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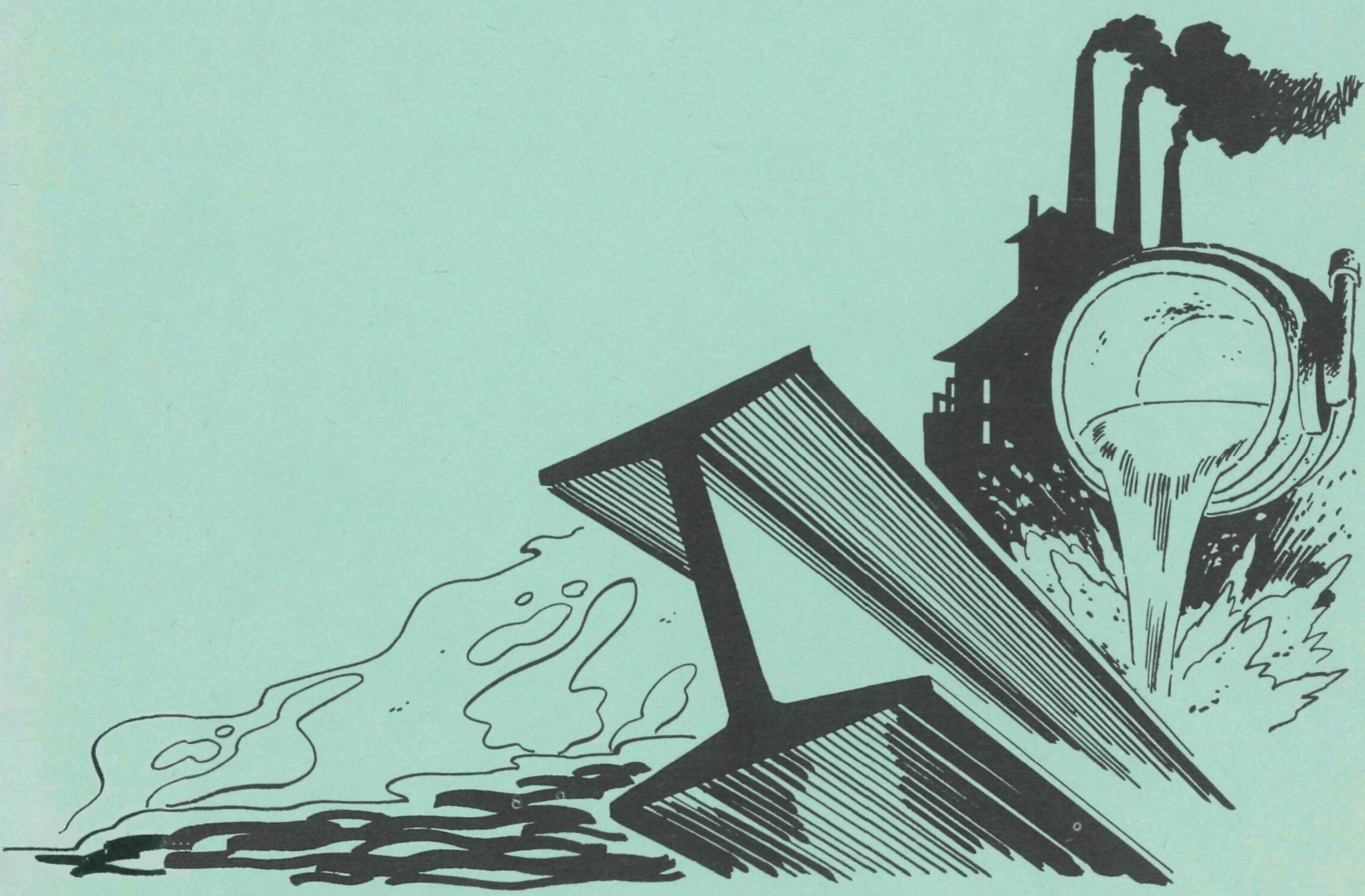
Brass Wire Mill Process Changes and Waste Abatement, Recovery and Reuse



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BRASS WIRE MILL PROCESS CHANGES AND WASTE ABATEMENT, RECOVERY AND REUSE

by

Volco Brass and Copper Company

Kenilworth, New Jersey 07033

for the

OFFICE OF RESEARCH AND MONITORING

ENVIRONMENTAL PROTECTION AGENCY

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Abstract

This report describes process changes and waste treatment, recovery, and reuse facilities installed by Volco Brass and Copper Company, Kenilworth, New Jersey. The plant produces 75 tons of wire per day.

An electrolytic system was installed to recover copper from the spent primary pickle solution and to regenerate the sulfuric acid for reuse. A hydrogen peroxide bright pickle replaced the chromate and fluoride bright pickles previously used. Copper from the bright pickle is also recovered in the electrolytic system. The electrolytic copper is reused on location in casting. An integrated copper treatment system was installed to treat bright pickle drag-out. Sludge from the integrated system is recovered for sale. Rinse water consumption was reduced from 150 gpm to 10 gpm. Former discharges of chromium, ammonium, and fluoride ions have been eliminated. Cost and operating data and effluent analyses are presented.

This report was submitted in fulfillment of Project No. 12010 DPF under the partial sponsorship of the Industrial Pollution Control Section, O R & M, of the Environmental Protection Agency.

Key Words: Peroxide pickling, chromate pickling, bright pickle, oxidizing pickle, brass mill wastes, wire pickling, copper treatment, chemical rinsing, copper recovery, copper sludge salvage, water reuse, pickle regeneration, electrolytic recovery, by-product recovery.

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SECTION I

CONCLUSIONS

1. Continuous electrolysis of the brass primary pickling solution regenerates the sulfuric acid pickle and recovers copper as high-purity metallic copper.

2. A peroxide bright (secondary) pickle has been successfully substituted for the conventional dichromate and dichromate-bifluoride bright pickles previously used for copper and copper alloy pickling.

3. Elimination of "lubricant shedding" chromate films has resulted in a 50% increase in die life in the first draw following pickling.

4. Installation of a non-dichromate bright pickle permits the economic recovery of metallic copper from the bright pickle and the recovery of a salable cuprous oxide sludge from the integrated waste treatment system.

5. Metallic copper can be recovered from the primary pickle and from the peroxide bright pickle in one common electrolytic copper recovery unit.

6. The integrated copper treatment (chemical rinsing) system to treat bright pickle drag-out also eliminates lubricant breakdown resulting from acid drag-in and reduces the number of coils requiring re-pickling due to staining.

7. "Chemical rinsing" plus water reuse were combined to reduce water consumption from the previous 150 GPM to 10 GPM.

8. The plant produces an effluent containing approximately one mg/l of copper or zinc ions and about 10 mg/l of suspended solids.

9. "Complete treatment" resulting from chemical rinsing, plus elimination of chromate and ammonium bifluoride usage, permits discharge to a storm sewer, thereby avoiding sanitary sewer rental charges.

10. Costs for current pickling, waste treatment, and recovery processes are $156 per day (operating) or $194 per day (operation plus amortization of capital investment in waste treatment and recovery facilities), as compared to $195 per day for the pickling processes and waste disposal methods formerly used (no waste treatment).

11. Estimated costs for the former pickling processes and an assumed treatment system (conventional) to treat spent solutions and dilute rinses would have averaged $386 per day (operating) or $540 per day (operating plus amortization).

12. Current pickling plus waste treatment and recovery costs are the same cost per ton of wire ($2.59) as the processes and waste disposal methods formerly used and compare with $7.20 per ton based on a conventional waste treatment design.

13. Current waste treatment and recovery costs (including amortization) amount to $46.72 per day or $0.62 per ton of wire product.

14. Based on an average "value added" by the manufacturing process of $800 per ton of copper or copper alloy wire, the current waste treatment and recovery costs (operating plus amortization) amount to 7.8 cents per hundred dollars of value added, or .078 percent of "value added."

15. The primary pickle bath (1,000 gal.) which was formerly disposed of monthly because of contamination, is no longer dumped with the installation of the new system.

16. The bright pickle bath (1,000 gal.), which was formerly disposed of weekly, is also no longer dumped with the installation of the new system.

SECTION II

RECOMMENDATIONS

Copper is recovered from both the primary and secondary pickles in its most valuable form, i.e. as electrolytic copper metal, whereas by-product copper recovery from waste treatment practices is in the form of a wet cuprous oxide sludge.

In view of the greater economic value of metallic copper, refiner apathy toward purchasing and refining copper sludge, and sludge shipping charges, it is felt that additional laboratory and pilot work is warranted. This work would be thus directed at the recovery of copper contained in the sludge in its ultimate form, as high-purity electrolytic copper.

