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Continuous Tritium Effluent Water Monitor at the Savannah River Site (U)

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Manager, Environmental Technology Section

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ABSTRACT

A continuous monitor for tritium in water has been installed in the secondary cooling water effluent from the K-Reactor at the Savannah River Site (SRS). The monitor is designed to provide early detection of a small leak of the tritiated heavy water moderator and facilitate rapid isolation procedures. The tritium detector consists of an analysis cell containing 0.1-0.25 mm diameter beads of plastic scintillator interposed between two photomultiplier tubes and standard fast-slow coincidence electronics. A small portion of the effluent stream is first filtered through a series of cartridge filters (0.2 μm final filter) and then chemically treated by ion exchange resin and activated charcoal before reaching the cell. Flow through the detector is ≈3 mL/min. The tritium effluent water monitor (TEWM) will alarm if the tritium in the outfall exceeds 56 Bq/mL during a 10 minute counting interval. The installation and performance of the TEWM are discussed.

INTRODUCTION

The development of a continuous monitor for tritium in aqueous solutions has progressed from laboratory testing to installation in the outfall from the K-Reactor. The K-Reactor is a heavy water moderated reactor at SRS. Secondary cooling of the reactor core is accomplished with water from the Savannah River in a once-through circulation mode. The primary coolant contains high concentrations of tritium which provides a radio-isotopic tracer for leak detection. Traditional methods of sampling and analysis by liquid scintillation counting, however, can result in a considerable delay in detecting a moderator leak. This was evident in the recent unanticipated release of ≈220 TBq of tritium from the reactor to the Savannah River through a leaking heat exchanger. The magnitude, circumstances, and consequences of this release are discussed elsewhere (1). Following the release, the laboratory prototype tritium monitor and pretreatment system were moved to the K-Reactor effluent canal.

The real-time monitoring of tritium provides reactor operators with prompt warning of a leak of moderator and permits rapid initiation of mitigation procedures. An operating TEWM is now a requirement for reactor operation (2). Figure 1 shows a schematic of the location of the TEWM as presently installed on the secondary cooling water outfall from the K-Reactor at the SRS. Transport modeling and dilution of the tritium released in December, 1991 demonstrates that detecting a 18 kg/hour leak of moderator within one hour will result in a concentration of tritium less than the 0.74 Bq/mL EPA guideline (3) at the nearest downstream drinking water intake in the Savannah River. This leak detection limit is based on conservative river flow and assumes the leak is isolated within four hours of detection. At full secondary coolant flow, the required alarm level of the monitor is 130 Bq/mL for tritium.

DESCRIPTION OF MONITOR

The tritium detector consists of a U-tube cell made from thin- walled, 4.8 mm ID FEP teflon filled 0.1-0.25 mm diameter beads of plastic scintillator. The selection of bead sizes and tubing type was chosen after extensive laboratory testing. (4) The analysis cell is placed in a commercially available radio-chromatographic analyzer (5) which consists of a pair of 51 mm diameter photomultiplier tubes and fast-slow coincidence electronics. Water flows through the cell continuously. The tritium beta particle interacts with the plastic scintillator to produce light proportional to the tritium content. The light is amplified and analyzed for amplitude and time coincidence (2t= 100 nsec) producing a pulse signal whose rate is proportional to the tritium concentration. Pulse height analysis discriminates the tritium beta from other background radiations. The tritium and background signals are fed to a data acquisition and analysis system to determine the count rates for a number of preset counting intervals. A more detailed description of the tritium detection system is given in reference 6.

It was determined during laboratory testing that the sample stream must be filtered using fine pore size media; even the slightest film on the beads reduced the tritium detection efficiency because the maximum range of the tritium beta particle is only 6 μm in water. Some chemical and biological species were found to interfere with tritium detection by chemi- or bio-luminescence. During monitor development, many samples from a liquid radioactive waste treatment facility at SRS and from the environment were circulated through the monitor to establish an acceptable chemical cleanup method. Reference 6 describes the sample recirculation system, testing protocols, and the tritium efficiency determination. It was found that luminescence effects were reduced by treating the filtered effluent by ion exchange, biocide, and activated charcoal.

Adequate sensitivity for detecting tritium in the aqueous outfall from the K-Reactor was demonstrated through laboratory testing with spiked and unspiked samples from the Savannah River. The results of one of these tests are summarized in Figure 2. A known, small quantity of tritium standard was added to a one-liter filtered sample of river water and circulated through the monitor. The monitor response was recorded for about 24 hours and another aliquot was added. A total of 10 aliquots of tritium standard were added to the river water sample over a 11-day period. Samples were removed daily for tritium analysis by liquid scintillation counting. The concentration range tested was 0-25 Bq/mL. The correlation coefficient for the linear fit of these data was 0.924. The slope of the data shown in Figure 2 is the tritium detection efficiency (cpm/dpm/mL) and is consistent with that measured in demineralized water standards before and after the spiked sample experiments.

