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Electrodialysis-Ion Exchange for the Separation of Dissolved Salts

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DISCLAIMER

PI.12 Electrodialysis-Ion Exchange for the Separation of Dissolved Salts

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Introduction

The Department of Energy generates and stores a significant quantity of low level, high level, and mixed wastes. As some of the DOE facilities are decontaminated and decommissioned, additional and possibly different forms of wastes will be generated. A significant portion of these wastes are aqueous streams containing acids, bases, and salts, or are wet solids containing inorganic salts. Some of these wastes are quite dilute solutions, whereas others contain large quantities of nitrates either in the form of dissolved salts or acids. Many of the wastes are also contaminated with heavy metals, radioactive products, or organics. Some of these wastes are in storage because a satisfactory treatment and disposal processes have not been developed.

Currently, it is anticipated that these wastes will be solidified for final disposal unless a better process can be demonstrated. Some of the wastes will be combined with cement, others will be solidified by calcination or vitrification. If they are disposed of as a grout or saltcrete, the volume is increased substantially. If calcined or vitrified, some of them produce a product with undesirable integrity. There is considerable interest in developing processes that remove or destroy the nitrate wastes, which DOE is investigating. These processes range from bionitrification to calcination. DOE needs a more economical process than calcination or vitrification and a process that produces a lower volume of highly stable wastes.

Electrodialysis–Ion Exchange (EDIX) is a possible process that should be more cost effective in treating aqueous wastes. EDIX is a process developed by Mr. Phil Grant of *WASTREN* in the 1970s. The process was developed to control the boron and lithium content of the primary coolant in Pressurized Water Reactors. This technique was never commercialized. A small research and development program was conducted at EG&G Rocky Flats in 1992 to determine the suitability of EDIX for processing streams containing low levels of nitric acid and small amounts of nitrate salts (~ 1.5 g/l). The program was exploratory in nature and limited in scope for processing selective waste streams at the Rocky Flats facility for the recovery of nitric acid. It did, however, yield some very promising results that justified conducting additional research and development.

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The purpose of this program, funded by METC, is to develop a process that can process rather dilute nitrate solutions. Thus, the wastes of interest are those generated at Rocky Flats and the contaminated ground water in Richland, Washington. It would be desirable to develop a process that would (1) remove the anions, primarily nitrate from the waste, free of radioactivity, in the form of an acid; (2) yield a stream of high quality water; and (3) produce a small stream containing the cations and radioactive metals. The cation stream might be processed further to separate the radioactive materials from the other cations.

This program will involve studying the suitability of the technology to treat aqueous streams containing low concentrations of organics, heavy metals, radioactive species, nitrates, and sodium. During the study, surrogate solutions typical of some of those in storage or being produced at some of the DOE sites will be evaluated.

The program will consist of a series of bench scale tests to develop the design and optimum operating conditions; two 100-hour runs to better understand the long term operation of the system; the design of a system to process 30 gpm; and the development of a cost estimate for processing 30 gpm in the EDIX system.

Objectives

The technical feasibility of EDIX has been demonstrated on a small scale. EDIX, however, has not been demonstrated as an economical process for treatment of aqueous streams containing various anions and cations. Therefore, the objective of this program is to demonstrate the suitability of the EDIX process for processing surrogate waste streams similar to those generated at some of the DOE sites. Specifically, the program is designed to determine the technical and economic potential of EDIX (1) to produce water meeting discharge criteria from a variety of waste streams containing small quantities of nitrates, chromium, sodium, uranium, and light organics; and (2) to produce waste streams containing the anions and cations in which the volume of these waste streams is less than 1/10th of the volume of the feed stream. During the program operational data will be obtained on the system through two extended runs so that a reliable economic analyses can be developed. These data will be used to design a 30 gpm system for treating one of the solutions tested in the program and to develop a capital and operating cost estimate for the 30 gpm system.

