

ANC/ES/SCP-82597

Conf-9505131--1

## RECYCLING ZINC BY DEZINCING STEEL SCRAP

Frederick J. Dudek  
Edward J. Daniels

Argonne National Laboratory  
9700 S. Cass Avenue  
Argonne, Illinois 60439, USA

William A. Morgan

Metal Recovery Industries U.S., Inc.  
415 E. 151st Street  
East Chicago, Indiana 46312, USA

### ABSTRACT

In response to the worldwide increase in consumption of galvanized steel for automobiles in the last fifteen years, and the increased cost of environmental compliance 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 in Hamilton, Ontario for batch treatment of 900 tonnes of mostly baled scrap. A pilot plant in East Chicago, Indiana has dezinced in a continuous process mode 900 tonnes of loose stamping plant scrap; this scrap typically has residual zinc below 0.1% and sodium dragout below 0.001%. This paper reviews pilot plant performance and the economics of recycling galvanized steel and recovering zinc using a caustic process.

The submitted manuscript has been authored by a contractor of the U. S. Government under contract No. W-31-109-ENG-38. Accordingly, the U. S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U. S. Government purposes.

---

KEYWORDS: caustic, dezincing, economics, electrowinning, recycling, zinc, electrolytic process, galvanized steel, pilot plant, steel scrap.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

GT

MASTER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

## **DISCLAIMER**

**Portions of this document may be illegible  
in electronic image products. Images are  
produced from the best available original  
document.**

## INTRODUCTION

Consumption of galvanized sheet steel for automobiles has increased four-fold in the last 15 years (Figure 1) with a commensurate increase in galvanized content in prompt scrap bundles. This change is being echoed in shredded scrap from obsolete autos. By the year 2000 the zinc contained in prompt and obsolete automotive scrap will approach 25% of the zinc consumed in the automotive producing centers of the world. Zinc recycling from galvanized steel scrap will be required, either before or after scrap melting. Black scrap will be difficult to find and lead to increased demand for scrap alternatives such as DRI, HBI and iron carbide. Steel- and iron-makers are sensitive to zinc, lead and other coating constituents of sheet steel scrap increasing the cost of environmental compliance [1,2,3].

Metal Recovery Industries U.S., Inc. (MRIUSI) and Argonne National Laboratory (ANL) are developing an electrolytically assisted process to separate and recover steel and zinc from galvanized steel scrap. An assessment of available dezincing technology was begun in 1987 and electrochemical stripping in hot caustic was selected as the most promising process. The technical and economic feasibility of the process was evaluated based on fundamental electrochemical studies and experimentally verified in a phased evaluation from bench-scale experiments through pilot plant operations that produced a total of almost 2000 tonnes of degalvanized scrap.

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 BOF furnaces, as measured by decreased zinc in the furnace dusts and hood water, is significantly improved.

A pilot plant designed 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 900 t of loose automotive stamping plant scrap, both shredded and flat clips, indicate zinc levels typically below 0.1% and sodium below 0.001%. The experimental plan for this plant calls for degalvanizing a total of 4500 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 \$30/t, with a 33% ROI, 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  $50 \times 10^6$  GJ ( $50 \times 10^{12}$  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 260 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 77-154 million/a.

## EXPERIMENTAL PLANT OPERATIONS

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 (250 - 440 g/L 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.

Development of the electrochemical dezincing process has been carried in phases from bench-scale studies in the laboratory to semi-works operation. Studies of the fundamental electrochemical behavior of zinc and steel in hot sodium hydroxide helped define the operating conditions of the process [4]. Two pilot plants were built for caustic dezincing process development. The first was located in Hamilton, Ontario, Canada and dezinced batches of commercial sheet, loose, and baled galvanized scrap. Lots as large as ten tonnes were dezinced in Hamilton culminating with accumulation of 580 tonnes of baled scrap for the AISI BOF melt campaign. A total of approximately 900 tonnes of galvanized scrap of various forms and coating types were treated in these batch processing studies [5]. This led to construction of a pilot plant in East Chicago, Indiana, USA, for continuous degalvanizing of loose scrap at a design capacity of 50 t/shift. This plant operated for dezincing a total of 900 tonnes of loose and shredded stamping plant scrap.

### Scrap Dezincing Trials

Batch Trials, Ten tonne Plant. The dezincing capacity of the Hamilton pilot plant comprised two 20,120 liter 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 dezincing trial to examine the technical and economic feasibility of dezincing and deleading of industry standard bales was conducted in this facility. The details of the degalvanizing campaigns at the Hamilton plant on loose, sheet and baled scrap, including the material for the AISI program, have been published previously [6] and are summarized in Table 1.