Several experiments were conducted in the laboratory which used large samples (30 liters) removed from one of the local streams. The circulation system was configured to pump the filtered water from one large carboy, through the ion exchange column and then the monitor, and back into a second large carboy. Thus, fresh river water was continuously flowing through the monitor, much the same as if it was in the field. A typical experiment ran continuously for about 10 days at ≈2 mL/min. The relative standard deviations of the monitor count rates in both the tritium and gross-beta counting channels (≈10%) were no different than those obtained with background runs of demineralized water. The tritium detection

efficiency, as determined by introducing a standard with known specific activity before and after the circulation of river water, was unchanged. The 95% confidence level tritium detection limit for a typical 10-day run was 28 Bq/mL in a 10-minute counting interval. These results confirmed adequate sensitivity for sensing a significant tritium release.

Field testing of the filtration system was performed at the outfall from a shutdown reactor of similar design. The results of the tests indicated that water in the effluent canal can be filtered using a 0.2 μm filter cartridge which produces low effluent turbidity (<1 NTU), adequate flow-rate, and acceptable throughput under various environmental conditions. An experiment was conducted for ≈80 days of continuous operation through a single filter cartridge with daily flow and pressure measurements. Samples of the influent and effluent were analyzed for turbidity, suspended solids, conductivity, and pH. Samples of the filtered effluent were periodically returned to the laboratory and circulated through the monitor as confirmation of the pretreatment system performance.

INSTALLATION IN THE K-REACTOR OUTFALL

Following the tritium release from K-Reactor, the components in the laboratory prototype system were assembled into a working system for installation in an existing building about 100 meters from the K-reactor effluent canal. Process tie-ins were made to existing piping (for continuous sampling of water in the canal) to permit near real-time tritium monitoring. A line diagram of the installation is shown in Figure 3. The TEWM consists of three independent, but closely coupled hydraulic systems. In the first system, water is pumped from the canal by a positive displacement tubing pump at 28 L/min (7.5 gal/min) and is pre-filtered through a nominal ≈10 μm pore size CUNO roughing filter. Using a small orifice in the line to develop appropriate back pressure, a 20-50 mL/min side stream is forced through the 0.2 μm polishing filter cartridge and is collected in a small (1000 mL) surge tank. A small portion of the filtered water is then removed from the surge tank and pumped through the analysis cell. The balance of the water from the roughing filter operation and from the surge tank returns to the effluent canal.

A suitable biocide can be introduced into the surge tank for biological control, when necessary. In addition, the surge tank provides positive pressure on the suction side of the metering pump for self-priming, helps remove the air from the super-saturated solution, and provides about 8 hours of holding time for filter changeouts, etc. The latter feature eliminates the need to turn off the monitor for routine system maintenance.

A HPLC metering pump removes water from the surge tank at ≈3 mL/min and pumps it through the analysis cell. The sample is drawn near the discharge line of the polishing filter in the surge tank to reduce response time and dilution. Small bore (1.6 mm ID) teflon and stainless tubing are used throughout this portion of the system to further reduce the response time. Before the filtered water reaches the detector, it passes through a small ion exchange column. The column is loaded with Dowex 50W-X8 strong acid cation exchange resin (50-100 mesh). The column produces an acidic effluent (pH ≈3.5) which minimizes the buildup of amorphous precipitates (e.g., iron or other metal hydroxides) on the scintillation beads. The column is replaced or can be recharged in place using dilute nitric acid. Under some conditions, activated charcoal is added to the ion exchange column to reduce the concentration of organic contaminants in the stream. The analysis cell effluent is collected as a composite sample for chemical and tritium analyses.

The electronic signals from the tritium and gross beta counting channels are analyzed by a firmware-based data acquisition and analysis system (5). This system calculates the count rates from each data channel and compares them to the preset alarm levels. Operating parameters (e.g., alarm levels, counting intervals, etc.) can be changed only by knowledgeable personnel. As presently configured, the system will alarm if the count rates exceed preset values for a 10 second count, a 10 minute count, and a 1 hour count. All of these alarms are received at a local status panel, in the reactor control room, and in the reactor Health Protection Office. The data acquisition system has a line printer to print all alarms and hourly data summaries. The TEWM also includes a strip chart recorder for a hardcopy record of the system count rate.

The TEWM contains flow meters in all three hydraulic systems and pressure gauges on all filters. Many of these sensors provide real-time alarms to operations personnel for any abnormal conditions. The system has provisions for introducing a flush solution and a tritium standard through the monitor for calibration. Grab samples of the pre-filtered influent can be obtained at the polishing filter drain valve.

