ABSTRACT

Radioactive liquid wastes generated by research and operations at the Los Alamos National Laboratory are processed through a central treatment facility that was constructed in 1963. The treatment process was changed in 1999 to address new and more stringent discharge requirements. While the new treatment processes successfully improved the quality of treated waters, they also generated more than 20 secondary and tertiary waste streams that add more than 50% to the volume of waste to be treated, resulting in severe process inefficiencies and increased treatment costs. These problems were tackled through a study that characterized the new treatment process, and that recommended process refinements that would eliminate the largest of the secondary waste streams. Recommendations implemented to date have succeeded as predicted by the study.

INTRODUCTION

The Radioactive Liquid Waste Treatment Facility (RLWTF) has been in operation at Technical Area 50 at the Los Alamos National Laboratory (LANL) since 1963. Until March 1999, the treatment process had consisted of two unit operations, and had generated but two secondary waste streams, clarifier sludge and sand filter backwash. Radioactive liquid wastes (RLW) were processed through a clarifier and sand filter in order to precipitate, and then filter out, radioactive impurities. This straightforward chemical and physical process was successful in removing about 99% of the radioactivity.

Changing Regulations

Discharge requirements recently became more stringent, however. In 1998, the New Mexico Environment Department (NMED) limited nitrate discharges to 10 milligrams per liter (mg/L) nitrate as nitrogen (NO$_3$-N). Then, the Department of Energy (DOE) imposed Derived Concentration Guidelines (DCGs) as discharge limits in 1999. The RLWTF failed to meet DCGs for one or more radioisotopes each year from 1990 through 1999. During this same time period, discharges averaged more than ten times the 1998 nitrate limit. In short, it was not possible to meet discharge limits with just the tried-and-true two-step treatment process that had been used since 1963.

Process Modification and Additions

To address the new requirements, two membrane operations, tubular ultrafiltration (TUF) and reverse osmosis (RO), were installed in March 1999, to replace the 36-year-old clarifier and sand filter treatment steps. Problems were encountered almost immediately. To counter these problems, additional unit operations were brought into service and/or installed, and additional storage tanks were acquired to accommodate off-quality waters. In a matter of months, treatment had grown from two to nine unit operations, as described in the next section. The modifications had some success, however, and the plant began meeting all discharge limits in December 1999.
The more complex treatment process presented a new set of problems, however. While the TUF and RO were good at removing impurities from the water, they ultimately created more than 20 secondary and tertiary waste streams. These streams are loaded with impurities, add to the volume of water processed through the main treatment process (MTP), require further treatment, and are expensive to treat. Plant capacity was also reduced.

**Problem Definition**

During 1999, the RLWTF changed from a two-step process that had been used to treat RLW for 36 years, to a more complex process that required multiple unit operations for the treatment of primary, secondary, and tertiary liquid waste streams. While the new process provided the ability to meet regulatory discharge limits, its complexity introduced many new secondary and tertiary waste streams. The treatment of these new streams was inefficient and expensive.

**PROCESS DESCRIPTION**

Installation of the new membrane processes led to a long period of start-up problems and process modifications. During this period, the MTP grew from two to nine unit operations, and did not settle into routine operations until late in 1999. The complete process is depicted in Figure 1 and briefly described below.

- **Clarifier, sand filter, and bag filter:** Membrane operations had difficulty cleaning plant influent, and membranes failed after only a few months in service. It became obvious that pretreatment was required before sending waters to the membrane units. Accordingly, the clarifier and sand filter were returned to service, and a bag filter installed as additional protection. Three chemicals are added at the clarifier – ferric sulfate, lime, and sodium hydroxide. The chemicals are used to adjust plant influent to a pH of about 10.5, to precipitate cations, and to assist with particle flocculation. The clarifier is over-sized, and has a retention time of about one day. The sand filter contains both anthracite and sand, and provides filtration to about 10 microns. Its function is to remove small particles that do not settle in the clarifier. The Ronningen-Petter (RP) filter is a bag filter typically fitted with nylon bags with pore size of 10 microns. Its primary function is as a redundant filter in the event of poor performance by the sand filter, as further protection for the membrane unit operations.

- **Tubular ultrafilter and reverse osmosis:** The TUF operates at typical throughputs of about 750 gallons per minute feed, 60 gallons per minute permeate, and recycle of the difference. In addition, about 1500 gallons of the recycled concentrate stream is purged daily to prevent buildup of impurities. TUF permeate is fed to the RO unit for final treatment. Carbon dioxide gas is first bubbled into the TUF permeate in order to adjust pH downward, from about 10.5 to about six. This reduces the formation of calcium carbonate which forms mineral scale on the concentrate side of the RO membrane. TUF membranes have a pore size of 10^5 molecular weight, or about 0.08 micron. The RO unit uses a high-rejection polyamide thin-film composite membrane, 8”x40”, with nominal NaCl rejection of 99%. Membrane operations improved dramatically once the clarifier and filtration pre-treatment steps were introduced. One negative effect of membrane operations, however, was the introduction of large-volume secondary waste streams, particularly RO concentrate.

- **Electrodialysis reversal (EDR) Unit and Evaporator:** These units concentrate the RO reject stream, reduce the volume of this secondary stream by a combined factor of 10-12. Further concentrations only result in precipitation of impurities. EDR permeate, about 80% of the RO concentrate, is recycled to the MTP; EDR concentrate is fed to the evaporator for additional concentration. The
Evaporator is a trailer-mounted mobile system comprised of a recirculating flash evaporator, a boiler, and a cooling tower, with a nominal capacity of 10 gallons of feed per minute. Evaporator downtime approaches 50% due to the high dissolved solids content of EDR concentrate.