The source and form of the scrap for the AISI trial 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 BOF melting trial conducted at LTV Steel, Indiana Harbor Works, to determine the effect on environmental performance of BOF operations. The use of dezinced scrap in this melt test significantly decreased zinc in furnace dusts and zinc in waste waters [1].

Approximately 6 t of impure zinc metal powder was produced from the 580 tonnes of galvanized scrap treated for the AISI. The zinc metal collected from the electrowinning system was a dendritic, non-adherent powder with a surface area typically over  $3 \text{ m}^2/\text{g}$ . 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.

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.

Continuous Pilot Plant, 50 t/shift. The purpose of the East Chicago, Indiana 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. A pictorial flow chart of the pilot plant is given in Figure 3.

A total of 900 t of prompt automotive scrap was processed for zinc removal. 200 t of shredded ( $960 \text{ kg/m}^3$ ) and 700 t of flat clips ( $640 \text{ kg/m}^3$ ) were treated. Retention times at  $70-85^\circ\text{C}$  were about two hours for almost the entire campaign. The process performs marginally better on shredded scrap. Figure 4 shows zinc removal effectiveness and sodium analysis for several types of galvanized material found in stamping plant clips.

## PROCESS ECONOMICS

The cost of electrolytic hot caustic processing of galvanized steel scrap for dezincing is estimated to be about \$US 30/t for a 30% ROI, including credit for the co-product zinc and depending on production volume, form, and zinc content of the scrap. In Table 2, 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. Figure 5 shows the sensitivity of plant capacity on the cost of dezincing with a 33% ROI.

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.

Experience with batch and continuous processing indicate that pieces of uncoated, loose scrap can be processed continuously in less than one hour, with high zinc removal efficiencies. The dezincing process time for bales can range from 6 to greater than 24 hours, depending on the bale preparation. If there is a need to dezinc baled scrap, it can be accomplished to a varying degree at increased costs.

## 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 or are currently under development. 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. Of these alternatives, degalvanizing with an anodically promoted process in hot caustic appears to have the lowest cost. 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. Degalvanized 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.

## ACKNOWLEDGMENTS

Work supported by the U.S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, under Contract W-31-109-Eng-38 with cost sharing by Metal Recovery Industries, US, Inc.

## 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. 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.
4. 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).
5. 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.
6. Dudek, F. J., E. J. Daniels, W. A. Morgan, Recycling Galvanized Steel: Operating Experience and Benefits, Proceedings of the World Zinc '93 Symposium, AusIMM and the CIM, Hobart, Tasmania, Oct. 10-13, 1993.

## LIST OF TABLES

Table 1: Summary of batch degalvanizing operations at the Hamilton pilot plant.

Table 2: Degalvanizing costs estimate, 100, 000 t/a plant, loose scrap in hot caustic.

## FIGURES

Figure 1 Galvanized sheet steel production and automotive consumption in Japan, Europe and North America: Historical data from AISI and projections from Cockerill Sambre, Consultation of Experts.

Figure 2: Flow chart of process for electrochemically assisted degalvanizing of ferrous scrap.

Figure 3: Pictorial flow chart of pilot plant for continuous degalvanizing of loose ferrous scrap.

Figure 4 Continuous pilot plant zinc removal performance and sodium analyses on prompt automotive scrap containing hot-dipped(HD), galvannealed(GA) and electrogalvanized coatings.

Figure 5 Cost factors vs production capacity for degalvanizing by dissolution of zinc in sodium hydroxide and recovery of zinc by electrowinning. Capital recovery is 33%.

Table 1 Summary of batch degalvanizing operations at the Hamilton pilot plant.

SCRAP				TREATMENT			
Form	Bulk Density (kg/m <sup>3</sup> )	Quantity (tonnes)	Type	Coating Wt. (%)	Time (h)	Anodic Assist	Zinc Removal (%)
Loose, in baskets	1500	20	Mixed	2.16	1-26	Yes	99.6
do	do	1	do	do	4	No	99.6
Bundles 1000x660x660 mm	1700	13	Hot dipped	1.53	17-26	Yes	78 avg. 68-83
do	do	1	do	do	71	No	36
Loose, in baskets	--	0.3	Galvalume	1.4 Zn 0.7 Al	--	Yes	Zn, 99.8 Al, not detected
Bales, auto stampings 330x360x400 mm	1900-3000	28	galvanneal	0.2-1.1 0.6 avg.	--	Yes	84
AISI bales 610x610x790 mm Sheet & coil ends	2500	170	Mixed	2.0 avg.	24	Yes	77
do	do	280	do	do	36	do	81
do	do	130	Mixed & Template	do	24	do	75

Table 2 Degalvanizing costs estimate, 100,000 t/a plant, loose scrap in hot caustic.

