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SPENT CATALYST PROCESSING WITH ELECTROCHEMISTRY

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November 13-17, 1994
Lake Buena Vista, Florida

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MASTER

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DISCLAIMER

SPENT CATALYST PROCESSING WITH ELECTROCHEMISTRY

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EXTENDED ABSTRACT

Increasing concern for pollution prevention and waste disposal has created a need for clean alternatives for spent catalyst processing. In addition, expanded use of catalysts for the production of fuels and chemical feedstocks will continue in response to 1) economic pressure to upgrade heavier crudes and other feeds having high levels of impurities, 2) competitive pressure to achieve higher conversions using less energy, and 3) pressure to increase reaction selectivities to minimize waste production. While the incentives for using catalysts are great, all catalysts gradually lose activity through coking; poisoning by metals, sulfur, or halides; or loss of surface area from sintering at high process temperatures. Regeneration is possible where the catalyst deactivation can easily be reversed. However, the economic life of a catalyst is ultimately limited by regeneration costs and extent of irreversible deactivation.

Electrochemical dissolution is a new technique to oxidize catalyst contaminants and dissolve catalyst metals in an aqueous solution for further recovery of the raw materials. The key to this process is adding spent catalyst to a solution containing small amounts of species that form kinetically active, strongly oxidizing ions such as cerium(IV) or silver(II). The oxidizing ions are regenerated at the anode; they act in a catalytic manner carrying electrons from the solid surface to the anode of the electrochemical cell.

A cerium oxidizer was used for the experiments described in this paper. For this procedure, solution is added to the anode side of an electrochemical cell. At the anode, aqueous cerium(III) is oxidized to cerium(IV). The cerium(IV), in turn, oxidizes organic material adhered to the catalyst to carbon dioxide and water. Many spent catalysts used in hydrogenations contain metal sulfides that have contaminated the catalyst surface during processing. Metal sulfides are oxidized to dissolved metal ions and sulfur species. Because cerium is continuously reoxidized to cerium(IV) at the anode, a small amount of cerium is needed to oxidize the spent catalyst.

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COPPER CHROMITE CATALYST

Copper chromite catalysts are used to reduce functional groups while maintaining the unsaturation of aromatic rings or alkyl chains. This class of catalyst is widely used in the oil and fats industry. Some copper chromite catalysts are stabilized with barium or manganese to slow reduction of the catalyst. It is not economic to treat spent copper chromite catalyst using conventional catalyst recovery methods because it is very insoluble even in concentrated acids or bases.

Fresh copper chromite catalyst was dissolved within 10 minutes using cerium(IV) oxidation in an electrochemical cell. No apparent dissolution was observed for electrochemical dissolutions without a redox agent such as cerium, or for dissolutions using acid alone.

A barium salt precipitate formed as the catalyst dissolution proceeded. The barium salt was filtered and easily dissolved in water. Therefore, the barium can be recovered separately from the other catalyst components and returned to the catalyst manufacturing processes in desired amounts.

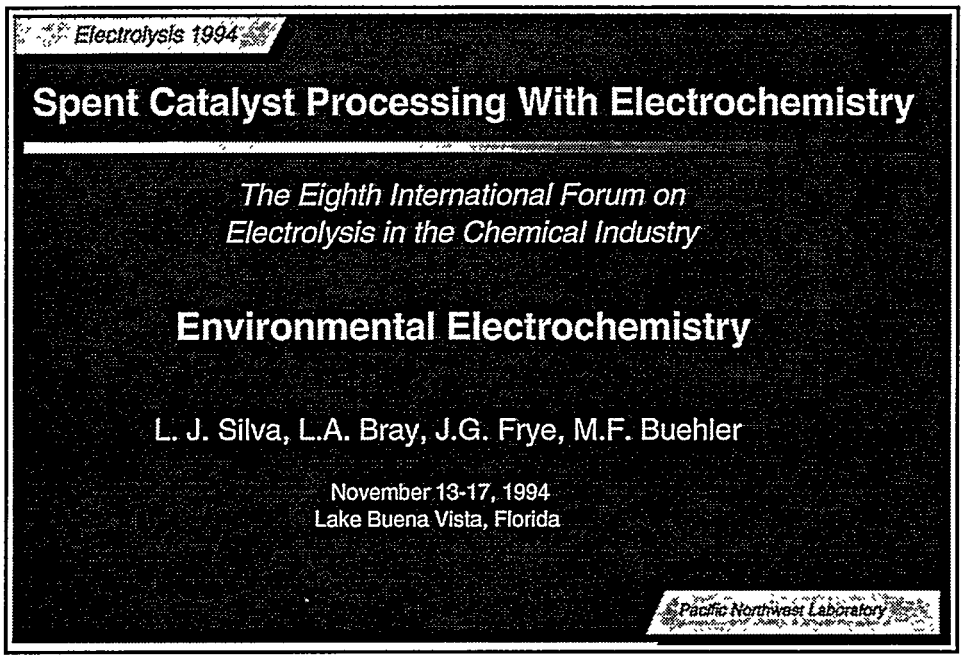
Cerium was selectively precipitated from the dissolved mixture by neutralizing the solution with ammonium. The cerium can be recovered and returned to the dissolution step. The remaining solution, containing copper and chromate ions, could be used as feedstock to produce fresh copper chromite catalyst. Two methods for preparing copper chromite catalyst are decomposition of copper ammonium chromate and decomposition of copper chromium nitrates. The solution could be returned from the catalyst preparation step for reuse in the dissolution step. A proposed flow scheme was prepared for processing spent copper chromite catalyst by cerium(IV) oxidation.

