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RECYCLING GALVANIZED STEEL: OPERATING EXPERIENCE AND BENEFITS

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ABSTRACT

In response to the increase in consumption of galvanized steel for automobiles in the last decade and the problems associated with remelting larger quantities of galvanized steel scrap, a process is being developed to separate and recover the steel and zinc from galvanized ferrous scrap. The zinc is dissolved from the scrap in hot caustic using anodic assistance and is recovered electrolytically as dendritic powder. The dezinced ferrous scrap is rinsed and used directly. The process is effective for zinc, lead, and aluminum removal on loose and baled scrap and on all types of galvanized steel. The process has been pilot tested for batch treatment of 900 tonnes of mostly baled scrap. A pilot plant to continuously treat loose scrap, with a design capacity of 48,000 tonnes annually, has been in operation in East Chicago, Indiana since early in 1993. The first 450 t of scrap degalvanized in the pilot plant have residual zinc below 0.01% and sodium dragout below 0.01%. Use of degalvanized steel scrap decreases raw materials, environmental compliance, and opportunity costs to steel- and iron-makers. Availability of clean degalvanized scrap may enable integrated steel producers to recycle furnace dusts to the sinter plant and EAF shops to produce flat products without use of high quality scrap alternatives such as DRI, pig iron, or iron carbide. Recycling the components of galvanized steel scrap saves primary energy, decreases zinc imports, and adds value to the scrap. The quantities of zinc available by the year 2000 from prompt and obsolete automotive scrap will approach 25% of zinc consumed in the major automotive production centers of the world. Zinc recycling from galvanized steel scrap, either before or after scrap melting, will have to be implemented.

INTRODUCTION

Metal Recovery Industries U.S., Inc. (MRIUSI) and Argonne National Laboratory (ANL), in cost-sharing collaboration, have developed an electrolytically assisted process to separate and recover steel and zinc from galvanized steel scrap. This work has been supported by the U.S. Department of Energy.

An assessment of available dezincing technology was begun in 1987 that (1) screened process concepts for separating and recovering zinc and steel from galvanized ferrous scrap, (2) selected electrochemical stripping in hot caustic as the most promising process, (3) evaluated the technical and economic feasibility of the selected process on the basis of fundamental electrochemical studies, (4) experimentally verified the technical and economic feasibility of the process in a phased evaluation from bench-scale controlled experiments through batch tests of actual scrap up to six ton lots, and (5) concluded that the process has technical and economic merit and requires larger-scale evaluation in a continuous mode as the final phase of process development.

Concentrations of zinc, lead, aluminum, and other coating constituents (except nickel) on loose scrap are reduced by a minimum of 98%, with zinc, in particular, reduced to below 0.1%. Removal efficiencies on baled scrap with bulk densities between 960 and 3,900 kg/m^3 range from 70 to 90% with removal effectiveness decreasing with increasing scrap density.

About 900 t of galvanized scrap bales have been treated in batch operation at Metal Recovery Industries, Inc. (MRII) in Hamilton, Ontario. The major portion of this scrap was prepared for an American Iron and Steel Institute (AISI) experimental scrap melting program to evaluate the degalvanizing process on bales for technical, economic, and environmental viability. Koros and Muhlhan have reported[1] on this AISI effort and concluded that degalvanizing of baled scrap by electrolytically aided caustic leaching is an industrially and economically viable process and that the environmental performance of the BOP furnaces , as measured by decreased zinc in the furnace dusts and hood water, is significantly improved.

A pilot plant for continuous treatment of 50 t/shift of loose scrap has been built by MRIUSI in East Chicago, Indiana, with operations started in early 1993. Results of degalvanizing the first 450 t of loose automotive stamping plant scrap, both shredded and flat clips, indicate zinc and sodium at levels below 0.01%. The experimental plan for this plant calls for degalvanizing a total of 4,500 t of various types of prompt industrial galvanized products (Galvalume, electrogalvanized, hot-dipped and nickel-zinc) as well as the ferrous fraction of shredded obsolete automobiles.

Current economic analysis indicates that the cost of processing ferrous scrap in a 100,000 t/a facility would be about $33/t, including credit for the co-product zinc and depending on production volume, form, and zinc content of the scrap.

Application of the degalvanizing process to only half of the nine million tonnes of galvanized ferrous scrap that will be available in the North American market in the year 2000 is estimated to (1) save 50 x 10^6 GJ (50 x 10^{12} Btu) of primary energy per year, (2) reduce raw materials costs to the iron and steel industry by $US 100-200 million/a, (3) create about $US 336 million/a in value-added manufacturing; and (4) eliminate the need for the U.S. to import about 70,000 to 140,000 tonnes of zinc per year at a value of $US 128-256 million/a.

DEZINCING PROCESSES ASSESSMENT

The need for removal of the metal coating on galvanized ferrous scrap to provide "specification-grade" or low coating residual scrap to the steel industry is not new. The need has now become critical because of the increased consumption of galvanized steel in the automobile producing centers of the world, as seen in Figure 1. Thermal and chemical degalvanizing 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.[2] The concept of anodically promoting the dissolution of zinc from galvanized steel scrap and electrowinning in hot caustic is 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.[3]

The degalvanizing process relies on the dissolution of zinc in caustic assisted by reverse electroplating. As shown in Figure 2, loose or baled galvanized scrap is fed to an electrolytic cell where it is made the anode by being placed in contact with the positive side of a high-current/low-voltage direct-current power supply. The cell (tank) is filled with a warm (70-90°C) water solution of 20-32% sodium hydroxide (NaOH), the electrolyte. The tank is fitted with a metal (e.g., steel sheet) cathode. An electrical potential is applied between the cathode and the scrap. Zinc and other common coating constituents are stripped (dissolved) from the scrap steel surface and simultaneously deposited on the metal cathode. The degalvanized scrap is conveyed from the tank and water rinsed to minimize loss of leaching solution that wets the steel. The washed scrap may then be shipped to the steel mill or foundry. Zinc deposited on the cathode is removed and recovered. The pregnant solution from the primary stripping tank is also sent to a purification circuit and to secondary electrolytic recovery cells for zinc recovery. The washed and mostly zinc solids may be sent to a zinc smelter or used directly. The liquids recovered from washing and filtration are sent to make-up tanks for eventual return to the stripping tank. The process consumes no chemicals other than drag-out make-up losses for treatment of most galvanized products and produces only small quantities of wastes. Treatment of galvanized alloy coatings containing aluminum results in consumption of caustic.

