OPTIMIZATION OF PERCHLORATE BIODEGRADATION: PERFORMANCE AND COST ASSESSMENT FOR THE THIOKOL PROTOTYPE

Final Report

Prepared for

The Air Force Research Laboratory
SSG 32.06
Contract No. F08637-98-C-6002

March 1999- March 31, 2000
ARA Project No. 4998

Submitted by

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OPTIMIZATION OF PERCHLORATE BIODEGRADATION: PERFORMANCE AND COST ASSESSMENT

1.0 Executive Summary

Applied Research Associates, Inc. (ARA) has been developing perchlorate biodegradation processes for the United States Air Force and private organizations for over eight years. ARA designed and managed the engineering and start-up of the perchlorate biodegradation prototype in building M-705A at Thiokol Corporations (Cordent Technologies) production facility near Brigham City, Utah. This prototype has been in continual operation since inoculation and startup on December 8, 1997. Incorporation of this prototype into the Thiokol's perchlorate recovery and wastewater treatment processes has optimized operations and reduced operating costs.

Previous research on micronutrients and alternate nutrients significantly demonstrated the potential to reduce operating costs. Several low-cost, carbohydrate-based wastes have been identified and evaluated for use as nutrients. Based on this data, ARA was awarded a contract to optimize the Thiokol process, reduce operating costs, and improve performance. A low cost nutrient that is a carbohydrate byproduct (CBP), was identified and evaluated as the best replacement for the brewer's yeast and cheese whey mixture in use at that time. CBP is a low-cost, pumpable byproduct from the food processing industry that contains amino acids, proteins, sugars, and micronutrients, which aid system performance. CBP demonstrated better performance than other nutrients and performed well over a broader concentration range.

The prototype was converted from the yeast-whey nutrient blend to CBP in May 1999. Since conversion, good performance has been maintained. Actual nutrient and chemical costs were reduced over 90%, from an average of $1.76 to $0.16 per pound of perchlorate reduced. During 1999, 15,400 pounds of perchlorate in wastewater were destroyed by the prototype at Thiokol. The weighted-monthly average perchlorate feed concentration ranged form 300 to 4400 mg/L.

ARA also performed bottle studies on three alternate effluents that could be co-processed with perchlorate wastewater: 1) Brulin (an aqueous degreaser); 2) isopropyl alcohol contaminated with HMX (IPA); and 3) ethylene glycol. Studies were performed to determine whether these organic materials had an inhibitory effect on perchlorate reduction and whether there was any contribution to system nutrient requirements. IPA exhibited some inhibition at concentrations above 1%. Ethylene glycol enhanced performance and could be used as a sole carbon source. Brulin solution had little affect on performance. Bottle studies were also performed on potential co-contaminants: boron, aluminum hydroxide, and cadmium. Some inhibition of perchlorate reduction occurred at higher concentrations of cadmium and boron. These contaminants could impact performance by bio accumulating in recycled biomass. The aluminum hydroxide ion, $Al(OH)_4$-, did not affect performance.

Based on this optimization study and other testing conducted by ARA, the Thiokol prototype process is currently operating at only 25-40% of potential capacity. ARA recommends several modifications that will improve performance. Operational changes recommended include reduction of residence time and temperature, operation of reactors in series, elimination of the clarifier and biomass recycle, and direct feed of undiluted nutrients and supplements. Minor hardware and software modifications will be necessary to achieve optimal performance. New programs associated with Minuteman III remanufacture and the Space Shuttle will result in even greater demands on the performance of the Biodegradation Prototype at Thiokol.

2.0 Background

2.1 The Thiokol Biodegradation Prototype

In the early 1990s, Thiokol Corporation, constructed an industrial wastewater treatment plant (IWTP) at its production facility near Brigham City, UT, and deactivated their evaporation ponds. Prior to the installation of the perchlorate biodegradation treatment system, aqueous treatment costs at Thiokol were in excess of $1.00 per gallon. These treatment processes generated sludges, spent activated carbon sorbents, spent ion exchange resins, salts, and brine solutions containing ammonium perchlorate (AP).

The Thiokol IWTP precipitates potassium perchlorate (KP) from concentrated AP effluents. These effluents are concentrated by evaporation and ion exchange followed by ammonia stripping. The ammonia is replaced by sodium. Excess potassium chloride (KCl) is added to effect the precipitation of KP. This results in a 10-30% salt (Na^+, K^+, and Cl^-) brine solution containing 3000-5000 ppm perchlorate and additional nitrate and nitrite.

In 1996, ARA performed treatability studies on both ammonium perchlorate and brine waste streams from Thiokol's perchlorate recovery and ion exchange processes. The brine stream contained high salt concentrations, nitrates, nitrites, and sodium perchlorate. Preliminary bench scale studies were conducted using brewer's yeast and cheese whey as nutrient sources, reduced temperatures, and flexible operation of two reactors in either parallel or series. These studies provided the necessary information for adapting an existing pilot scale system to meet Thiokol's needs.

In summer of 1997, the modified pilot scale system was shipped to Tyndall AFB, FL for testing. The system operated at residence times of 18-24 hours at temperatures of 35-40^{0}C for 8 weeks. After testing the system was shipped to Thiokol via flatbed trailer, erected, water tested and inoculated in December 1997 (See Figure 1). The system has operated exceptionally with no perturbations requiring re-inoculation.

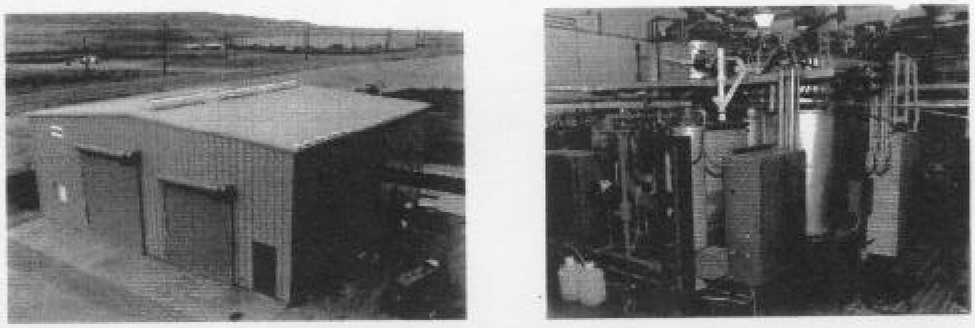

Figure 1. The Thiokol Biodegradation Prototype System

2.0 Micronutrients

In a laboratory process, that mimics the Thiokol prototype process with a stirred tank reactor (CSTR) followed by a clarifier to recycle biomass, micronutrient addition dramatically improved performance and reduced nutrient consumption. This result led to further alternate nutrient and micronutrient evaluations. These studies identified specific micronutrients necessary for the reduction of high concentrations of perchlorate. Further analysis of Thiokol source water shows a deficiency of micronutrients required for efficient perchlorate biodegradation. By providing proper micronutrients to the Thiokol prototype process, it is possible to reduce nutrient consumption, use low-cost alternate nutrients, and improve process performance.

2.1 Alternate Nutrients

The discovery of the benefits of micronutrient addition led to further evaluation of macronutrients (carbon sources) for perchlorate biodegradation. Perchlorate has been successfully reduced using many alternate nutrients. These include cheese whey, marshmallow waste, fruit juice wastes, sugars, starches, and acetate. The marshmallow waste was evaluated because it is a very abundant and very inexpensive ($10/ton). The marshmallow waste worked very well at concentrations equivalent to brewer's yeast, but had drawbacks. Another food processing waste, which was evaluated for use in this process, carbohydrate byproduct (CBP), showed more promise without the drawbacks of the marshmallow waste.

3.0 Objectives

The primary objective of this effort was to reduce nutrient consumption and cost. A combination of laboratory studies and operational changes to the Thiokol Prototype were employed to test alternate nutrient performance. In addition, the effect of other site wastewater and co-contaminants were evaluated. Specific sub-objectives for this effort included:

- **Eliminate the use of brewer's yeast as a nutrient.** Brewer's yeast is an expensive nutrient ($0.50-1.00 per lb) which could be eliminated without affecting perchlorate reduction performance.
- **Eliminate the use of cheese whey.** Addition of necessary trace nutrients allows a reduction in the total nutrient requirement. Addition of hydrolysate or alternate nutrients could further eliminate the need for cheese whey which costs approximately $0.20 per pound.
- **Simultaneously process alternate effluents.** The nitrate and nitrite in hydrolysates can be simultaneously reduced with perchlorate. In addition, organics in the hydrolysate (acetate, formate, formaldahyde, glycerol, etc.) provide additional nutrient for the process. Other alternate effluent candidates include ethylene glycol, isopropyl alcohol (IPA) contaminated with HMX, and Brulin solution (an aqueous degreaser).
- **Evaluate the effect of co-contaminants.** Co-contaminants of interest include aluminum, cadmium, and boron. Hydrolysis of aluminized propellants results in the potential for high concentrations of $Al(OH)_4$- in solution. Cadmium has been observed in wastewater from certain propellant removal operations. Boron originates either from boron containing igniter components or corrosion inhibitors used during propellant removal and recovery operations.