- Drying and Solidification: For final treatment, evaporator bottoms are shipped to a commercial facility (GTS Duratek) where they are dried to a solid residue. Solids are mixed with cement, allowed to solidify, and then returned to LANL for disposal as solid low-level radioactive waste. Bottoms are transported in a 5,000-gallon tanker, loaded into holding tanks at the Duratek facility, and added to drum ovens. Each drum is filled with about 40 gallons of bottoms, heated to 600 °F, and allowed to evaporate overnight to dryness. Residues are grouted using water and Portland cement. A net volume reduction factor of about 17 is achieved through the drying and solidification steps.

Each of these unit operations generates its own waste streams and has its own set of problems (e.g., 50% downtime for the evaporator). In addition, because so many of the secondary and tertiary streams are recycled to the Main Treatment Process (MTP), actual volumes of water treated are about 50% higher than the volume of influent waste water sent to the RLWTF.

SECONDARY STREAM STUDY

Problems created by the new secondary and tertiary waste streams were tackled beginning in the spring of 2000 by establishing a team to study the new secondary and tertiary waste streams. The team conducted a two-day test to characterize flows, concentrations, and material balances in the “new” main treatment process; identified and characterized secondary and tertiary waste streams; narrowed the study to focus on the four most troublesome streams; and then recommended solutions to bring process problems under control. Each of these study steps are described in succeeding sections.

The team developed two solution sets when formulating recommendations. The first set applied the waste minimization philosophy of “Reduce, Re-use, Recycle”. This solution set led to recommendations to eliminate or reduce the volume of secondary waste streams via direct modification to MTP operations. For example, chemical addition at the clarifier adds 12% to the volume of waters to be treated. A solution was found that eliminates this stream. Less desirable solutions, to treat the secondary streams themselves, were also identified. An example of this second set of solutions is to replace the current evaporator with an evaporator of a better design.

PLANT TEST

Because the MTP no longer resembled the treatment process employed for 36 years, a two-day plant test involving operators, engineers, and managers was conducted. A 50,000-gallon batch of feed was prepared, then fed through the MTP over a two-day period at normal throughput rates. The first day was used to flush the MTP, while the second was used to sample process streams at nine different locations over an eight-hour period. Nearly 400 samples were submitted to four different laboratories for a host of analyses. The results of this effort led to a clearer understanding of the MTP and to the construction of flow and material balances for many impurities. Many recommendations stem from observations that have resulted from the two-day plant test.

Test Preparations

Preparations for the test started by obtaining input and concurrence from operators, laboratory personnel, and management about (a) proceeding with a test and (b) details of the test. A 50,000-gallon batch of homogenous feed was then prepared, a step that required several days. Sampling details were also
attended to, including identification of sampling and support personnel, and the acquisition and labeling of 387 sample vials. Discussions were held with four analytical laboratories to provide advance notification, to discuss details such as sample size and preservative, and to distribute analytical workload to allow for rapid return of results.

**Sampling Points and Parameters**

Nine sampling points were selected within the MTP: feed to the clarifier, sand filter effluent, RP filter effluent, the TUF recycle and permeate streams, and RO feed, concentrate, and permeate streams. RO concentrate was the only secondary stream sampled during this plant test. Samples were analyzed for conventional parameters, metals, anions, and radioactive species.

**Plant conditions**

The first day of the test, 05/01/00, was used to flush the MTP; sampling was performed on the second day. Feed was drawn from the same homogenous batch on both days. Sampling personnel recorded relevant plant data to supplement data routinely recorded by the central control and data recording system at the RLWTF. Unit operations were conducted at typical flow rates, temperatures, and pressures. Samples were collected on the hour for eight hours.

**Flows**

All liquid flows were identified, starting with five streams that are fed to the clarifier. Storage tank volume changes were accounted for. Flows were either metered or measured. For example, measurement of the chemical feed streams to the clarifier, ferric sulfate and lime, showed a combined flow of six gallons per minute. Excellent flow balances were obtained; flow rates into and out of each piece of equipment balanced within five percent. Figure 1 shows plant flows as determined during the plant test, normalized to reflect one day of operation. (Flows are normalized because some streams, such as clarifier sludge sent to the vacuum filter, are intermittent, not continuous.)

**Test Results**

Flow rates were combined with sample results to obtain material balances for more than 20 different waste water parameters. The accuracy of mass balances was excellent, being within 5%-10% for most parameters at the final unit operation, reverse osmosis. These close results are an indication that flows were accurately determined; that analytical results were accurate; and that assumptions and mass balance equations were valid. Test data indicated that impurities are treated in one of four fashions:

a) Most multivalent metals (aluminum, barium, zinc, others) are removed at the clarifier.

b) Alpha radioactivity and TSS are removed at each unit operation.

c) Silica and a number of conventional impurities (COD, TKN, TOC) and metals (calcium, strontium) are partially removed at the clarifier, and then further removed at the RO.

d) Monovalent cations (sodium, potassium) and monovalent anions (chloride, nitrate, perchlorate) coast through the MTP until running into the RO unit, which removes more than 90% of these impurities. This is also true for sulfate, total alkalinity (as CaCO$_3$), and total dissolved solids.

Lesser conclusions drawn from the plant test include the following:
About 80% of the calcium added as lime at the clarifier precipitates in the clarifier. The balance remains in solution, and so is not filtered out until reaching the RO unit, where 98% of this divalent ion is removed.