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.[4] Anodically promoted detinning in caustic of tinplated scrap has been practiced commercially for many years and is directly analogous to the dezincing process reported on here.[5] A Belgian patent has been granted for use of electrolytic dissolution/electrowinning to recover the components of scrap galvanized steel.[6]

Apart from anodic dissolution processes are studies of recovery of zinc by electrolysis of alkaline or acid solutions derived from leaching of oxidic zinc ores [7,8,9,10] or zinc bearing residuals such as steel making furnace dusts.[11,12,13] These are distinctly 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 practiced economically in North America and Europe for many years.

The preliminary assessment of the technical and economic feasibility of the caustic electrolytic dezincing process was favorable. Experimental work was then directed to addressing uncertainties in extending the concept to commercial operation on scrap. These include determining: 1. maximum expected rate of dissolution, 2. selectiveness 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 various forms of scrap.

EXPERIMENTAL RESULTS

Work was done in four areas: 1. the electrochemical behavior of zinc and steel in hot caustic was explored in the laboratory, 2. small, 25 mm (1 in.) diameter, coupons of galvanized steel were stripped, and the zinc was recovered from caustic in a bench-scale stripping cell and 3. batches of commercial sheet, loose and baled galvanized scrap were dezinced, in two stages of scale-up, using anodic dissolution in hot caustic with recovery of clean scrap and electrodeposited zinc, and 4. a pilot plant for the continuous degalvanizing of ferrous scrap with a design capacity of 48,000 t/a was designed, constructed and has been in operation since early in 1993.

The first stage of scale-up was capable of treating 50 to 150 kg (110 to 330 lb) scrap lots in a 1500 liter (400 gal) tank. In the second stage, loose, sheet, and baled scrap was treated in lots as large as five tonnes culminating with the 580 tonne AISI campaign. A total of approximately 900 tons of galvanized scrap of various forms and coating types were treated in these batch processing studies. This led to construction of a pilot plant for continuous degalvanizing of loose scrap at a design capacity of 50 t/shift. In this paper, data is reported on the first 450 t of pilot plant operation for degalvanizing loose and shredded automotive stamping plant clips.

ELECTROCHEMICAL STUDIES

The purpose of this work was to determine the fundamental electrochemical behavior of zinc and steel in hot caustic solution. The detailed results of the electrochemical studies have been reported previously.[14]

The major results of the electrochemical behavior study are:

1. Zinc is anodically dissolved in hot caustic at maximum current densities about a factor of 1000 greater than for steel. This means that zinc can be selectively removed by anodic promotion from the surface of galvanized steel.
2. The passivation limited current densities for anodic dissolution of zinc in unstirred solution is about 1500 A/m^2. A typical galvanized

coating can then be stripped in a few minutes under ideal conditions. Fluoride (0.025 to 0.075 M), chloride (0.1 and 1.0 M) and sulfate ion (0.15 M) additions had no effect on passivation limited current densities in 90 °C, 5 M NaOH and 0.2 M ZnO.

3. Spontaneous dissolution (without the application of external electrical current) of zinc is thermodynamically possible, but kinetically limited. Dissolution will occur at a measurable rate only if the zinc metal is in electrical contact with another metal that catalyzes the evolution of hydrogen or if a strong oxidizing agent is added as a consumable reagent. Iron, nickel and aluminum will catalyze the dissolution of zinc at practical levels (equivalent to at least 1000 A/m^2) if the exposed area of the catalytic metal is about the same as that of the zinc. With alloyed zinc coatings, the alloying metal can suffice as the catalytic surface. Practical spontaneous dissolution rates in hot caustic are not obtained when the zinc content of the solution is above 0.1 M.
4. Anodic dissolution of zinc in the end of long, 150 mm (6 in.), narrow, 3 mm (0.25 in.) channels proceeds at current densities about a factor of 100 less than for parallel plate, line-of-sight geometry's. This suggests that electrolytic stripping of scrap with tortuous paths to the cathode, e.g. baled scrap, will require much longer processing times.
5. Current efficiencies for zinc deposition from hot caustic range from about 80 to 98%. Cathodic current efficiency increases with increasing current density and is strongly affected by choice of cathode material. None of the impurity ions tested (Al^{+3}, Fe^{+3}, Cd^{+2}, and Pb^{+2}) had any measurable effect on the current efficiency. Merrill and Lang observed a decrease in cathodic efficiency when iron was above 5 ppm but the iron was not in solution.[15]

BENCH SCALE STRIPPING TESTS

Electrolytic stripping of galvanized steel sheet disks was conducted in acid and in caustic solutions. The results of the acid and caustic stripping tests have been reported.[16,14] Caustic solutions were at 90 °C, 5 or 10 M NaOH, and with 0.1 to 0.4 M ZnO added. Stripping tests were run at various constant currents corresponding to a current density range of 400 to 3,800 A/m^2. The exposed stripping area was 520 mm^2 (0.8 in^2) and the electrode separation set at 15, 29 and 59 mm (0.6 1.1 and 2.3 in.) using cylindrical cells of different lengths.

