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OAK RIDGE Y-12 PLANT

AN OPERATIONAL GUIDE TO THE Y-12 DENITRIFICATION FACILITY

J. M. Napier

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**AN OPERATIONAL GUIDE TO THE Y-12
DENITRIFICATION FACILITY**

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Y-12 Development Division

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SUMMARY

Developmental studies have produced a recommended start-up procedure for the biological denitrification plant for reducing nitrate wastes into nitrogen gas. The pertinent parts of this procedure are as follows:

1. Maintain the reactor in the pH range of 7.0 to 8.3.
2. Add nitrate ions and calcium acetate in a carbon-to-nitrogen (C/N) weight ratio of 1.18 during the bacteria growth phase.
3. Start the reactor at an initial nitrate ion concentration of 500 ppm using *Pseudomonas stutzeri* bacteria. When the nitrate level in the reactor falls to <200 ppm of nitrate, feed flows should be started.
4. If the nitrate level in the reactor exceeds 4000 ppm, stop feed flows until the problem is identified and corrected.

The nitrate waste stream will contain free nitric acid and aluminum nitrate that must be neutralized before the biological process can function. The denitrification vessel will, therefore, be used as a neutralization tank and as a denitrification reactor. Chemical equations, representative of the neutralization reactions, are included in this report. Calcium carbonate, which is formed in the denitrification process, will be recycled and used as a primary neutralization agent. Process flow data included in this report indicate supplemental additions of carbonates or hydroxides may be required to control the pH of the reactor.

Two chemical equations are believed to represent the denitrification process and are discussed in this report. One equation represents a bacteria growth phase where excess biomass is produced. A second equation represents a steady state phase where the biomass is recycled to supply some organic carbon as a result of the decay of the bacteria.

Several process variables are expected to produce some operational problems. The pH control must be maintained in the range of 7.0 to 8.3 because the denitrification process will not function satisfactorily at a pH of <7.0. The C/N weight ratio must be controlled to ensure that sufficient excess carbon is available to decompose the nitrates. A C/N weight ratio in the feed during start-up should be 1.18 and should be reduced to 1.07 during stabilized operations. Other operational problems that may occur and suggested corrective actions are included in this report.

AN OPERATIONAL GUIDE TO THE Y-12 DENITRIFICATION FACILITY

J. M. Napier

ABSTRACT

A plant facility has been installed to recover and recycle part of the nitric acid and aluminum nitrate wastes generated in the uranium purification process. The residual nitrate waste solutions will be decomposed into nitrogen gas by denitrifying bacteria in a separate but sequential operation. This report contains a recommended start-up procedure for the denitrification process and information on operational parameters of the plant. The start-up procedure has been successfully used for repeated start-up of laboratory reactors. Critical control parameters are pH control, carbon-to-nitrogen balance in the reactor, and nitrate feed rate. Suggestions to control these plant variables are included in this report.

INTRODUCTION

Nitric acid and aluminum nitrate will be recovered for reuse from effluents generated by uranium salvage processes. A nitrate waste stream from the recycle plant will require additional processing to reduce the nitrate wastes to acceptable levels. This stream, called "mother liquor," will be mixed with a water-soluble organic carbon and biologically decomposed into nitrogen and carbon dioxide gases and solids containing aluminum hydroxide, calcium carbonate, and a biomass. The purpose and scope of the program have been outlined in other reports.¹⁻³

The biological denitrification plant will contain bacteria, a source of organic carbon, nitrate ions, and other ingredients. This will be a living system because of the presence of active bacteria. All living systems have common features and must have some of the following conditions to sustain the life cycle:

1. Water must be present.
2. A source of carbon that can serve as an energy source must be available.
3. A source of oxygen must be available to serve as the hydrogen ion acceptor as the organic carbon is decomposed into carbon dioxide gas. In this case, the oxygen is contained in the nitrate radical.

4. Nutrients that include nitrogen, must be present. Other trace elements are necessary for sustaining bacteria.
5. Proper environmental conditions, including pH, temperature, and pressure, must be maintained.

As previously stated, all living systems must have a source of carbon as an energy source. In our case, calcium acetate will be used, and the bacteria will decompose the acetate ion to produce carbon dioxide gas and a hydrogen ion. Because no oxygen will be present, the nitrate ion will accept the hydrogen ion, and the end products will be nitrogen gas and water. It should be emphasized that bacteria do not use the nitrate ion as a food supply; a small amount of nitrogen is required in the production of new bacteria, but the majority of the nitrate ions are decomposed only as a secondary reaction.

It should also be noted that the reduction by bacteria of acetate ions to carbon dioxide (CO_2) and nitrate ions to nitrogen (N_2) involves many chemical reactions, and all of the reactions for this reactor are not known.

