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ELECTROLYTIC DEMONSTRATION UNIT FOR COPPER REMOVAL FROM DISTILLATION PLANT BLOWDOWN

F. A. Posey

OAK RIDGE NATIONAL LABORATORY

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CHEMISTRY DIVISION

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F. A. Posey

ABSTRACT

The copper content of distillation plant blowdown brine (typically several tenths of a part per million) is of concern because of its likely toxic effect on sea life near brine outfalls. An electrolytic demonstration unit, based upon use of a packed bed of copper turnings operated as a porous cathode, has been designed, constructed, and tested. The unit, with a cross-sectional area of 1 ft², is capable of removing more than 90% of the dissolved copper from brine streams at a flow rate of 10,000 gpd. Details of the test unit and a closed loop assembly for measuring copper removal efficiency are described. An approximate theory of operation is discussed. Results of tests on simulated and actual blowdown brine are presented. An appendix contains a conceptual design and cost estimates for copper removal units capable of treating 1 and 10 mgd of distillation plant blowdown.

INTRODUCTION

Distillation plant blowdown streams contain dissolved copper in both cuprous and cupric forms at a concentration typically in the range of fractions of a part per million (1). Such copper concentrations are a consequence of normally occurring corrosion of Cu-Ni alloy tubing used in the heat-exchanger sections of distillation plants. The normal copper content of seawater is about 0.003 ppm in open ocean and the presence of much greater amounts of copper in blowdown brine is of concern because of its likely toxic effect on sea life near brine outfalls (1).

Up until now, there have existed no proven, economical methods for removing heavy metal ions, especially copper,

from distillation plant blowdown streams (2). Most proposed methods for copper removal would require the addition of various reagents and conventional chemical operations or would depend upon use of ion-exchange techniques. However, studies carried out by F. A. Posey, ORNL Chemistry Division, showed that reducible heavy metal ions could be removed from flowing streams very efficiently by appropriately designed and operated porous electrodes having a sufficiently large ratio of reactive surface area to solution volume.* Subsequently, an electrochemical demonstration unit for copper removal from brine streams was designed, constructed, and tested by F. A. Posey in collaboration with S. A. Reed, ORNL Reactor Chemistry Division.**

The device makes use of a packed bed (6" depth, 1 ft² cross-sectional area) of compressed light copper turnings, operated as a porous cathode, through which the stream to be treated is passed. Copper dissolved in the brine stream is deposited as metallic copper on the cathode surfaces and thereby removed from solution. The test unit is capable of treating at least 10,000 gpd (possibly up to 30,000 gpd) of blowdown brine with a removal efficiency of more than 90%.

This report presents results of a number of test runs carried out by use of a closed loop assembly in which synthetic or actual blowdown brine was circulated through the test unit with injection of appropriate amounts of copper into the test stream. The theory and mode of operation of the cell are discussed. In addition, a preliminary conceptual design and cost estimates are presented for units

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**Funds for construction and testing of the unit were provided by the Distillation Division, Office of Saline Water, U. S. Department of the Interior.

capable of treating 1 and 10 mgd of blowdown brine (cf. Appendix).

DESCRIPTION OF TEST UNIT

A schematic cross section of the copper removal cell is shown in Fig. 1, and Fig. 2 is a photograph of the cell. The walls of the cell are fabricated from Lucite for easy visibility of interior components. Copper-containing brine enters the cell from below through a 2" stainless steel pipe welded to the 3/8" stainless steel base plate (all stainless steel components were type 304L). A hose-and-clamp arrangement is used to connect the cell to the plastic (PVC) piping of the test loop. After entering the cell, the brine passes through two perforated stainless steel flow baffles and then through the cathode cage, which has a cross-sectional area of 1 ft² and a depth of 6 inches. The cathode cage contains approximately 9 pounds of finely divided, compressed copper turnings (Baker & Adamson Products, Specialty Chemicals Div., Allied Chemical Corp., Morristown, N. J.) on which copper dissolved in the brine is deposited as metallic copper. Electrical contact between the bed of copper turnings and the stainless steel base plate is provided by stainless steel studs and standoffs. The negative lead of the power supply is connected to the base plate. The top and bottom of the cathode cage are constructed from perforated stainless steel sheet to allow easy passage of brine, and porous polypropylene membranes (1/16" thickness, mean pore diameter ca. 120 microns) are used to contain the finely divided copper turnings. The sides of the cage are fabricated from stainless steel sheet, and fit closely with the Lucite cell walls. Two O-ring seals (neoprene) prevent flow of brine between the cathode cage and the cell walls. Stainless steel fittings (Swagelok) are provided through the cell wall at top and bottom of the cathode cage for connection of (saturated calomel) reference electrode assemblies. The reference

Fig. 1. Cross Section of Electrochemical Cell for Removal of Copper from Brine Blowdown of Distillation Plants (10,000 gpd Prototype).

Fig. 2. Photograph of Copper Removal Cell.

electrodes (Corning, Cat. No. 47600) are sealed into Pyrex glass tubes by use of a "home-made" compression fitting (rubber stopper, ground glass joint, and metal clamp assembly).

