VIRGINIA POWER LIQUID RADWASTE CHARACTERIZATION PROGRAM

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ABSTRACT

Virginia Power, utilizing B&W as a subcontractor, recently completed a 16 month program designed to characterize the liquid waste streams of the radwaste systems at the North Anna and Surry Nuclear Stations. Four hundred twenty samples were analyzed for up to forty different parameters. Sample stream selection, analysis selection, and required frequency of sampling for the characterization program were some of the key decision elements of this program; these were selected based on such factors as flow rates, suspected quantities of problem species present, existence of previous data and plant power history. The characterization program disclosed some previously unknown stream characteristics including the presence of oil, grease, and/or detergents in many streams. This characterization data is being used in the design of new radwaste treatment facilities at each of the Virginia Power plants.

INTRODUCTION

Virginia Power has made a decision to design and install a new radwaste treatment facility at both their North Anna and Surry Nuclear Power Stations. The program implemented to carry out this project has three phases: 1) conceptual design, 2) final design, and 3) equipment procurement and facility installation During the conceptual design phase, The Babcock & Wilcox Company was contracted to conduct a Liquid Radwaste Characterization Program involving the comprehensive analysis of over 400 radwaste samples taken at the two stations over 16 months. This paper will address 1) the purpose of the characterization program, 2) how the program was set up, in particular, such details as source stream selection, analysis selection, sample periodicity, supporting site data requirements, and sampling requirements, 3) how the sample batches were processed, 4) the results of the characterization program, and 5) how the resulting data was reduced and utilized in support of the radwaste facility design to date.

PURPOSE OF CHARACTERIZATION PROGRAM

Simple schematic diagrams of the liquid radwaste systems for each of the plants are shown in Fig. 1 and 2. Both plants are no longer using portions of the treatment systems because of higher than expected flowrates, undersized equipment, and subsequent difficulties with waste segregation.

Both stations generate large volumes of water contaminated with low levels of radioactivity. The streams also contain varied quantities of nonradioactive species dependent upon the stream's origin. Typical species will be cesium, cobalt, and iodine contamination, and dosium, chloride, magnesium, calcium, organics, and oil. The nonradioactive species may be present in concentrations 10^6 to 10^{12}-times higher than the radioactive species. Both radioactive and nonradioactive species characterization is necessary to properly design the required treatment systems. Typical questions which needed to be addressec in the treatment design include:

Is segregation of wastes necessary and, if so, to what degree?
Can partial segregation be achieved within the original design constraints?
Is pretreatment of an influent stream necessary?
Is ion-exchange or evaporation or both required?
Is a nonradioactive specie detrimental to a particular treatment?
What are proper materials of construction for the treatment systems?
What ion exchange resins would be appropriate for the radioactive species? What capacity equipment is required?

Since limited data was initially available at North Anna or Surry, a characterization program was instituted to help answer questions such as these.

Project Scope Definition

The chemical and radioactive characteristics of each waste stream must be understood to answer the questions posed above. The selection of the optimum waste treatment processes and systems, depends on the chemical species and quantity present in each stream. For example, with ion exchange processing being considered, one emphasis is on ion-exchange media and pretreatment selection; with characterization data, resin loading and filter fouling can be determined more easily. The radioactive species will help determine the life of system components based on the radiation levels expected from loaded resin beds and filters. Previous work at the Millstone plant helped B&W to identify chemical species that would contribute to premature loading of resins or fouling of filters. If these were identified in particular waste streams, arrangements could be made to eliminate the source of the problem species or pretreat the particular stream to eliminate or reduce the problem.

Analyses were selected on the basis of ion exchange and evaporation as the major waste treatment processes. Therefore ion loading, particulate loading, radionuclides, and detrimental species were the major concerns. A complete list of analyses is shown in Table I. With regard to stream selection, initially all the streams with potential for waste production were sampled. After a baseline of types and quantities of species present was established, and trends noted, only the sampling of streams with higher flowrates and higher concentration was continued. Streams initially monitored are those shown in Fig. 1 and 2 which had adequate flowrates to allow sampling. The initial sampling was at a frequency of once per week. As the program progressed, sampling frequency was reduced to twice a month and finally to once a month. Data was collected over an extended period to get maximum of each of the species in each of the major contributing streams during different operating modes such as normal, reduced power, transients, and outages.

