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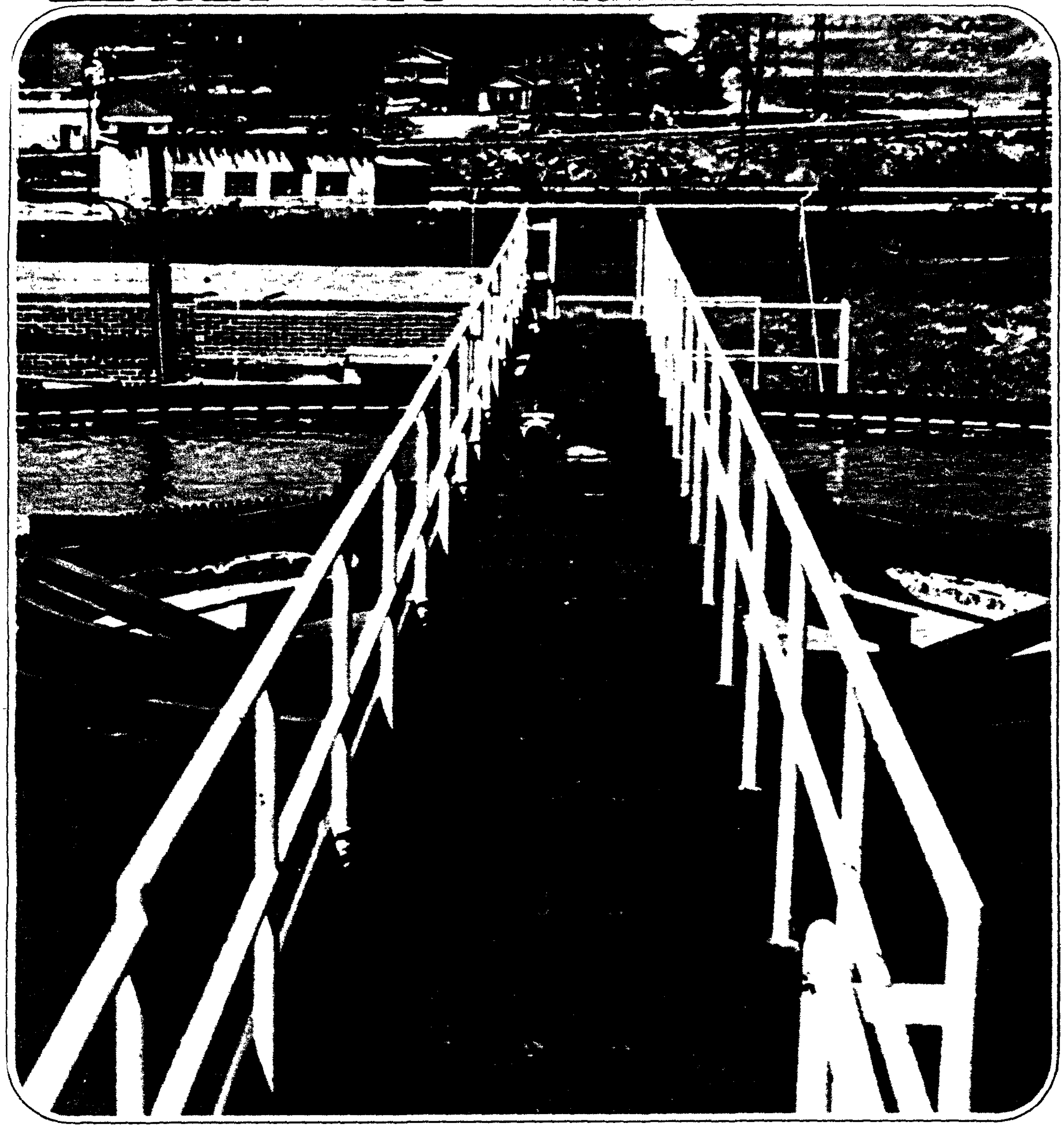
EPA TECHNOLOGY TRANSFER