After passage through the porous cathode (which is maintained at the proper electrode potential by a power supply, as described below), treated brine then flows through 16 Lucite flow ducts arranged in a square array which divert most ($> 99\%$) of the flow past the anode structure and out a 2" stainless steel pipe in the 3/8" stainless steel top plate. Where possible, stainless steel surfaces exposed to the brine were covered with a thin epoxy coating (90% Shell 815 resin + 10% Ciba 951 hardener) in order to minimize corrosion of structural components and to avoid galvanic effects as much as possible. During the loop tests it was necessary, of course, to provide means for external discharge and disposal of chlorine, the product of the anode reaction; otherwise use of a closed loop assembly for testing of copper removal efficiency would not have been feasible due to build-up of chlorine in the loop. A small portion of the total brine flow (typically 1 gal/hr) is allowed to pass into the anode compartment through a 3/16" porous polypropylene diaphragm (mean pore diameter ca. 120 microns). This flow of anolyte passes through holes in the 1" graphite anode, around the Lucite catholyte flow ducts, and out an anolyte exit fitting.* Anolyte flow is regulated by use of a Teflon stopcock and the reject stream is led by vinyl tubing to a collection vessel for disposal. The positive lead of the power supply is connected to the graphite anode by means of a stainless steel bus bar. The graphite anode and the stainless steel top and base plates are fastened to the Lucite cell walls by use of

*For operation at a distillation plant test site with once-through flow, the porous diaphragm assembly, catholyte ducts, and anolyte exit fitting are not needed and may be removed.

1/8" neoprene gaskets and stainless steel studs or bolts. External and gasketed surfaces of the graphite anode are covered with epoxy resin (Epoxi-patch, Hysol Div., Dexter Corp., Olean, N. Y.) to prevent seepage of brine into assembly stud holes and to the exterior of the cell.

The cell is cushioned by a 3/4" rubber pad and supported by a 1/2" aluminum plate through which the mounting studs are fastened. Mounting studs, washers, and nuts are insulated from the aluminum plate and thus from the instrument carbinet by use of Teflon bushings. The cell and its support are mounted in a standard steel instrument cabinet (6 ft.-7 in. high (including casters) x 24-1/2 in. wide x 22 in. deep) together with a power supply, voltmeter, pressure gauges, reference electrode assemblies, sampling valves, and observation light.

The power supply for the cell is a continuously adjustable, regulated, constant voltage/constant current unit (Hewlett-Packard Model 6256B, Series LVR-B, 0-10 V, 0-20 A) which operates on 115 V A.C.; power consumption at full output is 375 W. Panel meters on the power supply may be used to monitor the cell potential and the cell current. Provisions are available for operating the power supply in a remote sensing mode which compensates for any IR drop developed in the power leads during operation; this mode of operation is used in the demonstration unit.

The voltmeter used for monitoring the potential of the porous cathode is a solid-state VOM (Simpson Model 313) with 11 megohm input impedance. It is housed in a standard instrument rack panel together with a rotary switch which permits selection of four different quantities to be monitored; (a) E_1 , the potential (vs. saturated calomel electrode (SCE)) of the downstream (exit) end of the porous cathode; (b) E_2 , the potential of the upstream (entrance) end of the cathode bed; (c) ΔE , the difference between E_1 and E_2 , which is equal to the IR drop through the electrolyte phase within the porous cathode; and (d) V , the cell voltage (between the graphite anode and the exit end of the cathode bed).

The inlet line to the unit is standard 1 in. pipe; the reject line is 2 in. pipe, both of rigid polyvinyl chloride. The inlet and reject lines penetrate the left side of the instrument cabinet where they may be joined with appropriate unions to the test loop or other brine source. Pressure gauges (0 - 15 psig) are connected to the piping inside the cabinet upstream and downstream of the cell so that pressure drop through the unit may be monitored. In addition, small stainless steel valves are provided upstream and downstream of the cell for taking samples of inlet and reject streams for copper analyses and for ease in draining and flushing of the cell when needed. An observation light with swivel and flexible arm is provided to facilitate inspection of internal components of the cell during operation.

DESCRIPTION OF LOOP

A block diagram of the test loop is shown in Fig. 3, and Fig. 4 is a photograph of the loop with the test unit attached. Brine (typically 50 g/l NaCl) from the main reservoir (S_1) was circulated in 2" plastic pipe by the main pump (M_1 , Durco, 0 - 25 gpm) through the large rotameter (R_1 , Fischer & Porter tube no. B9-27-10/77) and the cell (E) back to the reservoir. Flow rate and pressure inside the cell could be adjusted by means of valves V_1 and V_2 . Pressures upstream and downstream of the cell were monitored by gauges P_1 and P_2 (P_2 is visible in Fig. 4 just above the cell). Tygon tubing (L) carried the chlorinated anolyte reject stream to receptacle W. Copper stock solution (typically $10^{-1}M$ $CuCl_2$ + $10^{-3}M$ HCl + 50 g/l NaCl) from the glass reservoir (S_2) was pumped through a rotameter (R_2 , Fischer & Porter tube no. FP-1/8-12-G-5) by a small pulsafeder pump (M_2 , Lapp Insulator Co., Leroy, N. Y., Model LS-10) and injected into the loop upstream of the test unit through a check valve (C). Not shown in Fig. 3 is a valve in the return line which allowed diversion of a small stream for continuous monitoring of the brine pH with a

Fig. 3. Block Diagram of Test Loop. S_1 , 55 gal stainless steel drum reservoir. S_2 , glass reservoir for copper stock solution (ca. 1 gal). M_1 , 25 gpm pump. M_2 , micro-pulsafeeder pump. R_1 , 0-30 gpm rotameter. R_2 , 0-20 cc/min rotameter. C , spring-loaded check valve. V_1 , V_2 , valves for flow and pressure control. P_1 , P_2 , pressure gauges. E , electrochemical cell. L , waste line for chlorinated anolyte. W , anolyte receptacle.

