Sulfuric acid batch pickling process promises no waste, no pollution

First U. S. installation will soon check performance claims of a Canadian developed system.

The future of sulfuric acid pickling may be brighter if a small Canadian based engineering group, KSF Chemical Processes Company (Scarborough, Ontario) can substantiate the claims it is making about the pickling process it has developed. Some of the claims: faster pickling rates, lower acid consumption, no liquid waste discharge. Any one of these results, let alone three, would be enough to interest steelmakers. In the next few months KSF will put its process claims on the line when Atlantic Wire Company (Branford, Conn.) goes on stream as the first U.S. user of the process. Start up date is now targeted for around September.

In describing its process KSF maintains that one of the mistakes in the past has been to separate the difficulties of steel pickling and those of water pollution into two distinct problems. KSF insists that it's the inefficiency of the traditional method of pickling steel which causes pollution problem. By making the pickling process efficient, they say, one simultaneously removes the pollution problem.

Before describing the KSF process it's probably a good idea to enumerate some of the major difficulties which arise in sulfuric acid pickling. Once these are understood it's easier to understand just what KSF is trying to do.

### COST DATA SUMMARY

**KSF Sulfuric Acid Pickling System**

**Before Installation**
- Acid used: 1000 t/y
- Steel pickled: 40,000 t/y
- Cost of removing pickle liquor: $25,000/y
- Water used: 300 gpm (cost: $18,000/y)

**After Installation**
- Capital cost of acid plant, water treatment plant and fume collector system: $135,000
- Total operating cost for labor, power, maintenance, depreciation (10% year), sludge removal and chemicals: $25,000
- Savings on acid recovery, production increase, pickle disposal costs, sale of crystals, and water recovery: $72,000

**Notes**
Under the above conditions the KSF plant would pay for itself in 2½ years. It takes approximately six months to fully engineer, design, supply, install and start up a complete system.

Here are the major benefits claimed for the KSF process:

1. Constant fast pickling time resulting in increased production.
2. Recovery of up to 50 percent of the acid presently purchased.
3. No delay in dumping and making up acid tanks.
4. Elimination of pickle waste disposal costs and problems.
5. Recovery of 90 percent of water purchased for rinsing.
6. Elimination of the fume problem by recovery of acid mist.
7. Elimination of water pollution.
8. Reduction of hydraulic load on municipal sewer and sewage plants.

Reprinted from August 1966, 33/ THE MAGAZINE OF METALS PROCESS

AR200742
The Problems of Pickling

The major problems usually associated with sulfuric acid pickling are:

1. Acid—It becomes progressively diluted by the formation of ferrous sulfate.
2. Spent pickle liquor—When the acid becomes ineffective it has to be disposed of in large quantities.
3. Rinse Water—Large quantities of acidified rinse water also have to be junked.
4. Acid vapor—Emission of this pungent vapor causes air pollution problems.

The plant which overcomes the above problems, must ideally: 1) Be simple to operate so that qualified engineers are not necessary for its routine operation. 2) Be corrosion resistant and mechanically sound so that it does not pose a maintenance problem. 3) Be economically viable.

The KSF Approach

KSF feels that not only does its process deal with the four major problems outlined earlier but it thinks it does it simply and economically. Here's how the company breaks down its attack.
The steel enters a conventional pickle tank (4) which is properly controlled for temperature, acid strength, agitation (6), and iron strength. It is then dunked in drag tank (3) to remove as much acid as possible prior to proper rinsing in tank (2). Pump (1) recirculates the rinse water via neutralization in tank (8) and through a clarifier (10) for removal of iron and is returned by pump (11) via the cooling coils of pickle acid crystallizer (12) for re-use. The only variable to control is the iron build up in pickle tank (4). When sufficient iron has formed the batch is rapidly pumped (7) to crystallizer (12). The previous batch having passed through the crystal vacuum box to remove crystals has been waiting and pre-heated in tank (14) is immediately returned to the pickle tank (4) for production to continue. This operation is set to take 60 minutes every 24 to 48 hours, consequently virtual continuous production can be maintained. The fumes are collected over the pickle tank by a push-pull system into a terephene filter collector and the acid is recovered by simple gravity drainage back to the pickle tank.

12-CRYSTALLIZER FOR IRON REMOVAL
13-CRYSTAL VACUUM BOX
14-RECOVERED ACID TANK
15-RECOVERED ACID PUMP
16-ACID STORAGE TANK

on the few problems (which, as mentioned, they see as actually a single interrelated problem):

The Acid Problems—KSF say that if steel pickling is to be done efficiently it must not not be regarded simply as method of cleaning by hot sulfuric acid but as a chemical process. When this is acknowledged then the conditions necessary for efficient chemical reaction can be firmly laid down. These conditions are: (a) temperature control (b) good agitation (c) correct acid strength.

