

Bench Scale Silver Recovery Unit for the  
MEO System

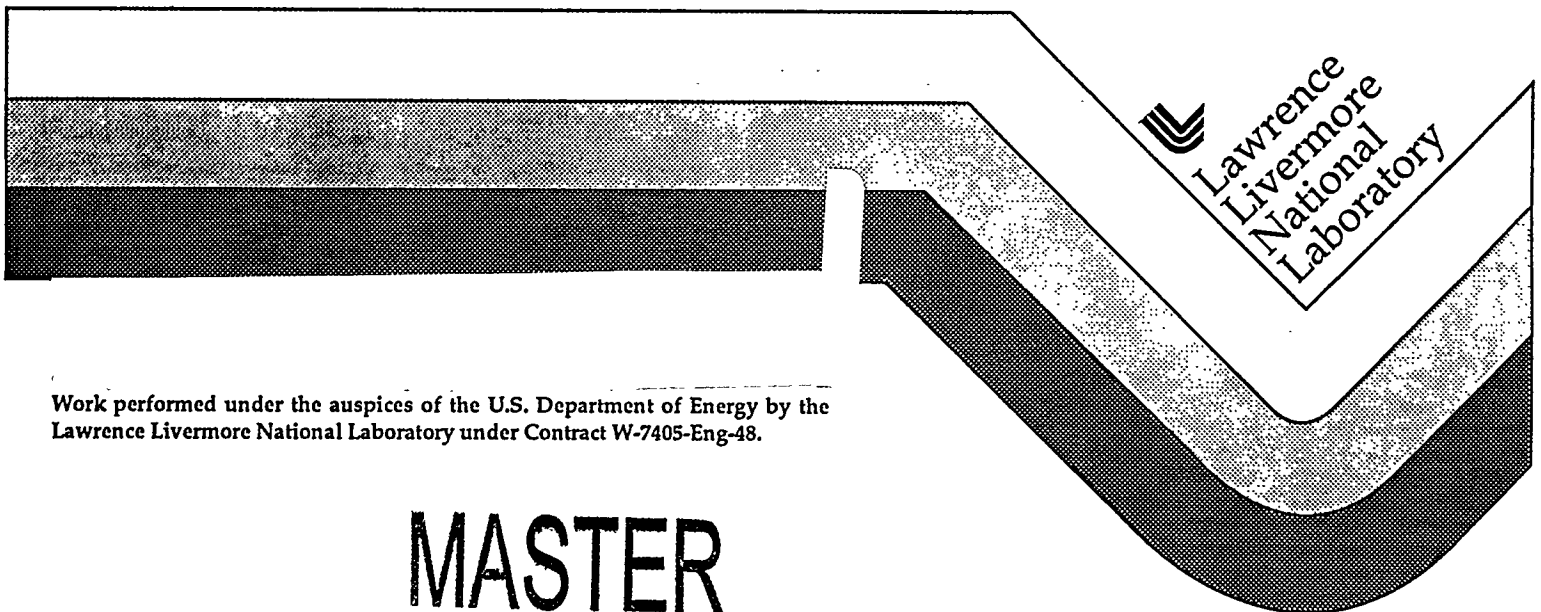
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# Bench Scale Silver Recovery Unit for the MEO System

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## I. Introduction

Mediated electrochemical oxidation (MEO) is one of several process technologies for the effective treatment of low-level radioactive, organic mixed wastes. MEO is a non-thermal process and is ideally suited for treating liquid and aqueous mixed wastes. When treating chlorinated organic compounds, MEO process generates silver chloride which needs to be recovered, converted into silver nitrate, and sent back to MEO for reuse in order to optimize process economics and reduce silver discharge to the environment. A silver recovery process which has been developed in a small lab-scale is capable of converting silver chloride into silver nitrate with 98% efficiency. A bench unit which is 30 times bigger than the lab-scale unit was built and successfully tested for the scaling effect of the silver recovery process. This article reports the operational experience we have learned from the bench scale unit.