Approach

EDIX is a water/waste water treatment technology that combines ion exchange resins and membranes with the conventional electrodialysis process. The ion exchange resins can be either organic or inorganic and provide the removal mechanism for all ionic forms within a given feed stream. Electrodialysis is a voltage driven process which is used to separate and transport ions to their respective compartments for the separation and concentration of specific salts. The collective EDIX process can be used to split waste salt streams into acids and bases, or concentrate waste salts with substantial volume reduction. The use of ion exchange resins, with continuous regeneration, provide substantial decontamination factors across the cell and can provide very pure effluent water.

The basic cell unit is illustrated in Figure 1. This cell contains three compartments, each separated by a cation or anion permeable membrane. A cation membrane allows passage of cations but not anions. The opposite is true for anion membranes (A). The outer compartments contain a cathode (-) or an anode (+). The center compartment is the deionization section containing mixed-bed ion exchange resins.

The anolyte compartment contains anion resins and the catholyte compartment can be arranged in parallel or in series with similar cell units to provide either a larger flow capacity or greater degree of water purification.

Process Chemistry

The process involves two basic mechanisms: ion exchange by resin and ion migration induced by current flow. The operation of the cell is best described by assuming the feed stream contains sodium (Na^+)

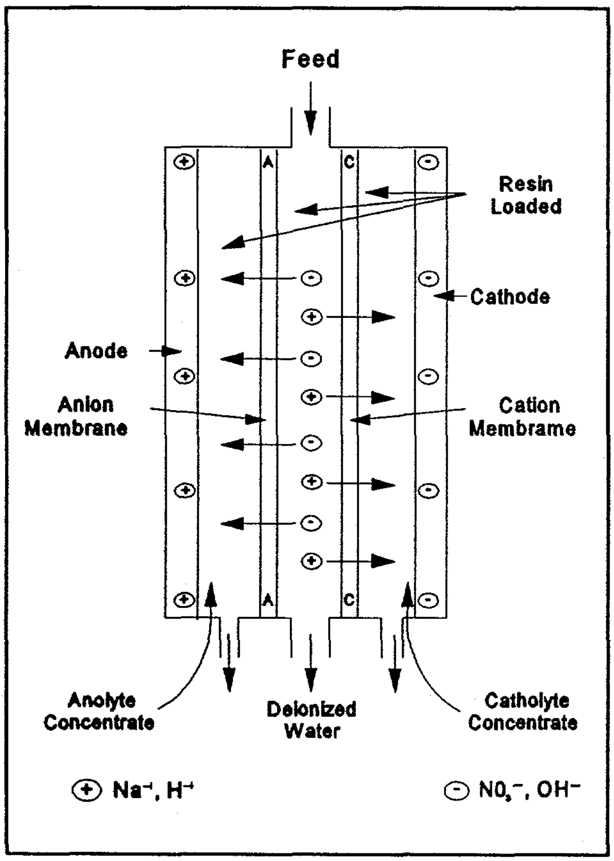

Figure 1. Electrodialysis–Ion Exchange (EDIX) Cell.

and nitrate ions (NO_3^-). The Na^+ ions exchange on the cation resin in the center compartment and displace hydronium (H_3O^+) ions. Under the induced current, the Na^+ ions migrate toward the cathode (-) through the porous resin particles, through the cation membrane, and into the catholyte compartment. In conjunction with the Na^+ transport, hydroxide ions (OH^-) are generated at the cathode from the electrolysis of water. The OH^- combines with the Na^+ to form a concentrated stream of sodium hydroxide (NaOH).

Similarly, the NO_3^- exchanges on the anion resin in the center mixed-bed compartment and then migrates with the induced current to the anolyte compartment. H_3O^+ generated from the electrolysis of water combines with the NO_3^- in the anolyte compartment to form nitric acid (HNO_3). If the solution residence time in the center compartment is sufficiently long, complete deionization occurs and all Na^+ and NO_3^- ions are removed from the feed stream.

The mixed-bed resins are constantly regenerated in place. In the feed compartment, Na^+ and NO_3^- exchange on their respective cation and anion resins. The dissociation of water molecules produces OH^- and H_3O^+. These ions displace their similarly charged Na^+ and NO_3^- from the cation and anion resins. The Na^+ and NO_3^- ions migrate to their respective anolyte and catholyte compartments as discussed above. This mechanism is a continuous electrolytical regeneration that precludes the need for regeneration by conventional acid and base techniques.