Fig. 4. Photograph of Test Loop Assembly.

combination pH electrode (Corning, Cat. No. 476056). A portable, battery-operated pH meter (Beckman Model N) was used with the combination electrode (cf. Fig. 4, on top of cabinet). Also not shown in Figs. 3 and 4 are means for deaeration and subsequent transfer of solution (typically 40-50 gal) to be circulated in the loop.

THEORY OF OPERATION

When the porous cathode is operated within the proper potential range (ca. -600 to -900 mV vs. SCE), the rate of removal of dissolved copper from the flowing stream onto the cathode surfaces is controlled by mass transport (convective diffusion). The principles used for selection of the proper operating potential are illustrated by the data of Fig. 5, which shows polarization curves for reduction of cupric ion on a solid pyrolytic graphite electrode in NaCl solution.* The blank (curve A) is largely due to reduction of residual oxygen (ca. 0.05 ppm) dissolved in the solution (deaerated with a stream of He). It is seen from curves B and C, which correspond to about 13 and 140 ppm Cu^{+2} respectively, that the reduction reaction takes place in two steps. Above a potential of about -300 mV vs. SCE, cupric ion is reduced to cuprous. Operation of a porous cathode bed at such a high potential would therefore lead to formation of soluble cuprous species instead of to an adherent metallic deposit. These curves have essentially the same significance as a polarogram and the vertical sections on curves B and C represent the limiting rate of convective diffusion to the electrode surface under the prevailing flow conditions.

*Data in Figs. 5 and 6 were obtained in previous studies on copper reduction on a variety of planar and porous electrodes. They are included here to illustrate the principle of operation of the demonstration unit. Similar results are observed for reduction of copper ions on the copper substrate of the demonstration unit.

Fig. 5. Reduction of Cu^{+2} on Pyrolytic Graphite.
 $T = 25^\circ\text{C}$, 0.67 M NaCl . A, 0.67 M NaCl ($\text{pH} \approx 5.6$). B,
 $0.67 \text{ M NaCl} + 1.96 \times 10^{-4} \text{ M Cu}^{+2}$ ($\text{pH} = 2.48$). C, 0.67 M
 $\text{NaCl} + 2.14 \times 10^{-3} \text{ M Cu}^{+2}$ ($\text{pH} = 2.48$).

Fig. 6. Effect of Flow Rate and Electrode Potential on Reduction of Cu^{+2} in a Porous Carbon Electrode (Carbocell 40). $T \approx 23^\circ\text{C}$, $0.67 \text{ M NaCl} + 10^{-4} \text{ M Cu}^{+2}$. Diameter = 0.25 in, length = 0.50 in, cross-sectional area = 0.317 cm^2 .

Between about -400 and -800 mV, cupric ions are reduced all the way to metallic copper, and this is therefore the proper potential region for operation of a porous carbon cathode as a copper removal device. Reduction of hydrogen ions to molecular hydrogen is encountered at potentials below about -800 mV; this region should be avoided because of increased power consumption. Similar considerations apply to the copper reduction reaction on solid and porous copper electrodes.

Figure 6 shows measurements on the influence of solution flow rate on the reduction of cupric ion, present at a concentration of about 6 ppm, in a small porous carbon electrode held at various potentials. The average pore diameter of the carbon was about 70 microns, the electrode length was 0.5 in., and the cross-sectional area was about 0.3 cm². Thus, the linear flow rate of solution through the porous electrode may be obtained by multiplying the values on the abscissa of Fig. 6 by a factor of about 3. In agreement with the polarization curves on the solid graphite electrode in Fig. 5, the current depends upon whether the cupric ions undergo a 1-electron or 2-electron reduction reaction, and this is determined by the electrode potential. At low flow rates, up to about 10 cm³/min (ca. 30 cm/min linear flow rate), the current increases directly with the flow rate. This means that the reduction reaction is proceeding with close to 100% efficiency. At higher flow rates, the efficiency drops off due to inadequate residence time of the fluid within the porous electrode (3). On the basis of such data it is possible to design porous electrode devices for efficient removal of certain electroactive substances from flowing solutions. (The flow rate indicated in Fig. 6 for use with a proposed device is not related to the present application.) This procedure was followed in the design of the demonstration unit for removal of copper from blowdown brine. Scale-up computations were based on the results of experiments

with a small column (2" diameter, 6" length) of compressed copper turnings.

In steady-state operation of the demonstration unit, the downstream (exit) end of the cathode is maintained by the constant-voltage power supply at a potential of about -800 mV vs. SCE. At the copper concentration levels to be expected in typical distillation plant blowdown, the upstream end of the cathode will operate at potentials which are estimated to be between -700 mV and -500 mV vs. SCE (all within the desired potential range). The potential drop through the porous cathode is a consequence of the distribution of the reaction within the packed bed and depends upon a number of factors, including the conductivity of the brine (see below).

