

# DESTRUCTION OF ORGANICS AND DECOMPOSITION OF NITRATES IN UST WASTES BY STEAM REFORMING

Terry R. Galloway  
Synthetica Technologies, Inc.

Robert G. Dosch and Jeremy L. Sprung  
Sandia National Laboratories

## ABSTRACT

Organic contaminants and nitrates in Hanford Underground Storage Tank (UST) wastes have been destroyed by exposure to high temperature steam during bench tests with a quartz reactor and full-scale tests that used Synthetica's commercial steam reforming waste destruction system. Thermal decomposition of nitrates at typical steam reforming feed system temperatures (300 to 600 C) was also examined by Thermal Gravimetric Analysis (TGA).

## INTRODUCTION

Sixty-one million gallons of highly radioactive wastes (265 MCi) are stored in 177 underground storage tanks on the Hanford site. The wastes contain large quantities of sodium nitrate, and smaller amounts of organic complexants (Na citrate, Na<sub>2</sub>EDTA) and solvents (CCl<sub>4</sub>, n-decane, tributyl phosphate), that were introduced into the wastes by PUREX processing (1) of the original waste streams.

After retrieval from the tanks, Hanford remediation plans call for separation of the radioactive materials into a small quantity of high-level waste, which will be vitrified, and a large amount of low-level waste (sodium nitrate and other inorganic salts), which will be immobilized in grout in on-site vaults. The radioactive separations will be performed using solvent extraction or ion exchange processes. Because they may interfere with both separation processes, the organic complexants and solvents in the wastes must be destroyed before either process is performed. Because nitrate is a hazard if it enters drinking water, it must be destroyed before the low-level wastes are grouted and placed in the on-site grout vaults. Otherwise leaching of nitrate from the low-level grouted wastes into groundwater will constitute a health hazard.

Gasification and mineralization of organics by steam is a well known process (2-7), as is the thermal decomposition of sodium nitrate to sodium oxide and oxides of nitrogen (8). This paper summarizes studies of the destruction of organic interferents and sodium nitrate found in Hanford wastes by exposure to high-temperature steam during both bench-scale experiments and full-scale tests performed with the Synthetica Detoxifier, a commercial steam reforming waste destruction system (4-6).

## SYNTHETICA DETOXIFIER

The Synthetica Detoxifier (see Fig. 1) is a high-temperature, atmospheric pressure, waste destruction system that consists of a drum feeder, a moving bed evaporator, and a high-temperature reactor. Organic wastes are gasified in either the drum feeder or the moving bed evaporator by exposure to steam at moderate temperatures (300 - 500°C). Hetero atoms in the gasified organic materials are released as mineral acids that will be immediately neutralized by the NaOH formed by reaction of the steam with the Na<sub>2</sub>O that is produced by thermal decomposition of the large amounts of sodium nitrate in the Hanford wastes. After gasification, the organic fragments are destroyed by exposure to 1100°C steam

in the high-temperature reaction chamber of the Detoxifier. Previous Detoxifier studies have demonstrated better than 99.99 percent destruction of a variety of organic compounds (alcohols, ketones, chlorocarbons, aromatics) (4-6). Pressure increases due to gasification of organic materials are relieved by venting the excess gas to the atmosphere through an oxidative automobile catalytic unit that converts the CO and H<sub>2</sub> formed by the steam reforming chemistry to CO<sub>2</sub> and H<sub>2</sub>O.

## TGA NITRATE DECOMPOSITION EXPERIMENTS

Decomposition of NaNO<sub>3</sub> crystals with and without added heavy metal nitrates and of NaNO<sub>3</sub> dispersed on silica supports was examined using TGA. In ambient air, weight loss by NaNO<sub>3</sub> crystals is not detected below 600°C, and decomposition (loss of weight at a significant rate) is not appreciable below 725°C. Use of ambient air saturated with water vapor lowered this decomposition temperature from 725°C to 550°C.

