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# Segregation of Metals-Containing Wastewater by pH

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MARTIN MARIETTA ENERGY SYSTEMS, INC.
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# SEGREGATION OF METALS-CONTAINING WASTEWATER BY pH

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# SEGREGATION OF METALS-CONTAINING WASTEWATER BY pH

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## ABSTRACT

A pH-based sampling system has shown that there is a high correlation between low pH and metals contamination for the wastewater from the 4500 area (manhole 190) and the 2000 area (pump station). Wastewater from the Radiochemical Engineering Development Center (REDC) and the High Flux Isotope Reactor (HFIR) has not shown any metals concentrations above the National Pollutant Discharge Elimination System (NPDES) permit limits for the Nonradiological Wastewater Treatment Plant (NRWTP).

It is recommended that pH be used as the diversion criteria for wastewater from manhole 190 and the pump station to be sent to the metals tank of the NRWTP. Any wastewater with a pH less than 6.0 or greater than 10.0 should be sent to the metals tank. Based on the results of 29 weeks of sampling, it is expected that on the order of 36 $m^3$/wk (9500 gal/wk) of wastewater will be diverted to the metals tank of the NRWTP. Wastewater from REDC and HFIR can be sent to the nonmetals tank, but it should be sampled periodically and analyzed by Inductively Coupled Plasma (ICP) spectrophotometer to confirm that the metals concentration is not increasing.

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## 1.0 INTRODUCTION

The Nonradiological Wastewater Treatment Plant (NRWTP), which is expected to start operation in the spring of 1990, contains both metals and organic removal processes. Most wastewater at ORNL does not require treatment for metals removal, so the bulk of the water will bypass the metals precipitation step and only be treated by air stripping and carbon adsorption for organic removal (see Fig. 1). The National Pollutant Discharge Elimination System (NPDES) Permit for this facility limits the concentration of certain metals in the effluent, as shown in Table 1. On-line instrumentation will be needed to automatically segregate the metals-containing water from the rest of the wastewater stream.