TABLE I

Parameters Measured

pH
Conductivity
Total Suspended Solids
Total Organic Carbon
Oil and Grease
Detergents
Boron
Silica
Ammonia
Hematite
Magnetite
Sulfate
Sulfite
Nitrate
Phosphate
Chloride
Calcium
Sodium
Potassium
Iron

Magnesium
Manganese
Chromium
Gross Beta
Colloidal Cobalt
Gamma Isotopes
Mn-54
Co-58
Co-60
I-131
Cs-134
Cs-137
Ru-106
Sb-125
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Fe-59
Zr-95
Nb-95
Ag-110m

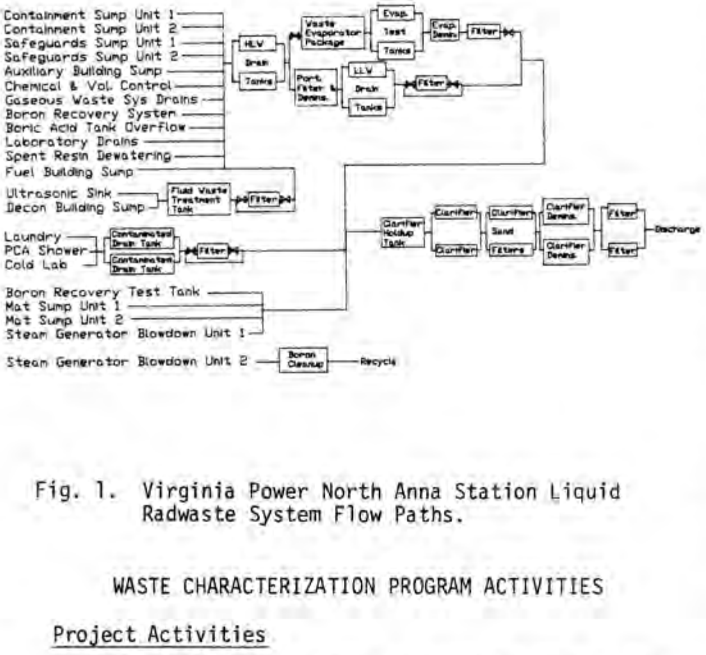

Fig. 1. Virginia Power North Anna Station Liquid Radwaste System Flow Paths.

WASTE CHARACTERIZATION PROGRAM ACTIVITIES

Project Activities

Virginia Power personnel collected samples from the individual sample sumps, tanks, and flow points. Where possible, tanks and sumps were recirculated to obtain representative samples. Sample lines were flushed to remove standing fluid. Three bottles were filled at each sample location-one 1000 ml glass bottle and two 1000 ml plastic bottles.

After sampling, the bottles were further processed in the Surry and North Anna chemistry laboratories. Five ml of sulfuric acid was added as a preservative to the 1000 ml glass bottle. The sample in one of the 1000 ml plastic bottles was filtered. The filtered liquid was transferred to a 125 ml plastic bottle and 0.5 ml nitric acid preservative was added. The remaining 1000 ml plastic bottle did not have any preservative added. During Phase III, a 125 ml aliquot of the filtered liquid from each of the High Level Waste Collection Tanks was transferred to another plastic bottle without preservative. The samples were then prepared for shipment to B&W's Lynchburg Research Center (LRC).

