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A NOVEL CHEMICAL NITRATE DESTRUCTION PROCESS

Potential Solution To Sillamae Nitrate Discharge Problem

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1. Abstract

Nitrates represent one of the most significant pollutant discharged to the Baltic Sea by the Sillamae hydrometallurgical plant. This article contains a brief overview of the existing nitrate destruction technologies followed by the description of a new process developed by the authors. The new chemical process for nitrate destruction is cost effective and simple to operate. It converts the nitrate to nitrogen gas which goes to the atmosphere.

2. Introduction

Sillamae hydrometallurgical ore processing plant located in Estonia on the shore of Baltic Sea has been in operation since 1948. During the Soviet era the plant was processing uranium ore along with rare earth and rare metals production. The city of Sillamae belonged to the group of so called closed cities in Soviet Union, a group of cities involved with weapons production effort. Since Estonia's independence the uranium processing stopped and only the rare earth metal processing continued, and at a smaller scale it is still continued today. A tailing pond has been established in 1959 right on the beach of the Baltic Sea. The pond collects the waste-water and slurry from the plant. A dike which separate the pond from the sea is permeable for water. The tailing pond is one of the largest of its kind in the world and certainly the largest in the Baltic Region. Naturally this location makes it a matter of concern for all Baltic countries [1].

The radioactive contaminants were the focus of the NATO Advanced Research Workshop in Tallinn, Estonia. However, chemical contamination from the pond may have equal if not larger impact on the ecology of the Baltic Sea. In the forefront of the chemical contamination there is discharge of nitrate salts. Nitrates, because of their high solubility, are not stopped or filtered by the dike material. They flow freely through the dike into the sea. Roughly 10 m^3 of nitrates at a concentration of 40 – 50 g/l are generated per 1 ton of processed raw material. The production capacity of the plant is currently a few thousand tons per year and the plant operates somewhat under the capacity [2].

Nitrate wastes are harmful to humans and the environment if not disposed of properly. Nitrates are especially dangerous for nursing mothers and infant babies

causing so called blue baby disease. Additionally, when nitrate waste contaminates a natural body of water, it causes excessive biological activity, vegetation growth, and precipitation of organic residue to the bottom. Excessive nitrate concentrations can transform healthy bodies of water into decaying marshes.

During the workshop very little discussion was dedicated to the nitrate discharge problem. A. Siinmaa and V. Petrenko [3] gave four reasonable ways to discontinue Baltic Sea contamination with nitrogen: (1) producing fertilizers, (2) producing explosives, (3) utilization as nitric acid, (4) denitration using plasma or by burning in a furnace. However they do not specifically discuss how to accomplish these solutions. This paper contains an overview of possible methods of nitrate destruction and presents a novel, non-biological and non-thermal process for converting nitrates to nitrogen gas.

3. Nitrate Elimination Literature Overview

Generally all nitrate destruction methods can be divided in two groups: biotreatment and physicochemical methods.

Biological denitrification involves reducing nitrate to a gaseous nitrogen species. The gaseous product is primarily nitrogen gas (N_2), but it may also be nitrous oxide (N_2O), or nitric oxide (NO). NO_3^- can be reduced by a relatively broad range of bacteria. Genera of bacteria that are known [4] to contain denitrifying bacteria include *Pseudomonas*, *Micrococcus*, *Archromobacter*, *Thiobacillus*, and *Bacillus*. Natural biological denitrification occurs, although not extensively, in a variety of aquifers in which a sufficient source of oxidizable organic carbon is present [5]. Water-treatment processes stimulate the denitrification by injection of nutrients. Such organic compounds as methanol, methane, glucose, and starch or mixtures (for example, a sugary brewery waste) [5] can be used as carbon sources.