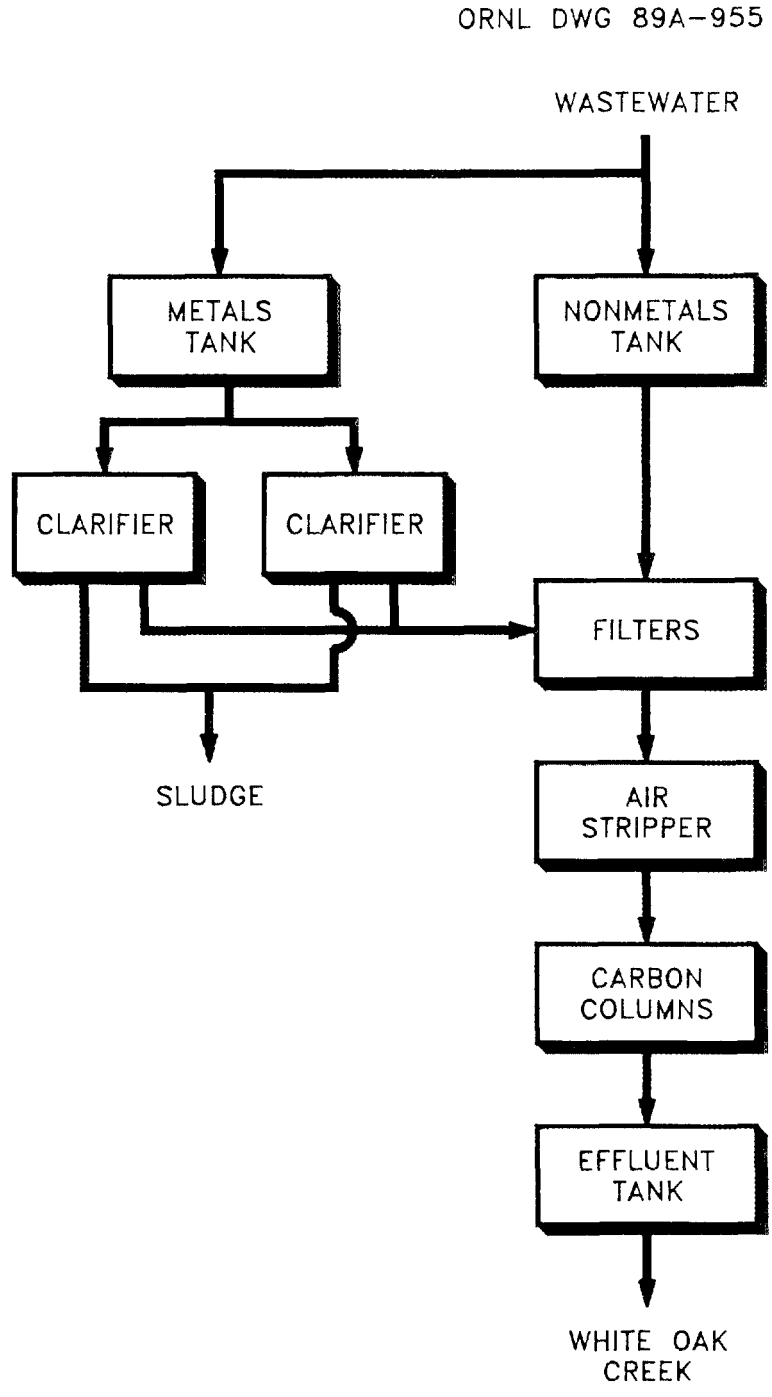


Fig. 1. Nonradiological wastewater treatment plant (NRWTP).

Table 1. NPDES metals concentration limits for the NRWTP

| | Concentration limit (mg/L) | |
|---|---|---|
| **Metal** | **Monthly average** | **Daily maximum** |
| Cadmium (Cd) | 0.26 | 0.69 |
| Chromium (Cr) | 1.71 | 2.77 |
| Copper (Cu) | 2.07 | 3.38 |
| Lead (Pb) | 0.43 | 0.69 |
| Nickel (Ni) | 2.38 | 3.98 |
| Silver (Ag) | 0.24 | 0.43 |
| Zinc (Zn) | 1.48 | 2.61 |

An On-Line Voltammetric Wastewater Analyzer (OVWA) that used a polarographic analyzer and voltammetric electrodes was previously developed to measure the concentration of metals in wastewater.[1] These laboratory instruments were modified several times to make them more rugged, but they still did not hold up well for on-line use. Therefore, an alternate method for segregating metals-containing wastewater was needed.

In the past it had been noticed that metals spikes normally occurred in conjunction with low pH wastewater. Two pH-driven sampling systems were used to determine if pH could be used to segregate the small amount of metals-containing wastewater from the bulk of the wastewater streams that will be treated at the NRWTP. Since pH meters are dependable, rugged and inexpensive, they would be ideal instruments for an on-line segregation system. The sampling protocol follows the specifications for NPDES samples at the NRWTP. Sampling systems were set up at manhole 190 and at the Radiochemical Engineering Development Center (REDC), and later at manhole 95 and the pump station (wastewater from manholes 95 and 240) (see Fig. 2).

