When uranium ores are leached underground we can guard against the contamination of groundwater by monitoring for the products of leaching, particularly toxic heavy metals. This paper describes a new geoelectrochemical method called polarographic logging (PL), and its effectiveness in monitoring groundwater contamination and its movement in a mining environment (Putikov, 1987).

Polarographic logging belongs to a group of nonlinear polarizational geoelectrochemical methods. These methods are based on recording of voltammograms (in the PL case polarograms) — the nonlinear dependence of the current on voltage between two special electrodes that must be placed in the medium to be investigated (Ryss, 1981).

To obtain borehole water polarograms, a dipping sonde on a cable is used (Putikov, 1987). This sonde contains a mercury dropping electrode and an auxiliary lead electrode. Using a container for the utilized mercury minimizes or eliminates pollution of the environment. In comparison with the well-known laboratory method of polarography, the PL method does not require the addition of a supporting electrolyte (a special neutral electrolyte of the high concentration) and allows us to make qualitative and quantitative analysis of water in boreholes, lakes and seas up to 1–2 km depths, in situ, without sampling.

At the present time, two models of the polarographic logging units have been developed — the direct current polarographic logging (DCPL) and the pulse polarographic logging (PPL). The potential of the mercury electrode is a linear function of time in the DCPL mode, with the addition of a pulse component by means of a synchronization system in the case of the PPL mode. Use of the PPL mode gives increased sensitivity in comparison with the DCPL mode, by approximately a factor of ten.

Polarographic logging allows the determination of the dissolved gaseous oxygen \( \text{O}_2 \), Fe\(^{++} \), Cl\(^- \), Mn\(^{+++} \), UO\(_2\)\(^{+++} \), VO\(_2\)\(^+ \), S\(^-\) and other components. The advantages of PL include real time measurements, increased reliability of analysis for volatile (\( \text{O}_2 \)) and unstable (Fe\(^{++} \)) components, and resulting high productivity.

Many years of experience using the PL in underground leaching sections have shown its effectiveness for all phases of the mining operation, during preparation of a section for exploitation, during exploitation itself, and during the later remediation.

The main components that need to be determined during preparation for exploitation of a mineral deposit are \( \text{O}_2 \), Fe\(^{++} \), Cl\(^- \), S\(^-\). Using PL we have found that we can easily obtain the levels and patterns of the background distribution of these ions in the groundwater, including the hydrochemical zonality. For example, polarogram trace number 2 in Figure 1 has two polarographic waves (steps) of the dissolved gaseous oxygen \( \text{O}_2 \), and is typical for boreholes that have crossed the oxygenized part of a seam. Polarograms 1 and 3 in Figure 1 correspond to the ore bodies and the non-oxygenized zones. In these zones we observe the absence of the oxygen polarographic waves, but the presence of the two-charged iron and the sulphide-ion polarographic waves. Concentration of the chlorine-ion (Figure 1, polarogram 4) is independent of zonality and practically constant (200–300 mg/l) within the boundary of the region.

For underground leaching, the sulphuric acid solution and the solutions enriched by dissolved oxygen are widely used as the production solutions. These solutions convert into the liquid phase not only the useful components but also a number of the associated elements and some components of the embedding rocks.

For example, in the case of the acid leaching there are the definite polarographic waves on the polarograms of Figure 2. By means of correlation with the chemical analysis data of the water samples and by the identification in laboratory and directly in the boreholes, it was established that these waves belong to uranium, vanadium, two-charged iron and manganese. It should be pointed out that the concentrations of iron and manganese in the production solutions has increased by tens and hundreds of times in comparison with the natural water.

The main task during the exploitation phase of the uranium underground leaching deposits is a determination of the uranium concentration in the production solution within the boreholes. But it is necessary to have a high sensitivity of analysis for resolution of this task. As is evident from the calibration for the uranile complex UO\(_2\)\(^{+++} \) (Figure 3), the PL method in the pulse mode (PPL) supplies a measure of the uranium in the borehole water with a threshold near 10 mg/l, quickly and without sampling.

