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REMOVAL OF GADOLINIUM NITRATE FROM HEAVY WATER

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CONTENTS

List of Tables

List of Figures

1.0 Executive Summary

Work was conducted to develop a cost-effective process to purify 181 55-gallon drums containing spent heavy water moderator (D_2O) contaminated with high concentrations of gadolinium nitrate, a chemical used as a neutron poison during former nuclear reactor operations at the Savannah River Site (SRS). These drums also contain low level radioactive contamination, including tritium, which complicates treatment options. Presently, the drums of degraded moderator are being stored on site. It was suggested that a process utilizing biological mechanisms could potentially lower the total cost of heavy water purification by allowing the use of smaller equipment with less product loss and a reduction in the quantity of secondary waste materials produced by the current baseline process (ion exchange).

Microbiological and chemical studies were initiated to evaluate the potential use of bacteria and algae for water purification of the drums. These studies along with recommendations for continued process development work are described herein. Principal components of the study included:

1) chemical and biological characterization of representative drums from the 181 drum inventory,
2) evaluation of the toxicity of gadolinium to various microbes,
3) evaluation of the effectiveness of gadolinium precipitation with phosphate and the hydrate composition of the precipitate, and
4) the comparative growth and nitrate removal capabilities of selected microbes subjected to nitrate salts at various concentrations and with four different anion components.

Results from the drum characterization studies showed substantial variability among drums in terms of pH, conductivity, heavy water content, and gadolinium nitrate concentration. Gadolinium concentrations ranged from 0.09 ppm to 203,800 ppm in eight drums selected for intensive sampling. Biological sampling demonstrated the presence of microorganisms in all eight of these drums and suggested that gadolinium may have a toxic effect on microbes since substantial growth could only be enhanced by nutrient addition in three of four drums with relatively low (<100 ppm) gadolinium concentrations. No significant increase in microbial density occurred in drums with Gadolinium concentrations of >100ppm with the addition of nutrients (glucose) to the drum water.

Experiments were then conducted to evaluate the toxicity of gadolinium to algae. Several species were tested for toxicity to various Gd concentrations at various pH conditions. At all pH conditions tested, algal growth decreased dramatically between 100 mg/l and 1000 mg/l. Based on these data it was concluded that algal growth is inhibited at gadolinium concentrations in this range. Since gadolinium levels in drums

are reportedly as high as 280,000 ppm, the use of algae or other microbes to sequester gadolinium and or nitrate in the absence of other treatment does not seem feasible. Since the toxicity experiments clearly demonstrated that Gadolinium is toxic to microorganisms at the higher concentrations present in some of the drums, we evaluated removal of the gadolinium by precipitation prior to nitrate removal. Experiments using $Na_3PO_4 \cdot 12H_2O$ as the precipitating agent demonstrated that virtually all dissolved gadolinium can be precipitated in a single precipitation step, that takes less than 30 minutes and can be done by a solid or liquid (solution) of Na_3PO_4. Dry or wet sodium phosphate worked equally well for the precipitation of Gadolinium as $GdPO_4$. The yield was close to 100% in both cases. Analyses of the precipitate indicated that it contained 10.43% phosphorus and 7.58% H_2O which corresponds to a compound like $GdPO_4 \cdot 1H_20$. Although it appeared that a precipitation step would result in a small loss of heavy water due to hydrate formation within the precipitate, that heavy water could be recovered by heating the hydrate to 150°C and condensing the vapor.

The final phase of the study involved testing the ability of selected microbes to remove nitrate from simulated contaminated moderator drum water following removal of gadolinium. Algal growth was better in nitrate salt solutions with Na, K and NH_4 as the cation compared to $GdNO_3$. Substantial nitrate reduction in response to algal growth was evident in many cases, especially at the lower salt concentrations. However, valid comparisons between algal growth and nitrate removal could not be made for many of the test conditions because of unexplainable variation in nitrate measurement results. Thus, additional experiments need to be conducted before firm conclusions can be made regarding comparative nitrate removal.

Based on the results of the studies, a four-step conceptual process has been developed. The gadolinium is removed by chemical treatment (e.g. precipitation with potassium phosphate) and subsequently processed for potential re-sale. Residual potassium nitrate is removed by a combination of electrochemical and biological methods. Nitrate is reduced to extremely low (ppb) levels by metabolically mediated uptake into live algal cells. The algal biomass is separated from the water by centrifugation or filtration, dried, and disposed of by incineration.

The proposed process has three significant advantages over the “baseline” technology, ion-exchange: (1)Gadolinium can be recovered and potentially sold as a valuable resource, rather than being included in the secondary waste stream, (2) less dilution of heavy water occurs in the process resulting in improved economics when the purified heavy water is sold for use in commercial reactors (3) secondary waste will be reduced more than three-hundred-fold (from approximately 300% of the original volume to <1% of the original volume). Additional process development is necessary to advance from the proof-of-concept stage to a working process that will convert a legacy waste into a valuable resource.

2.0 Introduction and Description of Problem

Nuclear reactors were operated for approximately 30 years at the Savannah River Site (SRS) near Aiken, SC to produce nuclear weapons materials for national defense. Throughout this period, a heavy water solution of gadolinium nitrate was utilized in a standby emergency shutdown system that could inject this chemical into the reactor moderator coolant water. The chemical was used for this purpose because the high neutron absorption cross sections of some gadolinium isotopes make gadolinium salts such as $GdNO_3$ effective in controlling nuclear activity in aqueous systems (Baumann, 1980; Gilbert et al., 1985, Rodenas et al. 1990). Currently, there is an inventory of approximately 181 55-gallon drums (37,680 liters overall) of this degraded heavy water containing gadolinium nitrate. The sale of some of the heavy water inventory at SRS for use in commercial nuclear power reactors is being negotiated, but the degraded heavy water containing $GdNO_3$ has been rejected. Thus, purification and up-grade is required for sale of this heavy water.

Existing gadolinium purification technology by ion exchange would generate large volumes of waste. Manufacture of the needed quantity of special resin, assembly of process equipment, and drum purification, with frequent resin bed changes and moderator dilution by flushes, would be required. Alternative treatment by the purification evaporator is not possible because nitrate salts would quickly foul the pot. Tritium in the evaporator flush water would complicate treatment and disposal. Much heavy water would be lost to the hydrated salt waste in the evaporator pot.

Failing to purify the $GdNO_3$-contaminated heavy water could be very costly. Because of the tritium content, storage of this high conductivity aqueous waste in stainless steel drums remains a liability and significant expense. A waste treatment/stabilization process would require development and would generate an even larger waste volume for costly disposal. In contrast, purification of the degraded heavy water such that it can be sold provides funds for a portion of the treatment and waste disposal expense. Rather than becoming a waste liability, the moderator becomes available for commercial nuclear power generation. Furthermore, the gadolinium that could be recovered may have commercial use.

Although this project focuses on the problems at SRS with the end user being the Spent Fuel Storage Division, Gadolinium nitrate is used as a neutron absorbent in heavy water nuclear power reactors world-wide and a cost-effective process for purification and re-use has considerable potential usage.

3.0 Drum Sampling

A total of 99 of the subject drums were sampled in December 1996 and January, 1997. All 99 were assayed for conductivity, pH tritium and gadolinium. Ninety-two (92) were assayed for mole% D_2O and 13 were assayed for nitrate. The results of these analyses were reviewed prior to selecting eight drums for more extensive chemical characterization and microbiological characterization in the present study. The eight drums that were selected represent a wide range of conditions. These conditions included relatively high and low values for gadolinium, pH, conductivity and % D_2O. One-liter samples were collected from each of the eight drums on 2/12/98. Aliquots of these drum samples were subjected to both chemical (including radiological) and microbiological analyses. The chemical/radiological analyses were conducted by SRTC/ADS personnel while microbiological analyses were conducted by SRTC/EBS personnel.

Methodology

Chemical parameters and the procedures used for each analysis are shown in Table 1. Water samples from Par Pond were processed along with the drum samples to provide reference data for microbial concentration quantities.

Aliquots from the drums were subjected to the following microbiological processing and analyses techniques:

Spread Plates: Duplicate plates were prepared using 10 microliters (ul) and 100 ul inoculums taken from each drum sample. The plate agar consisted of a 1 % peptone-tryptone-yeast-glucose mixture without cyclohexane. A glass "L" shaped glass rod and turntable were used to spread the inoculum evenly over the entire surface of the agar by rotating the plate and moving the rake back and forth. The glass rod was alcohol sterilized and flamed between each plate. The plates were covered and incubated in an inverted position at room temperature until plate counts were performed.

Direct Total Counts: Microscopic counts of cells were performed by spotting fifty microliters (ul) of well-mixed water onto toxoplasmosis slides and heat fixing at 65°C for 12 minutes. The samples were then stained with either fluorescein isothiocyanate (FITC) solution (0.04% FITC in a 0.5M $NaCO_3$ - phosphate buffer, pH 7.2) or acridine orange (AO) (0.1% AO in phosphate buffer) for two minutes, rinsed with deionized pre-filtered (0.2 µm pore size) water and air dried at room temperature. Stained microbial cells were counted using a Zeiss epifluorescence microscope and appropriate filter set. After counting the cells on each slide, the cellular density was calculated based on the sample volume, the area of each field for the microscope, and the total number of fields counted. Results are presented as a total count per milliliter and represents all the microorganisms, both living and dead, that were present in the collected water sample.

Table 1. Chemical/Radiological Characterization of Drum Samples: Parameters, Units and Procedures

Parameter	Methodology
pH (units)	Combination pH electrode
Gd (mg/l)	Inductively Coupled Argon Plasma Spectroscopy
D_2O (mole %)	Infrared Spectroscopy
Conductivity (μMhos)	Electrolytic method
NO3 (mg/l)	Ion Chromatography
Ca (mg/l)	Ion Chromatography
Fe (mg/l)	Inductively Coupled Plasma Emission Spectroscopy
Mg (mg/l)	Inductively Coupled Plasma Emission Spectroscopy
Mn (mg/l)	Inductively Coupled Plasma Emission Spectroscopy
Mo (mg/l)	Inductively Coupled Plasma Emission Spectroscopy
Zn (mg/l)	Inductively Coupled Plasma Emission Spectroscopy
K (ppm)	Atomic Absorption Spectrometry
Na (ppm)	Ion Chromatography
Alkalinity (mg/l CaCO3)	Atomic Absorption Spectrometry
Chloride (ug/ml)	Ion Chromatography
Fluoride (ug/ml)	Ion Chromatography
Formate (ug/ml)	Ion Chromatography
Nitrate (ug/ml)	Ion Chromatography
Nitrite (ug/ml)	Ion Chromatography
Oxalate (ug/ml)	Ion Chromatography
Phosphate (ug/ml)	Ion Chromatography
Sulfate (ug/ml)	Ion Chromatography
Ammonium ion (ug/ml)	Inductively Coupled Plasma Emission Spectroscopy
Inorganic carbon (ppm)	Total Organic Carbon Analyzer
Organic carbon (ppm)	Total Organic Carbon Analyzer
Beta count (dpm/ml)	Liquid Scintillation Counting
Tritium count (uCi/ml)	Liquid scintillation counting
Alpha count (dpm/ml)	Liquid scintillation counting

Nutrient Addition: Nutrient additions were made to the drum samples by first transferring 7.0 ml of each drum sample into sterile 15-ml centrifuge tubes. Then 250 ul of a glucose solution was added to each vial to yield a final glucose concentration of 0.34%. The vials were tightly capped and placed on a rotating shaker for 72 hours. The samples were then analyzed using the direct count method described above.

Results and Discussion

Complete results of chemical and microbiological analyses of the drum samples are shown in Table 2. The samples with the highest gadolinium concentrations generally displayed proportionally higher concentrations of NO_3, conductivity, Fe, Mg, Mn, Mo, P, Zn, K, and Na and organic carbon.

Drums with relatively high gadolinium concentrations also tended to have the lowest quantities of bacteria. Although only three of the drum samples produced culturable bacteria on 1% PTYG agar, bacteria (either viable or nonviable), were present in all drums. Initially, their total densities ranged from a little higher than in tap water to nearly as high as in a water sample from Par pond. Thus, the data indicate that some bacteria are present in all of the drums, including those containing > 99% D_2O with nitrate and gadolinium concentrations greater than 200,000 mg/l (Table 2).

