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PROGRESS IN CAUSTIC DEZINCING OF GALVANIZED SCRAP

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ABSTRACT

In response to the worldwide increase in consumption of galvanized steel for automobiles in the last fifteen years, and the cost of environmental compliance associated with remelting larger quantities of galvanized steel scrap, processes are being developed to separate and recover the steel and zinc from galvanized ferrous scrap. In the process discussed here, zinc is dissolved from the scrap in hot caustic 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. Pilot testing has been conducted in Hamilton, Ontario for batch treatment of 900 tonnes of mostly baled scrap. A pilot plant in East Chicago, Indiana, now in its second generation, has dezinced in a continuous process mode about 1,800 tonnes of loose clips and shredded stamping plant scrap; this scrap typically has residual zinc below 0.05% and sodium dragout below 0.001%. This paper reviews caustic dezincing pilot plant performance and economics.

Introduction

Consumption of galvanized sheet steel for automobiles has increased four-fold in the last 15 years, with a commensurate increase in galvanized content in prompt scrap. This change is being echoed in shredded scrap from obsolete autos. Eventually, the zinc recoverable in prompt and obsolete automotive scrap will approach the quantity of refined zinc produced in the U.S. 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 use of other iron units such as DRI, HBI, iron carbide, and pig iron. Steel- and iron-makers sensitive to zinc, lead and other coating constituents of sheet steel scrap increasing the cost of environmental compliance [1,2,3] should be eager to have dezinced scrap available.

Caustic Dezincing Process Development Review

Argonne National Laboratory and Metal Recovery Technologies, Inc. (MRTI), or MRTI's predecessors, in cost-sharing collaboration, have developed a process to separate and recover steel and zinc from galvanized steel scrap. This work, begun in 1987, has been supported by the U.S. Department of Energy. A technoeconomic assessment of dezincing process candidates led to the selection of electrochemical stripping in hot caustic as the most promising. Development of the 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 and dezinced batches of sheet, loose, and baled galvanized scrap. Lots as large as ten tonnes were dezinced with anodic assistance in Hamilton culminating with accumulation of 580 tonnes of baled scrap for an AISI BOF melt campaign [5]. A total of approximately 900 tonnes of galvanized scrap of various forms and coating types were treated in these batch processing studies [6]. This led to construction of a pilot plant in East Chicago, Indiana for continuous degalvanizing of loose clips or shredded scrap with a 200 cubic foot reactor capable of dezincing 1-4 tonne/hour. This plant operated in 1993 for dezincing a total of 900 tonnes of loose and shredded stamping plant scrap. The scrap was conveyed through the caustic bath on a pan belt conveyor with corrosive dissolution of the zinc on the steel scrap substrate. In 1996 the plant was dismantled and refurbished with the present rotary reactor. The new reactor has an active volume 670 cubic foot and a dezincing design capacity on shredded scrap of 12 tonne/hour. Operating experience with the first 900 tonnes of scrap dezinced in this plant indicates the reactor is exceeding its design performance. A commercial demonstration plant capable of dezincing 200,000 tonne/a with recovery of 3,400 ton/a zinc is planned for start-up in 1998.

Process Description

The degalvanizing process relies on the dissolution of zinc on a steel substrate in hot caustic. As shown in the process schematic, loose, shredded galvanized scrap is fed to a rotary dezincing reactor that is partially immersed in a tank. The tank is filled with a warm (70-90 °C) water solution of about 20-32% sodium hydroxide (250-440 g/L NaOH). Zinc and other common coating constituents are leached from the scrap steel surface as it is tumbled making its way from the feed to the discharge end of the rotary reactor. The degalvanized scrap is conveyed by rotary conveyors from the dezincing tank and water rinsed twice. The washed scrap may then be shipped to the steel mill or foundry. The pregnant solution from the leaching tank is sent to electrowinning cells for zinc recovery. Over 2.4 pounds of powdered zinc are collected on magnesium sheet metal cathodes for every 1000 ampere-hours of current passing through the electrolytic cell. Power utilization is about 2 kWh per pound of zinc recovered. Electrowinning the zinc regenerates the caustic solution and it is returned to the leach tank to dezinc more steel. The washed zinc solids may be dried and 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 leaching tank. The process consumes no chemicals other than drag-out losses for treatment of most galvanized products and produces only small quantities of wastes. 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 60 and 245 pounds per cubic foot range from 70 to 90% with removal effectiveness decreasing with increasing scrap density - bales require anodic promotion.

