# PILOT-PLANT EVALUATION OF THE MOBILE WET OXIDATION PROCESS

Stanley M. Finger
Herbert G. Sutter
Duratek Corportation
Allen Atwood
Bechtel Corporation

## ABSTRACT

The Wet Oxidation Process was originally developed and patented by JGC Corporation, Japan. Pilot-plant studies of the Wet Oxidation Process were conducted. This process oxidizes chelating agents in wastewaters generated during nuclear reactor cleaning operations. Test runs were made with solutions containing NTA/EDA, EDA, and EDTA. Key findings are summarized in Table I. Based on JGC's performance data, these studies were conducted to establish processability in treating wastewaters and to confirm the applicability of this process to Maine Yankee Waste.

## PROCESS DESCRIPTION

The Wet Oxidation Process is designed to oxidize chelating agents, e.g. EDA, NTA, EDTA, in wastewaters generated during nuclear reactor cleaning operations. The decomposition of the chelating agents would result in significantly lower disposal costs, providing an overall savings to the industry.

The basic process, shown in Fig. 1, consists of two stages: a Stripper/Concentrator and a Reactor. The Stripper/Concentrator removes free ammonia and concentrates dilute solutions for more rapid processing in the Reactor. The ammonia removed in the Stripper/Concentrator is neutralized with sulfuric acid in a separate tank and is released as ammonium sulfate.

The wastewater from the Stripper/Concentrator is fed to the reactor where it is reacted with hydrogen peroxide under acid conditions in the presence of a catalyst. Since foaming is a significant problem, antifoam chemicals are also added to the mix. Sodium hydroxide is added at the end of each run to neutralize the reaction mixture.

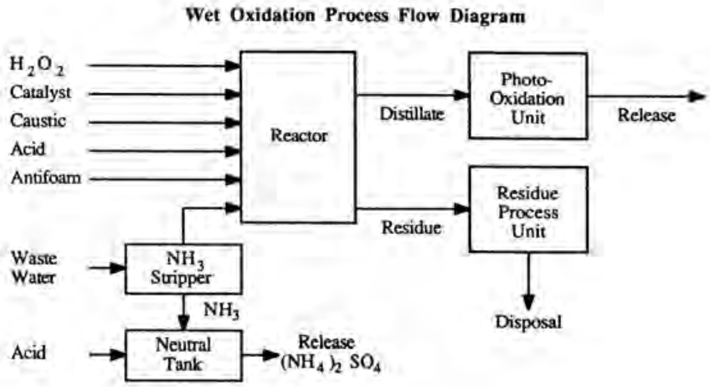


Fig. 1. Duratek Wet Oxidation Process.

### TABLE I

Key Findings

## Key Findings

- Foam can be controlled
  - pH
  - Anti-foam chemical
  - Anti-foam ring
  - Heater grid
  - Reactor design - large gas-liquid interface
- Distillate TOC directly related to reactor TOC; ratios fou
  - EDTA - 0.066
  - EDA - ≤0.13
  - NTA/EDA - 0.1
- Catalyst required

## SMALL PILOT-PLANT

The current series of experiments were carried out in a small pilot-plant designed for 10-20 mL/min (feed rate) operation. Stripping was done batch-wise in large flasks. The Reactor was a 14 L glass cylinder (6 in. diameter x 24 in. high) operated on a continuous basis (except for periods when the feed had to be shut off to control foaming). The solution volume in the Reactor was maintained at approximately 7 L. This allowed a large volume for foam expansion, although the interfacial area between the liquid and the headspace was small, contributing to the foaming. The reaction mixture was maintained at its boiling point with two 1kW immersion heaters (much of the heat required was supplied by the exothermic oxidation reactions taking place within the reaction mix).

An anti-foam ring was added to this pilot-plant system. Heated air was blown downward from the ring toward the surface of the liquid. The heated air dried and applied mechanical force to the foam bubbles. This technique was found to be quite effective in helping to control the foam.

