the zinc in the solution by more than 10% (from 0.2 M to 0.18 M).

A series of experiments was carried out without the addition of impurities to establish a base line. Drastically different behaviors were found depending on whether the zinc was plated onto a steel or zinc rod. The results for plating onto steel in stagnant solution is shown in Figure 10. The zinc deposition efficiency increases with time, but seems to level off after an initial time. The efficiency increases with current density and stirring (not shown). The efficiencies range between 70 and 95%. The results for plating onto zinc are shown in Figure 11. The zinc deposition efficiency increases with time, but levels off after a few minutes, and except for the initial few minutes, the efficiency is hardly affected by current density and stirring, and is practically 100% within the error of the measurements.

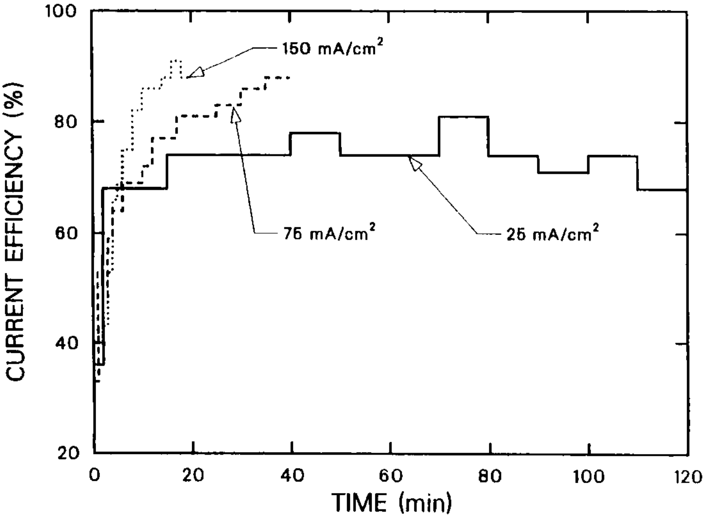

Figure 10. Current efficiency of zinc deposition on steel in 5 M NaOH with 0.2 M ZnO at 90 °C in stagnant solution.

A low initial current efficiency is expected on the steel electrode because of the much smaller hydrogen overpotential on this metal as compared to zinc. This, indeed, was observed. Apparently, as the plating proceeds, the steel base never becomes fully covered with zinc, probably because of the continued hydrogen evolution and the very porous nature of the deposited zinc. This would explain the much smaller current efficiencies on the steel base as compared to the zinc base. The initial increase of the current efficiency is explainable partially by the increased coverage of the electrode by zinc with time, and partially by the decrease of the effective current density as the high surface area zinc is deposited (the stated current densities are based on the original area of the base electrode). The second effect is operative also when plating on a zinc base. Stirring is expected to increase the current efficiency of the zinc deposition because it enhances the supply of zinc ions to the surface.

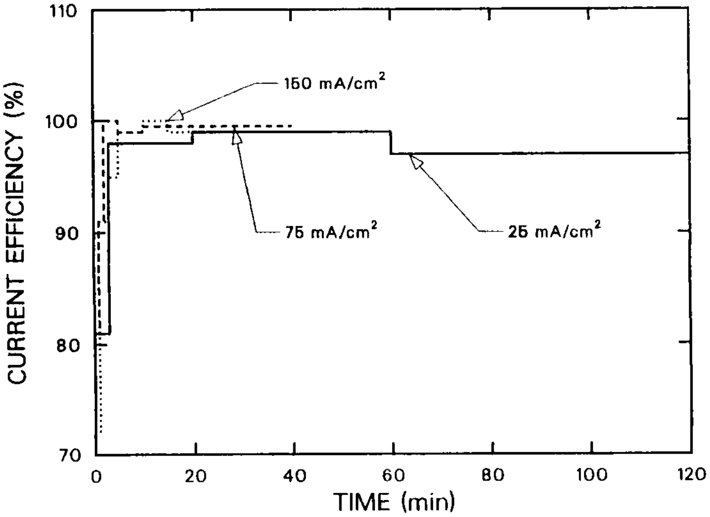

Figure 11. Current efficiency of zinc deposition on zinc in 5 M NaOH with 0.2 M ZnO at 90 °C in stagnant solution.

