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TESTING OF A MOBILE PILOT-SCALE CONTINUOUS COUNTERCURRENT ION EXCHANGE SYSTEM FOR TREATMENT OF LOW-LEVEL RADIOACTIVE WASTEWATERS

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ABSTRACT

A mobile pilot-scale continuous countercurrent ion exchange (CCIX) system is being operated at the Oak Ridge National Laboratory (ORNL) for the treatment of wastewaters that contain predominantly calcium, sodium, and magnesium bicarbonates and are slightly contaminated with ^{90}Sr and ^{137}Cs radioisotopes. A demonstration study is being conducted to evaluate the steady state performance and feasibility of a pilot-scale CCIX column for the selective removal of strontium from the wastewater. Initial test results show that the process sufficiently removes strontium from the water while significantly reducing the volume of secondary waste generation. This process has the potential for effective use in many diverse applications. However, it has not been frequently utilized by industries to date. This study shows that the CCIX process could offer an economical alternative for decontamination of wastewaters containing trace amounts of contaminants prior to discharge into the environment.

1. INTRODUCTION

Alternative methods for reducing secondary waste generation at the Oak Ridge National Laboratory (ORNL) are being developed. Process wastewater that is slightly contaminated with ^{90}Sr and ^{137}Cs radioisotopes has been routinely treated at the ORNL Process Waste Treatment Plant (PWTP) using chemical precipitation and filtration followed by fixed bed ion exchange columns containing strong acid cation resin.[1] The objective is to decontaminate process wastewater sufficiently for release to the environment while concentrating the radioactive materials (^{90}Sr and ^{137}Cs) into a nonhazardous solid waste form that can be safely stored with minimum surveillance.

New federal regulations on discharge limits for ^{90}Sr and ^{137}Cs along with higher costs for disposal of the concentrated secondary liquid low-level radioactive wastes (LLLW) produced during resin generation have prompted efforts to improve the efficiency of the PWTP. Therefore, extensive research, development, treatability studies, and analyses of alternatives were conducted to support PWTP upgrades and improvements.[2] Based on previous experience, the removal of ^{137}Cs from the process water can be achieved by the selection of an inorganic zeolite.[3] Studies indicated that calcium and magnesium compete with strontium and other radionuclides for sites on cation exchange resin making it more difficult to efficiently remove strontium from multicomponent wastewater. Finding a treatment process that will efficiently separate ^{90}Sr from Ca and many other components (Na, Mg, etc.) would be desirable to simplify the process flowsheet and reduce secondary waste generation.

A pilot-scale CCIX system, marketed by the CSA Company in Oak Ridge, Tennessee, was purchased as a potentially economical alternative method for treatment of slightly contaminated ORNL process wastewaters. The CCIX system has the potential for efficiently removing strontium from the wastewater while simultaneously minimizing secondary waste generation by (1) recycling the strip stream used in the removal of strontium and calcium from the waste stream, and (2) separating strontium from calcium followed by subsequent disposal of a concentrated strontium solid precipitate. One paramount feature of the CCIX process is the ability to selectively remove a preferred component, strontium, from many other

component ions, calcium, magnesium, etc., even at conditions where ion exchange separation factors are near unity.[4]

This report summarizes the results of a pilot-scale demonstration of the CSA CCIX System for treatment of process wastewaters generated from the multi-purpose research facilities at ORNL. Since the ORNL process wastewater is essentially tap water and groundwater that is slightly contaminated with ^{90}Sr and ^{137}Cs, the data and results discussed in this paper should be widely applicable to other systems with similar characteristics.

2. COMPOSITION OF ORNL PROCESS WASTEWATER

The process waste system at ORNL is used to collect liquid wastes that have the potential to be radioactively contaminated and liquid wastes that are slightly contaminated with radioactivity, including groundwater and condensate from evaporation of liquid low-level radioactive wastes (LLLW). Approximately 50 vol % of the process waste is surface and ground water which is slightly contaminated with radioactivity.

The process wastewater at ORNL contains a number of trace radionuclides, shown in Table 1, and relatively large amounts of competing ions (representative of city water and local groundwater in Oak Ridge, Tennessee) as shown in Table 2.[5] The major chemical constituents are (1) calcium, (2) sodium, and (3) magnesium bicarbonates, which are introduced by local river water and shallow drainage wells. The major radionuclides are ^{90}Sr and ^{137}Cs. The ^{90}Sr is the more hazardous contaminant because of its potential for introduction into the human and animal food chain. Discharge limits into the environment, as defined by the Code of Federal Regulations, Chapter 10, Part 20 (10CFR20), are 11 Bq/L for ^{90}Sr and 740 Bq/L for ^{137}Cs.

