Natural zeolites remove thallium from mining water

By Mark Reinsel and Scott Mason

Although a relatively obscure metal, thallium is found in many mining waters and, because of its toxic nature, must be removed to low levels. A low-cost natural zeolite, clinoptilolite, has been found to effectively remove thallium from water at a closed gold mine.

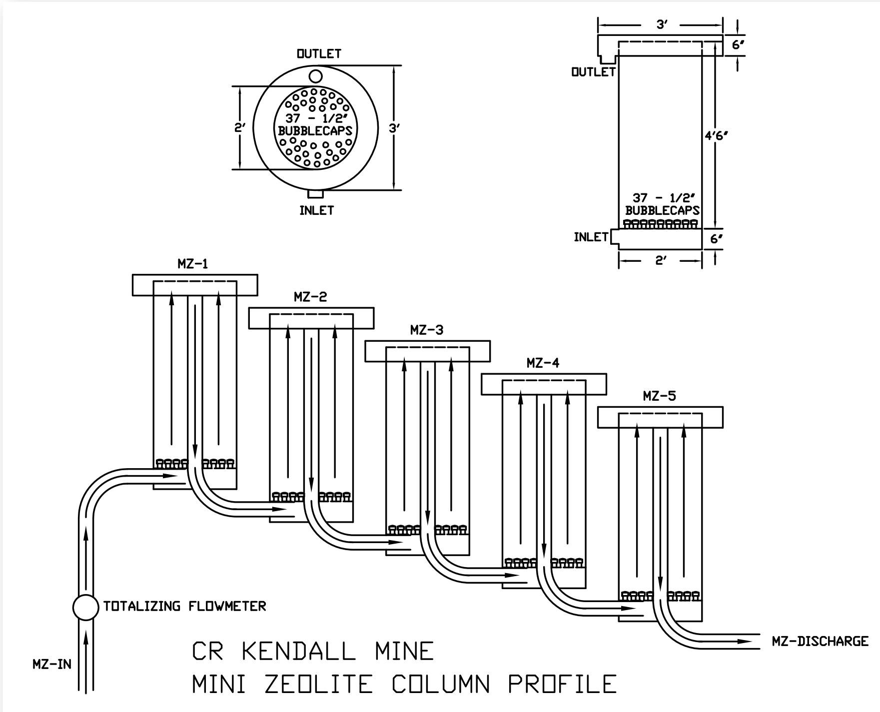
Thallium is a soft metal now used in electronics, pharmaceuticals and glass manufacturing. Due to its potential toxicity, it is the primary contaminant of concern at the Kendall Mine in Montana. Concentrations of thallium, cyanide, nitrate and other parameters in mine water are decreasing, but it is anticipated that water treatment will be required for the next 10 to 40 years. Treatment will cease once water quality standards and/or background levels are met.

Several water treatment technologies for thallium have been evaluated since 1996, including reverse osmosis, biological treatment, sulfide precipitation and other chemical treatment methods. However, none were found to perform as well as natural zeolites.

Zeolites have very effectively removed thallium from mine water in bench- and pilot-scale testing, and through operating a 100-gpm treatment system at the Kendall Mine for over 10 years. The zeolite treatment system is advantageous in that it is effective, simple to operate, and generates a nonhazardous waste product (spent zeolites). Toxicity Characteristic Leaching Procedure (TCLP) testing indicates that thallium is effectively sequestered on the zeolites, with less than 1% of the toxic metal being mobile.

This system, using a zeolite called chabazite (cab-a-zite), was very effective. However, a review of previous bench-scale testing, current operational results and discussions with zeolite providers, suggested that higher loading capacities might be achievable with different zeolite materials.

To evaluate performance of a lower-cost natural zeolite, clinoptilolite, several sets of bench tests were run using clinoptilolite of different size gradations and from different suppliers. Bench test results were promising and led Kendall personnel to operate two pilot tests on-site.



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Pilot Test #1

A new material, 14x40 mesh clinoptilolite from Steelhead Specialty Minerals, was used in Zeolite Pilot Test #1. The previously-used zeolites are a larger material, 8x20 mesh chabazite from St. Cloud Minerals. The pilot test system used five "mini-columns" in series with gravity flow, which was modeled after the existing full-scale system, which uses columns formerly filled with activated carbon for gold recovery. Each mini-column contained approximately 230 L (180 kg) of clinoptilolite.

The maximum flow rate, without overflowing the columns, was found to be 3.9 m^3/hr. After results showed that thallium removal improved at lower flow rates, flow was reduced to about 1 m^3/hr for the remainder of the test.

The human health standard for thallium, which is the effluent limit for the treatment system, is 0.002 mg/L. Influent concentration of mine water in this test was about 0.6 mg/L. "Breakthrough" was defined as the time when the thallium effluent concentration first exceeded detection limits. The pilot test was operated for 65 days, when consistent breakthrough was seen from Column 5 at the laboratory detection limit of 0.0002 mg/L.

A total of 1,840 m^3 were treated through the system. At the end of the test, Column 4 effluent was near the discharge limit of 0.002 mg/L but Column 5 effluent still comfortably met the limit. Other conclusions from Test #1 were that:

- Clinoptilolite in Column 1 achieved a thallium loading of 0.38%. Loading in downstream columns was progressively lower.
- Spent clinoptilolite was tested by TCLP and the adsorbed thallium was found to be essentially non-leachable, as less than 1% of the thallium was liberated.
- Water quality parameters other than thallium (pH, arsenic, selenium, sulfate, etc.)

were not affected by zeolite treatment.