## II. Process Development and Scale up

General principles for developing a new process are to start from a small unit (lab-scale) and scale up carefully. Due to the "unknown nature" of a new process, an early stage development of a new process requires many "try & error" runs. It is not uncommon to have over one hundreds experiments before a recipe can be discovered. Lab-scale unit needs less amounts of reagents, less time to accomplish a condition, and smaller hardware. Therefore it is the most economical way to start a new development from a lab-scale unit (about 50 different runs were tried for the silver recovery process in the lab-scale).

After an optimal recipe has been found in a lab-scale, scaling up must be proceeded very carefully. Table 1 shows scale up ratios for a number of processes from lab scale to commercial production. (Ref. 1)

Table 1

<u>Systems</u>	<u>Scale up Ratios</u>	
	<u>Lab scale to pilot scale</u>	<u>pilot scale to commercial plant</u>
Gas reactants, liquid or solid products	200 - 500	100 - 500
Liq and gas reactants, liq products	100 - 500	100 - 500
liq reactants, solid or viscous liq products,	20 - 200	20 - 250
<u>Solid reactants, solid products</u>	<u>10 - 100</u>	<u>10 - 200</u>

Table 1 provides a general guideline for scaling up a process. The silver recovery process, with NaOH, H<sub>2</sub>O<sub>2</sub> (in water), nitric acid, and AgCl as reactants, and silver/silver nitrate as products, would have 20 to 200 as scale up ratios from lab scale to pilot scale. Therefore a bench unit is required as part of the process development. Table 2 shows the scales of lab scale unit, bench-scale unit and MWMF scale.

Table 2

<u>System</u>	<u>Amounts of AgCl Treated</u>	<u>Location</u>	<u>Scale ratio</u>
Lab Scale	28.64 grams	B-241	1
Bench-Scale	860 grams	B-161	30
<u>Pilot-Plant</u>	<u>12,500 grams</u>	<u>MWMF</u>	<u>435</u>

Table 2 indicates that scale up ratios 30 from lab-scale to bench scale and 14.5 from bench scale to MWMW pilot scale. A successful operation of the bench scale unit would provide important design information to the MWMF pilot scale unit.