4.0 Discussion and Results of Laboratory Tests

4.1 General Procedures

Laboratory tests were conducted to screen the performance of alternate nutrients and determine the affect of nutrients, nutrient concentrations, co-contaminants, and co-contaminant concentrations on perchlorate reduction performance. The most rapid and useful screening tool employed is referred to as a bottle test, which is a small (100-1000-ml) inoculation test conducted in a glass bottle. The bottle tests are designed to evaluate one variable at a time while maintaining other parameters constant. A series of serum bottles are prepared and nutrient, or co-contaminant concentration is varied over a wide range. All components are added (nutrients, phosphate buffers, perchlorate, water, test compounds, etc.) to the series of bottles, the pH adjusted to 7.5-8.0, and then a 5-10% inoculum from an active culture is added to each bottle. Bottles are sealed and then transferred to an anaerobic chamber that is maintained with a gas mixture of 80% nitrogen, 10% carbon dioxide, and 10% hydrogen. Bottles are incubated at 35°C. Samples are withdrawn from the bottles for perchlorate analysis at approximately 24-hour intervals. If the pH drops to 6.8 or less, it is adjusted to 7.5 by the addition of 30% sodium hydroxide. While bottle test results do not directly correlate to continuous-stirred-tank-reactor (CSTR) performance, they do give an indication of factors that may affect perchlorate biodegradation rates.

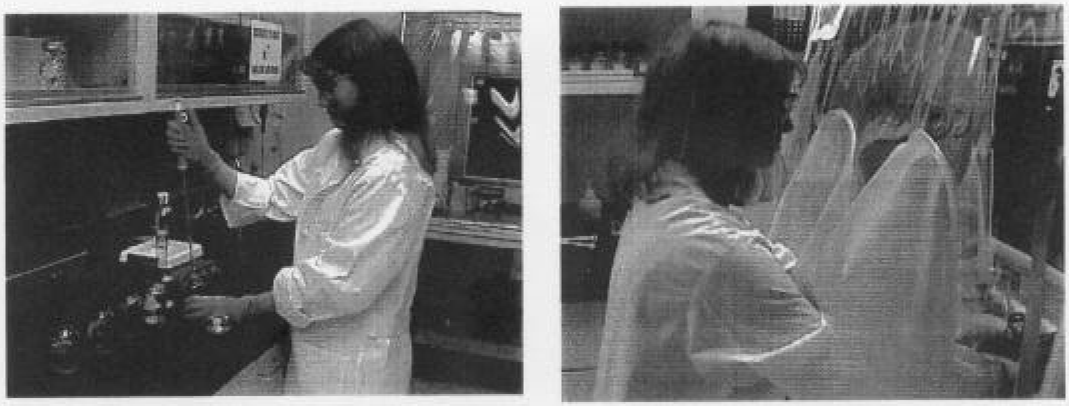

Figure 2. Conducting Bottle Tests at ARA's Panama City, FL Research Facility

4.2 Evaluation of Alternate Nutrients

Two nutrients were evaluated as alternatives to the brewer's yeast and cheese whey mixture used for Thiokol's prototype operation. A fruit juice waste previously evaluated under another effort demonstrated acceptable performance. This material could be obtained for transportation costs but had some drawbacks. Low nutrient value (sugar concentration of ~4%) and instability (i.e., this material would ferment easily), were a few of the drawbacks. The second alternative was a carbohydrate by-product (CBP) from a food processing operation. This liquid nutrient was concentrated in sugars, proteins, and minerals and, therefore, inherently stable providing the possibility of long term storage without fermentation or spoiling.

Two normalized parameters were used to compare nutrient performance. Nutrient concentration was based on the mass of biologically usable materials in the nutrient. These materials included sugars, amino acids, proteins, starches, cellulose, and other organic compounds typically determined by COD, BOD, or other chemical analyses. Nutrient ratio is defined as the ratio of mass of biodegradable organics in the nutrient to mass of perchlorate ion present. Typically, a nutrient ratio of 4 or less is necessary in the CSTR process.

Table 1 shows the first series of tests using fruit juice waste as a nutrient. Initial perchlorate concentrations were adjusted to approximately 160 mg/l (ppm). Bottles were inoculated with 5 ml of brewer's yeast inoculum.

Table 1. Bottle Test Series using Fruit Juice Waste Nutrient

Bottle Number	1	2	3	4	5
Nutrient Stock, ml	0.25	0.5	1	2	4
Nutrient Concentration g/L	0.36	0.72	1.44	2.85	5.60
Nutrient Ratio	2.19	4.43	8.71	17.38	34.80
Total, ml	115.25	115.5	116	117	119

A second series of tests were conducted concurrently with the fruit juice test using CBP as a nutrient. Initial conditions are shown in Table 2. Initial perchlorate concentrations were adjusted to approximately 160 mg/l. The bottles were also inoculated with 5 ml of brewer's yeast inoculum.

Table 2. Bottle Test Series using Carbohydrate Byproduct Nutrient (CBP)

Bottle Number	6	7	8	9	10
Nutrient Stock, ml	0.25	0.5	1	2	4
Nutrient Concentration g/L	0.43	0.87	1.72	3.42	6.72
Nutrient Ratio	2.65	5.22	10.58	21.23	45.12
Total, ml	115.25	115.5	116	117	119

<u>Results.</u> As observed in Figures 3 and 4 below, both of these nutrients effectively degraded perchlorate after a one to two day induction period. However, several significant differences in performance were observed. The fruit juice waste appeared to have a longer induction period before perchlorate reduction was observed. Perchlorate was reduced at a slower rate and appeared to be negatively impacted by both high and low nutrient concentrations.

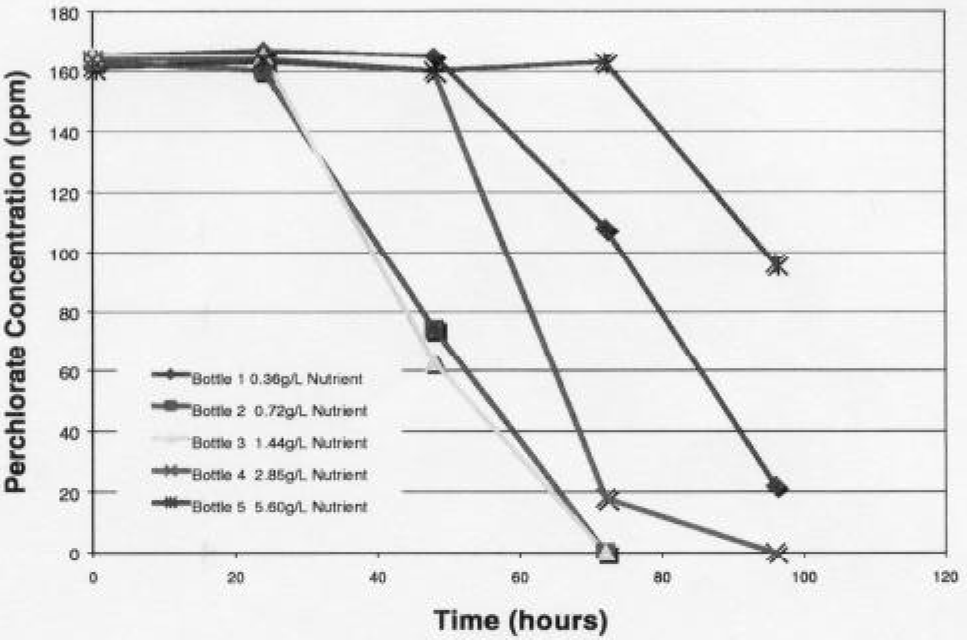

Figure 3. Bottle Test Results using Fruit Juice Waste as Nutrient

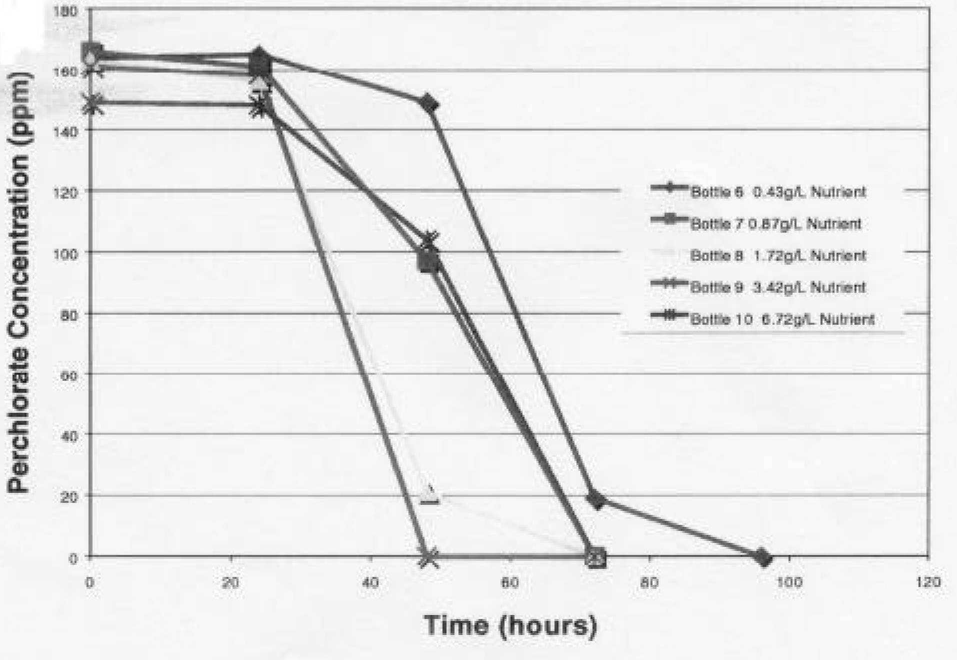

Figure 4. Bottle Test Results using CBP as Nutrient

To better evaluate the performance of these two nutrients, the perchlorate reduction rate observed at the 48-hour point in the test series was plotted against nutrient concentration. Figure 5 shows the CBP performed better than fruit juice waste and also over a broader concentration range than the fruit juice waste. Performance over a broader nutrient concentration is operationally significant for several reasons. Perchlorate concentration of the effluent water may vary considerably. The carbohydrate-based nutrient will be more tolerant of these fluctuations. Also, during process upsets, a typical recovery procedure is to increase nutrient concentration in the reactor. This is because the process is typically operated near a nutrient limited condition. The Thiokol prototype was very responsive to increasing brewer's yeast and cheese whey concentrations. The apparently narrow operating range of the fruit juice waste could possibly lead to operational problems resulting from over-feeding the reactor. The cause for this performance difference could be related to the relative oxygen or complex organic content of each nutrient. As a result of these tests, and operational and logistics considerations, the carbohydrate-based byproduct was selected as the nutrient for further laboratory testing and for the Thiokol Prototype Process.