The microbial density increased in six of the eight drum samples, as measured using the direct count method, when glucose was added to the drum samples. Bacteria densities increased more than two orders of magnitude with nutrient addition in three of the samples. All of these contained less than 100 ppm gadolinium. Cells in many of these samples were larger and/or in the process of dividing when viewed under the microscope indicating the presence of actively growing cells. The largest increase in cellular density occurred with the sample from drum #15435, which had a very low gadolinium concentration. This sample also had the largest number of viable bacteria as determined using the spread plate method. The addition of an organic carbon source, glucose, appeared to stimulate the growth of the bacteria that were already present in the samples.

Samples with little or no increase in bacterial density tended to contain the highest amounts of gadolinium. However, these samples were difficult to enumerate and the results are subject to error because the samples did not evaporate completely and left a slime layer on the microscope slides after being rinsed. The additional gadolinium in the sample appeared to increase the viscosity of the sample and increase its boiling point.

Although the presence of large amounts (>5000 ppm) of gadolinium may have affected either the growth of the bacteria or the ability to enumerate the cells using our direct count methods, dividing cells were observed in the sample from drum #18156, and viable cells were measured in drum sample #13749. This indicates that some bacteria

Table 2. Characterization Data: Drums of Spent Moderator Water

Drum #	18156	15208	15817	4600	15793	15861	15435	13749	Reference water	
Microbiological data									Tap Water	Par Pond
Direct Count Cells/ml	1.24E+05	6.14E+05	4.74E+04	1.29E+05	5.57E+04	8.25E+03	1.22E+06	9.28E+03	2.06E+03	1.93E+06
Spread Plate CFU/ml	0.00E+00	2.00E+01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	6.35E+03	6.20E+02		
72 hr. Nutrient Cell/ml	3.44E+05	2.03E+03	3.80E+04	2.08E+05	1.43E+06	1.38E+06	>1.0E+08	2.44E+04		
Chemical data										
Gd ppm	202500	203800	0.09	142	97	0.5	0.26	6118		
Nitrate (mg/l)	183936	279985	<1	179	63	<1	<1	5954		
PH	1.63	5.36	6.14	3.62	6.79	6.34	5.59	6.66		
D_2 0%	78.17	99.59	98.73	98.54	99.65	99.47	99.17	2.99		
Cond. (µmhos)	84400	97500	4.07	394	199	1.4	10.8	9020		
Ca (mg/l)	8.6	10.48	0.15	0.09	0.07	0.07	0.21	7.29		
Fe (mg/l)	24.62	8.53	0.06	0.15	0.02	0.01	0.02	0.24		
Mg (mg/l)	0.92	0.43	0.05	0.04	0.01	0.02	0.04	0.55		
Mn (mg/l)	5.21	5.06	0.06	0.02	<0.01	<0.01	<0.01	0.25		
Mo (mg/l)	50.9	63.91	0.56	0.06	0.03	<0.01	<0.01	2.52		
P (mg/l)	50.53	64.25	0.51	0.07	0.03	<0.02	0.02	2.27		
Zn (mg/l)	20.05	3.66	0.12	0.13	0.01	0.01	0.03	0.28		
K (mg/l))	0.545	0.765	<0.195	<0.195	<0.195	<0.195	<0.195	1.19		
Na (mg/l)	2.024	185.724	0.869	5.599	<0.198	<0.198	0.594	132.66		
Alkalinity (mg/l)	<250	<250	<250	<250	<250	<250	<250	<250		
Chloride (µg/l)	<200	<200	<200	<2	<0.2	<0.2	1	<200		
Fluoride (µg/l)	<200	<200	<200	<2	<0.2	<0.2	<0.2	<200		
Formate (µg/l)	<1000	<1000	<1000	<10	<1	<1	<1	<1000		
Nitrite (µg/l)	<1000	<1000	<1000	<10	<1	<1	<1	<1000		
Oxalate (µg/l)	<1000	<1000	<1000	<10	<1	<1	<1	<1000		
Phosphate (µg/l)	<1000	<1000	<1000	<10	<1	<1	<1	<1000		
Sulfate (µg/l)	<500	<500	<500	<5	<0.5	<0.5	<0.5	<500		
Ammonium ion (µg/l	<10	<10	<10	<10	<10	<10	<10	<10		
Inorganic carbon (mg/l)	0.246	10	0.319	0.259	0.223	0.182	0.104	2		
Organic carbon (mg/l)	44	26	14	14	12	6	10	6		
Radiological Data										
Beta count (dpm/ml)	4.57E+09	5.66E+07	7.18E+09	5.33E+09	4.29E+09	7.32E+09	4.66E+09	4.39E+08		
Tritium count (uCi/ml)	2.06E+03	2.55E+01	3.23E+03	2.40E+03	1.93E+03	3.30E+03	2.10E+03	1.98E+02		
Alpha count (dpm/ml)	<1.59E+05	<1.59E+05	<1.59E+05	<1.59E+05	<1.59E+05	<1.59E+05	<1.59E+05	<1.59E+05		

are viable in some environments with very high levels of gadolinium.

In summary, microbiological sampling demonstrated the presence of microorganisms in all eight of the drums sampled and suggested that gadolinium may have a toxic effect on microbes since substantial growth could only be enhanced by nutrient addition in three of four drums with relatively low (<100 ppm) gadolinium concentrations. No significant increase in microbial density occurred in drums with Gadolinium concentrations of >100 ppm with the addition of nutrients (glucose) to the drum water.

Table 3 shows the concentrations of gadolinium, NO_3, and conductivity along with the expected levels of nitrate based on the gadolinium measurements and the molecular weights of the elements in the $Gd(NO_3)_3 \cdot 6H_2O$ compound used in the reactor process where the water in the drums originated. Gadolinium, nitrate, and conductivity were strongly correlated with each other. Expected (calculated) and measured values of nitrate were generally similar. There was no clear evidence from these analyses that bacteria were reducing nitrate in the drums since some of the drums had measured nitrate levels higher than expected values based entirely on the stoichiometry (Table 3).

Table 3. Relationship between Gadolinium, Nitrate, and Conductivity in Spent Moderator Drums

Drum #	Gd (mg/l)	NO_3 (mg/l Expected*	NO_3 (mg/l) Measured	Conductivity (mmhos)
15208	203800	241503	279985	97500
18156	202500	239963	183936	84400
13749	6118	7250	5954	9020
4600	142	168	179	394
15793	97	115	63	199
15861	0.5	0.6	<1	1.4
15435	0.26	0.3	<1	10.8
15817	0.09	0.1	<1	4.1

*Based on molecular weight ratios for Gd and NO_3 in $Gd(NO_3)_3 \cdot 6H_2O$

4.0 Gadolinium Toxicity Studies

Metals are often toxic to microbes when present at concentrations substantially higher than natural environmental levels. Therefore, it was hypothesized that Gd may be toxic to selected microorganisms (algae and bacteria) at the very high concentrations present in most of the drums. The microbial characterization of the drum samples also suggested the presence of gadolinium toxicity to microbes because viable microbes were rare or absent from the drums with the highest Gd concentrations. To assess the feasibility of utilizing an in-drum biological treatment process for remediation, studies were designed to evaluate the capability of selected organisms to grow in $GdNO_3$ at concentrations bracketing the levels present in the drums requiring purification.

Methods

Three experiments were conducted to evaluate the toxicity of gadolinium to algae. Experimental designs for the three are summarized in the Appendix (Tables A-1 to A-3). In the initial experiment, four species of algae were inoculated into standard culture media with and without $GdNO_3$ substituted for conventional nitrate (e.g. $NaNO_3$) to provide $GdNO_3$ at concentrations resulting in Gd concentrations of 0, 10, 100, 1,000, 10,000, 80,000 and 260,000 ppm (thus, bracketing the quantities in all of the drums requiring treatment). Relative concentrations of Gd and NO_3 based on elemental atomic weights and the hydrate form of the gadolinium nitrate used in the experiments are shown in Table 4. Gd and NO_3 concentrations of the media were measures at the start of the experiment and after one and two weeks. Algal cultures included *Chlorella pyrenoidosa, Scenedesmus quadricauda, Closterium* sp. and *Cyanidium caldarum.* All four strains were obtained from the Carolina Biological Supply Company, Burlington, NC, USA. *Chlorella* and *Scenedesmus* were grown in modified Bold Basal (BB) medium (Nichols and Bold 1965). Closterium was grown in Alga Gro Freshwater Medium and *Cyanidium* in Doemel's *Cyanidium* medium (Carolina Biological Supply Co., 1978). These species were selected on the basis of one or more of the following criteria:

1. on hand or readily obtainable
2. known or suspected ability to grow in high D_2O concentrations
3. known or suspected high capability to assimilate nitrate

Culture media was prepared in 25 ml batches in 50 ml flasks prior to being autoclave sterilized. Flasks were subsequently inoculated with 600 µl of algal culture in accordance with the scheme shown in Table A-1. The flasks were then placed in a Pschrotherm shaker/ incubator (New Brunswick Scientific) for two weeks at 20°C, with a 12 h light (200 μE^{-2} s^{-1}):12 h dark illumination regime and 100 rpm rotation.

Control flasks, not inoculated with algae but otherwise treated identically with all

Table 4. Corresponding Gd and NO_3 Concentrations using $Gd(NO_3)_3 \cdot 6H_2O$ in Modified BB Media*

Amount $Gd(NO_3)_3 \cdot 6H_20$/l added	Gd (mg/l)	NO_3 (mg/l)
0.0286 g	10	11.85
0.2859 g	100	118.5
2.8593 g	1,000	1,184
28.5934 g	10,000	11,847
228.7472 g	80,000	94,777
743.4180 g	260,000	308,022

*Based on molecular weight ratios for Gd and NO_3 in $Gd(NO_3)_3 \cdot 6H_2O$

treatment conditions, were examined for nitrate and gadolinium concentrations at the start and conclusion of all three experiments.

The experimental design for Experiment #1 is shown in Appendix Table A-1. Densities of live algae were determined by examining aliquots from the flasks with an inverted microscope using fluorescence microscopy which allows the differentiation of live and dead cells by the detection of chlorophyll fluorescence when cells are subjected to excitation by blue or green light (Wilde and Fliermans,1979, Wood et al. 1985, Tsuji et al. 1986). Density estimates were made by randomly counting fields until a minimum of 400 cells were tabulated. These counts were performed after incubation periods of one- and two-weeks. After 250µl aliquots were collected from the flasks for microscopical observations, the remaining liquid was filtered (0.45µm pore size). The filters were labeled, dried and photographed. The relative amount of algae observed on the dried filters was compared to the quantitative count data.

Experiment 2 was conducted to further elucidate the toxicity of GdNO3 to algae. Based on the results of Experiment 1, the range of Gadolinium that the algae were exposed to was decreased and two additional algal strains were evaluated. These were isolates of the species, *Mastigocladus laminosus*, a thermophilic blue green alga. These isolates were derived from SRS reactor effluent streams and cultured in Medium ND (Castenholz 1982). Three different pH levels, 3.5, 4.5, and 5.5 were also compared (Table A-2). Algae were enumerated at the start of the experiment and at one- and two-week intervals. Otherwise, experimental protocols were identical to those described for Experiment 1.

Experiment #3 (Table A-3) was conducted to determine: (1) comparative toxicity of GdNO3, NaNO3, KNO3 and NH4NO3 to algae, (2) whether algae can live in high nitrate concentrations if Gd is replaced by other metals or ammonium, and (3) nitrate uptake by algae in relation to algal growth and nitrate compound form at various concentrations. Modified BB Medium was formulated to contain 10, 100, 1000, and 10,000 mg/l of Gd as $GdNO_3$, Na as $NaNO_3$, K as KNO_3, and NH_4 as NH_4NO_3. Triplicate samples containing each medium were inoculated with 600µl of a *Chlorella vulgaris* suspension and algal concentrations were determined immediately and after one week of incubation under pschrotherm incubator conditions previously described.