The critical results of the electrolytic stripping tests are:

1. Anodic promotion and chemical dissolution of zinc proceeds at higher rates in room temperature hydrochloric or sulfuric acid than in hot caustic, but those acids are not selective for just the zinc coating.
2. Coupons of electrogalvanized steel with a coating thickness of 0.02 mm (0.0008 in) were typically stripped in 3 to 8 minutes in hot caustic.
3. After stripping, the residual zinc on the steel was typically 0.05 wt%.
4. Anodic current efficiencies were over 100% because of chemical dissolution. Cathodic current densities ranged between 80 and 100%, increasing with current density, for deposition on zinc cathodes.

SCRAP DEZINCING TRIALS

Batch trials, 100 kg facility

Electrolytic stripping test capacity was first scaled-up to a 1500 liter (400 gallon) tank fitted with sheet steel cathodes; a typical batch size of 50 kg of loose or 150 kg of baled scrap could be dezinced. An anode basket for loose or bulk scrap was provided with adjustable side HDPE grid panels to provide 230 to 400 mm (9 to 16 inch) thicknesses of loose scrap. Bales of scrap were placed between the cathodes and were self-contained.

Loose scrap with apparent bulk density of 400 to 800 kg/m^3 (25 to 50 lb/ft^3) with a zinc coating weight of 2.3 -3.3% was stripped in 30 to 65 minutes to 0.002-0.04% residual zinc; power consumption was 1.5 to 2.4 kWh/kg zinc recovered. Bales averaging 1400 kg/m^3 (85 lb/ft^3) and zinc coating weight of 3.0% were stripped in 4.3 hours to 0.008-0.034% residual zinc; power consumption was 3.3 kWh/kg of zinc recovered. Bales averaging 2400 kg/m^3 (150 lb/ft^3) and zinc coating weight of 0.4% were stripped in 5 hours to 0.02-0.09% residual zinc; the anodic current efficiency was 28% and the power consumption was 10 kWh/kg of zinc recovered. Solution composition for the tests reported here were 5 M NaOH with 0.2 M ZnO added and the electrolyte was maintained at 70-80 °C.

Batch trials, 10 tonne facility

The second stage scale-up in dezincing capacity comprised two 20,120 liter (5,300 gal) primary treatment tanks, each able to accommodate five tonnes of bales. This was in line with a counter-current five-stage washing system for dezinced scrap; the pregnant dezinc solution was sent to an electrowinning cell for zinc recovery. This system was used to dezinc a total of approximately 900 tonnes of galvanized scrap of various types and forms. The 580 t AISI trial to examine the technical and economic feasibility of dezincing and deleading of industry standard bales was conducted in this facility. A summary of some of the experimental campaigns on loose, sheet and baled scrap follow, including the experimental AISI program.

Approximately 20 t of loose scrap, in 12 runs, were processed for galvanized coating removal. The scrap was loaded into steel baskets measuring 100x860x640 mm (39x34x25 in). The average bulk density was 1500 kg/m^3 (94 lb/ft^3), initial zinc weight was uniformly 2.16%, and the average residual zinc was 0.008%, independent of stripping time between 1 and 26 hours . A four hour test run on one ton of this loose scrap was made without anodic promotion with no significant difference in coating removal effectiveness.

Approximately 13 t of dealer bundles prepared from heavy galvanized construction sheet scrap were processed for coating removal. The bale dimensions were nominally 100x660x660 mm (44x26x26 in) with an average bulk density of 1700 kg/m^3 (107 lb/ft^3) and a zinc weight of 1.53%. Electrolytic treatment for 17 to 26 hours resulted in an average 78% and range of 68-83% zinc removal effectiveness; without anodic promotion and a residence time of 71 hours, the zinc removal effectiveness was 36%.

Approximately 300 kg of scrap Galvalume sheets with an average thickness of 0.94 mm (0.037 in.) and a coating of 1.4% zinc and 0.7% aluminum were processed for coating removal by electrolytic stripping. The stripped scrap analyzed 0.003% zinc and aluminum was not detectable.[17]

A total of 28 t of baled automotive stamping plant scrap nominally 330x360x400 mm (13 x 14 x 16 inches), weighing 120 to 170 kg with a density of between 1,900 and 3,000 kg/m^3 were processed for removal by electrolytic stripping of the predominantly galvannealed coating. The sheet thickness was mostly 0.71 mm (0.028 inch) and the zinc coating ranged from 0.2 to 1.1%, averaging 0.6% by weight. The stripped scrap contained residuals of zinc, 0.10%; water, 0.3%; aluminum, 0.006%; sodium, 0.004%; and lead, 0.003%; this was 84% zinc removal effectiveness based on the 0.6% average incoming zinc content.

580 tonnes of baled, galvanized steel produced from sheet steel and coil ends generated directly from steel mills were processed for dezincing. The source and form of this scrap were as provided in a multiple company cost-shared research program coordinated by the AISI Task Force on Recycling of Galvanized Steel Scrap. The dezinced scrap was used in a melting trial conducted at LTV Steel, Indiana Harbor Works, to determine the effect on environmental performance of BOF operations.[18]

Three dezincing campaigns were conducted for the AISI program and are summarized in Table 1: 1. 170 t of bales with no added lead content were treated for 24 hours, 2. 280 t of bales with no added lead content were treated for 36 hours, and 3. 130 t of bales with lead added as Terneplate were treated for 24 hours. On average, the bales were 610x610x790 mm (24x24x31 in), weighing 730 kg with an apparent bulk density of 2,500 kg/m^3. Using the degalvanizing performance data generated from the solution mass balances, the zinc removal for the regular and leaded bales processed for 24 hours were quite similar, at 1.53% and 1.49% respectively. For the regular bales treated for 36 hours, the zinc removal was marginally higher at 1.61%. Based on the average zinc content of the incoming scrap of 2.0%, the dezincing performance is 76% for the 24 hour bales and 81% for the 36 hour bales. The additional zinc removal observed for the 36 hour treatment is not likely to be economically justified.