One approach to consider would be the solubilization of cuprous oxide (insoluble in sulfuric acid) in muriatic acid, followed by the addition of sulfuric acid for the crystalization of the dissolved copper as cupric sulfate. The existing crystal filter and electrolytic copper recovery system would then be used for the ultimate recovery of the copper as metallic copper.

SECTION III

INTRODUCTION

The Volco Brass and Copper Company in Kenilworth, New Jersey, is a typical copper and cuprous alloy wire mill. Some of the products may be considered unique, but in general, the operation is typical. The plant processes copper and alloys of copper, such as various brasses, phosphor bronze, and German silver (an alloy of copper, nickel, and zinc). Approximately 75 tons of wire are produced per day, but since all materials go through the pickling process at least three or four times before the manufacturing is completed, the pickling process handles at least 250 tons per day of various wire gauges. The thinner the wire, the larger the surface area per ton of metal processed.

Production Operations

Copper and cuprous-alloy wire is produced in a wire-drawing operation where basically the wire is pulled through a succession of smaller diameter dies to provide the desired final gauge. The starting point in the case of copper is hot-rolled rod which the company purchases. The rod is produced by successive reductions from a metal billet, which is maintained hot enough through the rolling operation to allow plastic deformation to occur. The hot rolling results in a continuous coil of metal rod rolled to a uniform round dimension. After the hot rolling is completed, the continuous rod, which may be from 5/8" to 1/4" in diameter, is allowed to slowly cool to room temperature. This slow cooling effectively anneals the wire to a soft condition suitable for cold forming. The high temperatures required for hot rolling and/or extrusion, as is the case for alloy rod, causes the formation of oxide coatings or "scale" on the surface during the rolling, and/or extrusion, and cooling. Before the rod is further processed in cold rolling or drawing, it is necessary to remove the adherent scale in a pickling operation such as is shown in Figures 1 and 4. The pickling acids dissolve and remove the oxide coatings.

A soap-type lubricant is then applied to the surface and the rod is drawn through dies to reduce the rod to wire (Figure 5). Depending on the alloy, the cold forming develops a metallurgical condition recognized as hardness and embrittlement so that usually the drawing operation cannot be carried further than 50-80% reduction of the original diameter. At this stage, the wire has to be annealed to relax the strains developed in the body of the metal. Annealing causes the metal crystals to go through a transformation, called re-crystalization, which makes the metal soft and malleable again and allows further cold drawing. During the annealing state, the surface of the metal may again oxidize even though the atmosphere during the heat treatment is controlled by excluding oxygen or maintaining a reducing atmosphere. Some of the oxidation may be due to the vaporization of the lubricant oils that were left on the surface after the drawing operation. As a practical result, it is necessary to pass the coils of wire through the same acid treatment again to remove the oxides formed during the annealing operation. In this manner then, the same metal may be acid pickled three to four times before a finished wire product is produced. The number of pickling steps will depend on the extent of gauge reduction; i.e., the finer the wire, the more often the cleaning steps will be repeated.

The conventional pickling system uses a hot sulfuric acid solution of about 10-25% sulfuric acid by volume. This acid is capable of dissolving the cupric oxide and the oxides of the various alloying elements in a uniform manner and without undue attack on the basis metal. One serious shortcoming of this conventional pickling is that the black, cupric oxide scale is reduced during the reaction to the cuprous oxide state which is not soluble in sulfuric acid. As a result, the pickled rod is covered with an adherent cuprous oxide dust film called in practice "red copper dust." Any oxide dust remaining on the surface may become drawn into the body of the wire in the subsequent wire-drawing operation and thereby reduce the conductivity and the tensile strength of the wire. Also, some of the cuprous oxide dust falls into the lubricant that is applied and causes dust contamination of the lubricant oil and subsequent deterioration due to metal soap formation in the lubricant. To remove this cuprous oxide dust, many of the wire mills use a subsequent oxidizing acid cleaning system which will dissolve and remove the cuprous oxide. Such acid processes are based on chromic acid-sulfuric acid formulations; chromic acid-ammonium bifluoride mixtures; or nitric acid solutions as an oxidizing bath to remove the tenaciously adhering cuprous oxide film. The Volco Brass and Copper Company chose instead a new approach to solving this problem.

Past Practice

Prior to this project, the company utilized either of two types of secondary pickles following the hot sulfuric acid primary pickle. These secondary pickles consisted of the sulfuric-chromic acid or the ammonium bifluoride-chromic acid formulations. Since the surface area processed was large, the rinsing requirements between the various process steps was important. The waste water carried, in a dilute form, the constituents of the concentrated process solutions, such as sulfuric acid, chromic acid, ammonium bifluoride, and the salts of copper, zinc, tin, nickel, phosphorous, etc. The total flow rate was approximately 150 gallons per minute.

Waste disposal requirements arose from the necessity to dispose of spent pickling solutions and the rinse waters from the rinsing operations which followed the various cleaning steps. Disposal practice consisted of contract hauling of spent pickle concentrates at a fee of eight cents per gallon plus labor charges and disposal of rinse waters to the sanitary sewer for a fee of $0.25 per thousand gallons. The latter practice, however, had to be stopped when the company was advised that their effluent had been independently sampled, analyzed, and considered unacceptable by the Rahway Valley Sewerage Authority because of possible adverse effects to their Secondary Treatment Plant and processes.

It is noteworthy that prior to this sanitary discharge, the company had depended on cooling water dilution for treatment of their pickle rinses prior to discharge to the storm sewer. This prior practice was stopped after consultation with the New Jersey Health Department.

Having been excluded from both the storm and sanitary sewers, a new solution was now sought from outside professional help in order to protect community interests and to avoid court action and possible closure.

The Pollution Problem

Chemical treatment of high-volume, low-concentration rinse waters can be used to precipitate copper and to neutralize acids (1→5). However, chemical treatment following the use of the ammonium bifluoride-chromic acid pickling system would be only partially effective. Fluorides cannot be precipitated in a conventional manner to yield an effluent containing less than 12-15 ppm fluoride. In addition, the ammonia complexes the copper to form copper ammonium sulfate which cannot be easily precipitated. Two additional problems encountered in chemical treatment of rinse waters from metal finishing operations are effluent clarification and sludge handling. It is difficult to clarify the effluent to meet aesthetical requirements and to maintain low levels of suspended solids of metallic origin. The second problem is related to the volume of sludge generated, its drying, and its disposal (6). Precipitated metal hydroxides and the chromic hydroxide, which would result from the chromic acid type pickling system, yield very thin slurries containing not more than 0.5% dry weight of solids. Thus sludge concentration would require an excessive investment in equipment, maintenance, and labor costs to handle such low density sludges. Moreover, since the plant is located in a relatively congested area in Kenilworth, New Jersey, large tracts of land are not available for waste treatment purposes, such as are required for sedimentation basins and sludge drying beds when using a conventional waste treatment design.

Current Practice

To avoid these processing and waste treatment problems, the company installed a hydrogen peroxide bright pickle, an integrated system for drag-out treatment before dilution, and water and waste recovery systems. These facilities and the reasoning behind this selection are described in the following section.

SECTION IV

DISCUSSION

The cost of chemical treatment of dilute rinses, as originally proposed by Volco, could easily have been the most costly operation in the entire manufacturing process. The voluminous waste sludges that would have been generated would not have been amenable to economical recovery.

Experience with metal finishing waste treatment in various phases of plating and cleaning operations has shown that process modifications can sometimes be made to reduce the waste treatment problem to a reasonable level (7). Laboratory investigations and pilot plant studies in this plant indicated an opportunity to reduce costs by making process changes and by providing more extensive water treatment, reuse, and recovery facilities. The costs to be incurred by using more expensive chemicals for the cleaning process and for waste treatment could be off-set by recovering the significant quantities of metals that were previously lost in plant wastes. An additional objective to be considered to accomplish further cost reductions was the reduction of water consumption to 10% of what it had previously been to allow reduction in the size of the final treatment equipment and to reduce the water bill.

The process changes selected were far reaching and had to aim first for an improvement in the quality of the material in process and under no circumstances a reduction in quality. The innovations had to be accepted by the operating personnel which may be the greatest difficulty in view of the fact that most of the processes previously in use were based on unchanged practices going back to the turn of the century. Operators typically dislike change, especially if it requires closer analytical control of the processes to be utilized as compared to a minimum of control that is the usual practice throughout the country in such pickling operations.