TOC measurements taken throughout the runs were used to control the rate of feed addition, i.e. the feed rate was increased or decreased to keep the TOC of the reaction mix at about 1000-2000 ppm. However, the TOC of the reaction mix varied considerably due to the length of time it took to analyze a sample (measurements were made with a Dohrmann DC-80 TOC Analyzer). An on-line control system would make process control much more effective.

The performance evaluation test runs performed are listed in Table II. The feed for Run P-9 was Maine Yankee Waste Solvent. The composition of this EDTA wastewater is listed in Table III.

The feed rates and total amounts of each of the chemicals fed to the Reactor are summarized in Table IV.

**TABLE III**

Maine Yankee Waste Solvent Composition (Run P-9)

**Maine Yankee Waste Solvent Composition (Run P-9)**

| Component | Value |
|---|---|
| Fe | 12,645 ppm |
| Ni | 324 ppm |
| Mn | 177 ppm |
| Zn | 1,320 ppm |
| Cu | 5,552 ppm |
| Cr | 5.86 ppm |
| Co | < 1.0 ppm |
| TOC (EDTA as main component) | 55,625 ppm |
| pH | 7.0 - 7.5 |

## RESULTS

The performance of the small pilot-plant system in treating each of the wastewaters is summarized in Table V. Graphs of performance data (TOC vs time, distillate TOC vs reactor TOC, and oxidation efficiency vs time) are provided in Figures 2-8.

The distillate TOC was directly related to the TOC in the reaction mix. The ratio of distillate to reactor TOC was about 0.1 for all three cases. Much of the distillate TOC appeared to be caused by physical carryover. It is expected that distillate TOC can be significantly reduced by better reactor design to limit carryover.

Table V compares the oxidation efficiency found during the test runs with the theoretical efficiency, calculated from the stoichiometry of the oxidation reactions (assuming complete oxidation of the chelating agents). The

**TABLE II**

Test Runs

**Test Runs**

**P-5 - NTA/EDA**

- Feed conc. 2.92%/0.47% (4.38%/0.70% after concentration)

**P-8 - EDA**

- Feed conc. 2.07% (2.76% after concentration)

**P-9 - EDTA**

- Feed conc. 13.45%

**TABLE IV**

Performance

| Test | P-5 | P-8 | P-9 |
|---|---|---|---|
| Feed (to reactor) | NTA/EDA | EDA | EDTA |
| TOC, ppm | 14,235 | 11,000 | 55,625 |
| Rate, ml/min | 25-50 | 10-15 | 10-20 |
| Total, ml | 38,806 | 36,245 | 36,282 |
| 50% $H_2O_2$ | | | |
| Rate, ml/min | 10-13 | 10-14 | 10 |
| Total, ml | 21,395 | 74,475 | 36,980 |
| Anti-foam | | | |
| Rate | 100 ppm every hour | 100 ppm as required | 1-4 |
| Total, ml | 750 | 1,187 | 4,459 |
| $9NH_2SO_4$ | | | |
| Rate, ml/h | 100-200 | 50-150 | 80-180 |
| Total, ml | 5,662 | 2,958 | 6,450 |
| 11.75 N NaOH, ml | 777 | 540 | 2,400 |

**TABLE V**

**Performance**

| Test | P-5 | P-8 | P-9 |
|---|---|---|---|
| Feed | NTA/EDA | EDA | EDTA |
| Dist. TOC / Reac. TOC | 0.100 | ≤ 0.130 | 0.066 |
| Oxidation Eff., $gH_2O_2$/g chelate | | | |
| Experimental | 8.49 | 42.1 | 4.25 |
| Theoretical | 4.15 | 4.52 | 3.56 |
| Volume Reduction | ~ 28 | 9.6 | 8.0 |
| Final TOC, ppm | 80 | 362 | 271 |

NTA/EDA and EDTA wastewaters required about twice the theoretical amount of oxidant. The EDA wastewater, however, required almost ten times the theoretical requirement. This may be due in part due to the significant foaming experienced during the EDA run, requiring the feed to be discontinued while hydrogen peroxide addition was maintained. In future reactors, designed to minimize foaming problems through the use of anti-foam rings, heater grids and larger interfacial areas, the oxidation efficiency would be expected to improve.