Several denitrifying bacteria strains were obtained from the American Type Culture Collection (ATTC) and evaluated for their ability to grow and remove nitrate in liquid culture media (5% peptone tripticase yeast glucose) spiked with salt concentrations ranging from 0 to 2000 ppm Gd. Following sterilization of the media and inoculation of microbes in culture tubes, the samples were placed on shaking platforms and checked visually at regular intervals (at least once every two days) for visible growth. Tubes that

showed indications of growth were measured for turbidity and compared with uninoculated control tubes. Samples showing clear signs of growth were subsequently analyzed for nitrate content.

Results and Discussion

Comprehensive data results from the three algae experiments are presented in Appendix Tables A-4 to A-6. Observations of the relative amounts of algae on the dried filters led to the same conclusions regarding growth as the quantitative counts utilizing the microscope. Thus, labeling and photographing of the dried filters provided a quick screening method to qualitatively observe and document relative quantities of algal growth. This procedure eliminates the need to conduct laborious microscopic counts for all samples, particularly those where algal growth is clearly inferior based on naked eye assessments. Use of this technique allowed us to quickly eliminate several algal strains and media conditions from further consideration during the initial screening phase of process development.

The initial experiment showed that *Chlorella vulgaris* was more tolerant to gadolinium nitrate than *Scenedesmus quadricauda* or *Cyanidium caldarum* (Figure 1). The microscopical examinations also revealed some viable algal cells at gadolinium concentrations up to 260,000 mg/l. However, growth was greatly impeded at gadolinium concentrations between 100 mg/l and 1000 mg/l. The growth data in Figure 1 represent the change in algal populations between the first and second week of inoculation in the media. Figure 2 shows the amount of *Chlorella* growth in each of two consecutive 1-week periods when exposed to various concentrations of Gd and pH with BB media. At all pH conditions tested, algal growth decreased dramatically between 100 mg/l and 1000 mg/l. These data support the conclusion that algal growth is inhibited at concentrations in this range.

At pH 4.5 and 5.5, *Chlorella* grew much better when gadolinium concentrations were 0 and 100 mg/l compared to a gadolinium concentration of 10 mg/l (Figure 2) (This was also evident in Figure 1). This result, which may appear as a data anomaly at first glance, can be explained by the methodology. The 0 mg/l gadolinium samples were prepared with the standard modified BB media formulation which contains 182.5 mg/l of nitrate as $NaNO_3$; whereas, the formulations for 10 to 10000 mg/l gadolinium samples were prepared by substituting $Gd(NO_3)_3$ in place of sodium nitrate. Thus, the 0, 10, and 100 mg/l gadolinium formulations contained 182.5, 11.9, and 118.5 mg/l nitrate, respectively and the lower growth at 10 mg/l Gd, relative to the 0 mg/l and 100 mg/l concentrations was most likely due to nitrate limitation rather than gadolinium toxicity. The relationship between nitrate uptake and algal growth is further discussed in Section 6.0. Growth was substantially higher in the second week of incubation than in the first week with the exception of the 10mg/l Gd exposures at pH 4.5 and pH 5.5. Once again, the lower growth at 10 mg/l Gd is thought to be due to the depletion of nitrate after the

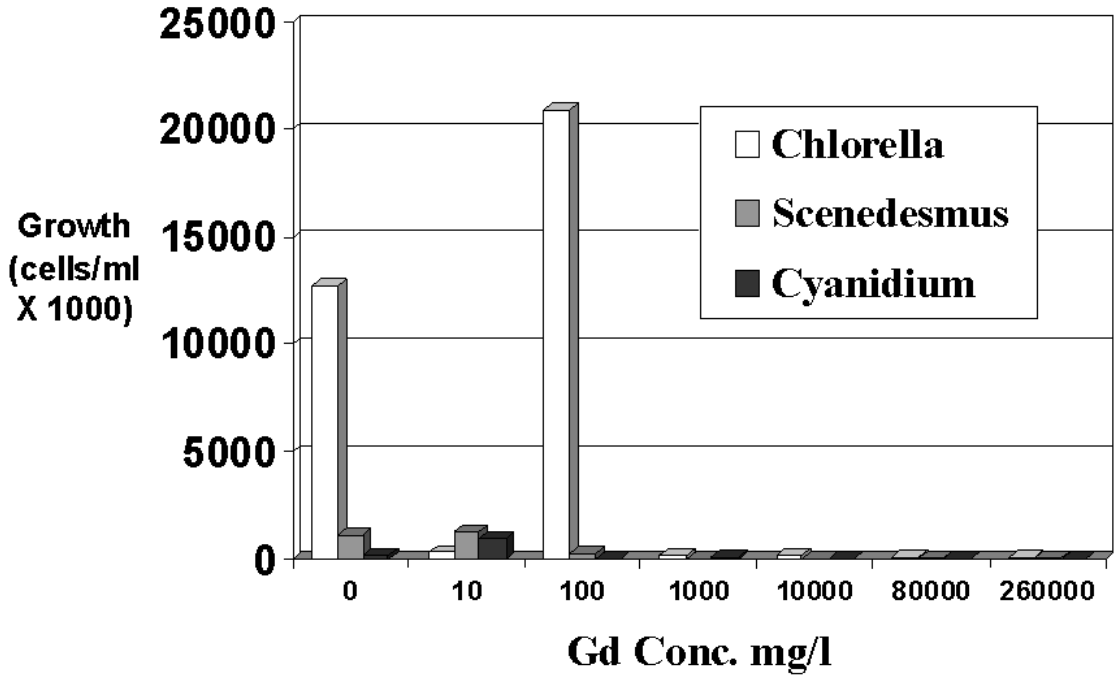

Figure 1. Growth of three species of algae exposed to various concentrations of gadolinium

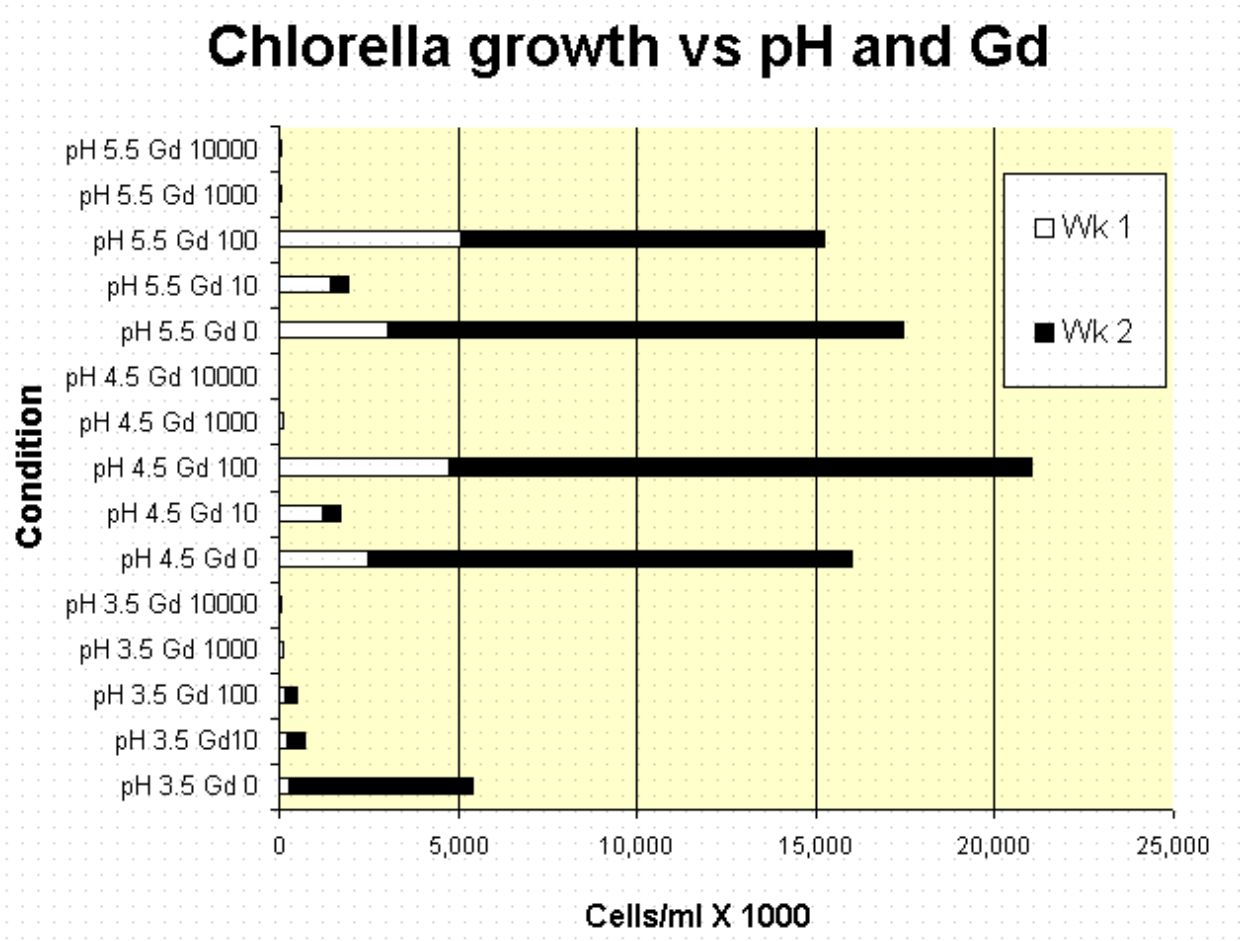

Figure 2. Growth of *Chlorella* during exposure to various pH and gadolinium concentrations (mg/l).

first week. The higher growth in week #2 compared to week #1 in the other samples may represent adaptation to the gadolinium in the medium.

Figure 3 shows the growth of*Chlorella* in modified BB media containing nitrate salts prepared with gadolinium, sodium, potassium and ammonium at concentrations of 0, 10, 100, 1000 and 10000 of the cationic portion of each compound. Gadolinium appears to stimulate growth at 10 mg/l but results in reduced growth at the higher concentrations. The highest growth occurred with sodium at 100 mg/l. However, at the highest concentration tested (10,000 mg/l) potassium resulted in the best growth.

Several of the bacteria strains demonstrated growth in the presence of Gd at concentrations as high as 2000 mg/l. Growth was generally better in nitrate salt solutions with Na, K and NH_4 as the cation than in nitrate salts with Gd NO_3. Of course, It had been previously demonstrated (Section 3.0) that some viable microbes were present in drums containing Gd concentrations as high as 203, 800 mg/l (Table 2). However these cells did not respond to nutrient enrichment.

Overall, it was concluded that although some microbes can survive at extremely high Gd concentrations, gadolinium is more toxic to algae and bacteria than the other cations tested.

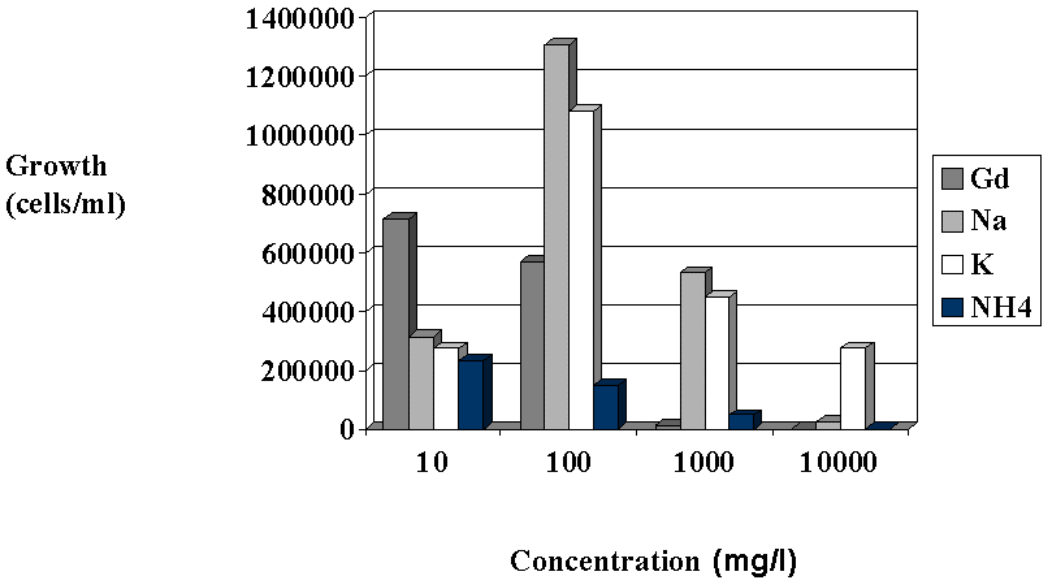

Figure 3. Comparative algal growth in four nitrate salt solutions

5.0 Precipitation of Gadolinium

The toxicity experiments (Section 4) clearly demonstrated that Gadolinium is toxic to microorganisms at the higher concentrations present in some of the drums. Furthermore, it would not be feasible to expect biological processes associated with microorganisms to remove a high percentage of the extremely high gadolinium concentrations (259K ppm maximum, 80K ppm mean) present in the drums. Thus, removal of the gadolinium by precipitation prior to nitrate removal was evaluated. It is well known that soluble Gadolinium salts like nitrate can be very easily precipitated from solution by using alkali metal salts like PO_4^{-3}, HPO_4^{-2}, etc., or that of ammonium ions. A general formula for the $GdPO_4$ precipitation is as follows:

$Gd(NO_3)_3$ + M_3PO_4 (solid or solution) ---> $GdPO_4$ (solid) + $3MNO_3$ (sol)

where M can be Na^{+1}, K^{+1} or NH_4^{+1}

Methods

Initially, we tested the following reaction:
$Gd(NO_3)_3$ (aqueous) + $Na_3PO_4 \cdot 12H_2O$ (solid) ------> $GdPO_4$ (solid) + $3Na^{+1}$ (aqueous) + $3NO_3^{-1}$ (aqueous)

A 13,939 ppm Gd solution as $Gd(NO_3)_3$ was prepared by adding 2 g (4.432 mmol) $Gd(NO_3)_3 \cdot 6H_20$ to 50 ml of DI H_2O in a 250 ml Erlenmeyer flask. A magnetic stir bar was placed in the flask and 1.6846g (4.432mmol) of sodium phosphate dodecahydrate, a solid, was added to the flask and the solution was stirred for on a magnetic stirrer for 5 min. The Gd (III) phosphate appeared to precipitate out immediately. The supernatant solution was filtered through a Corning 430711 (250 ml, 0.2 um nylon membrane) system using a vacuum pump. A 10 ml aliquot of the filtrate was measured for Gd(III) using Inductively Coupled Argon Plasma Spectroscopy. This experiment was repeated three times. The third time the experiment was conducted, the precipitate was washed three times with 5 m1 with DI water to make sure that all the water-soluble nitrates were washed out. It was then placed on an watch glass and dried overnight in a drying oven at 320° F. The precipitate sample was then submitted to an off-site laboratory (Galbraith Laboratories) for a determination of Karl Fischer Water, determined by coulometric titration and phosphorus using Inductively Coupled Plasma Optical Emission Spectroscopy. This was done to obtain an estimate of the hydrate concentration of the precipitate.

Results and Discussion

Initial experiments using $Na_3PO_4 \cdot 12H_2O$ as the precipitating agent demonstrated that virtually all dissolved gadolinium can be precipitated in a single precipitation step, that takes less than 30 minutes and can be done by a solid or liquid (solution) of Na_3PO_4.

There was no noticeable difference in the use of dry or wet sodium phosphate in the precipitation of Gadolinium as $GdPO_4$. The yield was close to 100% in both cases. Analyses of the precipitate indicated that it contained 10.43% phosphorus and 7.58% H_2O which corresponds to a compound like $GdPO_4 \cdot 1H_20$.

Four major concerns associated a Gd precipitation step are discussed below:

1. Can we easily and cost-effectively remove the metal from the drum? It was clearly demonstrated in this study and is generally well known that soluble Gadolinium salts like nitrate can be very easily precipitated from solution by using alkali metal salts like PO_4^{-3}, HPO_4^{-2}, etc., or that of ammonium ions.

2. Can the integrity of the heavy water be retained? (i.e. can the step be performed with minimal hydrate formation?) It appears the precipitation step will result in a small loss of heavy water due to hydrate formation within the precipitate. However, that heavy water can be recovered by heating the hydrate to 150°C and condensing the vapor.

3. Can the gadolinium be recovered in a reusable (salable) form? Gadolinium is a rare metal with very unusual properties including unique ferromagnetic characteristics. These properties give the element high market value potential. Gadolinium is presently used in presently used in numerous high-tech products and is a key element in MRI technology. The possible presence of trace levels of radionuclides in the precipitate could make this problematic.

4. Will the remaining solution in the drum, containing less toxic chemicals like $NaNO_3$, KNO_3 or NH_4NO_3 be amenable to further chemical and biological treatment to result in purified D_2O? The complete answer to this question is uncertain at this point and awaits further developmental work. However, the experimental work performed thus far has demonstrated several advantages of utilizing a precipitation step in the process of removing gadolinium from heavy water. Gadolinium is extracted out of the waste drums very easily. The process takes less than 1 hour and results in very little heavy water losses due to hydrate formation. The residual solution containing relatively non-toxic salts like $NaNO_3$ or KNO3 should be amenable to further purification by biological treatment and possibly by electrochemical treatment. If $(NH_4)_3PO_4$ is used as the precipitating agent, then the by-product left in the waste drum will be NH_4NO_3 for which there is an electrochemical (electrolysis) method documented in the literature (Voortmam, 1993). This precipitating agent would, of course, result in higher losses of heavy water to the precipitate than would be the case with sodium or potassium salts.

6.0 Microbial growth and uptake of nitrate

Studies were performed to assess the ability of selected microbes to remove nitrate from simulated contaminated moderator drum water. It is envisioned that biological nitrate removal, utilizing denitrification by bacteria or uptake by algae during growth would be employed as part of the overall process for removing gadolinium nitrate from the contaminated drums. The low levels of tritium in the drum waters made it impractical to conduct most of the initial nitrate removal studies in the laboratory using actual drum water samples.

Methods

Nitrate measurements were performed using ion chromatography on samples from each of the three algal experiments described in Section 4.0. The most comprehensive analysis of nitrate removal by algae was in experiment 3 where triplicate flasks of modified BB media were spiked with nitrate salts resulting in concentrations of Gd, Na, K, and NH_4 of 10, 100, 1000 and 10000 mg/l. The samples were analyzed for nitrate concentration before and after treatment with algae in which *Chlorella* (3.61E+05 cells/ml) was inoculated and allowed to grow in 25 ml of Modified BB Media in 50 ml flasks placed in a light programmed environmental chamber (New Brunswick Scientific) for two weeks at 20°C, with a 12 h light ($200 \mu E^{-2}\ s^{-1}$):12 h dark illumination regime and 100 rpm rotation. The nitrate concentration in triplicate "control" flasks (treated identically to the flasks containing algae with the exception of the algal inoculation) was also measured.

Strains of denitrifying bacteria were tested for their ability to remove nitrate in the form of $Gd(NO_3)_3$, and in the possible forms resulting from a precipitation step as described in Section 5.0. ($NaNO_3$, KNO_3, or $NH_4NO_{3)}$. Following screening tests utilizing various media spiked with 0-2000mg/l of the anionic component of the salt solution, the organisms showing the best growth were selected, Samples were incubated overnight and subsequently preserved prior to being tested for nitrate concentration as measured by ion chromatography.

Results and Discussion

Table 5 shows the results of the nitrate analyses of the samples spiked with four different nitrate salts. Nitrate reduction in response to algal growth was evident in many cases, especially at the lower salt concentrations. However, valid comparisons between algal growth and nitrate removal could not be made for many of the test conditions because of the considerable unexpected variation between the predicted quantities of nitrate, based on media preparation and the nitrate measurements of samples before and after treatment. Thus, additional experiments need to be conducted before firm conclusions can be made regarding comparative nitrate removal

Table 5. Nitrate Concentrations (mg/l) before and after Inoculation and Growth (1-week) of Algae (*Chlorella)* into Modified Bold's Basal Media Containing Various Nitrate Salts

Media salt composition	Calculated NO_3 Estimate before treatment	NO3 Measured before treatment*	NO3 Measured After Treatment with Algae*	NO3 Measured after Treatment with no algae*
10 ppm Gd as GdNO3	11.8	25.3±0.8	0.3±0.4	11.6±1.1
100 ppm Gd as GdNO3	118	37.4±1.7	20.9±4.7	30.8±14.1
1000 ppm Gd as GdNO3	1180	1098±20.6	2304±132	12907±1040
10,000 ppm Gd as GdNO3	11800	10549±218	11520±154	12344±319
10 ppm Na as NaNO3	26.95	27.4±0.4	2.8±4.0	27.3±0.5
100 ppm Na as NaNO3	269.5	58.4±20.0	50.1±11.9	74.9±1.0
1000 ppm Na as NaNO3	2695	3557±121	1782±47	1913±44
10,000 ppm Na as NaNO3	26950	19276±1432	17567±2714	21173±772
10 ppm K as KNO3	15.89	3441±80.0	192±309	6.5±4.3
100 ppm K as KNO3	158.9	200±12.3	60.0±6.0	97.7±0.6
1000 ppm K as KNO3	1589	1326±9	1297±33	1341±72
10,000 ppm K as KNO3	15890	16097±3291	14255±70	14636±368
10 ppm NH_4 as NH_4NO3	34.44	7.8±1.8	62.8±101.5	5.3±0.6
100 ppm NH_4 as NH_4NO3	344.4	312.7±10.8	317.3±8.6	316.3±5.0
1000 ppm NH_4 as NH_4NO3	3444	3266±242	3258±37	3197±25
10,000 ppm NH_4 as NH_4NO3	34440	31289±1449	39522±8882	34881±2416

*Mean and standard deviation of three replicates

by algae in the presence of various concentrations and anionic components of nitrate salts being considered for use in the heavy water drum purification project.

The results form the tests utilizing denitrifying bacteria are shown in Table 6. Substantial nitrate reduction occurred with all the nitrate salts evaluated. However, the data in this initial scoping study were insufficient to clearly delineate the best microbial strain or nutrient source to be used in the conceptual process.

Overall, the nitrate removal studies indicated feasibility of substantial nitrate removal by algal uptake and by bacterial denitrification. However, the utilization of either mechanism in the proposed drum purification process requires further refinement.

Table 6. Nitrate Removal by Denitrifying Bacteria under Various Conditions

Samp. #	Strain and Culture Cond.	Cation Concentration	Initial NO3 Conc. (mg/l) Calculated	Final NO3 Conc. (mg/l) Measured	Percent Removal
B1	#1 ptyg pH 6	Na 0 mg/l	0	0.1	0
B2	#1 ptyg pH 4	Na 0 mg/l	0	0.1	0
B12	#1Tol3 pH 4	Na 0 mg/l	0	0.1	0
B13	#1Tol3 pH 6	Na 0 mg/l	0	0.1	0
B21	#1Tol4 pH 4	Na 0 mg/l	0	0.2	0
B20	#1Tol4 pH 6	Na 0 mg/l	0	0.4	0
B22	#1Tol4 pH 4	Na 2 mg/l	5.4	4.6	14.8
B3	#1 ptyg pH 6	Na 2 mg/l	5.4	<0.1	>98.2
B4	#1 ptyg pH 4	Na 2 mg/l	5.4	<0.1	>98.2
B7	#1 m9c pH 4	Na 2 mg/l	5.4	0.1	98.2
B14	#1Tol3 pH 6	Na 2 mg/l	5.4	4.7	13.0
B5	#1 ptyg pH 4	Na 20 mg/l	54.0	7.4	86.3
B15	#1Tol3 pH 4	Na 20 mg/l	54.0	8.2	84.8
B16	#1Tol3 pH 6	Na 20 mg/l	54.0	55	0
B23	#1Tol4 pH 6	Na 20 mg/l	54.0	26	51.9
B6	#1 ptyg pH 6	Na 200 mg/l	540	404	25.2
B46	#1ptyg pH 4	Na 200 mg/l	540	97	82.0
B8	#1 m9c pH 4	Na 200 mg/l	540	269	49.8
B10	#1 m9c pH 4	K 0 mg/l	0	0.1	0
B11	#1 m9c pH 4	K 0 mg/l	0	0.1	0
B17	#1Tol3 pH 4	K 2 mg/l	3.2	1.8	43.8
B25	#1Tol4 pH 4	K 2 mg/l	3.2	9.8	0
B9	#1 m9c pH 4	K 20 mg/l	31.8	17	46.5
B18	#1Tol3 pH 4	K 20 mg/l	31.8	14	56.0
B26	#1Tol4 pH 4	K 20 mg/l	31.8	7.3	77.0
B19	#1Tol3 pH 4	K 200 mg/l	318	266	16.4
B27	#1Tol4 pH 6	NH4 2 mg/l	6.9	10.3	0
B28	#1Tol4 pH 6	NH4 20 mg/l	68.8	6.0	91.3
B29	#1Tol3 pH 6	NH4 200 mg/l	688	32	95.4
B30	#1 M9c/ptyg	Gd 0 mg/l	0	10.7	0
B33	#2 PTYG pH 6	Gd 0 mg/l	0	10.8	0
B39	#1 m9c pH 6	Gd 0 mg/l	0	1.1	0
B40	#1 m9c pH 4	Gd 0 mg/l	0	10.8	0
B34	#2 PTYG pH 6	Gd 1 mg/l	1.2	10.7	0
B35	#2 PTYG pH 4	Gd 1 mg/l	1.2	10.7	0
B41	#1 m9c pH 6	Gd 10 mg/l	11.8	<0.1	>99.1
B31	#1 M9c/ptyg?	Gd 10 mg/l	11.8	10.7	9.3
B36	#2 PTYG pH 6	Gd 10 mg/l	11.8	10.5	11.0
B42	#1 m9c pH 6	Gd 100 mg/l	118	10.7	90.9
B43	#1 m9c pH 4	Gd 100 mg/l	118	4	96.6
B32	#1 M9c/ptyg?	Gd 100 mg/l	118	29.6	25.1
B37	#2 PTYG pH 6	Gd 100 mg/l	118	3.4	97.1
B38	#2 PTYG pH 4	Gd 100 mg/l	118	4.1	96.5
B44	#1 m9c pH 6	Gd 1000 mg/l	1180	101	91.4
B45	#1 m9c pH 4	Gd 1000 mg/l	1180	102	91.4