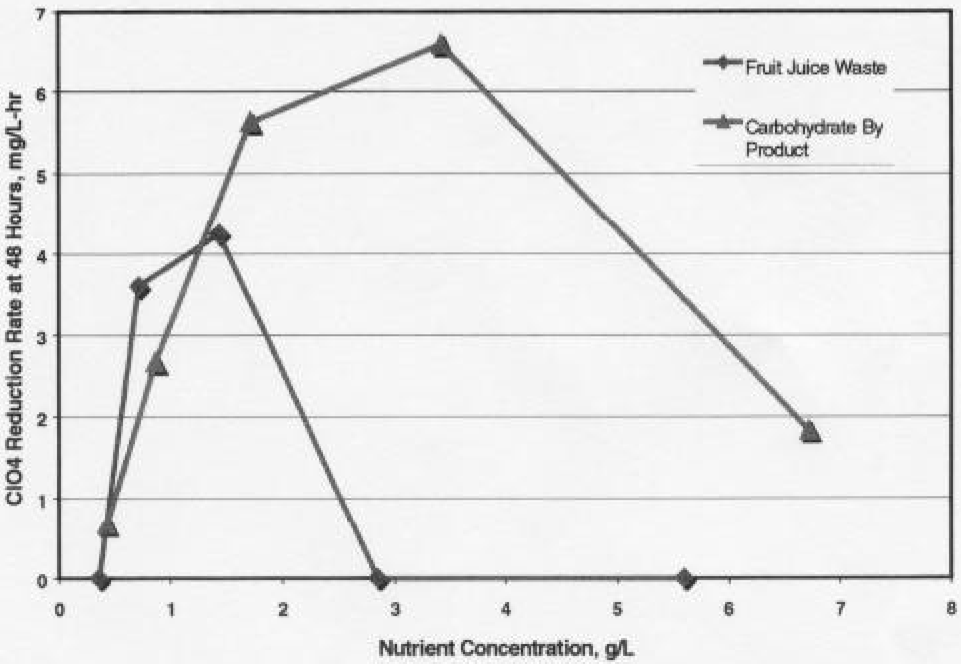

Figure 5. Comparison of Nutrient Performance

4.3 Evaluation of Alternate Effluents

4.3.1 General Procedures

Thiokol provided three alternate effluents by that could potentially be co-processed with perchlorate wastewater. These effluents were ethylene glycol, isopropyl alcohol (IPA), and Brulin solution. These organic-based materials also contained oxygen and were biodegradable. This provided two objectives for this study: 1) determine if perchlorate reduction performance is inhibited, and 2) determine if these materials could contribute to nutrient requirements for perchlorate reduction.

Thiokol wastewater is diluted as it is fed to the reactors which results in a 2% potassium chloride brine contaminated by perchlorate. To best simulate the co-processing of these alternate effluents, bottle tests were prepared with a 2% KCl solution. Initial perchlorate concentrations were adjusted to 400 mg/l using a 100,000-mg/l perchlorate standard. The bottles were then inoculated with 5 ml of brewer's yeast inoculum and incubated in the anaerobic chamber.

4.3.2 Ethylene Glycol

The ethylene glycol solution provided by Thiokol was a concentrated effluent from heat exchanger equipment and from vehicle use. The as-received material has a COD value of 595,000 mg/l. A stock solution was prepared by diluting to 50% with deionized water and adding micronutrients. The stock solution had a calculated nutrient value of approximately 0.2 g/ml. Table 3 below shows data for this bottle test series.

Table 3. Bottle Test Series for Ethylene Glycol

Bottle Number	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Ethylene Glycol Stock, (ml)	0	0	0.5	1.0	0.5	1.0	2.0	0.5	1.0	2.0
CBP Nutrient Value (g/L)	0.9	1.7	0	0	0.9	0.9	0.9	1.7	1.7	1.7
Total Nutrient Value, (g/L)	0.9	1.7	0.9	1.7	1.7	2.6	4.3	2.6	3.4	5.1
Total Volume (ml)	115.5	116.0	115.5	116.0	116.0	116.5	117.5	116.5	117.0	118.0
Calculated Initial ClO_4^- (mg/L))	433	431	433	431	431	429	426	429	427	424

Results. Figure 6 shows perchlorate reduction results with 0.9 g/l of the carbohydrate byproduct (CBP) nutrient added. In this test, addition of glycol improved performance in comparison to the control not containing glycol. However, as shown in Figure 7, when CBP nutrient concentration was increased, improvement in performance was less pronounced. This may have been caused by the possibility that CBP concentrations near 0.9 mg/l may be nutrient limited. But even at the higher nutrient concentration there appeared to be a synergistic improvement in performance compared to the control containing no ethylene glycol.

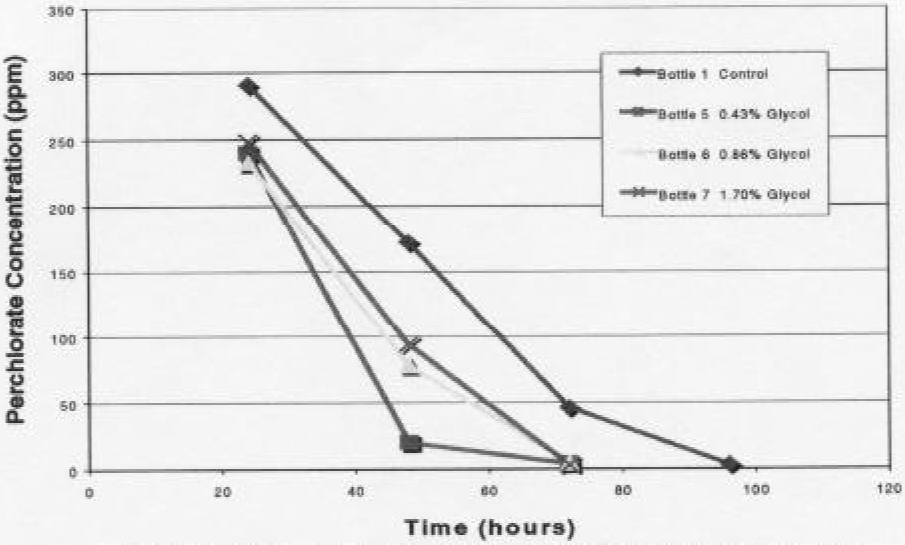

Figure 6. Glycol Bottle Test Results with 0.9 g/l CBP Nutrient

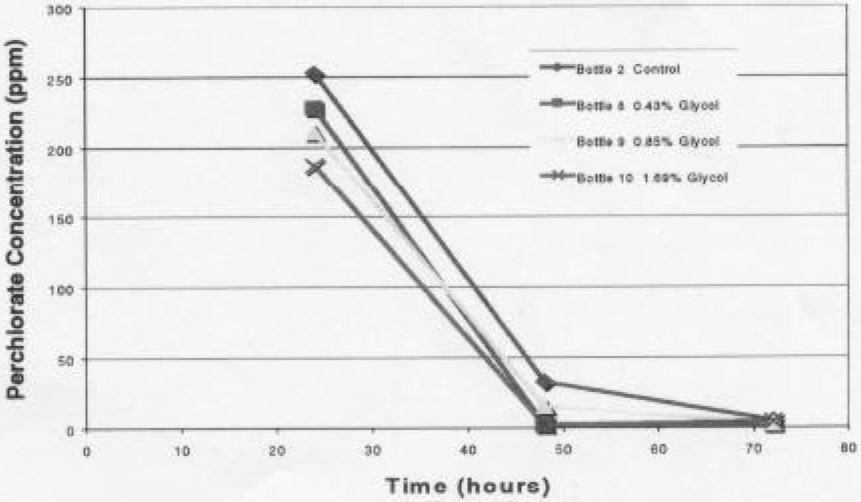

Figure 7. Glycol Bottle Test Results with 1.7 g/l CBP Nutrient

Figure 8 shows the perchlorate reduction performance of bottles 3 and 4. In these tests CBP was not added and perchlorate reduction was accomplished using ethylene glycol as the primary nutrient. The actual reduction rate observed was less than rates with CBP, but complete perchlorate reduction was demonstrated. These results show that not only could ethylene glycol be used in this process to enhance performance of CBP-type nutrients, but that it could also be used as a carbon nutrient.

