

# *Methods for Treating* **METAL-FINISHING WASTES**

An evaluation of various disposal methods and their  
applicability to specific waste control conditions



*Reference Data Publication compiled by*

**Metal-Finishing Industry Action Committee**

**OHIO RIVER VALLEY  
WATER SANITATION COMMISSION**



# OHIO RIVER VALLEY WATER SANITATION COMMISSION

*... an interstate agency representing  
Illinois, Indiana, Kentucky, New York,  
Ohio, Pennsylvania, Virginia and West  
Virginia, each of which is pledged by  
compact, approved by the Congress of  
the United States, faithfully to cooperate  
in the control of pollution in the  
waters of the Ohio River Valley.*

## ILLINOIS

Maurice E. Gosnell, Gosnell & Benecki  
Clarence W. Klassen, Chief Sanitary Engineer  
Franklin D. Yoder, M.D., Director of Public Health

## INDIANA

A. C. Offutt, M.D., State Health Commissioner  
Blucher A. Poole, Stream Pollution Control Board  
Joseph L. Quinn, Jr., The Hulman Company

## KENTUCKY

Minor Clark, Department of Fish and Wildlife Resources  
J. O. Matlick, Commissioner of Conservation  
Russell E. Teague, M.D., State Health Commissioner

## NEW YORK

Lyle W. Hornbeck, Bond, Schoeneck and King  
Hollis S. Ingraham, M.D., State Health Commissioner  
Joseph R. Shaw, Associated Industries of New York State, Inc.

## OHIO

Emmett W. Arnold, M.D., Director of Health  
Hudson Biery, Ohio Valley Improvement Association (ret.)  
Barton Holl, Logan Clay Products Company

## PENNSYLVANIA

Karl M. Mason, Department of Health  
Marion K. McKay, Sanitary Water Board  
Charles L. Wilbar, Jr., M.D., Secretary of Health

## VIRGINIA

E. Blackburn Moore, State Water Control Board  
William H. Singleton, State Water Control Board  
Ross H. Walker, State Water Control Board

## WEST VIRGINIA

N. H. Dyer, M.D., State Health Commissioner  
W. W. Jennings, State Water Commission  
Bern Wright, Division of Water Resources

## UNITED STATES GOVERNMENT

Edwin E. Abbott, Corps of Engineers  
Raymond E. Johnson, Fish and Wildlife Service  
Luther L. Terry, M.D., Public Health Service

## officers

Barton Holl, Chairman  
A. C. Offutt, M.D., Vice-chairman  
Fred H. Waring, Secretary  
Verna B. Ballman, Treasurer  
Edward J. Cleary, Executive Director and Chief Engineer  
Leonard A. Weakley, General Counsel

## staff

Edward J. Cleary, Executive Director and Chief Engineer  
Robert K. Horton, Assistant Director  
William L. Klein, Chemist-Biologist  
Robert J. Boes, Chemical Engineer  
David A. Dunsmore, Assistant Engineer  
Verna B. Ballman, Office Manager

Secretaries: Ruth C. Bergmeyer, Alice F. Courtney,  
Jane W. Renaldo, Grace B. Ziegler

Headquarters -- 414 Walnut Street, Cincinnati, Ohio 45202

Phone: 513-421-1151

Third Printing -- January 1965

# *Methods for Treating* **METAL-FINISHING WASTES**

Prepared by the

**METAL-FINISHING INDUSTRY ACTION COMMITTEE**

R. G. CHOLLAR, Director of Research  
National Cash Register Co.  
(Chairman of committee)

W. J. NEILL, Past-President  
American Electroplaters' Society  
Columbus Metal Products, Inc.

G. A. LOGSDON, Plating Superintendent,  
Louisville Works  
American Radiator & Standard  
Sanitary Corp.

C. L. PRICHARD, Manager  
Electrical Appliances and Dinette Furniture Plants  
Arvin Industries, Inc.

A. M. REED, Chemist  
Electric Auto-Lite Co.

K. S. WATSON  
Coordinator of Waste Treatment  
Manufacturing Policy Division  
General Electric Co.

DAVID MILNE, Chemical Engineer  
General Motors Corp.

H. S. KLINE, Director,  
Industrial Hygiene and Sanitary Engineering,  
Frigidaire Division  
General Motors Corp.

WALTER MILLER, Asst. Secretary-Treasurer  
Hamilton Manufacturing Corp.

W. L. PINNER, Manager Process Development Div.  
Houdaille-Hershey Corp.

W. H. TOLLER, JR., Chief Chemical Engineer  
Huntington Division  
Houdaille-Hershey Corp.

R. G. CHOLLAR, Director of Research  
National Cash Register Co.

L. J. HIBBERT, Head  
Finishes Laboratories  
National Cash Register Co.

C. C. CUPPS, Engineer  
Newton Falls Division  
Standard Steel Spring Co.

H. W. McELHANEY, Head Foreman  
Metal Finishing, Plating and Waste Disposal  
Talon, Inc.

HAROLD FARBER, Chief Chemist  
Mansfield Works  
Westinghouse Electric Corp.

J. E. KINNEY, Sanitary Engineer  
Ohio River Valley  
Water Sanitation Commission  
(Committee Coordinator)

of the

**OHIO RIVER VALLEY WATER SANITATION COMMISSION**

January, 1953

Price \$2.00

COPYRIGHT 1953  
Ohio River Valley Water Sanitation Commission

Third Printing - January 1965



## *Foreword*

This manual is one of a series of reference-data publications sponsored by the Ohio River Valley Water Sanitation Commission for the promotion of industrial waste control. These manuals are developed by men who are intimately associated with both manufacturing methods and the resultant problems of waste control. Thus their evaluation of remedial measures represents the practical viewpoint of proper concern to management.

This particular manual, "Methods For Treating Metal-Finishing Wastes", can be ranked as an outstanding contribution to industrial waste control practice. It represents a pooling of the knowledge and experience of a group of specialists who have been operating and appraising the various treatment methods described. For each method they evaluate the merits and the shortcomings, and then draw conclusions as to its applicability. The manual does not pretend to recommend any "best" method; however, it does provide a cogent array of facts on which the method best suited for a specific situation could be selected.

The authoritativeness of the manual, which was compiled under the direction of the Metal-Finishing Industry Action Committee of the Commission, is indicated by the membership of the sub-committee assigned to the task. This included: H. S. Kline, director of industrial hygiene and sanitary engineering, Frigidaire division, General Motors Corp.; David Milne, chemical engineer, production engineering section, General Motors Corp.; H. W. McElhaney, head foreman, metal-finishing, plating and waste disposal, Talon, Inc.; Allen M. Reed, chemist, Electric Auto-Lite Co.; C. C. Cupps, engineer, Newton Falls division, Standard Steel Spring Co. and L. J. Hibbert, head, finishes laboratory, National Cash Register Co.

The entire committee, under the chairmanship of Robert G. Chollar, director of research, National Cash Register Co., reviewed and approved the manuscript. This is the third manual produced by the committee. Prior publications, as listed on the back cover, deal with methods for measuring discharges and ways to control and minimize losses of solution and metals.

Coordination of committee activity and assistance in the assembly and preparation of the manual was provided by John E. Kinney, staff sanitary engineer. Drawings were made by Elmer Rohmiller of the Commission staff.

Cincinnati, Ohio  
January 2, 1953

EDWARD J. CLEARY  
Executive Director  
and Chief Engineer



# *Contents*

Introduction.....	5
Wastes From Metal Finishing Operations.....	9
Cyanide Treatment By	
Chlorination (gas).....	11
Hypochlorites.....	17
Chlorine Dioxide.....	20
Ozone.....	21
Conversion to Less Toxic Cyanide Complexes.....	23
Electrolytic Oxidation.....	25
Acidification.....	29
Lime Sulfur Method.....	31
Ion Exchange.....	33
Heating to Dryness.....	35
Chromium Treatment by Reduction and Precipitation.....	37
Chromium Treatment by Precipitation.....	41
Treatment by Neutralization and Chemical Precipitation.....	43
Disposal by Regulated Discharge.....	47
Disposal by Ponding.....	50
Oil Removal.....	51
Paint Spray Booth Wastes.....	54
Disposal of Waste Treatment Sludge.....	56
Metal Recovery by Ion Exchange.....	58
Solution Concentration and Recovery by Evaporation.....	61
References.....	66







# METHODS FOR TREATING METAL FINISHING WASTES

Each metal-finishing plant has the legal and moral responsibility of discharging its wastes in such manner as not to interfere with subsequent reasonable uses of the stream. This may be done by:

- (1) Reducing unnecessary waste of expensive and critical materials in the plant by practicing materials conservation.
- (2) Regulating the discharge of the waste so that slugs of contaminants do not cause damage.
- (3) Reducing the load or amount of contaminants by treatment so that the resulting concentrations will be below harmful levels.

Every metal finishing plant faced with a waste control problem should investigate methods for reducing the amount of material it is wasting. These methods fall under four general headings:

- (1) Employee education
- (2) Extension of solution life
- (3) Material recovery
- (4) Process substitution

The suggestions offered in the manual "Plating Room Controls For Pollution Abatement", together with the recovery methods presented in this manual, should be given every consideration before treatment of the waste is resorted to. Remember that treatment of a waste costs money - conservation saves money.

The degree of treatment required depends on local conditions peculiar to each plant. The extent of treatment necessary for a plant discharging its wastes to a stream depend on:

- (1) The uses of the stream (recreation, industrial or domestic water supply, animal watering).
- (2) Toxicity of the wastes.
- (3) Self-purification capacity of the stream.
- (4) Low stream flows that limit dilution.
- (5) Organic or inorganic constituents of the waste that interfere with natural stream functions.
- (6) Physical properties of the waste (color, odor, taste producing substances, settleable solids, floating materials).

When wastes are discharged into a municipal sewer, the municipality may define by ordinance the concentrations permissible after determining the loads or concentrations that interfere with sewerage maintenance, sewage treatment plant operation, or load



of contaminant that the city is permitted to discharge to the stream. The city may require pretreatment of a waste so that these limits will not be exceeded, and so that its effluent to the stream will meet state requirements.

When stream concentrations (limits or standards) are used for defining the waste load that can be discharged from a plant, the need for treatment and degree of treatment required depend upon the particular stream receiving the waste. The use of stream concentrations as standards may raise the problem of fair distribution between plants using the stream. In other words, an upstream plant may use the full capacity of the stream for dilution, leaving nothing for other industries further downstream. This problem may not exist until all companies have minimized their individual waste loads by good housekeeping and the uses of the stream have been defined. Then a knowledge of what can be expected from accepted methods of treatment at each plant will show whether or not the desired stream concentrations will be exceeded.

Permissible effluent concentrations theoretically set the same limitations on all plants, whether large or small, and regardless of the capacity or size of the stream. Actually, this regulation penalizes a plant that minimizes its water consumption. The need for treatment is arbitrarily established for all plants, not on the damage caused by the waste on downstream water users, but on a level that permits easier administration.

Treatment Plant Design for any particular waste problem is based on the following considerations:

- (1) Volume of waste - including variations in flow.
- (2) Load of contaminants - including variation in concentrations.
- (3) Physical and chemical characteristics of the waste.
- (4) Regulatory agency requirements.
- (5) Factory layout and its effect on ease of collection of wastes.
- (6) Separation of industrial wastes from storm or cooling waters and from domestic sewage.
- (7) Dilution available from plant process and cooling waters following treatment and from receiving stream.
- (8) Possibility of pretreatment at source.
- (9) Wastes that can neutralize each other.
- (10) Cost and availability of chemicals.



- (11) Recoverable products for reuse.
- (12) Space available for treatment plant facilities.
- (13) Land requirements for sludge disposal.
- (14) Availability of equipment that can be used or modified for use.
- (15) Ventilation.
- (16) Maintenance costs.
- (17) Operating costs.

#### Selection of Batch or Continuous Treatment

Metal-finishing industry wastes may be treated on a continuous flow basis or collected in tanks and treated by batch operation. In some cases it may be desirable to use a combination of both methods. The selection of the method to be used in any plant requires consideration of the volumes of wastes to be handled, strength of the waste, type of treatment, and quality of the waste effluent desired as well as area restrictions within the plant.

The principal differences in the two methods are:

##### A. Batch Treatment Plant

- 1. Provides facilities for retreatment of wastes should necessity arise.
- 2. Provides more time for analysis and recording before wastes are released.
- 3. Permits use of a minimum amount of treatment chemicals.
- 4. Allows positive control over the rate of discharge of treated waste.
- 5. Minimizes possibility of "slugs" or temporary high concentration getting through the treatment plant and into the sewers or streams without proper treatment.
- 6. Gives a more accurate check on water and chemical usage in a plant.
- 7. Allows holding capacity should breakdown of treatment equipment occur.

##### B. Continuous Flow Treatment Plant

- 1. Handles large volumes of waste with less tank capacity than batch treatment method.



2. Utilizes automatic controls and chemical feeding equipment with accompanying ease of operation.
3. Requires continuous maintenance and calibration schedule to insure satisfactory operation of automatic equipment.
4. Usually permits a less expensive installation for large plants.
5. Requires stand-by controls and equipment to assure proper treatment of waste should breakdowns occur.
6. Requires frequent analysis for marked changes in character of waste.
7. Requires design capacity for handling batch dumpings of concentrated solutions or provision for holding tanks to permit proper treatment of the concentrated wastes. These provisions are necessary if immediate volume dumping of spent or spoiled solutions is desired.

#### Separate Treatment of Wastes

Certain wastes are more easily treated before mixture with other wastes. Where plant layout permits, this separate treatment can reduce the chemicals and reaction time required. This separate treatment may be either complete in itself or a pretreatment step. Examples of wastes of this type are chromates, cyanides and emulsible or "soluble" oils. Treatment of these wastes is more efficient and convenient in the concentrated solutions. However, when these materials exist in rinse waters separate treatment may be required before blending with other wastes to prevent formation of toxic compounds and interference with treatment reactions.

Segregation of the various wastes, while highly desirable for many reasons, may be difficult in some of the older plants. It may be more economical in a few cases to provide larger treatment facilities than make the required changes to the sewers inside the plant.

Summary - The type of treatment plant required for a metal-finishing establishment will depend on local conditions. These conditions may be determined by making a plant survey, and it is suggested that the manual "Planning and Making Industrial Waste Surveys", developed by this committee and published by the Ohio River Valley Water Sanitation Commission, be consulted for this purpose. After a plant survey has been completed and the waste load from each source of contamination is known, the objectives can be determined by consultation with the regulatory authority.

This manual will then assist in the selection of the type of treatment that will satisfy the requirements.



# WASTES FROM METAL FINISHING OPERATIONS

Proprietary Solutions. Most metal-finishing plants use solutions which are prepared according to manufacturer's formulas. If the composition is not known, then the manufacturer should be consulted as to composition of the solution. Some of these proprietary mixtures are described in the Metal-Finishing Guidebook-Directory and this data may suggest possible treatment methods. Again, it must be remembered that each metal-finishing plant has the legal and moral responsibility of discharging its wastes in such manner as not to interfere with subsequent reasonable uses of the stream.

Cyanide Concentrates. This would include cyanide plating solutions, cyanide dips, etc., which contain relatively high concentrations. As these wastes are dumped only occasionally, a storage tank should be provided with capacity sufficient to hold solution from the largest process tank. This gives an opportunity to treat before mixing with more dilute waste water, or by controlling the rate of discharge to take advantage of dilution with other wastes.

Cyanide Rinse Waters. Waste cyanide rinse waters can be disposed of by separate treatment or by controlling the rate of discharge to take advantage of dilution with other wastes.

Concentrated Acid and Pickling Wastes. Storage should be provided for these wastes so that when possible they can be utilized for the treatment of other wastes or can be treated separately. The acid and ferrous sulfate from steel pickling processes can be used for treatment of chromates. The acid may also be used for neutralizing alkali wastes.

Strong Acid Rinse Waters. Rinses following acid dips, pickling solutions, and strong acid process solutions can be used for treatment of chromates or alkalies.

Chromates. Rinse waters containing chromium can be discharged with the acid rinses to the treatment tank for help in treatment of chromates. Concentrated solutions containing chromates can be stored for treatment, or by controlled discharge, combined with the chromate rinse waters.

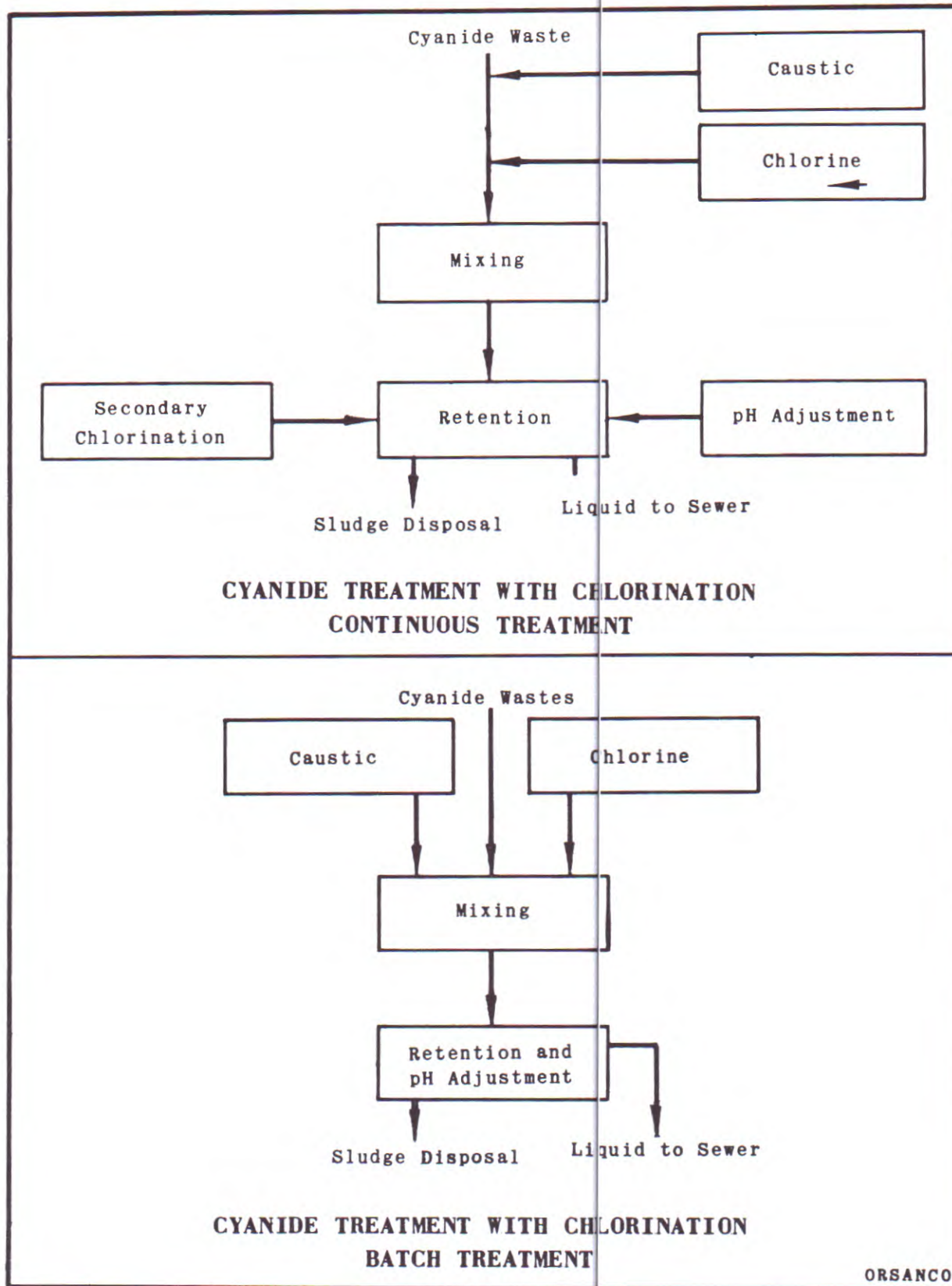
Concentrated Alkalies. These include spent alkaline cleaning solutions which are dumped periodically. The polluting materials are usually soaps, oils, and suspended solids. Storage should be provided for these solutions for controlled discharge or blending with acid wastes.

