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COPPER RECOVERY FROM BRASS MILL DISCHARGE BY CEMENTATION WITH SCRAP IRON

National Environmental Research Center
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COPPER RECOVERY FROM BRASS MILL DISCHARGE BY CEMENTATION WITH SCRAP IRON

By

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FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment -- air, water, and land. The National Environmental Research Centers provide this multidisciplinary focus through programs engaged in

- studies on the effects of environmental contaminants on man and the biosphere, and

- a search for ways to prevent contamination and to recycle valuable resources.

This report covers attempts to develop an economical way of recovering copper in brass mill discharge which otherwise might be wasted. The recovery process is non-polluting and incidentally reduces hexavalent chromium in an economical fashion.

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ABSTRACT

This report presents the results of studies of copper recovery and incidental simultaneous reduction of hexavalent chromium in brass mill discharge by passage of the discharge over scrap iron in a rotating drum. Effluent from the cementation system was treated by neutralization for the precipitation of residual copper and other metals which are settled in a clarifier and subsequently dewatered on a vacuum filter. The drum feed consisted of normal production discharge of combined pickle rinse water and spent sulfuric acid and sulfuric acid - dichromate pickle. About half of the total mill waste discharge over a period of 16 weeks was processed.

Four modes of drum operation were studied:

1. Continuous rotation
2. No rotation
3. Intermittent rotation (1 hr off - 5 min on)
4. Intermittent rotation (2-1/2 hr off - 10 min on)

Each mode was studied at 2 flow levels and 2 scrap iron surface area levels.

Data were evaluated in terms of percent cementation of available copper, excess iron consumption over theoretical, and completeness of chromium reduction.

Results indicate that the over-riding factor in the efficiency of copper cementation is the level of copper in the feed solution. Copper concentrations of over 300 ppm may yield recoveries of over 50% of the copper; concentrations below 100 ppm yield recoveries too small to be economically practical. Normal levels of hexavalent chromium are effectively reduced under a variety of conditions providing the pH is below 2.5.

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Work was completed as of November 1974.

CONTENTS

FIGURES

TABLES

ACKNOWLEDGMENTS

Charles R. Chamberlin manned the Waste Treatment Plant during the experimental runs and was responsible for all monitoring, sampling, field analytical work and data recording.

Kenneth F. Schneider performed the regression analysis of the data.

SECTION I

CONCLUSIONS

The inclusion of cementation facilities as part of the total wastewater treatment system for brass mill discharge is economically justified only if copper removal efficiencies approaching 50% can be achieved.

Cementation efficiencies high enough to be economically viable can only be achieved if the concentration of copper in the feed solution is kept at a high level; 300 ppm or greater.

A high concentration of copper in the feed solution can be maintained by water conservation measures which prevent unnecessary dilution of the waste stream.

Low pH enhances cementation of copper; a high concentration of hexavalent chromium inhibits it.

Any material likely to form a film on the surface of the iron reductant, such as oil or surfactants, may inhibit the cementation reaction. However, in practice the effect does not appear to be serious unless the contamination is gross.

A high cementation efficiency results in dissolution of considerably less EXCESS iron than a low cementation efficiency.

The mode of operation of the cementation drum and the flow/iron surface level combination have considerably less effect on the cementation efficiency than the characteristics of the feed solution. However, regression analysis of the data indicates the continuous mode of drum operation to be optimum and that flow/iron surface area and copper concentration/iron surface area ratios should be kept as small as practical.

The cemented copper can be converted to usable metal by conventional smelting and refining techniques.

The present study indicated an annual potential of approximately 77,000 pounds of copper in the waste stream, as well as an annual loading of 1,500 pounds of hexavalent chromium. Assuming the value of the copper in a usable form to be 75 cents per pound, the net annual return using 15-year amortization of equipment would be approximately:

$22,600	at 90% Copper Recovery
$16,200	at 75% " "
$ 5,200	at 50% " "
Break-even	at 35% " "

These returns DO NOT include the value of the simultaneous reduction of the hexavalent chromium which would have an annual cost of approximately $5,000 if another process were used.

Based on the results of this study the Anaconda American Brass Company will continue to utilize cementation for the recovery of copper and the simultaneous reduction of hexavalent chromium. Attempts will be made to increase the efficiency of copper recovery by in-plant water conservation measures designed to concentrate the copper in the waste streams.

SECTION II

RECOMMENDATIONS

Since the efficiency of cementation is dependent on the concentration of copper in the feed solution, means of concentration through water conservation should be explored.

Gross amounts of oil, soaps and similar film-forming materials must be removed from the waste stream prior to passage over the iron reductant. Segregation and separate disposal of such materials is recommended. Where this is not practical, gravity separation or similar pretreatment should be considered.

An alternate means of copper recovery through treatment of the clarifier sludge filter cake should be studied. This route offers potentially complete copper recovery and lower over-all waste treatment cost. The high-density clarifier sludge achieved through sludge recirculation should be especially suitable for such a process.

SECTION III

INTRODUCTION

The Valley Divisions of the Anaconda American Brass Company at Waterbury and Ansonia, Connecticut, are typical brass mills.

The Waterbury Division consists of three tube mills producing both copper and copper-alloy tube, while the Ansonia Division is essentially a rod mill which also produces some drawn copper shapes. Annual production from both divisions exceeds 100 million pounds.

Also located in the Waterbury area is the Anaconda Metal Hose Division which fabricates flexible hose from galvanized steel, stainless steel, aluminum and copper alloy strip and tube.

In all divisions, in-process material, as well as end products, may be pickled in sulfuric acid, or sulfuric acid plus sodium dichromate, or a combination of the two. Rinsewaters utilized in the process, as well as the spent pickles which are discarded, contribute copper, zinc, nickel, chromium and sulfuric acid to the waste stream; all of which must be separated or neutralized before discharge. All brass mills, and mills processing copper alloys, face similar problems in treating effluents.

To provide suitable treatment for the waste streams generated in the Naugatuck Valley Plants, the Anaconda American Brass Company has built treatment plants at Ansonia and Waterbury, each having a capacity of 500,000 gpd. Both plants are identical and utilize a unique process for simultaneously precipitating metallic copper in a recoverable form and reducing hexavalent chromium.[1]

Similar plants are in operation at Anaconda American Brass Company divisions at Toronto, Ontario and Kenosha, Wisconsin.

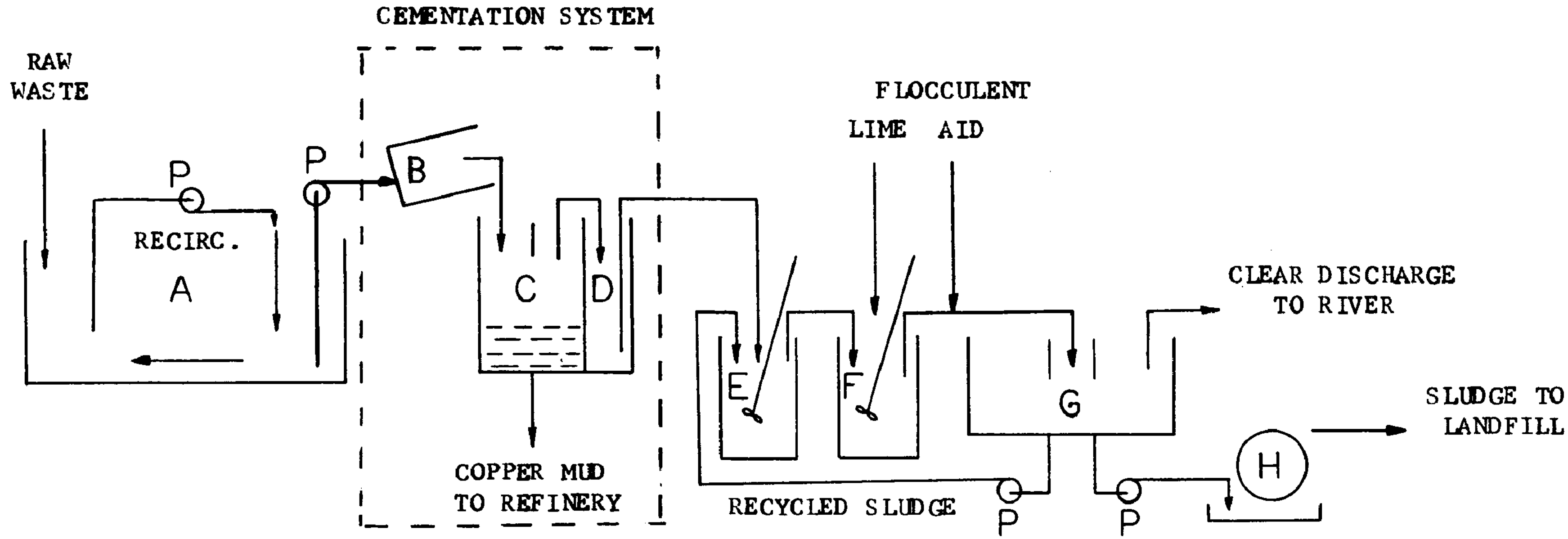
All of these plants perform in admirable fashion as far as waste treatment is concerned; however, the recovery of copper has been disappointing. Analyses of raw waste streams from the Valley Mills show the following copper potentials:

Waterbury	77,000 lbs/yr
Ansonia	75,000 lbs/yr

At current prices for copper, this is worth over $110,000 less recovery costs. Experience indicated that less than 50% of this potential was being realized.

The reason for the low copper recovery in the full-scale plant operations is not evident. A laboratory study carried out for the Connecticut Research Commission[2] and a similar study carried out for the Environmental Protection Agency[3] both demonstrated the feasibility of over 90% copper recovery, coupled with complete reduction of hexavalent chromium.

The present study was undertaken to determine the most significant factors influencing cementation efficiency under actual mill operating conditions and to determine the optimum procedure for operation of the cementation drums.



A - EQUALIZATION BASIN
B - CEMENTATION CHAMBER
C - SETTLING PIT
D - TRANSFER WELL

E - NO. 1 NEUTRALIZATION TANK
F - NO. 2 NEUTRALIZATION TANK
G - CLARIFIER
H - VACUUM FILTER

Figure 1. Schematic flow sheet for Waste Treatment Plant

SECTION IV

WASTE TREATMENT SYSTEM

GENERAL

The flow of waste material through the plant is shown schematically in Fig. 1 and the general plant layout is shown in Fig. 2.

Waste is collected and blended in a 100,000-gal. equalization basin where the pH is monitored, and adjusted to pH 2.5 or less by addition of sulfuric acid, if necessary. The blended waste is pumped to one of two revolving drums filled with scrap iron.

Passage of the feed solution through the scrap bed reduces hexavalent chromium and precipitates metallic copper. The finely divided metallic copper is carried in the stream flowing over the lip of the drum, and settles in a baffled pit.

Copper mud removed from the settling pits is air-dried to approximately 30 to 40% moisture and shipped to a copper refinery for recovery of the copper.

The overflow from the settling pit flows by gravity to a preliminary neutralizing tank where it is blended with settled sludge pumped from the bottom of a clarifier. The mixture flows by gravity to a second neutralizing tank where it is treated with lime slurry to bring the pH to 9.0. Polyelectrolyte floc aid is added and the neutral slurry passes to a clarifier where the sludge settles. The two-stage neutralization produces a dense sludge which is periodically dewatered on a vacuum filter.

The dewatered sludge has a solids content of approximately 35% and is disposed of as landfill.

The clarifier overflow meets all applicable effluent specifications and is discharged to the Naugatuck River.

The analysis of a typical discharge from the Waterbury Treatment Plant by the Connecticut Department of Environmental Protection Laboratory is shown in Table 1 on page 9. The effectiveness of the total treatment system may be judged by comparison of this analysis with the composition of the blended raw waste streams given on page 10.

