Copper Removal from A-01 Outfall by Ion Exchange

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COPPER REMOVAL FROM A-01 OUTFALL BY ION EXCHANGE (U)

SUMMARY

Chelex100, a commercially available ion exchange resin, has been identified in this study as having a significant affinity for copper and zinc in the A-01 outfall water. Removal of copper and zinc from A-01 outfall water will ensure that the outfall meets the state of South Carolina's limit on these heavy metals.

In this study, batch distribution coefficient (K_d) tests were performed with nine ion exchange resins using A-01 outfall test solutions (simulants) to identify the resin with the highest affinity for copper and zinc in the presence of other competing ions (iron, magnesium, calcium and others). Based on K_d test results, column performance tests were carried out using the ion exchange resin (Chelex100) with the highest combined affinity for copper and zinc. Column work was performed using a composite sample of collected A-01 outfall water. The copper concentration of the composite sample of A-01 outfall water, 12.5 $\mu\text{g/L}$ (ppb), was not within the expected range of 30-300 ppb.

Batch distribution coefficient (K_d) and column performance results are summarized below:

- K_d values for copper and zinc removal from A-01 outfall simulant solution using Chelex100 resin are 81,600 mL/g and 65,800 mL/g, respectively.

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- Approximately 53,040 bed volumes of A-01 outfall water can be processed to 50% breakthrough for copper on a Chelex100 resin column.
- Chelex100 treated A-01 outfall water showed a slight increase in pH and conductivity in the first column fraction. However, the pH and conductivity of the treated effluent returned to normal (pH 7.1 and conductivity of 72.5 $\mu\text{S}/\text{cm}$) after the first fraction.
- Both copper and zinc ions showed no breakthrough after processing over 26,000 bed volumes of A-01 outfall water with Chelex100 resin.
- Pre-filtration of A-01 outfall water is required for ion exchange treatment.
- The amount of resin required for treating A-01 outfall water depends on the concentration of iron, which is the principal trivalent competing ion. The other competing ions (calcium and magnesium), unlike iron, showed an early breakthrough in column performance study with Chelex100 resin.
- The amount of Chelex100 resin (bed volume) required for processing 630,833 liters of A-01 outfall water (one operating cycle of 8 hours) is approximately 11.8 liters (7.67 kg).
- Since the A-01 outfall water flow rate is about 1,892,500 liters (500,000 gallons) per twenty four hours, it will require about 35.4 liters (23.01 kg) of the resin for treating the A-01 outfall per day.
- The retail cost of Chelex100 resin, at 7.67 kg per operation cycle, is approximately \$3,758. Chelex100 resin cost for treating A-01 outfall at a flow rate of 1,892,500 liters per 24 hours (three operating cycles) is \$11,274. This resin cost estimate is based on the A-01 outfall metal concentrations as determined in this study.
- The regeneration of Chelex100 resin will depend on the presence or absence of trace radionuclides in the A-01 outfall water and the affinity of Chelex100 resin for such radionuclides.
- Composite column fractions from the A-01 outfall water study passed toxicity tests with the organism *ceriodaphnia dubia*.

1.0 INTRODUCTION

The discharge to A-01 outfall in the 700 area consists of non-contact cooling water, steam condensate, laboratory waste water, cooling tower overflow, well-flush water, steam cleaning rack waste water, ground water air stripper effluent from outfall A-1A, and storm water. This discharge from A-01 travels (regulatory compliance point for all the combined waste streams) about 100 yards before entering an ephemeral stream (waters of the state). This stream empties into Tim's Branch and ultimately into the Savannah River via upper Three Runs Creek.

The South Carolina Department of Health and Environmental Control (SCDHEC) regulates the amount of transition metals (Hg, Zn, Pb, Cu, etc) in the A-01 outfall water. Data analysis during 1996 permit negotiations indicated that copper and toxicity levels for the A-01 outfall would not meet the state's requirements. Since the effective date of the NPDES (National Pollution Discharge Elimination System) permit, A-01 monitoring

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data have shown copper at 1.4 to 14 times the 22 ppb upper limit requirement for copper. The source of this copper increase has been attributed to the corrosion of old copper supply piping and steam/air conditioning condensates. As part of an on going effort by the Environmental Compliance Group at the Savannah River Site (SRS) to bring the A-01 outfall into SCDHEC compliance, the Waste Disposal and Environmental Development Group (WD&ED) of the Waste processing Technology Section (WPTS) was asked to investigate the use of ion exchange materials. A treatability study was performed to:

- identify three ion exchange resins which could be used to solve the A-01 outfall water problem of high copper and occasionally high zinc concentrations.
- optimize the column performance for the most promising resin for A-01 outfall water treatment.