In case of the oxygen leaching, there are on the polarograms two well expressed polarographic waves of the dissolved oxygen and often the wave of two-charged iron. Also we have increasing chlorine-ion concentration in the production solutions up to 500–600 mg/l. The sulphide ion S\(_2\)\(^-\) is oxygenized into sulphate ion SO\(_4\)\(^2-\) and we see the absence its polarographic wave on the polarograms.

Table 1: Concentration of the micro-components in the residual solutions.

<table>
<thead>
<tr>
<th>Borehole number</th>
<th>Concentration, mg/l</th>
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<tbody>
<tr>
<td>Mo</td>
<td>Cd</td>
</tr>
<tr>
<td>4-11</td>
<td>7.077</td>
</tr>
<tr>
<td>10-7</td>
<td>3.173</td>
</tr>
<tr>
<td>6-12</td>
<td>8.900</td>
</tr>
<tr>
<td>18-1</td>
<td>23.500</td>
</tr>
<tr>
<td>The safe concentration</td>
<td>0.250</td>
</tr>
</tbody>
</table>

Figure 1: The logging polarograms of natural water at the uranium underground leaching site. 1: anodic, 2-4: cathodic.

Figure 2: Dependence of the logging cathodic polarogram shape on depth for a uranium underground leaching deposit. A: borehole 7 (sensitivity $-10^{-6}$ A); depth, m: 1 - 90, 2 - 95, 3 - 103; B: borehole 3H (sensitivity $-10^{-5}$ A); depth, m: 4 - 90, 5 - 98, 6 - 104, 7 - 107; 8 - borehole 3H (sensitivity $-10^{-5}$ A); depth - 98 m.

Figure 3: The pulse cathodic calibration polarograms for the uranile complex $\text{UO}_2^{2+}$. The initial solution of the underground leaching ($\text{pH} = 5.5$): 1 - before the blow-through, 2 - after the helium blow-through. The added $\text{UO}_2^{2+}$ concentration, mg/l: 3 - 12, 4 - 25, 5 - 37, 6 - 52, 7 - 77, 8 - 101, 9 - 126, 10 - 176, 11 - 225.
After completing the exploration of the uranium deposits by underground leaching, the high mineralized residual solution remains within the ore body boundaries. This residual solution contains \( \text{SO}^{4-} \), \( \text{Fe}^{2+} \), \( \text{Fe}^{3+} \), \( \text{Ca}^{2+} \), \( \text{Mg}^{2+} \), \( \text{Al}^{3+} \) as macro-components, with the total mineralization up to 20–25 g/l, as well as micro-components, including the heavy toxic metals—Zn, Co, Ni, Cd, Pb and others (Table 1). PL allows a determination of \( \text{Cd}^{2+} \), \( \text{Zn}^{2+} \) and other components. The detection limit is 5 mg/l for \( \text{Fe}^{2+} \) and 0.1 mg/l for \( \text{Cd}^{2+} \).

The remediation of a section may be accomplished by an artificially induced movement of the groundwater. During this movement there is interaction between the residual solution and the host rocks with increasing pH and decreasing heavy metals concentration, including \( \text{Fe}^{3+} \). The PL technique allows the monitoring of this process by measuring the \( \text{Fe}^{3+} \) concentration in the borehole water (Figure 4). The initial \( \text{Fe}^{3+} \) distribution before remediation, isoconcentration contour 100 mg/l, practically coincides with the lens of contaminated groundwater (Figure 4a). During remediation this lens was divided into two parts (Figure 4b), and then completely disappeared. By the end of remediation the \( \text{Fe}^{3+} \) concentration in the borehole water was less then 10 mg/l, pH 6.5–7.0, and mineralization <4–5 g/l. These parameters correspond to their values under natural conditions before leaching, and demonstrate that the remediation was successful.

**REFERENCES**