This report is oriented toward the operation of the biodenitrification part of the recycle facility and is intended to serve as a guide in the development of operational policies and procedures. Recommendations are based on laboratory and pilot-plant denitrification studies that have been documented in Report Y-1990 entitled *Denitrification of Acid Wastes from Uranium Purification Processes*.³

ACID WASTE DENITRIFICATION

START-UP PROCEDURE

Several start-up procedures have been successfully used during the laboratory and pilot-plant studies. All of the procedures were essentially the same except the amount of "seed" bacteria was varied and the chemicals used to control the pH were varied both in quantity and in type (i.e., calcium carbonate, calcium biocarbonate, calcium hydroxide, sodium carbonate, sodium biocarbonate, and sodium hydroxide have been used).

The following procedure is based on laboratory reactor operations and is recommended for the production plant:

1. Fill the 25,000-gal tank with process water. Do not use demineralized water.
2. Add 43 lb of sodium carbonate or bicarbonate to the 25,000 gal of water.

3. Mix for 30 min and check the pH and temperature in the vessel. If the pH is <6.8 , add additional sodium carbonate, bicarbonate, or hydroxide to raise the pH to the range of 7.0 to 8.3. If >8.3 , hydrochloric acid can be used to lower the pH.

If the temperature is $<20^{\circ}\text{C}$, apply steam to the reactor to increase the temperature to the range of 20° to 35°C (68° to 95°F).

If practical, bubble nitrogen gas into the solution to decrease the oxygen content in the reactor. This is not required but will aid in the start-up because the bacteria will use the oxygen in air in preference to nitrates.

4. Adjust the nitrate ion content of the reactor to 500 ppm by adding either commercial-grade calcium nitrate or raffinate. If commercial-grade calcium nitrate is used, 168 lb should be added to the reactor. If raffinate wastes are used, the nitrate concentration should be determined and an amount added to the reactor to achieve a 500-ppm nitrate level of the tank contents. The nitrate wastes may cause a pH drop, which must then be adjusted by adding one of the neutralization agents (calcium, sodium carbonate, or hydroxide).
5. Calcium acetate should be added to obtain a total organic carbon (TOC) level of 133 ppm of the tank contents. This will require 91.42 lb of calcium acetate (chemical composition equal to 30.3% carbon). If a water solution of 17% calcium acetate is used, then 54 gal of the solution should be added. The important point is to have a carbon-to-nitrogen (C/N) weight ratio of 1.18.
6. The reactor solution should be mixed for at least 30 min and the pH adjusted to a range of 7.0 to 8.3.
7. The equivalent of 20 ppm of phosphate, 10 ppm of magnesium sulfate, and 1 ppm of sodium molybdate should be added. These concentrations will result in adding the following amounts of chemicals:
 - (a) $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ —12 lb/25,000 gal of water
 - (b) $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ —4.2 lb/25,000 gal of water
 - (c) Na_2MoO_4 —0.45 lb/25,000 gal of water

The solution in the reactor should be stirred while these chemicals are added. They can be poured directly into the reactor or dissolved in water and then poured into the tank.
8. The reactor should be sealed to prevent air leaking into the vessel.

9. A nominal 215 gal of "seed" bacteria should then be added to the reactor. These bacteria will be supplied by Development Division personnel from cultures grown in the laboratory studies.
10. Record the following data:
 - (a) pH,
 - (b) temperature,
 - (c) gas flow reading,
 - (d) NO_3 , and
 - (e) TOC.
11. As soon as the nitrate level decreases to 200 ppm or less, the feed flow should be started at a rate equal to 1 g of nitrate/d/L of solution (208 lb of nitrate/d per reactor).

It is normal that 1 to 5 d will elapse before feed can be started. It is important that sufficient carbon be available in the tank to ensure reproduction of the bacteria. The carbon level in the reactor solution should be 200 or more ppm.
12. The pH should be maintained in the range of 7.0 to 8.3 by adding a neutralization agent (sodium carbonate, bicarbonate, or hydroxide preferred). The pH normally decreases in 3 to 7 d after feed flows start.
13. The following data should be taken at least once per shift during start-up:
 - (a) gas flow rate from the reactor,
 - (b) NO_3^- concentration of the reactor solution,
 - (c) pH of the reactor solution,
 - (d) TOC of the reactor solution, and
 - (e) temperature of the reactor solution.
14. The gas analyses should be <60% carbon dioxide, the pH in the range of 7.0 to 8.3, the nitrate ion concentration <4000 ppm, and the TOC in the range of 500 to 4000 ppm. If these conditions exist, the reactor can be assumed to be operating. The offgas rate should be in the order of 343 L/min using raffinate wastes (~0.44 L/min/g of nitrate ion decomposed).

15. The feed rate to the reactor can then be slowly increased as long as the nitrate ion concentration of the reactor contents does not exceed 4000 ppm and the pH is in the correct range (7.0 to 8.3).
16. If the nitrates exceed 4000 ppm, the feed flows should be stopped to allow the reactor to stabilize.
17. If the reactor was started using commercial-grade calcium nitrate, the nitrate feed can be changed to plant nitrate wastes after 5 to 8 d of operation.
18. When the reactor is operated on stabilized flow rates, the organic carbon flow should be reduced to a C/N weight ratio of 1.07. The carbon level of the reactor solution should normally be in the range of 500 to 1000 ppm with a maximum level of 2500 ppm.