2.0 EXPERIMENTAL

The first part of this study identifies the most promising ion exchange or chelating resin for the removal of copper and zinc from A-01 outfall water test solution (simulant). All chemicals used in the simulant preparation were reagent ACS grade quality. The concentration of the simulant components are summarized in Table 1 below. De-ionized water (conductivity less than 2 μ S/cm and pH of 6.8) was used in all preparations.

Resin comparisons are based on the magnitude of the batch distribution coefficient, K_d , as a measure of their abilities to remove metals from A-01 outfall water simulant in the presence of competing ions. The most promising resin, one with the largest K_d for copper and zinc, will be used in column performance experiments with A-01 outfall water to confirm its ability to remove the ions of interest. Resin characterizations will also include the determination of column flow parameters, ion exchange capacities, and breakthrough curve for copper and zinc.

The following resins were evaluated for copper and zinc uptake in the presence of competing divalent and trivalent cations: Chelex100 (Bio-Rad), 3T-73, IRC-50, and IRC-718 (Rohm & Haas), NASA-IEM-Ca (Dr. K. Street of NASA Lewis Research Center), SIR 300, WACG-Na and WBG30 (ResinTech, Inc.) and ZSM-5 zeolite (University of Florida-Gainesville).

Batch Distribution Coefficient Studies with A-01 Outfall Simulant Solution

The batch distribution coefficient (K_d , mL/g) is an equilibrium measure of the overall ability of a solid phase ion exchange material to remove ions of interest from solution. It represents the theoretical volume of solution that can be processed per a given mass of the ion exchanger under equilibrium conditions (1,2).

In these tests, a known quantity of the resin (approximately 0.1 grams, Table 2) was placed in contact with 25 ml of the simulant in a 50 ml polyethylene bottle. All samples were prepared in duplicates. The polyethylene bottles were placed in an orbital shaker and the mixture agitated for 24 hours at 26 ± 2 °C. After this contact time, the used resin was separated from the solution by decanting (filtering with a 0.2 micron nylon filter

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resulted in the absorption of the colored components of the simulant solution onto the membrane). The decanted portion, without resin was submitted for metal concentration analysis. The K_d value was obtained by determining the concentration of metal ions of interest before and after contact and calculating the amount of metal ions of interest on the resin by difference. K_d calculation was based on the equation below:

$$K_d = ((C_i - C_f)/C_f) * (V/m * F) \quad (1)$$

where C_i is the initial metal of interest concentration, C_f if the final metal of interest concentration after contact, V is the volume of simulant used, m is the resin exchanger mass and F is the F-factor (ratio by weight of dry resin to wet resin). In the above equation, it is assumed that the mass of dry ion exchange is approximately equal to that of wet ion exchange material used; $F \approx 1.0$.

The initial concentrations of metals of interest in the A-01 outfall simulant solution (copper, zinc, calcium, magnesium, iron, lead and strontium) are summarized in Table 1.

Cation of interest	Precursor	Target cation concentration (ppm)
Cu^{+2}	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	8
Zn^{+2}	ZnCl_2	8
Fe^{+3}	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	8
Ca^{+2}	$\text{Ca}(\text{OH})_2$	10
Mg^{+2}	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	16
Pb^{+2}	$\text{Pb}(\text{NO}_3)_2$	0.010
Sr^{+2}	$\text{Sr}(\text{NO}_3)_2$	0.010

Table 1. A-01 Outfall Simulant Composition.

Column Studies With A-01 Outfall Water

A composite sample of A-01 outfall water was used in the ion exchange column work. Three 2-liter A-01 outfall water samples were collected over a period of three days. These samples were decanted and the bottom part with sludge and suspended particles filtered through a Whatman glass fiber micro-filter. This decanted and filtered portions were mixed with about twelve liters of A-01 effluent collected on the fourth day. This gave a total volume of 18 liters of the composite A-01 outfall water samples. The composite A-01 outfall sample was stored in an 18-Liter storage plastic bottle.

A glass column, pre-treated with 2.0 M nitric acid solution overnight (column id = 0.9 cm, volume = 0.64 mL/cm), was loaded with a slurry of Chelex100 resin to a total volume of 2 mL. This is approximately 0.6 mL Chelex100 resin (one bed volume of Chelex100) since the resin is approximately 71% water. The gross volume of the ion exchange resin in a disc is termed the bed volume (BV). A small plug of nitric acid conditioned glass wool was used to hold the resin in place about 5 cm from the restriction above the column outlet. The conditioning of the Chelex100 resin in the column involved brief rinsing with de-ionized water for two hours before initiation of column operation with A-01 outfall water sample (2).