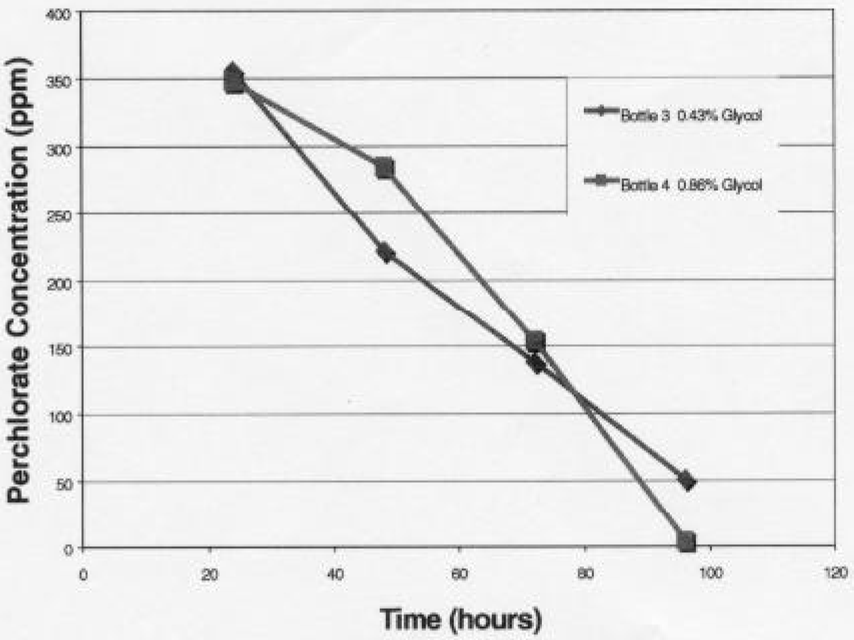

Figure 8. Glycol Bottle Test Results without CBP Nutrient

4.3.3 Isopropyl Alcohol (IPA)

Isopropyl alcohol and water solution is used to desensitize HMX during shipping. An IPA solution is recovered from HMX drying operations and typically contains low concentrations of HMX. Thiokol provided this "as received" IPA solution for these tests. The IPA content of this solution was approximately 50%. The nutrient content of this solution based on IPA content was estimated to be 0.2 g/ml. A bottle test series prepared in an identical manner to the ethylene glycol test series is shown in Table 4.

Table 4. Bottle Test Series for Isopropyl Alcohol

Bottle Number	1	2	3	4	5	6	7	8	9	10
IPA Solution, (ml)	0	0	0.5	1.0	0.5	1.0	2.0	0.5	1.0	2.0
CBP Nutrient Value (g/L)	0.9	1.7	0	0	0.9	0.9	0.9	1.7	1.7	1.7
Total Nutrient Value, (g/L)	0.9	1.7	0.9	1.7	1.7	2.6	4.3	2.6	3.4	5.1
Total Volume (ml)	115.5	116.0	115.5	116.0	116.0	116.5	117.5	116.5	117.0	118.0
Calculated Initial ClO_4^- (mg/L))	433	431	433	431	431	429	426	429	427	424

Results. A summary of perchlorate degradation performance is shown in Figures 9 and 10 for the two different CBP nutrient concentrations evaluated. In Figure 9 the addition of the IPA did not improve performance over the control, even though this may have been near a nutrient limited condition. Figure 10 shows that high concentrations of IPA may inhibit perchlorate reduction. Based on this data, "as received" IPA solution could be co-processed at approximately a 1% concentration without inhibiting perchlorate reduction performance. The fate of the HMX present was not determined. However, other studies have shown that the culture used in this process will completely remove the nitro functionality of explosive compounds (aromatic and non-aromatic). Therefore, it is likely that the HMX present was completely destroyed.

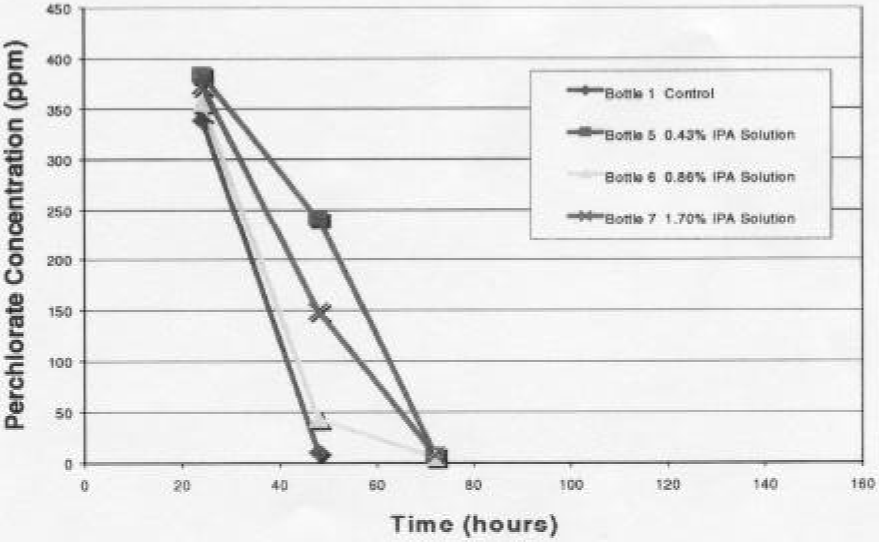

Figure 9. Isopropyl Alcohol Bottle Test Results with 0.9 g/l CBP Nutrient

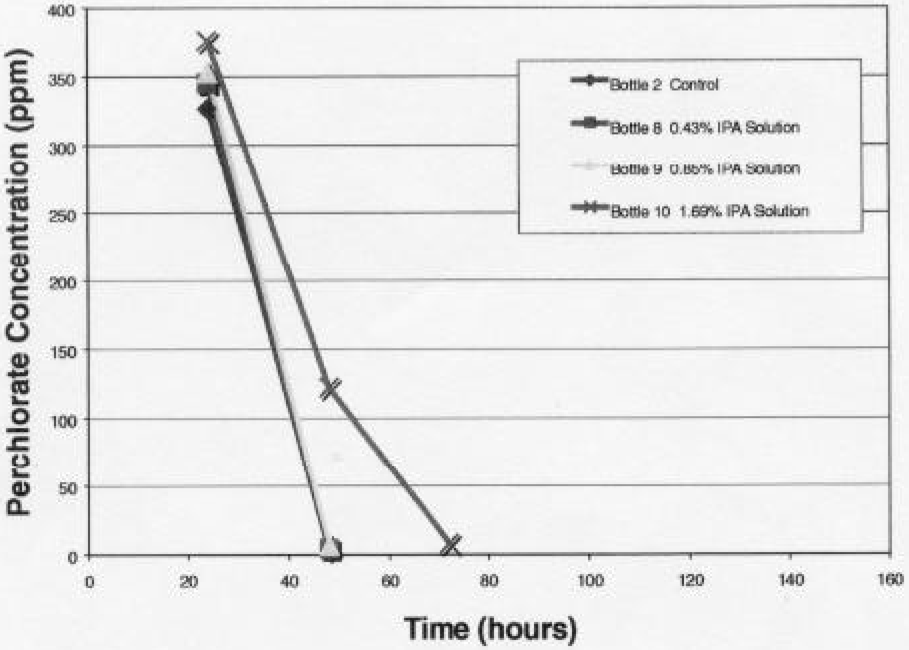

Figure 10. Isopropyl Alcohol Bottle Test Results with 1.7 g/l CBP Nutrient

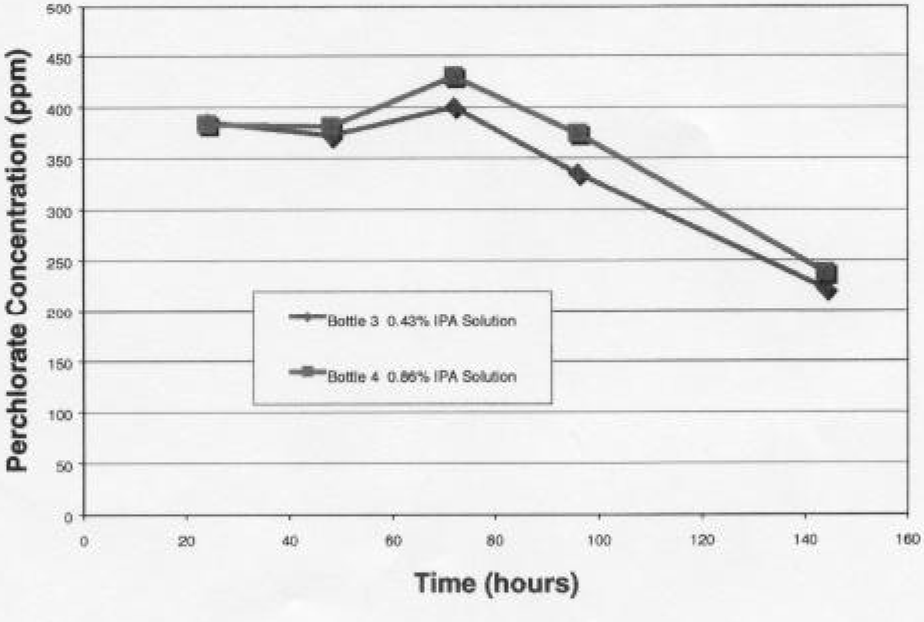

Figure 11. Isopropyl Alcohol Bottle Test Results without CBP Nutrient

Figure 11 shows perchlorate reduction performance for bottles 3 and 4. In these tests CBP was not added and perchlorate reduction was accomplished using IPA as the primary nutrient. After a 3-day induction period perchlorate was reduced, but at a much-reduced rate. After 144 hours, less than 50% of the perchlorate had been reduced. While this would indicate that IPA should not be used as a primary nutrient source, it is possible that acceptable performance might be obtained in a flow reactor after additional acclimation of the microbial culture to the IPA.

4.3.4 Brulin Degreaser Solution

Brulin degreaser solution is another effluent produced on site. Brulin is the trade name for an aqueous degreasing solution. Spent Brulin solution may contain organics and other contaminants, but a detailed analysis was not accomplished at this time. Again, bottles were prepared in a similar manner to the two previous tests. Brulin was a dilute solution compared to other effluents evaluated with a COD value of 1726 mg/L. Larger volumes of Brulin solution were used in this bottle test series as shown below in Table 5. However, nutrient contribution was minimal.