Other Wastes Requiring Treatment. In most metal finishing plants there are wastes which contain metal compounds, oils, soaps, and suspended solids which can be treated to cause precipitation. After removing the solid materials, the pH of these wastes may be further adjusted before discharge.

Waste Waters Not Requiring Treatment. Cooling water and other waste water which is substantially unchanged in quality can be discharged without treatment in order to reduce the volume of the wastes requiring treatment. This water may be used for dilution of other wastes.



Figure 1





# CYANIDE TREATMENT BY CHLORINATION (GAS)

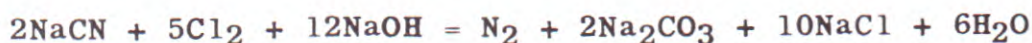
## Technique

This method involves the addition of chlorine gas, usually by means of a commercial chlorinator using either city water or waste under treatment as a carrying agent. The chlorine should be applied to a solution of high pH value, and sufficient alkali should be added to the waste solution to raise it to a pH value of approximately 11 before treatment. Chlorination of cyanide wastes must always be done with rapid and thorough agitation of the solution being treated. This is extremely important to insure complete contact between the chlorine and the cyanide and to avoid the formation of solid cyanide precipitates which may resist the action of chlorine in solution. Where free cyanides are being treated, the appearance of residual chlorine in the solution usually indicates the destruction of all of the cyanide. In some cases, however, the presence of metals allows the formation of metallic cyanide complexes which resist chlorination. In these cases it may be found that even in the presence of free residual chlorine a distillation test will show some cyanide still in solution. Under these conditions, chlorination is continued until no free cyanide is found by standard test methods, and then the pH value of the solution is lowered to below 7 by slow addition of an acid or by continued chlorination. If acid is used to reduce pH, chlorination must be continued to destroy the liberated cyanide. Indications are that hydrochloric or muriatic acid is more effective than sulfuric acid in destruction of cyanide complexes under these conditions.

If after chlorination a large excess of free chlorine remains in the solution, it may be necessary to remove this free chlorine by adding a material such as sodium bisulfite or sodium thiosulfate.

## Reaction

(Probable reaction with excess chlorine in presence of NaOH)

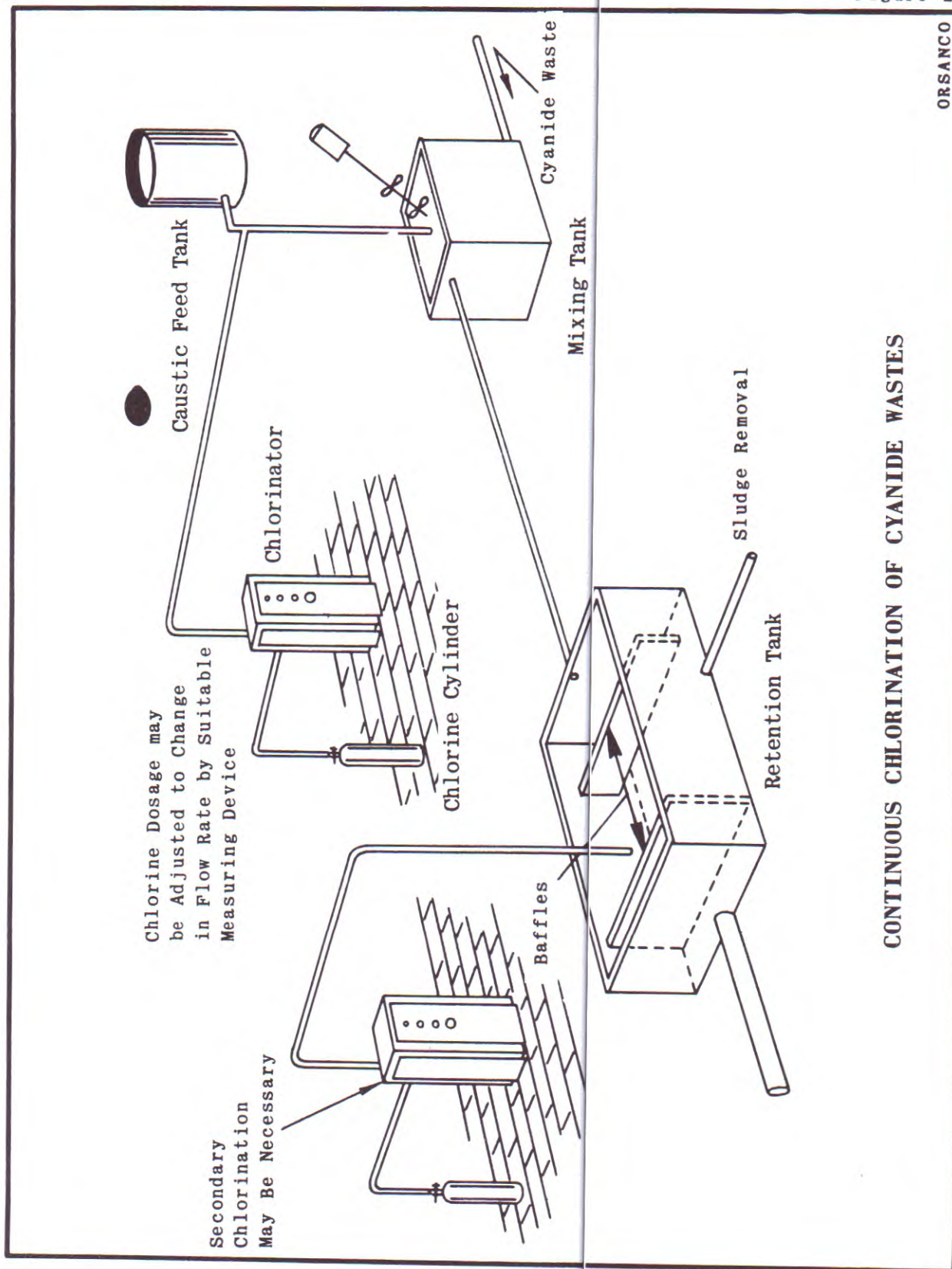


## Plants Using This Method or Have Used It In The Past

- A. Curtis Wright Corporation, Propeller Division, Caldwell, N.J.
- B. Talon, Inc., Meadville, Pennsylvania.
- C. King-Seeley Corporation, Ann Arbor, Michigan.
- D. Westinghouse Electric Corporation, Beaver, Pennsylvania.  
(Continuous flow with emergency provisions for semi-automatic)
- E. Electric Auto-Lite Company, Lockland, Ohio.

Figure 2

ORSANCO



# CONTINUOUS CHLORINATION OF CYANIDE WASTES



- F. Detroit Diesel Engine Division, GMC, Detroit, Michigan.
- G. Pontiac Motor Division, GMC, Pontiac, Michigan (no longer in use - now using sodium hypochlorite solution).
- H. General Electric Company, Erie, Pennsylvania.

#### Notes

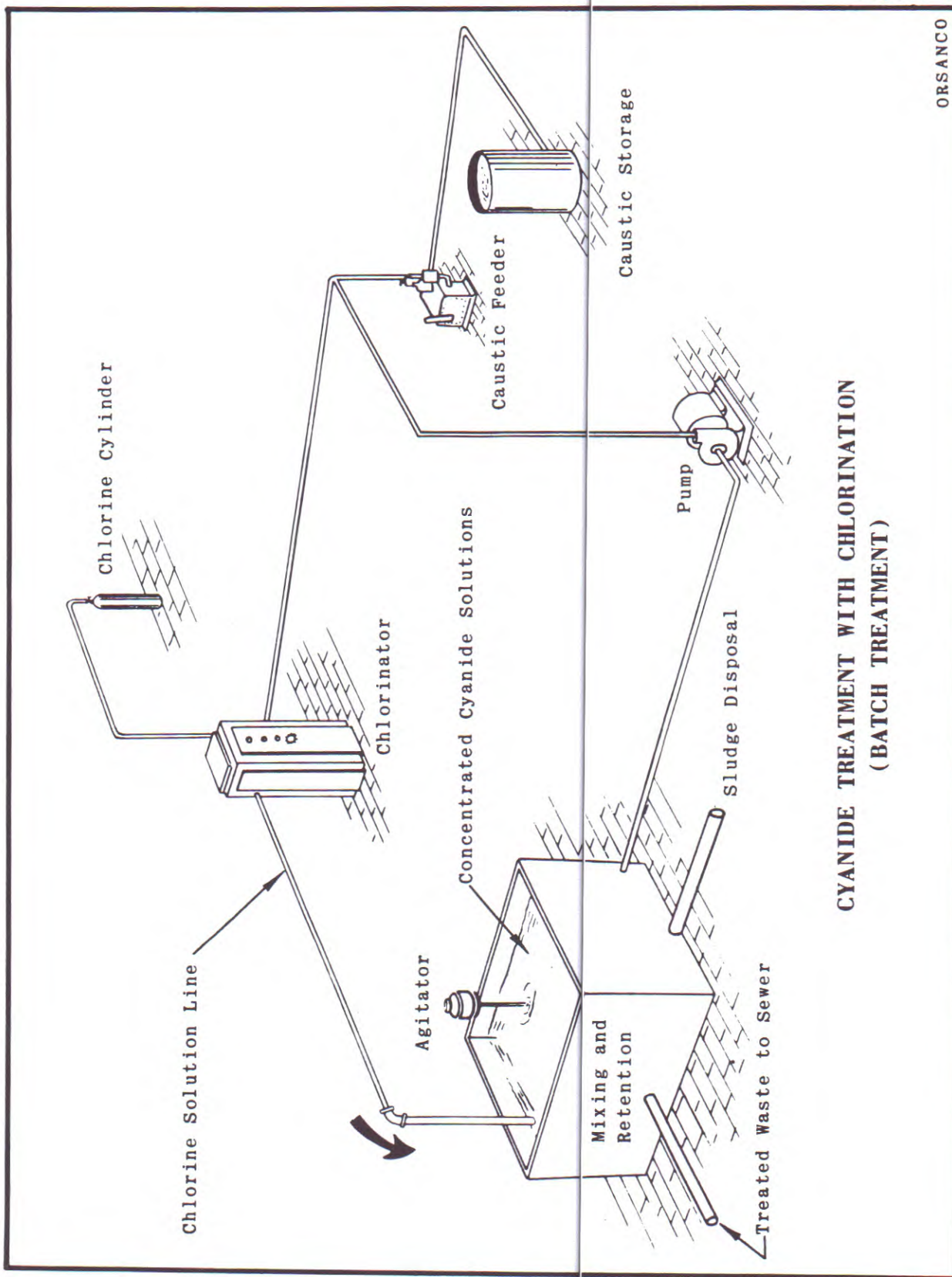
- A. Will destroy last traces of free cyanide with sufficient reaction time.
- B. Can be used for either batch treatment or continuous flow processes.
- C. Also will destroy cyanates if sufficient chlorine is added.
- D. The presence of heavy metals in waste may interfere with treatment by chlorination. These metals may form complexes with cyanides making them more resistant to chlorination and requiring adjustment of pH as described under Technique.
- E. Standard liquid chlorine feeders may be used for dispensing chlorine.
- F. Construction and operation costs compare favorably with other methods.
- G. Maintenance of pH above 10.5 is recommended for the destruction of free cyanides in order to minimize the evolution of toxic gases, to accelerate the reaction, and for economy.
- H. Use of gaseous chlorine sometimes extends treatment time of concentrated cyanide wastes to 24 - 30 hours because of limited solubility of the chlorine.
- I. Copper cyanide solutions containing Rochelle salts will contain copper tartrate complexes. Chlorination alone will not destroy the soluble copper compounds which may be toxic to stream life. Use of calcium or sodium hypochlorite in the presence of calcium chloride or calcium hydroxide will destroy the tartrate complex and precipitate the copper.

#### Design Considerations

Theoretical chemicals required (in pounds) to convert one pound of CN to:

Cyanate		N <sub>2</sub> and CO <sub>2</sub>	
Cl <sub>2</sub>	NaOH	Cl <sub>2</sub>	NaOH
2.73	3.08	6.83	6.16

Operators in some plants have found that the average usage of caustic soda is one pound for each pound of chlorine. Consid-



**CYANIDE TREATMENT WITH CHLORINATION  
(BATCH TREATMENT)**

ORSANCO



eration should be given to the available alkalinity in making these additions. Actual chlorine requirements will exceed theoretical amounts because of high chlorine demand of such substances as copper, wetting agents, organics and the like, contained in the wastes.

Thorough agitation is necessary to complete reaction. At least one hour retention time should elapse before chlorinated cyanide waste is mixed with any waste containing chlorine demanding substances.

Between pH 7-10, approximately 0.4 ounce of commercial lime would be needed for each ounce of Rochelle salt in solution. Solutions averaging from 4 to 8 ounces of Rochelle salt per gallon will need 1.6 to 3.2 ounces of lime per gallon of Rochelle solution to treat the tartrates present. Additional lime will be required to react with carbonates, either added to the solution or formed during its use. These quantities may be calculated by the usual methods.

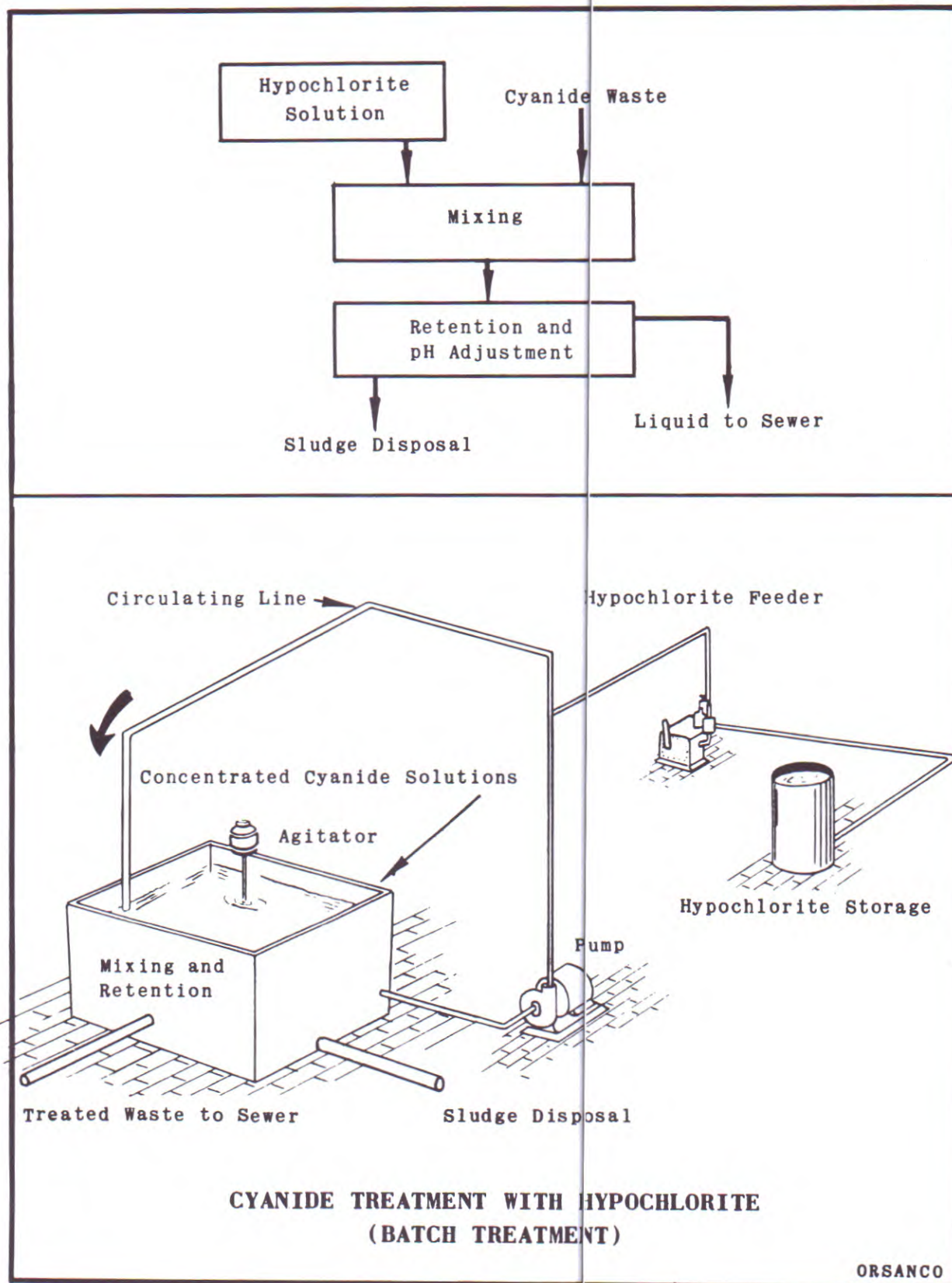
#### References

1, 11, 13, 14, 16, 17, 18, 23, 30, 35, 44, 48, 50.