The increase of the current efficiency with current density is unexpected, although observed by others (8) and in the work reported here under Stripping of Galvanized Steel Coupons. At high current densities, the mass-transport limitations of the zinc become important, while they are practically unchanged for hydrogen evolution; therefore, a decrease of the efficiency with current density would be expected. To explain the observed effects, one could assume that there are two parallel processes taking place: the deposition of zinc and a continuous corrosion of zinc with hydrogen evolution, with the latter process being practically independent of the applied current density. Zinc is thermodynamically unstable in basic solution, and it should dissolve with concurrent hydrogen evolution. In a pure system, this process is slow because of the high hydrogen evolution overpotential of zinc. In the presence of bare steel, a low hydrogen overpotential surface is available, and the corrosion can proceed much faster. This hypothesis was tested in two experiments as follows. The plating current was disconnected after some initial zinc deposition, but the hydrogen evolution rate was continued to be measured. Very strong hydrogen evolution was found from the zinc plated on a steel base, while very little was found for the zinc-based case. Einerhand et al. (23) also concluded that hydrogen is formed chiefly by corrosion of the zinc during electrodeposition of zinc from 8 M KOH electrolyte containing 1 M zincate.

The effect of impurities on the cathodic process was investigated using a zinc base for plating from stirred solutions at a current density of 150 mA/cm^2. The effect of Al^{+3}, Fe^{+3}, Cd^{+2}, and Pb^{+2} ions was tested. Aluminum and lead oxides are soluble in the basic solution; 0.1 M and 0.01 M solutions were used, respectively. Iron and cadmium oxides are practically insoluble; saturated solutions were prepared at room temperature and they were analyzed by atomic absorption spectroscopy, giving 0.4 and 11 ppm solubility, respectively. None of the impurities had any measurable effect on the current efficiency. Merrill and Lang (12) observed a decrease in cathodic current efficiency when iron was above 0.005 g/l. They noticed a pink color in the NaOH solution, but concluded that the iron was not in solution because it was removed by filtering through diatomaceous earth.

The morphology of the deposited zinc was a strong function of deposition conditions with the results shown in Table 1. None of the deposits were smooth. Qualitatively, the deposits can be classified in three classes; (a) rough, grainy type deposits, (b) bulky, sponge-type deposits, and (c) dendritic, needle and flake-like deposits. The compactness of the deposits decreased from (a) to (c). It was observed during the handling of the samples that the deposits were generally not strongly adherent. The results can be summarized as follows. Increasing current density and the absence of stirring will produce less compact deposits. This is understandable, since it is known that dendritic deposits are produced when the deposition is under mass-transport control. The deposits on the steel base seemed to be less compact than their counterparts on the zinc base. This may be due to

Table 1. Zinc Deposition Morphology

Base	Stirring	CD (mA/cm2)	Impurity	Zinc Morphology
steel	no	25	none	spongy
steel	no	75	none	small dendrites
steel	no	150	none	large dendrites
steel	yes	25	none	grainy
steel	yes	25	none	grainy
steel	yes	75	none	grainy
steel	yes	150	none	small dendrites
zinc	no	25	none	spongy
zinc	no	75	none	spongy/dendrites
zinc	no	150	none	dendrites
zinc	yes	25	none	grainy
zinc	yes	75	none	grainy
zinc	yes	150	none	grainy
zinc	yes	150	Al	grainy
zinc	yes	150	Cd	grainy
zinc	yes	150	Pb	heavy sponge
zinc	yes	150	Fe	grainy

the larger hydrogen evolution on the steel electrodes, since the gas evolution within the zinc structure would tend to weaken it. Among the impurities, only the lead seemed to influence the deposition morphology, i.e., it produced a very voluminous, spongy deposit. The chemical purity of the deposits was checked only in the case of the lead addition to the solution. The qualitative check revealed for this case that the deposit was contaminated with lead.