PETROLEUM HYDROTREATING CATALYST

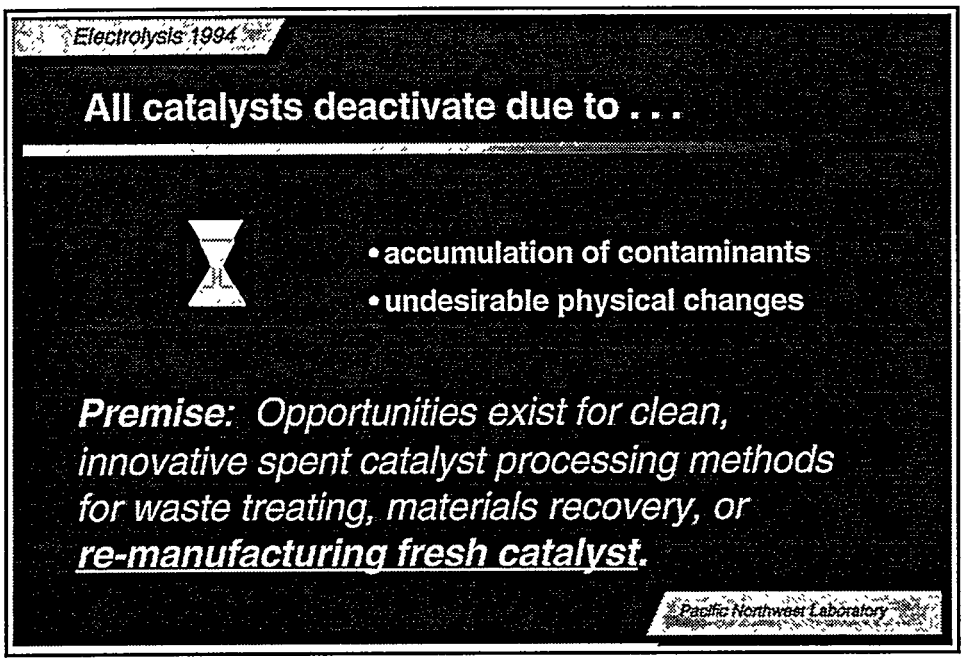
Metals such as Ni, Mo, Co, or W are commonly used in catalysts used to improve the quality of fossil fuels. The metals are conventionally incorporated on a support material and used in fixed-bed reactors. Recent developments include research using unsupported catalysts combined with liquids in a slurry reactor system to improve reactions for coal liquefaction or very heavy petroleum. Most of this research has focused on using iron as a cheap, disposable catalyst. However, this catalyst recovery technique could make more expensive metals more attractive.

An unsupported hydrotreating catalyst sample was prepared by deactivating fresh catalyst via coking and metal deposition. The spent catalyst sample contained the original catalyst metal plus contaminants such as Ni, V, S, carbon and hydrocarbons. The sample was pretreated to remove some of the adhered hydrocarbons. Pretreated samples completely dissolved in about 15-30 minutes using cerium(IV) oxidation in an electrochemical cell. Results from inductively coupled plasma/mass spectrometry analyses showed that the ratios of dissolved metal concentrations were about the same as the ratios of metals in the spent catalyst. For this case, then, the dissolution was not selective for particular catalyst components. After complete dissolution of the solid, the acidity of the anolyte was adjusted. The oxide of the transition metal used for the fresh catalyst subsequently precipitated.