Because alkaline earth and transition metal nitrates decompose directly to oxides releasing NO<sub>2</sub>, while alkali nitrates decompose first to nitrites by release of O<sub>2</sub> and then to oxides by release of N<sub>2</sub>O<sub>3</sub>, catalysis of NaNO<sub>3</sub> decomposition by addition of heavy metal nitrates was examined. Addition of two percent Ca(NO<sub>3</sub>)<sub>2</sub> or a mixture of other heavy metal salts found in UST wastes (iron, cadmium, chromium, lead, manganese, and mercury nitrates, sulfates, and/or phosphates) had no effect on the decomposition temperature in ambient air, indicating that non-alkali metal cations do not catalyze the decomposition of NaNO<sub>3</sub>.

Dispersal of NaNO<sub>3</sub> on two types of silica beads that had quite different surface areas (55 and 243 m<sup>2</sup>/g) led to complete decomposition in ambient air of the nitrate ions and lowered the decomposition temperature from 725°C to 280 and 260°C respectively. Thus, decomposition of NaNO<sub>3</sub> is strongly promoted by dispersal on a surface, although decomposition temperature is not strongly affected by surface area (degree of dispersal).

## BENCH-SCALE NITRATE DECOMPOSITION TESTS IN STEAM

In agreement with these results, only a twelve percent weight loss was attained when NaNO<sub>3</sub> crystals were exposed to 600°C steam in a quartz tube heated by a muffle furnace, while NaNO<sub>3</sub> coated on non-porous alumina spheres decomposed completely under the same conditions (nitrate concentrations on crushed spheres were 1425 mg/kg before exposure

