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CHROMIC ACID RECOVERY BY RECIPROCATING FLOW ION EXCHANGE

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ABSTRACT

A patented process for recovery of chromic acid from chrome plating rinsewaters has been developed and field proven in over fifty decorative and hard chrome installations over the past ten years. Utilizing a new technique called Reciprocating Flow Ion Exchange, the system offers a number of significant cost and size advantages over conventional ion exchange. Process fundamentals, field data, working experiences and installation photographs are presented. The process is adaptable to chrome recovery in tin free steel applications.

1. Introduction

Chromic acid is used in a variety of metal finishing processes. Rinsewater from these processes present major waste treatment problems, conventional reduction/precipitation techniques being expensive and difficult to operate.

Conventional ion exchange has been utilized for recovery of chromic acid from rinsewater to a limited degree for some time but have demonstrated a number of shortcomings. These include the following;

1. large equipment,
2. high resin replacement costs,
3. high chemical consumption,
4. low product concentrations,
5. long offstream times necessitating duplicate standby equipment.

A novel chromic acid recovery system based upon Reciprocating Flow Ion Exchange (RECOFLO) was first reported in 1971[1] which largely overcame these problems. Since that time over fifty systems have been installed in decorative and hard chrome plating installations all over the world.

2. Basic Ion Exchange Recovery Process

The basic ion exchange process for chromic acid recovery from rinsewater is as follows;

The rinsewater is first pumped through a strong acid cation exchanger in the hydrogen form (RH) to remove metallic impurities (M^{+++}) such as trivalent chrome (Cr^{+++}) and iron (Fe^{+++}). This is necessary to avoid precipitation of metallic hydroxide in the subsequent anion exchange bed. This exchange occurs according to the following equation (1);

$$3RH + M^{+++} \text{ -- } R_3M + 3H^+ \qquad (1)$$

Upon exhaustion, the cation resin must be regenerated with sulfuric acid according to equation (2);

$$2R_3M + 3H_2SO_4 \text{ -- } 6RH + M_2(SO_4)_3 \qquad (2)$$

It should be noted that a dosage of sulfuric acid several times greater than the stoichiometric amount is normally required to effect adequate regeneration.

The "decationized" chromic acid rinsewater is next directed through an anion exchanger in the hydroxl form (ROH) to remove the chromate (and polychromate, depending on the concentration) ions. The effluent leaving the anion exchanger will be deionized water. Uptake of chromate basically occurs according to equation (3) although the actual mechanism is somewhat more complex.

$$2ROH + H_2CrO_4 \text{ -- } R_2CrO_4 + 2H_2O \qquad (3)$$

Upon exhaustion, the anion exchanger is regenerated with dilute sodium hydroxide yielding sodium dichromate according to equation (4);

$$R_2CrO_4 + NaOH \text{ -- } 2ROH + Na_2CrO_4 \qquad (4)$$

If a strong base anion resin is employed, a considerable excess of sodium hydroxide is normally required. To minimize this excess, weak base resins are sometimes employed. Weak base resins are much more prone to oxidation by chromic acid, however, and weak base resin replacement cost usually become a factor to be considered.

The sodium dichromate produced through anion exchanger regeneration is passed through another cation exchanger in the hydrogen form (RH). The sodium chromate is converted to chromic acid and the excess sodium hydroxide is converted to water according to;

$$2RH + Na_2CrO_4 \text{ -- } 2RNa + H_2CrO_4 \qquad (5)$$
$$RH + NaOH(\text{excess}) \text{ -- } RNa + H_2O \qquad (6)$$

Neutralization of the excess sodium hydroxide by ion exchange generates considerable heat and as a result the cation resin is exposed to warm or even hot chromic acid, a severe oxidant. As a result, the cation resin can undergo serious degradation. The relatively long residence times employed in conventional ion exchange columns exaggerates this problem. The development of macroreticular cation resins has alleviated the problem somewhat, but cation resin life in this application is still severely limited.

A major limitation of the conventional ion exchange process is its apparent inability under practical circumstances to produce a chromic acid product in excess of CrO_3 = 50 g/L. This limitation remains, despite employment of elaborate regeneration techniques such as proportional and countercurrent regeneration.

3. Reciprocating Flow Ion Exchange

The basic RECOFLO technique is general and can show significant improvement in any ion exchange process. While the basic RECOFLO technique has been discussed in detail elsewhere[2], its features demonstrate particular advantage in the chromic acid recovery process and will be discussed briefly in this context.

Fine Resins

The fine resins employed (ie. 100-200 mesh vs standard 16-50 mesh) improve the kinetics of the ion exchange process, enabling very high flows and short chromic acid/resin contact times. This reduces resin degradation.

Short Beds

The height of the ion exchange bed (eg. 3 inches) is only slightly longer than the active exchange zone in the bed. This further reduces chromic acid/resin contact times, prolonging resin life. The small resin inventory renders resin replacement costs almost insignificant.

Countercurrent Regeneration

Recognized as the most efficient means of regeneration, the use of countercurrent regeneration yields more concentrated chromic acid products at lower chemical consumption.

Liquid Stratification

Dilution of solutions in the beds is minimized by always maintaining less dense fluids (eg. water) above denser fluids (eg. chromic acid) as the fluids are displaced in and out of the beds. Production of concentrated chromic acid product is thus facilitated.

Low Exchange Loadings

Only a portion of the ultimate exchange capacity of the resin is utilized. By using only the most accessible exchange sites, efficiency is improved. Moreover, a moderate loss in exchange capacity due to resin degradation does not effect system performance.

Short Cycles

High flow rates, short beds and low loadings result in very short cycle times. Short offstream times (15 minutes for this application) eliminate the need for standby equipment, providing semi-continuous flows of purified water.

Small Equipment

In addition to the small ion exchange beds, the rapid cycles allow use of small regenerant reservoirs, etc. It becomes feasible to pre-assemble and skid mount even high capacity, multiple bed processes such as this.

4. RECOFLO Chromic Acid Recovery Process

The above general RECOFLO features were considered in the design of a patented[3] ion exchange process for chromic acid recovery. The three basic steps in the process are illustrated in Figure 1. In addition to the above general features, there are two features specific to the chromic acid recovery process which are noteworthy -- the manner in which the sodium chromate regenerant solution emerging from the anion bed is passed directly into the cation bed and the manner in which the beds are washed (the term "wash" is used in place of the more usual "rinse" to avoid confusion with the plating rinse water). These features have a significant effect on the concentration of recovered chromic acid product, the amount of chemicals consumed and hence, the overall economics of the process. The effect of these features upon the operation of the process can best be understood by a detailed description of the nature of the solutions passing through the beds during the regeneration and wash steps and the void volumns found in the beds at the end of the regeneration step.