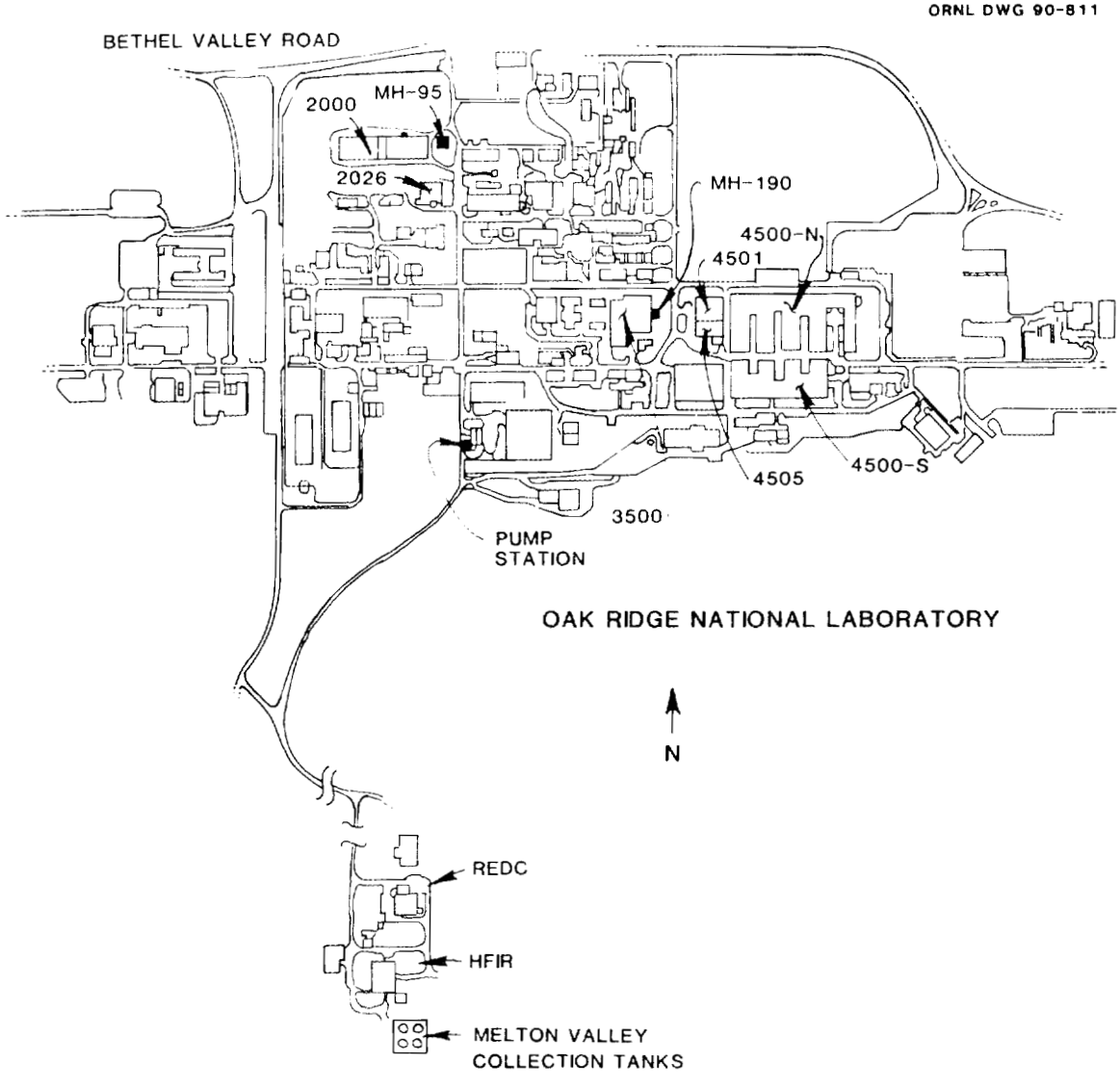


Fig. 2. Location of pH-based sampling stations.

# 2. METHODS

## 2.1 MANHOLE 190

The wastewater from the 4500 area buildings passes through manhole 190 (see Fig. 2), where there is an on-line pH meter that is tied into the Waste Operations Control Center (WOCC). The computer at the WOCC records the average pH every 10 min. The pH meter also has two alarm contacts that were utilized to drive two sampling pumps. The normal-pH pump is turned on anytime the pH is in the normal range (6.0 to 9.0). The alarm pump is turned on, and the normal pump is turned off, anytime the pH is outside this range. The pumps are used to collect 24-h composite samples, as is specified in the NPDES permit for the NRWTP.

The samples were analyzed locally using the polarographic analyzer for Cd, Cu, Pb, and Zn, and they were also sent to the lab for Inductively Coupled Plasma (ICP) spectrophotometer analysis of Ag, Cd, Cr, Cu, Ni, Pb, and Zn. The Analytical Services Request Form specified that any samples that show >0.3 mg/L of any of the metals should be rerun to confirm the result, in order to reduce the chance of false positives. The ICP results demonstrated that the polarographic analyzer was reasonably accurate (normally within ±20% for concentrations >1 mg/L). After ten weeks of sending daily samples to the lab, the procedure was changed to reduce analytical costs. The daily samples were still analyzed on the polarographic analyzer, but only weekly composites of the daily samples were sent to the lab for ICP analysis.