An approximate treatment of the mass-transport problem for operation of the porous cathode in the region of rate control by convective diffusion leads to the following relation for the ratio of copper concentration in effluent and input streams (assuming only a single copper species is present):

$$\frac{C(\ell)}{C_0} = \exp (-S\ell D/\delta U) \quad (1)$$

In this expression, C_0 is the copper concentration in the input stream, $C(\ell)$ is the copper concentration in the effluent, S is the cathode surface area per unit length of the porous electrode (cm^2/cm), ℓ is the length of the porous electrode (cm), D is the diffusion coefficient of the copper ions (cm^2/sec), δ is the effective diffusion layer thickness (cm), and U is volume flow rate (cm^3/sec). The derivation of Eq. (1), a one-dimensional approximation, is based upon a number of assumptions commonly used in the analysis of problems of this type. As a numerical example, based on quantities believed typical of the test unit, for $S = 10^{+4} \text{ cm}^2/\text{cm}$, $\ell = 6 \text{ in.} = 15.24 \text{ cm}$, $D = 10^{-5} \text{ cm}^2/\text{sec}$, $\delta = 10^{-3} \text{ cm}$, and $U = 10^{+4} \text{ gpd} = 4.38 \times 10^{+2} \text{ cm}^3/\text{sec}$, we estimate from

Eq. (1) that approximately 97% of the dissolved copper would be removed by the porous electrode. Thus the copper content of a stream containing initially 300 ppb of dissolved copper could be reduced to about 9 ppb by passage through a porous cathode having the stated characteristics and obeying Eq. (1).

For essentially complete removal of copper from the brine stream, the total current due to reduction of copper ions (in both cuprous and cupric forms) is given by

$$I = F U (C_1 + 2C_2) \quad (2)$$

where I is the current (A), F is Faraday's constant ($9.64867 \times 10^{+4}$ coulombs/equivalent), C_1 is the concentration of cuprous ions (moles/cm³), and C_2 is the concentration of cupric ions (moles/cm³). Thus, for a flow rate of $U = 10^{+4}$ gpd. = $4.38 \times 10^{+2}$ cm³/sec in the test unit, and for $C_1 = C_2 = 100$ ppb = 1.57×10^{-9} moles/cm³, we estimate from Eq. (2) that the current required for complete copper removal is about 0.2 A. Of course, trace amounts of other reducible substances (ferric ions, dissolved O₂, etc.) may also contribute to the observed current, as well as a small background current due to reduction of hydrogen ions and/or the solvent (water) on the electrode surfaces.

Under the same assumptions (including presence of a single reducible ionic species) used in the derivation of Eq. (1), it can be shown that the total potential drop through the porous electrode (ΔE , volts) is given, in the case of excess inert electrolyte (e.g., NaCl), by

$$\Delta E = (n F U C_0) R \left[1 - \left(\frac{\delta U}{S \ell D} \right) \left(1 - e^{-\frac{S \ell D}{\delta U}} \right) \right] \quad (3)$$

where R , the resistance of the solution phase inside the porous electrode, is equal to $\ell/\sigma A$ (σ = solution conductivity, mho/cm; A = cross-sectional area of solution phase, cm²), and n is the number of electrons involved in the reduction

reaction ($n = 1$ for Cu^{+1} ; $n = 2$ for Cu^{+2}). As a numerical example, using the same values for S , l , D , δ , and U as quoted above, and with $n = 1$, $C_0 = 300 \text{ ppb} = 4.72 \times 10^{-9} \text{ moles/cm}^3$, $A = 5 \times 10^{+2} \text{ cm}^2$ (ca. 54% porosity), and $\sigma = 5 \times 10^{-2} \text{ mho/cm}$, we find that $\Delta E \approx 88 \text{ mV}$. This rough calculation indicates that, for the copper concentration levels likely to be encountered in actual blowdown brine, it is very probable that the entire porous electrode may be operated in the potential region of rate control by convective diffusion of the copper ions in the solution phase to the cathode surfaces.

The input power required by the cell may be computed by use of the relation

$$P = V I / (60 U) \quad (4)$$

where P is the power consumption (KWH/Kgal), V is cell voltage (V), I is current (A), and U is flow rate (gpm). For the numerical examples presented above ($I = 0.2 \text{ A}$, $U = 10^{+4} \text{ gpd} = 6.94 \text{ gpm}$), and assuming that the cell voltage is 2.5 V, we find from Eq. (4) that the power requirement in such a case would be $1.2 \times 10^{-3} \text{ KWH/Kgal}$. From this result it can be inferred that the capital cost of the equipment is the major item of expense connected with the electrolytic method for copper removal from blowdown brine, since the operating power requirement is almost negligible for copper concentration levels which are likely to be encountered in blowdown from actual distillation plants.

TEST PROCEDURE*

The first few runs carried out in the test loop were unsuccessful because of a number of problems in loop design.

*Detailed procedures for assembly and operation of the components of the test unit are contained in an instruction manual which is provided with the test unit.

or in start-up procedure. It was found, first of all, that no loop components constructed of iron or mild steel could be tolerated; substantial corrosion of these materials in the aerated 50 g/l NaCl test solution soon interfered with both operation of the cell and analysis for the copper content of the solution. Consequently, all iron components of the loop were replaced with plastic (PVC) or stainless steel components. Subsequently, it was found that pH control ($\text{pH} < 6$) and deaeration of the circulating stream had to be achieved in order to prevent formation of large quantities of cuprous oxide on the internal surfaces of the copper packed-bed cathode during the start-up period. The operating procedure finally adopted, as described below, allowed a number of test runs on copper removal efficiency to be carried out successfully.

