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DENITRIFICATION OF ACID WASTES
FROM URANIUM PURIFICATION
PROCESSES

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OAK RIDGE Y-12 PLANT
OAK RIDGE, TENNESSEE

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ABSTRACT

Laboratory and pilot-plant investigations have shown the technical feasibility of removing nitrates from neutralized acid wastes by biological denitrification, a dissimilatory process in which the nitrate ion is reduced to nitrogen gas by specific bacteria. The process requires anaerobic conditions and an organic carbon source, as well as other life-sustaining constituents.

These denitrification studies have produced process design information on a columnar denitrification plant and on continuous-flow, stirred-bed reactors. Denitrification, using packed columns, has been found to be desirable for soluble salts, such as those of sodium and ammonium; denitrification, using stirred reactors, has been found to be desirable for mixtures containing insoluble salts, such as those of calcium and aluminum. Packed columns have been found to have denitrification rates ranging up to 122 grams of nitrate per day per cubic decimeter of column volume; stirred-bed reactors have been shown to have reaction rates near 10 grams of nitrate per day per cubic decimeter of reactor volume. The continuous-flow, stirred-bed reactors were selected for scaleup studies because of the solids-removal problems associated with packed columns when operating on feeds containing high concentrations of insoluble salts or ions which form insoluble salts with the products of the denitrification reaction.

In order to determine the effectiveness of a biological process, the specific waste stream must be considered. Minor changes in the composition of the wastes can cause major changes in the biological denitrification process.

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SUMMARY

FEASIBILITY OF THE COLUMNAR DENITRIFICATION SYSTEMS

Nitrate waste streams from two uranium processes were evaluated in the columnar denitrification studies. One stream, containing high concentrations of calcium and aluminum salts, was found to be unsuitable for feed to the column. Another stream, containing high concentrations of ammonium salts, was found to be effectively denitrified using packed columns.

The packed-column studies evaluated both straight and tapered columns, with the tapered column being the preferred design. Several column-packing media were studied including anthracite coal. Carbon in the form of methanol was used in the column studies.

Denitrification-rate studies showed decomposition rates up to 122 grams of nitrate per day per cubic decimeter of column volume. Scaleup calculations indicated that a 1.2-meter-long by 8-meter-diameter column could decompose five metric tons of nitrate per day where the inlet feed concentration would be in the range of 500 to 5000 g NO_3^-/m^3 , and the total feed flow would be in the range of 11.6 dm^3/s , producing a cross-sectional flow in the column of 0.23 $\text{dm}^3/\text{m}^3/\text{s}$. It should be noted that scaleup studies should be performed on plant waste streams to obtain engineering design information on specific systems.

STIRRED-BED REACTORS

Bench-scale studies were conducted to obtain design information on stirred-bed reactors. Excluding the startup period, four test reactors were satisfactorily operated for 428 days out of a total of 453 test days. The inlet feed concentration was a nominal 10 wt % nitrate, with a nominal 20-day residence time in the reactors. The effluent from the reactors contained less than 0.01 wt % nitrate, with the systems being operated at a reduction efficiency of greater than 99.9%. The maximum denitrification rate was not established, but nominal rates of 10 grams of nitrate per day per cubic decimeter of reactor solution were typical. Plant design data showed that a 94.5- m^3 (25,000-gal) vessel, operating on the same nitrate feed, could be expected to decompose more than 181,500 kgs (400,000 lbs) of nitrate per year. All bench-scale studies used calcium acetate as the carbon source. Also, the acidic wastes were not neutralized prior to adding them to the reactor. The excess calcium carbonate particles in the vessel served to neutralize the feed solution.

PILOT-PLANT STUDIES

The continuous-flow, stirred-bed reactor design was selected for scaleup studies because of the removal problems associated with the expected large volumes of calcium carbonate and aluminum hydroxide solids. A large vessel (15 m^3) was modified and operated as a stirred-bed reactor. Test data showed the same denitrification rates (nominally, 10 g $\text{NO}_3^-/\text{day}/\text{dm}^3$ of solution) were obtained in the pilot-plant reactor as were obtained in the laboratory studies. The maximum rate of denitrification was not determined in the pilot-plant tests.

A test was made in the pilot-plant studies using a feed solution containing a mixture of methanol and calcium acetate. The results showed that the system did not operate satisfactorily, because the calcium acetate was utilized in preference to the methyl alcohol as an organic carbon source.

Engineering design data for a plant-sized denitrification stirred-bed reactor have been completed.

INTRODUCTION

A development program has been completed at both the Oak Ridge National Laboratory and the Oak Ridge Y-12 Plant^(a), to develop process design information for the installation of facilities to curtail or eliminate the indirect release of acidic nitrate effluents from a uranium purification process. Essentially all of the nitrate waste streams are generated by uranium solvent extraction recovery processes as acidic evaporator condensates and aluminum nitrate-containing extraction raffinates. Pilot-plant studies have been completed on conventional distillation and recycling of the nitric acid-water evaporator condensate streams and the raffinate streams containing aluminum nitrate, calcium nitrate, and extracted impurities. Most of the aluminum nitrate will be recycled by the evaporation and recrystallization operations. A waste stream from the evaporation/recrystallization process (or the "mother liquor") will require further treatment.

Since the mother-liquor stream could not be recycled to the plant, an acceptable disposal method was required. Several approaches to this problem were considered, but the most promising method appeared to be biological denitrification. The principle of biological denitrification has been studied by many investigators. In general, the nitrate concentration in the waste streams previously studied was in the order of several hundred parts per million. In the case of the mother-liquor streams, nitrate concentrations up to 40 wt % were typical. To obtain feasibility data on the denitrification process, a research study was conducted at the Oak Ridge National Laboratory. This study used nitrate wastes obtained from several uranium processing plants which contained calcium, sodium, and ammonium salts. The experiments were focussed on columnar denitrification systems, and the significant findings are recorded in this report.

The mother-liquor stream from the Y-12 Plant contains high concentrations of aluminum and calcium salts which precipitate as hydroxides or carbonates during the biological denitrification process. These solids cause plugging of columnar reactors and, therefore, continuous-flow stirred-bed reactor studies were proposed and conducted. Laboratory and pilot-plant-sized equipment were operated to obtain the engineering design data.

(a) Both facilities are operated by the Union Carbide Corporation's Nuclear Division for the US Energy Research and Development Administration.

ACID WASTE DENITRIFICATION

THEORY

Biological denitrification is the reduction, by microorganisms, of nitrates or nitrites to gaseous molecular nitrogen or the oxides of nitrogen. "Dissimilatory biological denitrification" is nitrate reduction where the nitrate serves as the terminal electron (hydrogen) acceptor in the oxidation of an organic substrate by a large number of facultative anaerobic bacteria. This term should not be confused with "assimilatory denitrification", which is the reduction of nitrates or nitrites to ammonia for the synthesis of amino acids, amino sugars, and nucleotides in anabolic cell metabolism.

Biological denitrification can only occur under an anaerobic environment or at least a "reduced" environment where the redox potential is less than 250 mV. Optimum denitrification occurs in the pH range from 7.5 to 8.5. Two substrates must be available—nitrate and an energy source which is usually a hydrocarbon that also supplies carbon for additional cell synthesis.

COLUMNAR DENITRIFICATION STUDIES

Description of the Unit

A columnar denitrification unit is an enclosed reactor that contains submerged inert packing material which provides a large surface area for bacterial growth. The system is operated under flooded conditions with flow either upward or downward. Most columnar units are operated by directing the influent in an upward direction at a slow flow rate to promote separation of the microbial population from the effluent. A major portion of the microbial population is attached to the medium, but a small fraction is suspended in the effluent and consequently lost.

Materials and Methods

The packing medium used in this study included anthracite coal particles and polypropylene Raschig rings. Both are available commercially. The anthracite coal^(b) has an effective particle diameter between 2 and 3 mm. The particles are angular and irregularly shaped and have an average particle density of approximately 1.5 g/cm³. Initial bed porosity after placement in the column was 36%. The polypropylene Raschig rings^(c) are 1.6 x 1.6 cm in diameter and have a geometric surface of 3.2 m²/m³ and a free space of 92%.

All reactors were seeded from a microbial soil culture obtained in the following manner: Approximately 10 g of a soil from an organic horizon of an Emory slit loam on

(b) Identified by the trade name, "Filt-O-Cite 1.5" and was obtained from the Shamoking Filter Co, Inc, Shamokin, Pennsylvania.

(c) Identified by the trade name, "Flexirings" and were obtained from Koch Engineering Co, Wichita, Kansas.

ORNL property were added to 8 dm³ of Ca(NO₃)₂ solution containing approximately 1000 g NO₃⁻/m³ and 600 g CH₃OH/m³. Anaerobic conditions and occasional stirring every three to four days produced a healthy culture of denitrifiers after 10 - 20 days. Columnar units were seeded by recycling 80 dm³ of Ca(NO₃)₂ solution containing approximately 1000 g NO₃⁻/m³, 600 g CH₃OH/m³, and 2 - 3 dm³ of an active culture of denitrifiers. Recycling continued until a microbial population was established on the packing medium; subsequently, nitrate feed containing 0.6 g CH₃OH/g NO₃⁻ was passed slowly (0.61 to 2.9 dm³/hr) through the column. Influent solutions were made with spring water; and, in addition to the nitrate and carbon substrate, contained the following chemicals in moles per liter: KH₂PO₄, 3.2 × 10⁻⁴; MgSO₄, 7.7 × 10⁻⁴; FeCl₃ · 6H₂O, 2.75 × 10⁻³, and NaMoO₄ · 2H₂O, 4.13 × 10⁻⁷.

Nitrate measurements were made with an Orion Nitrate Specific Electrode, Model 92-07, connected to a Corning, Model 110, digital, expanded-scale pH meter. Interferences by nitrite were eliminated by complexing the nitrite with sulfanilamide in 0.01 N H₂SO₄ according to the procedure of Francis and Malone.⁽¹⁾ Use of the H₂SO₄ acts as an ionic strength adjustor and eliminates any interferences by HCO₃⁻ and CO₃⁻². Nitrite concentrations were determined colorimetrically according to Bremner,⁽²⁾ and CH₃OH concentrations with a gas chromatograph.

Two columnar units were used: the first, a glass column (120 by 15 cm diameter) and the second, a tapered column made of Plexiglas.

Method of Expressing Denitrification Rates

Assuming that an adequate carbon source is available, the nitrate removal rate is dependent on nitrate concentration and microbial cell concentration. Anaerobic columnar units (conventionally called "packed-bed reactors"), in which the influent nitrate stream is introduced at the bottom of the column, encourage maximum microbial cell concentrations in denitrification reactors due to the large surface area provided by the packing matrix. As cell buildup in the column exceeds that washed from the reactor, the hydraulic residence time in the column decreases at constant influent flow rates. Continued cell buildup eventually plugs the column unless such preventive measures as backwashing or flushing are taken. As denitrification progresses, the void spaces become filled with N₂ and CO₂ rather than substrate. Thus, any hydraulic residence time based on the initial void space is a maximum value, and the real hydraulic residence times after prolonged operation of a column are likely to be lower by a factor of 5 to 10. In this work, denitrification rates were not considered valid unless at least ten hydraulic residence times, based on the initial void space of the packing material, had elapsed. Valid denitrification rates in anaerobic columns should include current hydraulic residence times as well as microbial concentrations. This inclusion is made in the **DENITRIFICATION KINETICS** section; but, for the columnar studies, determinations of such parameters were considered impractical. For this reason, rates of denitrification are based on the initial volume of the packing medium in the following manner:

$$R = 24 (\Delta \text{NO}_3^-) (W)/V ,$$

where:

- R represents the denitrification rate, in $\text{g NO}_3^-/\text{day}/\text{dm}^3$,
- ΔNO_3^- the difference between the influent and effluent NO_3^- concentration, in $\text{kg NO}_3^-/\text{m}^3$,
- W the flow rate, in dm^3/hr , and
- V the initial volume of packing medium, in dm^3 .

Results and Discussion

Anthracite Coal Packing - Glass Columnar Column - Solutions made from three nitrate salts [$\text{Ca}(\text{NO}_3)_2$, NaNO_3 , and NH_4NO_3] and actual nitrate wastes from a UO_2 fuel fabrication plant were used as influent solutions in the columnar denitrification studies. As reported earlier,⁽³⁾ use of $\text{Ca}(\text{NO}_3)_2$ results in the formation of CaCO_3 , which causes high head losses (> 90 kPa) and eventually plugs the column. Calcium carbonate is the secondary reaction product formed from the calcium and CO_2 that are produced by the denitrification reaction. Continuous-flow, stirred-bed reactors appear to be a more realistic engineering design to denitrify nitrate wastes where the dominant complementary cations are Ca^{+2} or Al^{+3} .⁽⁴⁾

With influent solutions made from NaNO_3 or NH_4NO_3 , no insoluble carbonate compounds are formed to cause significant head losses. However, effluent pH values are considerably higher when using NaNO_3 and NH_4NO_3 rather than $\text{Ca}(\text{NO}_3)_2$, as noted in Table 1. The major difference in the denitrification of solutions containing NaNO_3 and NH_4NO_3 is that rather high concentrations of nitrite (as great as $1000 \text{ g NO}_2^-/\text{m}^3$) accumulate in the effluent of NaNO_3 feed solutions, as the data of Table 2 points out. On the other hand, maximum concentrations of nitrite in the effluent of NH_4NO_3 solutions did not exceed $10 \text{ g NO}_2^-/\text{m}^3$ at any time during the study. A similar observation was made in the stirred-bed reactor work. The addition of a small amount of ammonium ($10 - 15 \text{ g}/\text{m}^3$) to the NaNO_3 influent solutions did not lower the nitrite accumulation, indicating that the accumulation of nitrite is due to the levels of sodium rather than any possible ammonium nutrient deficiencies.

Table 1
INFLUENT AND EFFLUENT pH VALUES IN THE COLUMNAR
DENITRIFICATION OF VARIOUS NITRATE FORMS
(Anthracite Coal is the Packing Medium)

Nitrate Source	pH Value		Number of Observations
	Influent	Effluent	
$\text{Ca}(\text{NO}_3)_2$	$7.15 \pm 0.09^{(1)}$	7.62 ± 0.21	8
NaNO_3	7.46 ± 0.75	8.55 ± 0.76	20
NH_4NO_3	6.86 ± 0.09	8.25 ± 0.16	13
UO_2 Nitrate Wastes	6.93 ± 0.13	8.23 ± 0.13	10

(1) Standard deviation.

Denitrification rates with solutions containing NH_4NO_3 appear to be greater than those containing NaNO_3 (Table 2). For example, the average denitrification rate with influent solutions containing NaNO_3 was $21.2 \pm 13 \text{ g NO}_3^-/\text{day}/\text{dm}^3$, while influents containing NH_4NO_3 averaged $28.6 \pm 12.9 \text{ g NO}_3^-/\text{day}/\text{dm}^3$, an approximate 35% increase. This

difference indicates that denitrification of influent solutions containing NH_4NO_3 may be noticeably faster than for solutions containing NaNO_3 . However, this interpretation will be misleading if denitrification proceeds according to first-order kinetics, because the average concentration of nitrate in the NH_4NO_3 influents ($11.8 \text{ kg NO}_3^-/\text{m}^3$) was nearly twice the average nitrate concentration in the NaNO_3 influents ($6.5 \text{ kg NO}_3^-/\text{m}^3$). In addition, influents containing NH_4NO_3 followed those containing NaNO_3 , which introduces the possibility that a higher microbial population was present in the column for the NH_4NO_3 data.

Table 2
DENITRIFICATION IN AN ANTHRACITE COAL PACKING

Test Date (day)	Nitrate Concentration (kg/m^3)		Flow Rate (cm^3/hr)	Nitrite Concentration in Effluent (g/m^3)	Denitrification Rate ⁽¹⁾ ($\text{g NO}_3^-/\text{day}/\text{dm}^3$)
	Influent	Effluent			
Influent Containing NaNO_3					
1	4.43	1.15	3.1	970	13
2	5.76	2.30	3.3	1200	14
4	4.52	0.62	1.7	1020	9.2
5	5.54	1.28	0.83	164	9.2
8	8.19	1.42	3.1	1050	3.5
9	8.86	4.87	3.2	624	22
10	8.64	4.87	3.1	230	23
11	8.86	4.65	3.4	360	27
14	3.10	< 0.05	2.5	0.7	
15	3.94	0.50	4.1	624	23
16	3.80	0.17	3.6	296	25
17	1.24	< 0.05	3.4	< 33	
18	4.87	0.06	3.6	181	35
19	10.6	2.67	3.7	1250	51
Influent Containing NH_4NO_3					
20	3.76	< 0.05	3.9	< 0.7	
21	9.52	1.64	3.8	< 0.7	64
22	13.7	4.43	2.5	9.2	50
23	13.7	4.21	1.9	3.0	38
24	9.74	3.76	1.8	< 2.6	23
25	11.1	5.98	3.0	3.9	33
26	11.1	7.53	3.1	-	24
27	11.3	6.86	3.0	-	29
28	11.3	7.75	2.9	3.5	22
29	11.1	7.97	3.0	3.3	20
30	11.5	7.97	3.0	4.6	31
31	11.1	8.86	3.3	2.3	15
32	12.4	7.97	2.9	4.9	28
33	11.1	7.97	2.9	4.3	20
34	12.4	8.86	2.9	4.6	22
35	12.4	10.6	2.8	-	11
36	12.0	8.41	2.9	3.9	22
37	15.1	9.52	2.8	-	34

(1) Denitrification rate based on the initial volume of the packing medium (11.12 dm^3) in a $120 \times 15\text{-cm}$ -diameter glass column. For influents containing NaNO_3 , rates were corrected for NO_2^- accumulation.

Anthracite Coal Packing - Tapered Plexiglas Column - Columns packed with anthracite coal appear to be a highly effective method for denitrifying high nitrate wastes. However, in the 120-cm-long by 15-cm-diameter column, flotation of the bed occurred at flow rates that exceeded $2.9 \text{ dm}^3/\text{hr}$. Continued operation resulted in compaction of the bed against the top of the column which caused high head losses ($> 50 \text{ kPa}$). Floating of the anthracite bed was caused by the low density (1.5 g/cm^3) of the anthracite particles, large microbial growth on the coal surfaces, and high production of nitrogen gas. Use of the same anthracite coal in a tapered column alleviated compaction of the bed at the top of the column, even at flow rates of $18 \text{ dm}^3/\text{hr}$; and, under optimum operating conditions, took on many properties of a fluidized bed.

Denitrification kinetics (discussed later) indicated that rates of denitrification became nitrate-substrate inhibited at nitrate concentrations greater than $6.0 \text{ kg NO}_3^-/\text{m}^3$. Thus, greater denitrification should be obtained in tapered columns than in conventional columns because greater quantities of nitrate can be delivered to the unit at influent nitrate concentrations which do not inhibit denitrification; viz, a greater fraction of the microbial enzyme can be maintained in the active form at influent concentrations of $5 \text{ kg NO}_3^-/\text{m}^3$ and at a flow rate of $18 \text{ dm}^3/\text{hr}$ than at an influent concentration of $31 \text{ kg NO}_3^-/\text{m}^3$ at $3 \text{ dm}^3/\text{hr}$.

The column made of Plexiglas and tapered 0.23 rad deg outwardly (Figure 1) was filled with 32.5 dm^3 of the same anthracite coal used in the previously described columnar studies. The column was seeded with an active denitrifying culture in the manner previously described,

and an influent of NH_4NO_3 containing approximately $1 \text{ kg NO}_3^-/\text{m}^3$ with $0.6 \text{ kg CH}_3\text{OH}/\text{m}^3$ was fed to the unit for three weeks before the denitrification data presented in Figure 2 and Table 3 were collected. Visual observations revealed that the microbial growth was predominantly located in the lower one third of the column, indicating that an equilibrium microbial biomass had not been attained over the entire bed. Yet, the denitrification rate of $44 \text{ g NO}_3^-/\text{day}/\text{dm}^3$ observed the first day of measurement (Table 3) was considerably higher than the average observed rate ($29 \text{ g NO}_3^-/\text{day}/\text{dm}^3$) obtained with NH_4NO_3 in the 120-cm-long by 15-cm-diameter column.

Denitrification performance in the tapered column over a 41-day interval is reported in Figure 2. On the fifth day, an influent containing $11.1 \text{ kg NO}_3^-/\text{m}^3$ as NH_4NO_3 and acetic acid (neutralized with NaOH) (equivalent in terms of carbon to $0.6 \text{ g CH}_3\text{OH}/\text{g NO}_3^-$) was fed to the unit at

Figure 1. DESIGN OF THE TAPERED COLUMN.

13.4 dm³/hr (influent pH was 7.35). The following day, nitrate analyses of the influent and effluent, and the observation that there was no difference between the temperature of the two streams, indicated that denitrification had ceased.

Figure 2. INFLUENCE OF NITRATE AND CARBON SOURCE, BED EXPANSION, AND TIME ON DENITRIFICATION IN A TAPERED COLUMN.

To avoid loss of the established microbial population, methanol was substituted for sodium acetate as the carbon substrate. Nitrate analyses on the eighth and ninth day verified that denitrification had resumed but at a much lower rate. However, the high influent nitrate concentrations may have been partially responsible for the low rates. Switching to NaNO₃ as a nitrate source reduced the denitrification 75% after three days. The reduction was due either to continued exposure to nitrate concentrations greater than 15.0 kg NO₃⁻/m³ or to some specific effect associated with NaNO₃.

Taking into consideration the large quantities of nitrate detected in the NaNO₃ effluents from the 120 by 15-cm columns, reduction in the denitrification rate was likely due to the inability of the microorganisms to acclimatize quickly to NaNO₃. For example, a similar, but not as severe, reduction in denitrification was noted on the substitution of UO₂ fuel nitrate wastes (predominantly NH₄NO₃ and HNO₃ neutralized to a pH of 6.4) for NH₄NO₃ on the 26th and 27th day. The difference between these nitrate sources was rather subtle;

ie, the ratio of nitrate to ammonium, on a weight basis, in the UO_2 nitrate wastes was 5 to 1 rather than 3.5 to 1 as in NH_4NO_3 , and the influent concentration of calcium after dilution with spring water was about 600 g/m^3 compared to less than 20 g/m^3 for NH_4NO_3 influent. Even so, acclimatization for approximately three days was required before similar denitrification rates were attained.

Through the Plexiglas walls of the column, it could be seen that a large number of pores in the anthracite bed were filled with gas rather than nitrate solution, indicating that the packing material was not being utilized efficiently. On the 15th day, to maximize bed efficiency, the bed was expanded by pumping (for 30 s) approximately 5 dm^3 (flow rate of $600 \text{ dm}^3/\text{hr}$) of effluent from a sump every 0.25 hr. The manner in which this pumping was conducted is illustrated in Figure 3. This procedure agitated the packing medium so that the gaseous denitrification products were discharged, thus increasing the hydraulic residence time of fresh influent into the column. Bed expansion in this fashion was carried out every 0.25 hr until the 22nd day when visual observations and a sharp decline in the rate of denitrification indicated that microorganisms were being washed from the column faster than they were being produced. On the 23rd day, bed expansion was changed to every 2 hrs. Gaseous discharge during bed expansion was quite high (as great as 2 dm^3 , or approximately $240 \text{ dm}^3/\text{hr}$).

Table 3
DENITRIFICATION IN THE TAPERED COLUMN PACKED
WITH ANTHRACITE COAL

Test Date (day)	Nitrate Concentration (kg/m ³)		Flow Rate (cm ³ /hr)	Denitrification Rate ⁽¹⁾ (g NO ₃ ⁻ /day/dm ³)
	Influent	Effluent		
<u>Influent Containing NH₄NO₃</u>				
1	4.87	0.36	13.2	44
2	7.53	2.21	13.2	52
3	8.86	5.09	17.3	43
4	12.8	7.31	14.8	60
<u>Acetate Used as Carbon Source</u>				
8	22.1	15.5	4.4	22
9	22.1	15.5	4.5	22
<u>Influent Containing NaNO₃</u>				
10	23.0	19.5	4.8	12
11	20.4	17.7	4.8	9.5
12	17.7	15.9	4.8	6.0
<u>Influent Containing NH₄NO₃</u>				
With Bed Expansion Every 0.25 Hr				
15	7.31	3.19	8.1	24
16	7.75	1.02	8.1	40
17	12.0	0.55	7.7	65
18	15.5	7.75	9.6	55
19	12.8	8.19	9.6	33
With Bed Expansion Every 2 Hrs				
22	10.2	4.21	7.4	33
24	7.53	2.66	8.7	31
25	15.5	2.97	5.6	52
<u>UO₂Fuel Nitrate Waste</u>				
With Bed Expansion Every 2 Hrs				
26	11.1	2.57	6.3	40
27	7.97	5.31	9.9	19
28	10.1	3.10	5.3	28
29	12.8	3.10	8.0	58
30	12.2	5.53	9.2	45
31	13.7	5.31	9.4	58
32	13.3	3.10	9.2	69
34	22.1	11.9	9.1	68
37	15.9	8.6	16.8	91
38	11.5	4.43	17.5	92
39	12.4	4.43	16.4	96
40	12.4	3.81	16.1	102
41	15.5	5.31	16.2	122

(1) Denitrification rate based on the initial volume of packing medium (32.5 dm^3). Nitrite measurements were not routinely made; however, random effluent samples of NH_4NO_3 and UO_2 fuel nitrate wastes did not reveal any concentrations greater than $10 \text{ g NO}_2^-/\text{m}^3$.

Figure 3. PRINCIPAL COMPONENTS OF THE TAPERED-COLUMN DENITRIFICATION SYSTEM.

At the termination of the experiment, denitrification rates were established in excess of $100 \text{ g NO}_3^-/\text{day}/\text{dm}^3$ (Table 3). These rates are 10 - 15 times higher than those reported in continuous-flow, stirred-bed reactors.⁽⁴⁾

Gaseous Discharge - The primary gaseous products of denitrification are elemental nitrogen and carbon dioxide:

The gaseous discharge from the tapered column packed with anthracite coal and fed with UO_2 fuel fabrication wastes was approximately 92% N_2 and 8% CO_2 (Table 4). Considering the stoichiometric ratio of CO_2 to N_2 from the equation, the concentration of CO_2 in the gaseous discharge was extremely low. However, the pH of the effluent was approximately 8.2 (Table 1); therefore, the bulk of the carbon leaves the reactor in the form of HCO_3^- and CO_3^{2-} . Some carbon left the reactor in the form of microbial solids. Values for mixed liquor volatile suspended solids (MLVSS) in the effluents ranged from 100 to $900 \text{ g}/\text{m}^3$. Carbon was also retained inside the reactor as carbonates and microbial carbon.

Table 4
DENITRIFICATION GAS ANALYSES FROM
THE TAPERED COLUMN PACKED
WITH ANTHRACITE COAL

Sample	Gas (% by volume)					
	N_2	CO_2	O_2	NO	Ar	CH_3OH
1	95.42	4.54	0.008	0.01	0.03	0.002
2	90.36	9.42	0.0084	0.02	0.06	0.09
3	90.63	9.01	0.02	0.09	0.008	0.15
4	92.39	7.40	0.07	0.008	0.02	0.06
5	92.24	7.58	0.03	0.02	0.007	0.05
Average	92.21	7.59	0.027	0.03	0.025	0.07
Standard Deviation	2.02	1.92	0.026	0.03	0.021	0.05

Calcium and Phosphorus Retention -

When anthracite coal is used as the packing medium, 99% of the calcium is removed from influent streams that contain less than $1000 \text{ g}/\text{m}^3$ calcium (Table 5). X-ray diffraction patterns of suspended solids in stirred reactors show

that calcium is precipitated as CaCO_3 . The same is likely to hold true for columnar denitrification. Elements other than calcium were also removed; for example, phosphorus, for which the mechanisms responsible remain unclear. X-ray patterns characteristic of any calcium phosphates were not detected in the suspended solids from the stirred reactors. Quite likely, a relationship exists similar to that of phosphorus adsorption in alkaline soils; ie, phosphorus is either coprecipitated with or strongly occluded to CaCO_3 .

Table 5
ELEMENT REMOVAL DURING DENITRIFICATION
IN A TAPERED COLUMN PACKED
WITH ANTHRACITE COAL

Element	Element Concentration (g/m ³)		Extent of Removal (%)
	Influent	Effluent	
Calcium	645	7.0	99
	792	4.6	99
	615	5.7	99
Phosphorus	3.0	1.3	57
	5.1	0.52	90
	7.1	1.2	83
Zinc	0.15	< 0.005	> 96
Nickel	0.30	< 0.1	> 66
Copper	0.20	0.035	82
Cadmium	0.06	< 0.005	> 91

Trace-Element Retention - Reaction mechanisms governing the removal of the transition metals (Zn, Ni, and Cu) are unknown. Prolonged use of an anthracite bed for denitrification of influent streams containing appreciable quantities of these heavy metals will result in the accumulation of rather large quantities of these metals. It is also difficult to predict what effect the buildup of the metals will have on subsequent denitrification. Further research in this area is required. Cadmium likely behaves like calcium because its ionic radius is nearly equal to that of calcium. Cadmium probably precipitates as CdCO_3 , or in mixtures of $\text{CdCO}_3\text{-CaCO}_3$.