EXPERIMENTAL

The TEWM has operated continuously since January 3, 1992. The performance of the TEWM and the water purification system have been closely monitored by daily sampling and analyses, daily source checks, and weekly calibrations using tritium spiked solutions. The response time of the filtration portion of the system was determined by introducing dilute nitric acid upstream of the polishing filter with samples taken at the normal tritium standard inlet line (see Figure 3). Figure 4 shows the nitric acid concentration measured in samples removed from the inlet line after the injection of a 0.1N HNO_3 at a temporary polishing filter inlet connection. Thirty-five minutes after acid injection, the system was flushed with demineralized water. The results demonstrated adequate response and less than 10% dilution as the acid passed through the system. The response of the monitor to a tritium standard introduced at the tritium standard inlet during the weekly calibrations has repeatedly shown that an alarm is received about 10 minutes after injection. The time required to pump water from the effluent canal to the building is calculated to be less than 2 minutes. The results of these tests and calculations confirm that the time required to detect elevated tritium in the outfall is less than one hour.

Daily surveillances are performed which include a source check using a Cs-137 external standard, recording of the system flows and pressures, sampling of the influent, and analysis of the influent and effluent composite sample for pH, conductivity, turbidity, dissolved solids, and tritium concentration. These measurements, along with the monitor count rates, are used to evaluate the system performance on a daily basis and to determine when to replace filters, ion exchange resins, and measurement cells. Once per week, a full system calibration is performed using a standard tritium solution to determine the detection efficiency and verify alarm levels.

The results of the system calibrations have shown that the sensitivity of the monitor to tritium concentrations in the outfall changes as the cell is in-service. For a typical new cell, the sensitivity (as determined by a 2-sigma deviation in the background count rate) is $\approx$ 16 Bq/mL for a 10 minute count. Using the formalism of Currie (7), the minimum detectable

concentration is ≈29 Bq/mL. Table I summarizes the sensitivity for detecting tritium by

both methods for several preset counting intervals. Also included in the table are the alarm limits set for the monitor. The alarm limits are chosen to minimize the false alarms received in the control room (< 2E-4 probability). The efficiency of the cell has been shown to degrade about a factor of two over a one week period and is replaced on a 7 day frequency.

TABLE I. Tritium Detection Sensitivity (Bq/mL)

Count Time	2σ dev. background	Minimum* Detectable Concentration	Alarm Level
10 seconds	133	380	400
10 minutes	16	729	56
1 hour	7.4	11	22
		ATTENTION	19
10 hour	4.3	3.3	
24 hour	2.6	2.2	

* calculated per Curie (1968)

The efficiency and response time data confirm that the TEWM has been capable of alerting plant operators to a 18 kg/hr leak of primary coolant at full cooling water as required by the Plant Operating Specifications. Under reduced letdown flow conditions, the TEWM would have alarmed at a leak of primary coolant greater than 2.3 kg/hr. No moderator leaks of this magnitude have been detected to date.

SURVEILLANCE RESULTS

The results of the daily source checks using the external standard (daily source checks) are summarized in Figure 5. As can be seen, the data is consistent up to March 10, but then shows an abrupt decrease in count rate. On this date, larger diameter beads (0.25 mm instead of 0.1 mm diameter) were used in several cells as a test. The counting efficiency decreased because of the increased void volume. Only 0.1 mm diameter beads are now used in the analysis cell. While it was determined that the count rates produced by the external standard were not directly proportional to the tritium counting efficiency, this test provided a good indicator of the overall system performance.

The results of the chemical analyses are given in Table II. The pH of the influent and effluent samples demonstrate the effect of the strong acid ion exchange column when removing cations from the solution. The lower pH is also responsible for the increased conductivity of the effluent. The influent turbidity has a wide range due to changes in environmental conditions. However, the effluent turbidity is maintained <1 NTU at all times by the 0.2 micron polishing filter. While most of the filterable debris in the water is removed, slight bead discoloration is observed in used cells.

TABLE II. A Summary of the Results of the Water Quality tests on the water through the TEWM.

Parameter	Influent	Effluent
pH	6.9 ± 0.5	3.7 ± 0.4
Conductivity (μS/cm)	83 ± 10	150 ±45
Total Dissolved Solids (ppm)	41 ± 7	106 ±30
Turbidity (NTU)	18 ± 9	0.5 ± 0.3
Dissolved O_2 (ppm)	9	7.5

Nine measurement cells were replaced during the first 100 days of operation. With each cell change, a new ion exchange column was also installed. The first cell (Figure 6) was in service for about 500 hours at an average flow of 2.3 mL/min. It was removed from service on January 24 due to degradation in tritium counting efficiency. The average hourly background count rate for this cell was 5.02 ± 0.35 cpm. A new cell was installed and operated for about 415 hours before it was removed from service on February 10. This cell was flushed daily with 0.1 N HNO_3 in an attempt to increase cell life. No increase in performance was observed. The third cell experienced shortened life when an organic chemical was introduced into the outfall by drilling operations in the area. This chemical caused the monitor to alarm by chemical luminescence. An additional activated charcoal adsorbent was added to the ion exchange column to reduce the concentration of the interfering chemical. The performance of the fourth cell was reduced due to pump failures and filter breakthrough. Cells 5 and 6 contained larger diameter beads. Cells 7, 8 and 9 were typical of the performance expected from the cells. This data was used to develop a maintenance schedule for replacement of the analysis cells, the polishing filters, and the ion exchange resin columns. All are now replaced on a weekly schedule and daily surveillances have been reduced to weekly calibrations.