#### Summary

Considered to be one of the best methods for cyanide destruction.

Figure 4



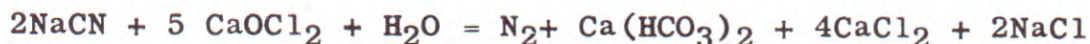
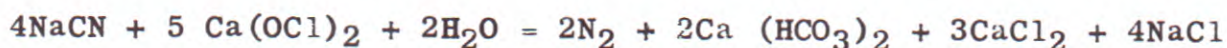
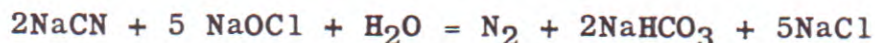


# CYANIDE TREATMENT BY HYPOCHLORITES

## Technique

In general, application of hypochlorite solutions should follow the same principles as those indicated for gaseous chlorine. The same precautions are necessary and the same controls should be used.

## Reactions (Probable)



## Plants Using This Method

- A. Pontiac Motor Division, GMC, Pontiac, Michigan.
- B. National Twist Drill, Rochester, Michigan.
- C. GMC Truck & Coach Division, GMC, Pontiac, Michigan.
- D. American Central Division, Avco Manufacturing Corp., Connersville, Indiana.

## Notes

- A. Hypochlorites Obtainable are:
  - NaOCl - - - Sodium hypochlorite
  - Ca(OCl)<sub>2</sub> - - Calcium hypochlorite
  - CaOCl<sub>2</sub> - - - Chloride of Lime  
(bleaching powder)
- B. Requires less special equipment than gas chlorination.
- C. Chlorine gas in aqueous solution reacts with an alkali (sodium or calcium) to form hypochlorite and chloride. The hypochlorite is then sold on the basis of the chlorine available for oxidation. This should be noted in comparing costs of hypochlorite and gaseous chlorine. In aqueous chlorine gas oxidation, half the chlorine is used up during the solution procedure in the formation of chlorides which have no effect on oxidation. However, in using either chlorine gas or hypochlorite, the same amount of chlorine available for oxidation will be required.
- D. No additional alkali needed with sodium hypochlorites. A small quantity may be necessary with calcium hypochlorite.
- E. Handling of liquid hypochlorite involves less problems and cost than handling of large numbers of chlorine gas cylinders, (eg. return of cylinders).



- F. The hypochlorites present less hazard than gaseous chlorine.
- G. Rapid addition of chlorine gas or hypochlorite may result in formation of a cyanide sludge when heavy metal cyanides such as copper or zinc cyanide are being treated. This will result in the reappearance of cyanide in the solution some time later. This effect can be minimized by vigorous agitation of the solution during treatment.
- H. Sodium hypochlorite is furnished as a solution and as such provides several advantages over solid calcium hypochlorite or bleaching powder.
- I. Chloride of lime (35% available chlorine) produces greatest sludge volume. Calcium hypochlorite (70% chlorine) produces a minimum amount of sludge and is preferred. Liquid sodium hypochlorite does not add sludge. Some difficulty with foaming may result when feeding calcium hypochlorites to solutions of high concentration.
- J. Control of temperature for sodium hypochlorite treatment is not so critical as with gas chlorination, as heat of gas solution is not developed. This permits more rapid addition of treatment agent.
- K. Rate of gas addition in gas chlorination is limited by slow solubility. Addition rate of liquid hypochlorites limited mainly by capacity of equipment.
- L. In batch treatment the use of liquid hypochlorites adds to the volume of solution to be handled.
- M. Copper cyanide solutions containing Rochelle salts will contain copper tartrate complexes. Chlorination alone will not destroy the soluble copper compounds which may be toxic to stream life. Use of calcium or sodium hypochlorite in the presence of calcium chloride or calcium hydroxide will precipitate the copper.

#### Design Considerations

Chemicals required in one plant to convert one pound CN:

	NaOCl (16% available Cl <sub>2</sub> )	Cl <sub>2</sub>
Copper Cyanide Solution	2.61 gallons	4.23 pounds

Storage facilities resistant to corrosion must be provided for sodium hypochlorite.

Lime requirements for treatment of Rochelle salt solutions described under "Design Considerations" of "Cyanide Treatment by Chlorination".

#### References

12, 13, 28, 50.



## Summary

Adaptable to any size treatment plant where addition of extra liquid volume is not objectionable. Suited to continuous or batch treatment. May be less expensive than chlorine gas depending on location and relative overall costs. Considered to be one of the best methods for cyanide destruction at the present time.

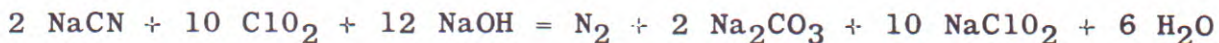
# CYANIDE TREATMENT BY CHLORINE DIOXIDE

## Technique

Chlorine dioxide is generated by reacting a solution of sodium chlorite with chlorine solution in a glass chamber or generator designed for this purpose. The solutions enter at the bottom of the glass generator which is filled with Raschig rings to aid in mixing the two solutions and the chlorine dioxide solution passes out the top through rubber hose into the cyanide waste to be treated. Chlorine dioxide treatment, like chlorination, must be done with rapid and thorough agitation of the waste being treated to insure complete contact between the chlorine dioxide and the cyanide.

## Reactions

(Probable reaction with chlorine dioxide in presence of NaOH)



## Plants Using This Method

Experimentally at Talon, Inc., Meadville, Pennsylvania.

## Notes

- A. Presence of heavy metals in waste appear to prevent 100% destruction of cyanide with chlorine dioxide. Metals complexed with cyanide are likely to be offenders.
- B. Can be used for either batch treatment or continuous flow processes.
- C. Standard chlorine dioxide generator may be used for dispensing chlorine dioxide with only intermittent inspection.

## Design Considerations

Since this process has only been in operation experimentally, no figure is available for chemical requirement. Experiments have been made varying the amounts of sodium chlorite between 0.5 to 2 pounds per pound of cyanide, and 1 to 3 pounds chlorine per pound of cyanide. Increasing the quantity of chlorine to 6.5 pounds per pound of cyanide will destroy all the cyanide, but this has no advantage over straight chlorination.

## Summary

More laboratory work and pilot plant application will be necessary before this system can be recommended for complete destruction of cyanides.



# CYANIDE TREATMENT BY OZONE

## Technique

Ozone is generated in commercially available equipment and passed through solutions containing cyanides. For efficient use, the ozone must be introduced in a manner insuring intimate contact with all parts of the solution. This may be done by the use of a bubble column or by dispersion of the ozonized air through diffuser plates at the bottom of the diffusion chamber. Certain metal catalysts are used where necessary.

## Reactions



## Plants Using This Method

This method is still in the experimental stage and so far has not been applied to full scale plant operation.

## Notes

- A. Certain complex cyanides require the use of catalysts such as iron, manganese or copper. Copper and nickel cyanide solutions need no catalyst for complete destruction.
- B. Because of the possibility of toxic effects from ozone, the system must be well ventilated. Maximum permissible concentration of ozone in air for prolonged exposure is 1 ppm by volume as compared to 10 ppm hydrogen cyanide.
- C. Loss of ozone from the system during treatment may result in rapid deterioration of rubber or other easily oxidized materials close to the treatment system.
- D. Ozone can be used for the treatment of relatively large volumes of solution containing less than 5 ppm cyanide (CN). This makes it adaptable to continuous treatment plants for the treatment of relatively dilute rinse waters.
- E. The oxidation of cyanide to cyanate by ozone is rapid in any case, and practically instantaneous in the presence of a trace of copper. Oxidation of the cyanate ion by ozone is apparently very slow.
- F. Ozone oxidizes the ferrocyanides to ferricyanides.
- G. pH seems to have little effect on oxidation within the range 3 to 12.5.

### Design Considerations

Ozone required is approximately 2.0 pounds per pound of cyanide reacted.

Plastics, wood, aluminum, stainless steel or black iron protected by an asphaltic enamel or paint should be used for construction of the ozonation system or any part of the system exposed to ozone.

### References

59

### Summary

More field work and pilot plant application will be necessary before this system can be recommended.



# CYANIDE TREATMENT BY CONVERSION TO LESS TOXIC CYANIDE COMPLEXES

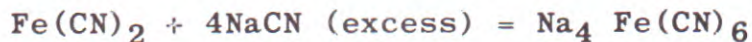
## Technique

Treatment with ferrous sulfate usually takes place in alkaline solution. Under these conditions the ferrous sulfate is first converted to ferrous hydroxide which then reacts with the cyanide to form ferrocyanide. The presence of oxygen from the air causes some oxidation of the ferrous hydroxide and consequent formation of ferric ferrocyanide or Prussian Blue. The use of ferrous sulfate is therefore invariably accompanied by the formation of quantities of dark blue sludge.

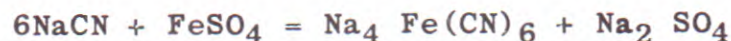
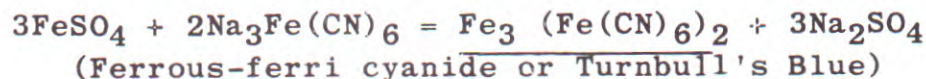
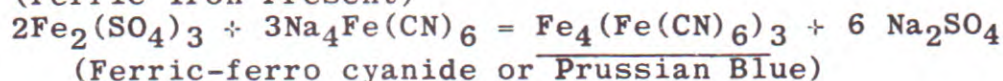
Treatment with other complex forming metals such as nickel from the nickel rinse results in the formation of the corresponding metal cyanide complex which is relatively non-toxic. Treatment with nickel rinses is only conducted to the point at which precipitation appears. At this point all free cyanide has been tied up in a complex.

## Reaction

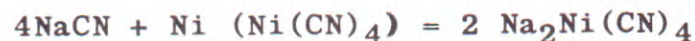
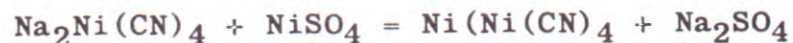
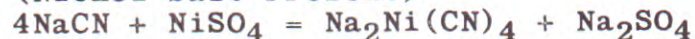
(Ferrous Iron Present)



(Ferric Iron Present)



(Nickel Salt Present)



## Plants Using This Method

No plants in the United States reported to be using these methods.

## Notes

- A. Tests have been conducted which indicate that in the presence of sunlight, ferrocyanides present in the stream would

be converted to cyanides.

- B. Large volume of sludge is produced if Prussian Blue or Turnbull's Blue is formed.
- C. Strong color of many ferro and ferri cyanides may be objectionable.
- D. Relatively inexpensive where waste ferrous sulfate or nickel rinses are available.
- E. Method affords only partial treatment leaving some cyanide compounds yet to be treated.

#### Design Considerations

Laboratory work has shown that 7 parts of  $\text{FeSO}_4$  are required to react with 1 part of CN (theoretical requirements are 2.3 parts  $\text{FeSO}_4$  to 1 part CN). Copper was completely removed as a sludge.

#### References

2, 8, 11, 13, 34, 41, 44.

#### Summary

These processes require more investigation and pilot plant scale application before being considered satisfactory treatment methods for cyanide.



# CYANIDE TREATMENT BY ELECTROLYTIC OXIDATION

## Technique

Cyanide solutions may be destroyed by passing electric current through the heated waste. Exhaust ventilation equipment should be provided to remove the gases from this process. This method is especially adapted to reducing concentrated solutions to a point where secondary treatment may satisfactorily remove remaining cyanide.

## Plants Using This Method

- A. Guide Lamp Division, GMC, Anderson, Indiana.
- B. National Cash Register Company, Dayton, Ohio.
- C. Doehler-Jarvis Co., Grand Rapids, Michigan.

## Notes

- A. Experience has shown that a high current density at the anode increases the efficiency of decomposition more than it does at the cathode.
- B. Some hydrogen cyanide gas is given off during the process and an exhaust system is necessary.
- C. The efficiency decreases as the cyanide concentration decreases and the method is not applicable to dilute solutions, such as rinse waters, because of the low conductivity.
- D. Although in most cases it may be necessary to further treat the solutions, the overall cost of disposal may be decreased by first using electrolytic decomposition.
- E. In some instances, the plating tank itself can be used by simply raising the temperature, installing anodes and cathodes and raising the current density. Temperature and agitation are important factors.
- (F) Experience has shown the process to be by far the cheapest method of decomposition of concentrated cyanide waste. Copper may be recovered from copper cyanide solutions in a form suitable for recasting into anodes.

## Design Considerations

Solution heated to about 200°F. and air may be used for agitation. The anode current density is maintained from 30 to 80 asf. As long as the anode current density is high, the ratio of anode to cathode area does not appear too important. A high ratio increases power costs and decreases the quality of the

Figure 5

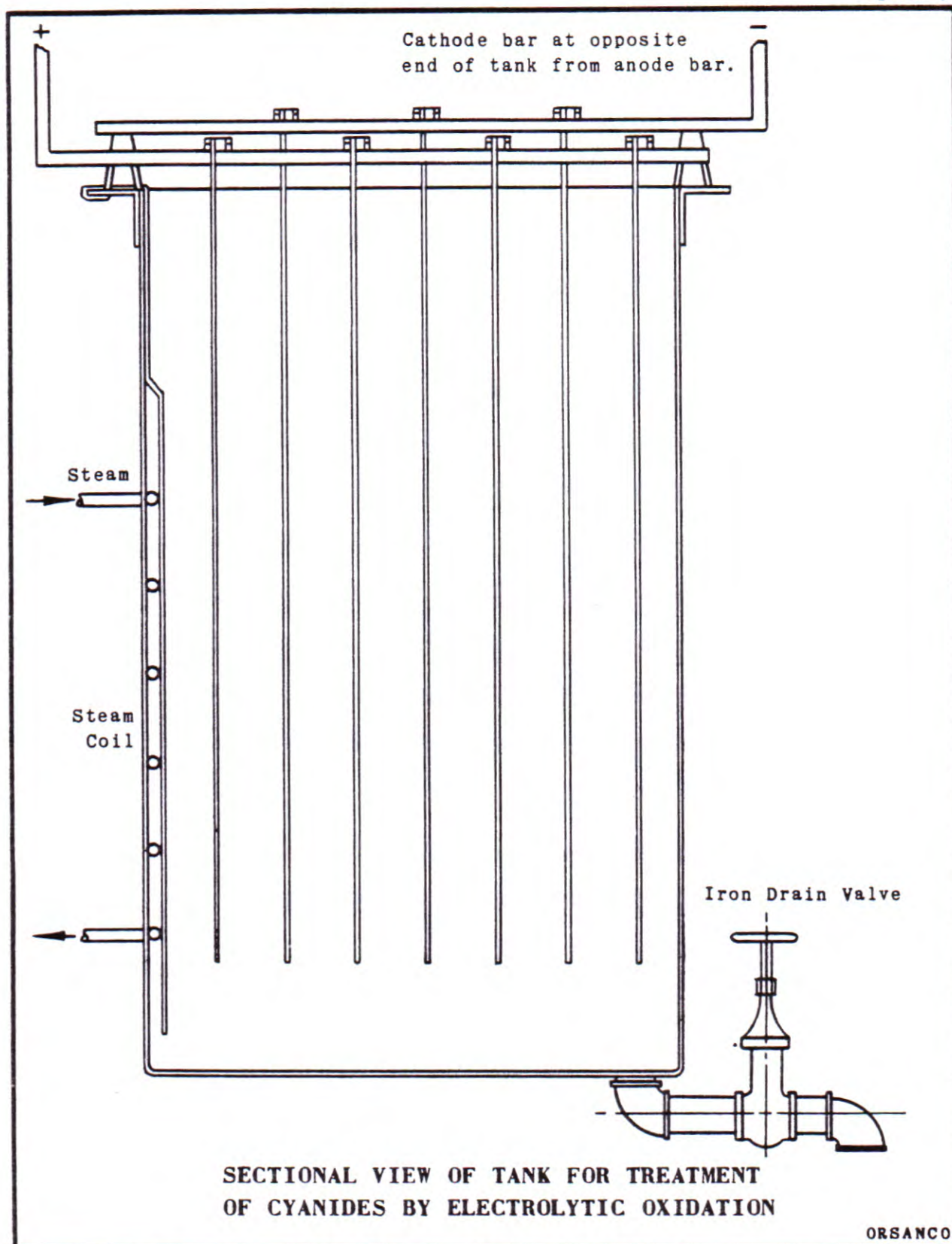




plate on the cathode. Copper anodes are of particular advantage in electrolysis of copper cyanide solutions, due to less difficulty with polarization and anode loss. Stainless steel or cold rolled sheet anodes may also be used. Stainless steel sheets give lower efficiency than cold rolled sheets. The steel anodes are corroded slowly, but this may be disregarded due to their lower costs. Reaction time will depend upon volume-current ratio and initial concentration and may vary from several hours to several days. Cyanide may be reduced to 5 ppm by this method but reduction below 1000 ppm may prove uneconomical. Metal residue will be negligible. From 2.5 to 3.5 KWH per pound of cyanide (CN) are required at 16 asf (6 volt generator at 70% efficiency).