Sulfate added to the clarifier, as ferric sulfate hexahydrate, remains in solution, and so is neither precipitated nor filtered out until reaching the RO unit. At the RO, 98% of this divalent ion is removed.

Data clearly showed that silica polymerizes and precipitates at the RO unit. The polymerized silica particles form a gel layer on the RO membrane. This gel layer decreases salt rejection of, and water recovery by, the membrane. The practice of soaking the RO membrane every night in a sodium hydroxide solution (Silica is very soluble at high pH) was therefore shown to be effective.

Figure 2 illustrates flows, concentrations, and quantities for one parameter, total suspended solids, for 05/02/00. Similar information was collected for more than 20 water quality parameters. Test data, coupled with plant performance at other times, also indicated that DCG concentrations for radioactivity can sometimes be achieved without the RO.

IDENTIFYING MAJOR PROBLEM STREAMS

The identification of secondary and tertiary waste streams was another step taken by the study team. A total of 25 secondary streams were identified, as listed in Tables 1 and 2. Once waste streams had been identified and qualitatively characterized, the magnitude of the secondary stream study was reduced and sharpened by deciding to focus on just four waste streams or types of waste streams.

Identification of Secondary and Tertiary Streams

Prior to the installation of the membrane unit operations in 1999, the RLWTF generated only two secondary waste streams, sand filter backwash and clarifier sludge. The streams were low in volume, and were generated only intermittently. The only tertiary stream resulted from operation of a rotary vacuum filter when treating the clarifier sludge – also an intermittent operation.

In sharp contrast, the “new” RLWTF, while producing higher quality effluent, has more unit operations, generates more secondary waste streams, more tertiary waste streams, and larger volumes of each. For example, RO concentrate is a new secondary stream. It is generated whenever the MTP operates, and is generated at the rate of 6,000 gallons for every 20,000 gallons of raw influent. This stream did not exist prior to March 1999.

A tabulation of the nine secondary streams appears in Table I, while 16 tertiary streams are enumerated in Table II. (Note: Clarifier chemicals are listed as a secondary stream. Although not generated as a result of MTP operations, this liquid stream adds significantly to the volume of waters processed through the MTP. It is included in this study because elimination of the stream or reduction of its volume would reduce quantities of most other secondary and tertiary streams.)

Volume estimates for the streams listed in Tables 1 and 2 come from a variety of sources, including the RLWTF annual reports, data from the plant test in May 2000, measurement of the flows of streams that are not metered, and estimates from experienced plant personnel. A summary of flows normalized to one day of operation is shown in Figure 1. The figure clearly shows the immense burden placed upon the RWLTF by the generation of so many secondary and tertiary streams. Because so many secondary
streams are recycled to the MTP, actual volumes of water treated are about 50% higher than the volume of waste waters sent to the RLWTF by LANL generators.

**Major Problem Streams**

Of all the secondary and tertiary waste streams presented in Tables 1 and 2, most problems can be represented and summarized in just four streams – RO concentrate (6,000 gallons per day or gpd), chemical addition to the clarifier (2,500 gpd), TUF concentrate (1,500 gpd), and waters used to clean, rinse, and backwash (1,800 gpd). Combined, these streams recycle about 10,600 gallons per day to the MTP (more than 50% of plant influent), and send another 1,200 gpd to the troublesome and expensive interim evaporator. They formed the focus for the remainder of the Secondary Stream Study.

**SOLUTIONS THAT ELIMINATE OR REDUCE SECONDARY STREAMS**

This section presents likely and potential solutions that would be achieved through MTP process modifications that would eliminate or reduce the four “focus” secondary streams. The team arrived at recommendations that would eliminate three of the four focus streams, with flows totaling 9,000 gallons per day. It is of note that no additional unit operations are required to achieve this elimination. The installation of tanks, piping, and controls will accomplish the task. Modifications that may reduce other secondary stream volumes were also recommended.

**Elimination Of RO Concentrate**

Meeting discharge limits without use of the reverse osmosis unit, and thereby eliminating the RO concentrate stream, was the most important recommendation to come out of the Secondary Stream Study. At 6,000 gallons per day, RO concentrate is the largest secondary stream. It is also the most troublesome stream to treat, and is processed through the EDR, the interim evaporator, drying, and solidification. Even worse, 80% of this stream is recycled back to the MTP for yet more treatment (EDR product, at a rate of 4800 gallons per day) because its radioactivity exceeds discharge limits. Finally, RO concentrate is easily the most expensive secondary stream to treat, requiring an estimated one-fifth of the RLWTF budget.

Despite the challenges presented by this secondary stream, operating experience showed that it can be eliminated. This was the case during the plant test in May 2000 (when influent radionuclide concentrations were about half those typically encountered), and also upon occasion in the months following the plant test. Elimination of the stream can occur when the TUF permeate meets discharge limits for radioactivity and nitrates and, therefore, can be discharged without further treatment.

In order to *routinely* achieve this level of water purity in TUF permeate, upgrades are needed to the clarifier and sand filter, and equipment and tanks must be installed that will allow improved MTP feed preparation. In addition, storage tanks are needed so that the TUF permeate can be routinely collected, sampled and analyzed, rather than being directly pumped to, and processed through, the RO unit. These MTP modifications are described in the following paragraphs.