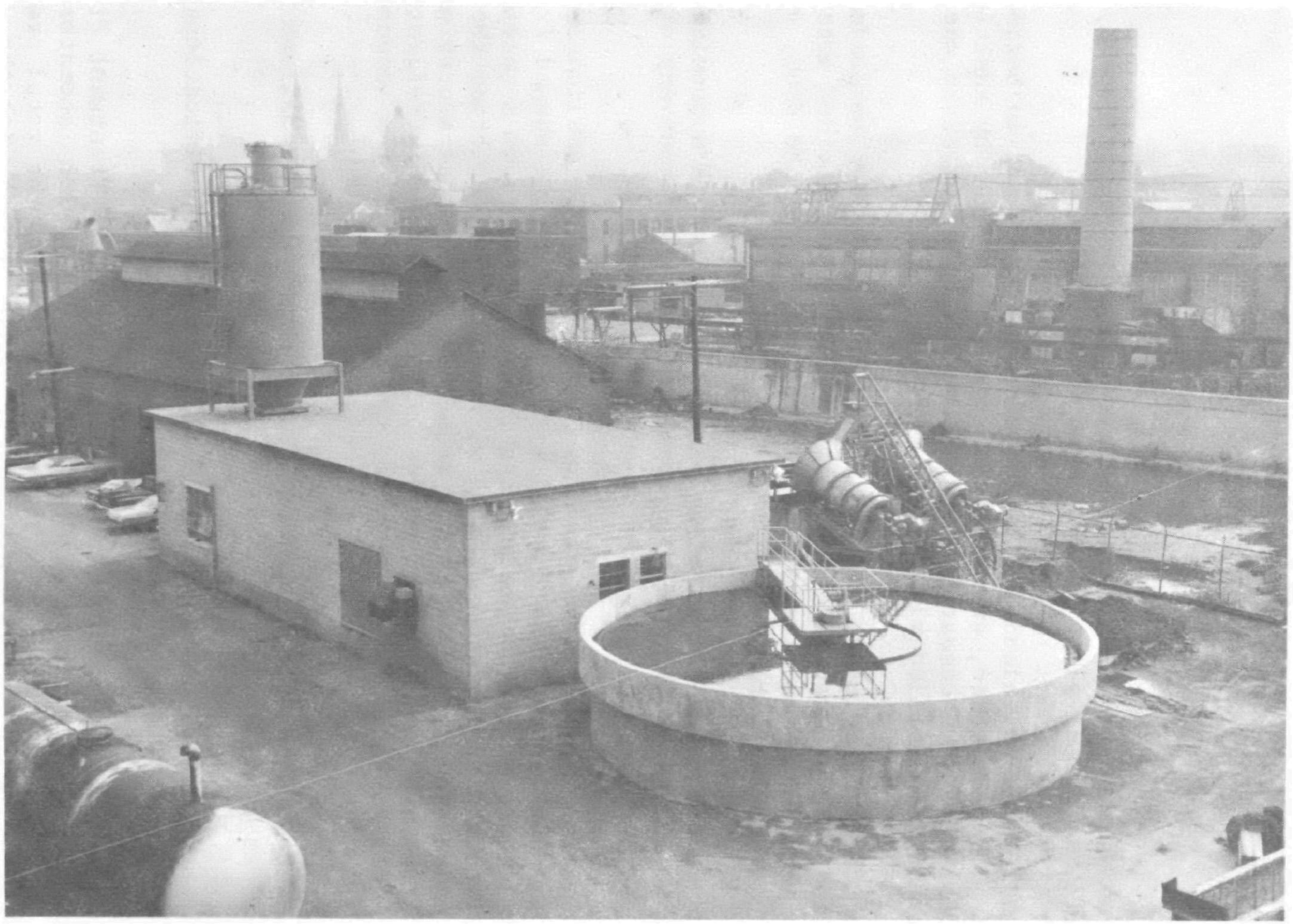


Figure 2. General view of Waste Treatment Plant

Table 1. TREATED WASTE DISCHARGE SAMPLED SEPTEMBER 5, 1974

Clarifier Effluent	Clear	
pH	8.2	
Methyl Orange Alk - pH 3.7	26	ppm
Phenolphthalein Alk - pH 8.3	0	ppm
Solids - Total	1798	ppm
- Fixed	1606	ppm
- Volatile	192	ppm
PO_4 - P	0.2	ppm
NH_3 - N	0.4	ppm
Tot Org Carbon (TOC)	6	ppm
Cyanide (CN)	0	ppm
Free Chlorine	0	ppm
Iron (Fe)	0.2	ppm
Copper (Cu)	0.3	ppm
Zinc (Zn)	<0.1	ppm
Cadmium (Cd)	<0.1	ppm
Nickel (Ni)	<0.1	ppm
Chromium - Total (Cr^T)	<0.1	ppm
Aluminum (Al)	<1	ppm

WASTE STREAM

The waste stream treated at the Waterbury Division Waste Treatment Plant consists of effluent from four mills:

1. East Tube
2. West Tube
3. Small Tube
4. Metal Hose (flexible tube)

All of these mills process copper and copper alloy tube, including pickling in sulfuric acid or sulfuric acid-dichromate solution to remove surface oxides. Effluents consist essentially of rinse water from pickling operations and the spent pickles themselves.

Although oils, alkaline cleaners, soaps, drawing lubricants and similar organic materials are not intentionally included in the waste stream, in practice small amounts of these materials do find their way into the stream and gradually form a sludge in the Treatment Plant equalization basin and occasional scum or foam on the surface.

Discharge from the East Tube Mill is collected in a sump in the mill and pumped to an intermediate lift station from which it is pumped to the Treatment Plant equalization basin.

Discharge from the West Tube Mill is collected in a sump in the mill from which it is pumped directly to the Treatment Plant equalization basin.

The Small Tube Mill is some distance away from the Treatment Plant, hence wastes are transported by tank truck and discharged into the lift station sump. In addition to sulfuric acid, dichromate and soluble metal salts this discharge may contain small amounts of hydrazine and elemental copper.

Discharge from the Metal Hose operation flows directly to the lift station. The lift station is equipped with two 1.14-klm (300-gpm) pumps which may be used singly or combined. The West Mill sump is equipped with two 0.757-klm (200-gpm) pumps which also can be used singly or in combination. It will be apparent that if all pumps are in operation a total of about 3.79 klm (1,000 gpm) can be delivered to the equalization basin. In practice the waste flow will rarely exceed half this amount.

The equalization basin is roughly 11.28 m (37 ft) long x 10.97 m (36 ft) wide x 3.66 m (12 ft) deep and has a capacity of about 453 kl (120,000 gal.). Thus, there is capacity for retaining at least 4 hours normal flow of effluent. The waste collected in the basin is blended by a 2.65-klm (700-gpm) recirculation pump.

The Cementation Drums are fed from inlets located 22.86 cm (9 in.) from the bottom of the basin. Three pumps of 0.662-klm (175-gpm) capacity feed the Drums. The pump valves are so arranged that the flow may go to either Drum or be split between them. However, not more than 1.32 klm (350 gpm) may be fed to one Drum.

The composition of the blended waste streams as fed to the Cementation Drums may vary widely as follows:

Copper	50-1300	ppm
Total Chromium	10- 750	ppm
Hexavalent Chromium	0- 40	ppm
Zinc	10- 90	ppm
Nickel	10- 35	ppm
Oil	5- 130	ppm
pH	1.5- 6.0	

The high metal and low pH values correspond with pickle dumps, whereas the lower metal values and high pH values are characteristic of dilute rinse water.

CEMENTATION DRUM

A cementation drum is shown schematically in Fig. 3.

It consists of a Type 316L stainless steel cylinder 1.372 m (4.5 ft) ID and 2.438 m (8 ft) long which may be inclined 25 to 35 degrees from the horizontal.

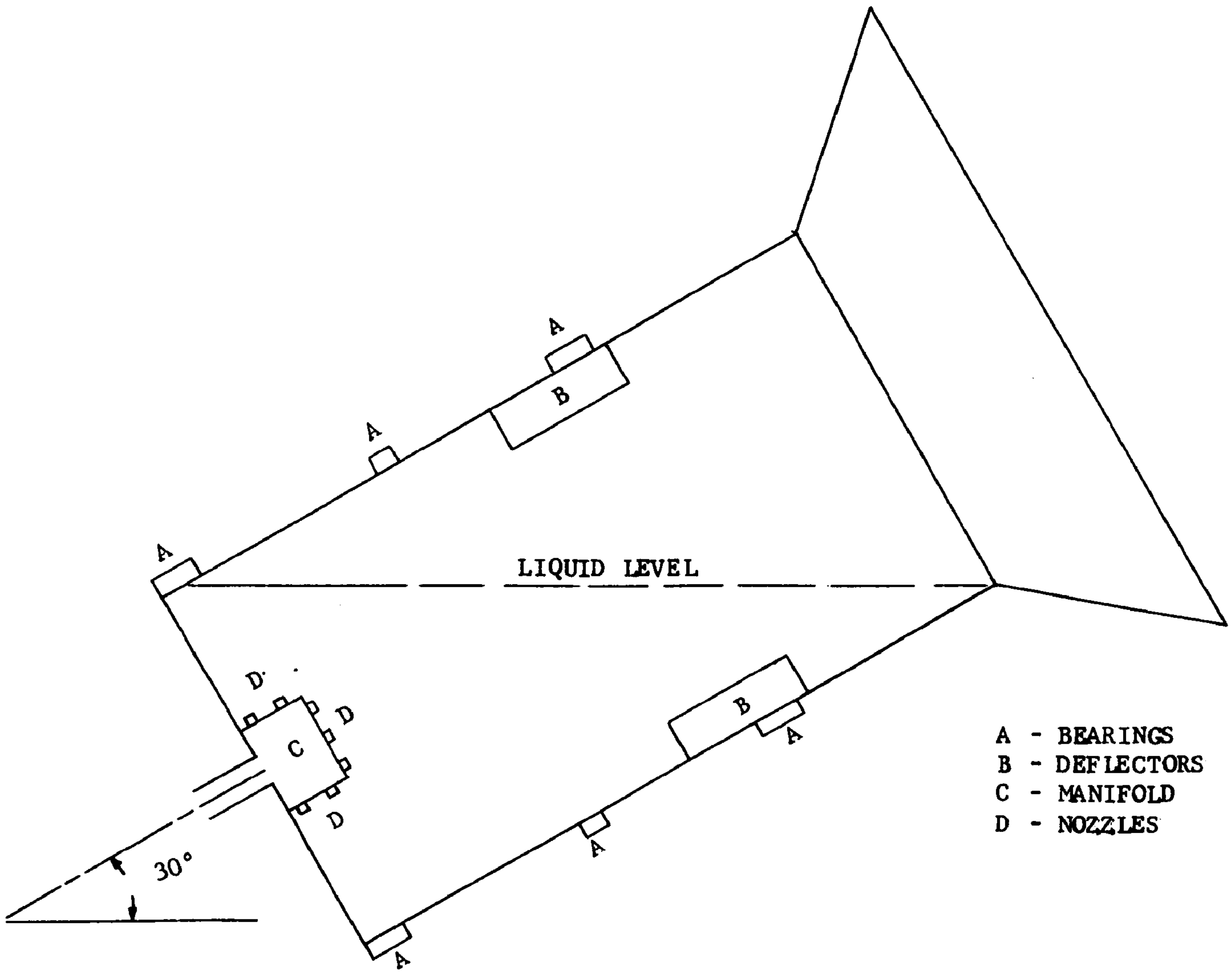


Figure 3. Schematic diagram of Cementation Drum

The influent end of the drum is fitted with a circular manifold 29.2 cm (11.5 in.) OD containing 18 spray nozzles 1.27 cm (0.5 in.) ID, 12 of which are directed in a lateral direction and 6 in a horizontal direction.

The discharge end of the drum is fitted with a flared lip which extends 64.14 cm (25.25 in.) from the cylinder and has a diameter of 2.438 m (8 ft) at the face.

The interior of the drum is fitted with four deflectors arranged to impart good tumbling action to the scrap iron charge.

