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A Low-Temperature Process for the Denitration of Hanford Single-Shell Tank, Nitrate-Based Waste Utilizing the Nitrate to Ammonia and Ceramic (NAC) Process

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MANAGED BY
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FOR THE UNITED STATES
DEPARTMENT OF ENERGY

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Chemical Technology Division

A LOW-TEMPERATURE PROCESS FOR THE DENITRATION OF HANFORD SINGLE-SHELL TANK, NITRATE-BASED WASTE UTILIZING THE NITRATE TO AMMONIA AND CERAMIC (NAC) PROCESS

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ABSTRACT

Bench-top feasibility studies with Hanford single-shell tank (SST) simulants, using a new, low-temperature (50 to 60°C) process for converting nitrate to ammonia and ceramic (NAC), have conclusively shown that between 85 to 99% of the nitrate can be readily converted. In this process, aluminum powders or shot can be used to convert alkaline, nitrate-based supernate to ammonia and an aluminum oxide-sodium aluminate-based solid which might function as its own waste form. The process may actually be able to utilize already contaminated aluminum scrap metal from various U.S. Department of Energy (DOE) sites to effect the conversion. The final, nearly nitrate-free ceramic-like product can be pressed and sintered like other ceramics. Based upon the starting volumes of 6.2 and 3.1 *M* sodium nitrate solution (probable supernate concentrations resulting from salt-cake/sludge removal from the Hanford SSTs), volume reductions of 50 to 55% were obtained for the waste form produced, compared to an expected 35 to 50% volume increase if the Hanford supernate were grouted.

Engineering data extracted from bench-top studies indicate that the process will be very economical to operate, and data were used to cost a batch, 1200-kg NO_3/h plant for working off Hanford SST waste over 20 years. Our total process cost analysis presented in the appendix, indicates that between $2.01 to 2.66 per kilogram of nitrate converted will be required. These costs are between one-third to one-half of the processing costs quoted for electrolytic and thermal processes based upon 1957 literature. Additionally, data on the fate of select radioelements present in solution are presented in this report as well as kinetic, operational, and control data for a number of experiments.

Additionally, if the ceramic product functions as its own waste form, it too will offer other cost savings associated with having a smaller volume of waste form as well as eliminating other process steps such as grouting. This work has been predicated on exactly this assumption: that the by-product from the reactor would be pressed uniaxially and sintered to produce a waste form. To consider mixing the solid formed [alumina hydrate (96%)/ sodium aluminate (4%), based on X-ray analysis of dried NAC solid product produced with sodium nitrate feed] with cement-based grout would not be possible due to flash set problems from the soluble aluminate fraction and possibly the alumina hydrate (gibbsite) and would obviate the large volume reduction possible with the NAC process. The sodium content and molecular speciation in the product solid are still uncertain and are a subject for further evaluation in FY 93. In order to aid in fixing the sodium present, the reactor product may be mixed with fine

silica (5 μm) and sintered by microwave. This approach is planned for FY 93 along with a greater emphasis upon product testing. Testing of actual mixed wastes from the Melton Valley Storage Tanks (MVSTs) (similar to Hanford SST waste in composition) is planned in FY 93.

1. INTRODUCTION

Sodium nitrate-based wastes are common to many U.S. Department of Energy (DOE) facilities throughout the United States. At facilities such as the single-shell tanks (SSTs) at the Hanford site, the Savannah River site, Melton Valley Storage Tanks (MVSTs) at ORNL, and the Pad A Waste at Idaho Falls, 1984 figures indicate that greater than 242,700 metric tons of nitrate wastes were stored. This study has been directed at a surrogate supernate representing solution resulting from dissolving and decanting the salt cake/sludge in the Hanford SSTs, of which there are 149 tanks with capacities of 1 million gal each.

Wastes at the Hanford site can be subdivided into high-level waste (HLW), transuranic (TRU), and low-level waste (LLW), with the HLW and TRU wastes targeted for vitrification and the LLW for immobilization in cement-based grout, although a final decision is not expected until 1996. The LLW contains most of the sodium nitrate and would be grouted in near-surface vaults, in a similar fashion to efforts at Savannah River using "salt stone".

Because the nitrate anion is very mobile and difficult to immobilize, especially in relatively porous, cement-based grout, it presents a major obstacle for cleanup efforts at the Hanford site. It would follow that processes that could decompose nitrate might be implemented to eliminate this problematic species and that these would be of interest to DOE and to federal and state regulators. In addition, a process that could be operated at a low temperature, coproduce its own ceramic-based waste form, and be cost-effective compared with other technologies would be of immense importance. Just such a process has been demonstrated in this bench-top feasibility study using Hanford supernate surrogates.

Nitrate in groundwater can pose a serious threat to public health. Reduction of nitrate to nitrite in the gut may cause methemoglobinemia in newborns as well as in some adults who may be deficient in the enzyme glucose-phosphate dehydrogenase. It is also postulated that nitrite in the stomach can form N-nitrosamines, a potential cause for many stomach cancers. Additionally, any nitrite entering the bloodstream can compete for sites on hemoglobin that would otherwise carry oxygen into or carbon dioxide out of the body. It is for this reason that the Environmental Protection Agency (EPA) has set the nitrate concentration limit in drinking water at 44 ppm as nitrate, or 10 ppm as monatomic nitrogen (N).

2. CHEMISTRY AND DISCUSSION OF THE NITRATE TO AMMONIA AND CERAMIC (NAC) PROCESS

2.1 BACKGROUND

Aluminum is the third most abundant element in the earth's crust, with only silicon and oxygen exceeding its 8.1% abundance. Aluminum is not found in a free form in nature as a metal (placer form), as is the case for metals such as gold and silver. This is because the metal is not thermodynamically stable in the presence of oxygen and quickly forms the oxide. It is this oxide coating on aluminum that makes it possible for aluminum to be used in the oxygen-rich atmosphere of this planet. The oxide coating, once formed, can allow the aluminum to exist for a useful length of time.

In the presence of water, the rate of oxidation is further enhanced because water can aid in transferring electrons from aluminum to water or some other species capable of being reduced. In an aqueous medium, especially one which is distinctly alkaline, the protective oxide is sparingly soluble. Upon abrasion or partial solubilization of the oxide, the metal dissolves by reducing the hydrogen component of water to gaseous hydrogen or reduces some other reducible species that may be present, such as nitrate or nitrite.

The free energy change associated with the oxidation of aluminum (-378 kcal/g-mol) to its most stable, water-free oxide, alumina (Corundum), is quite large and exothermic. This means that aluminum can function as a very powerful reductant. This fact is taken advantage of in the familiar process employed by self-serving "safe crackers" by which they sometimes successfully burn through thick, steel safe doors. To the chemist, this artisan is known to be dependent upon the reaction known as the Goldschmidt, or thermite reaction, in which the highly exothermic reduction of metal oxides of iron or chrome is effected by powdered aluminum metal. Upon using a heat source to initiate the reaction, such as burning magnesium and perchlorates, a blinding flash and temperatures far in excess of the metals' melting points result. The same reaction is used by the military to burn through hardened steel tanks microseconds before impact by explosive charges encased in rocket or artillery projectiles.

The thermodynamic driving force for aluminum metal to be oxidized, or, in other words, function as a strong reductant by giving up its outer shell electrons, is also evident by the fact that aluminum is present in nature as alumina. Alumina is found in association with silica and iron oxide and is known by the mineral name bauxite, $Al_2O_3 \cdot nH_2O$ (indefinite formula). Bauxite is the world's primary source of aluminum, and a very energy intensive (13—17 kWh/kg aluminum) electroreduction process is required to produce metal from this mineral. The process, known as the Hall-Herault process, named after the co-inventors, requires the use of a calcium fluoride-based molten salt bath and still remains the leading process for the consumption of the largest amount of electrical energy per unit of product produced in the modern world.

Interestingly, the process for nitrate reduction described in this report is also a type of electrochemical process which is related to the Hall-Herault process in that it is actually this process in reverse. Admittedly, a major difference is that it occurs in an alkaline, aqueous solution, rather than a water-free molten salt bath. In the Hall-Herault process, many amperes of electrical energy are added via large, consumable carbon anodes (+) to convert the oxide to metal. On the other hand, when using powdered aluminum metal as a reductant, the metal gives up 3 mol of electrons per 1 g-mol of metal, energy which was in effect added during the electroreduction in the Hall-Heroult cell. In a way, the aluminum metal can be considered to be like a charged capacitor or battery, ready to release its energy during the reduction of nitrate to ammonia gas, or, under some conditions, to reduce water to hydrogen gas.

We may then be able to take advantage of this source of stored electrons to reduce nitrate or nitrite ions to ammonia gas. It can be said, therefore, that the metal is electropositive, so much so that as an electrode it is highly irreversible and therefore its half cell cannot be measured directly and must be calculated from thermal data. The following standard reduction potentials, in aqueous solutions at 25°C, reveal how powerful a reductant aluminum metal is in alkaline solution:

$$Al(OH)_3 + 3\,e^- \rightarrow Al + 3OH^- \qquad E^\circ = -2.31 \text{ volts} \tag{1}$$

$$NO_3^- + 6H_2O + 8\,e^- \rightarrow NH_3\uparrow + 9OH^- \quad E^\circ = -0.16 \text{ volts} \tag{2}$$

From the magnitude of the difference of the absolute values of these reduction potentials, it can be seen that aluminum is indeed more than capable of reducing nitrate to ammonia. In addition, aluminum can reduce water to form hydrogen gas and hydroxide in accordance with Eq. (3). This reaction lowers efficiency and produces unwanted hydrogen:

$$2Al + 6H_2O \rightarrow 3H_2\uparrow + 6OH^- + 2Al^{3+}\,. \tag{3}$$

The electrical reduction potential minimum necessary to reduce water to hydrogen is a function of temperature, metal activity, the specific metal overvoltage, pH, and current density (A/cm^2 of exposed metal surface). Values for all these parameters have not been established; however, based upon Eq. (4) and a pH of 12 and an overvoltage (V) of 0.8 V for aluminum, we estimate:

$$E = -0.059\ pH - V\,. \tag{4}$$

A minimum theoretical reduction potential of at least −1.5 V might ideally be necessary to decompose water into hydrogen gas. As shown above, the nearly 2 V difference is sufficiently large enough to accomplish this. What helps us is that a greater difference exists between the nitrate anion reduction potential and aluminum as opposed to our estimate of 1.5 V for water; therefore, nitrate reduction is favored first.

Although the above standard potentials are only for ideal solutions and conditions, and the system is more complex than described, one can realize the order of magnitude differences involving thermodynamic driving forces for the reduction of nitrate and water. It is for this reason that this process using aluminum metal is able to work so well.

One missing parameter that does not figure into the thermodynamic picture is the protective oxide coating on the surface of the aluminum metal. This oxide protects the aluminum so well in air that it even protects aluminum from serious oxidation during melting. This oxide coating is actually alumina with some associated water and is written as $Al_2O_3{\cdot}3H_2O$, otherwise known as "gibbsite" and called "hydrargillite" in the ceramics industry. This form of aluminum oxide contains 34.6% water and 65.4% Al_2O_3.

This water-containing form of alumina has a more negative free energy of formation at STP than anhydrous alumina (corundum). Crystalline gibbsite has a free energy of formation of −555 kcal/g-mol. The waters associated with the oxide are not waters of hydration; rather, they are loosely bound by hydrogen/oxygen bonding and represent an average composition. This oxide is what rubs off on your hands if you run your hand over the surface of aluminum patio chairs that have been out in the weather for a long time.

The as-written formula for gibbsite can also be shown in another way, despite the fact that aluminum hydroxide, as written, does not really exist. This is because this formula represents an average ratio of aluminum to water, and as a fresh gel it is changing to approximate the crystalline mineral gibbsite. Therefore, we may write:

$$2Al(OH)_3 = Al_2O_3{\cdot}3H_2O \quad \text{("gibbsite")} . \tag{5}$$

This is the primary product that is formed in our reactor upon reducing nitrate to ammonia. This product is crystalline, white in color, hard (2.5 to 3.5 Mohs) and dense (2.42 g/cm^3). Upon aging, it is quite insoluble in nearly all acids and sparingly soluble in hot caustic.

As already discussed, aluminum metal is not stable in water and in, especially, alkaline solutions. The metal actually dissolves while functioning like an anode (+), giving up its electrons to nitrate, or, under some conditions, water. When added to solutions that are sufficiently alkaline, there is a delay in reactivity due to the presence of the protective oxide coating. The delay is accompanied by the absence of the expected rise in solution temperature due to the highly exothermic reaction. After several minutes at, for example, 50°C and pH 12, a marked rise in temperature is observed, accompanied by the evolution of ammonia gas.

The delay is most pronounced during start-up of the reactor and becomes shorter with time after each successive addition of metal. The oxide coating is partially broken down following metal addition and the reaction accelerates. Factors which can accelerate the reaction of metal with the solution and its electrolyte can be summarized as follows:

(1) High shear mixing can cause the oxide surfaces to be abraded.

(2) Both a high pH and high temperatures favor a faster reaction.

(3) The presence of increasing amounts of highly abrasive gibbsite in the reactor serves to remove oxide coatings; for this reason, early stages of reactor start-up can be expected to be inhibited, if not seeded with gibbsite.

(4) The physical configuration of the reactor, such as the presence of baffles or its shape, can serve to abrade oxide coatings and expose bare metal to solution faster.

Interestingly, some beaker tests that were performed to investigate the effect of having abrasive gibbsite added to the reactor before adding any aluminum metal revealed that, indeed, the presence of the gibbsite increased the reaction rate, as judged by nearly an immediate temperature rise and evolution of ammonia. Therefore, once enough abrasive gibbsite product has been formed, the aluminum metal can be expected to react not long after being added, thereby making it easier to control the reactor. The aluminum powder feed rate can be adjusted to maintain a desired temperature, generally 50 to 60°C. Experience has shown that if the temperature becomes too high, due to the highly exothermic reaction, it may become very difficult or impossible to control the reaction, resulting in a situation similar to test tube "bumping" in the chemistry lab.

The calculated heat of reaction for the reduction of nitrate to ammonia and the conversion of aluminum metal to oxide is −381 kcal/mol $NaNO_3$, and for this reason, an efficient cooling system must be an integral part of the reactor design. The heat of reaction is calculated based upon the free energy change between aluminum metal and its oxide and accounts for the major part of the overall free energy change of the overall reaction.

2.1.1 The Formation of Reactor Products

Upon adding aluminum powder to a 50°C solution which is alkaline (pH 11 to 12.5) and which contains ~.4 *M* $NaNO_3$, one obtains an initial delay and then a reaction which is associated with a rapid increase in temperature. During the early stage of the reaction, the solution remains clear until at some point, dense, white gibbsite begins to precipitate. Upon stopping the mixer, the solids quickly settle to the bottom of the reactor, much like sand. Figure 1 shows the thermodynamic relationship between the stability fields for soluble aluminate (AlO_2^-), gibbsite, and the aluminum cation as a function of pH.

As shown in Fig. 1, as aluminum metal is added to the alkaline solution in the pH range of 12 to 14, soluble aluminate anion predominates until, after a sufficiently large

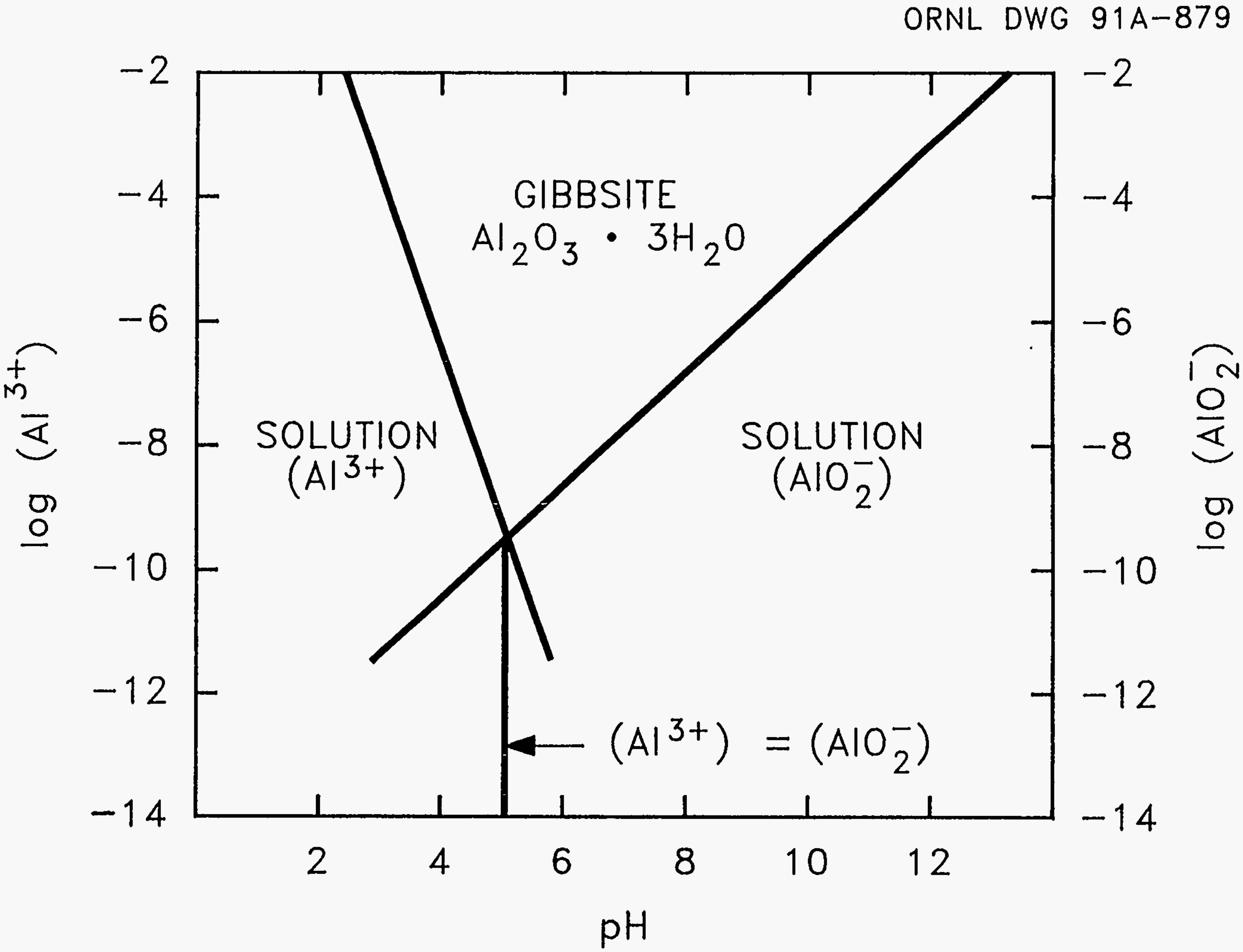

Fig. 1. Stability field diagram for the gibbsite, aluminate, free-cation system as a function of solution pH at STP.

quantity of aluminum has been added and reacted, we reach the gibbsite/aluminate equilibrium line separating the soluble aluminate and the gibbsite stability fields. After the solution reaches this point, any further addition of aluminum metal causes the formation of the highly insoluble gibbsite product. As the diagram shows, there is a solubility minimum for aluminum at about pH 5; and although the diagram indicates that we may work at a lower pH, the increase in the activity of the hydrogen cation will waste aluminum by forming hydrogen gas. For this reason, we must work at higher pHs to have a viable process.

Under any given set of conditions, especially pH and the availability of water, the aluminate anion will be in equilibrium with gibbsite and will react with water (in the presence of the sodium cation) to form more gibbsite in accordance with the reaction shown in Eq. (6):

$$NaAlO_2 + 2H_2O \rightarrow Al(OH)_3 + NaOH . \qquad (6)$$

Because of the well established aluminum industry and the modern day interest in producing high-purity alumina of uniform size for use in ceramics, there are a lot of data on the equilibrium relationships in the Na_2O-Al_2O_3-H_2O system at various temperatures.[1,2] We would therefore expect at the end of a reaction, when we start with sodium nitrate at pH >12, to have a final product containing some ratio of sodium aluminate and gibbsite, if we agree that these are the two predominant species, and they seem to be according to X-ray analysis. Laboratory samples of oven-dried (110°C) solids removed from beaker tests produced by reacting 4 *M* $NaNO_3$ with aluminum powder in the prior experiments, and from the bench-scale reactor following denitration of 6.2 and 3.1 *M* $NaNO_3$ this year, have revealed the following composition when wet chemical methods of analysis[3] were employed:

95.4 wt % $Al_2O_3 \cdot 3H_2O$
2.6 wt % $NaAlO_2$
2.0 wt % NaOH

The fate of the rest of the sodium present in the feed material has yet to be determined, and closing of a sodium balance around the reactor is a priority for FY 93.

In addition to wet chemical analysis, X-ray diffraction spectra were obtained on selected products, and results of one of the scans are presented in Appendix A. The scans show the analysis of a product produced in run DN-3 in which the 3.1 *M* nitrate feed was reduced to low ppm levels. Scans of sodium aluminate and gibbsite standards are also shown for comparison. These semiquantitative X-ray scans seem to agree in order of magnitude with our wet chemical methods. Diffraction results indicated the following composition:

95 wt % $Al_2O_3{\cdot}3H_2O$
3 wt % $NaAlO_2$
NaOH not detected (must be >5% to be detected)

In earlier beaker tests (FY 91), samples were obtained that contained no free sodium hydroxide that could be titrated by standard acid upon crushing the samples and mixing with water. The reason for the absence of sodium hydroxide on occasions is still unclear, for as Eq. (6) above shows, the sodium aluminate component should react with excess water to release caustic. Samples that were heated at 300°C and placed in the open air for more than a year did not take up water from the air, as might be expected if free caustic were present.

2.1.2 Relevant Chemical Reactions

A closely related technology to the NAC process would be the electroreduction technology, much of which has been developed and tested at the Savannah River Laboratory.[4] This similarity affords a good introduction to the use of active metal aluminum reduction by comparison with the electrolytic approach to denitration.

An overall reaction that might represent both anodic and cathodic reactions in an electrolytic cell is:

$$3NaNO_3 + 3H_2O \rightarrow N_2\uparrow + NH_3\uparrow + 3NaOH + 4.5O_2\uparrow \ . \qquad (7)$$

From reaction (7), we notice that for every mole of sodium nitrate reduced to ammonia and nitrogen we produce a mole of sodium hydroxide. This would mean that for every 85 kg of sodium nitrate we would produce 40 kg of sodium hydroxide. This is one of the many problems associated with the standard electrolytic process for decomposing nitrate which makes it unattractive; otherwise, it might be widely used today.

In the NAC process, aluminum dissolves, functioning similarly to a sacrificial anode, and, therefore, we can write the following equation for the sodium nitrate reduction reaction if it is assumed to be 100% efficient:

$$3NaNO_3 + 8Al + 12H_2O \rightarrow 3NH_3\uparrow + 5Al(OH)_3 + 3NaAlO_2 . \qquad (8)$$

The equation, as written, allows us to surmise four things: (1) if 100% efficient, 0.85 kg of metal would be required per kg of sodium nitrate (8 moles of aluminum for each 3 moles of sodium nitrate); (2) the reaction as written does not show sodium hydroxide as a product, instead sodium aluminate is present; also (3) if the reaction were correct as written, we might expect to have a product that contained 61% gibbsite as $Al_2O_3{\cdot}3H_2O$ and 39% sodium aluminate; and, lastly, (4) the reaction appears to consume a lot of water.

Our work with aluminum has never shown a stoichiometric relationship as per Eq. (8) above. In fact, generally 1.6 kg of metal is required per kg of sodium nitrate (~2 times stoichiometric) to reduce all the nitrate. Preliminary test work performed in FY 91 showed that half of the metal was consumed reducing the last 10% of the nitrate in solution due to the much lower nitrate concentration relative to the amount of water near the end of the reaction. During actual operation of a plant at steady state, one would be unlikely to lower the concentration of nitrate to this extent.

Instead of sodium hydroxide, reaction (8) above shows sodium aluminate, which is capable of reacting with water to form sodium hydroxide and more gibbsite. At the end of a reaction, when solids and some minimum amount of water are discharged from an operating reactor, we would expect some fixed ratio of these components. The ratios will be determined by parameters such as available water, pH, and, to a lesser extent, temperature. If the solids are dried, or sintered at higher temperatures, one can still expect a change in the gibbsite to sodium aluminate ratio as free water is removed.

Generally, our tests have required twice as much aluminum metal as predicted by Eq. (8) to reduce all of the nitrate initially present, and, as expected, the ratio of gibbsite to sodium aluminate has been very much different than would be predicted by this equation. As a result of using more than the theoretical amount of aluminum, both wet chemical and X-ray diffraction reveal that a dried product will contain approximately 96%

gibbsite and closer to 4% sodium aluminate and sometimes trace amounts of sodium hydroxide. The wet chemical analysis of the sodium aluminate component is complicated by the fact that it reacts with water to form caustic and more gibbsite, and, therefore, its exact composition is prone to some error.

Since our prior batch reaction tests have shown that we must use almost twice as much metal as predicted by Eq. (8) to convert all of the nitrate, we can write a reaction that reflects a situation in which we might run that batch reactor until nearly all the nitrate is converted to ammonia:

$$3NaNO_3 + 16Al + 36H_2O \rightarrow 3NH_3\uparrow + 12H_2\uparrow + 13Al(OH)_3 + 3NaAlO_2 . \qquad (9)$$

The reaction that best represents the actual active metal batch reduction of nitrate in this study presumably lies between this reaction and Eq. (8) above, but probably closer to the latter at present. Based upon Eq. (9), we would predict the use of 1.7 kg of metal per kg of sodium nitrate and produce reaction products composed of approximately 81% gibbsite and 19% sodium aluminate.

As both Eqs. (8) and (9) show, a large amount of water is consumed, much of which supplies aluminum with its oxygen component. This means that nearly all of the water contained in a 4 *M* nitrate solution is consumed during the reaction and water must be added during the reaction to facilitate mixing and enhance heat transfer to the cooling system.

As Eq. (9) indicates, in a batch reactor, we expect hydrogen gas as a product since we have added nearly twice as much metal, and, therefore, twice as many moles of electrons, which must reduce either nitrate or water in a solution of only these species. We expect that the hydrogen might be produced during the time when the nitrate concentration is low in comparison with the concentration of water and would be closely related to diffusion rates of reactants and products to and from exposed metal surfaces. Metal use, and, therefore, potential for hydrogen production, is related to the chosen steady state concentration of nitrate maintained in an operating reactor.

Since this process ultimately forms alumina, which is, on the average, associated with 3 mol H_2O at temperatures <300°C, Eq. (9) above may be rewritten to more accurately reflect this by-product. Upon relating Eq. (5) to reaction (9), we may write the following reaction when we utilize twice the theoretical amount of aluminum indicated in Eq. (8) in a batch reactor:

$$3NaNO_3 + 16Al + 36H_2O \rightarrow 3NH_3\uparrow + 12H_2\uparrow + 6.5Al_2O_3{\cdot}3H_2O + 3NaAlO_2\,. \quad (10)$$

2.1.3 Reaction Schemes

Although the purpose of this study was not to investigate reaction schemes or mechanisms, a task which would be challenging due to the complex and sensitive chemistry involved, we did develop a basic understanding of the system. Much of the knowledge on the formation of gibbsite from solutions comes from those companies which produce a pure, uniformly sized gibbsite for use in the ceramics industry.[5-7]

Interestingly, when aluminum metal is fed to our reactor, at first we experience a drop in pH, which can be as much as or more than a whole pH unit, and then a gradual rise in pH occurs. This drop becomes less pronounced with each successive aluminum addition, until, depending upon conditions, the change in pH is no longer evident. At this point, the reaction of the metal with nitrate becomes almost instantaneous. A pictorial, nonstoichiometric reaction scheme is presented in Fig. 2.

As Fig. 2 shows, after aluminum has reduced nitrate to ammonia, the highly charged aluminum III cation quickly surrounds itself with a cage of water molecules. After this occurs, the hydrated metal begins to age by eliminating hydrogen ions as the oxide is much preferred thermodynamically, accounting partially for a pH drop. Additionally, another hydrated aluminum cation nearby will condense with this species and form what we call the mineral gibbsite, which is actually $Al_2O_3{\cdot}3H_2O$, or also is called aluminum hydroxide, as shown in various reactions above. The free energy of formation at STP for amorphous $Al(OH)_3$ is -272 kcal/g-mol and that for $Al_2O_3{\cdot}3H_2O$ is -555 kcal/g-mol; therefore, it is easy to understand why the condensation reaction presented in Fig. 2 is favored with such a large thermodynamic driving force to form crystalline gibbsite.

In addition to the aluminum cation reacting with water, the cation will also lower the free hydroxide activity contributing to the initial solution pH by temporarily consuming it. Depending upon the starting pH, aluminum, being amphoteric, can become an anion, taking on four hydroxides, to later release hydroxide upon aging and move the pH upward again. The aluminate anion, which exists in equilibrium with gibbsite, water, and sodium

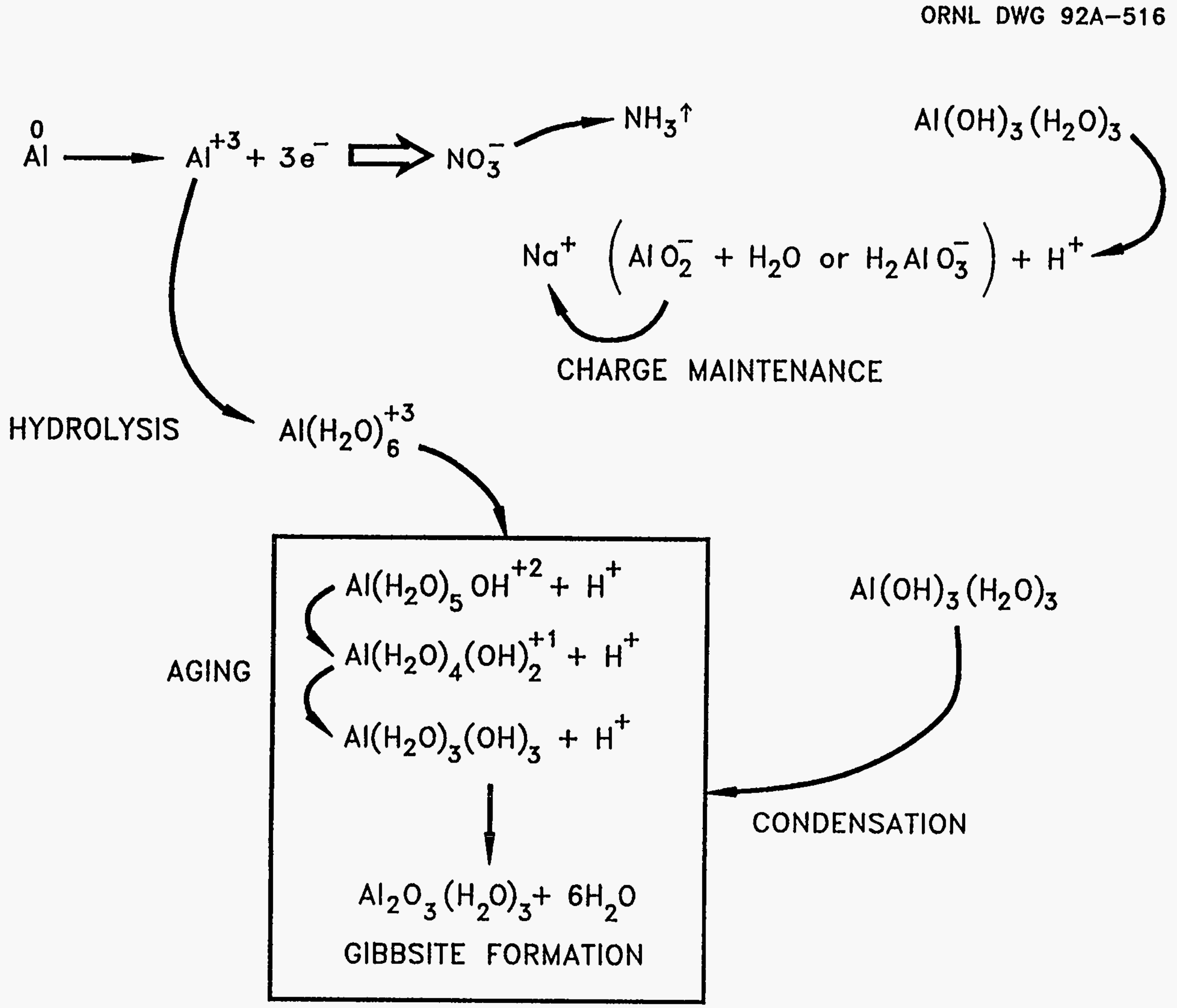

Fig. 2. Pictorial, nonstoichiometric reaction scheme for the nitrate to ammonia and ceramic (NAC) process.

hydroxide, also contributes to an additional rise in pH in the reactor depending upon the amount of available water.