CAUTION: This is an anaerobic process, and no oxygen (air) should be allowed to enter the reactor.

FLOW SHEET

Two process flow sheets, shown in Figs. 1 and 2, were made based on 1973 monthly effluent flows. The flow sheet shown in Fig. 1 represents expected flows during the startup phase of the reactor. The Fig. 2 flow sheet is expected to be valid during stable operations of the reactor. It is recognized that flows used in these figures do not represent present daily flow rates, but the current flows are not expected to be greater than used for this report.

Based on 1973 process data, the daily mother liquor waste stream from the chemical recycle plant would contain 2191 lb of nitrates/d and 264 lb of free nitric acid for a total daily output of 2455 lb of nitrate ions. The mother liquor stream would have a nominal specific gravity of 1.422 g/cm³ (11.8 lb/gal) and a daily flow rate of 371 gal/d (0.26 gal/min). As noted in Figs. 1 and 2, a water solution of calcium acetate will be added to the denitrification reactor. During start-up (Fig. 1), a daily total of 2,147 lb of calcium acetate and 12,629 lb of water will be required. This will be equal to an input flow rate of 1.05 gal/min or 1512 gal/d.

CHEMICAL REACTIONS

Startup Phase

The denitrification vessel will be used as a neutralization tank and as a denitrification reactor. The mother liquor stream will be neutralized by the excess calcium carbonate that is produced as a by-product of the denitrification reaction. The neutralization reactions are expected to be as follows:

Fig. 1. Startup phase of the denitrification process^a ^aEstimate based on 1973 flow data, Report Y-DA-6094.^bBased on lab tests, 50% of solids will precipitate in the reactor, thus reducing the solid contents to ~5 wt %. Also, the excess CaCO₃ may be less than shown (reference Table 5 of this report)

Fig. 2. Stabilized operations.

^aBased on lab tests, 50% of solids will precipitate in solid contents to ~4.3 wt %.

These two reactions will require 1274 lb/d of calcium carbonate, assuming discharge rates equal to those generated during 1973. It has been assumed that some of the nitrate wastes will not require additions of calcium carbonate because some amounts of calcium, sodium, and other cations will be present in the mother liquor stream. If this assumption is not valid, then calcium, sodium, or potassium ions will have to be added to control the pH of the denitrification solution.

During the start-up, the following equation is believed to be valid for the denitrification process:

As shown in Table 1, if 3242 lb/d of calcium nitrate are available, a total of 2147 lb/d of calcium acetate must be added to obtain a C/N weight ratio of 1.18.

**Table 1. Startup denitrification equation
(biomass growth phase)^a**

Chemicals	Production rate (lb/d)
<i>To reactor</i>	
$\text{Ca}(\text{NO}_3)_2$	
From free acid neutralization	344
From $\text{Al}(\text{NO}_3)_3$ reaction	1746
From miscellaneous chemical reactions	1152
Total $\text{Ca}(\text{NO}_3)_2$	3242
$\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$	2147 ^b
<i>From reactor</i>	
$\text{C}_5\text{H}_7\text{O}_2\text{N}$	112
CO_2	707
N_2	551
H_2O	645
$(\text{OH})^-$	50
CaCO_3^c	3336

^a $0.55 \text{ Ca}(\text{C}_2\text{H}_3\text{O}_2)_2 + 0.8 \text{ Ca}(\text{NO}_3)_2 \rightarrow 0.04 \text{ C}_5\text{H}_7\text{O}_2\text{N (biomass)}$
 $0.65 \text{ CO}_2 + 0.796 \text{ N}_2 + 1.35 \text{ CaCO}_3 + 1.45 \text{ H}_2\text{O} + 0.12 (\text{OH})^-$.

^bC/N weight ratio 1.18.

^c2563 lb of CaCO_3 is required for neutralization, leaving 773 lb/d of excess.

The denitrification process will produce 3336 lb/d of calcium carbonate in addition to the amounts of biomass and other materials shown in Table 1. However, 2563 lb/d of calcium carbonate will be used for neutralization, leaving an excess of 773 lb/d of calcium carbonate. This excess amount of calcium carbonate is estimated to be present if the miscellaneous chemicals in the mother liquor do not require neutralization. If this assumption is not valid, then the total amount of calcium carbonate required per day will be 3715 lb, which means the reactor will be deficient in calcium carbonate (379 lb/d). Laboratory tests have shown that ~50% of the calcium carbonate is precipitated on the sides of the reactor. This precipitated calcium carbonate will reduce the amount that can be used for neutralization. Therefore, it is very probable that the reactor will require additions of 50 to 100 lb/d of sodium or calcium ions, as hydroxide, to control the pH of the reactor.

