

## LOW-LEVEL RADIOACTIVE WASTE NITRATE

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### INTRODUCTION

Tail end waste treatment operations at nuclear facilities result in the generation of large quantities of low-level radioactive waste nitrates.

A description of where waste nitrates occur in the commercial fuel cycle and defense nuclear operations is necessary to understand the magnitude of the problem. An investigation into plant operations in both sectors was carried out in fiscal 1981. The quantities and composition of waste nitrates (both in storage and being generated) found in this investigation emphasize the need for continuing research into processes which will render the material environmentally acceptable.

An insight into the regulations (both proposed and in effect) which influence present and future waste management practices for waste nitrate is important. The proposed NRC Rule 10 CFR 61 establishes minimum waste form requirements which current waste nitrates will not meet. This rule is supplemented by EPA rule 40 CFR 141, the National Primary Drinking Water Quality Criteria (DWQC). This rule requires that all plant effluents, and ground water seepage from burial sites, do not exceed 10 mg/l elemental N (45 mg/l  $\text{NO}_3$ ). Concentrations above this limit are considered toxic to man.

### OBJECTIVE

The objective of this project is the development and demonstration of a process(es) to eliminate or drastically reduce the amount of toxic nitrates in LLW streams without the generation of objectionable oxides of nitrogen.

This project will provide the technology to convert these nitrate wastes to non-toxic carbonates or hydroxides, which

are more environmentally acceptable as well as being more amenable to a wider spectrum of immobilization options to meet future transportation and disposal criteria, and evaluate immobilized wastes for mechanical durability and chemical leachability.

## DISCUSSION

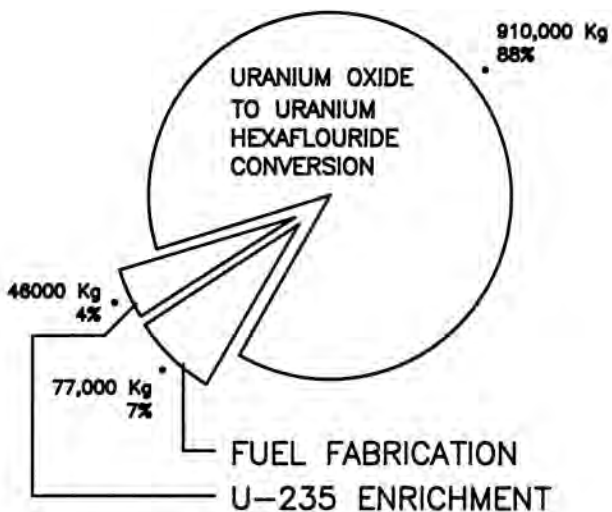
A brief description of the quantities of waste nitrate found, who the major generators are, and the proposed processes to be investigated for converting the waste to an environmentally acceptable substance is in order. This can best be accomplished by a summary of an investigation completed in fiscal 1981.<sup>1</sup> The results of that investigation shows the quantities of material to be enormous. The material generated in the commercial fuel cycle is tabulated in Fig. 1. The bulk of waste nitrate is associated with conversion of  $U_3O_8$  to  $UF_6$ . This process accounts for about  $9.1 \times 10^5$  kg annual production with the enrichment of  $^{235}U$  process accounting for an additional  $1.2 \times 10^4$  kg of waste nitrate. Fuel fabrication plants generate some nitrate. However, the quantities are small compared to the rest of the inventory. The total is estimated at 1,033,000 Kg annually.

No waste nitrate was found at power generators, and since there is no commercial fuel reprocessing currently going on, there is none being generated. However, the potential for nitrate waste from commercial fuel reprocessing is enormous. An example is the nitrate waste from commercial reprocessing stored at the Western New York Nuclear Service Center (WNYNSC). A survey of the commercial shallow land burial sites did not reveal reportable quantities.

An investigation into defense plant waste operations revealed still greater quantities of waste nitrates. The amount of low-level waste nitrate generated annually is now estimated at  $8.96 \times 10^5$  kg. The generation sites and quantities are shown in Fig. 2. But, the bulk of material which needs to be addressed is stored as HLW.