PLANT CAPITAL COST	
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
Credit, zinc recovery, 15 kg @ 0.60/kg	(9.00)
Total variable zinc recovery	(3.15)
Total Variable Dezinc and Zinc Recovery Operating Cost	11.76
Fixed costs	
Administrative labor	2.10
R&D	2.00x
Insurance, taxes & interest	2.61
General office	0.50
Total Fixed Operating Cost	7.21
Total Variable and Fixed Operating Cost	18.97
CAPITAL RECOVERY COST	
Return of 33% required on the total investment per tonne of annual operating capacity (\$US 4,090,000/100,000)	13.50
<b>TOTAL COST FOR DEGALVANIZING LOOSE SCRAP</b>	<b>32.47</b>

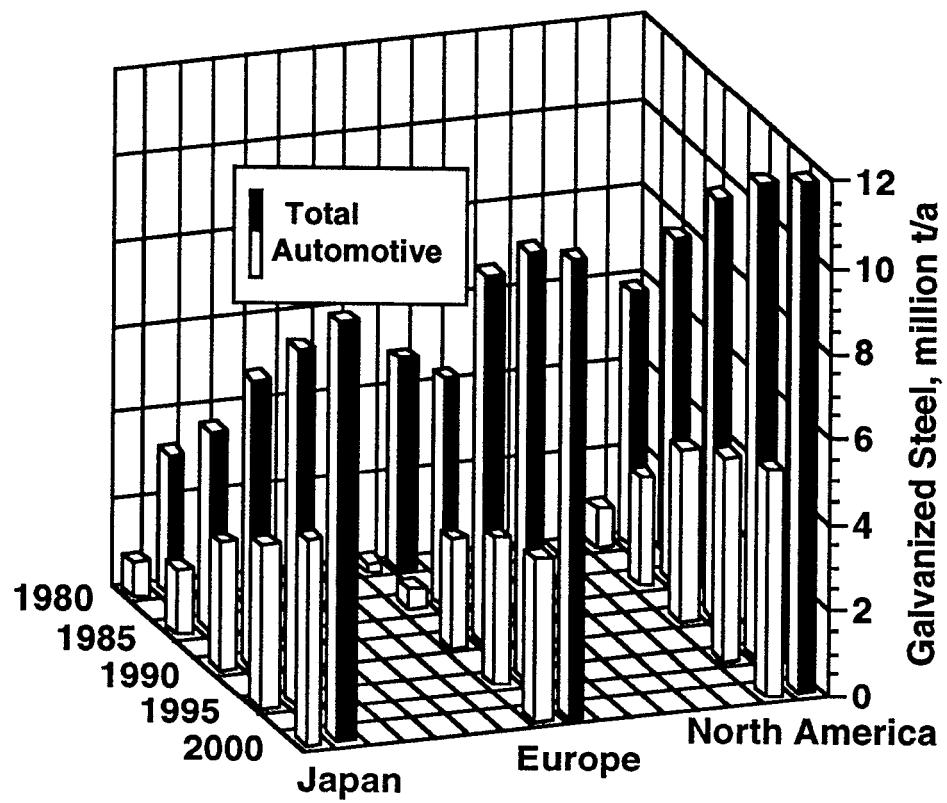


Figure 1 Galvanized sheet steel production and automotive consumption in Japan, Europe and North America: Historical data from AISI and projections from Cockerill Sambre, Consultation of Experts.