Stabilized Reactor Operations

As previously stated, the denitrification vessel will be used as a neutralization tank and as a denitrification reactor. When the reactor is operated at or near a constant flow for a period of time (estimated to be 10 to 60 d), the denitrification reaction is believed to change where the biomass is recycled and used as a carbon food supply in addition to the calcium acetate. The following equation is believed to represent stable operations:

As shown in Table 2, if 3242 lb/d of calcium nitrate are available, the amount of calcium acetate will be reduced to 1952 lb/d to obtain a C/N weight ratio of 1.07. The significance of this ratio is discussed later in the C/N ratio section of this report.

The stabilized denitrification process will produce 3212 lb/d of calcium carbonate plus the other wastes shown in Table 2. However, 2563 lb/d of calcium carbonate may be required for neutralization of the crystallizer mother liquor stream. An excess of 649 lb/d of calcium carbonate could be produced if the miscellaneous nitrates do not require neutralization. If this assumption is not valid, then the reactor will be deficient in calcium carbonate (503 lb/d). As previously mentioned, some calcium carbonate will precipitate and will not be readily available for neutralization of the mother liquor stream. It is very probable that some sodium or calcium ions will have to be added to control the pH of the solution.

NITRATE FEED

As previously mentioned, the nitrate feed, called mother liquor, will be an acid stream similar in composition to those noted in Figs. 1 and 2. The nitrate feed flow will be a typical 0.26 gal/min assuming

Table 2. Stabilized reactor operations^a

Chemicals	Production rate (lb/d)
<i>To reactor</i>	
Ca(NO ₃) ₂	3242
Ca(C ₂ H ₃ O ₂) ₂	1952 ^b
<i>From reactor</i>	
C ₅ H ₇ O ₂ N	0.0
CO ₂	761
N ₂	554
H ₂ O	667
(OH) ⁻	0
CaCO ₃ ^c	3213

^a0.5 Ca(C₂H₃O₂)₂ + 0.8 Ca(NO₃)₂ → 0.7 CO₂
+ 0.8 N₂ + 1.3 CaCO₃ + 1.5 H₂O.

^bC/N weight ratio 1.07.

^c2563 lb CaCO₃ is required for neutralization,
leaving 649 lb/d of excess.

plant effluent flows approximating the 1973 flow rates. The nitrate feed flow rate to the reactor can and may be expected to vary during the operation of the plant. If the nitrate feed flow rate is varied, the calcium acetate flow must also be adjusted to maintain a correct C/N balance to the reactor. If the nitrate content in the reactor is low (<500 ppm of nitrate), the feed can be increased if desired. The laboratory reactor vessels were operated at a maximum feed rate equivalent to 13 g of nitrate per day per liter of reactor solution. This amount would be equal to 2709 lb/d of nitrates per 25,000 gal of reactor solution, which is the size of each of the two reactors in the plant. Based on laboratory data, the production reactor was designed to decompose a nominal 1150 lb/d of nitrate wastes. If more than 1150 lb of nitrates are available, it is recommended that the production plant operate two reactors that have been designed to be operated individually or combined in series. One of the vessels can also be used as a backup unit in case of failure of the primary reactor. It is recommended that both reactors be started, but one reactor would receive only a very small daily amount of nitrate wastes and organic carbon. This would maintain a bacteria population in the reactor that would be sufficient in the event that the bacteria in the primary vessel were destroyed.

CARBON FEED

Laboratory studies have shown that the system works well using calcium acetate as the carbon source. Also, calcium ions are needed for neutralization, and a large part of the calcium will be supplied from the carbon feed.

Methyl alcohol has been used in development work in place of calcium acetate. However, the bacteria were found to be very sensitive to minor process variations. When methanol was used in laboratory studies, the bacteria population decreased from a "mixed" culture to a "narrow" culture, which was believed to be essentially two types of bacteria. Laboratory culture tests were made, and a tentative identification indicated a major shift in the types of bacteria present in the reactor.

Development tests were made to use a mixture of methanol and calcium acetate. In all tests, the calcium acetate was decomposed completely without any change in the methanol concentration. It is recommended that the organic feed to the reactor be calcium acetate because the bacteria will readily decompose this material and the calcium ion is needed during the neutralization operation.

CARBON-TO-NITROGEN RATIO

This is an important process parameter and must be closely controlled in the plant. A wide range of C/N weight ratios have been used in the development studies. However, during start-up or an increase in feed rates, a C/N weight ratio in the feed must be 1.18. This ratio will supply sufficient carbon to allow reproduction of bacteria at a faster rate than the death rate. It should be remembered that the organic carbon is the food supply for the bacteria. The nitrate ion serves as the only oxygen source for the discarded hydrogen ions that are produced in the organic decomposition reaction. This situation is established and is based on the fact that the system is anaerobic (oxygen-starved).

During stable operations, the production rate of new bacteria will equal the death rate. The dead bacteria will decompose, releasing organic compounds that supply organic carbon, which is believed to serve as a food supply for the manufacture of new bacteria. The C/N weight ratio in the feed must be reduced to 1.07 to prevent high carbon levels from occurring in the reactor.