The flow rate of the alarm sample pump was set at about 45 mL/min. The volume of alarm sample was measured each weekday, and this volume was used to estimate the amount of time the alarm pump was on. The pH data from the WOCC was also plotted weekly and compared to the alarm time calculated from the sample volumes. The average time that the alarm pump was on was used to estimate the amount of time that the wastewater stream would be diverted to the NRWTP metals tank during full-scale operation.

## 2.2 RADIOCHEMICAL ENGINEERING DEVELOPMENT CENTER (REDC)

A portable pH controller was used to sample the process wastewater from REDC (see Fig. 1). With the portable controller, only one set-point can be used. The normal-pH sample pump was turned on anytime the pH was above 6.0, and the alarm pump was turned on anytime the pH was 6.0 or below. During the first five weeks of sampling there was no alarm sample collected. After five weeks, the set-point of the pH controller was changed to 9.0, so that alarm samples were collected when the pH was 9.0 or above. In the next three weeks, there were two days when high pH alarm samples were collected, but they did not contain any higher concentrations of the NPDES metals than the normal pH samples. The daily composite samples were analyzed using the polarographic analyzer, and weekly composites of these samples were sent to the lab for ICP analysis.

After eight weeks of sampling, when the Melton Valley Collection Tanks (MVCT) began operation, the pH controller and sampling pumps were moved to manhole 95. From this time on wastewater from REDC, along with wastewater from the High Flux Isotope Reactor (HFIR), was sent to the MVCT. The water was sampled each time a tank was filled, and the samples were sent to the lab for ICP analysis. The water from the tanks is presently discharged to Melton Branch, but the water will be sent to the NRWTP after it begins operation.

## 2.3 MANHOLE 95

The sampling system that was originally used at REDC was used at manhole 95 (see Fig. 1) for nine weeks (5/23/89 to 7/25/89) to sample the wastewater from Bldg. 2000. The normal pH samples were collected anytime the pH was greater than 6.0, and the alarm samples have a pH of 6.0 or less. There were only three days when alarm samples were collected. All of the daily samples were analyzed using the polarographic analyzer, and the daily samples were composited weekly for ICP analysis.

### 2.4 PUMP STATION

The sampling system used at manhole 95 was moved to the pump station (see Fig. 1), which receives wastewater from Bldgs. 2000 and 2026, on 7/31/89, and used for nine weeks. The alarm settings and chemical analyses were the same as before. There were no alarm samples collected during nine weeks of operation at the pump station.

## 3. RESULTS

### 3.1 MANHOLE 190

The pH-based sampling system at manhole 190 was operated from 3/9/89 to 10/2/89. During this 29 week period, the normal pH samples never exceeded the NPDES limits for the NRWTP. The highest concentration of an NPDES metal measured by ICP in the normal pH samples was 0.46 mg/L Cu on 4/26/89, followed by 0.34 mg/L Cr and 0.33 mg/L Cu on 3/23/89. Table 2 lists the highest concentrations of metals detected in the normal pH daily samples (3/9/89 to 5/19/89), and Table 3 lists the highest concentrations in the weekly composite samples (5/22/89 to 10/2/89). By comparing the results in Tables 2 and 3 to the daily maximum and monthly average values, respectively, in Table 1, it can be seen that all of the measured concentrations are substantially below the NPDES limits.

The frequency and duration of the alarm samples decreased during the 29-week sampling period, but the proportion of the alarm samples that contained high concentrations of metals increased. The highest concentration for an NPDES metal measured in an alarm sample was 9.8 mg/L Cu on 3/21/89. The alarm samples have contained >0.3 mg/L of at least one of the NPDES metals 88% of the time, and have violated the NPDES limits 42% of the time overall. The daily alarm samples violated the NPDES daily maximum limits 4% of the time during the first 10 weeks (3/9 to 5/19/89), and the weekly composite samples violated the monthly average limits 62% of the time during the last 19 weeks. A list of the highest metals concentrations in the alarm samples is shown in Tables 4 and 5.