After assembly of the cell, reference electrodes, and electrical connections in the test unit, the reservoir and all valves were sealed and the entire loop assembly was purged with a vigorous stream of purified N_2 for several hours (sometimes overnight) to remove atmospheric oxygen. Simultaneously, solution to be added to the loop (ca. 180 liters) was deaerated by use of purified N_2 . After satisfactory deaeration ($< 5\%$ of initial O_2 content), as indicated by a Beckman Laboratory Oxygen Analyzer (Model 777), solution was pressurized into the loop. The solution used during most of the test runs was 50 g/l NaCl; one run was carried out using actual blowdown brine (with added copper) from the OSW test site at Wrightsville Beach, N. C. The main pump (M_1 , Fig. 3) was then started and flow rate was adjusted by use of the rotameter (R_1) and valves (V_1 and V_2). Internal pressure, as monitored by the gauge downstream of the cell (P_2 , Fig. 3), was adjusted in most cases to approximately 3 psig in order to provide adequate outflow of the chlorinated anolyte reject stream.

Subsequently, solution was admitted to the reference electrode compartments at top and bottom of the cathode bed, with adjustment of the liquid level to allow adequate immersion depth of the reference electrodes. Electrode potentials of each end of the cathode bed (E_1 and E_2) were then checked on the voltmeter to ensure that they were essentially the same ($\Delta E \cong 0$ with power supply disconnected). After attachment of the power and sensor leads from the power supply to the cell, power was turned on and the output voltage was slowly adjusted until $E_1 \cong -800$ mV vs. SCE (or other desired value). In general, the current was initially high (a few amperes) as residual oxygen and superficial oxide on the copper cathode surfaces were reduced. The current then dropped with time until only a small background current (0.1 - 0.2 A) was observed (some readjustment of power supply voltage was required during this time). It was necessary during the start-up period to monitor the pH of the solution in the loop and to add periodically quantities of acid (HCl) sufficient to ensure operation under slightly acidic conditions (pH ~ 5 - 6). (Attempted operation in alkaline solution greatly hindered polarization of the cathode and resulted in rapid and copious oxide formation on the copper surfaces, especially in the presence of dissolved oxygen.)

After the cathode bed was operating in the proper potential region, and the background current had attained a sufficiently low value, copper stock solution was injected into the loop upstream of the cell by use of the small pulsar-feeder pump (M_2 , Fig. 3) at a rate sufficient to provide the proper concentration level (200 ppb or higher). The entire system was then allowed to operate for some time (typically one hour) in a steady state at constant flow rate and incoming copper concentration. Several samples (ca. 125 ml) were taken upstream and downstream of the cell during this time for subsequent analysis of the copper content of incoming and exit streams and calculation of the efficiency of copper

removal by the porous cathode. Flow rate and/or copper injection rate were varied as desired to obtain data on the influence of flow rate and concentration level on copper removal efficiency over a reasonably wide range of conditions. Electrode potentials, cell voltage, current, pressures, and flow rate were monitored every few minutes during operation. At the conclusion of a run, the entire loop assembly was flushed repeatedly with demineralized water and drained.

ANALYSES

In addition to samples of the solution in the loop taken upstream and downstream of the cell during operation at various levels of copper injection, several samples were taken prior to copper injection. These were analyzed for both iron and copper content to establish that iron levels due to corrosion of stainless steel components were not high enough to interfere with the copper analyses and that copper levels were sufficiently low (less than about 10 - 20 ppb) at the beginning of a run. Also, at the conclusion of a run, another sample was taken for iron analysis to ensure that corrosion products accumulated during a run would not interfere with copper analysis procedures.

Sensitive spectrophotometric methods were used for both iron and copper analyses. Iron analyses were carried out by use of 1,10-phenanthroline in buffered acid solution according to a well-established method (4). Copper analyses for runs with 50 g/l NaCl were carried out by the "cuprethol" method with the reagent bis(2-hydroxyethyl)dithiocarbamate (5). In the loop test with brine from the Wrightsville Beach plant, copper analyses were carried out by use of the "bathocuproine" method using 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline with chloroform extraction (6). The bathocuproine method is free from interference by relatively large amounts of iron, calcium, and/or magnesium.

RESULTS AND DISCUSSION

Results of the loop tests are presented in Tables 1, 2, and 3, which contain flow rates, electrode and cell potentials, results of analyses of test samples for copper content, removal efficiencies, total power requirements, and power requirements per unit copper concentration. The results of Table 1 were obtained in 50 g/l NaCl, with the cathode bed packed with long strands of light copper turnings, as received from the vendor. In addition, the first perforated stainless steel flow baffle at the bottom of the cell (cf. Fig. 1) had a solid stainless steel disk (3" diameter) attached in the center just above the 2" entrance pipe. It was thought that without such a flow deflector the fluid flow would tend to be higher in the center of the cell than near the walls. Subsequent visual observations on flow distribution within the cell as a function of total flow rate showed that this was not true. With the baffle disk in place, it was observed that fluid flow was much faster near the edges of the cell than near the center. Furthermore, it appeared that relative flow rates near the edge and near the center of the cell remained approximately constant over the experimentally accessible flow range. Thus, the flow distribution within the cell, while nonuniform, remained reasonably constant at various total flow rates. The disk baffle was removed from the cell for the test results reported in Tables 2 and 3. This had the desirable effect of making the flow distribution somewhat more uniform across the cell, but on the other hand it was observed that the flow distribution across the cell was considerably more dependent upon the total flow rate. The more uniform flow distributions were observed at the higher flow rates, with more of a tendency for increased fluid flow near the walls relative to that near the center of the cell at low flow rates. The consequences of the nonuniform flow distribution and its variation with total flow rate are reflected in the performance of the demonstration unit.