CAPSULE REPORT

RECYCLING ZINC IN VISCOSE RAYON PLANTS BY TWO STAGE PRECIPITATION

U.S. ENVIRONMENTAL PROTECTION AGENCY INDUSTRIAL DEMONSTRATION GRANT



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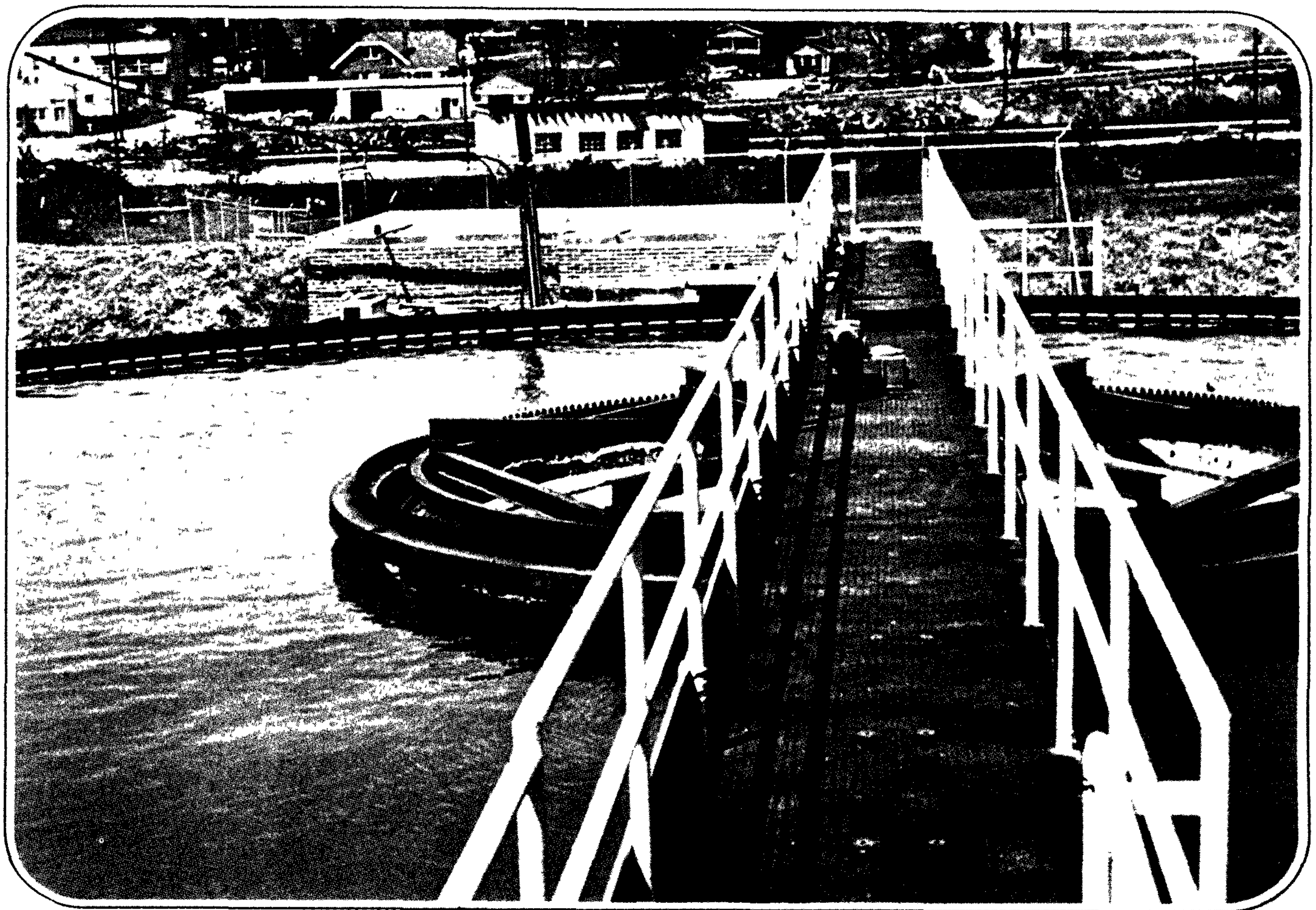


Densator Reactor

1. THE SIGNIFICANCE

Over 50 million lbs. of zinc sulfate are used annually in the United States for the manufacture of approximately one billion pounds of viscose rayon. Zinc is used as a regeneration retardant in the acid spinning bath. Since it is not consumed in any of the viscose reactions, these 50 million pounds of zinc represent process losses, through dragout by the filaments to the subsequent wash streams, filter backwashing, splashes, leaks and the washing of equipment.