Table 2. List of the highest metals concentrations in the normal-pH samples (pH = 6.0 to 9.0) from manhole 190 (daily composite samples 3/9/89 to 5/19/89)

| Dates | Metal | Concentration (mg/L) | Percentage of NPDES Daily Limit |
|---|---|---|---|
| 4/26 | Cu | 0.46 | 14.0 |
| 3/23 | Cr | 0.34 | 12.0 |
| 3/23 | Cu | 0.33 | 9.8 |
| 4/25 | Cu | 0.30 | 8.9 |
| 5/3 | Cu | 0.23 | 6.8 |
| 5/3 | Zn | 0.22 | 8.4 |
| 5/12 | Zn | 0.21 | 8.0 |

Table 3. List of the highest metals concentrations in the normal-pH samples (pH = 6.0 to 9.0) from manhole 190 (weekly composite samples 5/22/89 to 10/2/89)

| Dates | Metal | Concentration (mg/L) | Percentage of NPDES Weekly Limit |
|---|---|---|---|
| 5/30 to 6/5 | Cu | 0.29 | 14.0 |
| 6/6 to 6/12 | Cu | 0.27 | 13.0 |
| 7/11 to 7/17 | Cu | 0.18 | 8.7 |
| 5/22 to 5/30 | Cu | 0.17 | 8.2 |
| 6/13 to 6/19 | Zn | 0.16 | 11.0 |
| 6/13 to 6/19 | Cu | 0.14 | 6.8 |
| 6/20 to 6/26 | Zn | 0.14 | 9.5 |
| 7/11 to 7/17 | Zn | 0.14 | 9.5 |
| 8/22 to 8/28 | Cu | 0.14 | 6.8 |
| 6/27 to 7/5 | Zn | 0.13 | 8.8 |
| 8/22 to 8/28 | Pb | 0.13 | 30.0 |

Table 4. List of the highest metals concentration in the alarm samples (pH < 6.0 or > 9.0) from manhole 190 (daily composite samples 3/9/89 to 5/19/89)

| Date | Metal | Concentration (mg/L) | Percentage of NPDES Daily Limit |
|---|---|---|---|
| 3/21 | Cu | 9.8 | 290 |
| 4/10 | Cr | 2.4 | 87 |
| 4/25 | Cu | 2.2 | 65 |
| 4/20 | Cu | 2.0 | 59 |
| 3/22 | Zn | 1.7 | 65 |
| 3/13 | Cr | 1.6 | 58 |
| 4/21 | Zn | 1.6 | 61 |
| 4/13 | Zn | 1.4 | 54 |
| 4/20 | Pb | 1.2 | 170 |
| 4/24 | Cu | 1.2 | 36 |
| 3/21 | Cr | 1.0 | 36 |
| 4/5 | Zn | 1.0 | 38 |
| 4/24 | Zn | 1.0 | 38 |

Table 5. List of the highest metals concentration in the alarm samples (pH <6.0 or >9.0) from manhole 190 (weekly composite samples 5/22/89 to 10/1/89)

| Dates | Metal | Concentration (mg/L) | Percentage of NPDES Monthly Limit |
|---|---|---|---|
| 8/22 to 8/28 | Pb | 3.7 | 860 |
| 7/18 to 7/24 | Pb | 2.9 | 670 |
| 9/12 to 9/18 | Pb | 2.9 | 670 |
| 5/30 to 6/5 | Cu | 2.4 | 120 |
| 8/22 to 8/28 | Cu | 2.4 | 120 |
| 8/8 to 8/14 | Pb | 2.3 | 530 |
| 7/18 to 7/24 | Cu | 2.2 | 110 |
| 7/11 to 7/17 | Cu | 2.0 | 97 |
| 7/25 to 7/31 | Pb | 2.0 | 460 |

Based on the alarm sample volumes, the alarm pump at manhole 190 ran for an average of 136 min/week for the first 10 weeks and 42 min/week for the last 19 weeks, for an overall average of 75 min/week. If a pH-based diversion system is used for the NRWTP, it would be expected that about 9500 gal/week (36 $m^3$/week) would be diverted to the metals tank from manhole 190, assuming an average flow rate of 125 gal/min (0.47 $m^3$/min) at the manhole.