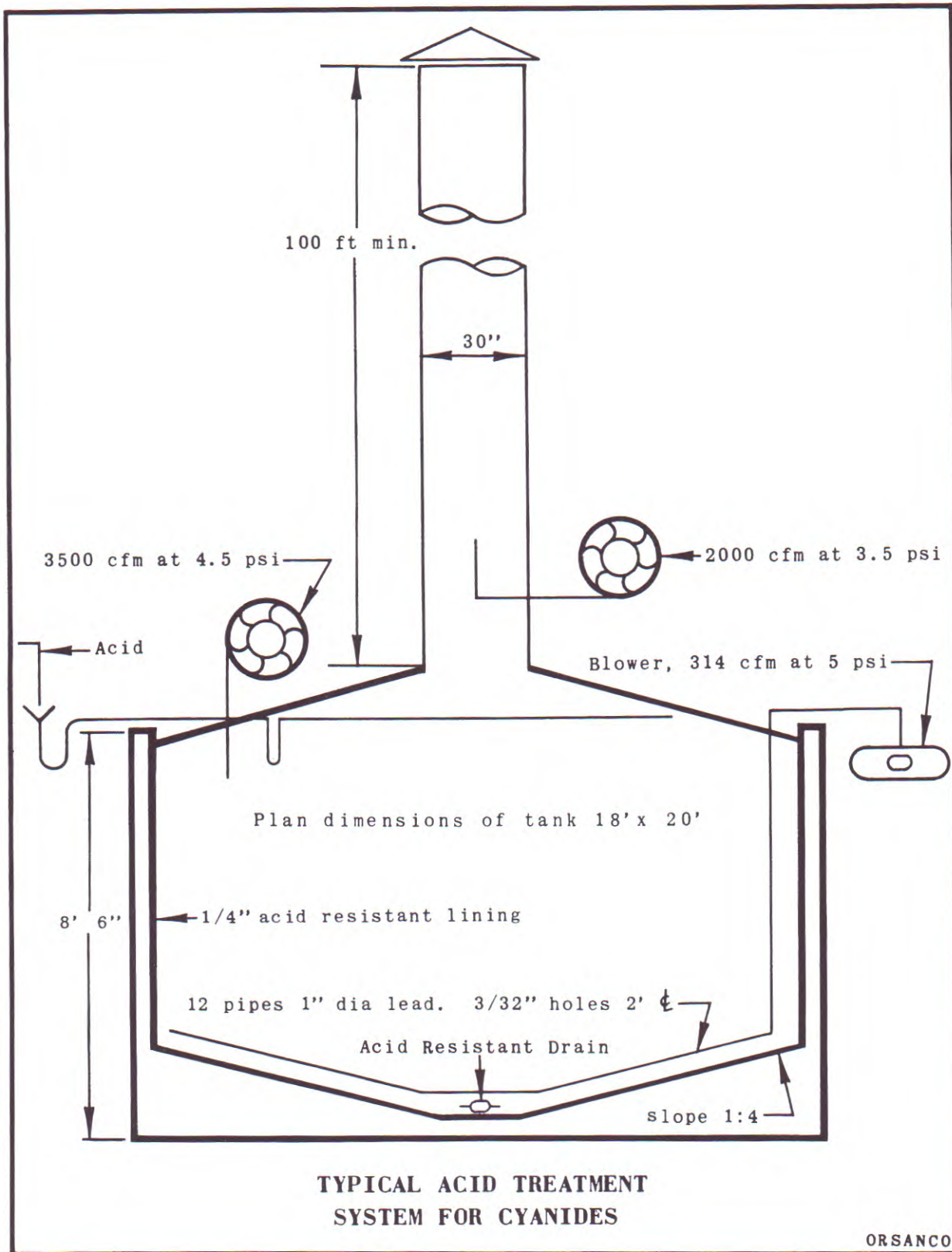
#### References

12, 17, 36, 42, 60.

#### Summary

A very satisfactory method for disposing of concentrated solutions, such as discarded plating baths, by batch treatment. Further treatment may be necessary depending on final analysis and plant conditions.

Figure 6



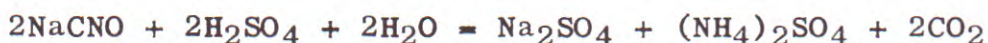


# CYANIDE TREATMENT BY ACIDIFICATION

## Technique

Either waste acid or new acid is added to cyanide wastes usually in a closed hooded reactor and fumes vented through high stack with large air dilution by means of blower or compressed air.

## Reaction



## Plants Using This Method or Have Used It In The Past

- A. Chevrolet Motor Division, GMC, Flint, Michigan. (No longer in use - process changes eliminated use of concentrated cyanides.)
- B. Kaiser-Frazer Corp., Willow Run Plant, Detroit, Michigan. (Not using process at present time.)
- C. Ternstedt Division, GMC, Trenton, N.Y. (Plant never used.)

## Notes

- A. Cyanide in effluent ranges from 0.1 to 1.0 ppm.

## Design Considerations

Acid required will depend on the amount of hydroxide, carbonates and cyanide present. Sixteen hours aeration time recommended. Acid proof and gas tight construction required throughout.

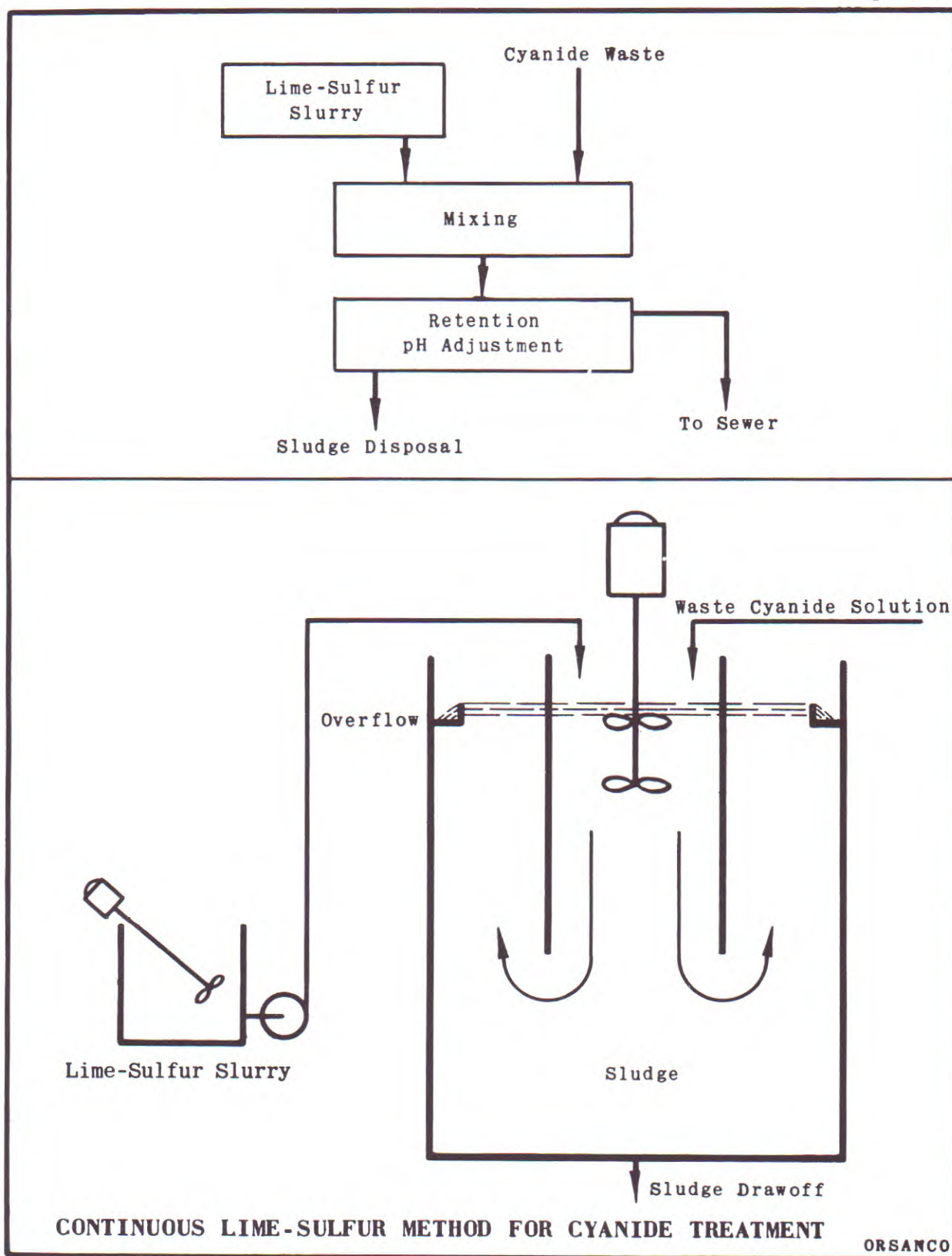
## References

5, 11, 15, 21, 22, 24.

## Summary

This method appears to lend itself to batch treatment rather than to continuous flow methods. Equipment and operation costs are more expensive than for chlorination method. Copper cyanide is deposited as a sludge and must be disposed of separately. The danger of hydrogen cyanide fume concentration under certain atmospheric conditions is always present. Because of the possibility of escaping deadly hydrocyanic acid gas, this method is not considered satisfactory.

Figure 7





# CYANIDE TREATMENT BY LIME SULFUR METHOD

## Technique

Two procedures are available for the treatment of cyanide solutions with lime sulfur. The first of these is a batch treatment method and requires only the addition of lime sulfur solution to the cyanide solution in a treatment tank until the resulting yellow solution becomes bright orange in color. Heating to about 140°F. may be necessary to bring this reaction to completion within a reasonable time.

The second method is continuous. Cyanide wastes are allowed to flow into a reaction tank and mixed with commercial lime-sulfur solution (spray material). The solution is then allowed to flow through a retention tank where solid matter settles out.

## Reaction

The reactions taking place are obscure, but it is believed that the calcium polysulfide obtained from the lime-sulfur mixture reacts with the cyanides to form calcium and sodium thiocyanate, with sodium sulfate, sodium carbonate, and free sulfur as by-products.

## Plants Using This Method

Hamilton Standard Division, United Aircraft Corporation, Hartford, Connecticut.

## Notes

- A. Quantities of sludge remain after treatment.
- B. Solution remaining is still somewhat toxic.
- C. Does not destroy all cyanide. It has been claimed that this method will not reduce cyanide below 100 ppm as CN.
- D. Contact of the treated solution with acid will produce hydrogen sulfide, which may result in objectionable odors and corrosion of equipment.
- E. Contact of the treated solution with chlorine or other strong oxidizing agents may result in release of hydrocyanic acid gas.

## Design Considerations

Two pints of lime sulfur solution, 32°Be', required to treat one pound sodium cyanide, or 3.76 pints per pound of CN. Another source states 3.5 pounds lime sulfur per pound of CN (1.84 pounds per pound NaCN).

## References

12, 13, 15, 21.

## Summary

This process limited in usage because of sludge and fumes produced during reaction of chemicals and cyanide wastes. Unless adequate dilution waters are available, the effluent requirements may not be satisfied.



# CYANIDE TREATMENT BY ION EXCHANGE

## Technique

This method is applied to rinse waters following the plating solution or to other relatively dilute cyanide wastes. In practice, the method consists of passing the dilute cyanide solution through a bed of ion exchange resins, so selected that the cyanide is removed either as cyanide or as a cyanide complex. When the resin bed has become saturated with cyanide, the system is regenerated by one of several methods. The system may be compared in operation to the use of a filter intended for the removal of suspended matter, as it virtually filters the dissolved cyanide from solution.

## Plants Using This Method

No knowledge. The system is being investigated at Yale University, Purdue University and several industrial and manufacturing organizations.

## Notes

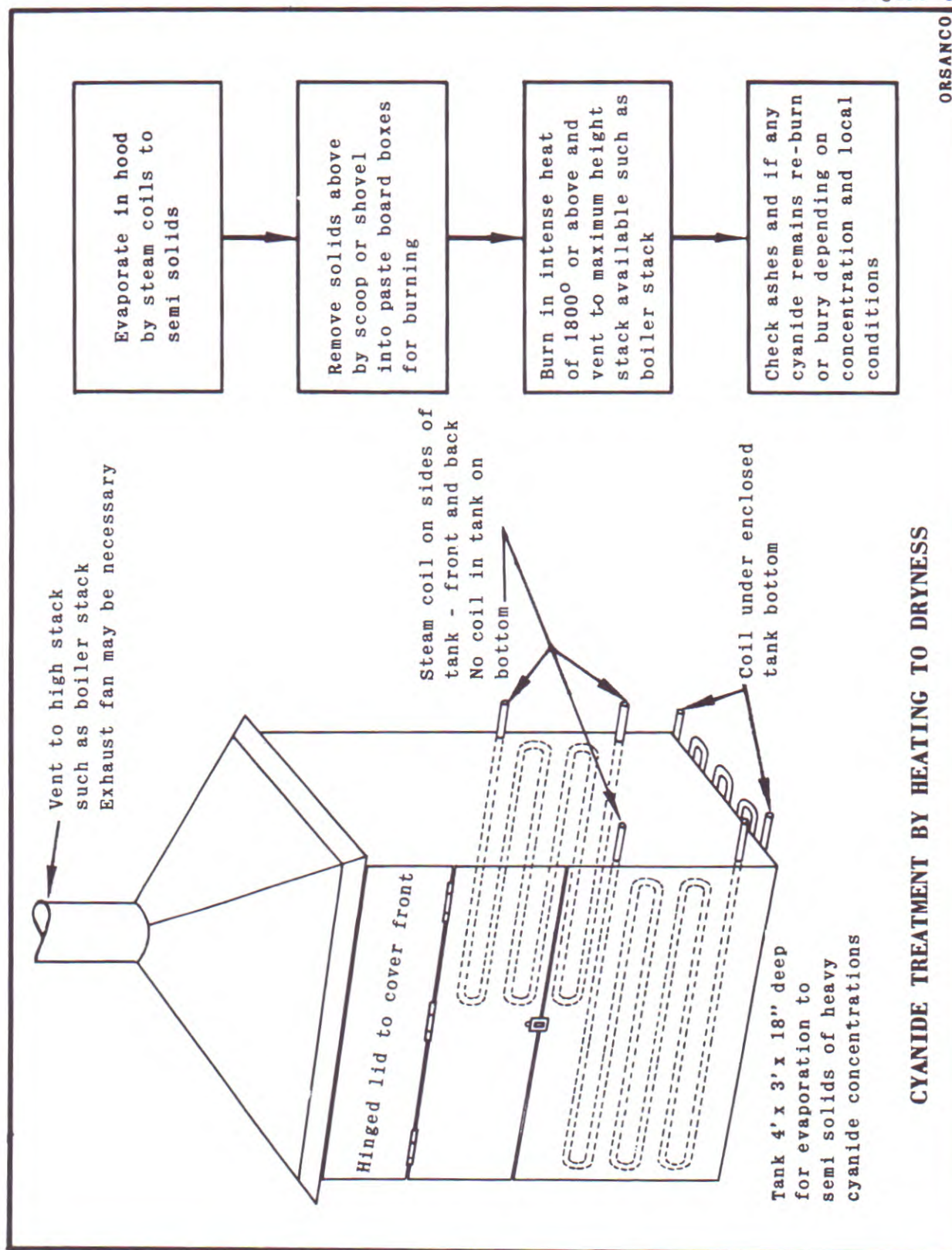
- A. This method is still in the experimental stage with respect to its application to cyanide solutions.
- B. With the proper selection of regenerating solutions there is some promise of reuse of the regenerated cyanides in the process.
- C. Unless reuse of the regenerated cyanide is intended, the method must be considered simply a means of concentrating the dilute cyanides. This concentrated cyanide must then be disposed of by some conventional method.
- D. The resin bed must be rinsed following regeneration. The rinse water will then contain some of the regenerating solution, which in some methods may be a cyanide. This makes it necessary to provide treatment for removal of the cyanides from the rinse water and presents an additional complication to the method.
- E. Selection of the proper resins may permit recovery of not only cyanides but of many of the metals also present in cyanide plating solutions.

## References

6

## Summary

This method offers considerable promise at present, but is still in the experimental stage and can not be recommended at this time for application in the metal finishing industry.



### CYANIDE TREATMENT BY HEATING TO DRYNESS



# CYANIDE TREATMENT BY HEATING TO DRYNESS

## Technique

Batch treatment only - evaporate to dryness, exhaust the fumes and then burn off any organics (brighteners) at temperatures greater than 1800°F. to decompose remaining cyanides. Residue would contain metals such as copper, zinc, etc., which should be disposed of in a safe manner.

## Plants Using This Method

Talon, Inc., Meadville, Pennsylvania (experimental).

## Notes

- A. Sludge remaining is of small volume and mostly insoluble and can be burned under controlled conditions above 1800°F.
- B. Not an economical process unless waste heat can be used or unless original batch is highly concentrated.
- C. Cyanide decomposition is not complete during evaporation. Complete destruction possible by burning.
- D. Some HCN fumes given off during evaporation.
- E. Applicable to badly contaminated solutions.

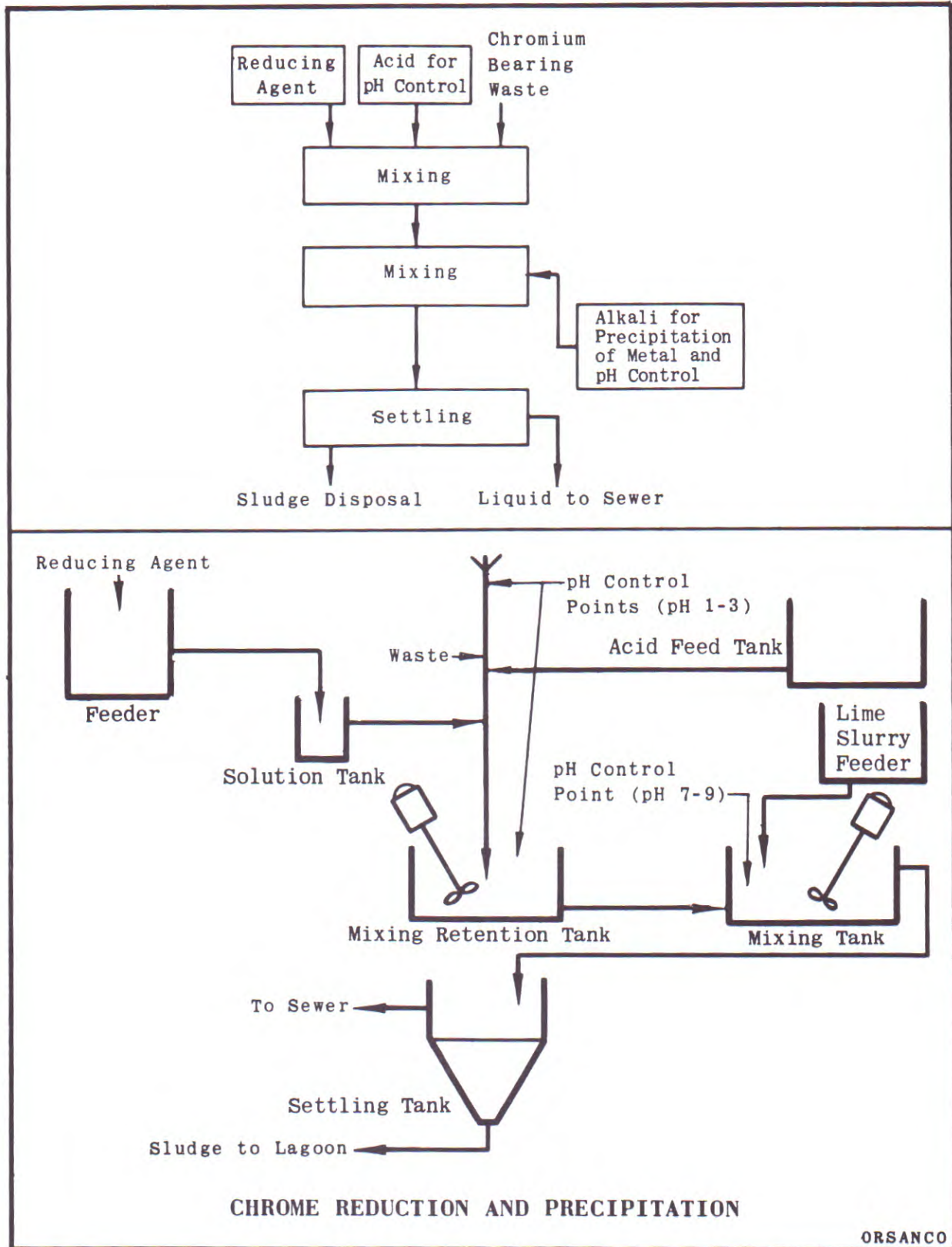
## References

13

## Summary

An effective means of destroying cyanide except that metals are not recovered.