A removable hatch cover approximately 50 cm x 50 cm (20 in. x 20 in.) is provided on one side of the drum for removing the scrap charge if this becomes necessary.

The drum may be rotated in a counter clock-wise direction at speeds varying from 0 to 10 RPM.

Variation in speed of rotation and angle of inclination are provided to permit optimum tumbling action for scrap iron shapes of widely varying geometrical configuration.

At an inclination of 30° the drum has a total capacity of 2.166 m^3 (76.5 ft^3). An installation normally includes two drums which may be operated simultaneously or separately. The drums are covered by U. S. Patent 3,748,124.[1]

COPPER SETTLING PITS

Each drum discharges into a settling pit of trapezoidal shape approximately 5.626 m x 2.781 m (18.46 ft x 9.13 ft) at the top, 5.283 m x 2.438 m (17.33 ft x 8 ft) at the bottom and 4.115 m (13.5 ft) deep, having a total capacity of 58.70 m^3 (2073 ft^3).

The end of the pit into which the drum discharges is segregated by a baffle which extends 1.194 m (3.92 ft) below the surface.

The discharge from each settling pit flows over a weir into a common transfer well, from which it flows by gravity to the neutralization system.

Cemented copper and other particulate matter discharged from the drum collects in the settling pit. After the pit becomes about one third full of particulate material the supernatent liquid is pumped down and the copper mud removed with a clam-shell bucket.

This is an inefficient method of removal, and settling pits in future installations will be modified so that the mud layer can be transferred to a decant storage tank at periodic intervals before it becomes too dense to pump.

SECTION V

EXPERIMENTAL PROGRAM

GENERAL

Factors known, or suspected, to influence the efficiency of copper cementation include:

1. Temperature
2. pH of feed solution
3. Concentration of copper in feed solution
4. Concentration of other metals in feed solution, especially hexavalent chromium
5. Oily material in feed solution
6. Flow rate of feed solution
7. Composition of iron contact material
8. Geometry of iron pieces
9. Surface area of iron
10. Surface films on iron, especially oil
11. Oxidation of cemented copper
12. Mode of operation of cementation drums; i.e., static, continuous or intermittent rotation
13. Geometry of settling pit
14. Flow pattern through settling pit
15. Particle size of cementate

Of these factors the only ones which can be controlled to a reasonable degree under mill operating conditions are:

1. Flow rate of feed solution
2. Surface area of iron contact material
3. Mode of operation of cementation drum

Some recent work[4] has indicated that copper previously deposited on an iron surface greatly increases the cementation rate by forming nucleii for subsequent cementation. Essentially the same conclusion was reached in an independent study of the cementation of copper on zinc.[5]

These findings led to the belief that the efficiency of copper cementation might be enhanced by leaving the scrap bed quiescent in the drum for various intervals, limiting rotation of the drum to brief periods for dislodging some of the deposited copper and realigning the scrap surfaces.

When the drum is operated without rotation it becomes essentially a plug-flow reactor, whereas with normal rotation it is a back-mix reactor.

It was decided to operate the drum in the following modes:

1. Continuous rotation
2. Static (no rotation)
3. Intermittent rotation

    A (1 hr off - 5 min on)
    B (2-1/2 hr off - 10 min on)

It was planned to study each mode of operation for one week at each of two flow levels for two iron contact surface levels. Thus, a total experimental period of 16 weeks was projected. Because of flow control problems operation in the Continuous Mode at low flow/low iron surface was repeated. Operation in the Intermittent Mode B at high flow/high iron surface was eliminated due to previous unpromising results in this mode.

Nadkarni and Wadsworth have studied the effect of ferric iron on the cementation of copper in considerable detail[6]. They concluded that ferric iron not only consumed excess metallic iron but also had a tendency to redissolve deposited copper and promote other undesirable side reactions. For this reason the percentage of ferric iron in the drum discharge was monitored each day.

It must be pointed out that there are inherent difficulties in attempting to carry out a controlled experiment under mill production conditions, since there are fluctuations in production schedules which affect the composition of the discharge and flow rates. It was found especially difficult to maintain uniform flow rates at desired levels. However, a substantial differential between high and low flow rates was fairly consistently achieved.

Occasional problems were encountered with unauthorized dumps of detergents which resulted in foaming and drawing lubricants which formed a scum on the surface of the equalization basin.

IRON REDUCTANT

The reducing medium utilized consisted of scrap punchings of low carbon steel (SAE 1009).

The material as received from the scrap dealer consisted of a large variety of configurations averaging about 0.25 cm (0.1 in.) in thickness and ranging from 0.6 cm (0.25 in.) to 7.5 cm (3 in.) in the largest dimension.

Previous experience had shown that the smallest pieces of scrap, especially disks, had a tendency to plug up the feed injection nozzles in the drum. Therefore, all scrap used in the experimental runs was classified with a metal screen having openings of a diamond configuration, the long axis being 3.81 cm (1.5 in.) and the short axis 1.75 cm

(0.6875 in.). This method of classification was found very effective in rejecting the smaller pieces of scrap.

A representative portion of screened scrap weighing approximately 6.48 kg (14 lbs) contained individual pieces as shown in Figs. 4 and 5. Data relating to the individual pieces are given in Table 2, pg. 18. The material contained a slight amount of oil equivalent to 13 g/m^2. The packing density of the screened scrap was estimated by filling a tared wooden box having a capacity of 0.0339 m^3 (1.2 ft^3) and weighing. Four trials gave an average packing density of 1540 kg/m^3 (96 lbs/ft^3).

Considering the density of 1009 steel as 7.871 g/cm^3, the packing density of the loose scrap (1.540 g/cm^3) indicates that the solid volume of the scrap is $\frac{1.540}{7.871} \times 100 = 19.57\%$ of the loose scrap volume.

The surface area per unit volume of the screened scrap was estimated by dividing the solid volume by the weighted average thickness of the individual pieces, multiplying by 2 and adding 10% for the edge area. Thus:

$$\frac{0.1957 \times 1{,}000{,}000}{0.2338 \times 10{,}000} \times 2 = 167.6 \text{ m}^2/\text{m}^3 + 10\% = 184 \text{ m}^2/\text{m}^3 \text{ (56 ft}^2/\text{ft}^3).$$

During the ninth week of the experiment, a fresh load of scrap was received. This lot had slightly different geometric characteristics because of the presence of a disk 4.1275 cm (1.625 in.) in diameter with a 1.113 cm (0.4375 in.) diameter hole in the center which had not been present in the original lot. This piece is identified as "M" in Fig. 4. Since the piece had a thickness of 0.2337 cm (0.092 in.) the weighted average thickness of the scrap was not materially changed.

The characteristics of the new lot of scrap were determined as previously described and found to be:

packing density - 199 kg/m^3 (124 lbs/ft^3)
surface area per unit volume - 238 m^2/m^3 (72.5 ft^2/ft^3).

This material contained an oil film equivalent to 8 g/m^2.

In determining intial charges for both low and high iron surface levels, the volume of scrap was estimated by multiplying the volume of the charging bucket (0.0566 m^3) by the number of bucket loads added. This was converted to weight by use of the appropriate factor. Periodic additions to the charge were measured by the actual weight of the scrap added.

