Caustic Dissolution of Chromium in Underground Storage Tanks at Hanford Site

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Background
Currently, there are approximately 200,000 m³ of radioactive waste in the 177 underground storage tanks located at the U.S. Department of Energy’s Hanford Site. As part of the remediation efforts for these underground storage tanks, DOE plans to retrieve, pre-treat, immobilize, and dispose of this radioactive waste.

Problem
The presence of chromium at Hanford waste tanks can interfere with the efficient vitrification of the waste by shorting of the heating electrodes and clogging of pour spout. For these reasons minimization of the residual chromium concentration in the tank waste is an important pretreatment objective.

Objectives
Conducted, studied, and performed experiments to determinate the concentration of chromium in caustic solution. By knowing concentration values in the waste, we can design an optimal process of chromium removal, which is vital for the efficient vitrification process of the waste.

Chemistry
- Caustic leaching is expected to remove a large fraction of the Aluminum & Chromium.
- The Aluminum will be removed by converting aluminum oxides/hydroxides to sodium aluminate.
  \[ \text{AlOOH(s)} + \text{NaOH(aq)} \rightarrow \text{NaAlO}_2(\text{aq}) + \text{H}_2\text{O} \]
  \[ \text{Al(OH)}_3(\text{s}) + \text{NaOH(aq)} \rightarrow \text{NaAlO}_2(\text{aq}) + 2\text{H}_2\text{O} \]
- Based on its known chemical behavior, Cr(III) was expected to be removed by caustic leaching according to the following equation.
  \[ \text{Cr(OH)}_3(\text{s}) + \text{NaOH(aq)} \rightarrow \text{Na}[\text{Cr(OH)}_4](\text{aq}) \]

Experimental
A reaction vessel was used for this experiment equipped with a mechanical stirrer, a thermocouple, and a port for sampling while being air-tight. The vessel had a heating strap around it to maintain a constant temperature. Samples of supernatant were taken at 0, 1, 2, 4, 8, and 24 hours and analyzed for chromium by inductively-coupled plasma optical emission spectroscopy (ICP-OES).

Results
- Oxalate is no longer a problem in the dissolution reaction as previously thought.
- When chromium and iron rich sludge are mixed, equilibrium is not reached in a 24 hour period.
- Chromium is reacting with the iron rich sludge in unusual ways.

Future Work
- Identify the different anions found in the Iron Rich Sludge.
- Once the anions are found, we can conduct more experiment to find the reason for incomplete chromium dissolution.

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