CONCLUSIONS

The TEWM has continuously monitored the outfall from the K-Reactor for an unanticipated release of moderator since January 3, 1992. Tritium analyses of the composite samples taken during the first 3 months of operation have shown an average tritium concentration of 0.96 ± 0.85 Bq/mL While these concentrations are well below the alarm threshold of the monitor, they were confirmed by analyses of the corresponding daily grab samples. This tritium concentration is consistent with the range observed for Savannah River Samples (8).

The performance of the TEWM installed on the outfall from the K-Reactor has confirmed that on-line techniques are possible for monitoring tritium in real time but that they require continued maintenance and surveillance (9). Techniques are under development to improve the system performance using advanced water purification methods and improved tritium detection sensitivity. Most failures have occurred in the water delivery and purification system. A second improved tritium monitor is being assembled which will utilize the same scintillation bead detector technology but will improve the response time through a redesigned water purification system. The system will be capable of operating at higher flows and will include graded filters, ion exchange resins, ultra-violet sterilization, and activated charcoal absorbents to reduce detector cell contamination. This system will operate in parallel with the existing system.

The performance of the monitor over a variety of environmental conditions has shown that this technique is adequate for near real-time detection of tritium in aqueous streams provided the sample is pre-treated to remove known impurities. Interferences from chemical and biological species have been identified and eliminated. Improvements to the design are proposed. Field experience with the monitor has demonstrated that the pre-treatment system must be reliable, inexpensive, simple to operate and maintain, and yet provide high quality effluent for the solid scintillator detector. Once the impurities are removed, this study has shown that detectors made from plastic scintillator can be used to monitor for tritium in aqueous solutions in near-real time.