7.0 Conceptual Process Design

Based on the experimental results of this study, a novel conceptual process for the purification of heavy water containing large concentrations of gadolinium nitrate has been developed (Figure 4). The process contains the following steps:

1. Chemical precipitation to remove gadolinium from the drum

2. Removal of the anionic precipitating agent (e.g. K) and much of the NO_3^- using electrochemical techniques

3. Complete (nitrate removal (e.g. to ppb level) by the growth and subsequent removal of select microbes

4. Upgrading D_2O purity as necessary for resale of the purified heavy water

5. Recovery and reprocessing, if necessary, to provide gadolinium for resale as a high value product.

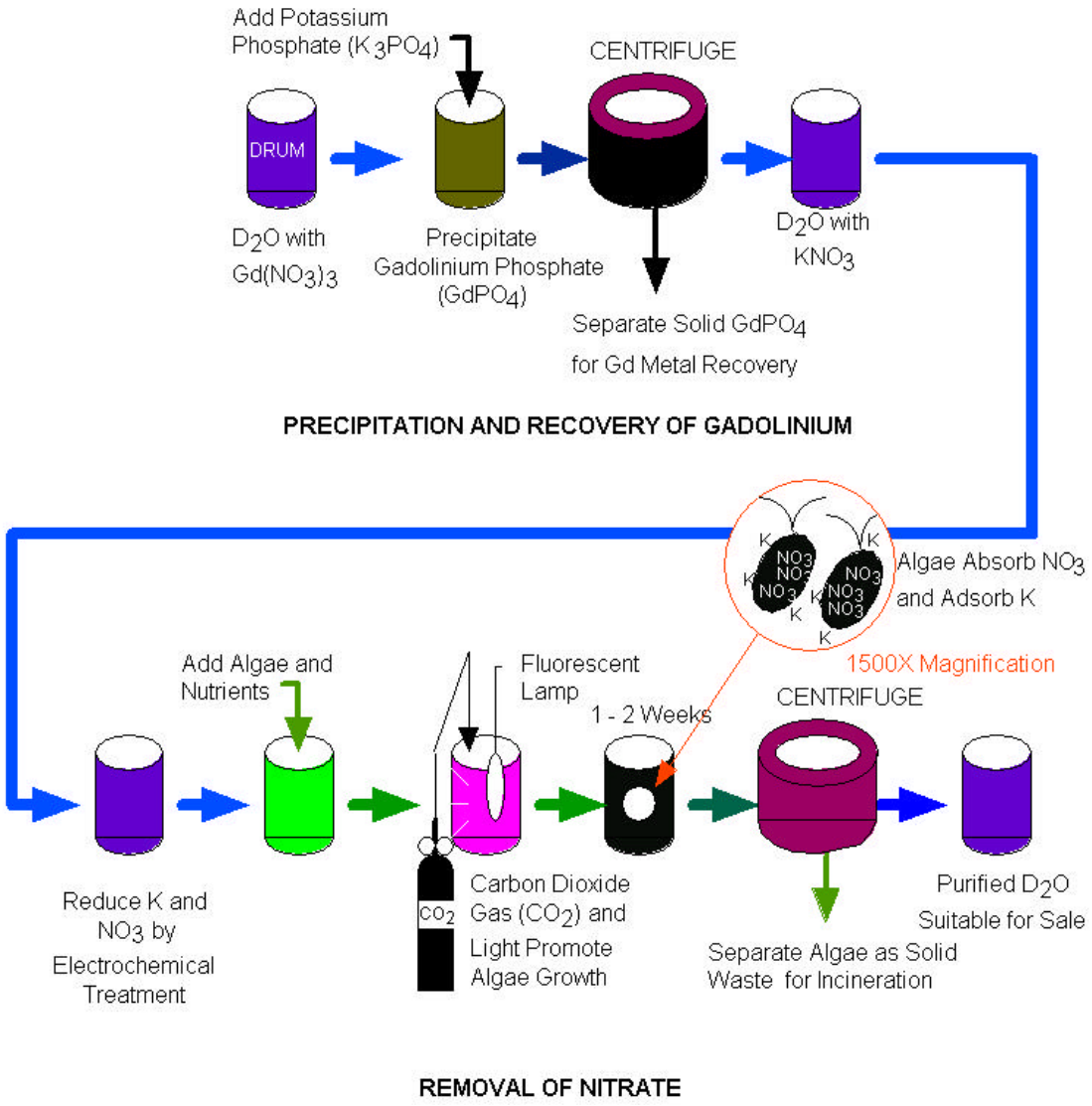

Figure 4. Conceptual Process for Purifying Drums of Heavy Water Containing $Gd(NO_3)_3$

8.0 Proposed Future Work

The study provided the development of a novel four-step conceptual process for the purification of heavy water containing large concentrations of gadolinium nitrate. The process would provide several key advantages over an ion exchange process. Encouraging results were obtained in the initial proof-of-concept experiments. However, continued development is required in the following areas:

Chemical Precipitation Step:
It remains to be demonstrated how the gadolinium can be optimally precipitated for the minimization of hydrate formation and processing costs along with the best suitability for further treatment for nitrate removal using actual heavy water with the candidate precipitating agents identified in the study.

Bulk Nitrate Removal Step:
Although microbiologically induced nitrate removal is deemed an integral part of the overall nitrate removal process, an inexpensive nitrate removal scheme that would generate very little secondary waste and efficiently reduce the very high nitrate levels remaining after the precipitation step (e.g. thousands of ppm) to levels more amenable to biological removal (e.g. tens to hundreds of ppm). Electrolysis processes appear most promising for this intermediate step in the overall nitrate removal scheme.

Microbiological Nitrate Removal Step:
It was demonstrated in the study that some strains of algae and bacteria are tolerant to nitrate salt concentrations up to the levels present in the drums. It is also well known and was documented in the study that that some microbes can grow in heavy water concentrations of >99% and that microbes can remove nitrate by denitrification and by incorporation of nitrate into biomass. Additional process development work is needed to distinguish the limits of these biological phenomena in relation to the chemical conditions of the subject drums.

Gadolinium Recovery Step:
The precipitate from the initial step in the process will be $GdPO_4$, an extremely rare compound which has unique properties and is the subject of several patents describing novel uses of the compound. For example, Nakagome et. al. 1998) have proposed the use of $GdPO_4$ for use in controlling a novel magnetic refrigerator. Thus, the resultant precipitate from the process could have considerable value as produced. Alternatively, the compound could be chemically treated to recover the gadolinium in a form that is more commonly available commercially. Additional research on gadolinium marketability and recovery methods is required to determine the overall cost-effectiveness of the proposed process described in this report.

9.0 Literature Cited

Baumann, E.W. 1980. Preparation and properties of nitrate-deficient gadolinium nitrate solutions. J. Inorg. Nucl. Chem. 42:1705-1709.

Castenholz, R.W. 1982. In: Starr, M.P. (ed.) The Prokaryotes, Springer-Verlag, New York. 236-246.

Gilbert, R. Lepine, L., Laurin, M., Ouellet, L., and R. Gauthier. 1985. Study of complexing reactions causing the depletion of gadolinium ions from the moderator of CANDU-PHW Nuclear Reactors. Can. J. Chem. Eng. 63:978-986.

Nakagome, H., Sdato, A, and Tasuda, S. 1998. Production of working material for a magnetic refrigerator. Patent Application EP223265.

Rodenas, L.G., Prini, R.F., and S.J. Liberman. Radiolysis of aqueous solutions of gadolinium nitrate. J. Radioanalytical and Nuclear Chem. Articles. 139: 277-286.

Tsuji, T. K. Ohki, and Y. Fujita. 1986. Determination of photosynthetic pigment composition in an individual phytoplankton cell in seas and lakes using fluorescence microscopy; properties of the fluorescence emitted from picoplankton cells. Mar. Biol. 93:343-349.

Voortman, W.J., An Evaluation of the Technical Feasibility of Removing Ammonium Nitrate from Aqueous Solutions with Electrolysis', Thesis MScEng, 1993. University of Natal, Pretoria South Africa.

Wilde, E.W. and C.B. Fliermans, 1979. Fluorescence microscopy for algal studies. Trans. Am. Microsc. Soc. 98:96-102.

Wood, A.M., Horan, P.K., Muirhead, K., Phinney, D.A.,Yentch C.M. and J.B. Waterbury. 1985. Discrimination between types of pigments in marine Synechococcus spp. by scanning spectroscopy, epifluorescence microscopy, and flow cytometry. Limnol. Oceanogr. 30:1303-1315.

10.0 Acknowledgements

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APPENDIX

Summary of Algae Experiments:

Exp. #	Scope	Algal Species Used	Table
1	Determine potential toxicity of $GdNO_3$ to algae by Evaluating capability of organisms to grow in $GdNO_3$ at concentrations bracketing the levels in the drums to be remediated.	*Chlorella* *Scenedesmus* *Closterium* *Cyanidium*	A-1, A-4
2	Determine potential toxicity of GdNO3 to algae by evaluating capability of species to grow in GdNO3 at concentrations deemed feasible based on Experiment 1. Results. Also, evaluate influence of media pH on growth.	*Chlorella* *Cyanidium* *Mastigocladus*	A-2, A-5
3	1. Determine comparative toxicity of GdNO3, NaNO3, KNO3 and NH4NO3 to algae. 2. Determine if algae can live in high nitrate concentrations if Gd is replaced by other metals or ammonium. 3. Determine nitrate uptake by algae in relation to algal growth and nitrate compound form at various concentrations.	*Chlorella*	A-3, A-6

Table A-1. Experimental Design for Experiment #1 showing number of flasks for each treatment

Medium	Chlorella	Scenedesmus	Closterium	Cyanidium	Control
BB pH 6.6 (standard formula)	3	3	3	3	
BB pH 5.5	3	3			
BB pH 5.5 w/ 10 ppm Gd as $GdNO_3$	3	3			1
BB pH 5.5 w/ 100 ppm Gd as $GdNO_3$	3	3			1
BB pH 5.5 w/ 1000 ppm Gd as $GdNO_3$	3	3			1
BB pH 5.5 w/ 10,000 ppm Gd as $GdNO_3$	3	3			1
BB pH 5.5 w/ 80,000 ppm Gd as $GdNO_3$	3	3			1
BB pH 5.5 w/ 260,000 ppm Gd as $GdNO_3$	3	3			1
BB pH 3.5 (standard formula)			3	3	
BB pH 3.5 w/ 10 ppm Gd as $GdNO_3$			3	3	1
BB pH 3.5 w/ 100 ppm Gd as $GdNO_3$			3	3	1
BB pH 3.5 w/ 1000 ppm Gd as $GdNO_3$			3	3	1
BB pH 3.5 w/ 10,000 ppm Gd as $GdNO_3$			3	3	1
BB pH 3.5 w/ 80,000 ppm Gd as $GdNO_3$			3	3	1
BB pH 3.5 w/ 260,000 ppm Gd as $GdNO_3$			3	3	1