### III. Operation of the Bench Scale Unit

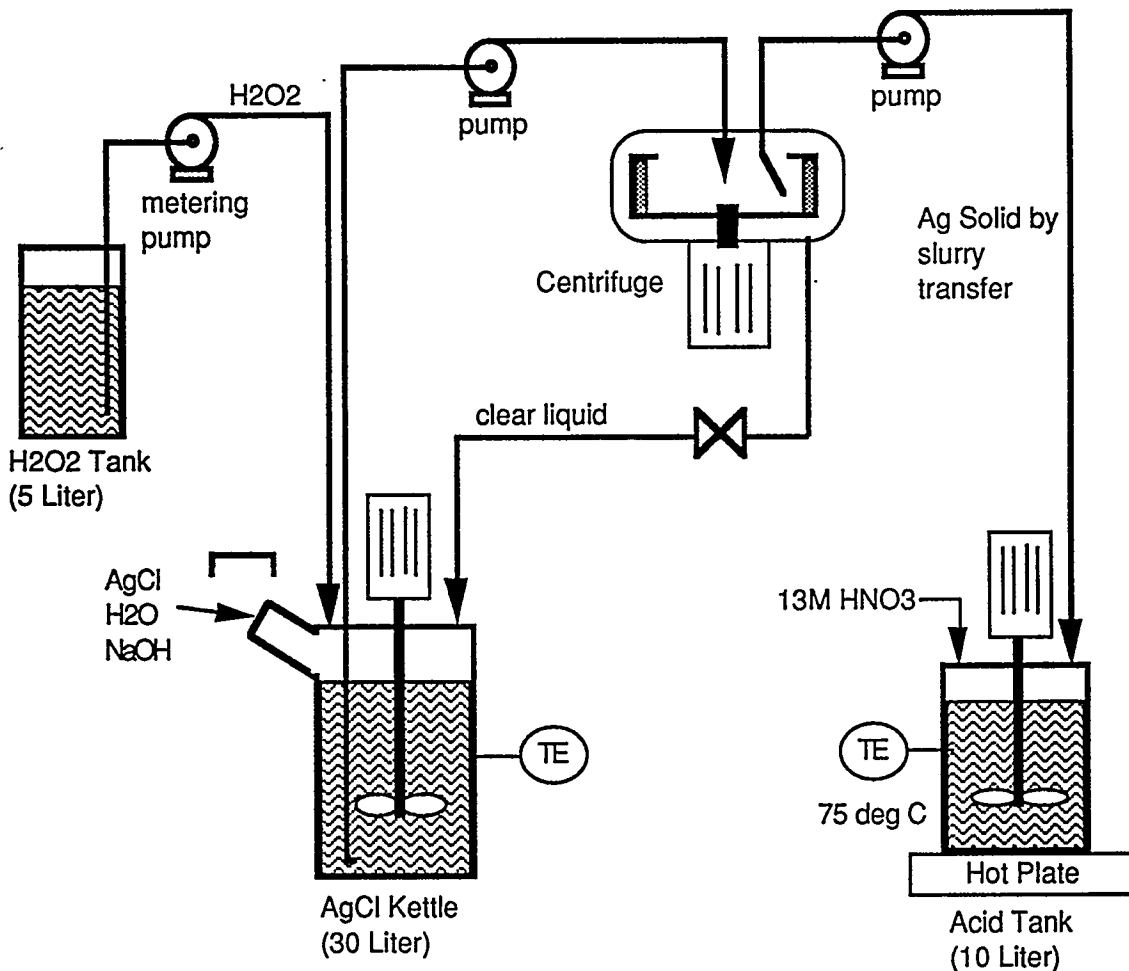
Fig. 1 shows the bench scale silver recovery unit. 3750 cc water was put into the AgCl kettle before mixing starts. 371 gram sodium hydroxide was then added into the kettle and the solution temperature increased quickly in 2 minutes from room temperature to a maximum 42 deg C. After 2 minutes, solution started to drop, an indication of complete dissolution of sodium hydroxide in water. Silver chloride was then put into the kettle and solution turned dark brown quickly, an indication of silver oxide formation. An

adjustment of mixing speed may be required in order to maintain a "just suspended" condition and assure a good contact between liquid and solid particles for interphase mass transfer. The definition of "just suspended mixing" is that no solid particle remains stationary on the bottom of the kettle for longer than one to two seconds.

Hydrogen peroxide (50%) was added into the kettle via a metering pump. The solution temperature rised very quickly due to the reaction of hydrogen peroxide with sodium hydroxide in the aqueous solution. A severe foaming also occurred with the release of oxygen. A careful addition of hydrogen peroxide into the AgCl kettle is very important to prevent the reaction medium from overheating and spilling over the kettle. A large free board schedule of the AgCl kettle is required. As the reaction proceeded, silver formed at the expense of silver chloride. Since silver is heavier than silver chloride, mixing speeds needed to be adjusted to ensure a good suspension of solid particles in the reaction medium. A thermocouple was used to monitor the solution temperatures during the course of reaction.

After a desired reaction time was reached, the solution slurry was transferred to a centrifuge by a varistaltic pump at a rate of 1.5 liters/min. for solid-liquid separation. The solution recycled back to the kettle and solids stayed in the centrifuge bowl. Several recycle passes were needed in order to achieve a good separation. After the solution in the kettle became clear, an indication of good separation, centrifugation stopped. The silver slurry was then transfer to the acid tank to convert into silver nitrate. Concentrate nitric acid was used to convert silver into silver nitrate. Brown NOx gas appeared vigorously in the first several minutes. A hot plate was used to heat up the acidic solution to 75 deg C to prevent the precipitation of silver nitrate. The reaction of silver with nitric acid at 75 deg C was fast and the reaction went to completion within one hour. The residual solids was then separated from the solution by filtration. Conversion efficiency can be calculated from the amounts of starting silver chloride and residual silver chloride.