Table 1. Results of Loop Tests on Efficiency of Copper Removal by Electrolytic Demonstration Unit

(Solution: 50 g/l NaCl)

Test No.	U		E ₁	E ₂	ΔE	V	I	C ₀	C(l)	Percent Removed	Power (P)	P/C ₀
	(gpm)	(gpd)	(volt)	(volt)	(volt)	(volt)	(amp)	(ppb)	(ppt)		(WH/Kgal)	(WH/Kgal-ppm)
1	5	7,200	-0.6	-0.480	0.120	2.15	0.7	1048	166	84.2	5.0	4.8
2	"	"	"	"	"	"	"	1074	146	86.4	"	4.7
3	7	10,000	"	-0.378	0.222	2.6	1.4	1534	358	76.7	8.7	5.7
4	"	"	"	-0.375	0.225	"	1.55	1545	378	75.5	9.6	6.2
5	"	"	-0.7	-0.466	0.234	2.7	1.5	1476	286	80.6	"	6.5
6	"	"	"	-0.470	0.230	"	"	1508	283	81.2	"	6.4
7	"	"	-0.8	-0.570	"	2.8	"	1439	259	82.0	10.0	6.9
8	"	"	-0.9	-0.672	0.228	2.9	"	1503	264	82.4	10.4	"
9	"	"	-0.8	-0.704	0.094	2.3	0.65	714	138	80.7	3.6	5.0
10	"	"	"	-0.370	0.430	3.6	2.95	3069	623	79.7	25.3	8.2
11	14	20,160	"	-0.380	0.420	3.8	3.30	1836	778	57.6	14.9	8.1
12	21	30,240	"	-0.309	0.491	4.8	5.15	2841	1756	38.2	19.6	6.9

Table 2. Results of Loop Tests on Efficiency of Copper Removal by Electrolytic Demonstration Unit

(Solution: 50 g/l NaCl, repacked cell)

Test No.	U		E ₁	E ₂	ΔE	V	I	C ₀	C(l)	Percent Removed	Power (P) (WH/Kgal)	P/C ₀ (WH/Kgal-ppm)
	(gpm)	(gpd)	(volt)	(volt)	(volt)	(volt)	(amp)	(ppb)	(ppb)			
1	2.5	3,600	-0.9	-0.760	0.140	2.4	0.7	1370	104	92.4	11.2	8.2
2	"	"	"	-0.757	0.143	"	0.8	1530	132	91.4	12.8	8.4
3	5	7,200	"	-0.777	0.123	2.45	0.7	790	72	90.9	5.7	7.2
4	"	"	"	-0.780	0.120	"	"	764	62	91.9	"	7.5
5	"	"	"	-0.781	0.119	"	"	707	58	91.8	"	8.1
6	7	10,080	"	-0.788	0.112	"	"	579	64	88.9	4.1	7.1
7	"	"	"	-0.790	0.110	"	"	595	63	89.4	"	6.9
8	"	"	"	-0.791	0.109	"	"	575	65	88.7	"	7.1
9	10	14,400	"	-0.782	0.118	2.5	0.8	405	48	88.1	3.3	8.1
10	"	"	"	-0.783	0.117	"	"	"	45	88.9	"	"
11	15	21,600	"	-0.770	0.130	2.6	1.05	285	"	84.2	3.0	10.5
12	"	"	"	-0.764	0.136	"	"	277	39	85.9	"	10.8
13	20	28,800	"	-0.710	0.190	2.75	1.4	231	42	81.8	3.2	13.9

Table 3. Results of Loop Tests on Efficiency of Copper
Removal by Electrolytic Demonstration Unit

(Solution: blowdown brine from OSW test site, Wrightsville Beach, N. C.)

Test No.	U (gpm)	U (gpd)	E ₁ (volt)	E ₂ (volt)	ΔE (volt)	V (volt)	I (amp)	C ₀ (ppb)	C(l) (ppb)	Percent Removed	Power (P) (WH/Kgal)	P/C ₀ (WH/Kgal-ppm)
1	7	10,080	-0.8	-0.697	0.103	2.6	0.75	429	14	96.8	4.6	10.7
2	"	"	"	-0.693	0.107	2.7	0.8	449	12	97.4	5.1	11.4
3	"	"	"	-0.691	0.109	"	"	488	16	96.8	"	10.5
4	15	21,600	"	-0.677	0.123	3.0	1.1	419	15	96.4	3.7	8.8
5	"	"	"	-0.675	0.125	"	"	381	20	94.9	"	9.7
6	25	36,000	"	-0.624	0.176	3.5	1.7	323	45	86.2	4.0	12.4
7	"	"	"	-0.614	0.186	3.55	1.75	242	37	84.9	4.1	16.9

The results in Table 1 were obtained with relatively high copper concentrations in the stream (1 - 3 ppm). Removal efficiencies varied from about 85% at 5 gpm to about 40% at 21 gpm. Change of electrode potential from -0.6 to -0.9 V at approximately constant copper content and total flow rate produced little change in either current requirement or removal efficiency, thus showing that the cathode bed may be operated anywhere within this potential range and demonstrating that the rate of the copper reduction reaction is indeed controlled by convective diffusion to the cathode surfaces. In addition, changes in the incoming copper concentration level had little effect on removal efficiency (Table 1, test nos. 7, 9, and 10), thus demonstrating one of the most important properties of flow-through porous electrodes for removal of trace quantities of electroactive substances. The total power requirement, amounting to several watt-hours per thousand gallons, depended on the flow rate, since incoming copper concentration was maintained fairly constant in the tests of Table 1. The specific power requirement was in the range of a few watt-hours per thousand gallons for each part per million of cupric ion.