ACKNOWLEDGMENT

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LIST OF FIGURES

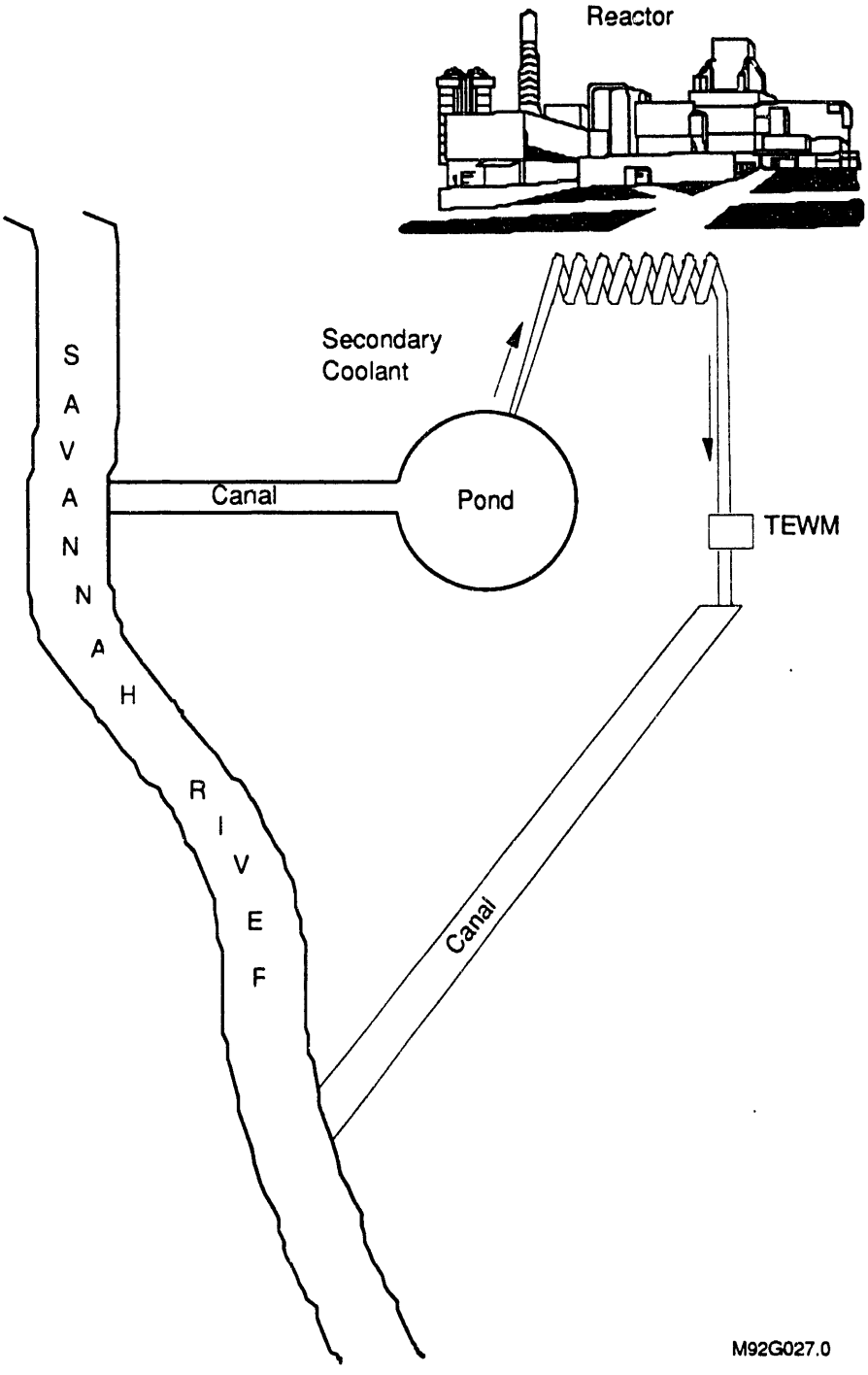

Figure 1. Illustration of TEWM Monitor Location.

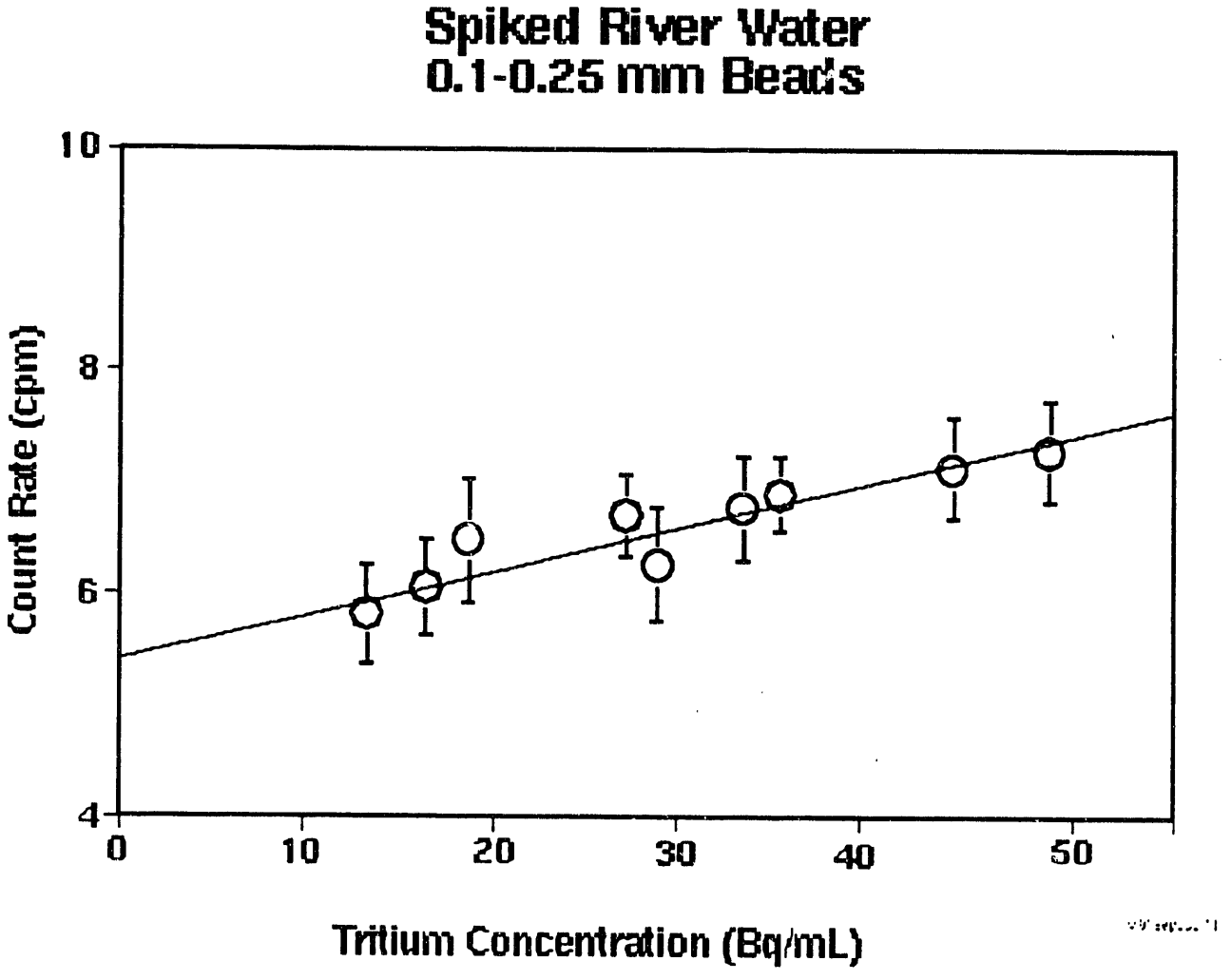

Figure 2. The monitor response to a tritium-spiked riverwater sample.