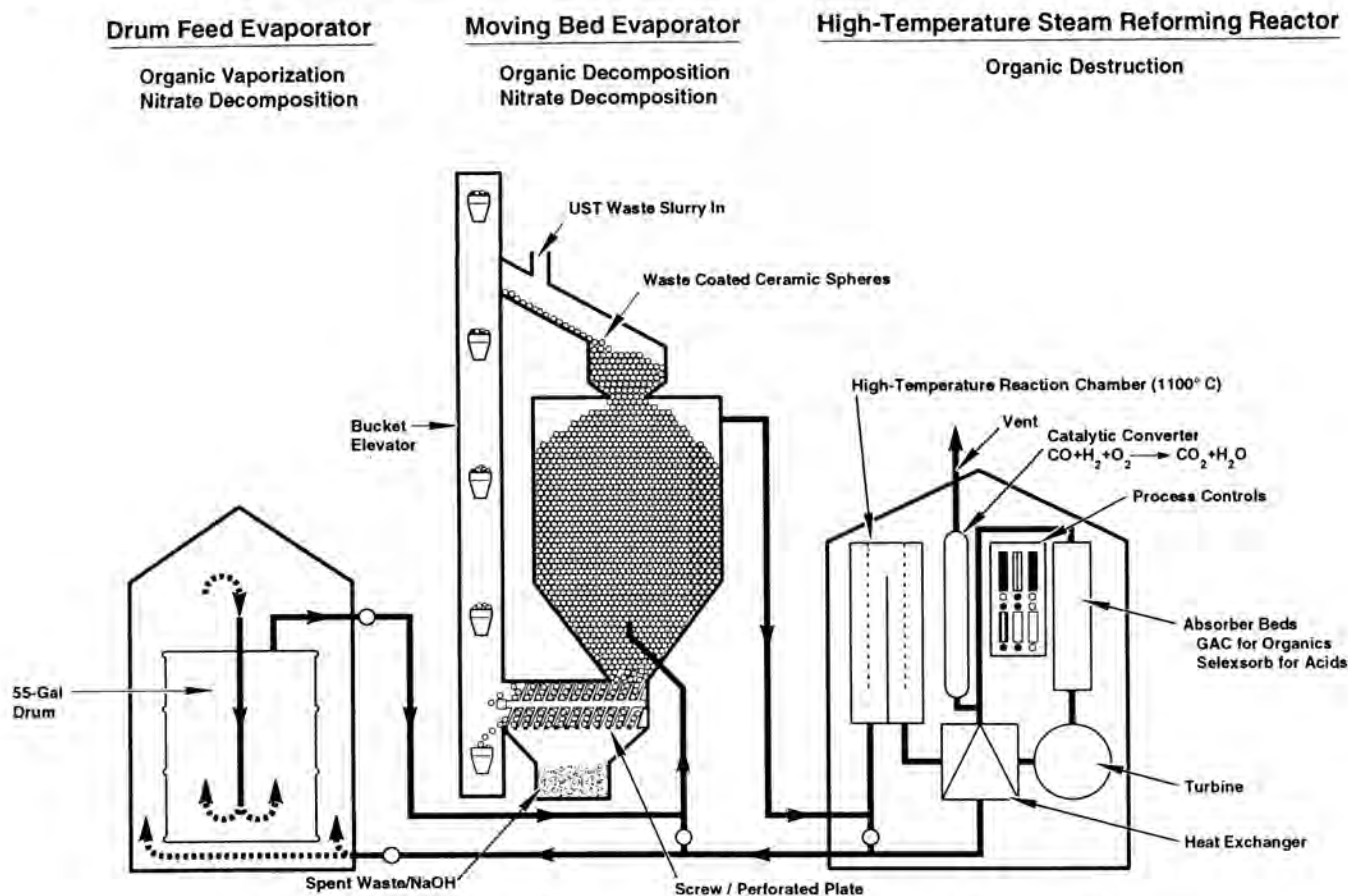


Fig. 1. Synthetica detoxifier: organic waste destruction, nitrate decomposition.

to steam and below the 5 mg/kg detection limit of ion chromatographic analysis after exposure).

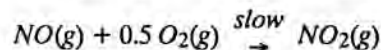
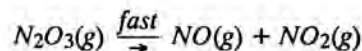
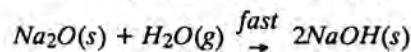
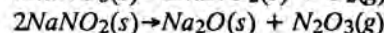
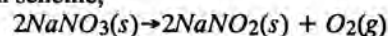
#### BENCH-SCALE ORGANIC GASIFICATION TESTS

Porous alumina spheres were soaked in a mixture of *n*-decane, tributylphosphate,  $\text{CCl}_4$ , and aqueous solutions of sodium citrate or disodium EDTA and then coated with a surrogate for UST single shell tank wastes prepared at Pacific Northwest Laboratory (PNL). Gasification of these organics was then examined by exposing the soaked, coated spheres to  $600^\circ\text{C}$  steam. After crushing, Total Organic Carbon (TOC) analyses of the soaked, coated spheres, before and after exposure to  $600^\circ\text{C}$  steam, showed that exposure to steam had gasified 99 percent of the organics (16000 ppm TOC before exposure to steam; 160 ppm TOC after). GC/MS analysis of a grab sample of the effluent steam stream showed that the concentrations of the starting organics in the effluent stream were below detection limits indicating that gasification had also led to quite complete destruction of the gasified organics (the quantities of organics used in this test were too small to allow destruction efficiencies to be measured).

#### FULL-SCALE NITRATE DECOMPOSITION TEST

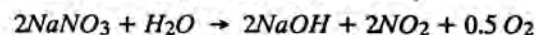
One hundred pounds of  $\text{NaNO}_3$  dissolved in water was injected into a moving (recirculating) bed of ceramic spheres through which high-temperature steam was flowing ( $500^\circ\text{C}$  at the bed inlet;  $200^\circ\text{C}$  at the bed outlet). Exposure to steam caused 92.2 percent of the nitrate to decompose and left a highly basic residue (wet pH paper registered pH 11 when in contact with the residue), presumably  $\text{NaOH}$ . Chemilumines-

cent analysis of grab samples of the Detoxifier effluent steam stream showed that it contained  $\text{NO}_2$  (850 ppm) and  $\text{NO}$  (100 ppm), which appears to be consistent with the following reaction scheme,



where qualitative agreement with experimental results would result if the conversion produced by the first two reactions is 92 percent, the third and fourth reactions are essentially quantitative, the conversion for the last reaction is about 80 percent, and the reverse of the last reaction is too slow to be significant at the experimental temperatures.