Biological denitrification has been extensively investigated for several reasons: denitrification is a major mechanism for loss of fertilizer nitrogen in nature resulting in a decreased efficiency of the fertilizer; denitrification can be used as a treatment process to remove nitrogen from such high-nitrogen waste materials as animal residues; and drinking water resources are facing a major nitrate contamination that may cause methaemoglobi, an infant disease. Biotreatment can remove nitrates down to 2-10 mg/L of total nitrogen [6]; a standard set by US EPA is 10 mg/L as nitrate-nitrogen. Many papers have covered both pure [5,6] and applied branches of science. Some recent reviews are listed [5-7; 10-13].

Biological denitrification is an effective nitrate-removal technology. The disadvantages of biological denitrification are that it is slow, is difficult to control, and produces an organic residue. Bacteria are sensitive to heavy metal ions. The process is also prone to microbe poisoning when the influent stream components change.

Chemical methods for destroying nitrate can be divided into two groups: nonspecific methods and methods designed for nitrate destruction. Since 1976, only 17 US patents deal with nitrate destruction. Six patents describe supercritical water oxidation reactors. Eight patents describe various thermal processes, during which nitrate destruction is achieved (in 6 methods nitrates are used as oxidizers; 2 address thermal nitrate self-destruction). Only 3 patents describe methods for nonthermal nitrate destruction: two of

them are electrolytic methods, and one is chemical. Among these 17 patents, only seven are directly dedicated to nitrate destruction.

From a chemist's viewpoint, all nitrate destruction methods are based on oxidizing power of NO_3^- .

Supercritical water oxidation (SCWO) is a nonspecific nitrate-destroying method. It is based on use various oxidizers (like O_2 , NO_3^- , Fe^{3+}) in supercritical water. The critical temperature and pressure of water are 705°F (374°C) and 3208 psi (22.9 MPa). In supercritical water (SCW), the hydrogen bond between water molecules is essentially eliminated, making SCW an excellent solvent for gases and most organics. Usually it allows an effective oxidation of organic compounds to H_2O and CO_2 ; sometimes addition of a heterogeneous catalyst is necessary. Further, inorganic salts are almost insoluble in SCW if the temperature is higher than 800°F (425°C). Any phosphorous, chlorine, or sulfur compounds exposed to SCWO are converted into chlorides, sulfates, and phosphates and may be easily precipitated and separated. SCWO has successfully treated various streams of wastes [14-17]. In some works, nitrate has been used as oxidizer [16-19]. Wet-air oxidation (WAO) is a similar technology, but it uses slightly lower temperatures (125 – 320°C) and pressures (0.5–20 MPa) [20]. Most developments in SCWO and WAO focus on destroying organics, with nitrate removal being an additional bonus. Both SCWO and WAO are energy-intensive processes and require high pressure. Consequently, special means must be used during treatment of radioactive wastes to modify the hazard of contamination.

Thermal methods of destruction can use the nitrate disproportionation reaction or the nitrate-reducer reaction. The first method may be used to decompose solid nitrates. A general disadvantage of this method is that toxic oxides of nitrogen are produced. The second method is based on using a chemical agent. Cox, Hallen, and Lilga [21] did experiments at 350°C and 2500–2900 psi using 6 various reducers. The best results have been received with formate: 100% efficiency of nitrate removal, 99.9% converted to N_2 , 0.1% to N_2O . The disadvantages of thermal methods are high temperature and pressure.

Low-temperature, low-pressure methods of nitrate reduction are based on cathodic electroreduction of NO_3^- or chemical reduction.

In the electrochemical methods, electric current is used to reduce nitrate. The ideal process consists of two reactions:

The real process is much more complicated and still not quite understood. Even the first step, $\text{NO}_3^- \rightarrow \text{NO}_2^-$, reduction is a multistep phenomenon with adsorption of different species [19-21]. The mechanism and efficiency of electrochemical nitrate reduction depend on cathode material. Usually a special catalytic electrode surface is necessary to achieve high efficiency of $\text{NO}_3^- \rightarrow \text{N}_2$ reduction. The industrial use of the process can be difficult; for example, if various metals are present, they will be deposited on cathodes, changing their catalytic properties. The second important factor is nitrate itself; NO_3^- is far less reactive than NO_2^- [22, 23, 25], but it becomes reactive in the presence of NO_2^- [24, 26, 27].