Denitrification columns packed with anthracite coal might be useful in uranium recovery operations. For example, NH_4NO_3 solution containing 5 - 10 g/m³ of uranium was lowered to less than 0.5 g/m³ in one pass through a column packed with 11.12 dm³ of anthracite coal. The uranium likely coprecipitated on the calcium and magnesium carbonates, or is converted to an insoluble phosphate mineral similar to that of apatite, which is known to selectively concentrate uranium. The chemistry of thorium and plutonium indicates that these elements would behave in a similar manner. Thus, columns of this type may be useful in removing low levels of plutonium from waste streams containing nitrates.

Influence of Temperature - Denitrification is an exothermic reaction. The difference between the influent and effluent temperatures on the 39th day was 12 degrees (295 vs 307 K). At a flow rate of 4.55 cm³/s, and assuming a water density of 1 kg/m³ with a specific heat of 4.48 J/g/K, the rate of energy required to raise the influent to 307 K would be 228 J/s. Presumably, this heat is generated by the oxidation of CH_3OH . The quantity of heat generated by the oxidation of CH_3OH can be calculated in the following manner: The observed denitrification rate was 36.3 mg NO_3^- /s. Methanol analysis of the influent and effluent showed that 0.52 g of CH_3OH was required to denitrify a gram of nitrate. Thus, the oxidation rate of CH_3OH was 18.9 mg CH_3OH /s. If the heat of combustion for CH_3OH is taken as 0.71 MJ/mol, then the rate of energy released on oxidizing is 422 J/s. Thus, the rate of heat generated is nearly twice that reflected by the increase in influent temperature. A portion of the remaining energy is used for microbial growth while the remainder is lost as heat to the surrounding environment.

A large unit, one capable of denitrifying five metric tons of nitrate daily and operating at this efficiency, will generate considerable energy (58.1 GJ/day), which is equivalent to 54.6×10^6 Btu/day. Quite likely the heat loss in a larger unit will be much less, which means that the heat generated may limit (up to a certain temperature may increase) the rate of denitrification. It appears that some type of cooling of larger units will be necessary if they are to operate at maximum efficiency.

Polypropylene Raschig Rings

Microbial populations were established faster on polypropylene Raschig rings than on the anthracite coal packing (viz, < 2 weeks on rings compared to 3 - 4 weeks on the coal). Maximum denitrification rates (Table 6), based on the initial bed size, were similar ($100 \text{ g NO}_3^-/\text{day}/\text{dm}^3$). However, on prolonged operation (> 40 days), denitrification rates began to decrease to $20 - 30 \text{ g NO}_3^-/\text{day}/\text{dm}^3$ after 50 - 60 days (Table 6). This reduction in denitrification rates was attributed to hydraulic short circuiting in the column due to excessive microbial growth.

For instance, after 30 - 35 days, areas of dark-colored microorganisms were observed in the lower portion of the column. Healthy denitrifiers are pink colored, and they rapidly turn black if they do not receive a sufficient supply of nitrate. Initially, the dark-colored organisms were suspected of being sulfate-reducing microorganisms even though no evidence of H_2S could be detected. Sulfate concentration in the influent was reduced by a factor of 10, but the dark-colored areas continued to grow. On the 45th day, the column was flushed for 0.33 hr at a flow rate of $414 \text{ dm}^3/\text{hr}$. Visual observation of the effluent or microbial mass in the column indicated that little biomass had been removed, and denitrification rates the following 10 days were not appreciably changed. At the end of the experiment, mixed liquor suspended solids (MLSS) were 28.7 , 37.6 , and $83.0 \text{ kg}/\text{m}^3$ at the top, center, and bottom

Table 6
DENITRIFICATION IN A COLUMN PACKED
WITH POLYPROPYLENE RASCHIG RINGS

Test Time (day)	Nitrate Concentration (kg/m^3)		Flow Rate (cm^3/hr)	Denitrification Rate ⁽¹⁾ ($\text{g NO}_3^-/\text{day}/\text{dm}^3$)
	Influent	Effluent		
10	2.43	0.71	2.6	4.7
11	2.21	1.20	0.9	0.95
12	2.21	1.33	2.6	2.4
13	2.08	0.95	2.0	2.3
14	3.10	1.20	2.9	5.6
15	2.71	0.93	2.0	3.9
16	2.74	0.75	3.0	6.1
17	2.30	0.55	3.6	6.6
18	2.26	0.06	2.7	6.0
19	2.21	< 0.05	3.7	> 8.4
20	2.61	< 0.05	6.7	> 18
22	2.26	< 0.05	9.8	> 22
23	3.19	< 0.05	19.3	> 64
24	3.10	0.82	19.1	44
25	3.45	0.66	18.8	54
27	2.66	< 0.05	18.7	> 50
31	2.83	0.56	18.5	43
36	4.87	< 0.05	17.2	> 86
37	5.09	0.16	21.3	108
38	5.31	0.93	19.2	86
41	4.98	0.80	18.6	80
42	4.65	0.83	18.7	74
43	5.53	0.74	18.6	92
45	4.03	1.90	18.8	41
46	4.43	2.26	18.6	42
47	4.21	2.79	18.6	27
49	5.53	3.32	14.8	34
52	5.53	3.50	19.3	41
56	5.20	2.21	18.2	56
57	3.59	2.43	18.0	21

(1) Denitrification rate based on an initial bed volume of 23.2 dm^3 .

portions of the column, respectively. These MLSS values are significantly higher than the maximum MLSS values of 5.55 kg/m^3 observed in stirred-bed reactors fed NH_4NO_3 .⁽⁵⁾ With the 1.6-cm-diameter Raschig ring, microbial growth fills the center of the ring and reduces the surface area exposed to nitrate solution. Possibly, larger-diameter rings would be more effective for long-term use.

Methanol Utilization

Numerous denitrification studies at low nitrate concentrations ($< 250 \text{ g NO}_3^-/\text{m}^3$) have shown that 0.6 g of methanol is required to denitrify one gram of nitrate.^(6,7) This work, at high nitrate concentrations ($> 1000 \text{ g NO}_3^-/\text{m}^3$), indicates that less CH_3OH is required

(Table 7). The stoichiometric CH_3OH requirement to denitrify one gram of nitrate is 0.43 g CH_3OH ; however, it does not provide sufficient carbon for microbial growth or deoxygenation of any dissolved oxygen present in the system.

Table 7
DENITRIFICATION METHANOL REQUIREMENTS

Packing Type	CH_3OH Utilization (g $\text{CH}_3\text{OH}/\text{g NO}_3^-$)(1)	Sample Number
Anthracite in the Columnar Column	$0.48 \pm 0.35^{(2)}$	18
Anthracite in the Tapered Column	0.45 ± 0.14	16
Polypropylene Raschig Rings	0.29 ± 0.14	14

(1) Grams of CH_3OH required to denitrify one gram of nitrate.

(2) Standard deviation.

The CH_3OH requirement for denitrification with Raschig-ring packing appears to be approxi-

mately 60% lower than with the anthracite packing (Table 7). In the case where 1.6-cm-diameter polypropylene rings were used for packing, excessive microbial growth caused hydraulic short circuiting in the column which resulted in appreciably lower denitrification rates after operation of the unit in excess of 40 days. The CH_3OH utilization constant observed with the polypropylene rings was below the stoichiometric CH_3OH requirement for denitrification, indicating that the microbial biomass (maximum of 83 kg MLSS/m^3 at the bottom of the column) was being utilized as an endogenous carbon source. The CH_3OH requirement decreased in proportion to the length of operation (Figure 4).

It appears that denitrification at high nitrate concentrations requires approximately 25% less CH_3OH than denitrification at low nitrate substrate concentrations. For example, the work of McCarty⁽⁶⁾ and Smith,⁽⁷⁾ where nitrate substrate concentrations were in the order of $5 - 10 \text{ g NO}_3^-/\text{m}^3$, required 0.6 g of $\text{CH}_3\text{OH}/\text{g}$ of NO_3^- while, in this work, where nitrate substrate concentrations were on the order of $500 - 5000 \text{ g NO}_3^-/\text{m}^3$, the CH_3OH requirement for each gram of nitrate was on the order of 0.4 to 0.5 g.

Figure 4. METHANOL UTILIZATION AS A FUNCTION OF THE TIME OF OPERATION.

Summary and Conclusions

Anaerobic columns packed with anthracite coal particles appear to be an effective method for the treatment of nitrate wastes associated with uranium recovery operations which use the ammonium diuranate process. Nitrate wastes generated in this process are predominantly HNO_3 and NH_4NO_3 . The quantity of nitrates in the waste streams from a commercial-scale facility might be expected to be as high as five metric tons of nitrate per day. To denitrify this quantity of nitrate at a denitrification rate of $100 \text{ g NO}_3^-/\text{day/dm}^3$, a bed volume of 50 m^3 would be required; so, for a bed four meters in diameter, the required height would be slightly more than four meters.

Denitrification kinetic data indicate that the most effective substrate nitrate concentrations are less than $6 \text{ kg NO}_3^-/\text{m}^3$. If $5 \text{ kg NO}_3^-/\text{m}^3$ is selected as the influent concentration, the required volume for five metric tons of nitrate per day would be 1000 m^3 , or a flow rate of $11.6 \text{ dm}^3/\text{s}$. The cross-sectional flow into a 4 by 4-m-diameter column would be $0.92 \text{ dm}^3/\text{m}^2/\text{s}$, about 0.4 of that in the tapered column used in these studies. Mechanical stirrers could be used to maintain bed integrity, or the bed could be fluidized in a tapered column by using anthracite of smaller particle size. A recycle system could be used if the pH levels and ammonium concentrations could be maintained at nontoxic conditions.

Extrapolations of laboratory-bench experiments to production-size facilities are often haphazardous and speculative; however, data presented here certainly justify pilot-plant tests at facilities where the disposal of large quantities of nitrate wastes is a problem.

DENITRIFICATION KINETICS

Introduction

Denitrification kinetics at low nitrate substrate concentrations has demonstrated that, as long as there is an adequate carbon supply, denitrification rates do not decrease until nitrate concentrations approach less than $0.30 \text{ g NO}_3^-/\text{m}^3$.⁽⁸⁻¹⁰⁾ At nitrate substrate concentrations greater than $1000 \text{ g NO}_3^-/\text{m}^3$, the kinetics of denitrification has not been investigated. The major purpose in evaluating denitrification kinetics is to determine the nitrate substrate concentrations that will provide optimum denitrification rates for various nitrate sources. In columnar studies it is difficult to properly evaluate denitrification kinetics because the concentration of substrate nitrate in an upward-flow column will decrease with increasing column height. In addition, such parameters as current hydraulic residence times and microbial concentrations should be measured periodically as they likely vary within the column over the interval of the experiment. Microbial concentrations are difficult, if not impossible, to determine without destroying the columnar unit. Thus, in the work described here, continuous-flow, stirred-bed reactors were used to evaluate denitrification kinetics.

Methods and Materials

Since wastes from UO_2 fuel fabrication processes contain large quantities of NH_4NO_3 , the ammonium salt was used as one of the nitrate materials. Other nitrate materials were KNO_3 , $\text{Ca}(\text{NO}_3)_2$, and actual nitrate wastes from a UO_2 fuel fabrication plant. Methanol was used

as a carbon source at a rate of $0.6 \text{ g CH}_3\text{OH/g NO}_3^-$. A reactor (illustrated in Figure 5), containing 8.8 dm^3 of microbial stock solution, was fed influent NH_4NO_3 solutions ranging in nitrate concentration from approximately 2 to $15 \text{ kg NO}_3^-/\text{m}^3$. A smaller reactor (2.2 dm^3) was used to evaluate the influence of CH_3OH concentrations on denitrification rates and establish specific removal rates for $\text{Ca}(\text{NO}_3)_2$. A combination magnetic stirrer/hot plate was used to maintain a stirred suspension of microbial solids at a reactor temperature of $29 \pm 2^\circ \text{C}$. Influent was pumped from a 40-dm^3 calibrated feed reservoir at a flow rate of $0.31 \text{ dm}^3/\text{hr}$. Four influent concentrations of NH_4NO_3 , in the following successive order, were used: 2.2, 5.0, 12, and $15 \text{ kg NO}_3^-/\text{m}^3$.

Figure 5. CONTINUOUS-FLOW, STIRRED-BED REACTOR SYSTEM.

Specific removal rates, U , were determined after three mean hydraulic residence times^(d) and expressed in days^{-1} :

$$U = \frac{C_i - C_r}{\gamma x},$$

where:

C_i represents the influent nitrate concentration in $\text{kg NO}_3^-/\text{m}^3$,

C_r the reactor nitrate concentration in $\text{kg NO}_3^-/\text{m}^3$,

γ the mean hydraulic residence time, in days, and

x the mixed liquor volatile suspended solids, in kg/m^3 .

(d) Mean hydraulic residence time is determined by the volume of the reactor divided by the flow rate—1.2 days.

Nitrate determinations were made by the method of Francis and Malone⁽⁵⁾ and nitrite was determined colorimetrically by the method of Bremner.⁽²⁾ Mixed liquor volatile suspended solids (MLVSS) were determined after filtering aliquots of the reactor mixed liquor through preheated (550° C for 0.5 hr) Gelman glass fiber Type A filters. After drying to 110° C for one hour, the weight loss at 550° C after 0.5 hour was expressed as MLVSS (in kg/m³). The concentrations of MLVSS as a function of time is presented in Figure 6. MLVSS values not measured directly were taken from this curve.

Results and Discussion

The kinetics of denitrification was evaluated using Lineweaver-Burk plots.⁽¹¹⁾ The Lineweaver-Burk equation is derived from the Michaelis and Menten relationship:

$$U = U_{\max}(S)/[K_S + (S)], \quad (1)$$

where:

$U_{\max}$ represents the maximum specific removal rate, in days⁻¹,

(S) the nitrate substrate concentration, in kg NO₃⁻/m³, and

K_S the Michaelis-Menten constant, which is equal to the nitrate concentration at 1/2 $U_{\max}$.

The Lineweaver-Burk equation:

$$(S)/U = (S)/U_{\max} + K_S/U_{\max} \quad , \quad (2)$$

is formed by taking the reciprocal of both sides of Equation 1 and multiplying the equation by (S) . Thus, $U_{\max}$ and K_S can be solved graphically by plotting $(S)/U$ on the linear ordinate as a function of (S) on the abscissa. The intercept is $K_S/U_{\max}$ and the slope is $1/U_{\max}$. The Lineweaver-Burk equation is more appropriate for $U_{\max}$ and K_S determinations at high substrate concentrations than the Michaelis-Menten equation.^(7,10,11)

Specific removal rates, U , for NH₄NO₃ ranged from 1.94 days⁻¹ at 3.99 kg NO₃⁻/m³ to 0.70 day⁻¹ at 9.30 kg NO₃⁻/m³ (Table 8). Plotted in the form $(S)/U$ as a function of (S) resulted in a concave upward curve at nitrate substrate concentrations greater than 6 kg NO₃⁻/m³ (Figure 7). At substrate concentrations less than 6 kg NO₃⁻/m³, linear regression analyses ($r = 0.992$) resulted in a value for $U_{\max}$ of 1.79 days⁻¹, a value slightly higher than the 1.37 days⁻¹ reported by Moore and Schroeder.⁽⁸⁾

Figure 6. MIXED LIQUOR VOLATILE SUSPENDED SOLIDS GROWTH CURVE.

Table 8
DENITRIFICATION SPECIFIC REMOVAL RATES AT VARIOUS
EFFLUENT NITRATE CONCENTRATIONS
(Using NH_4NO_3 Solutions in a Continuous-Flow, Stirred
Bed Reactor; Reactor Volume = 8.8 dm^3 , Flow Rate = $0.31 \text{ dm}^3/\text{hr}$)

Nitrate Concentration (kg NO ₃ ⁻ /m ³)		Hydrogen Ion Concentration (pH)	Mixed Liquor Volatile Suspended Solids (kg/m ³)	Specific Removal Rate, r ⁽¹⁾ (days ⁻¹)
Influent	Effluent			
2.44	1.42	8.26	0.64	1.33
2.88	0.07	8.58	1.43	1.64
11.5	3.99	8.35	3.22	1.94
13.3	5.98	8.34	3.64	1.68
13.3	9.30	8.25	3.96	0.84
12.0	7.97	8.27	4.09	0.82
15.0	9.74	8.28	4.35	1.01
12.8	9.30	8.28	4.16	0.70
15.9	8.86	8.26	4.19	1.76
5.1	0.38	8.53	4.36	0.90
5.1	0.01	8.58	4.20	1.01

(1) Determined after three residence times.

The ratio of CH_3OH to nitrate was maintained constant in the influent at $0.6 \text{ g CH}_3\text{OH}/\text{g}$ of NO_3^- throughout the study. Thus, CH_3OH concentrations at nitrate substrate concentrations of $10 \text{ kg NO}_3^-/\text{m}^3$ would be on the order to $6 \text{ kg CH}_3\text{OH}/\text{m}^3$ if 0.6 g of CH_3OH was oxidized for each gram of NO_3^- denitrified. To test the influence of CH_3OH substrate concentrations on the rate of denitrification, specific removal rates, r , were determined at CH_3OH substrate concentrations ranging from 1.41 to $11.6 \text{ kg CH}_3\text{OH}/\text{m}^3$ while maintaining the nitrate substrate concentration less than $5.0 \text{ kg NO}_3^-/\text{m}^3$. The high linear regression coefficient ($r = 0.973$) between $(S)/U$ and (S) in Figure 8, where (S) in this case represented CH_3OH substrate concentrations as high as $10 \text{ kg CH}_3\text{OH}/\text{m}^3$, indicated that excessive CH_3OH substrates were not responsible for the observed inhibition in denitrification rates at nitrate substrate concentrations greater than $6 \text{ kg NO}_3^-/\text{m}^3$. (Incidentally, $10 \text{ kg CH}_3\text{OH}/\text{m}^3$ is more than twice that of any CH_3OH substrate concentration observed during the evaluation of nitrate substrates on the denitrification rate.) The negative intercept (-0.07 in Figure 8), resulted in a negative Michaelis-Menten value for CH_3OH ($-164 \text{ g}/\text{m}^3$) and might imply some inhibition in the denitrification rate. However, the U_{max} value determined at various CH_3OH concentrations

The increasing upward curvature of the line in Figure 7 at nitrate substrate concentrations greater than $6 \text{ kg NO}_3^-/\text{m}^3$ is indicative of denitrification kinetics resulting from excessive nitrate substrate concentrations.⁽¹¹⁾ It, thus, appears from Figure 7 that nitrate substrate concentrations in excess of $6 \text{ kg NO}_3^-/\text{m}^3$ inhibit the denitrification rate. However, other constituents, such as excessive concentrations of the carbon substrate (CH_3OH) or ammonium, might be responsible for the observed decrease in the denitrification rates.

Figure 7. LINEWEAVER-BURK PLOTS, USING NITRATE AS A SUBSTRATE.

(Figure 8) was approximately 30% higher than $U_{\max}$ determined from the nitrate substrate concentrations below 6 kg NO_3^-/m^3 (Figure 7), indicating that the negative intercept was due to statistical variation rather than any inhibition of CH_3OH on the denitrification rate.

Maximum ammonium concentrations, using NH_4NO_3 influents in stirred-bed reactors at nitrate substrate concentrations between 7 and 10 kg NO_3^-/m^3 were approximately 3.3 kg NH_4^+/m^3 (Table 8). Specific removal rates obtained after adding $(\text{NH}_4)_2\text{SO}_4$ to NH_4NO_3 influents and lowering the pH with concentrated H_2SO_4 revealed a synergistic effect between the mixed liquor pH and the NH_4^+ concentrations (Table 9). For example, at approximately the same NH_4^+ concentrations, as the pH of the mixed liquor was decreased, the rate of denitrification increased sharply, implying that the inhibition was not due to NH_4^+ concentrations per se but due to ammonia concentrations because of the equilibrium reaction:

where: $K_d = (\text{NH}_3)(\text{H})/(\text{NH}_4^+) = 5.52 \times 10^{-10}$. Thus, the inhibition in denitrification observed in Figure 7 may be due to NH_3 toxicities rather than excessive nitrate substrate concentrations, since the averaged mixed-liquor pH value from 25 observations was 8.34 ± 0.16 .

Table 9

INFLUENCE OF AMMONIUM ION CONCENTRATIONS AND pH OF THE MIXED LIQUOR ON THE DENITRIFICATION SPECIFIC REMOVAL RATE
(Nitrate Substrate Concentration < 3 kg NO_3^-/m^3)

Mixed Liquor NH_4^+ (kg/ m^3)		Specific Removal Rate (days $^{-1}$)
	pH	
3.3	8.0	0.85
3.3	7.1	2.63
3.6	6.8	4.68

Figure 8. LINEWEAVER-BURK PLOTS, USING METHANOL AS A SUBSTRATE.

To test if concentrations of nitrate in excess of 6 kg NO_3^-/m^3 inhibited the rate of denitrification in the absence of the ammonium ion, $\text{Ca}(\text{NO}_3)_2$ and KNO_3 solutions were used as influents. In addition, specific removal rates were determined at substrate concentrations less than 6 kg NO_3^-/m^3 for some UO_2 fuel nitrate wastes. These wastes were made predominately of NH_4NO_3 and HNO_3 neutralized to a pH of 6.4 with CaCO_3 . The difference in chemical composition between the UO_2 fuel nitrate wastes and NH_4NO_3 was rather subtle (ie, the ratio of nitrate to ammonium, on the weight basis, in the UO_2 nitrate wastes was approxi-

mately 5 to 1 rather than 3.5 to 1 as in ammonium nitrate). The calcium concentration in the influents made of UO_2 fuel nitrate wastes was about $600 \text{ g Ca}^{+2}/\text{m}^3$ after dilution to the desired nitrate concentrations with spring water, while the calcium ion concentration in the NH_4NO_3 influents was less than $20 \text{ g Ca}^{+2}/\text{m}^3$.

There appeared to be little difference in the specific removal rates between NH_4NO_3 or $\text{Ca}(\text{NO}_3)_2$ at concentrations above or below $6 \text{ kg NO}_3^-/\text{m}^3$ (Table 10). Specific removal rates for $\text{Ca}(\text{NO}_3)_2$ at substrate nitrate concentrations less than $6 \text{ kg NO}_3^-/\text{m}^3$ were slightly larger than, though not significantly different from, the removal rates for NH_4NO_3 . The very low removal rates with $\text{Ca}(\text{NO}_3)_2$ at substrate concentrations greater than $6 \text{ kg NO}_3^-/\text{m}^3$ suggests that denitrification was substrate inhibited. Since only two measurements were made, additional work should be carried out to verify the existence of the inhibition.

Removal rates at substrate concentrations greater than $6 \text{ kg NO}_3^-/\text{m}^3$, using KNO_3 , were significantly higher than at similar nitrate substrate concentrations using either $\text{Ca}(\text{NO}_3)_2$ or NH_4NO_3 . However, the average removal rate was not as high as the average removal rates for $\text{Ca}(\text{NO}_3)_2$ and NH_4NO_3 at substrate concentrations less than $6 \text{ kg NO}_3^-/\text{m}^3$.

The highest average specific removal rate was observed using UO_2 fuel nitrate waste at substrate concentrations less than $6 \text{ kg NO}_3^-/\text{m}^3$ (Table 10). This rate is approximately ten times that determined by Requa and Schroeder⁽⁹⁾ in a packed-bed reactor, and over twice that reported by Moore and Schroeder⁽⁸⁾ in stirred-bed reactors.

Table 10
SPECIFIC REMOVAL RATES AS INFLUENCED BY THE
NITRATE SOURCE AND CONCENTRATION
(After Three Hydraulic Residence Times)

Source of Nitrate	Substrate Concentration ($\text{kg NO}_3^-/\text{m}^3$)	Specific Removal Rate, U (days^{-1})	Number of Determinations
NH_4NO_3	< 6	$2.18 \pm 0.80^{(1)}$	17
	> 6	1.03 ± 0.42	5
$\text{Ca}(\text{NO}_3)_2$	< 6	2.30 ± 1.04	5
	> 6	0.75 ± 0.20	2
KNO_3	< 6	ND ⁽²⁾	
	> 6	$1.85 \pm 0.31^{(3)}$	3
UO_2 Fuel Wastes	< 6	3.13 ± 0.56	3
	> 6	ND	

(1) Standard deviation.

(2) Not determined.

(3) Contained an average NO_2^- concentration of $2.09 \pm 0.32 \text{ kg}/\text{m}^3$ at an average nitrate substrate concentration of $11.5 \pm 0.9 \text{ kg}/\text{m}^3$ of nitrate to nitrite.

There is apparently considerable difference in the intermediate denitrification kinetics of nitrate as NH_4NO_3 compared to nitrate as KNO_3 . For example, in the denitrification of KNO_3 at substrate nitrate concentrations between $10 - 12 \text{ kg NO}_3^-/\text{m}^3$, approximately $2 \text{ kg NO}_2^-/\text{m}^3$ were detected in the equilibrium mixed liquor; while, at similar substrate nitrate concentrations as NH_4NO_3 , less than $10 \text{ g NO}_2^-/\text{m}^3$ were detected. The intermediate kinetics of the denitrification of KNO_3 must be similar to that of NaNO_3 , as appreciable quantities of NO_2^- (as high as $1250 \text{ g NO}_2^-/\text{m}^3$) were detected in effluents from columnar denitrification units when influents contained NaNO_3 as the nitrate source (Table 2). No significant nitrite concentrations were detected in the stirred-bed reactors

whose influents were made of $\text{Ca}(\text{NO}_3)_2$ until substrate nitrate concentrations exceeded 6 kg/m^3 .

Summary and Conclusions

Continuous-flow, stirred-bed reactors were used to determine the maximum denitrification specific removal rate for NH_4NO_3 solutions. Nitrate substrate concentrations ranged from $0.01 - 9.74 \text{ kg NO}_3^-/\text{m}^3$. Through use of Lineweaver-Burk equations, a graphical solution was used to obtain a U_{max} of 1.79 days^{-1} for nitrate substrates less than $6 \text{ kg NO}_3^-/\text{m}^3$. This value is slightly higher than the 1.37 days^{-1} reported by Moore and Schroeder(8) using NaNO_3 at reactor concentrations less than $60 \text{ g NO}_3^-/\text{m}^3$. The Michaelis-Menten constant ($159 \text{ g NO}_3^-/\text{m}^3$), determined by the intercept of the Lineweaver-Burk plot, was on the order of 300 times higher than that observed by Moore and Schroeder. At substrate nitrate concentrations greater than $6 \text{ kg NO}_3^-/\text{m}^3$, denitrification rates appeared to be inhibited. Inhibition may have been a result of either an excessive nitrate substrate or ammonia toxicities at pH values of the mixed liquor near 8. Data indicated that both inhibition processes likely occurred. Methanol concentrations as high as $11.6 \text{ kg CH}_3\text{OH}/\text{m}^3$ did not inhibit the denitrification rates. The highest specific removal rates recorded ($3.13 \pm 0.56 \text{ days}^{-1}$) were with influents made from NO_3^- fuel fabrication wastes.

Evaluation of maximum nitrate substrate levels that do not inhibit denitrification rates is of little value in regard to applied processes using continuous-flow, stirred-bed reactors, because effluent levels are usually designed to be low enough for direct disposal to the environment. These values, however, are important in applied processes using columnar denitrification, since influent nitrate substrate concentrations should not exceed the inhibiting levels for optimum utilization of the columnar unit. Stirred-bed reactor studies indicated that, for NH_4NO_3 and $\text{Ca}(\text{NO}_3)_2$ solutions, substrate nitrate concentrations should not exceed $6 \text{ kg NO}_3^-/\text{m}^3$. For NH_4NO_3 solutions which exceeded $3 \text{ kg NH}_4^+/\text{m}^3$, denitrification rates were approximately five times greater at a pH of 6.8 than at a pH of 8.0, indicating that ambient pH should be maintained between 6.5 and 7.0 for best results.

LABORATORY DENITRIFICATION STUDIES

Introduction

Table 11
OPERATING DATA ON FOUR
TEST REACTORS

Reactor	Total Test Days	Number of Satisfactory Test Days	Maximum Denitrification Rate ($\text{g NO}_3^-/\text{day/dm}^3$)
Mini I	84	76	11.2
Mini II	88	79	9.8
Mini III	149	142	11.0
Mini IV	132	131	7.6
Total	453	428	9.9

Stirred-bed reactor studies have been made to determine the feasibility of biologically decomposing nitric acid wastes. Process operating parameters and plant design data were collected during these studies. Excluding startup periods, four test reactors were satisfactorily operated, as reported in Table 11.

