Surface and deep shaft coal mining operations must meet EPA standards for the amount of acid, iron, and manganese in drainage waters. CAIROX® and ECONOX® are very effective for removing iron and manganese from acid rock drainage to meet discharge requirements.

**Benefits of CAIROX® and ECONOX®**
- Insure metal discharge limits are routinely met
- Fast and efficient reactions
- Safe and easy to handle
- Do not form chlorinated organics which can find their way into drinking water

**Manganese Removal**
- Permanganate is a powerful oxidant that quickly reacts with soluble manganese to remove it in the form of insoluble manganese dioxide.
  
  \[
  3\text{Mn}^{2+} + 2\text{MnO}_4^- \rightarrow 5\text{MnO}_2 \downarrow
  \]

- It may seem a paradox that one manganese compound, permanganate, would be used successfully to produce a treated water that is free of manganese contamination. It is the oxidation potency of permanganate that established its use to remove manganese from water and wastewater. Permanganate treatment of manganese is commonly practiced in the water treatment industry, world-wide.

**Case Study 1**

In Case 1, drainage water samples were taken at a coal mining operation in West Virginia. The initial pH was 3.9, iron 45.0 mg/L, and manganese 18.75 mg/L. The coal facility is required to reduce manganese levels to less than 1 mg/L.

**Case 1 Field Data**

<table>
<thead>
<tr>
<th>pH</th>
<th>ECONOX™ (NaMnO₄ mg/L)</th>
<th>Iron (mg/L)</th>
<th>Mn (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.9</td>
<td>0.0</td>
<td>45.00</td>
<td>18.75</td>
</tr>
<tr>
<td>7</td>
<td>10.0</td>
<td>0.35</td>
<td>0.75</td>
</tr>
<tr>
<td>8</td>
<td>5.0</td>
<td>0.10</td>
<td>4.60</td>
</tr>
<tr>
<td>8</td>
<td>7.5</td>
<td>0.00</td>
<td>3.50</td>
</tr>
<tr>
<td>8</td>
<td>10.0</td>
<td>0.25</td>
<td>0.50</td>
</tr>
<tr>
<td>9</td>
<td>10.0</td>
<td>0.50</td>
<td>0.00</td>
</tr>
</tbody>
</table>

After the pH was adjusted to 7.0 and above, most of the iron was precipitated and ECONOX® liquid permanganate was able to significantly lower the manganese concentration. In fact, 45.0 mg (33 mL) of the ECONOX® solution per one liter of drainage water at pH 7 produced acceptable results.

**Case Study 2**

At a coal mining facility in eastern Kentucky, tests were conducted on two drainage ponds being treated with lime and CAIROX® potassium permanganate.

The first pond had pH levels of 3.0 - 4.0, iron concentrations from 20 - 40 mg/L, and manganese concentrations from 30 - 40 mg/L. Lime is usually added to raise the pond water pH to 8.3 - 8.5. After pH adjustment and CAIROX® addition, the iron and manganese levels dropped to less than 1 mg/L.

**Field Data - Pond 1**

<table>
<thead>
<tr>
<th>pH</th>
<th>CAIROX® (KMnO₄ mg/L)</th>
<th>Iron (mg/L)</th>
<th>Mn (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.0</td>
<td>40.00</td>
<td>40.00</td>
</tr>
<tr>
<td>8.5</td>
<td>33.0</td>
<td>0.45</td>
<td>0.44</td>
</tr>
</tbody>
</table>

The second pond (pH 4.0) was treated with lime to a pH of 7.7. Iron concentrations in the pond dropped from 3.0 to 0.62 mg/L and manganese levels were reduced from 30 to 16.05 mg/L. CAIROX® was then applied at a rate of 2.0 mg/L for every 1.0 mg/L manganese.

**Field Data - Pond 2**

<table>
<thead>
<tr>
<th>pH</th>
<th>CAIROX® (KMnO₄ mg/L)</th>
<th>Iron (mg/L)</th>
<th>Mn (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.0</td>
<td>3.00</td>
<td>30.00</td>
</tr>
<tr>
<td>7.7</td>
<td>0.0</td>
<td>0.62</td>
<td>16.05</td>
</tr>
<tr>
<td>7.7</td>
<td>33.0</td>
<td>Pink after 1 hour</td>
<td></td>
</tr>
<tr>
<td>7.7</td>
<td>22.0</td>
<td>0.10</td>
<td>0.37</td>
</tr>
</tbody>
</table>

At a dosage of 33.0 mg/L, the sample was still pink after one hour, an indication of an overdose. After further testing, a lower dosage of 22 mg/L reduced the iron and manganese levels to within the discharge limits.

**Permanganate Evaluations**

Evaluating permanganate for the treatment of acid rock drainage requires the following steps:

1. Begin by collecting one or two gallons of the acid rock drainage that must be treated. Exercise care, since this wastewater is acidic! Using a lime solution, adjust the pH of the sample to 8.0. If lime is not available, any alkaline compound can be used to raise the pH. If chemical additions for pH control are already being made at the mine site, a sample of this pre-treated water can be used for the permanganate test.