**Feed Preparation**

The benefits of aging, oxidation, batch feed, and batch characterization are evident from the review of published literature at large, the review of RLW treatment processes at other DOE facilities, and bench-scale and full-scale tests conducted at the RLWTF. For example, a quick survey uncovered seven published articles that report evidence of microflocculation due to oxidation. Internally, a study was performed in which the gross alpha content of filtrate obtained by passing influent through a 0.45-micron
filter was reduced from 4,000 to less than 30 pC/L through periodic mixing and aeration over a 20-week period.

None of these feed preparation steps are undertaken at the RLWTF. For example, plant influent exhibits large variations in flow, chemical constituents, and constituent concentrations. In addition, on an irregular basis, significant quantities of surfactants, detergents, and chelating agents are in the stream. When this variable influent is mixed with the numerous secondary streams returned to the MTP, an even larger variation exists in the influent to the clarifier. The ability to collect and characterize large batches of feed would eliminate this variability, and the process upsets that result.

Feed preparation would require three large influent tanks (50,000-100,000 gallons each), similar to the systems employed at Savannah River and Hanford. (SRS uses three 500,000-gallon tanks, each providing about 50-hours of RLW inventory.) While one tank is being used to feed the MTP, a second tank is receiving fresh influent, and the third is being prepared (homogenization, sampling, and analysis) as the next batch of feed.

Engineering evaluation and bench-scale tests are needed before selection of the oxidation method. Techniques include aeration, chemical addition (ozone, chlorine, permanganate), or the use of mixed oxidants. Full-scale plant tests should be performed after completion and analysis of bench tests. Feed preparation could be achieved within a year of bench tests. Procurement and installation of the feed tanks could proceed in parallel with plant tests, and selected oxidation equipment subsequently installed.

**Clarifier Upgrades**

The clarifier is well-designed, and operates below normal industry loading rates of 400-600 gallons/day/ft$^2$ overflow rate and 10,000 gallons/day/linear foot weir loading. This fact, coupled with periods of good performance, suggests that periods of poor performance are related to influent variation and chemical feed problems rather than physical shortcomings. Evaluations and historical data show that the clarifier has the potential to be a true workhorse with reduction in radioactivity approaching a factor of 100 when it is operating well.

However, process control must be improved for this unit operation. The following facts are either well-known, documented, or both:

- There is non-functioning instrumentation for metering or controlling influent feed rates and chemical additive rates.
- The possible sequence for mixing influent and chemicals can be improved.
- Substitution of caustic soda for lime may greatly reduce problems encountered in the treatment of secondary streams. (Sodium is highly soluble; calcium is not.)
- Polymers are used universally to enhance coagulation, flocculation, and precipitation. Bench tests have also confirmed this fact, yet we do not use polymers.

Polymer and chemical addition tests have been limited to jar tests. Larger-scale testing should be considered prior to introducing process changes. Tests would also be justified to assess the effect of polymers on membranes and rotary vacuum filter cake.

Upon completion of tests, controls and instrumentation would be purchased and installed. Minor piping modifications would be required. A tank would be needed for polymer preparation. Another tank would be needed for storage of process waters (TUF permeate or sand filter effluent or EDR product) to be used for chemical make-up. Clarifier upgrades could be achieved within a year of completion of testing.
Sand Filter Upgrades

It has been documented that the existing sand filter has a capacity of 135-225 gallons per minute, or as much as four times as large as currently needed. While excess capacity is desirable, there is currently no method to isolate one of the two filter cells. Isolation would provide flexibility to, for example, refurbish one cell while the other is in use, or to filter overflow from the MTP in one cell while the other is used to filter overflow from the treatment of RO concentrate. In addition, channeling is widespread due to deterioration of the sand filter media, and much of the upper layer of anthracite has washed away. The unit is also original equipment, and risk of failure exists.

In the short term, additional anthracite should be obtained and installed to return layer thickness to its design basis. A tank should be installed for the storage of process waters to be used for backwashing, rather than tap water. (This could be the same tank used for storing process waters for chemical make-up, as discussed above.) In parallel, installation of a contained pressure sand filter should be evaluated. The pressure filter would provide redundancy and flexibility. All of these upgrades could be achieved within a year of approval and funding.

TUF Permeate Tanks

TUF permeate is known to meet DCG guidelines upon occasion. Whenever this occurs, the RO can be bypassed, and the RO concentrate stream, fully 30% of plant influent, is eliminated. Improvements brought about by recommendations for feed preparation, clarifier upgrades, and sand filter upgrades will increase the frequency with which this welcome event occurs.

In order to accommodate this new mode of operation, two or three tanks, each of about 20,000-gallon capacity, would need to be installed to collect, sample, and analyze TUF permeate. In the likely event that TUF permeate met DCG and nitrate limits, these would act as effluent tanks. Should TUF permeate exceed discharge standards, it would be directed to the RO unit for additional treatment. TUF permeate tanks could be operational within a year of approval and funding.

RO Operation at 90% Recovery

At least two years will be required for design, installation, and startup of process modifications needed to routinely generate discharge-quality TUF permeate. The study team recommended a process change that, in the interim, halved the volume of the RO concentrate secondary stream to 3,000 gallons per day.

When first installed in early 1999, the RO unit was operated with 90% recovery. At the time, however, RO concentrate was recycled directly to the MTP, and the clarifier was not being used. This process strategy re-introduced all the impurities that had been filtered out by the RO. The practice was abandoned, and recovery reduced to 80%, when fouling and scaling affected membrane quality and life. Since that time, however, the practice of recycling RO concentrate to the MTP has been discontinued. Part of the concentrate stream is now treated via evaporation, drying, and solidification, steps that provide a sink for removal of impurities.