Schematic flow diagrams are used to permit a rapid comparison of the installed system design (Figure 3) with a typical conventional pickling waste treatment design (Figure 2). A schematic of the previous pickling operation, having no waste treatment or recovery operations is shown in Figure 1.

Pictures of the present recovery and waste treatment installation and equipment are shown in Figures 8 through 13.

Primary Pickling Process Improvements

The hot sulfuric acid pickling system as used on copper and copper alloys is basically a good, fast, and economical solvent for the various oxides to be removed. It has the advantage of not attacking the unoxidized base metal to any significant extent, even if the work is allowed to be left in the pickling solution for hours. The removal of cupric oxide is based on the following reaction:

$$CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O$$

CuO	H_2SO_4	$CuSO_4$	H_2O
Cupric Oxide	Sulfuric Acid	Copper Sulfate	Water

The only disadvantage, as was mentioned earlier, is the fact that cuprous oxide is generated during the pickling process when the sulfuric acid as an electrolyte does not hinder the electrochemical reaction occurring between the metallic copper surface and the cupric oxide, the result being the formation of an insoluble cuprous oxide dust on the metal surface, which is not removed by the sulfuric acid.

Frequent dumping of the sulfuric acid pickle is usually necessary due to the increase in copper content, causing another electrochemical reaction on the brass surface that results in a metallic copper deposition, while the zinc from the brass is going into solution. It was thought that a continuous electrolytic removal of the copper would solve this problem and at the same time maintain a low copper concentration in the pickle acid and permit the most economical recovery of copper that is accumulating.

Similar electrolytic copper recovery systems were used earlier, but only in systems where only pure copper material was processed. In view of the harmful effects of the copper content of the pickling solution on brasses, most such pickling acids are dumped too frequently to allow the recovery of metallic copper by electrolysis. Another objection by the Trade to electrolytic recovery of copper from such pickling systems was that the zinc, tin, nickel, lead, etc., metallic content would interfere with the successful operation of an electrolytic recovery system. Our investigation has shown that electrolytic recovery of copper in an economical manner is possible, provided the cathode current density for electrolysis is kept within the range of 5 to 10 Amps/ft^2. Experience indicates that the copper concentration can be maintained at a constant low level of 15 gm/l so that the electrochemical plating-out of copper can be avoided on brass surfaces. It is therefore possible to avoid frequent dumping of the simple and economical sulfuric acid pickling solution. More importantly, it is possible to recover economically the copper that is accumulating and it is assumed that dumping may not be required, except at very infrequent intervals, such as two to three years, when the accumulation of zinc, nickel, tin, lead, etc., could be detrimental. The electrolytic copper recovery cell used to accomplish these objectives is shown in Figures 8 and 12.

Secondary or Peroxide Bright Pickling

The so-called "red copper dust," cuprous oxide, that cannot be removed in the sulfuric acid pickle, and which is to some extent formed during the pickling operation, has to be removed for efficient operation and for the best quality of product. Since the chromic-acid-type oxidizing acids can be harmful for wire drawing, create excessive die wear, form chromate salts which contaminate the copper values to be recovered, and on the other hand, nitric acid would create an air pollution problem, a new pickling process has been developed in which the oxidizing conditions are provided by inclusion of hydrogen peroxide in the make-up. The sulfuric acid bright pickle following the pre-pickle contains only sulfuric acid, 2-5% hydrogen peroxide, and stabilizing agents. The breakdown product of hydrogen peroxide is water; therefore this solution does not ever require dumping. The dissolution of the "red copper dust" in the peroxide pickle is based upon the following reaction:

$$Cu_2O + H_2O_2 + 2H_2SO_4 \rightarrow 2CuSO_4 + 3H_2O$$

Cu_2O	H_2O_2	$2H_2SO_4$	$2CuSO_4$	$3H_2O$
Cuprous Oxide	Hydrogen Peroxide	Sulfuric Acid	Cupric Sulfate	Water

The cupric sulfate that is formed in the pickling process can be periodically removed by simple crystalization and the cupric sulfate crystals can be added to the electrolytic copper recovery system or can be sold separately as a by-product.

The hydrogen-peroxide-containing bright pickle met all the requirements with regard to appearance of the finished product and it is yielding the cleanest copper or copper alloy metal surface that we have encountered. The cost of the hydrogen peroxide, which is consumed as cuprous oxide is dissolved, is offset by:

(a) Recovery of the copper;

(b) Elimination of the need to purchase chromic acid;

(c) Saving of the waste treatment costs with chromic acid and sludge handling that it would entail;

(d) Elimination of the frequent dumping of the process solution, thereby simplifying scheduling needs; and

(e) A surface far better for wire drawing, avoiding the detrimental after-effects of the chromic acid.

Production work loads of wire pickled in the peroxide bright pickle are shown for both intermediate wire (Figure 6) and fine wire (Figure 7).

Integrated Copper Treatment System (10)

The bright pickle is followed by a chemical treatment rinse that precipitates the copper and other metal salts dragged out of the pickling solution. The treatment solution is recirculated between the treatment wash tank and a reservoir tank. The reservoir tank serves the purpose of providing a larger solution reserve to avoid fluctuation of chemical concentration and as a settling basin for the precipitated copper and metals (8). The copper is precipitated in this system as cuprous oxide, a dense, reddish-brown powder with no occluded water. The sludge contains 50% dry weight in comparison to the standard neutralization systems where cupric hydroxide is precipitated with a sludge containing a dry solids weight of not more than .5%. The sludge volume actually compared to the standard neutralization system is less than 1%.

A high sludge density results from two mechanisms at work in the integrated treatment system. The first mechanism is chemical, wherein the drag-out is neutralized under the most desirable chemical conditions; that is, only concentrated acid drag-out is treated in the chemical rinse. In this manner, no dilution occurs prior to neutralization and thus the formation of light, hydrated flocculent metal hydroxides is avoided. Secondly, beneficial sludge compaction and aging are gained in the treatment reservoir as a result of new sludge contacting old sludge in the recirculated treatment system. The dense cuprous oxide resulting from this integrated treatment can be returned to the refiners without even filtration, just as the by-product of wet sludge. The dry weight of this sludge contains 86% copper.

The chemical rinse making up the integrated waste treatment system solution is a simple solution of caustic soda, soda ash, and a reducing agent, with no expensive chemical content. The pH controller automatically adds fresh chemicals whenever required.

The neutralization of the sulfuric acid drag-out is based upon the following reaction:

$$H_2SO_4 + Na_2CO_3 \rightarrow Na_2SO_4 + CO_2\uparrow + H_2O$$

The reaction between the reducing agent and the cupric ions at the pH involved is best represented by the following reaction:

$$4Cu^{+2} + N_2H_4 + 4OH^- \rightarrow N_2\uparrow + 4Cu^+ + 4H_2O$$

Since the cuprous (Cu^{+1}) ions are insoluble at a pH between 8 and 9, the reaction goes to completion with the complete removal of copper.

As sodium sulfate accumulates in this solution, some solution has to be periodically dumped, and to avoid batch dumps, a small volume of sodium sulfate solution is continuously discharged with the rinse water effluent. The sodium sulfate concentration is maintained in the range of 100-120 g/l.

Water Reuse

The chemical rinse accomplishes the main function of the water rinse, which is neutralization and elimination of acid on the wire. Therefore the following water rinse has to only remove excess alkalinity; no acid, and only minimal quantities of copper, enter this system. A rinse water effluent with less than 1 ppm copper content is easily achieved (9). If necessary, the copper concentration in the effluent can be maintained at one-tenth of this value.

Rinsing of coiled intermediate wire, as shown in Figure 6, had been a serious problem in the past. Hand spraying by the operators by high-pressure hoses using 150 GPM water was the previous processing method and the rinsing of each coil of wire consumed about one-half minute of time. Since there were 6-10 coils of wire on one loadbar, each load that was processed through the pickling system took 3-5 minutes for rinsing. Rinsing of fine wire ("shipping wire"), racked on loadbars as shown in Figure 7, consumed even more time. After the chemical rinse, on the other hand, a 30-second immersion or dip rinse is all that is required.

Equally important, the chemical rinse by itself has reduced water consumption to one-third of the volume of water needed without the copper treatment system. For even greater economy, a water reuse system was installed to permit the reuse of 80% of the total rinse water flow in recirculation. In operation, the rinse waters are collected, adjusted in pH, and are clarified for removal of hard water constituents prior to pumping back to the pickle line (Figure 13). From a maintenance standpoint, it is anticipated that the settling tank will require only annual desludging in view of the minor sludge load contributed by the hard water constituents contained in the 10 GPM fresh water input into the reuse water system.