Some attempts [28–30] have been made to use electrolysis to remove nitrate. The composition of N-containing gases produced during electrolysis depended on electrode material and current density. The best results were achieved [28] with Metcote ES-6 and cadmium cathodes (70–75% N_2 ; ~25% NH_3 ; ~2% N_2O), with an overall current efficiency 55%. The drawback of this method is a low destruction efficiency (64–99% of nitrate destroyed) and high residual NO_3^- concentrations. Even after the best runs, $NO_3^- + NO_2^-$ concentration exceeded 1500 ppm.

So far only two chemical reduction methods were proposed for nitrate removal. One uses aluminum as a reducer, the second gaseous hydrogen.

In the pH range 9–10.5, nitrate can be reduced to ammonia with aluminum powder [31]. Next, ammonia can be removed by air-stripping or by $MgNH_4PO_4$ precipitation. Oak Ridge National Laboratory later implemented this idea on a laboratory scale [29]. A bench-scale study [32] with relatively concentrated nitrate (0.1 to 1.0M $NaNO_3$) showed that up to 90% of the nitrate can be converted to ammonia, but residual concentrations of nitrates remain high ($\sim 0.03M \Leftrightarrow \sim 2000$ ppm). The authors did not consider the ammonia disposal problem. The other unsolved problem is a nitrite generation: an average NO_2^- concentration in treated waste was ~1000 ppm. Nitrite is considered much more toxic than nitrate.

Hydrogen can be used as nitrate scavenger in presence of a catalyst. Sometimes the energy of light must initiate the reaction [33]. The best results have been achieved with palladium catalyst [34]; 99.9% of NO_3^- was reduced to nitrogen; only 0.1 % formed ammonia. The drawbacks are that the catalyst is sensitive to poisoning by the presence of heavy metals. The process has been tested only at low concentration of the nitrate.

Proposed Process For Nitrate Conversion To Nitrogen Gas

The authors of this article have invented a novel, inexpensive, non-thermal, non-biological, simple process for converting nitrates to nitrogen gas. The patent for the invention is pending. The invention offers an effective method for reduction of nitrates to nitrogen gas. In the process a metal in presence of a catalyst is contacted with the nitrate containing solution or slurry. As a result, nitrates are quantitatively reduced to nitrites while the metal cations are released to this solution. Subsequently an organic reagent is added to the waste. As a result, the organic compound is oxidized by nitrite, and the nitrate is reduced to nitrogen gas which can be released to the atmosphere. The dissolved metal cations which were released into the solution are electrochemically reduced to metal, recovered, and reused. The block diagram below depicts the invented process.

The scope of the invention includes the process for reduction of nitrates to nitrogen gas. The process is distinguished by three major steps: (1) contacting of a metallic reagent with nitrates to reduce them to nitrites (2) reacting of an organic reagent with the nitrite solution to reduce the nitrite to nitrogen gas, and (3) electrochemical recovery of this metallic reagent from the solution and its reuse. These steps may be carried out in sequence or simultaneously. These steps when combined together represent a novel process for the reduction of nitrate to nitrogen gas. Such process represents an effective method for treatment of nitrate containing waste.