## 3.2 RADIOCHEMICAL ENGINEERING DEVELOPMENT CENTER (REDC)

No low-pH alarm samples were collected from the REDC wastewater during the first five weeks of sampling. After changing the set-point to 9.0, there were two high-pH alarm samples collected in three weeks. The ICP results for these two samples did not show any elevated metals concentrations. Table 6 shows the highest concentrations of metals measured in the normal-pH composite samples from the REDC. The two highest concentrations, 0.57 and 0.36 mg/L of Zn, occurred during a time when white paint was visible in the wastewater. None of the samples from the Melton Valley Collection Tanks, which receive wastewater from REDC and HFIR, has shown any elevated concentrations of metals. Sixteen tanks of water [average volume of 265 $m^3$ (70,000 gal) each] have been sampled during the 13 week period between 6/27 and 9/25/89.

## 3.3 MANHOLE 95

Table 7 shows the highest metals concentrations detected in the normal-pH composite samples from manhole 95 during nine weeks of sampling. These results, 0.13 to 0.19 mg/L of Zn, are just slightly above the normal Zn concentration in the local drinking water. There were three days when low-pH alarm samples were collected from manhole 95, on 6/16, 7/10 and 7/21/89. Two of these samples, on 7/10 and 7/21, contained elevated concentrations of NPDES metals. The highest concentrations of metals in the alarm/samples is shown in Table 8. The sample on 7/10 was the only sample from any of the locations that contained an elevated concentration of Ni.

Table 6. List of the highest metals concentrations in composite wastewater samples from the Radiochemical Engineering Development Center.

| Dates | Metal | Concentration (mg/L) | Percentage of NPDES Daily Limit |
|---|---|---|---|
| 4/29 to 5/5 | Zn | 0.57* | 38 |
| 5/6 to 5/15 | Zn | 0.36* | 24 |
| 8/14 to 8/21 | Cu | 0.29 | 14 |
| 8/5 to 8/14 | Cu | 0.22 | 11 |
| 6/28 to 7/5 | Zn | 0.20 | 14 |

*White paint visible in wastewater.

Table 7. List of the highest metals concentrations in the normal-pH samples (pH > 6.0) from manhole 95 (weekly composite samples 5/23/89 to 7/24/89)

| Dates | Metal | Concentration (mg/L) | Percentage of NPDES Monthly limit |
|---|---|---|---|
| 6/13 to 6/19 | Zn | 0.19 | 13.0 |
| 6/20 to 6/26 | Zn | 0.15 | 10.0 |
| 6/27 to 7/5 | Zn | 0.13 | 8.8 |
| 7/6 to 7/17 | Zn | 0.13 | 8.8 |
| 7/18 to 7/24 | Zn | 0.13 | 8.8 |

Table 8. List of the highest metals concentrations in the alarm samples (pH < 6.0) from manhole 95 (weekly composite samples 5/23/89 to 7/24/89)

| Dates | Metal | Concentration (mg/L) | Percentage of NPDES Monthly Limit |
|---|---|---|---|
| 7/6 to 7/17 | Ni | 1.9 | 80 |
| 7/18 to 7/24 | Zn | 1.6 | 110 |
| 7/6 to 7/17 | Pb | 1.5 | 350 |
| 7/6 to 7/17 | Zn | 1.5 | 100 |
| 7/18 to 7/24 | Cu | 0.5 | 24 |
| 7/18 to 7/24 | Pb | 0.5 | 120 |

### 3.4 PUMP STATION

The highest concentrations of metals in the normal-pH samples from the pump station are shown in Table 9. As with manhole 95, the concentrations listed are only slightly higher than in drinking water. There were no alarm samples collected from the pump station during the nine weeks of sampling. Although there were no alarm samples collected during this sampling period, the alarm samples that were detected at manhole 95 on 7/10/89 and 7/21/89 should have also been detected at the pump station if the sampling system had been in operation during this time period, since the flow from manhole 95 is a major part of the flow at the pump station.