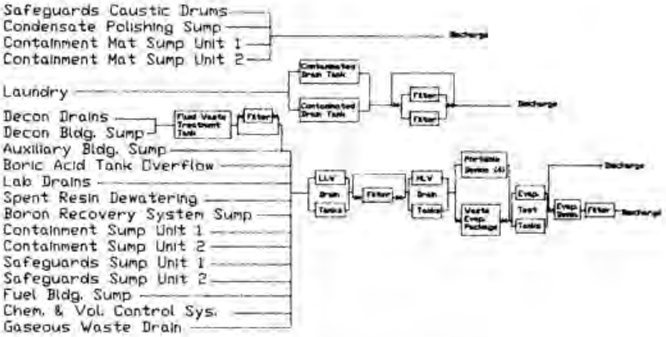

Fig. 2. Virginia Power Surry Station Liquid Radwaste System Flow Paths.

After sample receipt at LRC, the samples were separated for their subsequent analysis analysis. The glass bottle was used for total organic carbon (TOC) and oil & grease analysis. The TOC analysis required approximately 5-10 ml of sample. The oil and grease analysis used the remaining sample volume and the sample bottle was repetitively rinsed with solvent to extract the oil and grease. The 125 ml bottle with nitric acid was used for calcium, sodium, potassium, magnesium, iron, manganese, and molybdenum analysis by atomic adsorption. The 125 ml bottle without preservative was analyzed by atomic adsorption for total chromium.

The 1000 ml plastic bottle was used for the remaining analyses. First, the pH and conductivity were determined. The sample was then filtered through a 5.0 micron and 0.45 micron filter. The filters were used to determine the total suspended solids. The filters were subsequently counted by gamma spectrometry to determine the radiologic species. During Phase I, a portion of the original sample was filtered through a separate 0.45 micron filter which was analyzed for ferric oxide (hematite) and ferrous oxide (magnetite). The filtered liquid sample was then analyzed for boron by titration, detergents by surface tension, silica by calorimetric method, ammonia by titration, gross beta by liquid scintillation, chloride, sulfate, sulfite, nitrate, and phosphate by ion chromatography, and radiologic species by gamma spectrometry. During Phases II and III, colloidal cobalt was determined by ultrafiltration of the colloidal species and subsequent gamma analysis.

Because of the large number of samples, accurate tracking of the samples from the Virginia Power sites through the laboratory analytical process was a necessity. During the initial phase, as many as three batches of 33 samples with three sample bottles per sample were in the laboratory at one time. Each sample bottle was assigned a number based upon the sample point and the sampling batch. By the end of the program a total of 20 batches of samples had been analyzed. Data sheets for each of the batches of samples were used for record keeping. Subsequently the data was transferred to a computer spreadsheet for transfer to Virginia Power and for ultimate data reduction.

After the completion of Phase I, the data was evaluated to determine which streams and types of analysis should be modified. Analyses were deleted if they met three criteria: 1) the data obtained in batches 1 to 4 indicated no unusual or unexpected results, 2) no significant fluctuations in the data were expected with changes in plant operating status, and 3) additional data was not considered necessary to support data evaluation or comparison with other results. On the basis, gross beta, silica, iron oxides, molybdenum, and manganese were eliminated from the analysis program. In addition, the performance of several of the reamining analyses was limited to only certain samples.

Certain waste streams were also deleted at the end of Phase I. Selection for deletion was based upon the above criteria and if it had been determined that they would not be processed by the proposed radwaste facilities. Streams deleted from the program included the following North Anna streams: boron recovery system, laboratory drains, mat sump units I & 2, ultrasonic sink, and steam generator blowdown units I & 2. Deleted streams for Surry included: subsurface drains unit I & 2, yard pad sump, and boron recovery test tank.

Changes to the program for the final phase, Phase III were minimal. The concept was to ensure data was obtained during plant transitions such as power escalation, shutdown, and refueling, since a majority of the Phase I and II samples were obtained during full power periods. The ammonia and magnesium analyses were deleted.

The data produced was evaluated for trends at the end of the analysis program. Data reduction included maximums, minimums, averages, and standard deviations for each of the analyzed parameters for all of the streams. Graphs of parameters versus time for all the Phase III streams were made for the following parameters: pH, conductivity, boron, total suspended solids, total organic carbon, oil and grease, total anions from ion chromatography, total cations from atomic absorption, summation of gamma isotopes for the filtrate, and summation of the gamma isotopes for the filters.