The combined effect of chemical rinsing, plus water reuse, results in a spectacular water savings. The total effluent water discharged is approximately 10 GPM, compared to 150 GPM consumption which was the case previous to waste treatment. In summary, the waste water is high-quality water (Table 10) and is suitable for reuse for rinsing purposes back in the process. The main purpose of the 10 GPM effluent is to serve as "blow-down" of the water reuse system, thereby maintaining the dissolved solids level at an optimum value.

Economic Evaluation and Effluent Comparison

The economic data resulting from this study is detailed in Tables 1 → 3; "previous costs" before the waste treatment and recovery installation, being based on historical records over a one-year period, whereas "current costs" were based upon present-day practices. Estimated costs associated with a conventional waste treatment design for the given Volco pickling operation were included in the tabulated cost comparisons to permit a meaningful comparison (Tables 4 → 7). The cost of amortizing these installations is reflected in the cost comparisons in Table 8 and 9. The final effluent quality, previous and current, are compared in Table 10.

SECTION V

ACKNOWLEDGEMENTS

Supervision of the waste treatment and recovery installation and operation was provided by Volco Brass and Copper Company personnel, Mr. Al Izzo, Mr. John Ligenza, and Mr. Maxwell Gilbert.

Leslie E. Lancy, Ph.D., President of Lancy Laboratories, Division of Dart Industries, Inc., Chemical Group, Zelienople, Pennsylvania, supervised the design of the waste treatment and recovery operation and the preparation of this report. The report was prepared by Mr. Charles A. Forbes.

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SECTION VII

APPENDICES

Part A

Tables 1 through 11

Part B

Figures 1 through 13

TABLE I

Primary Pickle Bath Composition and Operating Conditions

Item	Previous	Current
Sulfuric Acid	10-25% Vol.	10-25% Vol.
Temperature	125-160° F	125-160° F
Alternate Primary Pickle		
Sulfamic Acid	8-12 oz./gal.	Use discontinued
Temperature	125-160° F	Use discontinued

TABLE IA

Primary Pickle Acid Purchases and Costs

Material	Previous Operations			Current Operations Dollar Cost
	Tons per Year	Annual Cost	Avg Daily Cost	
H_2SO_4 66° Bé	70*	$2,736*	$10.90	0 (acid is continuously regenerated)
Sulfamic Acid	18	5,235	18.10	0 (use discontinued)
Total		$7,971	$29.00	0

* A detailed breakdown of historical sulfuric acid purchase records is as follows:

25 Ton 66° Bé Sulfuric Acid at a purchased cost of $925 plus
45 Ton DuPont "Duclean #1" (Inhibited Sulfuric Acid) at a purchased cost of $1811

TABLE IB

Primary Pickle
Spent Acid Dumping Cost

Item	Previous Operations Annual Cost	Previous Operations Avg. Daily Cost	Current Operations Dollar Cost
Haulage charge ($.08/gal.)	$960	$3.84	0 (not dumped)
Associated Labor Charge	290	1.15	0 (not dumped)
Total	$1250	$4.99	0

TABLE 2

Secondary or Bright Pickle Bath Composition and
Operating Conditions

Pickling Chemical	Previous Operations	Current Operations
Sulfuric Acid	5-10% by Volume	10-15% by Vol.
Sodium Dichromate	4-8 oz./gal.	None
Ammonium Bifluoride*	4 oz./gal.	None
Temperature	Room	115-120° F
Hydrogen Peroxide (35%)	None	2-5% by Vol.
Stabilizer "BPX"**	None	2% by Vol.
Inhibitor "CPXI"**	None	2 oz./gal.
Inhibitor "CPXII"**	None	.4 oz./gal.

* In order to meet brightness requirements on certain customers' orders, an occasional addition of 4 oz./gal. of ammonium bifluoride was added to the conventional sulfuric dichromate bright pickle bath.

**Manufactured by Electrochemicals, Inc., Subsidiary of Dart Industries Inc., Chemical Group, Cleveland, Ohio, 44114.

TABLE 2A

Secondary Pickle
Purchased Acid Cost

Pickling Chemical	Previous Operations #/yr.	Previous Operations Annual Cost	Previous Operations Avg. Daily Cost	Current Operations Unit Cost	Current Operations Avg. Daily Cost
$Na_2Cr_2O_7 \cdot 2H_2O$	46,000	$7,820	$31.30	0*	0*
NH_4HF_2	1,250	312	1.25	0*	0*
H_2O_2				$1.67/gal.	$100.00
"BPX"				9.60/gal.	14.40
"CPXI"				.80/#	8.00
"CPXII"				.80/#	8.00
H_2SO_4**				.02/#	13.50
Total		$8,132	32.55		143.90

*Both the dichromate and dichromate ammonium bifluoride secondary pickles were eliminated.

**A sulfuric acid cost breakdown between primary and secondary pickles in previous operations is not available; therefore sulfuric acid cost for both purposes is included in Table IA.

TABLE 2B

Secondary Pickle
Spent Acid Dumping Cost

Item	Previous Operations		Current Operations
	Annual Cost	Avg. Daily Cost	Dollar Cost
Haulage Charge ($.08/gal.)	$3,840	$15.30	0 (not dumped)
Associated Labor Cost	1,200	4.80	0
Total	5,040	20.10	0

Note: All data in Tables 1, 1A, 1B, 2, 2A, and 2B were based on pickling operations run on a 3 shifts/day 5 days/week, 50 weeks/yr. common basis.

TABLE 3

Solution Composition and Operating Conditions For the Integrated Copper Treatment Solution

Copper Treatment Solution Composition

pH. . . . . 9.5-10.5[1].
Hydrazine (N_2H_4). . . . . 500 ppm[2].
Temperature . . . . Room

Chemical Feed Solution Make-up per 100 Gallons of Stock Solution:

Soda Ash. . . . . 200#
Caustic Soda. . . . . 25#
Hydrazine Hydrate, 85%. . . . 2-1/2 gal.

Notes:

1. Maintained in this range by automatic control instrumentation;
2. Hydrazine concentration may range from 300-700 ppm;
3. Daily sludge withdrawals are made for the by-product recovery of copper sludge as cuprous oxide.

TABLE 3A

Treatment Chemical Cost Integrated Copper Treatment System

Treatment Chemical*	Daily Consumption	Chemical Cost
Caustic Soda ($.055/lb.)	315 lbs.	$17.30
Soda Ash ($.033/lb.)	68 lbs.	2.25
Hydrazine Hydrate, 85% ($.95/lb.)	34.4 lbs.	32.72
Treatment Chemical Cost/Day		52.30

*The chemical feed solution contains caustic soda, soda ash, and hydrazine hydrate, and is fed "on demand" from an automatic pH controller for control of the copper treatment solution. (See Figure 11)

TABLE 4

Processing Cost Comparison
Daily Average Basis

Description	Previous Cost	Based On Conventional Waste Treatment Design	Current Cost Installed System Design
Primary Pickling: Sulfuric and Sulfamic Acid	$29.00[1]	$29.00	None
Secondary or Bright Pickling: Dichromate Pickle	32.55[2]	32.55	Dichromate Pickle Eliminated
Peroxide Bright Pickle			$143.90[2]
Process Rinse Water	54.00[3]	54.00[3]	3.60[4]
Total Processing Cost	115.55	115.55	147.50

Notes:

1. See Table 1A
2. See Table 2A
3. Previous rinse water consumption was 150 GPM or 216,000 gal./day. At a use cost of $.25/1000 gal., this represented a daily purchased water cost of $54/day.
4. Current rinse water consumption is 10 GPM or 14,400 gal./day, representing a purchased water cost of $3.60/day.

TABLE 5

Disposal, Chemical Waste Treatment and Recovery Cost Comparison

Daily Average Basis

Cost Item	Previous Cost	Based On Conventional Waste Treatment Design	Current Cost Installed System Design
Hauling Costs for Spent Acid Dumps	\$25.09[1]	None	None
Treatment Chemicals: NaOH, Na_2CO_3, N_2H_4	[2]		\$52.30[3]
$Ca(OH)_2$, $Na_2S_2O_5$, H_2SO_4 Polyelectrolyte	[2]	\$130.00 (est.)	
Labor: Waste Treatment Operator and Sludge Handling Cost	None[2]	86.50[4]	29.00[5]
Sanitary Sewer Cost	54.00[6]	54.00[6]	0[7]
Copper Recovery or Sav'gs (See Table 6 following)	0	0	(\$72.58)
Total	\$79.09	\$270.50	\$ 8.72

Notes:

1. See Table 1B, 2B
2. No waste treatment provided previously, except that waste acid dumps were hauled from the plant by an Industrial Waste Hauler.
3. See Table 3A.
4. Includes three operators per day or an annual operator cost of \$21,600.
5. One waste treatment operator controls the 24-hour per day operation on the day shift, annual operator cost = \$7,200.
6. Sanitary sewer rental charge is the same as the purchased water cost or \$.25/1000 gal., or \$54/day. (See Table 4)
7. Sanitary sewer rental charges are by-passed; completely treated effluent is discharged to the storm sewer.