It was possible, therefore, that 90% recovery could work. To test the theory, a full-scale plant study was undertaken. Plant conditions were closely monitored, and samples of RO and EDR streams analyzed for several weeks as recovery rates were slowly increased. Tests proved successful. Today, the RO unit is routinely operated at 88-90% recovery whenever used, and volume of the RO concentrate stream has been successfully halved.
Elimination of Clarifier Chemicals as a Secondary Stream

At 2,500 gallons per day, clarifier chemicals have a larger volume than all other secondary streams except for RO concentrate. The stream is generated by using tap water for the dissolution of chemicals (ferric sulfate and lime) added to the clarifier to promote flocculation and precipitation. This six gallons per minute must then be processed, as though it were RLW, through all five MTP unit operations. In turn, this processing contributes to the generation of all the other secondary streams. The use of tap water to dissolve chemicals is unnecessary, however, because the RLWTF produces several process streams that could be used instead of tap water and because the dissolution takes place entirely within a contaminated area.

The study team recommended that process water be used instead of tap water for dissolution of clarifier chemicals. Sand filter effluent would be preferable, but RP filter effluent or TUF permeate would also work. Two storage tanks with level controls would have to be purchased and installed. The system should be designed to draw make-up water from the preferred tank (sand filter effluent) first, and from the alternate tank (e.g., RP effluent) in case the first tank is empty. No studies or tests are required for implementation of this change, and the system could be installed within six months of approval and funding.

Elimination of Cleaning and Backwash Secondary Streams

At 1,800 gallons per day, cleaning and backwash waters are the third largest secondary stream. Cleaning solutions are needed for the three membrane unit operations – TUF, RO, and EDR. The sand and RP filters are the source of backwash waters. Currently, this 1,800-gallon-per-day stream is entirely recycled to the MTP, to be processed through all five MTP unit operations. In turn, this processing contributes to the generation of all the other secondary streams. The use of tap water for backwash is unnecessary because the RLWTF produces several process streams that can be used for this purpose.

It was recommended that process water be used instead of tap water for backwashing the sand filter and RP filter. As above, sand filter effluent would be preferable, but RP filter effluent or TUF permeate would also work. Higher-purity waters are needed for cleaning the TUF and RO membranes, and either RO or TUF permeate would be acceptable. Currently, there is no mechanism for collecting such high-quality permeate for process use. Accordingly, two or four storage tanks with level controls would have to be purchased and installed, one or two each for filter backwash and for membrane cleaning. No studies or tests are required, and the system could be installed within a year of approval and funding.

Other Possible Ways To Eliminate Or Reduce Secondary Streams

There may be other MTP process changes that can eliminate or reduce the volume of the four focus secondary streams. These changes all require study and pilot testing, however, before deciding upon whether or not to implement. The below sections describe the potential process changes. Schedule and cost information cannot be developed, however, until pilot studies have been conducted.

Nanofiltration: The RO uses a thin-film composite polyamide membrane, the very best available. The result is that nearly all impurities are removed; that discharge waters are of higher-than-necessary quality; and that impurity concentrations are increased in secondary streams, which increases processing costs. It would be preferable to allow some salts to be discharged to the environment within state and federal limits. While still yielding high-quality waters, nanofiltration would allow more salts to pass through into the permeate. Silica and monovalent ions like sodium, potassium, and chloride would more easily pass through the membrane, to be discharged to Mortandad Canyon. Design considerations would be needed, however, to limit the amount of monovalent nitrate that would pass through the membrane. Rigorous
pilot and full-scale plant tests would need to precede a commitment to this potential process change, in order to assure that discharge waters would still comply with DOE, EPA, and New Mexico limits.

**Ion Exchange**: Hanford and Savannah River employ ion exchange as a final polishing step after reverse osmosis. Hanford uses a mixed bed ion exchange unit; Savannah River uses anion beds followed in series by cation beds. This raises the distinct possibility that impurities with very tight discharge limits (radioactive species, perchlorates, nitrates) could be selectively removed from treated waters by ion exchange, while leaving acceptable concentrations of other impurities in discharge waters. Under this concept, one or more ion exchange units would be installed as a final polishing step. Ion exchange could replace RO, could be used to treat RO permeate, or could be coupled with the recommended nanofilter. A rigorous pilot test would need to precede a commitment to this process change, in order to assure that discharge waters would still comply with DOE, EPA, and New Mexico limits. The pilot test would also need to assess quantities of regenerant solutions, chemicals needed to regenerate the ion exchange beds, treatment of regenerant solutions, and/or the use of disposable ion exchange resins.

**Membranes That Can be Backwashed**: Several manufacturers have recently begun to offer membranes that can be cleaned by backwashing. These systems can be operated at low pressures (thereby improving process safety and costs), claim to extend membrane life, and swap a concentrate stream for a backwash secondary stream, possibly of lower volume. The primary advantage such a system would offer to the RLWTF, however, is simplicity and reliability since the existing TUF has more than 2,000 failure points (flanges, valves, and controls).

Accordingly, it may be possible to replace the existing TUF with an ultrafilter that can be backwashed, or to install a second, redundant ultrafilter that can be backwashed. Much is unknown about this emerging technology, however. Literature indicates that these membranes have been used in the production of drinking water for municipal systems, but not for the treatment of industrial waste waters. Volumes of backwash solutions would have to be assessed, and compared to volumes of TUF concentrate generated within the MTP. Permeate quality would need to be scrutinized, and compared to the quality obtained by the TUF.