The A-01 outfall composite water was delivered to the column head via a Masterflex® peristaltic pump through a size-14 Tygon® tubing (Figure 1). The measured flow rate of the effluent through the column was 1.3 ± 0.05 mL/min (204 mL/min/cm^2 or 0.204 L/min/m^2). At this flow rate it took about 12.8 hours to deliver a total fraction volume of approximately 1000 mL (130 BV/hr). Sixteen column fractions with a total volume of 15.7 L (26,133.3 BV) were collected.

3.0 RESULTS AND DISCUSSIONS

Batch Distribution Coefficient Results

In this study it is assumed that the batch distribution coefficient (K_d) for copper removal in a solution with ppm levels of copper (A-01 outfall simulant), is equal in magnitude to K_d for copper removal from a solution with ppb levels of copper (like the A-01 outfall water), when Chelex100 resin is used in both instances.

Table 2 contains a summary of the experimental parameters (initial and final cation concentration and weight of resins) used in determining the K_d values for the A-01 simulant (pH 7.10). The K_d values obtained for all the resins characterized for uptake of copper and zinc in the presence of competing ions (calcium, magnesium, iron, lead and strontium) are summarized in Table 3.

Chelex100 resin had the highest K_d value for copper (81,600 mL/g). This resin also showed high affinity for other competing divalent and trivalent cations. Calcium, magnesium and iron had K_d values of $1.35\text{E}7$, $2.55\text{E}7$ and 12,600 mL/g, respectively.

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GT-73 resin showed a good affinity for copper, with a K_d values of 53,300 mL/g and a smaller K_d value for zinc (6,500 mL/g).

The resin with the highest affinity for zinc was IRC-718 ($K_d = 73,600$ mL/g), although its affinity for copper is less than that of Chelex100 or GT-73. All other resins in the study had K_d values lower than 20,000 mL/g for copper. One interesting resin with a K_d for copper of 13,400 mL/g was the experimental resin from NASA Lewis center, NASA-IEM (calcium form). With release of the counter ion (Ca^{+2}) into the treated simulant, calcium concentration increased by almost a factor of four in the treated simulant. If this resin were used, there could be a potential increase in water hardness (A-01 outfall initially has a low water hardness).

Based on the magnitude of the K_d values for copper and zinc Chelex100 is the resin of choice for column work with A-01 outfall water. GT-73 has lower K_d values for copper and zinc, however, based on process knowledge it would be more efficient if mercury and lead contaminant (present as Hg^{+2} and Pb^{+2}) removal becomes a priority.

$$\lambda = K_d * \rho_b \quad (2)$$

In the above equation, Lambda (λ) is the theoretical number of bed volumes of solution that can be processed per volume of the ion exchange material (3). It is the product of K_d and the ion exchanger bulk density, ρ_b (g/mL). Lambda, also called the column K_d , is useful for estimating the 50% breakthrough point ($0.5 = C/C_0$) in column loading experiments.

Based on this equation, it should be possible to treat about 53,040 bed volumes of A-01 outfall water for copper before change out or regenerating the Chelex100 resin (assuming that there is no accumulation of radionuclides like strontium-90 on the resin). The value of 53,040 bed volumes was determined by multiplying the K_d (Chelex100) for copper (81,600 mL/g) times the bulk density of Chelex100 resin (0.65g/mL).

Column Test Results with A-01 Outfall Water

The first data line in Table 4 (0-initial column) contain the initial concentration of the principal cations (copper, zinc, calcium, magnesium and iron) in the A-01 outfall composite sample used for the column work. The pH of the composite sample was 7.11 and its conductivity was 72.5 $\mu\text{S}/\text{cm}$. Analysis for copper concentration was determined for all sixteen column fractions collected ($\approx 26,100$ BV, see Table 4). To cut down on analytical cost, concentration for other ions was only determined on fractions one, eight, and sixteen. The pH and conductivity of the first fractions was slightly higher than that of the other fractions, respectively, 8.9, and 92 $\mu\text{S}/\text{cm}$. The pH of the other fractions averaged 7.17 ± 0.50 and the conductivity averaged 72.7 ± 0.30 $\mu\text{S}/\text{cm}$ (Table 4). There was no evidence of copper breakthrough during the processing of the 26,100 BV. The concentration of copper going through the column was always lower than the

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initial copper concentration of 12.5 ppb. The average copper in all the sixteen fractions was 7.45 ppb.

It is well known that in waste streams with copper concentration at or below 10 ppb, copper is no longer present as a divalent ion. It instead complexes as neutral or anionic species. Hence, cationic resins and chelating agents will not be able to effectively bind to copper in such effluents with low level copper concentrations. With copper concentration at 12.5 ppb in the A-01 effluent, most of the copper may not be in the divalent state and so the copper removal efficiency of Chelex100 resin may not be as high as expected. The detection limit of the instrument (inductively coupled Argon plasma (ICP)) used in the A-01 analysis is in the ppb levels (5.4 ppb). Problems associated with detection limit, especially for those fractions with copper concentrations below 7 ppb, may be another source of error in quantifying the copper concentrations in A-01 outfall column fractions.