As these data indicate, the reactors operated 94.4% of the test times at an average maximum feed rate of 9.9 grams nitrate per day per dm^3 (liter) of reactor solution. This

feed rate is equivalent to a rate of 935 kgs (2060 lbs) of nitrate per day [341,000 kgs (752,000 lbs) per year] in the production-sized 94.5-m³ (25,000-gal) reactor. The operational data on each of the reactors are discussed in subsequent sections of this report.

Equipment

Continuous-Flow Stirred-Bed Reactors - The waste nitrate stream at the Y-12 Plant will contain a high level of aluminum, calcium, and other materials which precipitate as solids at pH levels of 7.0 (see **Reactor Feeds** section of the report, Page 28). It was decided that a continuous-flow, stirred-bed reactor design could be used as a denitrification reactor. A miniature version ($\sim 0.06 \text{ m}^3$) of a standard commercial water-softener vessel was designed (Figure 9). A variable-speed motor drives the agitator, producing a high turbulent mixing area beneath the impeller. The concentrated feed solutions are added in this zone. The

Figure 9. DESIGN OF THE ORIGINAL DENITRIFICATION REACTOR.

agitator pumps liquids over a baffle in the vessel and creates a relatively quiet zone which permits solids to settle and provides for the continuous withdrawal of the solids from the bottom of the reactor. While this design worked satisfactorily, a later design was also used (Figure 10). In the modified reactor, a nominal 10-cm-wide pocket was welded on top of the inside baffle for the collection of solids. A pipe-and-valve arrangement permitted withdrawal of the solids and eliminated solid withdrawal from the bottom of the reactor.

Figure 10. DESIGN OF THE MODIFIED DENITRIFICATION REACTOR.

A plastic cover was installed on top of the reactors to obtain an anaerobic vessel. A vent tube was installed in the cover so that the gases could escape to the atmosphere; also, the volume and composition of the gases could be determined. An inlet feed tube, a thermometer, and a pH electrode were also installed through the plastic cover. In addition, a spare hole was drilled in the cover to permit sampling of the reactor solution. In normal operation, this hole was plugged with a rubber stopper. The impeller agitator shaft passed through the center of the cover and was equipped with a water seal to prevent loss of gases from the reactor. Each entry port and the plastic top were made gas tight using a silastic adhesive.

Mechanically, this type of reactor has operated satisfactorily at solids levels in the reactor up to 6 wt %. Most of the laboratory studies used this reactor design, and the ultimate

production-size vessel has been designed with the solids withdrawn by using the "side-pocket" design.

Reactor Feeds

Nitrate Feed - The present nitrate waste stream from the Y-12 Plant is composed of a stream called "condensates" and another stream called "raffinates". These streams originate from a uranium purification process in the Y-12 Plant. The condensate waste stream is approximately a mixture of 10% nitric acid and 90% water, plus trace quantities of such impurities as chlorides, fluorides, and soluble organics. It is planned that this stream will be

evaporated and the nitric acid will be recycled back to the uranium purification system without any biological treatment. The raffinate stream contains a high level of aluminum nitrate, calcium nitrate, and nitric acid, plus impurities extracted in the uranium purification process. It is planned to process this stream through a crystallization operation, and purified aluminum nitrate nanohydrate solids will be recycled for reuse in the uranium purification plant. A waste stream (labeled "mother liquor") from this operation will be generated and will have the typical composition listed in Table 12. This stream, containing a high level of aluminum, calcium, and other impurities, cannot be economically recycled back to the uranium purification plant. This mother-liquor stream will be the nitrate feed solution used in the production denitrification plant.

Table 12
TYPICAL ANALYSIS OF
THE MOTHER LIQUOR

Component	Concentration (wt %)
Aluminum	4.4
Magnesium	0.4
Calcium	0.8
Sodium	0.2
Potassium	0.01 - 0.1
Lithium	0.01 - 0.1
Molybdenum	0.01 - 0.1
Zirconium	0.01 - 0.1
Silicon	0.01 - 0.1
Nickel	0.01 - 0.1
Fluorides	0.5
Free Nitric Acid	3.5
Total Nitrate	33.0
Water	59.1

During the development stages of the biodenitrification process, a variety of nitrate and organic feeds was used. A commercial grade of calcium nitrate containing about 4.0 wt

% ammonium nitrate was also used in some tests. However, the raffinate solution from the uranium purification plant was used as the source of nitrate for a majority of the continuous-flow, stirred-bed reactor studies. In the early stages, the raffinate solution was neutralized with lime prior to adding it to the reactors. Later studies have used raffinate with neutralization occurring in the reactor vessel by the reaction of the raffinate feed solution with calcium carbonate which is produced in the reactor vessel.

The raffinate stream does not have a constant chemical composition. As noted in Table 13, three different batches had significant variations in the amounts of calcium, aluminum, free nitric acid, and the total nitrate level. Once the production recycle plant is operational, some of the day-to-day variations will be present, and significant long-term changes in the impurity levels can be expected.

Organic Feed - Organic carbon sources used in the batch and column process development studies have included methyl alcohol, calcium acetate, and one experimental batch using sucrose. All of the continuous-flow, stirred-bed reactors have used calcium acetate as the organic feed source. The work of McCarty, et al,⁽⁶⁾ showed that the acetate ion was an effective carbon source.

Table 13
RAFFINATE ANALYSIS

Component	Concentration (wt %)		
	Batch 1	Batch 2	Batch 3
Aluminum	2.36	2.10	3.06
Calcium	0.29	1.70	
Magnesium	0.2	1.30	
Fluorine	0.24	-	
Sodium	-	0.03	
Lithium	-	0.04	
Potassium	-	0.002	
Free Nitric Acid	9.24	8.32	4.90
Total Nitrate	30.5	31.1	29.04
Uranium ($\mu\text{g/g}$)	0.06	0.06	0.01
Specific Gravity	1.280	-	1.273

In most of the stirred-bed experiments, the organic carbon was added to the raffinate feed solution as a calcium acetate solution. A typical analysis of a water solution of calcium acetate is noted in Table 14. Acetic acid and water were neutralized with agricultural-grade lime to obtain the calcium acetate solutions.

Reactor Feed Solutions - For the continuous-flow, stirred-bed reactor experiments, the majority of the feed solutions were made by mixing raffinate solution with an aqueous solution of calcium acetate. Total nitrate level was in the range of 10 to 13.5 wt %, and the total organic carbon level was in the range of 0

to 3.9 wt %. The organic carbon level was varied to study the C/N mole ratio, which will be discussed later in this report. The chemical compositions of several feed batches are given in Table 15. The feeds showing 0.3 to 0.58 wt % ammonium ion were made using commercial-grade calcium nitrate which contained ammonium nitrate as an impurity. The feeds showing no ammonium ion were made using plant raffinate solution.

Carbon-to-Nitrogen Mole Ratio - A source of organic carbon is required to provide the energy required for a bacterial reduction of nitrates. It is believed that nitrate reduction is coupled to the metabolism of the organisms involved, and the nitrate ion acts as the terminal hydrogen acceptor in the energy transport system. When an adequate concentration of a degradable organic material is present, many types of facultative bacteria are capable of nitrate reduction under anaerobic, or near anaerobic, conditions.

Several organic compounds have been shown to be a satisfactory carbon source. Methanol is commonly used because of engineering economics, ease of handling, and availability. McCarty, et al,⁽⁶⁾ showed that methanol, ethanol, acetone, sugar, and neutralized acetic acid could be used in the denitrification process. For the Y-12 studies it was decided that methanol and acetic acid, neutralized with lime, would be used to determine if the acetate carbon would produce higher denitrification rates using nitrate wastes from the Y-12 Plant. Table 16 lists the chemical equations which are believed to be valid for the methanol/calcium nitrate and calcium acetate/calcium nitrate reactions. The C/N weight ratio from the calcium acetate/calcium nitrate equation is shown to be 1.39.

Table 14
COMPOSITION OF THE CALCIUM ACETATE SOLUTION

Component	Range (wt %)	
Calcium	4.5	5.2
Carbon	5.4	6.3
pH	6.5	7.5
Trace Inorganics	0.001	0.2
Specific Gravity	1.1	1.15

During the continuous-flow experiments, a number of feed batches were used which had a C/N weight ratio of 1.3 to 1.65. While using these feeds, the carbon level in the reactor vessel always increased to about 0.4 wt %. Some tests were made at reduced C/N mole ratios, and it is now believed that an approximate 1.2 C/N weight ratio in the feed would be preferable. The carbon-to-nitrogen ratio is further discussed in later sections of this report.

Table 15
COMPOSITION OF THE FEED SOLUTIONS

Feed Number	NO ₃ ⁻ Concentration (vol %)	Concentration (wt %)			C/N(2) (wt ratio)	Hydrogen Ion Concentration (pH)	Density (g/cm ³)	Concentration (wt %)							
		NO ₃ ⁻	N	TOC(1)				NH ₄ ⁺	Ca	Mg	Al	Na	K	Li	Fe
F-7	11.52	10.08	2.27	1.29	0.57	-	1.143	0.31	-	-	-	-	-	-	-
F-8	12.86	11.10	2.51	3.36	1.34	-	1.158	0.58	-	-	-	-	-	-	-
F-9	12.10	10.51	2.37	2.67	1.13	-	1.151	0	-	-	-	-	-	-	-
F-10	12.58	10.90	2.46	4.07	1.65	3.63	1.156	0	-	-	-	-	-	-	-
F-11	12.94	11.10	2.51	3.43	1.37	6.40	1.170	0.46	-	-	-	-	-	-	-
F-12	13.47	11.60	2.62	3.50	1.33	4.90	1.163	0	3.47	0.27	0.92	0.035	0.02	0.006	0.11
F-13	13.88	11.90	2.69	3.04	1.13	-	1.166	0	3.54	0.27	0.94	0.034	0.02	0.007	0.12
F-14	12.80	10.49	2.48	3.34	1.35	-	1.158	0	-	-	-	-	-	-	-
F-15	13.71	11.80	2.66	3.52	1.32	3.45	1.165	0	-	-	-	-	-	-	-
F-16	13.82	11.90	2.69	3.71	1.38	3.40	1.166	0	-	-	-	-	-	-	-
F-17	14.42	12.20	2.75	3.68	1.34	3.50	1.186	0	-	-	-	-	-	-	-
F-18	14.49	12.20	2.75	3.93	1.43	3.75	1.190	0	4.25	0.60	0.60	0.01	0.001	0.02	0.01
F-18W	13.98	12.10	2.73	0	-	-	1.160	0	-	-	-	-	-	-	-
F-19	15.64	13.40	3.03	2.96	0.98	3.30	1.170	0	3.4	0.70	1.00	0.02	0.001	0.02	-
F-20	14.78	12.90	2.91	2.06	0.71	2.90	1.148	0	-	-	-	-	-	-	-
F-21	14.62	12.40	2.80	3.24	1.16	3.40	1.180	0	-	-	-	-	-	-	-
F-22	16.16	13.60	3.07	3.36	1.10	2.90	1.187	0	-	-	-	-	-	-	-
F-23	16.04	13.50	3.05	3.32	1.09	3.50	1.187	0	-	-	-	-	-	-	-
F-24	13.70	11.80	2.56	3.5	1.32	3.30	1.160	0	-	-	-	-	-	-	-
F-25	12.82	11.06	2.50	3.93	1.57	4.70	1.159	-	4.00	0.06	1.48	0.11	0.01	0.01	0.34
F-26	14.14	12.91	2.92	2.86	0.98	3.20	1.095	-	0.10	0.06	0.16	0.12	0.01	0.00	0.04
F-27	14.77	12.73	2.87	3.43	1.20	4.65	1.160	-	3.60	0.05	1.50	0.14	0.01	0.00	0.03
F-28	13.54	11.68	2.64	3.47	1.31	4.40	1.159	-	-	-	-	-	-	-	-
F-29	13.37	11.60	2.62	2.99	1.14	4.40	1.153	-	-	-	-	-	-	-	-

(1) TOC - total organic carbon.

(2) To obtain mole carbon/mole nitrogen ratio, multiply C/N weight ratio by a factor of 1.166.

Table 16
DENITRIFICATION CHEMICAL EQUATIONS

Methyl Alcohol⁽¹⁾

1.08 mol carbon to 1.0 mol nitrogen = C/N mol ratio of 1.08

12.96 g carbon to 14.0 g nitrogen = C/N wt ratio of 0.93

Calcium Acetate

2.60 mol carbon per 1.6 mol nitrogen = C/N mol ratio of 1.63

31.2 g carbon per 22.4 g nitrogen = C/N wt ratio of 1.39

(1) From McCarty.⁽⁶⁾

Identification of Active Bacteria

Two bacterial cultures, obtained from the Biology Division of the Oak Ridge National Laboratory, were initially used in the laboratory studies. These seed cultures were identified by the names, "Pseudomonas stutzeri" and "Pseudomonas denitrificans". The Pseudomonas stutzeri culture was predominantly used as the original base seed culture. After activation of a 0.21 m³ (55-gal) drum, the culture was used whenever a new system was started. No identification was made of the types of bacteria present in the reactor solutions.

One sample was taken from an active reactor, and photomicrographs were obtained using optical microscopy, transmission electron microscopy (TEM), and scanning electron microscopy (SEM). For record purposes, typical photographs are presented in Figures 11 and 12.

The optical examination included: evaporation of a drop of the culture, heat fixation, and staining with the classical Gram's stain. The organisms appeared as Gram negative bacilli. The SEMs were obtained by evaporation of the culture onto a glass cover slip and gold coating to provide electrical conductivity. TEM photographs involved dispensing the culture on collodion and staining with phosphotungstic acid to enhance contrast in the electron beam. Other than these examinations, no work was performed to identify or quantify the types and number of microbes.

Mini I Reactor

The first engineering version of a laboratory, stirred-bed reactor was a vessel having a liquid capacity of about 57 dm³ and a free gas volume capacity of about 12 dm³, as noted in Figure 9.

Reactor Feed Solutions - For the Mini I reactor tests, a synthetic feed was made using commercial-grade calcium nitrate and a chemically pure grade of calcium acetate (see discussion under **Reactor Feeds**, Page 28). In general, all feed solutions contained a nitrate level in the range of 10 to 13.5 wt % and the appropriate organic carbon level to obtain a

nominal carbon-to-nitrogen mole ratio of 1.6. The 1.6 C/N ratio was decided upon to insure that an excess of organic carbon was present in the reactor.

Test Data - The first 50-day test was started on January 23, 1974 and terminated on March 12. The inlet flow to the system was controlled using a gravity-flow method and was not satisfactory. The unit was started without flow and was operated as a batch-type operation for the first 14 days. Flow to the system was started on the 15th day and was stopped on the 41st day because of a high concentration of nitrate and nitrite ions in the reactor. The unit was operated nine additional days (to the 50th day) without flow. The nitrate level in the reactor decreased from 1.335 to 0.509 wt % during this nine-day period. It was estimated that an additional 9 to 18-day waiting period would be required before the nitrate level was low enough to accept feed. The test was terminated to conserve time, and a new solution was added and labeled "Test 2".

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Figure 11. SCANNING ELECTRON MICROGRAPH OF NITRATE-ACTIVE BACTERIA. (3000X)

Figure 12. TRANSMISSION ELECTRON MICROGRAPH OF NITRATE-ACTIVE BACTERIA. (4800X)

During the first test period, the nitrate feed rate was varied up to a maximum of 1.332 kg NO_3^- per day, which is equivalent to 23.4 g $\text{NO}_3^-/\text{day}/\text{dm}^3$ of reactor solution. The maximum feed rate of 1.332 kg NO_3^- per day caused the nitrate level in the tank to increase to an unreasonable level of 13,584 $\mu\text{g/g}$. Sudden feed-rate increases were made over a time period of eight days, starting with Day 34 and ending at Day 41. The system was not allowed to equilibrate after the flow increases occurred, and these sudden flow changes may have shocked the system.

Table A-1 (Appendix) is a tabulation of the experimental data which shows that the denitrification efficiency of converting the nitrate ion to nitrogen gas was usually above 98%, except during the last nine days of the first test period.

The second test period was initiated on the 51st test day and extended through 135 test days. The nitrate feed rate to the reactor during this test period was held below 636 g NO_3^- per day, which is equivalent to 11.16 g $\text{NO}_3^-/\text{dm}^3/\text{day}$ solution in the reactor. The reactor efficiency was a nominal 99.8% except for nine test days when the efficiency dropped to a low of 96.2% (Table A-1).

During this 84-day test period, the feed to the reactor was stopped four times for a total of nine days to allow the nitrate concentration in the reactor to decrease to an acceptable level (less than 500 $\mu\text{g/g}$ nitrate). The cause of the four perturbations in this test period is not known. The first upset occurred on Day 83, and the feed was stopped for one day. The nitrate ion level in the reactor had increased from less than 100 to a level of 4143 $\mu\text{g/g}$, the nitrite ion increased from less than 5 to 1030 $\mu\text{g/g}$, and the total organic carbon (TOC) level increased to 3450 $\mu\text{g/g}$. The carbon-to-nitrogen mole ratio in the reactor at this time was 2.76. In general, the carbon-to-nitrogen mole ratio in the reactor during satisfactory operations was greater than 20, but less than 100.

The second perturbation occurred on Day 117, and the feed was stopped for two days. The nitrate ion level in the reactor increased from a nominal 126 to 462 $\mu\text{g/g}$. At this time, the TOC level was a nominal 4050 $\mu\text{g/g}$, and the C/N mole ratio was 144, which is considered to be too high for satisfactory operation.

The third perturbation occurred on Day 130, and the flow was stopped for two days. The nitrate ion level in the reactor had increased to 1330 $\mu\text{g/g}$, the nitrite ion level had increased to 374 $\mu\text{g/g}$, and the TOC level was 1525 $\mu\text{g/g}$. The C/N mole ratio at this time was 3.69, which was below the desired operating range of 20 to 100.

The fourth upset occurred on Day 132 and is believed to be as a result of starting the reactor flow without adjusting the low C/N mole ratio.

Analytical Data - Analytical data on the effluent from the Mini I reactor are reported in Table A-2, Appendix. In all cases, the reported analyses were made on clear solutions obtained by centrifuging and filtering through a micro filter. Later samples were centrifuged using an ultra-high-speed centrifuge instead of a low-speed centrifuge. Analytical data were also occasionally obtained on as-taken samples, and the nitrate level usually was in agreement with the centrifuge/filter data. The TOC levels were decreased by the centrifuge/filtration of the samples.

Gas Analysis - Data on the gaseous products from the reactor are presented in Table A-3. The total gas volume was obtained by passing all of the gases through a wet-test flow meter. The amount of gas evolved per hour, reported in Table A-3, was normally an average of the overnight (16-hour) gas production and was used in an effort to minimize the effects of sample-withdrawal operations which normally occurred during the day.

The carbon dioxide content of the evolved gases was determined by standard gas chromatographic techniques using a sample injected into the instrument. Periodically, the instrument was calibrated using a gas mixture containing a known amount of carbon dioxide and nitrogen gases. Also, occasional gas samples were analyzed using mass spectrographic techniques.

The nitrogen gas volume, noted in Table A-3, was calculated as the difference between the amounts of carbon dioxide and the total gas volume. The nitrogen calculation is believed to be valid, based on the analysis obtained from the mass spectrographic data. Trace impurities in the gas of a normal functioning reactor consisted of argon and oxygen which was always less than a total of 1%. During abnormal operations, nitric oxide gas was generally present, and the level could be as high as 13%. The gas chromatograph instrument used for this study detected both nitrogen oxide and carbon dioxide gases as only carbon dioxide. In all cases when the carbon dioxide level, noted in Table A-1, was above 55%, and if nitric oxide gas were also present, the reactor was found to be operating at an unsatisfactory level.

Total Organic Carbon Data - Early analytical TOC data were obtained on "settled" samples from the reactor. About Day 50, the TOC data (Table A-2) were obtained by using low-speed centrifuged and filtered samples. Low-speed centrifuge techniques did not produce a "clear" or biomass-free sample. Centrifuged solutions were then filtered through a 0.33-micrometer-pore-sized paper filter to obtain a "clear" and biomass free solution. Later analyses were obtained using an ultra-high-speed centrifuge followed by filtration through a micro pore filter. TOC values thus obtained were lower, and the difference between these TOC values and the previous lower-speed centrifuged and filtered samples appears to have been due to biomass or insoluble organic constituents in the solutions.

Ammonium Ion - Analytical data on the ammonium ion concentration in the reactor is presented in Table A-2. The ammonium ion was present in the synthetic feed solution which has previously been discussed in the **Reactor Feeds** section of this report. The concentration increased in the reactor to a nominal 4500 $\mu\text{g/g}$, which was approximately the level in the feed solution. This level of ammonium ion caused no detectable adverse effects on the reactor performance. A nominal 30 days were required for the ammonium ion to increase from a level of 300 to 4500 $\mu\text{g/g}$.

Phosphate - A nominal 20 $\mu\text{g/g}$ of phosphate was routinely added on a once-per-day batch basis to the reactor and was added as a potassium phosphate solution. Phosphate analyses, given in Table A-2, indicate that less than 5 $\mu\text{g/g}$ of soluble phosphate was present in the reactor solution. The low phosphate level was caused by the low solubility of the phosphate ion in the reactor solution. Excess phosphates probably precipitated from the solution as calcium phosphate solid. In any event, the daily addition of soluble phosphate ions was required. When this ion was not added, the reactor efficiency was always adversely affected because phosphates are a required nutrient for the reproduction of microbes.

Hydrogen Ion Measurements - A radical change in the pH of the reactor solution will act as a shock to the denitrifying bacteria. In the anaerobic denitrification reaction, which is highly buffered by carbonate and bicarbonate ions, and with an excess of CO_2 gas present, the pH of the solution seeks and maintains its unique level. The pH of a normal working reactor lies between 6.5 and 7.6, with an average value of 6.8.

Temperature - The temperature of the reactor solution inside the reactor was typically 2 to 5°C above ambient temperatures and was dependent on the denitrification rate.

Mini II Reactor

Design of the Mini II reactor was the same as Mini I except that the liquid volume was increased to 67.2 dm^3 . The free-gas-volume capacity remained at about 12 dm^3 . The vessel was equipped the same as Mini I, and the same measurements were routinely made.

Reactor Feed Solutions - The reactor tests were started on April 2, 1974, using a solution containing an inoculum from a batch reactor. Approximately 25 vol % of the "seed" solution and 75 vol % water were added to the vessel. The starting nitrate level was approximately $250\text{ }\mu\text{g/g}$. Approximately a month was required before denitrification occurred at a reasonable rate. The vessel was periodically batch-fed nitrate and organic carbon solutions during this acclimation period. On the 31st test day, continuous feed to the vessel was started using a solution of commercial-grade calcium nitrate and sufficient calcium acetate solution to obtain a carbon-to-nitrogen mole ratio of 1.3. After four days of operation (Day 35), the feed solution was changed to nitric acid-raffinate wastes from the production plant. The organic carbon source and the carbon-to-nitrogen mole ratio were not significantly changed.

Test Data - As previously stated, a batch-type operation was conducted during the first 30 days of the test, with feed occasionally introduced into the reactor. During this period, the stirring motor failed and other equipment problems were resolved. The reactor was started on continuous feed on the 31st test day using a commercial grade of calcium acetate. After four days (Table A-4), the nitrate feed was changed to nitric acid-raffinate wastes from the Y-12 Plant. The acid wastes were mixed directly with the calcium acetate solution. As previously stated, it was assumed that the acid solution would be neutralized by the calcium bicarbonate ions and carbonate solids in the reactor solution. This operational change eliminated the need for a neutralization step; therefore, a significant amount of capital equipment was cancelled in the design of the plant.

After two satisfactory operating days (Day 37), the inlet feed valve to the reactor failed and a large volume of acid feed was suddenly dumped into the reactor. The pH of the reactor solution immediately dropped from 6.4 to 3.9, and the nitrate level in the reactor increased from 53 to $12,000\text{ }\mu\text{g/g}$ (Table A-4). A water slurry of calcium hydroxide was added to the reactor to adjust the pH to a nominal value of 6.2. For the next 12 days, a pH level of 5.8 to 6.4 was maintained by additions of calcium hydroxide. This operational procedure appeared to minimize the "shock" effect to the reactor, and continuous feed was again started after a 12-day delay (Day 50). During the first four days of the 12-day offstream time, the nitrate level decreased from $12,000\text{ }\mu\text{g/g}$ to less than $200\text{ }\mu\text{g/g}$ (Day 42). Feed was not restarted until Day 50 in order to redesign the feed system. A mechanical pump was installed in the feed system to provide a "fail safe" feed condition.

Continuous feed flow was administered successfully until Day 80. At this time, half of the reactor solution was taken from the Mini II reactor and used to activate a new reactor (Mini IV). Water was added to the Mini II reactor to refill the vessel. The feed rate was decreased from 4.80 to 0.93 g $\text{NO}_3^-/\text{day}/\text{dm}^3$ of reactor solution, then progressively increased over the next eight days to the level of 4.4 g $\text{NO}_3^-/\text{day}/\text{dm}^3$ of reactor solution. There was no evidence that the reactor performance was affected by this procedure.

During the next 64-day period, feed-flow variations ranged from 1 to 9 g $\text{NO}_3^-/\text{day}/\text{dm}^3$ of reactor solution. The feed was cut off on Day 114 and restarted on Day 124. The nitrate level in the reactor had increased from a nominal 60 $\mu\text{g}/\text{g}$ (Day 112) to 2445 $\mu\text{g}/\text{g}$ (Day 113). On Day 114, the nitrate level had decreased to 1562 $\mu\text{g}/\text{g}$ and the feed flow was stopped to allow the level to decrease to below 100 $\mu\text{g}/\text{g}$, which occurred on Day 123. The cause of the increased nitrate level is not known, but the feed flow to the reactor had been doubled on Day 108. This sudden flow increase may have caused a "shock" to the reactor. In any case, the reactor returned to normal operational conditions within 10 days.

As previously stated, the feed was resumed on Day 124 at a level of three grams of nitrate per day per dm^3 of reactor solution. This feed level was maintained for five days (Day 125) and then the flow was abruptly increased to nine grams of nitrate per day per dm^3 of reactor solution (Day 130). The higher flow rate was about equal to the flow rate which was present when abnormal operations occurred on Day 114. There were no obvious adverse effects observed after the feed flow was increased. The reactor test was terminated on Day 133 in order to use the reactor vessel for other biological studies.

Analytical Data - Analytical data of the effluent from the reactor are summarized in Table A-5. In all cases, the reported analyses were made on "clear" solutions obtained by centrifugation and filtration of the solution. These data show that the effluent from the reactor was normally less than 200 $\mu\text{g}/\text{g}$, and the TOC level was more than 900, but less than 3800 $\mu\text{g}/\text{g}$. The nitrate concentration was normally not detectable except during abnormal operating conditions (Table A-5). As noted in Table A-5, the phosphate level was always less than 5 $\mu\text{g}/\text{g}$, which was the detectable level of the analytical procedure. The ammonium ion concentration, reported in Table A-5, was a result of feeding commercial-grade calcium nitrate which contained a nominal 4.8% by weight of ammonium nitrate. Ammonium nitrate contaminant was not normally present in the nitric acid-raffinate feed from the uranium purification process.

Gas Analysis - Gas analyses from the reactor gaseous effluent are presented in Table A-6. In general, the carbon dioxide concentration in the offgases was a nominal 38 wt % when using commercial-grade calcium nitrate feed, and a nominal 58 wt % when using nitric acid-raffinate feeds. Carbon dioxide was higher with the acid feeds because the acid was neutralized in the reactor with excess calcium salts, and carbon dioxide was liberated by this reaction. A significant change in the carbon dioxide concentration was always an indicator of abnormal operating conditions. Also, a change in the gas evolution rate was an indicator of reactor problems. In general, the total gas evolved in a normal operating reactor using nitric acid-raffinate feed was 0.450 dm^3/g nitrate feed to the reactor.

Total Organic Carbon Data - As noted in Table A-5, the TOC level in the reactor ranged from 900 to 3800 $\mu\text{g}/\text{g}$. The majority of the reactor test days were run at TOC levels ranging from 900 to 2000 $\mu\text{g}/\text{g}$.

Hydrogen Ion Measurements - The Mini II reactor operated at a pH range of 6.6 to 7.3. Normally, a pH of 6.8 was noted in the reactor solution.

Phosphates - The phosphate level in the reactor was consistently less than 5 $\mu\text{g/g}$, which was the analytical detectable level (Table A-6).

Temperature - The reactor operated between 21 and 31 $^{\circ}$ C. Typically, the solution was 2 to 5 $^{\circ}$ C above ambient temperature and always increased with increased feed rates.

Mini III Reactor

Mini III reactor design was a duplicate of the Mini II reactor and was operated in order to determine if the performance of the Mini II reactor could be duplicated. It was also intended to study higher feed rates in this reactor.