When the anion bed is regenerated with sodium hydroxide, the sodium hydroxide passes through the bed and a sodium chromate salt solution leaves the top of the anion bed. At first, the solution leaving the top of the anion bed is practically pure sodium chromate solution, then it is a mixture of sodium chromate and sodium hydroxide, and finally, when the bed is regenerated, it is substantially pure sodium hydroxide. In the conventional process, the solution emerging from the anion exchange bed would be collected in a reservoir, forming a solution having a uniform concentration of sodium hydroxide and sodium chromate. This solution would then be passed from the reservoir through the cation exchange bed.

In the cation exchange bed, the sodium chromate is converted to chromic acid, and any sodium hydroxide is converted to water. To the extent that the sodium hydroxide is converted to water there is a loss of sodium hydroxide to the system. In the conventional process, where a solution having a uniform concentration of

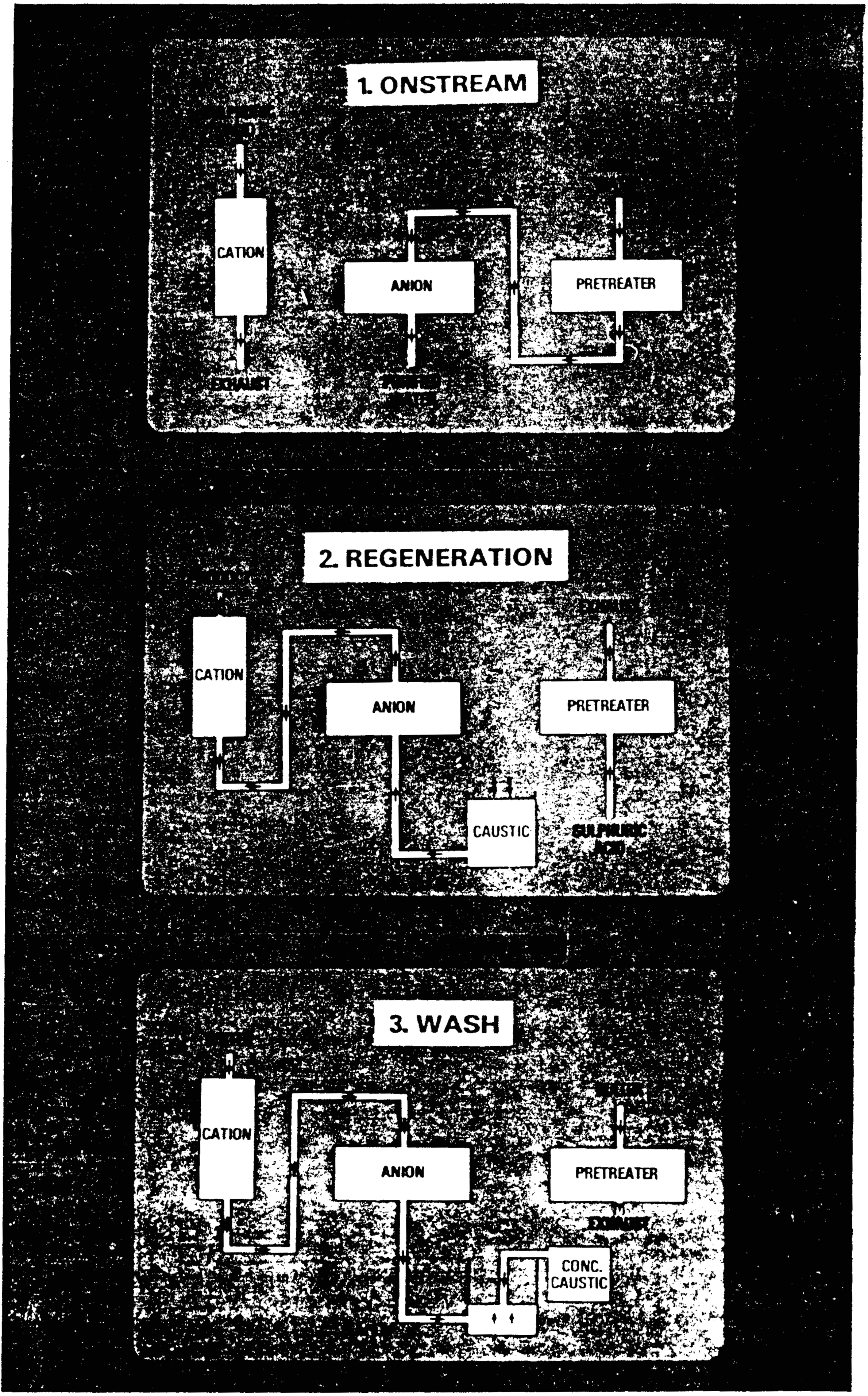


Figure 1 - Basic RECOFLO Chromic Acid Recovery Process

sodium hydroxide and sodium chromate salts is passed through the bed, the bed will at first take up sodium ions, but the sodium ions will be taken up from both sodium hydroxide and sodium chromate. In this way, a substantial amount of the sodium hydroxide will be converted to water and lost to the system.

In the RECOFLO process the solution leaving the anion exchange bed is passed directly to the cation exchange bed. The first solution to pass through the cation exchange bed is substantially pure sodium chromate solution. This is followed by a mixture of sodium hydroxide and sodium chromate and finally by a solution of virtually pure sodium hydroxide. The cation exchange bed is at first in a highly regenerated state, and will readily take up sodium ions from the solution. At this stage, the solution is substantially pure sodium chromate. As the bed becomes more loaded with sodium, its ability to pick up sodium ions decreases, so that by the time pure sodium hydroxide reaches the cation exchange bed, the bed is so loaded with sodium ions that little of the sodium hydroxide will be converted to water, and it will be retained in the bed where it can be recovered for re-use as described below.

Following completion of the passage of the regenerant solution through the beds, the cation exchange bed contains as void volume substantially pure chromic acid at the top, sodium chromate salts in the middle, and sodium hydroxide at the bottom, and the anion exchange bed contains as void volume a small amount of sodium chromate at the top with the rest of the void being primarily pure sodium hydroxide.

If both beds are washed separately as in the conventional process, the effluent from the cation exchange bed will be a sodium chromate solution. This sodium chromate solution would be either diverted to waste or converted in subsequent cycles to product.

However, in the RECOFLO process the beds are coupled together and the washing can be carried out in a single step. Water enters the top of the cation exchange bed, the solution from the cation bed passing directly into the anion exchange bed. This solution is at first sodium hydroxide, then sodium chromate and then chromic acid. At this stage, the anion exchange bed is highly regenerated, and therefore the sodium chromate is converted to sodium hydroxide which goes to the sodium hydroxide reservoir where it can be used for regeneration. Any chromic acid would be converted to water and also goes to the sodium hydroxide reservoir where it merely tends to dilute the solution in the sodium hydroxide reservoir and in effect act as make-up water. A small amount of 50% sodium hydroxide is added each cycle as chemical make-up.