Tables Showing Basis for
Copper and Copper Sludge Recovery Values

TABLE 6

Copper Recovery from Primary Pickle

Recovered Material	Previous	Conventional Waste Treat Design	Current Operations			
			#/day	Value	Recovery Cost[1]	Net Value Recovered
Electrolytic Copper[2]	0	0	40#	$.50/#	$1.20/ day	$18.80/ day

TABLE 6A

Copper Recovery from Secondary Pickle

Recovered Material	Previous	Conventional W. Tr. Design	Current Operations			
			#/day	Value	Recovery Cost[1]	Net Value Recovered
Electrolytic Copper[2]	0	0	46#	$.50/#	$1.40/ day	$21.60/ day

Notes:

1. The electrolytic recovery cost is based on a power cost of $.02/Kw hr.
2. The electrolytic copper is reused on location in casting operations.

TABLE 6B

Copper Sludge Recovery from Copper Treatment System

Recovered Material	Previous	Conventional W. Tr. Design	Current Operations		
			#/day	Value	Net Value Recovered
Copper Sludge	0	0	585	$.055/#[1]	$32.18[2]

Notes:

1. Based on a recent sale of 40,000 lbs. of copper sludge.

2. Future plans are based on ultimate recovery of copper in the sludge as electrolytic copper for use on location as a source of metallic copper in casting operations.

TABLE 7

Detailed Comparison of Processing, Disposal, Waste Treatment, and Recovery Costs

	Daily Average Basis - In Dollars		
	Previous	Conventional	Current
Primary Pickle Chemicals	29.00	29.00	0
Disposal by Hauling	4.99	0	0
Bright Pickle Chemicals	32.55	32.55	143.90
Disposal by Hauling	20.10	0	0
Process Rinse Water - Water Cost	54.00	54.00	3.60
Sanitary Sewer Cost	54.00	54.00	0
Integrated Copper Treatment Chemicals	0	0	52.30
Labor	0	0	29.00
Recovered Values	0	0	
Cu El. Primary Pickle	0	0	(18.80)
Cu El. Bright Pickle	0	0	(21.60)
Cu Sludge - Int. Treat.	0	0	(32.18)
Conventional Tr. Costs			
Chemicals	0	130.00	0
Labor	0	86.50	0
Total	194.64	386.05	156.22
Amortization Costs (15 yrs)	0	154.00[1]	38.00[2]
Total	194.64	540.05	194.22

Notes:

1. The cost of a conventional waste treatment installation was calculated to be $598,000. This total includes a waste treatment equipment cost of $248,000, an installation cost of $250,000, a new waste treatment building (80' x 50') cost of $60,000, and engineering fees of $40,000.

2. The installed system cost was $141,000. This total included waste treatment and recovery equipment ($42,000); installation, $61,000; engineering fees ($20,000); and a new waste treatment building cost of ($18,000).

TABLE 8

Summary Comparison of Processing, Disposal, Waste Treatment and Recovery Costs

Cost Item	Daily Average Basis - In Dollars		
	Previous	Conventional	Current
Processing Costs (Table 4)	115.55	115.55	147.50
Disposal/Treatment/ Recovery Costs (Table 5)	79.09	270.50	8.72
Amortization Costs (Table 7)	0	154.00	38.00
Total	194.64	540.05	194.22

TABLE 9

Comparison of Amortized Costs per Unit of Wire Product Daily Average Finished Wire Production of 75 Ton

A. Unit Cost Based on Processing, Disposal, Waste Treatment and Recovery Costs, Including Amortization

Cost Item	Previous	Conventional	Current
Processing, Disposal, Waste Treatment and Recovery Costs, Including Amortization (Table 7)	$194.64	$540.05	$194.22
Cost/Ton	$ 2.59	$ 7.20	$ 2.59

B. Unit Cost Based on Disposal, Waste Treatment and Recovery Costs, Including Amortization

Cost Item	Previous	Conventional	Current
Disposal, Waste Treatment and Recovery Costs, Including Amortization (Tables 5, 7)	$79.09	$424.50	$ 46.72
Cost/Ton	$ 1.05	$ 5.66	$ .62

TABLE 10

Pickling Effluent Quality and Quantity Comparison

Item (ppm, except pH)	Previous		Current				
	1/23/67[1]	7/7/67	1/25-2/5/71 Composite	2/8-2/17/71 Composite	2/17/71	5/12/71	5/13/71
pH	3.81	3.83	8.0	8.09	7.9	8.0	8.7
Cr^{+6} as CrO_3	70	96.9	No such process used		No such process used		
Cr^{+3}	27	---	No such process used		No such process used		
Cu^{+2}	124	75	.65	.50	.3	.25	.85
Zn^{+2}	374	36	.08	None	None	1.60	.30
Ni^{+2}	---	---	None	None	None	< .05	<.05
Sn^{+2}	---	---	---	---	None	None	None
Solids:							
Suspended, ppm	71.5	2.4	---	---	10	3.4	33.2
Dissolved, ppm	1551	---	---	---	---	760	814
Flow, GPM[2]	150	150	10	10	10	10	10

Notes: 1. United States Testing Company Report #90314 dated 2/10/67; all other results by Lancy Laboratories.

2. The 10 GPM, current effluent flow rate, corresponds to the freshening water input of 10 GPM into the Water Reuse System.

TABLE 11

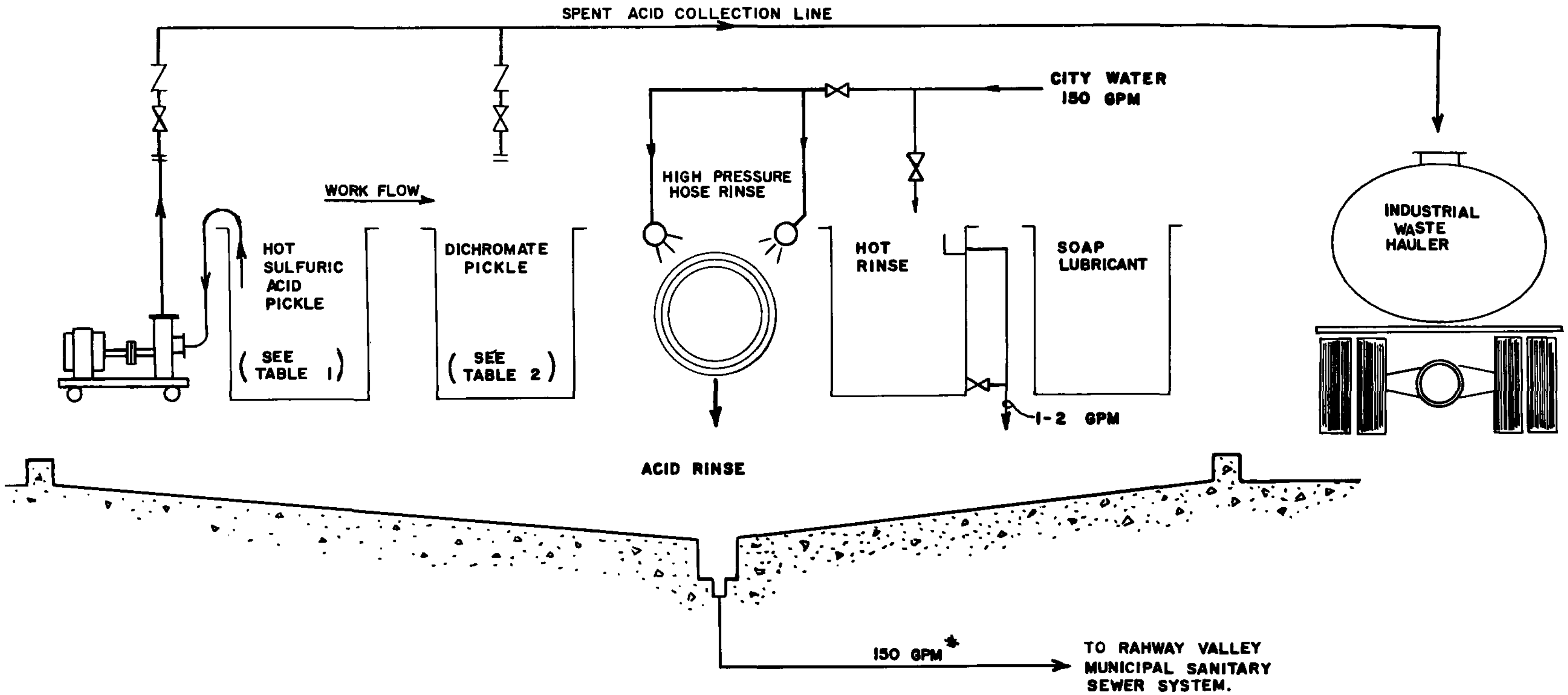
Capital Equipment Cost

Summary - Copper Recovery, Bright Pickle, and Waste Treatment Equipment Cost

Integrated Copper Treatment System. . . .	$ 10,370
Bright Pickle System.	8,720
Electrolytic Copper Recovery System . . .	5,830
Deionized Water System.	2,880
Batch Waste Treatment System.	1,920
Final pH Adjustment and Water Reuse System.	3,330
Auxiliary Equipment	4,900
Integrated Copper Treatment System (Flat Wire Mill).	4,165
	$ 42,115