Similarly, after processing about 26,100 bed volumes, there was no breakthrough for zinc, which had an initial concentration of 35.6 ppb (Figure 2, Table 4). Average zinc concentration in the sixteen fractions was 3 ppb. There was, however, a breakthrough for calcium and magnesium, some where between 13,000 and 26,000 bed volumes (Table 4). This last observation will ensure that the water hardness of A-01 outfall water is maintained even after treating the outfall with Chelex100 resin. The highest calculated resin capacity for treating 630,833 liters of A-01 outfall water, based on Chelex100 nominal total capacity of 0.7 meq/mL and worst case iron concentration of 4.5 mg/L (highest competing charged ion), is 23.28 kg/cycle (one cycle is 8hrs), and the lowest capacity based on observed A-01 outfall iron concentration (0.0155 mg/L) is 7.67 kg/cycle (16.95 lbs/cycle); see Appendix A.

Chelex100 resin used in this study was the sodium form (Resin-Na). With this resin the sodium ion (counter-ion on the resin) is replaced by equivalent amount of the target ion in solution (Cu^{+2} or other ions). Copper uptake, for example, is shown below:

It is the concentration of the accumulated sodium ions in solution which is responsible for slightly changing the pH and conductivity of the first column fraction of the treated A-01 effluent.

The regeneration process for Chelex100 resin requires a two step process to form the sodium salt after loading with metals (4). In the case of loading with copper, for example, the regeneration process would proceed as follows (in a molar solution of hydrochloric acid and sodium hydroxide, respectively):

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The regeneration sequence is 2 bed volumes of the metal-loaded resin (Resin-Cu) in a molar solution of hydrochloric acid, 5 bed volumes water rinse, 2 bed volumes of the proton form of the resin (Resin-H) in a molar solution of sodium hydroxide and finally 5 bed volumes of water rinse. For larger column operations back-washing is normally recommended after each operating cycle.

Sample Identification			Concentration (mg/L)				
Resin Type	LIMS #	Resin Weight (g)	Cu	Zn	Ca	Mg	Fe
NONE*	3-94071	---	6.28	7.45	9.15	15.40	7.126
NONE*	3-94072	---	6.93	8.54	11.50	15.30	NA
Chelex100	3-94073	0.1005	0.02	0.03	<0.00019	<0.00015	0.1470
Chelex100	3-94074	0.1011	0.02	0.03	<0.00019	<0.00015	0.1269
GT-73	3-94077	0.1025	0.03	0.29	0.17	4.67	0.881
GT-73	3-94078	0.1030	0.03	0.29	0.17	4.58	1.010
IRC-50	3-94075	0.1030	0.21	0.04	0.04	0.07	0.4546
IRC-50	3-94076	0.1022	0.24	0.04	0.04	0.07	0.3702
SIR-300	3-94079	0.1012	1.12	0.43	<0.00019	0.35	0.0183
SIR-300	3-94080	0.1006	1.13	0.60	<0.00019	0.47	0.0169
IRC-718	3-93732	0.1000	0.08	<0.002	<0.00019	<0.00015	0.4546
IRC-718	3-93733	0.1000	0.09	0.05	<0.00019	<0.00015	0.3702
NASA-IEM	3-94262	0.1010	0.12	0.191	36.5	6.21	NA
WACG-Na	3-94757	0.1000	0.5857	0.3755	0.0729	0.0348	NA
ZSM-5	3-94413	0.1001	1.93	6.09	9.34	15.00	NA
WBG-30	3-94754	0.1000	3.138	2.5	9.574	15.00	NA

NA = Not analyzed

* Initial A-01 concentration.

Volume of simulant used = 25 ml.

Table 2. Batch Distribution Coefficient (K_d) Data Summary

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Resin Type	Average K_d Values (ml/g)					Comments
	Cu	Zn	Ca	Mg	Fe	
Chelex100	81,600	65,800	1.35E07	2.55E7	12,600	Highest combined K_d for copper & Zinc
GT-73	53,300	6,500	1.45E04	560	1,600	High K_d for copper
IRC-50	7,000	48,500	6.26E04	53,400	4,000	High K_d for zinc
SIR-300	1,200	3,600	1.35E07	9,000	100,100	
IRC-718	19,200	73,600	1.36E07	2.56E07	4,100	Highest K_d for zinc
NASA-IEM	13,400	10,100	-180	400	NA	Calcium form of the resin was used
WACG-Na	4,100	5,100	35,200	110,000	NA	
ZSM-5	600	80	26	10	NA	
WBG30	280	550	20	10	NA	

NA = Not analyzed

Table 3. Summary of Batch Distribution Coefficient (K_d) Values.