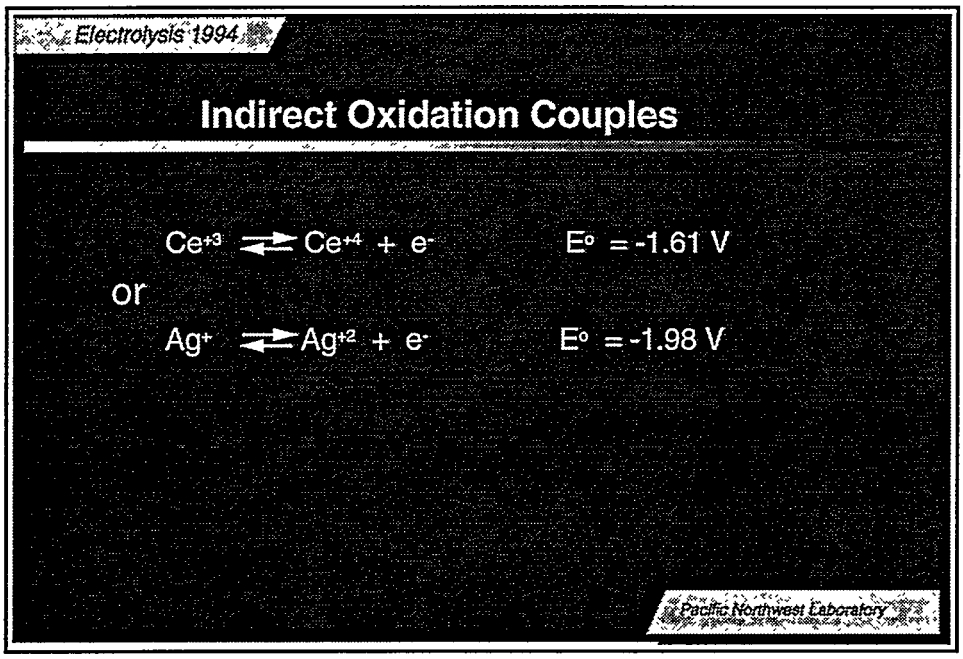
An experiment was also conducted in which spent catalyst was contacted with nitric acid solution overnight without an oxidizer present. The solids did not dissolve under these conditions, but did dissolve within a few minutes after adding cerium(IV). Therefore, an oxidizer is needed for this process.



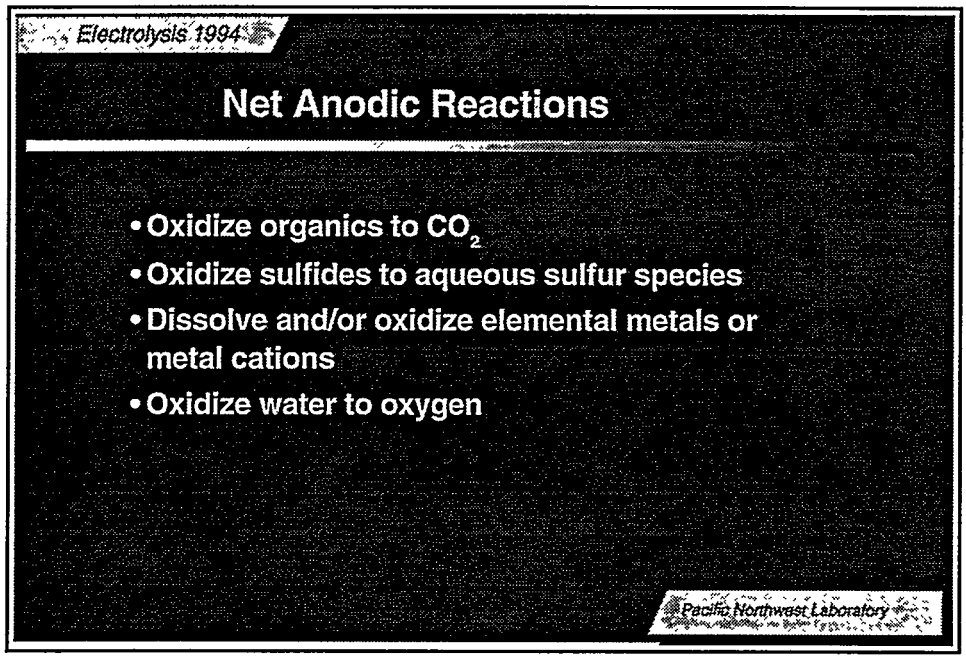
Spent Catalyst Processing With Electrochemistry



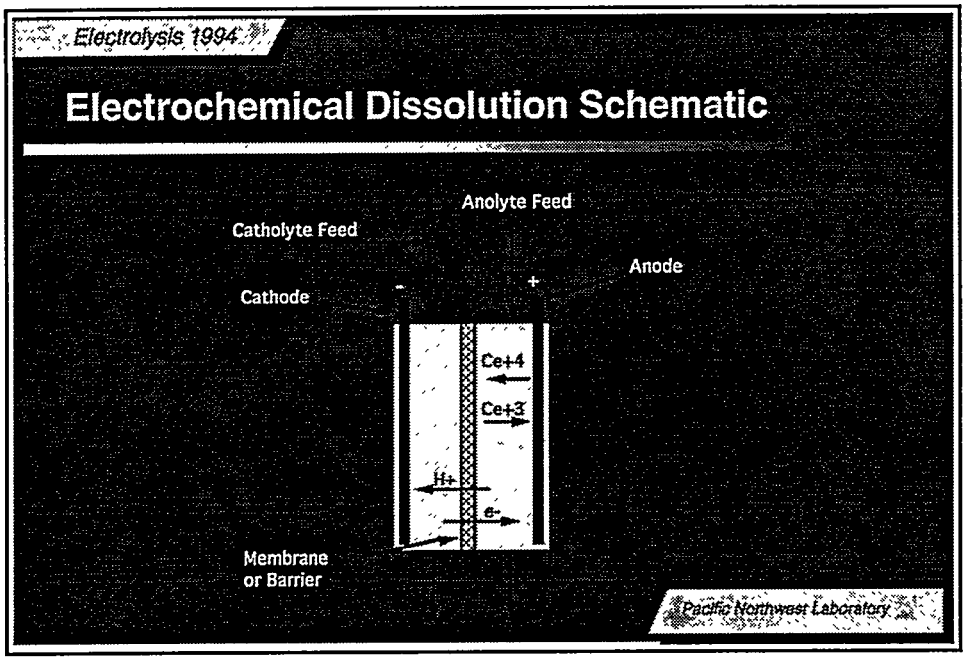
All catalysts deactivate due to . . .