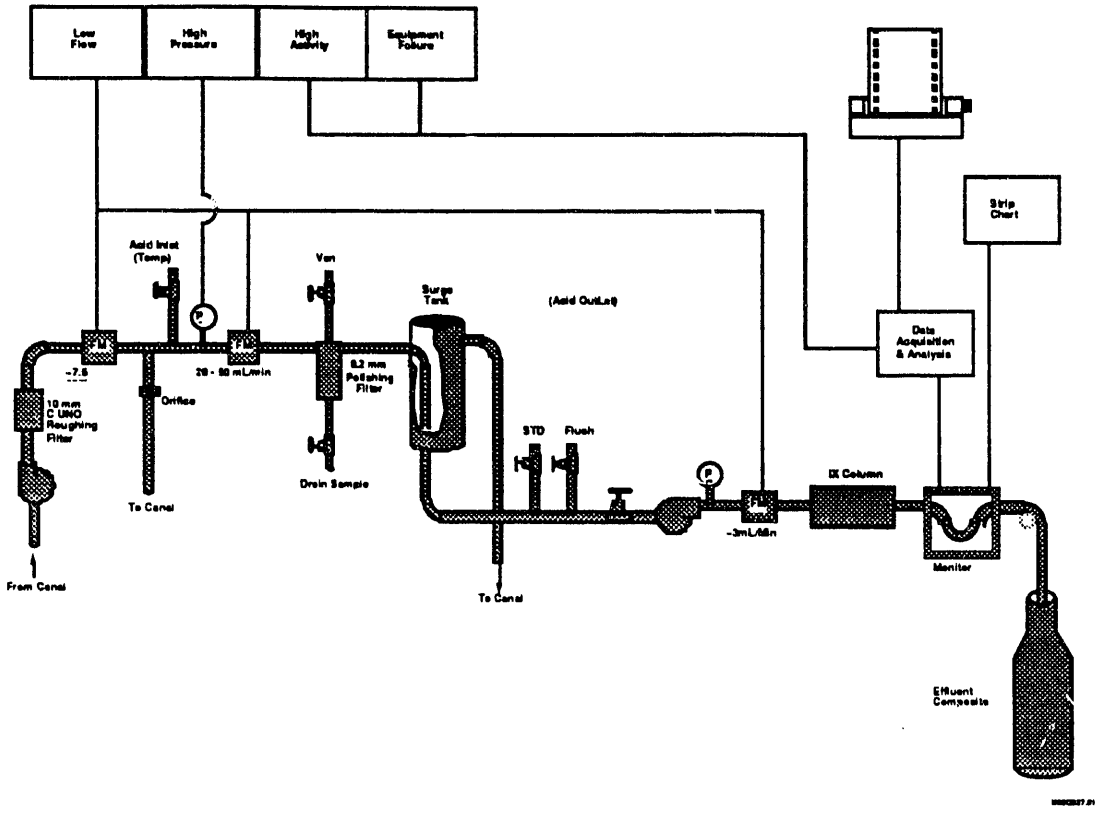

Figure 3. Line diagram of the tritium effluent water monitor as installed in the outfall from the K-Reactor.