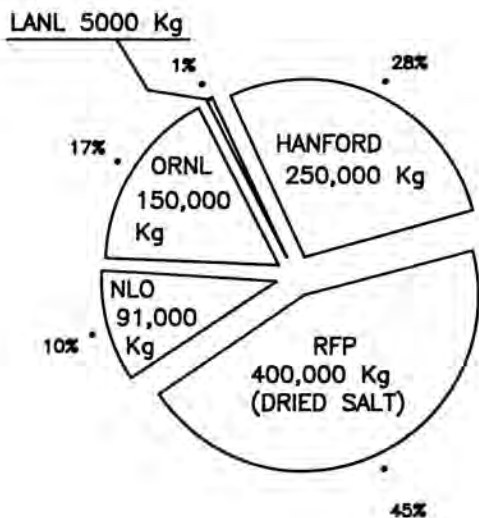
With the pending construction and operation of the Defense Waste Process Facility (DWPF) at the Savannah River Plant (SRP), HLW nitrate becomes a defense low-level waste disposal problem because the bulk of the HLW stored is converted to LLW nitrate during the DWPF process. Therefore, the inventory and generation rates shown in Fig. 3 are potential LLW. WNYNSC waste is shown here because DOE has title to it.

The total mass stored is on the order of  $4.2 \times 10^8$  kg with the nitrate content varying from 54% to 90%. Generation rates through year 2000 are estimated at  $6.1 \times 10^6$  kg per year. These quantities justify an increased effort to treat or immobilize them. Since nitrates are strong oxidizers, organic binders such as resin or bitumen are not applicable.



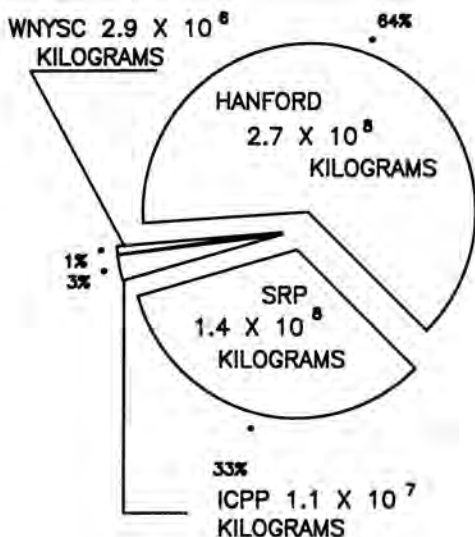
TOTAL: 1,033,000  
KILOGRAMS

FIG. 1. ANNUAL GENERATION RATE OF LOW LEVEL WASTE NITRATE IN THE COMMERCIAL FUEL CYCLE



TOTAL: 896,000 Kg  
 PER YEAR AS  
 MONATOMIC  
 NITROGEN

FIG. 2: ANNUAL LOW-LEVEL WASTE  
 NITRATE EFFLUENTS  
 GENERATED AT DOE  
 FACILITIES



TOTAL: 423,900,000  
 KILOGRAMS STORED  
 AS NITRATE COMPOUNDS

FIG. 3. DOE LOW-LEVEL WASTE  
 NITRATE STORED AS  
 HIGH-LEVEL WASTE

Cement is the immobilizing medium of choice for dispersion control at most plants.

The present DWPF waste management scheme requires mixing the nitrates with cement and interment in shallow land burial as "salt-crete." This material requires a 55% increase in weight from cement which is also costly. SRP is concerned that the cementitious mixtures of nitrate salt will leach nitrates quite rapidly. Consequently, their scientists have expressed interest in a process which will convert the material to an environmentally acceptable form and not jeopardize their DWQC permit for nitrate in ground water.

#### IMMOBILIZATION EXPERIMENTS

Leach results from experiments to immobilize RFP spray dried evaporator salts indicate the SRP concern is valid. The chemical composition of the RFP waste is analagous to the SRP waste, i.e., 80-90%  $\text{NaNO}_3$  and  $\text{KNO}_3$  with the remainder chlorides, fluorides and sulfates.

A cement made up of Portland I cement and 20% fly ash was selected as the immobilization medium. Cylindrical specimens with a 196  $\text{cm}^2$  surface area were prepared at a 36% by weight loading of nitrate and leach tested after curing for 10 days.

A standard static leach test using deionized water at room temperature was used. Weight losses were determined by evaporating the leachate to dryness and weighing the residue. Leach rate was determined by the following equation.

$$L = \frac{A_t}{A_o} \times \frac{W_o}{ST}$$

where  $L = \text{gm/cm}^2 \text{ day}$

$A_t =$  leached residue weight

$A_o =$  weight of material A in specimen

$W_o =$  initial specimen weight

$S =$  Surface area  $\text{cm}^2$

$T =$  leach period (days)

$A_t/A_o =$  Fraction leached

Leach rates determined are shown in Table I. The high initial leach rate can be attributed to a high surface concentration of nitrates that are in direct contact with the water. After this surface concentration has been leached away, the leach rate drops to a diffusion limited value.