The effects of zinc as a pollutant are well documented. Concentrations as low as 1.0 ppm have been shown to be harmful to fish. In addition, there is some evidence indicating that zinc has a synergistic property when associated with copper.

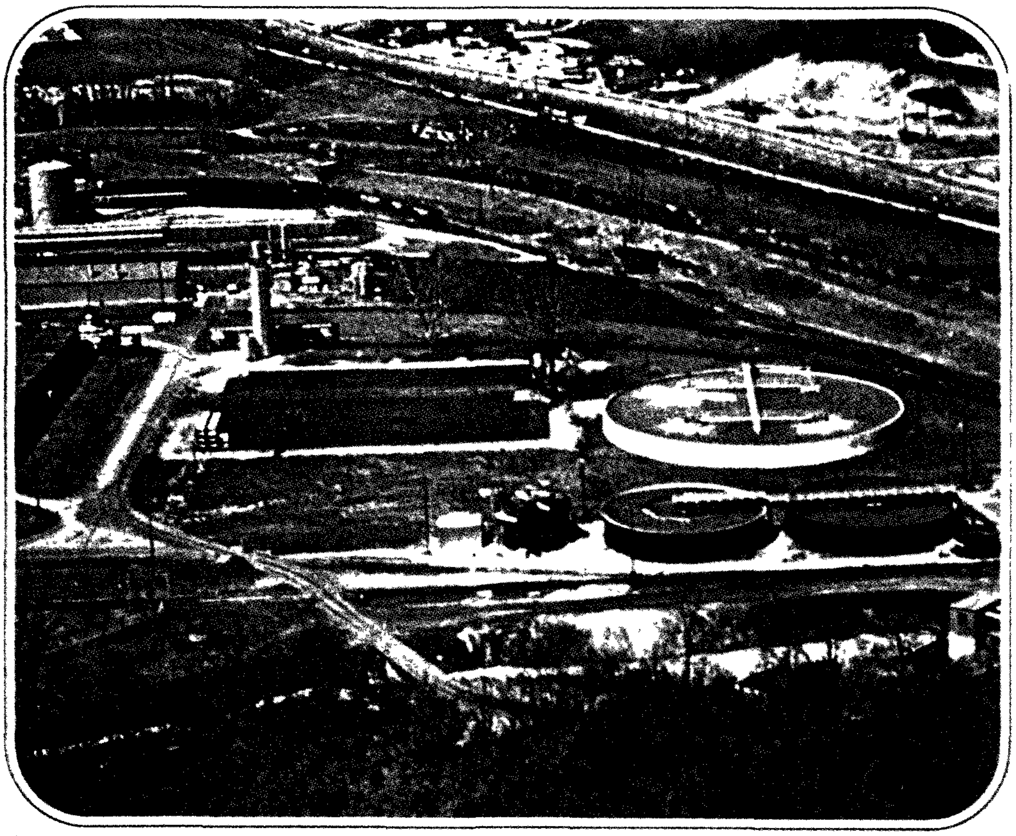
Although it has been known that zinc can be precipitated from the acid waste streams by the use of lime, the resultant sludge has been of low zinc assay, contaminated with other compounds, and with very poor settling characteristics. In commercial operations, the sludge presented a disposal problem and recovery of zinc suitable for recycle was impossible.

In this EPA demonstration grant with the American Enka Company, a process for precipitating a dense sludge of high zinc assay was proven. The zinc in the sludge was recovered and recycled to the rayon manufacturing plant. This recycling of zinc was shown to have no ill effects on the rayon yarn.

There are 10 viscose rayon manufacturing plants in the United States, all of which are believed to use zinc sulfate in their spinning bath.

This process greatly enhances the economics of removing this source of zinc pollution, allowing neutralization of the acid stream and recovery of the zinc of a good profit for industrial yarns and at a moderate cost for textile yarns.