Another unique feature of this process is the ability to clean the system without disassembly. Cleaning, or purging in this instance, involves reversing the cell polarity similar to the process for conventional electrodialysis. Reversing cell polarity transports the contaminants along with Na^+ and NO_3^- into the feed compartment where they are flushed as unrecovered waste. If the goal is to produce high quality water and the composition of the anolyte and catholyte is unimportant, it may not be necessary to conduct reverse polarity operations.

Equipment Description

EDIX System

The EDIX cell and associated support system are designed to collect and store highly concentrated chemicals. The EDIX system consists of a stack of cells, an electrical rectifier, holding tanks, pumps, flowmeters, pressure gauges, and conductivity meters. The EDIX system is configured in a three-loop flow configuration as shown in Figure 2.

The alkaline and acid streams are circulated through individual tank systems to build up concentrations. The solutions are collected in the acid tank for the acid loop and the alkaline tank for the alkaline loop. These solutions are piped to their respective pumps and pumped through control valves and rotameters to the cell stack. From the cell stack the streams discharge into conductivity pots and drain into their respective holding tanks. Heat builds up in these loops from the pumps and cell voltage. The heat is removed with cooling coils submersed in the acid and alkaline tanks. The feed solution is introduced into the EDIX system via the feed tank. When the cell is energized, the stream will become demineralized through the loss of anions through the anion membrane and the loss of cations through the cation membrane.

The EDIX system is equipped with instrumentation for regulating and monitoring the operating parameters. Each tank is equipped with a conductivity pot for measuring the conductivity and pH level of the stream entering the tank. The tanks have temperature gauges to

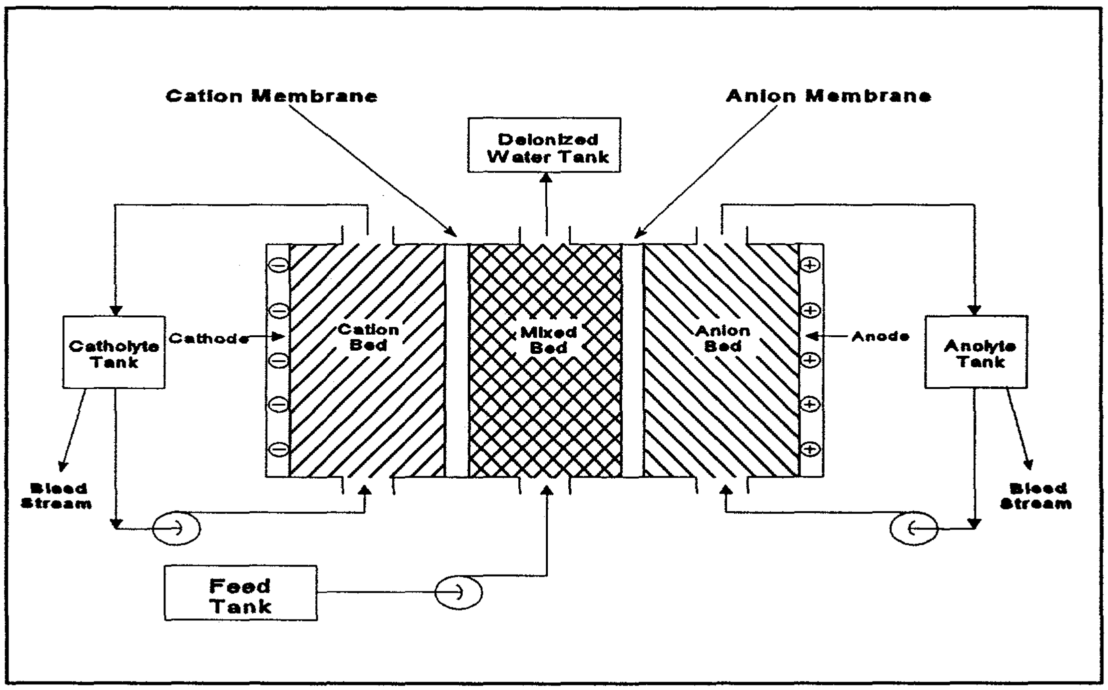

Figure 2. EDIX System—Three-Loop Flow Configuration.