Temperature control is great importance because it dramatically affects the rate of reaction.

Good agitation is of fundamental importance to most chemical reactions yet the majority of pickle plants don't agitate their acid tanks. KSF does agitate the tanks and says that the evaporation caused by air agitation offsets the increase of the acid solution which is caused by heating with live steam. This eliminates the problem of overflowing tanks and, more importantly, concentrates the iron sulfate so that it can be crystallized easily in the acid recovery plant.

Correct acid strength is related directly to the rate of reaction with iron and the subsequent
rate of cleaning. Yet, says KSF, virtually no pickle plant has at present the means of maintaining consistent acid strength.

The sulfuric acid is allowed to become weaker and weaker while the pickling takes longer and longer. From a desire to cut costs the acid is allowed to decline to half its efficient strength before dumped. KSF says it maintains the acid at its most effective strength. It does this economically by recovering acid from the pickling process by means of its acid recovery unit. When enough iron has built up in the pickle tank the batch is pumped into the crystallizer where the iron is crystallized as ferrous sulfate heptahydrate. The crystals are run into a vacuum filter box where they are washed (and possibly sold for pigment manufacture). The acid is drained off and pumped back to bring it up to strength. The cooling water which is used in the crystallization process is then utilized for steel rinsing. It’s this cooling system which helps over corrosion and/or maintenance problems.

The Spent Pickle Liquor Problem: Spent pickle liquor, the second of the four major problems connected with pickling is, says KSF, no longer a major problem because of the provision in its process for acid recovery.

The Rinse Water Problem: In the KSF process there’s no need to dispose of large quantities of acidified rinse water. After rinsing, the water is pumped to a neutralization system, clarified of its iron and then recirculated via the cooling coils of the crystallizer. To maintain a fixed balance of impurities in the rinse water, 10 percent is run off to the sewer and fresh makeup water is added.

The Acid Vapor Problem: On the KSF process a terylene fibre installed on the fume exhaust collects acid vapors and runs them to the pickle tank. This removes the problem of air pollution and simultaneously recovers waste acid.

If KSF can convince steelmakers that its process is as economical and simple to operate as it claims there should be a steady trek of steelmakers beating a path to their door. (For an interview with the engineer-developer of the KSF process, see following story.)

ATLANTIC WIRE COMPANY:

First in the U.S. to install a KSF unit

As a long standing practice, the Atlantic Wire Company (Branford, Conn.) has been batch pickling wire rod with sulfuric acid prior to drawing. In keeping with U. S. environmental trends, the company is now under orders from the State Water Resources Commission to end pollution of the Branford River with acid waste waters.

William Hitchcock, Jr., president of Atlantic Wire gives the following report on the company’s decision to be the first in the U. S. to install the KSF system: “Last Fall our representatives visited a KSF system in a Canadian plant. Early in 1966 another plant in Canada installed similar equipment and this was also visited by representatives from our company.

“In October we were sufficiently impressed to ask KSF to design a system suitable for the Atlantic Wire Company and in December an order was placed for the necessary equipment, subject to the approval of the plans by the State of Connecticut Water Resources Commission. With an investment exceeding $135,000 in this special equipment our company had to make sure this method of solving its industrial waste problem would be satisfactory to the Commission. Understandably the Commission also wanted to be sure this new system will correct Atlantic Wire’s industrial waste problem. Several conferences between representatives of the Commission and engineers representing the company were held and recently (March 1966) the green light was given by the Commission to proceed with installation of the KSF equipment which we had ordered on December 7, 1965.

“Basically, the new equipment will deal with the spent pickle solutions in a manner which will recover all acids, extract ferrous sulfate crystals and effectively control and treat any remaining waste waters. The acid will be used over again. The ferrous sulfate crystals, looking something like rock salt, will be marketed, although the sales value will largely be offset by handling and transportation costs.

“It will be the first unit of its kind in the United States and about the third in the steel industry anywhere.”

Hitchcock commented further to 33:

“We’re looking forward to the operation of the KSF sulfuric acid system. Just the same, you’ll notice that we have a muriatic acid (hydrochloric acid) tank in our smaller pickling room. There’s no doubt that muriatic does a good job on certain kinds of wire. The surface is better than from sulfuric pickling. Also, there’s much less chance of over pickling.

“Unfortunately, we can’t run both acids through the KSF system so we can’t use muriatic except for special wire. If we were building a new plant and had the room I’d sure take a good look at having both acids working in my plant.”