Approximately 6 t of impure zinc metal powder was produced from the 580 tons of galvanized scrap treated for the AISI. Purification tests were performed in the laboratory, and to a limited extent, in the pilot plant. Iron, lead, copper and nickel in caustic solution can be readily controlled by cementation with zinc dust; tin and antimony were not significantly affected by cementation. Evaluation of the different grades of zinc powder produced will be required by the potential users to determine suitability. The high surface area and high reactivity of the zinc powder makes it desirable for chemical production, fertilizers, animal micro-nutrients, or as a zinc supply for inert anode zinc electroplating systems, but may result in excessive loss to oxide if used for melting.

The zinc metal collected from the electrowinning system was a dendritic, non-adherent powder with a surface area typically over 3 m^2/g. The purity varied from 77 to 95% by weight, on an "as produced" basis, with the degree of oxidation the largest variable. Washing and drying of freshly produced electrodeposited zinc under non-oxidizing atmosphere produced zinc powder with an analysis of 97% zinc and 1.8% oxygen.

Sludge was generated from the dezincing and washing systems at a combined rate of 1.1 kg (dry weight) per tonne of mill scrap. This material contains iron, zinc, lead and other heavy metals which would require that it be classified as and disposed of as a hazardous waste. From dezincing solution analysis, aluminum was present in the baled scrap at a level of 0.25%. Laboratory tests indicate that the solution may be treated with calcium hydroxide to precipitate the aluminum. Aluminum sludge would be generated at a rate of 11 kg/t of scrap; it is not hazardous and might be used to aluminize cement. No quantities of oil or grease were collected from the dezincing system during the AISI trials.

The bales of galvanized steel prepared for this trial should be considered as some of the most difficult to degalvanize. This is due to the fact that they were made exclusively with sheet steel and coil ends; some bales were wrapped with sheet. There were no "through holes" present to allow solution to pass to the center of the bale, as would be the case if stamping plant scrap had been used. Also, steel generated from a stamping plant or shredder would be bent and produce wrinkles in the scrap when baled, allowing solution to travel more freely within the bale. For the bales prepared for this trial, the smooth sheets tended to laminate when baled, which restricted movement in the bale. Most of the steel surfaces were wetted due to capillary action of the dezincing solution; however, diffusion of solute and movement of the wash water between these sheets is limited.

Continuous pilot plant, 50 t/shift

The purpose of the pilot plant effort is to demonstrate the technical viability and to refine the economics of a continuous degalvanizing process on a credible scale and to provide ample market development samples of degalvanized scrap and recovered zinc for evaluation by potential customers. Various types of galvanized prompt scrap will be degalvanized to determine the effect they have on the process. The ferrous fraction of shredded obsolete auto scrap will also be treated as it is the largest source of ferrous scrap in the U.S. A pictorial flow chart of the pilot plant is given in Figure 3.

Table 2 provides a summary of the pilot plant performance on selected types of electrogalvanized and hot dipped prompt scrap from automotive and industrial sources that were degalvanized soon after the plant was started. Retention times were about two hours and at 80 °C.; zinc removal effectiveness is uniformly in excess of 99.99%.

Table 3 provides a summary of process performance on the first 450 t of prompt automotive scrap. Similar quantities of shredded (960 kg/m^3) and flat clips (640 kg/m^3) were processed with the shredded (balled) material processed first. Retention times at 70-85 °C were about two hours for almost the entire campaign for the shredded material and were less than one hour for the flat clips. The zinc and sodium analysis range on the degalvanized scrap is for several analyses done on grab samples by MRII in Hamilton, Ontario. Zinc removal is no less than 97%. The higher sodium levels were measured before improvements were made to the washing system conveyors.

PROCESS ECONOMICS

The cost of electrolytic hot caustic processing of galvanized steel scrap for dezincing is estimated to be about $US 33/t, including credit for the co-product zinc and depending on production volume, form, zinc content of the scrap, and desired rate of return on investment. In Table 4, costs are estimated for a "greenfield" site with a design capacity of 100,000 t/a of loose ferrous scrap with 50% of the incoming material coated. Treatment time is taken at four hours. The average zinc weight is taken at 1.5% or a total of 1,500 t/a. Plant operation is based on two operations, degalvanizing and zinc recovery. Operations are assumed to run 19 shifts/week or 7,600 h/a.

The processing time, rectification requirements and power consumption for the removal of zinc from galvanized steel are variables which are greatly dependent on the physical form of the scrap and, to a lesser extent, on the type of galvanized steel to be processed. The type of galvanized steel affects the rate and completeness of coating removal and the associated processing time, anodic current efficiencies, rectification and power costs. Alloy coatings of zinc such as galvanneal, galvalume and zinc/iron all react relatively faster in the hot caustic process because of spontaneous chemical dissolution of zinc. Relatively pure hot dipped or electrogalvanized zinc coatings react slower to hot caustic unless an oxidizing agent or anodic promotion is provided. Zinc-nickel coatings tend to be the most resistant to the hot caustic process as the nickel is essentially inert and hinders access of the caustic solution to the zinc.

The physical form of the scrap is the most significant variable to the dezincing process. Estimates based on batch processing indicate that pieces of uncoated, loose scrap can be processed continuously in less than one hour, with high zinc removal efficiencies. Dezincing of baled scrap encounters the problems of solution contact with the zinc, solution removal and washing of the bale (even more difficult than solution contact), the lack of any distinct current density in the center of the bale, the inability to physically dislodge protective coatings from the internal scrap surfaces, and the collection of gas bubbles within the bale which subsequently displaces dezincing solution reducing process efficiency. If there is a need to dezinc baled scrap, it can be accomplished to a varying degree at increased costs. The main variables to performance and cost of dezincing bales are the size of the bale, the tightness of the bale, the physical nature and size of the scrap used in the bales, (i.e. full sheets, coils ends and stamping plant refuse) which directly affect the porosity of the bale, and the presence of protective coatings. Protective coatings may be dissolved over time in the hot alkaline solution, while other coatings may act as gasketing material. The dezincing process time for bales can range from 6 to 24 hours, depending on the variables identified above. Even though most baled scrap will have a greater bulk density than loose scrap, the longer process residence time means that a larger dezincing facility would be required for baled as compared to loose scrap.