Table 5. Bottle Test Series for Brulin

Bottle Number	1	2	3	4	5	6	7	8	9	10
Brulin Solution, (ml)	0	0	5.0	10.0	5.0	10.0	20.0	5.0	10.0	20.0
CBP Nutrient Value (g/L)	0.8	1.6	0	0	0.8	0.8	0.8	1.6	1.6	1.6
Total Nutrient Value, (g/L)	0.8	1.6	0.07	0.14	0.87	0.94	1.08	1.67	1.74	1.87
Total Volume (ml)	125.5	126.0	125	125	125.5	125.5	125.5	126.0	126.0	126.0
Calculated Initial ClO_4^- (mg/L))	433	431	433	431	431	429	426	429	427	424

Results. A summary of the perchlorate degradation performance is shown in Figures 12 and 13 for the two different CBP nutrient concentrations evaluated. Figure 12 shows that the addition of Brulin did not appear to improve performance over the control, even though this may have been a nutrient limited condition. Higher concentrations of Brulin may slightly inhibit perchlorate reduction. Figure 13 shows that higher concentrations of CBP overwhelm any inhibitory effect Brulin may have on perchlorate reduction.

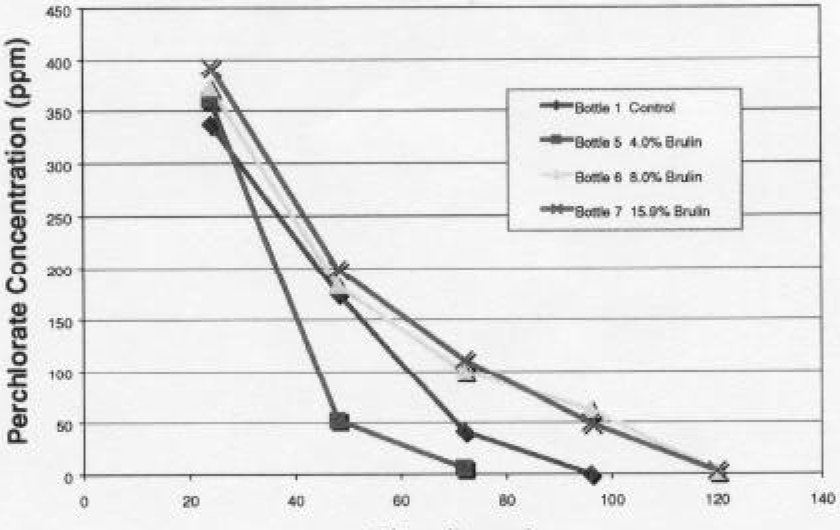

Figure 12. Brulin Bottle Test Results using 0.8 g/l CBP

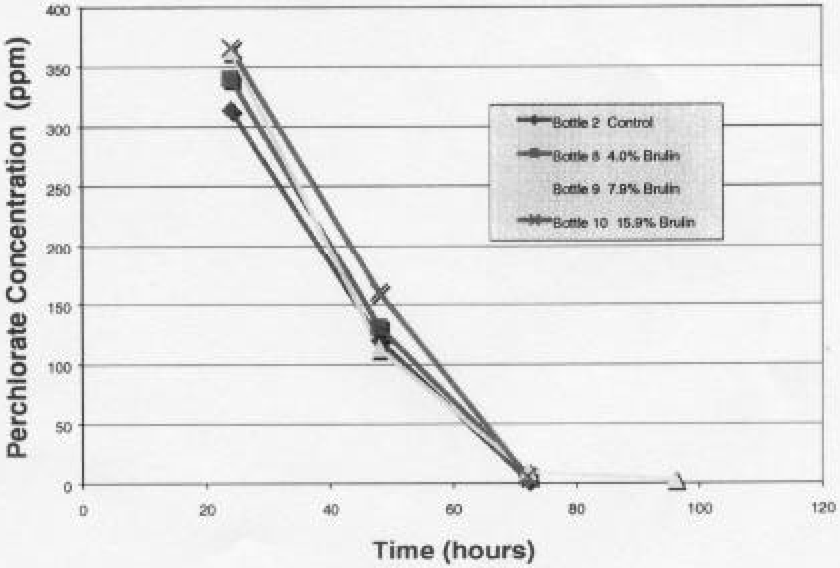

Figure 13. Brulin Bottle Test Results with 1.6 g/l CBP

Figure 14 below shows perchlorate reduction performance of bottles 3 and 4. CBP was not added and perchlorate reduction was accomplished using Brulin as the primary nutrient. After an induction period, perchlorate was reduced at a lower rate. After 120 hours more than 50% of the perchlorate had been reduced. While this would indicate that Brulin should not be used as a primary nutrient source, it is possible that acceptable performance might be obtained in a flow reactor after additional acclimation of the microbial culture to the Brulin. Results indicate that Brulin may be co-processed at concentrations up to 10-20% without inhibiting perchlorate reduction.

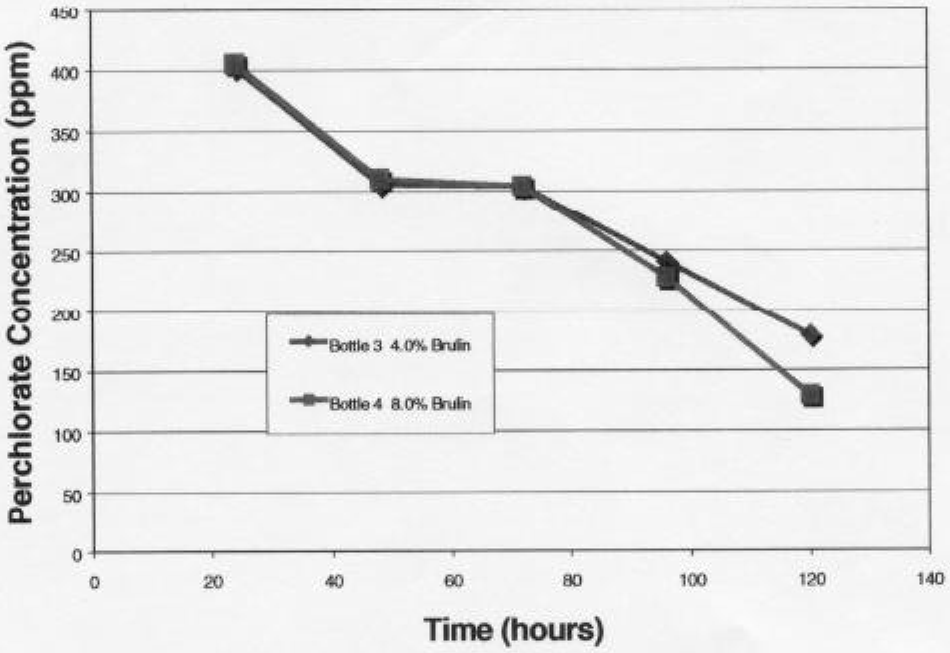

Figure 14. Brulin Bottle Test Results without CBP Nutrient

4.4 Evaluation of Inorganic Co-contaminants

Several inorganic co-contaminants were evaluated for their affect on perchlorate reduction performance. These contaminants originate from propellant washout operations (propellant and case constituents) and propellant hydrolysis operations. Bottles in each test series were prepared as previously discussed except where noted.

4.4.1 Boron

Boron contamination may originate from rocket motor igniters that are not removed during propellant washout operations or from borate-containing corrosion inhibitors. This test series was prepared in a 2% KCL solution to simulate Thiokol perchlorate-containing effluents. A 10,000 mg/l boron standard was prepared by dissolving 8.83 g of sodium borate in 100 ml of deionized water. Bottles were inoculated using 5 ml of inoculum from a culture maintained with CBP. Only one CBP nutrient concentration was evaluated as shown in Table 6.

Table 6. Bottle Test Series for Boron

Bottle Number	1	2	3	4	5
10,000 mg/L Boron Standard, (ml)	0	0.625	1.250	2.500	6.250
Calculated B, (mg/L)	0	50	100	200	500
CBP Nutrient Value, (g/L)	1.6	1.6	1.6	1.6	1.6
Calculated Initial ClO_4^-, (mg/L)	400	400	400	400	400
Total Volume, (ml)	125	125	125	125	125

<u>Results.</u> As shown in Figure 15, only the highest concentration of boron tested (500 mg/l) appeared to inhibit perchlorate biodegradation. However, boron can bio-accumulate and affect microbial growth. This mechanism of inhibition may not be evident in bottle tests. However, in the Thiokol process where biomass is recycled, boron may become toxic. If significant boron is anticipated in process wastewater for a prolonged period of time, consideration should be given to wasting all the biomass generated in the process. Other studies have shown that this method of operating CSTRs reduces or eliminates inhibition of perchlorate biodegradation caused by co-contaminants known to bio-accumulate.

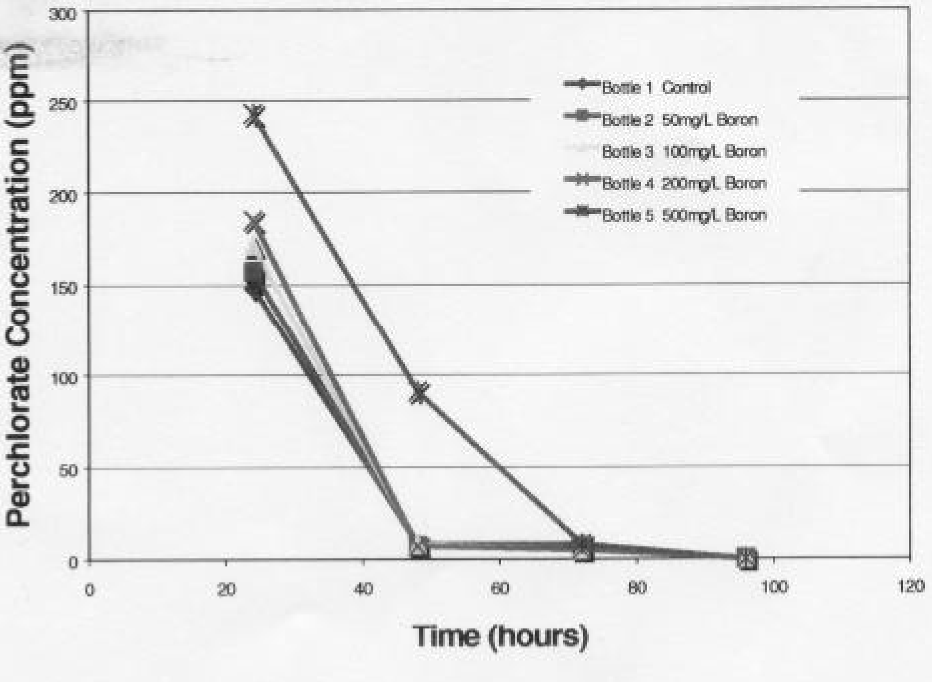

Figure 15. Boron Bottle Test Results

4.4.2 Cadmium

Cadmium contamination may originate from cadmium plated components of small pyrotechnics and rocket motors exposed to perchlorate and water washout processes. A 5000-mg/l cadmium stock solution was prepared by dissolving 10.159 grams of cadmium chloride in 1 liter of deionized water. In this bottle test series, tap water was used instead of the 2 % KCl solution. Also, 250 mg/l of nitrate was included as a co-contaminant. Bottles were inoculated with 5 ml of inoculum from a brewer's yeast culture. A single CBP nutrient concentration was used in these bottle tests as shown in Table 7.