Figure 9





# CHROMIUM TREATMENT BY REDUCTION AND PRECIPITATION

## Technique

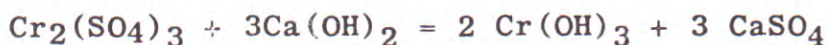
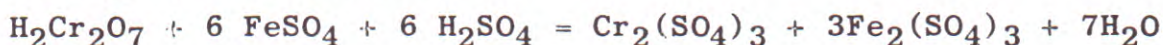
Hexavalent chromium (chromic acid or chromates) in the plant wastes is reduced to trivalent chromium by reducing agents, such as ferrous sulfate, sodium bisulfite, sulfur dioxide and other forms of  $\text{SO}_2$ . Sufficient free mineral acid should be present to combine with the reduced chromium and also maintain a residual pH of 3.0 or lower to insure complete reaction.

After reduction, an alkali, usually lime slurry, is added to effect neutralization of the acid and precipitation of the metal salts. The neutralization and sedimentation of the reduced chromium wastes can be done concurrently and in the same equipment with other plating wastes.

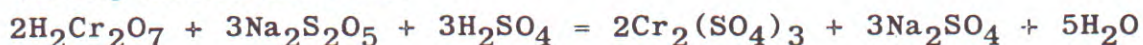
The addition of the reducing agents can be controlled either by analysis for hexavalent chromium or by the oxidation-reduction potential. Control using the oxidation-reduction potential is impractical above 2.5 pH. In using either method, great care must be exercised to define and maintain conditions that will insure complete treatment. It is convenient to control the acidity during reduction and alkalinity during neutralization by means of pH.

## Reactions

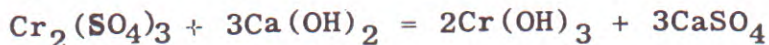
(Using ferrous sulfate)



(Using metabisulfite)



Using sulfur dioxide)



## Plants Using This Method

- A. King-Seeley Corp., Ann Arbor, Michigan. (Chromium waste pH adjusted prior to treatment and sulfur dioxide and lime used.)



- B. The Electric Auto-Lite Plant, Lockland, Ohio. (Ferrous sulfate and lime used originally. Using sodium bi-sulfite and lime at present time.)
- C. Talon, Inc., Meadville, Pennsylvania. (Ferrous sulfate and lime used.)
- D. Kaiser-Frazer Corporation, Willow Run, Michigan. (Ferrous sulfate and lime used with sludge disposal in lagoons.)
- E. Standard Steel Spring Company, Newton Falls, Ohio. (Continuous flow with ferrous sulfate additions automatically controlled. Use of evaporation process has reduced the amount of chromic acid in wastes.)
- F. New Departure Division, GMC, Sandusky, Ohio. (Continuous flow introducing controlled amount of sodium bisulfite or waste pickle acid prior to precipitation.)
- G. General Electric Co., Erie Plant, Erie, Pennsylvania. (pH adjusted prior to treatment when necessary. Ferrous sulfate introduced to reduce chromium. Lime added and sludge removed.)
- H. General Electric Co., Brockport, New York. (pH is controlled and chromium reduced by a mixture of ferrous sulfate and sulfuric acid. Soda ash added in agitator tank and sludge removed in a settling tank.)
- I. Ranco, Inc., Delaware, Ohio. (Batch treatment with sodium metabisulfite.)

#### Notes

- A. Ferrous sulfate, sodium bisulfite or sulfur dioxide may be used depending on the economics of the problem as to supply of the reagent, volume of resulting sludge, type of feeding equipment required, etc. Sodium bisulfite and sulfur dioxide give less sludge.
- B. Both ferrous sulfate and sodium bisulfite may present problems by caking and bridging while in storage due to their capacity for picking up moisture from the air.
- C. The ferrous sulfate available in waste pickle liquors may be used.
- D. In general, the efficiency of chrome reduction increases with reduction of pH. With certain reducing agents, however, chromate reduction can take place under alkaline conditions. If ferrous sulfate is used as a reducing agent under alkaline conditions, no control can be exercised over the characteristics of the sludge formed. The sludges resulting from neutralization after reduction of chromium in acid solution are usually more dense and settle faster. Economic considerations should be studied in each specific problem.



- E. Barium sulfide has been used, but is not recommended because it is expensive and excess barium in the wastes is toxic.
- F. The amount of alkali required for precipitation of metallic wastes should be determined for each specific waste by actual test because of variation of buffering action.
- G. The reactions as shown by the equations given above may not be complete unless sufficient free mineral acid is also present to give a residual pH of 3.0 or less. This extra acid will increase the quantity of lime required for neutralization. An excess of reductant is usually required to give a practical rate of reaction and insure complete reduction.
- H. Hexavalent chromium can be reduced in basic solution. However, where the reduction of chromium is carried out in rather concentrated solutions, the formation of precipitates may result in entrainment of hexavalent chromium and thus obviate the waste treatment. Carrying out the reduction on the acid side prevents the formation of the precipitate. It is possible, however, to reduce small quantities of hexavalent chromium in basic solutions by the use of sulfur dioxide.
- I. Trivalent chromium in solution will be oxidized to chromates if chlorine is added. The oxidation appears to proceed more rapidly if the waste is chlorinated on the acid side before the addition of lime. However, some oxidation can take place in an alkaline solution.

### Design Considerations

Theoretical quantities of chemicals used and sludge produced are given for each process:

#### Using ferrous sulfate

##### Chemicals

- 1 ppm Cr requires 16.03 ppm Copperas ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ )
- 1 ppm Cr requires 6.01 ppm Sulfuric Acid, (66°Be')
- 1 ppm Cr requires 9.48 ppm Lime (90%) for precipitation of both metallic sulfates.

##### Sludge

- 1 ppm Copperas (thru  $\text{Fe}_2(\text{SO}_4)_3$ ) produces 0.38 ppm  $\text{Fe}(\text{OH})_3$
- 1 ppm Lime (as  $\text{Ca}(\text{OH})_2$ ) produces 1.84 ppm  $\text{CaSO}_4$  (not all sludge)
- 1 ppm Chromium (as Cr) produces 1.98 ppm  $\text{Cr}(\text{OH})_3$

#### Using sodium metabisulfite

##### Chemicals

- 1 ppm Cr requires 2.81 ppm sodium metabisulfite (97.5%)
- 1 ppm Cr requires 1.52 ppm Sulfuric Acid, (66°Be')
- 1 ppm Cr requires 2.38 ppm Lime (90%)

### Sludge

1 ppm Lime (as  $\text{Ca(OH)}_2$ ) produces 1.84 ppm  $\text{CaSO}_4$  (not all  
1 ppm Chromium (as Cr) produces 1.98 ppm  $\text{Cr(OH)}_3$  sludge)

Using sulfur dioxide

### Chemicals

1 ppm Cr requires 1.85 ppm  $\text{SO}_2$  (100%)  
1 ppm Cr requires 2.38 ppm Lime (90%)

### Sludge

1 ppm Lime (as  $\text{Ca(OH)}_2$ ) produces 1.84 ppm  $\text{CaSO}_4$  (not all  
1 ppm Chromium (as Cr) produces 1.98 ppm  $\text{Cr(OH)}_3$  sludge)

### References

1, 17, 20, 22, 24, 27, 29, 30, 40, 46, 49, 51.

### Summary

This appears to be the most generally used method for treatment of acid plating wastes containing chromium.



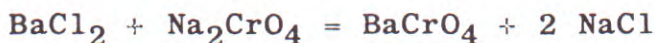
# CHROMIUM TREATMENT BY PRECIPITATION

All barium salts except barium sulfate are highly toxic. This should be remembered when this method of treatment is considered

## Technique

Waste chromate solutions are pumped to settling tanks, neutralized with soda ash or waste cleaners, and precipitated with barium chloride. Rigid chemical control is necessary in order to insure addition of correct amounts of barium chloride, as any excess of this poisonous compound would pass through the filter and be discharged into the stream. The solution is agitated and the precipitate is then allowed to settle. The relatively clear supernatant liquid is passed through a diatomaceous earth filter unit. The filtrate is discharged to the stream and the barium chromate plus the filter-aid is back-washed to a collecting tank and allowed to settle. The supernatant liquid from this settling is again filtered.

## Reaction



## Plants Using This Method

Ternstedt Instrument Division, GMC, Plymouth, Michigan.  
Ternstedt Manufacturing Division, GMC, Trenton, New Jersey.

## Notes

- A. The precipitated barium chromate may be of some value in the paint pigment industry.
- B. The presence of sulfate or sulfuric acid in the wastes will increase the amount of barium chloride used. Under these conditions, barium sulfate precipitates until all of the sulfate is used up and, at this point, barium chromate begins to precipitate.
- C. If the barium chloride is added under alkaline conditions, an additional precipitate of barium phosphate or barium hydroxide may be formed. As the barium chromate is less soluble than barium phosphate or hydroxide, the chromate will precipitate first.
- D. Sludges from this process are toxic and may present some problem in disposal.

## Design Considerations

Filtering equipment of the diatomaceous earth type should be installed for removal of the very fine precipitate. Plant experience has shown that one pound of technical barium chloride

September 3, 1952

will remove five pounds of chromium expressed as  $\text{CrO}_3$ . (Note - These figures do not check stoichiometrically.)

### Summary

This method is not recommended unless adequate laboratory control can be maintained over the process.



# TREATMENT BY NEUTRALIZATION AND CHEMICAL PRECIPITATION

## Technique

Metal bearing wastes and those containing solids, soaps, greases, acids and alkalies are usually combined with previously oxidized cyanide and reduced chromium wastes, for subsequent and final treatment. The operational steps involved in the subsequent treatment are the same whether single batch tanks or a full-automatic continuous operation with a series of tanks or compartments for each step are used.

## Neutralization and Precipitation

The combined waste-bearing waters are brought to a tank or compartment equipped for vigorous mixing. If the waste is acid, an alkali (usually 5 to 10% lime slurry) is added to effect neutralization and precipitation. During the reaction the pH is maintained within a range that will result in precipitation to the degree required to produce a final effluent satisfactory for discharge to the receiving stream. The development of a buffer curve for the specific waste under consideration will be helpful in determining the optimum pH range to obtain the desired results. Wastes from metal finishing plants will vary widely in concentration and may require prolonged mixing of the more concentrated wastes to insure complete reaction. In the case of continuous systems 2 or more mixing tanks in series are sometimes used.

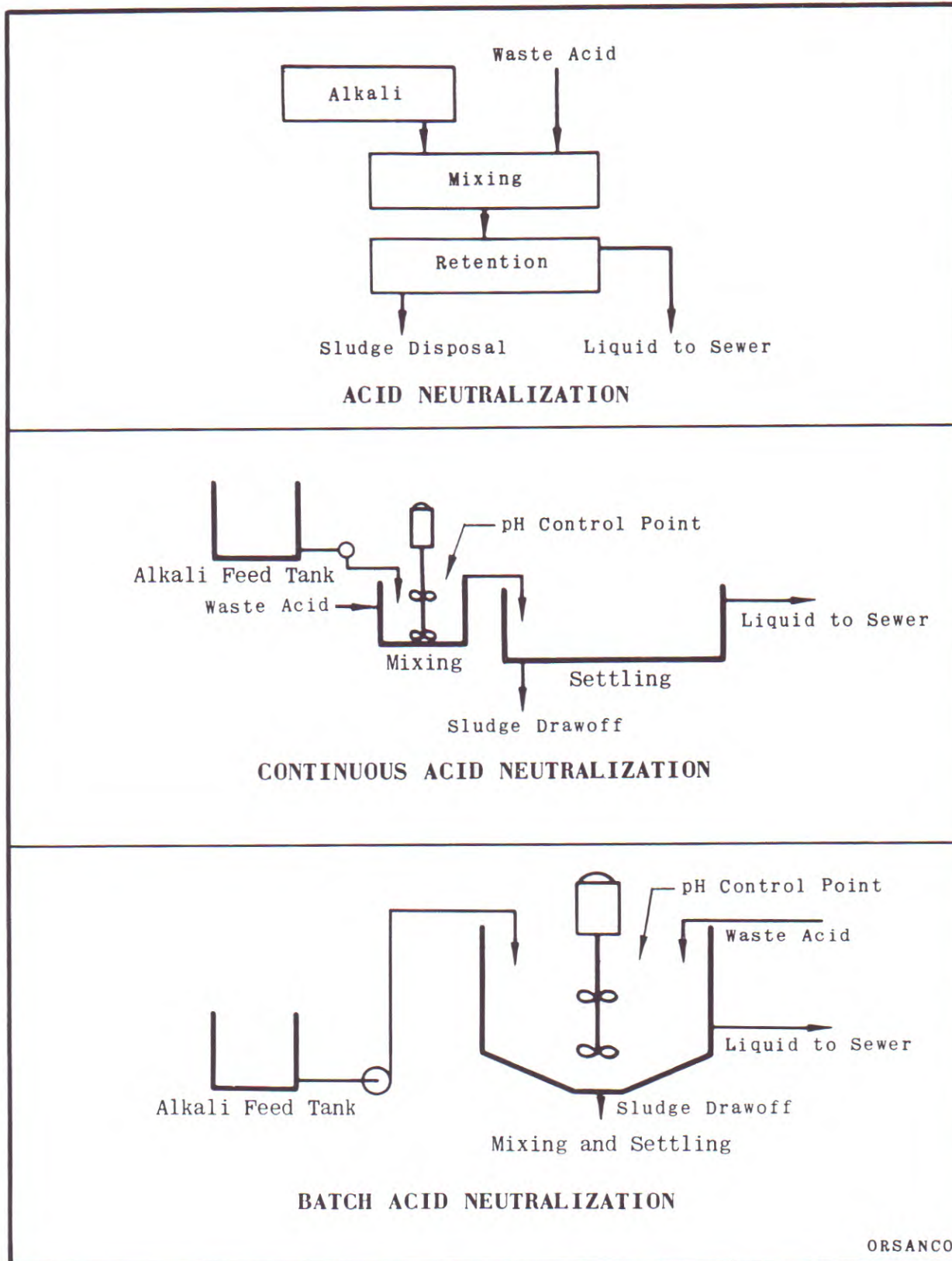
## Flocculation

The settling characteristics of the precipitates can in some cases be improved by slow stirring after the initial reaction. The floc produced from plating wastes is usually large and does not as a rule require the same degree of flocculation as that required in water treatment plants.

## Sedimentation and Settling

Sedimentation is the process by which the suspended material in the waste is allowed to settle from the liquid phase. This is accomplished by decreasing the velocity of flow to a point at which the solids, with a specific gravity greater than that of the liquid, will settle to the bottom of the tank or compartment. The longer the retention time, within limits, the higher the efficiency of sedimentation. The sludge consisting of the wet solids that have settled to the bottom is removed for final disposal as described in another chapter. Some tanks are equipped with scrapers and collectors to facilitate removal of the sludge. The factors governing the quality of the supernatant liquor are: pH,

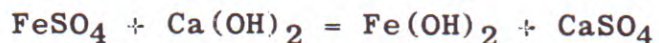
Figure 10





rate of flow, retention time, settling characteristics of suspended solids, rate of sludge removal, temperature, quantity of sludge producing materials in plant waste and degree of prior treatment. Compounds of the metals commonly encountered in metal finishing wastes such as chromium, copper, nickel, lead, calcium, magnesium, iron, aluminum, zinc, etc., are removed to the extent that they can be rendered insoluble and collected in the sludge.

### Reactions



### Plants Using This Method

- A. Irvin, Pennsylvania, Works of Carnegie-Illinois Steel Corp. (Use hydrated lime and later "pond" after aeration)
- B. Hercules Powder Co., Wilmington, Delaware. (Continuous treatment in multiple unit chamber - two point pit control using dolomite lime slurry).
- C. Talon, Inc., Meadville, Pennsylvania. (Batch treatment - use of unslaked quick lime to neutralize spent pickle liquor and precipitate toxic metals).
- D. New Departure Division, GMC, Sandusky, Ohio. (Four stage treatment (continuous) in which third stage is neutralization by lime).
- E. Western Electric Company, Allentown, Pennsylvania. (Caustic soda treatment).
- F. Standard Steel Spring Company, Newton Falls, Ohio. (Feeding of dolomitic lime slurry automatically controlled by pH)
- G. Olds Forge Division, GMC, Lansing, Michigan. (Use acetylene sludge and well water of high alkalinity.)

### Notes

- A. High sludge volume when lime is used. Less sludge from caustic soda treatment but soluble salts in discharge are increased. Use of dolomitic lime results in less sludge volume.
- B. Metal hydroxide sludges are slow drying.
- C. Land may be necessary for lagooning.
- D. Caustic soda may be cheaper when purchased in solution form and is easier to handle.
- E. Neutralization of nitric and hydrochloric acids with lime



will add soluble calcium salts to the effluent which will increase its hardness and the hardness of the receiving waters.

- F. Under some conditions the neutralized waste can be pumped directly to a lagoon for settling, in lieu of the sedimentation setup as described in the technique. This may be advantageous where the percentage of suspended solids are high or where the total volume is low.
- G. Acetylene sludge, alkaline cleaners, caustic strip solutions, water softening and boiler blowdown, and the like, may be used as neutralizing agents.
- H. Where relatively large quantities of lime are required, it may be more economical to purchase the calcium or dolomitic quicklime and install slaking equipment for hydration.
- I. Reference should be made to "Disposal of Spent Sulfate Pickling Solutions" prepared by the Steel Industry Action Committee of the Ohio River Valley Water Sanitation Committee.