The C/N ratio in the reactor is important for successful facility operations. The acetate carbon level in the vessel must be slightly higher than the nitrate content. Typical values of a satisfactorily operating reactor would be an acetate carbon level of >100 ppm if the nitrate level is <50 ppm. During the laboratory studies, operational troubles have occurred if the acetate carbon has exceeded 4000 ppm while the nitrate concentration was <50 ppm. It is recommended that the acetate carbon level be maintained in the reactor in the range of 100 to 2000 ppm; a level of ~500 ppm of acetate carbon is the target concentration.

Normally, laboratory analyses report the TOC and, upon request, can determine the amount of free acetate ions in the reactor solution. The TOC values represent all soluble organic carbon, including some bacteria. The TOC value will normally be 300 to 600 ppm at an acetate level of <10 ppm. The acetate level determines the useful organic carbon, and if only a TOC value is obtained, the reactor will normally stop functioning at a TOC level of <600 ppm.

FLOW RATE

A common cause of poor reactor operations can be a high liquid flow to the reactor. High flows will eject bacteria from the reactor at a faster rate than is formed. This phenomenon is called "wash out" in a standard aerobic sewage plant. The denitrification vessel was designed to have a minimum liquid residence time of 10 d which means the total liquid flow to the reactor should be <2500 gal/d (1.74 gal/min). Longer residence times will not harm the reactor performance, and up to 40-d residence times have been successfully used in laboratory studies. It is recommended that the residence time or inlet flow rate be controlled to maintain a minimum residence time of 10 d.

NITRATE CONCENTRATION IN REACTOR

The overall nitrate level in the reactor should normally <100 ppm. However, reactors have been successfully operated at nitrate levels as high as 8000 ppm. During start-up it will be desirable to have a starting nitrate level of 500 ppm to have sufficient nitrogen to obtain a high bacteria growth rate. During stabilized operations, a level of <100 ppm of nitrate will be common. If the nitrate level increases rapidly, it is probably caused by one or more of the following items:

1. low pH,
2. insufficient amount of organic carbon,
3. insufficient amount of nutrients (phosphates),
4. a sudden increase in the reactor feed,
5. low reactor temperature,
6. a poisoning agent in the reactor, or
7. other unusual process perturbations.

The primary process corrective action is to cut off the reactor feed flow until the cause of the nitrate increase is determined. Low pH levels can be corrected by additions of caustic, carbonates, or bicarbonates. This problem will be discussed in more detail in the pH section of this report. A low carbon level can be detected by laboratory analysis, but this even will not occur suddenly. A low carbon level can usually be predicted several days in advance of trouble.

A low nutrient level will not occur rapidly, and reactor operational problems will occur over a few days. This problem can be corrected by adding nutrients to the reactor (~20 ppm of soluble phosphate ion in the reactor solution). Sodium hypophosphate, which is highly soluble in water, is specified as the source of the phosphate ion.

A sudden increase in the feed flow rate can cause the nitrate level in the tank to increase. If the increased nitrate flow rate causes a flow increase in the exhaust gases and if the carbon dioxide concentration does not significantly increase, then the reactor nitrate level will decrease within a few hours. If the nitrate level approaches 4000 ppm, the feed flows should be stopped until the nitrate level is reduced to <500 ppm.

Low reactor temperatures will cause a decrease in the microbial growth rate. Temperatures <20°C (68°F) should be adjusted by adding steam to the reactor solution. Temperatures >35°C (95°F) should also be avoided by spraying cooling water on the outside of the tank. Laboratory reactors have been successfully operated up to 42°C (106°F), but it is recommended that the production vessel not be operated at >35°C (85°F) for long time periods.

A poisoning agent may enter the reactor during normal operations. Common poisoning agents include soluble mercury, lead, cadmium, and other metal ions. In the laboratory studies there have been no operational problems related to poisoning agents. The reactor solution should precipitate or complex the common metal poisons. If, however, the microbes are killed because of a poisoning agent, the solution should be pumped to the S-3 ponds, and the vessel should be thoroughly washed with water. The source of the poisoning agent should be eliminated, and the reactor should be restarted.

DENITRIFICATION BACTERIA

The plant will be started using bacteria that originated from a culture of *Pseudomonas stutzeri*. Representative samples of the bacteria that will be used in the plant are in storage. "Seed" bacteria for the plant can be produced from those in storage within a few weeks (<8 weeks). It is possible that a change in the stored bacteria population has occurred and that a mixed population will be available for start-up operations.

The number of bacteria per unit volume of the reactor determines the amount of nitrate that can be decomposed per unit time. The exact number per volume is not known, but typical sewage plants have a population ranging from 2000 to 5000 ppm. Because of the high solid contents of the denitrification reactor, common techniques to determine the population cannot be used. During laboratory studies, data were not collected to determine the bacterial population. The number will change depending on process operating conditions. Photographic examinations were occasionally made during laboratory studies to obtain the typical shape and size of the microbes. In general, the bacteria were rod

shaped and about the same length; however, bacteria were different lengths and were not rod shaped. These data indicated a mixture of bacteria were present in the reactor. During one test period when abnormal operations occurred, the population was found to consist of only two shapes and sizes of bacteria. The reactor did not operate at a high high feed rate until reseeded with the original culture. The cause of the shift to essentially two types of bacteria in the test reactor was not determined.

