POLLUTION ABATEMENT:

Pollution Instrumentation Techniques

Besides improving the plant's relationship with the community, many aspects of this environmental protection program have literally paid for themselves by reducing the loss of expensive products and/or raw materials.

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UNION CARBIDE'S PETROCHEMICAL PLANT AT Institute, W. Va. is located on an 850 acre plot approximately 10 mi. "down" the Kanawha River from the state capital, Charleston. Some 20- to 30 chemicals are produced at rates in the millions of pounds per year, and about 200 others are produced at lesser rates by the approximately 2,000 people employed here. The original plant was built by the U.S. Government in 1941 to produce raw materials, such as butadiene and styrene, for the production of synthetic rubber.

When the State Division of Water Resources and municipalities and industrial firms of the Kanawha Valley began a river cleanup program in 1958, there was only one waste treatment plant along the 95 mi. Kanawha River. Along a 30 mi. stretch of the river, there are ten major chemical plants and seven communities with a total population of more than 150,000. With this combined industrial and municipal waste load, the Kanawha River became a virtual cesspool during the warm summer months when the river flow was at its lowest. In order to determine where the cleanup program should begin, a comprehensive survey of the Kanawha River was made by personnel from the State Division of Water Resources and valley industrial people. A team of some 40 people—working on a round-the-clock basis—carried out the survey over a period of 26 days. Although some data were obtained in the field, most of the river samples were transported to the industrial laboratories for analysis.

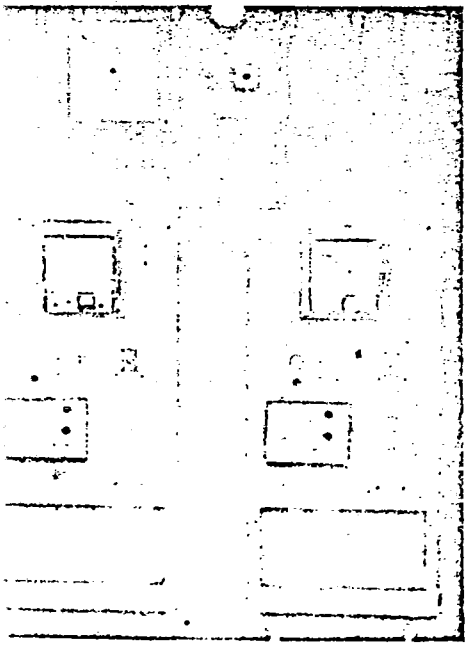


Figure 1. Total Carbon Analyzer monitoring inlet cooling water from the Kanawha River (left), and an analyzer monitoring cooling water being discharged into the river from one of the main collecting sewers (right).

When the results of the survey were studied, it was obvious that the pollution problem in the Kanawha River was too complex to be corrected by simple means. The state decided that a phased cleanup program was the most satisfactory solution, and proceeded to initiate such a plan.

Phase I of the plan called for all municipalities to provide primary treatment for their wastes, and industry was required to reduce the biological oxygen demand (BOD) of their waste by 40%. The compliance date for Phase I was June 30, 1963. Most of the towns and industries met this goal; however, those not meeting the deadline did comply within six months.

Upon completion of Phase I, a re-evaluation of the lower Kanawha River conditions showed that the BOD loading was still sufficient to completely deplete the disolved oxygen during warm weather, low flow periods. During Phase I, the state required each industry to supply periodic waste load reports. These reports were of considerable value during the planning of Phase II.

Phase II required municipalities to provide secondary treatment. Industrial plants were handled on an individual basis in order to correct the most serious problems, but, in general, the requirement was for a 50% reduction in the remaining waste load. June 30, 1966 was designated as the end of Phase II and most of the industrial plants met their goals. The municipal program, however, ran into financing problems. When you consider that seven of the twelve communities in the upper stretch of the river have populations of less than 3,000, then this financial problem becomes understandable.

We are now approaching the end of Phase III (January 1, 1973), and things are getting progressively tougher. All cities must complete their secondary treatment facilities; industry may have to add tertiary treatment in some cases. To meet water quality standards set by the state and federal government, some wastes will have to be removed for which there is no known treatment process technically feasible. These reductions may have to be met by costly process changes or shut down of the facility.