monitor the system temperature. Flowmeters and control valves regulate the flow of solution to the cell stack. Pressure gauges monitor the pressures in the three compartments of the cell. The AC to DC rectifier provides power to the stack of cells. The rectifier is housed in a control box. A 220 V, single-phase, 50-60 cycle AC inlet power source is required for the rectifier. The cell current and cell voltage are recorded on an ammeter and voltmeter.

Cell Stack

The cell stack assembly consists of electrodes and one or more cell pairs. A cell pair is made up of an anode, an anolyte compartment, an anion membrane, a feed compartment, a cation membrane, a catholyte compartment, and a cathode. The cell is arranged in a stack unit, assembled, and compressed by end plates and tie-rods as shown in Figure 3.

The alkaline stream (i.e., NaOH) is concentrated in the catholyte compartment. The acid stream (i.e., HNO_3) is concentrated in the anolyte compartment. The feed stream enters the feed compartment and is deionized. The streams flow through channels; each channel is bounded on both sides by a combination of an

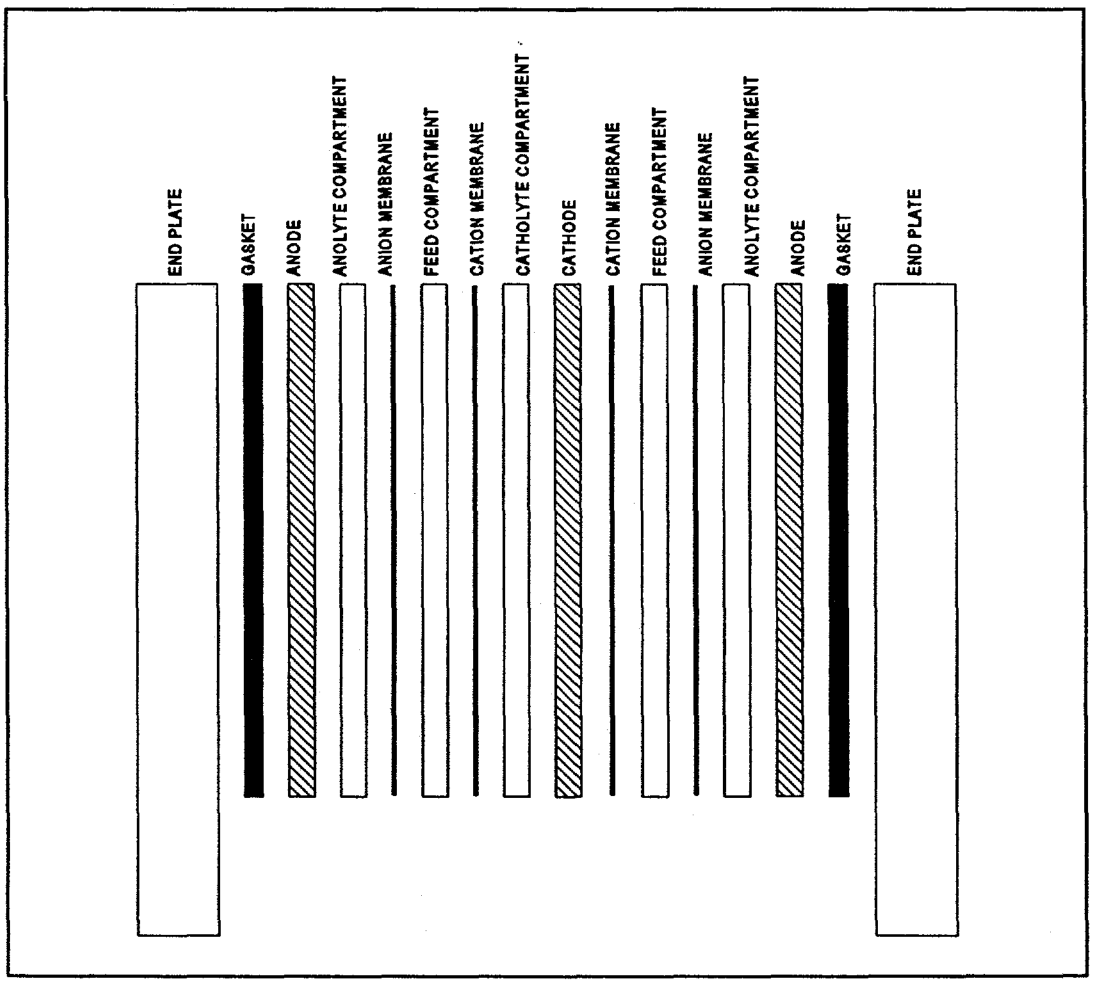

Figure 3. EDIX Cell Stack Configuration.

anion membrane, cation membrane, or electrode. The channels furnish the flow paths, keep the membranes separated, act as gaskets, and contain the ion exchange resins.

Project Description

The purpose of this experimental program is to determine whether EDIX can be used economically to process aqueous waste streams containing small quantities of radioactive materials, nitrates and other anions, heavy metals and other cations, and organics. The goal is to produce a product stream of high purity water containing the organics, an acidic stream free of radioactivity, and a cation stream containing the radioactive materials and other cations.

The process would be considered technically successful if the volume of cation and anion streams are no more than 1/10th of the volume of the feed stream. The overall success will be dependent upon the economics of the process.

The chemistry and fundamentals of processing solutions containing mixtures of dissolved salts, organics, and heavy metals are not well understood. Therefore, a matrix of bench scale tests is planned in which the composition of the feed stream, flow rate, power, and type of resins and membranes are varied. The composition of the feed solution will vary and, in most of the tests, neither radioactive materials or organics will be in the feed stream. The composition of the effluent can also vary. By reducing the throughput and increasing power, removal efficiencies can be attained that meet the desired discharge limits. The experimental program consists of six tasks as described below.