In reducing the sodium hydroxide requirements, the load on the cation bed is reduced with a savings in sulfuric requirements for regeneration of that bed. Total chemical requirements for chromic acid recovery are shown in Table 1.

Table 1 - Chemical Consumption and Operating Costs

basis: 1 kg. CrO_3 recovered

50% sodium hydroxide	1.7 kg. @ \$0.20 =	\$0.34
66° Be sulfuric acid	2.9 kg. @ \$0.066 =	\$0.191
water	150 L. @ \$0.00025 =	\$0.038
resin replacement		\$0.027
	Total Operating cost	\$0.596
		(\$0.27/lb.)

In reducing chemical consumption the chemical wastes generated are also reduced. RECOFLO techniques also minimize wastewater volumes. It is significant that the process is 99.5% efficient in chromic acid recovery.

Table 2 - Wastewater

basis: 1 kg. CrO_3 recovered

sodium sulfate	1.5 kg.
sulfuric acid	1.77 kg.
chromic acid	0.005 kg.
pH	less than 1.0
flow	150 L.

By the various means described above it is possible to recover a chromic product at concentrations exceeding those normally achieved by conventional ion exchange. About one anion bed volume of chromic acid product can be produced each cycle consistently in the range of CrO_3 = 75-100 g/L.

The process has been assembled into a pre-piped skid mounted package called a Chrome Recovery Unit or "CRU". The CRU basically consists of a pre-filter, two cation beds, an anion bed and the various pumps, valves and controls necessary for fully automated operation (see Figure 2).

As discussed above, the ion exchange beds are extremely small by conventional ion exchange standards. The cation "pretreater" and

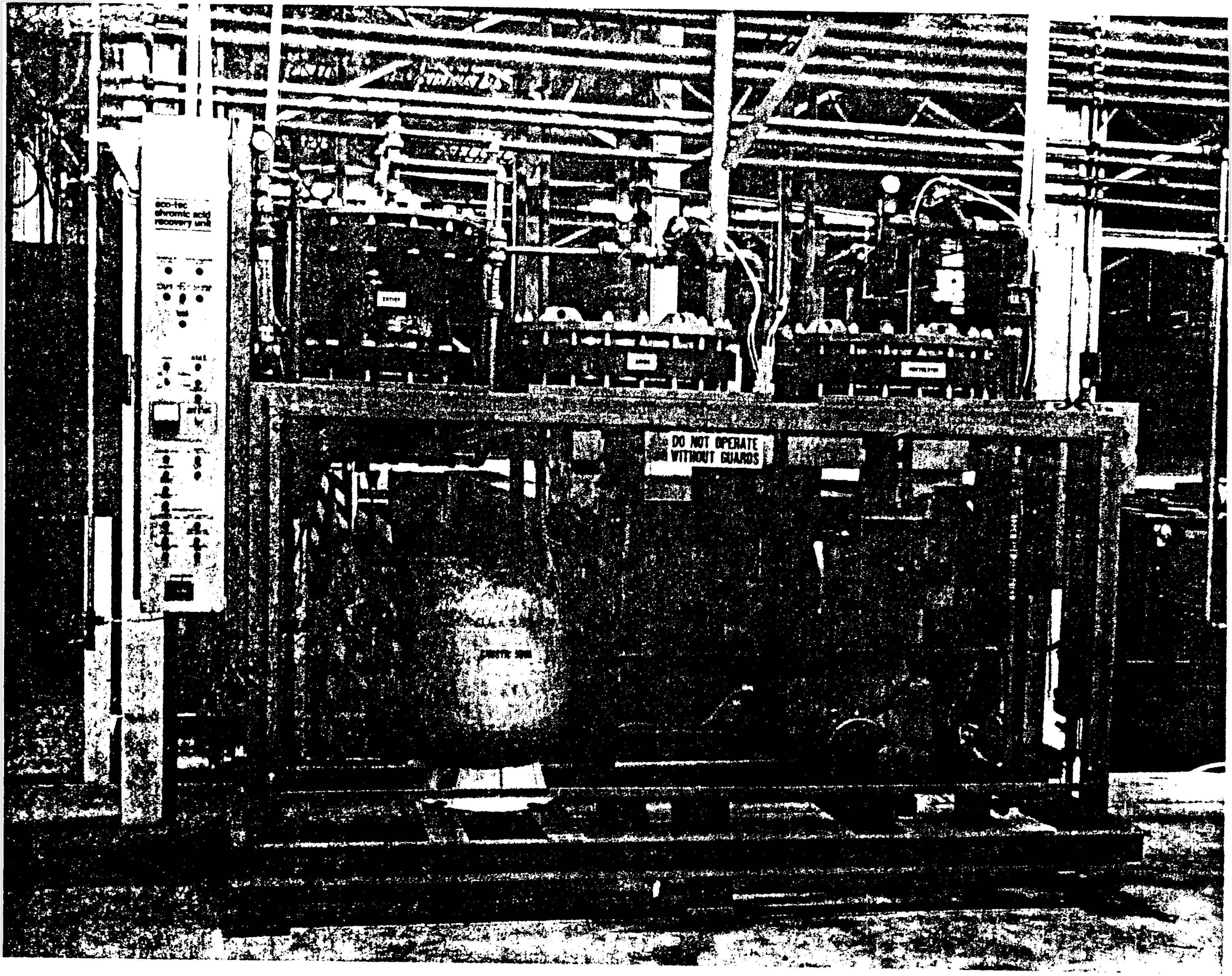


Figure 2 - Typical Chromic Acid Recovery Unit

anion bed are each approximately 7.6 cm. (3 inches) high. The second cation bed utilized for chromate conversion is approximately 30 cm. (12 inches) high. Scaleup is achieved by increasing bed diameters. Bed heights stay constant regardless of system capacity.

Service flow rates are extremely high by normal standards - 480 bed volumes per hour (60 US gpm/ft^3).

5. Installation Configurations

Figures 3, 4 and 5 show onstream breakthrough profiles of chromic acid rinsewater at different feed concentrations. It can be readily seen that the quality of the de-ionized water produced is a function of the feed concentration. Assuming one wants to maintain final rinse purity at less than 5 mg./L. CrO_3, water at more than this concentration is not acceptable for use in the final rinse. At a feed concentration of 390 mg./L. approximately 24 minutes of acceptable water can be produced. At a feed concentration of 700 mg./L. this time is reduced to 5 minutes and at 900 mg./L. essentially instantaneous breakthrough occurs.