Plant laboratory program

At the Institute plant, the first step in determining a program that would meet the requirements of this three-phase program required extensive laboratory analysis of plant wastes. In 1959 two significant laboratory programs were begun. In the plant quality control laboratory one of the authors, L. G. Cochran, began investigating the

DSW 296030

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assibility of using laboratory gas chromatographs to identify specific wastes in the plant sewers (*1*). Since most of the products manufactured at the Institute plant were organic materials, hydrogen flame ionization detectors were used in order to achieve detection levels in the low parts per million range. The first sample tested was a "clean water" outfall which had been exerting a considerable load on the river. In excess of 20 peaks were observed with the chromatograph. This demonstrated the potential capability of this tool and a long range program was initiated. Since that time, more than 400 separate chemical species have been identified at one time or another in the waste streams.

The second laboratory program was to develop an on-stream carbon analyzer. This project was assigned to Union Carbide's Special Instrumentation Department, located a few miles away in South Charleston, W. Va. Details of this development program have been described elsewhere (*2*). Within a few months a prototype total carbon analyzer was being tested at the Institute plant. Subsequently, this device was marketed commercially, and is now used extensively in Union Carbide plants around the world.

A brief assay of the present quality control laboratory effort dedicated to pollution control analytical work is as follows: 1) a battery of chromatographs which is used to routinely identify the major contaminants in the 24 hr. composite samples brought to the laboratory each day; 2) laboratory carbon analysis equipment which is used to quickly identify the carbon loading of each waste stream; 3) a chemical oxygen demand (COD) apparatus which is used to generate data that is reported to the state; and 4) a Perkin Elmer atomic absorption spectrometer which is used to identify traces of heavy metals.

Additional laboratory analytical tests include:

1. Biochemical oxygen demand (BOD)—Data are reported to the state giving weekly averages for both cooling water inlet and outlet streams; also, 7 day composited samples of the waste water treatment unit inlet and effluent streams are analyzed for BOD.
2. pH
3. Nitrogen—Reported as ammonia, as nitrate, as nitrite, and as organic nitrogen.
4. Carbon absorption—Kanawha River samples and municipal water samples from the nearest downstream water treatment plant are checked periodically for organic contaminants.
5. Oil and grease—To assure that levels, as established by discharge permit, are not exceeded.
6. Residues—Waste treatment unit effluent is checked for total, filterable, and fixed residues.
7. Bacteriological examination—coliform count.
8. Miscellaneous chemical analyses—titrimetric, colorimetric, gravimetric, etc.

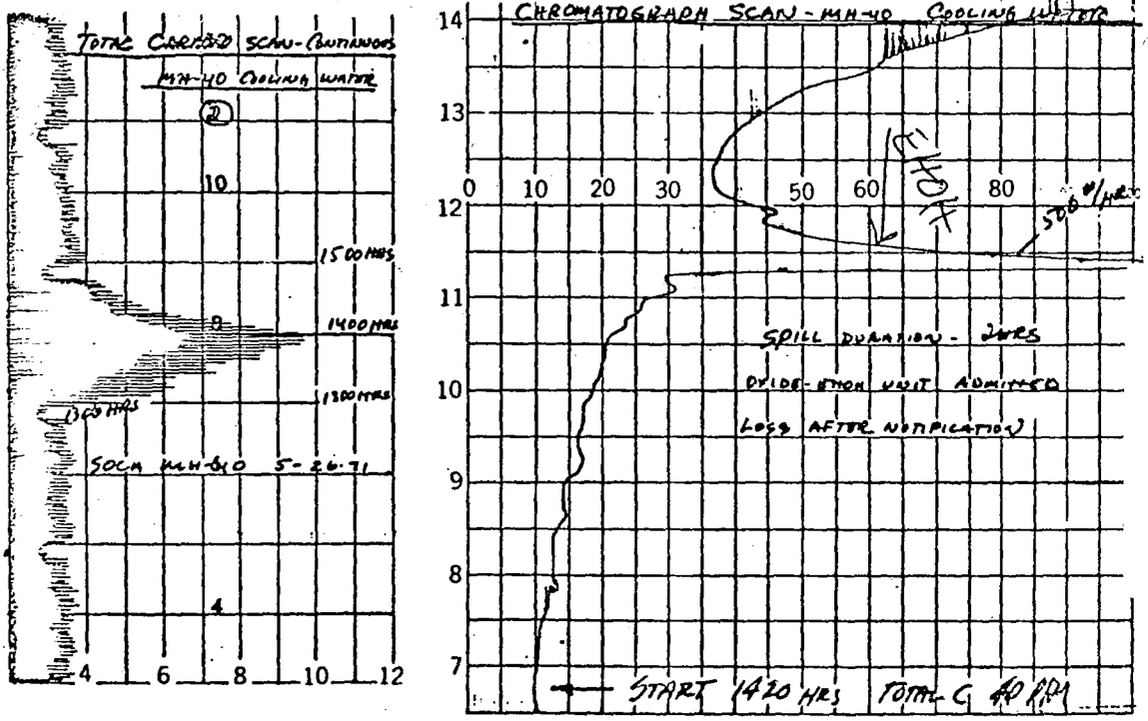
The development of analytical methods to improve our ability to detect and, thus, eventually control environmental contaminants is an on-going program. At the present time we are evaluating systems for measuring trace amounts of sulfur compounds. We are also utilizing liquid chromatography to identify high molecular weight or unstable molecular species that sometimes reach the plant sewers.