Fig. 1 Bench Scale Ag Recovery Unit



#### IV. System Description

##### 1. AgCl Kettle

A 30 liters vat made of glass was used as the AgCl kettle. Although its size was greater than required, it allowed us to observe the severity of foaming during the addition of hydrogen peroxide. The transparent nature of the glass also allow us to observe and adjust mixing conditions.

##### 2. Mixer

The mixing speed was maintained at about 500 rpm by a Variac to achieve a good mixing. The impeller width was 4 inch. The shaft was made of stainless steel to avoid corrosion.

### 3. H<sub>2</sub>O<sub>2</sub> Tank

The tank volume is 5 liter and made of glass.

### 4. Metering Pump

The metering pump is capable of delivering hydrogen peroxide at 20 to 700 cc/min.

### 5. Pump

The varistaltic pump was used to transfer slurry from AgCl kettle to centrifuge. Pump capacities were from 1 to 5 liters per minute.

### 6. Centrifuge

The bowl volume of the centrifuge is 2 liters. The centrifuge's g-value is 500 and revolution is 1725 rpm.. The bowl was made of stainless steel.

### 7. Acid Tank

It is a 10 liters container made of glass which allows the mixing conditions to be observed.

### 8. Tubing and Fittings

All the tubing is made of flexible polymers (Tygon) for the ease of operation. Fittings are made of PP.

## V. Test Results

### 1. Blank Test of the Centrifuge

A model slurry solution was used to test the capability of the centrifuge for solid liquid separation. The formula of the slurry is shown in table 3.

Table 3

<u>Components</u>	<u>Amounts</u>	<u>Notes</u>
Sands	500 g	35 to 50 mesh
Activated Alumina	500 g	40 to 60 mesh
Fly Ashes	91 g	
Water	7 liters	

As shown in the Table 3 the solid content in the slurry is 13.5% wt. which is still pumpable under mixing. The slurry was transferred to the centrifuge at 1.5 liters per minute by a pump and its residence time in the centrifuge was 1.33 minutes per pass. The solution exit the centrifuge and returned back to the kettle. It was found that at least 4 recycle passes were required to separate solids from the liquid. One problem with this centrifuge was that small portion of solid particles would spin out due to the configuration of the centrifuge bowl. These particles would have to be recovered manually. Nonetheless, the results indicated that the centrifuge had good capability of separating small and light particles such as fly ashes from the liquid.

## 2. Conversion Efficiencies

The first step in the scale up process is to demonstrate efficiencies of a larger unit by using an optimal condition which has been found in a smaller unit. For this reason, two tests, namely BS-1 & BS-2, were conducted in the bench unit by using the optimal condition developed in the lab scale. Table 4 shows the results.