The conventional approach is to go offstream as soon as breakthrough occurs. It has been found, however, that regeneration yields a more concentrated chromic acid product if the unit is left onstream until the anion bed is completely saturated, ie. the effluent rises to the same concentration as the feed.

Taking into account the shape of these breakthrough profiles, three different CRU installation configurations have been devised.

Single Feed/Double Return (SF/DR) (see Figure 6)

Rinsewater at less than CrO_3 = 700 mg./L. is pumped from the first rinse tank to the CRU. The deionized water produced at the beginning of the cycle flows to the final rinse in the counterflowing series. As soon as breakthrough occurs the effluent flow is diverted from the final rinse directly back to the first rinse. The contents of the first rinse are recirculated through the CRU until saturation, at which point the unit goes offstream.

A typical cycle at a feed concentration of CrO_3 = 300 mg./L. consists of about 30 minutes of "purified return", 15 minutes of "breakthrough return" and 15 minutes offstream (ie. regeneration and wash). Thus the CRU completes one complete cycle each hour.

Single Feed/Single Return (SF/DR) (see Figure 6)

The onstream cycle of the CRU shortens up, providing a corresponding increase in chromic acid recovery capacity when the concentration of the rinsewater feed increases. As shown by Figure 5, the effluent water is not acceptable for final rinsing if the feed