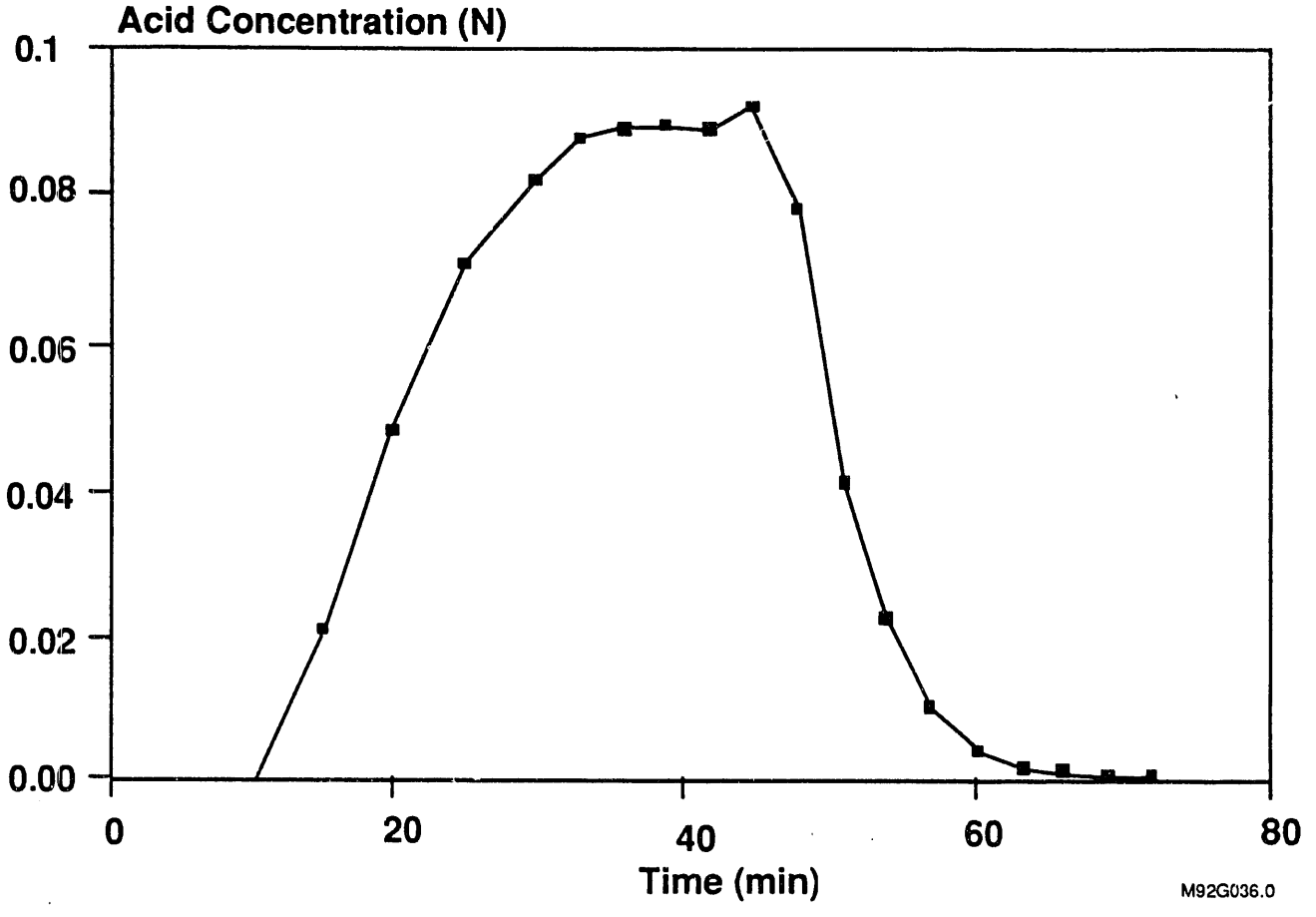

Figure 4. Time response of the filtration portion of the TEWM as determined by the injection of a 0.1 N HNO_3 solution.