Concentration spikes have occurred occasionally due to drainages from construction sites, leaks in underground piping, etc. Feed composition may vary between 500 and 8000 Bq/L ^{90}Sr and 200 and 1000 Bq/L ^{137}Cs. Process wastewater is collected in a series of centralized holding tanks, chemically treated, and ultimately disposed in the environment.

3. LABORATORY-SCALE SCREENING TESTS

Experimental, small-scale column tests were made to determine distribution coefficients and separation factors for strontium and calcium using a Dowex HGR-W2, sodium-form, cation exchange resin and ORNL process wastewater feed. Distribution coefficients of 1730 and 1245 were measured for strontium and calcium, respectively, during continuous loading on the ion exchange resin. Results from these tests indicated that a separation factor of only 1.4 between calcium and strontium was realized. Removal of strontium and calcium from the loaded resin was performed using a 1 M NaCl solution yielding distribution coefficients of 11.5 and 3.8, respectively, and a separation factor of 3 between strontium and calcium.

To maximize production efficiency and produce low volumes of secondary waste in a pilot-scale operation under conditions of low distribution coefficients, poor separation factors, and high production rates, a continuous countercurrent ion exchanger is preferred over a fixed bed ion exchanger, since the countercurrent operation is more efficient in utilizing the resin exchange capacity than a fixed-bed system.[6]

4. CONTINUOUS COUNTERCURRENT ION EXCHANGE (CCIX) TREATMENT OF ORNL PROCESS WASTEWATERS

A pilot-scale CCIX system shown in Fig. 1 has been operated at ORNL to test the selective removal of strontium from ORNL process wastewater prior to discharge into the environment. The CCIX system employs use of a well known, often used water softening technique to perform the relatively difficult separation between strontium and calcium and many other component ions (^{137}Cs, Mg, Na, etc.) found in ORNL wastewaters. This system is mounted on a mobile trailer bed to allow easy transport. The pilot CCIX column is sized to treat 3 gpm (11 L/min) of process wastewater as a test demonstration. The column is 27 ft (8.2 m) in height and is composed of four subsections -- (1) loading, (2) scrub (3) strip/rinse, and (4) a pulse section -- each connected in a closed loop.[7] A Dowex HGR-W2 cation exchange resin (10% cross linkage) was chosen to perform the separation between the multicomponents based on the resin's affinity for

Ca and Sr relative to Na, cost and availability, and high throughput capability.

4.1 CCIX LOADING SECTION

Resin [(20-50 mesh) 0.84 - 0.30 mm] is initially charged into the loading section of the CCIX column. Process wastewater was fed to the column at a constant flow rate of 3 gpm (11 L/min) in a countercurrent direction with respect to the resin flow. The pressure drop at this flow rate was normally in the range of 30 to 40 psig (207 to 275 kPa). During column operation, resin was pulsed around the column loop using approximately one gallon (3.8 L) of 50 psig (344 kPa) water supply per pulse. Strontium and calcium were loaded on the resin in this loading section. Magnesium and the other components of the process wastewater were only partially loaded onto the resin because of calcium competition and higher resin selectivity for strontium and calcium, respectively. As a result, magnesium and all other components breakthrough into the effluent stream. At optimum conditions, the effluent contains 100% of the calcium and magnesium and essentially 0% strontium.

Generally, the process wastewater feed rate was fixed leaving only the time length of the loading cycle variable. The loading cycle time length (normally 30 to 40 min) was programmed using a programmable controller. Samples of the effluent were analyzed for calcium total hardness after the start of a run to achieve optimum loading conditions. After the loading cycle time had been determined, the column was allowed to operate continuously. Resin was pulsed a distance of ~1 ft (30 cm) at the end of each loading cycle. The loading section for the pilot-scale column in Fig. 1 was a 5 ft (150 cm) length, 4 in. (10 cm) ID PVC pipe.

4.2 PULSE SECTION

Resin, loaded primarily with calcium and strontium, was pulsed up into the backwash section, where the resin was fluidized to remove any fine particles that might accumulate during processing. Fine particles were recovered in the Resin Recovery Tank. The backwashed, loaded resin dropped down into the pulse vessel by gravity flow (Fig. 1) when valve V-A

was automatically opened during the programmed cycle. The pulse chamber was equipped with ultrasonic probes to indicate resin levels and thus provide an evenly measured amount of resin during each pulse cycle. The overall resin flow rate may be controlled over a wide range, by varying the length of the stroke and/or the frequency of movement.