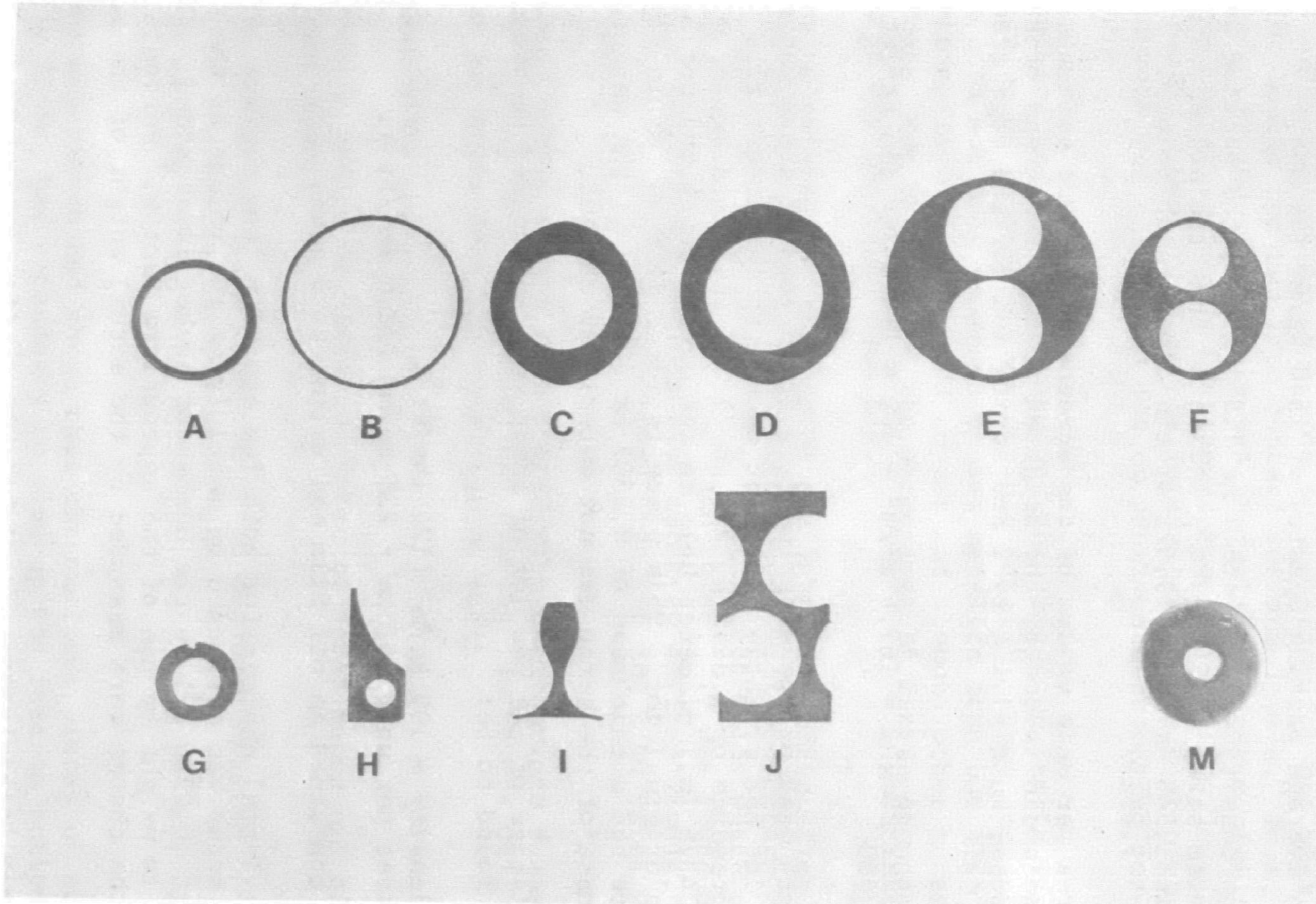


Figure 4. Typical Scrap Iron Punchings

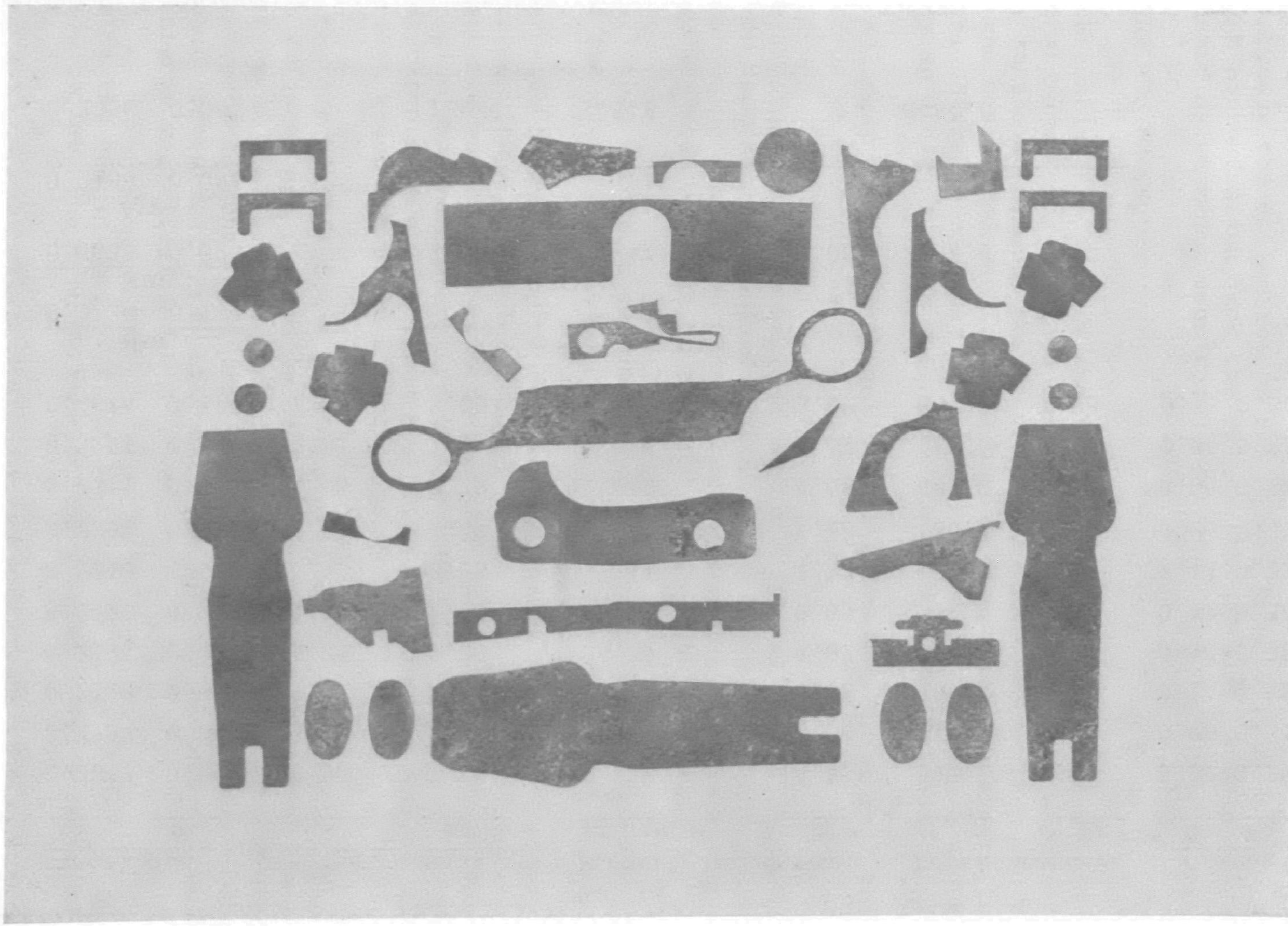


Figure 5. Miscellaneous Scrap Iron Punchings

Table 2. CHARACTERISTICS OF TYPICAL PIECES OF SCRAP IRON IN DRUM CHARGE

Type	Thickness		Greatest Dimension		No. of Pieces in Sample	Percent by Type	Total Wt, g	Percent by Wt	Composition,%		
	cm	in.	cm	in.					C	Mn	Other
A	0.2337	0.092	3.96	1.56	75	14.45	398.1	6.14	0.07	0.29	Cu 0.02
B	0.1702	0.067	5.72	2.25	95	18.30	359.1	5.54	0.08	0.31	
C	0.2108	0.083	5.41	2.13	71	13.68	1395.7	21.52	0.14	0.45	
D	0.2134	0.084	6.03	2.38	25	4.82	363.4	5.60	0.10	0.38	Pb 0.02
E	0.2032	0.080	6.83	2.69	50	9.63	1735.0	26.76	0.11	0.34	
F	0.2210	0.087	5.40	2.13	11	2.12	197.2	3.04	0.11	0.32	
G	0.2337	0.092	2.54	1.00	30	5.78	180.1	2.78	0.06	0.31	
H	0.2311	0.091	4.45	1.75	75	14.45	595.0	9.18	0.05	0.22	
I	0.3251	0.128	3.81	1.5	24	4.62	160.4	2.47	0.06	0.23	
J	0.4674	0.184	7.62	3.00	16	3.08	491.7	7.58	0.13	0.36	
	Max.										
	0.3734	0.147									
	Min.										
Misc.	0.0635	0.025		7.00	47	9.06	608.9	9.39			
	Avg.										
	0.2184	0.086									
Weighted Average	0.2338	0.092		Total	519		6484.6				

The average iron contact surface area for each run was estimated as follows: weight of iron remaining at end of previous run plus weight of iron added during run minus weight of iron consumed during run multiplied by the appropriate conversion factor.

Admittedly the estimation of the actual iron surface is only a very rough approximation, and the values thus obtained should only be considered as relative magnitudes.

OPERATING PROCEDURE

Each combination of flow and iron surface level for each mode of drum operation was run for five consecutive days, with the exception of the run in the Continuous Mode at high flow/low iron surface and the run in the Static Mode at low flow/high iron surface which were for four days. Normally each day's run was for a full 8 hours, although occasionally an early shutdown was necessitated by lack of feed.

In all runs the drum was inclined 30° above the horizontal and during periods of roation was rotated at 3 RPM.

The experimental drum was cut into the line at 8:30 A.M. each morning after recording the volume of feed which had passed through the standby drum during the period when the experimental drum was off line and feed flow adjusted as close to the desired level as possible.

Brailsford automatic samplers were set up to sample both the drum feed and the drum discharge.

Every two hours the pH of both feed solution and drum discharge was checked with a glass electrode pH meter. At the same time the drum discharge was checked colorimetrically for the presence of hexavalent chromium and the temperature of the feed solution taken. Manual flow measurements were also taken every two hours at the Parshal flume through which the plant discharge passed.

In the early afternoon a grab sample of drum discharge was taken. This was filtered and divided in half. Ferrous iron was determined in one portion of the sample by immediate titration with standard potassium dichromate and the total iron was determined in the other portion by atomic absorption. From this data the percent of ferric iron in the discharge was calculated.

During the day weighed portions of screened scrap estimated to be sufficient to keep the iron surface at the desired level were added to the drum.

At 4:30 the experimental drum was shut down and the standby drum cut in. The Brailsford samplers were shut down and the samples removed.

Specimens of the composite sample of feed were transferred to appropriate containers and sent to the laboratory for the following determinations:

Copper
Chromium[T]
Oil (Tuesday and Thursday only)
Zinc " " " "
Nickel " " " "

The hexavalent chromium in the composite was determined immediately by adding a measured excess of standard ferrous ammonium sulfate and back titrating with standard potassium dichromate.

The composite sample of drum discharge was filtered (to remove particulate copper and iron) and specimens transferred to appropriate containers and sent to the laboratory for determination of copper and iron.

Once each week a sample of copper mud was withdrawn from the top of the mud blanket in the settling pit and allowed to settle for 24 hrs, after which the supernatant layer was poured off. The density of the settled layer was determined and analysis made for moisture, copper and iron.

An attempt was made to measure the increase in depth of the mud layer each week, but this was never reliably accomplished; perhaps due to constant shifting of the surface of the layer by currents in the pit.

Twice a week a sample was taken of overflow from the settling pit and the concentration of particulate copper determined. The data were not reliable due to the ever-present possibility of including particulate copper inadvertently dislodged from the lip of the weir. For this reason the data are not included in the report.

Sludge which settled in the clarifier was normally vacuum filtered once each week. The volume of the filter cake was estimated and determination made of density, moisture, copper and iron.

Once each week representative specimens of scrap were withdrawn from the drum and examined for the nature of any film on the surface and the progress of dissolution.

SECTION VI

EXPERIMENTAL RESULTS

GENERAL

In all instances cementation efficiencies were disappointingly low. As previously mentioned, laboratory experiments have consistently shown copper recoveries of over 90%[3]. Recoveries in the present study were not only much lower, but data related to optimum conditions for recovery presented a confusing pattern. It is evident that many factors, not readily isolated, bear upon the effectiveness of copper recovery in a full-scale mill operation. One of these factors may well be the presence of oil or other film-forming materials in the waste stream, although the effect of oil did not appear marked unless the amount was gross.

The single factor which appeared to bear most heavily on the effectiveness of cementation was the concentration of copper in the feed solution. In general, the higher the concentration, the greater the percentage of recovery.

A high concentration of copper is invariably the result of a pickle dump which has the concomitant effect of producing low pH and relatively high concentrations of metal salts besides copper, such as nickel, zinc and chromium. The low pH is desirable; high concentrations of hexavalent chromium are not.

Little difficulty was experienced in reducing hexavalent chromium at any level encountered. Only on one or two occasions were traces of hexavalent chromium detected for short periods in the discharge and these were readily corrected by the addition of sulfuric acid to the drum feed.

CALCULATIONS

Because the primary criterion for judging the effectiveness of any set of parameters was the cementation efficiency attained, data were arranged according to the conditions under which maximum and minimum cementation was obtained for each series of runs. Also included in the data are the AVERAGE conditions for the series of runs and the AVERAGE cementation efficiency attained.

Note that data related to maximum and minimum cementation define the conditions ONLY for the respective run. Averaged data are the arithmetic means of weekly (5-day) data.

Calculations from data were made as follows:

Vol Feed, 1×10^{-6} =

$$\frac{\text{Avg daily flow in l/min} \times \text{hrs of operation} \times 60}{1{,}000{,}000}$$

Cu Cemented, kg =

Cu in drum feed in ppm - Cu in drum discharge in ppm x vol feed in 1×10^{-6}

Cr^{+6} Reduced, kg =

Cr^{+6} in drum feed in ppm - Cr^{+6} in drum discharge in ppm x vol feed in 1×10^{-6}

Fe dissolved, kg =

Fe in drum discharge in ppm x vol feed in 1×10^{-6}

Fe required, kg =

Cu cemented in kg x 0.8789 + Cr^{+6} reduced in kg x 1.611

Fe excess, % =

$$\frac{\text{Fe dissolved in kg} - \text{Fe required in kg}}{\text{Fe required in kg}} \times 100$$

Cu cemented, % =

$$\frac{\text{Cu in drum feed in ppm} - \text{Cu in drum discharge in ppm}}{\text{Cu in drum feed in ppm}} \times 100$$

OPERATION IN THE CONTINUOUS MODE

Data and calculations are given in Appendices A and B, pages 40 and 41. Table 3 summarizes the significant data for the four combinations of flow and iron surface levels.

Table 3. SUMMARY OF DATA FOR OPERATION IN THE CONTINUOUS MODE

Combination	Cementation Efficiency, %		Composition of Drum Feed			Composition of Drum Discharge	
			Cu ppm	Cr^{+6} ppm	pH	Fe^{+3}%	Fe excess,%
Low flow/ Low iron surface	60.00	max	345	3.5	2.5	8.14	1.83
	35.71	min	700	12.6	2.3	7.81	112
	42.24	avg	431	9.7	2.4	4.91	99.03
Low flow/ High iron surface	35.61	max	132	6.5	2.3	5.37	205
	17.20	min	93	2.0	2.7	7.62	704
	27.20	avg	92	3.5	2.6	3.83	283
High flow/ Low iron surface	28.50	max	200	10.8	2.3	13.75	92.75
	14.29	min	56	1.52	3.1	14.10	280
	22.49	avg	150	11.8	2.5	13.89	82.28
High flow/ High iron surface	30.00	max	100	2.0	2.7	9.75	190
	16.22	min	74	2.0	2.9	5.00	307
	21.95	avg	82	1.7	3.0	10.60	227

As previously mentioned, the original run in the Continuous Mode with the low flow/low iron surface level was repeated because of flow control problems. The data, however, are given in Appendix I, page 48.