The results of Table 1 are plotted in Fig. 7 (open circles) in the manner suggested by Eq. (1), according to which the slope of the line should be equal to $-S\ell D/\delta$. The fit is reasonably good considering the approximate nature of the derivation leading to Eq. (1). As noted above, this series of tests was carried out with the disk flow baffle in place, and the flow distribution within the cell, while nonuniform, was evidently reasonably constant as a function of flow rate, thus probably accounting for the good fit of the data by Eq. (1).

The removal efficiencies in Table 1 were somewhat disappointing since considerably better results had been obtained previously in laboratory experiments on a small column of compressed copper turnings. It was felt that some

Fig. 7. Copper Removal as a Function of Flow Rate.

channeling of fluid flow was taking place within the packed-bed cathode due to somewhat nonuniform packing of the long strands of copper turnings. Consequently, the cell was disassembled and repacked with short lengths (ca. 1/2") of copper turnings in an effort to provide a more uniform cathode structure. Simultaneously, 1/16" porous polypropylene membranes were provided at the top and bottom of the cathode cage (cf. Fig. 1) for containment of the finely divided copper turnings. In addition, the disk flow baffle was removed from the cell.

Results of the tests carried out with the repacked cell in 50 g/l NaCl are presented in Table 2 and the results are also plotted in Fig. 7 (solid circles). All tests were carried out at a cathode potential of -0.9 V vs. SCE with a constant rate of injection of copper stock solution into the loop. Consequently, as total solution flow increased, the incoming copper concentration decreased. Removal efficiencies were much better in this run, varying from about 92% at 2.5 gpm to about 82% at 20 gpm, probably as a result of better packing of the cathode bed. However, the results are not described satisfactorily by Eq. (1). At low total flow rates the distribution of fluid flow within the cell was such that a great part of the flow was channeled up the edges of the cell, with a smaller part flowing through the large central section of the packed-bed cathode. Consequently, the linear flow rate near the edges of the cell was much higher than the average linear flow rate, and removal efficiency was thus much lower than would be expected for a uniform flow distribution across the cell. With increasing total flow rate, a larger fraction of the flow went through the central portion of the packed-bed cathode, and at flow rates above about 15 gpm, the flow distribution across the cell appeared to be much more uniform. A dashed line is drawn through the 20 gpm data point in Fig. 7 to indicate the performance which would be expected on the basis of Eq. (1) for uniform flow within the cell.

From this it may be seen that it should be possible to remove about 99% of the dissolved copper at a flow of 10,000 gpd if uniform flow could be achieved, assuming the validity of Eq. (1). Specific power consumption was found to be approximately 7 watt-hours per 1000 gal for each part per million of dissolved cupric ions at a total flow rate of 10,000 gpd/ft². The increase in specific power consumption at high flow rates, with a constant rate of copper injection into the loop, is largely a consequence of reduction of residual oxygen in the loop solution.

Table 3 presents results of a test run using blowdown brine from the OSW test station at Wrightsville Beach, N. C. Removal efficiencies were especially good in this case, varying from about 97% at 7 gpm to about 85% at 25 gpm. As may be seen in Fig. 7, performance was similar to, but better than, the run recorded in Table 2. It is felt that the increased performance was due to the following circumstances. The brine run of Table 3 was carried out after the 50 g/l NaCl run of Table 2 without dismantling and cleaning of the cell. During the time elapsed between runs the cell had been allowed to remain with a very moist atmosphere inside (due to rinsing of the cell with demineralized water after the 50 g/l NaCl run). Consequently, a considerable quantity of oxide corrosion product was accumulated on the cathode surfaces prior to the brine run. After deaerated brine was admitted to the loop and cell assembly and the solution was made slightly acid, dissolution of the oxide corrosion product in the brine resulted in accumulation of a large amount (probably ca. 3×10^{-2} M) of cuprous ions in the solution within the loop. Initial attempts to polarize the cathode bed to the desired operating potential (-800 mV vs. SCE) required several amperes and the observed potential with no polarization showed that the bed of copper turnings was functioning essentially as a reversible copper-cuprous ion electrode. Continued application of current led eventually to reduction of all cuprous

ions contained in the loop solution on the cathode surfaces, and finally it was possible to adjust the cathode potential to -800 mV vs. SCE with eventual attainment of a sufficiently small background current. However, deposition of such large amounts of cuprous ion on the cathode surfaces resulted in copious formation of dendritic growths of metallic copper. Presence of the dendrites evidently increased the ratio of cathode surface area to solution volume inside the cathode bed as well as promoting better mixing. Consequently, once it became possible to carry out the tests on copper removal efficiency, it was found that a higher percentage of copper could be removed at various flow rates than had been observed previously using the same cell. The dashed line through the data in Fig. 7 (open squares) shows the approximate performance to be expected for uniform flow, assuming the validity of Eq. (1).