## 4. RECOMMENDATIONS

The sampling that was done for this project has shown that low pH is highly correlated with significant metals concentrations in the wastewater from the 4500 area (manhole 190) and the 2000 area (pump station). Although none of the high-pH alarm samples collected during this project have contained elevated concentrations of metals, some metals,

Table 9. List of the highest metals concentrations in the normal-pH samples (pH > 6.0) from the pump station (weekly composite samples 7/31/89 to 10/2/89)

| Dates | Metal | Concentration (mg/L) | Percentage of NPDES Monthly Limit |
|---|---|---|---|
| 7/31 to 8/7 | Zn | 0.14 | 9.5 |
| 8/8 to 8/14 | Zn | 0.13 | 8.8 |
| 8/15 to 8/21 | Zn | 0.11 | 7.4 |
| 8/22 to 8/28 | Zn | 0.11 | 7.4 |
| 9/6 to 9/11 | Zn | 0.11 | 7.4 |
| 9/12 to 9/18 | Zn | 0.11 | 7.4 |
| 9/19 to 9/25 | Zn | 0.11 | 7.4 |

particularly zinc, are soluble at high pH. Zinc hydroxide has a solubility of 1 mg/L at a pH of 11, so setting the high pH limit at 10.0 for sending water to the nonmetals tank would provide a large margin of safety for meeting the NPDES limits.

It is recommended that pH be used as the criteria for diverting wastewater to the metals tank of the NRWTP. Wastewater from manhole 190 and the pump station should be diverted to the metals tank anytime the pH is below 6.0 or above 10.0. It is recommended that a new pH meter be installed in the discharge line of the pumps at the wet well downstream from manhole 190. The wet well will help modulate any rapid changes in the pH of the wastewater, and will make the timing of the valve response at the NRWTP tanks much easier. A pH meter should also be installed at the pump station. It is recommended that the water from the Melton Valley Collection Tanks (wastewater from REDC and HFIR) be sent to the nonmetals tank of the NRWTP, since no metals spikes have been detected over 21 weeks of sampling. This wastewater should be sampled and analyzed by ICP periodically to assure that the metals concentration does not increase.

## 5. CONCLUSIONS

The use of two pH-based sampling systems has shown that there is a high correlation between low pH and metals contamination in the wastewater from the 4500 area (manhole 190) and the 2000 area (pump station). The low-pH samples from manhole 190 have contained greater than 0.3 mg/L of at least one of the NPDES medals 88% of the time and have violated the NPDES limits 42% of the time overall. Low-pH samples from the 2000 area occur less frequently, but two of the three samples collected contained high concentrations of metals. Wastewater from the Radiochemical Engineering Development Center (REDC) and the High Flux Isotope Reactor (HFIR) has not shown any metals concentrations above the NPDES permit limits for the Nonradiological Wastewater Treatment Plant (NRWTP).

It is recommended that pH be used as the diversion criteria for wastewater from manhole 190 and the pump station to be sent to the metals tank of the NRWTP. Any wastewater with a pH less than 6.0 or greater than 10.0 should be sent to the metals tank. Based on the results of 29 weeks of sampling, it is expected that on the order of 36 $m^3$/week (9500 gal/week) of wastewater will be diverted to the metals tank of the NRWTP. Wastewater from REDC and HFIR can be sent to the non-metals tank, but it should be sampled periodically to confirm that the metals concentration is not increasing.

Although the correlation between low pH and higher metals concentrations has only been demonstrated for selected wastewater streams at ORNL, heavy metals are generally not soluble in neutral pH water unless a high concentration of chelating agents are present, so these results would probably be applicable for a wide range of other wastewaters.

## 6. REFERENCE

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