Considering the averaged data, the low flow/low iron surface combination appears to have a significant advantage, although the efficiency in terms of excess iron requirements is not quite as good as that of the high flow/low iron surface combination. Note that by chance the low flow/low iron surface combination had by far the highest copper concentration in the feed solution and this fact may well overbalance any other influence.

The fact that for the low flow/low iron surface combination a lesser cementation efficiency was obtained at a higher level of copper in the feed solution is an anomaly. The reason may possibly be related to the high chromium level in the feed.

The proportion of ferric iron in the drum discharge is least for the low flow combinations, probably because of the longer contact periods per unit iron surface area.

OPERATION IN THE STATIC MODE

Data and calculations are given in Appendices C and D, pages 42 and 43. Table 4 summarizes the significant data for the four combinations of flow and iron surface levels.

Table 4. SUMMARY OF DATA FOR OPERATION IN THE STATIC MODE

Combination	Cementation Efficiency,%		Composition of Drum Feed			Composition of Drum Discharge	
			Cu ppm	Cr^{+6} ppm	pH	Fe^{+3} %	Fe excess %
Low flow/	21.61	max	545	0.0	2.2	10.42	52.36
Low iron surface	15.97	min	119	0.88	2.7	5.68	179
	18.12	avg	470	1.56	2.5	12.75	58.86
Low flow/	28.50	max	107	2.2	2.3	6.94	141
High iron surface	20.92	min	76.5	2.0	2.4	2.70	103
	24.67	avg	86	1.2	2.4	2.62	96.85
High flow/	23.67	max	414	6.5	2.2	37.65	74.72
Low iron surface	7.53	min	146	3.5	2.4	33.52	91.40
	13.56	avg	163	2.4	2.6	17.96	124
High flow/	50.00	max	600	0.0	1.9	5.36	52.59
High iron surface	15.63	min	160	8.2	2.6	52.01	0
	31.63	avg	245	3.2	2.4	19.57	55.58

It should be pointed out that due to previously mentioned difficulty in flow control, the difference in flow between the low flow/high iron surface combination and the high flow/high iron surface combination is much less than desired.

The data indicate the high flow/high iron surface combination to give the best results. That this is not entirely due to a higher copper concentration in the feed solution is attested to by the fact that equivalent or higher copper concentrations did not give as good recoveries in other flow/iron surface combinations. In all combinations, however, higher copper concentrations gave the best recoveries.

Generally large excess iron dissolution was associated with lower copper recoveries, however, in the high flow/high iron surface combination this phenomenon was reversed, although the excess iron dissolved was not great.

OPERATION IN THE INTERMITTENT MODE (A)

Data and calculations are given in Appendices E and F, pages 44 and 45. Table 5 summarizes the significant data for the four combinations of flow and iron surface levels.

Table 5. SUMMARY OF DATA FOR OPERATION IN THE INTERMITTENT MODE (A)

Combination	Cementation Efficiency,%		Composition of Drum Feed			Composition of Drum Discharge	
			Cu ppm	Cr^{+6} ppm	pH	Fe^{+3} %	Fe excess %
Low flow/ Low iron surface	17.27	max	139	1.3	2.4	7.68	197
	7.38	min	122	3.0	3.2	52.54	323
	11.66	avg	125	2.4	2.7	22.51	279
Low flow/ High iron surface	57.71	max	584	2.0	2.1	-	108
	22.73	min	110	3.0	2.6	0	241
	37.51	avg	220	2.2	2.4	4.57	123
High flow/ Low iron surface	13.58	max	81	0.4	2.65	6.93	287
	2.08	min	96	2.6	2.8	4.82	285
	8.04	avg	82	1.2	2.6	8.51	297
High flow/ High iron surface	23.53	max	170	2.0	2.7	4.82	77.00
	6.60	min	212	37.3	2.5	-	29.81
	15.69	avg	197	14.3	2.8	14.48	50.57

It is evident that the low flow/high iron surface combination gave the best results. However, this is not conclusive since the copper in the feed solution was much higher during this run than in others.

The low flow combinations showed less excess iron dissolution for the higher cementation efficiencies as expected; however, this was reversed for the high flow combinations.

The minimum cementation efficiency for the high flow/high iron surface combination is surprisingly low when it is considered that the concentration of copper in the feed solution was over 200 ppm. Again, this appears to be due to a higher than normal concentration of hexavalent chromium in the feed solution. It is also of interest to note that the effect of the hexavalent chromium appears to have superseded the normally positive cementation effect of a low pH. The concentration of hexavalent chromium was sufficiently high so that for a short period, complete reduction was not achieved, and during this period at least, no cementation of copper would occur.

OPERATION IN THE INTERMITTENT MODE (B)

Data and calculations are given in Appendices G and H, pages 46 and 47. Table 6 summarizes the significant data for three combinations of flow and iron surface levels.

Table 6. SUMMARY OF DATA FOR OPERATION IN THE INTERMITTENT MODE (B)

Combination	Cementation Efficiency,%		Composition of Drum Feed			Composition of Drum Discharge	
			Cu ppm	Cr^{+6} ppm	pH	Fe^{+3} %	Fe excess %
Low flow/	12.00	max	50	0.1	2.9	0	907
Low iron surface	1.12	min	89	1.3	2.3	9.41	2,549
	7.64	avg	85	2.9	2.7	13.60	501
Low flow/	55.37	max	1183	2.0	1.9	32.72	35.04
High iron surface	4.59	min	54.5	1.3	3.0	1.76	574
	21.74	avg	290	1.5	2.7	11.02	51.31
High flow/	9.68	max	62	0.7	2.9	0	243
Low iron surface	1.32	min	76	2.0	2.8	0	533
	5.82	avg	85	1.4	2.8	-	278
High flow/	Not						
High iron surface	Run						

As previously explained, the high flow/high iron surface combination was not run in this mode due to generally unpromising results for other combinations.

The low flow/high iron surface gave a fair maximum copper recovery, but it will be noted that the copper concentration in the feed solution was enormously high. It is interesting to note that even with such a high concentration of copper, the excess dissolution of iron was extremely low.

The concentration of copper in the feed solution for all of the other combinations run was too low for data to be interpreted, except in a very general way.

SUMMARY OF DATA FOR OPERATION IN ALL MODES

Data are summarized in Table 7.

Table 7. SUMMARY OF DATA FOR OPERATION IN ALL MODES

	Max Cu Recovery %	Fe Excess %	Fe^{+3} %	Cu in Feed, ppm	Cr^{+6} in Feed, ppm	pH
Continuous Mode						
Low flow/low Fe surface	60.00	1.83	8.14	345	3.5	2.5
Low flow/high Fe surface	35.61	205	5.37	132	6.5	2.3
High flow/low Fe surface	28.50	92.75	13.75	200	10.8	2.3
High flow/high Fe surface	30.00	190	9.75	100	2.0	2.7
Static Mode						
Low flow/low Fe surface	26.61	52.36	10.42	545	0.0	2.2
Low flow/high Fe surface	28.50	141	6.94	107	2.2	2.3
High flow/low Fe surface	23.67	74.72	37.65	414	6.5	2.2
High flow/high Fe surface	50.00	52.59	5.36	600	0	1.9
Intermittent Mode (A)						
Low flow/low Fe surface	17.27	197	7.68	139	1.3	2.4
Low flow/high Fe surface	57.71	108	-	584	2.0	2.1
High flow/low Fe surface	13.58	287	6.93	81	0.4	2.65
High flow/high Fe surface	23.53	77.00	4.82	170	2.0	2.7
Intermittent Mode (B)						
Low flow/low Fe surface	12.00	907	0	50	0.1	2.9
Low flow/high Fe surface	55.37	35.04	32.72	1183	2.0	1.9
High flow/low Fe surface	9.68	243	0	62	0.7	2.9
High flow/high Fe surface			Not Run			

Data for runs where 50% or better copper recovery was achieved are arranged in Table 8, page 28.

It is interesting to note that one run in each mode gave a copper recovery of 50% or better. Although in all instances the copper concentrations in the feed solution were higher than normal, the percentage of recovery was not strictly proportional to the copper concentration, indicating that other factors besides the copper concentration exert an influence. For instance, operation in Intermittent Mode (A) with the low flow/high iron surface combination gave slightly better copper recovery than operation in Intermittent Mode (B) under the same conditions with twice the copper concentration in the feed solution. This, however, was at the expense of dissolution of about 3 times the amount of excess iron.

Table 8. DATA FOR RUNS GIVING 50% OR BETTER COPPER RECOVERY

Mode	Flow	Iron Surface	Cu Recovery, %	Fe Excess, %	Fe^{+3} %	Cu in Feed, ppm	Cr^{+6} in Feed, ppm	Feed pH
Cont	Low	Low	60.00	1.83	8.14	345	3.5	2.5
Static	High	High	50.00	52.59	5.36	600	0.0	1.9
Inter.(A)	Low	High	57.71	108	-	584	2.0	2.1
Inter.(B)	Low	High	55.37	35.04	32.72	1183	2.0	1.9

The data given in Appendices A through I were analyzed on an IBM 370 computer using a Stepwise Regression technique whereby only the significant variables are retained in the final equation.

The following variables were entered into the analysis:

a) % Cu cemented = y = dependent variable
b) Mode = time drum was off = x_1

There were four modes:

1) Continuous = 0
2) Intermittent (A) = 55
3) Intermittent (B) = 140
4) Static = 450

c) Feed flow in l/min = x_2
d) Iron surface area in m^2 = x_3
e) Feed concentration of Cu in ppm = x_4
f) Feed concentration of Cr^{+6} in ppm = x_5
g) pH of feed solution = x_6
h) Feed concentration of oil in ppm = x_7
i) Feed temperature in °C = x_8

j) Interaction of $\frac{\text{flow}}{\text{Fe area}} = x_9$

t) Interaction of $\frac{\text{Conc}_{\text{Cu}}}{\text{Fe area}} = x_{19}$

v) Interaction of $\frac{(\text{flow})(\text{Conc}_{\text{Cu}})}{\text{Fe area}} = x_{21}$

x) Interaction of $\frac{(\text{flow})(\text{Fe area})}{\text{Conc}_{\text{Cu}}} = x_{23}$

To cover the fact that these variable effects were probably not linear, a second order term, or variable, was included for each of the above 12 independent variables; i.e., Mode^2, Flow^2, etc. This made the total number of independent variables entering the analysis = 24.

The following variables proved significant:

a) Cu concentration
b) Mode
c) Cr^{+6} concentration
d) pH
e) Flow/Fe area
f) ConcCu/Fe area

The following equation with a multiple correlation of 0.924 was determined from the analysis:

$$
\begin{aligned}
\%\ \text{Cu cemented} \pm 13.18 = {} & 43.34397 + .09512\ (\text{Conc}_{Cu}) \\
& - .000038\ (\text{Conc}^2_{Cu}) - .18312\ (\text{Mode}) \\
& + .000333\ (\text{Mode}^2) - .74124\ (\text{Cr}^{+6}) \\
& - 1.32452\left(\frac{\text{Flow}}{\text{Fe area}}\right) - .92799\ \left(\frac{\text{Conc}_{Cu}}{\text{Fe area}}\right) \\
& - 2.42109\ (\text{pH}^2)
\end{aligned}
$$

where 13.18 = standard error at 95% confidence.

From the above equation and within the limits of the experiment, the following conclusions can be made:

a) Better cementation efficiency can be obtained with higher concentrations of copper. (However, the maximum for the quadratic expression for concentration is about 1,251 ppm.)

b) A continuous mode of drum operation; i.e., time drum off = 0, will improve the cementation efficiency.

c) The lower the hexavalent chromium, the better the efficiency.

d) The higher the pH value, the less efficient will be the cementation.

e) Because both the $\frac{\text{flow}}{\text{Fe area}}$ and the $\frac{\text{Conc}_{Cu}}{\text{Fe area}}$ interaction have a negative effect on cementation efficiency, these terms should be made as small as possible. Increases in the flow and/or copper concentration will require substantial increases in iron surface area.