Table V also shows that significant volume reductions (ranging from 8 to approximately 28) were achieved and that the final TOC of the residue in the reactor was well under 1000 ppm. The final TOC was essentially controlled by the duration of continued treatment after the feed was stopped. Thus, residue TOC's could be lowered further, if desired, but this would probably not be necessary.

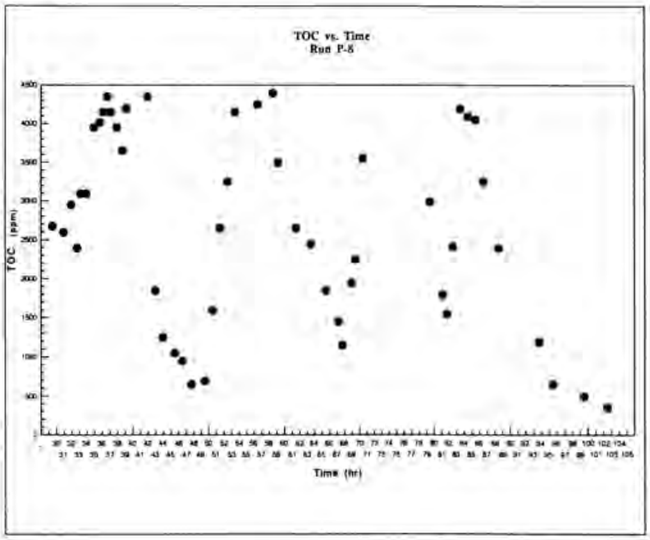


Fig. 3. TOC vs. Time -- Run P-8.

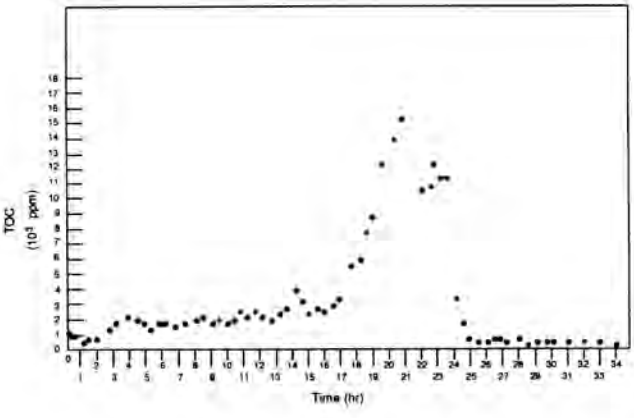


Fig. 2. TOC vs. Time -- Run P-5.

Table VI summarizes the composition of the bottoms remaining in the reactor at the conclusion of the test runs. The sludges were filterable by a 5 micron filter. Residual TOC's were low and metals content were also generally low or undetectable. Thus, the sludge is not expected to cause serious disposal problems.

## T-PLANT

Scale-up calculations for a large pilot-plant (1 gpm) system were performed based on the results of these test runs. The requirements for the large pilot-plant system are summarized in Figure 9. The size of the large pilot-plant was chosen to be able to treat 10,000 gallons of wastewater in approximately one week, operating around the clock.

The size of the Reactor, based on a direct scale-up of the small pilot-plant system, would be 1,050 gallons. However, one of the main problems with the tall cylindrical reactor used in the small pilot-plant was its relatively small interfacial area, which contributed significantly to foaming problems. We believe that the reactor size for the large