4.3 CCIX SCRUB SECTION

Resin loaded with strontium and calcium was pulsed around the CCIX loop into the scrub section. A 0.5 to 1.0 M NaCl solution was pumped to the scrub section countercurrent with respect to the resin flow to remove calcium from the resin leaving 80 to 100% of the strontium. Since calcium has a lower affinity than strontium, calcium was preferentially displaced into the scrub recycle and blended with the process wastewater feed. The amount of calcium that was removed from the resin can be controlled by varying the concentration of salt (NaCl) scrub feed solution and the pump rate. The objective was to adjust the flow ratio of scrub-to-resin, Sc/R, so that bulk calcium travels with the salt solution in the scrub recycle leaving bulk strontium on the resin. The pump rate was controlled by a programmable timer that was set to vary the length of time the pump was operated. The column scrub section is a 9 ft (2.7 m) length, 2 in. (5 cm) id PVC pipe.

4.4 CCIX STRIP/RINSE SECTION

Resin, loaded primarily with strontium, was pulsed around the CCIX loop from the scrub into the strip/rinse section. A 5 M NaCl solution was pumped to the strip/rinse section countercurrent with respect to the resin flow to remove 100 % of the strontium from the resin. The strip section feed pump was controlled by a programmable timer to vary the length of strip cycle time. After strontium had been stripped from the resin, it was then washed with water prior to entering the loading section of the column. Strontium rich eluate was precipitated as the carbonate by addition of sodium carbonate. Strontium, along with any residual calcium carbonate precipitates are filtered and ultimately disposed as solid

waste. The column strip/rinse section is a 14 ft (4.3 m) length, 2 in. (5 cm) id PVC pipe.

5. CCIX TREATMENT RESULTS

Test results from the near-steady-state operation of the CCIX system for > 700 h have indicated that a removal of better than 99.7% of the strontium from the process wastewater onto the resin has been achieved. The raffinate stream (i.e., strip waste stream) from the CCIX system contains 40 to 60% of the calcium and 90 to 99% of the strontium originally in the feed. Test results show that 90% of the strontium and calcium in the raffinate (strip waste stream) can be chemically precipitated by stoichiometric addition of sodium carbonate (with 0.3 M excess sodium carbonate) forming a carbonate solid waste sludge. The effluent stream from the loading section of the column contains <0.005 ppm (5 μg/L) total strontium and approximately 3.4 Bq/L radioactive strontium, which is below the federal discharge limit of <11 Bq/L for radioactive strontium.

6. DISPOSAL COST COMPARISON OF CCIX AND ORNL CURRENT PROCESS WASTE TREATMENT METHODS

6.1 ORNL CURRENT PROCESS WASTE TREATMENT SYSTEM

A flow diagram of the current PWTP system at ORNL is shown in Figure 2. The PWTP generates both concentrated and dilute LLLW and solid sludge precipitates that consists primarily of calcium carbonate. The dilute waste is generated during column regeneration with nitric acid and comprises approximately 5800 gallons/year (22 m^3/year). Dilute waste is evaporated in the LLLW evaporator and disposed at a cost of $7/gallon ($1.8/L). The concentrated waste [(4200 gallons/year) 16 m^3/year] is combined with LLLW evaporator concentrate and stored for future processing. Disposal cost for concentrated LLLW is $50/gallon ($13/L). Approximately 3900 ft^3 (110 m^3) of sludge is generated at the PWTP each year as a result of the clarifier precipitations. Sludge is disposed at a cost of $40/$ft^3$ ($1400/$m^3$). Total waste disposal costs for the currently used treatment plant are on the order of $500,000/year.

6.2 CCIX PRODUCTION-SCALE WASTE TREATMENT SYSTEM

A flow diagram of the CCIX process is shown in Figure 3. Based on pilot-scale test results, the secondary solid waste sludge generation in the strip waste stream is estimated to be 2340 ft^3/yr (66 m^3/yr) for a production scale CCIX process [150 gpm (567 L/min) design feed rate]. An order of magnitude disposal cost estimate based on performance results of the current PWTP show the CCIX process secondary solid waste disposal cost to be on the order of $100,000/yr.