The exact conditions of pH, temperature, mixing, concentrations, seeding, and cool down of solutions are still a mixture of industrial art and science in the ceramics manufacturing industry, and much data are available from the literature on the topic.[8,9] The importance of such research is unquestionable since the gibbsite product is the material which is calcined to form the ultimate alpha alumina component of modern-day ceramics.

2.1.4 Properties of Reactor Products

The primary product from the reaction of aluminum with a basic solution of sodium nitrate is gibbsite with a small percentage (3 to 4%) of sodium aluminate and possibly a trace amount of caustic. Although the physical and chemical properties of these products were not studied in depth this year, we know from scoping tests done during the inception of this process that we can form a true ceramic product with many of the advantages offered by such a medium: that is, it is readily pressed and sintered.

As already discussed, the product exiting the reactor is quite sandlike and easily dewatered. The product, however, if allowed to stand in the reactor for a number of hours, will "age" and become quite hard and, in fact, afterwards cannot even be dissolved in acid. After this type of aging, in which three-dimensional bonding between aluminum and oxygen and some hydrogen occurs, the product can only be dissolved in boiling sodium hydroxide solutions, with difficulty.

The reaction product can be dried and then calcined at various temperatures to produce different types of alumina, with different properties, as is done in the ceramics industry. Each of the higher forms of alumina becomes successively more chemically inert following calcination. In addition, higher-temperature sintering of product causes fusion to occur between alumina particles where contact is made between them, thereby increasing the physical strength.

Early work performed in FY 91 showed that the crude, noncompressed, nonsintered product possessed an unconfined compressive strength of 255 psi. Upon sintering at only 300°C, the strength increased to 521 psi. Sintering the gibbsite at 300°C converted it to "boehmite," which is $Al_2O_3{\cdot}H_2O$. This product is often called European bauxite, as opposed to American bauxite (gibbsite). There is actually no bauxite in the United States; rather, various Caribbean islands provide most of the U.S. supply. If the dried product is pressed and then sintered, we expect strengths of many thousands of psi to result. Work to study such properties is scheduled for next year.

Additionally, the size of the gibbsite particles forming in situ in our reactor are known to be mostly submicron, based upon the literature, and upon observing material pass through filter paper in the laboratory. Because of these small, dense particles, we have an opportunity to produce a solid with much smaller pores than any cement-based material. Therefore, the capillary pore pressure resistance inside such a solid will be very high. Water from the outside will not be able to penetrate, as it can with cement-based grout or even high-grade structural concrete.

2.1.5 Potential for Large Volume Reductions

Work performed in FY 91 with product from stirred beaker tests, using 4 *M* sodium nitrate, was used to gauge volume changes based upon the starting volume. In these tests, we generally reduced the nitrate concentration to ~5 ppm. This meant that we used 1.6 kg Al/kg $NaNO_3$; as already discussed, there may not be a need to achieve such a complete conversion of the nitrate, and, therefore, less metal would be required. It should also be noted that for those tanks which contain large amounts of nitrite, less aluminum will be needed to convert this species to ammonia, compared with that required for nitrate.

In these tests, we dried the reactor product at 110°C and then pressed the product uniaxially at 5000 psi for a final volume reduction of 55%; that is, one unit volume of waste becomes 0.45 unit volumes of hard solid. Studies this year also looked at pressing (2000 psi) dried or sintered product from our reactor tests and obtained similar results. It is felt that dried reactor product can be pressed to even smaller volumes prior to sintering.

If a nitrate-based waste is immobilized in a cement-based grout, as is done at Savannah River or at Oak Ridge's Melton Valley, we can expect a volume increase of from 35 to 50%, depending upon the formulation used. In Oak Ridge's Melton Valley, we are grouting 4 *M* $NaNO_3$ and obtaining a 38% increase in volume. Figure 3 shows this relative volume change between cement-based grout and the NAC process.

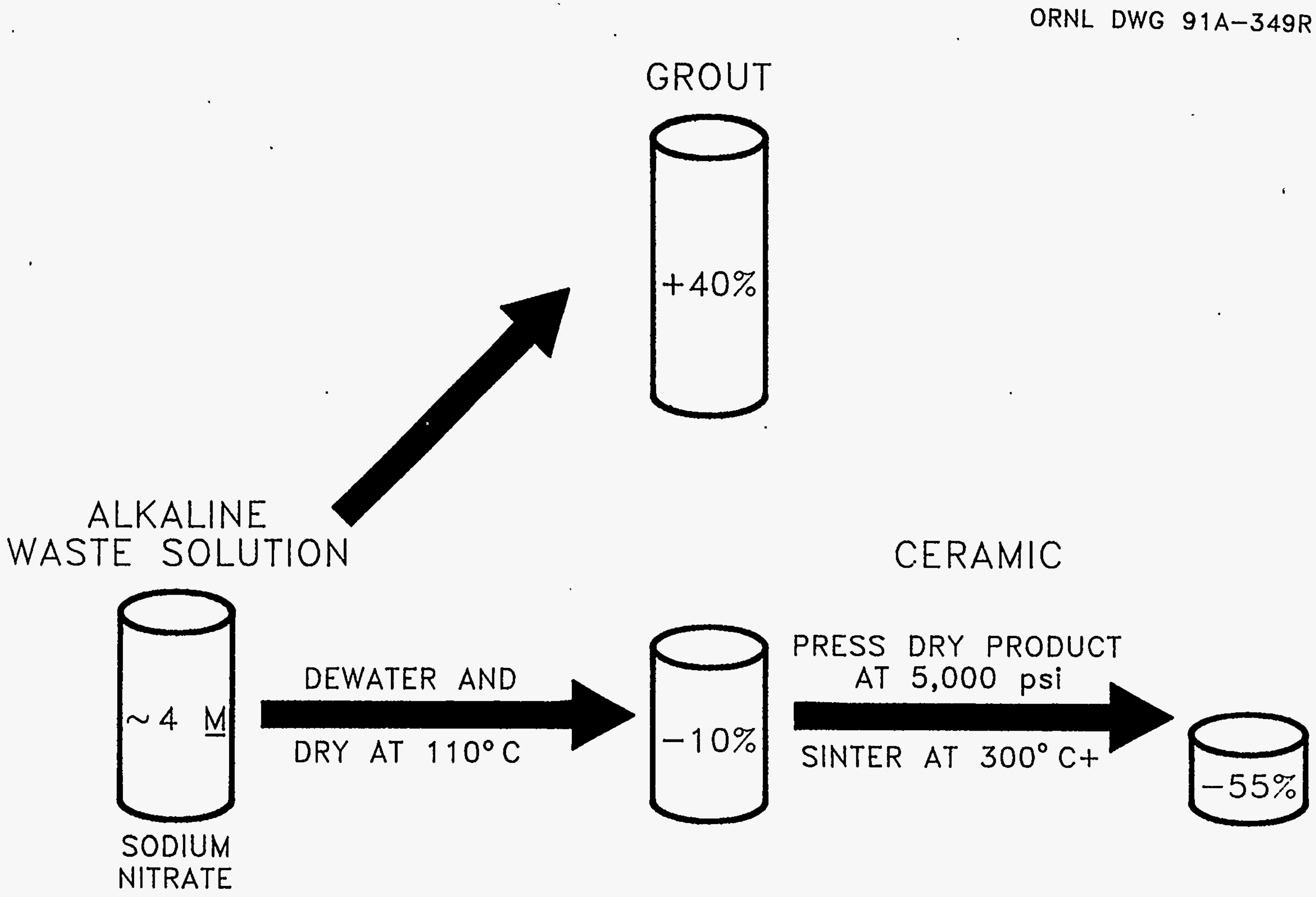

Fig. 3. Relative volume reduction efficiencies of the NAC process compared with grout.

2.1.6 The Fate of Other Waste Solution Cations

This process has an added bonus aside from converting nitrate to ammonia; that is, it also precipitates most cations, metallic and nonmetallic, from solution forming "highly" insoluble aluminates. Since aluminate is an important intermediate species in our reaction, this anion is always present and forms what are referred to as "spinels" in the material science field. These spinels for mono- and divalent cations are represented as $R_2O \cdot 11Al_2O_3$ and $RO \cdot 6Al_2O_3$, respectively. In fact, the spinel calcium aluminate is the active ingredient in portland cement ($\sim$10%) and is quite insoluble, as we know. As a result, we would expect that the sister alkaline earth species, strontium, will form a spinel with similar properties to calcium. The higher the positive charge to ion radius ratio of the cation, the more insoluble is the resulting spinel.[5,10] This fortuitous chemical property of aluminum means that most metal and nonmetal cations will enter the dense, solid ceramic matrix as a very insoluble mineral. Additionally, some chemical species in the waste solution may be adsorbed onto the large specific surface area of the reactor product; this may also include some organics. This study investigates the fate of just a few of these waste species of concern at Hanford; next year the investigation will be expanded.

2.1.7 Ammonia Disposal

It is obvious that we produce large amounts of ammonia upon reducing nitrate. Nitrate passes through nitrite on its way to ammonia, so any nitrite that may be present would also produce ammonia. In our laboratory tests, we scrub the ammonia into dilute hydrochloric acid; but in our planned pilot plant, we will scrub it into dilute sulfuric acid to form the sulfate salt. This scrubbing option is only one of several that can be utilized for ammonia disposal. The following are a few possibilities which are "off-the-shelf" technologies:

1. The ammonia can be scrubbed into dilute acid to form ammonium salts.
2. The gas can be cooled and pressurized into liquid ammonia for reuse.
3. The ammonia can be burned in a heated, catalytic bed tower to nitrogen and water vapor.[11] This is likely the preferred disposal scenario.
4. The ammonia can be reoxidized to form nitric acid for reuse on-site.

2.1.8 Drying or Sintering Reactor Products

The discharged gibbsite product from the reactor is very amenable to microwave drying and sintering since it is primarily alumina. If dewatered, dried, and compacted uniaxially in a container prior to sintering, a hard ceramic may be produced using microwaves in the 28-GHz range. Microwave use lowers the temperature necessary to sinter alumina by 300 to 400°C compared with conventional heating modes.[12] The activation energy associated with sintering with microwave energy is 170 J/mol, while with thermal systems, it is 570 J/mol alumina.

What is also fortuitous about the use of microwave processing is that alumina is well suited to microwave use since it is transparent to microwaves. It has a large "skin depth," up to from 3 to 6 m compared to only a few centimeters into a sodium nitrate-based solution. This means uniform heating and potential to sinter at much lower temperatures[12] than conventional convective heating systems.

3. PERCEIVED ADVANTAGES OF THE NAC PROCESS OVER OTHERS

Because nitrate is such a very mobile anion, it is difficult to immobilize it in materials such as, for example, polyethylene and bitumen, which are subject to osmotic pressure swelling over time and can burn on their own, once ignited with difficulty, since nitrate carries its own oxygen. Additionally, no cement-based formulation is known that can prevent the fairly rapid diffusion of nitrate or nitrite out into the environment when a leach solution is present.

Because of the ease with which nitrate is leached from grout, we place the grout inside concrete vaults to slow release. The pore water inside the vault walls will eventually equilibrate with the nitrate ions in the grout pore water, and then the release to the environment begins. In this case, the vault is another barrier which will also eventually release nitrate as well, but only to a smaller degree. This vault itself is also subject to degradation by the elements and the forces of nature.

In the case of cement-based grout, we pay a large price for the volume increase that results when we place an aqueous waste in such a matrix. We can expect from 35 to 50% increase in the overall volume upon grouting, depending upon the formulation and waste loading.

Instead of immobilizing nitrate in a porous, solid matrix such as grout, the option of converting it to another form such as a gas exists, thereby obviating the problem of nitrate release. However, such processes may be hindered by problems associated with off-gas processing (e.g., NO_x scrubbing). Four possible options are (1) thermal conversion to NO_x, (2) electroreduction to N_2 and NH_3, (3) biodenitrification to N_2, and (4) organic reduction to NO_x at low pH.

3.1 THERMAL CONVERSION

Although the reported values for the initial temperature of thermal decomposition of sodium nitrate vary widely, depending upon the reference source, decomposition starts at about 588°C and is 70% complete at about 940°C. This conversion to NO_x and sodium oxide can only occur after all water has been evaporated, a very energy intensive process step. Different types of such decomposition are reported throughout the literature.[13-16]

A problem for such technology is that the scrubbing of NO_x is still partly science and partly art. The lower oxides of nitrogen such as NO(g), which have a low aqueous solubility, are often not removed and need to be reoxidized and rescrubbed in many stages, only to produce another nitrate/nitrite-contaminated waste stream, possibly containing radioelements. Additionally, radioelements that become volatile in the temperature range between 588 and 1200°C must be scrubbed out, thereby producing yet another separate waste stream.

In addition to problems with NO_x and radioelement scrubbing, organics present in the nitrate-based waste may initiate an explosion depending upon concentration and other catalyzing metals or species which may be present in the waste.

3.2 ELECTROREDUCTION

A number of different electrolytic cell configurations exist, and, depending upon the cell, can produce a mixture of gases such as NH_3, N_2, O_2, and H_2.[4,17-19] Such cells are subject to a number of problems:

1. Such cells produce 40 kg of sodium hydroxide for every 85 kg of sodium nitrate processed. The NAC process produces aluminum oxide and sodium aluminate instead and brings with it the benefits associated with these components as discussed above.

2. In-cell crystallization of salts, due to evaporating liquid, fouls electrodes and lowers current efficiency. Criticality issues may become a concern with Hanford wastes.

3. Trace amounts of chromium (<36 ppm) can drop cell efficiency (%) from the high nineties down to the thirties due to cyclic oxidation and reduction of chromium in such cells; the result is that decomposition times may quadruple. The NAC process is unaffected by chromium since this species can form a highly insoluble aluminate, as discussed in the literature.

4. Many metals and some radioelements plate out on electrode surfaces and lower cell efficiency.

5. The electrolytic process does not bring with it the potential for producing its own waste form as does the NAC process, and the associated chemistry which makes alumina such a good host matrix.

3.3 BIODENITRIFICATION

The biodenitrification process produces nitrogen and calcium carbonate when run anaerobically,[20-24] which happens to be the most efficient mode. The bacteria must be fed a carbon source, such as calcium acetate, which is oxidized to carbon dioxide while reducing nitrate. Also, a phosphate-containing salt for intercellular energy transfer and storage must be added. This produces large volumes of calcium carbonate which must be disposed of.

The biggest problem with the use of bacteria is that they must operate in the proper pH range (7 to 8.5) and therefore will require pH adjustments downward for Hanford waste. Additionally, certain concentrations of various metals can be toxic to bacteria cultures. Also, if the total salt concentration is too high, the bacteria will die due to osmotic pressure imbalance; thus, initial dilution of the Hanford waste may also be required.

3.4 ORGANIC REDUCTION

This technology is very old and was developed in Europe by the Germans.[22,25,26] In this process, the nitrate-containing solution "must" be acidic before it can be utilized; therefore, vast amounts of acid would likely have to be added to the Hanford waste, depending upon waste buffering capacity. In this process, acidic, nitrate-based solutions are heated, and an organic compound such as sucrose, formaldehyde, or formic acid is slowly added to produce NO_x and carbon dioxide as well as a lot of heat.

The process is difficult to control and is sometimes explosive. In addition, upon adding an acid of choice to lower the pH of the Hanford solution, there will be problems associated with any acid chosen. Corrosion problems will follow the use of hydrochloric acid. Sulfuric acid will produce large amounts of the high-volume hydrated calcium sulfate (gypsum). Nitric acid may be the only remaining choice, adding more nitrate to be removed later. Since nitric acid, like hydrochloric acid, only provides one proton, vast amounts of acid (and nitrate) would become necessary if these acids were utilized.

4. EXPERIMENTAL APPARATUS

4.1 BATCH REACTOR

The reactor system chosen for the initial tests of the active metal denitration system was a stirred-tank-type batch reactor. A diagram of the vessel and associated instrumentation is shown in Fig. 4. The reactor is a 700-mL total volume, 350-mL maximum working volume, glass vessel made by New Brunswick (Bio-flo model C-30) as a fermentation reactor (Fig. 5); a photograph of the reactor is shown in Fig. 6. It contains a four-bladed, magnetically driven stainless steel turbine agitator, four stainless steel baffles, an electrical heating rod with temperature controller, and various other lid openings for other equipment. For these tests, a cooling coil was constructed of 1.52-m long, 3.2-mm-OD stainless steel tubing and inserted into the reaction area of the vessel. Cooling was provided by a Lauda K-4/R refrigerated circulating bath of 1600-W cooling capacity. For pH monitoring, an Orion semimicro Ross glass combination electrode was placed into the vessel during the reaction. An Orion model 920A pH meter was used as the indicator and connected to a Linear recorder for a record of the pH during the reaction. A 3.2-mm stainless steel, Type K thermocouple was connected to an Omega monitor and Linear recorder to monitor the reaction temperature.

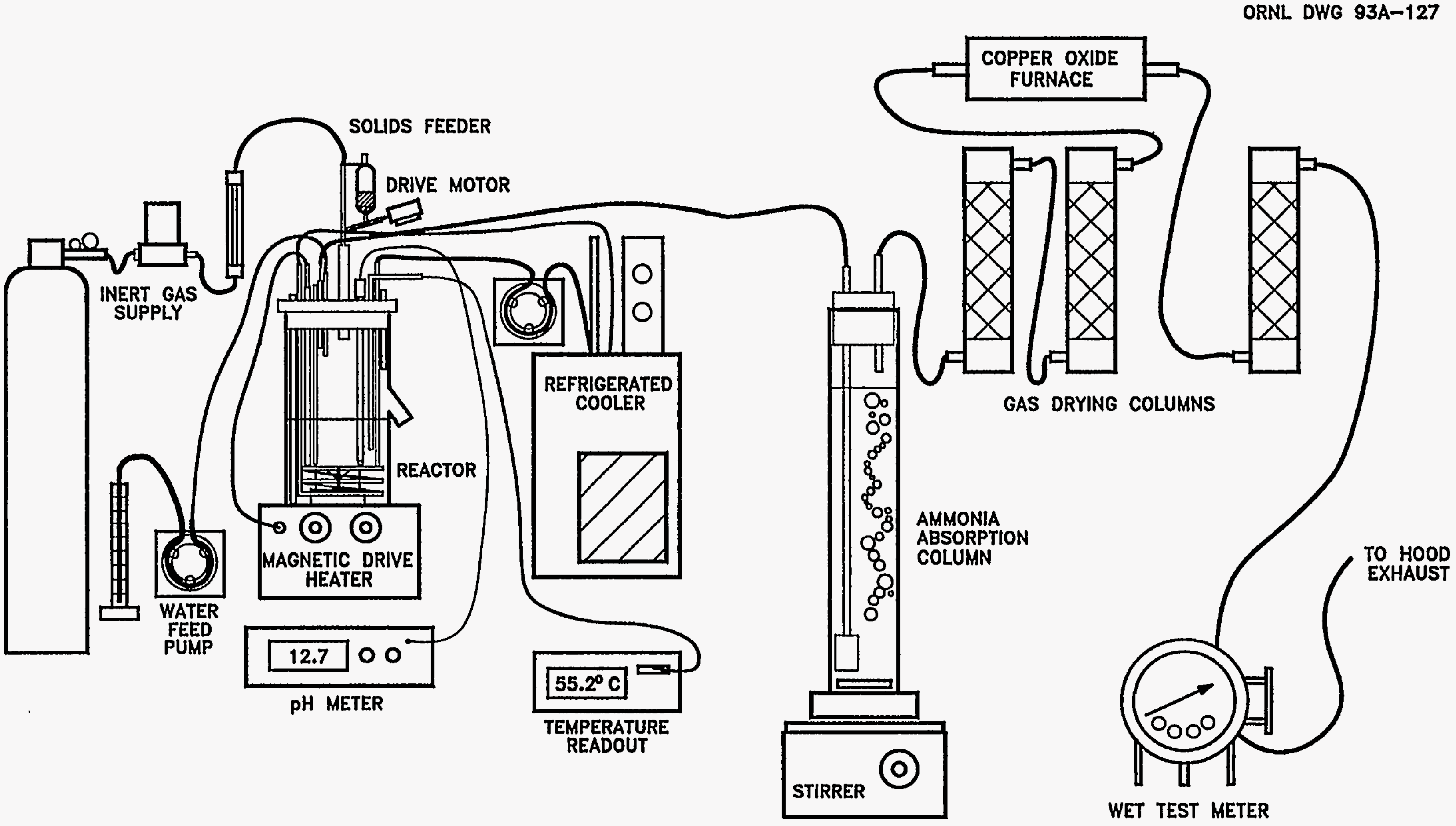

Fig. 4. Experimental nitrate conversion apparatus.

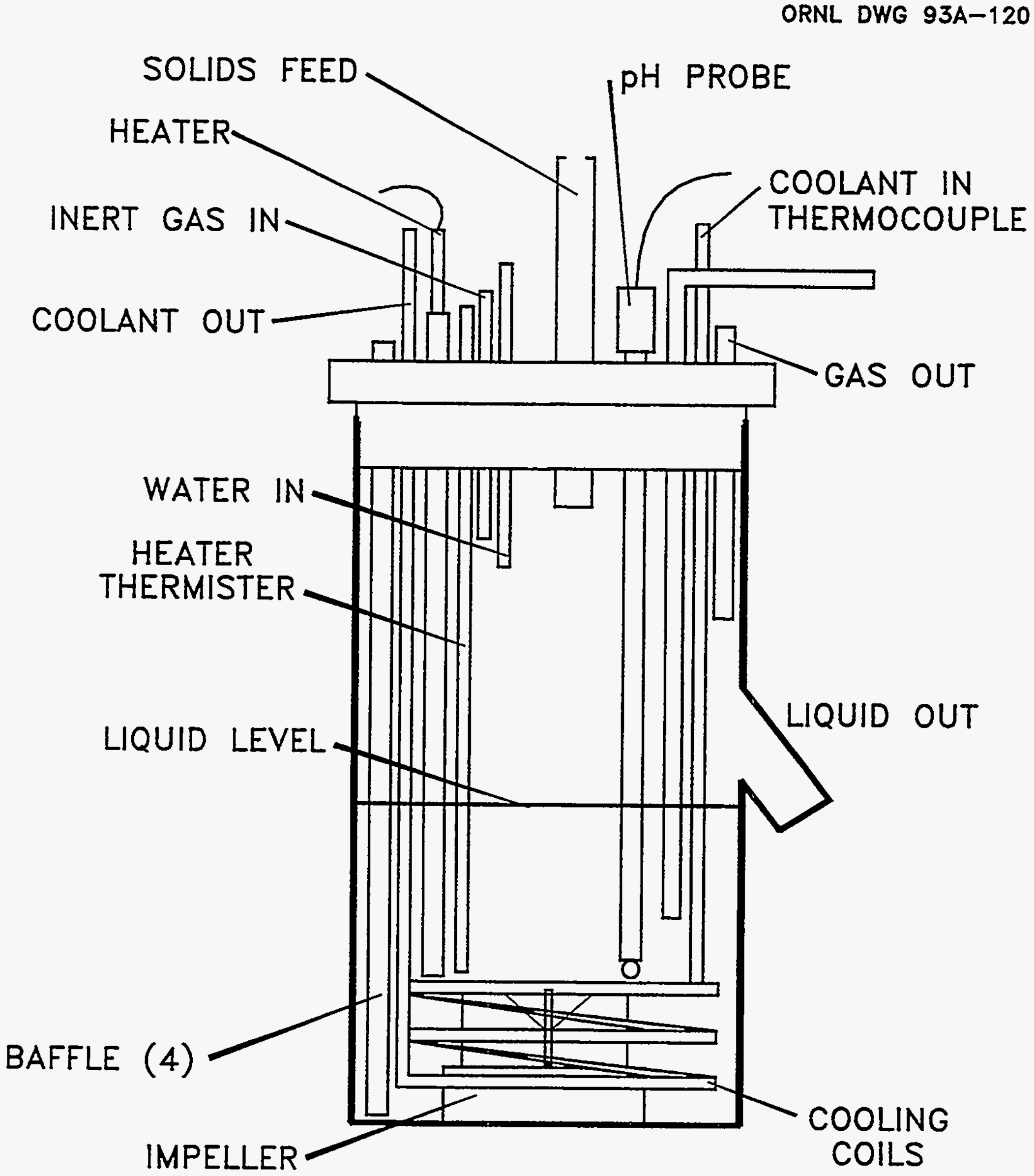

Fig. 5. Experimental reactor.

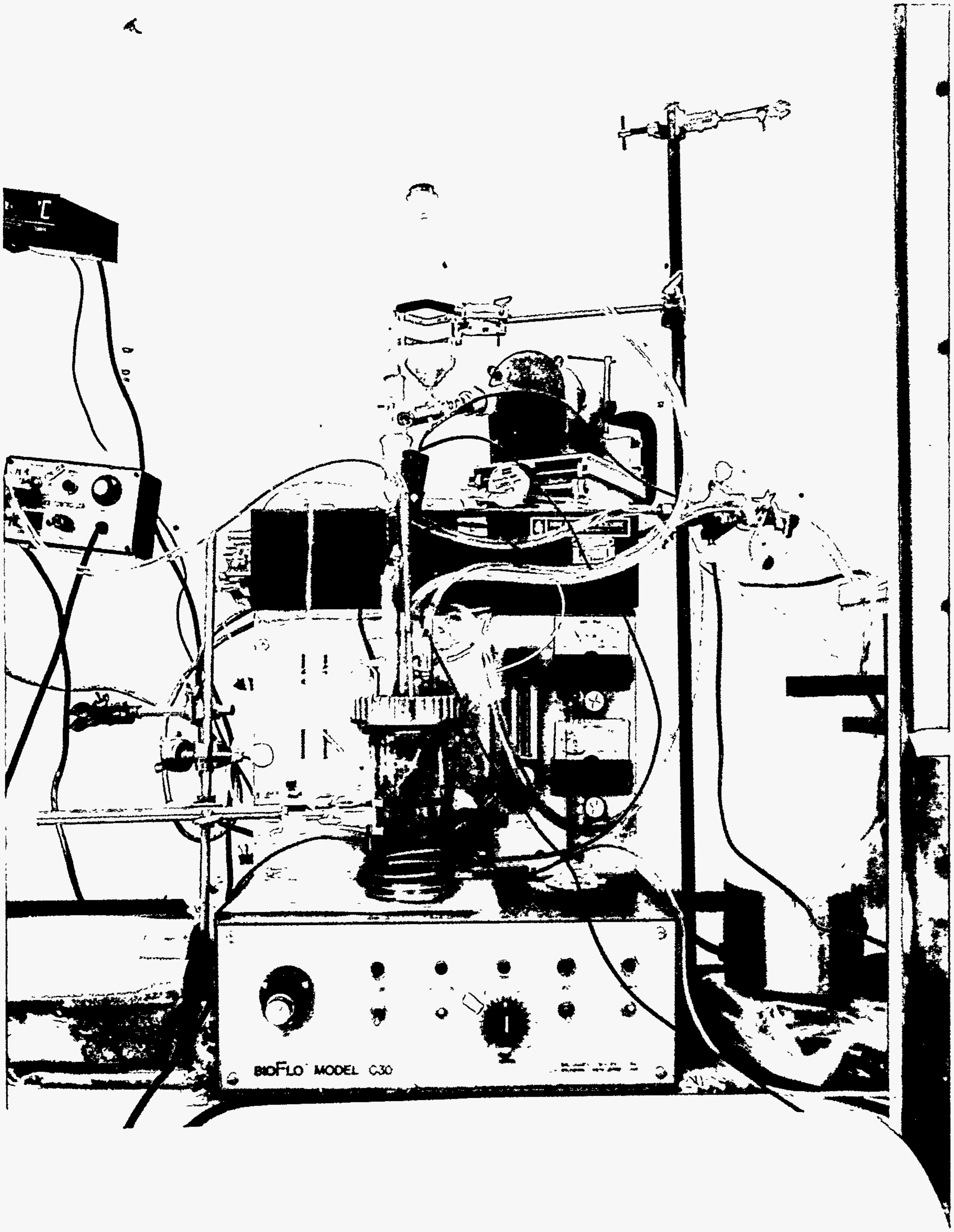

Fig. 6. Photograph of experimental apparatus.

4.2 NITRATE FEED AND REACTANTS

The feed solutions for the first six batch reactor experiments consisted of solutions of sodium nitrate in water with the pH adjusted to 10 to 13 with sodium hydroxide. Solutions of 6.2 and 3.1 *M* $NaNO_3$ were chosen for use in the initial batch reactor tests to permit nitrate material balances to be obtained across the reactor. Sodium nitrate is the largest component of the Hanford SST salt cake waste, as shown in Table 1. Sodium nitrite contributes almost 5%, but nitrite is on the pathway for the nitrate reduction and was not included in the initial formula for simplicity. The composition is based on the mean concentrations of the SST sludge components analyzed from the core samples of 18 SSTs at Hanford.[27] The composite synthetic salt cake recipe was developed from the tank analysis data. Because the processing necessary to remove the salt cake/sludge from the tanks will probably generate a supernate containing primarily the sodium nitrate, it was chosen as the baseline feed. Since the ORNL MVSTs also contain supernate with an average sodium nitrate concentration of 4.4 *M,* which constitutes ~95% of the soluble salts in the tanks,[28] this supernate will make a good surrogate material to demonstrate the NAC process on an actual waste containing radioactive and other components.

Table 1. Composition of synthetic SST salt cake

Component	Dry weight (%)
$NaNO_3$	75.2
$NaNO_2$	4.8
Na_2SO_4	2.4
Na_2CO_3	4.3
$NaAlO_2$	4.3
Na_3PO_4	4.6
NaOH	4.4
Total	100.0

The aluminum was fed to the reactor as small pellets or powders with an Ace Glass model B7234 powder dispensing funnel driven by a Cole-Parmer Servodyne power drive system. The powder dispensing funnel could dispense powders from 25 mesh (0.7 mm) to 270 mesh (0.002 mm). Particles smaller than 270 mesh tended to plug and not feed. Midrange-size (60 to 130 mesh) particles fed very uniformly and predictably. In order to keep the finest feedable powders from caking in the small diameter feed due to moisture from the reactor, dry nitrogen was fed through the powder feed tube and through the reactor. Small-scale tests showed that small powders could also be fed using a slurry of the aluminum powder in neutral pH water. Nitrogen also carried the gaseous reaction products through the gas separation and analysis sections of the apparatus. In the first run, the solids feed tube entered at the side of the reactor top. Because of aluminum buildup on the vessel internals, the inlet was moved to the center of the reactor above the agitator for subsequent runs.