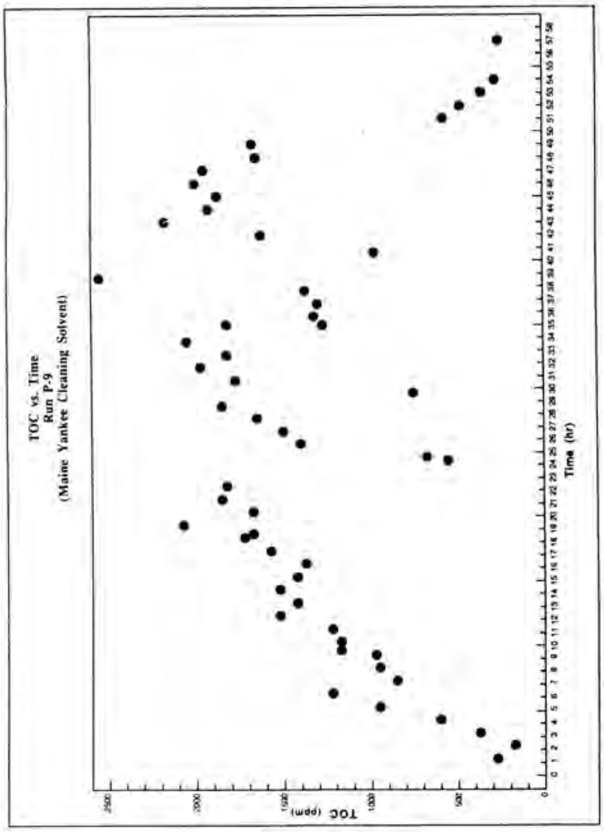


Fig. 4. TOC vs. Time -- Run P-9.

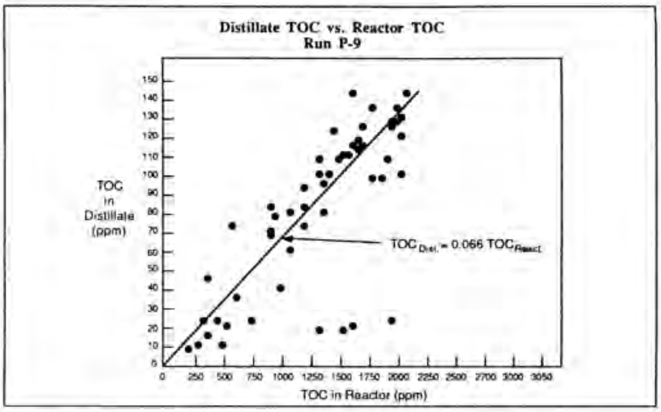


Fig. 6. Distillate TOC vs. Reactor TOC -- Run P-9.

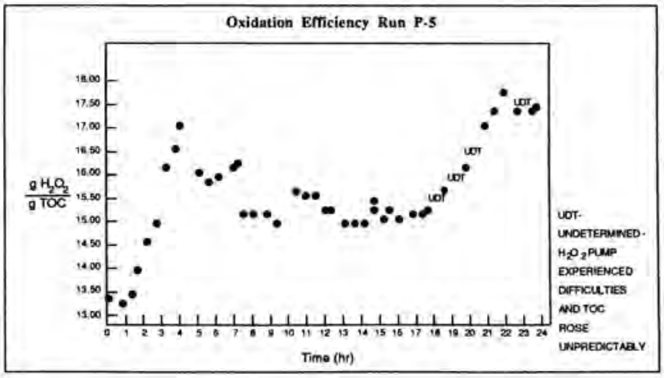


Fig. 7. Oxidation Efficiency -- Run P-5.

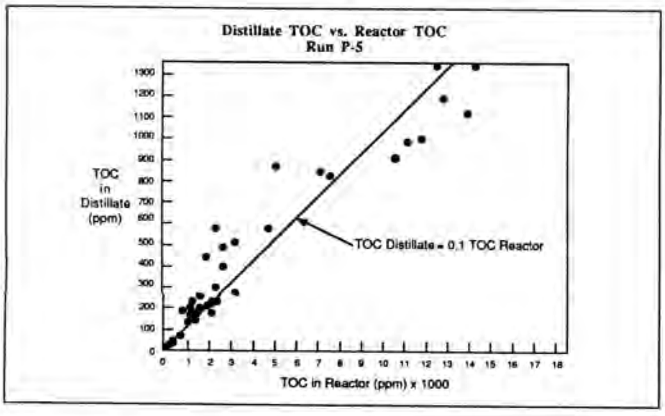


Fig. 5. Distillate TOC vs. Reactor TOC -- Run P-5.

pilot-plant can be reduced considerably by using a reactor with larger interfacial area per unit liquid volume, i.e. a reactor with a low height-to-cross-sectional area ratio.