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Fraction Number	Bed volumes	Concentration; $\mu\text{g/L}$ (ppb)					pH	Ω $\mu\text{S/cm}$
		Cu	Zn	Ca	Mg	Fe***		
0 (Initial)	0.0	12.5	35.6	1,150.5	221.5	15.5	7.11	72.5
One	1633	9.0	3.5	2.0	1.8	26.2	8.90	92.0
Two	3,267	5.5	NA	NA	NA	NA	7.50	73.8
Three	4900	6.8	NA	NA	NA	NA	7.40	73.6
Four	6533	5.4*	NA	NA	NA	NA	6.98	73.2
Five	8167	6.1	NA	NA	NA	NA	7.00	74.0
Six	9800	6.9	NA	NA	NA	NA	7.20	72.5
Seven	11,433	6.5	NA	NA	NA	NA	7.20	73.0
Eight	13,067	8.1	1.8	22.3	6.6	6.5**	7.40	73.0
Nine	14,700	6.5	NA	NA	NA	NA	7.30	72.8
Ten	16,333	9.6	NA	NA	NA	NA	7.23	71.6
Eleven	17967	6.1	NA	NA	NA	NA	7.25	71.8
Twelve	19,600	8.2	NA	NA	NA	NA	7.14	71.8
Thirteen	21,233	9.2	NA	NA	NA	NA	7.10	72.2
Fourteen	22,867	8.3	NA	NA	NA	NA	7.30	72.2
Fifteen	24,500	7.9	NA	NA	NA	NA	7.20	72.2
Sixteen	26,133.3	9.3	3.0	1,059	261.1	10.6	7.20	72.3

* Detection limit for copper is 5.4 ppb

** Detection limit for iron is 6.2 ppb

*** Possible contamination on first fraction iron concentration

NA = Not analyzed

Table 4. Concentration of ions, pH and Conductivity in A-01 (initial) and in Column Fractions.

4.0 CONCLUSIONS

The concentration of copper in A-01 outfall water (12.5 ppb), as determined in this study, was out of the expected range of 1.4 to 14 times the 22 ppb upper limit (30-300 ppb) for copper. This discrepancy in copper concentration in the outfall may be due to differences in sampling method and sample preparation for the A-01 outfall water. In the past, sampling at A-01 outfall involved inclusion of sedimentary particulates, followed by digestion of the sample. This would seem to indicate that the goal was to obtain total recoverable ions and not just dissolved ion as is the case with ion exchange work reported here. In this study, because particulates would accumulate on the resin column and potentially cause reduction in flow (high pressure drop), suspended materials were filtered from collected A-01 outfall water samples. The fact that the copper concentration in the initial A-01 outfall was so low relative to what was expected, may indicate that the source of the higher copper is due to particulates (i.e., A-01 stream bed components) collected during the sampling procedure and not from the A-01 outfall water. To test this idea, sampling of A-01 outfall water for copper or other ions should be carried out in a manner so as to minimize the inclusion of soil sludge or solids.

Of the nine commercial resins tested for copper removal from A-01 outfall simulant, the chelating resins Chelex100 and GT-73 had the highest combined affinity for copper (highest combined K_d values). The commercial resin IRC-718 had the highest batch distribution coefficient (K_d) for zinc removal from A-01 outfall simulant. Based on the magnitude of the batch distribution coefficient for copper removal with Chelex100 resin, 53,040 bed volumes of A-01 outfall water can be processed without copper breakthrough. The corresponding bed volumes with Chelex100 resin for zinc is 42,770.

The Chelex100 resin column was operated at a flow rate of 0.204 L/min/m² (130 BV/hr). The manufacturer recommends (4) a minimal Chelex100 resin bed depth of 0.61 meters (2 feet). At the flow rate used in this study, there were no breakthroughs for copper and zinc after processing 26,133 bed volumes or 15.7 liters of the effluent. There was, however, a breakthrough for calcium and magnesium somewhere after 13,000 bed volumes. Iron breakthrough was estimated to occur after 26,000 bed volumes. Chelex100 treated A-01 outfall water showed a slight increase in pH and conductivity in the first column fraction (1600 bed volumes). The pH and conductivity of the treated effluent returned to their normal values after the first fraction.