The aluminum was purchased in various sizes and purities ranging from 6.4-mm pellets to 5-μm particles and 98 to 99.9% purity from Cerac, AESAR Johnson Matthey, and Aldrich Chemical Company. The aluminum was in either a nonoxidized (packed under nitrogen or argon) or oxidized state. The aluminum was sieved into narrow size ranges for each run, and a range such as −25+30 mesh or −200+230 mesh was used for a particular run. In addition to the aluminum, water could also be fed to the reactor to make up for the water used in the reaction and to help slurry the product solids as they built up during the reaction. Additional inert gas (saturated with water vapor or dry) could also be fed through the reactor to sweep out any product gas to the downstream analysis system. The nitrate feed was prepared as a 6.2 *M* solution from sodium nitrate and deionized water. It was used at that concentration (Run DN-1 and DN-2) or diluted to 3.1 *M* (DN-3—DN-6) for each run. The starting pH was adjusted to the desired level (pH 10 to 13) with concentrated sodium hydroxide.

When radioactive tracers were used, ^{85}Sr, ^{137}Cs, and ^{144}Ce (with ^{60}Co contamination) were added for gamma spectroscopy. The ^{137}Cs and ^{144}Ce were available from sources at ORNL, and the ^{85}Sr was purchased from New England Nuclear. The samples were counted using an intrinsic germanium detector (Princeton Gammatech) and an Accuspec multichannel analyzer computer data acquisition board (Canberra) in an IBM-XT computer with AccuSpec ASAP Radionuclide Analysis Software (Canberra) for data analysis. The counting system was calibrated using an efficiency standard from Amersham provided by W. Arnold of ORNL. Technetium-99 was obtained at ORNL and was counted on a β-scintillation counting system.

4.3 HANFORD SLUDGE SURROGATE

A feed material was also prepared for run DN-7 using the Hanford surrogate formula for combined salt cake and sludge[27] to prove that nitrate could be reduced in the presence of the other species and solids. The formula for the synthetic salt cake was shown in Table 1. The composition of the synthetic sludge is shown in Table 2, while the procedure for preparing the sludge is shown is Table 3. The proportions called for by the Hanford recipe include 55% sludge and 45% salt cake by weight of dry material. Run

Table 2. Composition of synthetic sludge

Component	Dry weight (%)
Al_2O_3, $Al(OH)_3$	38
$BiPO_4$	10
FeOOH, Fe_2O_3, $FePO_4$	15
SiO_2	17
Organic Salts	2
Na_2SO_4	2
Ce_2O_3 (for U)	2
CaO	1
Cr_2O_3	1
Na_2O, NaOH	1
La_2O_3	1
Oxides, Hydroxides, Phosphates (<1% each of Pb, Mg, Ag, Zn, Mn, Zr, Sr) and waters of hydration	10
Total	100

Table 3. Procedure for synthetic sludge

Container A — 4-L beaker

To 600 mL H_2O add:
143.35 g $Al(NO_3)_3 \cdot 9H_2O$

Stir 1 h

While stirring add:
2.31 g $Ca(NO_3)_2 \cdot 4H_2O$
0.30 g $Pb(NO_3)_2$
0.80 g $MgNO_3 \cdot 6H_2O$
0.04 g $AgNO_3$
0.14 g $Zn(NO_3)_2 \cdot 6H_2O$
0.09 g $Zr(O)(NO_3)_2 \cdot 2H_2O$
0.36 g $Ce(NO_3)_3 \cdot 6H_2O$
14.73 g $Fe(NO_3)_3 \cdot 9H_2O$
0.95 g $Cr(NO_3)_3 \cdot 9H_2O$

Stir 1 h

Adjust pH to 9.5 with 25% NaOH

Container B — 100-mL beaker

To 100 mL H_2O: Dissolve 0.21 g $KMnO_4$; add 0.20 g $Mn(NO_3)_2$ dissolved in 2 mL H_2O

Add well-stirred **Container B** to **Container A**

Stir 1 h, adjust to pH 9.5

Container C — 1-L beaker

To 400 mL H_2O add:
13.6 g $Fe(NO_3)_3 \cdot 9H_2O$
1.48 g $Cr(NO_3)_3 \cdot 9H_2O$
0.98 g $La(NO_3)_3 \cdot 6H_2O$

Stir 1 h

Dissolve 0.21 g $Nm(NO_3)_2$ in 2-mL H_2O.
Add to above solution while stirring.
Mix 10 min

While stirring add 3.45 g 85% H_3PO_4.
Stir until dissolved

Add 7.82 g $Bi(NO_3)_3 \cdot 5H_2O$
(ppt will form); mix 10 min

While stirring add:
10.09 g $Na_3PO_4 \cdot 12H_2O$
2.07 g $Ce(NO_3)_3 \cdot 6H_2O$
0.49 g $Zr(O)(NO_3)_2 \cdot 2H_2O$

Stir 1 h
Adjust pH to 10 with 25% NaOH while stirring vigorously

While stirring add:
0.38 g $Ni(NO_3)_2 \cdot 6H_2O$
0.09 g $Sr(NO_3)_2$

Stir 1 h; adjust to pH 10.0

Add Container C to Container A

Wash: Add pH 10 H_2O to the 3.5-L mark; mix
Let sit overnight; pump off clear liquid
Repeat wash 2 more times

Add: 0.17 g NaF
1.42 g K_2SO_4
27.99 g 30 SiO_2 solution
0.62 g EDTA (MW = 372.2 g/mol)
0.53 g citric acid

Mix; Dry at 110°C; Pulverize — Yield = ~62 g

DN-7 included ^{85}Sr and ^{137}Cs as tracers. The surrogate sludge-salt cake made such a thick slurry with many large chunks of sludge at ~3 *M* nitrate concentration that it could not be stirred, and some of the solids had to be removed (~50%) before the agitator would turn and the run could begin.

4.4 PRODUCT ANALYSIS SYSTEMS

4.4.1 Gas Analyses

The reactor off-gas was purged from the reactor using inert gas flow of nitrogen or argon. The inert gas flow was controlled at a known flow rate using a Tylan general mass flow monitor/controller. From the reactor, the gas passed into the bottom of a 2000-mL graduated cylinder, modified with a sparge tube extending into the bottom of the cylinder. The graduate was agitated by a magnetic stirrer. Two additional ports were added above the liquid level to enable sparger liquid sampling and the addition of a pH probe into the sparger liquid. The sparger contained ~2 L of dilute (~0.1 *M* HCl) acid to react with any ammonia produced in the reaction and carried off with the purge gas stream. The ammonia dissolved in the HCl, neutralizing the acid. The sparger was sampled periodically during the reaction, and the acid remaining at any time was titrated to pH 7.00 with standard base to determine the quantity of ammonia that had been produced in the reaction. The remaining gas then was sent through two Drierite® columns in series to remove water vapor before the conversion reaction to measure hydrogen production. The gas passed through a tube furnace containing CuO at ~400°C to convert any hydrogen produced in the reaction to H_2O. The loss of weight of the furnace tube could then be correlated to the hydrogen produced during the reaction. The water produced in the CuO reactor was then absorbed on a Drierite column and the weight gain measured. Finally, the remaining gas exited the system through a wet test meter.

In an attempt to determine when the hydrogen was produced during the reaction, the water from the CuO reactor was condensed before the Drierite column and dripped into dilute phosphoric acid. The conductivity change of the acid could be correlated with the amount of water added. The signal from the YSI model 32 conductivity meter was then recorded so that the decrease in conductivity could be correlated with the reaction. Unfortunately, the sensitivity of the conductivity to temperature was such that the small conductivity changes due to water addition were masked by the larger fluctuations due to small (<1°C) temperature changes in the conductivity cell. Therefore, hydrogen/combustible gas detectors were obtained for the qualitative determination of when hydrogen was produced.

4.4.2 Liquid Analyses

The liquid products of the reaction were obtained by filtering the product slurry on Whatman No. 2 filter paper in a Buchner funnel. The clear liquid was analyzed for nitrate (Method 418 A. Ultraviolet Spectrophotometric Screening Method);[29] when radioactive materials were used as tracers, it was also counted to determine the activity present. Some samples were also neutralized with hydrochloric acid to determine the content of soluble aluminate present at the end of the reaction.

4.4.3 Solids Analyses

The solid products were characterized after removal from the reactor in several steps. First, the slurry was filtered on the No. 2 filter, and the resultant wet filter cake weighed. It was allowed to air dry and reweighed. A portion of the solids was dried at 105 to 110°C to constant weight (4 to 6 h) and the weight recorded. A second portion was heated to 300 to 305°C to constant weight (4 to 6 h) and the weight recorded. Samples of the solids from each of the three drying procedures were then washed with three separate portions of DI water. The solids were broken up into a powder using a mortar and pestle, put into bottles, then agitated for a set period of time, allowed to settle, and the supernate decanted. The three wash supernates were analyzed for nitrate. In the runs using the radioactive tracers, the washes were analyzed for the radioactivity present in the wash solution. In the tracer runs, samples of the solids were counted before and after the washing steps.

Additional tests on the solids included loose-packed and compressed density measurements. The loose-packed density was measured by tapping a known mass of powder into a graduated cylinder to measure the volume. The compressed density was achieved by compressing product powder using a small, 6.4-mm (¼-in.)-diameter Parr pellet press with a 2000-lb total force capacity on the die punch. Pellets were formed using stearic acid (~5 wt %) as a lubricant and binder mixed with the product powder in mortar and pestle. The pellets were weighed, and the volume of water displaced by the pellet was measured from which the density was calculated. These measurements were made for runs DN-1—DN-5. Two samples of the filtered ambient dried solids were also analyzed by thermogravimetric analysis and differential scanning calorimetry from room temperature to 800°C to further characterize the products.

4.5 OTHER REACTOR CONFIGURATIONS

Several small batch reactions were carried out in open or closed Pyrex beakers ranging in volume from 25 to 1500 mL and stirred using a magnetic stirrer and stir bar. They were heated with laboratory hot plates and cooled by addition of cold water to the pan of water they sat in on the hot plate. In these tests, aluminum was added as a nonoxidized powder, water slurry, oxidized powder, or pellets to determine qualitative reaction rates and the feasibility of feed configurations and to develop reaction control procedures. Technetium distribution between the liquid nitrate solution and the aluminum hydroxide product was also tested in one of the beaker reactors so that only a minimum of equipment would be contaminated.

The tests of oxidized and nonoxidized aluminum powder involved using 3.1 *M* $NaNO_3$ at a starting pH of 13.0. The oxidized aluminum powder was apportioned in small bottles and added in increments while following the reactor temperature and reaction pH. For the nonoxidized run, conditions were the same except that the aluminum was placed into the glass vials under argon and double bagged in an inert gas glove bag. The aluminum was added to the reactor under a blanket of nitrogen gas and the reaction pH and temperature noted. The nitrate and nitrite remaining at the end of the reaction was measured using EM® Quant® ion-specific nitrate and nitrite test strips. A combustible gas detector was used to monitor the reaction off-gas for ammonia and hydrogen. In some of these beaker tests, the beaker was closed and inert gas purged through it into a hydrochloric acid trap to collect the ammonia produced. The gas leaving the trap was then checked with the combustible gas detector for the presence of hydrogen.

A packed-bed-type reactor was also tested. It consisted of a tube filled with 10 g of large aluminum pellets, a stirred liquid reservoir containing the sodium nitrate solution, a gas distribution and collection system, and a liquid circulation pump (Fig. 7). The reaction

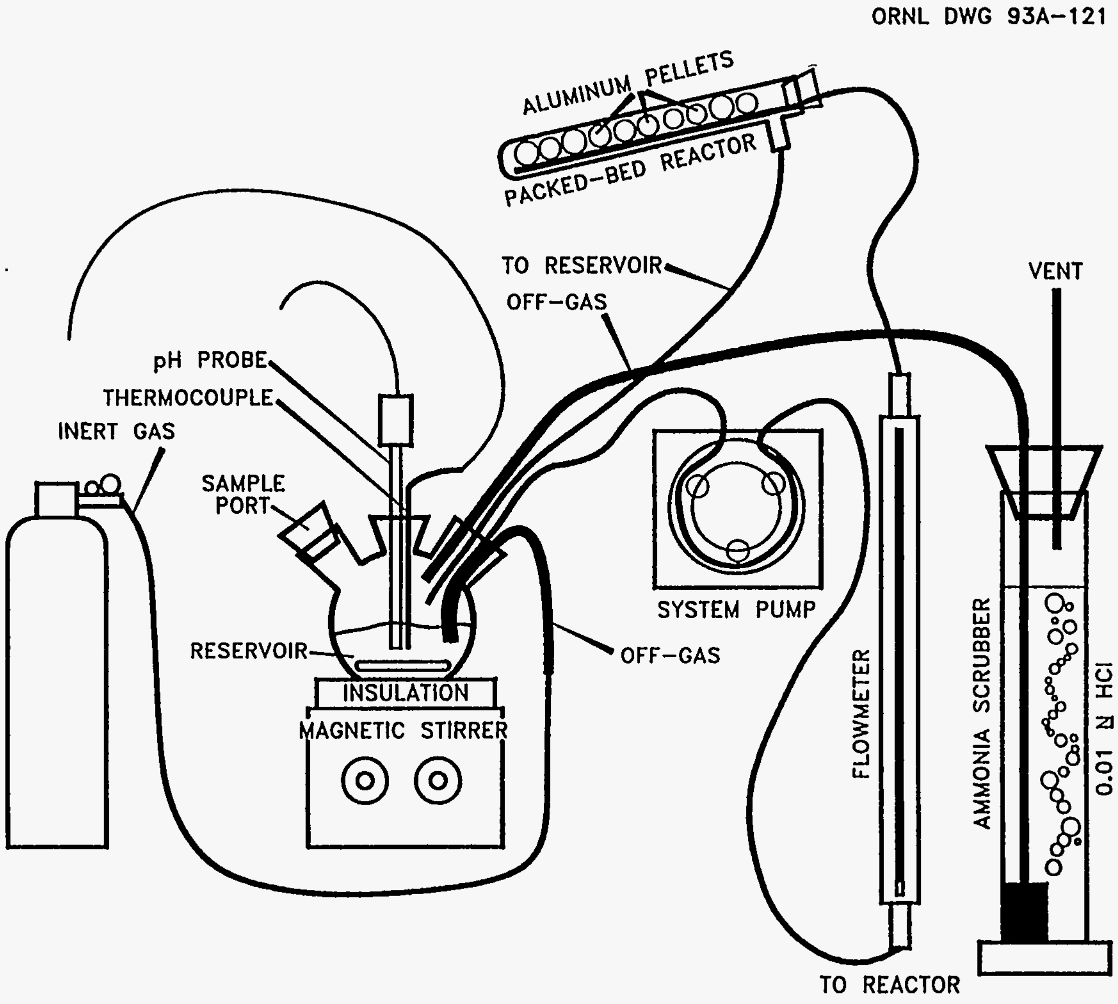

Fig. 7. Packed-bed reactor.

was followed by taking periodic samples from the reservoir and from the ammonia absorption trap in the gas system as described earlier. The temperature and pH of the reservoir were also monitored. The ammonia produced, the nitrate destroyed, and the aluminum reacted were then determined, and reaction rates were calculated based on the mass of aluminum lost from the pellets or the total pellet surface area and the volume of liquid in circulation.

5. RESULTS AND DISCUSSIONS

5.1 BATCH REACTIONS WITH $NaNO_3$ AT 6.2 *M*

5.1.1 Initial pH of 10.5

The initial batch reaction was carried out with starting materials of 6.2 *M* $NaNO_3$ at pH 10.5 and a reactor temperature of 50°C. The aluminum was in the form of 200 to 230 mesh particles with an oxide surface coat. In this test, the aluminum was added very slowly to prevent any occurrence of the exothermic reaction of NO_3^- and aluminum heating the solution to the boiling point and causing a steam pressurization of the reactor. The $NaNO_3$ solution was placed in the reactor at pH 10.5 and heated to 50°C with the reactor internal heater. At this time, 2 g of Al powder was added with the feeder. The pH of the solution dropped to ~8.5 over a 15—20 min period and then gradually increased to 10.2—10.5 over a 4-h period. Since no appreciable reaction had taken place, the experiment was stopped for the 2-d weekend by cooling to ~9°C and shutting off heat, stirring, and sweep gas. The aluminum that had been added was still present in suspension, and the ammonia trap showed that no ammonia had been produced.

The reaction was restarted on Monday by turning all systems back on, heating the reactor to 50°C, and adding an additional 2 g of Al powder. At this point, immediate heating took place and the reactor cooling was required to hold the temperature <60°C. Reactor pH dropped 0.3 units almost immediately after the Al addition and then gradually increased to a higher level than the starting pH. The aluminum was added in 2-g increments until ~90 g were added. This was approximately the theoretical amount of aluminum required to convert all of the nitrate to ammonia gas assuming 8:3 mole ratio of Al to NO_3, as shown in Eq. (8). Some of the aluminum added caught on the inlet tube walls, reactor walls, and vessel internals and was present as agglomerates when the reactor was shut down and cleaned. Some aluminum (~5 to 10 g) was lost when the feeder required repair during the run. As the reaction progressed, the solids produced in the reaction became thicker and stirring became more difficult; feeding aluminum powder was very difficult because the slurry was so thick that mixing of Al powder and slurry was severely impeded. After the theoretical Al had been added, the reactor was allowed to continue stirring with inert gas flow for another day since the reaction was apparently continuing slowly. When shut down, the reactor temperature was still ~3°C above ambient, indicating an ongoing, slow, exothermic reaction.

Shown in Fig. 8 is a plot of the results of the experiment. The percent nitrate destroyed is based on the ammonia produced, the percent theoretical aluminum added, and the efficiency as (% NO_3/% theoretical Al). Approximately 80% of the nitrate was destroyed as measured by the ammonia produced, and that was associated with about an 80% efficiency of aluminum usage. Also note that nitrate did not begin to disappear until ~30% of the theoretical aluminum had been added. This was consistent for most of the runs.

A 1-mL sample of the 29 mL of filtrate from the run was titrated with 1 *N* HCl after a 1:10 dilution. The results are shown in Fig. 9. At the first break (pH ~12.4), a gel-like precipitate started to appear as the acid was added and then disappeared as it was mixed. When the pH reached ~11.2, the precipitate stayed and became more pronounced until the pH dropped below 3.0, where it again disappeared. Analysis of the filtrate for nitrate showed ~0.6 to 0.85 *M* nitrate remaining in the 29 mL. This is about 95% destruction of the nitrate that was initially present, assuming that the liquid with the solids also contained this concentration of nitrate. There is considerable discrepancy between the destruction values based on nitrate analysis and the values based on ammonia recovery. The density of the filtrate at 20°C measured in a 2-mL Thomas 8350 B16 pycnometer was 1.442 g/cm^3. The results of the solids analyses will be described later.

5.1.2 Initial pH of 13.0

A second run with 6.2 *M* $NaNO_3$ was completed with the feed initially adjusted to pH = 13.0. Again, 200 mL of feed was heated to 50°C, and 200 to 230 mesh aluminum powder was fed with the powder feeder. Gas evolution and heating began immediately,

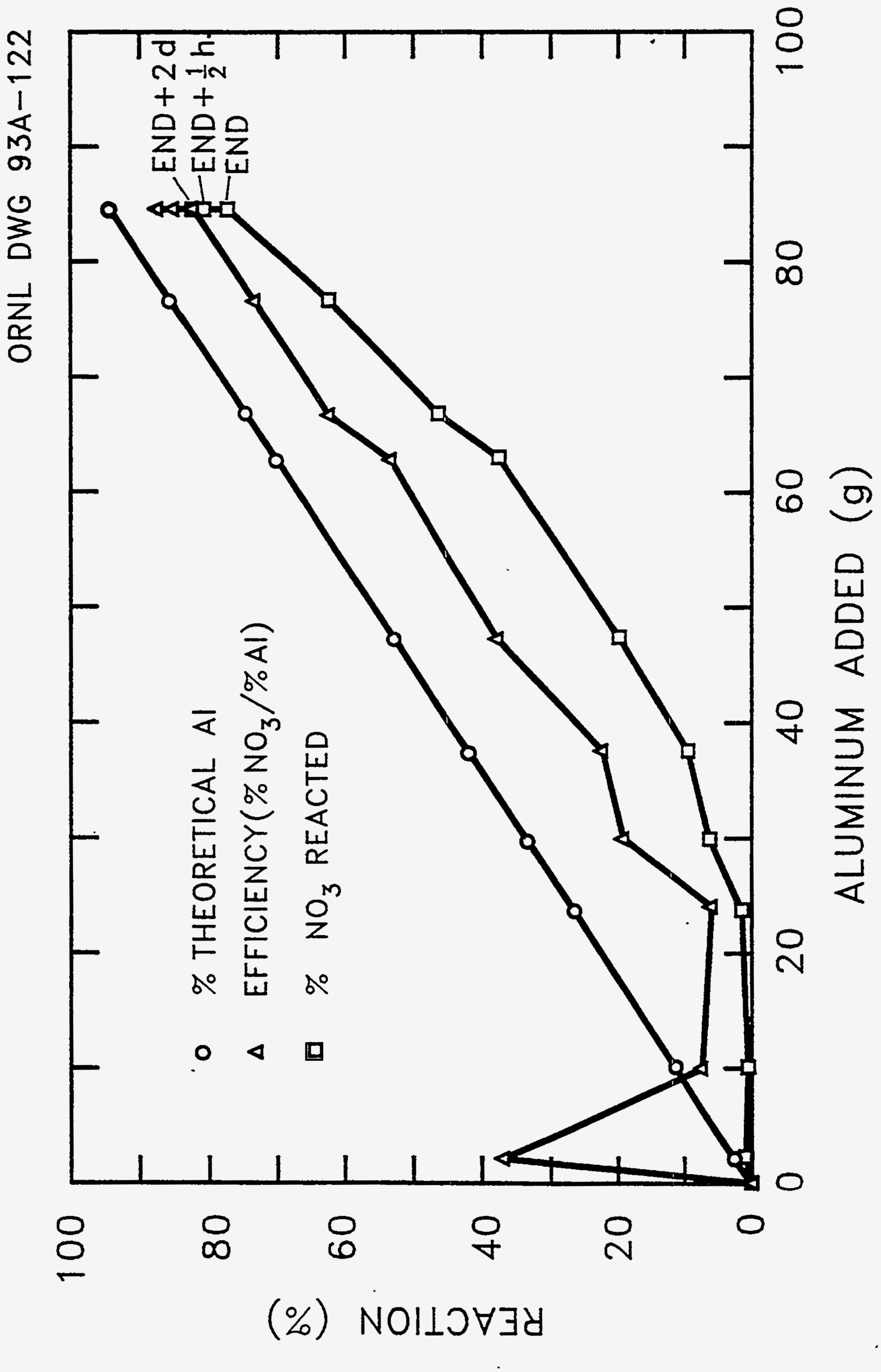

Fig. 8. Run 1 results.

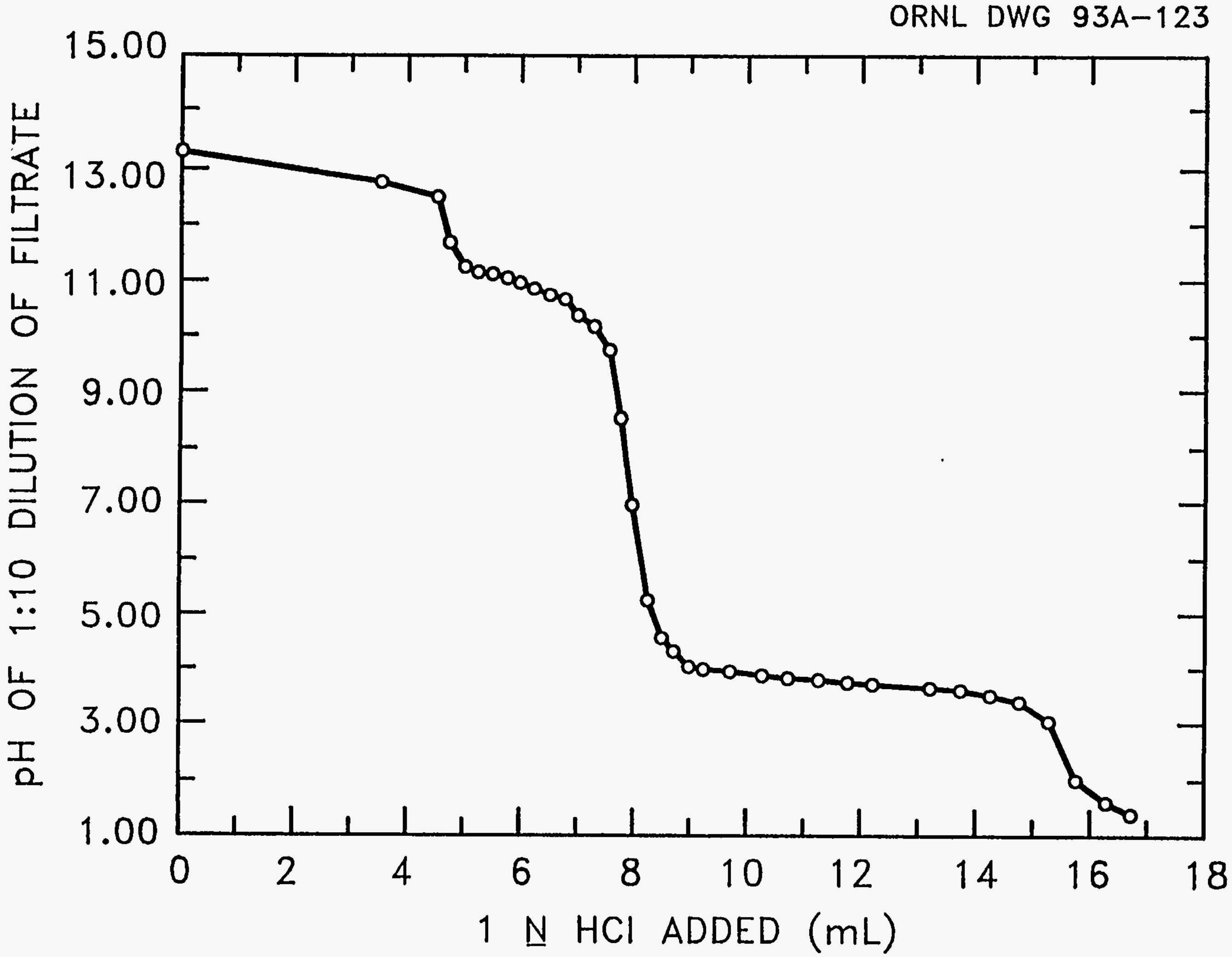

Fig. 9. Titration of Run 1 filtrate.

and the pH dropped from ~12.0 to ~10.5. As the pH dropped <11.0, the reaction slowed to a very slow rate. As the pH gradually increased past 11.0 to 11.5, the reaction began producing heat and gas again, and the reactor cooling had to be used. As long as the indicated pH remained above ~11.5, adding aluminum produced an immediate reaction with heating and gas evolution. A total of ~92 g Al was fed during 225 min for a feed rate of 0.41 g/min. The ammonia analyses indicated that ~83% of the original nitrate was destroyed using ~103% of the theoretical Al required. Nitrate analyses on the product filtrate (19 mL) showed 0.516 *M* NO_3, and the wash (500 mL) of the reactor showed 0.04 *M* NO_3. Figure 10 shows the reaction progress during run DN-2.

Near the end of the run (the last 20% of the aluminum addition), the slurry became so thick that agitation, feeding, and heat transfer were difficult. The gas produced had trouble exiting the slurry and caused froth to fill the reactor volume and cake up the aluminum feed tube by wetting the powder in the end of the tube. The thick slurry also prevented mixing of fresh aluminum as it was fed, and hot spots and more foaming resulted. The additional 75 mL of water added during the run was not sufficient to keep the slurry mixable, although after the run, the slurry did pour slowly but easily out of the reactor, with 95% removed by pouring.

In this run, the 322.92 g solids remained after filtration, which decreased to 267.14 g after drying at 105—110°C. A balance on the nitrate showed that of the initial nitrate present, 5% could be accounted for in the product slurry. The solids became more powdery as it dried, but some of it did become chunky and had to be broken up.

5.2 BATCH REACTIONS WITH $NaNO_3$ AT 3.1 *M*

5.2.1 Small (200—230 mesh) Aluminum Feed

The next run (DN-3) was started with 200 mL of 3.1 *M* $NaNO_3$ at a pH of 13.0 (at room temperature) using aluminum particles from the same batch as previous runs (200—230 mesh). The solution was heated to 50°C before aluminum was added with the powder feeder. The feed was started for 2 min (~3 g Al) and the reaction observed. The pH rapidly dropped from ~12.5 to 10.5, and the cooling requirement was negligible after the pH decreased. After ~¾ h, the pH had returned to 11.1. It then rapidly increased to 11.5, where the reaction was again exothermic and required cooling. After

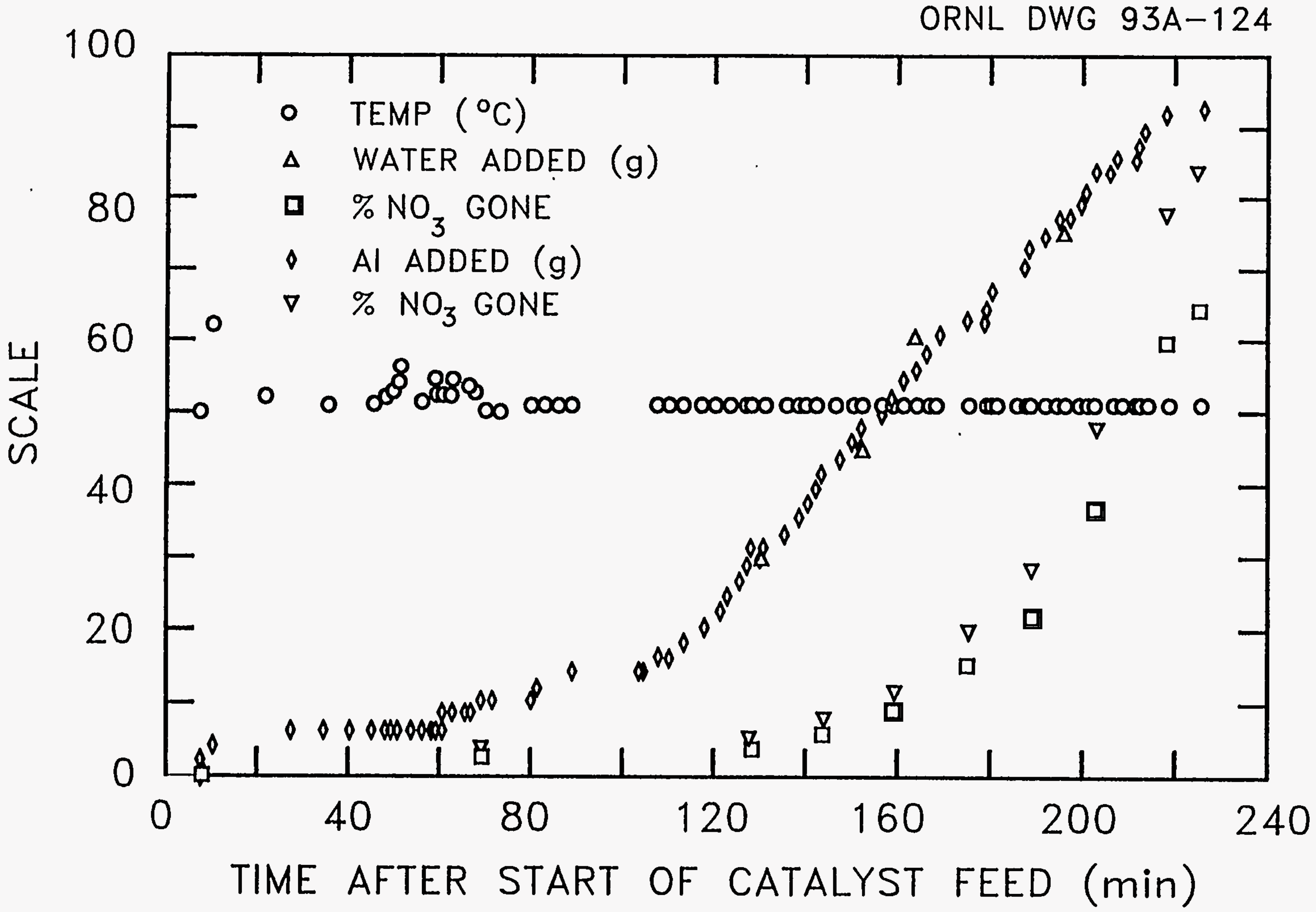

Fig. 10. Reaction progress in Run 2.

the reaction appeared to be over, aluminum feeding was begun at a rate of 1.4 g/min until the theoretical amount of Al (44 to 45 g) had been added in ~30 min. Cooling was used to control the temperature near 50°C. The reaction was allowed to slow down until cooling was not required, and samples were taken.