2. THE NEW PROCESS



American Enka Waste Treatment Facilities

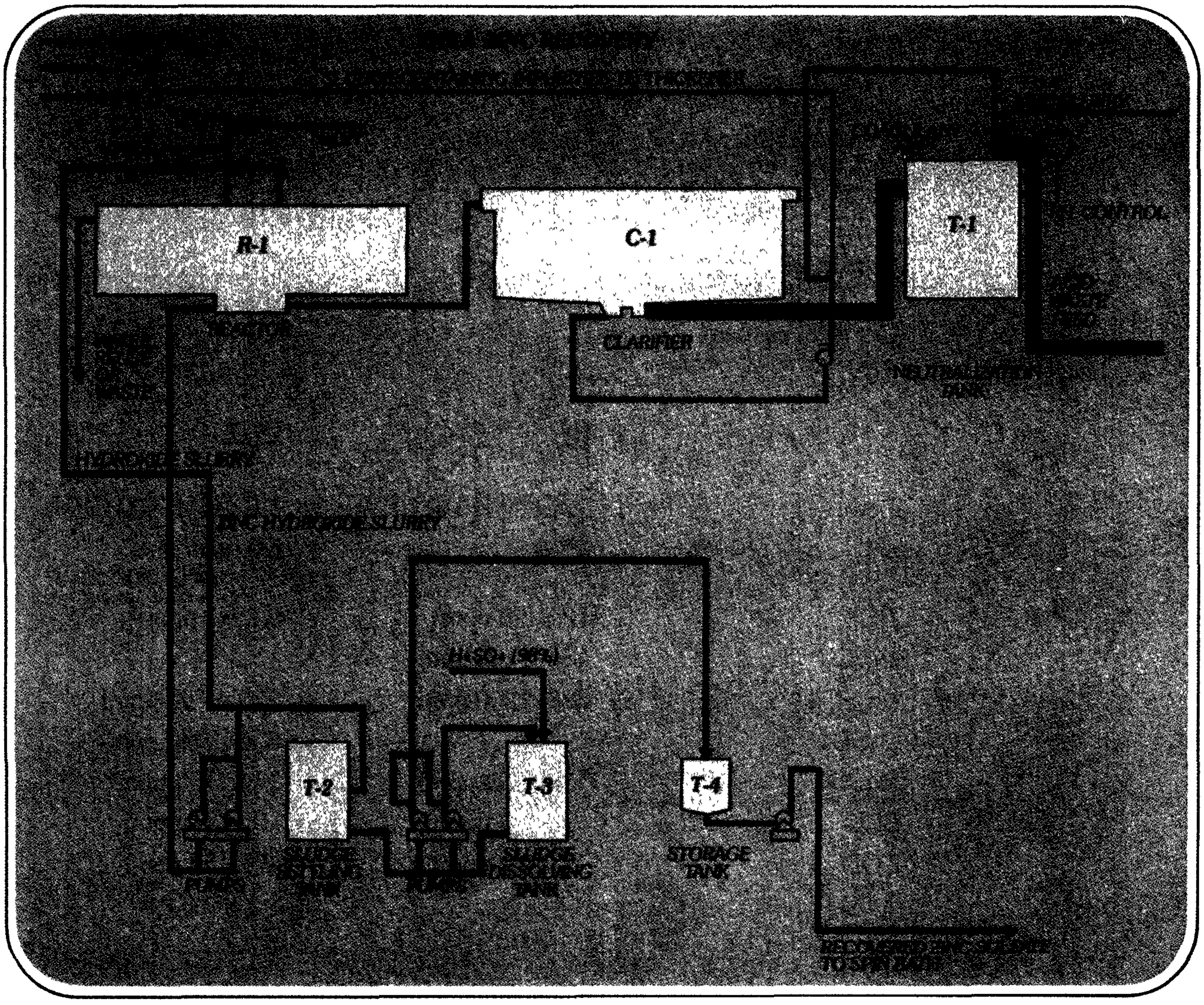
The key to this zinc recovery process is a two-stage precipitation with the second precipitation taking place under careful pH control, using sodium hydroxide, in contact with a circulating slurry of zinc hydroxide crystals. All of the zinc precipitates in the second step, most of the impurities in the first.

Referring to the flow sheet, Figure 1, the elements of the process are as follows:

Acid and alkaline waste streams are collected in a neutralization tank (T-1). Here sufficient lime is added to raise the pH to 6.0. At this point, no zinc hydroxide will precipitate but a portion of the iron, calcium sulfate, and other impurities will form a light precipitate. With a coagulant aid, the mixture is sent to a clarifier (C-1) where a clear overflow containing the dissolved zinc is obtained.