REACTOR pH

The pH of the reactor is a very important parameter and may be the most difficult to control during reactor operations. The bacteria will not survive a pH level <6.8 but can operate satisfactorily at least up to a pH of 8.3.

The reactor solution can be considered as a buffered solution. Calcium acetate and nitrate solutions, when a trace of free acetic or nitric acid is present, have a pH in the range of 5.5 to 6.5. When carbon dioxide gas is present, the pH will be lowered because of the formation of carbonic acid. No denitrification will occur at pH 6.5 or less with the type of bacteria that will be present in the reactors.

A second buffered range in the reactor solution occurs at a pH of 6.8 to 6.9. The reactor will operate at a satisfactory rate at a pH of 6.8, but normally the pH will drop to 6.5 or less within a few days (1 to 3 d) unless additional soluble hydroxide cations are added.

A third buffered range in the reactor occurs at a pH range of 7.1 to 7.2. A variety of microbes tends to buffer solutions at a pH of 7.2 and is the most desirable pH for most bacterial reproduction to occur.

A fourth buffered range has been found at or near a pH of 7.8, particularly when the reactor was operating at a high feed rate but a low nitrate level in the reactor (<50 ppm).

A fifth pH range has been frequently noted at 8.3 when the reactor was operating at a high denitrification rate, with a low nitrate level in the reactor and with some sodium ions present in the solution.

Reactions in the reactor can be expected to change frequently, depending on the impurities extracted during the uranium purification operations that ultimately enter the mother liquor stream. In any event, pH control of the reactor must be maintained to obtain a satisfactory denitrification rate. The amount of calcium ions should be in excess of that needed for the neutralization process. However, some calcium ions will be precipitated as calcium carbonate, which will not be very effective in the neutralization operation. In the laboratory studies, batch additions of calcium carbonate, calcium hydroxide, sodium carbonate, sodium bicarbonate, and sodium hydroxide have been used to control the reactor pH. In general, low pH values will occur over a long time span (several hours to several days). When the pH is adjusted, denitrification rates have always increased within a few hours.

TEMPERATURE

The laboratory reactors have normally been operated in the range of 20 to 35°C (68 to 95°F). As previously mentioned, one reactor was operated up to 42°C (106°F) without any abnormal effects being noted. Consultations with biologists have indicated that the optimum temperature for many species of bacteria is 37°C (98.6°F). Some bacteria have a doubling of the reproduction rate with each 10°C increase in temperature. Because the reactor vessel will also be the neutralization vessel, heat will be generated by neutralization of the acid wastes. It is not likely that temperatures <20°C (68°F) will occur in the vessel. However, if this occurs, steam can be injected directly into the vessel to raise the temperature of the solution. The number of bacteria that will be killed by the hot steam injection should be low. In any event, raising the temperature to at least 20°C (68°F) will cause an increase in the reproduction rate, which will more than compensate for the bacteria destroyed by the steam.

A high temperature is probable during the hot summer months, particularly August. High temperatures [i.e., >35°C (95°F)] can be avoided by spraying cooling water onto the walls of the vessel. As previously stated, temperatures up to 42°C (106°F) have not been found to be detrimental to the operation of the process.

NUTRIENTS

All living reproduction processes require the addition of trace nutrients, particularly phosphorus and sulphates. There is much controversy as to the minimum amount and as to the different materials that must be added. During the development of the process, daily additions equal to 20 ppm of phosphate ions, 10 ppm of sulfate ions, and 1 ppm of molybdenum were added. It is known that most of the phosphate ions combined with calcium in the reactor, and a nominal 5 ppm of phosphate were all that remained in solution. It is also known that when the phosphate was not added, the denitrification process did not function at a high rate, and after a few days' period, the reactor performance dropped to unacceptably low denitrification rates.

There are no positive laboratory data available that show the effects of adding sulfates and molybdenum.

Nutrients have been routinely added once or twice per day (batch fed). However, one reactor was operated by using a continuous feed of nutrients, and it appears that batch or continuous feed is an acceptable method. Also, the amount per day added does not appear to be critical. Sudden changes in the phosphate concentration in the reactor probably will not occur. In any case, daily additions of the nutrient solution (Figs. 1 and 2) should be sufficient to prevent problems arising from low nutrient levels in the reactor.