Table A-2. Experimental Design for Experiment 2 showing number of flasks for each treatment

Medium	Chlorella pH 3.5	Chlorella pH 4.5	Chlorella pH 5.5	Cyanidium pH 3.5	Mastigocladus 113D pH 5.5	Mastigocladus M1 pH 5.5	Control no algae
BB Std.	2	2	2	2			2 (pH5.5)
BB w/10ppm Gd	2	2	2	2			2 (pH5.5)
BB w/ 100 ppm Gd	2	2	2	2			2 (pH5.5)
BB w/ 1000 ppm Gd	2	2	2	2			2 (pH5.5)
BB w/ 10000 ppm Gd	2	2	2	2			2 (pH5.5)
C Std . wo/$(NH4)_2SO4$				2			2
C w/ 10ppm Gd				2			2
C w/ 100 ppm Gd				2			2
C w/1000 ppm Gd				2			
C w/ 10000 ppm Gd				2			2
ND Std pH 5.5					2	2	2
ND w/ 10 ppm Gd					2	2	2
ND w/ 100 ppm Gd					2	2	2
ND w/ 1000 ppm Gd					2	2	2
ND w/ 10000 ppm Gd					2	2	2

Table A-3 Experimental design and sample numbering scheme for Experiment #3

Medium (Ph=5.0)	T=0	T=1 wk Chlorella	T=1 wk Control no algae
BB w/10 ppm Gd as $GdNO_3$	X3-1 X3-2 X3-3	X3-49 X3-50 X3-51	X3-97 X3-98 X3-99
BB w/ 100 ppm Gd as $GdNO_3$	X3-4 X3-5 X3-6	X3-52 X3-53 X3-54	X3-100 X3-101 X3-102
BB w/ 1000 ppm Gd as $GdNO_3$	X3-7 X3-8 X3-9	X3-55 X3-56 X3-57	X3-103 X3-104 X3-105
BB w/ 10000 ppm Gd as $GdNO_3$	X3-10 X3-11 X3-12	X3-58 X3-59 X3-60	X3-106 X3-107 X3-108
BB w/10ppm Na as $NaNO_3$	X3-13 X3-14 X3-15	X3-61 X3-62 X3-63	X3-109 X3-110 X3-111
BB w/ 100 ppm Na as $Na\ NO_3$	X3-16 X3-17 X3-18	X3-64 X3-65 X3-66	X3-112 X3-113 X3-114
BB w/ 1000 ppm Na as $NaNO_3$	X3-19 X3-20 X3-21	X3-67 X3-68 X3-69	X3-115 X3-116 X3-117
BB w/ 10000 ppm Na as $NaNO_3$	X3-22 X3-23 X3-24	X3-70 X3-71 X3-72	X3-118 X3-119 X3-120
BB w/10 ppm K as KNO_3	X3-25 X3-26 X3-27	X3-73 X3-74 X3-75	X3-121 X3-122 X3-123
BB w/ 100 ppm K as KNO_3	X3-28 X3-29 X3-30	X3-76 X3-77 X3-78	X3-124 X3-125 X3-126
BB w/ 1000 ppm K as KNO_3	X3-31 X3-32 X3-33	X3-79 X3-80 X3-81	X3-127 X3-128 X3-129
BB w/ 10000 ppm K as KNO_3	X3-34 X3-35 X3-36	X3-82 X3-83 X3-84	X3130 X3-131 X3-132
BB w/10 ppm NH_4 as NH_4NO_3	X3-37 X3-38 X3-39	X3-85 X3-86 X3-87	X3-133 X3-134 X3-135
BB w/ 100 ppm NH_4 as NH_4NO_3	X3-40 X3-41 X3-42	X3-88 X3-89 X3-90	X3-136 X3-137 X3-138
BB w/ 1000 ppm NH_4 as NH_4NO_3	X3-43 X3-44 X3-45	X3-91 X3-92 X3-93	X3-139 X3-140 X3-141
BB w/ 10000 ppm NH_4 as NH_4NO_3	X3-46 X3-47 X3-48	X3-94 X3-95 X3-96	X3-142 X3-143 X3-144

Table A-4. Experiment #1 Results: Gd (mg/l), NO3 (mg/l) and algal densities (cells/ml) before during and after a two week incubation period

#	Alga	Medium	Gd Before	Gd After	NO3 calc. Estimate	NO3 Meas. Before	NO3 Meas. After	Algae After 1 wk	Algae After 2 wk
1	Chlorella	BB Std. (pH 6.6)	<0.05	<0.05	182.5	146	22	5.66E+06	1.41E+07
2	Chlorella	BB Std. (pH 6.6)	"	<0.05	182.5	"	25		
3	Chlorella	BB Std. (pH 6.6)	"	<0.05	182.5	"	26		
4	Chlorella	BB pH 5.5	0.07	<0.05	67	150	44	5.28E+06	1.80E+07
5	Chlorella	BB pH 5.5	"	<0.05	67	"	42		
6	Chlorella	BB pH 5.5	"	<0.05	67	"	36		
7	Chlorella	BB pH 5.5 w/ 10 ppm Gd*	11	0.097	12	58.5	35	2.10E+06	2.44E+06
8	Chlorella	BB pH 5.5 w/ 10 ppm Gd	"	lost	12	"	missing		
9	Chlorella	BB pH 5.5 w/ 10 ppm Gd	"	1	12	"	33		
10	Chlorella	BB pH 5.5 w/ 100 ppm Gd	109	7.1	118	94.1	15	3.17E+06	2.41E+07
11	Chlorella	BB pH 5.5 w/ 100 ppm Gd	"	7.6	118	"	15		
12	Chlorella	BB pH 5.5 w/ 100 ppm Gd	"	7.9	118	"	18		
13	Chlorella	BB pH 5.5 w/ 1000 ppm Gd	981	1263	1184	896.6	830	1.75E+05	3.44E+05
14	Chlorella	BB pH 5.5 w/ 1000 ppm Gd	"	1168	1184	"	912		
15	Chlorella	BB pH 5.5 w/ 1000 ppm Gd	"	854	1184	"	884		
16	Chlorella	BB pH 5.5 w/ 10,000 ppm Gd	9796	11,410	11843	7557.1	10828	8.51E+04	2.56E+05
17	Chlorella	BB pH 5.5 w/ 10,000 ppm Gd	"	11,610	11843	"	16123		
18	Chlorella	BB pH 5.5 w/ 10,000 ppm Gd	"	11,585	11843	"	14011		
19	Chlorella	BB pH 5.5 w/ 80,000 ppm Gd	77960	81,475	112,066	64851.5	91170	1.61E+05	2.44E+05
20	Chlorella	BB pH 5.5 w/ 80,000 ppm Gd	"	88,975	112,066	"	184195		
21	Chlorella	BB pH 5.5 w/ 80,000 ppm Gd	"	90,350	112,066	"	99744		
22	Chlorella	BB pH 5.5 w/ 260,000 ppm Gd	200,100	457,750	364,000	123480.2	c	1.43E+05	2.20E+05
23	Chlorella	BB pH 5.5 w/ 260,000 ppm Gd as GdNO3	"	466,000	364,000	"	c		
24	Chlorella	BB pH 5.5 w/ 260,000 ppm Gd as GdNO3	"	468,500	364,000	"	c		
25	Scenedesmus	BB Std. (pH 6.6)	<0.05	14.2	67	146	27	2.59E+05	2.25E+06
26	Scenedesmus	BB Std. (pH 6.6)	"	1.9	182.5		31		
27	Scenedesmus	BB Std. (pH 6.6)	"	0.33	182.5		26		
28	Scenedesmus	BB pH 5.5	0.07	0.14	182.5	149	24	1.98E+05	1.34+E06

Table A-4. (Cont.)

#	Alga	Medium	Gd Before	Gd After	NO3 calc. Estimate	NO3 Meas. Before	NO3 Meas. After	Algae After 1 wk	Algae After 2 wk
29	Scenedesmus	BB pH 5.5	"	<0.05	182.5		31		
30	Scenedesmus	BB pH 5.5	"	<0.05	182.5		35		
31	Scenedesmus	BB pH 5.5 w/ 10 ppm Gd as GdNO3	11	1	12	58	25	1.31E+05	1.41+E06
32	Scenedesmus	BB pH 5.5 w/ 10 ppm Gd as GdNO3	"	64.8	12		38		
33	Scenedesmus	BB pH 5.5 w/ 10 ppm Gd as GdNO3	"	71.8	12		9		
34	Scenedesmus	BB pH 5.5 w/ 100 ppm Gd as GdNO3	109	47.2	118	94	41	5.70E+04	3.43+E05
35	Scenedesmus	BB pH 5.5 w/ 100 ppm Gd as GdNO3	"	2.5	118		31		
36	Scenedesmus	BB pH 5.5 w/ 100 ppm Gd as GdNO3	"	2.5	118		58		
37	Scenedesmus	BB pH 5.5 w/ 1000 ppm Gd as GdNO3	981	819	1184	886	175	1.53E+04	1.53E+04
38	Scenedesmus	BB pH 5.5 w/ 1000 ppm Gd as GdNO3	"	922	1184		210		
39	Scenedesmus	BB pH 5.5 w/ 1000 ppm Gd as GdNO3	"	916	1184		94		
40	Scenedesmus	BB pH 5.5 w/ 10,000 ppm Gd as GdNO3	9796	13,120	11843	7216	16904	1.65E+04	1.26E+04
41	Scenedesmus	BB pH 5.5 w/ 10,000 ppm Gd as GdNO3	"	12,385	11843		19787		
42	Scenedesmus	BB pH 5.5 w/ 10,000 ppm Gd as GdNO3	"	14,320	11843		24116		
43	Scenedesmus	BB pH 5.5 w/ 80,000 ppm Gd as GdNO3	77960	96,025	112,000	64852	101665	1.56E+04	1.81E+04
44	Scenedesmus	BB pH 5.5 w/ 80,000 ppm Gd as GdNO3	"	88,825	112,000		96332		
45	Scenedesmus	BB pH 5.5 w/ 80,000 ppm Gd as GdNO3	"	91,225	112,000		102741		
46	Scenedesmus	BB pH 5.5 w/ 260,000 ppm Gd as GdNO3	200100	285,125	364,000	123480		7.94E+03	1.43E+04
47	Scenedesmus	BB pH 5.5 w/ 260,000 ppm Gd as GdNO3	"	250,500	364,000				
48	Scenedesmus	BB pH 5.5 w/ 260,000 ppm Gd as GdNO3	"	267,625	364,000				
49	Closterium	BB Std. (pH 6.6)	<0.05	64.2	182.5	146	29		
50	Closterium	BB Std. (pH 6.6)	"	0.49	182.5		41		
51	Closterium	BB Std. (pH 6.6)	"	2.2	182.5		38		
52	Cyanidium	BB Std. (pH 6.6)	<0.05	0.2	182.5	146	68	7.26E+05	7.10E+05
53	Cyanidium	BB Std. (pH 6.6)	"	0.18	182.5		83		
54	Cyanidium	BB Std. (pH 6.6)	"	0.41	182.5		75		
55	No Alga	BB pH 5.5 w/ 10 ppm Gd as GdNO3	11	0.74	12	58	75		

Table A-4. (Cont.)