Figure 3 - Onstream Breakthrough Profile

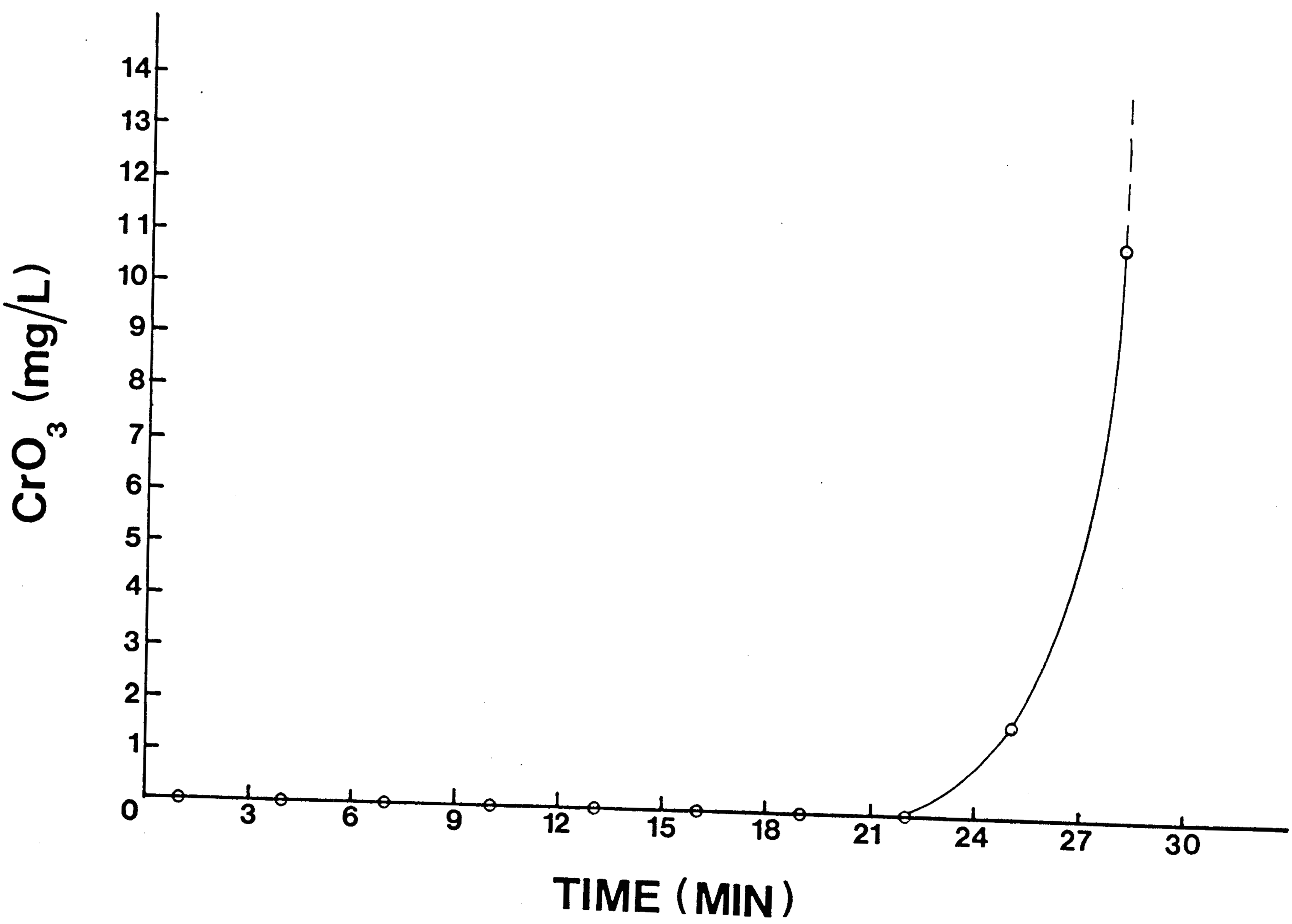


Figure 4 - Onstream Breakthrough Profile

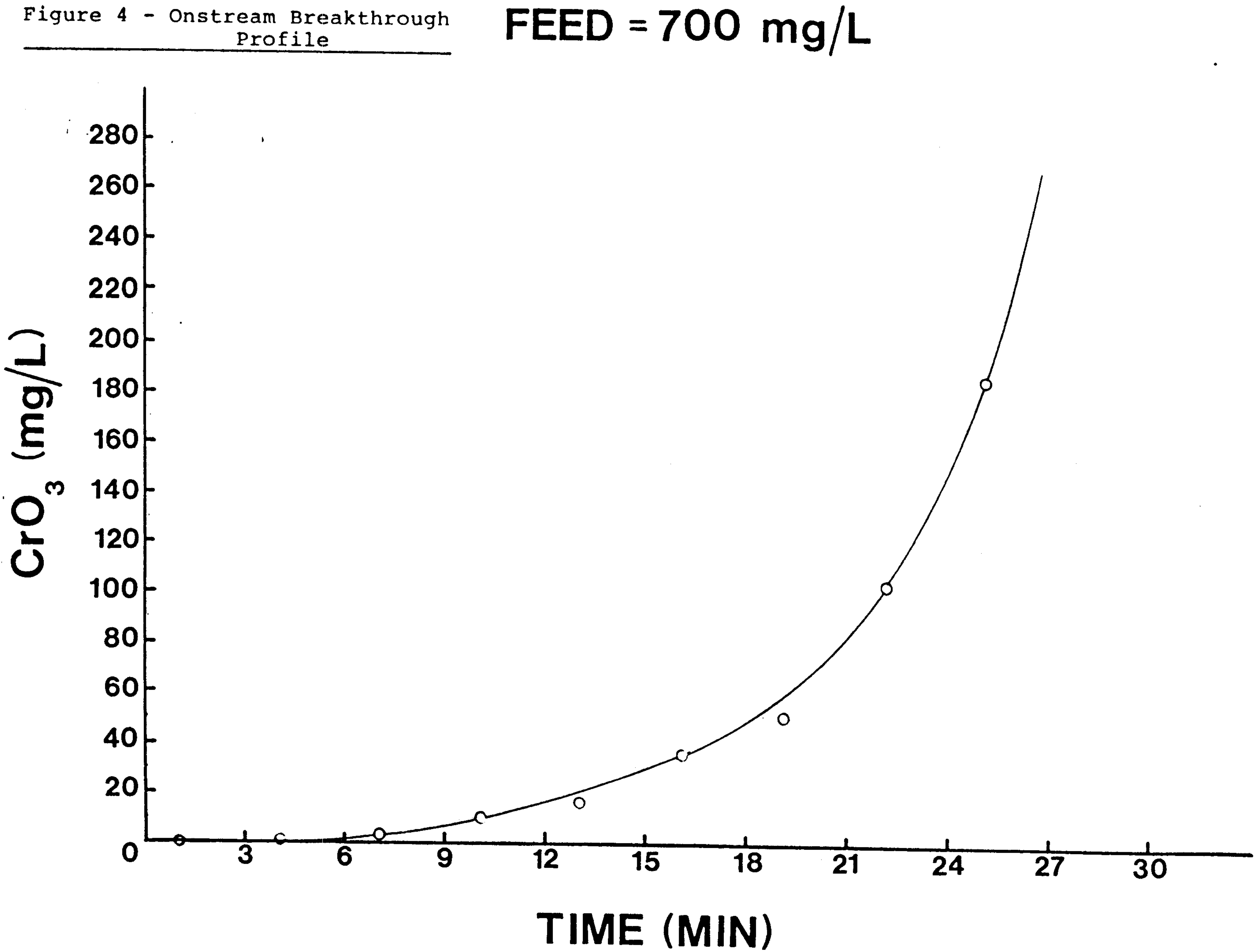
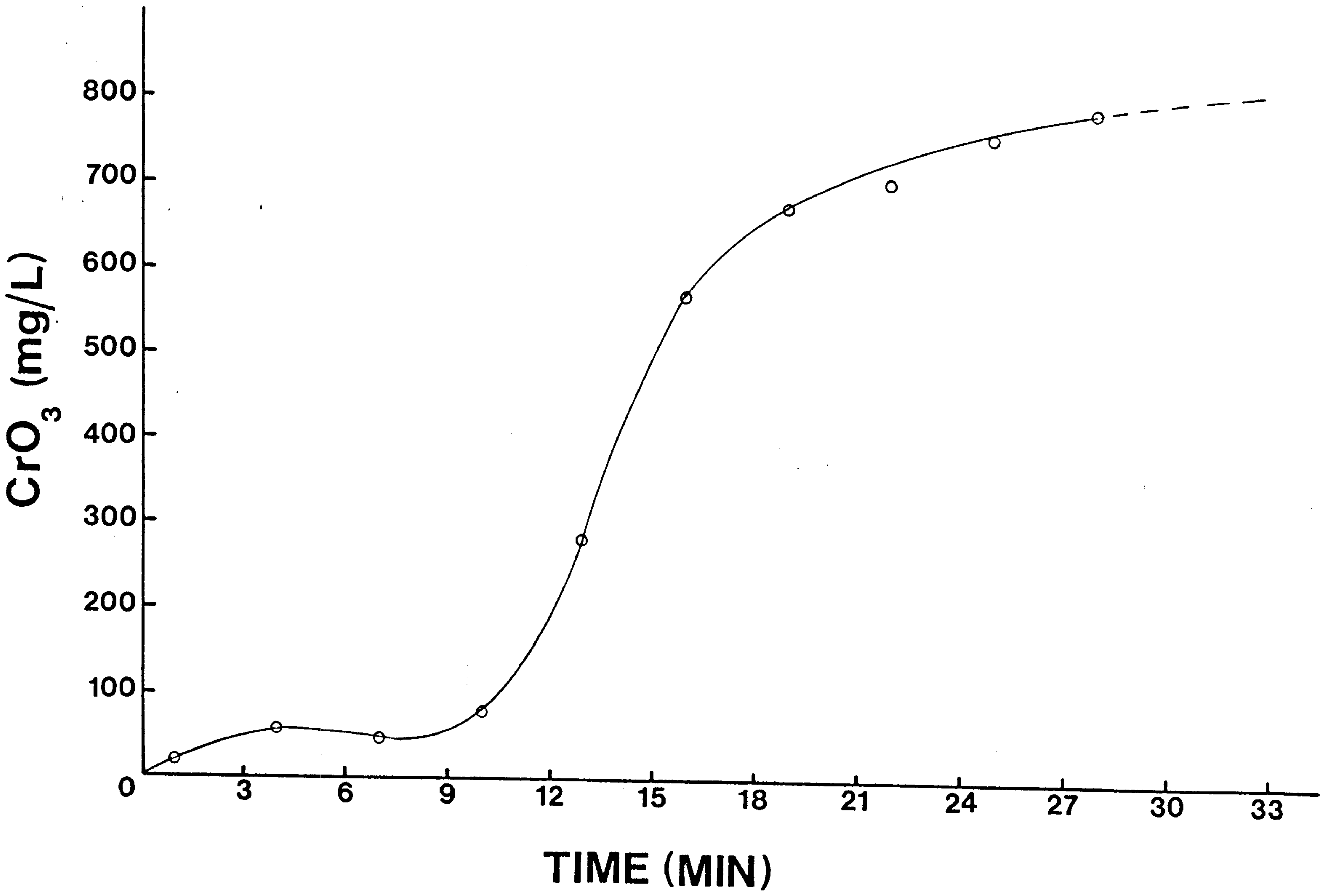


Figure 5 - Onstream Breakthrough Profile

FEED = 900 mg/L



exceeds about CrO_3 = 900 mg./L. In this case, rinsewater from the first rinse only is recirculated through the CRU. Final rinse quality is achieved through use of an "open loop" running rinse which is allowed to overflow to the plant waste treatment system.