Economics and Market

Economic analysis indicates that the cost of processing shredded ferrous scrap would be about $15 to $40/tonne for plant capacities of 50,000 to 500,000 tonne/a, respectively, including credit for the co-product zinc, and capital recovery.

Critically important to the economics of dezincing is the recovery of the zinc. At the current LME price of $1,200 for SHG slab zinc, the estimated 38 pounds of zinc recoverable per tonne of galvanized scrap dezinced is worth over $20. Metal Recovery Technologies, Inc. is targeting growing into five million tonnes of dezincing by the year 2010. This market penetration is half of the approximately ten million tonnes of zinc coated scrap forecast to be available in the U.S. The average coating weight of zinc on steel sent to automotive applications in the U.S. in 1995 was 1.7%; on five million tonness of scrap this would be 85,000 tonnes of zinc worth about $100 million in today's market. Zinc recovery from scrap steel would be the largest zinc mine in the U.S. Equivalent needs for dezincing are in Japan and Europe.

At first, dezincing plants will use as raw feed prompt manufacturing scrap, preferably from auto plants. Prompt scrap is clean and auto scrap contains the largest percentage of galvanized material - on average 50%. This material is sheared and then shredded in a hammermill to fist size chunks. The abrasion in the hammer mill increases the number of zinc/iron electrochemical corrosion sites and promotes more rapid and effective dezincing in the hot caustic solution. The ferrous product from dezincing plants is a shredded zinc-free low-carbon steel. This material may then be baled if the customer so wishes. Work is ongoing at Argonne National Laboratory to extend the dezincing process to obsolete scrap, but shredded obsolete auto scrap contains about 0.25% of tramp metallic copper as well as zinc coated material. The copper is more troublesome than the zinc because it causes metallurgical problems such as hot shortness. Excluding diluting the copper content with other low residual scrap or iron units, copper removal, as well as zinc removal, would have to be a part of a successful treatment of obsolete auto scrap.

The constituents of galvanized coatings on scrap impose environmental compliance, yield, nuisance, and opportunity cost penalties on most iron and steel making. To be relieved of these costs, iron and steel makers need zinc-free and otherwise low residual iron units. These may be provided by clean "black" scrap, dezinced scrap, or scrap alternatives such as Direct Reduced Iron (DRI), Hot Briquetted Iron (HBI), iron carbide and other pig irons. At present, with clean black scrap hard to find and at high premiums, and in the absence of dezincing capability, most iron and steel making operators are putting zinc coated steel into their cupolas or furnaces. They absorb the costs because of the high quality of the underlying steel and, in the case of EAF operations, the credit for zinc which partially offsets the cost of EAF dust treatment.

Competing Processes

The need for cost effectively degalvanizing scrap steel was the subject of a CMP report [2] prepared by O. F. Angeles and E. F. Petras of United States Steel in 1986. This seminal report identified the problems in using zinc coated scrap and estimated the cost of degalvanizing processes. They found no process economic but suggested that further work in the area would be desirable.

Of the several chemical, electrochemical, and pyrometallurgical ways for recycling galvanized scrap that have been the subject of R&D subsequent to the CMP report, two technical approaches to dezincing survive in pilot-scale development. One is the electrochemical corrosive attack of zinc on steel in hot aqueous caustic; this is the method employed in the MRTI/ANL process. This approach is also being developed by Hoogovens Groep in Europe [7]. The second approach uses vacuum evaporation of the zinc from the steel substrate; this is most recently being done by Ogihara and also Toyokin in Japan [8,9]. The Hoogovens process is being piloted successfully in France in a 50,000 net ton per year (Nt/year) plant using essentially the same flowsheet as the MRTI/ANL process but they do not use a rotary reactor. The MRTI/ANL process is being piloted successfully in a 75,000 tonne/year plant in East Chicago, Indiana. Ogihara is operating a 1,000 ton/month plant in a batch mode on bales and Toyokin has a vacuum-aided recycling system (VARS) in pilot stage with a capacity of 5,000 Nt/month of shredded scrap.

Technical and Economic Benefits

A scrap dezincing process could save the nation approximately 50 trillion Btu per year; the operating cost benefits to the steel industry are estimated to be $140 million per year compared to the historical cost of using HBI; and the United States could realize a $100 million decrease in foreign exchange deficit through a reduction in the need to import 85,000 tonnes of zinc and doubling the zinc recycling rate. The process also has major environmental benefits. The removal of zinc from steel scrap increases the recyclability of steelmaking fume and eliminates zinc from wastewater streams. Dust disposal and wastewater treatment costs are estimated at $1-3 per tonne of hot metal for BOP operations. Koros and Bauer [10] have reviewed the consequences of use of galvanized scrap in iron foundries.