Following this, 35 g were added in 4 h to complete the scheduled test. The feeder was then run intermittently for 1 min at a time until 200% of the theoretical Al (~85 g in 350 min) had been added. Cooling was required at each Al addition. The slurry became thicker, and the agitator speed was increased to enable the Al powder to mix with the slurry. At the end of the run, the slurry was white, thick with a consistency like "chunky peanut butter," with chunks of Al powder agglomerates in it. The reaction progress is shown in Fig. 11. The reactor was allowed to cool and settle over the weekend after the pH probe had been removed. The slurry did not settle, and there was no free liquid over the solids after the weekend. The slurry clung to the vessel internals as the reactor was dissembled and were scraped off and the solids filtered on the No. 2 Whatman filter paper. The filtrate resulting was 18.8 mL, and 195.8 g of damp solids was produced. After washing the reactor and filtering the wash slurry, the total solids produced was 327.21 g. Drying at 105 to 110°C removed 68.76 g water.

The analysis of the ammonia trap showed that ~95% of the nitrate was converted to ammonia and trapped. UV analysis of the product liquid for nitrate showed that ~400 ppm ammonia remained. The wash solution contained about 15 ppm nitrate by UV analysis. Rates of reaction based on the volume of liquid at the start ranged up to 159.7 g $NaNO_3$ L^{-1} fluid h^{-1} maximum with an overall rate for the total reaction of 42 g $NaNO_3$ L^{-1} h^{-1}. Based on the aluminum fed, the rate was a maximum of 86.5 g $NaNO_3$ L^{-1} h^{-1} g^{-1} Al. This probably came from nitrate deposited on vessel internals above the liquid level during the heatup of the reactor before aluminum addition. White crystals were seen on the internals above the liquid level.

5.2.2 Large (25—30 mesh) Aluminum Feed

An identical test (DN-4) was run with the only difference the size of the aluminum particles. The particles were 25—30 mesh (0.595—0.707-mm diameter) Al of ~98% purity (impurities were 6600 ppm Fe, 4010 Mn, 2850 Mg, 2450 Si, 890 Cu, 140 Ga, 60 Ni, and 4 Cd) that had been well exposed to air so that their surfaces were well oxidized.

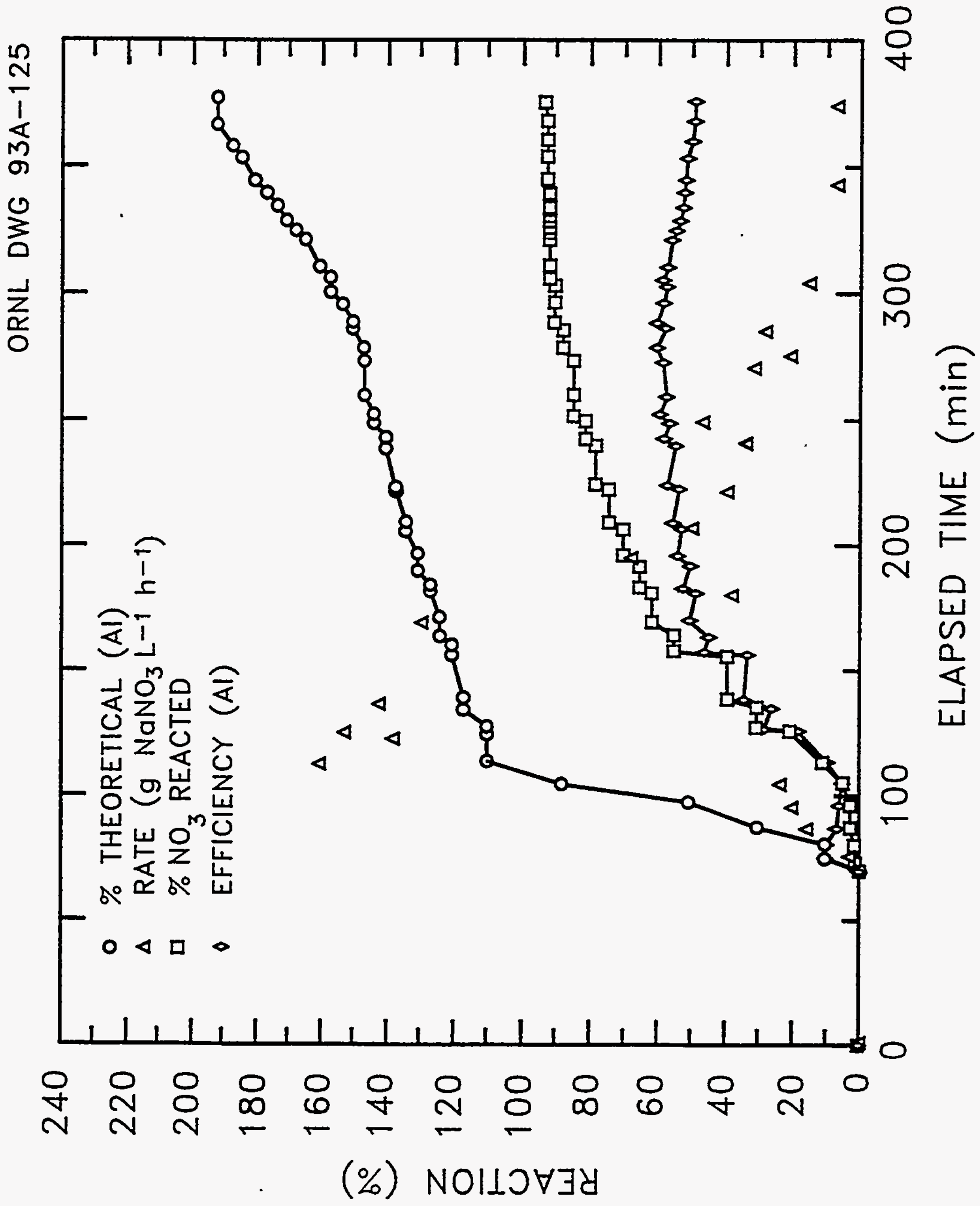

Fig. 11. Reaction progress in Run 3.

The large particles of aluminum had a specific surface area of ~37 cm^2/g, while that of the previous particles of 230 mesh was 325 cm^2/g. This surface area difference made a significant difference in the heat evolved after aluminum was added, with the large particles evolving much less heat during the equivalent period of time compared to that evolved by the small particles. The system containing 200 mL of 3.1 *M* $NaNO_3$ at pH 13.0 was again heated to 50°C, and ~4 g of Al beads were added. As seen in the previous runs, a slow reaction took place. A total of 13.4 g of Al was fed in the first portion of the run, during which time, ~4.5% of the NO_3 was converted to ammonia. During the overnight shutdown period of ~15.5 h, inert gas was left on to sweep any ammonia into the scrubber and the remaining Al in the slurry continued to react converting an additional 4.5% of the NO_3.

The system was reheated to 50°C in the morning, and the continuous feed of aluminum was continued for 1 h at a rate of ~0.5 g/min. Feed was stopped for 1 h, then started for another 1 h and 15 min, and stopped for 2½ h. Aluminum feed was started and stopped two more times before finally being stopped when the slurry was too thick to stir and aluminum would not penetrate the slurry surface. The pH probe and water and Al feeders were disconnected and the slurry left in the reactor over the weekend with an inert gas purge.

The larger particles tended to stay in the reactor as particulates which were visible as the slurry was agitated. The aluminum particles became black during the reaction after they were fed and visibly shrank in size as the reaction continued during periods of no aluminum addition. When the slurry was removed from the reactor, it was dark instead of the white of previous runs and contained only 2 mL of liquid which could be removed by filtration. This liquid showed no nitrate when tested with the EM Quant nitrate test strip. About 2 g of Al were present in the bottom of the vessel as metal, and black particles were visible throughout the slurry, so there was a significant portion of the aluminum (~3 to 5 g) that was fed that remained as aluminum when the reactor was shut down. The wash solution used to remove solids from the reactor showed just a trace of nitrate, probably splashed on the upper areas of the reactor during the starting heatup.

The results of the fourth run are shown in Fig. 12. Analysis of the ammonia trapped in the absorber showed that ~100% of the original nitrate had been converted to ammonia. About 1.8 times as much aluminum was added as would be theoretically

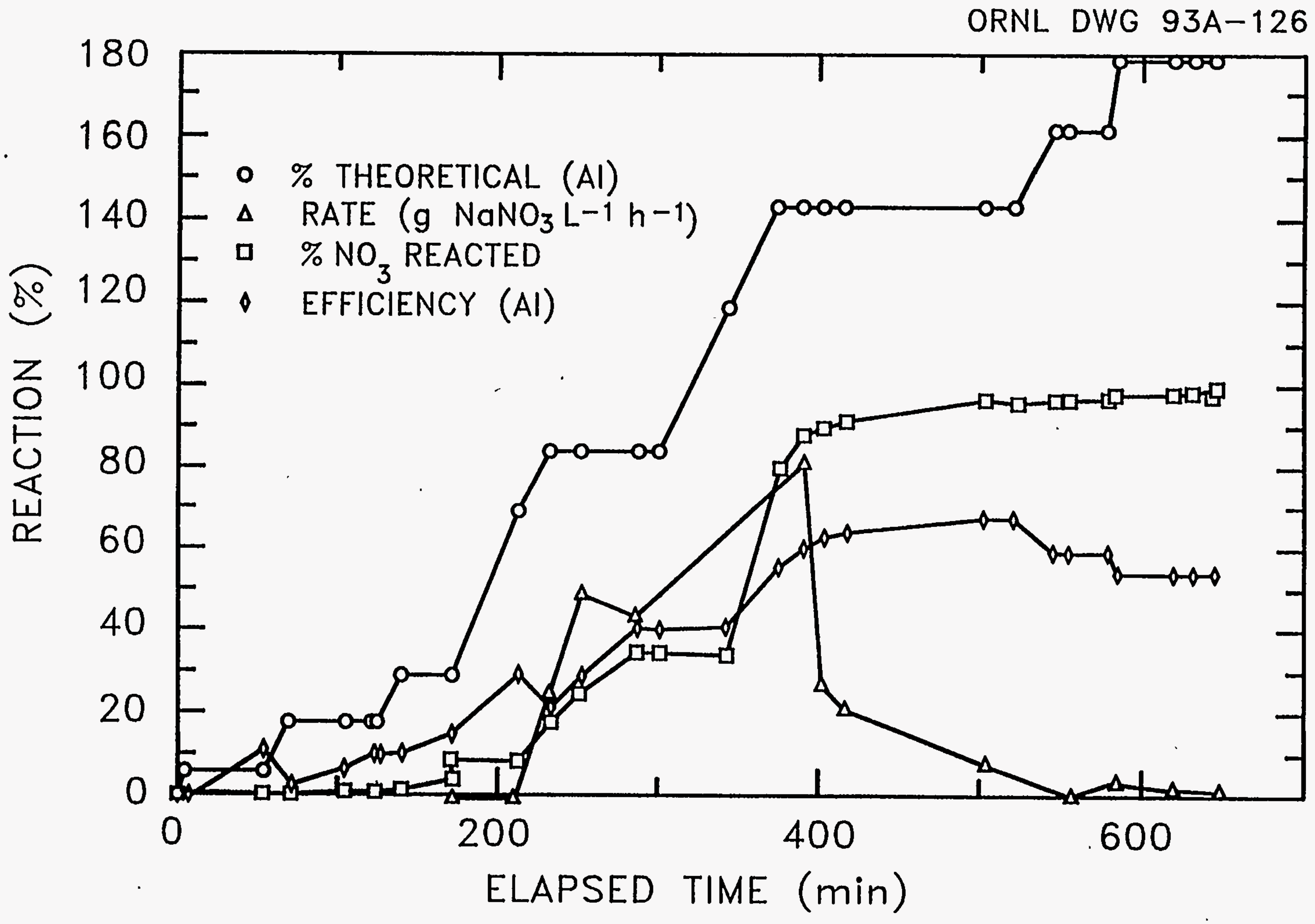

Fig. 12. Experimental results for Run 4.

required, but ~97% conversion was achieved at 140% of the aluminum added. The reactor required significantly less cooling than in previous runs, suggesting that surface area available for reaction is a controlling mechanism for the reduction. As can be seen, the nitrate conversion does not follow the aluminum fed until the Al reaches 70—90% of the theoretical requirement, or until ~30% of the nitrate is destroyed. The efficiency during the early portion of the reaction is very low, and then during the latter stages, is much higher until ~90—95% of the nitrate is destroyed, and then decreases again. The reaction rate follows the same trend, peaking during the 30—90% nitrate destruction region.

Samples of the filtrate from each of runs DN-3 and DN-4 were diluted 1:5 with DI water and titrated to a pH 7 endpoint to determine the approximate amount of aluminum hydroxide/sodium aluminate present in solution after the reaction. As the pH drops, the aluminate is converted to the hydroxide and the aluminum hydroxide precipitates as a gel-like solid. The initial pH of the diluted DN-3 filtrate was 13.4, and the diluted DN-4 filtrate pH was 13.31. DN-3 required 208 mL of 0.1 *N* HCl and 4 mL of 1.0 *N* HCl to get to pH 7.0, while DN-4 needed 108 mL of 0.1 *N* HCl and 25.0 mL of 1.0 *N* HCl. The solutions were settled for 2 d and the "gel" filtered out on a Whatman No. 1 filter paper. The dried product was 0.4176 g from 5 mL of DN-3 filtrate and 0.9514 g from 5 mL of DN-4 filtrate. The dried solids gained 0.085 and 0.109 g after exposure to ambient air for 3 d.

5.2.3 Small (230—270 mesh) Aluminum Feed Particles

Run DN-5 used 200 mL of 3.1 *M* $NaNO_3$ feed at a starting temperature of 60°C and pH 13.0. The 230—270 mesh (0.053—0.063 mm) aluminum was fed as in previous runs with the powder feeder. In this run, the copper oxide furnace tube was used to convert any hydrogen gas produced in the reaction to water vapor for collection in a conductivity cell or a Drierite column. The hydrogen produced could be determined from the weight lost by the CuO as it was reduced to metallic copper. Hydrogen production in the reaction resulted in the formation of 0.2 mol hydrogen, which is approximately equivalent to 8.45% of aluminum fed during this reaction. During the run, the conductivity cell reading cycled with the temperature of the cell to such an extent that the results were unusable.

The run was started by heating to 57°C and then adding ~4.3 g of the aluminum powder. After 15 to 20 min, the pH dropped to 11.4, and after ~1 h returned to 12.4 and another ~4.3 g Al was added. Each 15 to 20 min thereafter, another 4.3 g of aluminum powder was added (7 more times). After the last addition, the feed tube was found plugged and had to be cleared. Another feed attempt again plugged the tube, so the run was ended. The slurry was frothing so badly that the feed tube was wet causing the powder to cake and plug at contact. After disassembly, the feed tube plug was found to contain 3.63 g Al.

The results for run DN-5 are shown in Fig. 13. The aluminum addition was fairly uniform for the time between ~50 and 180 min, but the conversion of nitrate was very slow, reaching only 45% at the end of the run when over 100% of the theoretical Al had been added. In the run, 47.21 g aluminum reacted with 17.43 g NO_3, or 23.9 g $NaNO_3$. This is 0.37 g NO_3/g aluminum or 0.51 g $NaNO_3$/g aluminum. Conversion did not rise above 10% until ~70% of the Al had been added. This continues the pattern observed during the earlier runs 2, 3, and 4. The incremental volumetric reaction rate also increased greatly after 60 to 70% of the Al had been added.

Solids from the run were removed and filtered, resulting in 128.49 g air-dried solids and 115 mL of liquid filtrate. An additional 16.49 g of air-dried solids were scraped and washed from the reactor with 280 mL of wash water. The solids were analyzed in the same manner as the previous runs for water loss on heating and nitrate present after drying and washing.

5.2.4 Discussion of Initial Batch Reaction Results

The problems discovered in the series of batch reactions using sodium nitrate and aluminum feeds centered around feeding aluminum powders and maintaining agitation near the end of the batch reaction period. The feeding problems are primarily associated with the small diameter tubes used to feed the aluminum powders for the research-scale reactor. The small size tubing allowed the easy bridging of the powder in the end of the tube where it was close to the moisture in the reactor. Dry nitrogen feed helped this problem and allowed feed until near the very end of the reaction. Small-scale tests showed that an aluminum-water slurry could also be fed, and this would overcome the plugging problem entirely.

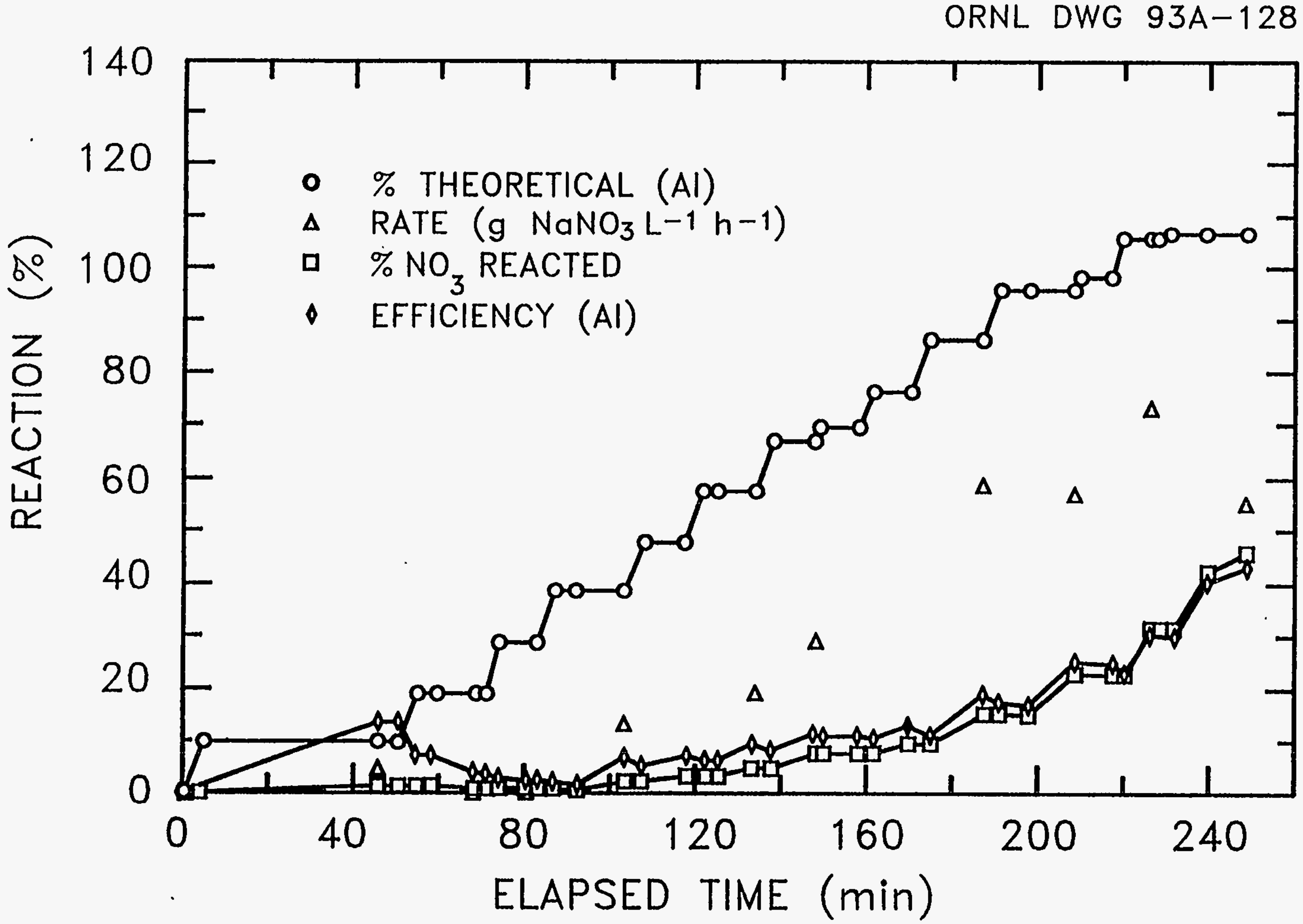

Fig. 13. Results of denitrification Run 5.

The results of slurry thickening at the end of the reaction — off-gas bubbling which entrained liquid and slurry, lack of aluminum feed mixing with the slurry, and lack of agitation capability — were caused by the reaction itself using up the water originally present. The batch method of operation in which it was attempted to react all of the nitrate present in the 3 or 6 *M* starting solution was tried but did not lend itself to keeping an easily stirred slurry. When enough water is added to the reaction to replace the reacted water, plus water to keep the slurry fluid, these problems are decreased. Operation in a continuous-stirred reactor mode, with aluminum-water slurry feed, product withdrawal, solids separation, and liquid recycle to the reactor, is planned for the pilot-scale operation. In addition, the magnetic-drive stirrer used in the reactor could be decoupled if the slurry got too thick. A direct-drive agitation device would be limited only by the power of the motor.

5.3 BATCH REACTION WITH ^{137}Cs, ^{85}Sr, ^{144}Ce, AND ^{60}Co

One run (DN-6) was completed using 230—270 mesh particles and a reaction temperature of 50°C. In this run, nitrate solution was spiked with ^{144}Ce, ^{137}Cs, ^{60}Co, and ^{85}Sr as tracers to give a preliminary indication as to their disposition after the reaction. Results of the denitration are shown in Fig. 14. Approximately 20% of the aluminum fed was converted to hydrogen. Gamma-ray spectroscopy of the product solids and the filterable liquid products indicated that the cesium remained with the liquid filtrate and was easily removed from the wet or dry solids by simple washing. The strontium and cerium (cerium was used as a stand-in for plutonium and other alpha emitters) reported to the solid and were not washed out by the simple washing technique used. Some of the cobalt remained in the solids and some was washed out, as expected. The solids washing results are shown in Table 4 and presented in Fig. 15 as a bargraph for the four isotopes added to the reaction mixture. The gamma counting results are shown in detail in Appendix E.

The gamma-ray spectroscopy data are shown for several of the samples in Appendix E. They are presented for the product filtrate from the reactor, the solid product from the reactor, the washes of the dried and heat treated solids, and the various dried solids after washing. The data plots record the log of the counts versus the energy/channel number. The results of the peak search and analysis are also shown.

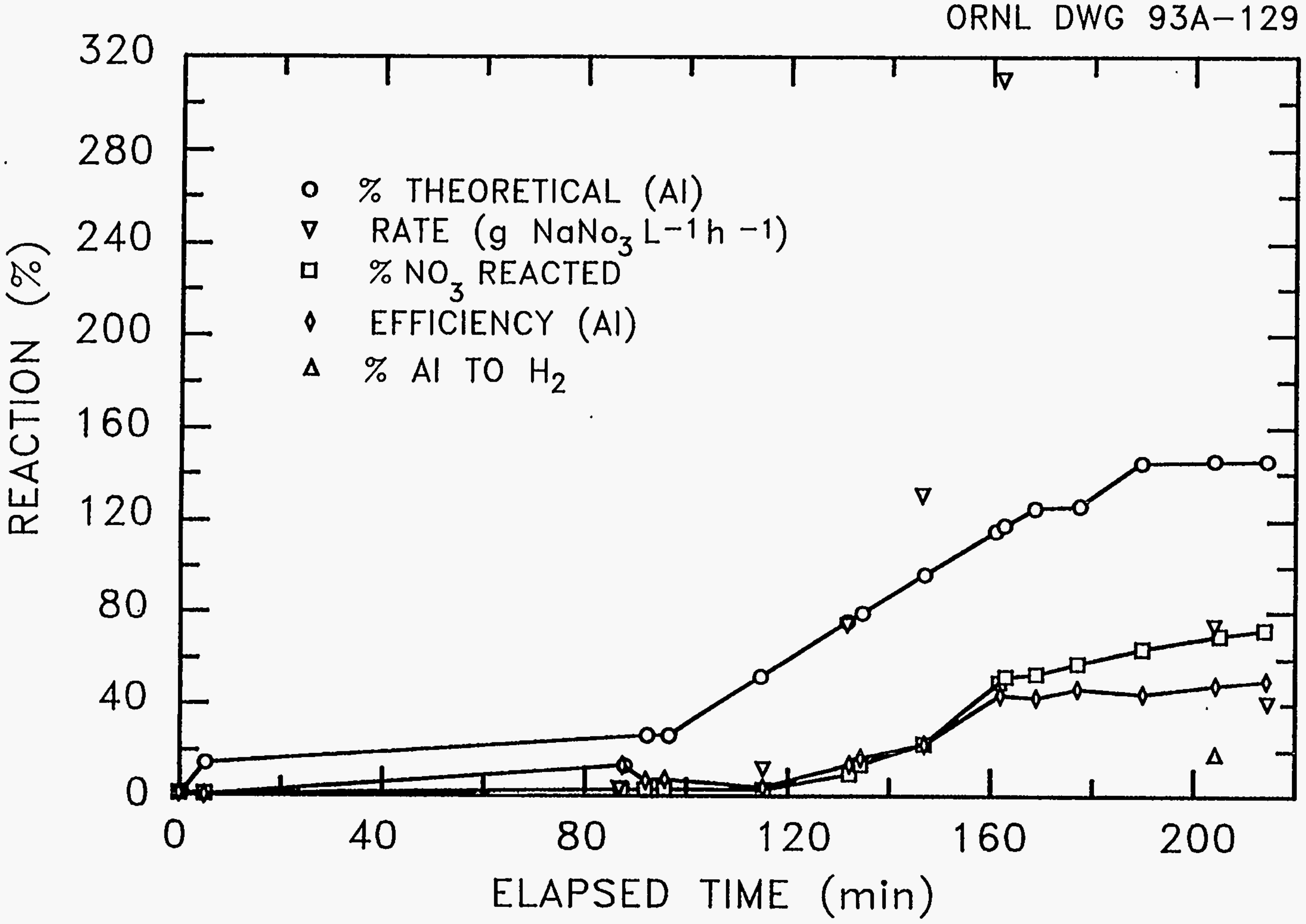

Fig. 14. Results of DN6 reaction using tracers.

Table 4. Radiochemical analysis of the DN-6 feed and products

200 mℓ of 3.1 M NaNO$_3$ feed was spiked with ^{85}Sr, ^{137}Cs, and ^{144}Ce. The ^{144}Ce had a small amount of ^{60}Co with it, and this was also followed. After the reaction, the solids were removed, filtered, and the solids and filtrate counted. Small samples of each were also counted. A sample of the solids was counted and then washed with DI water and the resultant filtrate was counted. Another sample was dried at 100°C, and a third at 300°C. These were both sampled, then washed and the wash water counted to see if any radioactivity could be easily washed out.