Table 4

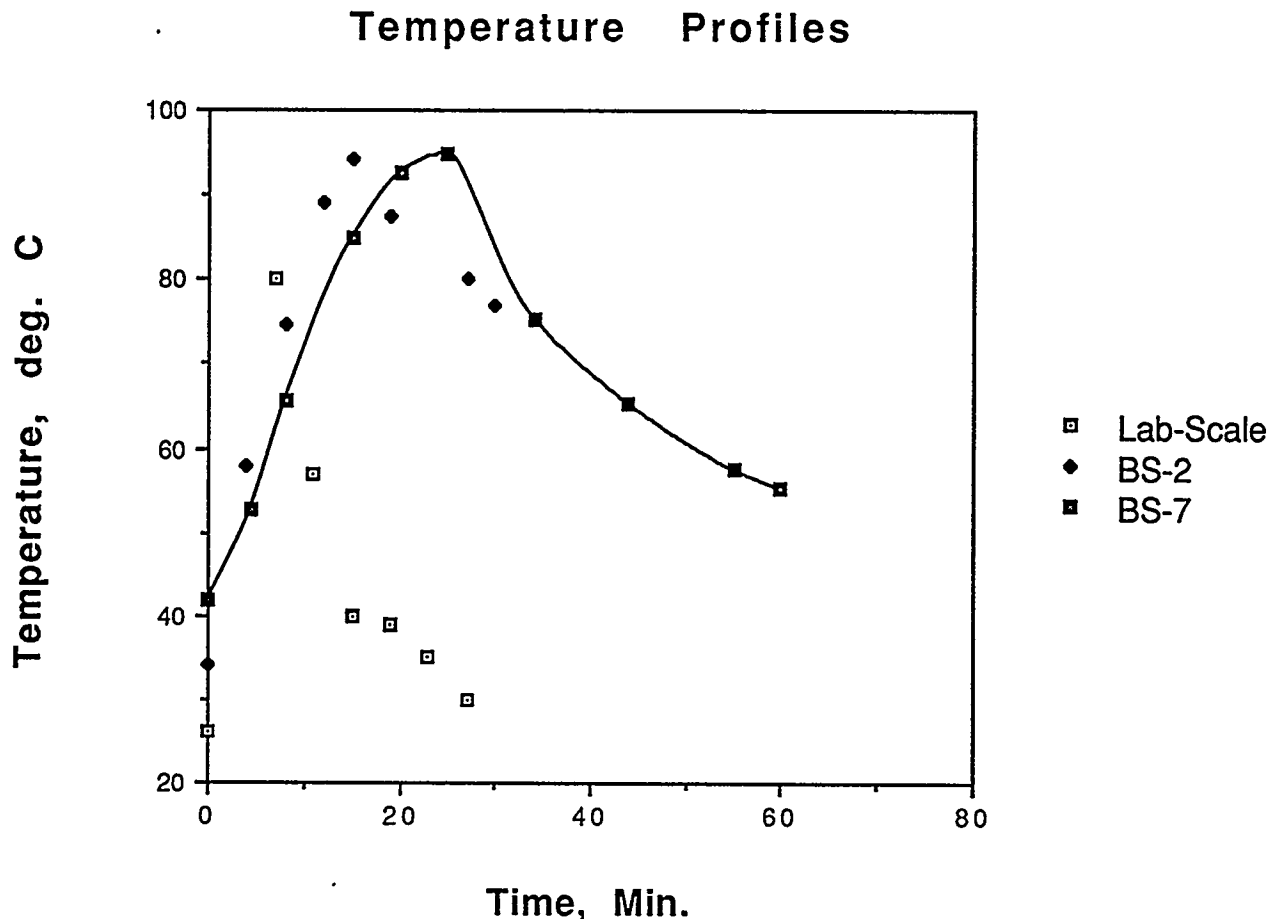
<u>System</u>	<u>Conditions *</u>	<u>Reaction Time</u>	<u>Conversion Eff.</u>
Lab-scale	1.25X NaOH, 10.32X H <sub>2</sub> O <sub>2</sub>	30 min.	98.1%
BS-1	1.25X NaOH, 10.32X H <sub>2</sub> O <sub>2</sub>	30 min.	85.6%
BS-2	1.25X NaOH, 10.32X H <sub>2</sub> O <sub>2</sub>	30 min.	84.6%

\* Please see Ref. 2

Table 4 indicates that the bench scale unit did not perform as well as lab scale unit at the optimal condition. Consequently, the lab scale optimal condition needs to be modified for the bench scale unit.