#	Alga	Medium	Gd Before	Gd After	NO3 calc. Estimate	NO3 Meas. Before	NO3 Meas. After	Algae After 1 wk	Algae After 2 wk
56	No Alga	BB pH 5.5 w/ 100 ppm Gd as GdNO3	109	10	118	94	97		
57	No Alga	BB pH 5.5 w/ 1000 ppm Gd as GdNO3	981	884	1184	886	859		
58	No Alga	BB pH 5.5 w/ 10,000 ppm Gd as GdNO3	9796	13,280	11843	7216	14959		
59	No Alga	BB pH 5.5 w/ 80,000 ppm Gd as GdNO3	77960	100,975	112,000	64851	61833		
60	No Alga	BB pH 5.5 w/ 260,000 ppm Gd as GdNO3	200100	291,125	364,000	123480	c		
61	Closterium	BB pH 3.5	<0.05	2	182.5	150	32		
62	Closterium	BB pH 3.5	"	120	182.5		34		
63	Closterium	BB pH 3.5	"	6.2	182.5		28		
64	Closterium	BB pH 3.5 w/ 10 ppm Gd as GdNO3	5	4.8	12	59	36		
65	Closterium	BB pH 3.5 w/ 10 ppm Gd as GdNO3	"	3.3	12		17		
66	Closterium	BB pH 3.5 w/ 10 ppm Gd as GdNO3	"	2.3	12		18		
67	Closterium	BB pH 3.5 w/ 100 ppm Gd as GdNO3	98	11	118	94	176		
68	Closterium	BB pH 3.5 w/ 100 ppm Gd as GdNO3	"	9.7	118		229		
69	Closterium	BB pH 3.5 w/ 100 ppm Gd as GdNO3	"	10	118		140		
70	Closterium	BB pH 3.5 w/ 1000 ppm Gd as GdNO3	1003	1003	1184	896	1609		
71	Closterium	BB pH 3.5 w/ 1000 ppm Gd as GdNO3	"	1039	1184		1244		
72	Closterium	BB pH 3.5 w/ 1000 ppm Gd as GdNO3	"	1079	1184		1988		
73	Closterium	BB pH 3.5 w/ 10,000 ppm Gd as GdNO3	9872	15425	11843	7557	20504		
74	Closterium	BB pH 3.5 w/ 10,000 ppm Gd as GdNO3	"	17535	11843		19053		
75	Closterium	BB pH 3.5 w/ 10,000 ppm Gd as GdNO3	"	15020	11843		17622		
76	Closterium	BB pH 3.5 w/ 80,000 ppm Gd as GdNO3	70840	107800	112,000	50169	46505		
77	Closterium	BB pH 3.5 w/ 80,000 ppm Gd as GdNO3	"	116375	112,000				
78	Closterium	BB pH 3.5 w/ 80,000 ppm Gd as GdNO3	"	93450	112,000				
79	Closterium	BB pH 3.5 w/ 260,000 ppm Gd as GdNO3	197900	281000	364,000	106182	c		
80	Closterium	BB pH 3.5 w/ 260,000 ppm Gd as GdNO3	"	274125	364,000		c		
81	Closterium	BB pH 3.5 w/ 260,000 ppm Gd as GdNO3	"	354250	364,000				

Table A-4. (Cont.)

#	Alga	Medium	Gd Before	Gd After	NO3 calc. Estimate	NO3 Meas. Before	NO3 Meas. After	Algae After 1 wk	Algae After 2 wk
82	Cyanidium	BB pH 3.5	<0.05	1.8	182.5	150	186	1.17E+06	1.37E+06
83	Cyanidium	BB pH 3.5	"	2.8	182.5		177		
84	Cyanidium	BB pH 3.5	"	11.1	182.5		160		
85	Cyanidium	BB pH 3.5 w/ 10 ppm Gd as GdNO3	5	3	12	59	16	6.46E+05	1.59E+06
86	Cyanidium	BB pH 3.5 w/ 10 ppm Gd as GdNO3		2.9	12		45		
87	Cyanidium	BB pH 3.5 w/ 10 ppm Gd as GdNO3	"	2.7	12		17		
88	Cyanidium	BB pH 3.5 w/ 100 ppm Gd as GdNO3	98	4.6	118	94	140	6.61E+05	5.20E+05
89	Cyanidium	BB pH 3.5 w/ 100 ppm Gd as GdNO3	"	4.9	118		119		
90	Cyanidium	BB pH 3.5 w/ 100 ppm Gd as GdNO3	"	4.5	118		222		
91	Cyanidium	BB pH 3.5 w/ 1000 ppm Gd as GdNO3	1003	10.57	1184	897	1780	5.83E+05	6.73E+05
92	Cyanidium	BB pH 3.5 w/ 1000 ppm Gd as GdNO3	"	976	1184		1722		
93	Cyanidium	BB pH 3.5 w/ 1000 ppm Gd as GdNO3	"	908	1184		1688		
94	Cyanidium	BB pH 3.5 w/ 10,000 ppm Gd as GdNO3	9872	13495	11843	7557	16187	4.16E+05	4.03E+05
95	Cyanidium	BB pH 3.5 w/ 10,000 ppm Gd as GdNO3	"	13815	11843		15346		
96	Cyanidium	BB pH 3.5 w/ 10,000 ppm Gd as GdNO3	"	13250	11843		15802		
97	Cyanidium	BB pH 3.5 w/ 80,000 ppm Gd as GdNO3	70840	102875	112,000	50169	46505	1.91E+05	1.73E+05
98	Cyanidium	BB pH 3.5 w/ 80,000 ppm Gd as GdNO3	"	90975	112,000		c		
99	Cyanidium	BB pH 3.5 w/ 80,000 ppm Gd as GdNO3	"	94200	112,000		c		
100	Cyanidium	BB pH 3.5 w/ 260,000 ppm Gd as GdNO3	197900	340625	364,000	106183	98822	1.82E+05	1.63E+05
101	Cyanidium	BB pH 3.5 w/ 260,000 ppm Gd as GdNO3	"	331,000	364,000		c		
102	Cyanidium	BB pH 3.5 w/ 260,000 ppm Gd as GdNO3	"	299,500	364,000		c		
103	No Alga	BB pH 3.5 w/ 10 ppm Gd as GdNO3	5	139	12	59	52		
104	No Alga	BB pH 3.5 w/ 100 ppm Gd as GdNO3	98	9.5	118	94	87		
105	No Alga	BB pH 3.5 w/ 1000 ppm Gd as GdNO3	1003	795	1184	897	1042		
106	No Alga	BB pH 3.5 w/ 10,000 ppm Gd as GdNO3	9872	12,940	11843	7557	7391		
107	No Alga	BB pH 3.5 w/ 80,000 ppm Gd as GdNO3	70840	100,500	112,000	50169	46505		
108	No Alga	BB pH 3.5 w/ 260,000 ppm Gd as GdNO3	197900	299,125	364,000	106182	c		

Note: c= cancelled By D-Area chemist because results appeared erroneous

Table A-5 Experiment #2 Results

#	Alga	Medium	Gd (mg/l) Before	Gd (md/l) After	NO3 (mg/l) Est.	NO3 (mg/l) Measured Before	NO3 (mg/l) Measured After	Algae (cells/ml) Inoculation	Algae (cells/ml) After 1 wk	Algae (cells/ml) After 2 wk
1	Chlo	BB Std. pH 3.5		cancel	182.5		90.9	131,020	464,496	7,472,649
2	Chlo	BB Std. pH 3.5		0.18	182.5		76.4	203,719	461,950	3,841,327
21	Chlo	BB pH 3.5 w/10 ppm Gd		2.8	11.8		5.6	202,715	245,562	1,289,438
22	Chlo	BB pH 3.5 w/10 ppm Gd		2.8	11.8		5.4	218,849	576,032	677,501
41	Chlo	BB pH 3.5w/100 ppm Gd		2.6	118.4		98.8	170,724	279,620	606,941
42	Chlo	BB pH 3.5w/100 ppm Gd		2.9	118.4		99.6	172,852	373,191	836,953
61	Chlo	BB pH 3.5w/1000 ppm Gd		801	1,184.0		876.8	230,413	306,812	367,045
62	Chlo	BB pH 3.5w/1000 ppm Gd		956	1,184.0		985.3	233,785	331,404	356,508
81	Chlo	BB pH 3.5w/10,000 ppm Gd		13,472	11,843		9,314.4	213,866	222,631	306,132
82	Chlo	BB pH 3.5w/10,000 ppm Gd		13,020	11,843		9,139.9	209,183	312,993	333,057
3	Chlo	BB Std. pH 4.5		0.16	182.5		3.0	167,355	1,956,857	10,475,503
4	Chlo	BB Std. pH 4.5		0.09	182.5		3.1	219,930	3,351,990	22,050,441
23	Chlo	BB pH 4.5 w/10 ppm Gd		1.5	11.8		10.0	249,838	1,314,949	1,623,494
24	Chlo	BB pH 4.5 w/10 ppm Gd		1.5	11.8		3.8	213,345	1,617,810	2,368,380
43	Chlo	BB pH 4.5w/100 ppm Gd		5.5	118.4		7.2	244,951	5,922,118	18,760,376
44	Chlo	BB pH 4.5w/100 ppm Gd		6.2	118.4		1.2	282,330	4,056,899	23,887,978
63	Chlo	BB pH 4.5w/1000 ppm Gd		948	1,184.0		932.3	257,363	371,435	342,148
64	Chlo	BB pH 4.5w/1000 ppm Gd		886	1,184.0		942.9	237,672	352,995	384,958
83	Chlo	BB pH 4.5w/10,000 ppm Gd		13,216	11,843		8,275.7	238,257	318,457	359,142
84	Chlo	BB pH 4.5w/10,000 ppm Gd		12,220	11,843		8,721.0	246,784	276,308	320,798
5	Chlo	BB Std. pH 5.5		<0.05	182.5		2.8	211,784	4,701,760	14,035,281
6	Chlo	BB Std. pH 5.5		0.05	182.5		2.9	157,667	1,717,834	21,315,427
25	Chlo	BB pH 5.5 w/10 ppm Gd		1.1	11.8		3.4	160,399	1,871,776	2,110,542
26	Chlo	BB pH 5.5 w/10 ppm Gd		1	11.8		4.9	176,498	1,338,776	2,221,623
45	Chlo	BB pH 5.5w/100 ppm Gd		8.4	118.4		1.2	312,213	5,908,118	13,482,608
46	Chlo	BB pH 5.5w/100 ppm Gd		cancel	118.4		ND	232,661	4,783,429	17,598,352
65	Chlo	BB pH 5.5w/1000 ppm Gd		874	1,184.0		1,026.6	278,315	262,471	353,873
66	Chlo	BB pH 5.5w/1000 ppm Gd		901	1,184.0		959.6	229,851	316,115	411,451
85	Chlo	BB pH 5.5w/10,000 ppm Gd		13,002	11,843		7,361.6	252,282	225,917	352,995
86	Chlo	BB pH 5.5w/10,000 ppm Gd		12,710	11,843		8,532.6	215,947	271,625	344,627
9	none	BB pH 5.5 Std	0.08	0.23	182.5	25.0	135.9			
10	none	BB pH 5.5 Std		<0.05	182.5		138.3			
29	none	BB pH 5.5 w/10 ppm Gd	9.5	0.99	11.8	1.5	10.8			
30	none	BB pH 5.5 w/10 ppm Gd		0.92	11.8		11.7			
49	none	BB pH 5.5 w/100 ppm Gd	91.7	2.1	118.4	17.0	101.6			
50	none	BB pH 5.5 w/100 ppm Gd		176	118.4		99.1			
69	none	BB pH 5.5 w/1000 ppm Gd	1005	855	1,184.0	869.0	979.0			
70	none	BB pH 5.5 w/1000 ppm Gd		815	1,184.0		994.6			
89	none	BB pH 5.5 w/10,000 ppm Gd	10,800	9,072	11,843	8,396.0	9,483.3			
90	none	BB pH 5.5 w/10,000 ppm Gd		9,574	11,843		8,595.1			
7	Cyan	BB Std pH 3.5		0.35	182.5		130.6	754,930	1,188,594	1,637,779
8	Cyan	BB Std pH 3.5		0.037	182.5		142.8	928,396	1,149,255	1,657,850
27	Cyan	BB pH 3.5 w/10 ppm Gd		2.9	11.8		14.0	992,836	871,073	1,811,314
28	Cyan	BB pH 3.5 w/10 ppm Gd		3.2	11.8		15.9	875,396	1,401,651	1,342,515
47	Cyan	BB pH 3.5 w/100 ppm Gd		2.1	118.4		91.9	816,882	964,737	922,949
48	Cyan	BB pH 3.5 w/100 ppm Gd		1.8	118.4		108.9	810,861	1,039668	935,917
67	Cyan	BB pH 3.5 w/1000 ppm Gd		978	1,184.0		831.4	430,853	820,896	705,991
68	Cyan	BB pH 3.5 w/1000 ppm Gd		1096	1,184.0		868.2	768,043	814,875	716,528
87	Cyan	BB pH 3.5 w/10,000 ppm Gd		12,600	11,843		9,857.6	647,841	612,265	629,108
88	Cyan	BB pH 3.5 w/10,000 ppm Gd		12,814	11,843		7,928.1	641,597	636,914	677,685
11	Cyan	C Std pH 3.5		0.18	182.5		3.9	1,126,642	1,115,937	1,270,706
12	Cyan	C Std pH 3.5		0.28	182.5		<1.0	814,875	1,206,784	1,661,864
31	Cyan	C pH 3.5 w/10 ppm Gd		0.34	11.8		10.1	671,257	890,527	1,075,431
32	Cyan	C pH 3.5 w/10 ppm Gd		0.25	11.8		9.8	1,032,643	427,508	1,256,032