## CONCLUSION

The tests with the small pilot-plant were successful in demonstrating the processability of wastewaters (including Maine Yankee Waste Solvent) by the Wet Oxidation Process. These tests pinpointed problems, such as foaming, to be resolved in future reactor designs and provided the necessary data for scale-up to a large (1 gpm) pilot-plant system.

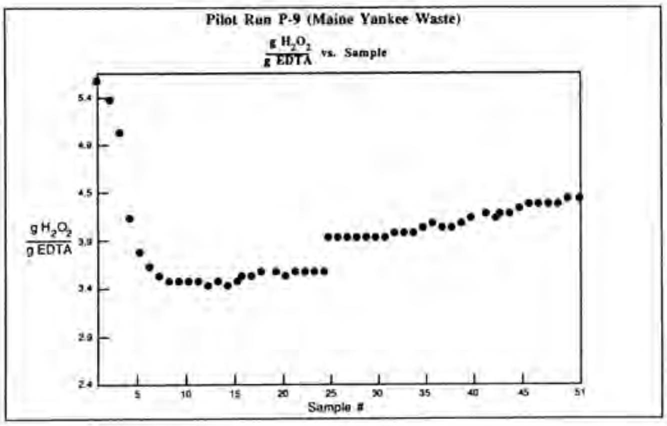


Fig. 8. Pilot Run P-9 (Maine Yankee Waste).

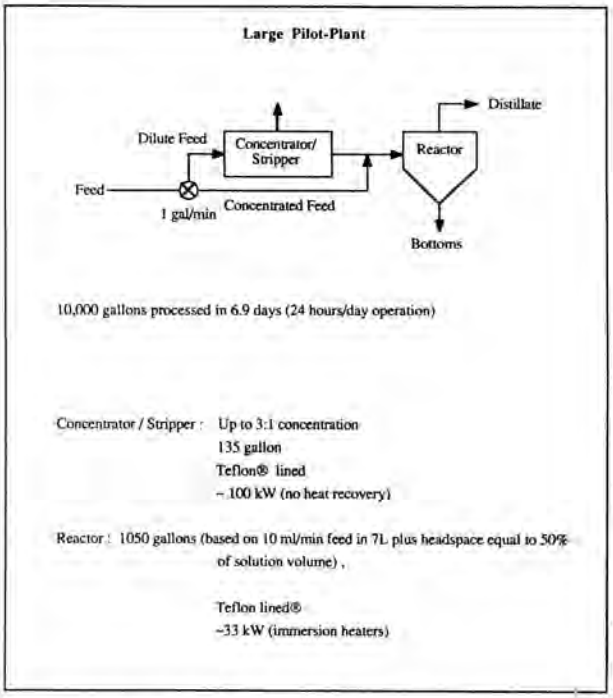


Fig. 9. Large Pilot -- Plant.

## TABLE VI
## Bottoms

**Bottoms**

Run P-5 (NTA/EDA)
- Brown sludge
- All captured by 5 um filter
- Filtrate crystallized - clear filtrate and solid white crystals

  - Filtrate - < 100 ppm TOC
  - Crystals - 163 ppm Na<br>2.22 ppm Si<br>0.244 ppm K<br>245 ppm $SO_4^{-2}$<br>7 ppm $Cl^-$<br>18 ppm $NO_3^-$<br>all metals < D.L.

Run P-8 (EDA)
- Filter cake grey-green mud
- Captured by 5 um filter
- Filtrate (dark blue) did not crystallize
- Filtrate analysis - 325 ppm TOC

Run P-9 (EDTA)
- Filter cake dark brown sandy sludge
- Captured by 5 um filter
- Dark blue filtrate