7. SUMMARY AND CONCLUSION

Removal of strontium from ORNL process wastewater using continuous countercurrent ion exchange is a more efficient process for minimization of secondary waste generation than the currently used PWTP. The CCIX process is shown to be a potentially cost effective technique for treatment of low level radioactively contaminated process wastewaters. Recycling of regeneration streams and separating strontium and calcium from the process wastewater significantly reduces secondary waste disposal costs.

Table 1. Radiochemical composition of process wastewater at ORNL

Radionuclide	Concentration (Bq/L)[a]
Gross alpha	5
Gross beta	6000
^{60}Co	25
^{90}Sr	4000
$^{95}ZrNb$	50
^{106}Ru	10
^{137}Cs	400

[a] 1 Bq = 1 disintegration per second = 2.7×10^{-11} Curies

Table 2. Chemical composition of ORNL process wastewater (pH = 7.7)

Cation	Concentration (mg/L)	Anion	Concentration (mg/L)
Ca	40	HCO_3	60
Mg	10	SO_4	18
Na	20	Cl	6
Si	2	NO_3	4
K	2	F	1
Sr	0.2	PO_4	0.2
Al	0.1		
Fe	0.05		
Zr	0.05		
Cu	0.02		
Ni	<0.02		
Cr	<0.02		
U	<0.001		