In-plant monitoring

The second step in the Institute plant's program to control environmental pollution involved the installation

IN PLANT CONTROL PROGRAM

1. LOCATION: MH-40-COOLING WATER
2. TIME: 1420 HOURS
3. DURATION: 2 HOURS
4. TOTAL LBS.: 1000



REMARKS CHEMICAL IDENTIFIED BY ON-STREAM G.C.
40 MINUTES AFTER START OF SPILL.

DSW 296031

Figure 2. Concurrent charts from the cooling water effluent Total Carbon Analyzer or TCA (left), and the Specific Organic Carbon Analyzer, a temperature programmed gas chromatograph, identifying the spill detected by the TCA as ethanol.

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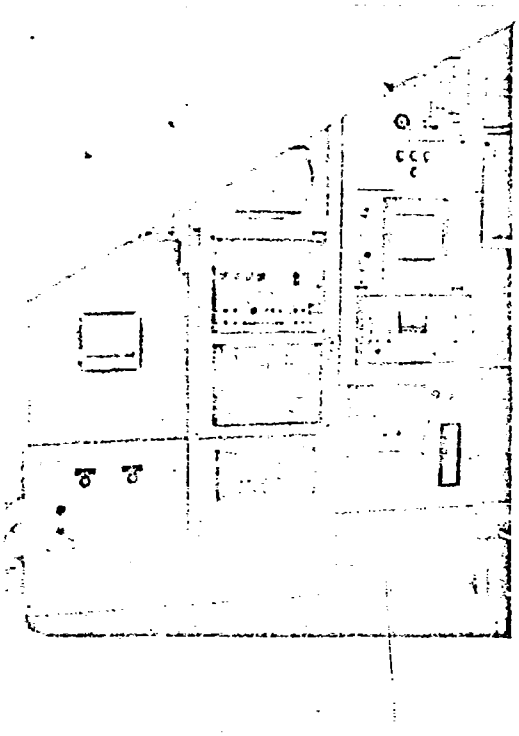


Figure 3. The telemetry recorders, Total Carbon Analyzer, and the Specific Organic Carbon Analyzer in the control room of the Institute plant.

of automatic on-stream analyzers to provide continuous indication of the level of contaminants. This program is divided into three phases: 1) monitoring of the cooling water system, both inlet and effluent lines; 2) monitoring the process or contaminated water sewers; 3) monitoring the waste water treatment unit operation.

The inlet cooling water is monitored in order to establish base loads existing in the river, Figure 1. Without this information, monitoring of the effluent cooling water would be meaningless since there are a number of large industrial plants further upstream. A large spill from one of these plants might be detected and interpreted as a malfunction of process equipment in the Institute plant. Composite samplers are used to collect 24 hr. samples for analysis by the quality control laboratory.