Table 7. Bottle Test Series for Cadmium

Bottle Number	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
5000mg/L Cd Standard, (ml)	0	0	1.0	1.0	5.0	5.0	10.0	10.0	20.0	20.0
Calculated Cd (mg/L)	0	0	41.7	41.7	208.3	208.3	416.7	416.7	833.3	833.3
CBP Nutrient Value, (g/L)	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
Total Volume (ml)	120.0	120.0	120.0	120.0	120.0	120.0	120.0	120.0	120.0	120.0
Calculated Initial NO_3^- (mg/L)	251	251	250	250	250	250	250	250	250	250
Calculated Initial ClO_4^- (mg/L))	418	418	417	417	417	417	417	417	417	417

Results. Figure 16 shows the results of the cadmium test series. Duplicate test results agreed with each other, especially the control and 42 ppm tests (bottles 1-4). Higher cadmium concentration tests all performed in similar fashions. Concentrations of cadmium above 42 ppm caused the induction period to increase from 1 day to 4 days. However, after 6 days all perchlorate was reduced. It is not clear how this result might manifest itself in the Thiokol CSTR process. Clearly some inhibition or loss of performance occurs in the presence of high cadmium concentrations. As stated previously with other contaminants, proper acclimation of the culture to these elevated concentrations of cadmium may result in acceptable perchlorate reduction as evidenced by bottle tests at 208 and 833 ppm.

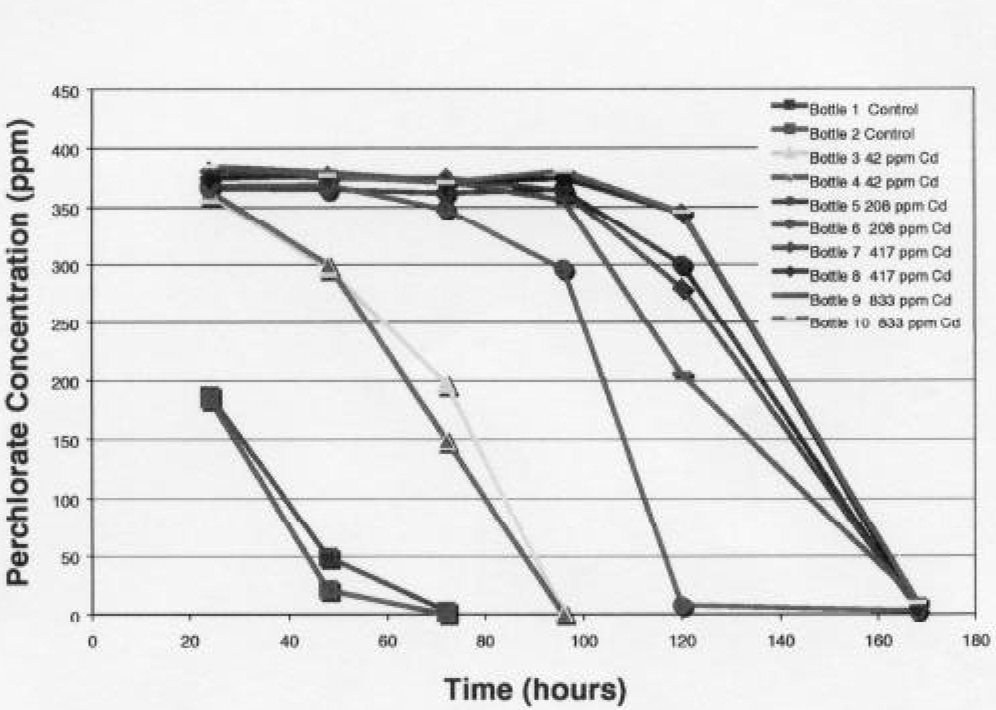

Figure 16. Cadmium Bottle Test Results

4.4.3 Aluminum Hydroxide – $Al(OH)_4^-$

Aluminum hydroxide ion, $Al(OH)_4^-$, can be formed when aluminized propellants are hydrolyzed with sodium hydroxide. $Al(OH)_4^-$ ion stock solution was prepared by dissolving 5 grams of aluminum shot in 50% NaOH then diluting to 1 liter. The resulting solution was 5000 mg/l as Al and 17,690 mg/l as $Al(OH)_4^-$. Tests were conducted at two different nutrient levels in tap water vs. 2% KCl solution. Table 8 shows a summary of the test series.

Table 8. Aluminum Hydroxide Test Series

Bottle Number	1	2	3	4	5	6	7	8
5000mg/L Al Standard, (ml)	0	0	0.5	1.0	2.0	0.5	1.0	2.0
Calculated Al, (mg/L)	0	0	75	150	300	75	150	300
CBP Nutrient Value, (g/L)	0.9	1.7	0.9	0.9	0.9	1.7	1.7	1.7
Calculated Initial ClO_4^-, (mg/L)	433	431	431	429	426	429	427	424
Total Volume, (ml)	115.5	116.0	116.0	116.5	117.5	116.5	117	118

Results. Figures 17 and 18 show perchlorate reduction performance at low and high nutrient concentrations, respectively. Slight inhibition of perchlorate reduction may occur at the higher aluminum concentrations (150 and 300 mg/l).

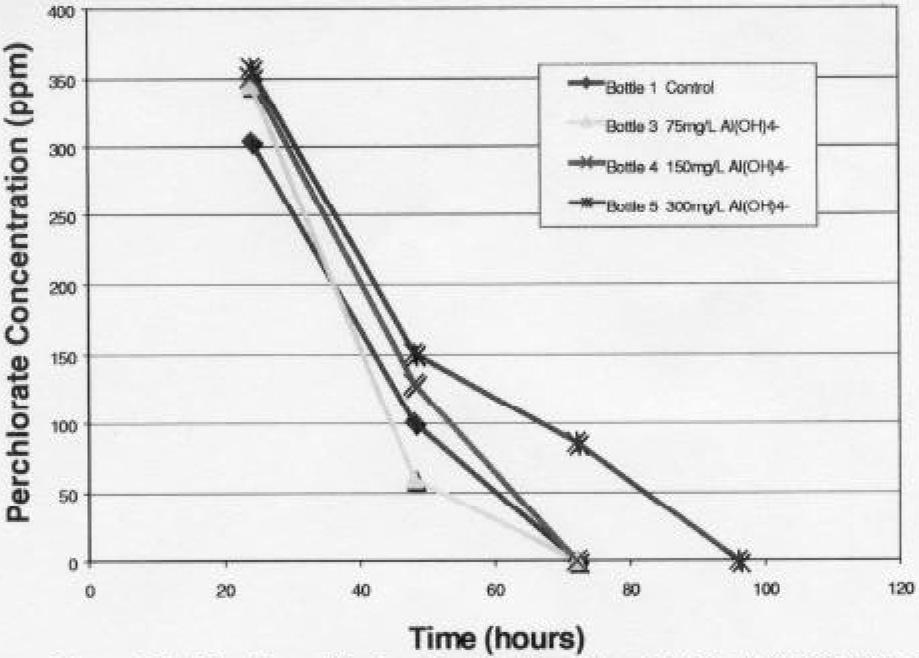

Figure 17. Aluminum Hydroxide Test Results with 0.9 g/l CBP Nutrient

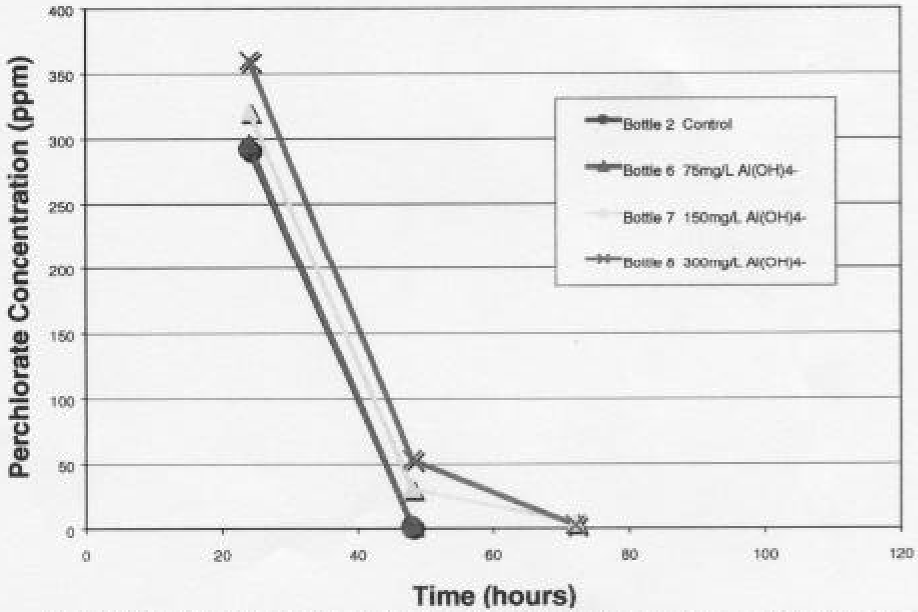

Figure 18. Aluminum Hydroxide Test Results with 1.7 g/l CBP Nutrient

5.0 Summary of Prototype Operational Performance

5.1 Transition to Alternate Nutrients

A primary objective for the prototype operation was to convert the process to a low-cost alternate nutrient. A secondary objective was to demonstrate the treatment of hydrolysate, but unavailability of hydrolysate precluded this objective from being met. During May 1999, the prototype process was transitioned from a brewer's yeast/cheese whey mixture to whey, then to a whey/CBP mixture, and finally to CBP in a period of five weeks. Additional micronutrients were fed to the process during this transition.