Reactor Feed Solutions - Most of the nitrate feed solutions to this reactor were from the nitric acid-raffinate waste stream from the uranium purification plant. Feeds F-13 through F-24 (Table 15) were used, starting on the 56th test day and ending on the 198th test day.

Reactor Test Data - The Mini III reactor was started as a batch operation. Continuous flow was started on the 24th test day (Table A-7). A nominal flow of 2 g $\text{NO}_3^-/\text{day}/\text{dm}^3$ of reactor solution was maintained from the 24th to the 35th test day (11 days), then the flow was doubled to a nominal 4 g $\text{NO}_3^-/\text{day}/\text{dm}^3$ of reactor solution. Reactor operating data, including feed flow rates, are noted in Figure 13. On the 40th test day, the feed valve failed and the reactor vessel was quickly filled with nitric acid-raffinate solution. Consequently, the nitrate level in the vessel increased to more than 4 wt %. Calcium hydroxide was added to adjust the pH of the solution and the feed was stopped. On the 48th test day, the reactor solution was discarded and replaced with a viable solution from an existing batch test. Continuous feed to the reactor was started on Day 50 at a nitrate feed rate of 2.2 g $\text{NO}_3^-/\text{day}/\text{dm}^3$ of reactor solution. Flow was then slowly increased up to a nominal 9 g $\text{NO}_3^-/\text{day}/\text{dm}^3$ (Figure 13). On Day 112, the flow was stopped for a 48-hour period because the nitrate level in the tank had suddenly increased from a nominal less than 300 $\mu\text{g/g}$ to 10,528 $\mu\text{g/g}$ (Table A-8). TOC in the reactor had reached a level of 4360 $\mu\text{g/g}$ on Day 108. On Day 112, the TOC level had increased to 6450 $\mu\text{g/g}$, which was significantly higher than the normal operating TOC level of 2000 to 3000 $\mu\text{g/g}$.

After the flow was stopped on Day 112, the nitrate and TOC concentrations in the reactor dropped to 289 $\mu\text{g/g}$ NO_3^- and 4010 $\mu\text{g/g}$ TOC on Day 114. Flow was resumed on Day 114 at a nominal 1.47 g $\text{NO}_3^-/\text{day}/\text{dm}^3$ of reactor solution and was increased to a nominal 7 g $\text{NO}_3^-/\text{day}/\text{dm}^3$ on Day 120 (Figure 13). On Day 122, flow was stopped for a 24-hour period to allow the nitrate concentration in the reactor to decrease from a nominal 5600 to 90 $\mu\text{g/g}$. TOC concentration was approximately 4500 $\mu\text{g/g}$, and additional carbon was added which may not have been needed.

Flow was restarted on Day 123 and continued until Day 171. During this test period, the TOC concentration in the tank was reduced from a nominal 4500 $\mu\text{g/g}$ to a low of 370 $\mu\text{g/g}$ by adding feed solutions which were deficient in organic carbon. On Day 170, the nitrate concentration in the reactor increased to 3447 $\mu\text{g/g}$ with a TOC concentration of 1820 $\mu\text{g/g}$.

Figure 13. AMOUNT OF NITRATE REDUCED IN THE MINI III REACTOR.

(Table A-8). Flow was restarted on Day 174 when the nitrate level had decreased to 121 $\mu\text{g/g}$ and the TOC concentration was 1170 $\mu\text{g/g}$.

The feed flow, noted in Figure 13 and Table A-7, was continued at a high flow rate from Day 174 to Day 176. The nitrate concentration in the reactor again increased to 4381 $\mu\text{g/g}$ and the feed flow was again stopped for a 24-hour recovery period. Flow was restarted on Day 178 and continued through Day 200 with satisfactory operation.

Analytical Data - Analytical data on the liquid discharge from the Mini III reactor are given in Table A-8. These data show that the reactor normally operated at a nitrate effluent concentration of less than 200 $\mu\text{g/g}$. Nitrite ions were only present when the reactor was not operating properly.

Total Organic Carbon Data - The reactor solution contained a wide variation in the organic carbon, as noted in Table A-8 and Figure 14. These data show that the TOC concentration consistently varied during the 200-day test period. The last 60 days of the test had a TOC concentration span ranging from a low of 400 to a high of 2000 $\mu\text{g/g}$. The TOC level in the reactor was dependent on the carbon-to-nitrogen weight ratio in the inlet feed, which is tabulated in Figure 14. The optimum carbon-to-nitrogen weight ratio in the inlet feed was not established during the 200-day test period. A "best-estimate" carbon-to-nitrogen weight ratio of 1.10 to 1.20 appears to be a ratio which would maintain a near constant level of organic carbon in the reactor.

During the last 60 days of the test period, a few chemical analyses were made to determine both the acetate carbon and the TOC in the reactor solution. The available data are reported in Table 17. These data show that the difference between the TOC and the acetate carbon is an average value of 545 $\mu\text{g/g}$ lower. In other words, when the TOC concentration approaches a value of 545 $\mu\text{g/g}$, there is no acetate carbon available for denitrification. During the Mini III test period, low TOC values were observed beginning at about Day 140 and extending through Day 160. Extra acetate carbon was added six times, as noted in Table A-8, in order to keep the reactor operating at a satisfactory rate.

Table 17
ACETATE CARBON AND
TOTAL ORGANIC CARBON
CONCENTRATIONS

Test (day)	Total Organic Carbon ($\mu\text{g/g}$)	Acetate Carbon ($\mu\text{g/g}$)	Difference ($\mu\text{g/g}$)
136	1905	1275	630
140	630	90	540
141	650	30	620
142	380	< 25	355
146	675	283	392
147	535	156	379
148	555	13	542
154	370	7	363
Average Concentration Difference			545

Gas Analysis - Available gas analyses from the Mini III reactor operation are presented in Table A-9 and Figure 15. The carbon dioxide level normally was in the range of 50 to 60 vol % in the offgases. When the CO_2 content was above 60 vol % (which occurred 11 times during the 200-day test period), the reactor solution contained a nitrate concentration of more than 300 $\mu\text{g/g}$ and was not operating satisfactorily.

Exclusive of the first 60 days of test, the average amount of carbon dioxide generated in the reactor was 0.2379 dm^3 of CO_2 per gram of nitrate decomposed in the reactor. The average total gas volume from the reactor, exclusive of the first 60 days of test, was 0.4478 dm^3 per gram of nitrate decomposed in the reactor.

Figure 14. TOTAL ORGANIC CARBON CONCENTRATION IN THE MINI III REACTOR.

Figure 15. CARBON DIOXIDE CONCENTRATION OF THE EFFLUENT GAS FROM MINI III.

Hydrogen Ion Measurement - The pH of the reactor normally ranged from 6.7 to 7.3, with a typical value of 7.0.

The lower limit of total organic carbon in the reactor appears to be near $600 \mu\text{g/g}$. At this level, the acetate carbon concentration is normally less than $100 \mu\text{g/g}$, and there is not a sufficient supply of carbon available for the denitrification reaction.

Mini IV Reactor

The Mini IV reactor was designed to permit removal of solids from the side of the reactor (Figure 10). A sedimentation "pocket" was constructed inside the reactor where the solids could settle and be removed from the pocket through a drain-pipe arrangement. This solid-withdrawal method worked very satisfactorily, and this Mini IV design was selected for the scaled-up denitrification vessels for the Y-12 Plant installation.

Reactor Feed Solutions - Feed solutions used during this test period ranged from Batches F-13 through F-23 (Table 15). The operating time periods for each of the feed solutions are also noted (Figure 16). In all cases, the carbon-to-nitrogen weight ratio of the feeds ranged from 0.71 to 1.43. In some cases, additional carbon was added on a batch basis when using low carbon feeds (C/N weight ratio < 1.0).

Reactor Test Data - The reactor was inoculated on June 19, 1974 by transferring an active biological solution from the Mini I reactor. Continuous feed flow was started on June 20. Daily nitrate feed rates are reported in Figure 16 and Table A-10. The reactor operated for a total test period of 134 days.

The first 35-day test period showed normal operations, with the effluent from the reactor containing less than $200 \mu\text{g/g}$ nitrate ion (Table A-11 and Figure 16). High nitrate levels in the reactor were detected on the 36th day, so the feed rate was decreased from a nominal six grams of nitrate per day per dm^3 of reactor solution to one gram. The feed rate was again increased, starting with Day 41. Pump-plugging problems occurred about Day 47 and equipment repairs were made. The feed flows were again increased to six grams of nitrate per day per dm^3 of reactor solution. High nitrates were detectable in the reactor on Days 71, 72, 79, and 80. Consequently, the feed flow was reduced on Day 81 to a nominal $1 \text{ g NO}_3^-/\text{day}/\text{dm}^3$, but again raised the next day. A high nitrate level was again detected in the reactor on Days 97, 107, 108, 113, and 119. In each case, high nitrate levels decreased to less than $200 \mu\text{g/g}$ nitrate within 24 hours.

Analytical Data - Analytical data on the liquid effluent from the Mini IV reactor are reported in Table A-11. These data show that the reactor operated for 114 days out of the 134 test days at a nitrate discharge level of less than $400 \mu\text{g/g}$.

Total Organic Carbon Data - The TOC level in the reactor varied over a wide range, as noted in Table A-11 and Figure 17. The TOC level was dependent on the C/N weight ratio in the feed solution; and, in general, a TOC range of 1000 to $4000 \mu\text{g/g}$ produced a satisfactory denitrification rate. A few analyses were also made to determine both the TOC and the acetate carbon levels. The available data are given in Table 18. The acetate carbon

Figure 16. MINI IV REACTOR FEED RATES.

Figure 17. TOTAL ORGANIC CARBON CONCENTRATION IN THE MINI IV REACTOR.

concentration was usually 10 to 33% less than the TOC values. A brief review of the TOC data shows that the TOC concentration progressively increased from the starting date of the reactor until about Day 50. At this point, the TOC level remained at about the 5000 $\mu\text{g/g}$ level until Day 70. A decrease in the TOC concentration occurred by adding feeds containing a low C/N weight ratio. The TOC was allowed to decrease to a nominal 240 $\mu\text{g/g}$, which occurred on Day 90. The TOC concentration was then increased to a nominal 1000 $\mu\text{g/g}$, where it remained at approximately this level until Day 135.

Hydrogen Ion Measurement - The pH of the Mini IV reactor has remained in the range of 6.6 to 7.3.

Temperature - The temperature of the reactor remained in the range of 20 to 30°C, and normally was 1 to 4°C higher than the ambient temperature.

Gas Composition - Gas flows and the gas composition from the Mini IV reactor are tabulated in Table A-12. As revealed by these data, an average of 0.486 dm^3 of gas per gram of decomposed nitrate was generated in the reactor. The reactor released an average of 52.6% carbon dioxide, which is equivalent to 0.256 dm^3 of CO_2 gas per gram of nitrate decomposed. As was noted with the other reactors, the reactor performance could be observed by monitoring the CO_2 level in the effluent gas. If levels above 60% were noted, a high concentration of nitrate was always found in the effluent from the reactor.

Removal of Solids

Solids were routinely taken from the reactors in an attempt to establish a material balance around the reactors. As noted in Table 19, a daily average of 2242 grams of feed solution was added to both the Mini II and Mini III reactors. The total flow of liquid and solids from these reactors had an average daily weight of 2694 grams. The higher weight of material from the reactor can be partially explained by the fact that a nominal 100 grams of a solution of water and trace nutrients containing phosphate ions were added daily to the reactors.

A calculated material balance, based on the data listed in Tables 19 and 20, indicates that about 45% of the calcium is removed daily in the effluent. The aluminum from Mini II showed that 126% of this element was removed daily; and, from Mini II, a nominal 60% of the aluminum was removed, for a combined average value of 93.2%. The high aluminum

Table 18
TOTAL ORGANIC CARBON AND
ACETATE CARBON IN THE
MINI IV REACTOR

Test (day)	Total Organic Carbon ($\mu\text{g/g}$)	Acetate Carbon ($\mu\text{g/g}$)	Difference ($\mu\text{g/g}$)
73	4270	2825	- 1445
77	2240	1210	- 1030
78	1570	1250	- 320
79	1420	1205	- 215
80	1105	1125	+ 20
83	935	775	- 160
84	1030	781	- 249
85	965	675	- 290
91	542	358	- 184
97	1272	1228	- 44
98	1072	988	- 84
99	1085	1007	- 78
100	-	953	-
101	-	955	-
105	1075	1075	0
111	1045	796	- 249
113	1025	859	- 166
114	840	796	- 44
115	770	707	- 63
118	750	732	- 18
119	942	990	+ 48
120	768	724	- 44
Average Difference			231

Table 19
MATERIAL BALANCE DATA FOR THE FOUR REACTORS

Reactor	Daily Average Feed to the Reactor		Daily Average Withdrawal from the Reactors (g)			Grams of Dry Solids per Gram of Nitrate
	(g NO ₃ ⁻ /day)	(g liq/day)	Solids and Water	Filtered Cake	Dry Cake	
Mini II	333.6	2242	2629	1307	275	0.82
Mini III	247.0	2243	2760	1190	173	0.72

Chemical Analysis of the Feed Solution

Feed	Uranium Content (μg/g)	Total Nitrate (%)	Specific Gravity	Impurity Content (%)									
				Al	Ca	Mg	Cu	Fe	Na	Cl	Li	CO ₂	Organic Carbon
12	< 0.04	14.13	1.163	0.92	3.47	0.27	0.001	0.11	0.035	-	0.006	-	-
13	< 0.04	13.88	-	0.94	3.54	0.27	0.001	0.12	0.034	-	0.007	-	-
14	-	13.70	1.160	1.26	3.56	0.04	-	0.03	0.11	0.007	0.006	-	-
Average	< 0.04	13.90	1.161	1.04	3.52	0.19	0.001	0.09	0.06	0.007	0.006	-	-

Chemical Analysis of the Discharge from the Reactors (dried solids in the effluent)

Reactor	Impurity Content (%)									
	Ca	Mg	Al	Fe	P	Na	K	Li	CO ₂	Organic Carbon
Mini II(1)	13.63	0.55	10.67	0.62	-	0.17	-	0.016	19.89	7.56
Mini III(2)	13.68	0.57	10.14	0.59	-	0.16	-	0.015	21.14	6.23
Mini II(3)	14.90	0.50	9.38	0.58	-	0.14	-	0.02	21.56	6.49
Mini III(3)	19.53	2.44	7.31	0.06	0.28	0.04	0.30	0.02	-	-
Mini IV(3)	16.97	2.91	8.54	0.06	0.38	0.06	0.53	0.04	-	-

Solution from the Reactor after Filtration

Reactor	Impurity Content (%)							
	Total NO ₃ ⁻	Al	Ca	Mg	Na	K	Li	Organic Carbon
Mini IV	0.017	< 0.01	0.04	0.30	0.02	0.04	0.01	0.43

- (1) Dried solids taken from the bottom of the reactor.
 (2) Dried solids taken from the reactor solution.
 (3) Dried solids taken from the overflow stream.

value from Mini II cannot be explained since it was impossible to remove this amount of aluminum based on the available chemical analysis data.

Solids were deposited inside of the reactor vessel; and, after a nominal 100-day test, the vessels were opened for inspection. The chemical composition of these solids, given in Table 19, was equivalent to the solids removed in the discharge stream, which was expected. The amount of solids deposited in the reactor was not exactly determined, but an approximate weight per day indicated that the amount of solids in the reactor after the 100-day tests was equal to the amount which was leaving the reactor. The amount of solids to be deposited in the plant-sized unit cannot be estimated from the laboratory studies since the plant unit will not have the same surface area-to-liquid volume ratio as the laboratory unit.

PILOT-PLANT STIRRED-BED REACTOR STUDIES

Introduction

Due to the success of the laboratory stirred-bed reactors, a 15 m³ vessel was modified to serve as a pilot plant. A schematic diagram and a photographic view of the system are provided in Figures 18 and 19. Feeds to the pilot plant consisted, initially, of neutralized slurries of the nitrate acidic wastes from the plant. Later studies used nitric acid and acidified aluminum nitrate (AAN).

Initially, the pilot plant was operated on a batch basis (from August through October 1973). After some equipment modifications, continuous-flow studies were conducted (from February to August 1974). In order for a facility to be attractive, it must demonstrate a capability for continuous operation, have minimum equipment failures, and be relatively free from toxic effects induced by abrupt changes in the feed composition, pH,

Table 20
SOLIDS REMOVAL CALCULATIONS

<u>Mini II</u>			
Feed to Reactor	Liquid Volume (g/day)		2242
	Calcium (%)		3.52
	Aluminum (%)		1.04
	Equivalent Calcium Carbonate (g/day)		1.97
	Equivalent Aluminum Hydroxide (g/day)		58
	Total Solids (g/day)		255
Feed from Reactor	Weight Dry Solids (g/day)		275
	Calcium (%)		13.63
	Aluminum (%)		10.67
	Equivalent Calcium Carbonate (g/day)		93.7
	Equivalent Aluminum Hydroxide (g/day)		73.4
	Total Solids (g/day)		167.1
	CaCO ₃ Recovered (%)		47.6
	Al(OH) ₃ Recovered (%)		126.6
<u>Mini III</u>			
Feed to Reactor	Liquid Volume (g/day)		2243
	Calcium (%)		3.52
	Aluminum (%)		1.04
	Equivalent Calcium Carbonate (g/day)		197
	Equivalent Aluminum Hydroxide (g/day)		58
	Total Solids (g/day)		255
Feed from Reactor	Weight Dry Solids (g/day)		275
	Calcium (%)		19.5
	Aluminum (%)		7.8
	Equivalent Calcium Carbonate (g/day)		86.8
	Equivalent Aluminum Hydroxide (g/day)		34.7
	Total Solids (g/day)		121.5
	CaCO ₃ Recovered (%)		44.1
	Al(OH) ₃ Recovered (%)		59.8
<u>Combined Mini II and Mini III</u>			
	CaCO ₃ Recovered (%)		45.8
	Al(OH) ₃ Recovered (%)		93.2

temperature, or other unknown effects. This section of the report describes the operation of the continuous-flow, stirred-bed pilot-plant reactor.

Figure 18. PRINCIPAL COMPONENTS IN THE BIODENITRIFICATION PILOT PLANT.

Experimental Work

Batch Operation of the Pilot Plant - Eight batch-type experimental biodenitrification runs were successfully completed in the pilot-plant facility over a three-month operating period (August through October 1973). Individual batch operations varied from 4 to 22 days in duration, depending on the operating conditions. Reaction kinetics was dependent on a number of parameters such as: feed rates, cell-growth rates, nutrient concentrations and ratios, and variations in temperature and pH. Varying degrees of biological shock can occur in the system if any of these parameters are abruptly or drastically changed.

Data from a typical biodenitrification pilot plant run are given in Table 21. The feed material used in this batch run was Y-12 Plant evaporator condensate neutralized with lime hydrate and supplied as calcium acetate solution and trisodium phosphate. Daily nitrate ion, total carbon, and TOC concentrations are noted in Table 21. Curves showing progressive carbon-to-nitrogen ratios (C/N) versus the percent nitrate reduction and a plot of daily temperature variations with nitrate reduction rates are given in Figures 20 and 21.

Lime hydrate-neutralized solution was difficult to prepare in the available neutralization equipment, particularly when plant raffinate effluents were neutralized. The gel-like

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Figure 19. BIODENITRIFICATION PILOT-PLANT FACILITY.

precipitate was a heterogeneous, sticky, and lumpy mass that was difficult to convert to a homogeneous, free-flowing slurry without vigorous agitation or excessive dilution.

Because of the difficulties associated with lime hydrate neutralization of raffinates, flake sodium hydroxide was dissolved in water and added to a 1:1 solution of water and raffinate. Neutralization with sodium hydroxide was far less complicated and formed a slurry that was more readily pumped than the lime hydrate slurries. Also, the final carbonate effluent solution could be readily pumped back to the neutralization tank for reuse, if desired. Tests showed, however, that the calcite sludge produced in the reactor could be used equally as well to neutralize raffinate when properly slurried. Later, experimental tests also indicated that raw condensates and raffinates could be pumped directly into the reactor, there being sufficient hydroxide and carbonate ions in solution with calcite in the reactor to effect neutralization. This procedure was followed in subsequent continuous operations with injections of 70% nitric acid or acidified aluminum nitrate.

Results from a batch run using flake sodium hydroxide to neutralize raffinate are presented in Table 22. In comparing the two runs, many similarities are evident; however, there was a significant reduction in the carbon-to-nitrogen ratio (C/N) which was 0.8:1 for the sodium hydroxide batches versus a C/N of 1.11:1 for the lime hydrate-neutralized batches.

Table 21
PILOT-PLANT OPERATING CONDITIONS AND PERFORMANCE
(Run 4; Tank Volume, 14,440 dm³)

Date (1973)	Time	Nitrate Concentration		Total Organic Carbon		Hydrogen Ion Concentration (pH)	Offgas Evolution Rate (m ³ /hr)	Temperature (K)
		(wt %)	(kg)	(wt %)	(kg)			
8-21	1400	1.0151	146.6	0.1825	26.4	6.9	0.030 - 0.170	303
8-21	2000	0.9802	141.5	0.1750	25.3	6.8	0.270 - 0.680	303
8-22	0800	0.8956	129.3	0.1188 ⁽¹⁾	17.2	6.7	0.250 - 0.350	303
8-22	1600	1.3625	196.7	0.1688	32.4	7.0	0.360 - 0.520	303
8-23	0800	1.0354	149.5	0.3866 ⁽¹⁾	48.6	7.0	0.340 - 0.500	304
8-24	1030	0.5177	74.8	0.2588	37.4	7.0	0.610 - 0.680	307
8-25	1500	0.0720	10.4	0.1538	22.2	8.7	0.300 - 0.400	309
8-26	1500	0.0415	6.0	0.1513	21.8	8.9	0.030 - 0.100	311
8-27	0800	0.0393	5.7	0.1538	22.2	8.8	0.030 - 0.040	307

$$(146.6 - 129.3) + (196.7 - 5.7) = 208.3 \text{ kg (nitrate conversions)}$$

$$(26.4 - 22.2) + 47.7 = 51.9 \text{ kg (TOC consumed)}$$

$$208.3 \times 0.2259 = 47.05 \text{ kg N}$$

$$\text{C/N Consumptive Ratio} = 51.9/47.05 = 1.10:1$$

$$\text{C/N Molar Ratio} = 1.29:1$$

(1) Net addition, 47.7 kg.

X-ray diffraction patterns of composited sludge samples removed from the bottom of the suspended-bed reactor (Table 23) indicated that the major constituent in the dry sludge was calcite (CaCO_3) with a hexagonal crystal structure. These composites of naturally thickened sludges contained residues from six batch runs using lime hydrate and one batch run using sodium hydroxide for neutralization.

No X-ray pattern for Na_2CO_3 was detected, due to its solubility. Aluminum, which was one of the major chemical components in the spectrographic analysis (Table 23), did not show

Figure 20. PROGRESSIVE DENITRIFICATION VERSUS THE CARBON-TO-NITROGEN RATIOS.

in the X-ray pattern due to the amorphous nature of aluminum hydrate. Moisture determinations on this settled sludge after two weeks and decanting excess water indicated that the sludge contained 36% solids. Spectrochemical analyses (Table 23) of the two composite dry residue samples are very similar in composition, with calcium, aluminum, and carbon predominating. Lesser quantities of iron, potassium, magnesium, sodium, phosphorus, and silicon (which are classified as micronutrients),

Table 23
ANALYSES OF CUMULATIVE DRIED RESIDUES

Runs (%)			Runs (%)		
Element	6	7	Element	6	7
<u>Spectrographic</u>					
Ag	< 0.005	< 0.005	Na	0.3	1.0
Al	2.5	1.5	Nb	< 0.02	< 0.02
Au	< 0.02	< 0.02	Ni	< 0.01	< 0.01
B	< 0.01	< 0.01	P	< 1.0	< 1.0
Ba	< 0.002	< 0.002	Pb	< 0.01	< 0.01
Be	< 0.001	< 0.001	Pd	< 0.002	< 0.002
Bi	< 0.01	< 0.01	Rb	< 0.15	< 0.15
Ca	> 20.0	> 20.0	Sb	< 0.04	< 0.04
Cd	< 0.04	< 0.04	Si	0.25	0.08
Co	< 0.005	< 0.005	Sn	< 0.005	0.01
Cr	< 0.01	< 0.01	Ta	< 0.15	< 0.15
Cs	< 0.6	< 0.6	Th	< 0.04	< 0.04
Cu	< 0.005	< 0.005	Ti	< 0.01	< 0.01
Fe	0.3	0.05	U ⁽¹⁾	0.0002	0.00003
Hf	< 0.02	< 0.02	V	< 0.005	< 0.005
K	0.04	0.08	W	< 0.08	< 0.08
Mg	0.5	0.3	Zn	< 0.08	< 0.08
Mn	0.01	0.005	Zr	< 0.002	< 0.002
<u>Chemical</u>					
C	1.0	1.110	NO ₃ ⁻⁽²⁾	0.205	0.136
Ca		29.88	CO ₃ ⁻²		46.23
N	0.202	2.58	LOD ⁽³⁾	6.32	2.40

X Ray

CaCO₃ (calcite), hexagonal structure

- (1) By fluorimetric uranium analyses.
 (2) Water-soluble NO₃⁻ leached from dried solids.
 (3) LOD - loss on drying, after initial air drying.

effluents. Similar results occur when sodium hydroxide is used to neutralize the raffinates except that final precipitation is limited to the small amount of calcium carbonate originally contained in the organic solution. Sodium carbonate remains in solution because of its solubility. Samples from the suspended bed reactor confirms, in all cases, that a pH rise at the end of the batch run results in subsequent clarification of the reactor solution.

Mass spectrographic analyses of gaseous effluents resulting from biological denitrification are presented in Table 24. The analyses represent gas compositions at various denitrification rates for different batch runs. Run 5 represents idealized reactor conditions, with the offgases consisting primarily of nitrogen and carbon dioxide. The other analyses indicate less than ideal conditions with varying percentages of nitric oxide in the effluent gases.

Table 24
ANALYSES OF GASEOUS EFFLUENTS FROM DENITRIFICATION

Sample Date (1973)	Denitrification Rate		Gaseous Effluent ⁽¹⁾ (vol %)						
	Number of Runs	(g/day/dm ³)	CO ₂	Ar	O ₂	N ₂	H ₂	NO	CH ₄
8-23	4	1.75	68.50	0.0028	0.044	22.85		8.60	
			69.47	0.0019	0.042	21.82		8.67	
9-4	5	3.25	32.22	0.006	0.05	67.69		0.03	
			31.82	0.0003	0.05	68.10		0.03	
9-5	5	2.90	38.30	< 0.0005	0.03	58.77		2.90	
			37.30	< 0.0005	0.03	57.77		2.89	
10-24	8	5.4	26.42	0.04	0.10	67.00	0.03	5.43	0.98
			26.42	0.04	0.10	67.00	0.03	5.43	0.98

- (1) Analyses are by mass spectrometry.

Calculations based on recorded temperature reading observed during periods of steady-state denitrification operation indicate that the heat of reaction is approximately 65.6 kcal per gram mole of nitrate decomposed. Because of this energy release, the reactor temperature ranged from 303 to 311 K, depending on the vigor of the reaction.

Continuous Pilot-Plant Operations - Subsequent to the completion of the eight batch runs in the bionitrification pilot plant, minor modifications were made to permit the facility to operate in a continuous mode. Initial batch operations had adequately demonstrated the feasibility of operating the pilot plant on acid condensates and raffinates (plant acidic nitrate wastes). However, continuous operation of the facility would consume more nitrate wastes than it would be possible to properly withdraw because of uranium criticality safety limitations and the lack of nuclear safe storage tanks to hold the acid wastes until analytical results confirmed that it was safe to introduce the waste solutions into the reactor. Therefore, other sources of nitrate ion were investigated.

Industrial-grade calcium nitrate was available on a tonnage basis. This chemical contained, nominally, 81% calcium nitrate, Table 25. No toxicity from its use was anticipated and none developed, although it contained 4.8 wt % ammonium nitrate. A nominal 546 kg of calcium nitrate was dissolved in 0.6 m³ of water in the dissolver tank to give a dissolved calcium nitrate concentration of 910 kg/m³ (~50 wt %). Nitrate solution was then diluted with water and mixed with proportional quantities of water and either calcium acetate solution or methanol to provide the necessary soluble organic carbon substrate requirement. Adjusted feeds containing approximately 10 wt % ion were then transferred to the 3.8 m³ feed tank for continuous metering into the suspended-bed reactor.