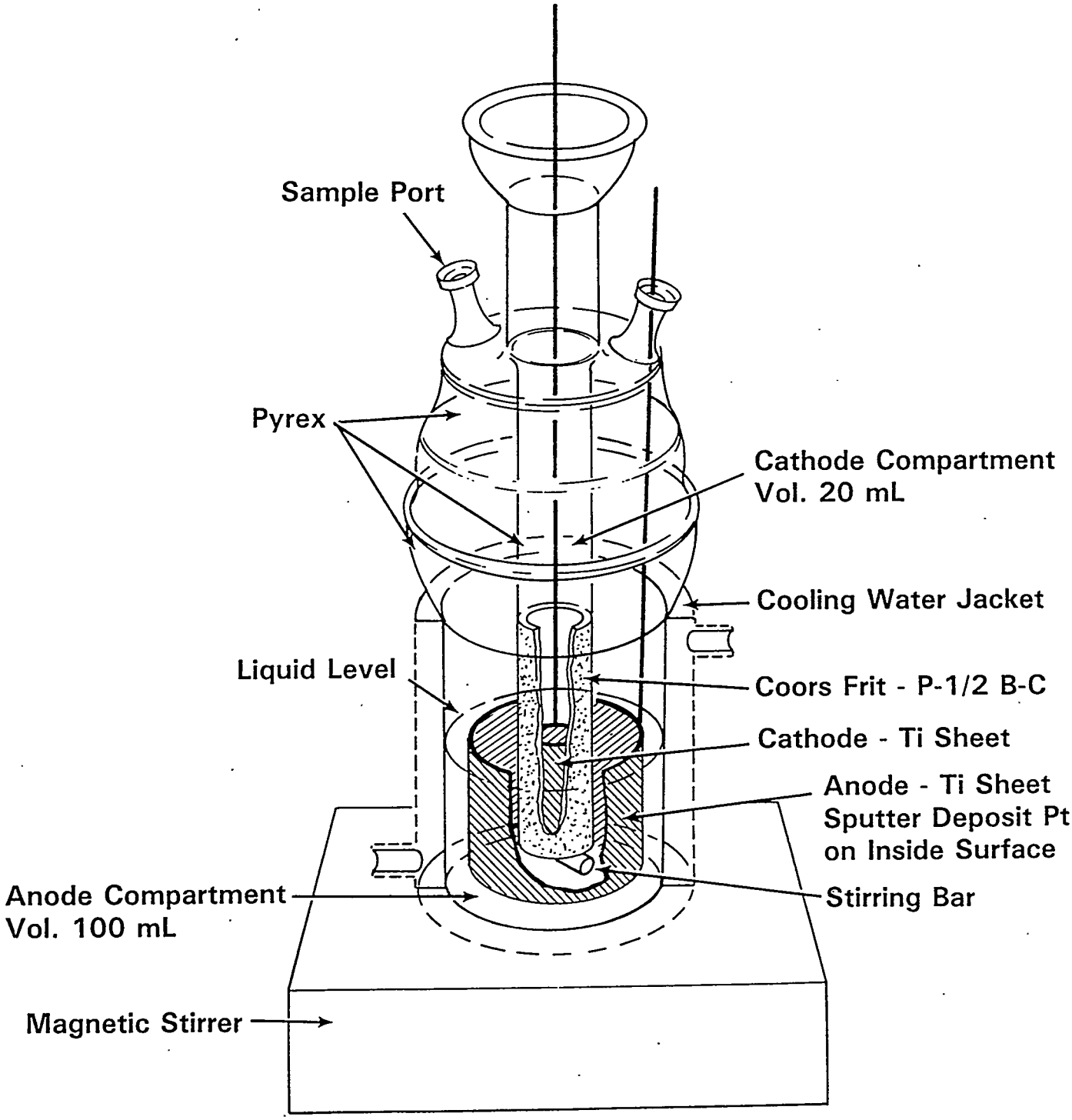
Indirect Oxidation Couples

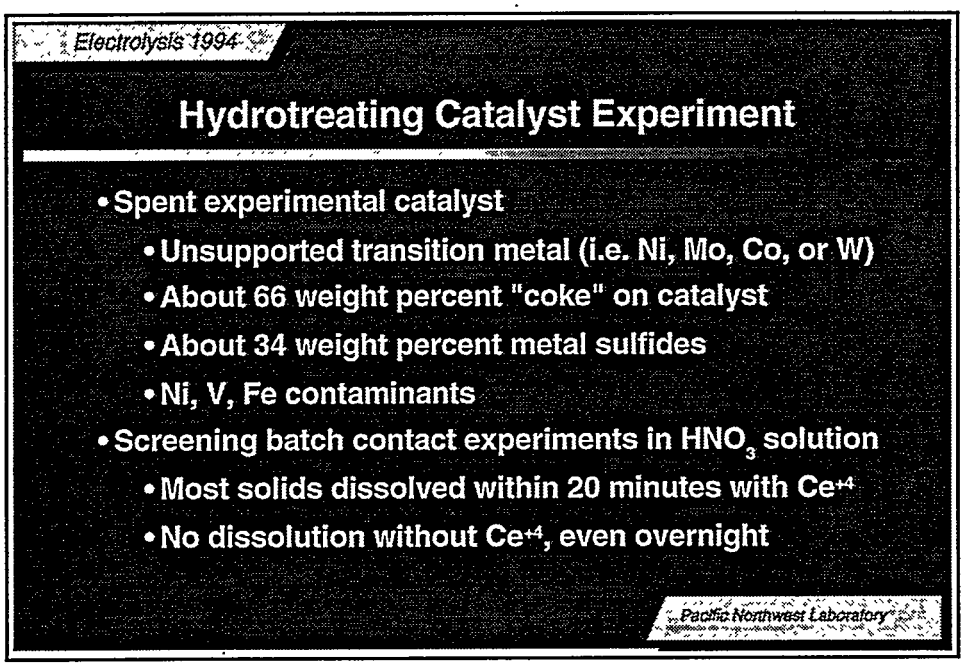


Net Anodic Reactions

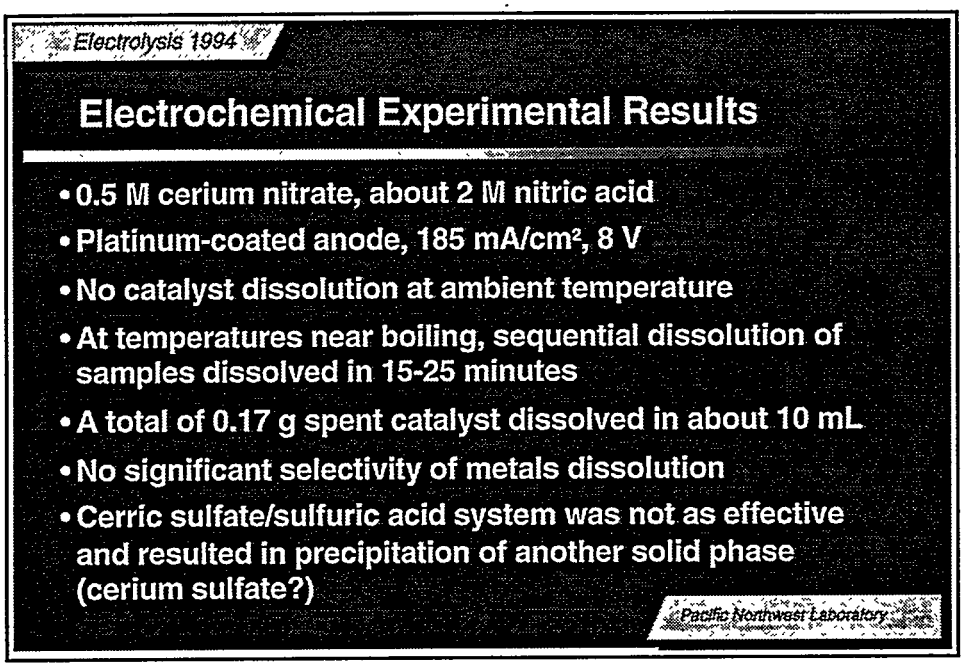


Electrochemical Dissolution Schematic

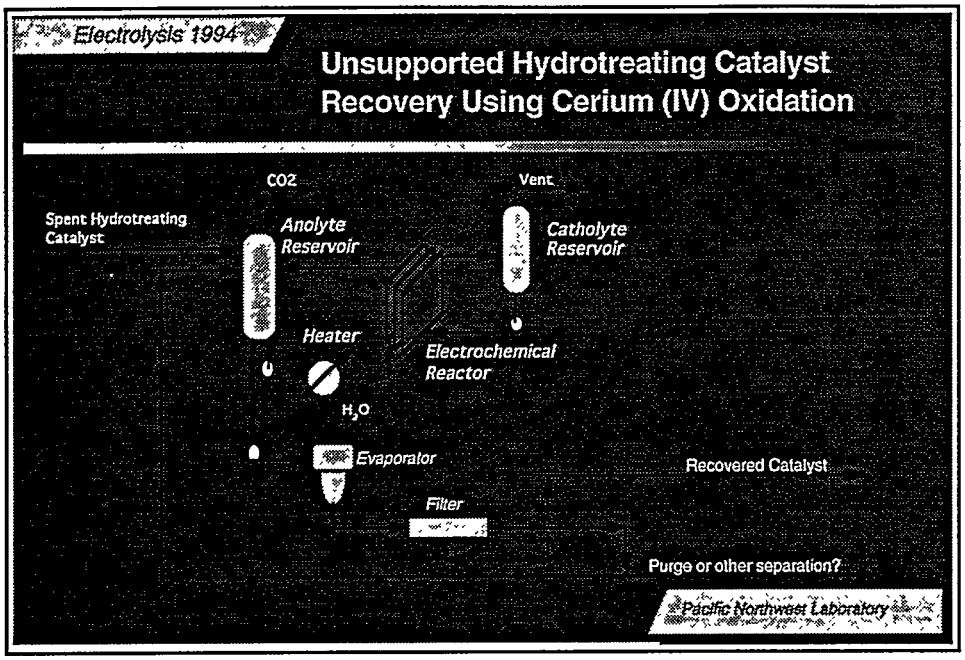

Sample Port
Pyrex
Cathode Compartment
Vol. 20 mL
Cooling Water Jacket
Liquid Level
Coors Frit - P-1/2 B-C
Cathode - Ti Sheet
Anode - Ti Sheet
Sputter Deposit Pt
on Inside Surface
Anode Compartment
Vol. 100 mL
Stirring Bar
Magnetic Stirrer