Sample ID	Total mass or volume	Counting sample mL or g	Raw ^{137}Cs Cts/s	Final ^{137}Cs μCi/g (or mL)	Total ^{137}Cs μCi	Total μCi of solids ^{137}Cs	Raw ^{85}Sr Cts/s	Final ^{85}Sr μCi/g (or mL)	Sample ^{85}Sr μCi	Total μCi of solids ^{85}Sr	Raw ^{144}Ce Cts/s	Final ^{144}Ce μCi/g (or mL)	Sample ^{144}Ce μCi	Total μCi of solids ^{144}Ce	Raw ^{60}Co Cts/s	Final ^{60}Co μCi/g (or mL)	Sample ^{60}Co μCi
1st portion solids (wet)	223.89 g	All	5920	0.1023	22.904		5050	0.0633	14.163		2780.00	0.0875	19.597		--------		
Room T dried & washed solids	28.64 g	All	23.4	0.0032	0.074		23.3	0.0023	0.053		16.90	0.0041	0.097		0.11	0.0000	0.000
2nd solids washed	23.42 g	All	6.59	0.0011	0.025		185.0	0.0229	0.151		166.00	0.0501	0.330		0.24	0.0000	0.001
2nd portion wash liquid DN62PW	465.17 mL	All	289	0.0024	1.121		----				----				0.19	0.0000	0.001
RT dried solid sample DN61PST0	28.64 g	0.61 g	23.4	0.1484	4.250	33.225	18.10	0.1115	3.193	24.964	21.10	0.2593	7.426	58.055	0.15	0.0011	0.031
RT wash water (g)	77.17 g	1.00 g	16.4	0.0637	4.914										0.14	0.0005	0.041
100 dry sample DN61PST1 25.48 g (wet)	20.83 g (dry)		11.6	0.2505	5.218	45.849	7.93	0.1624	3.383	29.724	9.73	0.4045	8.426	74.036	0.166	0.00319	0.067
300 dry Sample DN61PST3 25.64 g (wet)	13.42 dry	0.15 g	22.6	0.5835	7.831	68.377	7.27	0.1906	2.558	22.335	8.47	0.4287	5.753	50.237	0.16	0.0038	0.051
100 dried sample wash DN61P1W	123.35 g	1.00 mL	8.0	0.0313	3.860		----				----				0.17	0.0006	0.070
300 dried sample wash DN61P3W	46.96 g	1.00 mL	0.57	0.0022	0.103		----				----				0.18	0.0006	0.030
Trash after getting ready for run DN6TRASH	?	all	16.6	0.0642			9.65	0.0270			37.70	0.2647			0.25	0.0008	
Feed DN6BEG (mL)	200. mL	200 mL	323,000	6.2400	1248		46300	0.6524	130		6480.00	0.2292	45.840		--------		
Filtrate DN61FIL1 (mL)	55.20 mL	All	1790	0.3513	19.392		----				----				--------		
Filtrate DN61FIL1 (mL)	55.20 mL	1 mL	169	0.6534	36.068		----				----				0.18	0.0006	0.031
Empty Reactor DN6EMPV	100.0 g	All	16	0.0003	0.032		9.65	0.0001	0.014		37.70	0.0013	0.132		0.25	0.0000	0.000

SUMMARY	Filtrate I (μCi)	Wash I (μCi)	Solids I (μCi)	Solids II (washed) (μCi)	Solids I all (μCi)	Solids dried at 100°C (μCi)	Solids dried at 300°C (μCi)
Cesium	36.0676	1.12	33.2253	0.0255	22.90	38.9673	68.3770
Strontium	---------	----	24.9637	0.1508	14.16	25.7525	22.3353
Cerium	---------	----	58.0547	0.3302	19.60	65.5617	50.2369

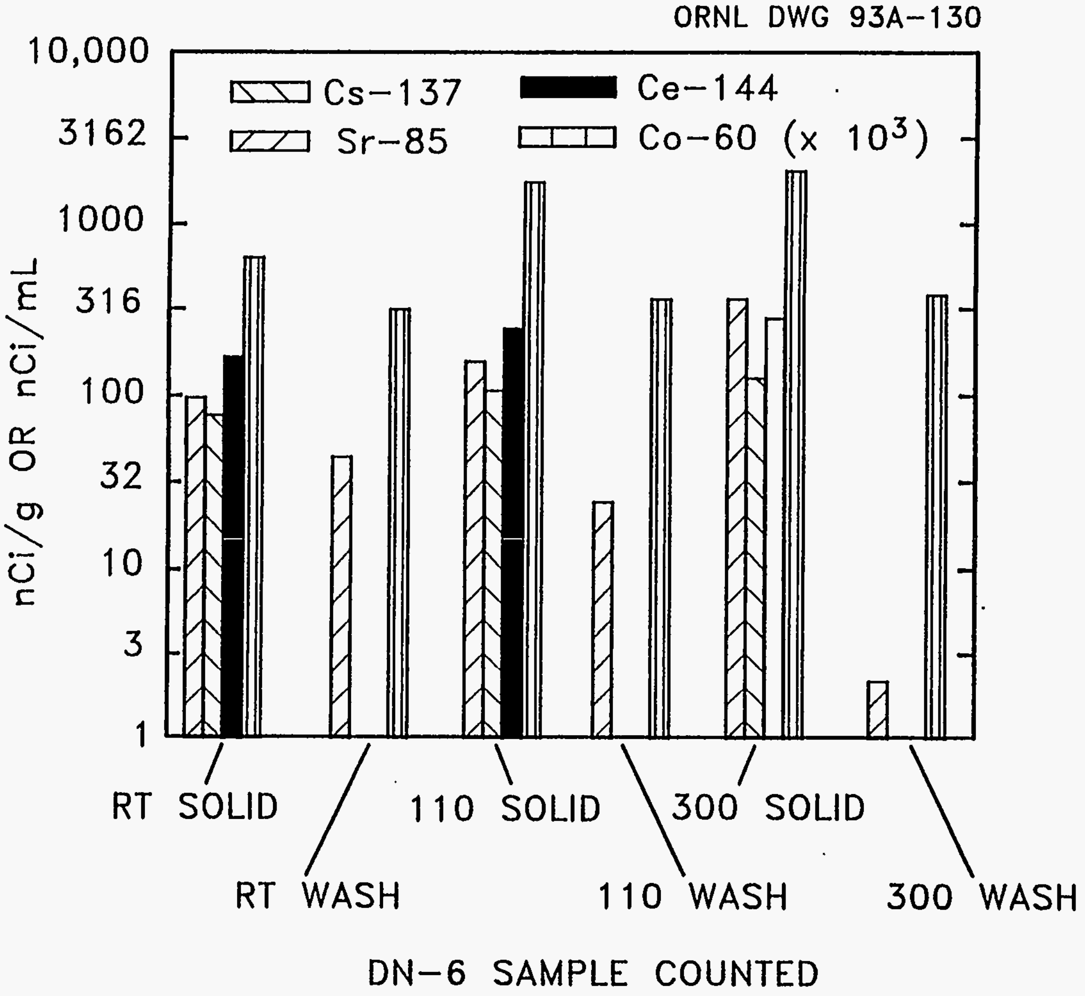

Fig. 15. Results of solids washing experiments.

5.4 BATCH REACTION USING THE HANFORD SLUDGE/SALT CAKE

Run DN-7 was completed using aluminum particles of 30—35 mesh (about 0.5—0.6 mm), the composition and treatment as in the earlier DN-4, and a reaction temperature of 50°C. Cesium-137 and ^{85}Sr were spiked as tracers to give a preliminary indication as to their disposition after the reaction. Cobalt-60 and ^{40}K were also followed because trace amounts of the cobalt were present in the cesium spike and the ^{40}K was present as a contaminant in some of the salts in the surrogate mixture. The feed for this run was composed of portions of the Hanford surrogate sludge mixture, initially 55% sludge/45% salt-cake, plus water to make a slurry of ~2.7 to 2.8 *M* in nitrate. The initial pH of this mixture at room temperature was ~11.5. In order for the reactor system agitator to turn and to process this mixture, some of the insoluble sludge "rocks" had to be removed (~50%) to allow for mixing and heat transfer. Because of the low initial pH and the lower concentration of nitrate in the reaction mixture, a very long induction period ensued, very similar to run DN-1. After 3.5 h of the start-up portion of the reaction, sodium hydroxide was added three times at ~1-h intervals to increase the pH to hasten the onset of a sustained reaction. After the reaction was sustained, the supernate remaining after removing the "rocks" and settling was added back to the reactor. Water that was used to wash the "rocks" was added to the reactor during the run to increase the processing capacity and return nitrate and radioactive tracers to the reaction mixture. An additional effect of the presence of the sludge was to decrease the apparent reaction rate with a resulting decrease in the heat load on the cooling system and a minimal requirement for cooling to control the reaction temperature.

Results from the Hanford sludge/salt-cake surrogate run showed that ~40% of the initial nitrate had been reduced to ammonia using 110% of the theoretical aluminum. The results are shown in Fig. 16. At least 9% of the aluminum fed produced hydrogen gas as measured by the loss of oxygen in the CuO furnace. After the experiment was complete, samples of the solids produced were separated into three fractions. One fraction was washed, and the solids and wash water were counted for ^{137}Cs, ^{85}Sr, ^{144}Ce, and ^{60}Co present. The second portion was dried at 110°C and then washed, and both portions were counted. The third portion was dried at 300°C, washed, and both portions counted. Results are summarized in Table 5 and in bargraph form in Fig. 17. The results shown

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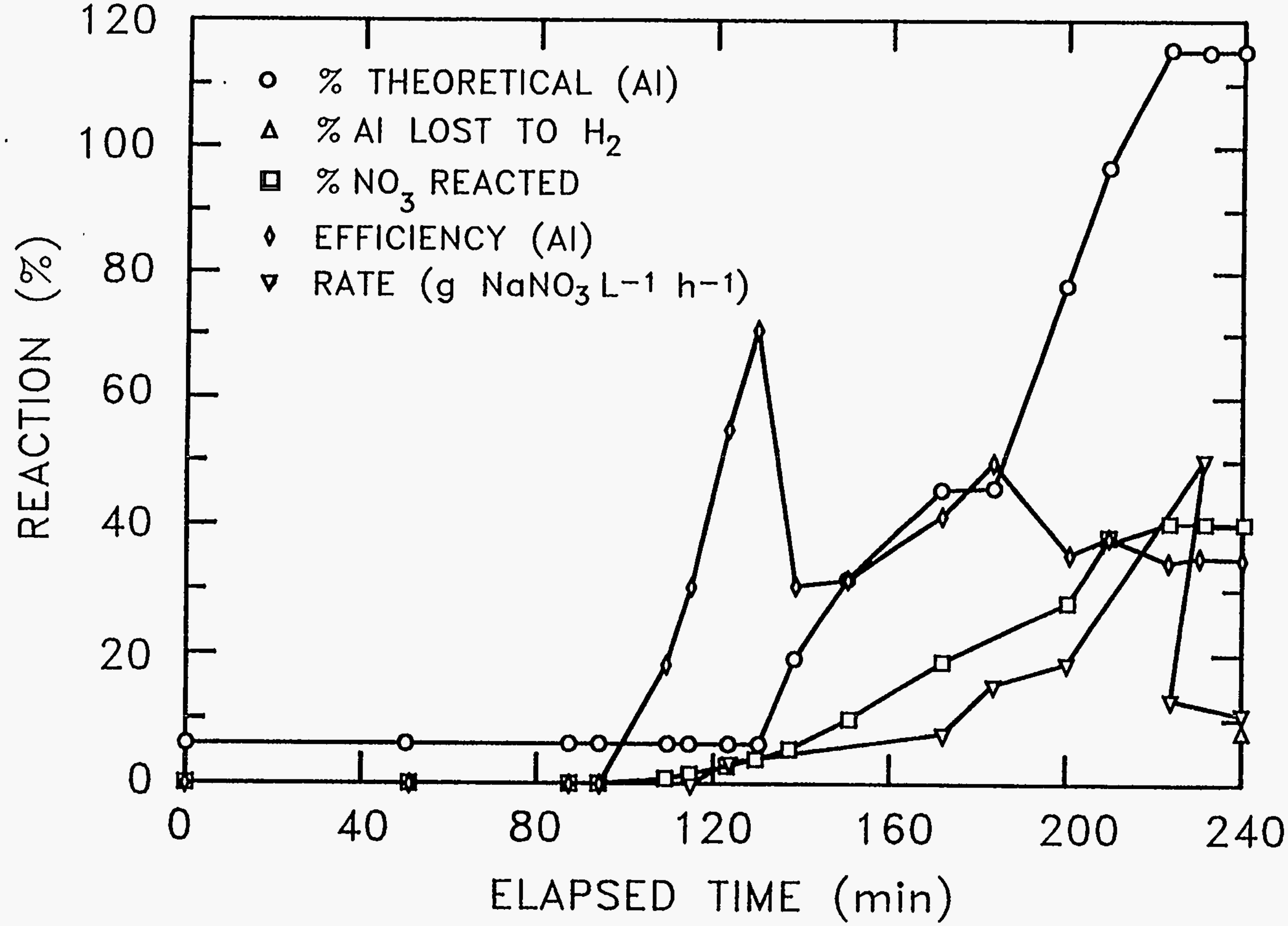

Fig. 16. Results for Hanford surrogate.

Table 5. Analysis of DN-7 solids and radioactive tracer disposition

DN-7 Hanford surrogate solids and radioanalysis	Mass or volume	^{137}Cs (μCi/unit)	^{137}Cs total (μCi)	^{85}Sr (μCi/unit)	^{85}Sr total (μCi)	^{60}Co (μCi/unit)	^{60}Co total (μCi)	^{40}K (μCi/unit)	^{40}K total (μCi)
Feed (26.619 g NO_3^-)	200 mL	0.4196	83.92	0.9826	16.53	0.0059	1.18	0.0058	1.17
First filtrate	49.4 mL	0.2018	9.97	—	0.0	0.0057	0.28	0.0042	0.21
Second solids wash	281.2 mL	0.0185	5.20	—	0.0	0.0006	0.17	0.0008	0.23
Theoretical solids if Al→$Al(OH)_3 \cdot 3H_2O$ (dry at 105°C)	173.92 g								
Theoretical solids if all Al→$Al(OH)_3$ (dry at 300°C)	102.76 g								
Theoretical Solids if all Al→Al_2O_3 (dry at >900°C)	79.04 g								
105°C solids + sludge	201.22 g								
300°C solids + sludge	130.06 g								
900°C solids + sludge	106.34 g								
105°C solids based on sample	169.34 g		28.61		11.82		2.09		1.94
300°C solids based on sample	116.94 g		75.64		30.25		1.28		1.70
First solids damp weight	248.99 g	0.1497	44.28	0.0467	13.82	0.0056	1.66	0.0074	1.83
Second solids damp weight	46.79 g	0.1145	5.36	0.0632	2.96	0.0045	0.21	0.0031	0.14
Sludge removed before reaction (dried)	27.7 g	0.4969	13.76	0.2156	5.97	0.0032	0.09	0.0024	0.07
Sludge left in reactor (by difference)	27.3 g								
Product solids sample	23.01 g	0.1470	3.38	0.828	1.90	0.0077	0.18		
Product solids wash	51.79 mL	0.0304	1.57	0.0003	0.01	0.0006	0.03	0.0004	
Product solids after wash	23.01 g	0.1518	3.49	0.0873	2.01	0.0073	0.17	0.0060	
Product to dry at 105°C	30.03 g								
Product dried at 105°C	11.47 g	0.1689	1.94	0.0698	0.0123	0.80	0.14	0.0144	
Dried product wash	47.18 mL	0.0259	1.22	—	0.0	0.0005	0.06	0.0052	
Water lost on drying	126.4 g = 42.74%								
Product to dry at 300°C	17.68 g								
Product dried at 300°C	6.99 g	0.6468	4.52	0.2587	4.57	0.0110	0.19	0.0145	
Dried droduct(300°C) wash	64.67 mL	0.0207	1.34	—	0.0	0.0006	0.04	0.0004	
Dried product after wash	6.99 g	0.1486	1.04	0.0905	0.63	0.0112	0.08	0.0080	
Water lost on drying	178.84 g = 60.46%								

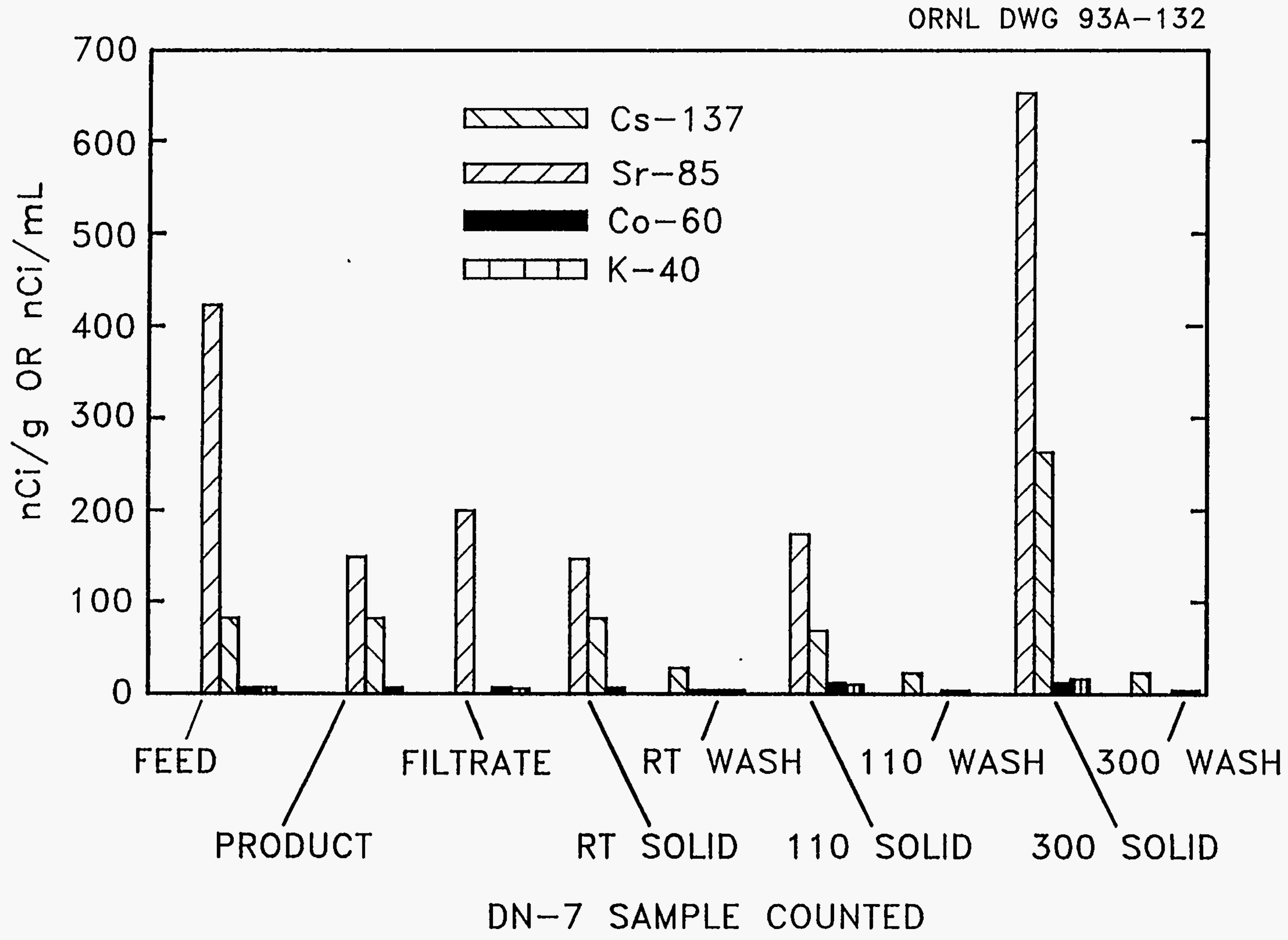

Fig. 17. Results of solids washing on tracers.

are for the samples as counted. As was seen in the previous run with tracers, the strontium was immobilized in the solids and was not washed out by distilled water, nor was it present in the reactor product filtrate. The cesium was present in the filtrate and was washed out of each solid sample to varying degrees, depending on the amount of wash solution, agitation, etc, and some still remained with the solids. It appeared that the drying slightly stabilized the solids with respect to cesium loss. The weight loss on drying amounted to ~60% for 300°C dried material and ~43% for drying at 110°C. Because of the weight loss on drying, the amounts of tracers present in the 110 and 300°C solids are higher than solids dried at room temperature, based on a unit of solid counted. These amounts are greater than was seen for feed materials starting with sodium nitrate only in which a weight loss of ~30% was seen and the difference can be attributed to the nonreactive sludge and salts. The counting results are given in detail in Appendix E.

The operational problems associated with this run were slightly different than those encountered with the sodium nitrate solution feed runs. The presence of the initial sludge solids caused agitation problems in which the solids would wedge under the magnetic stirrer and prevent it from turning. Finer grinding of the solids or a direct-drive agitator that was not in contact with the flat vessel bottom would help prevent this, as would running a more dilute slurry in a larger reaction vessel during the reaction. The more concentrated that the nitrate feed slurry is, the larger the amount of added water needs to be. Most of this water would be recycled from the solid/liquid separation step in a continuous process.

5.5 OTHER REACTION CONFIGURATIONS

5.5.1 Surface Preparation Effects

A set of bench-top open-beaker runs were completed to test the effect of the surface condition of the aluminum prior to the reaction. The first run was made using 175—200 mesh aluminum powder which had been exposed to the atmosphere. The reaction started with 100 mL of 1.55 *M* $NaNO_3$ at pH 12.1 and ~50°C reaction temperature. This first run followed the course seen in the regular reactor runs. The pH dropped rapidly upon addition of the aluminum powder and then gradually increased. Until over 3 g was added (25 to 30% of the theoretical Al), the reaction produced little excess heat; but after this point, heat evolution was very pronounced and rapid. After 6 h and the addition of ~7 g Al (63% of theoretical Al), the pH was 13. The additions were continued until ~29 g Al was added.

The second bench-top experiment was similar to the above, but −200 mesh 99% aluminum which had been stored under nitrogen was used. It was transferred to the reaction flask under argon to prevent any surface oxidation before encountering the solution. Similar conditions to those above were used, but the reaction started with 50 mL of 1.55 *M* $NaNO_3$ at pH 12.1 and 28°C. The Al powder was added to the beaker containing the reaction mixture under an argon blanket. After the first 0.29 g Al was added, the pH dropped from 11.55 to 10.7, and the temperature increased from 44°C to 62°C. The intense reaction lasted ~1 to 2 min, and the reaction solution cleared completely in ~4 min. A combustible gas detector (detects both hydrogen and ammonia) showed in excess of 1000 ppm combustible gas leaving the reactor. Olfactory sensing and the formation of ammonium chloride vapor in the presence of HCl revealed the presence of ammonia. A second addition of 0.3 g resulted in a pH drop from 10.8 to 10.17 and a temperature increase to 55°C. Due to the constant argon purge for a blanket, the volume in the reaction vessel had decreased to almost 10 mL and water was added to bring the volume back up. The solids forming in the reactor gradually turned from light gray to white and settled easily when agitation was removed. After 2 g Al (36% theoretical) was added (five separate additions), the pH was 10.6. After 4.4 g, or 80% of theoretical (5.6 g of theoretical Al for nitrate present), the pH was 11.3 and the precipitate in the reactor was white.

In comparing the two runs, the second, with "clean" aluminum, showed a much more rapid initial reaction, producing more heat, and the immediate presence of ammonia in the product gas. Ammonia was noted after each addition of aluminum, along with combustible gases in excess of 1000 ppm when feeding the "clean" aluminum.

5.5.2 Technetium Disposition

One bench-top run was made using 22.66 g of <325 mesh aluminum powder in slurry with 99.44 g deionized water, and using 100 mL of 1.55 *M* $NaNO_3$, at pH 13.0 and ~42°C reaction temperature. This run was used to test the addition of aluminum feed as a water slurry instead of as the dry powder or particles. Slurried aluminum was added in 1- to 1.5-mL portions over an ~2.5-h period. Temperatures during reaction reached 75°C. As has been seen in the regular reactor runs, the pH dropped rapidly upon addition of the aluminum slurry and then gradually increased. Technetium-99 was used in tracer amounts to determine its disposition during the reaction.

The initial solution and the supernate remaining after complete destruction of the nitrate and settling of the solid product overnight were counted using a scintillation counter. The technetium was not removed to any appreciable extent in the solids. Results showed more technetium present in the final supernate than was present in the feed material (87 mL product liquid vs 100 mL feed). Tests on the product solids are in progress, including drying and washing tests as in previous runs, and showed that the ^{99}Tc was not permanently fixed and could be washed out of the solids. Additional tests on the supernate to determine if the ^{99}Tc would precipitate with the aluminum hydroxide gel as the pH is reduced to 7—8 did not show appreciable fixation of the ^{99}Tc in the solids.

5.5.3 Reaction Rate Experiments

Two runs were completed using a 1.55 *M* $NaNO_3$, pH 13.0 solution in an experiment to determine the reaction rate based on the particle surface area. The surface area of the ~7- to 10-mm-diam aluminum pellets was determined, and ~10 g of these (9 to 12 pellets) were placed in a small column and the nitrate solution passed over them at a controlled flow rate and temperature, and the reservoir sampled over time. Changes in the concentration of nitrate in the solution and the production of ammonia with time were followed to determine the extent of reaction versus time, and from these data, a reaction rate. The total external surface area of the particles was calculated based on particle measurements and used to give a rate per unit surface area. The mass of the particles remaining after the experiment was determined, and the aluminum used in the reaction was obtained by difference to give the mass rate of reaction. The two runs were made under similar conditions, and the results compare favorably with each other as shown in Fig. 18. The rates were then compared to the approximate rates for the runs in the

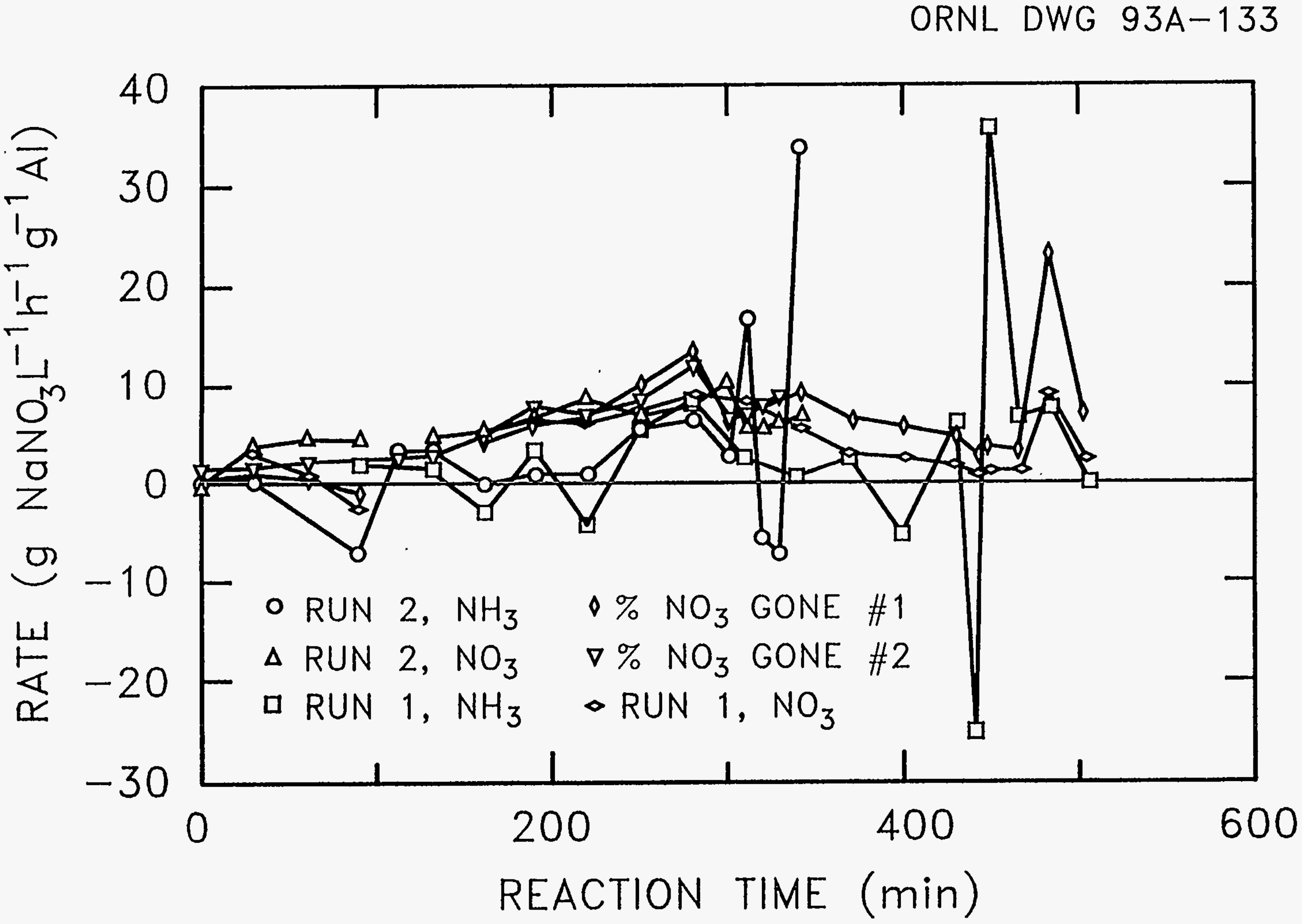

Fig. 18. Results of two reaction rate runs.

regular reactor using other particle sizes and are shown in Table 6. The detailed results are shown in Table 7 for the first run.

Table 6. Comparison of mass and area based reaction rates

Run No.	Al size (mm)	Feed $NaNO_3$ (*M*)	Mass rate (g L^{-1} h^{-1} g^{-1} Al)	Area rate (g L^{-1} h^{-1} cm^{-2} Al)
DN-2	0.0685	6.2	1—2	0.0007-0.001
DN-3	0.0685	3.1	20—86	0.01—0.05
DN-4	0.65	3.1	1—3	0.002—0.02
DN-5	0.058	3.1	1—17	0.002—0.035
DN-6	0.058	3.1	0.5—7.2	0.0002—0.002
RR1	7—10	1.55	1—9	0.2—0.4
RR2	7—10	1.55	4—10.5	0.15—0.37

Behavior during reaction was consistent with the stirred-cell reactions in which pH dropped and then slowly rose with increasing reaction rate as the pH passed 11. The reaction was taken to about 10% nitrate destruction, to the point where significant solids formed in the solution and operation as a recirculating reactor became difficult because of those solids. Results showed that rates of 6 to ~8 g $NaNO_3$ L^{-1} starting material h^{-1} reaction g^{-1} aluminum were used for both runs. Based on aluminum surface area, the rates were 0.2 to ~0.4 g $NaNO_3$ L^{-1} starting material h^{-1} reaction cm^{-2} Al surface. The rates per unit mass are all consistent, but the rates based on surface area are significantly higher (orders of magnitude) for the pellets than for small particles except for run DN-3.