Task 1: Design of the EDIX System and Experimental Program. For the laboratory experiments, a system having a capacity of at least one liter per minute will be required. The system will be required to process a variety of waste streams. However, the concentration of the contaminants (organics, heavy metals, nitrate, and radioactive materials) will be relatively small and in general < 3,000 ppm for any one constituent. The basic hardware will be designed and selected for these conditions. *WASTREN* will review the literature and hold discussions with the resin and membrane suppliers and select the membranes and resins that will have the highest probability of performing as required.

Task 2: Procure, Assemble, and Check Out the System. After the design of the system has been completed, *WASTREN* will purchase the equipment, membranes, resins, and chemicals needed to prepare surrogate solutions. After the equipment is received, it will be assembled into a complete EDIX system. The system will be checked out using deionized water and very dilute salt solutions to determine if there are any leaks; the throughput of the system; and the ability to control flow, pressure drop, voltage, and other operational parameters. Once the system passes these tests it will be ready for testing with the surrogate solutions.

Task 3: Conduct Bench Scale Tests. The experimental program will be divided into three phases. Phase 1 will be to run a series of about ten tests to determine the most suitable resins and membranes, voltages, and flow rates to transfer the anions and cations.

Phase 2 will be to run a series of forty tests in which the composition of the feed stream is varied, with the chief variables being levels of nitrate, sodium, and chromium metals. A proposed test matrix is shown in Table 1.

These experiments are designed to:

a. Determine if the anions and cations are removed selectively or in bulk;

b. Establish the conditions necessary to achieve the desired water quality;

c. Determine what concentration factors can be achieved for both the cation and anion streams;

d. Determine if precipitates are formed in the cation cell because of the high pH and determine what effect, if any, these cations have on overall system performance; and

e. Determine the operating conditions that are needed to preclude the deleterious effects of precipitates in cation cells.