2. A pH adjustment to near 8.0 is important because:
   - It raises the drainage pH to within EPA guidelines (pH between 6-9)
   - The iron precipitates in the wastewater as Fe(OH)₃
   - It reduces the CAIROX® demand by removing some of the manganese, thus saving money.

   **THE PERMANGANATE METHOD FOR REMOVING MANGANESE FROM ACID ROCK DRAINAGE**
**pH ADJUSTMENT**
- Prepare an alkaline solution in water. Lime is often used as a 1 gram/liter solution.
- Measure the pH of the sample using an appropriate device, e.g., a pH meter, litmus paper, etc.
- Titrate the sample using the prepared alkaline solution until the pH is 8.0.

**ANALYZE SAMPLE FOR DISSOLVED IRON AND MANGANESE**
- The sample is analyzed for dissolved iron and manganese.
- Allow the solids in the jar to settle and filter some of the sample through 0.22 micron filter paper.
- Determine the amount of dissolved iron and manganese in the filtered solution by standard test procedures.*
- It is possible that with pH adjustment alone the sample may be within EPA standards. If not, the remaining iron and manganese can be removed by treating the sample with CAIROX® potassium permanganate or ECONOX® agent
  - The procedures can be found in the most recent edition of Standard Methods, for the Examination of Water and Wastewater, Part 3000 prepared and published jointly by the APHA, AWWA, and WPCF, New York.

**CAIROX® AND ECONOX™ TEST SOLUTIONS**
Prepare a “master” 1% permanganate solution by dissolving 5 grams of CAIROX® potassium permanganate (be sure all of the CAIROX® is dissolved) with distilled water in a 500 mL flask. A 1% permanganate solution can also be prepared by pipetting 25 ml of ECONOX® agent into a 500 mL flask and fill with distilled water. This master solution should be sufficient to run a complete evaluation.

For the tests, dilute this “master” solution further. To make a “standard” test solution, dilute 10 mL of the 1% solution to 100 mL with distilled water. One ml of this dilute solution will give a dosage of 1.0 mg/L permanganate when added to one liter of drainage water.

**DETERMINE DEMAND**
If a spectrophotometer is available, determine permanganate demand by using Carus Analytical Method 105. An alternative method is to conduct a jar test as follows: Using a beaker, accurately measure a 1 liter volume of the pH-adjusted mine drainage. To determine the approximate permanganate demand, titrate this sample with the standard permanganate test solution. Note the amount of standard test solution that has been added. The test is complete when the pink color remains in the jar for about two minutes. Mixing the sample while titrating will help to determine the end point.

Example: If 20 mL of permanganate solution is required to produce a two-minute pink end point, the permanganate demand would be approximately 20 ppm. Additional tests can be conducted to determine if a lower permanganate concentration can be used to meet discharge requirements. If the analysis of iron and manganese does not meet discharge standards, repeat the test using a concentration of permanganate above the two-minute demand. After settling and filtering, analyze the sample for iron, manganese and pH. If all of these analyses meet the discharge standards, then this concentration of permanganate should be fed in a plant trial.

**Economics**
To determine the theoretical cost of successful treatment, proceed in the following manner:

Assume a dose of 20 mg/L resulted in satisfactory removal of iron or manganese. This dose is equivalent to 20 x 8.34 lbs, or 166.8 lbs of CAIROX® per million gallons of water to be treated.

Using the appropriate cost of CAIROX®, multiply 166.8 pounds times $/lb of CAIROX® to obtain the cost of treating one million gallons.

To determine actual costs, a plant trial may be required.

ECONOX® agent is a highly concentrated (20%) liquid permanganate that is easy to handle, feed, and is more effective at lower temperatures (12 °C). The cost of treatment for the above example is 20 ppm x 37.5 lbs or 748 pounds of ECONOX® x $/lb of ECONOX® agent.

**Carus Value Added**

**LABORATORY SUPPORT** - Carus Chemical Company has technical assistance available to its potential and current customers to answer questions or perform laboratory testing. Carus has complete laboratory testing capabilities including:

- Feasibility Studies
- Toxicity Evaluations
- Treatability Studies
- Analytical Services

**FIELD SERVICES** - As an integral part of our sales support, Carus provides extensive technical field assistance to potential and current customers. These evaluations can be useful in determining dosing requirements and equipment needs.

**EQUIPMENT SERVICES** - Standard feeders are designed specifically for potassium permanganate. Various options and accessories are available to meet a wide range of applications.

Custom-Engineered Feed Systems are complete, pre-engineered and pre-packaged systems that provide efficient, dust-free methods of storing, mixing, and feeding CAIROX® potassium permanganate. System designs are customized to meet specific applications.

**CARUS CHEMICAL COMPANY** - During its more than 85-year history, Carus’ ongoing reliance on research and development, as well as its emphasis on technical support and customer service, have enabled the company to become the world leader in permanganate, manganese, oxidation, and base-metal catalyst technologies.

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Form #CX 5752

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