SLURRY GROWTH: THE CHARACTERIZATION OF A UNIQUE PHENOMENON AT THE HANFORD SITE

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ABSTRACT

A unique phenomenon, known as "slurry growth," is occurring in certain tanks of high-level defense waste stored on the Hanford Site. Slurry growth is the increase in volume of waste contained in a tank without the addition of new waste. This phenomenon has been occurring for many years at the Hanford Site, with first recorded growth in 1976.

Slurry growth is caused by gas entrapment within concentrated waste slurries. The trapped gas causes the slurry to swell, much like bread dough. The surface of the slurry, which is a crust-like layer formed during storage, rises in the tank. The rise continues until pressure buildup beneath the crust or the weight of the slurry over the gas becomes great enough to cause the surface of the slurry to collapse, releasing gas into the void space of the tank. This cycle may be repeated many times.

No safety-related problems resulting from slurry growth have been observed. To date, there have been no indications that barrier integrity (tank walls and filter systems) has been breached in any fashion. However, to maintain high standards of safety and control of stored wastes, the volume of waste added to a tank is sufficiently conservative to compensate for slurry growth without exceeding tank fill specifications. Detailed monitoring programs have been established to ensure that no radioactivity is being vented directly to the atmosphere as a result of pressurizations.

The volume of waste is reduced using a vacuum evaporator-crystallizer to minimize the number of waste tanks required for storage. However, slurry growth increases with increases in chemical concentration. Therefore, some of the waste volume reduction attained by evaporation may be negated by slurry growth. A balance between waste volume reduction and projected growth must be obtained to minimize the final waste volume. Since tank space is both expensive and limited, experimental laboratory studies have been under way for some time to examine the causes and mechanisms of slurry growth at the Hanford Site. These studies allow accurate predictions of potential slurry growth in Hanford Site wastes. The predictions, in turn, will minimize utilization of waste tank storage space without jeopardizing safety values.

Laboratory experiments have determined that both chemical and physical parameters have major affects on slurry growth. The studies have shown that gas generation is caused by decomposition of organic complexing agents in the waste. Three organics have been identified as the primary source of degradation. They are N-hydroxyethylethylenediaminetriacetate (HEDTA), ethylenediaminetetraacetate (EDTA), and hydroxyacetate (glycolate). These chelating agents were added during byproduct waste processing operations (solvent extraction) to remove ^{90}Sr from certain wastes.

The degradation of HEDTA, EDTA, and glycolate is a function of many parameters. The chemical composition of the waste is a major factor, with respect to both specific constituents present and their concentrations. For example, hydroxide concentration is directly correlated to the amount of gas generated. Iron acts as a catalyst for chemical decomposition of HEDTA and EDTA in synthetic wastes. Increasing temperature increases gas generation and, therefore, slurry growth. The presence of oxygen (which is, of course, a major constituent of air) is necessary for the decomposition reaction to proceed. Other components in the waste (such as aluminate, nitrate, and nitrite) are also involved in the reaction.

As the organics degrade, gases are generated. The major gases generated are H_2, N_2, N_2O, NO_x, and CO_2. As mentioned earlier, oxygen is consumed in the reaction, acting as an oxidizing agent. The product gases are then trapped within the slurry causing it to rise, much like bread dough. Evidence suggests that the primary degradation products may continue to degrade, thus allowing continued gas generation. Degradation products identified in actual high-level waste include oxalate and EDTA.

Slurry growth is also affected by physical parameters. The viscosity of the slurry (naturally related to slurry composition and slurry temperature) is directly related to growth. Higher viscosity allows more gas to be trapped, increasing growth. Growth is also affected by vessel geometry. Experiments have been conducted on a bench scale (graduated cylinders and beakers), a pilot plant scale (800 gal tank), and *actual waste that has been* stored in a 1-million gal (75-ft-diameter) double-shell tank.

Some of the above experimental data have been integrated into predictive equations for volume of gas generated and amount of slurry growth. This paper discusses the details of experimentation, as well as the explanation of the predictive equations. A discussion of recent developments in solving the slurry growth problem (experimentation and results) is also included.

INTRODUCTION

Waste management operations at the Hanford Site have been systematically removing liquid wastes from existing single-shell tanks. The liquid waste streams have been reduced in volume, by way of vacuum evaporation, to slurries. The slurries, viscous mixtures with suspended solids, are presently stored in high-integrity double-shell tanks, hence the name double-shell slurry (DSS). A unique phenomenon has been observed at the Hanford Site. The slurry volumes of DSS have increased with no addition of new waste. It is this phenomenon, slurry growth, that is the subject of this paper.