Pilot Test #2

Pilot Test #2, using another fine-grained low-cost material, 16x50 mesh clinoptilolite from St. Cloud Minerals, was operated immediately afterward for 120 days. A total of 3,290 m^3 were treated prior to breakthrough from Column 5. Results showed that:

• The average influent thallium concentration of 0.38 mg/L was somewhat lower than Pilot Test #, but is still within anticipated future mixed mine water quality.
• Clinoptilolite in Column 1 achieved a thallium loading of 0.32%.
• Spent clinoptilolite was again found to be essentially non-leachable.

Column 1 material was completely “spent” at the end of the test. As at the end of Test #1, Column 4 effluent was at the discharge limit, while Column 5 effluent was comfortably below it.

Treatment costs

Based on these results, estimated operating costs for full-scale treatment using St. Cloud clinoptilolite (Test #2) are shown in Figure 1. Costs are based on a 0.32% thallium loading rate in the first column and a price of $0.24/lb for zeolites. This is based on the quoted price for clinoptilolite ($0.14/lb) plus estimated shipping costs ($0.10/lb).

Figure 1 includes scenarios for three flow rates (low, average and maximum) and two concentrations (average and maximum). Anticipated annual average flow rates range from 36 to 110 gpm (8 to 25 m^3/hr). Anticipated thallium concentrations range from 0.30 to 0.46 mg/L.

At the loading rate seen in Pilot Test #2 and a St. Cloud clinoptilolite cost of $0.24/lb, anticipated treatment costs are quite low (about $7,500/yr. for the base case at average flow and average concentration). Chabazite currently used at the Kendall Mine costs $0.95/lb, plus shipping. Assuming the same loading rate as with St. Cloud clinoptilolite, which was shown to be true in bench tests, the current zeolite cost is approximately $33,000/yr. Therefore, switching to clinoptilolite will save the mine about $25,000/yr., over the remaining 10 to 40 years of water treatment.

Proposed treatment system

The selected method for long-term removal of thallium at the Kendall Mine, which is awaiting regulatory review and approval, is zeolite adsorption. Approximately 1,800 kg of clinoptilolite will be loaded into each of five columns in series. The proposed water treatment system comprises:

• Water storage and equalization in two ponds.
• Multimedia filtration to remove suspended solids prior to zeolite treatment.
• Zeolite treatment in the existing column system, using clinoptilolite as the preferred material. Chabazite may also be used, although it is more expensive.

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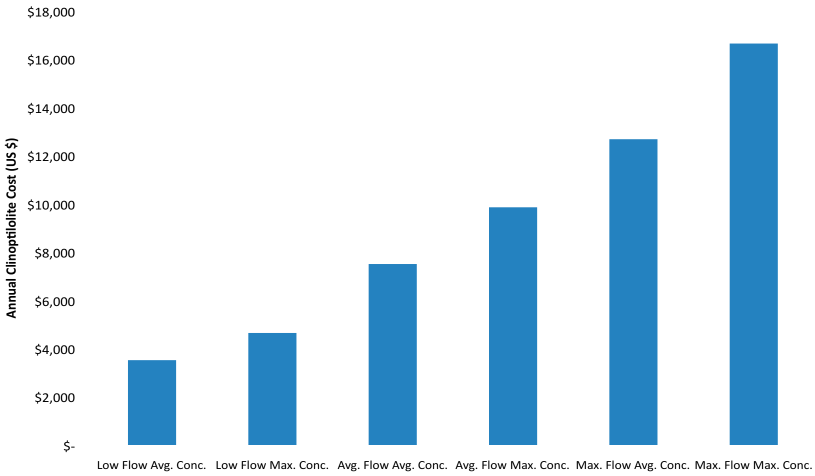
Figure 1. Annual Clinoptilolite Cost for Various Flow and Concentration Scenarios



• Effluent quality monitoring to ensure proper operation and thallium removal prior to groundwater discharge.
• Placement of water treatment residuals (spent zeolites and suspended solids) in a high-capacity lined pond.

Inflow rate to the storage ponds will vary seasonally. Total average annual flow is expected to be approximately 16 m^3/hr. The typical treatment flow rate will be 18 m^3/hr, which will partially fluidize zeolites in the columns, but still provide adequate contact time. If inflow rates do not provide enough water to meet minimum treatment system flows, treatment will be temporarily suspended until water is available.

Initial influent water quality will be similar to the range of concentrations predicted by the mixing model. Influent concentrations will decrease over time due to improving mine water quality.

Pilot testing and previous full-scale operations have shown that zeolites will adsorb more thallium when exposed to higher concentrations, as is typical with adsorbents. To maximize thallium loading, zeolite in each column will be transferred backward (upstream) periodically, with fresh material being loaded into Column 5 (the effluent or downstream end of the system), and material from Column 1 (the beginning or influent end of the system) being discarded.

It is anticipated that zeolite will be transferred by slurrying it with treated water, and pumping it from one column to another. Influent concentrations may be managed by adjusting source flows to increase removal efficiency.

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