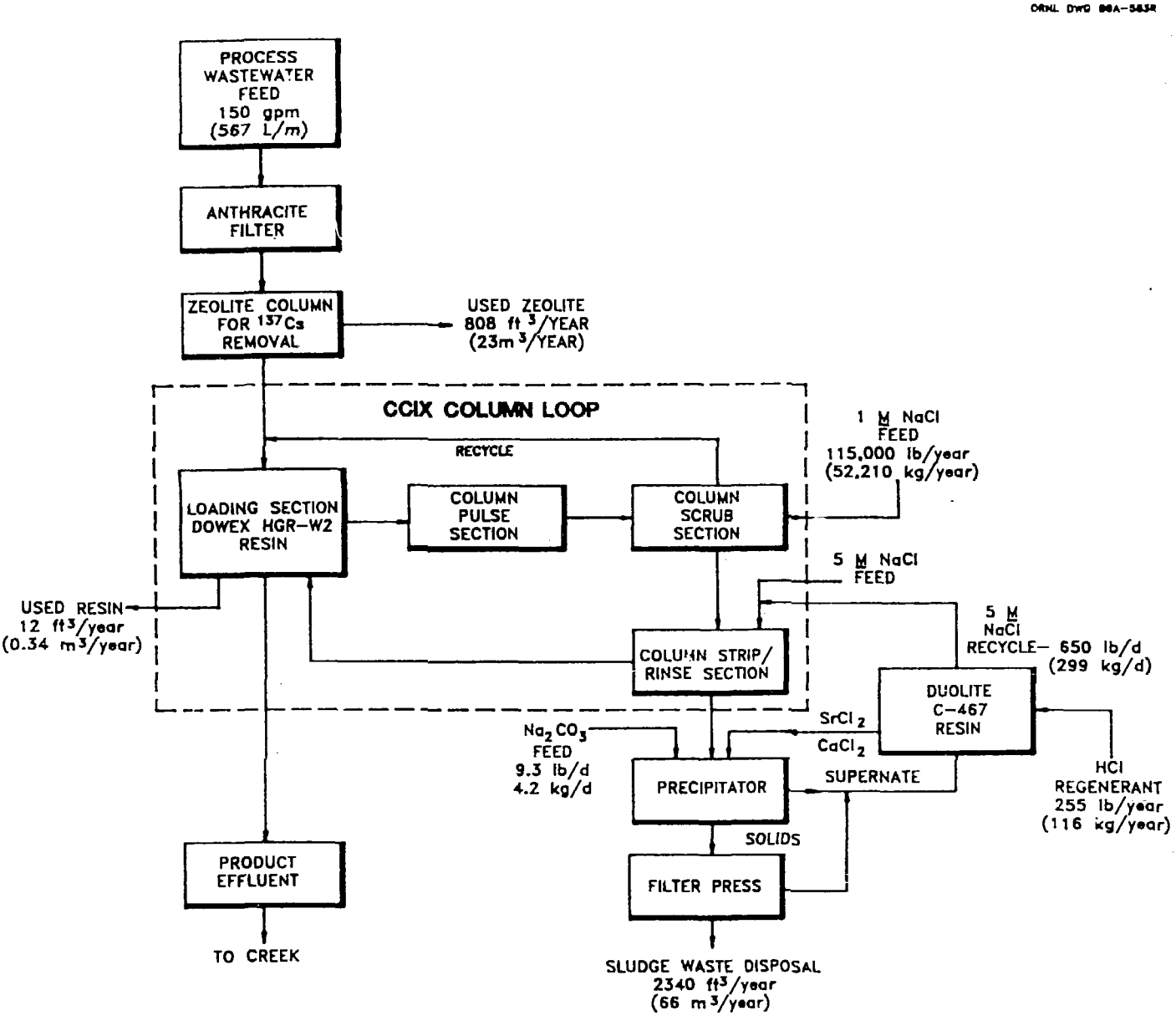

Fig. 1. Flowsheet for Full-Scale CCIX System Based on Experimental Pilot-Scale Results