Table 1. Suggested Experimental Program Test Matrix.

Nitrate Level ppm	Chromium Conc, ppm	Sodium Concentration, ppm		
		18	200	2000
30	20	X	X	X
30	200	X	X	X
30	2000	X	X	X
300	20	X	X	X
300	200	X	X	X
300	2000	X	X	X
3000	20	X	X	X
3000	200	X	X	X
3000	2000	X	X	X

Phase 3 will be a series of twelve tests in which some of the solutions tested in Phase 2 will be spiked with various levels of organics and depleted uranium to see if organics adversely affect the process and if the uranium concentration in the discharge streams (product and anion streams) are low enough to label them as non-radioactive.

Task 4: 100-Hour Extended Runs. After the bench scale tests have been completed, two 100-hour continuous campaigns on two different surrogate solutions will be conducted. These campaigns will determine if the performance of the cell changes with time and how frequently it will be necessary to regenerate the resins.

Task 5: Recommend processes for Treating the Catholyte and Anolyte Streams. The results of the 100-hour runs should provide information on the composition of the anolyte and catholyte streams. *WASTREN* will suggest means of processing these streams, but will not conduct any experiments.

Task 6: Design of a 30 gpm system. Based on the results from the 100-hour extended runs, an EDIX system to process 30 gpm of feed solution will be designed. The design will not include any processing schemes for the anolyte and catholyte solutions generated in the EDIX system. The system designs will be used to develop capital and operating costs. The cost of processing 1000 gallons of the desired water quality will be calculated.

WASTREN was authorized to begin work on the project in March 1995. The tentative schedule shown in Figure 4 will require about 20 months to complete. If the entire program is conducted and the schedule met, the program will be completed in November 1996.

The project manager is Dr. Barcoh of *WASTREN*, and the test program will be conducted at the Colorado Minerals Research Institute in Golden, Colorado. Mr. John Litz will be the project engineer for Acta Resources.

Results

The project began in March with the design of the system. Several vendors of electrodialysis cells were contacted and *WASTREN* evaluated the system capabilities and cost. The Electro Syn Cell provided by ElectroSynthesis was selected for the test program. As an electrodialysis cell it has a capacity of three liters per minute when processing a solution containing 200 ppm of sodium, 200 ppm chromium as chromate (CrO_4^-), and 300 ppm nitrate. The throughput when the cell contains ion exchange resins and higher concentrations of contaminants will be determined in the experimental program.

Based on discussions with the suppliers of the membrane and ion exchange, the following membranes and ion exchange resins were selected.

Item	Primary	Secondary
Anion Membrane	Tokuyama Sodium Neosepta AMX	Ultrex AMI-7000
Cation Membrane	Tokuyama Sodium Neosepta CMX	Ultrex CMI-7000
Anion Resin	Dowex 21	Reilex HPG
Cation Resin	Dowex G26	Dowex M33

The experimental equipment has been erected and the operational testing is in progress. No data have been generated at the time of publication of this paper.

Applications

The primary focus is on anticipated process performance, cost, and expected advantages and improvements over existing