The differences in conversion efficiencies may be a combination of solution temperature profiles and shear rates. Fig. 2 shows solution temperature profiles. Solution temperatures rised due to the reaction of hydrogen peroxide in the alkaline solution. The peak of each curve indicated the end of hydrogen peroxide addition. After stopping the addition of hydrogen peroxide, solution temperatures started to drop. The lab scale reaction mixture cooled off fairly quickly due to the higher surface area per unit volume of solution. The solution temperatures in the bench scale unit, due to the larger mass and lower surface area per unit volume, did not drop quickly, as indicated by BS-2 and BS-7. The rate of hydrogen peroxide addition for BS-2 is twice as the rate of hydrogen peroxide addition for BS-7. The

jacket-type of kettle design which allows cooling medium to enhance the heat transfer will provide the MWMF silver recovery system a good control of solution temperature profiles.



### 3. Time of Reaction

The rate of silver chloride conversion depends on many factors such as temperatures, reagent concentrations as well as mass transfer. The mass transfer between solid particles of silver chloride and liquid play an important role in determining when the conversion will go to completion. This interphase mass transfer can be facilitated with a good mixing pattern. However, maintaining a same mixing pattern during scaling up is inherently difficult, if not impossible, (Ref. 3). Installation of baffles will improve mixing sheer and turbulence for high viscous fluid, but it is impractical for the silver recovery process which has a low viscous mixture laden with solid particles. At lab scale unit, high sheer and rapid circulation were easily attainable, consequently the high conversion efficiency was achieved in 30 minutes. The mass transfer in bench scale unit which is 30 times greater than the lab scale might be slower, therefore prolonging the time of reaction may improve conversion efficiencies. Several tests were conducted in order to investigate the effect of reaction time on conversion efficiencies and the

results are shown in Table 5. As the conversion efficiency with one hour of reaction time is quite acceptable, the conversion can nearly reach completion in 3.5 hours. It clearly indicates that reaction times play a very significant role on the silver recovery process.

Table 5

Condition: NaOH 1.25X , H<sub>2</sub>O<sub>2</sub> 10.32X, NaOH molarity 2M

<u>Run #</u>	<u>Time of Reaction</u>	<u>Conversion Efficiencies</u>
BS-1*	30 minutes	85.6%
BS-7	1 hour	96.0%
BS-6	3.5 hours	99.4%
BS-8	3.5 hours	99.7%

\* Rate of H<sub>2</sub>O<sub>2</sub> addition was greater for this run.

The results of BS-6 & BS-8 are identical, an indication of good reproducibility of the tests.

#### 4. Effect of Sodium Hydroxide Molarity

Hydrogen peroxide served as a reducing agent for silver chloride. Its "reducing power" depends on solution temperatures and reagent concentrations. Table 6 shows the effect of sodium hydroxide molarity on conversion efficiencies. It indicates that 2M sodium hydroxide solution is more preferable.

Table 6

Condition: NaOH 1.25X , H<sub>2</sub>O<sub>2</sub> 10.32X, time of reaction 3.5 hours

<u>Run #</u>	<u>NaOH Molarity</u>	<u>Conversion Efficiencies</u>
BS-5	1 M	92.5%
BS-6	2 M	99.4%
BS-8	2 M	99.7%

## 5. Optimal Conditions

Table 7 shows the optimal conditions for both lab scale unit and bench scale unit. While the optimal times of reaction are different, the reagents requirement for both units remain the same. Conversion efficiencies of silver chloride are excellent in both units.

Table 7

Condition: NaOH 1.25X , H<sub>2</sub>O<sub>2</sub> 10.32X, NaOH Molarity 2M

<u>Run #</u>	<u>Time of Reaction</u>	<u>Conversion Efficiencies</u>
Lab-Scale	30 Minutes	98.1%
BS-7	1 hour	96.0%
<u>BS-6 &amp; BS-8</u>	<u>3.5 hours</u>	<u>99.4% &amp; 99.7%</u>

## VI Conclusions

The silver recovery process developed in the lab-scale unit has been successfully scaled up to the bench scale which is 30 times larger than the lab-scale unit. The conversion efficiencies of silver chloride from both units achieved 98%. The reagents requirements for both units remain the same. The results from the bench unit test provide a very useful information for the design and operation of the MEO silver recovery system.

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