Other sources of nitrate feed materials for the pilot-plant operation were acidified aluminum nitrate solution, approximating the composition of a concentrated raffinate solution (45 to 50% NO₃⁻), and 70% nitric acid. These acidic materials were added directly to the reactor for two reasons: (1) to dissolve the calcite, and (2) to determine their effect in the reactor. There appeared to be no significant biological shock as a result of periodic additions because the acidic materials rapidly reacted with the accumulated basic ions and calcite in the recirculating system or the sludge in the bottom of the reactor. Acidic materials were very effective in dissolving the hard accretions of calcite scale deposited in the piping and pump check valves. Plugged lines and checks were formerly a source of difficulty, resulting in loss of time for maintenance repairs and, if for an extended period of time, it always resulted in hydraulic shock to the microorganisms. During use of acidic feed materials, some decrease in the pH frequently occurred due to carbon dioxide generation resulting from additions of the feed solution. Low pH values were raised by the addition of lime hydrate slurry or sodium hydroxide solution.

Table 25
COMPOSITION OF INDUSTRIAL-
GRADE CALCIUM NITRATE

Chemical	Content (%)
Calcium Nitrate [as Ca(NO ₃) ₂]	81.0
Magnesium Nitrate [as Mg(NO ₃) ₂]	1.0
Ammonium Nitrate [as NH ₄ NO ₃]	4.8
Water [as H ₂ O]	14.0
	(mg/kg)
Insolubles in Water	100
Phosphorus (as P ₂ O ₅)	Nil
Sulfates (as SO ₄ ⁻²)	350
Chlorine (as Cl ⁻)	15
Strontium	Nil
Manganese (as Mn)	20
Sodium (as Na)	100
Iron (as Fe)	2
Copper (as Cu)	0.05
Heavy Metals (as Pb)	1

Phosphates were dissolved in measured volumes of filtered water and the solutions metered into the reactor as required. Experience indicated that most micronutrients were present as impurities in the various feed materials, and supplemental additions were unnecessary.

Gaseous and aqueous effluents leaving the pilot-plant reactor were measured and analyzed to obtain daily material balance data from which it was possible to evaluate the operating performance. Settled solids were removed periodically (in 0.1 m³ withdrawals approximately every ten days) through a bottom drain valve into drums for transport to the solid wastes burial ground.

Continuous operation of the suspended-bed denitrification pilot plant facility began on February 13, 1974. Feed composition was approximately 10 wt % nitrate ion, 2.35 wt % TOC, a pH of 8.76, and a specific gravity of 1.1245. In an initial incubation period, required to develop the biological log-growth phase which is essential for continuous operation, the solution in the suspended-growth reactor analyzed 2.86 wt % nitrate. As a result, minimal feed introduction at a rate of 0.75 g NO₃⁻/day/dm³ was maintained for approximately three days (Table A-13) to reduce the concentration in the reactor. By the third day, the nitrate effluent loss was 0.074 g NO₃⁻/day/dm³ with an average of 7.0 g NO₃⁻/day/dm³ being reduced. An increase in the feed rate was then made as biological activity improved. Average nitrate feed rate for the 15 days of February was 50.97 kg/day (5.1 g/day/dm³) with 48.436 kg/day (4.84 g NO₃⁻/day/dm³) being reduced for a 95.03 % nitrate reduction efficiency. These rates indicated that the reactor performance was exceeding the designed throughput rates of 40 kg/day (4 g NO₃⁻/day/dm³).

By the sixteenth day (March 1, 1974) the biological log growth phase was sufficiently established to support continuous feeding, as evidenced by the high level of nitrate reduction efficiency which followed over the next 50 days of operation, up to April 20, 1974 (Tables A-14 and A-15). Nitrate-reduction efficiencies during this period ranged from 98.42 to 99.97%. Effluent losses were well below 0.1 kg per day (0.01 g/day/dm³) practically every day from March 1 to April 20, 1974. Total nitrate ion reduced was 1777 kg—a daily average of 35.54 kg/day (3.55 g NO₃⁻/day/dm³).

A drastic change in the reduction efficiency occurred on April 20, 1974, brought on by slowly changing the organic feed from calcium acetate to methanol. Prior to this introduction, the microorganisms had become well adjusted to acetate carbon as their energy source. Minimal feeding [15.3 kg (1.5 g/day/dm³) of methanol over 12 days (Table A-15)] was used prior to Day 66, since a gradual transition to methanol was planned. The first evidence that biological shock was occurring was a sharp increase in the nitrate ion in the effluent. This upset resulted in a 9.6% decrease in the nitrate reduction efficiency (to 90.35%). Simultaneously, the nitrate concentration in the reactor recirculating system rose from 0.05 to 2.2 wt % NO₃⁻. Nitrate feed was stopped for the next five days and an additional 92.7 kg (9.27 g CH₃OH/dm³) of methanol carbon were added to alleviate an apparent carbon deficiency. Because of the high effluent nitrate values, the effluent was recycled from April 25 through May 13, 1974, except for one day [April 30, 1974 (Tables A-15 and A-16)]. It soon became apparent that the microorganisms were in a state of shock and methanol carbon was not biologically acceptable as a carbon energy source to the then-existing biological population. The quantity of useable acetate carbon had gradually been exhausted since it had been reduced in quantity in favor of methanol.

Supplemental additions of calcium acetate carbon were resumed throughout the month of May to maintain a viable population of microorganisms. As a result of dual feeding of organic carbon (acetate plus methanol) the TOC rose to approximately 1.7 wt % during May. Analysis indicated that the organic remaining was largely methanol carbon, which was apparently unacceptable to the microorganisms.

A further complication, occurring on April 22, 1974, aggravated the biological shock already induced by a change in the organic feed. A two-inch suction line to the diaphragm pump and its check valves became inoperative due to accumulations of calcite deposits. Approximately 16 hours of maintenance time were required to clean the recirculating system, inducing hydraulic shock to this system. Nitric acid was used to dissolve the calcite deposits by installation of an acid-injection nozzle at the bottom of the reactor in the pump suction line (Figure 18). A total of 115 kg (0.0115 kg/m^3) of nitric acid nitrate were introduced in the lines which were completely cleaned of calcite scale. An additional 57 kg (0.0057 kg/m^3) of acid were added between April 30 and May 12, 1974. This addition was supplemented with approximately 30 kg (0.003 kg/m^3) of calcium acetate carbon (Table A-16). When all effluents were recycled from May 1 through May 12, the nitrate content in the reactor decreased from 1.5 to 0.015 wt %. This change indicated that an active population of microorganisms could be revitalized if the feed contained acetate carbon. With two types of organic carbon being supplied to the reactor, the C/N ratio in the feed rose to 2.5:1. It appeared from the results of daily gas chromatograph analyses that possibly 40% of the methanol was being assimilated along with the acetate carbon, although the latter was more acceptable to the microorganisms. As reported in Table A-16, daily nitrate reductions during early May are 12-day averages because of effluent recycling.

On May 13, 1974 (Day 89, Table A-16), feeding and removal of effluents were resumed. Feed composition introduced was 9.47 wt % nitrate ion as calcium nitrate, 1.6 wt % methanol carbon, and 1.4 wt % acetate carbon. Initially, this effluent contained less than 0.01% NO_3^- ; however, in three days, the effluent rose to 0.4245 wt % nitrate with a drop in reduction efficiency. Recycling was resumed again with further supplemental feeding of calcium acetate carbon. Daily analyses indicated that methanol carbon was increasing in the reactor (0.8 - 0.9 wt %) and that the microorganisms were consuming only the acetate carbon. After the addition of 13 kg of acetate carbon and by recycling the effluent, the nitrate content was again lowered to 0.01 wt %, permitting resumption of continuous feeding through May 27, 1974, at which time recycling of the effluent was again required. During May, the C/N ratio in the feed was 2.12:1, which is based on the two organic substrates employed.

A characteristic of incomplete reaction was the presence of 0.02 to 0.09 wt % nitrite ion in the reactor recirculating system. Nitrite ion concentrations in the reactor during normal efficient operation are usually less than 0.0005%, increasing in value only due to unstable operating conditions. High nitrite values were generally evident when the pH was below 6.8. Above 6.8, nitrite values normally remained low. For example, when the pH values dropped below 6.8, from May 23 to May 29, inclusive (Table A-16), the nitrite concentration in the reactor increased to 0.1 vol % and remained at that level until the pH was maintained consistently above 7.0. High nitrate ion concentration is a precursor for high nitrite ion concentrations in the effluent and, consequently, lower reduction efficiencies.

Due to the difficulty in getting the acetate carbon microorganisms to accept a methanol carbon substrate for cell reproduction and synthesis, overall nitrate reduction in May was reduced to a daily average of 12.69 kgNO₃⁻/day (1.27 g NO₃⁻/day/dm³), compared to 51.0, 37.8, and 27.2 kg/day (5.1, 3.78, and 2.72 g/day/dm³) in February, March, and April, respectively (Tables A-13 through A-16).

Indicative of methanol substrate rejection was the C/N ratio of 2.12:1 for the total carbon feed versus a C/N ratio of 1.14:1 for the calcium acetate carbon input. The latter was comparable to 1.15:1 for both February and March when the substrate electron donor was acetate carbon. It appears that acetate-adjusted microorganisms will require an acclimation period prior to acceptance of a different carbon substrate.

As the month of May ended, very unstable conditions prevailed in the reactor, requiring recycling of the effluent to reduce excessive nitrate loss. Concentrations in the reactor recirculating system were 1.19% nitrate ion, 1.44% TOC, 0.071% nitrite ion, and 0.08% ammonium ion. Due to these high values, no blends of calcium nitrate-calcium acetate feed were used in June. In fact, no organic feed was required throughout June due to the initial high concentration of carbon in the reactor. Nitrate feeds utilized in June (Table A-17) consisted of occasional low-volume injections of 70% nitric acid for calcite removal from the recirculating system, four additions of calcium nitrate solution, and injections of acidified aluminum nitrate (AAN). Due to the absence of any organic and because the nitrate feed materials consisted primarily of concentrated nitrate ions (HNO₃ or AAN), no discards of effluents were made during the entire month of June.

During June, a total of 317.6 kg of nitrate ion were decomposed (Table A-17). The average daily nitrate reduction amounted to 10.59 kg/day (1.06 g NO₃⁻/day/dm³). Likewise, the TOC utilization was 126.66 kg (0.422 g C/day/dm³), resulting in an overall C/N ratio of 1.74:1 for June. It appears from this higher-than-normal consumptive ratio that there was some forced acceptance of methanol carbon. Both the nitrite and ammonium ions were lowered during the month.

As was the case in June, no effluent was withdrawn from the suspended growth reactor in July 1974, also due to continued utilization of concentrated nitrate feeds and minimal additions of organic solution (Table A-18). By July 12, TOC analyses indicated that organic carbon had dropped to 0.51 wt %; however, the nitrate concentration in the reactor had increased from 0.255 to 1.01 wt % after feeding 86.54 kg of AAN and 56.20 kg of calcium nitrate solution. Although the C/N ratio in the reactor was 1.52:1, there appeared to be an insufficiency of carbon (TOC) because the TOC present was largely methanol carbon and was not being utilized by the microorganisms. Further additions of AAN resulted in a further increase in the reactor nitrate concentration (1.2%). Five kilograms of calcium acetate were added on July 18 in an effort to reactivate the microorganisms. An immediate response occurred, with approximately 55 kg of nitrate being reduced over the next 12 days (0.46 g NO₃⁻/day/dm³). An additional 22.6 kg of acetate carbon were added up to the end of July, with a nitrate reduction of 24.58 kg on July 31.

Total nitrate reduced in July was 158.56 kg, a daily average of 5.11 kg/day (0.511 g NO₃⁻/day/dm³). Based on three months of generally unstable operation of the pilot plant

using methanol calcium acetate as the energy substrate, it was concluded that acetate carbon was superior to a methanol acetate carbon substrate under conditions existing in the reactor.

Mass spectrographic analyses of the effluent gases generated in the reactor were taken at intervals to identify the gases involved (Table 26). Sample 1, taken April 2, 1974, represents a typical gas analysis during a period of sustained high-reduction efficiency where effluent gases are largely carbon dioxide and nitrogen. Samples 2, 3, and 4 (taken April 26 and 29) represent deteriorating reactor conditions resulting from the gradual introduction of methanol into the reactor. Nitrogen was being partially replaced by nitric oxide gas. Due to high nitrate analyses, the effluent was being recycled. During this period of operation, the nitrate concentration in the reactor rose from 0.03 to 2.0 wt %, and the nitrite ion increased from 0.0005 to 0.27%. Sample 5 (May 3) was taken during a period when nitrogen gas was being used to pressurize the reactor. Samples 6 through 11 represent gas analyses which showed relatively high methane concentrations in the effluent gases, indicative of unstable reaction kinetics resulting from additions of methanol carbon substrate. As shown by Table 26, methanol also is exerting a slight vapor pressure in the reactor.

Table 26
MASS SPECTROGRAPHIC ANALYSES OF THE EFFLUENT GAS FROM THE REACTOR

Sample Number	Date (1974)	Gas Concentration (vol %)							Remarks
		CO ₂	Ar	O ₂	N ₂	CH ₃ OH	NO	CH ₄	
1	4-2	41.68	0.006	0.16	58.15	-	-	-	After PO ₄ ⁻³ .
2	4-26	40.10	0.01	0.14	48.98	0.07	10.69	-	CH ₃ OH added. Recycling effluent.
3	4-26	49.00	0.01	0.15	37.78	0.09	12.97	-	CH ₃ OH added. Drain sludge; add feed.
4	4-29	60.72	0.01	0.77	23.78	0.23	14.48	-	Recycling.
5	5-3	4.84	0.02	0.06	93.78	0.03	1.25	-	Nitrogen purge.
6	5-14	28.00	-	0.16	65.59	0.14	0.08	6.03	Feeding 50% CH ₃ OH 50% Ca(C ₂ H ₃ O ₂) ₂ .
7	5-15	32.21	0.001	0.19	60.26	0.14	0.56	6.63	Continuous operation.
8	5-16	46.06	0.004	0.15	44.11	0.12	2.78	6.77	Continuous operation.
9	5-17	56.18	0.007	0.33	35.85	0.26	3.92	3.45	Recycling; no effluent.
10	5-20	53.47	0.006	0.24	37.63	0.24	0.53	7.98	Feeding CH ₃ OH + Ca(C ₂ H ₃ O ₂) ₂ .
11	5-24	61.86	0.03	0.30	25.41	0.21	7.30	4.84	Feeding CH ₃ OH + Ca(C ₂ H ₃ O ₂) ₂ .

The reactor tests were stopped on July 31, 1974, but will be reactivated at a later date if additional engineering design data are required.

CONCLUSIONS

Columnar Denitrification Studies

These studies have shown that denitrification of nitrate acid wastes can be successfully accomplished by using columns packed with coal or plastic rings. The system will operate on feeds containing such soluble carbonate salts as sodium, potassium, and ammonium. Insoluble carbonate salts, such as calcium, will cause plugging of the column. Denitrification rates up to 122 grams of nitrate per day per cubic decimeter of packing material were obtained in these studies.

Laboratory Denitrification Studies

Four stirred-bed reactors were operated for a total of 453 days, and design information was obtained for scaleup to a plant-sized unit. Denitrification rates of up to 10 grams of nitrate per day per cubic decimeter of reactor solution were obtained. The following conclusions can be made from these studies:

Mini I Reactor - It was demonstrated that:

1. Denitrification of calcium nitrate using calcium acetate as the carbon source was successful.
2. Gravity feed systems were not satisfactory because the low liquid flows to the reactor could not be adequately controlled or maintained.
3. Feed solutions containing 10 to 14 wt % nitrate ions were successfully fed to the reactor.
4. The carbon-to-nitrogen mole ratio in the feed and in the reactor solution is an important variable. The data suggest that a low C/N mole ratio and also a very high C/N mole ratio may be detrimental. A "best-guess" satisfactory C/N mole ratio in the reactor range may be 20 to 100.
5. The system requires phosphate ions, and a level of 5 $\mu\text{g/g}$ appears to be satisfactory.

Mini II Reactor - The first 30 days of reactor operation were used to start the reaction. Continuous feed was started, but a valve failure occurred and a large volume of acid feed was dumped into the vessel. The pH of the solution was adjusted with calcium hydroxide; and, within 12 days, continuous feed was resumed (Day 50). From this date, the reactor satisfactorily operated 74 days out of a total of 83 test days.

Mini III Reactor - Exclusive of the first 50 days of the test period, the Mini III reactor operated 150 test days. During this 150-day period, the feed flow was turned off four times for a total of seven days with the maximum period being three days. The exact reasons for the four shutdowns are not fully understood, but two of them are believed to have been caused by an excessive amount of organic carbon in the denitrification vessel.

Mini IV Reactor - Mini IV operated satisfactorily for 114 test days out of a total 134 test-day period. The reactor flow was temporarily cut off or reduced for one or more days when high nitrates were noted in the effluent from the reactor.

Pilot-Plant Stirred-Bed Studies

A 15 m³-sized vessel was successfully operated as a stirred-bed denitrification reactor. The denitrification rate obtained on this unit was 10 grams of nitrate per day per cubic decimeter of reactor solution, which is the same as that found on the laboratory-sized vessels.

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APPENDIX
OPERATIONAL DATA ON THE FOUR MINI REACTORS

Table A-1
REDUCTION OF NITRATE IN THE MINI I REACTOR

Day	Nitrate Feed to the Reactor		Nitrate from the Reactor		Nitrate Reduced (g NO ₃ ⁻ /day/dm ³)	Nitrate Reduction (%)
	(g NO ₃ ⁻ /day)	(g NO ₃ ⁻ /day/dm ³)(11)	(μg NO ₃ ⁻)	(g NO ₃ ⁻ /day/dm ³)		
1	Startup of the Reactor					
2	0	-	-	-	-	-
3	0	-	-	-	-	-
4	-	-	-	-	-	-
5	-	-	-	-	-	-
6	-	-	-	-	-	-
7	0	-	-	-	-	-
8	0	-	-	-	-	-
9	0	-	-	-	-	-
10	0	-	-	-	-	-
11	-	-	-	-	-	-
12	-	-	-	-	-	-
13	0	-	-	-	-	-
14	0	-	359	0.0056	-	-
15	95	1.68	224	0.0034	1.377	99.80
16	105.6	1.85	300	0.0050	1.345	99.73
17	141.6	2.48	183	0.0041	2.476	99.84
18	345.6	6.06	-	-	-	-
19	326.4	5.73	-	-	-	-
20	297.6	5.22	239	0.0013	5.209	99.78
21	492.0	8.63	< 1	-	-	-
22	549.6	9.64	19	0.0017	9.338	99.98
23	568.8	9.98	276	0.0250	9.355	99.75
24	444.0	7.79	975	0.0690	7.721	99.11
25	412.8	7.24	-	-	-	-
26	376.8	6.61	-	-	-	-
27	-	-	-	-	-	-
28	268.8	4.72	1895	0.0813	4.339	98.28
29	537.6	9.43	6823	0.5832	8.3477	93.8
30	297.6	5.22	2998	0.1417	5.0783	97.3
31	324.0	5.68	1085	0.0560	5.3240	99.0
32	362.4	6.36	-	-	-	-
33	314.4	5.52	-	-	-	-
34	271.2	4.76	261	0.0013	4.7487	99.8
35	396.0	6.95	1846	0.1162	6.3338	98.3
36	648.0	11.37	340	0.0350	11.3350	99.7
37	532.8	9.35	221	0.0177	9.3323	99.8
38	1056.0	18.53	136	0.0228	18.2072	98.3
39	1332.0	23.37	10358	2.1940	21.1760	90.6
40	1190.4	20.88	-	-	-	-
41	964.8	16.93	-	-	-	-
42	0	0	13346	-	-	-
43	0	0	12837	-	-	-
44	0	0	13584	-	-	-
45	0	0	8864	-	-	-
46	0	0	-	-	-	-
47	0	0	-	-	-	-
48	0	0	7811	-	-	-
49	0	0	5773	-	-	-
50	0	0	5094	-	-	-
51	Startup of the Reactor					
52	177.6	3.12	91	0.0026	3.1174	99.9
53	213.6	3.75	-	-	-	-
54	-	-	-	-	-	-
55	201.6	3.54	102	0.0033	3.5367	99.9
56	187.2	3.28	136	0.0040	3.276	99.9
57	163.2	2.86	< 200	0.0052	2.8548	99.8
58	158.4	2.79	< 200	0.0050	2.785	99.8
59	196.8	3.45	< 200	0.0063	3.4437	99.8
60	189.6	3.33	-	-	-	-
61	-	-	-	-	-	-
62	204.0	3.58	< 200	0.0065	3.5735	99.8
63	180.0	3.16	< 200	0.0057	3.1543	99.8
64	252.0	4.42	272	0.0109	4.4091	99.8
65	244.8	4.29	306	0.0119	4.2781	99.7
66	415.2	7.28	29	0.0019	7.2781	99.9
67	-	-	-	-	-	-
68	-	-	-	-	-	-
69	393.6	6.91	35	0.0022	6.9078	99.9
70	400.8	7.03	50	0.0032	7.0268	99.9
71	357.6	6.27	40	0.0023	6.2677	99.9
72	321.6	5.64	42	0.0021	5.6379	99.9
73	336.4	5.94	59	0.0032	5.9368	99.9
74	-	-	-	-	-	-
75	-	-	-	-	-	-
76	237.6	4.17	70	0.0026	4.1674	99.9
77	326.4	5.73	79	0.0041	5.259	99.9
78	333.6	5.85	87	0.0046	5.8454	99.9
79	96.0	1.68	78	0.0012	1.6788	99.9
80	-	-	-	-	-	-
81	192.0	3.37	-	-	-	-
82	-	-	-	-	-	-
83	266.4	4.67	4143	0.1755	4.4945	96.2
84	0	0	679	-	-	-
85	26.4	0.46	-	-	-	-
86	184.8	3.24	146	0.0043	3.2357	99.9
87	40.8	0.72	127	0.0008	0.7192	99.9
88	348.0	6.11	-	-	-	-
89	-	-	-	-	-	-
90	314.4	5.52	107	0.0053	5.5147	99.9
91	350.4	6.15	102	0.0057	6.1443	99.9
92	338.4	5.94	110	0.0059	5.9341	99.9
93	321.6	5.64	249	0.0127	5.6273	99.8
94	321.6	5.64	110	0.0056	5.6344	99.9
95	-	-	-	-	-	-
96	-	-	-	-	-	-
97	338.4	5.94	134	0.0072	5.9328	99.9
98	348.0	6.11	165	0.0091	6.1009	99.9
99	316.8	5.56	200	0.0101	5.5499	99.8
100	456.0	8.00	138	0.0100	7.9900	99.9
101	422.4	7.41	127	0.0085	7.4015	99.9
102	-	-	-	-	-	-
103	432.0	7.58	-	-	-	-
104	408.0	7.16	127	0.0082	7.1518	99.9
105	398.4	6.99	141	0.0089	6.9311	99.9
106	384.0	6.74	144	0.0088	6.7312	99.9
107	362.4	6.36	135	0.0078	6.3522	99.9
108	328.8	5.77	175	0.0091	5.7309	99.8
109	360.0	6.32	-	-	-	-
110	-	-	-	-	-	-
111	343.2	6.02	136	0.0074	6.0128	98.6
112	-	-	106	-	-	-
113	316.8	5.56	102	0.0051	5.5549	99.9
114	324.0	5.68	126	0.0065	5.6735	99.9
115	463.2	3.13	462	0.0340	8.0960	99.6
116	444.0	7.79	-	-	-	-
117	0	0	-	-	-	-
118	0	0	171	-	-	-
119	446.4	7.83	122	0.0086	7.8214	99.9
120	376.8	6.61	115	0.0069	6.6031	99.9
121	355.2	6.23	121	0.0068	6.2232	99.9
122	352.8	6.19	134	0.0075	6.1825	99.9
123	-	-	-	-	-	-
124	-	-	-	-	-	-
125	417.6	7.33	-	-	-	-
126	-	-	34	-	-	-
127	-	-	136	-	-	-
128	458.4	8.04	110	0.0080	8.032	99.9
129	536.0	11.16	1330	0.1345	11.03	98.8
130	0	0	-	-	-	-
131	0	0	-	-	-	-
132	540.0	9.47	-	-	-	-
133	0	0	900	-	-	-
134	0	0	1000	-	-	-
135	0	0	900	-	-	-

(1) g NO₃⁻/day/dm³ is defined as grams of nitrate per day per dm³ of reactor solution. Volume of reactor was 0.057 m³.

Table A-3
MINI I GAS ANALYSIS

Test Day	Nitrate to the Reactor (g NO ₃ ⁻ /day/dm ³)(1)	Gas Flow from the Reactor (dm ³ /g NO ₃ ⁻ to reactor)	Gas Composition (% CO ₂)(2)	Amount of CO ₂ (dm ³ CO ₂ /g NO ₃ ⁻ to reactor)	Amount of N ₂ (dm ³ N ₂ /g NO ₃ ⁻ to reactor)(3)
1	Startup of the Reactor				
2	0	-	-	-	-
3	0	-	-	-	-
4	0	-	-	-	-
5	0	-	-	-	-
6	0	-	-	-	-
7	0	-	-	-	-
8	0	-	-	-	-
9	0	-	-	-	-
10	0	-	-	-	-
11	0	-	-	-	-
12	0	-	-	-	-
13	0	-	-	-	-
14	0	-	-	-	-
15	1.68	0.221	-	-	-
16	1.85	0.179	-	-	-
17	2.48	0.100	-	-	-
18	6.06	0.188	-	-	-
19	5.73	0.222	-	-	-
20	5.22	0.189	-	-	-
21	8.63	0.177	-	-	-
22	9.64	0.269	-	-	-
23	9.98	0.368	-	-	-
24	7.79	0.355	-	-	-
25	7.24	0.339	-	-	-
26	6.61	0.359	-	-	-
27	-	-	-	-	-
28	4.72	0.311	-	-	-
29	9.43	0.94	92	-	-
30	5.22	0.568	-	-	-
31	5.68	0.362	-	-	-
32	6.36	0.377	-	-	-
33	5.52	0.362	-	-	-
34	4.76	0.346	-	-	-
35	6.95	0.341	-	-	-
36	11.37	0.299	-	-	-
37	9.35	0.314	46.5	0.146	0.168
38	18.53	0.312	94	0.293	0.013
39	23.37	0.215	-	-	-
40	20.88	0.199	-	-	-
41	16.93	0.096	-	-	-
42	0	-	-	-	-
43	0	-	-	-	-
44	0	-	-	-	-
45	0	-	-	-	-
46	0	-	-	-	-
47	0	-	-	-	-
48	0	-	-	-	-
49	0	-	-	-	-
50	0	-	2.5	-	-
51	Startup of the Reactor	-	13.5	-	-
52	3.12	0.235	25	0.059	0.176
53	3.75	0.277	41.5	0.115	0.162
54	-	-	-	-	-
55	3.54	0.293	43	0.126	0.167
56	3.28	0.320	43	0.138	0.182
57	2.86	0.326	45	0.147	0.179
58	2.79	0.374	46	0.172	0.202
59	3.45	0.300	46	0.138	0.162
60	3.33	0.320	43	0.138	0.182
61	-	-	-	-	-
62	3.58	0.305	44	0.134	0.171
63	3.16	0.320	42	0.134	0.186
64	4.42	0.308	43.5	0.134	0.174
65	4.29	0.327	46	0.150	0.177
66	7.28	0.293	44	0.129	0.164
67	-	-	-	-	-
68	-	-	-	-	-
69	6.91	0.278	44	0.122	0.156
70	7.03	0.290	43	0.125	0.165
71	6.27	0.310	43	0.133	0.177
72	5.64	0.329	47	0.155	0.174
73	5.94	0.302	48	0.145	0.157
74	-	-	-	-	-
75	-	-	-	-	-
76	4.17	0.285	47.5	0.135	0.150
77	5.73	0.244	45.5	0.111	0.133
78	5.85	0.191	44.5	0.085	0.106
79	1.68	0.095	50	0.47	0.47
80	-	-	-	-	-
81	3.37	0.165	54	0.89	0.76
82	-	-	-	-	-
83	4.67	0.339	88	0.298	0.41
84	0	-	7	-	-
85	0.46	0.506	11	0.056	0.450
86	3.24	0.352	25	0.088	0.264
87	0.72	0.178	40	0.071	0.107
88	6.11	0.310	42	0.130	0.180
89	-	-	-	-	-
90	5.52	0.331	36.5	0.121	0.210
91	6.15	0.347	43	0.149	0.198
92	5.94	0.347	44	0.153	0.194
93	5.64	0.341	48	0.164	0.177
94	5.64	0.343	46	0.158	0.185
95	-	-	38.3	-	-
96	-	-	40.0	-	-
97	5.94	0.360	46	0.166	0.194
98	6.11	0.343	78	0.267	0.076
99	5.56	0.384	42	0.161	0.223
100	8.00	0.280	41.5	0.116	0.164
101	7.41	0.233	46	0.107	0.126
102	-	-	-	-	-
103	7.58	0.245	42.5	0.104	0.141
104	7.16	0.250	43	0.107	0.143
105	6.99	0.241	48.5	0.117	0.124
106	6.74	0.229	54.5	0.125	0.104
107	6.36	0.231	66	0.152	0.079
108	5.77	0.188	50	0.094	0.094
109	6.32	0.299	-	-	-
110	-	-	46	-	-
111	6.02	0.289	43	0.124	0.165
112	-	-	49	-	-
113	5.56	0.281	47.5	0.133	0.148
114	5.68	0.257	52	0.134	0.123
115	8.13	0.215	85	0.183	0.032
116	7.79	0.162	78	0.126	0.036
117	0	-	22	-	-
118	0	-	25.5	-	-
119	7.83	0.234	37	0.086	0.148
120	6.61	0.263	41	0.108	0.155
121	6.23	0.277	41	0.114	0.163
122	6.19	0.263	43	0.113	0.150
123	-	-	38.5	-	-
124	-	-	36.5	-	-
125	7.33	0.217	34.5	0.075	0.142
126	-	-	38.0	-	-
127	-	-	32.5	-	-
128	8.04	0.229	35	0.080	0.149
129	11.16	0.249	61	0.152	0.097
130	0	-	64	-	-
131	0	-	16	-	-
132	9.47	0.395	6	0.024	0.371
133	0	-	-	-	-
134	0	-	82	-	-
135	0	-	-	-	-

(1) g NO₃⁻/day/dm³ is defined as grams of nitrate per day per dm³ of reactor solution. Volume of reactor was 57 dm³.
(2) % CO₂ obtained using gas chromatograph (see text for additional information).
(3) Amount of N₂ obtained by subtracting amount of CO₂ from the total gas flow.