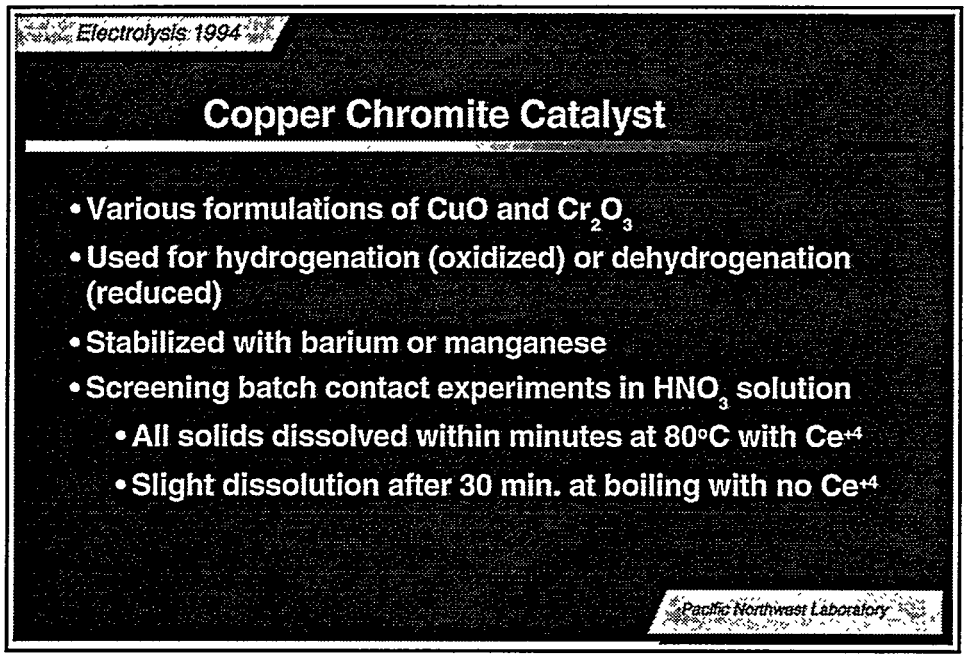
Hydrotreating Catalyst Experiment



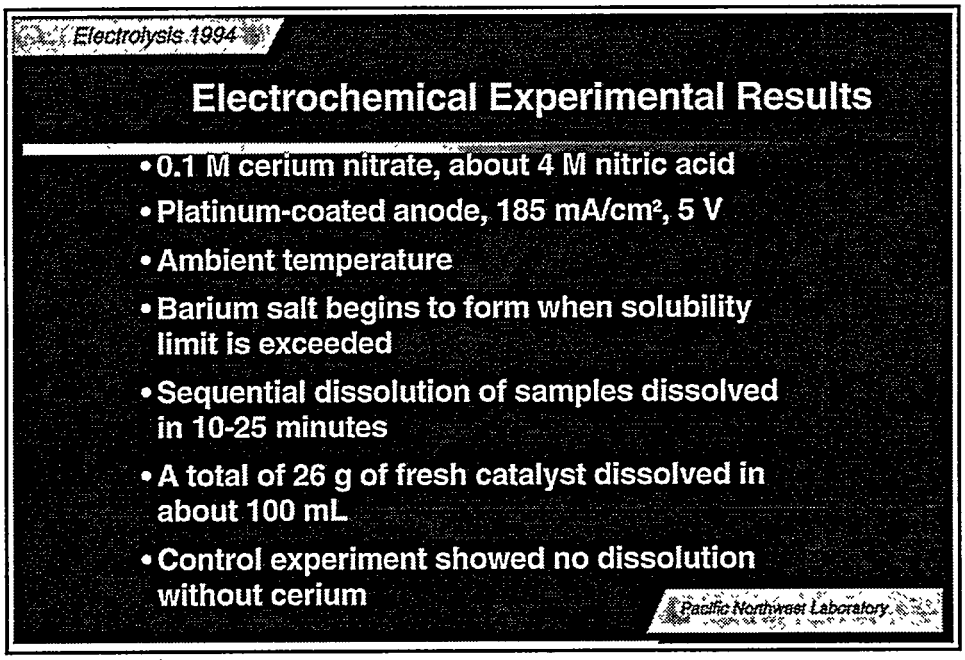
Electrochemical Experimental Results



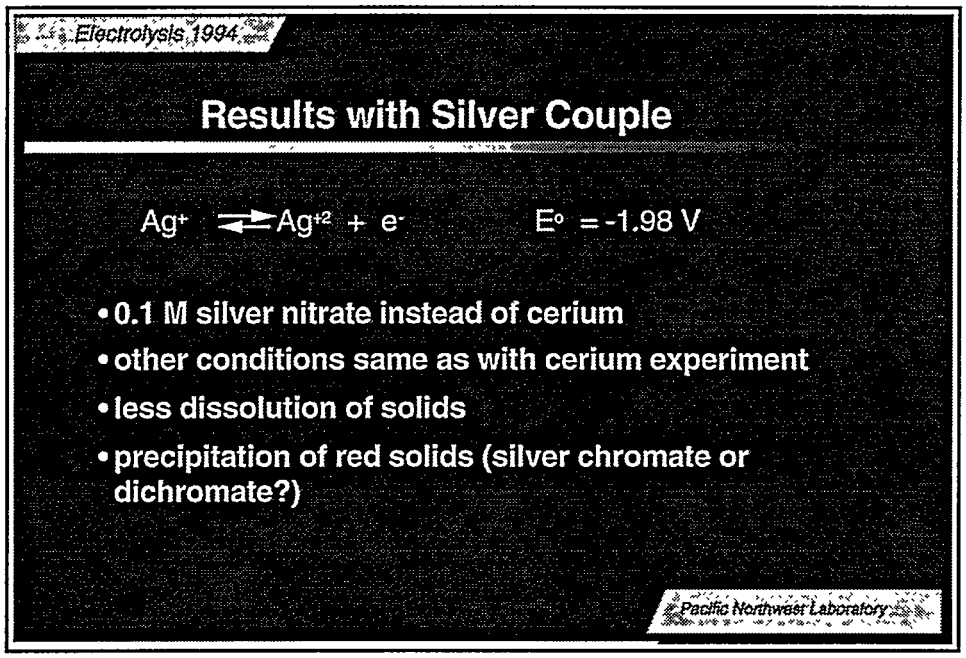
Unsupported Hydrotreating Catalyst Recovery Using Cerium (IV) Oxidation