Stripping of Galvanized Steel Coupons

All stripping experiments were conducted using electrogalvanized steel coupons 0.74 mm (0.029 in) thick for anodes and cathodes with a measured zinc coating thickness on each side of 0.019 to 0.023 mm (0.0008 to 0.0009 in). Stripping tests were completed in times ranging between 13 and 700 seconds; the end of each stripping test was marked by an increase in voltage across the cell indicating passivation of the anode due to either excessive current density or exhaustion of the zinc. The following trends were noted: 1. anodic current efficiency decreases and cathodic efficiency increases with ZnO concentration increasing from 0 to 0.4 M ZnO in both 5 and 10 M NaOH at 90 °C, 2. anodic and cathodic current efficiencies increase with increasing current density, but with 0.2 M ZnO added the measured efficiencies were typically 100 plus or minus 20%, 3. anodic stripping effectiveness, constrained by anodic passivation, decreases with ZnO concentration increasing from 0 to 0.4 M ZnO, 4. the total electrode polarization voltage in 5 M NaOH and 0.2 M ZnO increases from 0.03 to 0.23 V with current density increasing from 40 to 150 mA/cm^2 and 5. the cathodic zinc deposits are flaky and friable above and nodular and adherent below a current density band of 80 to 100 mA/cm^2.

Anodic current efficiencies above 100% are attributed to corrosion of the zinc. The increase in cathodic efficiency with increasing current density has been discussed in the laboratory results section. Decreasing anodic stripping effectiveness with increasing ZnO concentration is consistent with a dissolution-precipitation mechanism for anodic stripping in caustic. Using the method of Meisenhelder et al. (9), the total electrode polarization voltage was determined by plotting the cell voltage vs. electrode spacing for each of three different current densities, 40, 80 and 150 mA/cm^2 ; the intercept of the line, V_O, fit to the $V = CD \cdot rho \cdot l + V_O$ relation, is the total electrode polarization voltage and *rho* is the resistivity of the solution; *CD* and *l* are the current density and electrode separation, respectively. The resistivity of the solution was determined to be in the range of 0.85 to 1.4 ohm-cm which is in agreement with published values for the resistivity of caustic (24) at 90 °C. The polarization voltage determined for the stripping cell is also consistent with values tabulated in the work of Meisenhelder et al. (9).

Stripping of Loose Bulk and Baled Galvanized Scrap

Two forms of scrap galvanized steel were treated in the 26 ft^3 cell: 1. loose hot dipped galvanized scrap called clippings which is prompt scrap from automobile body panel manufacturing and 2. baled mixed galvanized scrap with densities of 85 lb/ft^3 (550 lb bale) and 150 lb/ft^3 (300 lb bale). The loose scrap before treatment contained 2.3-3.3% zinc, the 550 lb and the 300 lb bale contained about 3 and 0.4% zinc, respectively. Ninety to one hundred-eighty pound batches of loose scrap were put in the stationary basket with the width adjusted from 8 to 16 inches. The anodic current density was 5.7 A/lb (the surface area of the scrap is unknown). Some scrap pieces were dezinced in 30 minutes but batch completion, as marked by a plateau in the voltage required to maintain constant current, consistently took about 65 minutes. Power consumption increased from 0.67 to 1.06 kWh/lb zinc recovered with basket width increasing from 8 to 16 inches. Analysis on the stripped scrap indicated 0.002-0.035% zinc. At lower anodic current density of 1.2 A/lb, the stripping time was increased to 107 minutes and the power consumption was 0.12 kWh/lb zinc recovered. The 85 lb/ft^3 bale was stripped at anodic current densities of 1.5 to 1.8 A/lb for 4.3 hours with a power consumption of 1.5 kWh/lb. Residual zinc analysis was 0.008-0.034%. The 150 lb/ft^3 bale was stripped at 1 A/lb for 5 hours and the residual zinc was 0.020-0.085%. The anodic current efficiency was 28% and the power consumption was 4.5 kWh/lb of zinc recovered.