The calculated resin capacity per an eight hours cycle is 7.67 kg/cycle (16.95 lbs/cycle) for lower A-01 outfall iron concentration (0.0155 mg/L), and 23.28 kg/cycle (51.45 lbs/cycle) for high iron concentration (4.5 mg/L). This gives a processing bed volume of 11.8 Liters when iron concentration in the A-01 outfall is 0.0155 mg/L, and 35.813 liters when iron concentration is 4.5 mg/L. Based on the lambda value obtained using equation 2, the theoretical volume of A-01 outfall water that can be treated for copper with 7.67 kg/cycle of Chelex100 resin is 625,872 Liters (53,040*11.8 L), and the experimental volume is 630,833 liters. The difference between the experimentally

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determined volume of A-01 outfall water which can be treated and the theoretical volume which is predicted using equation 2 is less than one percent.

The composite A-01 outfall water sample used in the column study was clear and contained no suspended solids after it was decanted and filtered. In an actual ion exchange process, pumping will probably disturb the soil sludge on the bottom of the A-01 outfall, generating enough suspended particles which may plug the ion exchange column or generate high pressure drops. Therefore, filtration of A-01 outfall water is required prior to pumping onto an ion exchange column.

A stand alone bed of Chelex100 or mixed resin bed (beds in series) of Chelex100 and GT-73 could be used to remove heavy metals from A-01 outfall. A mixed resin bed would be more appropriate especially if, in addition to copper and zinc problems, mercury and lead levels in the A-01 outfall water approached regulatory limits. GT-73 resin in a mixed bed system would help extend the life and efficiency of Chelex 100 resin.

In this study, it is assumed that the ion exchange facility for A-01 treatment would be fully automated, meaning that the length of a service run for resin regeneration would be 8 hours (one cycle: 8 hours between resin regeneration). Therefore, resin cost calculations for A-01 facility operation are based on 8 hours between resin regeneration (see Appendix A). If the facility is based on manual equipment operation, a 24 hours service run would be more appropriate to reduce labor cost. Therefore, all resin costs have to be multiplied by a factor of three for 24 hours service runs. The retail cost for 7.67 kg/cycle of Chelex100 resin, at 49 cents per gram, is approximately \$3,758 (4). This resin cost estimate is based on the current A-01 outfall metal ion concentrations for copper, iron, zinc, calcium and magnesium as determined in this study. For different metal concentrations, new resin bed volumes have to be determined (as shown in Appendix A), and a new cost estimate based on the new resin requirements (BV) calculated. Different metal concentrations will also affect the total volume of A-01 outfall water that can be treated for copper and other metals. In this case, the new BV will affect the magnitude of λ (equation 2), the column K_d .

Composite column fractions (composite of 16 fractions) from the A-01 outfall water study passed toxicity tests with the organism *ceriodaphnia dubia*. Toxicity test results are summarized in Attachment A.

The identity and quantity of possible traces of radionuclides that could be found, if any, in A-01 outfall would have to be known before considering the possibility of regenerating Chelex100 resin. However, the regeneration of Chelex100 resin or GT-73 is not recommended if traces of radionuclides are present in the A-01 outfall.

5.0 QUALITY ASSURANCE

Data obtained from this study can be found in WSRC-NB-96-655. All analytical work was performed by the SRTC Analytical Development Section (ADS), using standards that are traceable to the National Bureau of Standards. Other relevant documents to this report include WSRC-RP-97-295 (copper treatment options), WSRC-RP-97-302 (TTP) and WSRC-RP-97-303 (QA plan).

Design Check

M. J. Barnes, Waste Processing Technology

Date

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- (3) Samuelson Olof, "Ion Exchange Separations in Analytical Chemistry", John Wiley & Sons, New York 1963.
- (4) Bio-Rad bulletin # 1224, Bio-Rad, Chemical Division, 2200 Wright Avenue, Richmond, Ca. 94804 (415-234-4130 or 1-800-4-BioRad).

Figure 1. Process Layout for Chelex100 : Column Performance Test Set Up.

Figure 2. Column Work with A-01 Outfall.
 No Breakthrough of Copper or Zinc.

(C_0, Cu = initial copper concentration; C_0, Zn = initial zinc concentration)
 (C_f = copper or zinc fraction concentrations)

Appendix A

Chelex100 resin capacity to remove copper ions from A-01 outfall water in the presence of Zn, Ca, Mg, and Fe as competing ions.

A) Analytical concentration of important A-01 ions¹ : [Cu] = 0.0125 mg/L,
[Zn] = 0.0356 mg/L,
[Ca] = 1.1505 mg/L,
[Mg] = 0.22145 mg/L
[Fe] = 0.0155 mg/L

B) Chelex100 data:

- Moisture content = 71-76%
- Wet mesh range = 100-200 spherical
- Nominal total capacity = 0.7 meq/mL resin bed; 2.9 meq/dry bed
- Bulk density = 0.65 g/mL

C) Total weight of metal ions in A-01 per 8hrs (cycle)[^].