PROGRAM RESULTS

Each of the 25 chemical parameters and 29 radiochemical parameters analyzed for each batch of samples was reported. The data in this form can lead to dubious design results due to the unknown uncertainty associated with the data. Therefore, all the batches of data were statistically reduced. The statistical data document the actual ranges of the parameters. Radwaste system design would rely heavily on the maximum or average values for each parameter depending upon the parameter. Most of the minimum values are actually the chemical analytical lower limit. Many of the parameters did show wide variations over the sampling period. A plot of conductivity versus time for three samples at North Anna is shown in Fig. 3. Plots of this type can be compared to the plant status to determine the effect of various plant perturbations such as shutdown and power escalation.

PRELIMINARY DATA EVALUATIONS AND APPLICATION

Thorough evaluation of data will be part of the future activities associated with detailed equipment and facility engineering, however, following are noteworthy conclusions from the data evaluation performed to date, along with their impact on the conceptual design (Refer to Table II for supporting data):

1. Oil and grease contamination levels are in the range 5 ppm to 1,800 ppm which is significantly high. A gross oil separator followed by a fine oil separator to lower the oil contamination down to 5 ppm is planned. Observation of data from individual streams indicates that about five sources contribute more to oil contamination than others. Corrective actions are planned to reduce oil from these sources.

2. Radioactivity levels average 2.2E-3 uCi/cc at North Anna and 2.6E-2 uCi/cc at Surry which are an order or two magnitude higher than normal. Several instances of significant primary system leaks were observed during this program. High activity levels indicate that primary system leaks must be significantly reduced. Because of such high levels of activity and Virginia Power's goal of discharging nearly zero activity to the environment, evaporation has been planned as a "primary" means of treating liquid waste. The "secondary" means of liquid waste treatment will be by ion-exchange but the characterization data is expected to help determine optimum resin loading.

3. The proportion of soluble radionuclides in the composite stream (excluding laundry waste) is approximately one-third of the total which is unusually high. In the laundry waste, up to one-half of the radionuclides are present in the soluble form. Normal means of treating laundry, i.e. by filtration would result in significant amount of radioactivity being discharged to the environment and not help meet the discharge goal. Chelating agents are suspected to be the cause of this problem. Alternate laundry detergents that contain lower concentrations of chelating agents are being investigated. Other ideas being considered are: application of newly developed laundry filters, wash laundry twice, once without and then with a detergent; laundry waste from the first wash to be treated by the evaporator whereas that from the second wash filtered and discharged.

4. The concentration of suspended solids greater than 5 micron is very high at both stations. Two major sources have been identified. A pretreatment to remove suspended solids is planned.

5. Sump samples are contaminated with soap and detergents, especially during outages. Use of decontamination solutions, soaps, and detergents only at designated points is planned.

6. Boron concentration in the composite waste stream is very high (up to about 2000 ppm). High boron concentration is likely to load up the ion-exchangers fairly rapidly. High boric acid concentration also limits evaporator capability in processing liquid waste. Major source of boric acid is confirmed to be primary system leakage. Concentration of boric acid as moderator has been reduced as a result of recent

modifications. Virginia Power is also engaged in an R&D effort to determine the feasibility of using enriched boron.

7. The chloride levels at Surry are higher compared to North Anna. This was expected since Surry is a salt water site whereas North Anna is a fresh water site. Although chloride levels are not alarmingly high, present plans are to construct liquid waste treatment system of materials resisting chloride attack such as Alloy 20 and Inconel 625.

8. Other chemical contaminants of note are sulfates, phosphates, TOC, potassium, calcium, and sodium. All of these will contribute to IX loading. Waste streams containing higher than normal concentrations of these chemicals will be segregated as high level and treated by evaporation.

PROBLEMS

This program has not been very successful in characterizing liquid waste considering all plant transients. During plant transients when the waste characteristics are most likely to reach maximums, the plant operator availability was limited due to the urgency of the transient.