The Regression Analysis confirms the conclusions reached by visual examination of the data and adds the not immediately apparent facts that drum operation in the continuous mode is advantageous and that flow/iron surface area and copper concentration/iron surface area ratios have significant influence.

It seems apparent that the static mode of drum operation does not have the hoped-for effect of increasing cementation efficiency. Even though the previously deposited copper may have the predicted effect of nucleating further cementation, other factors cut down on the over-all efficiency. Probably the principal negative factor is the reduction in effective iron contact surface by layering of adjacent pieces.

COPPER MUD

The characteristics of the copper mud collected in the settling pit during the course of the experimental runs are shown in Appendix J, page 49.

The characteristics are those of the mud after settling for 24 hrs. Longer settling, coupled with air-drying, of course would greatly increase the density and diminish the moisture content.

There is no obvious correlation between the characteristics of the mud and the conditions of drum operation.

The copper is probably largely in the elemental form, but substantial quantities of oxides are also present.

The moist mud also contains small quantities of copper, chromium, zinc, iron and nickel salts, as well as a small quantity of particulate iron.

A typical specimen of the mud was thoroughly washed with water and dried. Analysis showed the following composition:

Copper	78.50%
Iron	1.32
Zinc	0.11
Nickel	0.18
Aluminum	0.05
Calcium	0.01

Obviously, part of the copper and iron are in the form of oxides.

The air-dried copper mud may be mixed with other salvaged copper-bearing materials such as skimmings, and the copper reclaimed by conventional smelting and refining practices. However, an attractive optional method for recovery which eliminates the smelting operation is a hydrometallurgical process which involves leaching the mud with ammonium carbonate, separating the copper by liquid ion exchange, and finally depositing the copper electrolytically. The application of this process to copper mud is currently being studied at The Anaconda Company, General Mining Division, Research Laboratories, at Tucson, Arizona. Preliminary results are favorable.

SLUDGE FILTER CAKE

Any copper not precipitated by cementation and trapped in the settling pit is included in the sludge filter cake. The characteristics of the filter cake collected during the course of the experimental runs are shown in Appendix K, page 50.

To date, in spite of considerable effort, no practical way of reclaiming copper from the filter cake has been devised, and the material is discarded as land fill.

The major problem in reclaiming the copper is the presence of a substantial amount of chromium in the cake which attacks the lining of smelting furnaces.

Experiments with hydrometallurgical processes for recovery of copper from the cake are underway, and if successful a comparison will be made as to the cost of removing all the metal by chemical precipitation vs. the inclusion of cementation for copper recovery. This will also be dependent on the ability to improve the cementation efficiency beyond the capability shown in the present study.

BEHAVIOR OF IRON SCRAP

The mechanism of cementation and hexavalent chromium reduction by metallic iron is discussed in a previous report.[3]

The reactions appear to be concentrated at selected sites where progressively deeper pitting occurs. This is illustrated in Fig. 6, page 33.

During periods of continuous rotation, the pieces of scrap were coated with a bright lustrous film of copper which was continuously ground off and discharged as particulates.

During static operation, the copper film was dull and amorphous, and was generally not dislodged until the drum was rotated.

Generally, the scrap pieces tumbled well, but at the higher surface level there was a slight tendency for the pieces to stack in layers around the inlet nozzles.

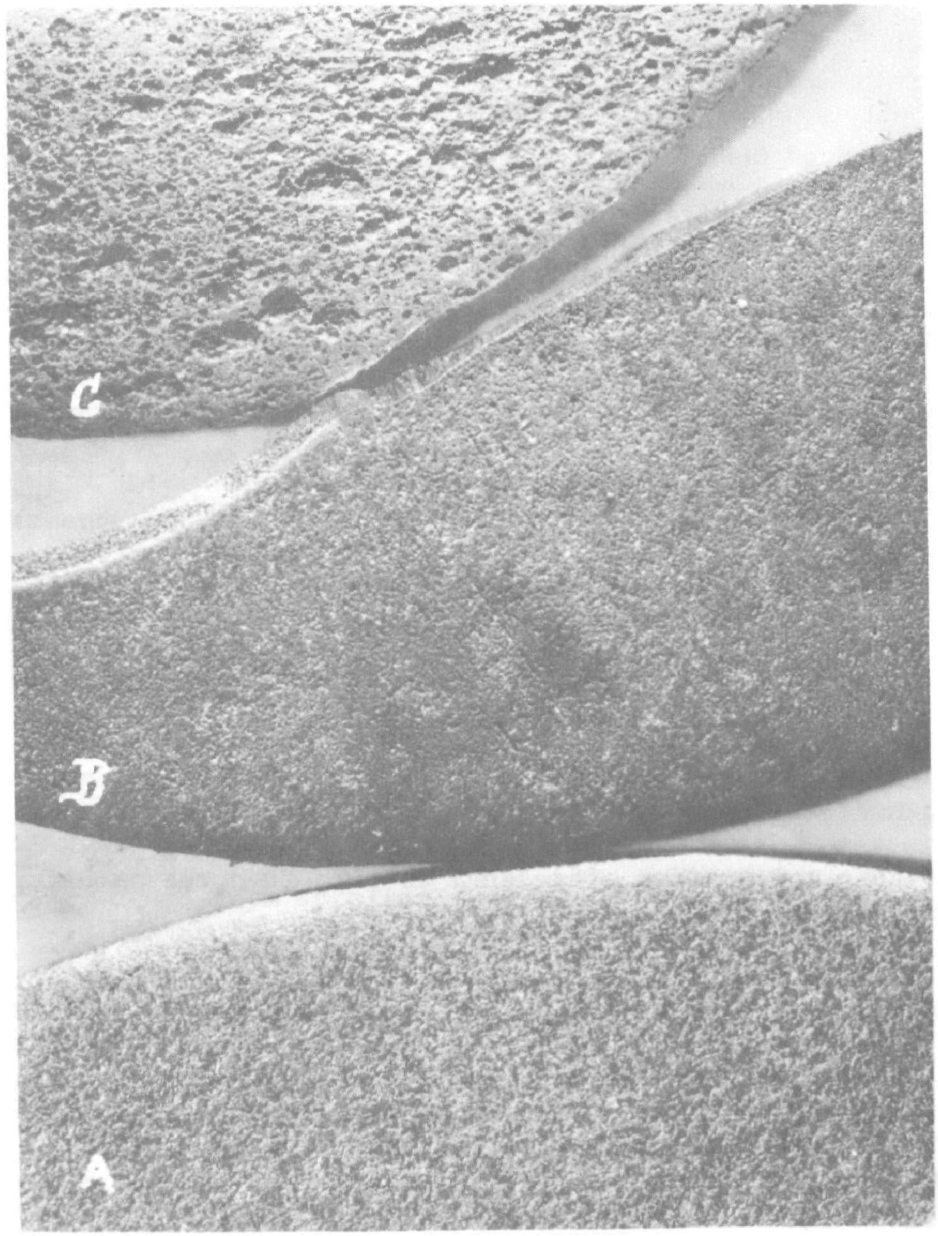


Figure 6. Appearance of Scrap Iron Surface After Various Periods of Use 5 X

A. Unused piece; original surface
B. Piece after short use; still original gauge
C. Piece after prolonged use; less than half original gauge

SECTION VII

ECONOMIC CONSIDERATIONS

During the 16 weeks of experimental runs, the copper concentration in the feed solution averaged 188 ppm, and the concentration of hexavalent chromium 3.69 ppm. The average flow was 697 l/min for 8 hours per day, and 46.60% of the total plant discharge was processed.

In terms of the total amount of available copper, this comes to:

$$\frac{694 \text{ l/min} \times 60 \times 8}{1{,}000{,}000} \times 188 = 62.63 \text{ kg Cu/day}$$

$$\frac{62.63 \text{ kg Cu/day} \times 5 \times 16}{0.4660} = 10{,}751 \text{ kg Cu/16 weeks}$$

$$10{,}751 \text{ kg Cu} \times \frac{52}{16} = 34{,}943 \text{ kg Cu/year, or } 77{,}047 \text{ lbs Cu/year.}$$

Calculated on the same basis, the total amount of hexavalent chromium to be reduced is equal to 868 kg/yr (1513 lbs/yr).

Assuming that cementation efficiency is 50%, then the annual potential copper recovery is:

> 34,942 kg Cu x 0.5 = 17,471 kg Cu (38,524 lbs) and the annual potential value is 38,524 lbs Cu at 75 cents = $28,893.

Whether or not any recovery of copper is attempted, it is mandatory that treatment facilities be provided to bring plant discharge into conformity with Federal and State effluent standards, hence only the ADDITIONAL cost of providing facilities and services for copper recovery need be considered in assessing the economic value of a copper recovery program.

The cost of a complete cementation unit including two drums, scrap conveyor, settling pits, pumps, etc. installed in Kenosha, Wisconsin, in 1972 was $164,000. If it is considered that the present cost would be increased by 10% and the equipment has a useful life of 15 years, then the amortized capital cost would be:

$$\frac{\$164{,}000 + 10\%}{15} = \$12{,}027/\text{year}$$

The iron required for cementing 17,471 kg of Cu and reducing 686 kg of hexavalent chromium may be calculated as follows:

17,471 kg Cu x 0.8789	=	15,355 kg Fe
868 kg Cr^{+6} x 1.611	=	1,105 " "
		16,460 kg Fe
plus 50% excess		8,230
		24,690 kg Fe
$\frac{24,690 \text{ kg Fe} \times 2.205}{2,000}$	=	27.22 tons Fe/year
27.22 tons Fe at $118	=	$3,212

Annual copper recovery costs may be summarized as follows:

Equipment (15-year depreciation)	$12,027
Maintenance at 5%	601
Electricity for drum operation (40 hp x 0.7457 x 8 hrs x 6 days x 52 weeks x 3.2 cents)	2,382
Scrap Iron	3,212
Labor (charging drum with scrap) 1.5 hr/week x 52 at $15	1,170
Removing Cu mud from settling pits - 16 hrs at $25	400
Shipping Cu mud to refinery - 48 tons at $20	960
Refining Costs - 38,524 lbs Cu at 7-1/2 cents	2,889
Total Annual Cost	$23,641
Total Annual Gain $28,893 - 23,641	$ 5,252

In considering the value of the annual gain it should be pointed out that if the cementation process were not utilized, an alternate process for the reduction of hexavalent chromium would have to be provided on which there would be no return on either capital or operating costs. Such a process would probably have a minimum annual cost of $5,000.

If only a 25% cementation efficiency is assumed, calculations on the same basis show an annual loss of $5,573 which may not be sufficient to cover the cost of hexavalent chromium reduction by another process.

Fig. 7, shows graphically the possible net annual return in recovered copper value for various cementation efficiencies. Note that the "break-even" point is at approximately 35% recovery.

The profitability of cementation is, of course, tied to the price of copper which may fluctuate widely. At 61 cents per pound the only gain from the cementation process (at 50% copper recovery) is the value of the chromium reduction.

It is apparent that the process is economically viable only if a cementation efficiency approaching 50% can be maintained. The present study indicates that this efficiency can only be maintained by keeping a high concentration of copper in the feed solution. This can best be achieved by eliminating all unnecessary dilution of the waste stream. Rinsing practices are notoriously wasteful in water usage and it is not uncommon for water to be left running continuously and serious leaks to go unrepaired. By implementing simple water conservation measures, it should not be difficult to upgrade the copper content of the feed solution to the point where copper recovery becomes profitable.

This is of especial importance because the waste stream must be treated in any event at considerable cost, and any copper which is not recovered by the cementation process is lost. There is at present, to our knowledge, no practical way of recovering copper from the filter cake precipitated by neutralization of brass mill discharges.