By holding the first rinse at CrO_3 = 2000 mg./L. the total onstream can be reduced to about 10 minutes. With a 15 minutes offstream, 2.4 cycles can be completed each hour with a corresponding increase in chromic acid recovery capacity. By using this configuration the size and capitol cost of the CRU can be reduced considerably at the sacrifice of a small reduction in rinsewater recovery efficiency.

Double Feed/Double Return (DF/DR) (see Figure 7)

The features of the above configuration can be combined to maximize recovery capacity while at the same time produce rinsewater of final rinse quality. Rinsewater at a concentration of CrO_3 = 100-300 mg./L. is pumped from the second rinse to the CRU where it is deionized and directed to the final rinse. This continues for a period of about 7.5 minutes. At the end of this period, rinsewater is drawn from the first rinse instead of the second rinse, which is held at CrO_3 = 1000-3000 mg./L. The rinsewater from the first rinse can be only partially purified by the CRU and so is recycled directly back to the same tank. This continues for about 7.5 minutes, after which time the CRU goes offstream. The total cycle time of 30 minutes allows completion of 2 cycles per hour.

Taking into consideration service flow rates, offstream times, etc., the net flow rates of "purified return", "breakthrough return" and recovery capacity can be calculated for any size system. Table 3 summarizes this information for two CRU's of different sizes - 12 inch diameter anion bed (C12) and 30 inch diameter anion bed (C30).

6. Sulfate, Fluoride and Chloride Recovery

Other anions present in the rinsewater are recovered with the chromate. This is advantageous for chrome plating applications since sulfate and fluoride are required as catalysts. Chloride ion, however, is a highly undesirable contaminant. For this reason use of low chloride caustic soda is highly recommended as a regenerant.

In some cases, an excess of sulfate in the recovered product is experienced. This can be adjusted by addition of barium carbonate which precipitates barium sulfate from the product. Semi-automatic batch treatment systems have been devised for this purpose.