The Phase III sampling dates were scheduled to coincide with plant outages and pre-outage transients. On several occasions, the plant outage schedule was shifted and the sampling time missed the transient. Because of the changes in plant operating schedules, an on-site person able to identify impending radwaste system transients is needed.

TABLE II

Liquid Waste Composite Stream
Significant Characteristics

Characteristic	North Anna	Surry
Suspend Solids (>5u) (ppm)	307 (max.) 1 (min.) 60 (ave.)	3600 10 778
Suspended Solids (0.45-5u) (ppm)	12 1 2	248 1 24
Specific Activity (uCi/cc)	1.5 E-2 2.2 E-3 1.3 E-4	1.4 E-1 2.6 E-2 5.4 E-4
Conductivity (s/cm)	3.4 E-4 6.5 E-5 1.8 E-4	3.4 E-4 8.1 E-5 1.9 E-4
Boron (ppm)	1280 46 316	2110 131 691
Oil & Grease (ppm)	1800 5 183	1200 16 330
Total Organic Carbon (ppm)	168 8 37	71 5 23
pH	7.24 6.33 6.67	7.08 5.82 6.61
Chlorides (ppm)	11.2 0.02 3.31	49.8 0.05 22.48

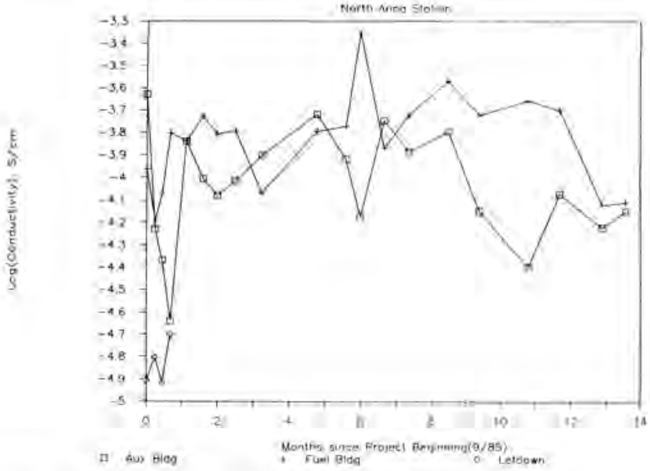

Fig. 3. Building Sump Conductivity at North Anna.

Flowrate data are critical to the radwaste system design. Acquisition of this data was partially successful. Much of the instrumentation is inadequate and will be replaced in the new system. The flowrates obtained were only instantaneous rates rather than accumulative flowrates. Much of the system is operated on a batch basis; therefore, very little can be deduced from the current flowrate data.

CONCLUSIONS

The Virginia Power liquid waste characterization program has been quite beneficial in drawing some obvious conclusions such as the need for source reduction, especially from primary leaks and oil contamination. Some of the not so obvious results such as the presence of high concentration of soluble radionuclides has helped in choosing the treatment options. Raw characterization data has been reduced to usable levels; however, further analysis and interpretation of data is necessary. Continued stream characterization is required to support the new radwaste facility operation. As equipment or operational modifications in the plant are made, the radwaste streams will change, requiring subsequent radwaste operational changes.

Some level of waste stream characterization would be beneficial to all major waste generators. An understanding of the chemical and radiochemical makeup of the waste streams, should serve to identify better ways to operate existing systems or the need for system modifications. For example, characterization would provide a better understanding of the particular sources of detrimental species. Highly chemically contaminated waste streams could be identified and segregated from stream requiring minimal treatment. Radiochemically clean streams could be identified and excluded from the radwaste treatment system. As the radwaste streams change, the data can be used to specify optimum ion exchange media and other waste processing materials. Where problems are from improper usage of materials, administrative controls can be changed to eliminate the problem. In summary, without characterization data, unknown chemical and radiochemical problems could be adversely affecting liquid radwaste processing equipment operation. With such data, the makeup of the plant streams can be understood and system operations modified to best treat the waste streams.