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ON-LINE MONITORING OF TOXIC MATERIALS IN SEWAGE AT THE LAWRENCE LIVERMORE LABORATORY

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ABSTRACT

It is becoming increasingly important for industry to prevent releases of potentially toxic material to the environment. The Lawrence Livermore Laboratory, a U.S. Department of Energy research facility, has developed a system to monitor its sewage effluent on a continuous basis.

A representative fraction of the total waste stream leaving the Plant is passed through a detection assembly consisting of an x-ray fluorescence unit which detects high levels of metals, sodium iodide crystal detectors that scan the sewage for the presence of elevated levels of radiation, and an industrial probe for pH monitoring. With the aid of a microprocessor, the data collected is reduced and analyzed to determine whether levels are approaching established environmental limits. Currently, if preset pH or radiation levels are exceeded, a sample of the suspect sewage is automatically collected for further analysis, and an alarm is sent to a station where personnel can be alerted to respond on a 24-hour basis. In the same manner, spectral data from the x-ray fluorescence unit will be routed through the 24-hour alarm system as soon as evaluation of the unit is complete.

The monitoring system has played an important role in averting treatment plant problems when a spill has occurred. The design of the system and operational experience will be discussed.

INTRODUCTION

Since its beginning in 1952, the Lawrence Livermore Laboratory (LLL), Livermore, California has supported an environmental surveillance program to determine its impact, if any, on the local environment. The Laboratory, located in a suburban valley 65 km east of San Francisco, is involved in widely varied research and development programs for the U.S. Department of Energy. The main efforts are in nuclear and nonnuclear weapons, magnetic and laser fusion energy, biomedical research, and nonnuclear energy technologies, such as geothermal power and fossil fuel utilization. These programs and the support efforts involved in carrying them out generate waste products that could present a negative impact on the environment if not properly managed. Although the Laboratory has an extensive program to control and dispose of all potentially toxic materials at the source, the environmental monitoring program serves as a check on control procedures. An important part of this monitoring program is the on-line wastewater monitoring system, which detects elevated radiation, metal concentration, and pH levels.

BACKGROUND

The Laboratory's sanitary sewer system is a possible route for the escape of toxic materials. Its effluent, which is approximately 350,000 gallons per day, is processed by the municipal Livermore Water Reclamation Plant. The plant is a secondary treatment operation, whose output is discharged to several different sources. Until very recently, most of this effluent was returned to a creek which eventually recharged a groundwater basin. A portion of the effluent is used for irrigating vegetation along roadways and a few local crops. Earlier this month, however, a transport pipeline to the San Francisco Bay was completed, and most of the treated effluent now flows to the Bay. The sewer monitoring system was designed and constructed to detect toxic material releases and to facilitate immediate response action when they occur. This is necessary in preventing damage to the city treatment plant and regions receiving discharged effluent. If toxic materials are detected at levels that exceed predetermined LLL alarm limits, signals are sent to a central alarm station that is manned 24-hours a day and a sample of the suspect toxic effluent is automatically collected. Since two hours pass before LLL effluent reaches the treatment plant, sufficient time is available to alert emergency personnel, evaluate the situation and, if necessary, arrange for diversion of the material to emergency holding basins at the treatment plant. The toxic waste can be treated in the basins or removed without destroying or cutting down on the efficiency of the treatment plant.

MONITORING SYSTEM COMPONENTS

The on-line monitoring system consists of several components. The flow route to these components starts at a point in a manhole where all Laboratory sewage discharge lines converge. As the sewage flows through a Parshall flow-measuring flume, approximately 40 l/min of it is pumped to an aboveground building where the detection instrumentation is located. Inside this building, the sample enters a tank housing the high- and low-energy radiation detectors, pH probe, and a sample line leading to the metal analyzer unit. After it is scanned, the sample is returned to the sewer via an outlet pipe.