**DIRECT TREATMENT OF SECONDARY STREAMS**

Direct treatment serves as a last option to resolve problems created by secondary streams. Due to the low priority given direct treatment, only three direct treatment options were presented by the study team for consideration, two for RO concentrate and one for TUF concentrate.

**Precipitation of RO Concentrate**

Reverse osmosis concentrates soluble water impurities in its reject stream. In particular, silica and calcium are present in the RO concentrate stream to the extent that they precipitate out during the ensuing EDR and evaporation treatment steps. It would be beneficial, therefore, to precipitate impurities from the RO concentrate, before unplanned and unwanted precipitation occurs at downstream locations.

This could be accomplished by using Clarifier #1, which has been idle for four years, to treat and precipitate impurities from RO concentrate. This may allow the EDR and evaporation units to more highly concentrate the RO reject stream, thereby lowering the cost to treat this secondary stream. There is also an outside chance that clarification pretreatment could result in an EDR product stream that meets DCG limits. If so, the EDR product stream could be discharged directly, and would not be recycled back through the MTP.
Bench-scale studies have indicated some potential benefits from this treatment. Full-scale testing in Clarifier #1 is needed, however, before routine implementation. If full-scale tests were successful, small chemical supply tanks, controls, and additional piping would be procured and installed. Full-scale testing would require several months. Equipment procurement and installation could subsequently be completed within six months of approval and funding.

**Evaporation of RO Concentrate**

The interim evaporator is designed to process solids-free waste waters. Its 50% downtime has amply proven that it is not designed to process either RO concentrate or EDR concentrate, both of which have high levels of dissolved solids. In contrast, it is known that many different types of evaporator designs exist for processing high-solids waters, and that some evaporators are designed to evaporate liquids to dryness.

Accordingly, one possible solution to the secondary stream problem is the procurement and installation of an evaporator (a) that is designed to process waters that are high in dissolved solids and (b) that is designed to evaporate such waters to dryness. Solar evaporation would be one possible design; mechanical evaporators would provide competing designs.

Available evaporator designs and manufacturers would need to be surveyed, followed by an engineering study to identify advantages and disadvantages of each, including costs. The system could be operational within two years of approval and funding.

**Treatment of TUF Concentrate**

When membrane unit operations were first brought on-line in March 1999, the reject stream from the TUF was further concentrated through a centrifugal ultrafilter, or CUF. Abrasive solids present in high concentrations caused failure of the CUF membrane, however, and the CUF was removed from service. This process scheme was used at a time when the clarifier was not being used and when RO concentrate was recycled directly to the MTP, thus re-introducing all the impurities that had been filtered out by the RO. RO concentrate is no longer directly recycled, so that fewer impurities are re-introduced to the MTP. Other impurities are removed in the clarifier. As a result, fewer solids are now present in the TUF concentrate stream, and it may be possible to return the CUF to service.

A CUF pilot test would be conducted on a portion of the TUF concentrate stream, followed by a full-scale test. Tests would require about six months. If the tests prove successful, the CUF could be returned to service without the need for new equipment, piping changes, or other actions.

**SUMMARY OF RECOMMENDATIONS**

During 1999, the RLWTF changed from a two-step process that had been used to treat RLW for 36 years, to a more complex process that required multiple unit operations for the treatment of primary, secondary, and tertiary liquid waste streams. While the new process provided the ability to meet regulatory discharge limits, its complexity introduced many new secondary and tertiary waste streams. The treatment of these new streams was inefficient and expensive.

In order to correct problems introduced by these new waste streams, a secondary stream study was initiated. In order to arrive at solutions, the study team conducted a full-scale two-day plant test in May 2000 to quantify flows, concentrations, and other information about the new RLWTF processes. The team identified more than 20 secondary and tertiary streams and those four secondary streams that cause most of the processing problems. The team then developed solutions to reduce secondary stream
problems by using personal operational knowledge, results of the plant test, and published studies of RLW treatment at LANL and other DOE sites.

Consistent with universal waste minimization practices, the majority of the problem-solving effort was devoted to the identification of MTP process changes that would eliminate or reduce the generation of secondary waste streams. These solutions are summarized in Table 9-1. The set of recommendations, if implemented, would eliminate the three most offensive secondary streams, which have a total flow of 8,500 gallons per day: RO concentrate, the clarifier chemical addition stream, and filter backwash waters. In addition, RO permeate that does not meet all discharge criteria, but is still of high quality, would be collected for use in flushing and cleaning the TUF and RO membranes, thus eliminating another secondary stream. This solution set requires no additional unit operations, just the installation of tanks, piping, and controls. Table III also summarizes actions that could be implemented in the near-term to reduce some of these flows while the elimination strategies are being pursued.

As an alternative to eliminating and reducing secondary streams, direct treatment of secondary streams was also considered by the team. Possible courses of action are identified in Table IV.

**ACTIONS AND RESULTS TO DATE**

In the months since the RLWTF Secondary Stream Study was completed, two of the recommendations have been implemented, and several others started.

The recommendation to operate the reverse osmosis unit at 90% recovery was implemented almost immediately. Recovery was inched upward in one- or two-percent steps over a four-week period. Effects on operations and other processes were evaluated before deciding to incrementally increase recovery again. Today, the RO is routinely operated at 88%-90% recovery, which approximately halves the volume of the RO concentrate stream.

Substitution of process water for tap water for the preparation of clarifier chemicals has also been accomplished. Piping modifications now direct a portion of sand filter effluent to the chemical dissolution tanks. The net result is a reduction in secondary stream volume of about 2,500 gallons per day.