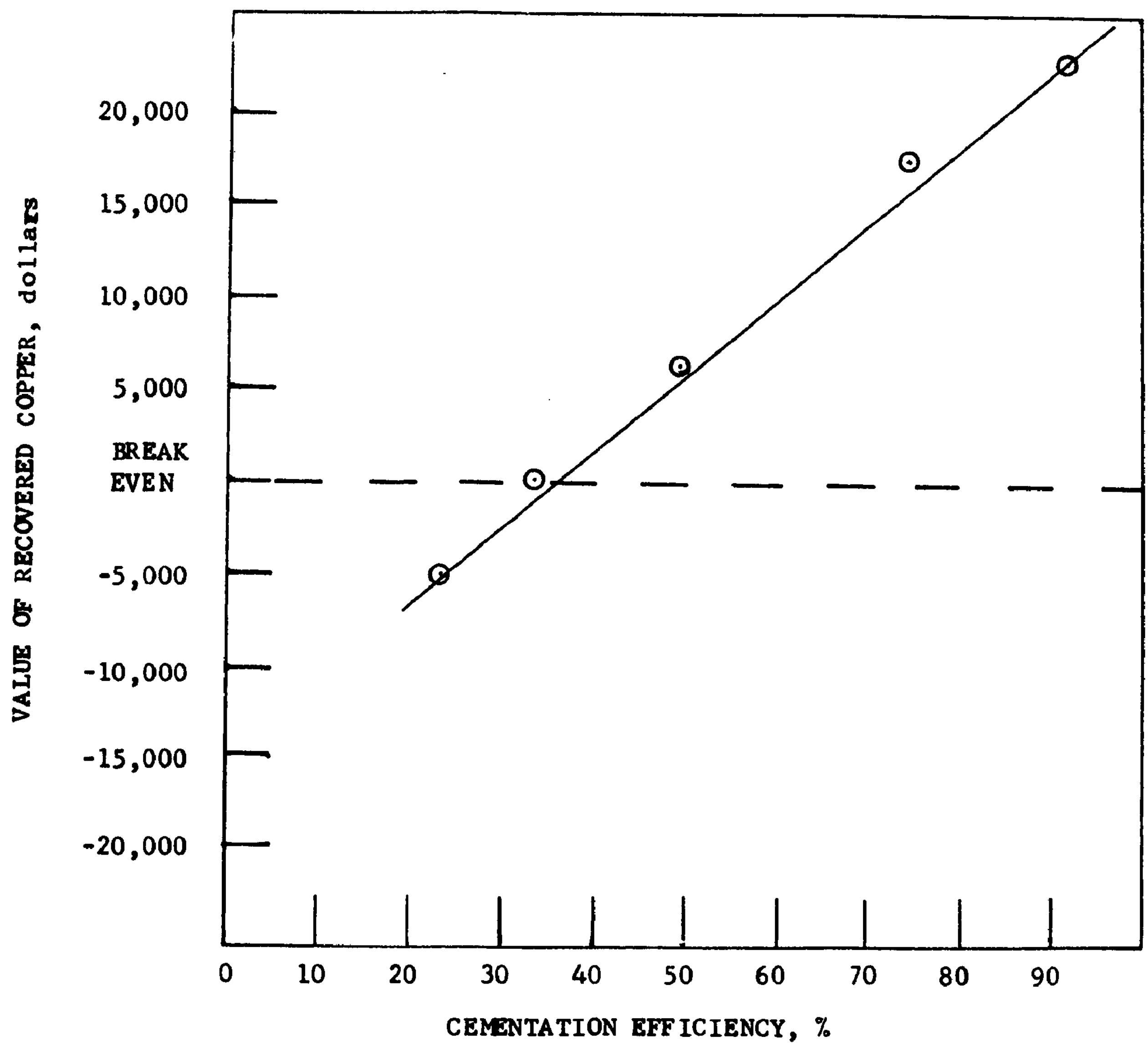


Figure 7. Net Annual Return Realized from Recovered Copper at Various Cementation Efficiencies

SECTION VIII

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SECTION IX

APPENDICES

APPENDIX A

DATA AND CALCULATIONS FOR OPERATION IN CONTINUOUS MODE

		Low Flow Low Iron Surface			Low Flow High Iron Surface		
		Cementation Efficiency			Cementation Efficiency		
		Max	Min	Avg	Max	Min	Avg
	Flow, l/min	379	492	416	727	507	601
	Iron Surface, m^2	124	124	124	322	322	322
DRUM FEED	Cu, ppm	345	700	431	132	93	92
	Cr^{+6}, ppm	3.5	12.6	9.7	6.5	2.0	3.5
	Cr^T, ppm	97	341	196	76	47	53
	Zn, ppm	18	91	54.5	11.4	14	14
	Ni, ppm	6.1	7	6.6	19	12	12
	Oil, ppm	10.2	23	16.6	39	61	61
	pH	2.5	2.3	2.4	2.3	2.7	2.6
	Temp, °C	30.5	30	29	26	28	26
DRUM DISCHARGE	Cu, ppm	138	450	253	85	77	65
	Cr^{+6}, ppm	0	0	0	0	0	0
	Fe^T, ppm	191	509	342	158	139	111
	Fe^{+3}, %	8.14	7.81	4.91	5.37	7.62	3.83
	pH	2.9	2.5	2.9	2.7	4.2	3.95
CALCULATIONS	Vol Feed, $l \times 10^{-6}$	0.18168	0.24356	0.19734	0.35972	0.25105	0.29031
	Cu Cemented, kg	37.6	60.9	35.1	16.9	4.02	7.7
	Cr^{+6} Reduced, kg	0.64	3.07	1.91	2.34	0.50	1.02
	Fe Dissolved, kg	34.7	124	67.5	56.8	35	32.2
	Fe Required, kg	34.1	58.5	33.9	18.6	4.34	8.4
	Fe Excess, %	1.83	112	99.03	205	704	283
	Cu Cemented, %	60.00	35.71	42.24	35.61	17.20	27.20

APPENDIX B

DATA AND CALCULATIONS FOR OPERATION IN CONTINUOUS MODE

		High Flow, Low Iron Surface, Cementation Efficiency			High Flow, High Iron Surface, Cementation Efficiency		
		Max	Min	Avg	Max	Min	Avg
	Flow, l/min	806	931	869	659	1105	1002
	Iron Surface, m^2	129	129	129	281	281	281
DRUM FEED	Cu, ppm	200	56	150	100	74	82
	Cr^{+6}, ppm	10.8	1.52	11.8	2.0	2.0	1.7
	Cr^{T}, ppm	111	22	86	39	38	38
	Zn, ppm	41	5	23	11	12	11
	Ni, ppm	8	3	5.2	6	6	6
	Oil, ppm	89	3	46	54	36	54
	pH	2.3	3.1	2.5	2.7	2.9	3.0
	Temp, °C	29	25	28	25	26.5	25
DRUM DISCHARGE	Cu, ppm	143	48	114	70	62	64
	Cr^{+6}, ppm	0	0	0	0	0	0
	Fe^{T}, ppm	130	36	92	86	56	61
	Fe^{+3}, %	13.75	14.10	13.89	9.75	5.00	10.60
	pH	2.5	3.4	2.8	4.4	4.0	4.2
CALCULATIONS	Vol Feed, $l \times 10^{-6}$	0.36279	0.43296	0.37904	0.31612	0.53050	0.44500
	Cu Cemented, kg	20.7	3.46	13.6	9.5	6.37	8
	Cr^{+6} Reduced, kg	3.9	0.66	4.5	0.63	1.06	0.76
	Fe Dissolved, kg	47.2	15.6	35	27.2	29.7	27.1
	Fe Required, kg	24.5	4.1	19.2	9.4	7.3	8.3
	Fe Excess, %	92.75	280	82.28	190	307	227
	Cu Cemented, %	28.50	14.29	22.49	30.00	16.22	21.95

APPENDIX C

DATA AND CALCULATIONS FOR OPERATION IN STATIC MODE

		Low Flow, Low Iron Surface			Low Flow, High Iron Surface		
		Cementation Efficiency			Cementation Efficiency		
		Max	Min	Avg	Max	Min	Avg
	Flow, l/min	424	390	420.	708	719	728
	Iron Surface, m^2	109	109	109	329	329	329
DRUM FEED	Cu, ppm	545	119	470	107	76.5	86
	Cr^{+6}, ppm	0	0.88	1.56	2.2	.2.0	1.2
	Cr^T, ppm	89	43	86	54	31	38
	Zn, ppm	85	52	69	10	9	9
	Ni, ppm	17	7	12	11	8	8
	Oil, ppm	81	36	58	88	46	47
	pH	2.2	2.7	2.5	2.3	2.4	2.4
	Temp, °C	29.5	30.5	30	30	28	28
DRUM DISCHARGE	Cu, ppm	400	100	374	76.5	60.5	64.5
	Cr^{+6}, ppm	0	0	0	0	0	0
	Fe^T, ppm	194	51	138	73	35	48
	Fe^{+3}, %	10.42	5.68	12.75	6.94	2.70	2.62
	pH	2.3	2.8	2.6	2.4	2.6	2.65
CALCULATIONS	Vol Feed, l x 10^{-6}	0.21619	0.18128	0.20710	0.34696	0.35943	0.35659
	Cu Cemented, kg	31.3	3.44	19.9	10.6	5.75	7.67
	Cr^{+6} Reduced, kg	0	0.16	0.32	0.76	0.72	0.43
	Fe Dissolved, kg	41.9	9.2	28.6	25.3	12.6	17.1
	Fe Required, kg	27.5	3.3	18	10.5	6.2	8.7
	Fe Excess, %	52.36	179	58.86	141	103	96.85
	Cu Cemented, %	26.61	15.97	18.12	28.50	20.92	24.67

APPENDIX D

DATA AND CALCULATIONS FOR OPERATION IN STATIC MODE

		High Flow Low Iron Surface Cementation Efficiency			High Flow High Iron Surface Cementation Efficiency		
		Max	Min	Avg	Max	Min	Avg
	Flow, l/min	772	855	800	840	905	878
	Iron Surface, m^2	117	117	117	309	309	309
DRUM FEED	Cu, ppm	414	146	163	600	160	245
	Cr^{+6}, ppm	6.5	3.5	2.4	0	8.2	3.2
	Cr^T, ppm	220	92	84	19	81	53
	Zn, ppm	-	-	-	27	19	19
	Ni, ppm	-	-	-	10	9	9
	Oil, ppm	20	17.7	20	49	105	105
	pH	2.2	2.4	2.6	1.9	2.6	2.4
	Temp, °C	29	27	29	21	25	24.5
DRUM DISCHARGE	Cu, ppm	316	135	135	300	135	147
	Cr^{+6}, ppm	0	0	0	0	0.09	<0.01
	Fe^T, ppm	169	44	64	402	43	142
	Fe^{+3}, %	37.65	33.52	17.96	5.36	52.01	19.57
	pH	2.3	2.6	2.75	1.7	2.8	2.5
CALCULATIONS	Vol Feed, l x 10^{-6}	0.38220	0.42342	0.39607	0.39072	0.40707	0.39778
	Cu Cemented, kg	37.5	4.66	11.1	117	10.2	39
	Cr^{+6} Reduced, kg	2.48	1.48	0.95	0	8.1	1.27
	Fe Dissolved, kg	64.6	18.6	25.3	157	17.5	56.5
	Fe Required, kg	37	9.7	11.3	103	22	36.3
	Fe Excess, %	74.72	91.40	124	52.59	0	55.58
	Cu Cemented, %	23.67	7.53	13.56	50.00	15.63	31.63

APPENDIX E

DATA AND CALCULATIONS FOR OPERATION IN INTERMITTENT MODE (A)