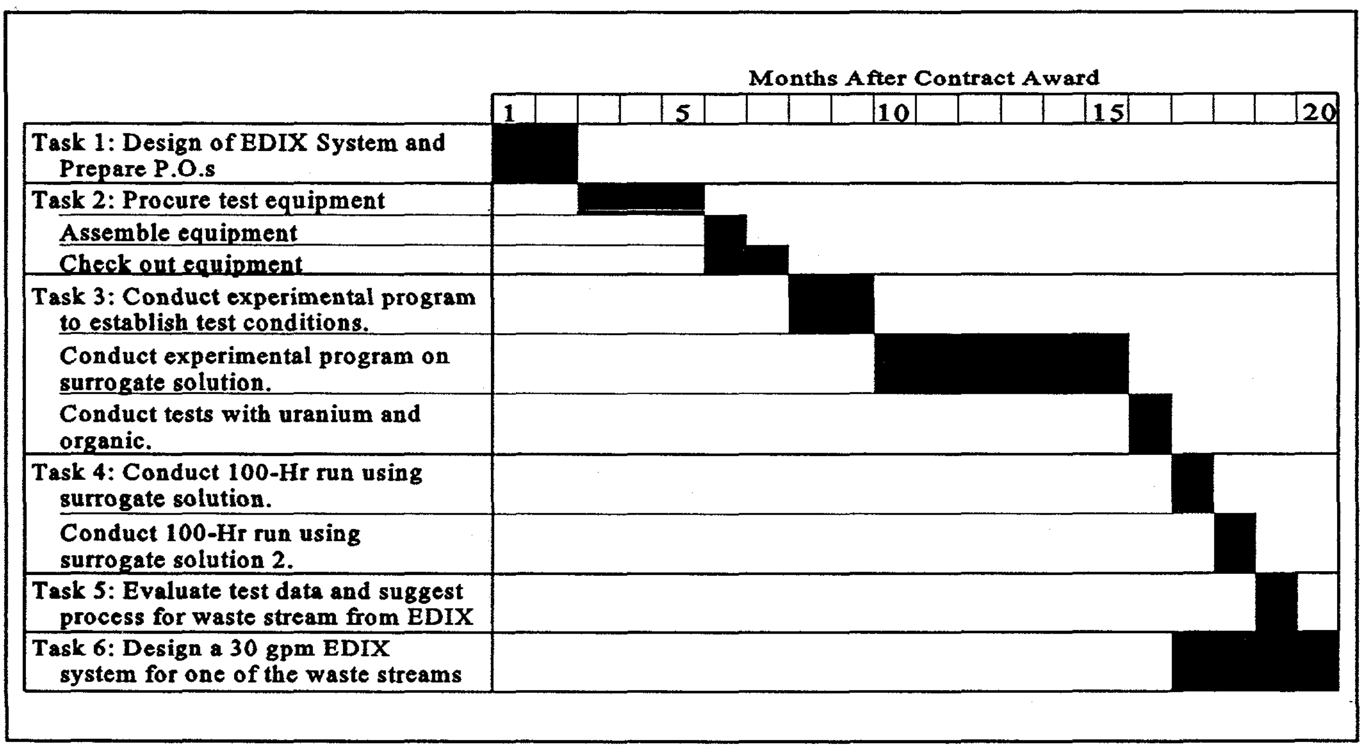

Figure 4. Schedule for EDIX Project.

technologies. EDIX is an emerging technology with only limited development for nitric acid recovery and water purification. Therefore, conclusions on performance and benefits are premature until the test program has been completed.

A major aspect in predicting EDIX operational performance is that each of the conventional ion exchange (IX) and electrodialysis (ED) technologies used in EDIX has extensive performance data and cost information which lends itself to evaluating the combined merits of the proposed technology. Additionally, the preliminary testing of the EDIX technology at Rocky Flats, while limited, also provides a source of empirical data on performance expectations for technology.

The EDIX technology applies two proven and commonly used water treatment technologies, ion exchange and electrodialysis, in a single, self-regeneration process for waste water treatment. The conventional ion exchange process is a relatively low cost ($0.50 - $1.50 per 1000 gallons) technology which can be used for ion substitution and high purity water recovery, but requires resin regeneration and/or resin discard, and has limited ionic capacity. The use of conventional electrodialysis is also low cost ($0.35 - $0.50 per 1000 gallons) and can be used to split salt streams, reduce waste volumes, and recover selective ions as acids and bases. The conventional ED process does not produce a higher effluent quality when compared to IX. The EDIX process benefits from these two conventional processes in that the IX resins are regenerated in place, high purity water can be recovered in a single step, additional flow capacity can be added without major retrofit, and a wider range of chemical/contamination concentrations can be treated than either IX or ED as a stand-alone process.