The most significant immediate result of the Secondary Stream Study, however, has been a change to plant operating philosophy. The RO is now viewed as a reserve process step, to be used only if TUF permeate does not meet discharge standards. TUF permeate is now routinely sampled for water quality, and the RO used only when necessary as a final polishing step. Currently, the RO is pressed into service less than half the time. When feed preparation equipment upgrades discussed in Section 6 have been implemented, use of the RO unit should drop to less than 10% of the time. Whenever the RO is bypassed, the EDR, evaporator, and drying operations can be idled. The net result is a reduction in secondary stream volume of about 6,000 gallons per day.

Finally, several recommended pilot and plant studies have been started. These include feed oxidation plant tests, and bench tests for polymer addition, nanofiltration, and ion exchange. In addition, sand filter refurbishment is underway.

As a result of recommendations already implemented, operations have quieted significantly compared to one year ago. Secondary stream volumes have been nearly halved, and five unit operations are idle more often than they are in service. With most recommendations from the Secondary Stream Study yet to be implemented, it becomes increasingly likely that processing problems will be controlled as projected.
REFERENCES


Table I. Secondary Waste Streams

<table>
<thead>
<tr>
<th>Unit Operation</th>
<th>Secondary Stream</th>
<th>Normalized Flow (^a)</th>
<th>Current Disposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clarifier</td>
<td>Chemicals</td>
<td>2,500 gpd</td>
<td>Clarifier</td>
</tr>
<tr>
<td>Clarifier</td>
<td>Sludge (^b)</td>
<td>380 gpd</td>
<td>Vacuum filter</td>
</tr>
<tr>
<td>Sand filter</td>
<td>Backwash solution</td>
<td>680 gpd</td>
<td>MTP (^c)</td>
</tr>
<tr>
<td>RP filter</td>
<td>Backwash solution</td>
<td>320 gpd</td>
<td>MTP</td>
</tr>
<tr>
<td>RP filter</td>
<td>Cartridge filters</td>
<td>---</td>
<td>Solid waste</td>
</tr>
<tr>
<td>TUF</td>
<td>Concentrate</td>
<td>1,500 gpd</td>
<td>MTP</td>
</tr>
<tr>
<td>TUF</td>
<td>Cleaning solution</td>
<td>300 gpd</td>
<td>MTP</td>
</tr>
<tr>
<td>RO</td>
<td>Concentrate</td>
<td>6,000 gpd</td>
<td>EDR</td>
</tr>
<tr>
<td>RO</td>
<td>Cleaning solution</td>
<td>500 gpd</td>
<td>MTP</td>
</tr>
</tbody>
</table>

\(^a\): Based upon 20,000 gallons of influent  
\(^b\): Volume of sludge and water pumped from the clarifier  
\(^c\): Recycled to the head of the Main Treatment Plant

Table II. Tertiary Waste Streams

<table>
<thead>
<tr>
<th>Unit Operation</th>
<th>Tertiary Stream</th>
<th>Normalized Flow (^a)</th>
<th>Current Disposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sludge Tank</td>
<td>Decant</td>
<td>250 gpd</td>
<td>MTP</td>
</tr>
<tr>
<td>Vacuum filter</td>
<td>Filter cake</td>
<td>220 drums/yr.</td>
<td>Solid waste</td>
</tr>
<tr>
<td>Vacuum filter</td>
<td>Filtrate</td>
<td>1,000 gpd</td>
<td>MTP</td>
</tr>
<tr>
<td>EDR</td>
<td>Product</td>
<td>4,800 gpd</td>
<td>MTP</td>
</tr>
<tr>
<td>EDR</td>
<td>Concentrate</td>
<td>1,200 gal/d</td>
<td>Evaporator</td>
</tr>
<tr>
<td>EDR</td>
<td>Off-spec product</td>
<td>b</td>
<td>Evaporator</td>
</tr>
<tr>
<td>EDR</td>
<td>Electrode waste</td>
<td>b</td>
<td>EDR</td>
</tr>
<tr>
<td>EDR</td>
<td>Cleaning solution</td>
<td>b</td>
<td>Evaporator</td>
</tr>
<tr>
<td>EDR</td>
<td>Cartridge filters</td>
<td>---</td>
<td>Solid waste</td>
</tr>
<tr>
<td>Evaporator</td>
<td>Condensate</td>
<td>900 gpd</td>
<td>Outfall</td>
</tr>
<tr>
<td>Evaporator</td>
<td>Bottoms</td>
<td>300 gpd</td>
<td>Off-site solidification</td>
</tr>
<tr>
<td>Evaporator</td>
<td>Cleaning solution</td>
<td>100 gpd</td>
<td>Off-site solidification</td>
</tr>
<tr>
<td>Evaporator</td>
<td>Cleaning solution rinse</td>
<td>100 gpd</td>
<td>MTP</td>
</tr>
<tr>
<td>Evaporator</td>
<td>Cooling tower bleed</td>
<td>3,000 gpd</td>
<td>Sewage plant</td>
</tr>
<tr>
<td>Evaporator</td>
<td>Boiler blowdown</td>
<td>200 gpd</td>
<td>MTP</td>
</tr>
<tr>
<td>Off-site solidification</td>
<td>Evaporator solids</td>
<td>50 drums/yr.</td>
<td>Solid waste</td>
</tr>
</tbody>
</table>

\(^a\): Based upon 20,000 gallons of influent  
\(^b\): Included in EDR concentrate stream
Table III. Solutions That Eliminate or Reduce Secondary Streams