Radiation detectors

Radioisotopes being used at LLL that could be released in quantities that would exceed continuous exposure maximum permissible concentration (MPC) levels are ^{90}Sr, ^{235}U, ^{238}U, ^{237}Np, ^{238}Pu, ^{239}Pu, ^{241}Am and ^{244}Cm. All of these, with the exception of ^{90}Sr, emit heavy element x-rays and low energy gamma rays during decay. For ^{90}Sr, low energy bremsstrahlung photons give an indication of specific activity. With this in mind, the radiation detection system was designed (1). The primary detector, a 3 x 127 mm sodium iodide crystal separated from the sample by a thin polycarbonate plastic sheet, allows recognition of the low energy x-rays, gamma rays, and bremsstrahlung photons in the energy range of 10 to 100 keV. In addition, a 50 x 50 mm sodium iodide crystal detector is mounted immediately adjacent to the sample tank to provide detection of higher energy (100 - 1000 keV) events.

The electronics associated with the detectors includes single channel analyzers and an Intel 8008 microprocessor which analyzes the data and decides whether preset levels have been exceeded. The alarm system for radiation detection has been set at a level that corresponds to less than 2% of the allowable monthly discharge limit for a continuous release of ^{90}Sr or less than 0.5% of the monthly allowable discharge limit for a continuous release of ^{239}Pu (2).

pH monitor

A commercial industrial pH probe is housed in the tank holding the radiation detectors. Output from the pH sensor is sent to the Intel 8008 microprocessor where the data is evaluated. If the pH drops below 3 or exceeds 11 for five minutes within a "floating" ten minute block of time, the alarm system is activated.

Metal detection

The deleterious effect of excess concentrations of heavy metals on sewage treatment plant operations has been demonstrated in a number of studies. The Laboratory has had two incidents in the past when inadvertent releases of toxic metals have created operating problems at the sewage treatment plant. In one incident, copper-cyanide solution destroyed 50% of the bacteria in the trickling filter unit, and in the other, excess chrome significantly reduced the efficiency of one of the two digestor units. These events prompted a search for a continuous metal detection system that would prevent the recurrence of plant down-time caused by a metal release to the sewer. When the search was started about two years ago, commercial units available appeared to be unsuitable for sewage analysis. The units required pre-analysis filtering, which would affect the representability of the sample and which would require a considerable amount of maintenance. A monitoring unit capable of detecting hazardous concentrations of ions found to be most harmful to the bacteria in the treatment plant process, specifically copper, nickel, chrome and zinc was then designed. The system, meets the requirements placed on a continuous system: it is fairly reasonable in cost, especially when contrasted to the cost of reseeding a treatment plant; works on-line and in real time; does not require extensive pretreatment of the sample, thereby preserving representability; and requires minimal maintenance.

The unit providing metals detection is an x-ray fluorescence analyzer (XRFA). Its design is based on the principle that elements emit characteristic x-ray lines when excited by a radiation source. These x-ray lines can be measured by energy dispersion techniques to determine their energy, which permits species indentification, while the intensity of the lines is proportional to concentration.

A portion of the sample stream that flows through the tank described previously is routed through a macerator to reduce any solids to particles 100 microns or less in diameter. The flow is then introduced through a nozzle into a flume inclined at 45°. The flow spreads to a sheet 1 mm in depth before it reaches the source/detector region of the unit. A thin plastic window backed by air is positioned under the stream in this region to prevent detection of the chrome and nickel in the stainless steel flume. A ^{109}Cd source is used to excite the elements of interest if they are present in the stream, and a commercial xenon-CO_2 mixture x-ray proportional counter is the detector used. The output from the detector goes to amplifiers, then through an analog-to-digital converter interfaced to a Digital Equipment Company LSI-11 microprocessor.

A dual register system for the data output allows both a rapid response to high metal concentrations (500 sec count) and a more sensitive response to low concentrations released over a longer time frame (5000 sec accumulated count). The data counting system also provides for advisories at concentrations that are elevated, but not at alarm levels. Minimum advisory and alarm levels are shown in Table 1.