5.6 PHYSICAL CHARACTERISTICS OF TEST PRODUCTS

5.6.1 Density and Compressibility Measurements

The solids from each run were sampled, and the series of tests described earlier were made for physical properties, loss of remaining nitrate, and loss of weight upon drying and heating. Table 8 gives the results for the solids analyses. Table 9 shows the results for

Table 7. Reaction rate run No. R1

Molarity of solution = 1.55 *M* volume at start = 275 mL; 96.1 g/L NO_3 = 96,100 ppm NO_3 = 21.7 g/L N = 21,700 ppm N; aluminum: 10.00 g = 21 pellets (surface area = 222.2 mm^2/pellet) = 46.662 cm^2/10 g [ammonia trap: 0.5 mL of HCl sample diluted to 25.0 mL with 24.5 mL DI water]

1st NO_3 dilution: 0.10 mL of sample + 10.00 mL of 0.001 N HCl + 0.10 mL of 0.01 N HCl; 2nd NO_3 dilution: 0.10 mL of 1st NO_3 dilution + 5.00 mL of 0.001 N HCl

											Incremental rate: From Ammonia Data:		From Nitrate Data	
Reaction time (min)	Reservoir temp. (°C)	Reservoir pH	Sample ID	0.001 *M* NaOH mL	mmol HCl	mmol HCl = NH_3 = NO_3	Incremental mg NO_3 gone	mg NO_3/L/g Al/min	mg NO^3/L/cm^2 Al/min	g $NaNO_3$/L/h	g $NaNO_3$/L/h/g Al	g $NaNO_3$/L/h/cm^2 Al	g $NaNO_3$/L/h/g Al	g $NaNO_3$/L/h/cm^2 Al
0	27.1	12.999	H0	5.60	1.120									
30	28.2	12.976												
35	28.6	12.968	H1	5.60	1.120	0							3.2829	0.1168
65	30.0	12.916	H2	5.60	1.120	0							1.0101	0.0359
95	30.8	12.854	H3	5.50	1.100	0.02	0.248	0.007359	0.000203	0.000215	1.9168	0.0530	-2.4190	-0.0861
125	31.1	12.771	H4	5.42	1.084	0.036	0.1984	0.010067	0.000278	0.000294	1.5335	0.0424		
160	31.6	12.690	H5	5.58	1.116	0.004	-0.3968	0.000874	0.000024	0.000026	-2.6288	-0.0727	5.1295	0.1825
185	31.4	12.625	H6	5.43	1.086	0.034	0.372	0.006424	0.000178	0.000187	3.4503	0.0954	6.4770	0.2304
217	31.5	12.526	H7	5.67	1.134	-0.014	-0.5952	-0.00225	-0.000062	-0.000066	-4.3129	-0.1192	6.1270	0.2180
245	31.7	12.438	H8	5.40	1.080	0.04	0.6696	0.005707	0.000158	0.000167	5.5452	0.1533	7.7717	0.2765
245	25.9	12.497	H9	5.50	1.100	0.02	-0.248	0.002853	0.000079	0.000083			8.1067	0.2884
283	31.0	12.418	H10	5.13	1.026	0.094	0.9176	0.011610	0.000321	0.000339	8.8654	0.2451	9.3962	0.3343
315	33.3	12.274	H11	4.96	0.992	0.128	0.4216	0.014204	0.000393	0.000414	3.0550	0.0845	8.5980	0.3059
340	34.2	12.141	H12	4.91	0.982	0.138	0.124	0.014187	0.000392	0.000414	1.1501	0.0318	5.6002	0.1992
370	34.6	11.996	H13	4.76	0.952	0.168	0.372	0.015871	0.000439	0.000463	2.8753	0.0795	3.5491	0.1263
400	34.7	11.827	H14	5.00	1.000	0.12	-0.5952	0.010486	0.000290	0.000306	-4.6004	-0.1272	2.9546	0.1051
430	34.7	11.703	H15	4.68	0.936	0.184	0.7936	0.014957	0.000413	0.000436	6.1339	0.1696	2.2140	0.0788
442	34.8	11.753	H16	5.20	1.040	0.08	-1.2896	0.006327	0.000175	0.000185	-24.919	-0.6889	1.4112	0.0502
450	34.8	12.019	H17	4.70	0.940	0.18	1.24	0.013982	0.000387	0.000408	35.9408	0.9936	1.6779	0.0597
466	34.8	12.286	H18	4.50	0.900	0.22	0.496	0.016502	0.000456	0.000482	7.1882	0.1987	1.6203	0.0576
485	34.8	12.411	H19	4.24	0.848	0.272	0.6448	0.019603	0.000542	0.000572	7.8691	0.2175	9.4425	0.3359
505	34.8	12.466	H20	4.23	0.846	0.274	0.0248	0.018965	0.000524	0.000553	0.2875	0.0079	2.9253	0.1041
Overall mass rate = 0.00537 g $NaNO_3$/L/h/g Al; Overall area rate = 0.000190 g $NaNO_3$/L/h/cm^2 Al									Averages = 0.0001602		3.986	0.110	4.490	0.160

Table 8. Solids analysis results

Sample	Weight (g)			Amount of water in wash (mL)		
	Before washes	After washes and drying	"Amount lost"	Wash 1	Wash 2	Wash 3
DN-1	50.00	41.29	8.71	77.0	102.0	91.0
DN-2	49.98	39.88	10.10	80.5	91.0	98.0
DN-3	49.98	41.50	8.48	77.0	94.3	99.4
DN-4	50.00	37.37	12.63	78.0	89.5	89.0
DN-5, 1st	50.00	27.81	22.19	100.0	100.0	100.0
DN-5, 2nd	10.01	6.73	3.27	40.0	40.0	40.0

Table 9. Results of density measurements

Sample	100°C dry "loose" packed	300°C dry "loose" packed	100°C dry "compressed"	300°C dry "compressed"
	(g/mℓ)	(g/mℓ)	(g/mℓ)	(g/mℓ)
DN-1	0.938	0.774	1.738	2.197
	0.918	0.800	1.713	1.647
	0.952	0.785	1.502	1.453
	0.942	0.753	1.871	2.057
	Hi-Lo=0.034 Avg=0.937	Hi-Lo=0.047 Avg=0.778	Hi-Lo=0.369 Avg=1.706	Hi-Lo=0.784 Avg=1.754
DN-2	0.988	0.857	1.513	1.715
	0.987	0.789	1.875	2.075
	0.973	0.765	1.728	2.064
	0.914	0.748	1.594	1.768
	0.915	0.744	1.665	1.732
	Hi-Lo=0.074 Avg=0.955	Hi-Lo=0.113 Avg=0.780	Hi-Lo=0.391 Avg=1.643	Hi-Lo=0.359 Avg=1.871
DN-3	0.912	0.776	1.672	2.116
	0.929	0.810	2.208	1.994
	0.916	0.756	1.507	2.131
	0.928	0.770	2.152	1.950
	0.890		2.008	
	Hi-Lo=0.039 Avg=0.915	Hi-Lo=0.054 Avg=0.778	Hi-Lo=0.701 Avg=1.909	Hi-Lo=0.181 Avg=2.025
DN-4	1.051	0.838	2.252	1.924
	1.066	0.765	1.965	1.734
	1.007	0.784	2.040	1.797
	1.068	0.809	1.932	2.035
	0.969	0.752	1.868	1.904
	Hi-Lo=0.099 Avg=1.032	Hi-Lo=0.086 Avg=0.790	Hi-Lo=0.385 Avg=2.011	Hi-Lo=0.301 Avg=1.879
DN-5	0.8043	0.9474	1.634	1.378
	0.8313	0.9455	1.584	1.149
	0.8683	0.9034	1.766	1.421
	0.8593	0.8702	1.545	1.426
	Hi-Lo=0.0640 Avg=0.8408	Hi-Lo=0.0772 Avg=0.917	Hi-Lo=0.221 Avg=1.632	Hi-Lo=0.275 Avg=1.344

the determination of loose and compressed densities after washing and then drying at 100 and 300°C. Portions of each of the solid products were dried at 105°C to constant weight, then washed three times with distilled water, and dried again at 105°C to constant weight. Another portion of each was heated to 300°C to constant weight and the same washing procedure followed. The samples were then tested for loose-packed and compressed density after drying at both 105 and 300°C. The average loose-packed densities for the 4 runs dried at 105°C were 0.937, 0.955, 0.915, and 1.032 g/cm^3, while the compressed densities were 1.706, 1.643, 1.909, and 2.011 g/cm^3 for DN-1—DN-4, respectively. The loose-packed densities after heating at 300°C were 0.778, 0.780, 0.778, and 0.790, while the compressed densities were 1.754, 1.871, 2.025, and 1.879, respectively. The compressed densities were measured on pellets using 5% stearic acid as a lubricant/ binder. The weight loss upon drying at 300°C was very consistent for each sample at 29%. This is slightly less than was obtained in a TGA/DTA analysis of samples of DN-3 and DN-4 (see Appendix D for the TGA/DTA recordings), which showed a 36% weight loss upon heating to 800°C, but compares favorably with the 30% loss as the temperature passed through 300°C.

5.6.2 Product Washing: Nitrate and Tracer Washout

The washes of the solids from runs 3 and 4, which were carried to completion, showed very little nitrate present, as would be expected from the ammonia trapped during the reaction. The washes from the product solids from the first two runs had very large amounts of nitrate remaining in the solids. These results are shown in Table 10.

Additional calculations were made to determine the final volumes of the various waste forms versus the starting volumes of liquid nitrate solutions. In runs 1 and 2, using the 6.2 *M* $NaNO_3$ solutions, 200 mL of starting liquid and 90 g aluminum (33 mL at 2.7 g/cm^3) produced about 320 g of damp filter cake. After drying at 100 and 300°C, the densities were 0.94 and 0.78, respectively, for a volume of 290 mL and 250 mL loose. The volumes after compaction were 117 and 101 mL, respectively, for the solids heated to 300°C. That is a 42% and a 50% volume reduction, respectively. Runs 3 and 4 produced 90.6 and 100 mL compacted volumes, respectively, for 200 mL of 3.1 *M* $NaNO_3$ feed and 85 and 80 g of Al, respectively. This is a 55% and a 50% volume reduction, respectively.

Table 10. Nitrate analytical results for runs DN-1—DN-5

Sample	Absorb.	Dilution	N (ppm)	NO_3 (ppm)	NO_3 (g)	NO_3 on 50 g solids	Total NO_3 on solids	76.9 g measured
Feed	1.134	20,000	86,842.16	384,430				
DN1 W1	1.044	100	399.28	1,767.53	0.1361	0.1733	0.945	65.089 g NO_3 acct for 84.66% acct for
DN1 W2	0.901	20	68.77	304.43	0.031052			
DN1 W3	0.406	10	15.20	67.28	0.006122			
DN2 W1	0.320	1020	1,210.20	5,357.32	0.431264	0.5195	2.777	68.55 g NO_3 acct for 89.15% acct for
DN2 W2	0.963	50	183.94	814.27	0.074099			
DN2 W3	0.853	10	32.52	143.98	0.01411			
DN3 W1	0.554	20	41.87	185.35	0.014272	0.0158	0.082	36.52 g NO_3 acct for 95.22% acct for
DN3 W2	0.047	20	2.57	11.36	0.001071			
DN3 W3	0.041	10	1.05	4.65	0.000462			
DN4 W1	0.218	20	1.13	4.99	0.000389	0.0008	0.004	38.032 g NO_3 acct for 98.941% acct for
DN4 W2	0.129	20	0.67	2.95	0.000264			
DN4 W3	0.142	10	0.37	1.63	0.000145			
DN5(1) W1	0.233	500	419	1,853	0.1853			17.43 g reacted
DN5(1) W2	0.190	100	67.25	198	0.0198			
DN5(1) W3	0.320	10	11.7	52	0.0052	0.2103	0.555	
DN5(2) W1	0.571	1	2.1	9.4	0.00038			
DN5(2) W2	1.776	2	13.5	60	0.0024			
DN5(2) W3	0.323	2	2.4	10.5	0.00042	0.0032	0.0053	
5-Filt, 1st	1.598	500	3,029.70	13,411.86	1.542			
5-Filt, 2nd	0.147	250	126.99	562.16	0.157			

If one could densify to the theoretical Al_2O_3 density of 3.6 g/cm^3, these volumes would be 57, 53, 51, and 52 mL, respectively, for runs 1—4, approximately a 75% volume reduction for the four runs. There is not an appreciable difference in the solids volumes produced for the 6.2 or 3.1 M $NaNO_3$ feeds when the same amount of aluminum is used.

5.7 CONCEPTUAL DESIGN AND COST ESTIMATE

A preliminary design for a plant to reduce the nitrate in the Hanford SSTs was completed, and the costs associated with construction and operation were estimated. The analysis and cost estimates, along with the assumptions used in the evaluation and a conceptual design drawing, are given in detail in Appendixes B and C. The cost estimate assumes a batch, single-stage stirred tank-type reactor capable of removing 8500 kW of heat, processing only the current tank inventory of 125,000 t NO_3, around the clock processing at a 60% availability over 20 years, and a resulting 1200-kg NO_3/h rate.

Conclusions from this assessment are: (1) the NAC process is feasible and competitive with other processes for removing nitrates, (2) the reactor design is crucial because of the multiphase exothermic reaction, and (3) the waste/product streams are readily handled. The capital cost for this system was estimated at $20,200,000 in FY 92 fourth-quarter dollars. Operating costs over the 20-year life of the plant were estimated to be $2.01 to $2.66/kg NO_3 destroyed, depending on the aluminum requirement, with the lower value signifying the stoichiometric aluminum to nitrate ratio, and the higher value, the results of experimental work when the nitrate was reduced to ppm levels. As can be seen in the Appendix B estimate, 56% of the operating cost is due to aluminum, assuming that aluminum is available at $0.88/kg, as scrap. This compares to new aluminum powder at $3.60/kg, which would raise operating costs accordingly from $2.01— $2.66/kg NO_3 to $4.50—$7.29/kg NO_3, depending on the aluminum efficiency. This compares to published literature costs for the electrolytic process and thermal process in 1957 of $5.13/kg of nitrate.

The bench-scale tests and the overall process were carefully appraised to identify any potential flaw in the process. No serious problems were discovered, although the highly exothermic nature of the reactions and the solids handling elements of the process present a challenging design task. The reactor system is large but reasonable, given the size of the nitrate waste stream to be treated, yielding a 10,000-gal (37,800-L) vessel with its associated mixing and heat-exchange equipment. In addition, a rotary vacuum dryer and a calciner for the solid product are required, and a catalytic burner to convert the ammonia and hydrogen produced to nitrogen and water vapor is shown for handling the reaction products. The raw materials required include ~45,400 kg/d of aluminum metal, 2000 L/d of 50% sodium hydroxide, and 283.2 m^3/min of air for the catalytic ammonia burner.

6. CONCLUSIONS

The experimental results obtained to date confirm that the NAC process will reduce nitrate present in Hanford aqueous sodium nitrate-based waste to ammonia, hydrated alumina "gibbsite" (96%), and solid sodium aluminate (4%). The reaction is exothermic and requires cooling to control the reactor temperature when a pure solution of sodium nitrate, representing sludge-free supernate, is used. Upon using a motorized auger to feed aluminum powder to an ethylene glycol-cooled batch reactor, we have shown that the reaction can be easily controlled at temperatures between 50 to 60°C.

When the Hanford surrogate containing the solid sludge and salt cake waste mixture was used as a starting material, the rate of heat production was substantially reduced and the need for cooling was diminished. Using sludge-free supernate at concentrations of 6.2 and 3.1 *M* sodium nitrate, 85—99% of the nitrate present could be converted to ammonia, primarily dependent upon the ability of the mixing system in the reactor to stir the solid/liquid slurry. When more dilute slurries were used, more complete reactions at higher reaction rates could be achieved due to better mixing and therefore better heat transfer as well.

The method of feeding the fine, dry aluminum powder into the reactor tended to cause problems as the reaction neared completion. When the slurry was too thick, foaming occurred as the gas produced in the reaction had trouble escaping. The resulting foam caused the aluminum feed tube to plug, and the reaction had to be curtailed. An alternate feeding method that proved successful on a smaller scale, and is planned for the future continuous reaction tests, used a feed of the aluminum as a slurry of aluminum powder and distilled water using a peristaltic pump to meter the aluminum to the reactor. This has the advantage of adding needed water to the reactor to replace the water taken up as the aluminum reacts to form crystalline oxide.

Addition of the aluminum to the reactor as larger particles reduced the problems encountered with the fine, dry powder feed by preventing caking in the feed tube. The larger particles of aluminum also reacted more slowly than the fine powders and required less cooling and temperature control.

The reaction rates for the various experiments were calculated to give a rough idea of what might be expected for a pilot plant design. The rates were based upon a differential nitrate reduction at a point in the reaction where nitrate was being actively reduced, usually at a point when between 70 and 150% of the theoretical amount of aluminum had been added. These rates were between 80 and 300 g $NaNO_3$ L^{-1} of starting reactor volume h^{-1}. Based upon these numbers, a preliminary estimate for a full-size plant to treat the Hanford SST waste at 1200 kg NO_3/h over a 20-year period was made. The estimate and its assumptions are presented in Appendices A and B.

The cost estimate for a full-scale nitrate processing plant assumes a batch reactor with the unit costs to process the Hanford waste nitrate over 20 years found to be between $2.01 and $2.66/kg of nitrate when aluminum is obtained as scrap. Purchased aluminum drives the cost up and makes reaction efficiency most important. The operating cost compares to published literature costs for the electrolytic process and thermal process in 1957 of $ 5.13/kg nitrate. No fatal flaws in the process were discovered.

Results of this study have shown that the product exiting the reactor can be uniaxially pressed as any other ceramic to result in a 55% volume reduction, compared to the starting volume of the original waste solution, for either 6.2 or 3.1 *M* $NaNO_3$. All the water associated with the waste solution is consumed by the aluminum to form oxide,and more must be added for this purpose, as well as for efficient mixing and heat transfer. Indications are that we may still be able to obtain a greater volume reduction and sinter the product into a dense ceramic waste form. Work next year will include the addition of fine silica (5 μm) to the reactor along with aluminum so as to form a low-temperature sintering ceramic which ties up any residual sodium as is present in the sodium aluminate component of the product.

We have also shown that ^{137}Cs and ^{99}Tc do not enter the insoluble reactor product, and some ^{60}Co that was present was also not fixed as insoluble aluminate "spinels"; this may have been due to stable organic complexation of the cobalt, for cobalt is known to form an insoluble spinel. Strontium 85 and ^{144}Ce (stand-in for plutonium) reported to the solid product and could not be washed out. It is well known that the aluminate component of our product will form highly insoluble spinels with most metal and nonmetal cations on the periodic table, an additional useful property of aluminum and its chemistry.

The relatively simple technology described in this report is based on the use of the aluminum metal reduction of nitrate to ammonia and ceramic (NAC), and based on research to date, is best suited for use with alkaline, sludge-free supernates. The use of supernates with tank sludges in slurry form as feeds to the NAC process appears feasible as long as the slurry is dilute enough and the solids are crushed enough to be maintained in suspension by the agitation present. The effective treatment of the Hanford nitrate-based wastes is dependent upon the development of simple and effective technologies such as described in this feasibility study. Continued work in FY 93 will focus upon achieving greater volume reductions (approaching 75%) and forming silica-alumina-based ceramics for waste form testing studies by adding fine silica to the denitration reactor along with the aluminum metal.

7. RECOMMENDATIONS

The experimental results obtained during this period have answered many of the questions concerning the "NAC" process and its applicability to the Hanford SST nitrate waste. Many more questions remain to be answered before a pilot- or full-size plant can be built. Some of the major issues are:

1. Reduce the amount of aluminum required to react with the nitrate present to closer to the theoretical amount. Currently, 1.5—1.8 times theoretical amount has been required for nitrate reduction to very low nitrate levels (low ppm range).

2. Determine the design and operational parameters for the future pilot plant. This includes the size and type of reactor, such as batch or continuous, and whether it is single or multistage. The method of feeding aluminum and type of aluminum required need to be resolved. Also to be decided is whether other materials (e.g., for sodium fixation) can be efficiently utilized.

3. Determine the maximum acceptable amount of nitrate in the waste form, if any. This will define the extent of the nitrate reduction required in the reaction to meet that limit.

4. Determine the characteristics and acceptability of the ceramic waste form resulting from the NAC process. This would include leachability studies on the various possible solid forms for the leaching of any remaining nitrate, radioelements, and RCRA hazardous metals. Also required are the structural and physical properties of the various ceramic waste forms and the processing steps necessary to produce them, such as pressing and heating to various temperatures.

5. Ascertain the fate of the total sodium present, and how best to control its form. This may require the addition of other minerals, such as silica, to tie up the sodium in molecular compounds or in solid solutions which are not leachable.

6. Determine the operability of the reaction system and the characteristics of the solids produced using an actual "hot" supernate, under proposed processing conditions, from the LLW waste storage tanks at ORNL.

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APPENDIXES

APPENDIX A. X-RAY DIFFRACTION SPECTRA OF REACTOR PRODUCT

The following X-ray diffraction spectra were obtained on a selected product from the denitrification of a 3.1 *M* sodium nitrate solution using aluminum powder and carried to completion. The nitrate remaining was in the low-ppm range in the liquid product. Results of the scans are presented. The scans show the analysis of the product produced in run DN-3. Scans of sodium aluminate and gibbsite standards are also shown for comparison.

Table A-1. Summary of the X-ray scan peaks for sample No. DN-3-1PSTI

```
 PEAKLISTER SUMMARY:
 -------------------

FILENAME> CT1450C               STEP> 0.020    WAVELENGTH> 1.540600
SAMPLE IDENT> AL-OXIDE #DN-3-1PSTI                    CORRECTION> NONE


      BEST       BEST     PK-TOP   PK-TOP                 REL   FWHM
### 2-THETA       D       (CPM)    (CPS)    PK-AREA  C1  INT   (DEG)  H   K   L   C2
--- --------  ---------  -------  -------  --------- --  ---  ------  --  --  --  --

  1  18.3666   4.82663   192420   3207.0    78621.6 DC 100   0.243   0   0   0
  2  18.7640   4.72530    29640    494.0    18228.9 DC  15   0.108   0   0   0
  3  20.2951   4.37215   116160   1936.0    31660.4 DC  60   0.153   0   0   0
  4  20.5076   4.32730    49980    833.0    15711.2 DC  25   0.151   0   0   0
  5  26.5158   3.35885     7320    122.0     2836.7 DC   3   0.131   0   0   0
  6  26.9005   3.31168    12540    209.0     6095.4 DC   6   0.173   0   0   0
  7  27.5234   3.23813     6300    105.0     8000.6 DC   3   0.536   0   0   0
  8  27.8183   3.20447     6480    108.0     5672.8 DC   3   0.400   0   0   0
  9  27.9935   3.18481     7800    130.0     3101.8 DC   4   0.193   0   0   0
 10  28.7201   3.10586     3900     65.0     2216.9 DC   2   0.192   0   0   0
 11  32.3504   2.76514     7920    132.0     3890.8 DC   4   0.300   0   0   0
 12  33.1507   2.70019     1920     32.0     3182.5 DC   0   0.122   0   0   0
 13  33.3644   2.68338     2400     40.0      982.2 DC   1   0.147   0   0   0
 14  33.5767   2.66690     4680     78.0     1758.2 DC   2   0.166   0   0   0
 15  36.4098   2.46562    11880    198.0     8744.7 DC   6   0.423   0   0   0
 16  36.6273   2.45148    12180    203.0     2656.6 DC   6   0.133   0   0   0
 17  37.0968   2.42152     4740     79.0     1671.6 DC   2   0.130   0   0   0
 18  37.6978   2.38429    22260    371.0    27373.7 DC  11   0.433   0   0   0
 19  39.3279   2.28913     4920     82.0     3986.1 DC   2   0.232   0   0   0
 20  40.1677   2.24319    11340    189.0     6213.7 DC   5   0.326   0   0   0
 21  40.5708   2.22183    15000    250.0     9926.1 DC   7   0.283   0   0   0
 22  41.6658   2.16593     8160    136.0     5323.3 DC   4   0.322   0   0   0
 23  43.5276   2.07751     1440     24.0     1311.3 DC   0   0.329   0   0   0
 24  43.8419   2.06334     3360     56.0     2330.6 DC   1   0.226   0   0   0
 25  44.1803   2.04832    15180    253.0     9154.7 DC   7   0.198   0   0   0
 26  45.4304   1.99482     9180    153.0     5490.1 DC   4   0.260   0   0   0
 27  46.1815   1.96410     1620     27.0      405.0 DC   0   0.144   0   0   0
 28  47.3482   1.91839     6660    111.0     3603.6 DC   3   0.281   0   0   0
 29  50.5372   1.80456     9420    157.0     1927.0 PF   4   0.160   0   0   0
 30  50.8922   1.79281     1380     23.0      253.0 PF   0   0.140   0   0   0
 31  52.2147   1.75047    11280    188.0     2308.0 PF   5   0.060   0   0   0
 32  53.1512   1.72181     6120    102.0     1258.0 PF   3   0.100   0   0   0
 33  53.4725   1.71222     1680     28.0      130.0 PF   0   0.140   0   0   0
 34  53.9603   1.69789     1380     23.0      108.0 PF   0   0.040   0   0   0
 35  54.3928   1.68540     7620    127.0     1558.0 PF   3   0.100   0   0   0
 36  55.3587   1.65826     2640     44.0      481.0 PF   1   0.120   0   0   0
 37  55.8475   1.64490     2820     47.0      435.0 PF   1   0.160   0   0   0
 38  56.1766   1.63604     2040     34.0      420.0 PF   1   0.160   0   0   0
 39  57.1300   1.61098     1500     25.0      277.0 PF   0   0.160   0   0   0
 40  57.4797   1.60201     1380     23.0      182.0 PF   0   0.160   0   0   0
 41  57.8781   1.59193     1740     29.0      312.0 PF   0   0.060   0   0   0
 42  58.1447   1.58526     1860     31.0      243.0 PF   0   0.100   0   0   0
 43  58.5947   1.57415     4320     72.0      891.0 PF   2   0.160   0   0   0
 44  61.4022   1.50874     1440     24.0      257.0 PF   0   0.120   0   0   0
 45  63.7719   1.45827    19560    326.0     4003.5 PF  10   0.080   0   0   0
 46  64.6038   1.44148     7860    131.0     1616.3 PF   4   0.100   0   0   0
 47  66.1381   1.41171     5820     97.0     1196.6 PF   3   0.080   0   0   0
 48  66.6191   1.40268     4500     75.0      931.1 PF   2   0.160   0   0   0
 49  67.0181   1.39530     1740     29.0      362.0 PF   0   0.160   0   0   0
 50  67.1644   1.39261     1680     28.0      265.0 PF   0   0.120   0   0   0
 51  68.8178   1.36313     2700     45.0      489.0 PF   1   0.160   0   0   0
 52  69.3181   1.35451     1980     33.0      253.0 PF   1   0.160   0   0   0
 53   0.3600   1.33698     2460     41.0      126.0 PF   1   0.160   0   0   0
 54  70.6591   1.33206     4140     69.0      850.0 PF   2   0.020   0   0   0
 55  71.0231   1.32612     1380     23.0      217.0 PF   0   0.100   0   0   0
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Table A-1 (continued)

```
 56  71.3056   1.32156    1380     23.0      106.0 PF   0  0.120  0  0  0
 57  71.4541   1.31918    1680     28.0      265.0 PF   0  0.160  0  0  0
 58  71.5147   1.31821    1560     26.0      323.0 PF   0  0.140  0  0  0
 59  74.7738   1.26862    1260     21.0       98.0 PF   0  0.160  0  0  0
 60  75.8428   1.25338    1740     29.0      365.0 PF   0  0.160  0  0  0
 61  76.1834   1.24862    1200     20.0      128.0 PF   0  0.040  0  0  0
 62  78.5650   1.21663    2520     42.0      519.0 PF   1  0.160  0  0  0
 63  78.8519   1.21292    2640     44.0      551.0 PF   1  0.040  0  0  0
 64  81.5344   1.17966    1380     23.0      286.0 PF   0  0.040  0  0  0
 65  84.6144   1.14440    1320     22.0      244.0 PF   0  0.120  0  0  0
 66  86.5953   1.12323    1800     30.0      138.8 PF   0  0.140  0  0  0
 67  86.7000   1.12214    1320     22.0       68.3 PF   0  0.160  0  0  0
 68  86.8000   1.12111    1260     21.0      267.6 PF   0  0.160  0  0  0

 CORRECTIONS HISTORY:

    ORIGINAL  CORRECT   DELTA                                          CSIZE
### 2-THETA   2-THETA   2-THETA  PROGRAM OF ORIGIN  INTERNAL STD        (A)   C3
--- --------  --------  -------  ----------------   --------------     -----  --

  1   0.0000   18.3666  0.00000  PROFILE FITTING
  2   0.0000   18.7640  0.00000  PROFILE FITTING
  3   0.0000   20.2951  0.00000  PROFILE FITTING
  4   0.0000   20.5076  0.00000  PROFILE FITTING
  5   0.0000   26.5158  0.00000  PROFILE FITTING
  6   0.0000   26.9005  0.00000  PROFILE FITTING
  7   0.0000   27.5234  0.00000  PROFILE FITTING
  8   0.0000   27.8183  0.00000  PROFILE FITTING
  9   0.0000   27.9935  0.00000  PROFILE FITTING
 10   0.0000   28.7201  0.00000  PROFILE FITTING
 11   0.0000   32.3504  0.00000  PROFILE FITTING
 12   0.0000   33.1507  0.00000  PROFILE FITTING
 13   0.0000   33.3644  0.00000  PROFILE FITTING
 14   0.0000   33.5767  0.00000  PROFILE FITTING
 15   0.0000   36.4098  0.00000  PROFILE FITTING
 16   0.0000   36.6273  0.00000  PROFILE FITTING
 17   0.0000   37.0968  0.00000  PROFILE FITTING
 18   0.0000   37.6978  0.00000  PROFILE FITTING
 19   0.0000   39.3279  0.00000  PROFILE FITTING
 20   0.0000   40.1677  0.00000  PROFILE FITTING
 21   0.0000   40.5708  0.00000  PROFILE FITTING
 22   0.0000   41.6658  0.00000  PROFILE FITTING
 23   0.0000   43.5276  0.00000  PROFILE FITTING
 24   0.0000   43.8419  0.00000  PROFILE FITTING
 25   0.0000   44.1803  0.00000  PROFILE FITTING
 26   0.0000   45.4304  0.00000  PROFILE FITTING
 27   0.0000   46.1815  0.00000  PROFILE FITTING
 28   0.0000   47.3482  0.00000  PROFILE FITTING
 29  50.5372   50.5372  0.00000  PEAKFINDER
 30  50.8922   50.8922  0.00000  PEAKFINDER
 31  52.2147   52.2147  0.00000  PEAKFINDER
 32  53.1512   53.1512  0.00000  PEAKFINDER
 33  53.4725   53.4725  0.00000  PEAKFINDER
 34  53.9603   53.9603  0.00000  PEAKFINDER
 35  54.3928   54.3928  0.00000  PEAKFINDER
 36  55.3587   55.3587  0.00000  PEAKFINDER
 37  55.8475   55.8475  0.00000  PEAKFINDER
 38  56.1766   56.1766  0.00000  PEAKFINDER
 39  57.1300   57.1300  0.00000  PEAKFINDER
 40  57.4797   57.4797  0.00000  PEAKFINDER
 41  57.8781   57.8781  0.00000  PEAKFINDER
 42  58.1447   58.1447  0.00000  PEAKFINDER
 43  58.5947   58.5947  0.00000  PEAKFINDER
 44  61.4022   61.4022  0.00000  PEAKFINDER
 45  63.7719   63.7719  0.00000  PEAKFINDER
 46  64.6038   64.6038  0.00000  PEAKFINDER
```

Table A-2. Aluminum hydroxide (gibbsite) standard