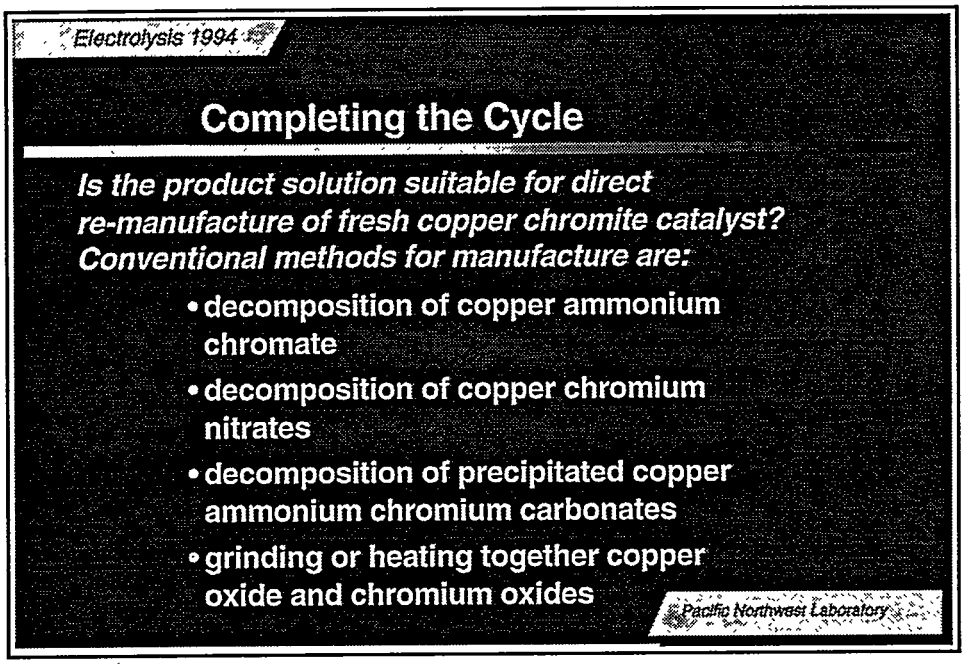
Copper Chromite Catalyst



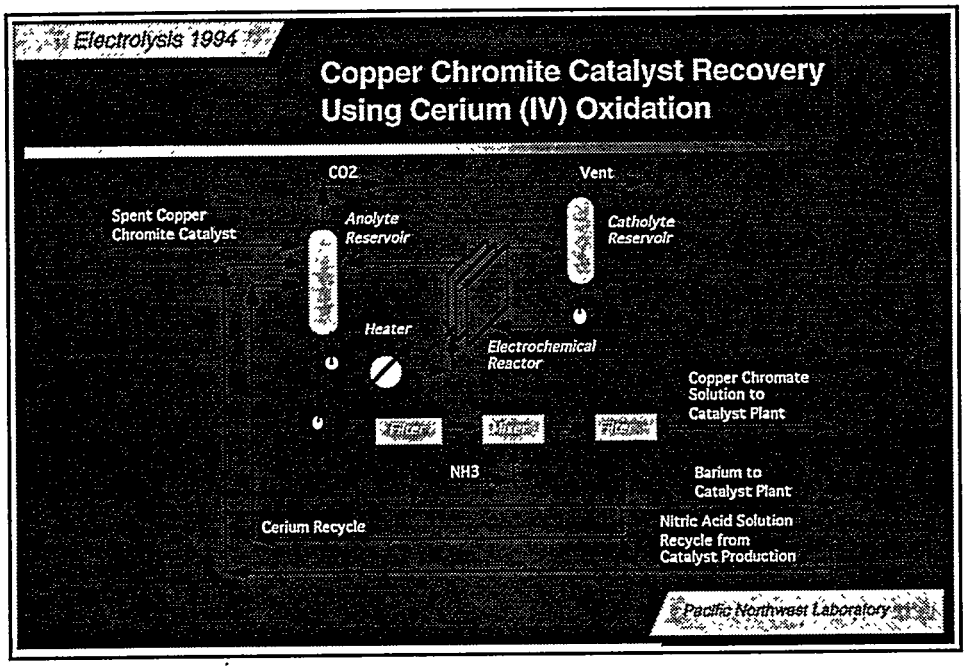
Electrochemical Experimental Results



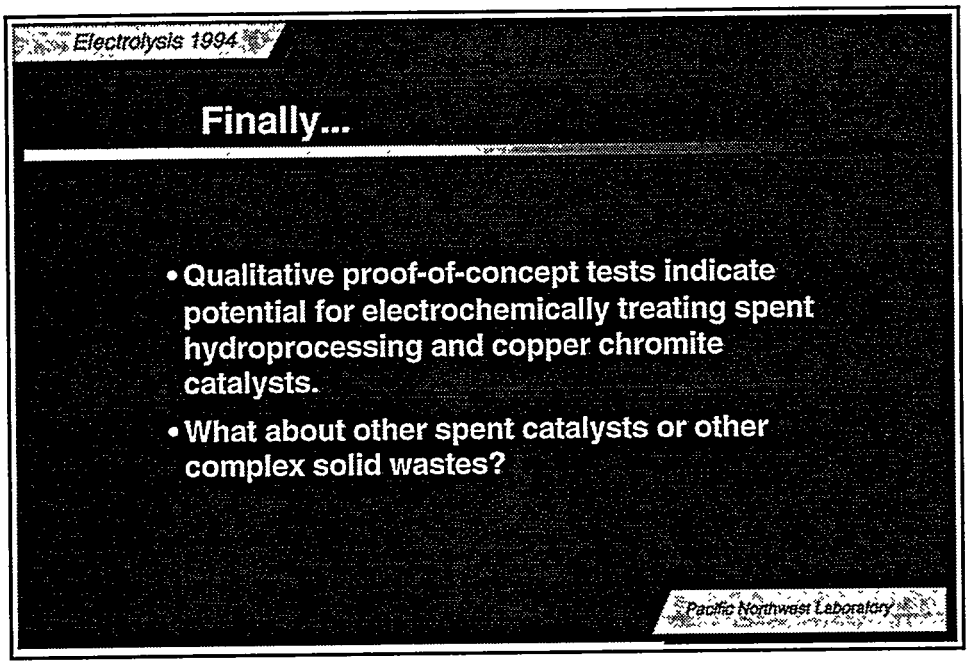
Results with Silver Couple



Completing the Cycle



Copper Chromite Catalyst Recovery Using Cerium (IV) Oxidation


Electrolysis 1994
Finally...
• Qualitative proof-of-concept tests indicate potential for electrochemically treating spent hydroprocessing and copper chromite catalysts.
• What about other spent catalysts or other complex solid wastes?
Pacific Northwest Laboratory

Finally...