5.2 Summary of Operational Data

A summary of the Thiokol operational data for 1999 is shown in Table 9 below. A total of 84,321 gallons of brine containing 7.7 tons of perchlorate from Thiokol's perchlorate recovery and ion exchange units were treated.

Table 9. Summary of Effluent Treated in 1999

Month	Volume of Brine Treated (gallons)	Average ClO_4^- Concentration (mg/l)	Perchlorate Destroyed (lbs.)
January	6,128	10,232	527
February	6,465	2,797	152
March	3,173	36,009	961
April	3,827	41,303	1,330
May	4,979	16,271	681
June	7,790	18,559	1,216
July	9,294	16,716	1,307
August	9,812	24,735	2,041
September	8,960	21,830	1,645
October	11,626	19,442	1,901
November	8,151	39,567	2,713
December	4,116	26,788	927
Total	**84,321**		**15,402**

The Thiokol perchlorate recovery and ion exchange processes produce a brine stream containing high salt concentrations, nitrates, nitrites, and sodium perchlorate. The perchlorate and TDS concentrations of the effluent varied significantly. Occasionally, alternate effluents and inorganic contaminants were processed through the system. For example, 0.14% IPA waste stream was processed 10-17 February. The effluent in Table 9 was diluted to 10-20% as it is fed to the reactors in order to reduce TDS. Figure 19 shows the weighted-average monthly concentrations of perchlorate and TDS processed in the reactors (after dilution) and the resulting effluent concentrations.

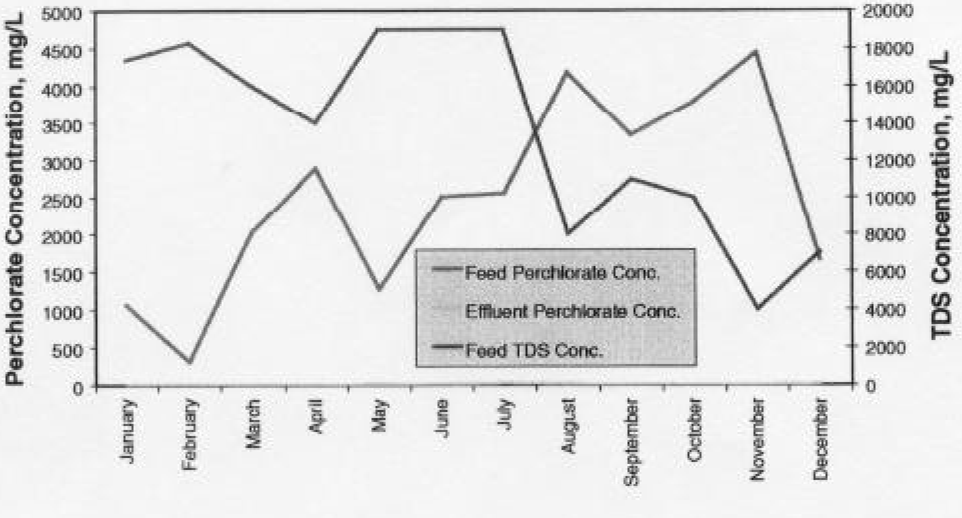

Figure 19. Reactor Perchlorate and TDS Concentration

The monthly average of perchlorate feed concentration delivered to the reactors varied from 305 mg/L to 4,624 mg/L. TDS concentration to both reactors ranged from 4000 to 19,000 mg/L. Average percent brine fed to the system ranged from 7-20%. The reactors performed extremely well despite being fed varying concentrations of perchlorate and TDS and being operated in the single-stage configuration. Figure 20 shows the daily variation in perchlorate feed concentration for the month of June 1999 and the resulting effluent perchlorate concentration.

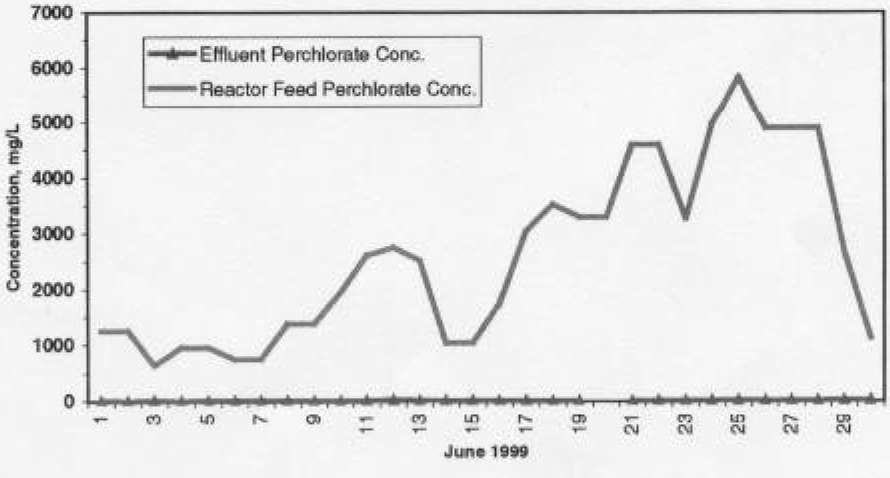

Figure 20. Variation of Perchlorate Concentration in Reactor Feed Composite

Effluent perchlorate concentration is measured prior to discharge at the effluent storage tanks by the IonChem analyzer using a perchlorate ion specific electrode (ISE). The monthly average effluent concentrations ranged from 2.74 and 24.95 ppm using this method. Effluents at Thiokol have high TDS concentrations and several anions known to interfere with perchlorate ISE's. Interfering anions such as chloride (Cl^-) and nitrite (NO_2^-) cause measurements to vary over 10% at perchlorate concentrations between 1 and 100 ppm. In addition, low ppm measurements are at the limit of capability for the ISE methods. Spot checks of samples using laboratory IC low concentration methods have confirmed that samples reading 0-30 ppm using the IonChem/ISE method are actually non-detect to low ppb (4-400 ppb).

5.3 Prototype Process Capability

Recent laboratory studies have shown that the prototype system is being operated at only 25-40% of its potential capacity. Performance parameters that were used as a basis for the 1997 configuration versus the current capability are shown in Table 10. The system is capable of processing a greater amount of perchlorate at reduced cost due to changes in the nutrient feed operating parameters. Equipment and software constraints prevent the system from being operated at optimal performance.

Table 10. 1997 Design Basis vs. Current Capability

Reactor Performance Parameters	1997 Bases for Prototype	Current Design Bases
Retention Time, hours	18-36	4-8
Operating Temperature, °C	35-40	<20
Perchlorate Treatment Range	1000-15,000 ppm	1-15,000 ppm
Perchlorate Destruction	< 1 ppm	< 4 ppb
Brine Tolerance, TDS	< 2%	> 5%
Co-contaminants Reduced	NO_3-	NO_2^-, NO_3^-, ClO_3^-, Cr (VI)
Nutrients	Brewer's Yeast Yeast-Whey Blends	Carbohydrates Food Process Byproducts

6.0 Summary of Prototype Equipment Modifications

6.1 Accomplished Modifications

Several modifications to the system have taken place since the system was commissioned in 1997 (see Figure 21). Changing the nutrient from a brewer's yeast/cheese whey mixture to a CBP solution has been the most significant change. The existing nutrient pumps performed well with the new nutrient, however, some nutrient dilution was required to maintain proper flow rate. Additionally, citric acid was substituted for sulfuric acid for pH control soon after system startup. Citric acid is safer, cheaper, less corrosive, and consumption in the process is minimal. Studies have shown that citric acid may also provide nutritional value to the system.