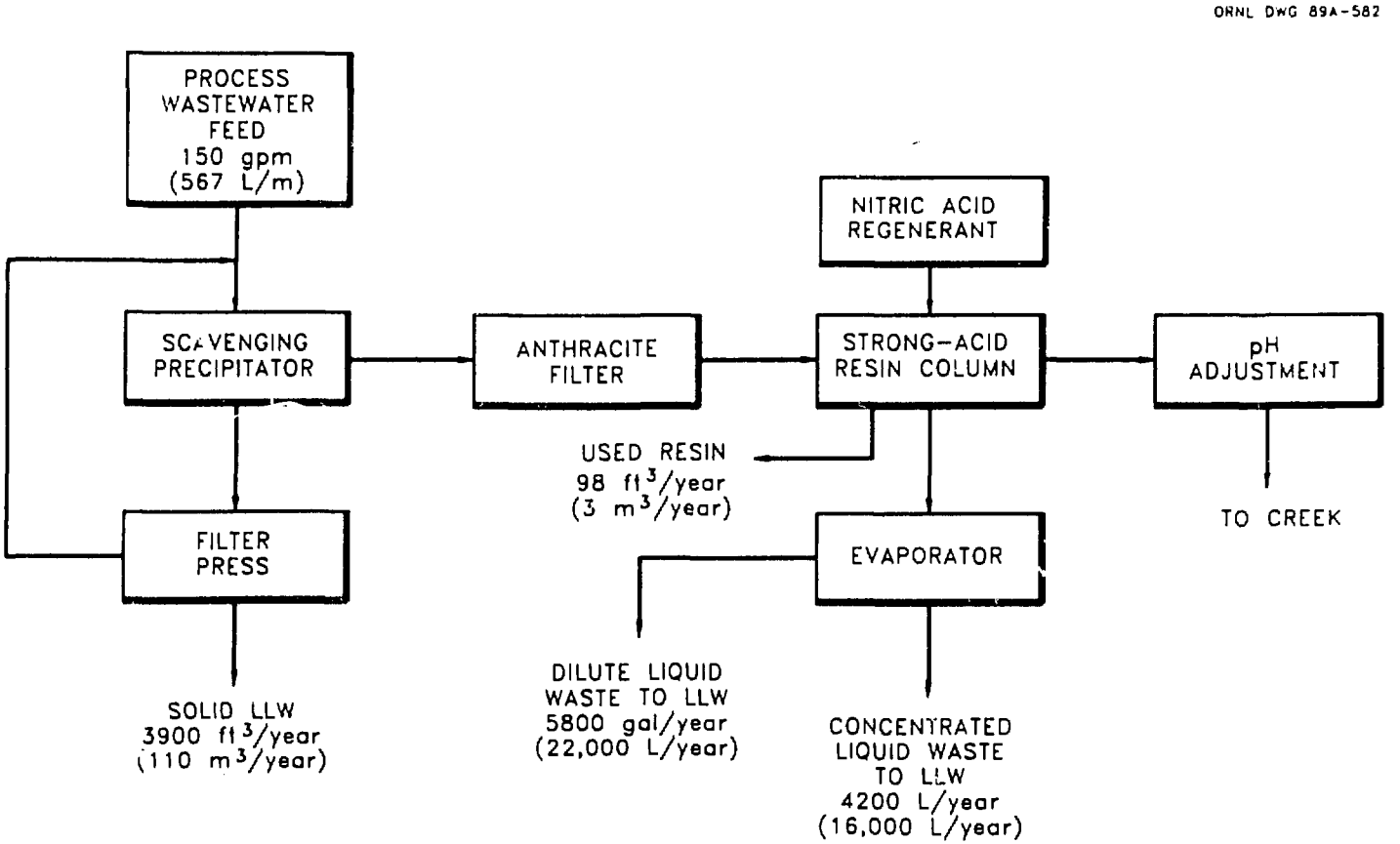

Fig. 2. Flowsheet for ORNL Process Waste Treatment Plant

ORNL DWG 88A-581R

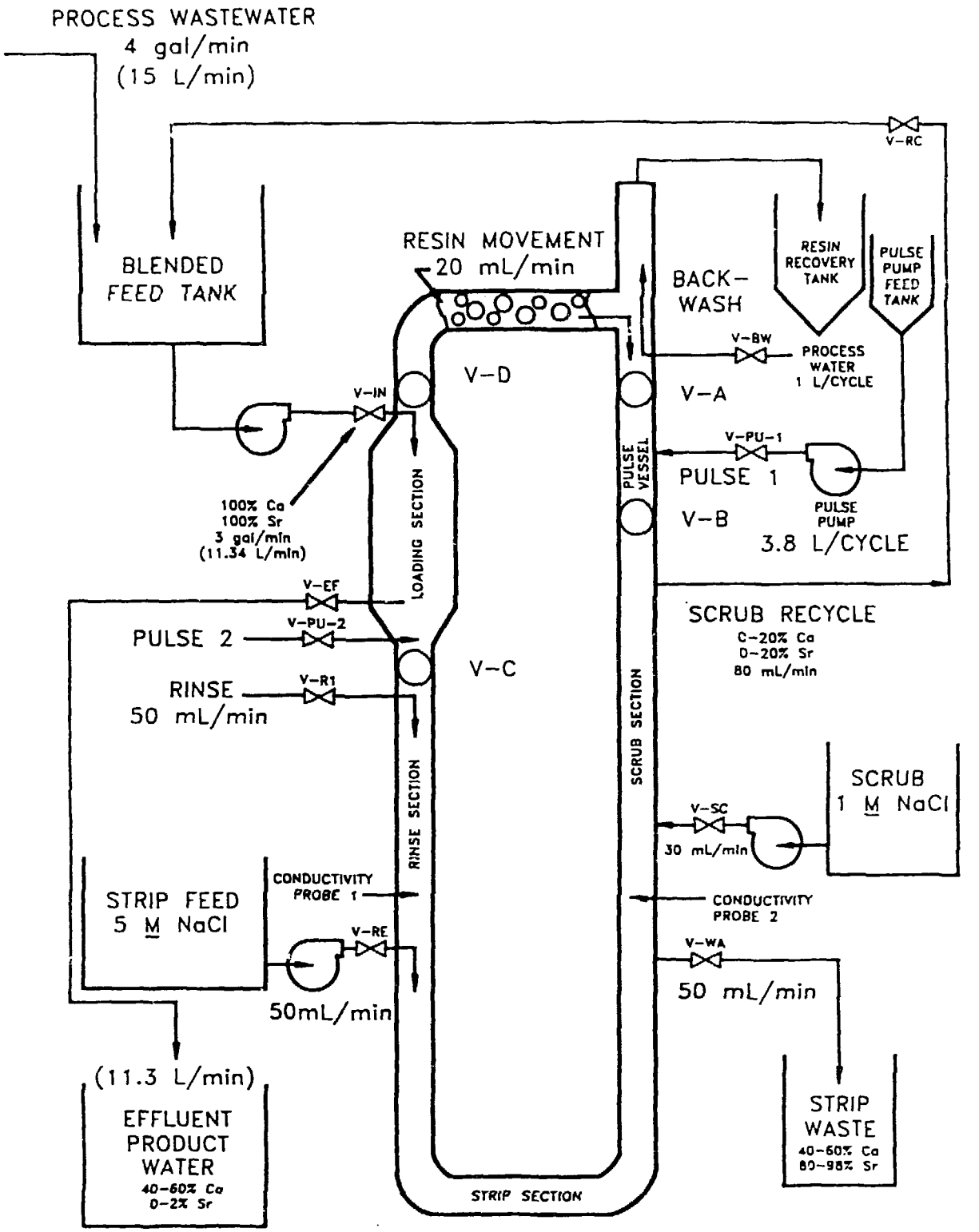

Fig. 3. Schematic of Pilot-Scale CCIX Unit Tested Using ORNL Process Wastewater

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