This clear overflow is contacted in a reactor (R-1) with a circulating stream of previously precipitated sludge containing zinc hydroxide. The pH is raised subsequently to 9.5—10.0 with sodium hydroxide. The bulk of the zinc precipitates onto the existing crystals in the circulating slurry. At steady state conditions, a withdrawal of the circulating slurry stream is made equivalent to the zinc being added. This dense sludge is then settled (T-2). The settled sludge of 4-7% zinc assay is converted back to zinc sulfate with sulfuric acid (T-3) and sent back to the spinning bath. If desired, the sludge can be filtered or centrifuged to 18% solids before dissolving with acid.

The zinc content of the overflow water from the densator-reactor is set by the pH-solubility relationship of zinc in water and results in a zinc content of 0.5—1 ppm at pH = 10. Once the precipitated zinc is removed from the wastewater, the pH can be readjusted to a lower value.



R-1
REACTOR
C-1
CLARIFIER
T-1
NEUTRALIZATION TANK
ZINC HYDROXIDE SLURRY
T-2
SLUDGE SETTLING TANK
PUMPS
T-3
SLUDGE DISSOLVING TANK
T-4
STORAGE TANK
TO SPIN BATH

3. THE OLD EFFLUENT VS. THE NEW

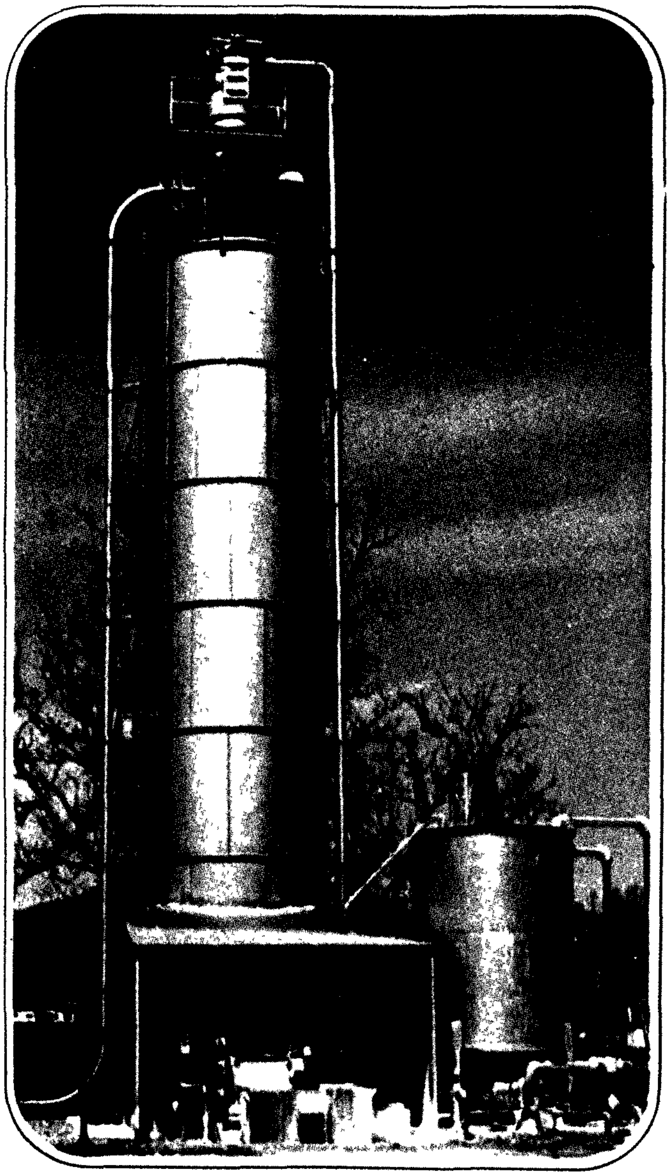
Typical Influent vs. the Treated Effluent at American Enka's North Carolina Plant