The results of the loop tests of the demonstration unit* show clearly that dissolved copper may be removed efficiently and economically by a properly designed packed bed of copper turnings operated as a porous cathode through which the brine to be treated is passed. Computations based on the results reported in Table 2, together with the assumptions which led to the derivation of Eq. (1), suggest that a packed-bed cathode (6" depth) operating at 90% efficiency at a flow of 10,000 gpd/ft² on brine having a copper content of 300 ppb Cu⁺¹ should be able to operate for approximately one year before the cross-sectional area of solution within the electrode is reduced by about 10% due to copper deposition on cathode surfaces. Thus, once in steady-state operation, it should be possible for electrolytic copper removal units to operate virtually unattended for long periods of time without need for replacement of the cathode bed. In large-scale units, use of a bed depth of 12 inches is certainly

*The device has become known as the "Copper Stopper."

feasible and would ensure virtually complete ($> 99\%$) removal of dissolved copper at flows on the order of 10,000 gpd/ft². This may be inferred from the data in Fig. 7 together with Eq. (1) where the fraction of copper remaining in the treated brine depends exponentially on bed length (ℓ), all other factors being equal. On the basis of the favorable test results reported above, a conceptual design and cost estimates have been prepared for units capable of treating 1 and 10 mgd of blowdown brine; these are presented below in the Appendix.

The demonstration unit has been shipped to the OSW test station at Freeport, Texas, for extended testing on actual blowdown brine. Results of these tests will be reported at a later date.

APPENDIX

Conceptual Design of 1 Mgd Copper Removal Unit*

A conceptual design for a unit capable of removing dissolved copper from 1 mgd of distillation plant blowdown brine is shown in Fig. 8. The cathode and anode structures are housed in a buried, square concrete tank, 9 ft in length on each side, and 4 ft in depth. The semi-open tank (or vat) is fitted with a loose cover. Brine blowdown enters the tank through a series of headers and passes upward through sixteen modular cathode baskets (constructed from iron or carbon steel) which contain York mesh type pads of metallic copper one foot thick. Although a bed of compressed copper turnings was used as the cathode structure in the demonstration unit described above, and in the following cost estimates, it is felt that iron shot or scrap would be cheaper and equally satisfactory. All cathode baskets and their packed-bed copper mesh pads are polarized by a suitable

*Conceptual design developed by E. C. Hise, ORNL Reactor Division.

ORNL-DWG. 72-13728

Fig. 8. Conceptual Design of 1 Mgd Copper Removal Unit.

constant-voltage power supply (commercially available) to the proper electrode potential (ca. -800 mV vs. SCE) for deposition of the copper contained in the flowing brine. The anode structure in this design consists of 64 graphite rods (3 in. diameter, 12 in. long) spaced on one foot centers. These are supported by a rubber-coated grid (not shown in Fig. 8) constructed of 6 in. "I" beams and are connected to one another by copper cable. After passage through the modular packed-bed cathodes, copper-free brine passes through the anode structure, where an amount of chlorine equivalent to the original copper content is released, and out an overflow and drain system which is integral with the concrete tank. Brine flow is sufficient in this configuration to prevent diffusion of atmospheric oxygen (or of chlorine evolved at the anode) down into the cathode structures; such diffusion, of course, would result in increased power consumption due to reduction of oxygen (or chlorine) on the cathode surfaces. Replacement of the cathode beds, when required, could be accomplished simply by emptying and refilling the cathode baskets. It is also possible that the copper removed from the brine could be recovered, if desired.

Cost Estimates for 1 Mgd and 10 Mgd
Copper Removal Systems*

Cost estimates, based upon the conceptual design shown in Fig. 8 and discussed above, are presented below for copper removal units capable of treating 1 mgd and 10 mgd of distillation plant blowdown brine.

*Cost estimates by S. A. Reed, ORNL Reactor Chemistry Division.

Cost Estimate for 1 Mgd Advanced Plant.

Capital cost:

1 concrete vessel 9' x 9' x 4'	\$2,300
Cathodes, copper wire mesh (York mesh)	3,759
Anodes, graphite rods and assembly	2,000
Pipes and valves	1,500
Instrumental and electrical	1,125
Total direct capital	<u>\$10,684</u>
Contingency, overhead, profit	10,684
Total capital cost	<u>\$21,368</u>

At 7% annual charge \$1,496

Capital charge at 218×10^6 gal blowdown/year =
0.69¢/1000 gal bd.

Operating cost:

1/2 cathode replacement annually	\$1,880
Power at 1¢/KWH	15
Total operating cost	<u>\$1,895 =</u> 0.87¢/Kgal

Total charge: 1.56¢/1000 gal blowdown

Cost Estimate for 10 Mgd Advanced Plant.

Capital cost:

1 concrete vessel 28' x 28' x 4'	\$7,500
Cathodes, copper wire mesh (York mesh)	35,730
Anodes, graphite rods and assembly	18,750
Pipes and valves	12,000
Instrumental and electrical	9,500
Total direct capital	<u>\$83,480</u>
Contingency, overhead, profit	83,480
Total capital cost	<u>\$166,960</u>

At 7% annual charge \$11,687

Capital charge at $2,180 \times 10^6$ gal bd/year =
0.54¢/1000 gal bd.

Operating cost:

1/2 cathode replacement annually	\$17,865
Power at 1¢/KWH	150
Total operating cost	<u>\$18,015 =</u> 0.83¢/Kgal

Total charge: 1.37¢/1000 gal blowdown

As noted above, savings could be effected by use of a steel shot instead of a copper mesh cathode. Furthermore, an amount equal to 100% of the total direct capital has been allowed for contingency, overhead, and profit, on the assumption that the unit may be built commercially. In spite of the rather liberal capital allowances, the estimated cost of treatment comes to only about 1.5¢/Kgal for both the 1 mgd and the 10 mgd plants. It should be realized, however, that verifying experiments (perhaps long-term tests carried out with a single modular unit) are needed before final cost figures can be developed. Nevertheless, these figures show clearly that the electrolytic process is expected to be more economical than any other alternative method of copper removal which is capable of efficiently treating large volumes of blowdown brine.

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