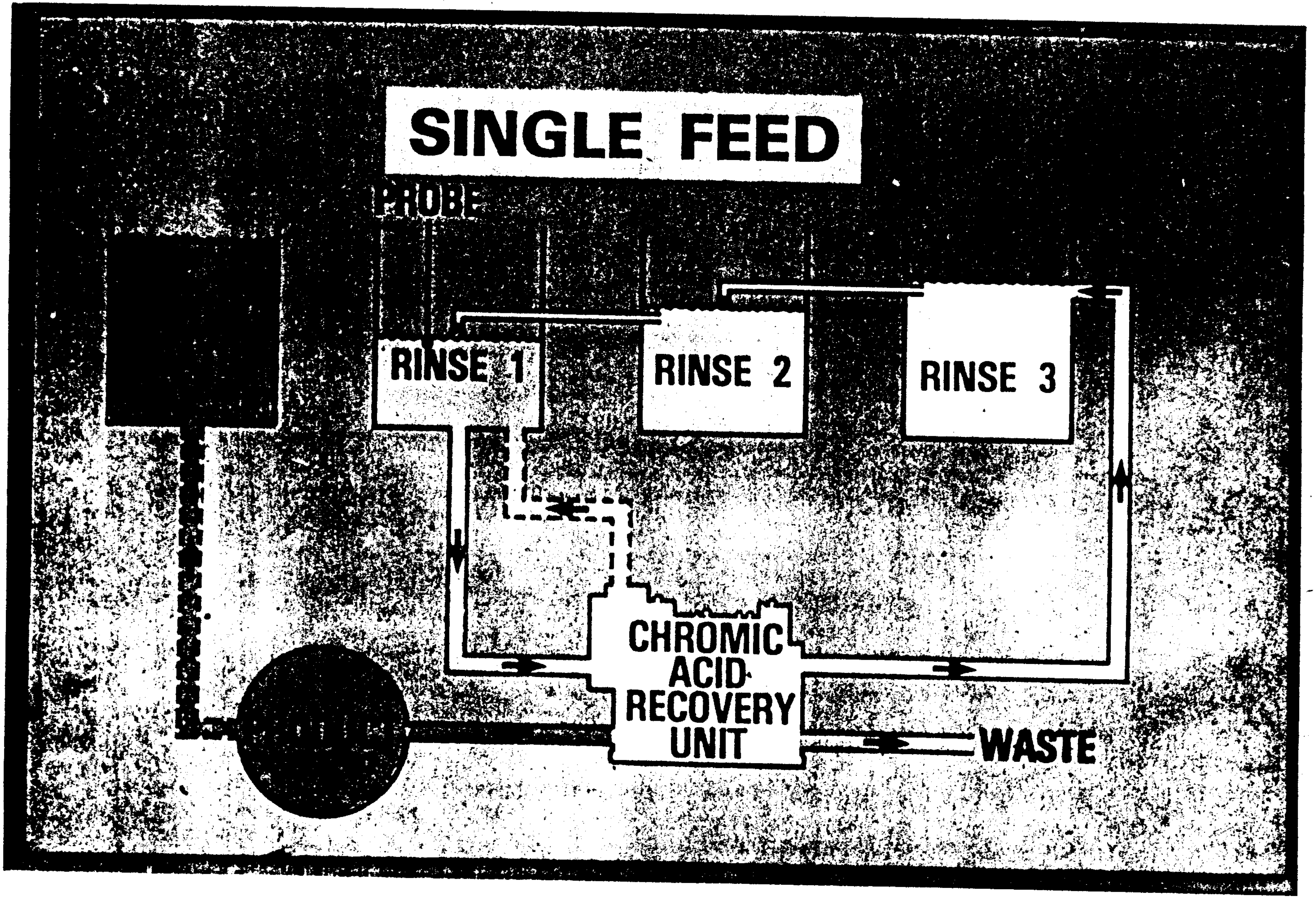


Figure 6 - Single Feed Installation Configuration

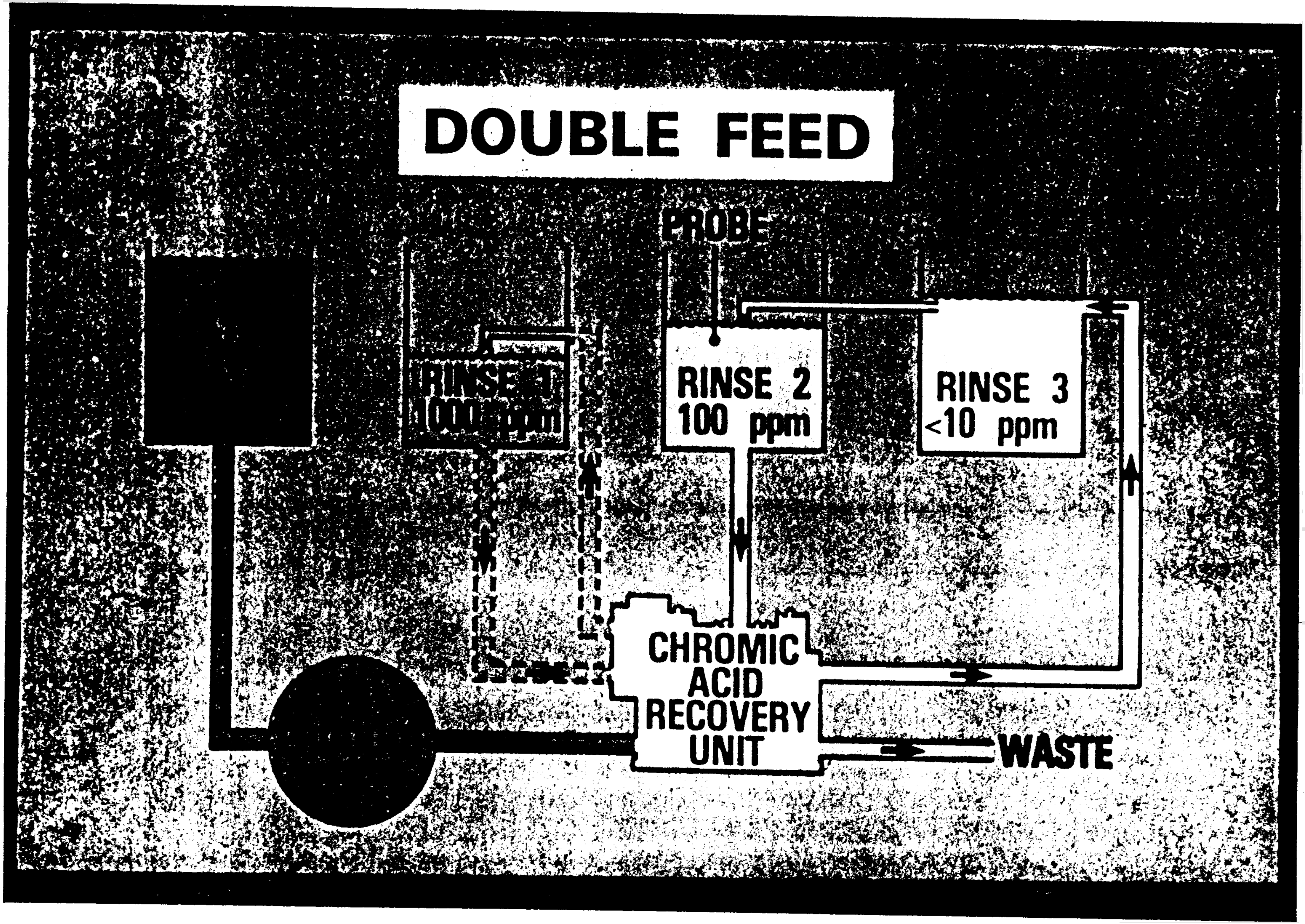


Figure 7 - Double Feed Installation Configuration

Table 3 - Typical System Specifications

	SF/DR		SF/SR		DF/DR	
	C12	C30	C12	C30	C12	C30
recovery capacity kg/h (lb/h)	0.48 (1.06)	2.97 (6.53)	1.15 (2.53)	7.13 (15.7)	0.95 (2.09)	5.9 (13)
service flow m^3/h (gph)	2.7 (714)	16.7 (4418)	2.7 (714)	16.7 (4418)	2.7 (714)	16.7 (4418)
purified return flow m^3/h (gph)	1.35 (357)	8.42 (2228)	0	0	0.34 (90)	2.09 (553)
breakthrough return flow m^3/h (gph)	0.68 (180)	4.21 (1113)	1.08 (286)	6.68 (1767)	0.34 (90)	2.09 (553)

7. Supplementary Product Concentration

In many cases the recovered product at CrO_3 = 75-100 g./L. is not sufficiently concentrated to permit full recycle back to the process bath.

In such cases, simple atmospheric type evaporators have proven ideal for increasing the chromic acid concentration to the necessary value. Because of the inefficiency of the chrome plating process large amounts of waste electrolytic heat are generated. The atmospheric evaporator can be operated directly off the bath, removing the necessary water to permit product recycle while at the same time cooling the bath.

Figure 8 shows an atmospheric evaporator designed to remove up to 75 litres per hour of water from a chrome plating bath. Warm chrome plating electrolyte is sprayed over packing in the tower. Plant air is forced through the tower, cooling the solution through evaporation of water. The cooled electrolyte flows by gravity back to the plating bath.

8. Field Experience

A large number of CRU's have been installed since 1971. Detailed logs have been maintained for each of these units so that a wealth of practical experience has been accumulated. Although the basic