When summed, the above reactions yield



This suggests that the molar rate of nitrate decomposition should have been about the same as the molar rate of  $\text{NO}_x$  generation and that a small increase (about 0.5 percent) in bulk gas oxygen levels should have been observed. In fact, bulk gas oxygen levels increased by about 2 percent, and the molar rate of nitrate decomposition was about 0.7 moles per minute, while 950 ppm of  $\text{NO}_x$  and a bulk gas flow rate of 35 cubic meters per minute gives a generation rate for  $\text{NO}_x$  of only 0.03

moles per minute. This discrepancy may be explicable if  $\text{NO}_2$  and  $\text{NO}$  are being converted either to  $\text{N}_2\text{O}$  or  $\text{N}_2$  in the high-temperature reactor of the Detoxifier. If conversion to  $\text{N}_2$  is occurring, then the amount of oxygen released would have produced an increase of about two percent in bulk gas oxygen levels, which agrees well with the experimental data. Clearly, this experiment needs to be repeated monitoring the production rates of  $\text{N}_2\text{O}$  and  $\text{N}_2$ .

#### FULL-SCALE ORGANIC GASIFICATION TEST

Finally, 50 lbs of the PNL UST surrogate waste was prepared using a recipe supplied by PNL and then was spiked with  $\text{CCl}_4$ , n-decane, and tributylphosphate (the recipe contained sodium citrate, and disodium EDTA). When the spiked waste was pumped onto a bed of Raschig rings in a 55 gallon drum through which high-temperature steam was flowing ( $440^\circ\text{C}$  inlet,  $315^\circ\text{C}$  outlet), before and after TOC analyses of the spiked surrogate waste showed that 97.5 percent of the organics had been gasified out of the waste, and before and after nitrate analyses showed that 96.9 percent of the nitrate ions had decomposed. Although the small quantities of organics in the spiked surrogate were too small to allow organic destruction efficiencies to be measured, past Detoxifier results (4-6) suggest destruction efficiencies in excess of 99.99 percent for gasified organic materials. Higher nitrate decomposition and organic gasification efficiencies should be obtained by operating the Detoxifier feed system at a somewhat higher temperature (for example, feed system inlet and outlet temperatures of  $600$  and  $450^\circ\text{C}$  respectively).

#### FIELD-OPERABLE STEAM REFORMING SYSTEM CONCEPT

Since the large-scale tests were performed using the drum feed system (the 50 lb surrogate waste test) and the moving bed evaporator feed system (the 100 lb nitrate test) of Synthetica's high-temperature steam reforming waste destruction system, these results suggest that the organic contaminants and the nitrates in Hanford UST wastes can be efficiently destroyed by exposure to high-temperature steam using existing commercial equipment that has a unit processing rate of two tons of aqueous slurried waste per day. Although considerable experimentation must be performed to confirm this conclusion, it is not premature to ask whether a steam reforming system can be conveniently sized to operate in the field, mounted for example on a flat-bed trailer.

Figure 2 presents a conceptual sketch of such a trailer-mounted system. Preliminary calculations suggest that use of two Moving Bed Evaporator units, both slightly larger than the current test unit, will provide a processing rate for UST waste slurry of about 20 gallons per minute (5 GPM of waste, 15 GPM water), that the water in this amount of slurry can be continuously vaporized by exposure to 5000 scfm of  $600^\circ\text{C}$

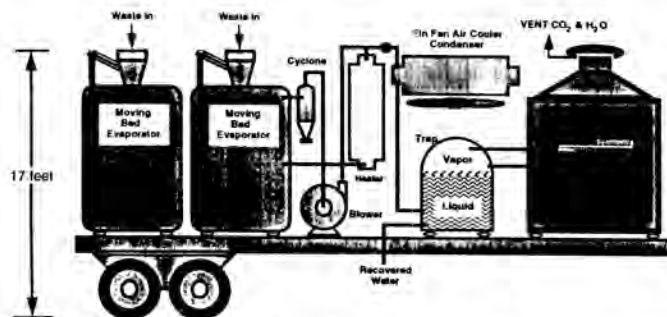


Fig. 2. Trailer-mounted UST organic/nitrate destruction system concept.

steam, and that the vaporized water can be condensed using a fin fan cooler condenser. The organics left in the vapor space in the water collection reservoir would then be destroyed by passage through the high-temperature reaction chamber of the current Detoxifier, which has more than enough capacity to handle the amounts of organics that would be vaporized by a waste processing rate of 5 GPM.

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