Table A-4
REDUCTION OF NITRATE IN THE MINI II REACTOR

Test Day	Nitrate Feed to the Reactor		Nitrate from the Reactor		Nitrate Reduced	Nitrate Reduction
	(g NO ₃ ⁻ /day)	(g NO ₃ ⁻ /day/dm ³)	(μg NO ₃ ⁻ /g)	(g NO ₃ ⁻ /day/dm ³)	(g NO ₃ ⁻ /day/dm ³)	(%)
1	Startup of the Reactor					
2	-	-	256	0.0008	0.4992	99.84
3	0.5	0.01	54	0.0010	6.539	99.98
4	6.54	0.11	1358	-	-	-
5	Batch Fed	-	-	-	-	-
6	Batch Fed	-	-	-	-	-
7	Batch Fed	-	7471	-	-	-
8	Batch Fed	-	6249	-	-	-
9	Batch Fed	-	5773	-	-	-
10	Batch Fed	-	5668	-	-	-
11	Batch Fed	-	-	-	-	-
12	Batch Fed	-	-	-	-	-
13	Stirrer Stopped	-	-	-	-	-
14	Stirrer Stopped	-	5298	-	-	-
15	Stirrer Stopped	-	5502	-	-	-
16	Stirrer Stopped	-	-	-	-	-
17	Stirrer Stopped	-	-	-	-	-
18	Stirrer Stopped	-	5705	-	-	-
19	Stirrer Stopped	-	-	-	-	-
20	Stirrer Stopped	-	-	-	-	-
21	Stirrer Stopped	-	1027	-	-	-
22	Stirrer Stopped	-	263	-	-	-
23	Stirrer Stopped	-	204	-	-	-
24	Stirrer Stopped	-	208	-	-	-
25	Stirrer Stopped	-	195	-	-	-
26	Stirrer Stopped	-	-	-	-	-
27	Stirrer Stopped	-	-	-	-	-
28	Stirrer Stopped	-	119	-	-	-
29	Stirrer Stopped	-	57	-	-	-
30	Stirrer Stopped	-	272	-	-	-
31	261.6	4.59	30	0.0011	4.589	99.98
32	261.6	4.59	490	0.0186	4.571	99.59
33	261.6	4.59	-	-	-	-
34	261.6	4.59	-	-	-	-
35	276.0	4.84	25	0.0010	4.839	99.98
36	367.2	6.44	47	0.0018	6.438	99.97
37	367.2	6.44	53	0.0027	6.437	99.96
38	Feed Valve Failed	-	11988	-	-	-
39	-	-	12056	-	-	-
40	-	-	-	-	-	-
41	-	-	-	-	-	-
42	-	-	< 200	-	-	-
43	-	-	176	-	-	-
44	-	-	132	-	-	-
45	-	-	160	-	-	-
46	-	-	-	-	-	-
47	-	-	-	-	-	-
48	-	-	-	-	-	-
49	-	-	106	-	-	-
50	242.4	4.25	95	0.0032	4.247	99.92
51	218.4	3.83	106	0.0032	3.827	99.92
52	196.8	3.45	94	0.0026	3.447	99.92
53	196.8	3.45	103	0.0028	3.447	99.92
54	242.4	4.25	-	-	-	-
55	199.2	3.49	-	-	-	-
56	208.8	3.66	-	-	-	-
57	-	-	234	-	-	-
58	196.8	3.45	391	0.0107	3.439	99.70
59	206.4	3.62	117	0.0034	3.617	99.91
60	192.0	3.37	107	0.0029	3.367	99.91
61	-	-	-	-	-	-
62	256.8	4.51	19	0.0007	4.509	99.98
63	268.8	4.72	30	0.0011	4.719	99.98
64	256.8	4.51	-	-	-	-
65	273.6	4.80	-	-	-	-
66	230.4	4.04	90	0.0029	4.037	99.93
67	273.6	4.80	-	-	-	-
68	259.2	4.55	-	-	-	-
69	249.6	4.38	-	-	-	-
70	240.0	4.21	136	0.0041	4.206	99.90
71	295.2	5.18	170	0.0063	5.174	99.88
72	261.6	4.59	50	0.0016	4.588	99.96
73	273.6	4.80	107	0.0037	4.796	99.92
74	273.6	4.80	62	0.0021	4.798	99.96
75	273.6	4.80	-	-	-	-
76	249.6	4.38	-	-	-	-
77	252.0	4.42	126	0.0040	4.416	99.91
78	232.8	4.08	95	0.0028	4.077	99.93
79	273.6	4.80	68	0.0023	4.798	99.95
80	52.8	0.93	20	0.0001	0.9299	99.99
81	50.4	0.88	19	0.0001	0.8799	99.99
82	103.2	1.81	-	-	-	-
83	100.8	1.77	-	-	-	-
84	103.2	1.81	30	0.0004	1.8096	99.98
85	156.0	2.74	200	0.0043	2.736	99.84
86	160.8	2.82	40	0.0009	2.819	99.97
87	196.8	3.45	31	0.0008	3.449	99.98
88	249.6	4.38	360	0.0124	4.368	99.72
89	249.6	4.38	32	0.0011	4.379	99.97
90	273.6	4.80	34	0.0012	4.799	99.98
91	273.6	4.80	35	0.0012	4.799	99.98
92	273.6	4.80	35	0.0012	4.799	99.98
93	280.8	4.93	35	0.0013	4.929	99.97
94	-	-	-	-	-	-
95	264.0	4.63	39	0.0014	4.629	99.97
96	268.8	4.72	-	-	-	-
97	-	-	-	-	-	-
98	283.2	4.97	38	0.0014	4.969	99.97
99	331.2	5.81	40	0.0017	5.808	99.97
100	333.6	5.85	30	0.0017	5.848	99.97
101	328.8	5.77	42	0.0018	5.768	99.97
102	326.4	5.73	40	0.0016	5.728	99.97
103	324.0	5.68	35	0.0014	5.679	99.98
104	-	-	-	-	-	-
105	309.6	5.43	44	0.0017	5.428	99.97
106	309.6	5.43	42	0.0016	5.428	99.97
107	288.0	5.05	54	0.0020	5.048	99.96
108	544.8	9.56	55	0.0038	9.556	99.96
109	561.6	9.85	60	0.0041	9.846	99.96
110	-	-	59	-	-	-
111	-	-	-	-	-	-
112	398.4	6.99	60	0.0038	6.986	99.95
113	238.0	4.00	2445	0.1079	3.892	97.30
114	0	-	1562	-	-	-
115	0	-	1380	-	-	-
116	0	-	859	-	-	-
117	0	-	920	-	-	-
118	0	-	-	-	-	-
119	0	-	662	-	-	-
120	0	-	652	-	-	-
121	0	-	565	-	-	-
122	0	-	475	-	-	-
123	0	-	80	-	-	-
124	177.6	3.12	-	-	-	-
125	170.4	2.99	-	-	-	-
126	170.4	2.99	136	0.0028	2.987	99.91
127	182.4	3.20	425	0.0094	3.191	99.71
128	175.2	3.07	122	0.0026	3.067	99.92
129	165.6	2.91	93	0.0019	2.908	99.93
130	482.4	8.46	100	0.0059	8.454	99.93
131	504.0	8.84	96	0.0059	8.834	99.93
132	451.2	7.92	80	0.0044	7.916	99.94
133	427.2	7.49	119	0.0062	7.484	99.92

Table A-5
COMPOSITION OF LIQUID FROM THE MINI II REACTOR

Test Day	Analysis of Liquid from the Reactor (µg/g)					Test Day	Analysis of Liquid from the Reactor (µg/g)				
	NO ₃ ⁻	TOC	NO ₂ ⁻	NH ₄ ⁺	PO ₄ ⁻³		NO ₃ ⁻	TOC	NO ₂ ⁻	NH ₄ ⁺	PO ₄ ⁻³
1	Startup of the Reactor					68	-	-	-	-	-
2	256	-	52	157	< 5	69	-	-	-	-	-
3	54	-	131	166	< 5	70	136	-	< 5	-	< 5
4	1358	-	290	120	< 5	71	170	1930	1	-	< 5
5	-	-	-	-	-	72	50	-	-	-	-
6	-	-	-	-	-	73	107	1930	< 5	-	< 5
7	7471	-	1651	388	< 5	74	62	-	-	-	-
8	6249	1300	1484	526	-	75	-	-	-	-	-
9	5773	3150	2465	508	-	76	-	-	-	-	-
10	5668	3125	2070	490	-	77	126	1800	< 5	-	< 5
11	-	-	-	-	-	78	95	-	-	-	-
12	-	-	-	-	-	79	68	-	-	-	-
13	-	-	-	-	-	80	20	-	-	-	-
14	5298	2550	2151	490	-	81	19	-	-	-	-
15	5602	1626	269	14	-	82	-	-	-	-	-
16	-	-	-	-	-	83	-	-	-	-	-
17	-	-	-	-	-	84	20	-	-	-	-
18	5705	2950	660	90	4	85	200	190	-	-	-
19	-	-	-	-	-	86	40	750	< 5	-	< 5
20	-	-	-	-	-	87	31	260	< 5	-	-
21	1027	1800	< 10	554	< 5	88	360	-	-	-	-
22	263	1675	< 5	554	< 5	89	32	-	-	-	-
23	204	1675	< 5	351	< 5	90	34	-	-	-	-
24	200	1550	< 5	647	< 5	91	36	-	-	-	-
25	195	1250	< 5	647	< 5	92	35	-	-	-	-
26	-	-	-	-	-	93	35	-	-	-	-
27	-	-	-	-	-	94	-	-	-	-	-
28	119	950	< 10	490	< 5	95	39	920	1	-	-
29	57	-	< 5	508	< 5	96	-	-	-	-	-
30	272	825	< 5	443	< 5	97	-	-	-	-	-
31	30	900	< 5	416	< 5	98	38	-	-	-	-
32	490	775	126	471	< 5	99	40	1600	-	-	-
33	-	-	-	-	-	100	39	-	-	-	-
34	-	-	-	-	-	101	42	-	-	-	-
35	25	800	< 5	395	< 5	102	40	-	-	-	-
36	47	600	< 5	610	< 5	103	35	-	-	-	-
37	53	1100	< 5	600	< 5	104	-	-	-	-	-
38	11988	5850	165	924	< 5	105	44	-	-	-	-
39	12050	5050	112	022	< 5	106	42	2400	-	-	-
40	-	-	-	-	-	107	54	-	-	-	-
41	-	-	-	-	-	108	55	-	-	-	-
42	< 200	2400	< 10	379	< 5	109	60	2540	-	-	-
43	176	2275	20	425	< 5	110	59	-	-	-	-
44	132	2600	< 5	277	< 5	111	-	-	-	-	-
45	160	2650	< 5	92	< 5	112	60	-	-	-	-
46	116	1995	< 5	< 100	< 5	113	2445	3850	1483	-	< 5
47	-	-	-	-	-	114	1562	-	1790	-	-
48	-	-	-	-	-	115	1380	-	-	-	-
49	106	1850	< 5	< 100	< 5	116	857	3450	1314	-	-
50	95	1650	< 5	< 100	< 5	117	920	-	-	-	-
51	106	-	< 5	-	< 5	118	-	-	-	-	-
52	94	-	< 5	-	< 5	119	662	3490	1102	-	-
53	103	-	< 5	-	-	120	002	3400	1227	-	-
54	-	-	-	-	-	121	565	-	-	-	-
55	-	-	-	-	-	122	478	-	-	-	-
56	-	-	-	-	-	123	80	-	-	-	-
57	234	-	< 5	-	< 5	124	-	-	-	-	-
58	391	-	< 5	-	< 5	125	-	-	-	-	-
59	117	-	< 5	-	< 5	126	136	-	< 5	-	-
60	107	1050	< 5	-	< 5	127	425	3840	8	-	-
61	-	-	-	-	< 5	128	122	2980	< 5	-	-
62	19	-	-	-	-	129	93	2800	-	-	-
63	30	-	-	-	-	130	100	-	-	-	-
64	-	-	-	-	-	131	96	-	-	-	-
65	-	-	-	-	-	132	80	-	-	-	-
66	90	-	-	-	-	133	119	1580	< 5	-	-
67	-	-	-	-	-						

Table A-6
MINI II GAS ANALYSES

Test Day	Nitrate to the Reactor		Gas Flow from the Reactor (dm ³ /g NO ₃ ⁻ to reactor)	Gas Composition (% CO ₂)	Amount of CO ₂ (dm ³ CO ₂ /g NO ₃ ⁻ to reactor)	Amount of Nitrogen (dm ³ N ₂ /g NO ₃ ⁻ to reactor)
	(g NC ₃ ⁻ /day)	(g NO ₃ ⁻ /day/dm ³)				
1	Startup of the Reactor					
2	-	-	-	4.0	-	-
3	0.5	0.01	-	8.0	-	-
4	6.54	0.11	-	23.5	-	-
5	0	-	-	-	-	-
6	0	-	-	-	-	-
7	0	-	-	96.0	-	-
8	0	-	-	95.0	-	-
9	0	-	-	-	-	-
10	0	-	-	91.0	-	-
11	0	-	-	-	-	-
12	0	-	-	-	-	-
13	Stirrer Stopped					
14	0	-	-	-	-	-
15	0	-	-	-	-	-
16	0	-	-	-	-	-
17	0	-	-	-	-	-
18	0	-	-	-	-	-
19	0	-	-	-	-	-
20	0	-	-	-	-	-
21	0	-	-	-	-	-
22	0	-	-	-	-	-
23	0	-	-	57	-	-
24	0	-	-	-	-	-
25	0	-	-	43.5	-	-
26	0	-	-	-	-	-
27	0	-	-	-	-	-
28	0	-	-	35.5	-	-
29	0	-	-	38.5	-	-
30	0	-	-	38.5	-	-
31	261.6	4.59	0.195	37.5	0.075	0.124
32	261.6	4.59	0.172	42.5	0.073	0.099
33	261.6	4.59	0.345	-	-	-
34	261.6	4.59	0.386	38.5	0.149	0.237
35	276.0	4.84	0.292	37.5	0.110	0.182
36	367.2	6.44	0.285	49	0.140	0.175
37	367.2	6.44	0.461	58	0.267	0.194
38	Feed Valve Failed					
39	-	-	-	-	-	-
40	-	-	-	20	-	-
41	-	-	-	25	-	-
42	-	-	-	-	-	-
43	-	-	-	-	-	-
44	-	-	-	34	-	-
45	-	-	-	40	-	-
46	-	-	-	53	-	-
47	-	-	-	55	-	-
48	-	-	-	54	-	-
49	-	-	-	53	-	-
50	242.4	4.25	0.383	49.5	0.190	0.193
51	218.4	3.83	0.443	52.5	0.233	0.210
52	196.8	3.45	0.478	52.5	0.251	0.227
53	196.8	3.45	0.458	52.5	0.240	0.218
54	242.4	4.25	0.446	54	0.241	0.205
55	199.2	3.49	0.670	52	0.348	0.322
56	208.8	3.66	0.454	52	0.236	0.218
57	-	-	-	52.5	-	-
58	196.8	3.45	0.454	54	0.245	0.209
59	206.4	3.62	0.373	54.5	0.203	0.170
60	192.0	3.37	0.418	60	0.251	0.167
61	-	-	-	59	-	-
62	256.8	4.51	0.424	59	0.250	0.174
63	268.8	4.72	0.378	59	0.223	0.155
64	256.8	4.51	0.409	59	0.241	0.168
65	273.6	4.80	0.378	58	0.219	0.159
66	230.4	4.04	0.418	54	0.226	0.192
67	273.6	4.80	0.376	59	0.222	0.154
68	259.2	4.55	0.454	61	0.277	0.177
69	249.6	4.38	0.465	63.5	0.295	0.170
70	240.0	4.21	0.500	61	0.305	0.195
71	295.2	5.18	0.391	58	0.227	0.164
72	261.6	4.59	0.468	60	0.281	0.187
73	273.6	4.80	0.449	55	0.247	0.202
74	273.6	4.80	0.448	56.5	0.253	0.195
75	273.6	4.80	0.457	-	-	-
76	249.6	4.38	0.509	59	0.300	0.209
77	252.0	4.42	0.333	56	0.186	0.147
78	232.8	4.08	0.424	55	0.233	0.191
79	273.6	4.80	0.478	59	0.282	0.196
80	52.8	0.93	0.158	12	0.019	0.139
81	50.4	0.88	0.228	16	0.036	0.192
82	103.2	1.81	0.251	25	0.063	0.188
83	100.8	1.77	0.388	40	0.155	0.233
84	103.2	1.81	0.430	52.5	0.226	0.204
85	156.0	2.74	0.442	50	0.221	0.221
86	160.8	2.82	0.587	52	0.305	0.282
87	196.8	3.45	0.497	55	0.274	0.223
88	249.6	4.38	0.457	55.5	0.254	0.203
89	249.6	4.38	0.501	53	0.266	0.235
90	273.6	4.80	0.466	55.5	0.259	0.207
91	273.6	4.80	0.487	57	0.278	0.209
92	273.6	4.80	0.478	56	0.268	0.210
93	280.8	4.93	0.493	57	0.281	0.212
94	0	-	-	-	-	-
95	264.0	4.63	0.484	57.5	0.278	0.206
96	268.8	4.72	0.496	52	0.258	0.238
97	0	-	-	-	-	-
98	283.2	4.97	0.458	58	0.266	0.192
99	331.2	5.81	0.460	59.5	0.274	0.186
100	333.6	5.85	0.482	59.5	0.287	0.195
101	328.8	5.77	0.439	60	0.263	0.176
102	326.4	5.73	0.460	60	0.276	0.184
103	324.0	5.68	0.460	59	0.271	0.189
104	-	-	-	-	-	-
105	309.6	5.43	0.470	60.5	0.284	0.186
106	309.6	5.43	0.466	60	0.280	0.186
107	288.0	5.05	0.449	61	0.274	0.175
108	544.8	9.56	0.483	61.5	0.297	0.186
109	561.6	9.85	0.415	59.5	0.247	0.168
110	-	-	-	54	-	-
111	-	-	-	-	-	-
112	398.4	6.99	-	62	-	-
113	228.0	4.00	0.308	94.5	0.291	0.017
114	0	-	-	86	-	-
115	0	-	-	83	-	-
116	0	-	-	81.5	-	-
117	0	-	-	79	-	-
118	0	-	-	-	-	-
119	0	-	-	75	-	-
120	0	-	-	71	-	-
121	0	-	-	71.5	-	-
122	0	-	-	62.5	-	-
123	0	-	-	44.5	-	-
124	177.6	3.12	0.353	30.0	0.106	0.247
125	170.4	2.99	0.397	40.5	0.161	0.236
126	170.4	2.99	0.420	43	0.181	0.239
127	182.4	3.20	0.069	44	0.030	0.039
128	175.2	3.07	0.494	50	0.247	0.247
129	165.6	2.91	0.462	47	0.217	0.245
130	482.4	8.46	0.545	46	0.251	0.294
131	504.0	8.84	0.428	48	0.206	0.223
132	451.2	7.92	0.478	49	0.234	0.244
133	427.2	7.49	0.386	57	0.220	0.166

Table A-7
REDUCTION OF NITRATE IN THE MINI III REACTOR

Test Day	Nitrate Feed to the Reactor		Nitrate from the Reactor		Daily Volume of Effluent (dm ³)	Nitrate Reduced (g NO ₃ ⁻ /day/dm ³) ⁽¹⁾	Nitrate Reduction (%)
	(g NO ₃ ⁻ /day)	(g NO ₃ ⁻ /day/dm ³)	(μg NO ₃ ⁻ /g)	(g NO ₃ ⁻ /day/dm ³)			
1	Startup of the Reactor						
2	0	-	187	-	-	-	-
3	52.8	0.93	93	0.0030	0.200	0.927	99.68
4	52.8	0.93	-	-	0.200	-	-
5	0	-	-	-	-	-	-
6	0	-	85	-	-	-	-
7	-	-	72	-	-	-	-
8	0	-	29715	-	-	-	-
9	0	-	33281	-	-	-	-
10	0	-	26319	-	-	-	-
11	0	-	-	-	-	-	-
12	0	-	-	-	-	-	-
13	0	-	35313	-	-	-	-
14	0	-	31753	-	-	-	-
15	Tank Emptied - Restarted		2106	-	-	-	-
16	0	-	2163	-	-	-	-
17	12.0	0.21	1379	0.0024	0.100	0.208	98.86
18	0	-	-	-	-	-	-
19	0	-	-	-	-	-	-
20	0	-	345	-	-	-	-
21	17.0	0.30	303	0.001	0.135	0.299	99.67
22	6.0	0.11	236	0.0002	0.050	0.110	100.00
23	Added Inoculum		-	-	-	-	-
24	120.0	2.11	45	0.008	0.954	2.109	99.95
25	129.6	2.27	-	-	1.030	-	-
26	187.2	3.28	-	-	1.488	-	-
27	180.0	3.16	34	0.0009	1.431	3.159	99.97
28	180.0	3.16	27	0.0005	1.431	3.159	99.97
29	180.0	3.16	25	0.0006	1.431	3.159	99.97
30	129.6	2.27	22	0.0004	1.030	2.27	100.00
31	129.6	2.27	28	0.0005	1.030	2.269	99.98
32	129.6	2.27	-	-	1.030	-	-
33	129.6	2.27	-	-	1.030	-	-
34	129.6	2.27	33	0.0007	1.030	2.269	99.98
35	144.0	2.53	42	0.0008	1.145	2.529	99.97
36	235.2	4.13	42	0.0014	1.870	4.129	99.97
37	240.0	4.21	42	0.0014	1.908	4.209	99.97
38	240.0	4.21	49	0.0016	1.908	4.208	99.95
39	278.4	4.88	-	-	2.213	-	-
40	Solenoid Feed Valve Failed		31000	-	-	-	-
41	Added Ca(OH) ₂		-	-	-	-	-
42	0	-	41100	-	-	-	-
43	0	-	34300	-	-	-	-
44	0	-	37016	-	-	-	-
45	0	-	-	-	-	-	-
46	0	-	-	-	-	-	-
47	0	-	-	-	-	-	-
48	Tank Emptied - Restarted		1500	-	-	-	-
49	0	-	350	-	-	-	-
50	132.0	2.32	-	-	1.020	-	-
51	129.6	2.27	60	0.0010	1.002	2.269	99.96
52	134.4	2.36	-	-	1.039	-	-
53	256.8	4.51	-	-	1.985	-	-
54	225.6	3.96	250	0.0076	1.743	3.952	99.81
55	189.6	3.33	357	0.0092	1.465	3.321	99.73
56	208.8	3.66	34	0.0009	1.504	3.321	99.98
57	213.6	3.75	30	0.0008	1.539	3.749	99.98
58	213.6	3.75	28	0.0008	1.539	3.749	99.98
59	278.4	4.88	23	0.001	2.006	4.879	99.98
60	285.6	5.01	-	-	2.058	-	-
61	273.6	4.80	-	-	1.971	-	-
62	278.4	4.88	93	0.0033	2.006	4.877	99.93
63	276.0	4.84	42	0.0015	1.988	4.838	99.97
64	276.0	4.84	42	0.0015	1.988	4.838	99.97
65	283.2	4.97	43	0.0015	2.040	4.968	99.97
66	288.0	5.05	88	0.0032	2.075	5.047	99.94
67	288.0	5.05	-	-	2.075	-	-
68	285.6	5.07	-	-	2.058	-	-
69	264.0	4.63	53	0.0018	1.902	4.628	99.96
70	261.6	4.59	102	0.0041	2.278	4.586	99.91
71	266.4	4.67	105	0.0038	2.081	4.666	99.91
72	266.4	4.67	68	0.0025	2.081	4.668	99.96
73	345.6	6.06	52	0.0025	2.700	6.058	99.96
74	312.0	5.47	48	0.0021	2.438	5.466	99.96
75	307.2	5.39	47	0.0020	2.400	5.388	99.96
76	307.2	5.39	76	0.0032	2.400	5.387	99.94
77	295.2	5.18	49	0.0020	2.306	5.178	99.96
78	292.8	5.14	49	0.0020	2.288	5.138	99.96
79	292.8	5.14	-	-	2.288	-	-
80	297.6	5.22	144	0.0059	2.325	5.214	99.89
81	256.8	4.51	-	-	2.006	-	-
82	256.8	4.51	-	-	2.006	-	-
83	256.8	4.51	51	0.0018	2.006	4.508	99.96
84	357.6	6.27	493	0.0226	2.608	6.247	99.64
85	364.8	6.40	47	0.0022	2.661	6.398	99.97
86	376.8	6.61	52	0.0025	2.748	6.608	99.96
87	496.8	8.72	100	0.0063	3.595	8.714	99.93
88	468.0	8.21	44	0.0026	3.386	8.207	99.97
89	468.0	8.21	-	-	3.386	-	-
90	434.4	7.62	51	0.0028	3.143	7.617	99.96
91	427.2	7.49	188	0.0102	3.091	7.480	99.86
92	408.0	7.16	55	0.0028	2.952	7.157	99.96
93	525.6	9.22	61	0.0041	3.803	9.216	99.96
94	499.2	8.76	140	0.0089	3.612	8.751	99.90
95	-	-	-	-	0	-	-
96	-	-	-	-	0	-	-
97	468.0	8.21	60	0.0036	3.386	8.206	99.96
98	470.4	8.25	209	0.12	3.262	8.238	99.85
99	273.6	4.80	85	0.0028	1.897	4.797	99.94
100	616.8	10.82	95	0.0071	4.277	10.813	99.93
101	624.0	10.94	204	0.0155	4.327	10.924	99.86
102	624.0	10.94	92	0.0070	4.327	10.933	99.94
103	-	-	-	-	-	-	-

Table A-7 (Continued)