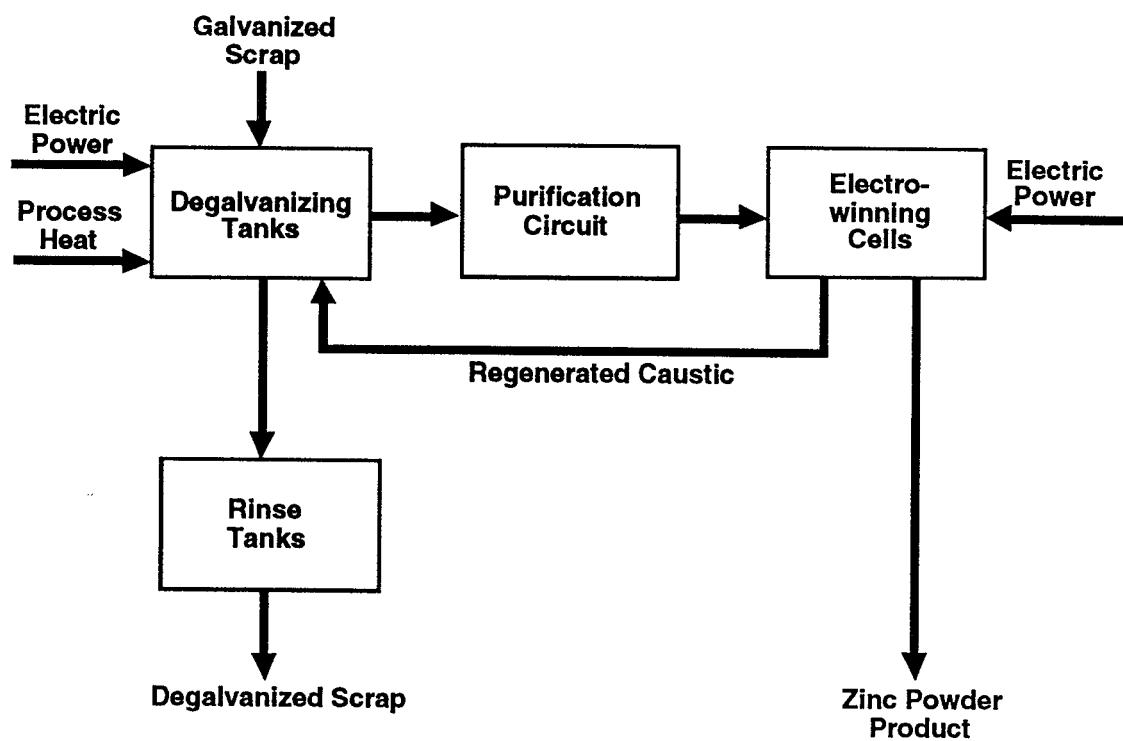


Figure 2 Flow chart of process for electrochemically assisted degalvanizing of loose ferrous scrap.

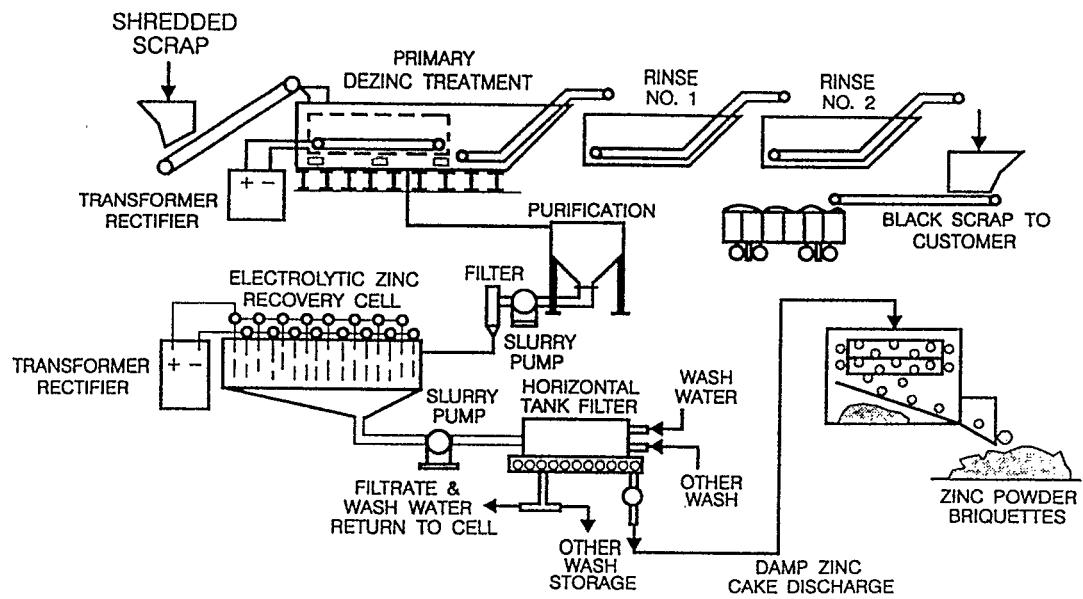


Figure 3: Pictorial flow chart of pilot plant for continuous degalvanizing of loose ferrous scrap.