- Flow rate of A-01 per cycle = 630,083.3 L/cycle (0.5 MG/24 hrs.)
- Total concentration of metal ion per cycle = 1.43555 mg/L
- Average mole. wt. of relevant A-01 metal ions ($\sum^n$ gram formula wt.)/n = average molecular wt. = 49.832 g/mole (an approximation)
- Total wt of metal ions = (1.43555 mg/L)* 630,833.3 L/cycle = 905.59 g/cycle.

D) Weight of total metal to equivalence (average equivalent is 11/5 = 2.2)

- (Total wt of metal ions)/(Average mo. wt.)/2eq/gmw =
(905.59(g/cycle))/(49.832(gmw))/(2.2eq/gmw) = 8.260 eq/cycle

E) Daily needed capacity

- Calculated capacity/ Chelex100 wet capacity =
8.260 eq/cycle/ 0.0007 eq/mL =
11,800 ml (11.800 liters of Chelex100/ cycle) = One Bed Volume (BV)

F) Weight of Chelex100

- capacity volume (liters/day)*(Chelex100 density) =
11.800 Liters/cycle * 0.65kg/Liter = 7.67 kg/cycle (16.95 lbs/cycle).

If the iron concentration for A-01 is 4.5 mg/L plus 1.42005 mg/L of other ions, then the combined Chelex100 capacity is 35.813 liters of Chelex100/ cycle (24.140 +11.673 L) =One bed Volum (BV);

G) Weight of Chelex100 resin is then

- capacity volume (liters/day)*(Chelex100 density) =
35.813_Liters/cycle * 0.65kg/Liter = 23.28 kg/cycle (51.45 lbs/cycle)

¹Divalent and trivalent competing ions with concentrations greater than that of copper.

[^]Typical industrial length of service run (between resin regeneration) for automated ion exchange facility is 8 hours.

Attachment A

Toxicity Test Results With Chelex100-Treated A-01 Outfall Column Fractions.

Author: Winona Specht at SRCCA13
Date: 9/17/97 3:41 PM
Priority: Normal
TO: Lawrence Oji
Subject: TOXICITY VERBAGE FOR YOUR REPORT

WSRC-RP-97-767, Rev. 0

Larry-

This should be sufficient verbage on the results of the toxicity test.
Let me know if I can be of further assistance.

A chronic definitive toxicity test following U.S. EPA protocol was performed on a sample of A-01 effluent after it had been treated by the ion exchange column. The results of the toxicity test indicate that the sample was not toxic (NOEC >100% effluent).

(864) 877-6942 • FAX (864) 877-6938

P.O. Box 16414, Greenville, SC 29606 • 4 Craftsman Court, Greer, SC 29650

7 Day Chronic Definitive Survival and Reproduction Bioassay

Method: EPA/600/4-91/002

Test Organism: *Ceriodaphnia dubia*

**Facility: WSRC
Sample ID: A-01**

**Aiken County
NPDES#: NA
ETT#: T8242**

Sample ID: August 19, 1997

CHRONIC DEFINITIVE SURVIVAL AND REPRODUCTION TEST

Survival and Reproduction Results

Client: WSRC
 Sample Identification: A-01
 Test Date: August 19, 1997

County: Alken
 NPDES#: NA
 BTT #: T8242

Reproduction at 0.0% Concentration						
Rep.	Day 3/4	Day 5	Day 6	Day 7	Day 8	Total
1	9	0	12	0	0	21
2	4	8	11	0	0	23
3	7	8	14	0	0	29
4	5	6	10	0	0	21
5	5	9	12	0	0	26
6	6	7	3	0	0	16
7	6	10	12	0	0	28
8	5	10	15	0	0	30
9	4	6	11	0	0	21
10	4	11	11	0	0	26

Reproduction at 6.25% Concentration						
Rep.	Day 3/4	Day 5	Day 6	Day 7	Day 8	Total
1	10	0	13	0	0	23
2	4	3	12	0	0	19
3	5	9	9	0	0	23
4	4	8	11	0	0	23
5	5	7	8	0	0	20
6	5	8	10	0	0	23
7	4	9	11	0	0	24
8	4	8	11	0	0	23
9	5	8	12	0	0	25
10	5	7	0	13	0	25

Reproduction at 12.5% Concentration						
Rep.	Day 3/4	Day 5	Day 6	Day 7	Day 8	Total
1	10	0	14	0	0	24
2	4	8	9	0	0	21
3	4	8	12	0	0	24
4	4	7	0	12	0	23
5	3	10	4	X	X	17
6	4	7	11	0	0	22
7	5	8	11	0	0	24
8	6	7	11	0	0	24
9	6	4	10	0	0	20
10	5	7	0	12	0	24