Maximum permissible discharge concentrations for copper, chrome, nickel, and zinc have been established at LLL based on studies of the effects of toxic metals on sewage treatment and the dilution factors resulting from the intermixing of LLL's effluent with the domestic sewage from the Livermore city population. These concentrations, as well as the 500- and 5000-sec alarm limits for the elements of concern, are shown in Table 2. Although only zinc will cause an alarm in 500 sec if its LLL limit is exceeded, copper, chrome and nickel will cause alarms in 5000 sec or less if their limits are exceeded. This will provide adequate response time.

System monitor

In addition to detecting high- and low-energy radiation, pH excursions, and heavy metal releases, the monitoring system trips an alarm when an equipment malfunction occurs. A signal is sent to the central alarm station if problems such as a count rate lower than background, power failure, or flow malfunction occurs.

Grab sampler

An important part of the monitoring system is a mechanism that extracts a sample from the waste stream as soon as an alarm is tripped. This sample is often valuable in identification of the toxic material involved and in the evaluation of the situation.

TABLE 1

Minimum Advisory and Alarm Levels
for the XRFA Monitor

Element	500 sec Advisory, ppm	500 sec Alarm, ppm	5000 sec Advisory, ppm	5000 sec Alarm, ppm
Cr	36	119	11	37
Mn	23	78	7	25
Fe	15	50	5	16
Co	10	33	3	10
Ni	6	21	2	7
Cu	5	16	2	5
Zn	4	14	1	4
As	2	7	1	2
Se	2	7	1	2
Hg	5	17	2	5
Pb	4	12	1	4

TABLE 2

Comparison of LLL Maximum Permissible Metal Discharge Limits and XRFA Alarm Limits

Single metal	LLL limit, ppm	XRFA alarm limit 500 sec, ppm	XRFA alarm limit 5000 sec, ppm
Cr	100	119	37
Cu	10	16	5
Zn	50	14	4
Ni	10	21	7

Combinations: total concentration to be less than 100 ppm

Teletype printouts

Both the LSI-11 and Intel 8008 are interfaced to teleptypes. The printouts provide responding personnel with current as well as historical data on effluent releases.

OPERATING EXPERIENCE

For the most part, the existing monitoring system has proved to be very effective. Since it has been in operation, there have been several occasions when diversion of the Laboratory's flow at the Livermore treatment plant was deemed necessary. In all instances, alarms were set off because of inadvertent acid releases. These incidents alone have proved the worth of the system since restoring the treatment plant to normal operation would have been more costly than the investment made in designing, constructing, operating and maintaining the monitoring system.

In addition to the pH excursions, there have been a number of radiation alarms. In all instances, grab samples analyzed have shown that the material triggering the alarm was a radiopharmaceutical, generally ^{99}Tc from brain scans or ^{131}I from thyroid treatments. These alarms are caused by the radiopharmaceutical being excreted by outpatients who return to work following medical treatment.

Although the alarm system has not yet been hooked up for the x-ray fluorescence analyzer, an inadvertent release of about 40 ppm chrome from a plating operation was noted on the teletype printout.

SUMMARY AND CONCLUSIONS

The on-line sewer monitoring system cannot in itself prevent the accidental discharge of toxic materials into sewers. However, by rapidly detecting releases and sounding alarms to alert emergency personnel to respond, actions can be taken to prevent damage to the environment. Because it is a real-time system, Laboratory personnel can more easily locate the source of a toxic discharge and take corrective action to prevent its recurrence.

REFERENCES

1. Cate, J. L., Jr. and T. D. Hoeger, "A Radioisotope Monitoring System for Sewage Effluent," American Industrial Hygiene Journal, 693-699 (October 1972).
2. U. S. Department of Energy, "Standards for Radiation Protection," DOEM 0524 (1975).

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