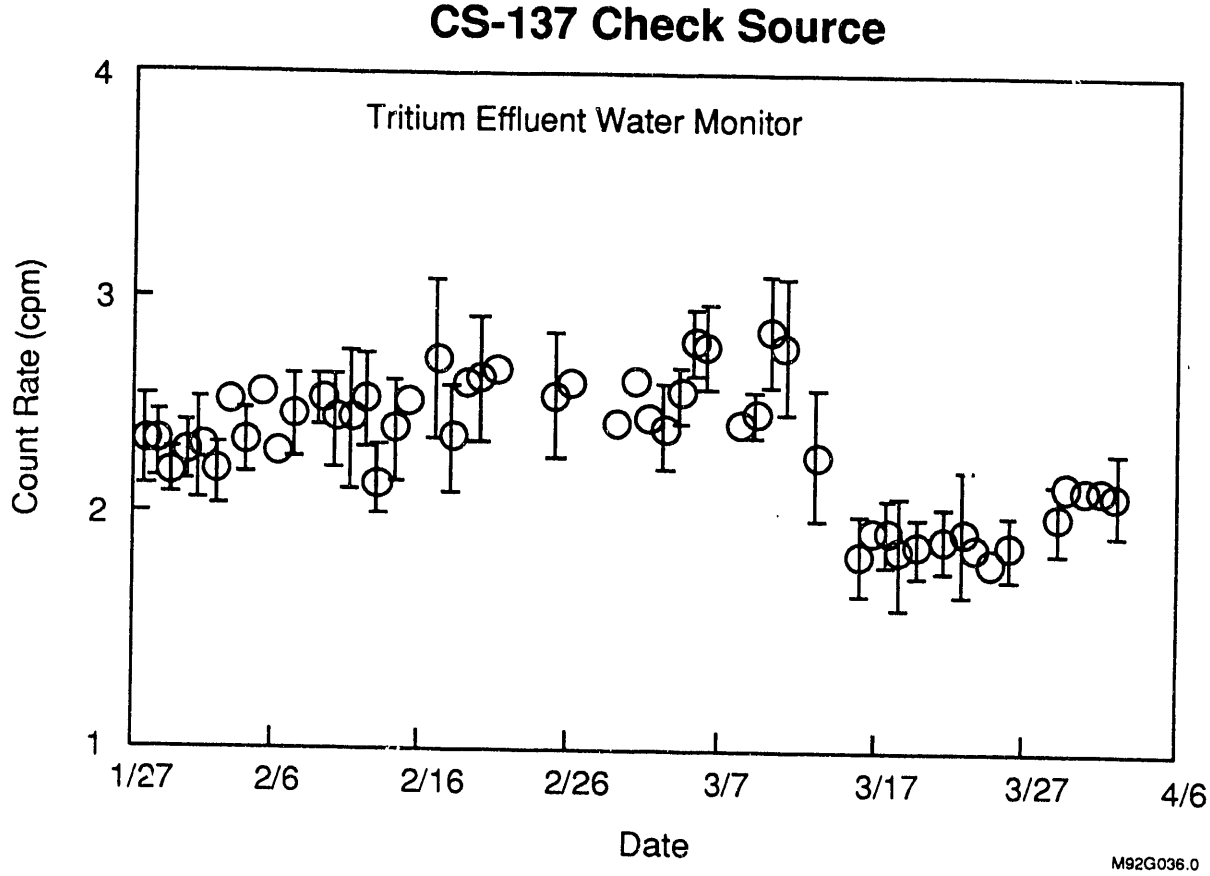

Figure 5. Count rate response of the tritium monitor when exposed to a Cs-137 external standard source.

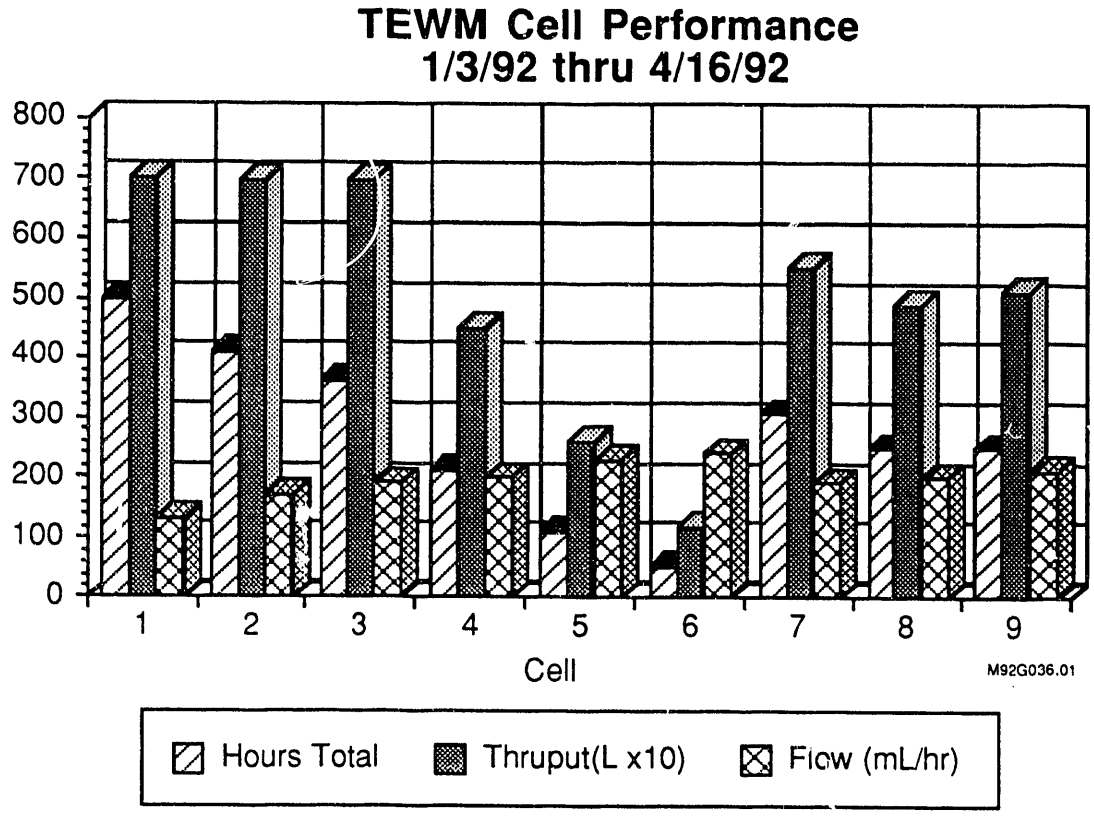

Figure 6. Summary of performance of the first nine cells used in the first 100 days of operation in the K-Reactor outfall.

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