<table>
<thead>
<tr>
<th>Stream</th>
<th>Recommended Solution</th>
<th>Benefit</th>
<th>Risk</th>
</tr>
</thead>
<tbody>
<tr>
<td>RO Concentrate (6,000 gpd)</td>
<td>1. Generate TUF permeate that meets DCGs via:</td>
<td>1. Eliminates the stream.</td>
<td>1. Need to closely monitor nitrate concentration in TUF permeate.</td>
</tr>
<tr>
<td></td>
<td>a) Feed preparation</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>b) Clarifier upgrades</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>c) Sand filter upgrades</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>d) TUF product tanks</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2. Operate the RO at 90% recovery</td>
<td>2. May reduce stream volume by 50%.</td>
<td>2. Will likely reduce membrane life.</td>
</tr>
<tr>
<td></td>
<td>3. Nanofilter (Requires a pilot test.)</td>
<td>3. May reduce the stream.</td>
<td>3. May not remove nitrates.</td>
</tr>
<tr>
<td>Clarifier Chemicals (2,500 gpd)</td>
<td>1. Reduce makeup flow rates.</td>
<td>1. May reduce stream volume by 50%.</td>
<td>1. Plugging of chemical feed lines.</td>
</tr>
<tr>
<td></td>
<td>2. Use sand filter effluent, RP filter effluent, or TUF permeate instead of tap water.</td>
<td>2. Eliminates the stream.</td>
<td>2. Use of contaminated waters.</td>
</tr>
<tr>
<td></td>
<td>3. Characterize waste; meter chemical addition via feed preparation and clarifier upgrades.</td>
<td>3. Likely reduces the stream by 50-60%.</td>
<td>3. Chemical reduction can result in TRU sludge.</td>
</tr>
<tr>
<td>TUF Concentrate (1,500 gpd)</td>
<td>1. Modify TK-72 flows, and then the frequency of TK-72 purges.</td>
<td>1. Reduces the stream by 50-75%.</td>
<td>1. None.</td>
</tr>
<tr>
<td></td>
<td>2. Install membranes that can be backwashed. (Requires pilot tests.)</td>
<td>2. Reduces the stream by 70-80%.</td>
<td>2. New technology.</td>
</tr>
<tr>
<td>Cleaning and Backwash Solutions (1,800 gpd)</td>
<td>1. Use sand filter or RP filter effluent instead of tap water to backwash the sand and RP filters.</td>
<td>1. Eliminates the backwash stream.</td>
<td>1. None.</td>
</tr>
<tr>
<td></td>
<td>2. Use TUF permeate for cleaning and flushing of the TUF, EDR, and CUF. Use RO permeate for cleaning and flushing of the RO.</td>
<td>2. Reduces the cleaning stream by 70%.</td>
<td>2. None.</td>
</tr>
</tbody>
</table>
Table IV. Solutions That Directly Treat Secondary Streams

<table>
<thead>
<tr>
<th>Stream</th>
<th>Potential Solution</th>
<th>Benefit</th>
<th>Disadvantage</th>
</tr>
</thead>
<tbody>
<tr>
<td>RO Concentrate (6,000 gpd)</td>
<td>1. Treat EDR Product in Clarifier #1. (Requires a pilot test.)</td>
<td>1. May eliminate the recycle of EDR Product stream (4800 gpd).</td>
<td>1. Still leaves 1200 gpd to process through the evaporator.</td>
</tr>
<tr>
<td></td>
<td>2. Install different evaporator. (Requires an engineering study and pilot tests.)</td>
<td>2. Reduces evaporator costs. May eliminate shipments of bottoms to Tennessee.</td>
<td>2. Still leaves 4800 gpd of EDR product recycled to the MTP.</td>
</tr>
<tr>
<td>Clarifier Chemicals (2,500 gpd)</td>
<td>None.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TUF Concentrate (1,500 gpd)</td>
<td>1. Re-install the CUF</td>
<td>1. Removes suspended solids and organics that would otherwise be recycled to the MTP.</td>
<td>1. Generates CUF filtrate, which must be recycled to MTP.</td>
</tr>
<tr>
<td>Cleaning and Backwash Solutions (1,800 gpd)</td>
<td>None.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fig. 1. Normalized RLWTF Flow Rates

Cemented Sludge to TA-54

Figures are gallons per day. * Small, occasional flows

Caustic wastes

Influent 20,000

TUF Concentrate 1500

EDR Product 4800

Clearing Solutions 800

Filter Backwash 1000

Vacuum Filter 350 Decant & Filtrate 44

Filter Pre-coat 14

Sludge to TA-54

Chemicals (2500)

28,500 Clarify

Sand Filter Backwash

RP Filter Backwash

TUF Concentrate 380 Backwash

1500

RO 29,100

6000

EDR Product 4800

1200

Evaporator 900

Solidify 300
to TA-54

High-nitrate wastes

Concentrate 4800

Product 1500

Filter Sludge High-nitrate Backwash to TA-54
Fig. 2. RLWTF Process Data for 05/02/00 Parameter: Total Suspended Solids

**Volume (LPH):**
- CLI 75K Tank 10,700
- Chemicals + seal water 1,400
- TK71 570
- TK72 620
- TK-9 3,300
- ROP 13,200

**Conc. (mg/L):**
- CLI 1,400
- 75K Tank 119
- ROP 0

**Mass (g/h):**
- CLI 1,280
- Chemicals + seal water 190
- TK71 1
- TK72 7
- TK-9 1
- ROP 0

* Estimate