Monitoring of cooling water sewers is divided into two areas: some equipment is located in specific operating units that have a high potential for excessive pollution, and other analyzers monitor the main collecting sewers that ultimately conduct the cooling water to the plant outfalls at the Kanawha River, Figure 1. The output signal from many of these carbon analyzers is telemetered via telephone lines to the waste treatment plant, approximately 1 mi. west of the main plant.

The main purpose in carrying out two types of cooling water sewer monitoring is to provide detection in the most effective places. Those units that, by their nature, will be frequent potential contamination sources are monitored at the unit, whereas other areas can be adequately monitored by analysis of the main sewer serving several units, thus providing adequate detection capability at a minimum cost.

A grab sampling system can be actuated by the waste treatment plant operator via a telemetry link in the event a spill is detected by this effluent monitor. A 1 qt. container holds enough sample to permit subsequent laboratory analyses that will identify the nature of the loss.

An automatic gas chromatograph (Specific Organic Carbon Analyzer, or SOCA) is located in the same shed with two of the carbon analyzers and grab sample apparatus described above. This analyzer is normally maintained in a standby operating condition; its analysis cycle can be started by the waste treatment operator by means of another telemetery link. In the event a spill is detected by the carbon analyzer, the treatment plant operator can remotely inject a sample into this gas chromatograph. This chromatographic signal is also telemetered to the waste treatment plant control room.

Case history

The following is a case study of an actual spill and how instrumentation first determined a spill had occurred and pinpointed its location, Figure 2. On May 26, 1971 around 1:00 p.m., the carbon loading at the cooling water effluent started to increase from its normal level of less than 20 parts/million. The Total Carbon Analyzer at that location detected the spill. All production units discharging into this sewer were notified that a spill had occurred but none of the units admitted any difficulties. At 1:05 p.m., the waste treatment plant operator initiated operation of the gas chromatograph. Within 40 min. the spill was identified as ethylhexyl alcohol. When the specific operating unit was notified, they were able to locate the source of the spill; a decanter level control had failed to function and caused an over-run. Within 2 hr. of the detection of the spill, the cooling water effluent load had returned to normal.

On-stream pH analyzers are also used to detect spills of acidic and caustic materials that are not detected by the carbon analyzers. In addition, one of the cooling water systems that is subject to contamination by surface active agents is monitored by a foam detector. This device is an optical system and requires periodic cleaning in order to function properly. A recently developed foam detector using a fluidic sensor will be installed later this year.

The same types of environmental equipment that we have previously described are also used to monitor the contaminated sewer system. One major difference is that pH monitoring equipment for the contaminated sewers telemeter their output signals to the waste treatment plant, and several of them are used to control the addition of caustic or acid to the sewers. This is necessary because sudden pH changes at the waste treatment plant have an adverse effect on the biological organisms that constitute the major waste removal process.

The third phase of the plant monitoring program is associated with the waste water treatment unit, which is located on the north bank of the Kanawha River approximately 1 mi. down river from the Institute plant. It is composed of a control building and three large basins making up the activated sludge system, each containing approximately 5 million gal. Each basin contains ten surface aerators (5- to 100 h.p. and 5- to 75 h.p.) to provide the oxygen required by the biological growths which remove some 90% of the organic load from the contaminated water before it is returned to the river.

The control building houses some of the monitoring instrumentation. There are six telemetry receivers for five of the in-plant Total Carbon Analyzers and the in-plant Specific Organic Carbon Analyzer. An additional Specific Organic Carbon Analyzer, installed in the control building, is used to monitor either the influent or the effluent stream of the treatment plant. There is, also, a Total Carbon Analyzer that is used to monitor either the plant influent or the plant effluent, Figure 3.

In addition to these analyzers, each of the three treatment basins is monitored by a Union Carbide developed dissolved oxygen analyzer, a pH meter, and temperature monitor. Voltage to current transducers transmit signals to electrical recorders inside the control room.