Figure 1. Block Diagram of the LANL Nitrate Destruction Process

The process may be arranged in many different ways. It may be carried out in a batch, as well as continuous arrangement. In a batch process the metallic reagent may be contacted with the nitrate containing solution in many different ways. For example, a metallic powder may be mixed with the nitrate solution. Alternatively, the nitrate containing solution may be passed through a bed of dispersed metal. In another method, the solution may be contacted with a solid non-dispersed metal structure, such as metal sheets, spheres or cylinders. Such solid metal structures may be connected to a current source and metal recovery by electroplating may be carried out in the same vessel as nitrate reduction. The metal recovery may be carried out simultaneously to nitrate reduction, or in a sequence, after the reduction is completed. The organic reagent is added to the solution containing nitrite to further reduce it to nitrogen. The reduction to nitrogen may be carried out simultaneously to the nitrate reduction or in a sequence following the nitrate reduction. It may be done in the same vessel as nitrate reduction or the solution may be pumped to another vessel. When organic reagent has reacted with the nitrite solution to produce nitrogen the remaining solution may be subsequently subjected to electrochemical recovery of the metallic reagent. In this recovery the electrodes are immersed in the solution and electric current is applied. As a result the metal is reduced and deposited on cathodes. This reaction may be done in a different vessel, or in the same vessel as the nitrogen release reaction. The metal recovery may be performed as a final step of the process, or it may be carried out simultaneously with nitrite to nitrogen reduction, or nitrate to nitrite reduction. After the three reaction steps are completed the batch is released to the environment or to further treatment for other components if such treatment is necessary. The vessel(s) are filled with fresh solution.

In a continuous process the nitrate containing solution is continually pumped through a reactor with the metallic reagent. This reactor may be a tank reactor with agitation, or a plug flow type of a reactor with a bed of metal. The metal may be in

powdered, dispersed, or solid form. The metal recovery may be performed simultaneously with the nitrate-nitrite reduction step, or as a subsequent step. The solution after the reduction of nitrate to nitrite may continually flow to another reactor where the organic reagent is continually added. Nitrite will be reduced to nitrogen gas in this second reactor and released from the reactor. It may be released to the atmosphere or captured. Alternatively the same reactor as for nitrate-nitrate reduction may be used for nitrite-nitrogen reduction. In such scenario the metallic reagent will be contacted with the influent solution simultaneously with the addition of the organic reagent, and the nitrate-nitrite reduction will be carried out simultaneously with the nitrite-nitrogen reaction. The metallic reagent recovery step may be performed continually in a separate or the same reactor. The reduced solution containing cations of the metallic reagent may continuously flow to the electrochemical cell. In such cell the metal will be recovered from the solution by electrochemical reduction on cathodes. The denitrated solution may be released from this cell to the environment, or directed to further processing when additional to denitrification processing is required. Alternatively, the electrodes may be in contact with the solution in the same reactor as used for nitrate-nitrite reactor or nitrite-nitrogen reactor and metal recovery performed there.

The above described process may be used for denitrification of various solutions at various nitrate concentrations. For example, it may be used for treatment of radioactive waste-water effluents which are high in nitrate concentration, or for remediation of contaminated natural waters with low level of nitrate. Solid nitrate salts, or heterogeneous solids containing nitrate salts, can be processed by mixing them with water and subjecting to the same treatment.

Status Of The New Process.

The process has undergone bench scale testing. During the testing initial concentration of nitrates ranging from .. to ... were successfully eliminated to less than 10 ppm. Some of the tests were performed under the argon gas blanket in order to eliminate nitrogen from air and capture the exiting gas for analysis. Typical gas analysis during bench testing is shown in Table 1. It shows that nitrogen was indeed generated with negligible quantities of oxides of nitrogen.

TABLE 1. GAS COMPOSTION FROM BENCH SCALE TESTING.

Mole %:
H2=.013
NH3=Not Detected(<.05)
N2=78.5
NO=0.2
O2=<.01
Ar=21.3
CO2=.044
N2O=.01
NO2= Not Detected (<.05)

The process is currently being evaluated for implementation at Los Alamos National Laboratory. Pilot scale testing is currently under way using the solution mimicking the effluent from the Radioactive Waste-water Treatment Plant at Los Alamos. The composition of this solution is shown in Table 2.