#### Design Considerations

Reaction tanks must be constructed of suitable resistant materials and should have at least three feet of freeboard to prevent overflowing due to foaming, etc. Lime slurry tanks require agitators to control suspension of slurry and should have a means of measuring the amount of slurry being used during reaction. Lagooning of sludges is the most economical means of sludge disposal, providing land is available. Evacuation of lagoons and hauling dried sludge to other disposal sites or vacuum filtration methods may increase sludge disposal costs two or three times. The amounts of lime or caustic soda necessary can be computed by determining the neutralizing factor of the alkali in ratio to the acid waste.

#### References

9, 10, 15, 19, 21, 25, 26, 30, 31, 33, 37, 38, 45, 46, 61.

#### Summary

This is the most generally accepted method in use at present and accomplishes the two-fold purpose of neutralization of acids and precipitation of metals.



## DISPOSAL BY REGULATED DISCHARGE

In place of or as a supplement to the foregoing chemical methods for treatment of industrial wastes, regulated discharge of certain waste solutions to public waters may be satisfactory. Dilution of wastes is a part of nearly every type of treatment. In special cases, dilution may be used alone as the method of disposal provided controls are properly instituted and water quality objectives in the receiving stream are met.

### Technique

As the name indicates, this procedure involves dilution of wastes by waters from the plant under strict supervision and control by the plant personnel. Haphazard dilution is not considered satisfactory for industrial waste disposal. Solutions should not be discharged directly from the process tank, but should be conducted to a holding tank for controlled disposal. Definite knowledge of stream standards, effluent and low stream flows, concentration and calculated dilution rates of each waste solution, and analysis of dilution waters is necessary. Orders should be written specifying the solution to be discarded, the discharge rate and time for disposal, and the chemical analysis of the material. By coordinating the engineering, laboratory and maintenance departments in the discarding of waste solutions, a program of regulated discharge may be entirely satisfactory in many plants.

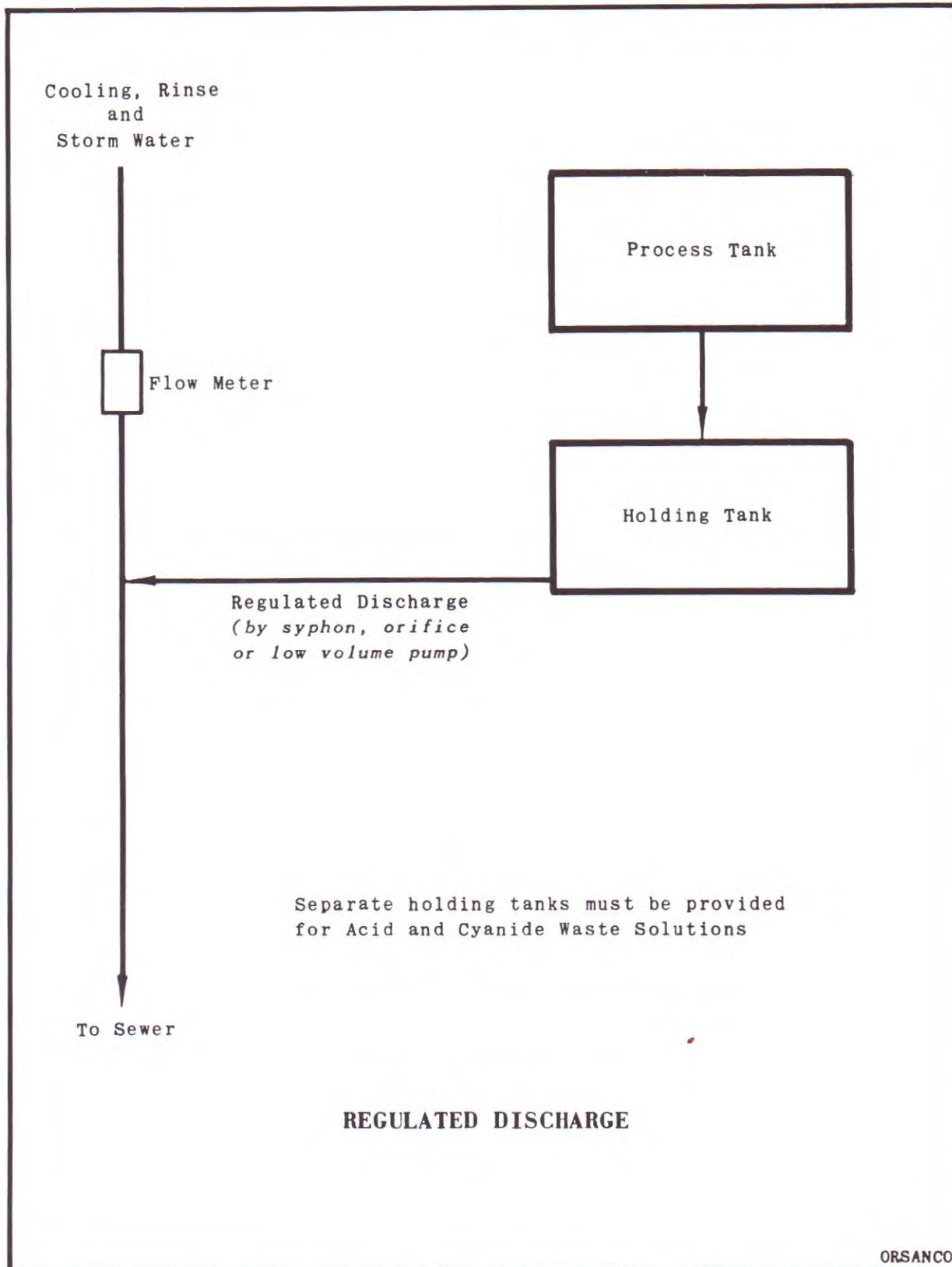
### Plants Using This Method

- A. National Cash Register Company, Dayton, Ohio.
- B. Frigidaire Division, GMC, Dayton, Ohio. (Concrete tanks receive segregated wastes which are slowly discharged at constant rate.)
- C. Aeroproducts Division, GMC, Vandalia, Ohio. (Large baffled tanks are provided to assure mixing of wastes before final discharge to stream).
- D. Ternstedt Division, GMC, Trenton, New Jersey. (Concrete mixing basins.)
- E. The Dow Chemical Company, Midland, Michigan. ("Inventory ponds" used for storage and leveling of wastes and controlled discharge.)

### Notes

- A. Proper scheduling must be arranged so other solutions in the plant are not discarded simultaneously.
- B. Method may not be suitable for highly colored solutions.
- C. Continuous automatic pH and flow records should be made of

Figure 11





- the effluent, together with catch sample analyses.
- D. Method should not be used for oil bearing wastes or wastes containing large sludge volumes.

### Design Considerations

Consideration should be given to the necessity for uniform distribution of the discharge into the stream so that its full dilution capacity may be used. The system should be designed to be usable under properly defined minimum flow conditions, as agreed upon by consultation with the regulatory agency. Holding tanks may require protective linings to resist action of acids and similar chemicals.

### References

13, 21.

### Summary

Under certain conditions this method of industrial waste disposal is adequate and will satisfy stream standards.

# DISPOSAL BY PONDING

## Technique

Metal finishing wastes may be disposed of by storing them in ponds formed by earth embankments allowing the liquids to evaporate or seep into the ground.

The mechanism and chemistry of cyanide disposal by ponding is dependent entirely upon the production of a lower pH value in the liquid. As this lower pH value is attained by absorption of carbon dioxide or other acid gases from the atmosphere, the ratio of free hydrocyanic acid to cyanide ion is increased tremendously. Hydrocyanic acid is lost from solution by hydrolysis and by escape to the air.

## Reaction (for cyanide solutions in air)



## Notes

- A. This method is dangerous and unsatisfactory.
- B. Seepage may contaminate streams and underground water supplies.
- C. Children may gain access to water in pond.
- D. Capacity of a pond is limited.
- E. There exists some question as to whether complete oxidation of cyanide ever occurs.

## References

4, 11, 15, 54.

## Summary

Considered to be a very dangerous practice for metal finishing wastes, it should not be used under any circumstances.



# OIL REMOVAL

## Technique

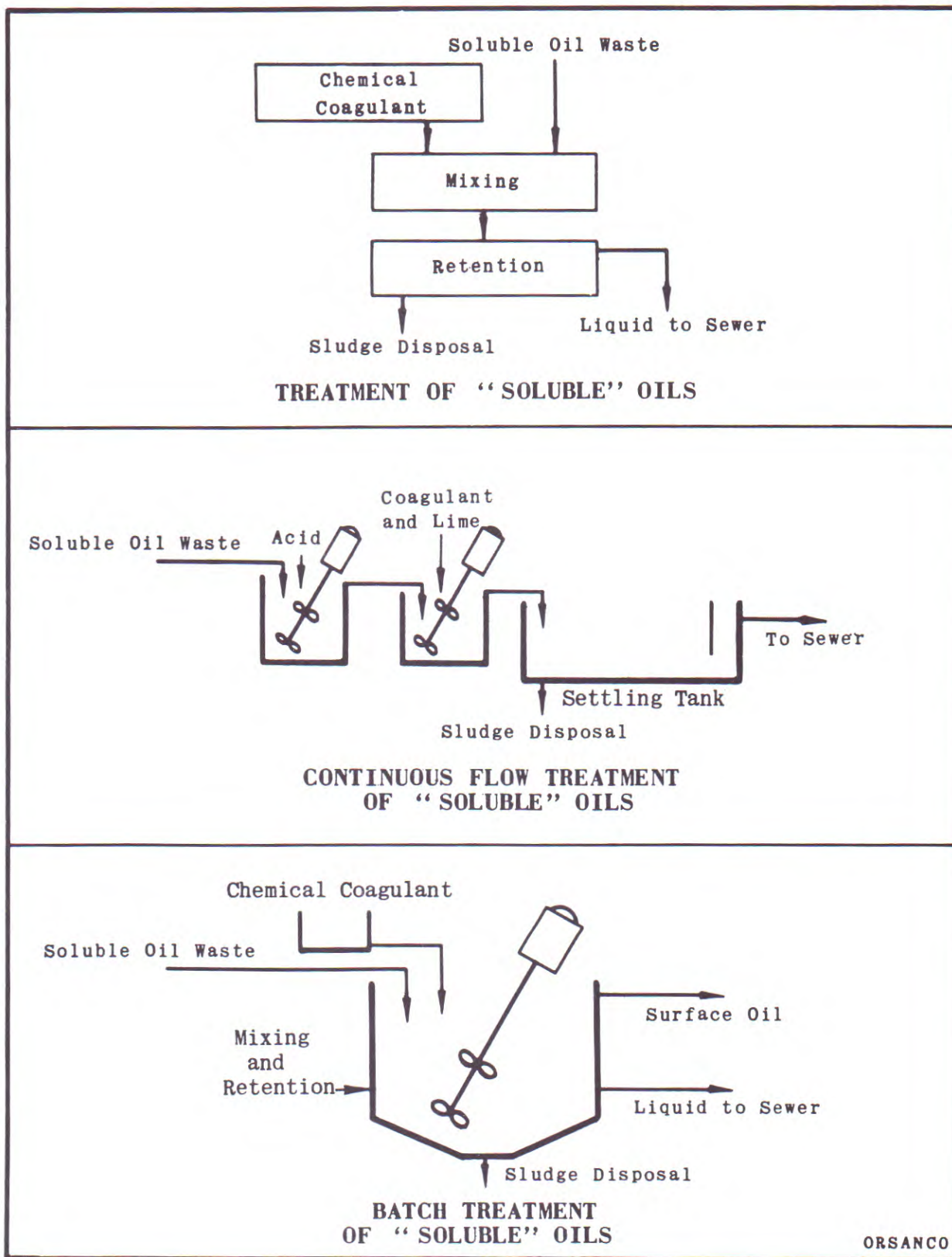
Floating oil is removed in a gravity type separator, using baffles to permit separation of oil from water before discharging to the sewer.

Two general and widely differing techniques are used in handling emulsified oil wastes. One method makes use of flotation and aeration equipment installed in a central soluble oil distributing system to maintain the oil in a condition such that it need not be wasted. Experience has shown that in a system like this the oil may be used for several years before disposal becomes necessary. The second technique makes use of emulsion breaking chemicals and treatment to destroy the emulsifying agents and cause the oil to separate and rise to the surface. Part of the oil may become enmeshed in the coagulating chemicals and is removed by sedimentation.

## Plants Using These Methods

- A. Cooper-Bessemer Corporation, Grove City, Pennsylvania. (Wastes collected and decanted from heated tanks after treatment to break the emulsion. After two hours the wastes are passed through gravity rapid flow filters.)
- B. New Departure Division, GMC, Sandusky, Ohio. (This is a continuous treatment system used on the small amount of oil obtained from washing and spillage. pH value is maintained from 5 to 6 in a primary clarifier for initial oil separation. Coagulating chemicals added either intentionally or produced by reduction of chromic acid wastes help to break the emulsion and remove the oil. The floating oil is removed by gravity to a storage tank. Residual oil scum is removed in a final clarifier. New Departure practices oil conservation on soluble oils.)
- C. Talon, Inc., Meadville, Pennsylvania. (This is a batch treatment. The emulsion is broken by the addition of raw acids and the later formation of precipitates carries down the oil.)
- D. Chevrolet Division, GMC, Flint, Michigan. (Two stage separation using low pH value in the first stage and a coagulant in the second stage.)
- E. Delco Products Division, GMC, Dayton, Ohio. (Separation of floating oil in a gravity type separator.)
- F. General Electric Company, Erie Plant, Erie, Pennsylvania.
- G. Cadillac Tank Division, GMC, Cleveland, Ohio. (Oil removal plant using chemical treatment.)

Figure 12





## Design Considerations

Data at one plant show coagulation of a 1000 ppm oil emulsion requires 2 to 3 pounds alum and 5 pounds caustic per 1000 gallon batch. Detention time required is 30 to 60 minutes in first stage and 20 to 30 minutes in second stage. Following settling there is a 1 to 2 hour quiescence period before discharging treated wastes.

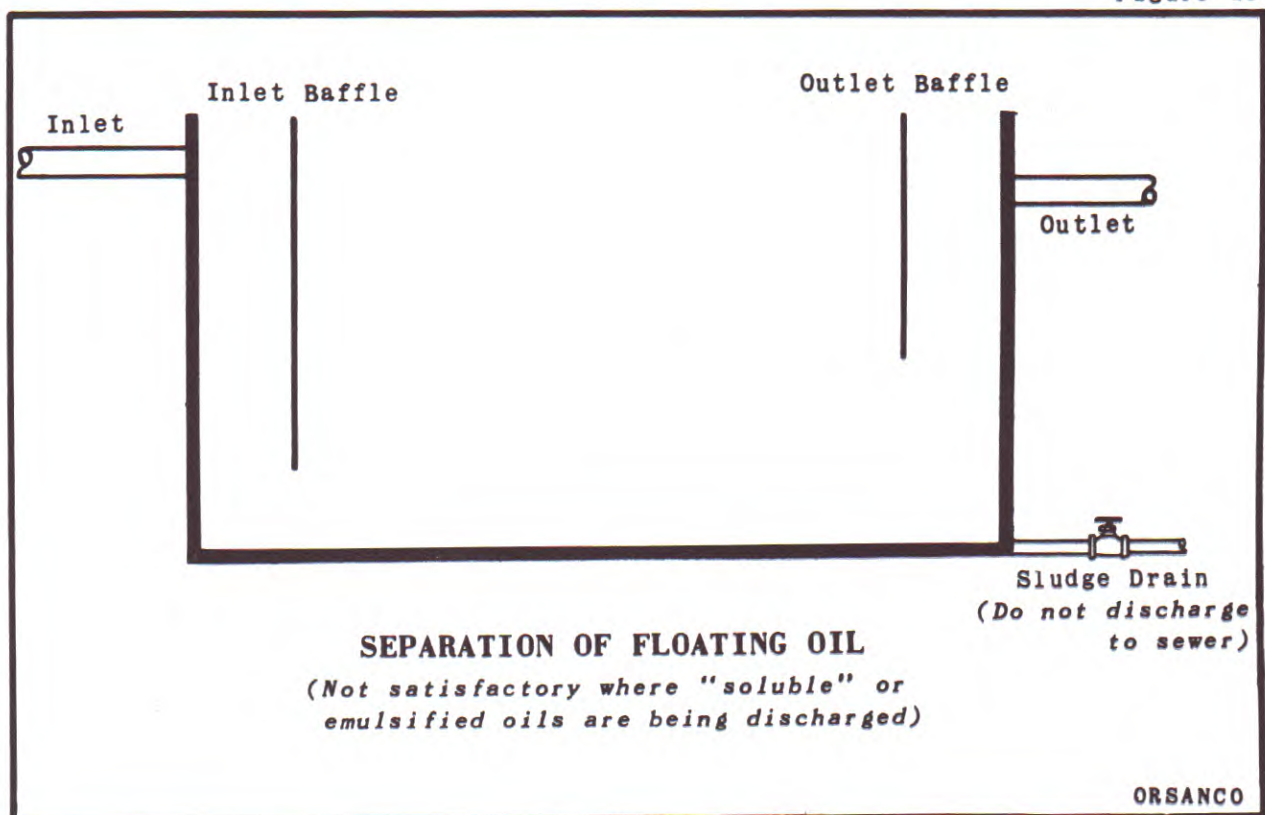
## References

37, 39, 46, 47, 50.

## Summary

In many types of industrial wastes, oil must be removed either before treatment by breaking the emulsion and subsequent decanting or by precipitation into sludge during treatment to prevent oil being discharged into sewers or streams. Recovered oil may, in some cases, wholly or in part, justify added expense.

Figure 13



## PAINT SPRAY BOOTH WASTES

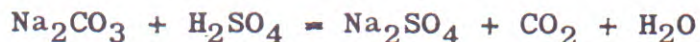
Many metal finishing plants make use of paint spraying operations to add an attractive appearance or provide a protective coating to their products. This paint coating is applied in spray booths in which water is circulated to cut down contamination of the air by paint spray particles and to minimize cleaning problems in the booth. The water used in this wet spray booth must be treated chemically to "kill" the paint particles; otherwise, these particles tend to adhere to the surface of the booth and the piping through which the water is circulated. Efficient operation of these booths requires that the circulating solution be replaced at frequent intervals, depending upon the amount of work going through the booth and the amount of paint sprayed. When the solution has become loaded with paint particles to the point of inefficiency, then it must be discarded and a fresh solution made up.