APPENDICES

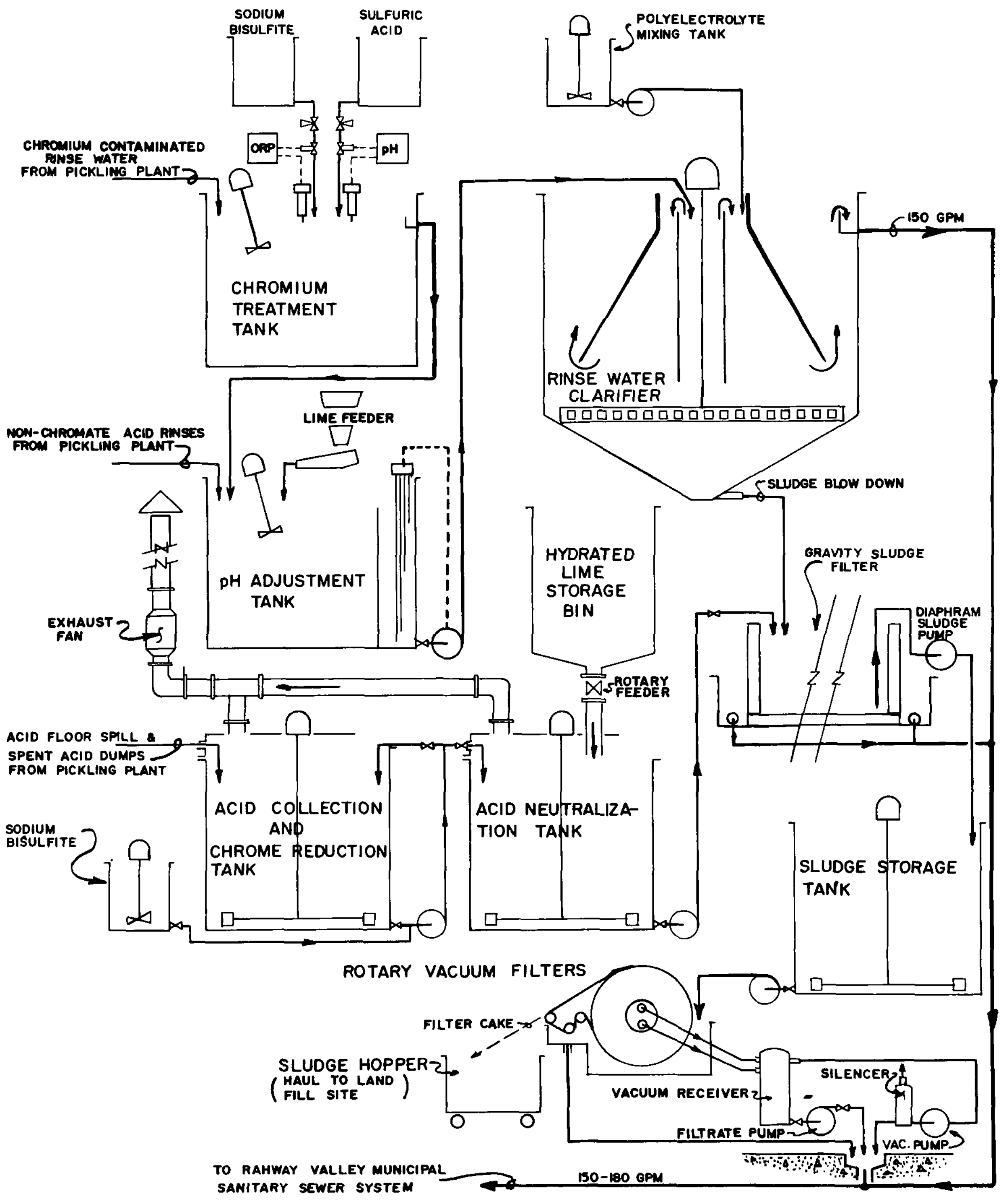
Part B



* SEE TABLE 10 FOR TYPICAL "PREVIOUS" EFFLUENT ANALYSIS.

Figure 1

Pickling Operations and Waste Disposal
Previous to this Project
Volco Brass & Copper Company