Reproduction at 25.0% Concentration						
Rep.	Day 3/4	Day 5	Day 6	Day 7	Day 8	Total
1	10	0	12	0	0	22
2	4	5	14	0	0	23
3	6	8	10	0	0	24
4	5	8	12	0	0	25
5	4	7	13	0	0	24
6	4	6	11	0	0	21
7	5	7	12	0	0	24
8	4	7	10	0	0	21
9	4	11	9	0	0	24
10	3	9	12	0	0	24

Reproduction at 50.0% Concentration						
Rep.	Day 3/4	Day 5	Day 6	Day 7	Day 8	Total
1	9	0	11	0	0	20
2	4	0	12	5	0	21
3	6	9	10	0	0	25
4	5	9	11	0	0	25
5	4	7	9	0	0	20
6	4	8	12	0	0	24
7	5	8	11	0	0	24
8	5	9	11	0	0	25
9	4	11	9	0	0	24
10	4	7	0	11	0	22

Reproduction at 100.0% Concentration						
Rep.	Day 3/4	Day 5	Day 6	Day 7	Day 8	Total
1	4	2	6	11	0	23
2	4	0	11	14	0	29
3	6	7	0	10	0	23
4	6	0	12	0	0	18
5	4	3	0	8	0	15
6	3	6	8	0	0	17
7	4	6	8	1	0	19
8	4	9	9	0	0	22
9	3	4	0	7	0	14
10	4	6	12	0	0	22

CHRONIC DEFINITIVE SURVIVAL AND REPRODUCTION TEST

Statistical Analyses

Client: WSRC
 Sample Identification: A-01
 Test Date: August 19, 1997

Test for Normality

Test Used: Kolmogorov D D= 1.000
 critical 1.035

The data are normal in distribution

Test for Homogeneity of Variance

Test Used: Bartlett's Test B= 19.67
 critical 15.1

The data are not homogeneous in variance

Test for Differences in Reproduction

Test Type Used: Fishers Exact Test for Survival
 Test Type Used: Wilcoxon's Test for Reproduction

t Test		Test Concentration					
	Control	6.3%	12.5%	25.0%	50%	100%	
t Value		0.97	1.34	0.67	0.82	2.90	
critical t		2.33	2.33	2.33	2.33	2.33	
reproduct	24.1	22.8	22.3	23.2	23.0	20.2	
survival	100%	100%	90%	100%	100%	100%	
CV= 18%		MSD= 3.13					

Wilcoxon's Test		Test Concentration			
				50%	100%
rank sum				96.5	82.5
critical value				74	74

NOEC: Survival: >100% Reproduction: >100%
 LOEC: Survival: >100% Reproduction: >100%
 Chronic Value: >100%

Effluent Conc. vs. Reproduction

Summary

The effluent is not acutely or chronically toxic.

CHRONIC DEFINITIVE SURVIVAL AND REPRODUCTION TEST

Water Chemistry

Client: **WSRC**
 Sample Identification: **A-01**
 Test Date: **August 19, 1997**

pH (After Renewal)

	Test Concentration					
	Control	6.25%	12.50%	25.00%	50%	100%
Initial		7.94				7.58
Day 1	7.85	7.87				7.53
Day 2		7.24				7.83
Day 3	7.89	8.05				7.82
Day 4	7.79	8.03				7.89
Day 5	7.68	7.91				7.28
Day 6		7.74				7.64

pH (Before Renewal)

	Test Concentration					
	Control	6.25%	12.50%	25.00%	50%	100%
Day 1	8.24	8.28				8.15
Day 2		7.70				6.74
Day 3	8.21	8.20				
Day 4	8.22	8.19				7.96
Day 5	8.24	8.27				8.00
Day 6		7.89				7.53
Final		8.29				8.12

Dissolved Oxygen (After Renewal)

	Test Concentration					
	Control	6.25%	12.50%	25.00%	50%	100%
Initial		8.3				9.4
Day 1	8.4	8.3				8.9
Day 2		8.4				8.8
Day 3	8.4	8.4				8.7
Day 4	8.4	8.5				8.6
Day 5	8.6	8.6				8.6
Day 6	8.4	8.4				8.4

Dissolved Oxygen (Before Renewal)

	Test Concentration					
	Control	6.25%	12.50%	25.00%	50%	100%
Day 1	8.4	8.3				8.5
Day 2		8.3				9.7
Day 3	8.3	8.3				8.4
Day 4	8.2	8.3				8.5
Day 5	8.3	8.4				8.4
Day 6	8.2	8.2				8.1
Final		8.2				8.4

Dilution Water:
MHSF

Temperature

Incubator °C	
Initial	24.3
Day 1	24.2
Day 2	24.4
Day 3	24.4
Day 4	24.6
Day 5	24.4
Day 6	25.2
Final	25.2

Test Results Reviewed and Approved By: *R. V. [Signature]*