```
29-1165    JCPDS-ICDD Copyright (c) 1991    Radiation:  1.54050  Quality: i
------------------------------------------------------------------------------------------------------------------------------
|                                                                                        |  d A    | Int.|      h k l        |
| Na Al O |6H O                                                                         |---------+-----+-------------------|
|   2  2 4   2                                                                          |         |     |                   |
|                                                                                        | 5.7     | <5  |    0  0  2        |
| Sodium Aluminum Oxide Hydrate                                                         | 5.26    | 20  |    2  0  0        |
|                                                                                        | 4.78    | 100 |    2  0  1        |
|                                                                                        | 4.71    | 100 |    2  1  0        |
|- --------------------------------------------------------------------------------------| 4.52    | 10  |    1  1  2        |
| Rad:            Lambda:                  Filter:                d-sp:                 |         |     |                   |
| Cutoff:         Int: Visual              I/Icor:                                       | 4.35    | 70  |    2  1  1        |
| Ref: Elliot, A., Huggins, J. Am. Ceram. Soc., 58 497 (1975)                           | 3.19    | 15  |    3  1  1        |
|                                                                                        | 2.83    | 10  |    3  2  1        |
|----------------------------------------------------------------------------------------| 2.75    | 90  |    1  0  4        |
| Sys: Tetragonal              S.G.:                                                    | 2.66    | 60  |    2  2  3        |
| a: 10.53          b:                  c: 11.40         A:             C: 1.0826      |         |     |                   |
| A:                B:                  C:               Z:             mp:            | 2.57    | 10  |    4  0  1        |
| Ref: Ibid.                                                                            | 2.48    | 15  |    3  3  0        |
|                                                                                        | 2.42    | 15  |    3  3  1        |
| Dx:            Dm:           SS/FOM: F(22)=5.5(0.033,120)                             | 2.35    | 70  |    4  2  0        |
|----------------------------------------------------------------------------------------| 2.23    | 70  |    1  0  5        |
| ea:               nwB:              ey:              Sign:      2V:                   |         |     |                   |
| Ref:                                                                                  | 2.21    | 20  |    3  0  4        |
|                                                                                        | 2.07    | 5   |    4  3  1        |
|----------------------------------------------------------------------------------------| 2.05    | 15  |    2  1  5        |
| Mwt: 272.03.  Volume[CD]: 1264.04.                                                    | 2.00    | 30  |    4  2  3        |
|                                                                                        | 1.93    | 15  |    5  2  1        |
|                                                                                        |         |     |                   |
|                                                                                        | 1.72    | 30  |    5  3  2        |
|                                                                                        | 1.61    | 10  |    1  0  7        |
|                                                                                        |         |     |                   |
|                                                                                        |         |     |                   |
|                                                                                        |         |     |                   |
|                                                                                        |         |     |                   |
|                                                                                        |         |     |                   |
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this job was run by OBC1
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Table A-3. Sodium aluminum oxide hydrate (sodium aluminate) standard

```
33-18      JCPDS-ICDD Copyright (c) 1991    Radiation:  1.54050  Quality: i
--------------------------------------------------------------------------------------------------------------
|                                                                   |   d A    | Int.|          h k l          |
| Al(OH)                                                            |----------+-----+-------------------------|
|      3                                                            |          |     |                         |
|                                                                   |  4.8486  | 100 |          0  0  2        |
| Aluminum Hydroxide                                                |  4.3711  |  70 |          1  1  0        |
|                                                                   |  4.3187  |  50 |          2  0  0        |
| Gibbsite, syn                                                     |  3.3590  |  17 |          2  0 -2        |
|-------------------------------------------------------------------|  3.3122  |  30 |          1  1 -2        |
| Rad: CuKa1      Lambda: 1.54060        Filter:            d-sp: Diff.        |     |                         |
| Cutoff:         Int: Diffractometer    I/Icor: 1.0                |  3.1829  |  25 |          1  1  2        |
| Ref: Cisar, A., Poulsen, K., Dow Chemical Company, Freeport, Texas, USA., JCPDS  |  3.1054  |  13 |          1  0 -3        |
| Grant-in-Aid Report, (1979)                                       |  2.4658  |  25 |          3  1 -1        |
|-------------------------------------------------------------------|  2.4522  |  40 |          0  2  1        |
| Sys: Monoclinic            S.G.: P21/n (14)                       |  2.4224  |  15 |          0  0  4        |
| a: 8.6552       b: 5.0722        c: 9.7161        A:        C:    |          |     |                         |
| A:              B: 94.607        C:               Z:  8     mp:   |  2.3851  |  55 |          3  1  1        |
| Ref: Ibid.                                                        |  2.3471  |   4 |          1  2  1        |
|                                                                   |  2.2899  |  15 |          3  1 -2        |
| Dx:  2.44     Dm:  2.40     SS/FOM: F(30)=10.2(0.025,116)         |  2.2464  |  20 |          0  2  2        |
|-------------------------------------------------------------------|  2.1924  |   2 |          1  2 -2        |
| ea: 1.577       nwB: 1.577       ey: 1.595       Sign: +    2V:   |          |     |                         |
| Ref: Dana's System of Mineralogy, 7th Ed., 2 663                  |  2.1647  |  27 |          3  1  2        |
|                                                                   |  2.0845  |   4 |          1  1  4        |
|-------------------------------------------------------------------|  2.0489  |  40 |          3  1 -3        |
| Color: White                                                      |  2.0234  |   3 |          2  2 -2        |
| Sample of reagent grade chemical from Matheson, Coleman, and Bell.  Optical data  |  1.9944  |  28 |          0  2  3        |
| on artificial material; measured density on crystals.  C.D. Cell: a=9.716,       |          |     |                         |
| b=5.072, c=8.655, beta=94.61, a/b=1.9156, c/b=1.7064.  PSC: mP56.  To replace    |  1.9637  |   6 |  1  2 -3,    2  2  2    |
| 12-460.  Mwt: 78.00.  Volume[CD]: 425.17.                         |  1.8042  |  30 |          3  2 -2        |
|                                                                   |  1.7517  |  30 |          0  2  4        |
|                                                                   |  1.7365  |   4 |          1  2 -4        |
|                                                                   |  1.6974  |   4 |          1  2  4        |
|                                                                   |          |     |                         |
|                                                                   |          |     |                         |
|                                                                   |          |     |                         |
--------------------------------------------------------------------------------------------------------------

------------------------------------------------------------------------------------------------------
|   d A    | Int.|          h k l         |   d A    | Int.|         h k l          |   d A    | Int.|         h k l         |
|----------+-----+------------------------+----------+-----+------------------------+----------+-----+-----------------------|
|          |     |                        |          |     |                        |          |     |                       |
| 1.6845   |  30 |        3  1  4         | 1.4021   |  13 |        3  1 -6         | 1.1791   |   4 |        1  1 -8        |
| 1.6576   |   9 |  1  3  0,    2  2 -4   | 1.3808   |   6 |        3  3  2         | 1.1452   |   4 |        6  2 -4        |
| 1.5926   |   7 |        4  1 -4         | 1.3620   |  10 |        0  2 -6         | 1.0933   |   3 |        4  4  0        |
| 1.5865   |   7 |        3  1 -5         | 1.3311   |   7 |        1  2  6         | 1.0826   |   4 |        6  3 -2        |
| 1.5739   |   8 |  5  0 -3,    2  3  0   | 1.3247   |   4 |        2  2 -6         |          |     |                       |
|          |     |                        |          |     |                        |          |     |                       |
| 1.5525   |   3 |        2  0 -6         | 1.2999   |   3 |        4  1 -6         |          |     |                       |
| 1.4846   |   4 |  2  1 -6,    2  3  2   | 1.2316   |   3 |        6  2 -2         |          |     |                       |
| 1.4577   |  30 |  3  2  4,    3  3  0   | 1.2267   |   2 |        3  3  4         |          |     |                       |
| 1.4405   |  18 |        4  1 -5         | 1.2160   |   6 |  4  2  5,    2  4  0   |          |     |                       |
| 1.4115   |  19 |        3  3 -2         | 1.2116   |   7 |        1  4  2         |          |     |                       |
------------------------------------------------------------------------------------------------------

this job was run by OBC1
```

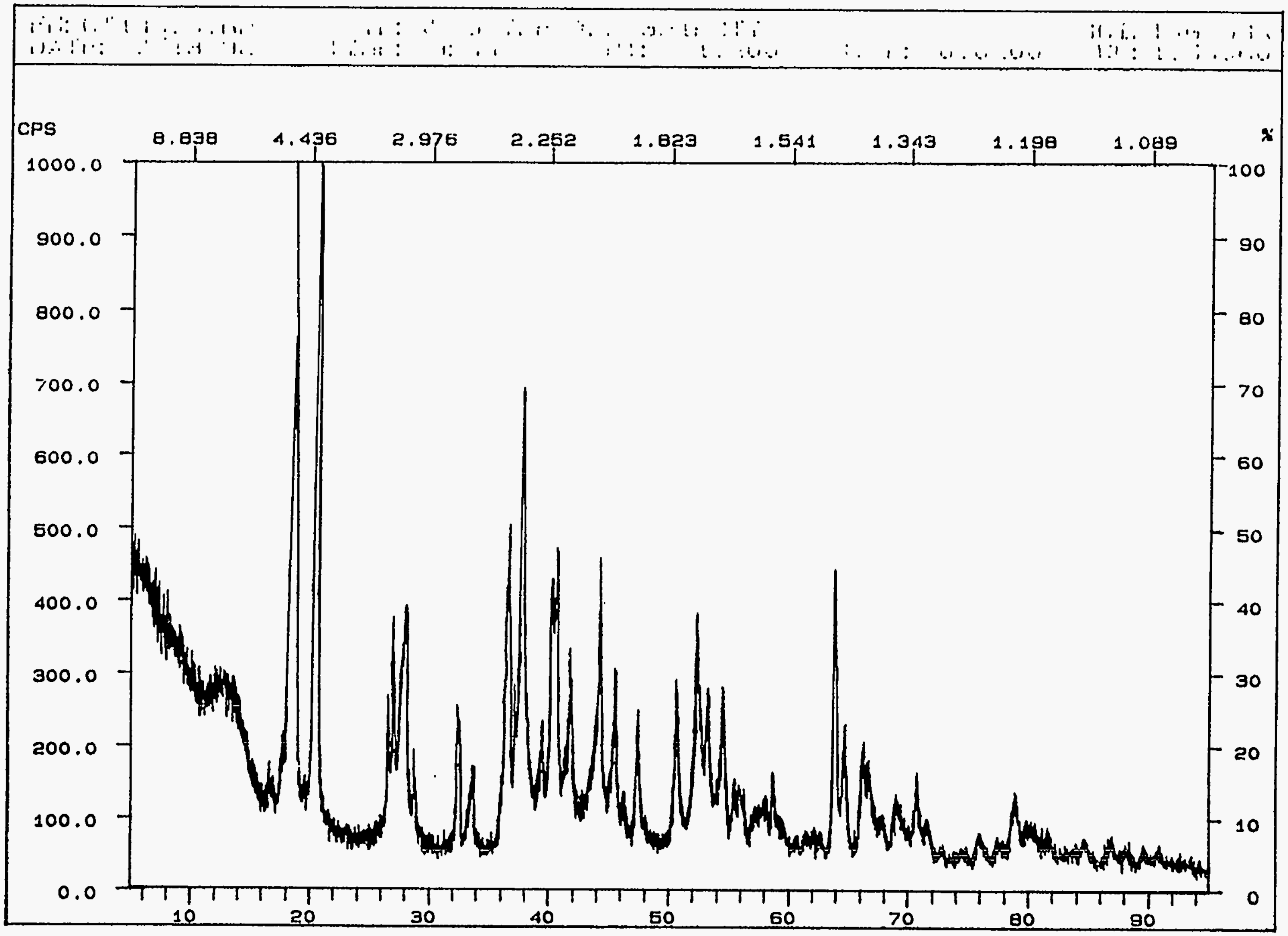


Fig. A-1. Scan of sample No. DN-3-1PSTI.

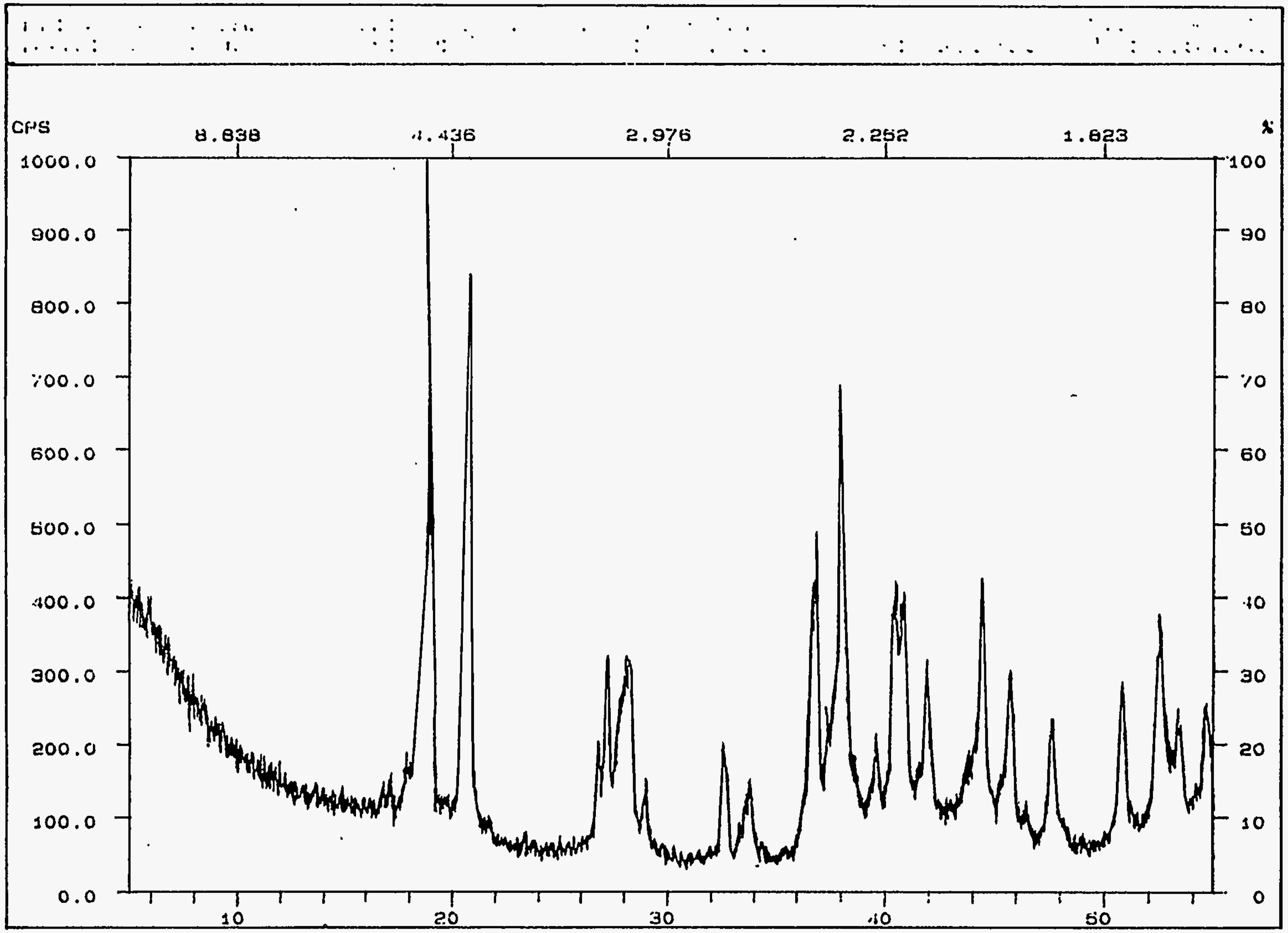


Fig. A-2. Expanded scan of sample No. DN-3-1PSTL.

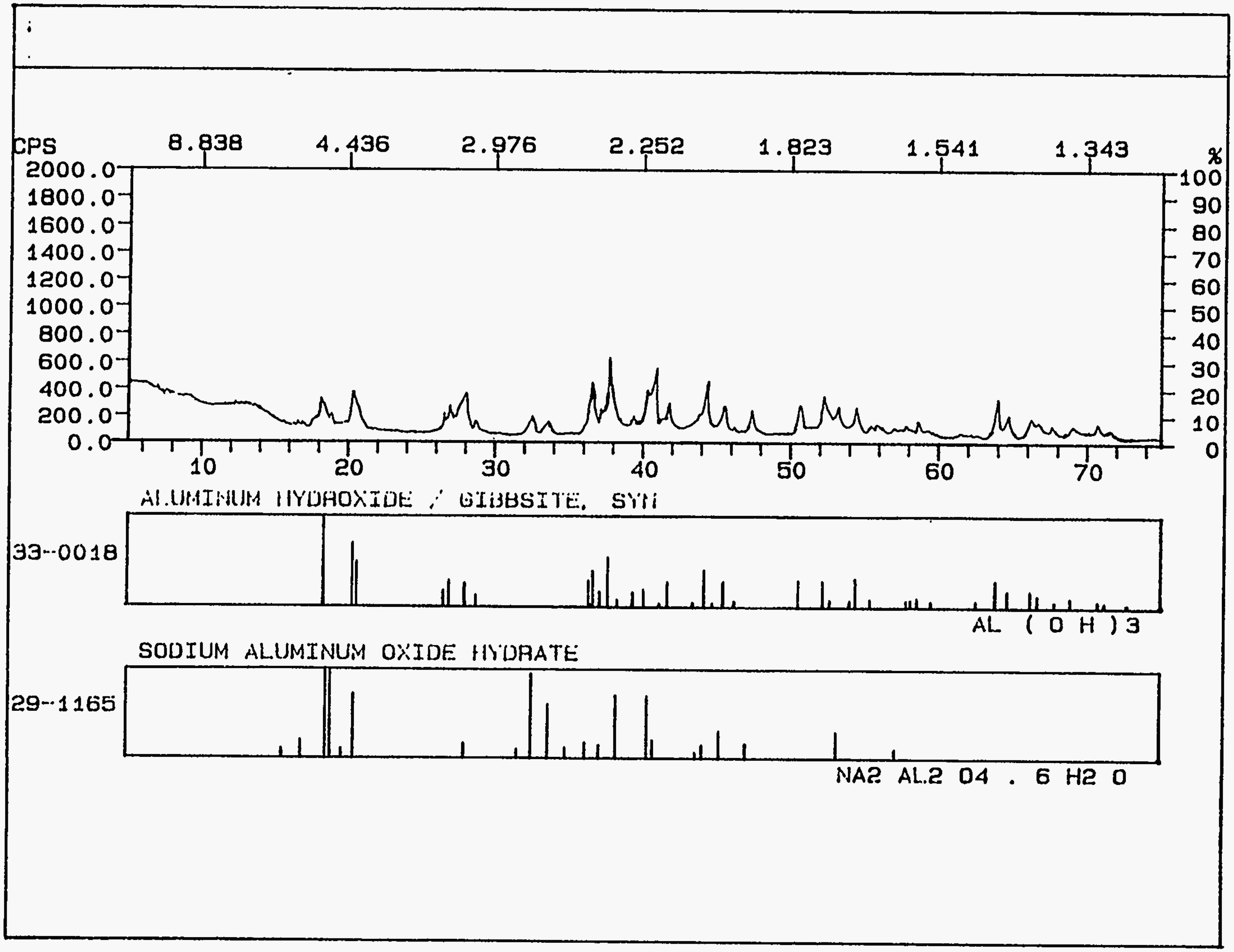
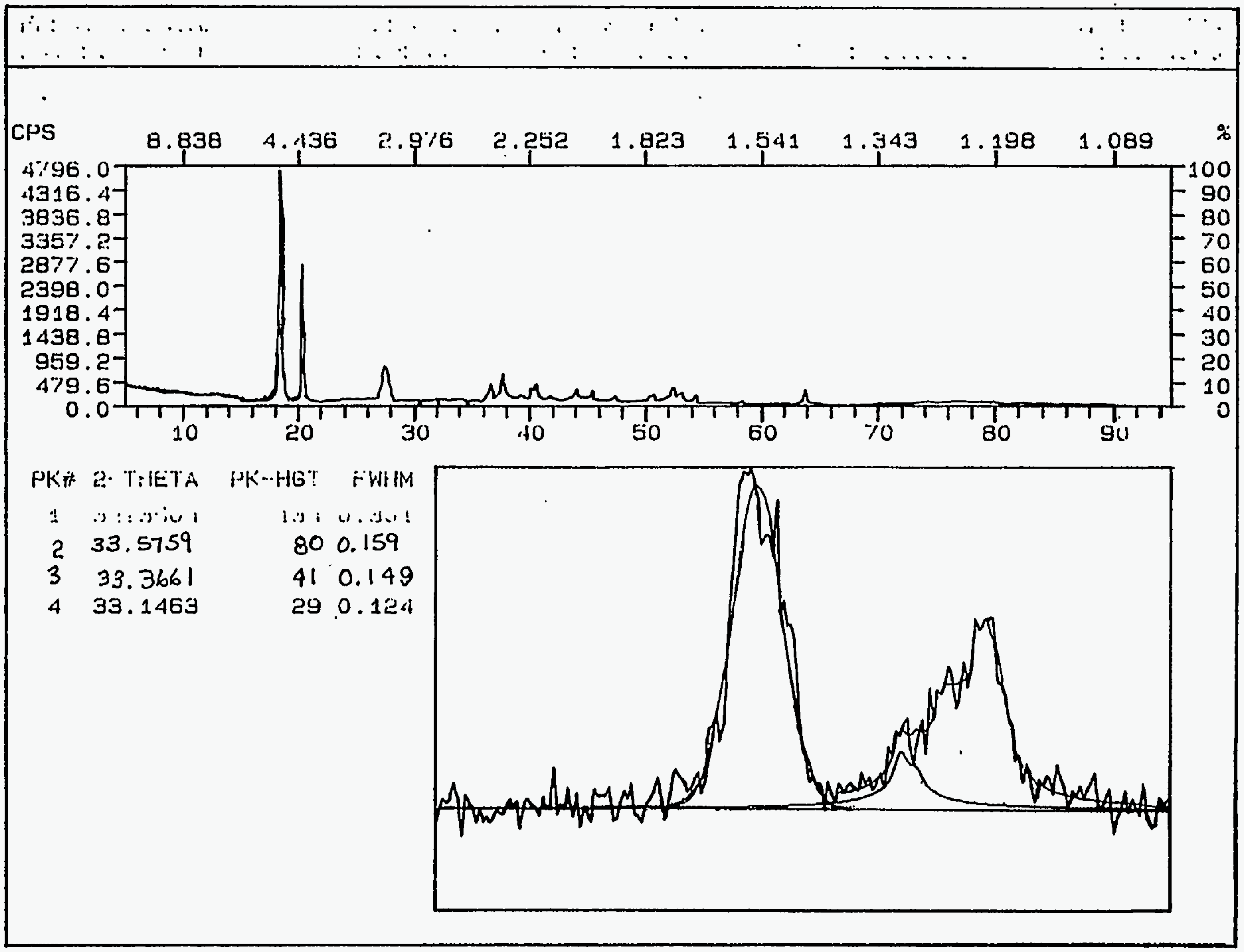
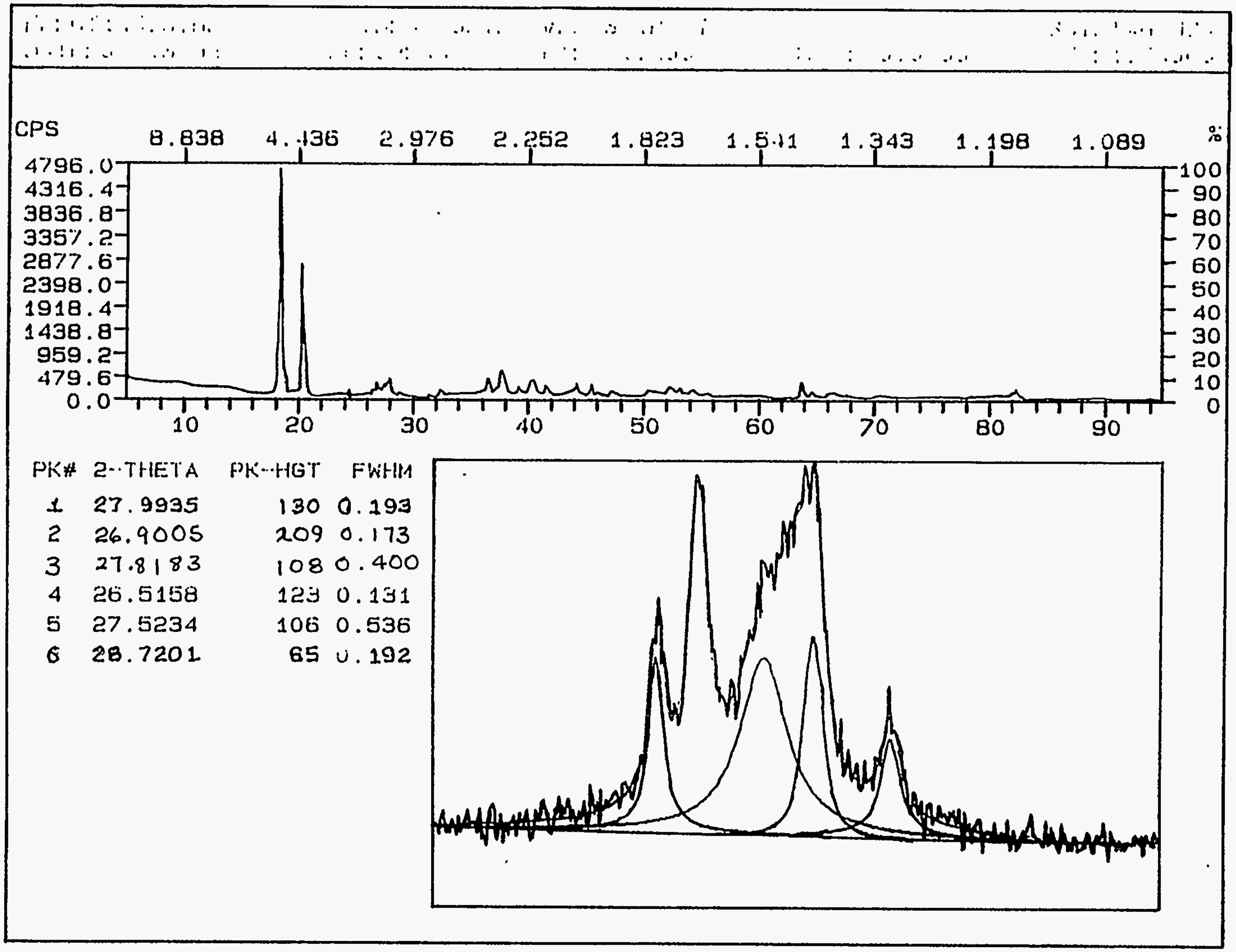


Fig. A-3. Scan of sample No. DN-3-1PSTI with $Al(OH)_3{\cdot}3H_2O$ and sodium aluminate standards.



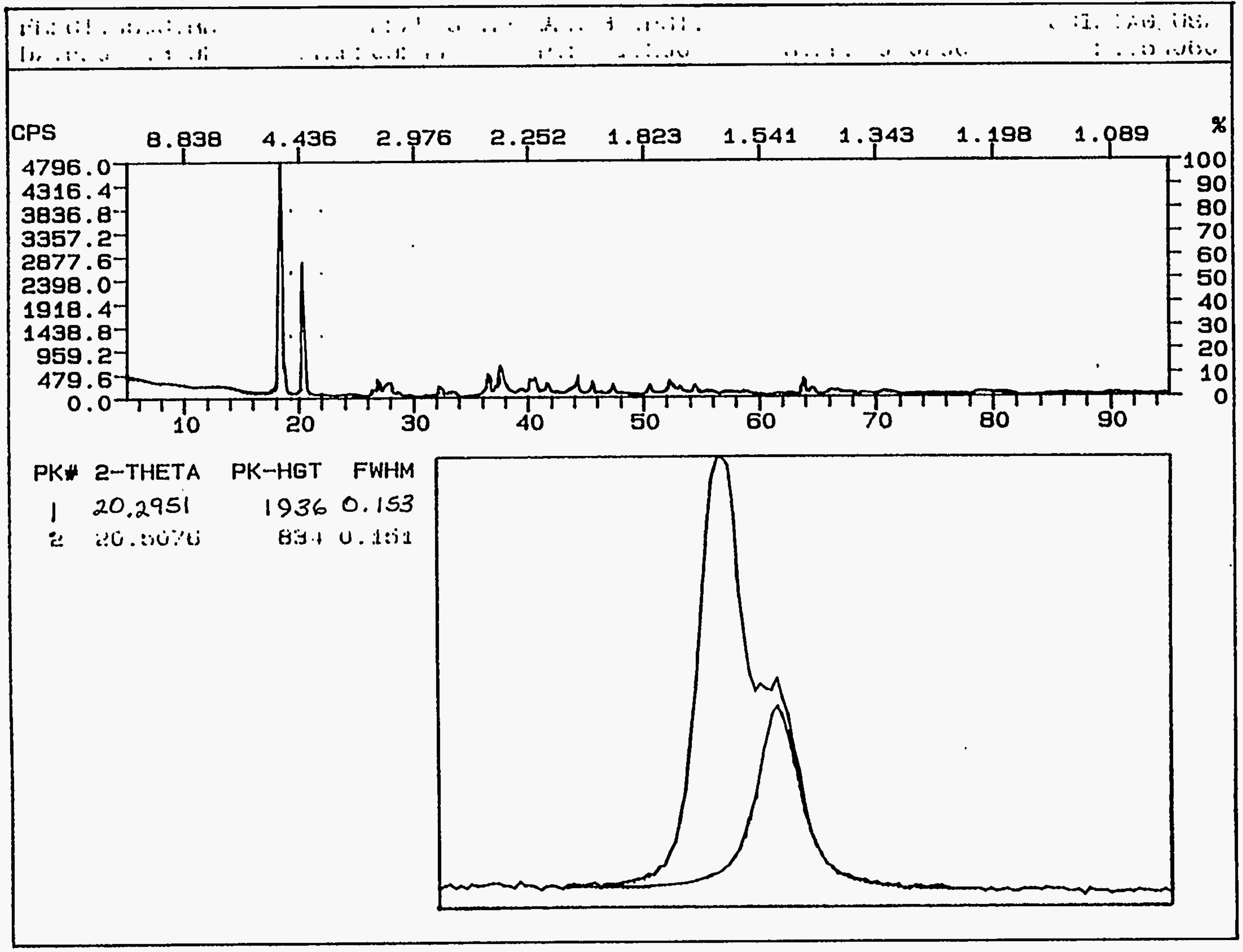
PK#	2· THETA	PK--HGT	FWHM
1	[illegible]	[illegible]	[illegible]
2	33.5759	80	0.159
3	33.3661	41	0.149
4	33.1463	29	0.124

Fig. A-4. Scan showing expanded region at 31—35.



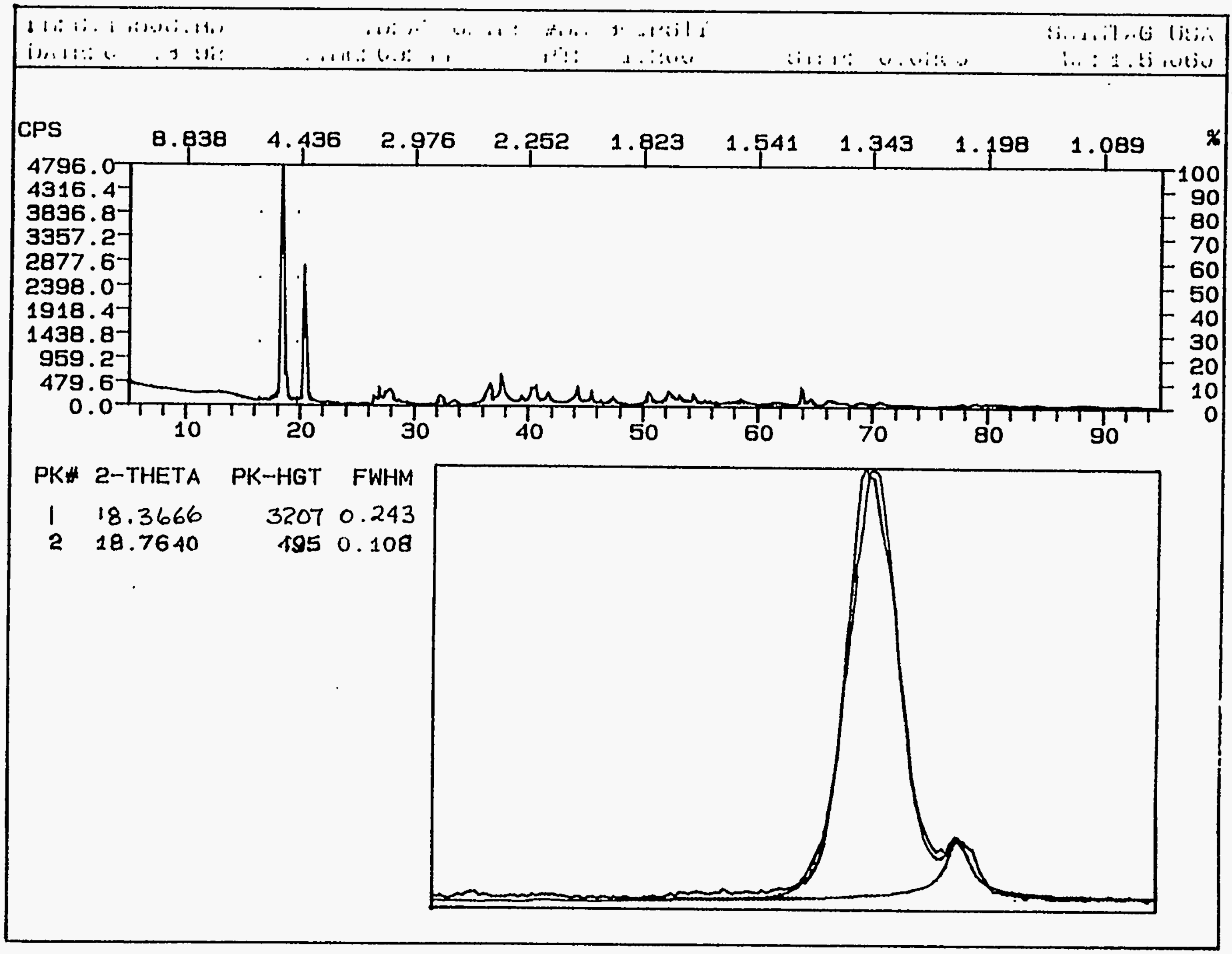
PK#	2-THETA	PK-HGT	FWHM
1	27.9935	130	0.193
2	26.9005	209	0.173
3	27.8183	108	0.400
4	26.5158	123	0.131
5	27.5234	106	0.536
6	28.7201	65	0.192

Fig. A-5. Scan showing expanded region at 24—31.