Another unique part of the EDIX technology is that by combining IX and ED into a single process, the effective range of feed flow rates and stream composition can be increased to include both low concentrations (ppm), high flow input as well as high concentrations, low volume feed streams. The use of IX resins within an EDIX cell provides greater ion retention and more efficiency for ion removal than conventional ED and therefore can produce exceptionally high quality water at a lower cost. The EDIX process should provide cost effective resin and membrane regeneration as part of the process and provides substantial waste volume reduction when compared to conventional technologies like reverse osmosis and membrane filtration systems. The following represents *WASTREN's* judgment on the potential of EDIX:

- Removal of > 99.9% of the ionic sources from the feed stream

- Waste volume reduction factors of up to 200 depending on the composition of the feed stream and the solubility limits of the constituents

- Continuous in-place regeneration of ion exchange resins and selective membrane materials

- Effluent water of high quality to meet all expected recovery and recycle requirements except for dissolved organics where present

- Design flexibility with capacity to treat small to high volume throughput without major design and operational changes

- Concentrated anion and cation waste streams (up to solubility limit of chemical forms) as a function of input feed concentrations

- Low energy cost (~$0.60/1000 gal.) and low pressure (< 50 psig) operations
- Longevity of equipment and materials expected to be > ten years based on equipment vendor testing data and proposed life cycle studies
- Potential for small amount of secondary waste generation which could be treated by conventional technologies or possibly could be recycled or returned to feed stream

Cost Comparisons with Existing Technologies

The anticipated technologies with which EDIX would compete include evaporation, reverse osmosis, conventional electrodialysis, ion exchange, and possibly utrafiltration and/or other membrane separation technologies. None provide the single step process proposed in the EDIX technology to produce three separate streams which include clean water (possibly with dissolved organics), a concentrated acid stream, and concentrated base stream containing the radioactive metals.

The anticipated costs for equipment and unit operations are based on *WASTREN's* engineering judgment for the EDIX technology because of the lack of specific performance and operations cost data. However, some assumptions can be made relative to the size of a large scale system and the associated operations. Table 2 shows the relative treatment and capital costs for a variety of techniques processing 72,000 gallons per day.

The major cost savings incentives are associated with volume reduction of the wastes, production of high purity water, and the potential to recycle chemicals for reuse. *WASTREN* believes that the EDIX technology can provide volume reductions up to the solubility limits of the feed salts and bases in the catholyte solution. For highly concentrated feed solutions, the volume reduction can be relatively low. Secondary cost incentives can be associated with water recycle and water management, especially for sites or facilities attempting to reduce plant effluents to near zero. Other potential cost savings incentives could be associated with chemical recovery, lower

Table 2. Technology Treatment with Capital and Operating Costs for a 5 gpm System

Technology	System Costs	Operating Costs
Evaporator	$2.0M - $2.5M	$4.50 - $6.50 per 1000 gallons
UF/Reverse Osmosis	$280K - $350K	$0.80 - $0.95 per 1000 gallons
Electrodialysis	$120K- $150K	$0.35 - $0.50 per 1000 gallons
Ion Exchange with Regeneration System	$350K	$0.50 - $1.50 per 1000 gallons
UF/Nano-Filtration	$450K	$1.00 - $1.50 per 1000 gallons
EDIX (Potential)	$150K - $175K	$0.50 - $0.60 per 1000 gallons

equipment and operating costs, flexibility in adding system capacity without major system reconfiguration, and operator ease in establishing waste stream process control programs.

Future Activities

The experimental program to determine the optimum conditions for treating the various solutions will begin in October, Task 3 as shown in Figure 4. These tests will require about nine months to complete if the entire test program is completed. Two 100-hour continuous runs will be run during the summer of 1996. During the fall of 1996, the 30 gpm system will be designed and the economics of the process will be calculated.

Acknowledgment

We appreciate the assistance and guidance William Huber, METC Contracting Officer's Representative, has provided to *WASTREN*. This contract began in March 1995 and should be completed in November 1996. *WASTREN* has a contract with Acta Resources of Golden, Colorado, to be responsible for the laboratory work. Mr. John Litz is project manager for Acta Resources. This work is being conducted as part of the Low-Level Mixed Waste Processing, Item 2, Separation of Suspended and Dissolved Solids program of DOE.