SLURRY GROWTH

Slurry growth is defined as the significant increase in volume of DSS without the addition of new waste. Slurry growth is caused by gases being generated from degradation of organics present in the waste, with subsequent gas entrapment within the slurry beneath the slurry crust. The slurry swells, much like bread dough, causing the surface to rise. The slurry continues to rise until either the pressure beneath the surface of the crust becomes great enough or the weight of the slurry above the gas becomes great enough to cause the slurry to collapse. The rise and fall of slurry surface level is cyclical, repeating itself many times. The slurry growth phenomenon has not created any observed safety-related problems. There have been no indications to date that barrier integrity, both tank walls and ventilation systems, has been breached. The tank contents are being constantly monitored. Exhaust systems continually provide vapor space changes, exhausting gaseous effluents through high-efficiency particulate air (HEPA) filters. The waste volumes are also constantly monitored. A periodic lancing program has been instituted to stimulate release of the trapped gas, allowing the crust to collapse. Thus, lancing relieves gas pressure and slurry volume. These and other programs have been established to ensure that no radioactive material is being released directly into the environment.

PROCESS OVERVIEW

For effective waste management at the Hanford Site, liquid waste is concentrated using a continuous, vacuum evaporator-crystallizer. The basic process is shown in Fig. 1. The products of evaporation are off-gases (treated by scrubbing), process condensate (which is further decontaminated by ion exchange), and the concentrated waste form.

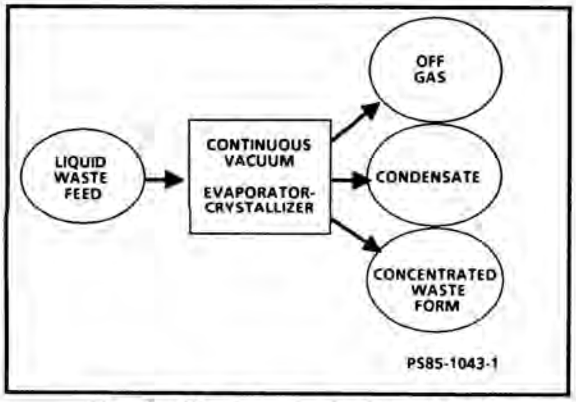

Fig. 1. Waste Concentration Process.

The evolution of the slurry growth phenomenon was a result of processing changes instituted in 1980 at the Hanford Site. Although some "growth" was observed as early as 1976, significant growth first occurred in 1980. The fundamental differences in processing mentioned above are shown in TABLE I.

TABLE I. Processing Changes.

Components	Pre-1980	1980
Feed	Primarily dilute	Primarily concentrated
Organic	Low or segregated	Mixed
Product form	Crystalline + liquid	Slurry
Specific gravity	1.4 - 1.6	1.8 - 1.9

The feed before 1980 was primarily a dilute waste. The product, salt crystals and supernatant, were segregated from significant concentrations of organics. The product also had specific gravity in the 1.4 to 1.6 range and a relatively low viscosity. In contrast, DSS was produced in 1980. The feed for DSS was primarily concentrated wastes, including the pre-1980 supernatant product. The DSS (with a specific gravity range of 1.8 to 1.9) was mixed with a concentrated organic product. This highly viscous material was the waste form that experiences slurry growth.

LABORATORY EXPERIMENTATION

Effective waste management of the slurry growth phenomenon required an understanding of the causes, mechanism, and anticipated affects of slurry growth. To that end, laboratory experiments were undertaken with the following objectives: define gas composition, define the causes of the slurry growth (both chemical and physical causes), model gas generation, and predict growth.

The approach to the laboratory study was threefold. First, scouting studies were undertaken to identify significant parameters, as well as verify the effects of known parameters. The ranges of the parameters were typical of the chemical and physical characteristics of DSS and DSS feeds. Second, a detailed statistically designed experiment was developed to determine relative importance of the parameters. This experiment utilized the data obtained from the scouting study. Third, the primary output of the statistical experiment was developed. The desired outcomes of the statistical experiment were to quantify gas volumes and gas production rates as a function of chemical variables and temperature.

The independent variables (HEDTA[a], GLY[b], NaOH, $NaAlO_2$, $NaNO_2$, $NaNO_3$, Fe(III), and temperature) were arranged in a fractional factorial experimental design. A major advantage of this design was that an empirical equation could be developed from experimental data. The dependent variable was gas volume as a function of time. The complete rate equation was developed by monitoring reactants' concentration as a function of time.

[a]N-hydroxyethylethylenediaminetriacetate
[b]glycolate

Finally, simulated waste forms were prepared and monitored to develop a predictive equation for slurry growth. The simulated wastes, based on actual waste analyses, were used to reduce radiation exposure to laboratory personnel. Synthetic feeds were reduced in volume using a bench scale batch evaporator. The resulting products were monitored for gas evolution (composition and volume) and physical growth.

Based on the laboratory results, the gas composition was determined. The gases present are primarily H_2, N_2, N_2O, NO_x, and CO_2. The relative ratios of these gases are dependent upon slurry composition, but several researchers established the major gases evolved. Ranges established for the various gases are shown in TABLE II.