GASES FROM THE REACTOR

Two gases will be generated during the process (as noted in Figs. 1 and 2). During start-up operations or feed increase periods, a nominal 200 L/min of carbon dioxide and 140 L/min of nitrogen will be evolved from the reactor (Table 3). Carbon dioxide will be formed by the free nitric acid and the aluminum nitrate neutralization, plus the bacterial decomposition of the organic carbon. The nitrogen gas will be released as a result of the decomposition of the nitrate ions. Usually, the gas mixture will be 59% carbon dioxide and 41% nitrogen. Normal operations will generate 202 L of gas per pound of nitrate decomposed (444 cm³/min/g nitrate).

Table 3. Gas balance—startup phase

Source compound	Reaction rate (lb/d)	CO ₂ produced	
		mol	L
<i>CO₂ production</i>			
HNO ₃	92.2	951	21,302
Al(NO ₃) ₃	469	4,839	108,394
Ca(NO ₃) ₂	707	7,295	163,408
Total			293,104 ^a
<i>N₂ production</i>			
Ca(NO ₃) ₂	551	8,934	200,122
Total			200,122 ^b

^aRate of CO₂ flow is 203.5 L/min.

^bRate of N₂ flow rate is 139 L/min.

NOTE: If NO₃ feed rate is 2,451 lb/d (1.7 lb of NO₃/min), then the total gas flow = 342.5 L/min (CO₂ = 59.4%; N₂ = 40.6%). This will equal 444 cm³/min of gas per gram of NO₃ decomposed (201.6 L/lb of NO₃).

During stabilized operations, the quantity of carbon dioxide gas generated will increase to ~212 L/min and the nitrogen gas will increase to ~140 L/min (Table 4). The composition of the gas will change to 60% carbon dioxide and 40% nitrate. The gas flow evolved will be equal to 207 L/lb of nitrate (456 cm³/min/g nitrate).

The concentration of carbon dioxide will be continuously monitored in the production reactor. Concentrations <60% will be observed during

startup until the reactor solution becomes saturated with carbon dioxide gas and all of the available chemical reactions are complete (i.e., formation of bicarbonates and carbonates). Low carbon dioxide levels during start-up should be expected, and no corrective action should be taken.

During stable operations, low carbon dioxide levels can be an indication that the reactor is deficient in organic carbon. If this is the problem, the nitrate level in the reactor will increase, and the total gas flow will decrease. Low carbon dioxide levels can also indicate that the feed composition has changed, and less neutralization is required. Again, the total gas flow will decrease, but the nitrate level in the reactor will not increase. In all cases, the carbon dioxide level can be expected to vary from 50 to 60% during routine operation of the reactor. This should be considered to be a normal range, and no corrective actions should be taken while in this range.

Table 4. Gas balance - stabilized phase

Source compound	Reaction rate (lb/d)	CO ₂ produced	
		mol	L
<i>CO₂ production</i>			
HNO ₃	92.2	925	21,302
Al(NO ₃)	469	4,839	108,394
Ca(NO ₃) ₂	761	7,852	175,888
Total			305,584 ^a
<i>N₂ production</i>			
Ca(NO ₃) ₂	554	8,983	201,213
Total			201,213 ^b

^aRate of CO₂ flow is 212.2 L/min.

^bRate of N₂ flow is 139.7 L/min.

NOTE: If NO₃ feed rate is 2,451 lb/d (1.7 lb of NO₃/min), then the total gas flow is 351.9 L/min (CO₂ = 60.3%; N₂ = 39.7%), that is, 456 L/min of gas per gram of NO₃ decomposed (207 L/lb of NO₃).

High carbon dioxide levels (>60%) can occur during start-up and also during stabilized operation of the reactor. High carbon dioxide levels are an excellent indication of poor reactor performance. The nitrate level in the reactor will increase if the feed rate is maintained. The best corrective action is to cut the feed rate immediately until the problem can be isolated and corrected. Nitrogen oxide gas will be evolved from the reactor when the carbon dioxide level is >80%. The high carbon dioxide level can be caused by a variety of reasons, but the most probable reason is that the bacterial population is too low for the nitrate feed rate. A sudden drop in the pH of the reactor will also cause a sharp increase in the carbon dioxide concentration. Carbonates and bicarbonates will be decomposed, and carbon dioxide gas will be released. Adding a neutralizing agent will correct the pH problem and cause a sudden drop in the carbon dioxide level because of formation of carbonates and bicarbonates. As previously stated, carbon dioxide levels above 60% indicate abnormal reactor operations, and the cause of the problem should be located and corrected.

REACTOR SOLIDS

As noted in Table 5, the amount of solids produced each day during startup, using 1973 effluent flow rates, will be 1590 lb. The expected volume of water per day is 12,851 lb (1,886 gal). The water and solids

Table 5. Waste products from reactor—start-up phase^a

Waste product	Flow rate (lb/d)
<i>Solids^b</i>	
C ₅ H ₇ O ₂ N	112
CaCO ₃	773
Al(OH) ₃	554
(OH) ⁻	151
Total solids	1,590
<i>Water^c</i>	
Reaction water	645
Water in feed	12,206
Total water ^d	12,851

^aBased on laboratory tests, a maximum of 50% of the solids will precipitate on the walls of the vessel. If this occurs, the solids from the reactor will be 795 lb/d and the water will be 12,851 lb/d, assuming 1973 effluent flows.