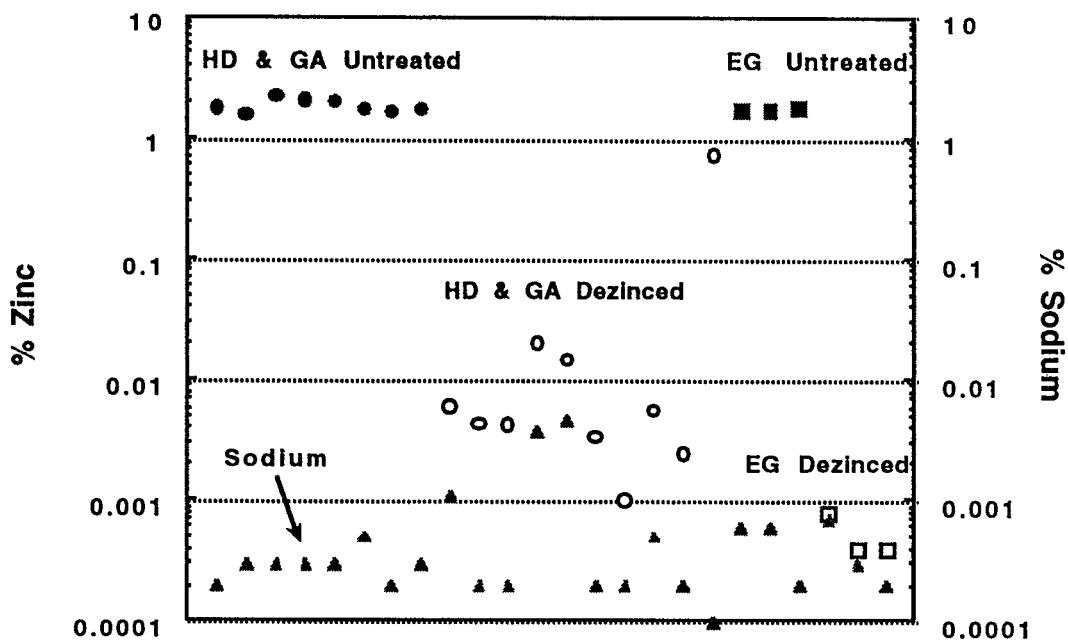


Figure 4      Continuous pilot plant zinc removal performance and sodium analyses on prompt automotive scrap containing hot-dipped(HD), galvannealed(GA) and electrogalvanized coatings.

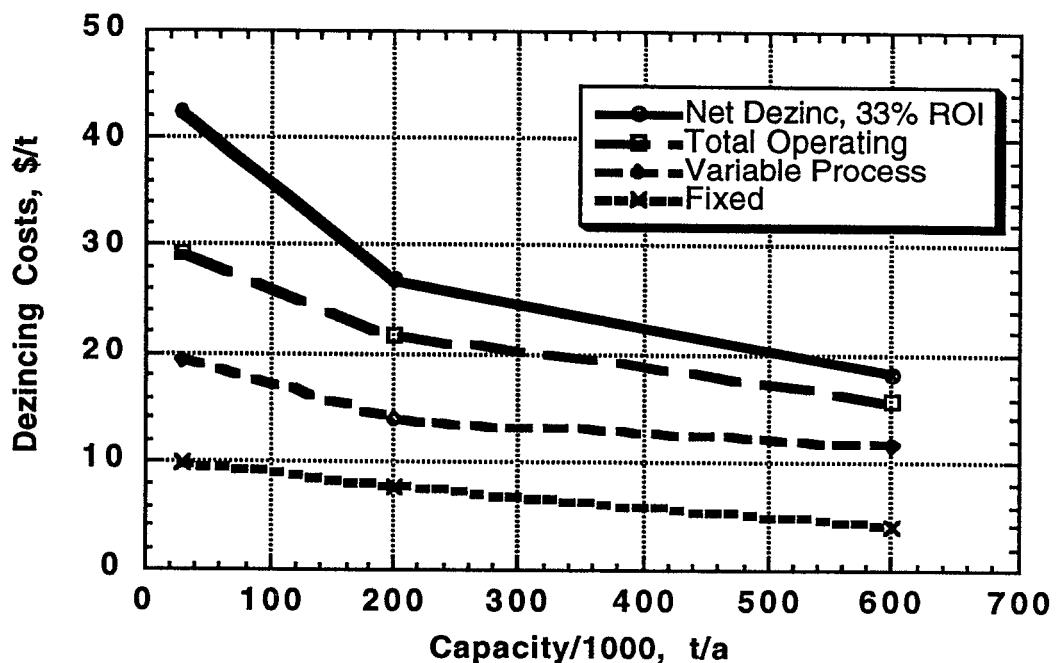


Figure 5 Cost factors vs production capacity for degalvanizing by dissolution of zinc in sodium hydroxide and recovery of zinc by electrowinning. Capital recovery is 33%.