PROCESS ECONOMICS

The results of the experimental effort on the single-step process provided a re-evaluation of caustic dezincing process economics using the two-stage cost estimates from the Angeles report for the CMP (3) as a base case. The costs are summarized in Table 2 for both the two-stage and single-step process. Each process has a design capacity of 100,000 tons per year of galvanized scrap feedstock. The zinc content of the scrap is taken as 3.5% by weight.

Whereas the two-stage process was estimated to have a capital cost of $12.3 million, the single-step process capital cost is estimated at $5.0 million. The cost difference is due to faster stripping rate and lower power requirements for the single-step process which reduces the cost of power supplies by two-thirds. The estimated variable operating costs of the single-step process are about $10/net ton less than those of the two-stage process due to the reduction in power consumption and lower labor costs. Chemicals costs are also expected to be lower because no oxidation reagent such as sodium nitrate is required in the single-step process. Administrative costs which are a function of direct labor costs are also lower.

Fixed operating costs are typically estimated as a percentage of the initial capital investment. And the required return on the initial investment is also substantially higher for the two-stage process relative to the single step process.

Both processes should produce an equivalent quality zinc product. At a by-product credit of $0.25 per pound of zinc recovered, the net cost of dezincing one ton of ferrous scrap in the single-step process is estimated at about $21 per ton compared to a cost of $64 in the two-stage process.

Table 2. Cost Comparison of Two-Stage and Single-Step Dezinc Processes

Basis: 100,000 tons per year of scrap input @ 3.5% zinc.

PROCESS	TWO-STAGE	SINGLE-STEP
CAPITAL COST , $ million	12.3	5.0
VARIABLE OPERATING COSTS *		
Chemicals	0.88	0.63
Electricity ($0.06/kWh)	6.53	2.09
Water and Fuel	0.66	0.66
Labor ($20/manhour)	10.89	8.17
Administrative (@ 50% of Labor)	5.45	4.09
SUBTOTAL	24.41	15.64
FIXED OPERATING COSTS		
Maintenance (5% of Investment)	6.37	2.59
Supplies (1% of Investment)	1.27	0.52
Services (1% of Investment)	1.27	0.52
Taxes & Insurance (1% of Investment)	1.27	0.52
SUBTOTAL	10.18	4.15
GROSS PROCESSING COSTS	34.59	19.79
CAPITAL RECOVERY, (30% ROI)	47.16	19.17
GROSS SUBTOTAL	81.75	38.96
ZINC CREDITS (@ $0.25/POUND)	18.13	18.13
NET COST ($/TON OF RECOVERED FERROUS SCRAP)	63.62	20.83

* Costs in 1985 dollars per net ton of recovered ferrous scrap.

CONCLUSIONS

The research conducted on the single-step process indicates that the process is technically and economically feasible. However, the research has only been conducted under bench-scale laboratory and larger batch scale testing conditions. The difficulty in stripping high density and low zinc content baled scrap is evident from the trends in anodic current efficiency and power utilization noted in batch testing with such scrap. The zinc removal effectiveness for all forms of scrap so far tested has been remarkably satisfactory as measured by the standards set for residuals by detinning. The process needs to be optimized for cost effective treatment of high density scrap.

The single-step process is fast, effective, selective for zinc, and the zinc product should be easy to recover in a powder form. The process appears robust in the presence of several anionic and cationic impurities that might be expected to be present. The process is the lowest cost pretreatment option so far developed and is consistent with the industry needs of reducing costs of steel and iron making while conserving capital. Implementation of the process would conserve energy and make use of scrap more attractive, thereby decreasing exports of a valuable national resource.

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