CONVENTIONAL PICKLING WASTE TREATMENT DESIGN

SCHEMATIC FLOW DIAGRAM

FIGURE 2

VOLCO BRASS AND COPPER
KENILWORTH, NEW JERSEY

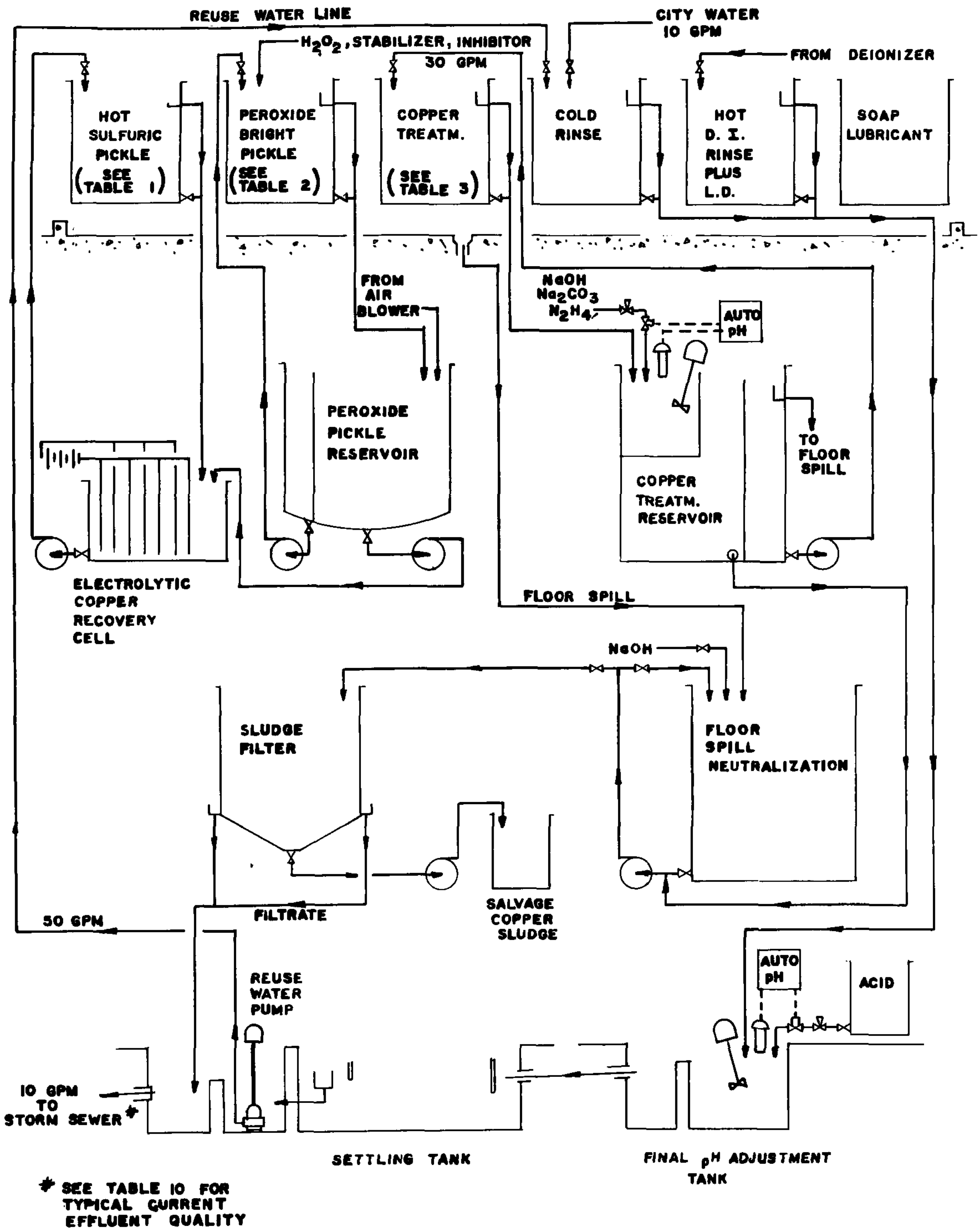
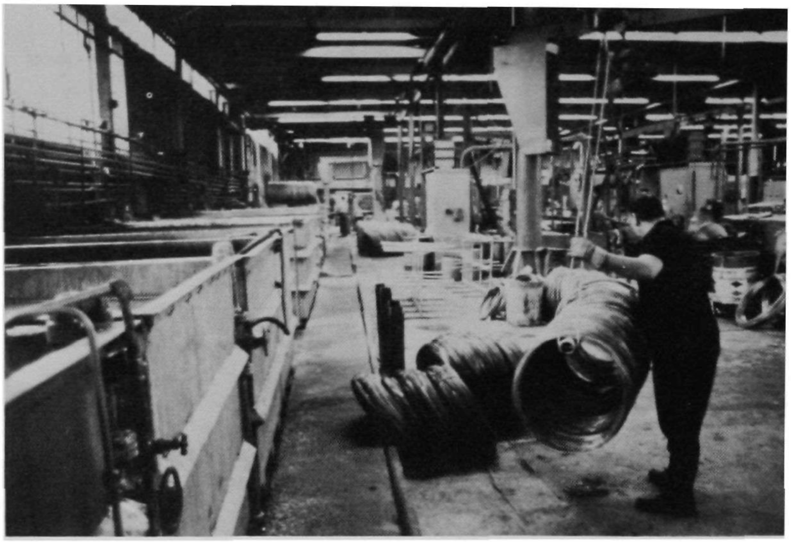
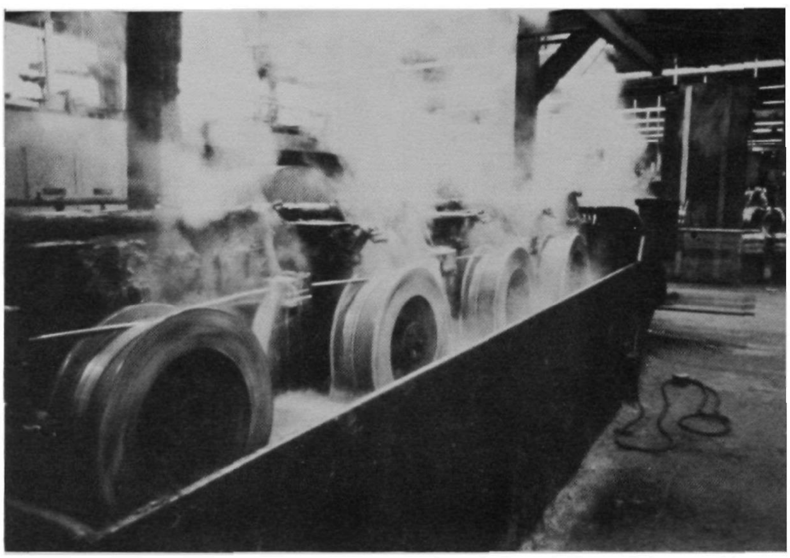


Figure 3

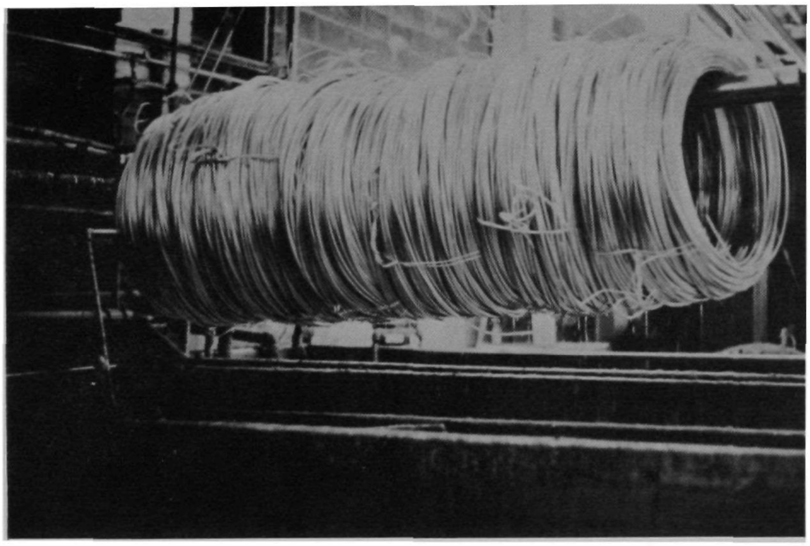
Pickling Operations, Copper Recovery, Waste Treatment, & Water Reuse System Currently in use at Volco Brass & Copper Co.



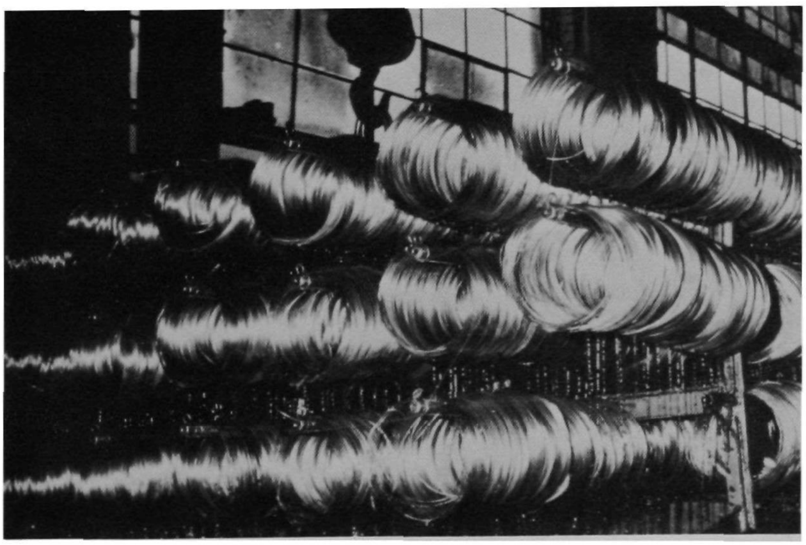
OVERALL VIEW OF VOLCO BRASS & COPPER PICKLING LINE
FIGURE 4



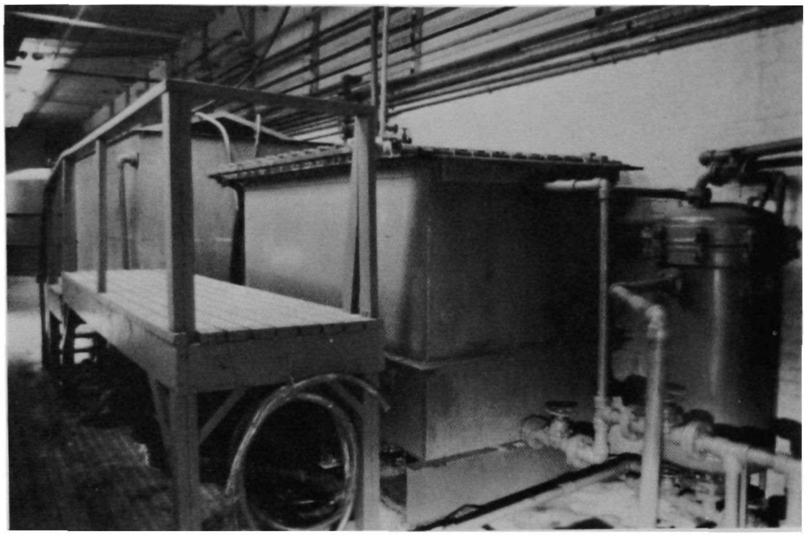
HEAVY WIRE DRAWING (.620" dia. to .400" dia., 5 Reductions)
FIGURE 5