BENEFITS OF DEGALVANIZING FERROUS SCRAP

The constituents of galvanized coatings in the scrap charge impose environmental compliance, yield, nuisance, and opportunity cost penalties on iron- and steel-making. Zinc-coated scrap increases the volume and cost of baghouse dust disposal. Cost penalties in excess of $US 50/t of galvanized scrap consumed have been estimated by some integrated BOF shops for disposal of dusts that do not pass the TCLP test for lead. For operations with wet gas scrubbers, zinc concentrations in waste water are exceeding the limit for discharge. Waste water treatment for zinc removal is estimated by the AISI to increase costs by $US 1-3/t liquid steel. Use of degalvanized steel scrap in BOF operations offers the strong potential for avoiding disposal of dry dusts as hazardous waste, avoiding treatment to decrease zinc concentration of waste water and enabling recycling of ferrous dusts to the sinter plant. In EAF operations, loss of control of the arc and zinc fuming on charging, tapping and casting is troublesome. In BOF and EAF operations anecdotal evidence indicates that zinc may contribute to high porosity in billets and to breakthroughs in continuous casting operations. In foundries, galvanized scrap also causes operating problems, such as: 1. zinc fuming when charging and pouring, 2. furnace shaft size reductions due to zinc oxide accretions, 3. recuperator inefficiencies due to oxide coatings on the checkerwork and 4. increased porosity in castings. Use of a specification grade scrap may enable the founder to use some quantities of lower cost scrap feeds such as post consumer tin-coated steel cans.

The savings in raw materials costs to the iron and steel industry in using high-quality recovered scrap depends on the marginal costs of alternative iron sources to each segment of the industry. Dudek et al [19] have calculated the total savings potential for the U.S. foundry, integrated and mini-mill industries at $US 142 million.

For each tonne of pig iron or DRI that is replaced by a tonne of clean black scrap, about 12 GJ (12 million Btu) are conserved. This is about 70% of the primary energy that would otherwise be required to produce one tonne of hot metal from primary ore or via DRI. In the long term, the scrap market will be burdened by about 9 million t/a of galvanized scrap, depending on the recovery rate of obsolete scrap. If this scrap is cost-effectively stripped of the zinc coating, the underlying steel is equivalent to the highest-quality scrap available in today's market. In the absence of a process for removing the zinc, scrap exports will increase, and domestic production of steel will require more pig-iron or DRI to replace the lost scrap. Because the primary problems associated with the use of low-quality scrap are derived from environmental regulations that affect the costs of disposing of the residuals resulting from low-quality scrap, it is more likely that the scrap will be exported to countries that do not have environmentally imposed costs. The long-term net effect could be a loss in domestic steel production. If half the 9 million t/a of galvanized scrap were treated and provided as a substitute for pig-iron, about 50 million GJ per year would be conserved. However, if the 4.5 million tonnes of scrap were exported (at a price of about $100/t) and finished steel products were imported (at a price of about $500/t) to make up for a decrease in domestic production, the impact on the U.S. federal trade deficit would amount to $US 1.8 billion/a -- an increase of 3% of the 1991 U.S. federal trade deficit.

CONCLUSIONS

A number of alternative technologies for responding to the increase in coated scrap by removing the coating before remelting have been considered in the recent past. These include: high-temperature preheating, heat treatment and shot-peening, heating and vacuum volatilization, and chemical leaching. Also, substitution of ferrous scrap by direct reduced iron or other alternative iron sources is being adopted by some steelmakers. None of these alternatives appear as cost-effective as degalvanizing with an anodically promoted process in hot caustic. The process can treat effectively all common forms of loose and baled galvanized scrap and is the most advanced option for dealing with the increase in galvanized ferrous scrap. The low carbon steels normally specified for automotive body use and which are under the galvanized coatings have specified limits on carbon, manganese, phosphorus and sulfur. These steels, without the galvanized coating, are an ideal scrap feed to iron and steel furnaces. This scrap provides the necessary quality and also cost savings, in most cases, over the use of pig iron and may enable the use of other lower cost scrap by dilution. Environmental compliance costs may be reduced if the lead content of furnace dusts and the zinc content of waste waters can be sufficiently controlled through use of low-residual scrap.

Large quantities of loose prompt and baled dealer bundles and mill scrap have been degalvanized successfully in batch operations using the primary steps of the electrolytic caustic process. The process is now being demonstrated in a pilot plant in East Chicago, Indiana. This plant treats 5-10 t/h in continuous operation; at this writing approximately 500 t of prompt automotive scrap have been successfully degalvanized. The process will also be demonstrated on galvanized obsolete scrap, which will constitute 40-50% of the total U.S. supply of galvanized scrap in the next decade and beyond. The process has technical and economic merit. Completion of the development effort and first commercial practice of the process is anticipated before the end of 1993.

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REFERENCES

1. Koros, P. J. and R. P. Muhlhan, "Zinc and Steel Scrap - Continued Recyclability and Zinc Recovery," Proceedings of the Second International Zinc Conference, AZA, Section 7, 1-15, Scottsdale, Arizona, Feb. 21-24, 1993.

2. Angeles, O. F. Jr. and E. F. Petras, "Dezincing of Galvanized Sheet Steel Scrap, A Scoping Study," Center for Metal Production Report 86-1F, October 1986.

3. Dudek, F. J., E. J. Daniels and W.A. Morgan, "Benefits of Recycling Galvanized Steel Scrap for Recovery of High-Quality Steel and Zinc Metal," Proc. of the Conf. "Minerals, Metals and the Environment," The Institution of Mining and Metallurgy, Manchester, England, Feb. 4-6, 1992.

