The Pickliq Process for Recovering Acid and Metal Salts from Pickling Liquors

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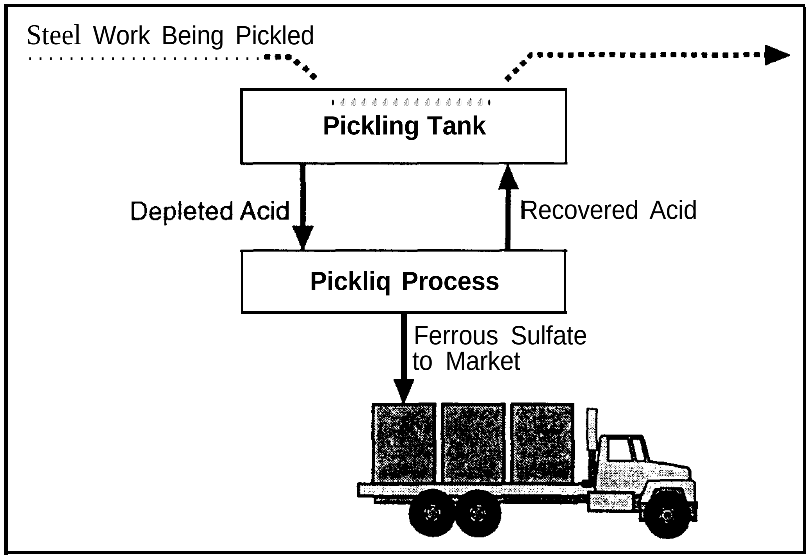
The Pickliq process can purify and recycle acids from pickling liquors at the point of use. The process also recovers the metal salts, which can be sold.



Pickliq Process

Introduction

Sulfuric and hydrochloric acid are top-ranking wastes in the national Toxic Release Inventory. Much of this waste comes from pickling liquors from the primary metals and metal finishing industries. A typical sulfuric-acid pickling operation requires an acid bath that must be pumped out as waste when the acid strength is depleted. That bath then must be replaced with a new bath made up from fresh sulfuric acid and water.

Current acid recovery systems have high maintenance costs and corrode. When acid recovery is not used, waste pickling bath is typically neutralized with caustic soda and land-filled or injected into deep wells. These treatments typically require the waste acid to be transported in tank trucks over the highway for considerable distances. These operations carry a high cost and an environmental risk because of the corrosive materials being handled.

Concept Description

The Pickliq process is being developed to recover and reuse purified sulfuric acid onsite and to produce crystalline ferrous sulfate heptahydrate (metal salts) for the market. Ferrous sulfate is used in substantial quantity in water treatment, agricultural chemicals, and pigments. The process uses membrane diffusion dialysis, cold crystallization, and heat interchange in a unique combination that requires low energy and produces a nonhazardous product. While this combination of technologies is unique, key elements have been used for several years in analogous solutions.

As the figure shows, in the Pickliq process, a side stream of depleted acid is taken from the pickling tank. Heat and acid are removed from the stream and added to the purified stream that is returned to the pickling tank. The ferrous sulphate heptahydrate from the pickling tank stream is crystallized at a low temperature. The crystals are dewatered in a centrifuge and dropped into bulk shipping containers. The liquid from the centrifuge is sent to the diffusion dialysis portion of the system, where it recovers the acid and returns it to the pickling tank.

A unique advantage of this process is its ability to produce a nonhazardous material because the acid is removed by diffusion dialysis. This feature lowers the cost of construction materials and extends equipment life because the Pickliq process takes place in a less corrosive solution. The product may be shipped as a non-corrosive material because the pH is above 2.0.

The process saves energy in several ways: recovered acid uses less energy to make than new acid; the need for treatment with caustic soda is eliminated; and the transportation cost of shipping used acid offsite is eliminated. Fuel, personnel hours, and material are also saved because higher average acid strengths reduce pickling times and a constant acid level minimizes rejected work caused by insufficient pickling.

Economics and Market Potential

The concept's economics were estimated using a galvanizing plant. The plant currently galvanizes 20 million lb of steel per year, resulting in >4000 gal/wk of pickling acid waste that must be hauled away and treated at a cost of >$1/gal. This waste liquid contains both acid and ferrous sulfate and is eventually neutralized and landfilled.

The facility's optimal capacity has been estimated to be 40 million lb of steel per year. The Pickliq process could eliminate acid purchases and waste hauling costs, and generate ~$3 15,000 in savings each year. While these savings are very good, this facility is "small" compared with steel strip mills and larger galvanizing facilities, which would produce substantially larger savings. Equipment payback for the Pickliq process is estimated at 1 to 2 years.

The process has widespread application in the primary metals industries for pickling operations. It also is applicable in all metal-working industries for metal pickling and cleaning, and in the metal finishing and the circuit board industries for recovering the acid and metal salts from all types of etches and metal strips. Acids that can be recovered are hydrochloric, sulfuric, nitric, hydrofluoric, phosphoric, and others (including nonmineral acids). The metals whose salts can be recovered include ferrous, nickel, copper, zinc, tin, manganese, and aluminum.

Key Experimental Results

The physical chemistry of ferrous sulfate in sulfuric acid is documented in the literature and well understood. Crystallizing ferrous sulfate from sulfuric acids at various acid strengths and temperatures is an essentially simple operation and requires minima1 development work.

From commercial operations and from bench and pilot operations, data were obtained for diffusion dialysis on pickling acids containing sulfuric acid and ferrous sulfate. Experiments have shown that production pickling acid can be deacidified to a pH of above 2.0. A pilot unit operating on a side stream of a production unit was also used to demonstrate the recycling of acid to the diffusion dialysis membranes and the crystallization of the deacidified pickling liquor.

Yet to be demonstrated is the energy and material balance from a production sized unit that is operated continuously. These data will demonstrate conclusively the operating economics and product characteristics for the market.

Future Development Needs

Future funding is needed to further commercialize the process, including testing and documenting the prototype performance, further defining and promoting the market, and developing technology transfer media. Assistance is also needed for the post-prototype design and commercial process marketing.

A technology demonstration project of a system prototype at a galvanizing plant in Utica, New York, is expected to verify system performance and confirm the energy balance and the exact product characteristics. Technology transfer can then be initiated to begin ultimate commercialization of the system.

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