The chemicals used for treatment of wet spray booths are usually similar in nature to cleaning compounds and will therefore contain large amounts of caustic soda, sodium phosphate, soda ash, or sodium silicate. One compound in use at present also contains starch and formaldehyde. These solutions are frequently made up to a concentration of 1/4 and 1/2 ounce per gallon and have a pH value ranging from ten to eleven. The treatment of these solutions on discharge will therefore be similar to that given to acids and alkalies. In other words, simple neutralization should be sufficient to take care of the objectionable high alkalinity.

### Technique

The paint spray booth wastes are discharged to a settling tank, where the paint sludge and other solid materials are permitted to settle out. Latest design of paint spray booths incorporate automatic sludge removal equipment. When this equipment is used the size of the settling tank may be reduced. Following the settling period the wastes are treated by the addition of acids until neutralized and are then discharged. The plant should take advantage of any dilution water available for this process.

### Reactions



### Plants Using This Method

In common use.



## Notes

- A. Where possible, paint sludges should be recovered for re-use. This may involve installation of special equipment and use of carefully selected spray booth compounds.
- B. Most of the solutions used for wet spray booths are highly buffered and some experimentation will be necessary to determine the exact quantities of acid required.
- C. The settled spray booth solutions are only objectionable because of their high alkaline quality. If sufficient dilution water is available, neutralization with acid may not be necessary.
- D. Paint sludge removed from these wastes may be difficult to dispose of. The most satisfactory method at present appears to be incineration in suitably designed equipment.
- E. The alkaline quality of these wastes may make their use as neutralizing agents for acids possible.

# DISPOSAL OF WASTE TREATMENT SLUDGE

The final disposal of the sludge can be the most troublesome and expensive part of waste treatment. This is particularly true if the plant is located in a congested area where land values are high or where land is scarce. Lagoons are usually provided for the ultimate detention and dewatering of the sludge.

## Technique

Where the lagoon can be located within reasonable distance from the treatment plant, sludge from the sedimentation tanks is pumped through pipelines to the lagoon. Further dewatering and settling of the sludge takes place in the lagoon. The supernatant liquor in the lagoon can safely be discharged to the stream if, during prior treatment, precautions as outlined in the previous chapters have been adhered to. Sludges pumped to lagoons should be those obtained from accepted treatment processes and not untreated sludges from process tanks. Clarified liquid discharged to the receiving stream should be analyzed periodically for control and record of performance.

A second method is to provide lagoons to be used in rotation. While one lagoon is being filled, the sludge in the other lagoons is allowed to settle and is excavated and trucked to the final disposal site. Each lagoon should have capacity for a minimum of one year of sludge production.

A third method is to further dewater the sludge from the sedimentation tanks in thickeners and/or vacuum filters so it can be trucked more easily to the final disposal site.

## Plants Using This Method

- A. Standard Steel Spring Company, Newton Falls, Ohio. (Sludge pumped to lagoons which are excavated or abandoned when full.)
- B. New Departure Division, GMC, Sandusky, Ohio. (Primary and final clarifiers equipped with scrapers that empty into sumps from which further processing is done and sludge eventually pumped to lagoon.)
- C. Talon, Inc., Meadville, Pennsylvania. (After decanting clear treated effluent, sludge is mechanically thickened and dewatered to 5% by weight and hauled by truck to lagoon.)
- D. Kaiser-Frazer Corp., Willow Run, Michigan. (Pumped by pipeline to lagoon.)
- E. General Electric Company, Erie Plant, Erie, Pennsylvania. (Sludge resulting from various treatments are pumped to blending and conditioning tank. After standing, sludge is pumped to rotary vacuum filters. Sludge cake is discharged to trucks and hauled away.)



F. General Electric Company, Brockport Plant, Brockport, New York. (Settling tanks and/or lagoons.)

### Notes

- A. Recent experimental data and plant experiences point to successful use of vacuum filtration of some sludges.
- B. Lagooning presents a problem in that the lagoon eventually is filled to capacity. Walls of lagoon should be constructed with proper thickness and slope to prevent washes and breaks. To date lagooning appears to be the most generally accepted method for disposal.
- C. Sometimes arrangements can be made with municipal authorities to dump regulated amounts of sludge into sanitary sewers.

### Design Considerations

The disposal of sludge from industrial wastes treatment is an exceedingly variable problem. Space requirements in lagoons will vary depending upon bulk density of sludge. The quantity of solids (dry basis) that will be produced, after treatment, can readily be calculated from the plant survey; however, the bulking characteristics of the sludge vary at different plants and can best be determined by experimentation and experience. Regardless of the method used, the weight of dry solids per unit volume of sludge will become the same after several years standing. Therefore the space required for final containment will be the same for any of the different methods of disposal.

Sludge from primary sedimentation equipment will usually contain less than 5% solids. Centrifugal pumps will handle this type of sludge. A velocity of 2-1/2 feet per second or higher should be maintained in pipelines to prevent clogging. A swing pipe outlet located at the opposite corner of the lagoon from the inlet is a convenient method for draining off the supernatant liquor. The lagooned sludge is difficult to handle with shovels and open trucks in less than two years settling time. It is far less expensive, where land is available, to abandon the lagoon when filled with sludge and build a new one than clean it out for re-use. Abandoned lagoons should be properly marked.

### References

1, 15, 24, 25, 30, 32.

### Summary

The disposal of sludge removed from industrial wastes is a difficult problem in planning an industrial waste system unless there is adequate land available. Methods for sludge disposal should be given early attention.



# METAL RECOVERY BY ION EXCHANGE

## Technique

Waste treatment through ion exchange is only a new application of tried methods of water softening. It offers great potential for material and water conservation if the proper approach is used in utilization of the process. The best application of ion exchange is the treatment of rinse waters following plating operations. Rinse water is passed through beds of cationic and anionic resins, selected for the particular application in mind. The deionized water is recycled through the rinse tank. The exchanger beds are treated periodically with a solution designed to regenerate the resins, and therefore the regenerating solution will contain the concentrated salts originally in the rinse water. Further treatment may be required to reclaim the metal salts in a suitable form for re-use.

## Plants Using This Method

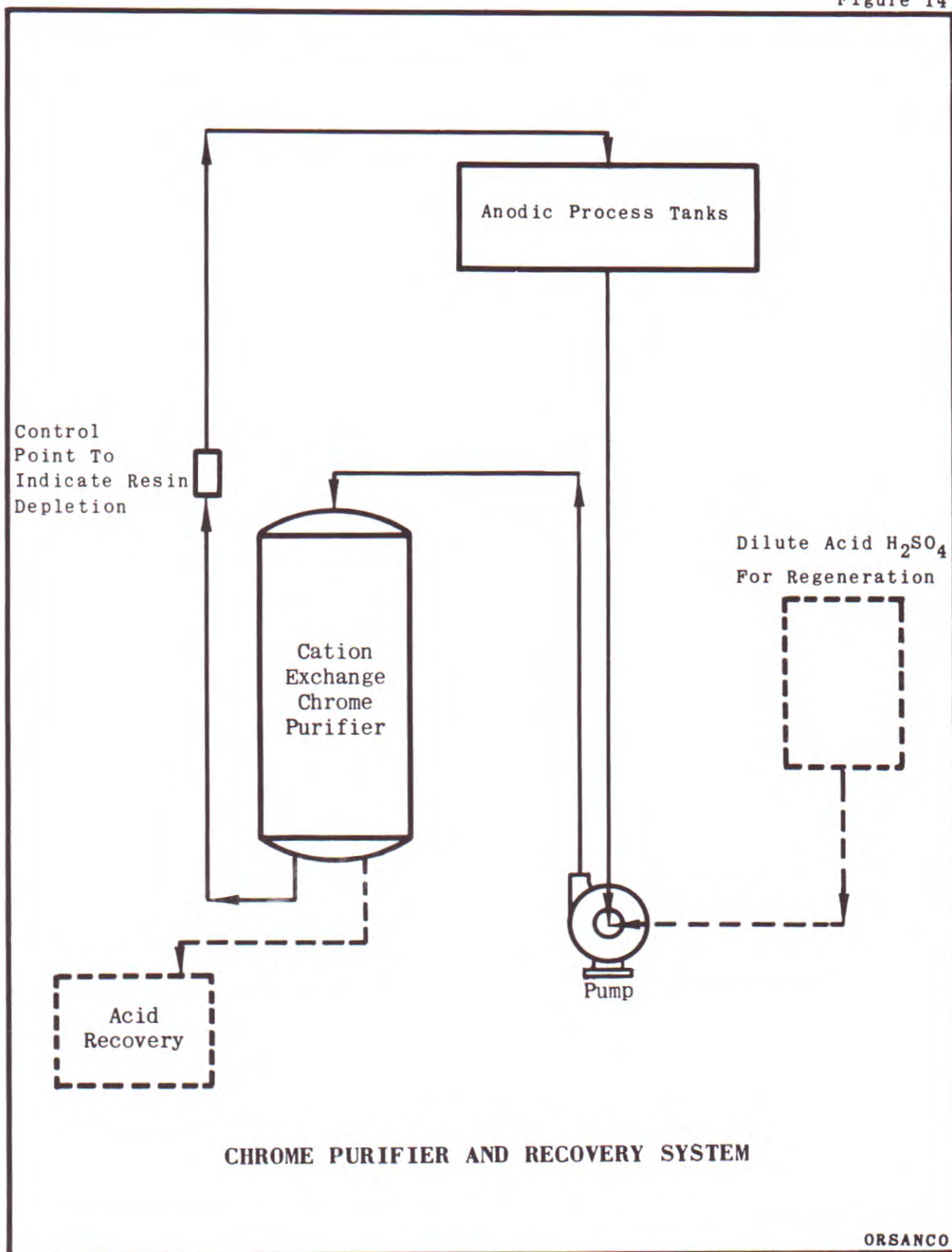
- A. Buick Motor Division, GMC, Flint, Michigan.
- B. Ternstedt Manufacturing Division, GMC, Trenton, New Jersey (pilot plant work completed.)
- C. Rock Island Arsenal, Ordnance Department, U.S. Army, Rock Island, Illinois.
- D. Grumman Aircraft Corporation, Long Island, New Jersey.
- E. Fisher Body Division, GMC, Plant 2, Grand Rapids, Michigan.

## Notes

- A. Some metals may be recovered from the concentrated regenerated solutions provided their recovery is found economical and feasible.
- B. The method may be applied to the removal of contaminating metals from chromic acid solutions on a continuous basis, returning chromic acid solution to the process tank. Iron, aluminum and trivalent chromium can be removed from chromic acid solutions because they are cationic contaminants, whereas the chromic acid is anionic and therefore would not be extracted. In the case of nickel and copper plating solutions, both the contaminating metals and the metal to be plated are cationic, and therefore all will be extracted.
- C. In the evaporative process for recovery of chromic acid (see Solution Recovery) the parts being plated are immersed in a still dip immediately following the plating bath. When this dip has arrived at a predetermined concentration, the solution is transferred to an evaporator and the concentration increased to a point closer to that in the plating



Figure 14



solution. This concentrate is then transferred to the plating solution. Any metals introduced to the still dip as a result of solution of metal from parts during the plating process are naturally included in this concentrate and will in time build up in the plating bath. To eliminate this possibility the still dip solution can be passed through a cation resin exchanger before transfer to the evaporator. This will remove the contaminating metals and permit recovery of relatively pure chromic acid.

- D. The most obvious application is the removal of metals from rinse waters. Unless recovery procedures are contemplated, this is simply a concentration method and some means of treatment for the regenerated solution must be used.
- E. The chemicals used for regenerating the resin beds may also require special treatment before disposal and the rinse water following regeneration may also have to be treated. In some cases acid regenerants may be added to metal pickling processes.
- F. pH value of the solution may require adjustment before passing through the ion exchange equipment to permit efficient operation.
- G. The presence of organic materials in some plating solutions (brighteners, wetting agents, etc.) may have a pronounced detrimental effect on the performance of the resin.
- H. Leaching of organic materials from certain resins may have a bad effect on the plate produced by solutions prepared from the regenerated metals.

### References

3, 6, 7, 20, 52, 53, 56, 57.

### Summary

This method promises to be of very great use in the treatment of dilute metal bearing wastes, and for the purification of concentrated chrome baths which in the past could not be salvaged. Some difficulty has been experienced in the past with incomplete regeneration of the resins and with the deterioration of resins in use, especially in contact with solutions such as chromic acid which are strongly oxidizing. The newer cation exchange resins used in treatment of chromium plating solutions have proved inert to the action of the solutions at the recommended concentrations treated. As many as 500 cycles of regeneration have been obtained without appreciable breakdown.

The method is under investigation by many universities and industries and is being installed by some industries. It appears to be well worth considering for application to metal finishing wastes.



# SOLUTION CONCENTRATION AND RECOVERY BY EVAPORATION

## Technique

Chrome, nickel and copper acid type plating solutions may be reclaimed from the rinse tank by evaporation in glass-lined equipment or other suitable evaporators and the concentrated solution returned to the plating system. Atmospheric or vacuum systems may be used. Vacuum systems are better where organic materials are present as they reduce the possibility of decomposition by permitting evaporation at low temperatures. The water condensed from the steam is then used as rinse water in the first rinse following the plating tank to eliminate buildup of natural water salts. So far this process has been confined to acid solutions recovered in still dip tanks immediately following the plating solution. Supplemental chemical treatment may be necessary to maintain the solutions in balance.

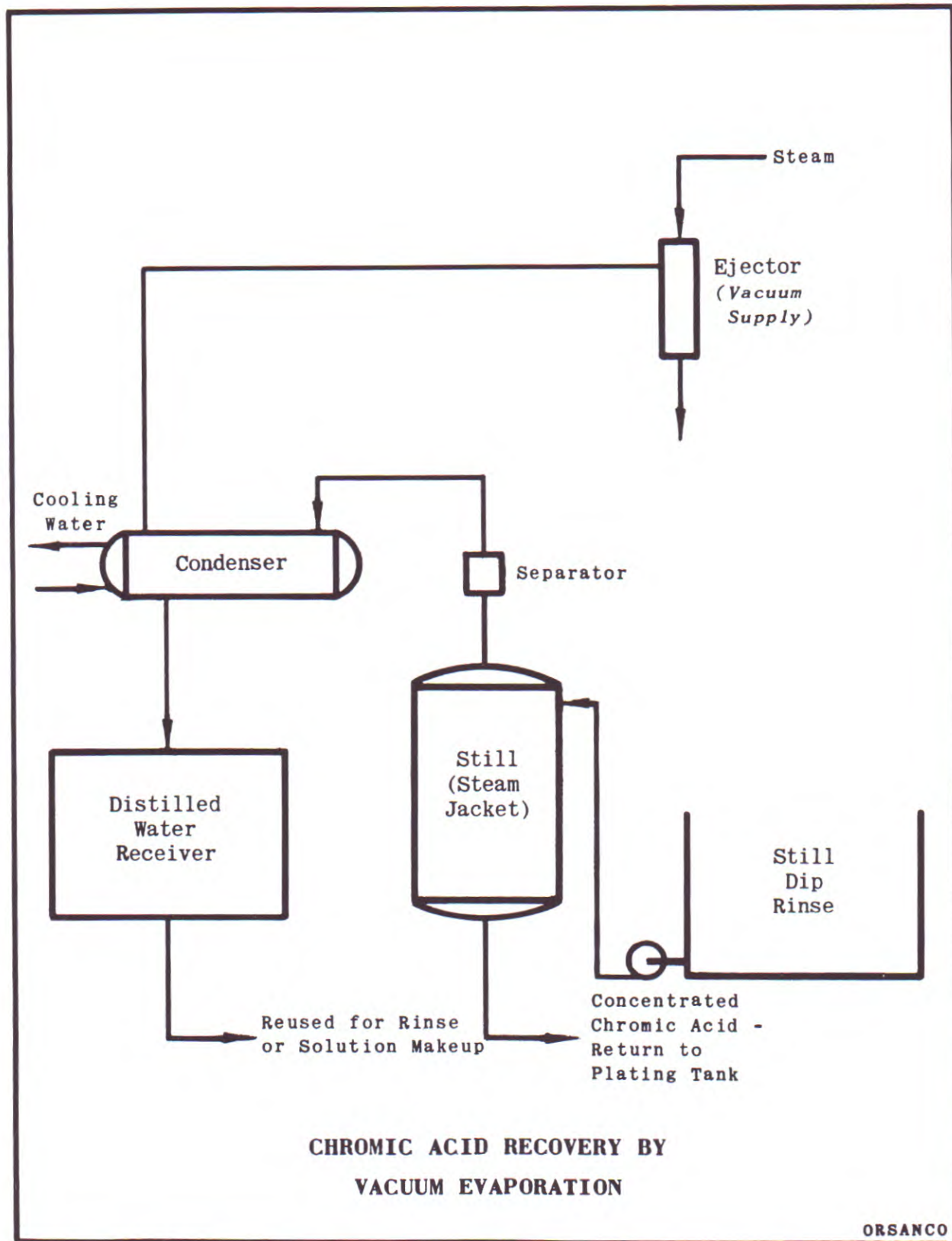
## Plants Using This Method

- A. Chevrolet Motor Division, GMC, Flint, Michigan. (Evaporation of chromic acid rinse water.)
- B. Talon, Inc., Meadville, Pennsylvania.
- C. Standard Steel Spring Company, Newton Falls, Ohio.
- D. Pontiac Motor Division, GMC, Pontiac, Michigan.

## Notes

- A. This process provides an excellent means for recovery of valuable metal salts.
- B. Initial cost of equipment is high, and the quantity of chemical to be recovered plus the expected cost of operation of a treatment system if recovery were not practiced would have to justify use of the system.
- C. This process does not completely eliminate toxic materials from the plant effluent since it is only applied to the first rinse following the plating system. Subsequent rinses will still discharge relatively small quantities of the polluting agent.
- D. Natural water salts or other contaminating materials may build up in solutions and limit the number of cycles of this process.
- E. Ion exchange resins can be used to remove contaminating metals before evaporation. See "Metals Recovery by Ion Exchange".

Figure 15





## Design Considerations

Data on an 800 gallon batch operation in one plant indicates concentration of a solution containing from 1 to 4 ounces per gallon chromic acid to 10 to 35 ounces per gallon final product, which may be returned to plating bath. Equipment is rated at a maximum of 450 pounds of steam per hour at 90 psig; it is operated at 27 inch vacuum for 8 hours.