The hypothetical amount of nitrate that would be leached the first day from a concreted nitrate waste form cast the size of a standard 0.21  $\text{m}^3$  drum and having a surface area of  $2 \times 10^4 \text{ cm}^2$  would be 9.8 kg. The leach rate then decreases and at the end of 36 days the total lost would be 29 kg of nitrates, assuming unsaturated water was in contact with the

TABLE I

Leachability of Concrete Nitrate Salt Specimen  
 $L = \text{g/cm}^2 \text{ day} \times 10^{-1}$

Days	Specimen No.				
	1	2	3*	4**	5***
1	4.9	4.9	5.6	4.2	5.5
2	3.3	3.4	4.1	3.0	3.7
3	2.7	2.7	---	2.4	2.9
4	2.2	2.3	2.7	2.1	2.4
7	1.5	1.5	1.6	1.4	1.5
14	0.9	0.9	0.9	0.9	0.9
22	0.6	0.6	0.7	0.6	0.6
36	0.4	0.4	0.5	0.4	0.4

\* Glycol added

\*\* Silicone added

\*\*\* Polymer added

TABLE II

Process Application to Waste Type

Process	Waste Type		
	Dilute $\text{NO}_3$ Stream	Concentrated $\text{NO}_3$ Stream	$\text{NO}_3$ Salt
Direct Thermal Decomposition			X
Direct Thermal Conversion			X
Thermal Reduction			X
Redox Systems	X	X	
Biological System	X		
Incorporation			X
Recovery	X	X	

waste form. A lysimeter study being conducted at SRP will confirm or deny this hypothesis in a full scale test.

Transport of nitrate in the environment was confirmed by work at Hanford<sup>2</sup> on liquid waste disposal cribs. Fig. 4 describes how monitoring wells were used to map transport of radionuclides and nitrates from old cribs. Analytical results on effluent collected from these wells show that while most heavy metal elements are retained by the soil beneath the cribs nitrates have penetrated deeply into the underlying strata and water table. The ease of transport coupled with the difficulty to immobilize nitrates suggests responsible management can only be achieved by converting them to a less toxic substance.

#### DESTRUCTION PROCESSES

Seven basic processes were studied which might have application to convert the waste streams to a less toxic substance. The waste streams were categorized as dilute nitrate, concentrated nitrate, and dried nitrate salt. Table II is a matrix of the processes and their application. No attempt has been made at applying risk factors to the processes, but the thermal processes are of major interest at this time for dried salts.

Nitrate salts have been successfully converted to carbonates on a laboratory scale without creating  $\text{NO}_x$  by reacting them with carbon in a fluidized bed. Carrying out the reaction at a higher temperature in a molten sodium carbonate bath has more potential for a production process. Direct thermal reduction to nitrogen gas without creating  $\text{NO}_x$  is possible but has not been demonstrated. Either technique will yield the desired result of converting the nitrate to a non-toxic substance and reducing the volume by 30 to 60% respectively.

Chemical reduction of aqueous nitrate waste streams using compounds such as urea has been demonstrated on a laboratory scale. Further characterization of the reaction products for toxic compounds is necessary before pilot scale demonstration is possible.

#### CONCLUSIONS

Several conclusions can be drawn from the work to date. Sufficient quantities of low-level waste nitrate exists to warrant developing a specific waste management technology. Toxic levels of nitrate compounds are easily transported in the environment, and difficult to immobilize. Nitrates can be converted to non-toxic compounds which are easier to immobilize for radionuclide retention. Reduced volume for disposal is an added benefit from these processes.



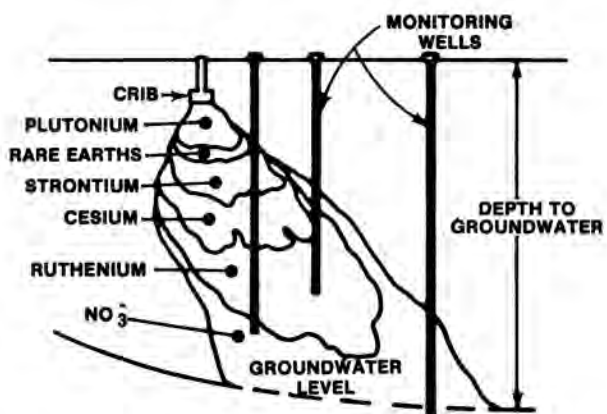


Fig. 4. Movement of Specific Ions from Cribs (Straub).

## REFERENCES

1. A. J. Johnson and J. J. Blakeslee, The Low-Level Waste Nitrate Challenge, RFP3283, Published Proceedings of The Third Annual Information Meeting, DOE Low-Level Waste Management Program, ORNL/NFW-81/34, Dec. 1981.
2. U.S. Energy Research and Development Administration Final Environmental Impact Statement, Waste Management Operations, Hanford Reservation, Richland WA, ERDA-1538, Vol 1 and 2, Dec. 1975.