Development Plans

Plans for the remainder of 1997, 1998, 1999 and 2000 include design, construction, and operation of a commercial demonstration dezincing plant tolling nominally 200,000 tonne/a of steel scrap for an integrated steel producer or for the captive foundry of an automaker. Product and process research will be conducted on the issues of development of a fluid bed zinc electrowinning cell, zinc purity, zinc melting techniques, and tramp copper removal from obsolete auto scrap. The R&D work will be conducted at Argonne National Laboratory, the MRTI East Chicago, Indiana pilot facility, and the University of California Berkeley.

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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. 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, Tasmaania, Oct. 10-13, 1993.

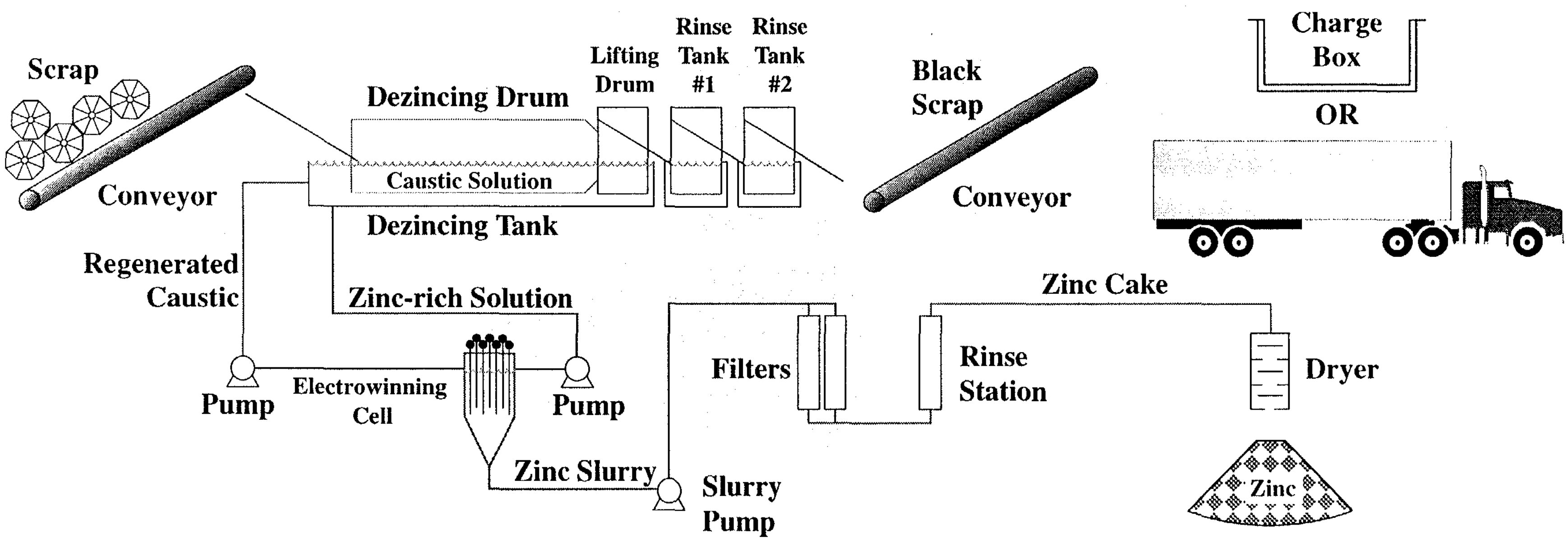
7. Mooij, J. N. and J. H. O. J. Wijeberg, Dezincing of Galvanized Steel Scrap in Hot Caustic Soda, Proceedings of the 2nd International Conference on the Recycling of Metals, ASM International, 1994, p. 199.

8. Saotome, Y., et al., Vacuum Aided Degalvanizing as a High Quality Materials Recycling Technology of Ecofactory, Galvatech '95 Conference Proceedings, pp. 569-576.

9. Okada, Y., et al., Development of a Method for Removal of Zinc from Automobile Body Scraps, Galvatech '95 Conference Proceedings, pp. 549-554.

10. Koros, P. J. and M. E. Bauer, Consequences of Galvanized Scrap Use in Iron Foundries and Technologies for Degalvanizing Scrap, 101st Congress of the AFS, Seattle, WA, April 20-23, 1997, AFS Paper No. 97-162

Dezincing Process



Schematic, MRTI/ANL caustic dezincing process