Another plant concentrates the rinse water following the chromium plating tank by a continuous evaporation process. The solution is circulated through a pyrex glass heat exchanger into the top of a tower through which air is forced counter-current to the flow of the solution. Temperature of the solution entering the concentrator tower is 178°F. It requires 682 pounds of steam per hour to evaporate the water from a solution having a concentration of 37 ounces per gallon at a rate of one gallon per minute.

## References

53, 55, 58.

## Summary

This process appears to be an excellent one where chemical quantities involved are relatively large and would justify recovery.

# TYPE OF WASTE      CHARACTERISTICS OF WASTE

		CHEMICALS IN WASTE REQUIRING TREATMENT										WASTE WATER FLOWS		
		NaCN	CuCN	ZnCN	Alkali	CrO <sub>3</sub>	CuSO <sub>4</sub>	NiSO <sub>4</sub>	H <sub>2</sub> SO <sub>4</sub>	HCl	FeSO <sub>4</sub>	gpm	gpd	
		#/day	#/day	#/day	#/day	#/day	#/day	#/day	#/day	#/day	#/day			
1	Cyanide Concentrates	Avg _____ Max _____										_____	_____	Storage Tank
2	Cyanide Rinse Water	Avg _____ Max _____										_____	_____	
3	Concentrated Acid Pickling Liquors	Avg _____ Max _____										_____	_____	Storage Tank
														Oxidation Reducti Control Point
4	Strong Acid Rinse Water	Avg _____ Max _____										_____	_____	
5	Chromate Wastes	Avg _____ Max _____										_____	_____	
6	Concentrated Alkalies	Avg _____ Max _____										_____	_____	Storage Tank
7	Other Wastes Requiring Treatment	Avg _____ Max _____										_____	_____	
8	Waste Waters Not Requiring Treatment	Avg _____ Max _____										_____	_____	
	Quantity Totals	Avg _____ Max _____										_____	_____	



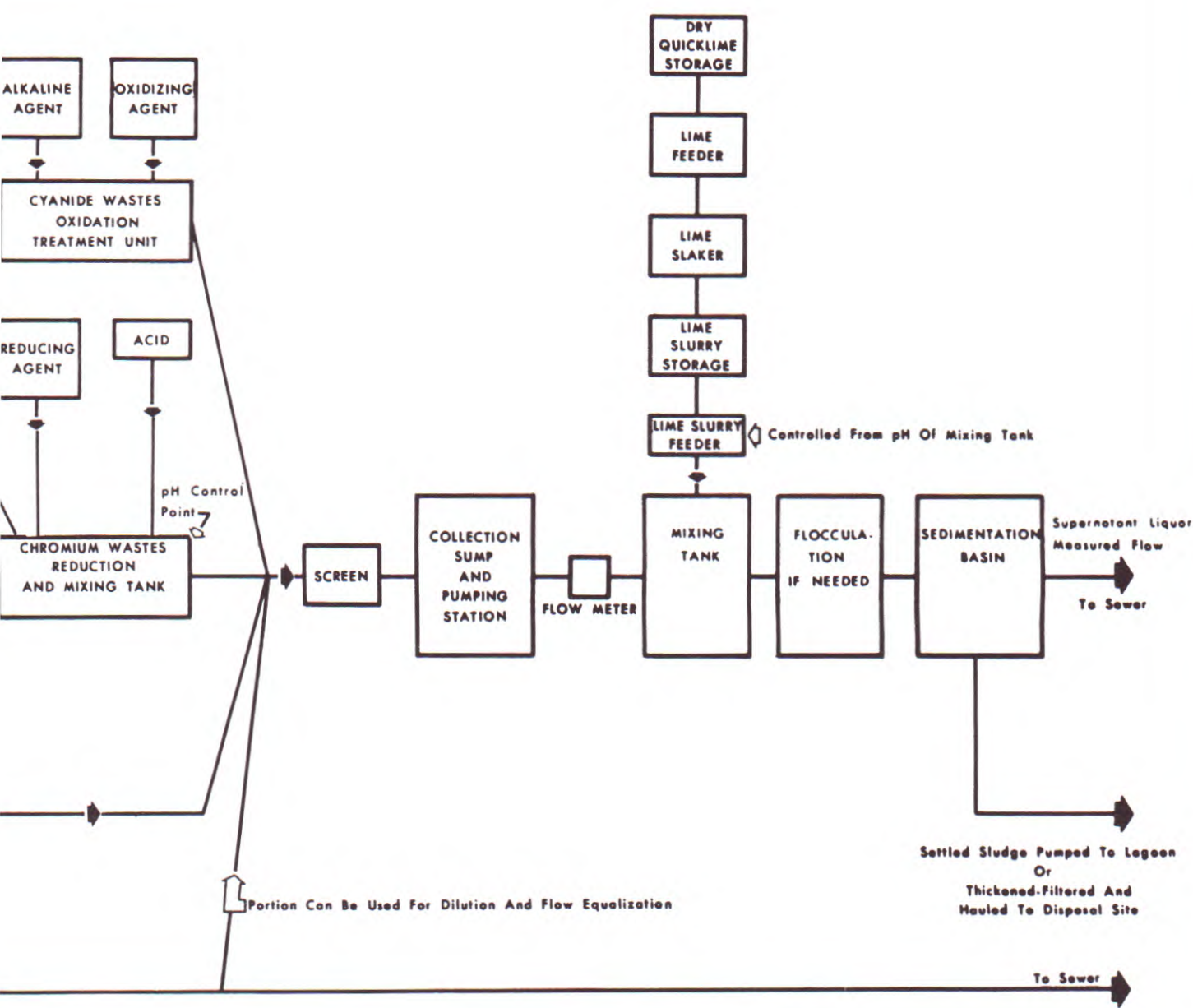
46. Unwin, Harry D., "Metallurgical Plant Wastes and Their Treatment", Water and Sewage Works, 96 (October, 1949), 399-405.
47. Walker, D. J., "Treatment For Disposal of Spent and Contaminated Soluble Oil Mixtures", Proceedings of the Fifth Industrial Waste Conference, Purdue University, Extension Series No. 72, (November, 1949), 63-67.
48. "Curtis Wright Plant Treats Cyanide Wastes", Chlorination Topics, Wallace and Tiernan Company, Newark, New Jersey, 4 (March, 1940), 45.
49. Wise, W. S., "The Industrial Waste Problem", Sewage Works Journal, 20 (January, 1948), 96-100.
50. AES Research Report #10. Progress Report (December 6, 1951). Sterling Laboratory, Yale Univ., New Haven, Conn.
51. Gard, C. M., Snively, C. A., and Lemon, D. J., "Design and Operation of a Metal Wastes Treatment Plant", Sewage and Industrial Wastes, 23 (November, 1951), 1429-1438.
52. Costa, Raymond L., "Regeneration of Chromic Acid Solutions By Cation Exchange", Industrial and Engineering Chemistry, 42 (February, 1950), 308.
53. "Chromium Salvage", Chemical Industries Week, 68, 7 (March 3, 1951), 21, 23.
54. Davids, H. W., and Lieber, M., "Underground Water Contamination by Chromium Wastes", Water and Sewage Works, 98 (December, 1951), 528-534.
55. Keller, F. R., Cupps, C. C., and Shaw, R. E., "Recovery of Chromic Acid From Plating Operations", Plating, 39 (February 1952), 152.
56. McGarvey, F. X., Tenhoor, R. E., and Nevers, R. P., "Cation Exchange For Metals Concentration From Pickle Rinse Waters", Industrial Engineering Chemistry, 44 (1952), 534-541.
57. Paulson, C. F., "Wastes Recovery By Ion Exchange", Wastes Engineering, 23 (1952), 208-209.
58. Neben, E. W., and Swanton, W. F., "Recovery of Chromic Acid From Plating Rinse Waters", Plating, 38 (1951), 457-460, 470.
59. Tyler, R. G., Maske, W., Westin, M. J., and Matthews, W., "Ozonation of Cyanide Wastes", Sewage and Industrial Wastes, 23 (September, 1951), 1150-1153.
60. U.S. Patent No. 2,520,703.
61. Steel Industry Action Committee of the Ohio River Valley Water Sanitation Commission, "Disposal of Spent Sulfate Pickling Solutions", (1952).

# NOTES



RETREATMENT

NEUTRALIZATION AND SEDIMENTATION



This outline indicates data on pollution loads and volumes required for design of treatment facilities -- and suggests a possible sequence of treatment steps. Individual operations in the plant must be evaluated before an overall treatment program is selected. In brief, the logical approach is to:

Separate your wastes,  
Determine their characteristics, then  
Select your treatment process.

## REFERENCES

1. Barnes, George E., "Treatment Works for Plating Wastes Containing Toxic Metals and Cyanides", Water and Sewage Works, 94 (August, 1947), 267-271.
2. Barnes, George E., and Braidech, M., "Treating Pickling Liquors for Removal of Toxic Metals", Engineering News Record, 129 (October 8, 1942), 86-89.
3. Beohner, H. L., and Mindler, A. B., "Ion Exchange in Waste Treatment", Industrial Engineering Chemistry, 41 (March, 1949), 448.
4. Billings, Norman, "Ground Water Pollution in Michigan", Sewage and Industrial Wastes, 22 (December, 1950), 1596-1600.
5. Bleiweis, Jerome, "Plating Waste Disposal", Iron Age, 163 (June 16, 1949), 78-83.
6. Bloodgood, D. E., and Losson, F. J., "Removal of Toxic Substances From Metal Plating Wastes by Ion Exchange", Proceedings of the Third Industrial Waste Conference, Purdue University, Extension Series No. 64 (1947), 196-208.
7. Bloodgood, D. E., and Strickland, A., "Chromium Removal by Ion Exchange", Water and Sewage Works, 97 (January, 1950).
8. Burdick, G. E., and Lipschuetz, Morris, "Toxicity of Ferro and Ferricyanide Solutions to Fish, and Determination of the Cause of Mortality", Transactions of the American Fisheries Society, 78 (1950), 192-202.
9. Reidl, A. L., "Limestone Used to Neutralize Acid Wastes", Chemical Engineering, 54, 7 (July, 1947), 100-101.
10. Dickerson, B. W., and Brooks, R. M., "Neutralization of Acid Wastes", Industrial and Engineering Chemistry, 42 (April, 1950), 599-605.
11. Dobson, John G., "Disposal of Cyanide Wastes", Metal Finishing, 45, (February, 1947), 78-81.
12. Dobson, John, "Disposal of Cyanide Wastes", Metal Finishing, 45 (March, 1947), 68-71.
13. Dodge, B. F., and Reams, D. C., "Disposal of Plating Room Wastes", A.E.S. Research Report #14, 8-9, 17-19, 22, 24-25, 27, 29, 30-33, 35.
14. Editorial. "Waste Disposal", Chemical Engineering, 56 (March, 1949), 96-106.



15. Eldridge, E. F., Industrial Waste Treatment Practice, New York and London: McGraw-Hill Book Company, 1942, 289, 290, 291, 294-299.
16. Friel, F. S., and Weist, G. T., "Cyanide Removal From Metal Finishing Wastes", Water and Sewage Works, 92 (March, 1945), 97-98.
17. Gray, Dr. Allen G., "Practical Methods for Treatment of Plating Room Wastes", Products Finishing, 14, 11 (August, 1950), 68-84.
18. Gray, Allen G., "Finishing Clinic", Products Finishing, 12 (March, 1948), 74-86.
19. Gray, Dr. Allen G., "Use of Limestone Beds to Neutralize Waste From Acid Dipping and Pickling Operations", Products Finishing, 12, 1 (October, 1947), 78, 80.
20. Grindley, J., "Treatment and Disposal of Waste Waters Containing Chromate", Journal of the Society of Chemical Industries, 64 (1945), 339-344.
21. Gurnham, Fred C., "Disposal of Metal Finishing Wastes", Metal Finishing Guidebook - 19th Edition (1950), 107-117.
22. Gurnham, Fred C., "Stream Pollution and the Plating Industry", Products Finishing, 14, 6 (March, 1950), 26-40.
23. Haseltine, T. R., "Determination of Cyanides", Water and Sewage Works, 94 (May, 1947), 187-191.
24. Herda, Nicholas, "Treatment of Cyanide and Acid Plating Wastes", Sewage Works Journal, 18 (1946), 499-502.
25. Hoak, Richard; Lewis, Clifford; Sindlinger, Charles; and Klein, Bernice, "Lime Treatment of Waste Pickle Liquor", Industrial and Engineering Chemistry, 39 (February, 1947) 131-135.
26. Hoak, R. D., Lewis, C. J., Hodge, W. W., "Treatment of Spent Pickling Liquors with Limestone and Lime", Industrial and Engineering Chemistry, 37 (June, 1945), 553-559.
27. Hoover, C. R., and Masselli, J. W., "Disposal of Waste Liquors From Chromium Plating", Industrial Engineering Chemistry, 33 (January, 1941), 131-134.
28. Eden, G. E., Hampson, B. L., and Wheatland, A. B., "Destruction of Cyanide in Waste Waters by Chlorination", Journal of the Society of Chemical Industry, 69, (1950), 244-249.
29. Kelch, James L., and Graham, A. Kenneth, "Electrometric System for Continuous Control of Reduction of Hexavalent Chromium in Plant Wastes", Plating, 36 (October, 1949), 1028-1031.



30. Kominek, E. G., "Treatment of Plating Wastes", Metal Finishing, 47 (March, 1949), 56-62.
31. "For Effective Neutralization of Industrial Wastes (Micro-max Automatic pH Control)", Bulletin ND44-96-708 (1949), Leeds and Northrup Company, 4907 Stenton Avenue, Philadelphia 44, Pennsylvania.
32. Lewis, C. J., "Dry Lime Treatment of Waste Pickle Liquor", Iron Age, 163 (January 20, 1949), 48-53.
33. Lime, Handling, Application and Storage, Bulletin of National Lime Association, Washington 5, D.C.
34. Milne, D., "Disposal of Cyanides by Complexation", Sewage and Industrial Wastes, 22 (September, 1950), 1192-1199.
35. Milne, D., Uhl, P. W., Hauri, C. F., and Roy, E. J., "Experiences With Chlorination of Cyanides in the General Motors Corporation", Sewage and Industrial Wastes, 23 (January, 1951), 64-81.
36. Oyler, R. W., "Disposal of Waste Cyanides by Electrolytic Oxidation", Plating, 36 (April, 1949), 341-342.
37. Pennsylvania Clean Streams (June, 1950), 3, 6.
38. Pennsylvania Clean Streams (December, 1948), 3, 5
39. Pratt, M. A., "Extended Use of Oil Emulsions to Minimize Disposal Problems", Sewage and Industrial Wastes, 22 (March, 1950), 331-335.
40. Reed, Allen, "Treatment of Plating Wastes at Electric Auto-Lite Plant, Lockland, Ohio", Sewage and Industrial Wastes, 22 (October, 1950), 1338-1342.
41. "Report of the Water Pollution Research Board", 1939 to 1945, Department of Scientific and Industrial Research, London. (Available from British Information Services, 30 Rockefeller Plaza, New York 21, N.Y.), 49-51.
42. Sperry, L. B., and Caldwell, M. R., "Destruction of Cyanide Copper by Hot Electrolysis", Plating, 36, (April, 1949), 343-347.
43. Sussman, S., Nachod, F. C., and Wood, W., "Metal Recovery by Anion Exchange", Industrial Engineering Chemistry, 37 (July, 1945), 618-624.
44. Tarman, John, & Priester, M., "Treatment and Disposal of Cyanide Bearing Wastes", Water and Sewage Works, 97 (September, 1950), 385-389.
45. The Use of Lime in Industrial Trade Waste Treatment, Bulletin of National Lime Association, Washington 5, D.C., Trade Waste Bulletin No. 1 (April 1, 1948).



# NOTES

## ADDITIONAL MANUALS

devoted to waste control in metal-finishing plants, which are available from the Ohio River Valley Water Sanitation Commission, are:

### PLATING-ROOM CONTROLS FOR POLLUTION ABATEMENT

A manual of principles and practice for curbing losses of solutions and metals that otherwise might find their way into water courses. Compiled by the Metal-Finishing Industry Action Committee, this manual describes methods for reducing wastes by reducing dragout, rinsing effectively, preventing losses, and purifying contaminated solutions. (20 pp., 8 illus.) Price 50¢

### PLANNING AND MAKING INDUSTRIAL WASTE SURVEYS

Detailed instructions for measuring volume of flow, obtaining representative samples and calculating waste loads. The manual is designed to aid those people who have had little or no experience in measuring industrial waste. Diagrams show how to construct and install measuring and sampling devices. Tables are included to assist in computing the rates of flow. The manual was compiled by the Metal-Finishing Industry Action Committee. (44 pp., 27 illus.) Price \$1.00

### DISPOSAL OF SPENT SULFATE PICKLING SOLUTIONS

An evaluation of methods for treating spent solutions resulting from sulfuric acid pickling to reduce stream pollution. Compiled by the Steel Industry Action Committee of the Commission, this manual describes methods for neutralization of acid solutions and for recovery of acid and iron salts. Flow diagrams and a nomograph for determining weight of alkaline agent required to neutralize acid solutions are included. (76 pp., 17 illus.) Price \$2.00



# Regulatory Agencies of the Signatory States

ILLINOIS	Technical Secretary State Sanitary Water Board Springfield, Illinois 62706 Phone: 525-2000 — Ext. 6580
INDIANA	Technical Secretary Indiana Stream Pollution Control Board 1330 West Michigan Street Indianapolis, Indiana 46207 Phone: 633-4420
KENTUCKY	Executive Director and Chief Engineer Kentucky Water Pollution Control Commission 275 East Main Street Frankfort, Kentucky 40601 Phone: 227-4531
NEW YORK	Director Bureau of Water Resource Services Division of Environmental Health Services New York State Department of Health 84 Holland Avenue Albany, New York 12208 Phone: 474-2060
OHIO	Chief Engineer Division of Engineering Ohio Department of Health Columbus, Ohio 43215 Phone: 469-4470
PENNSYLVANIA	Sanitary Water Board Box No. 90 Harrisburg, Pennsylvania 17120 Phone: 787-2367
VIRGINIA	Executive Secretary State Water Control Board P. O. Box 5285 Richmond, Virginia 23220 Phone: 644-4111 — Ext. 2437
WEST VIRGINIA	Executive Secretary State Water Resources Board 1709 Washington Street, East Charleston, West Virginia 25311 Phone: 343-4411 — Ext. 2107





ILLINOIS • INDIANA • KENTUCKY • NEW YORK  
OHIO • PENNSYLVANIA • VIRGINIA • WEST VIRGINIA