(Basically Textile Yarn Nominally 50 Million lbs. Per Year)

lbs./1000 lbs. yarn
unless otherwise noted

	IN	OUT
Flow	131,000 (1500 GPM)	131,000 (1500 GPM)
pH	1.5-3.0	8.0 (after final pH adjustment)
Zn	12.5 (95 ppm)	0.13 (1 ppm)
H_2SO4	184 (1400 ppm)	- - -
Na_2SO4	288 (2200 ppm)	320 (2440 ppm)
CaSO4	- - -	256 (1940 ppm)
MgSO4	13.8 (105 ppm)	13.8 (105 ppm)
BOD	3.1 (24 ppm)	3.1 (24 ppm)
COD	7.0 (53 ppm)	7.0 (53 ppm)

4. THE ECONOMICS



Lime Slaking System

The conventional technique for removing zinc from the spinning acid waste stream has been direct lime precipitation to a pH of about 10, with no zinc recovery. The economics of this approach are compared to the American Enka Zinc Recycle Process. In order to protect proprietary spinning information relating to acid/zinc ratios for a given product mix of yarns, it has been necessary to choose a hypothetical product mix and acid ratio which, although reasonable for economic evaluation, does not correspond to an actual production situation of the American Enka Plant.

The economics of recovery are a very strong function of the amount of zinc used in the preparation of the yarn and the ratio of acid to zinc in the spinning bath. In manufacturing industrial yarns and tire cords, it is common to use 4.5—7.5 pounds of zinc per 100 pounds of yarn. This high concentration of zinc makes recovery extremely attractive. Textile yarns use less zinc and although recovery is still the most economic solution, it offers less of a return. These two cases are presented as extremes, with many plants falling between the two values.

For the 50 MM lbs./yr plant considered, the use of two stage precipitation combined with zinc recycle offers a savings of $383,000 over neutralization for a plant producing industrial yarns and a savings of $68,000 for textile yarns. Many plants produce a mix of the two and results would be between these values. The costs associated with the more extensive sludge handling and storage in neutralization and precipitation only aren't included.

The cost of installing the complete neutralization and zinc recycle system would

50 MM/LBS./YR.
OF
TEXTILE YARN

(Acid/Zn SO4 = 5.5)
lbs./Zn
100 lbs. yarn = 1.5

	Conventional Lime Neutralization Precipitation	**Two Stage Precipitation With Zinc Recycle**
Total Investment (including engineering)	$425,000	$625,000
Operating Costs (all costs in $/yr.)		
I Wages	5,000	10,000
II Electric Power @ 8 mils	7,000	9,300
III Maintenance (3% on Invest./yr.)	12,800	18,800
IV Laboratory	All on-site, included in wages	
V General Plant Overhead	8,000	10,000
VI Raw Materials		
Lime ($20/ton)	72,900	64,800
NaOH ($40/ton)	- - -	20,800
Polyelectrolyte	- - -	5,500
Total Materials	72,900	91,100
Total Operating Cost	105,700	139,200
Fixed Charges		
Depreciation @ 15 yrs.	28,300	41,600
Taxes, Insurance	2,000	3,000
Total Fixed Charges	30,300	44,600
Zinc Credit (@ 15.5/lb.)	0	[116,000]
Net Yearly Cost Total	136,000	67,800

Net Yearly Advantage (Recycle over Conventional Neutralization) 68,200

Pretax Return on Differential Investment $\frac{\$\ 68{,}200}{\$200{,}000} = 34.1\%$

50 MM LBS./YR. OF INDUSTRIAL YARN

(Acid/Zn SO4 = 2.0)