4. Geltsharp, F., "Note on the Electrolytic Recovery of Tin," Trans. Faraday Society, 1, 111-117(1905).

5. Westerdijk, E.P., "New detinning plant for tinplate scrap of the Netherlands Detinning Plant (Hoogovens Group)," Leewarden, Iron and Steelmaking, 14(3),139-141(1987).

6. Centre D'Etude Et De Documentation De L"Environnement (C.E.B.E.D.E.A.U.), Belgian Patent 892,897, "Process and Apparatus for the Recovery of the Components of Galvanized Steel," Oct. 19, 1982.

7. Baroch, C.T., R.V. Hilliard, and R.S. Lang, "The Caustic Electrolytic-Zinc Process," J. Electrochem. Soc., 100(4),165-172 (1953).

8. Meisenhelder, J.H., A.P. Brown, R.O. Loutfy and N.P. Yao, "An Evaluation of the Alkaline Electrolysis of Zinc," Argonne National Laboratory Report ANL/OEMP-81-2 (1981).

9. Kappes, D.W., "Zinc Recovery by Caustic Leaching," Presented to the AIME Annual Meeting, Phoenix, Jan. 28, 1988.

10. Meek, R. L., "An Alkaline Process for Electrolytic Zinc," Proc. of the Extractive Metallurgy Div. Symp., Cleveland, OH, Dec. 2-3, 1968, T.A. Henrie, D.H. Baker, Jr., Eds., AIME, New York, NY, 306-319 (1969).

11. Pooley, F.D., J.M. Mallowan, B.I. Wheatley and W.R. Gurr, British Patent 1,600,287, "Heavy Metal Recovery from Flue Dusts," Oct. 14, 1981, Assigned to University College Cardiff .

12. University College Cardiff, British Patent 1,568,362, "Heavy Metal Recovery in Ferrous Metal Production Processes," May 29, 1980.

13. Duyvesteyn, W.P.C. and R.F. Hogsett, U.S. Patent 4,610,722, "Process for Metal Recovery from Steel Plant Dust," Sept. 9, 1986, Assigned to AMAX, Inc..

14. Dudek, F. J., E. J. Daniels, Z. Nagy, S. Zaromb and R. M. Yonko, "Electrolytic Separation and Recovery in Caustic of Steel and Zinc from Galvanized Steel Scrap," Separation Science and Technology, 25(13-15)2109-2131 (1990).

15. Merrill, C.C. and R.S. Lang, "Experimental Caustic Leaching of Oxidized Zinc Ores and Minerals and the Recovery of Zinc from Leach Solutions," Bureau of Mines Report 6576(1964).

16. Zaromb, S., A.V. Fraioli, E.J. Daniels, G.V. Queen, and R.M. Bozen, "$ZnCl_2$-HCl Plating Baths for Stripping and Recovery of Zinc from Galvanized Iron Scrap," presented at the 173rd Meeting of the Electrochemical Society, Chicago, Ill., Oct. 1988.

17. Metal Recovery Industries, Inc., "Dezincing of Scrap Galvalume Steel Sheets," Internal Report, Feb. 25, 1991.

18. Koros, P. J., "Recycling of Galvanized Steel Scrap - Issues and Solutions," 75th Steelmaking Conference Proceedings, ISS-AIME, 75, 679-685, Toronto, Ontario, Apr. 5-8, 1992.

19. Dudek, F. J., E. J. Daniels, W. A. Morgan, A W. Kellner and J. Harrison, "A Recycling Process for Dezincing Steel Scrap," 75th Steelmaking Conference Proceedings, ISS-AIME, 75, 743-748, Toronto, Ontario, Apr. 5-8, 1992.

LIST OF TABLES

FIGURES

Table 1: Summary of 580 tonne AISI program for batch degalvanizing of baled mill scrap

Quantity (tonnes)	Treatment time (hour)	Zinc removal* (%)
170	24	76.5
280	36	80.5
130	24	74.5

* Solution mass balance

Table 2: Zinc coating weights on untreated and after continuous degalvanizing treatment on various types of scrap

Sample type	Zinc coating weight (%) Untreated	Degalvanized
Automotive source A Electrogalvanized, clips	2.12	0.001
Automotive source B Electrogalvanized, balled	1.05	0.001
Automotive Source B Hot dipped, balled	2.23	0.002
Automotive Source C Electrogalvanized, balled	1.17	0.004
Industrial Construction Hot dipped, clips	2.25	0.004