TABLE II. Typical Gas Composition During Slurry Growth.

Gas	Composition range (mole %)
H_2	5 - 20
N_2	20 - 60
N_2O	13 - 55
NO_x	0.5 - 1.5
CO_2	3

Gas generation, causing slurry growth, is itself caused by decomposition of organics present in the waste. The organic chelating agents are in the waste due to previous chemical processing of the waste, primarily to effect the recovery of ^{90}Sr. Organic degradation is caused by thermal, radiolytic, and chemical reactions.

The key organics are HEDTA, ethylenediaminetetraacetate (EDTA), and hydroxyacetate (GLY). These organics, shown in Fig. 2, may degrade into either a stable chelating agent or a more reactive organic, producing additional gas.

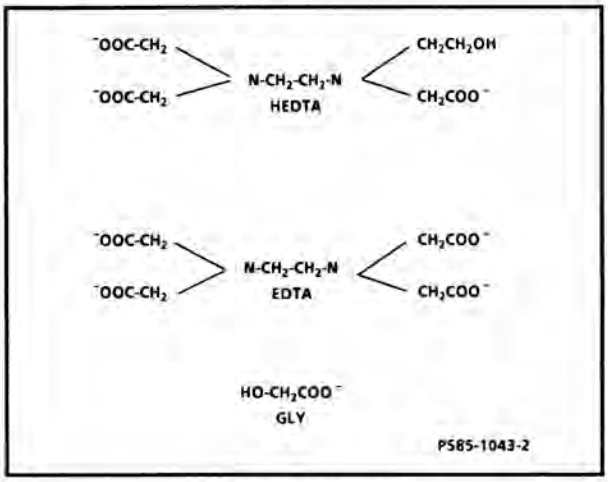

Fig. 2. Organics.

The degradation of the organics is dependent upon chemical composition. The scouting study indicated that gas generation is dependent on HEDTA, GLY, NaOH, $NaAlO_2$, $NaNO_2$, $NaNO_3$, and Fe(III). Also, it was determined that oxygen is required for the reaction to occur, and the reaction is temperature dependent.

The statistical study referred to earlier provided the relative importance of the various parameters. The parameters are in order of importance: temperature, GLY, NaOH, HEDTA, and Fe(III). This knowledge enabled an equation expressing the initial rate of gas generation to be developed. The initial rate, shown in Eq. (1), has an R^2 of 0.88 (88% of the variability in the data can be explained by the equation).

$$r_0 = \text{initial rate} = \text{mL gas/h/100 mL slurry}$$
$$\ln(r_0) = 41.95 + 0.14[\text{NaOH}] - 16{,}610.14 / T(°K) + 8.60[\text{GLY}] - 7.67[\text{GLY}]^2 + 0.28[\text{HEDTA}][\text{NaOH}] - 44.04[\text{HEDTA}][\text{Fe(III)}] \quad (1)$$

The volume of gas generated is directly related to the amount of slurry growth, for a specific composition concentration of DSS. The amount of slurry growth could not be quantified until physical parameters were examined. Laboratory experiments determined that slurry viscosity, itself a function of composition and temperature, played a predominant role in predicting the actual amount of slurry growth. In addition, vessel geometry was found to be important. Bench scale, pilot plant, and actual plant data were compared. Generally, the smaller the vessel, for a specific material, the greater the growth that was observed. The differences were attributed to wall affects. However, the equation developed to predict maximum growth, Eq. (2), shows excellent agreement with actual plant slurry growth.

Maximum growth (volume %)

$$\text{Growth} = 4.39 + 0.0253\ (\text{viscosity, Cp}) + 775\ (r_0)^* \quad (2)$$

This equation has enabled waste streams to be blended and scheduled for processing such that slurry growth is minimized and waste tank utilization is maximized.

CONCLUSIONS

Slurry growth, unique to the Hanford Site, is a significant increase in the volume of waste contained in a waste storage tank without the addition of new waste.

Slurry growth is caused by gas entrapment within waste slurries which causes the slurry to swell, like bread dough. The surface of the slurry rises until either gas pressure is great enough or the weight of the slurry over the gases is great enough to cause the surface of the slurry to collapse.

The gases causing slurry growth are generated from decomposition of organics present in high-level nuclear waste (HEDTA, EDTA, GLY). Predominant gases are H_2, N_2, N_2O, NO_x, and CO_2. More gas is generated, and at a faster rate, as the temperature increases.

*Refer to Eq. (1).

Slurry growth, although not completely eliminated, is being safely and effectively controlled. The parameters affecting slurry growth have been defined, and predictive equations have been established. The knowledge gained through laboratory experiments contributes to continued safe and efficient high-level waste management practices at the Hanford Site.