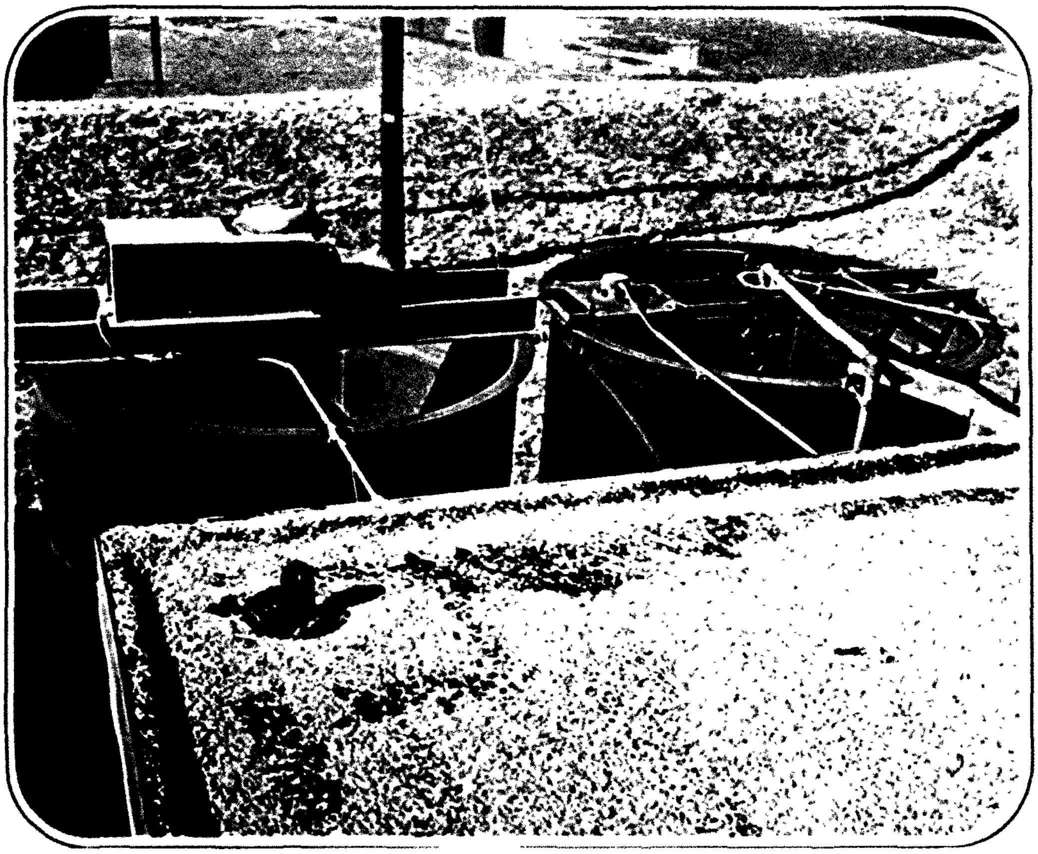
$\frac{\text{lbs. Zn}}{\text{100 lbs. yarn}} = 6.0$

	Conventional Lime Neutralization Precipitation	Two Stage Precipitation With Zinc Recycle
Total Investment (including engineering)	$425,000	$625,000
Operating Costs (all costs in $/yr.)		
I Wages ½, 1 man @ $10,000/yr.	5,000	10,000
II Electric Power @ 8 mils	7,000	9,300
III Maintenance (3% on Invest./yr.)	12,800	18,800
IV Laboratory	All on-site, included in wages	
V General Plant Overhead	8,000	10,000
VI Raw Materials		
Lime ($20/ton)	123,500	94,000
NaOH ($40/ton)	- - -	76,000
Polyelectrolyte	- - -	5,500
Total Materials	123,500	175,500
Total Operating Cost	156,300	223,600
Fixed Charges		
Depreciation @ 15 yrs.	28,300	41,600
Taxes, Insurance	2,000	3,000
Total Fixed Charges	30,300	44,600
Zinc Credit (@ 15.5/lb.)	0	[465,000]
Net Yearly Cost Total	186,000	[197,000] Credit

Net Yearly Advantage (Recycle over Conventional Neutralization) **383,600**

Pretax Return on Differential Investment $\frac{383{,}600}{200{,}000} = 192\%$

Pretax Return on Total Zn Pollution Control Facility $\frac{\$197{,}000}{\$625{,}000} = 31.5\%$