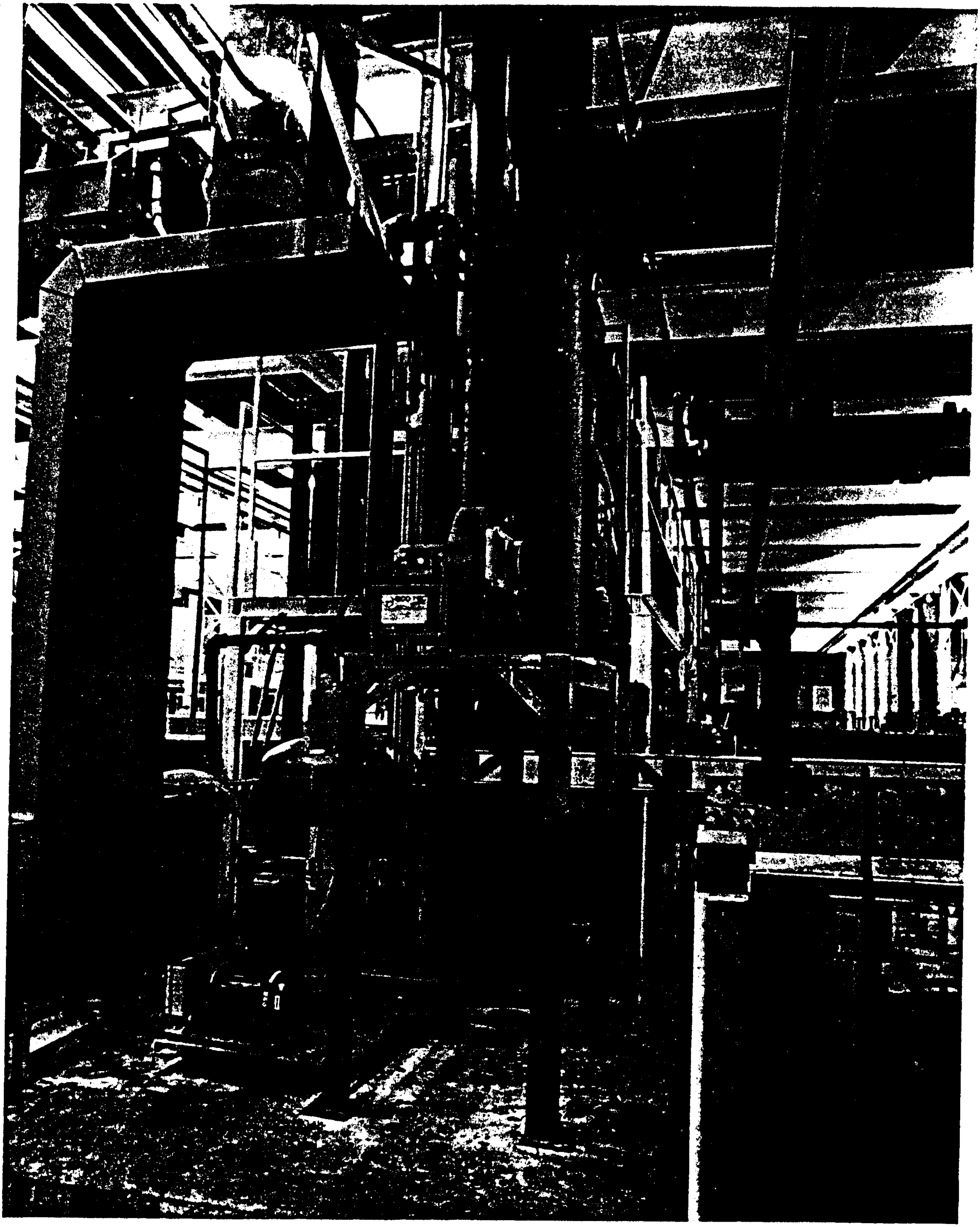


Figure 8 - Typical Atmospheric Evaporator

process has remained the same, field experience has resulted in a number of minor equipment and procedure modifications that together with an extensive trouble-shooting guide have maximized the reliability of the system. A number of experiences and problems that have been common to several installations are worth noting;

Bed Design

Standard ion exchange column designs were of course not applicable to the short RECOFLO beds. Early designs were somewhat prone to leakage. Development of a new gasketing design in 1975 corrected this problem and the problem was also rectified on existing units in the field. Leakage is no longer a problem.

Anion Bed Fouling

Unusually high metallic cation concentrations in the rinsewater or an interruption in the sulfuric acid supply results in precipitation of metallic hydroxide on the surface of the anion resin beads. This impedes anion exchange efficiency and results in poor quality deionized water and low product concentrations. The most common cause was found to be clogging of the sulfuric acid metering valve due to dirty acid. Installation of cartridge filters on the concentrated acid supply and monitors on the acid dispensing system largely alleviated this problem. In unusual circumstances installation of an oversized cation pretreater bed has been necessary to handle high cation loads. Such anion bed fouling can usually be corrected by "rejuvenating" the anion resin with a dilute sulfuric acid wash.

Resin Life

Resin life in the anion and cation "pretreater" beds has been good ... typically 2 - 5 years. Life of resin in the second cation bed has been more limited, however, due to exposure to warm chromic acid product. Typical cation resin life in this bed has been 6 - 12 months. This cation resin has been found to swell and then begin to soften. At this point it must be changed.

Fortunately, due to the small resin inventories, the cost of resin replacement is still small - about $.027 per kg. CrO_3.

Filtration

Chrome plating baths are not usually filtered and due to sloughing off of lead chromate from the anodes and barium carbonate additives for sulfate adjustment, the level of fine suspended solids in the system is often high. Inadequate filtration of the rinsewater prior to ion exchange treatment results in partial clogging of the cation pretreater bed. This in turn leads to difficulties in washing sulfuric acid regenerant from the bed and ultimately leads to high sulfate levels in the product. Proper attention to filtration requirements has been found to be a major consideration in the design of a successful chrome recovery system.

Regenerant Handling

Handling 10% sulfuric acid and caustic soda regenerant solutions can be a difficult problem. Excellent reliability has been achieved in this regard through use of hydropneumatic pump tanks, eliminating the use of centrifugal pumps and their attendant high service requirements.

Controls and Valves

Question frequently arises as to the life of valves and controls which are required to cycle several thousand times per year. Experience has shown this not to be a particular problem. The cycling is well within acceptable limits for all the components and, if anything, frequent actuation of valves prevents sticking.

A case in point is the 50% caustic soda valve which on occasion seizes up after several days of inoperation (a normal cycle for a conventional ion exchange system).

Maintenance Requirements

A survey of a large number of installations indicated that an average of about thirty minutes of maintenance time must be devoted to the chrome recovery system for each shift of operation. Included in this time is a highly recommended monitoring and log sheet program on the equipment. Allowance of this amount of time for a trained technician to maintain the equipment will result in a successful recovery installation.

9. Chromium Phosphate Aluminum Conversion Coating

Chromic acid is often employed in conjunction with large amounts of other chemicals. For example, phosphoric acid and ammonium bifluoride are used with chromic acid in aluminum conversion coatings. Economic feasibility studies on the recovery applications determined that when disposal of spent regenerants and resulting sludge were taken into account, that recovery of all three components was not a viable proposition.

Strong base resins demonstrate a dramatic preference for chromate over phosphate, fluoride and most other ions. Thus it is possible to selectively recover chromic acid from conversion coating rinsewater, discharging the remaining phosphate/fluoride bearing rinsewater to the waste treatment system. The economics of this process are excellent since chromic acid is the major pollutant and represents the major cost in making up the bath and disposing of the rinsewater.

Any move towards chrome free conversion coating processes should be considered, taking into consideration chrome recovery.

10. Other Metal Finishing Recovery Applications

RECOFLO cation exchange has been extensively used for purification of chromate process baths themselves, such as chrome plating baths, and zinc chromate passivation baths. Removal and regeneration efficiencies are excellent and resin replacement costs are small for the same reasons as those discussed above.

RECOFLO has been applied to a wide variety of other metal finishing recovery problems with excellent success. These include recovery of copper, nickel, tin, cobalt, and zinc salts from rinsewaters as well as removal of metallic salt contamination from sulfuric, hydrochloric, nitric and phosphoric acid pickling, etching and anodizing baths. Its unique features allow the employment of ion exchange in applications which were previously not technically and/or economically feasible.

11. Conclusion

A novel ion exchange system for chromic acid recovery from metal finishing rinsewater has been developed and field proven in a large number of commercial installations since 1971. The system has largely overcome the shortcomings inherent in conventional ion exchange chromic acid recovery systems. By utilizing the experience gained in previous installations it is possible to avoid many of the problems previously encountered when attempting to recover chromic acid by this method.

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