Test Day	Nitrate Feed to the Reactor		Nitrate from the Reactor		Daily Volume of Effluent (dm ³)	Nitrate Reduced (g NO ₃ ⁻ /day/dm ³) ⁽¹⁾	Nitrate Reduction (%)
	(g NO ₃ ⁻ /day)	(g NO ₃ ⁻ /day/dm ³)	(μg NO ₃ ⁻ /g)	(g NO ₃ ⁻ /day/dm ³)			
104	225.6	3.96	204	0.0056	1.564	3.954	99.86
105	218.4	3.83	221	0.0059	1.515	3.824	99.85
106	360.0	6.32	97	0.0042	2.496	6.316	99.94
107	432.0	7.58	85	0.0045	2.996	7.576	99.94
108	451.2	7.92	338	0.0186	3.129	7.901	99.76
109	518.4	9.09	-	-	3.595	-	-
110	492.0	8.63	-	-	3.412	-	-
111	482.4	8.46	10528	0.6178	3.345	7.842	92.70
112	0	-	7743	-	0	-	-
113	0	-	3871	-	0	-	-
114	84.0	1.47	289	0.0029	0.580	1.467	99.80
115	216.0	3.79	106	0.0028	1.491	3.787	99.93
116	201.6	3.54	98	0.0024	1.391	3.538	99.93
117	146.4	2.57	70	0.0012	1.010	2.569	99.95
118	276.0	4.84	85	0.0028	1.905	4.837	99.94
119	273.6	4.80	275	0.0091	1.888	4.791	99.81
120	386.4	6.78	1290	0.0604	2.667	6.72	99.11
121	120.0	2.11	5600	0.0813	0.828	2.029	96.15
122	0	-	3480	-	0	-	-
123	48.0	0.84	90	0.0005	0.331	0.84	100.0
124	72.0	1.26	-	-	0.497	-	-
125	72.0	1.26	82	0.0007	0.497	1.259	99.94
126	74.4	1.31	120	0.0011	0.532	1.309	99.92
127	199.2	3.49	246	0.0062	1.425	3.484	99.82
128	196.8	3.45	214	0.0053	1.408	3.445	99.85
129	91.2	1.60	224	0.0025	0.629	1.598	99.84
130	309.6	5.43	< 100	0.0037	2.137	5.426	99.93
131	309.6	5.43	-	-	2.137	-	-
132	309.6	5.43	191	0.0072	2.137	5.423	99.87
133	170.4	2.99	-	-	1.176	-	-
134	427.2	7.49	-	-	2.948	-	-
135	391.2	6.86	187	0.0089	2.700	6.851	99.87
136	432.0	7.58	194	0.0094	2.762	7.573	99.90
137	429.6	7.54	-	-	2.747	-	-
138	415.2	7.28	-	-	2.655	-	-
139	415.2	7.28	-	-	2.655	-	-
140	415.2	7.28	487	0.0227	2.655	7.257	99.69
141	400.8	7.03	306	0.0146	2.712	7.015	99.79
142	408.0	7.16	2571	0.1245	2.760	7.036	98.83
143	408.0	7.16	4279	0.2072	2.760	6.953	97.11
144	132.0	2.32	-	-	0.893	-	-
145	199.2	3.49	30	0.0007	1.348	3.489	99.98
146	192.0	3.37	190	0.0043	1.299	3.366	99.88
147	213.6	3.75	172	0.0040	1.322	3.746	99.89
148	369.6	6.48	517	0.0207	2.287	6.459	99.68
149	379.2	6.65	165	0.0068	2.346	6.643	99.90
150	364.8	6.40	177	0.0070	2.257	6.393	99.89
151	362.4	6.36	-	-	2.242	-	-
152	369.6	6.48	-	-	2.287	-	-
153	345.6	6.06	1195	0.0448	2.139	6.015	99.26
154	328.8	5.77	172	0.0062	2.050	5.764	99.89
155	175.2	3.07	136	0.0026	1.092	3.067	99.92
156	374.4	6.57	130	0.0053	2.334	6.565	99.92
157	439.2	7.71	-	-	2.738	-	-
158	372.0	6.53	-	-	2.319	-	-
159	372.0	6.53	-	-	2.319	-	-
160	379.2	6.65	126	0.0052	2.364	6.645	99.92
161	360.0	6.32	297	0.0117	2.244	6.308	99.81
162	103.2	1.81	728	0.0082	0.643	1.802	99.56
163	127.2	2.23	119	0.0017	0.793	2.228	99.92
164	192.0	3.37	127	0.0027	1.197	3.367	99.92
165	232.8	4.08	-	-	1.451	-	-
166	235.2	4.13	-	-	1.466	-	-
167	235.2	4.13	1640	0.0422	1.466	4.088	98.98
168	256.8	4.51	89	0.0025	1.601	4.508	99.94
169	232.8	4.08	-	-	1.451	-	-
170	105.6	1.85	3447	0.0398	0.658	1.812	97.96
171	0	-	2598	-	-	-	-
172	0	-	-	-	-	-	-
173	0	-	-	-	-	-	-
174	124.8	2.19	121	0.0016	0.778	2.188	99.93
175	249.6	4.38	-	-	1.556	-	-
176	388.8	6.82	4381	0.1863	2.424	6.634	97.27
177	0	-	2904	-	-	-	-
178	48.0	0.84	805	0.0042	0.299	0.836	99.52
179	93.6	1.64	-	-	0.584	-	-
180	93.6	1.64	-	-	0.584	-	-
181	86.4	1.52	110	0.0010	0.539	1.519	99.93
182	67.2	1.18	102	0.0007	0.419	1.179	99.94
183	134.4	2.36	521	0.0090	0.981	2.351	99.62
184	103.2	1.81	-	-	0.753	-	-
185	96.0	1.68	158	0.0016	0.701	1.678	99.88
186	88.8	1.56	-	-	0.648	-	-
187	88.8	1.56	-	-	0.648	-	-
188	88.8	1.56	91	0.0010	0.648	1.559	99.94
189	105.6	1.85	-	-	0.771	-	-
190	96.0	1.68	-	-	0.700	-	-
191	144.0	2.53	-	-	1.051	-	-
192	134.4	2.36	102	0.0018	0.981	2.358	99.92
193	133.4	2.34	-	-	0.974	-	-
194	133.4	2.34	-	-	0.974	-	-
195	136.2	2.39	102	0.0018	0.994	2.388	99.92
196	208.8	3.66	-	-	1.524	-	-
197	245.9	4.31	-	-	1.795	-	-
198	239.1	4.19	59	0.0018	1.745	4.188	99.95

(1) Defined as grams of nitrate per day per dm³ of reactor solution. Volume of reactor was 57 dm³.

Table A-8
COMPOSITION OF LIQUID FROM THE MINI III REACTOR

Test Day	Analysis of Liquid from the Reactor (µg/g)					Test Day	Analysis of Liquid from the Reactor (µg/g)		
	NO ₃ ⁻	TCC	NO ₂ ⁻	NH ₄ ⁺	PO ₄ ⁻³		NO ₃ ⁻	TCC	NO ₂ ⁻
1	Startup of the Reactor					100	95	-	-
2	167	3675	16	1108	< 5	101	204	3260	< 5
3	93	2600	< 10	877	< 5	102	92	-	-
4	-	-	-	-	-	103	-	-	-
5	-	-	-	-	-	104	204	3660	< 5
6	85	1550	< 10	1727	< 5	105	221	3500	< 5
7	72	2230	< 5	201	< 5	106	97	-	-
8	29715	10800	529	1616	< 5	107	85	-	-
9	33231	9650	1197	1895	< 5	108	338	4360	< 5
10	26314	9000	561	2032	< 5	109	-	-	-
11	-	-	-	-	-	110	-	-	-
12	-	-	-	-	-	111	10528	-	< 5
13	35318	10900	2047	2263	35	112	7743	5450	1
14	31753	10050	1942	1921	< 5	113	3871	5520	< 5
15	2106	900	121	185	24	114	289	4010	< 5
16	2163	950	72	134	11	115	106	-	-
17	1379	825	< 5	185	< 5	116	98	-	-
18	-	-	-	-	-	117	70	-	-
19	-	-	-	-	-	118	85	-	-
20	345	525	< 5	< 10	< 5	119	275	4120	< 5
21	303	375	45	77	16	120	1290	-	< 5
22	236	300	173	72	15	121	5600	-	-
23	-	-	-	-	-	122	3480	-	-
24	45	1300	< 5	249	< 5	123	50	-	-
25	-	-	-	-	-	124	-	-	-
26	-	-	-	-	-	125	82	-	-
27	34	675	< 5	92	< 5	126	120	4590	< 5
28	21	725	-	-	-	127	246	3310	-
29	25	425	< 5	187	< 5	128	214	2190	-
30	22	350	< 5	92	< 5	129	224	2030	-
31	28	360	< 5	3694	< 5	130	< 100	-	-
32	-	-	-	-	-	131	-	-	-
33	-	-	-	-	-	132	131	2245	-
34	38	430	< 5	< 100	< 5	133	-	-	-
35	42	450	< 5	< 100	< 5	134	-	-	-
36	42	-	< 5	-	< 5	135	187	1990	< 5
37	42	-	< 5	-	< 5	136	194	1905	-
38	49	-	< 5	-	-	137	-	-	-
39	-	-	-	-	-	138	-	-	-
40	31000	-	-	-	-	139	-	-	-
41	-	-	-	-	-	140	437	630	< 5
42	41100	-	-	-	25	141	306	650	6
43	34300	-	7	-	< 5	142	2571	380	29
44	37015	-	3	-	< 5	143	4279	895	288
45	-	-	-	-	-	144	-	-	-
46	-	-	-	-	-	145	30	-	-
47	-	-	-	-	-	146	190	675	< 5
48	1500	-	-	-	-	147	172	535	-
49	350	-	-	-	-	148	517	555	-
50	-	-	-	-	-	149	165	605	-
51	60	-	-	-	-	150	177	745	-
52	-	-	-	-	-	151	-	-	-
53	-	-	-	-	-	152	-	-	-
54	250	-	-	-	-	153	1195	390	-
55	357	250	< 5	-	-	154	172	370	-
56	34	710	< 5	-	< 5	155	136	755	-
57	30	-	-	-	-	156	130	430	-
58	28	320	< 5	-	< 5	157	-	-	-
59	28	-	-	-	-	158	-	-	-
60	-	-	-	-	-	159	-	-	-
61	-	-	-	-	-	160	126	644	-
62	93	990	< 5	-	< 5	161	297	722	45
63	42	-	-	-	-	162	728	1298	300
64	42	-	-	Discontinued Analysis		163	119	-	< 5
65	43	-	-			164	127	-	< 5
66	88	770	< 5			165	-	-	-
67	-	-	-	-	-	166	-	-	-
68	-	-	-	-	-	167	1640	1495	12
69	53	-	-	-	-	168	89	1345	< 5
70	02	250	-	-	-	169	-	-	-
71	105	1200	69	-	-	170	3447	1820	60
72	68	730	< 5	-	-	171	2598	1615	76
73	52	-	-	-	-	172	-	-	-
74	48	-	-	-	-	173	-	-	-
75	47	-	-	-	-	174	121	1170	< 5
76	76	950	< 5	-	-	175	-	-	-
77	49	-	-	-	-	176	4381	2085	22
78	49	-	-	-	-	177	2904	1440	17
79	-	-	-	-	-	178	805	980	1.2
80	144	1380	-	-	-	179	-	-	-
81	-	-	-	-	-	180	-	-	-
82	-	-	-	-	-	181	110	685	< 5
83	51	-	-	-	-	182	102	732	< 5
84	493	1610	-	-	-	183	521	730	2.4
85	47	-	-	-	-	184	-	-	-
86	52	-	-	-	-	185	158	750	-
87	100	2170	< 5	-	-	186	-	-	-
88	44	-	-	-	-	187	-	-	-
89	-	-	-	-	-	188	91	862	< 5
90	51	-	-	-	-	189	-	-	-
91	188	2000	-	-	-	190	-	-	-
92	55	-	-	-	-	191	-	-	-
93	61	-	-	-	-	192	102	1000	-
94	140	2240	-	-	-	193	-	-	-
95	-	-	-	-	-	194	-	-	-
96	-	-	-	-	-	195	102	1175	-
97	60	-	-	-	-	196	-	-	-
98	209	2700	< 5	-	-	197	-	-	-
99	85	-	-	-	-	198	55	1199	-

Table A-9
MINI III GAS ANALYSES

Test Day	Nitrate to the Reactor		Gas Flow from the Reactor (dm ³ /g NO ₃ ⁻ to reactor)	Gas Composition (% CO ₂)	Amount of CO ₂ (dm ³ CO ₂ /g NO ₃ ⁻ to reactor)	Amount of N ₂ (dm ³ N ₂ /g NO ₃ ⁻ to reactor)
	(g NO ₃ ⁻ /day)	(g NO ₃ ⁻ /day/dm ³)				
1	-	-	-	13	-	-
2	-	-	-	5	-	-
3	0.93	52.8	0.762	-	-	-
4	0.93	52.8	1.954	27.5	-	-
5	-	-	-	-	-	-
6	-	-	-	37.5	-	-
7	-	-	-	38	-	-
8	-	-	-	-	-	-
9	-	-	-	89	-	-
10	-	-	-	92	-	-
11	-	-	-	-	-	-
12	-	-	-	-	-	-
13	-	-	-	87.5	-	-
14	-	-	-	-	-	-
15	Tank Emptied - Restarted		-	-	-	-
16	-	-	-	-	-	-
17	0.21	12	0.244	3	-	-
18	-	-	-	-	-	-
19	-	-	-	-	-	-
20	-	-	0.050	12	-	-
21	0.30	16.8	-	-	-	-
22	0.11	2.6	-	-	-	-
23	Added Inoculum		-	-	-	-
24	2.11	120	0.323	17.5	0.056	0.267
25	2.27	129	-	-	-	-
26	3.28	187	0.215	37.5	0.081	0.134
27	3.16	180	0.409	38	0.155	0.254
28	3.16	180	0.272	40	0.109	0.163
29	3.16	180	0.263	40.5	0.106	0.157
30	2.27	129	0.351	39	0.137	0.214
31	129.6	2.29	0.356	40	0.142	0.214
32	129.6	2.29	0.376	44	0.165	0.425
33	129.6	2.27	0.405	51	0.206	0.199
34	129.6	2.27	0.389	52.5	0.204	0.185
35	144.0	2.53	0.341	50	0.170	0.171
36	235.2	4.13	0.209	55	0.115	0.94
37	240.0	4.21	0.437	53	0.232	0.205
38	240.0	4.21	0.299	53.5	0.160	0.139
39	278.4	4.88	0.391	55	0.215	0.176
40	Solenoid Feed Valve Failed		-	89	-	-
41	Added Ca(OH) ₂		-	91	-	-
42	0	-	-	46	-	-
43	0	-	-	4	-	-
44	0	-	-	-	-	-
45	0	-	-	-	-	-
46	0	-	-	-	-	-
47	0	-	-	-	-	-
48	Tank Emptied - Restarted		-	-	-	-
49	0	-	-	-	-	-
50	132.0	2.32	0.290	21	0.061	0.229
51	129.6	2.27	0.291	24	0.070	0.221
52	134.4	2.36	0.312	28.5	0.089	0.223
53	256.8	4.51	0.374	40	0.150	0.224
54	225.6	3.96	0.421	46.5	0.196	0.225
55	189.6	3.33	0.391	45	0.176	0.215
56	208.8	3.66	0.441	38	0.168	0.273
57	213.6	3.75	0.354	43	0.152	0.202
58	213.6	3.75	0.414	48	0.199	0.215
59	278.4	4.88	0.455	53	0.241	0.214
60	285.6	5.01	-	55	-	-
61	273.6	4.80	0.521	57.5	0.300	0.221
62	278.4	4.88	0.491	54.5	0.268	0.223
63	276.0	4.84	0.465	54	0.251	0.214
64	276.0	4.84	0.450	55	0.248	0.202
65	283.2	4.97	0.468	56	0.262	0.206
66	288.0	5.05	0.436	56	0.244	0.192
67	288.0	5.05	0.461	54	0.249	0.212
68	285.6	5.01	0.414	54	0.224	0.190
69	264.0	4.63	0.415	62.5	0.259	0.156
70	261.6	4.59	0.371	57	0.211	0.160
71	266.4	4.67	0.503	54	0.272	0.231
72	266.4	4.67	0.597	56	0.334	0.263
73	338.4	6.06	0.470	55	0.258	0.212
74	312.0	5.47	0.462	56	0.259	0.153
75	307.2	5.39	0.554	56.5	0.313	0.241
76	307.2	5.39	0.514	57.0	0.293	0.221
77	288.0	5.18	0.488	58.5	0.285	0.203
78	292.8	5.14	0.496	59	0.293	0.203
79	297.6	5.14	-	-	-	-
80	297.6	5.22	0.476	56.5	0.269	0.207
81	256.8	4.51	0.637	57.5	0.366	0.271
82	256.8	4.51	-	-	-	-
83	256.8	4.51	0.332	57.5	0.191	0.141
84	357.6	6.29	0.450	63	0.284	0.166
85	364.8	6.40	0.448	60	0.269	0.179
85	376.8	6.61	0.462	59	0.273	0.189
87	496.8	8.72	0.470	58.5	0.275	0.195
88	468.0	8.21	0.474	58	0.275	0.199
89	468.0	8.21	-	-	-	-
90	434.4	7.62	0.459	59.5	0.273	0.186
91	427.2	7.49	0.440	58.5	0.257	0.183
92	408.0	7.16	0.452	55.5	0.251	0.201
93	525.6	9.22	0.465	59.0	0.274	0.191
94	499.2	8.76	0.462	57.0	0.263	0.199
95	-	-	-	59.5	-	-

Table A-9 (Continued):

Test Day	Nitrate to the Reactor		Gas Flow from the Reactor (dm ³ /g NO ₃ ⁻ to reactor)	Gas Composition (% CO ₂)	Amount of CO ₂ (dm ³ CO ₂ /g NO ₃ ⁻ to reactor)	Amount of N ₂ (dm ³ N ₂ /g NO ₃ ⁻ to reactor)
	(g NO ₃ ⁻ /day)	(g NO ₃ ⁻ /day/dm ³)				
96	-	-	-	-	-	-
97	468.0	8.21	0.443	59.5	0.264	0.179
98	470.4	8.25	0.483	57.5	0.278	0.205
99	273.6	4.80	0.465	53.0	0.246	0.219
100	616.8	10.82	0.472	53.0	0.250	0.222
101	624.0	10.94	0.490	53.0	0.260	0.230
102	624.0	0.94	0.476	53.0	0.252	0.224
103	-	-	-	-	-	-
104	225.6	3.96	0.152	54.5	0.083	0.069
105	218.4	3.83	0.408	42.0	0.171	0.237
106	360.0	6.32	0.478	56.0	0.258	0.210
107	432.0	7.58	0.465	52.5	0.244	0.221
108	451.2	7.92	0.490	50.5	0.247	0.243
109	518.4	9.09	0.303	56	0.170	0.133
110	492.0	9.63	0.864	62.5	0.540	0.324
111	482.4	3.46	0.289	69	0.199	0.090
112	0	-	-	47	-	-
113	0	-	-	34	-	-
114	84.0	1.47	0.711	30.5	0.217	0.494
115	216.0	3.79	0.360	39	0.140	0.220
116	201.6	3.54	0.528	46	0.243	0.285
117	146.4	2.57	-	52	-	-
118	276.0	4.84	0.369	48	0.177	0.192
119	273.6	4.80	0.475	49.5	0.235	0.240
120	386.4	6.78	0.392	55	0.215	0.176
121	120.0	2.11	1.035	64	0.662	0.373
122	0	-	-	38	-	-
123	48.0	0.84	0.096	38.5	0.036	0.060
124	72.0	1.26	-	-	-	-
125	72.0	1.26	0.298	38	0.113	0.185
126	74.4	1.31	0.363	41	0.149	0.214
127	199.2	3.49	0.377	40	0.15	0.226
128	196.8	3.45	0.353	38	0.134	0.219
129	91.2	1.60	0.882	44	0.388	0.494
130	309.6	5.43	0.500	55.5	0.278	0.222
131	309.6	5.43	-	-	-	-
132	309.6	5.43	0.504	51.5	0.260	0.244
133	170.4	2.99	0.358	49.5	0.177	0.181
134	427.2	7.49	0.385	48.5	0.187	0.198
135	391.2	6.86	0.480	52.5	0.252	0.228
136	432.0	7.58	0.443	48.5	0.215	0.228
137	429.6	7.54	0.389	47	0.183	0.206
138	415.2	7.28	0.414	48	0.199	0.215
139	415.2	7.28	-	-	-	-
140	415.2	7.28	0.393	58.5	0.230	0.163
141	400.8	7.03	0.372	67	0.249	0.123
142	408.0	7.16	0.266	78	0.207	0.059
143	408.0	7.16	0.314	86	0.270	0.044
144	132.0	2.32	0.514	23.5	0.120	0.394
145	199.2	3.49	0.161	38	0.061	0.100
146	192.0	3.37	0.324	46	0.149	0.175
147	213.6	3.75	0.260	52.5	0.136	0.124
148	369.6	6.43	0.443	51.5	0.228	0.215
149	379.2	6.65	0.528	48	0.253	0.275
150	364.8	6.40	0.486	49	0.238	0.248
151	362.4	6.36	0.652	48	0.313	0.339
152	369.6	6.48	0.085	48	0.041	0.044
153	345.6	5.06	0.447	46.5	0.208	0.239
154	328.8	5.77	0.532	47.0	0.250	0.282
155	175.2	3.07	0.339	39	0.132	0.207
156	374.4	6.57	0.391	47.5	0.186	0.205
157	439.2	7.71	0.374	52	0.194	0.180
158	372.0	6.53	0.413	68.5	0.283	0.130
159	372.0	6.53	-	-	-	-
160	379.2	6.65	0.450	45.5	0.205	0.245
161	360.0	6.32	0.313	79.0	0.247	0.066
162	103.2	1.81	0.764	86.5	0.661	0.103
163	127.2	2.23	0.534	40	0.214	0.320
164	192.0	3.37	0.367	44	0.161	0.206
165	232.8	4.08	0.314	-	-	-
166	235.2	4.13	-	-	-	-
167	235.2	4.13	0.389	56	0.218	0.171
168	256.8	4.51	0.193	49	0.095	0.098
169	232.8	4.08	0.273	66	0.180	0.086
170	105.6	1.85	0.538	70	0.377	0.161
171	0	-	-	64.5	-	-
172	0	-	-	-	-	-
173	0	-	-	-	-	-
174	124.8	2.19	0.183	27	0.049	0.134
175	249.6	4.38	0.281	46.5	0.131	0.150
176	388.0	6.82	0.258	67	0.173	0.085
177	0	-	-	66	-	-
178	48.0	0.84	1.364	26	0.355	1.009
179	93.6	1.64	-	-	-	-
180	93.6	1.64	0.356	-	-	-
181	86.4	1.52	0.379	39.5	0.150	0.229
182	67.2	1.18	0.404	40	0.162	0.242
183	134.4	2.36	0.376	50	0.188	0.188
184	103.2	1.81	0.523	48.5	0.254	0.269
185	96.0	1.68	0.503	53.5	0.269	0.234
186	88.8	1.56	0.504	-	-	-
187	88.8	1.56	0.504	-	-	-
188	88.8	1.55	0.504	59	0.297	0.207
189	105.6	1.85	0.491	55	0.270	0.221
190	96.0	1.68	0.498	55.5	0.276	0.222
191	144.0	2.53	0.491	57.5	0.282	0.209
192	134.4	2.36	0.517	58.5	0.302	0.215
193	136.8	2.40	0.517	-	-	-
194	136.8	2.40	0.517	-	-	-
195	136.8	2.40	0.517	58	0.300	0.217
196	208.8	3.66	0.305	47	0.143	0.162
197	245.9	4.31	0.509	61	0.310	0.199
198	239.1	4.15	0.502	57	0.286	0.216

Table A-10
REDUCTION OF NITRATE IN THE MINI IV REACTOR

Test Day	Nitrate Feed to the Reactor		Nitrate from the Reactor		Daily Volume of Effluent (dm ³)	Nitrate Reduced (g NO ₃ ⁻ /day/dm ³)	Nitrate Reduction (%)
	(g NO ₃ ⁻ /day)	(g NO ₃ ⁻ /day/dm ³)	(μg NO ₃ ⁻ /g)	(g NO ₃ ⁻ /day/dm ³)			
1	Startup of the Reactor						
2	254.4	4.46	66	0.0021	1.833	4.458	99.95
3	276.0	4.84	129	0.0045	1.988	4.836	99.92
4	278.4	4.88	-	-	2.005	-	-
5	273.6	4.80	-	-	1.971	-	-
6	283.2	4.97	69	0.0025	2.040	4.968	99.95
7	228.0	4.00	102	0.0032	1.781	3.997	99.92
8	259.2	4.55	36	0.0013	2.025	4.549	99.97
9	259.2	4.55	170	0.0060	2.025	4.544	99.87
10	256.8	4.50	58	0.0020	2.006	4.498	99.96
11	264.0	4.63	48	0.0017	2.062	4.628	99.96
12	254.4	4.46	35	0.0012	1.988	4.459	99.97
13	254.4	4.46	131	0.0046	1.988	4.455	99.90
14	254.4	4.46	55	0.0019	1.988	4.458	99.96
15	266.4	4.67	55	0.0020	2.081	4.668	99.96
16	266.4	4.67	-	-	2.081	-	-
17	266.4	4.67	53	0.0019	2.081	4.668	99.96
18	252.0	4.42	-	-	1.969	-	-
19	Pump Plugged						
20	194.4	3.41	51	0.0014	1.519	3.409	99.96
21	314.4	5.52	50	0.0022	2.456	5.518	99.96
22	372.0	6.53	50	0.0025	2.906	6.528	99.97
23	367.2	6.44	55	0.0026	2.678	6.437	99.96
24	348.0	6.10	47	0.0021	2.538	6.098	99.96
25	352.8	6.19	39	0.0017	2.553	6.188	99.97
26	348.0	6.10	-	-	2.518	-	-
27	331.2	5.82	43	0.0018	2.397	5.818	99.97
28	326.4	5.73	352	0.0146	2.362	5.715	99.74
29	326.4	5.73	44	0.0018	2.362	5.728	99.97
30	350.4	6.15	47	0.0021	2.535	6.148	99.96
31	348.0	6.10	144	0.0064	2.518	6.094	99.90
32	362.4	6.36	49	0.0019	2.513	6.358	99.97
33	232.8	4.08	-	-	1.614	-	-
34	232.8	4.08	48	0.0014	1.614	4.079	99.96
35	338.4	5.94	80	0.0023	1.614	5.938	99.96
36	350.4	6.15	1500	0.0618	2.347	6.088	99.00
37	237.6	4.17	3950	0.1685	2.430	4.002	96.00
38	62.4	1.09	80	0.0023	1.648	1.088	99.79
39	81.6	1.43	120	0.0009	0.433	1.429	99.94
40	72.0	1.26	-	-	0.566	-	-
41	72.0	1.26	95	0.0008	0.499	1.259	99.94
42	199.2	3.49	73	0.0006	0.499	3.489	99.98
43	175.2	3.07	78	0.0019	1.381	3.068	99.94
44	273.6	4.80	80	0.0017	1.215	4.798	99.96
45	268.8	4.72	80	0.0027	1.897	4.717	99.94
46	192.0	3.37	-	-	1.331	-	-
47	19.2	0.34	-	-	0.133	-	-
48	38.4	0.67	45	0.0002	0.266	0.67	100.00
49	120.0	2.10	104	0.0015	0.832	2.098	99.93
50	81.6	1.43	1630	0.0162	0.566	1.414	98.87
51	117.6	2.06	170	0.0024	0.816	2.058	99.88
52	187.2	3.28	3736	0.0847	1.292	3.195	97.42
53	216.0	3.79	250	0.0065	1.491	3.784	99.83
54	319.2	5.60	100	0.0039	2.203	5.596	99.93
55	324.0	5.68	3500	0.1373	2.236	5.553	97.76
56	340.8	5.98	3124	0.1289	2.352	5.851	97.84
57	350.4	6.15	1450	0.0615	2.418	6.088	99.00
58	328.8	5.77	130	0.0052	2.269	5.765	99.91
59	312.0	5.47	171	0.0065	2.153	5.464	99.88
60	367.2	6.44	130	0.0058	2.534	6.434	99.91
61	367.2	6.44	-	-	2.534	-	-
62	367.2	6.44	124	0.0055	2.534	6.434	99.91
63	362.4	6.36	153	0.0067	2.501	6.353	99.89
64	355.2	6.23	151	0.0065	2.451	6.224	99.90
65	357.6	6.27	150	0.0065	2.468	6.264	99.90
66	-	-	166	-	-	-	-
67	151.2	2.65	250	0.0046	1.043	2.645	99.83
68	-	-	-	-	-	-	-
69	348.0	6.10	157	0.0066	2.402	6.093	99.89
70	350.4	6.15	-	-	-	-	-
71	386.4	6.78	1868	0.0810	2.471	6.699	98.80
72	177.6	3.12	3736	0.0745	1.136	3.046	97.61
73	187.2	3.28	139	0.0029	1.197	3.277	99.91
74	376.8	6.61	-	-	2.409	-	-
75	199.2	3.49	-	-	1.348	-	-
76	264.0	4.63	-	-	1.786	-	-
77	264.0	4.63	105	0.0033	1.786	4.627	99.93
78	256.8	4.50	1041	0.0326	1.786	4.467	99.28
79	264.0	4.63	2574	0.0784	1.737	4.552	98.31
80	120.0	2.10	3281	0.1029	1.788	1.997	95.10
81	40.8	0.72	< 100	0.0014	0.812	0.719	99.80
82	249.6	4.38	< 100	0.0005	0.276	4.38	100.0
83	249.6	4.38	87	0.0026	1.689	4.377	99.94
84	247.2	4.34	82	0.0025	1.707	4.338	99.94
85	254.4	4.46	75	0.0022	1.691	4.458	99.95
86	364.8	6.40	75	0.0023	1.740	6.398	99.96
87	403.2	7.07	71	0.0031	2.495	7.067	99.96
88	415.2	7.28	-	-	2.569	-	-
89	410.4	7.20	-	-	2.540	-	-
90	391.2	6.86	204	0.0087	2.420	6.851	99.87
91	398.4	6.99	84	0.0037	2.484	6.986	99.95
92	400.8	7.03	84	0.0037	2.499	7.026	99.95
93	393.6	6.90	-	-	-	-	-
94	398.4	6.99	-	-	-	-	-
95	412.8	7.24	-	-	-	-	-
96	412.8	7.24	-	-	-	-	-
97	422.4	7.41	1100	0.0508	2.633	7.359	99.31
98	117.6	2.06	87	0.0011	0.733	2.059	99.95
99	163.2	2.86	85	0.0015	1.017	2.858	99.95
100	256.8	4.50	89	0.0025	1.601	4.498	99.94
101	254.4	4.46	85	0.0024	1.586	4.458	99.95
102	259.2	4.55	-	-	2.239	-	-
103	259.2	4.55	-	-	-	-	-
104	146.4	2.57	465	0.0074	0.913	2.563	99.71
105	69.6	1.22	547	0.0042	0.434	1.216	99.66
106	124.8	2.19	-	-	0.778	-	-
107	148.8	2.61	2581	0.0420	0.928	2.568	98.39
108	-	-	1219	-	-	-	-
109	-	-	-	-	-	-	-
110	-	-	-	-	-	-	-
111	148.8	2.61	85	0.0014	0.928	2.609	99.95
112	199.2	3.49	-	-	1.242	-	-
113	189.6	3.33	412	0.0085	1.182	3.322	99.74
114	55.2	0.97	76	0.0005	0.344	0.97	100.00
115	112.8	1.98	69	0.0008	0.703	1.979	99.96
116	67.2	1.18	-	-	-	-	-
117	67.2	1.18	-	-	-	-	-
118	12.0	0.21	93	0.0007	0.418	0.209	99.67
119	86.4	1.52	1104	0.0104	0.539	1.510	99.32
120	-	-	196	-	-	-	-
121	66.2	1.16	-	-	0.483	-	-
122	113.4	1.99	75	0.0010	0.828	1.989	99.95
123	110.0	1.93	-	-	0.802	-	-
124	110.0	1.93	-	-	0.802	-	-
125	110.0	1.93	68	0.010	0.802	1.929	99.95
126	111.1	1.95	-	-	0.811	-	-
127	108.8	1.91	-	-	0.794	-	-
128	106.9	1.88	-	-	0.780	-	-
129	103.8	1.82	137	0.0018	0.758	1.818	99.90
130	109.5	1.92	-	-	0.799	-	-
131	109.5	1.92	-	-	0.799	-	-
132	109.5	1.92	81	0.011	0.799	1.919	99.94
133	163.0	2.86	-	-	1.190	-	-
134	244.5	4.29	-	-	1.785	-	-