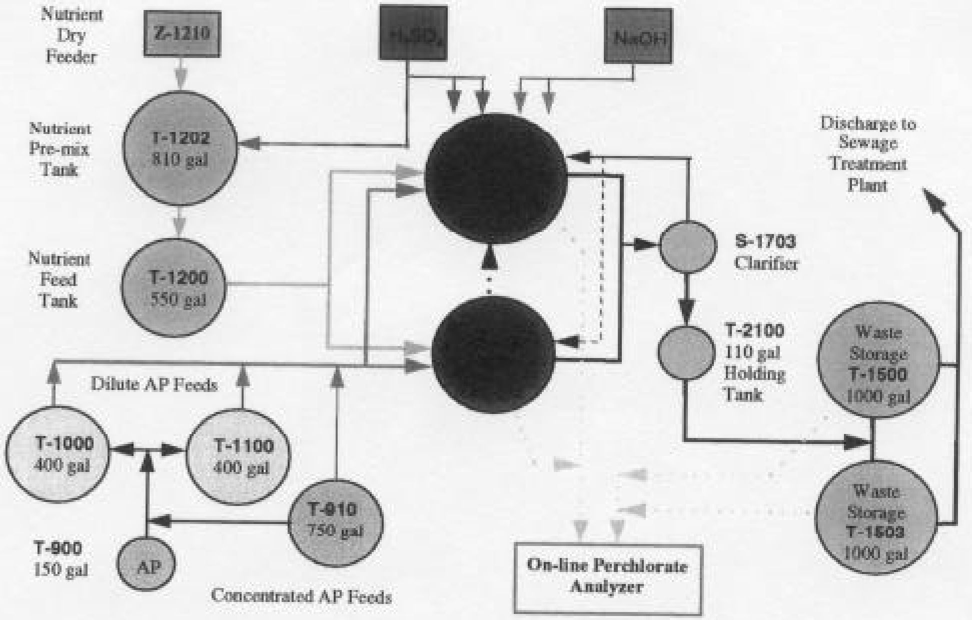

Figure 21. 1997 Thiokol Configuration

Stainless steel (304) brine feed storage tanks, T-1000 and T-1100 (400 gallons/ea.) have both been removed from service due to corrosion which led to leaking. They were replaced with two fiber reinforced polyethylene (FRP) tanks that are considerably larger and provide more brine storage capacity. One tank is 775 gallons, and the other 540 gallons. During installation, it was necessary to remove strong perchlorate tank T-900 from the perchlorate feed skid. In the future it will be used as a feed tank for metering alternate nutrients and other contaminants into the reactors.

6.2 Recommended Modifications

System operations are monitored and adjusted at the operator interface (O/I) using a computer that interfaces with a programmable logic controller (PLC). The computer and PLC are currently using obsolete software packages that need to be upgraded. It is recommended that the computer and control software packages both be upgraded to meet current industry standards. In addition, many of the recommended physical modifications will also require software changes.

Bench scale studies have shown that the system operates more effectively in series at shorter residence times (4-8 hrs.). At this time the reactors cannot be run at the lower residence times due to physical limitations. Dilution water flowmeters and control valves are currently undersized. These flowmeters and control valves provide the dilution water necessary for maintaining perchlorate effluent feed TDS and perchlorate at acceptable levels. Increasing the Cv's of the control valves and installing larger flowmeters would provide the system with the capability of operating at reduced residence times. These changes would require minor software changes.

Studies have also shown that the process operates efficiently at a temperature of 25°C or less. To operate the system at lower temperatures several modifications need to take place. The current heaters must be repositioned to prevent overheating and burning out of coil elements. Recently, it has been discovered that the heating coils were designed to be positioned horizontally, but during construction were mounted vertically. In addition, a five (5) horsepower centrifugal pump circulates glycol through a heating loop. This pump is oversized for this application, and needs to be replaced. This pump transfers a significant amount of heat to the glycol making glycol temperature difficult to control. The pump also creates excess pressure within the glycol loop and the current means of pressure relief for the loop is inadequate. Once these minor modifications are made, the system could be run at ambient temperatures (20-35°C) during warmer times of the year and be more easily controlled during colder times of year.

Nutrient feed contamination has been a problem in the nutrient storage tank with the brewer's yeast and cheese whey nutrient mixture. Currently, CBP is prepared by placing micronutrients and CBP in the nutrient pre-mix tank where they are diluted with water. This feed solution is then transferred to the nutrient feed tank where it is pumped to the reactors using a magnetic drive pump. Some feed contamination has continued occurred during the preparation of dilute CBP. Since concentrated CBP will not support bacterial growth, storing and feeding undiluted CBP by means of a dosing or metering pump can prevent nutrient contamination. Nutrient flow control valves could then be removed from service, reducing maintenance on the nutrient feed system. Software changes would be required for this modification.

It is also recommended that the clarifier and recycle pump be removed from service. Bench scale studies have shown that the solids or cell recycle is not necessary and at times harmful to the process. Recycled effluents and cells may enable bioaccumulation of contaminants that can inhibit perchlorate reduction. Effluent from the reactors should instead be fed to a larger intermediate holding tank where it would then be discharged to the sewage treatment plant. This modification also involves software changes.

7.0 Cost Assessment

7.1 Operating Cost Analysis

A summary of actual maintenance and operating costs for 1999 is presented in Table 11. Data was obtained from quarterly reports provided by Thiokol to the USAF and ARA under terms of the CRDA signed in 1997. Costs are shown as monthly averages and totals for 1999. Nutrient costs are shown only for the months that particular nutrient was used. During January through April 1999, brewer's yeast and cheese whey were used as the nutrients. In May the nutrient was transitioned to CBP and a supplement. The nutrient unit cost basis was \$0.20/lb for cheese whey; \$0.75/lb for brewer's yeast; and \$0.14/gal (\$25/ton) for CBP.

As can be seen in Table 11, the monthly average nutrient cost was reduced by over 20%, however, this does not reflect the increase in perchlorate destruction that was accomplished in the second half of the year. Total nutrient and chemical cost savings are better represented on a normalized basis. In Figure 22 the actual average cost is shown on a pound-of-perchlorate basis. This shows a reduction in costs from \$1.76 to \$0.16 per pound of perchlorate treated, or over a 90% cost reduction.

Table 11. Operating and Maintenance Costs for 1999

	Operating Costs for CY 1999	
	Monthly Average	Annual Total
Yeast And Whey (Jan-May, 4.5 mo.)	\$1068	\$4806
CBP (May-Dec, 7.5 mo.)	\$164	\$1230
Caustic (NaOH)	\$37	\$444
Nutrient Supplement (Jun-Dec, 7 mo.)	\$44	\$308
Maintenance (Materials)	\$753	\$9036
Maintenance (Labor)	\$800	\$9600
Operating Labor	\$3640	\$43,680
Annualized Total Based on CBP:	\$5438	\$64,256

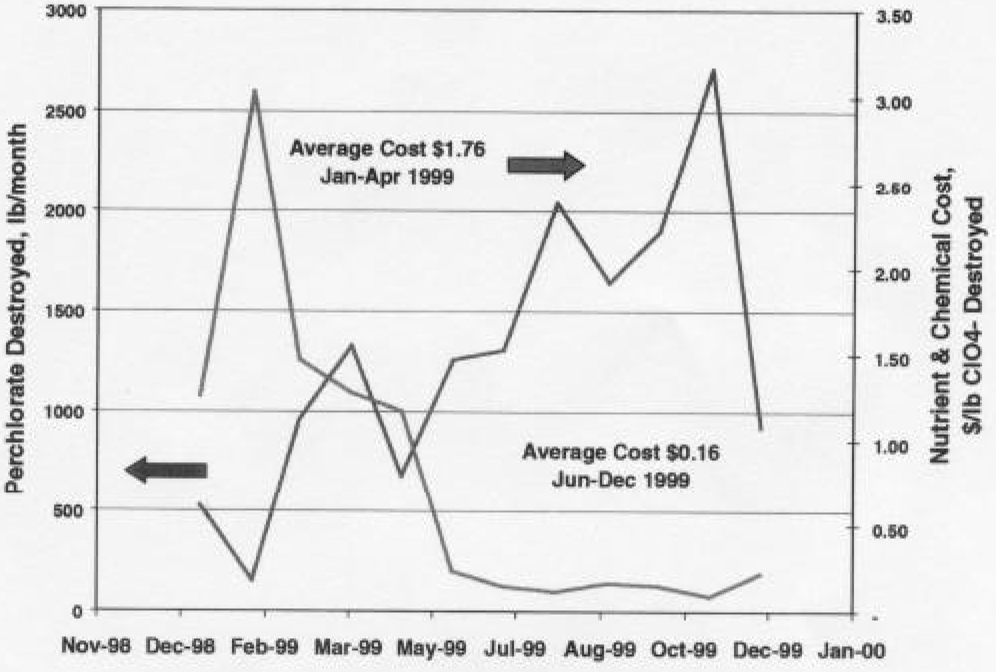

Figure 22. Summary of Nutrient and Chemical Costs

Operating Labor is based on a part-time technician at approximately 75% of full-time. Maintenance materials and labor are based on actual expenditures. This prototype which is based on an R&D pilot system, is projected to have greater maintenance, support, and operating cost than a comparable commercial production design.

7.2 Capital Cost Analysis

ARA recently designed and prepared budgetary cost estimates for a treatment facility similar in scale to the Thiokol prototype. The design for the capital costs presented in Table 13, is based on a process with two 1600-gallon reactors operated in series. These are approximately the same size reactors and tanks that are in the Thiokol Prototype. However, the capacity of the commercial system is 2-4 times greater (~4 GPM) which must be taken into consideration when comparing costs to the prototype. The commercial system is skid mounted like the Thiokol Prototype, however, the controls are simplified and the materials of construction are mostly fiber reinforced plastic (FRP) and high-density cross-linked polyethylene (HDPE).

Table 12. Capital Cost for Commercial 4 GPM Process

Cost Data Table, in $1000

	Project Phase			
Cost Category	Start-up	Annual O & M	Demobilization	Life-Cycle
Labor	20	25	-	-
Training & O&M Manual Prep.	35	-	-	-
Site-Specific Treatability Studies	100	-	-	-
Design/Engineering	80	-	-	-
Site Preparation	100	-	-	-
Equipment Installation	75			
Analysis/monitoring	15	5	-	-
Contracting	-	-	-	-
Permits/Regulatory Requirements	-	-	-	-
Capital Equipment	225	-	-	-
Modifications	-	-	-	20
Scheduled Maintenance	-	20	-	-
Consumables	-		-	-
- Nutrient		2		
- Acid, Caustic, Chemicals		1		
- Electricity		4		
Ancillary Equipment	-	-	-	-
Effluent Treatment	-	-	-	-
Equipment Decontamination	-	-	5	-
Equipment Removal	-	-	15	-
Site Restoration	-	-	-	-
Future Liability	-	-	-	-