		Low Flow Low Iron Surface Cementation Efficiency			Low Flow High Iron Surface Cementation Efficiency		
		Max	Min	Avg	Max	Min	Avg
	Flow, l/min	643	379	537	662	583	603
	Iron Surface, m^2	117	117	117	304	304	304
DRUM FEED	Cu, ppm	139	122	125	584	110	220
	Cr^{+6}, ppm	1.3	3.0	2.4	2.0	3.0	2.2
	Cr^T, ppm	71	57	64	371	44	124
	Zn, ppm	13	13	13	14	10	12
	Ni, ppm	9	9	9	34	7	21
	Oil, ppm	26	40	26	131	77	104
	pH	2.4	3.2	2.7	2.1	2.6	2.4
	Temp, °C	33	29.5	32	21	25	24
DRUM DISCHARGE	Cu, ppm	115	113	111	247	85	116
	Cr^{+6}, ppm	0	0	0	0	0	0
	Fe^T, ppm	68	54	61	624	78	211
	Fe^{+3}, %	7.68	52.54	22.51	-	0	4.57
	pH	2.5	3.7	3.0	2.3	3.5	2.8
CALCULATIONS	Vol Feed, l x 10^{-6}	0.31850	0.18735	0.26714	0.30800	0.28853	0.28923
	Cu Cemented, kg	7.6	1.69	3.74	104	7.2	30
	Cr^{+6} Reduced, kg	0.41	0.56	0.64	0.62	0.87	0.64
	Fe Dissolved, kg	21.7	10.1	16.3	192	22.5	61
	Fe Required, kg	7.3	2.39	4.3	92.4	6.6	27.4
	Fe Excess, %	197	323	279	108	241	123
	Cu Cemented, %	17.27	7.38	11.66	57.71	22.73	37.51

APPENDIX F

DATA AND CALCULATIONS FOR OPERATION IN INTERMITTENT MODE (A)

		High Flow, Low Iron Surface, Cementation Efficiency			High Flow, High Iron Surface, Cementation Efficiency		
		Max	Min	Avg	Max	Min	Avg
	Flow, l/min	802	977	887	889	818	896
	Iron Surface, m^2	107	107	107	301	301	301
DRUM FEED	Cu, ppm	81	96	82	170	212	197
	Cr^{+6}, ppm	0.4	2.6	1.2	2.0	37.3	14.3
	Cr^T, ppm	36	46	38	83	127	112
	Zn, ppm	7	9	8	29	11	20
	Ni, ppm	7	7	7	42	6	24
	Oil, ppm	9	19	14	124	63	94
	pH	2.65	2.8	2.6	2.7	2.5	2.8
	Temp, °C	32	30	30.5	25	26	25
DRUM DISCHARGE	Cu, ppm	70	94	75	130	198	166.5
	Cr^{+6}, ppm	0	0.	0	0	12 for < 1 hr	< 1
	Fe^T, ppm	40	23	32	68	94	75
	Fe^{+3}, %	6.93	4.82	8.51	4.82	-	14.48
	pH	2.8	3.25	2.8	3.2	3.1	3.3
CALCULATIONS	Vol Feed, $l \times 10^{-6}$	0.39334	0.48338	0.43299	0.44029	0.25753	0.35955
	Cu Cemented, kg	4.33	0.97	3.03	17.6	3.61	11
	Cr^{+6} Reduced, kg	0.16	1.26	0.52	0.88	9.61	5.14
	Fe Dissolved, kg	15.7	11.1	13.9	29.9	24.2	27
	Fe Required, kg	4.06	2.88	3.5	16.9	18.6	17.9
	Fe Excess, %	287	285	297	77.00	29.81	50.57
	Cu Cemented, %	13.58	2.08	8.04	23.53	6.60	15.69

APPENDIX G

DATA AND CALCULATIONS FOR OPERATION IN INTERMITTENT MODE (B)

		Low Flow Low Iron Surface Cementation Efficiency			Low Flow High Iron Surface Cementation Efficiency		
		Max	Min	Avg	Max	Min	Avg
	Flow, l/min	579	496	512	526	556	569
	Iron Surface, m^2	129	129	129	284	284	284
DRUM FEED	Cu, ppm	50	89	85	1183	54.5	290
	Cr^{+6}, ppm	0.1	1.3	2.9	2.0	1.3	1.5
	Cr^T, ppm	20	61	52	740	25	172
	Zn, ppm	15	20	20	9	7	8
	Ni, ppm	5	5	5	296	4	102
	Oil, ppm	81	54	54	34	11	22
	pH	2.9	2.3	2.7	1.9	3.0	2.7
	Temp, °C	29	33	31	22	18	21
DRUM DISCHARGE	Cu, ppm	44	88	78	528	52	152
	Cr^{+6}, ppm	0	0	0.1	0	0	0
	Fe^T, ppm	55	79	64	780	29	187
	Fe^{+3}, %	0	9.41	13.60	32.72	1.76	11.02
	pH	2.9	2.4	2.9	2.0	3.35	3.1
CALCULATIONS	Vol Feed, l x 10^{-6}	0.29256	0.24781	0.25620	0.25253	0.25304	0.26866
	Cu Cemented, kg	1.76	0.25	1.79	165	0.63	37
	Cr^{+6} Reduced, kg	0.03	0.32	0.72	0.51	0.33	0.40
	Fe Dissolved, kg	16.1	19.6	16.4	197	7.34	50.2
	Fe Required, kg	1.6	0.74	2.73	146	1.09	33.2
	Fe Excess, %	907	2549	501	35.04	574	51.31
	Cu Cemented, %	12.00	1.12	7.64	55.37	4.59	21.74

APPENDIX H

DATA AND CALCULATIONS FOR OPERATION IN INTERMITTENT MODE (B)

		High Flow, Low Iron Surface: Cementation Efficiency			High Flow, High Iron Surface: Cementation Efficiency		
		Max	Min	Avg	Max	Min	Avg
	Flow, l/min	912	912	893			
	Iron Surface, m^2	104	104	104			
DRUM FEED	Cu, ppm	62	76	85			
	Cr^{+6}, ppm	0.7	2	1.4			
	Cr^T, ppm	25	35	34			
	Zn, ppm	6	6	12		NOT RUN	
	Ni, ppm	4	4	6			
	Oil, ppm	14	14	24			
	pH	2.9	2.8	2.8			
	Temp, °C	28	28	28			
DRUM DISCHARGE	Cu, ppm	56	75	80			
	Cr^{+6}, ppm	0	0	0			
	Fe^T, ppm	22	26	25			
	Fe^{+3}, %	0	0	-			
	pH	3.1	3.1	3.0			
CALCULATIONS	Vol Feed, l x 10^{-6}	0.43784	0.45153	0.43948			
	Cu Cemented, kg	2.63	0.45	2.2			
	Cr^{+6} Reduced, kg	0.31	0.90	0.62			
	Fe Dissolved, kg	9.63	11.7	11.0			
	Fe Required, kg	2.81	1.85	2.9			
	Fe Excess, %	243	533	278			
	Cu Cemented, %	9.68	1.32	5.82			

APPENDIX I

DATA AND CALCULATIONS FOR OPERATION IN CONTINUOUS MODE (ORIGINAL RUN)

		Low Flow Low Iron Surface Cementation Efficiency			High Iron Surface Cementation Efficiency		
		Max	Min	Avg	Max	Min	Avg
	Flow, l/min	568	530	473			
	Iron Surface, m^2	149	149	149			
DRUM FEED	Cu, ppm	287	97	238			
	Cr^{+6}, ppm	1.7	0	1.3			
	Cr^T, ppm	117	39	104			
	Zn, ppm	26.5	17	27			
	Ni, ppm	5	4	5			
	Oil, ppm	61	79	61			
	pH	2.4	2.8	2.5			
	Temp, °C	29	26.5	28.5			
DRUM DISCHARGE	Cu, ppm	132	63	124			
	Cr^{+6}, ppm	0	0	0			
	Fe^T, ppm	190	211.5	200.5			
	Fe^{+3}, %	4.12	7.94	5.35			
	pH	2.7	2.75	2.7			
CALCULATIONS	Vol Feed, l x 10^{-6}	0.27252	0.21460	0.21954			
	Cu Cemented, kg	42.2	7.3	25			
	Cr^{+6} Reduced, kg	0.46	0	0.29			
	Fe Dissolved, kg	51.8	45.4	44			
	Fe Required, kg	37.8	6.42	22.4			
	Fe Excess, %	36.96	607	96.25			
	Cu Cemented, %	54.01	35.05	45.92			

APPENDIX J

CHARACTERISTICS OF COPPER MUD

Mode of Operation	Flow	Iron Surface	Total Cu Cemented, kg	Composition of Mud				
				Density,g/cc	H_2O,%	Fe,%	Cu,%	Other,%
Continuous	Low	Low	176	1.0760**	80.3	0.93	12.21	6.56
"	Low	High	39	1.2820	65.1	0.84	25.09	8.97
"	High	Low	55	1.1290	79.7	1.20	9.28	9.82
"	High	High	40	1.3906	60.1	0.76	30.32	8.82
Static	Low	Low	99	1.0520	69.0	0.68	22.32	8.00
"	Low	High	31		No Sample			
"	High	Low	55	1.3180	63.4	1.13	23.42	12.05
"	High	High	195	1.1758	76.1	0.79	15.98	7.13
Inter.(A)	Low	Low	19	1.2196	71.8	0.82	20.22	7.16
"	Low	High	129	1.3426	60.5	1.00	28.57	9.93
"	High	Low	15	1.3126	64.8	1.02	25.20	8.98
"	High	High	46	1.3320	62.7	0.98	30.40	5.92
Inter.(B)	Low	Low	9	1.2402	67.9	1.48	18.94	11.68
"	Low	High	186	1.2506	66.2	0.85	23.97	8.98
"	High	Low	11	1.3680	58.7	0.95	30.10	10.25
"	High	High			No Sample			
	Average			1.2625	66.62	0.96	23.37	9.05

**Limited settling period; values excluded from averages

APPENDIX K

CHARACTERISTICS OF FILTER CAKE

Mode of Operation	Flow	Iron Surface	Vol Filter Cake, m^3	Composition of Filter Cake: Density, g/cc	H_2O, %	Fe, %	Cu, %
Continuous	Low	Low	4.21	1.2366	69.4	5.20	5.51
"	Low	High	Filter Not Run				
"	High	Low	4.21	1.1960	68.6	5.12	6.22
"	High	High	2.68	1.2366	64.5	5.53	8.24
Static	Low	Low	4.21	1.1970	68.6	5.65	5.97
"	Low	High	5.35	1.2306	67.0	5.19	6.47
"	High	Low	3.82	1.2046	66.9	5.00	6.16
"	High	High	3.82	1.2820	66.2	5.30	6.84
Inter. (A)	Low	Low	3.06	1.2560	68.5	4.91	6.87
"	Low	High	3.82	1.2486	65.6	6.12	6.74
"	High	Low	4.01	1.2336	67.6	4.89	6.41
"	High	High	3.82	1.2580	65.2	5.39	7.62
Inter. (B)	Low	Low	4.01	1.1976	68.9	4.63	5.94
"	Low	High	Filter Not Run				
"	High	Low	6.9	1.2606	67.6	5.02	6.55
"	High	High	No Sample				
	Average		3.59*	1.2337	67.28	5.23	6.58

*Filter cake generated per week

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

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16. ABSTRACT

This report presents the results of studies of copper recovery (and incidental reduction of hexavalent chromium) in brass mill discharge by passage of the discharge over scrap iron in a rotating drum. The drum feed consisted of normal production discharge of combined pickle rinse water and spent sulfuric acid and sulfuric acid - bichromate pickle. About half of the total mill waste discharge over a period of 16 weeks was processed. Four modes of drum operation were studied: (1) continuous rotation, (2) no rotation, (3) intermittent rotation (1 hr of - 5 min on), and (4) intermittent rotation (2-1/2 hr off - 10 min on). Each mode was studied at two flow levels and two scrap iron surface area levels. Data were evaluated in terms of percent cementation of available copper, excess iron consumption over theoretical, and completeness of chromium reduction. Results indicate that the over-riding factor in the efficiency of copper cementation is the level of copper in the feed solution. Hexavalent chromium is effectively reduced providing the pH is below 2.5.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Water pollution	*Copper recovery	13B
*Metal finishing	*Hexavalent chromium reduction	
*Materials recovery	Water pollution abatement	
Industrial wastes	Metal finishing wastes	
Waste water	Metal recovery	
	Cementation	
	Iron reductant	

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