Operation of the activated sludge system converts a portion of the water pollution load into an air pollution problem. A portion of the lighter organic materials are stripped from the water by the action of the aerators and some of these materials have objectionable odors. Since a community of some 20,000 people is located directly across the river from the waste treatment plant, this air pollution must be controlled to eliminate its nuisance

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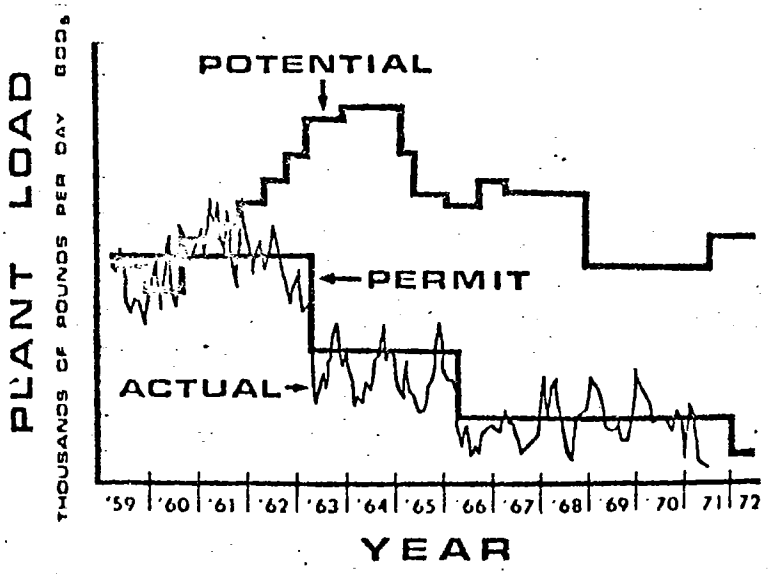


Figure 4. Potential, permitted, and actual Institute plant waste discharge.

value in the community. A Chem-Screen system installed at the waste water treatment unit is used to counteract the effect of these airborne pollutants. Drums contain a chemical odorizer that is distributed into the atmosphere by perforated pipe located along the riverbank separating the community and the waste treatment plant. It is claimed that this odorant does not merely mask objectionable odors, but reacts chemically with organic molecules in the atmosphere to convert them into non-objectionable species.

In addition to this type of development program, other on-line monitoring systems are periodically evaluated. In the very near future, an automatic liquid chromatograph will be used to monitor one of the process sewers for the presence of a toxic insecticide. This material will normally be destroyed by reaction with caustic before reaching the sewer, but because there is a possibility of a process upset or a failure of the caustic neutralization system, it is necessary to monitor the sewer continuously. Several automatic chemical analyzers will also be installed to control the neutralization of waste streams or to improve the control of scrubbing systems, and thus, reduce the caustic or acid load on the sewers.

All process instrumentation requires a basic amount of maintenance and environmental monitoring equipment is no exception. Because the sampling conditions are generally more severe, environmental instrumentation in general will require more maintenance than regular process instrumentation. The foregoing statement suggests the major problem area with most environmental monitors—the sampling system. Since most environmental samples contain suspended solids, are corrosive or involve trace quantities of reactive materials (and frequently all three), the sampling problems are often nearly impossible.

Results to date

The Institute plant's potential water pollution load would have increased in the past 10 yr. if there had been no effort to regulate the plant discharge, Figure 4. The state has permitted specific levels of discharge during this period with planned reductions as established by the three-phase river cleanup program. The cost of implementing and operating such a program for a large petrochemical plant is significant. To date, Union Carbide has expended approximately $4 million to install water pollution control equipment, and the yearly operating cost of these facilities is $1 million. This does not include the $6.5 million invested in air pollution control and solid waste disposal; together these represent an additional annual operating expense of $750,000.

The benefits from such a program are also significant. In addition to improving our relationship with the community and reducing the hazards of living in the same neighborhood, many aspects of the environmental protection program have literally paid for themselves by reducing the loss of expensive products and/or raw materials. The prospects are good that we will continue to pay for a significant portion of any environmental protection facilities by doing an even better job of designing our production facilities in the future. #

Literature cited

1. Cochran, L.G., and F.D. Bess, *J. Water Pollution Control Federation*, No. 12, 38, (December 1966).
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DSW 296033


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