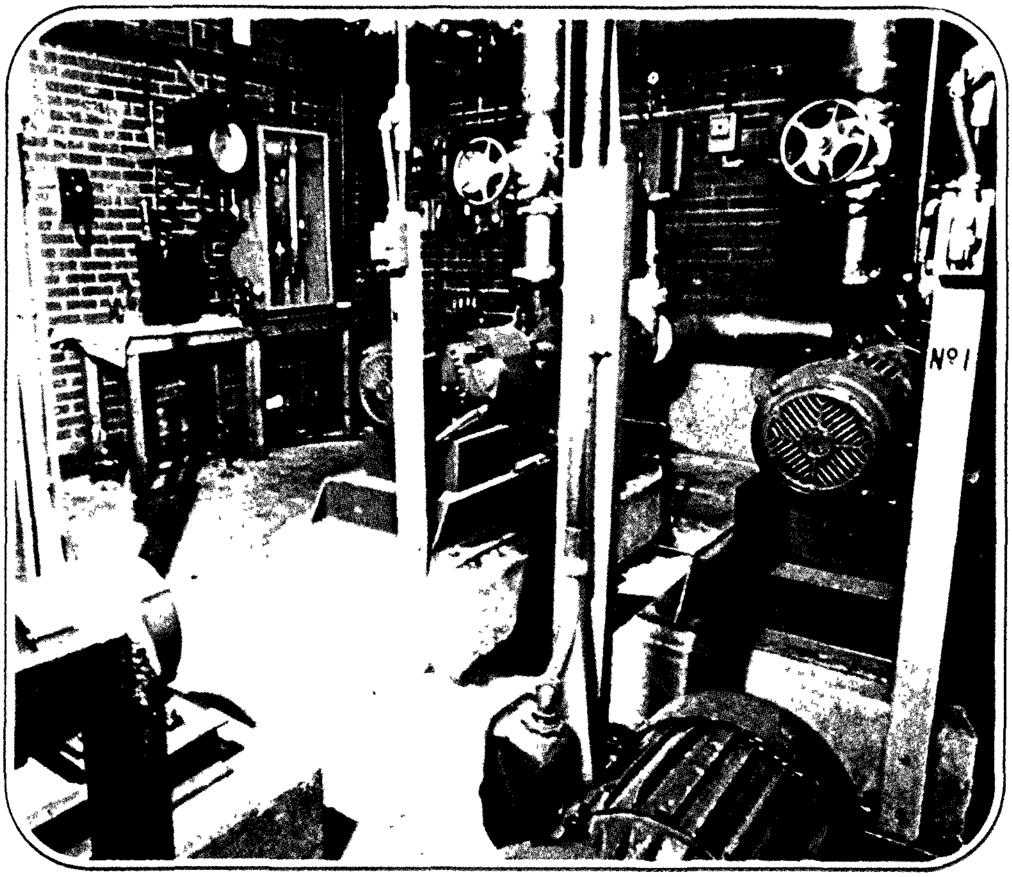
Sludge Settling and Sludge Dissolving Tanks

have negligible economic impact on the rayon industry, running from \$.40/100 lbs. profit to a \$.13/100 lbs. cost compared to selling prices of \$30-35/100 lbs. of staple, \$70-80/100 lbs. of tire yarn, and \$100-150/100 lbs. of filament. Zinc oxide manufacturers face the loss of the bulk of a 50 million lb./year market as this product is reused rather than wasted. At the present rate of consumption, the known world zinc reserves are estimated to last 23 years. Allowing for an estimated yearly increase in consumption of 2.9%, these reserves would last only 18 years. Thus, the recycling of zinc in the rayon industry is desirable to extend the domestic supply.

5. AREAS OF APPLICATION

This technology, with only small modifications to conform with local plant conditions, could have immediate application in any viscose rayon plant with soluble zinc in the plant waste stream. The techniques of initially precipitating the impurities which would prohibit zinc recycle as well as the use of a sludge recirculation process to obtain a dense sludge are excellent examples of good process engineering being applied to a waste problem.

In a broader sense this technology could have application to any waste stream containing soluble zinc in a form which can be precipitated by lime or caustic addition. The possibility of recycling the



Pump Room

precipitated zinc would depend upon the nature of the process considered and may require further work. Examples of other areas with zinc containing wastes are ground-wood pulp, metal plating, zinc refining, and recirculating water systems. To our knowledge, no R&D activity to demonstrate the economics and effectiveness of this technology in these applications is in evidence to date.

For further information:

Detailed information on this project, including equipment list, is available from the Superintendent of Documents as EPA Report 12090 ESG "Zinc Precipitation and Recovery from Viscose Rayon Wastewater".

Or write:

***Technology Transfer
Environmental Protection Agency
Washington, D.C. 20460***

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