TABLE 2. WASTE COMPOSITION USED IN PILOT TESTS

synthetic waste composition			
analytical data			
	mg/L	mmoles/L	mmoles/L
SiO ₂	100	1.66417 Na ₂ SiO ₃	1.66417
Na ⁺	800	34.79774 NaHCO ₃	3.736541
K ⁺	75	1.918159 NaNO ₃	14.70378
Ca ²⁺	100	2.49501 Na ₂ HPO ₄	0.484363
Mg ²⁺	40	1.645413 Na ₂ SO ₄	3.258041
HCO ₃ (-)	228	3.736541 NaCl	5.544264
SO ₄ (2-)	313	3.258041 CaCl ₂	2.49501
Cl ⁻	569	16.05078 MgCl ₂	1.645413
NO ₃ (-) as N	206	14.70378 KCl	2.225665
F ⁻	11	0.578947 KF	0.578947
PO ₄ (3-)	46	0.484363	
cations		44.99674	
anions		44.70339	
pH	8		
COD	75		
alpha nCi/L	30		
Tritium pCi/L	20000		

The testing is performed using 20 gal batches. A schematic flow diagram for the pilot process is shown in Figure 2. The pilot operation is successful. Typical results shown in Table 3 and Table 4.

TABLE 3. RESULTS OF THE PILOT TESTING

Initial ppm	After removal ppm
229 N/NO ₃	0.2 N/NO ₃
0.01 N/NO ₂	0.00 N/NO ₂
2 N/NH ₃	5.65 N/NH ₃
220 N/NO ₃	2.9 N/NO ₃
0.02 N/NO ₂	4.9 N/NH ₃
2 N/NH ₃	0.00 N/NO ₂

TABLE 4. GAS ANALYSIS FOR PILOT TESTS

Mole %
 Ar=73.9%
 N₂=23%
 O₂=2.28%
 CO₂= 0.81%
 N₂O =.04%
 H₂= <.01%
 NH₃ =trace
 N₂O =nd
 N₂O = nd

The results show that the process successfully reduces nitrates to nitrogen gas. The gas analysis was taken during a test conducted under argon purge. Some oxygen present in the off-gas resulted from air leakage into the reactor tank.

The process is planned to be implemented at LANL in 1999. The predicted operating costs of the process are \$2 per kg of nitrate destroyed. The capital costs for a 2000 gal per day batch operation at 1 g/L of NO₃⁻ are \$200,000.

A comparison of the known nitrate destruction processes with our process is given in Table 5.

Conclusions.

Nitrates represent a major part in Sillamae waste-water problem. A new non-biological and non-thermal simple process has been recently developed and tested at Los Lamos National Laboratory. This process may be considered to address the Sillamae waste problem.

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Figure 2. Scheme of the Pilot Plant

TABLE 4. COMPARISON OF NITRATE DESTRUCTION METHODS.

Nitrate destruction method	Maturity	Nitrate concentration in the influent.	Major nitrate conversion product	Byproduct	Advantages	Disadvantages
biological denitrification	commercial, industrially applied process	Medium or low	N ₂	biomass, NH ₃ , N ₂ O	well established, most suitable for non-industrial effluents	sensitive to poisoning and influx changes, slow, secondary waste (biomass)
supercritical water oxidation	bench to pilot scale	Medium to low	N ₂	NO _x , NH ₃	nonspecific method, a variety of organics and oxidizers may be destroyed at the same time	high pressure, high temperature required, high capital cost
direct electrolysis	bench scale	High	N ₂ , NH ₃	-	room temperature, ambient pressure method, no secondary waste	high residual nitrate concentration (g/L), produces ammonia, difficult to control
reduction with aluminum	bench to pilot scale	high to medium	NH ₃	Al hydroxides	simple, low capital cost	produces ammonia, high residual nitrate concentration (g/L), may reduce SO ₄ ²⁻ to H ₂ S, high reagent costs
reduction with gaseous hydrogen	bench scale	low	N ₂	-	suitable for drinking water, no secondary waste	expensive catalyst prone to poisoning, works only with low concentrations
thermal destruction	bench to pilot scale	solid nitrates	NO _x	metal oxides	separates nitrates from solid waste	energy intensive, produces NO _x , may be explosive if organics are present
proposed process	bench scale	high to low	N ₂	-	room temperature, ambient pressure, simple, easy to control, broad range of nitrate concentrations, low capital cost, no secondary waste	needs engineering development

High nitrate concentration: 10 - 100 g/L; medium 0.1 - 10 g/L; low - below 0.1 g/L