Table A-5 (Cont.) Experiment #2 Results

#	Alga	Medium	Gd (mg/l) Before	Gd (mg/l) After	NO3 (mg/l) Est.	NO3 (mg/l) Measured Before	NO3 (mg/l) Measured After	Algae (cells/ml) Inoculation	Algae (cells/ml) After 1 wk	Algae (cells/ml) After 2 wk
51	Cyan	C pH 3.5 w/100 ppm Gd		0.34	118.4		98.0	1,136,738	769,916	1,443,594
52	Cyan	C pH 3.5 w/100 ppm Gd		0.16	118.4		96.7	788,649	808,854	768,043
71	Cyan	C pH 3.5 w/1000 ppm Gd		804	1,184.0		930.4	666,574	946,004	1,002,203
72	Cyan	C pH 3.5 w/1000 ppm Gd		714	1,184.0		946.8	584,462	799,889	927,272
91	Cyan	C pH 3.5 w/10,000 ppm Gd		12,398	11,843		9,709.5	638,475	771,790	600,434
92	Cyan	C pH 3.5 w/10,000 ppm Gd		13,020	11,843		8,396.9	595,702	699,173	627,054
13	none	C Std pH 3.5	0.17	0.15	182.5	ND	ND			
14	none	C Std pH 3.5		0.11	182.5		ND			
33	none	C pH 3.5 w/10 ppm Gd	10.4	0.12	11.8	1.4	10.5			
34	none	C pH 3.5 w/10 ppm Gd		2	11.8		13.0			
53	none	C pH 3.5 w/100 ppm Gd	91.9	0.09	118.4	16.0	97.0			
54	none	C pH 3.5 w/100 ppm Gd		1.7	118.4		92.3			
73	none	C pH 3.5 w/1000 ppm Gd	838	788	1,184.0	1,2960	909.3			
74	none	C pH 3.5 w/1000 ppm Gd		774	1,184.0		927.9			
93	none	C pH 3.5 w/10,000 ppm Gd	9340	14,010	11,843	12,996	10,305.6			
94	none	C pH 3.5 w/10,000 ppm Gd		12,500	11,843		9,631.1			
15	Mast 113D	ND Std pH 5.5		0.1	0		ND			
16	Mast 113D	ND Std pH 5.5		0.74	0		2.0			
35	Mast 113D	ND pH 5.5 w/10 ppm Gd		2.9	11.8		10.7			
36	Mast 113D	ND pH 5.5 w/10 ppm Gd		3.1	11.8		11.4			
55	Mast 113D	ND pH 5.5 w/100 ppm Gd		17.2	118.4		149.4			
56	Mast 113D	ND pH 5.5 w/100 ppm Gd		19.7	118.4		154.3			
75	Mast 113D	ND pH 5.5 w/1000 ppm Gd		1822	1,184.0		1,462.5			
76	Mast 113D	ND pH 5.5 w/1000 ppm Gd		1517	1,184.0		1,477.1			
95	Mast 113D	ND pH 5.5 w/10,000 ppm Gd		14,450	11,843.0		14,236.3			
96	Mast 113D	ND pH 5.5 w/10,000 ppm Gd		19,340	11,843.0		14,466.3			
17	Mast M1	ND Std pH 5.5		0.08	0		1.6			
18	Mast M1	ND Std pH 5.5		0.09	0		1.6			
37	Mast M1	ND pH 5.5 w/10 ppm Gd		3.1	11.8		1.9			
38	Mast M1	ND pH 5.5 w/10 ppm Gd		3	11.8		ND			
57	Mast M1	ND pH 5.5 w/100 ppm Gd		19	118.4		140.1			
58	Mast M1	ND pH 5.5 w/100 ppm Gd		20.7	118.4		149.0			
77	Mast M1	ND pH 5.5 w/1000 ppm Gd		1380	1,184.0		1,478.0			
78	Mast M1	ND pH 5.5 w/1000 ppm Gd		1531	1,184.0		1,541.2			
97	Mast M1	ND pH 5.5 w/10,000 ppm Gd		19,490	11,843.0		13,968.0			
98	Mast M1	ND pH 5.5 w/10,000 ppm Gd		14,480	11,843.0		9,121.4			
19	none	ND Std pH 5.5	<0.05	1		<1	2.2			
20	none	ND Std pH 5.5		<0.05			2.3			
39	none	ND pH 5.5 w/10 ppm Gd	9.4	3	11.8	1.8	17.9			
40	none	ND pH 5.5 w/10 ppm Gd		3.8	11.8		21.4			
59	none	ND pH 5.5 w/100 ppm Gd	87.7	16.9	118.4	17.0	152.7			
79	none	ND pH 5.5 w/1000 ppm Gd	895	1546	1,184.0	896.0	1,505.0			
80	none	ND pH 5.5 w/1000 ppm Gd		1731	1,184.0		1,556.1			
60	none	ND pH 5.5 w/100 ppm Gd		125	118.4		153.4			
99	none	ND pH 5.5 w/10,000 ppm Gd	10,185	17,890	11,843	11,306.0	6,786.9			
100	none	ND pH 5.5 w/10,000 ppm Gd		17,670	11,843		3,401.3			

Table A-6 Experiment #3 Results (Growth of Chlorella in different media formulations)

Sample Numbers		#1-48	#49-96	#97-144			
BB Media variations	NO_3 (mg/l) Estimate.	NO_3 (mg/l) Meas. Before	NO_3 (mg/l) Measured. After Algal Growth	NO_3 (mg/l) Meas. After Treatment W/ No Algae	Algae (cells/ml) Inoculation	Algae (cells/ml) after 1-week	Growth?
10 ppm Gd as $GdNO_3$	11.8	24.7	0.7	10.4	3.61E+05	1.19E+06	x
10 ppm Gd as $GdNO_3$	11.8	25.1	<0.1	12	3.61E+05		
10 ppm Gd as $GdNO_3$	11.8	26.2	<0.1	12.5	3.61E+05	9.58E+05	x
100 ppm Gd as $GdNO_3$	118	38.9	17	32.3	3.61E+05	9.92E+05	x
100 ppm Gd as $GdNO_3$	118	37.7	19.5	44	3.61E+05		
100 ppm Gd as $GdNO_3$	118	35.5	26.1	16	3.61E+05	8.71E+05	x
1000 ppm Gd as $GdNO_3$	1180	1106	2167	11,753	3.61E+05	3.64E+05	x
1000 ppm Gd as $GdNO_3$	1180	1114	2432	13,773	3.61E+05		
1000 ppm Gd as $GdNO_3$	1180	1075	2314	13,196	3.61E+05	3.86E+05	x
10,000 ppm Gd as $GdNO_3$	11800	10715	11,586	12,423	3.61E+05	3.24E+05	0
10,000 ppm Gd as $GdNO_3$	11800	10630	11,629	11,993	3.61E+05		
10,000 ppm Gd as $GdNO_3$	11800	10302	11,344	12,617	3.61E+05	3.06E+05	0
10 ppm Na as $NaNO_3$	26.95	27.8	7.4	27.8	3.61E+05	6.96E+05	x
10 ppm Na as $NaNO_3$	26.95	27.4	<0.1	26.8	3.61E+05		
10 ppm Na as $NaNO_3$	26.95	27	0.84	27.2	3.61E+05	6.56E+05	x
100 ppm Na as $NaNO_3$	269.5	68.2	38.6	74.1	3.61E+05	2.79E+06	x
100 ppm Na as $NaNO_3$	269.5	71.7	62.4	74.5	3.61E+05		
100 ppm Na as $NaNO_3$	269.5	35.4	49.3	76	3.61E+05	5.46E+05	x
1000 ppm Na as $NaNO_3$	2695	3676	1815	1959	3.61E+05	9.79E+05	x
1000 ppm Na as $NaNO_3$	2695	3561	1748	1871	3.61E+05	8.03E+05	x
1000 ppm Na as $NaNO_3$	2695	3434	cancel	1908	3.61E+05		
10,000 ppm Na as $NaNO_3$	26950	20250	19,079	20,362	3.61E+05	6.63E+05	x
10,000 ppm Na as $NaNO_3$	26950	17631	14,434	21,259	3.61E+05		
10,000 ppm Na as $NaNO_3$	26950	19946	19,189	21,899	3.61E+05	5.22E+05	x
10 ppm K as KNO_3	15.89	3487	549	3.7	3.61E+05		
10 ppm K as KNO_3	15.89	3349	18.1	4.3	3.61E+05	3.84E+05	x
10 ppm K as KNO_3	15.89	3488	8.1	11.6	3.61E+05	8.85E+05	x
100 ppm K as KNO_3	158.9	190	60.3	97	3.61E+05		
100 ppm K as KNO_3	158.9	214	53.8	98	3.61E+05	1.93E+06	x
100 ppm K as KNO_3	158.9	197	65.8	98	3.61E+05	9.49E+05	x
1000 ppm K as KNO_3	1589	1328	1261	1259	3.61E+05		
1000 ppm K as KNO_3	1589	1334	1307	1392	3.61E+05	7.96E+05	x
1000 ppm K as KNO_3	1589	1317	1324	1371	3.61E+05	8.21E+05	x
10,000 ppm K as KNO_3	15890	19877	14,316	14,950	3.61E+05		

Table A-6 (Continued) Experiment #3 Results (Growth of Chlorella in different media formulations)

Sample Numbers		#1-48	#49-96	#97-144			
BB Media variations	NO_3 Est.		NO_3 Meas. (mg/l) After Algal Growth	NO_3 Meas. (mg/l) After Treatment W/ No Algae	Algal Inoculation (cells/ml)	Algae at 1 wk (cells/ml	
10,000 ppm K as KNO_3	15890	13863	14,178	14,728	3.61E+05	6.66E+05	x
10,000 ppm K as KNO_3	15890	14550	14,271	14,231	3.61E+05	6.00E+05	x
10 ppm NH4 as NH_4NO_3	34.44	5.8	180	6	3.61E+05	7.70E+05	x
10 ppm NH4 as NH_4NO_3	34.44	9.2	2.4	5.2	3.61E+05	4.19E+05	x
10 ppm NH4 as NH_4NO_3	34.44	8.5	5.9	4.8	3.61E+05		
100 ppm NH4 as NH_4NO_3	344.4	305	325	311	3.61E+05	6.35E+05	x
100 ppm NH4 as NH_4NO_3	344.4	325	308	317	3.61E+05	3.85E+05	x
100 ppm NH4 as NH_4NO_3	344.4	308	319	321	3.61E+05		
1000 ppm NH4 as NH_4NO_3	3444	3135	3232	3176	3.61E+05	5.42E+05	x
1000 ppm NH4 as NH_4NO_3	3444	3545	3284	3191	3.61E+05	2.74E+05	0
1000 ppm NH4 as NH_4NO_3	3444	3117	Cancel	3225	3.61E+05		
10,000 ppm NH4 as NH_4NO_3	34440	32736	34,019	32,174	361+E+05	321E+05	0
10,000 ppm NH4 as NH_4NO_3	34440	31291	49,769	36,819	3.61E+05	2.35E+05	0
10,000 ppm NH4 as NH_4NO_3	34440	29839	34,778	35,651	3.61E+05		