INTERMEDIATE WIRE FOLLOWING PEROXIDE BRIGHT PICKLING
FIGURE 6



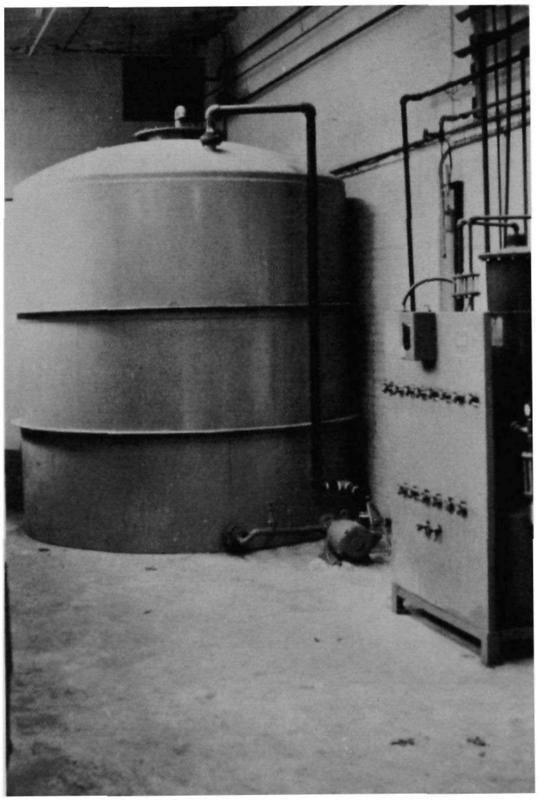
FINE WIRE FOLLOWING BRIGHT PICKLING
FIGURE 7

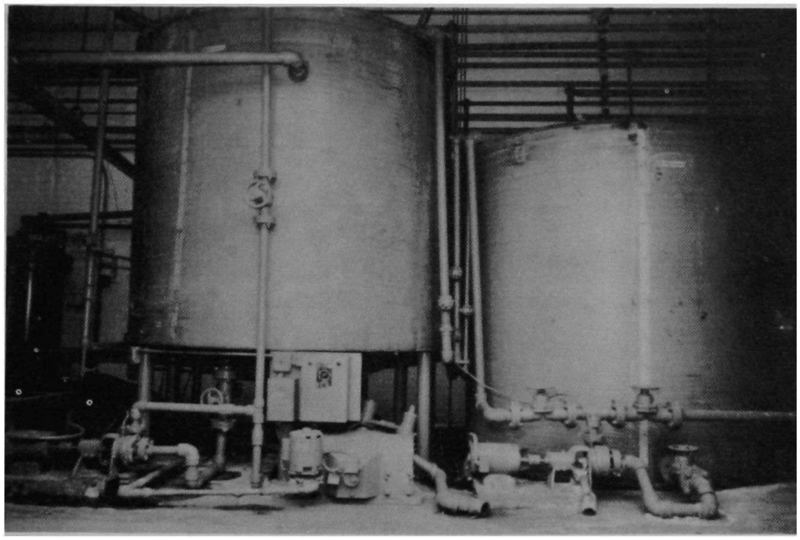


COPPER RECOVERY AND WASTE TREATMENT EQUIPMENT
(Right to Left: Crystal Filter, Electrolytic Copper Recovery Cell, Copper Treatment Reservoir, 50% Caustic Soda Supply Tank) FIGURE 8

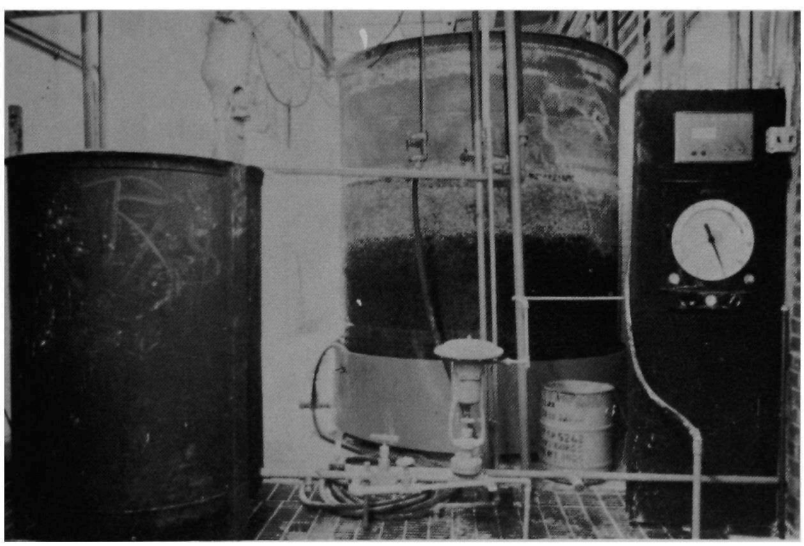
50% Caustic Soda Storage Tank and Deionizer

FIGURE 9





PEROXIDE PICKLE RESERVOIR TANK (LEFT), FLOOR SPILL NEUTRALIZATION TANK (RIGHT), STEAM CONDENSATE MONITOR AND PUMP (CENTER FOREGROUND)
FIGURE 10

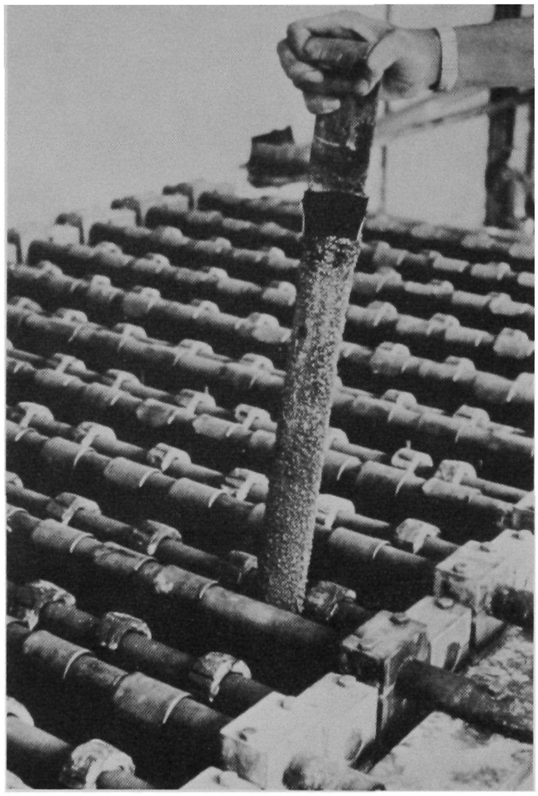


CHEMICAL SUPPLY TANK (LEFT, GRAVITY SLUDGE FILTER (CENTER) AND AUTOMATIC pH CONTROLLER (RIGHT)
FIGURE 11

ELECTROLYTIC COPPER RECOVERY CELL

(Cathode of Flattened Scrap Copper Tubing Being Removed for Inspection)

FIGURE 12



REUSE WATER PUMP INSTALLED IN RINSE WATER SETTLING TANK
FIGURE 13

1 Accession Number	2 Subject Field & Group	
W	Ø5D	**SELECTED WATER RESOURCES ABSTRACTS** **INPUT TRANSACTION FORM**

5 *Organization*

Volco Brass and Copper Company, Kenilworth, New Jersey 07033

6 *Title*

Brass Wire Mill Process Changes and Waste Abatement, Recovery and Reuse

10 *Author(s)*

Leslie E. Lancy
Charles A. Forbes

16 *Project Designation*

12010 DPF 11/71

21 *Note*

22 *Citation*

Lancy Laboratories, Inc., Zelienople, PA. 16063

23 *Descriptors (Starred First)*

25 *Identifiers (Starred First)*

Brass wire mill wastes, wire pickling, pickle regeneration, electrolytic copper recovery, chemical rinsing, copper sludge salvage, water reuse, by-product recovery.

27 *Abstract*

This report describes process changes and waste treatment, recovery, and reuse facilities installed by Volco Brass and Copper Company, Kenilworth, New Jersey. The plant produces 75 tons of wire per day.

An electrolytic system was installed to recover copper from the spent primary pickle solution and to regenerate the sulfuric acid for reuse. A hydrogen peroxide bright pickle replaced the chromate and fluoride bright pickles previously used. Copper from the bright pickle is also recovered in the electrolytic system. The electrolytic copper is reused on location in casting. An integrated copper treatment system was installed to treat bright pickle drag-out. Sludge from the integrated system is recovered for sale. Rinse water consumption was reduced from 150 gpm to 10 gpm. Former discharges of chromium, ammonium, and fluoride ions have been eliminated. Cost and operating data and effluent analyses are presented.

This report was submitted in fulfillment of Project No. 12010 DPF under the partial sponsorship of the Industrial Pollution Control Section, OR&M, of the Environmental Protection Agency.

Abstractor Edward L. Dulaney | *Institution* Industrial Pollution Control Section, ORM, EPA

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