^bSolids content = 11.0 wt %.

^cWater content = 89.0 wt %.

^dTotal water = 1,543 gal/d; 1.07 gal/min).

will be taken from the reactor simultaneously, and the liquid slurry will have a maximum concentration of solids of ~11 wt %. The total amount of solids taken from the reactor will be less than the 1590 lb/d because some of the solids will precipitate in the reactor. In laboratory studies, ~50% of the solids were deposited in the vessel. In production it is not known how much of the solids will precipitate in the reactor. The production reactor will have to be drained and cleaned after some period of time. The operating time between clean-outs was 4 to 6 months in the laboratory reactors. In the production reactor, the clean-out times will have to be determined.

The expected wastes from stabilized operations (Table 6) will be reduced to 1203 lb/d, assuming 1973 flow rates. The solid content in the waste water will be reduced to a maximum of 8.5 wt %. As previously mentioned, precipitated solids in the reactor will reduce the total expected daily amount.

Table 6. Waste products from reactor—stabilized phase^a

Waste product	Flow rate (lb/d)
<i>Solids^b</i>	
C ₅ H ₇ O ₂ N	0
CaCO ₃	649
Al(OH) ₃	554
(OH) ⁻	0
Total solids	1,203
<i>Water^c</i>	
Reaction water	667
Water in feed	12,206
Total water ^d	12,873

^aBased on laboratory tests, a maximum of 50% of the solids will precipitate on the walls of the vessel. If this occurs, the solids from the reactor will be 602 lb/d and the water will be 12,873 lb/d, assuming 1973 effluent flows.

^bSolids content = 8.5% wt %.

^cWater content = 91.5% wt %.

^dTotal water = 1,545 lb/d; 1.07 gal/min.

The solids will primarily be calcium carbonate and aluminum hydroxide. The water and solids are expected to be either buried in the sanitary landfill or placed in one of the S-3 acid ponds. If they are buried, the solids may produce an odor caused by the decay and decomposition of biomass. The solids should be covered with soil within 5 d to eliminate undesirable odors being released from the solids and water.

If the solids and water are placed in one of the S-3 ponds, some amount of neutralization will occur although it may be several years before any detectable change occurs in the pH of the S-3 ponds. The aluminum hydroxide will settle to the bottom of the pond or react to form aluminum nitrate, and the bottom may ultimately be sealed, but at a very slow rate, and should not be a major problem. It is recommended that the wastewater and solids be transferred to the S-3 ponds. The effects on the ponds should be monitored to determine any adverse effects.

ODORS FROM THE PLANT

The reactors will vent the nitrogen and carbon dioxide gases to a roof vent, and no detectable odors should be noted in the exhaust gases. The solid and liquid wastes taken off each day should not have an offensive odor if buried or dumped into the S-3 ponds within 5 d. This waste solution will putrefy with time if left standing in the waste disposal container for more than 5 d, and an offensive odor that may contain a trace amount of hydrogen sulfide will be released. If putrefaction occurs, air can be bubbled into the container, and within a few hours the offensive odors will be stopped. The bacteria present in the tank begin to die, and other bacteria use the organic carbon from the dead microbes. If nitrate ions are present, no offensive odors are released because nitrogen gas is evolved. If the solution is void in nitrates, the sulfate ions act as the terminal hydrogen acceptor in the energy transport system. One of the end products of sulfate reduction is the release of hydrogen sulfide. As previously mentioned, if odors are emitted from the waste container, injecting air (i.e., oxygen) into the vessel will prevent the production of hydrogen sulfide because the oxygen will combine with the hydrogen ions to form water.

CONCLUSIONS

Laboratory and pilot-plant studies have been undertaken to develop a biological denitrification process suitable for disposing of nitrate wastes generated in the uranium purification process at the Y-12 Plant. A plant that will recycle ~67% of the nitric acid-aluminum nitrate wastes and biologically decompose ~33% of the wastes has been engineered and installed.

The biodenitrification process will use a stirred bed reactor similar in design to a commercial water-softening vessel. Nitrate wastes, a soluble organic carbon (calcium acetate), and denitrifying bacteria will decompose the materials into nitrogen gas, carbon dioxide, and biomass.

Solids made in the process will primarily be aluminum hydroxide and calcium carbonate. The nitrate reduction efficiency of the process is expected to be >99.9% in the biological process. Expected operation programs that may occur in the plant have been documented in this report.

There will be process perturbations that cannot be predicted, and the cause of these perturbations may not be immediately clear. Biological systems have been studied in depth, but technical information on a system such as our reactors is very limited. Most of the reported technical data on denitrification of wastes were obtained on waste streams containing <50 ppm of nitrate. More than 2 years of development have been done on this process, but there are many parameters that have not been completely studied. Questions that cannot be answered about this system will arise. Therefore, some new problems may arise, and solutions to these problems will be found during plant operations.

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