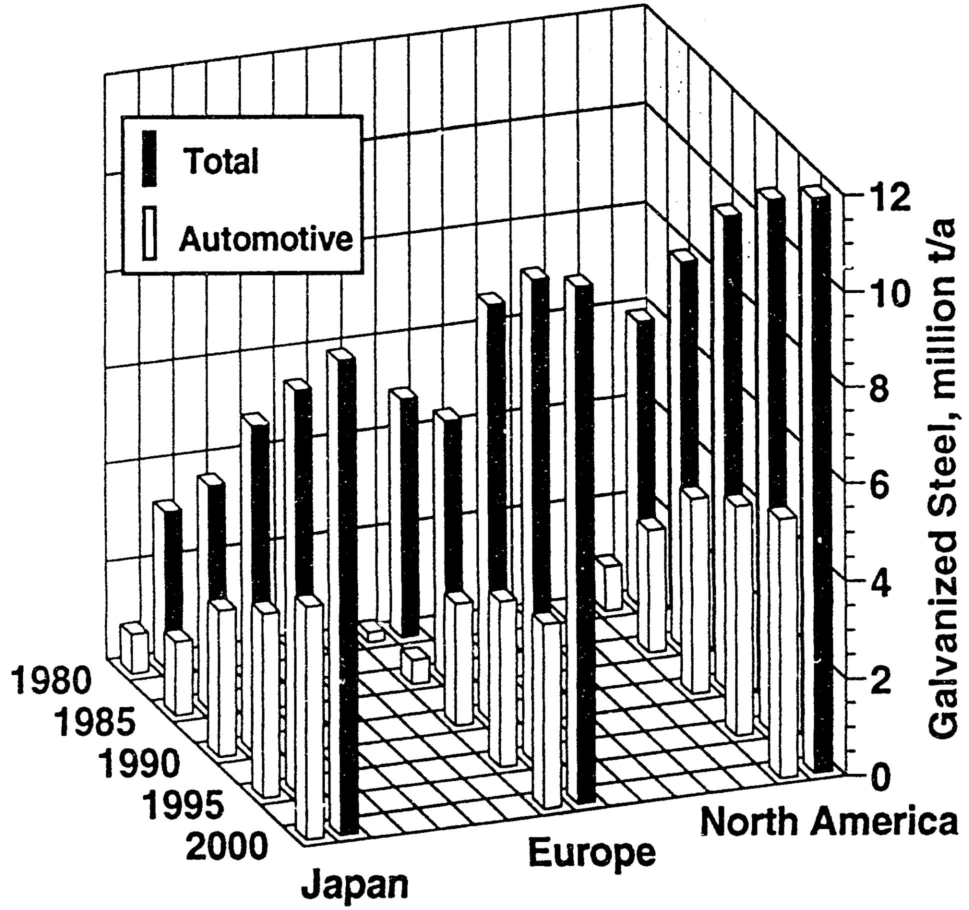
Table 3: Summary of scrap analysis on first 450 tonnes of continuous degalvanizing pilot plant operation

Sample type	Quantity (tonnes)	Degalvanized Zn (%)	Degalvanized Na (%)
Automotive source A Mixed galvanized, balled	200	0.001-0.02	0.001-0.05
Automotive source A Mixed galvanized, clips	250	0.01-0.07	0.001-0.002

Table 4: Degalvanizing costs estimate, 100,000 t/a plant, loose scrap in hot caustic.

PLANT CAPITAL COST	
Site	$US 500,000.
Buildings	760,000.
Yard equipment	560,000.
Process equipment	2,270,000.
Total plant cost	$US 4,090,000.
OPERATING COSTS	Cost ($US /t)
Variable dezinc costs	
Labor	7.14
Energy	1.60
Maintenance	0.50
Raw materials & supplies	1.47
Waste disposal	0.20
Royalties	4.00
Total variable dezinc costs	14.91
Variable zinc recovery costs	
Labor	1.37
Energy, 4.4 kWh/kg, $0.06/kWh	3.96
Packaging, 1,500 t	0.30
Other	0.22
Total variable zinc recovery	5.85
Total Variable	20.76
Fixed costs	
Administrative labor	2.10
Depreciation	3.59
Insurance, taxes & interest	2.61
General office	0.50
Total fixed costs	8.80
Total Degalvanizing Process Costs	29.57
Credit, zinc recovery, 15 kg @ 0.66/kg	(9.90)
Net Degalvanizing Process Costs	19.67
Return on investment, 33%	13.50
TOTAL COST FOR DEGALVANIZING LOOSE SCRAP	33.16

FIGURE 1



Data: AISI and Cockerill Sambre

FIGURE 2

[redacted]