Table A-11
COMPOSITION OF LIQUID FROM THE MINI IV REACTOR

Test Day	Analysis of Aqueous Effluent from the Reactor (µg/g)					Test Day	Analysis of Aqueous Effluent from the Reactor (µg/g)				
	NO ₃ ⁻	TOC	NO ₂ ⁻	NH ₄ ⁺	PO ₄ ⁻		NO ₃ ⁻	TOC	NO ₂ ⁻	NH ₄ ⁺	PO ₄ ⁻
1	Startup of the Reactor					69	157	4680	-	-	-
2	66	-	-	-	-	70	-	-	-	-	-
3	129	1970	< 5	-	-	71	1868	4370	-	-	-
4	-	-	-	-	-	72	3736	4780	-	-	-
5	-	-	-	-	-	73	139	4270/2825 ⁽¹⁾	-	-	-
6	69	-	-	-	-	74	-	-	-	-	-
7	102	1070	0.9	-	-	75	-	-	-	-	-
8	36	1938	< 5	-	-	76	-	-	-	-	-
9	170	850	< 5	-	-	77	105	2240/1210	-	-	-
10	58	-	-	-	-	78	1041	1570/1250	-	-	-
11	48	-	-	-	-	79	2574	1420/1205	-	-	-
12	55	-	-	-	-	80	3281	1105/1125	-	-	-
13	131	1240	< 5	-	-	81	< 100	-	-	-	-
14	55	-	-	-	-	82	< 100	-	-	-	-
15	55	-	-	-	-	83	00	395/775	-	-	-
16	-	-	-	-	-	84	87	1030/781	-	-	-
17	53	1560	1.7	-	-	85	75	965/675 ⁽¹⁾	-	-	-
18	-	-	-	-	-	86	75	835	-	-	-
19	Pump Plugged					87	71	700	-	-	-
20	51	-	-	-	-	88	-	-	-	-	-
21	50	3950	-	-	-	89	-	-	-	-	-
22	50	-	-	-	-	90	204	240	-	-	-
23	55	-	-	-	-	91	84	542/358	-	-	-
24	47	3290	< 5	-	-	92	84	355	-	-	-
25	39	-	-	-	-	93	-	-	-	-	-
26	-	-	-	-	-	94	-	-	-	-	-
27	43	-	-	-	-	95	-	-	-	-	-
28	352	2850	-	-	-	96	-	-	-	-	-
29	44	-	-	-	-	97	1100	1272/1228	634	-	-
30	47	-	-	-	-	98	87	1072/988	< 5	-	-
31	144	3450	-	-	-	99	85	1085/1007	-	-	-
32	49	-	-	-	-	100	89	-/953	-	-	-
33	-	-	-	-	-	101	85	-/955	-	-	-
34	48	-	-	-	-	102	-	-	-	-	-
35	80	3720	5	-	< 5	103	-	-	-	-	-
36	1500	-	-	-	-	104	465	1125/-	207	-	-
37	3950	-	-	-	-	105	547	1075/1075	< 5	-	-
38	00	3990	< 5	-	-	106	-	-	-	-	-
39	120	-	-	-	-	107	2581	1570/-	506	-	-
40	-	-	-	-	-	108	1219	1415/-	856	-	-
41	95	4920	< 5	-	-	109	-	-	-	-	-
42	73	-	-	-	-	110	-	-	-	-	-
43	78	-	-	-	-	111	85	1045/796	< 5	-	-
44	80	-	-	-	-	112	-	-	-	-	-
45	80	3970	< 5	-	-	113	412	1025/859	234	-	-
46	-	-	-	-	-	114	76	840/796	-	-	-
47	-	-	-	-	-	115	69	740/707	< 5	-	-
48	46	-	-	-	-	116	-	-	-	-	-
49	404	4140	< 5	-	-	117	-	-	-	-	-
50	1630	5520	< 5	-	-	118	93	750/732	< 5	-	-
51	170	5080	< 5	-	-	119	1104	942/990	63	-	-
52	3700	-	< 5	-	-	120	196	768/724	127	-	-
53	250	-	-	-	-	121	-	-	-	-	-
54	100	-	-	-	-	122	75	888/-	-	-	-
55	3500	-	-	-	-	123	-	-	-	-	-
56	3124	5660	-	-	-	124	-	-	-	-	-
57	1400	-	-	-	-	125	68	1030/-	< 5	-	-
58	130	-	-	-	-	126	-	-	-	-	-
59	171	4290	-	-	-	127	-	-	-	-	-
60	130	-	-	-	-	128	-	-	-	-	-
61	-	-	-	-	-	129	137	-	-	-	-
62	124	-	-	-	-	130	-	-	-	-	-
63	153	5360	-	-	-	131	-	-	-	-	-
64	151	4630	-	-	-	132	81	1345/- ⁽¹⁾	-	-	-
65	150	4590	-	-	-	133	-	-	-	-	-
66	166	4630	-	-	-	134	-	-	-	-	-
67	250	-	-	-	-	135	-	-	-	-	-
68	-	-	-	-	-	-	-	-	-	-	-

(1) Acetate carbon.

Table A-12
MINI IV GAS ANALYSES

Test Day	Nitrate to the Reactor		Gas Flow from the Reactor (dm ³ /g NO ₃ ⁻ to reactor)	Gas Composition (% CO ₂)	Amount of CO ₂ (dm ³ CO ₂ /g NO ₃ ⁻ to reactor)	Amount of N ₂ (dm ³ N ₂ /g NO ₃ ⁻ to reactor)
	(g NO ₃ ⁻ /day)	(g NO ₃ ⁻ /day/dm ³)				
1	Startup of the Reactor					
2	254.4	4.46	0.452	55	0.249	0.203
3	276.0	4.84	0.480	56	0.269	0.211
4	278.4	4.88	0.501	54	0.270	0.231
5	273.6	4.80	0.438	51.5	0.226	0.212
6	283.2	4.97	0.455	59	0.268	0.187
7	228.0	4.00	0.521	50	0.260	0.261
8	259.2	4.55	0.466	50.5	0.235	0.225
9	259.2	4.55	0.472	55.5	0.262	0.210
10	256.8	4.63	0.438	56	0.245	0.193
11	264.0	4.46	0.476	56	0.267	0.209
12	254.4	4.46	-	58.5	-	-
13	254.4	4.46	0.495	58	0.287	0.208
14	254.4	4.46	0.477	57	0.272	0.205
15	266.4	4.67	0.446	60	0.268	0.178
16	266.4	4.67	-	-	-	-
17	266.4	4.67	0.450	56	0.252	0.198
18	252.0	4.42	0.464	61	0.283	0.181
19	Pump Plugged					
20	94.4	3.41	0.454	59	0.268	0.186
21	314.4	5.52	0.458	57.5	0.263	0.195
22	372.0	6.53	0.469	57.5	0.270	0.199
23	367.2	6.44	0.477	60	0.286	0.191
24	348.0	6.10	0.484	57	0.276	0.208
25	352.8	6.19	0.455	55.5	0.252	0.203
26	348.0	6.10	-	-	-	-
27	331.2	5.82	0.552	57	0.315	0.237
28	326.4	5.73	0.430	58	0.249	0.181
29	326.4	5.73	0.478	56	0.268	0.210
30	350.4	6.15	0.507	56	0.284	0.223
31	348.0	6.10	0.498	54.5	0.271	0.207
32	362.4	6.36	0.400	51	0.204	0.196
33	232.8	4.08	-	-	-	-
34	232.8	4.08	0.314	53.5	0.168	0.146
35	338.4	5.94	0.428	53.5	0.229	0.199
36	350.4	6.15	0.391	51	0.199	0.192
37	237.6	4.17	0.505	58.5	0.354	0.251
38	62.4	1.09	0.870	52	0.452	0.418
39	81.6	1.43	0.606	50.5	0.306	0.300
40	72.0	1.26	-	-	-	-
41	72.0	1.26	0.414	53	0.219	0.195
42	199.2	3.49	0.458	46	0.211	0.247
43	175.2	3.07	0.576	55	0.317	0.259
44	273.6	4.80	0.458	52.5	0.240	0.218
45	268.8	4.72	0.468	48.5	0.227	0.241
46	192.0	3.37	0.528	71	0.375	0.153
47	19.2	0.34	2.294	50	1.147	1.147
48	38.4	0.67	0.688	50.5	0.347	0.341
49	120.0	2.10	0.406	44	0.179	0.227
50	81.6	1.43	0.766	61.5	0.471	0.295
51	117.6	2.06	0.341	46	0.157	0.184
52	187.2	3.28	0.276	61.5	0.170	0.106
53	216.0	3.79	0.400	46	0.184	0.216
54	319.2	5.60	0.368	52.5	0.193	0.175
55	324.0	5.68	0.547	53	0.290	0.257
56	340.8	5.98	0.482	48	0.231	0.251
57	350.4	6.15	0.475	48	0.228	0.247
58	328.8	5.77	0.550	46	0.253	0.297
59	312.0	5.47	0.454	49	0.222	0.232
60	367.2	6.44	0.467	50	0.234	0.233
61	367.2	6.44	-	-	-	-
62	367.2	6.44	0.476	52	0.248	0.228
63	362.4	6.36	0.520	50	0.260	0.260
64	355.2	6.23	0.497	49	0.244	0.253
65	357.6	6.27	0.476	48	0.228	0.248
66	-	-	-	54	-	-
67	151.2	2.65	0.549	60	0.329	0.220
68	-	-	-	-	-	-
69	348.0	6.10	0.478	52	0.248	0.228
70	350.4	6.15	0.462	50	0.231	0.231
71	386.4	6.78	0.368	54	0.199	0.169
72	177.6	3.12	0.812	55	0.447	0.365
73	187.2	3.28	0.317	32.5	0.103	0.214
74	376.8	6.61	0.335	54	0.181	0.154
75	199.2	3.49	0.564	44	0.248	0.316
76	264.0	4.63	-	-	-	-
77	264.0	4.63	0.422	45	0.190	0.232
78	256.8	4.50	0.243	47	0.114	0.129
79	264.0	4.63	0.322	52	0.167	0.155
80	120.0	2.10	0.838	47	0.394	0.444
81	40.8	0.72	0.838	30	0.251	0.587
82	249.6	4.38	0.326	38	0.124	0.202
83	249.6	4.38	0.414	43	0.178	0.236
84	247.2	4.34	0.439	50	0.220	0.219
85	254.4	4.46	0.429	47	0.202	0.227
86	364.8	6.40	0.408	51	0.208	0.200
87	403.2	7.07	0.391	50	0.196	0.195
88	415.2	7.28	0.396	50	0.198	0.198
89	410.4	7.20	0.416	49	0.204	0.212
90	391.2	6.86	0.424	50	0.212	0.212
91	398.4	6.99	0.467	48	0.224	0.243
92	400.8	7.03	0.441	48	0.212	0.229
93	393.6	6.90	0.418	59	0.247	0.171
94	398.4	6.99	0.511	48.5	0.248	0.263
95	412.8	7.24	0.429	58.5	0.251	0.178
96	412.8	7.24	-	-	-	-
97	422.4	7.41	0.398	75.5	0.300	0.098
98	117.6	2.06	0.103	24	0.025	0.078
99	163.2	2.86	0.404	66	0.267	0.137
100	256.8	4.50	0.380	54	0.205	0.175
101	254.4	4.46	0.472	47	0.222	0.250
102	259.2	4.55	0.431	-	-	-
103	259.2	4.55	-	-	-	-
104	146.4	2.57	0.632	78	0.498	0.134
105	69.6	1.22	0.876	39	0.342	0.534
106	124.8	2.19	0.293	38.5	0.113	0.180
107	148.8	2.61	0.357	76.5	0.273	0.084
108	-	-	-	71	-	-
109	-	-	-	-	-	-
110	-	-	-	-	-	-
111	148.8	2.61	0.123	32	0.039	0.084
112	199.2	3.49	0.374	65	0.243	0.131
113	189.6	3.33	0.394	54	0.213	0.181
114	55.2	0.97	0.689	36.5	0.251	0.438
115	112.8	1.98	0.368	35.5	0.245	0.123
116	67.2	1.18	0.412	-	-	-
117	67.2	1.18	0.412	-	-	-
118	12.0	0.21	0.468	46.5	0.218	0.250
119	86.4	1.52	0.430	53	0.228	0.202
120	-	-	-	57	-	-
121	66.2	1.16	-	47	-	-
122	113.4	1.99	0.462	50.5	0.233	0.229
123	110.0	1.93	0.484	-	-	-
124	110.0	1.93	0.484	-	-	-
125	110.0	1.93	0.484	58	0.281	0.203
126	111.1	1.95	0.508	58.5	0.297	0.211
127	108.8	1.91	0.500	58.5	0.292	0.208
128	106.9	1.88	0.625	57.5	0.359	0.266
129	103.8	1.82	0.498	57.5	0.286	0.212
130	109.5	1.92	-	-	-	-
131	109.5	1.92	-	-	-	-
132	109.5	1.92	0.519	59.5	0.309	0.210
133	163.0	2.86	0.520	54	0.218	0.239
134	244.5	4.29	0.509	60	0.305	0.204
135	-	-	-	-	-	-

Table A-13
PILOT PLANT NITRATE REDUCTION DATA
(February 1974)

Date	Feed (kg NO ₃ ⁻)	Effluent (kg NO ₃ ⁻)	Reduced (kg NO ₃ ⁻)	Reduced (g NO ₃ ⁻ /day/dm ³)	Reactor (pH)	Reactor (K)
14	37.9	1.25	36.65	3.005	6.70	310
15	89.9	0.80	89.10	8.910	6.56	315
16	86.2	0.74	85.46	8.546	6.62	311
17	58.0	1.52	56.48	5.648	7.02	311
18	37.9	2.67	35.23	3.523	6.93	311
19	42.7	3.08	39.62	3.962	7.00	310
20	49.5	3.06	46.44	4.644	7.04	308
21	72.9	4.04	68.86	6.886	7.14	308
22	52.1	3.58	48.52	4.852	6.59	309
23	60.5	4.18	56.32	5.632	6.56	308
24	34.9	2.37	32.53	3.253	7.08	309
25	32.4	1.85	30.55	3.055	6.97	310
26	42.2	3.12	39.08	3.908	6.76	309
27	42.8	3.91	38.89	3.889	6.86	310
28	25.7	1.84	23.86	2.386	6.92	310
Total	785.6	38.01	725.59			
Daily Average	50.97	2.534	48.44	4.844	6.85	310

C/N Ratio in Feed = 197.5(1) ÷ 172.95 = 1.14:1
C/N Mole Ratio = 1.33:1

(1) Total organic carbon initially present plus additions during month.

Table A-14
PILOT PLANT NITRATE REDUCTION DATA
(March 1974)

Date	Feed (kg NO ₃ ⁻)	Effluent (kg NO ₃ ⁻)	Reduced (kg NO ₃ ⁻)	Reduced (g NO ₃ ⁻ /day/dm ³)	Reactor (pH)	Reactor (K)
1	17.1	0.17	16.83	1.683	8.85	311
2	24.4	0.08	24.32	2.432	8.53	316
3	23.9	0.04	23.86	2.386	8.26	316
4	18.4	0.08	18.34	1.834	8.17	314
5	22.0	0.03	21.97	2.197	7.98	313
6	12.2	0.05	12.15	1.215	7.71	311
7	31.2	0.06	31.14	3.114	8.07	313
8	48.3	0.11	48.19	4.819	7.86	310
9	32.4	0.06	32.34	3.234	7.84	318
10	44.6	0.17	44.43	4.443	7.88	320
11	42.8	0.30	42.50	4.250	7.73	320
12	40.1	0.07	40.03	4.003	7.84	320
13	45.8	0.08	45.72	4.572	8.03	320
14	39.1	0.04	39.26	3.926	7.74	319
15	43.38	0.04	43.34	4.334	7.75	317
16	34.90	0.05	34.85	3.485	7.61	317
17	40.92	0.05	40.87	4.087	7.61	316
18	39.12	0.04	39.08	3.908	7.77	315
19	39.69	0.04	39.65	3.965	7.59	315
20	50.77	0.10	50.67	5.067	7.79	315
21	50.11	0.05	50.06	5.006	7.67	316
22	47.05	0.03	47.62	4.762	7.71	316
23	48.30	0.04	48.26	4.826	7.99	316
24	49.54	0.04	49.50	4.950	7.72	316
25	44.62	0.04	44.58	4.458	7.49	316
26	45.18	0.03	45.15	4.515	7.42	316
27	44.62	0.04	44.58	4.458	7.40	317
28	52.57	0.04	52.53	5.253	7.39	317
29	36.66	0.02	36.64	3.664	7.45	318
30	31.16	0.02	31.14	3.114	7.32	317
31	30.60	0.02	30.58	3.050	7.41	310
Total	1171.99	2.01	1169.99			
Daily Average	37.806	0.065	37.74	3.774	7.70	310

C/N Ratio in Feed = 303.28 ÷ 264.75 = 1.15:1
C/N Mole Ratio = 1.34:1

Table A-15
PILOT PLANT NITRATE REDUCTION DATA
(April 1974)

Date	Feed (kg NO ₃ ⁻)	Effluent (kg NO ₃ ⁻)	Reduced (kg NO ₃ ⁻)	Reduced (g NO ₃ ⁻ /day/dm ³)	Reactor (pH)	Reactor (K)	Supplemental Feeding (kg)
1	39.12	0.028	39.092	3.909	7.51	316	
2	30.60	0.025	30.575	3.057	7.47	317	
3	15.25	0.009	15.241	1.524	7.17	316	
4	21.41	0.007	21.403	2.140	7.38	316	
5	19.51	0.014	19.496	1.949	7.22	315	
6	19.51	0.012	19.498	1.949	7.20	311	
7	19.51	0.017	19.493	1.949	7.45	311	
8	19.51	0.020	19.490	1.949	7.45	310	
9	39.69	0.030	39.660	3.966	7.39	308	
10	35.43	0.027	35.403	3.540	7.24	309	6.6 CH ₃ OH/C(1)
11	33.62	0.024	33.596	3.359	7.18	309	3.3 CH ₃ OH/C
12	31.83	0.038	31.792	3.179	7.29	310	
13	42.82	0.035	42.785	4.278	7.46	312	
14	42.15	0.026	42.124	4.212	7.56	316	
15	28.13	0.147	27.983	2.798	7.69	319	5.4 CH ₃ OH/C
16	50.11	0.032	50.078	5.008	7.92	316	
17	48.31	0.048	48.262	4.826	8.47	314	
18	31.83	0.057	31.773	3.177	8.35	315	
19	38.46	0.024	38.436	3.844	8.61	315	
20	29.67	2.477	23.193	2.319	6.79	315	
21	31.03	3.451	28.379	2.838	7.20	314	
22	68.27(2)	3.731	64.539	6.453	5.72	313	50.0 HNO ₃ /NO ₃ ⁻ (2)
23	54.59	0.229	54.461	5.446	6.55	311	51.0 HNO ₃ /NO ₃ ⁻
24	2.46	0.229	2.231	2.231	8.63	311	33.9 CH ₃ OH/C
25		Recycling Effluents			6.91	311	3.0 CH ₃ OH/C
26		Recycling Effluents			6.65	313	17.1 CH ₃ OH/C
27		Recycling Effluents			6.85	313	33.0 CH ₃ OH/C
28		Recycling Effluents			7.09	312	5.7 CH ₃ OH/C
29		Recycling Effluents			8.58	311	
30	25.00	2.046	22.954	2.206	0.10	313	14.0 HNO ₃ /NO ₃
Total	814.72	12.783	801.937				
Daily Average	27.157	0.426	26.781	2.678	7.47	313	

C/N Ratio in Feed = 286.72 ÷ 184.05 = 1.56:1

(1) Methanol carbon,
(2) HNO₃ added to recirculating system to remove calcite scale.

Table A-16
PILOT PLANT NITRATE REDUCTION DATA
(May 1974)

Date	Feed (kg NO ₃ ⁻)	Effluent (kg NO ₃ ⁻)	Reduced		Reactor		Supplemental Addition Calcium Acetate Carbon (kg)
			(kg NO ₃ ⁻)	(g NO ₃ ⁻ /day/dm ³)	(pH)	(K)	
1	9.8 (1)	Recycling	5.7 (2)	0.575	8.22	315	6.84
2	-	Effluent	5.75	0.575	9.32	316	-
3	13.3	Effluent	5.75	0.575	9.28	316	-
4	7.1	Effluent	5.75	0.575	8.43	311	-
5	7.1	Effluent	5.75	0.575	7.72	315	-
6	-	Effluent	5.75	0.575	7.06	315	-
7	4.4	Effluent	5.75	0.575	6.69	315	2.77
8	3.7	Effluent	5.75	0.575	7.49	313	0.73
9	2.0	Effluent	5.75	0.575	7.06	314	0.52
10	1.7	Effluent	5.74	0.574	7.10	310	4.54
11	3.3	Effluent	5.74	0.574	7.92	311	12.12
12	4.6	Effluent	5.74	0.574	8.64	314	2.85
13	17.71	0.002	5.74	0.574	8.04	312	1.60
14	21.74	0.017	21.723	2.172	7.60	312	-
15	21.98	0.249	21.731	2.173	7.45	313	-
16	47.92	Recycling	14.055	1.405	7.35	311	-
17	4.8	Recycling	14.055	1.405	6.88	311	3.08
18	-	Recycling	14.055	1.405	7.53	313	4.80
19	3.5	0.082	14.055	1.405	7.69	313	5.13
20	28.47	0.051	28.419	2.841	7.12	311	6.73
21	24.21	0.055	24.155	2.415	6.72	312	2.28
22	33.87	0.055	33.815	3.381	6.96	313	7.98
23	42.69	0.089	42.601	4.260	6.78	313	-
24	16.62	0.846	15.774	1.577	6.74	315	5.24
25	23.15	0.518	22.634	2.263	6.60	313	6.50
26	38.09	3.542	34.548	3.454	6.20	311	6.04
27	11.65	2.198	9.452	0.945	5.99	311	6.84
28	-	Recycling	6.020	0.602	6.09	314	-
29	-	Recycling	6.020	0.602	5.97	310	-
30	-	Recycling	6.020	0.602	8.15	310	14.80
31	3.7	Recycling	6.020	0.602	7.73	310	-
Total	393.40	7.072	386.328				101.39
Daily Average	12.69	0.228	12.462	1.246	7.36	313	

C/N Ratio in Feed = 188.90 ÷ 88.87 = 2.12:1

- (1) HNO₃ supplemental additions added to remove calcite in the recirculation system.
(2) Reductions are averaged as indicated for the recycling periods.

Table A-17
PILOT PLANT NITRATE REDUCTION DATA
(June 1974)

Date	Feed (kg NO ₃ ⁻)	Effluent (kg NO ₃ ⁻)	Reduced		Reactor	
			(kg NO ₃ ⁻)	(g NO ₃ ⁻ /day/dm ³)	(pH)	(K)
1	3.70(1)		6.97	0.697	8.70	311
2			8.81	0.881	8.14	312
3			3.26	0.326	7.62	312
4			10.78	1.078	6.55	312
5			17.96	1.796	6.52	314
6			8.06	0.806	6.62	314
7			11.21	1.121	6.46	311
8	5.60(1)		5.92	0.592	6.51	311
9			8.15	0.815	6.53	311
10			9.80	0.980	6.56	311
11			5.88	0.588	6.56	311
12	7.90(1)		7.53	0.753	6.89	311
13			4.90	0.490	7.62	312
14	1.76		3.40	0.340	7.04	311
15	26.44(2)		-	-	6.48	311
16	1.76		1.42	0.142	6.28	310
17	3.52		17.56	1.756	6.88	311
18	-		8.49	0.849	6.87	310
19	-		12.01	1.201	6.83	308
20	13.52(2)		6.66	0.666	6.67	307
21	69.54(2)		-	-	6.42	310
22	49.63(2)		-	-	6.45	311
23	-		15.35	1.535	6.53	311
24	3.52		15.93	1.593	6.63	311
25	7.04		36.42	3.642	7.06	311
26	3.52		24.08	2.408	7.37	312
27	7.04		11.94	1.194	7.96	311
28	7.04		9.33	0.933	8.27	311
29	10.56		14.48	1.448	8.38	311
30	3.52		31.27	3.127	8.23	311
Subtotal	225.61 + (95.77)		317.57			
Total	321.38		317.57			
Daily Average	10.71		10.59	1.059	7.05	311

C/N Ratio in Feed = 126.66 ÷ 72.60 = 1.74:1

- (1) Nitric acid/NO₃⁻.
(2) Calcium nitrate/NO₃⁻. All other additions were acidified aluminum nitrate solution to simulate concentrated raffinate.

Table A-18
PILOT PLANT NITRATE REDUCTION DATA
(July 1974)

Date	Feed (kg NO ₃ ⁻)	Effluent (kg NO ₃ ⁻)	Reduced		Reactor	
			(kg NO ₃ ⁻)	(g NO ₃ ⁻ /day/dm ³)	(pH)	(K)
1	5.28(1)		2.99	0.299	8.32	312
2	8.80		10.69	1.069	8.00	313
3	7.95		13.57	1.357	7.97	313
4	13.40		10.58	1.058	8.25	313
5	56.20(2)		4.17	0.417	7.34	312
6	6.81		16.61	1.661	7.78	312
7	-		5.87	0.587	7.31	312
8	9.09		0.61	0.061	7.21	314
9	6.81		0.93	0.093	7.05	312
10	11.60		0.07	0.007	7.07	312
11	13.63		1.23	0.123	6.90	313
12	3.27		0.65	0.065	6.80	312
13	6.81		-	-	-	312
14	2.27		-	-	-	312
15	-		-	-	-	312
16	4.54		-	-	-	312
17	6.81		1.50	0.150	6.91	312
18	5.00		9.57	0.957	7.00	314
19	2.50		4.57(3)	0.457	-	312
20	2.50		4.57	0.457	-	312
21	-		4.58	0.458	-	311
22	-		4.58	0.458	-	311
23	-		4.58	0.458	-	311
24	-		4.58	0.458	7.00	311
25	2.50		4.58	0.458	-	312
26	1.25		4.58	0.458	-	311
27	1.25		4.58	0.458	-	309
28	-		4.58	0.458	-	307
29	-		4.58	0.458	-	311
30	2.5		4.58	0.458	7.98	312
31	2.5		24.58	2.458	7.90	312
Subtotal	183.17 - (13.71)		158.56		7.30	313
Total	169.46		158.56			
Daily Average	5.47		5.11	0.511		

C/N Ratio in Feed = 49.25 ÷ 38.28 = 1.29:1

- (1) Nitrate feed for the entire month, except on the 5th, was acidified aluminum nitrate to simulate concentrated raffinate feed.
(2) Food for the 5th was calcium nitrate solution.
(3) Reductions averaged over a 12-day period.

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