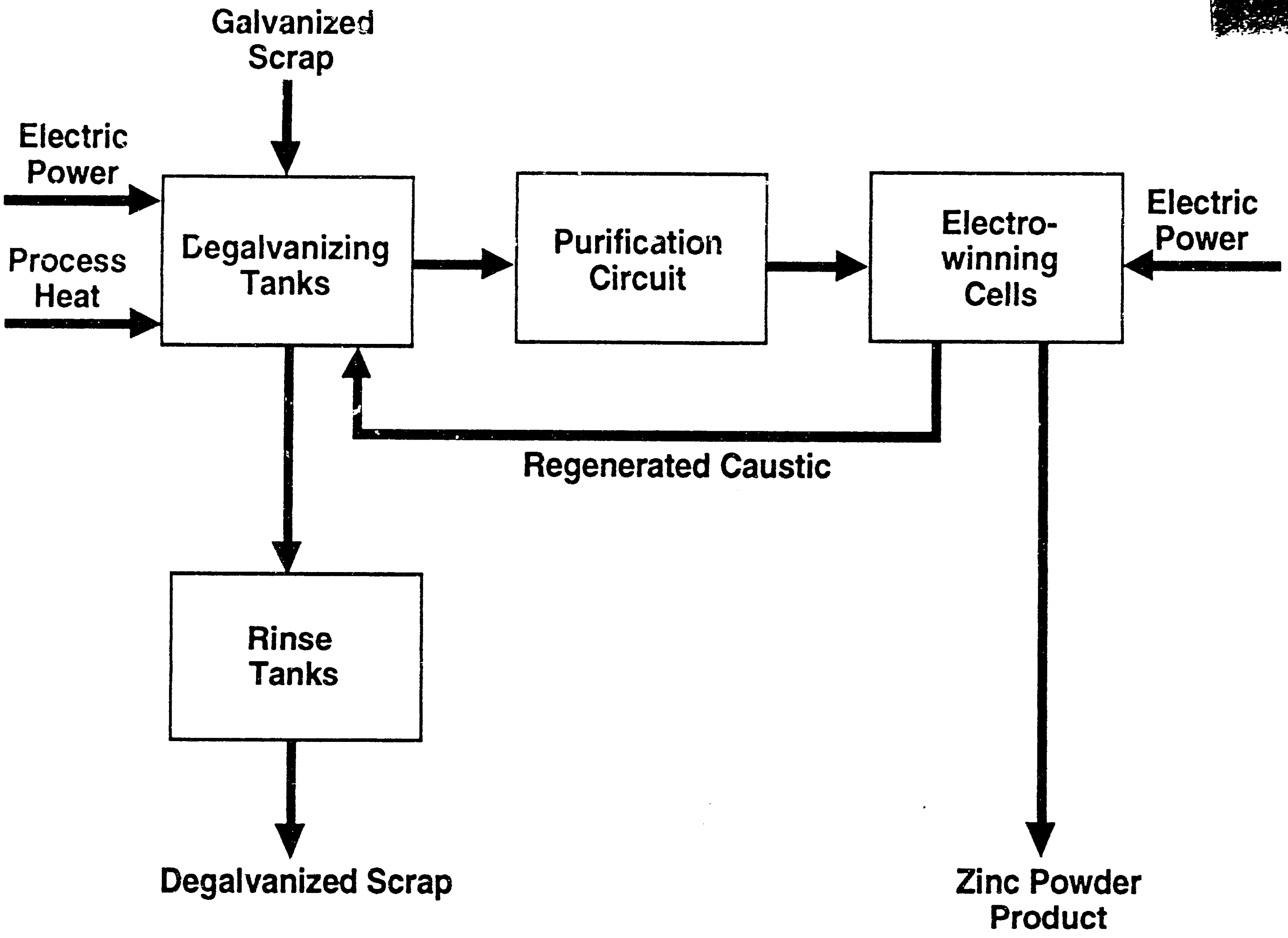
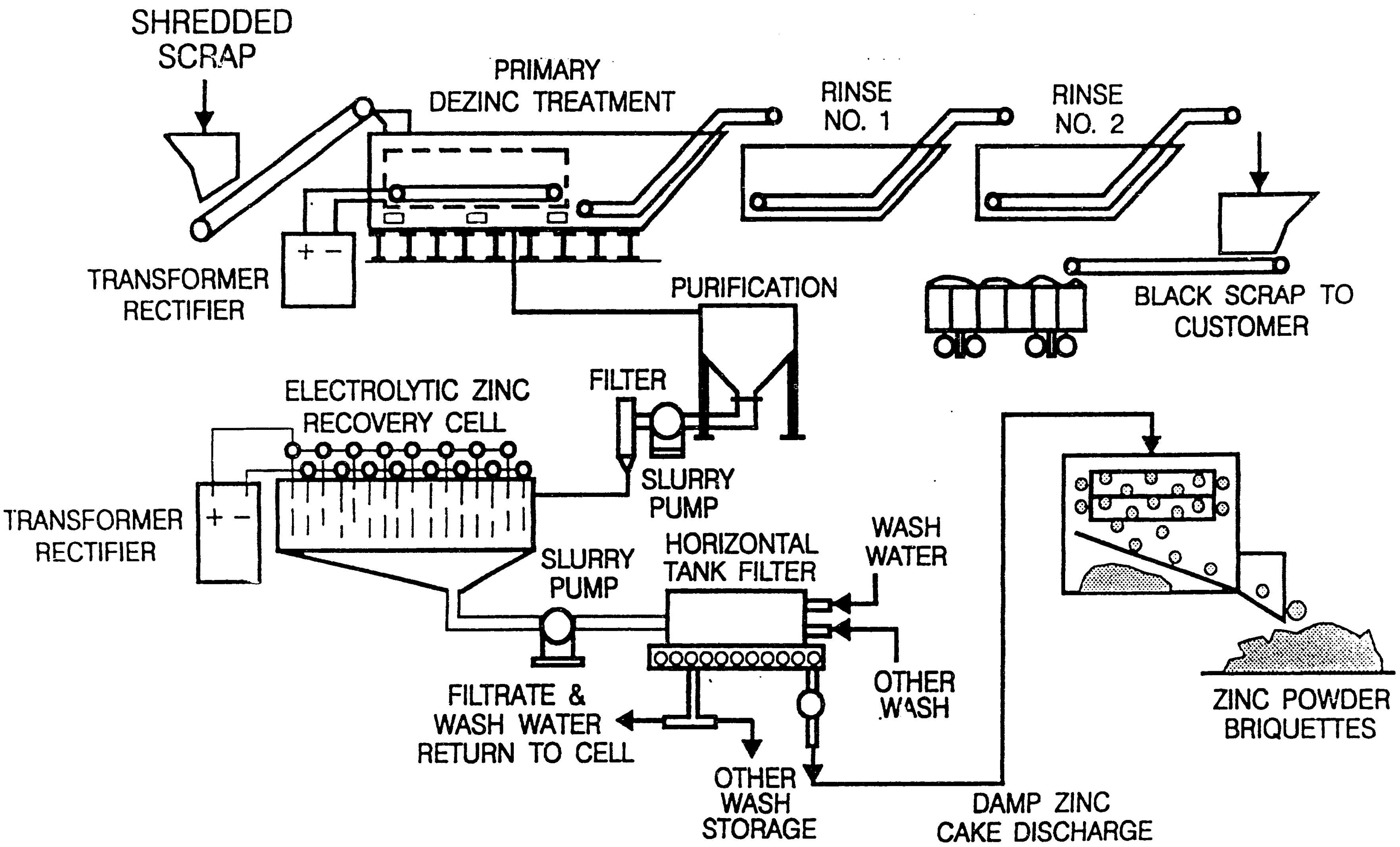


FIGURE 3


SHREDDED SCRAP
PRIMARY DEZINC TREATMENT
RINSE NO. 1
RINSE NO. 2
TRANSFORMER RECTIFIER
+ −
PURIFICATION
BLACK SCRAP TO CUSTOMER
ELECTROLYTIC ZINC RECOVERY CELL
FILTER
SLURRY PUMP
TRANSFORMER RECTIFIER
+ −
SLURRY PUMP
HORIZONTAL TANK FILTER
WASH WATER
OTHER WASH
FILTRATE & WASH WATER RETURN TO CELL
OTHER WASH STORAGE
DAMP ZINC CAKE DISCHARGE
ZINC POWDER BRIQUETTES

END

DATE
FILMED

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