PK#	2-THETA	PK-HGT	FWHM
1	20.2951	1936	0.153
2	20.5070	834	0.161

Fig. A-6. Scan showing expanded region at 19—22.



PK#	2-THETA	PK-HGT	FWHM
1	18.3666	3207	0.243
2	18.7640	495	0.108

Fig. A-7. Scan showing expanded region at 16—19.

APPENDIX B. COST ANALYSIS AND PROCESS CONCEPTUAL DESIGN

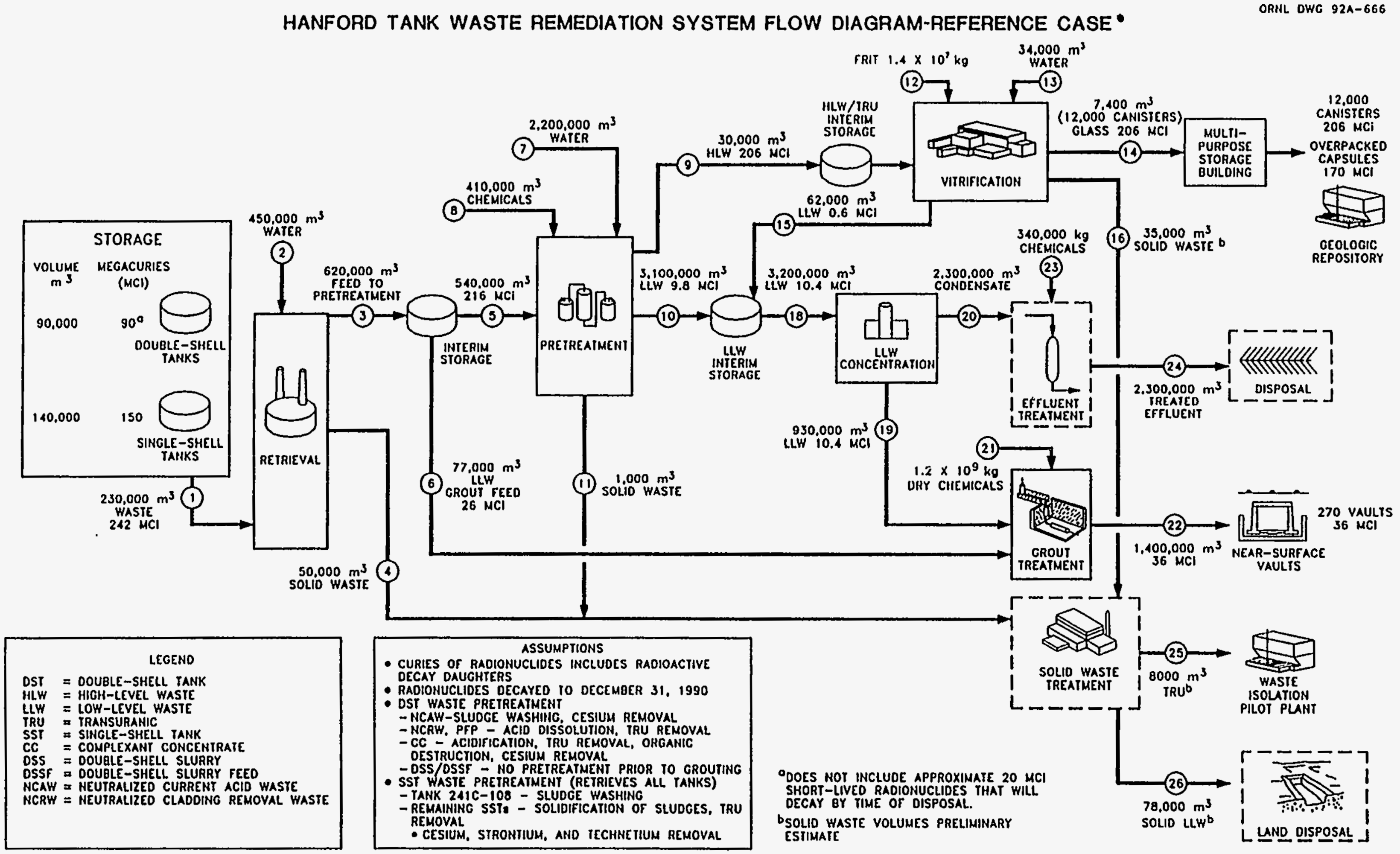
COST ANALYSIS AND CONCEPTUAL DESIGN OF THE NITRATE DESTRUCTION PROCESS

W. W. Pitt

INTRODUCTION

Much of the waste awaiting disposal at U.S. Department of Energy (DOE) facilities contains high concentrations of nitrate. This is especially true of the reprocessing waste produced at Hanford, Savannah River, and Idaho Falls sites where a survey conducted in 1981 and updated in 1984 indicated 145-, 83-, and 13-million kilograms, respectively, of nitrate waste are stored.[1] The bulk of the nitrate waste at Hanford is stored in single-shell tanks (SSTs), and DOE is currently examining several storage and disposal options for these tank wastes. The base case (Fig. B-1) is retrieval from the tanks, pretreatment to separate the HLW and TRU wastes from the LLW, and disposal of the LLW, which would contain nearly all of the nitrate, in near-surface vaults in a grout matrix. The HLW and TRU would be vitrified and placed in the geologic repository.[2]

The high solubility of virtually all nitrate compounds and the low limit for nitrate (45 mg/L) in plant effluents and groundwater make the presence of nitrate in disposed waste highly problematic and provide a strong incentive to destroy the nitrate prior to either storage or disposal. This problem was addressed by a project funded by the National Low-Level Waste Management Program and conducted at the Rocky Flats Plant.[1] An objective of that project was to evaluate existing nitrate destruction technologies; seven potentially successful technologies were identified. Five of these technologies were thermal (high temperature), one biological, and one aqueous. A promising new aqueous nitrate destruction technology is evaluated in this study. Its technical feasibility was established, and a preliminary cost estimate was prepared based on bench-scale tests.



HANFORD TANK WASTE REMEDIATION SYSTEM FLOW DIAGRAM-REFERENCE CASE*

ORNL DWG 92A-666

LEGEND

DST = DOUBLE-SHELL TANK
HLW = HIGH-LEVEL WASTE
LLW = LOW-LEVEL WASTE
TRU = TRANSURANIC
SST = SINGLE-SHELL TANK
CC = COMPLEXANT CONCENTRATE
DSS = DOUBLE-SHELL SLURRY
DSSF = DOUBLE-SHELL SLURRY FEED
NCAW = NEUTRALIZED CURRENT ACID WASTE
NCRW = NEUTRALIZED CLADDING REMOVAL WASTE

ASSUMPTIONS

- CURIES OF RADIONUCLIDES INCLUDES RADIOACTIVE DECAY DAUGHTERS
- RADIONUCLIDES DECAYED TO DECEMBER 31, 1990
- DST WASTE PRETREATMENT
  - NCAW–SLUDGE WASHING, CESIUM REMOVAL
  - NCRW, PFP – ACID DISSOLUTION, TRU REMOVAL
  - CC – ACIDIFICATION, TRU REMOVAL, ORGANIC DESTRUCTION, CESIUM REMOVAL
  - DSS/DSSF – NO PRETREATMENT PRIOR TO GROUTING
- SST WASTE PRETREATMENT (RETRIEVES ALL TANKS)
  - TANK 241C-108 – SLUDGE WASHING
  - REMAINING SSTs – SOLIDIFICATION OF SLUDGES, TRU REMOVAL
    - CESIUM, STRONTIUM, AND TECHNETIUM REMOVAL

[a] DOES NOT INCLUDE APPROXIMATE 20 MCI SHORT-LIVED RADIONUCLIDES THAT WILL DECAY BY TIME OF DISPOSAL.

[b] SOLID WASTE VOLUMES PRELIMINARY ESTIMATE

*ADAPTED FROM UNPUBLISHED PRELIMINARY DRAFT INTEGRATED TECHNOLOGY PLAN FOR HTW REMEDIATION, MARCH 1992

Fig. B-1. Base case Hanford LLW disposal.

BACKGROUND

Although the process described herein is applicable to nitrate waste throughout the DOE system, this study was funded specifically to consider its application in the remediation of the Hanford Tank Wastes. The Final Environmental Impact Statement (EIS) for the Disposal of Hanford Defense High-Level, Transuranic, and Tank Wastes[2] showed an estimate of 110,000 t of nitrate and 14,000 t of NO_2. An estimated 1000 t of NO_3 and NO_2 have been produced since, for a total of 125,000 t. The base case shown in Fig. B-1 provides for the incorporation of the bulk of the nitrates in a cementitious grout and disposal in near-surface vaults. While this is adequate with appropriate engineered barriers in the vault system, destruction of the soluble nitrates and conversion of the associated cations to insoluble solids would reduce the cost of final disposal. In addition, the ceramic aluminum oxide produced in this process is potentially an excellent waste form for final disposal and thus obviate the use of cement grout.

PROCESS BASIS AND ASSUMPTIONS

The process evaluation which follows is based on a unit (kg) of NO_3 fed. The rate of feeding can be estimated using the following assumptions:

1. Only the current tank inventories of NO_3 and NO_2 are considered; any nitrate added in the pretreatment (which could double the total) will be considered separately.

$$\frac{125*10^6\ kg\ NO_3}{3.1*62\ g/L} = 650{,}000\ m^3\ . \tag{1}$$

2. All NO_2 will exist as NO_3 and the feed will be 3.1 M nitrate. This results in an overestimate of the aluminum required. Thus the total =
3. The inventory will be processed over a 20-year period.

$$6.25 * 10^6\ \text{kg/year or } 32{,}500\ \text{m}^3\text{/year}$$

4. Around the clock operations with 60% availability yields

$$\frac{32{,}500\ m^3/year}{0.6*365*24\ h/year} = 6.18\ m^3/h\ , \tag{2}$$

or 1200 kg NO_3/h.

The feed is assumed to contain other constituents as described by Jones, Colton, and Bloom.[3] Although the actual chemistry is complex with multiple reactions (e.g., see Fig. B-2), the overall, stoichiometric reaction can be assumed to be:

$$3NaNO_3 + 8Al + 12H_2O \rightarrow 3NH_3 + 5Al(OH)_3 + 3NaAlO_2 ,$$

or

$$3NaNO_3 + 8Al + 4.5H_2O \rightarrow 3NH_3 + 4Al_2O_3 + 1.5Na_2O .$$

The Heat of Reaction = −1142 kcal

The Entropy of Reaction = +0.919 cal/K

An undesirable competing reaction is:

$$3H_2O + 2Al \rightarrow Al_2O_3 + 3H_2 .$$

PROCESS PARAMETERS

Bench-scale tests using both sodium nitrate solutions and simulated SST waste[3] have established the following process parameters and characteristics:

1. The desired reaction temperature is between 50 and 80°C; below 50°C the reaction is slow to start and above 80°C it is difficult to control and leads to rapid steam production.
2. A pH above 11 (preferably 12 to 13) is required to initiate and maintain a reasonable reaction rate. The addition of about 50 g NaOH raises a 3.1 *M* $NaNO_3$ solution to about pH 13.
3. The addition of aluminum in the form of spheres >200 μm in diameter to fresh 3.1 *M* nitrate solution lowers the pH to <10 and delays onset of the reaction for about 4 h. Use of nonoxidized aluminum or fine aluminum powder avoids this reaction delay. It has also been shown that a seed of the gibbsite product from the reaction promotes instant start of the reaction.
4. Although the heat of reaction was not determined, the highly exothermic nature of the process was confirmed.
5. To obtain 100 ppm or less nitrate in the reactor effluent requires about twice the stoichiometric amount of aluminum: thus, 2.3 kg Al/kg nitrate or 1.7 kg Al/kg sodium nitrate. Further development could result in less aluminum required.

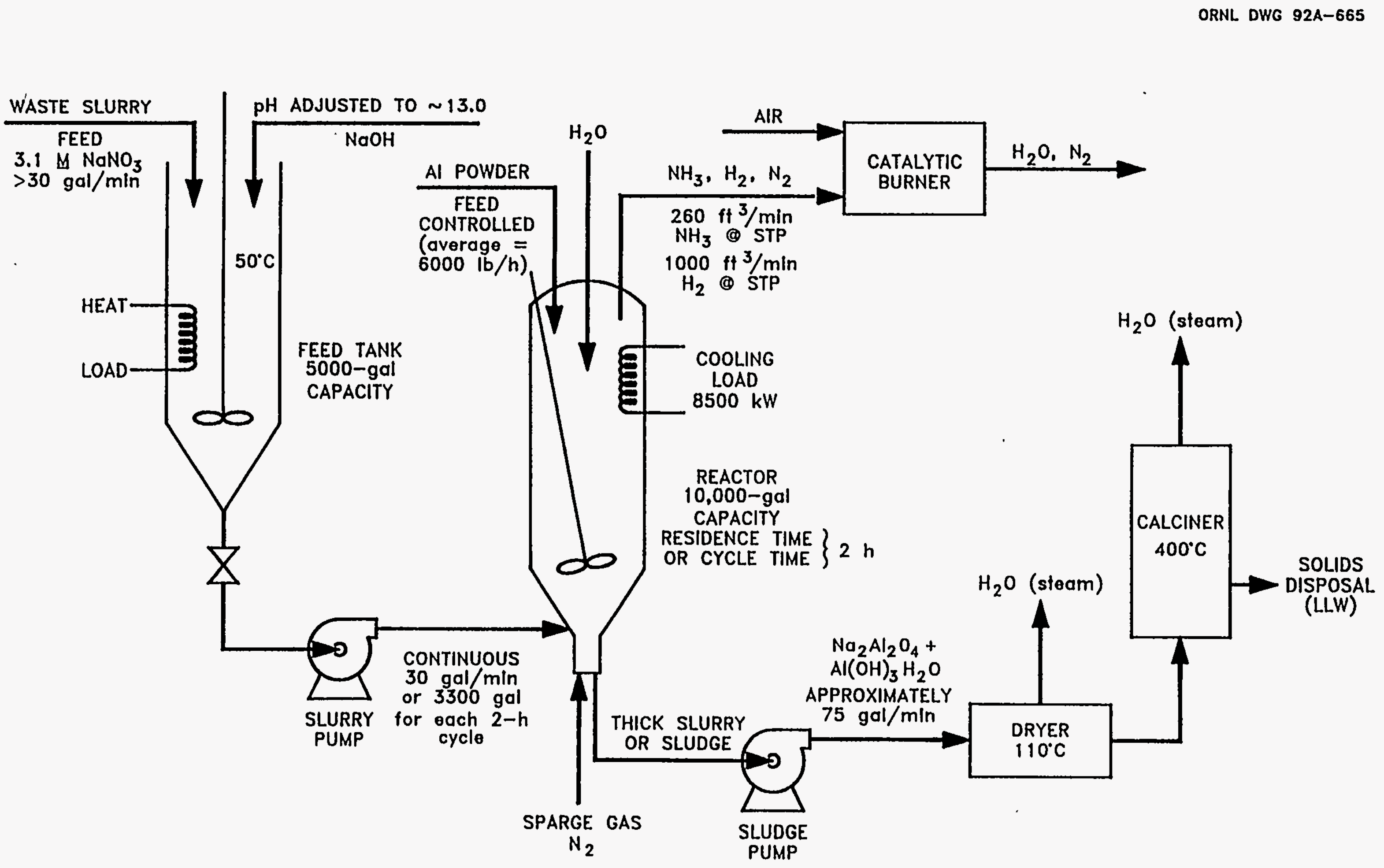


Fig. B-2. Pilot plant for Hanford nitrate waste denitrification.

6. Under these conditions, the resulting products per kg of nitrate destroyed are −365 L NH_3 at STP, 1450 L H_2 at STP, and a slurry consisting of 94% $Al(OH)_3$ (gibbsite) and 6% $NaAlO_2$ by dry weight.
7. Although the rate of reaction was not precisely determined, it was observed that about 1 to 2 h were sufficient to reduce the nitrate concentration to ≤100 ppm. Again conservatism prevailed, and a 2-h requirement was assumed.

OVERALL FLOWSHEET

The overall process that was evaluated and priced is shown in Fig. B-2.

Equipment list. The list of major equipment with required sizes for a throughput of ~4 m^3/h (~1 L/s) is shown in Table B-1. The list of required utilities and process support is shown is Table B-2.

Raw materials. Aluminum metal is the principal raw material required; ~50 t/d are consumed. This could be either raw aluminum metal ingot, recycled beverage cans, or contaminated aluminum scrap from various DOE sites. Approximately 1900 L/d (500 gal/d) of 50% sodium hydroxide is required. A supply of ~283 m^3/m (10,000 ft^3/min) of unconditioned air to the catalytic burner is needed.

Utilities. Power consumption is mainly for electrical loads for the pumps, feed tank heating, cooling tower fans and pumps, and agitator drives. Additional heat must be supplied for the product drier and calciner.

PROCESS EVALUATION AND COST ESTIMATE

Neither an analysis of the results from bench-scale tests to date nor the careful consideration of other aspects of the overall process has identified any fatal flaw for this process. It is a technically feasible process with a large but reasonable size plant required to work off the existing Hanford SST wastes in 20 years. The highly exothermic nature of the reactions and the solid reaction products do present a challenging task in designing the reactor for the process.

Table B-1. Major process equipment list

Component	Size	Cost	Comments/remarks
Feed tank	5,000 gal	50,000	pH adjustment; stir
Reactor vessel	10,000 gal	500,000	Heating/cooling, agitator
Aluminum hopper	1,000 cu ft	100,000	Powder or small shot
Aluminum feeder	5,000 lb/h	150,000	Screw auger or conveyor
Slurry feed pump	300 gpm	125,000	30 gpm if continuous
Reactor discharge pump	75 gpm	45,000	Sludge pump
Reactor cooler	8,500 kW	500,000	600-ton cooling tower
Sludge dryer	10,000 lb/h	150,000	Rotary vacuum dryer
Extruder	7,500 lb/h	100,000	Heated enclosed screw
Calciner	7,500 lb/h	300,000	400°C maybe 1100°C
Ammonia burner	2,500 cfm	80,000	Catalytic burner
Feed mixer	10 hp	10,000	
Piping and valving		500,000	Carbon steel A-53
Structural support	500 tons	750,000	For tanks, pumps, and piping
Feed heater	100 kW	10,000	Electric in-tank heater
NaOH supply system	500 gal/d;	250,000	5,000-gal tank
Subtotal—process equipment		3,620,000	

Table B-2. Utilities, support equipment and facilities

Component	Size	Cost	Comments/remarks
1000KW transformer		250,000	With switch gear, etc.
Air compressor		15,000	
NPDES monitoring station		150,000	For pollution monitoring
Isokinetic sampler		150,000	For gas discharge stack
HEPA filtered area	10,000 CFM	300,000	Calciner and solids area
65,000 SF building	40' eave height	2,250,000	With 30-ton crane, exhaust, heat, office, change house, etc.
Outside utilities/site work		250,000	
Dry product handling		500,000	From calciner, and other miscellaneous equipment
Process instrumentation and controls		400,000	Includes data acquisition
Subtotal—utilities and support equipment		4,265,000	

SUMMARY

Total Equipment and Facilities	**$7,885,000**
Construction Management at 25%	**$1,915,000**
Engineering at 25%	**$2,450,000**
Project Management at 10%	**$1,200,000**
Subtotal	**$13,450,000**
Contingency at 50%	**$6,750,000**
Total FY 92 4th QTR $	**$20,200,000**

A preliminary cost estimate based on the preceding assumptions has been prepared (Appendix C, prepared by Dave Brashears) and is summarized below.

Cost Estimate

Capital Costs		$20,000,000
Amortized over 20 years		$1,000,000/year
Operating & Maintenance		
Operating labor (4-shifts)		$3,375,000/year
Support labor		$640,000/year
Supplies (excluding aluminum)		$425,000/year
Analytical and HP surveillance		$475,000/year
Utilities	(?)	$350,000/year
Aluminum (recycled at 0.40/lb)		$9,375,000/year
Maintenance (5% Capital/year)		$1,000,000/year
Total O&M (less utilities)		**$15,640,000/year**

Total Cost of Process = $16,640,000 or $16,640,000/6,250,000 kg = $2.66/kg NO_3 destroyed. This could be reduced to about $2.01/kg if the required aluminum was nearer the stoichiometric amount.

This compares to $5.13/kg NO_3 by an electrolytic process evaluated in 1957[4] and similar costs for the thermal processes.[1]

CONCLUSIONS

The following conclusions have been drawn by this study:

1. The nitrate to ammonia and ceramic process is technically feasible and competitive with other feasible processes for removing the nitrates contained in the Hanford Tank Wastes. The sugar or formic acid nitrate destruction processes are not capable of obtaining the low nitrate levels required, and the biological denitrification would require an extremely high dilution of the feed. Although not addressed in this study, it is likely that the cost of not removing the nitrates would exceed the cost of implementing this process.

2. The design of the reactor is a crucial element in the successful application of this process. The reactor must be capable of handling the thick slurry or gel which is produced and provide for the removal of ~8500-kW heat.
3. The waste streams which result are tractable; the hydrogen and ammonia are readily burned to nitrogen and steam, and upon calcination, the aluminum hydroxide should be suitable for land disposal as a refractory alumina.
4. Before this process can be applied, additional development is needed and warranted.

RECOMMENDATIONS

It is recommended that development activities continue on this promising process in at least the following areas:

1. Conduct additional bench-scale tests with the objective of determining the parameters required for reactor design.
2. Design, construct, and test a prototype engineering-scale reactor.
3. Conduct bench-scale reductions of surrogate HLW with and without radioactive tracers and prepare sufficient quantities of solid waste material to perform waste form evaluations: leach rates, leachate composition, compressive strength, durability, etc.

ACKNOWLEDGMENTS

The author is very grateful to Al Mattus for the many enlightening discussions regarding the chemistry and other aspects of the process. David Brashears provided the capital cost estimate based on a rough flowsheet supplied by the author who accepts full responsibility for any gross errors in this estimate. The O&M cost estimate is directly based on an estimate for a pilot plant operation of a similar operation (a much smaller scale) made by Karl Haff and graciously provided to the author.

REFERENCES

1. A. J. Johnson and P. M. Arnold, *Waste Generation Reduction - Nitrates Comprehensive Report of Denitrification Technologies*, RFP-3899, Rockwell International, Rocky Flats Plant, Golden, CO, March 1986.
2. *Final Environmental Impact Statement Disposal of Hanford Defense High-Level, Transuranic and Tank Wastes*, DOE/EIS - 0113, December 1987.
3. E. O. Jones, N. G. Colton, and J. R. Bloom, "Hanford Single-shell Tank Waste, Preliminary Pretreatment Testing of Simulated Waste," in **Proceedings of the 7th Annual DOE Model Conference on Waste Management & Environmental Restoration**, October 14-17, 1991.
4. H. W. Alter et al., *Electrolytic Recycle Method for the Treatment of Radioactive Nitric Acid Waste*, KAPL-1721, June 1957.

APPENDIX C. COST ESTIMATE FOR HANFORD TANK WASTE TREATMENT STUDY

SUMMARY

	Dollars × 1000
Equipment and Facilities	$7,885
Construction Management at 25%	$1,915
Engineering at 25%	$2,450
Project Management at 10%	$1,200
Subtotal	$13,450
Contingency at 50%	$6,750
Total FY 92 4th quarter dollars	$20,200
Use	$20,000

RANGE $20,000 TO $25,000

BASIS OF ROUGH ORDER OF MAGNITUDE COST ASSESSMENT

- Cost assessment is based on very rough flow sheet sketch of a proposed full-scale nitrate waste treatment process at Hanford Site in Washington State.
- This cost assessment is a very rough order of magnitude, and much more additional definition is required before any "concrete" cost assessments can be made.
- Cost assessment assumes that land is available to construct this facility on.
- Utilities, sufficient electrical power, and water are available within reasonable distance (i.e., 200 LF) at the proposed site.
- Engineering, project management, construction management, and contingency have been included at levels as identified based upon previous experience with similar type processes.
- The proposed site of construction would NOT be contaminated, no security problems, no extraordinary site difficulties.
- Dollars are presented in FY 4th quarter. NO escalation for future years is included.

HANFORD TANK WASTE TREATMENT NITRATE DESTRUCTION UNIT

R.O.M. Estimate Per Attached Flow Sheet

Equipment

\$50,000	1.	Feed tank 5,000 gal with conical bottom, carbon steel coated with epoxy with supports
\$10,000	2.	Mixer, assume 20 H.P.
\$125,000	3.	Moyno slurry pump, 300 G.P.M., assume 40' head, assume reactor fill in ~11 min
\$500,000	4.	Reactor 10,000 gal capacity ● material of construction S.S. 304L ● conical bottom ● water cooled jacket cooling load 8500 kW ● 3 each mixer, assume 20 H.P.
\$45,000	5.	Moyno slurry pump, 75 G.P.M.
\$150,000	6.	Rotary vacuum dryer 110°C, 3' diam × 4'6" LG 29 CR working capacity
\$300,000	7.	Calciner 400°C, 2' diam × 8' LG
\$80,000	8.	Catalytic burner to "burn" NH_3, H_2, N_2, 2500 CFM NH_3/250—500 CFM H_2
\$100,000	9.	Screw conveyors between dryer and calciner, enclosed and heated, 20 CFM capacity, C.S. construction
\$1,360,000		SUBTOTAL

Equipment

$10,000	10. Electric heater, assume 100 kW submerged inside feed tank
$500,000	11. Piping and valving, assume carbon steel A-53 largest size piping 4" diam
$750,000	12. Supports for tanks, pumps, and piping, allow 500 tons of structural steel

Utilities Requirements

$150,000	13. Aluminum oxide feeder with screw conveyor and handling equipment
$500,000	14. 600 ton cooling tower
$250,000	15. NaOH caustic system 5,000 gal with associated pumps, etc.
$250,000	16. 1000 kW transformer with switch gear, etc.
$100,000	17. Aluminum power silo, allow for 1000 CF silo
$15,000	18. Air compressor

Support Equipment and Facilities

$150,000	19. NPDES monitoring station
$150,000	20. Isokenetic sampler on stack
$300,000	21. HEPA filtered area for calciner and solids packaging area, assume 10,000 CFM
$2,250,000	22. Pre-engineered building with 40' eve height with diked concrete slab, 30-ton crane, minimum heat, exhaust system, office area, change house, etc. — 15,000 SF
$250,000	23. Outside utilities and site work for building
$5,625,000	SUBTOTAL
$500,000	24. Handling equipment for removal of dried material from calciner and other miscellaneous handling equipment
$400,000	25. Instrumentation and controls for process, including process control and data acquisition
$900,000	SUBTOTAL
$7,885,000	**TOTAL EQUIPMENT AND FACILITIES**

APPENDIX D. TGA AND DTA ANALYSES OF DENITRATION PRODUCT

Samples of DN-3 and DN-4 room temperature dried product were characterized by thermogravimetric analysis and differential thermal analysis.

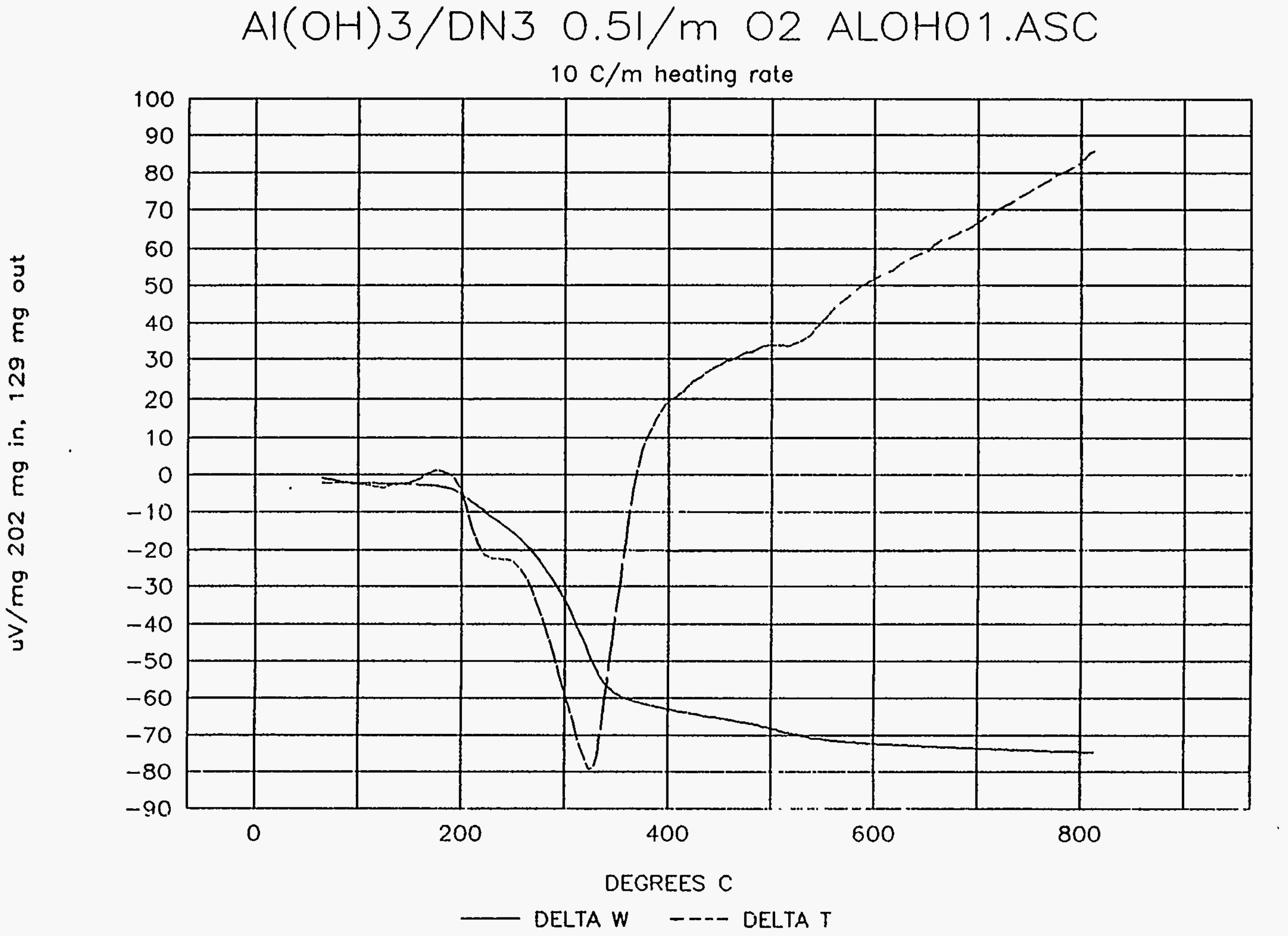


Fig. D-1. TGA and DTA analyses of DN-3 product.

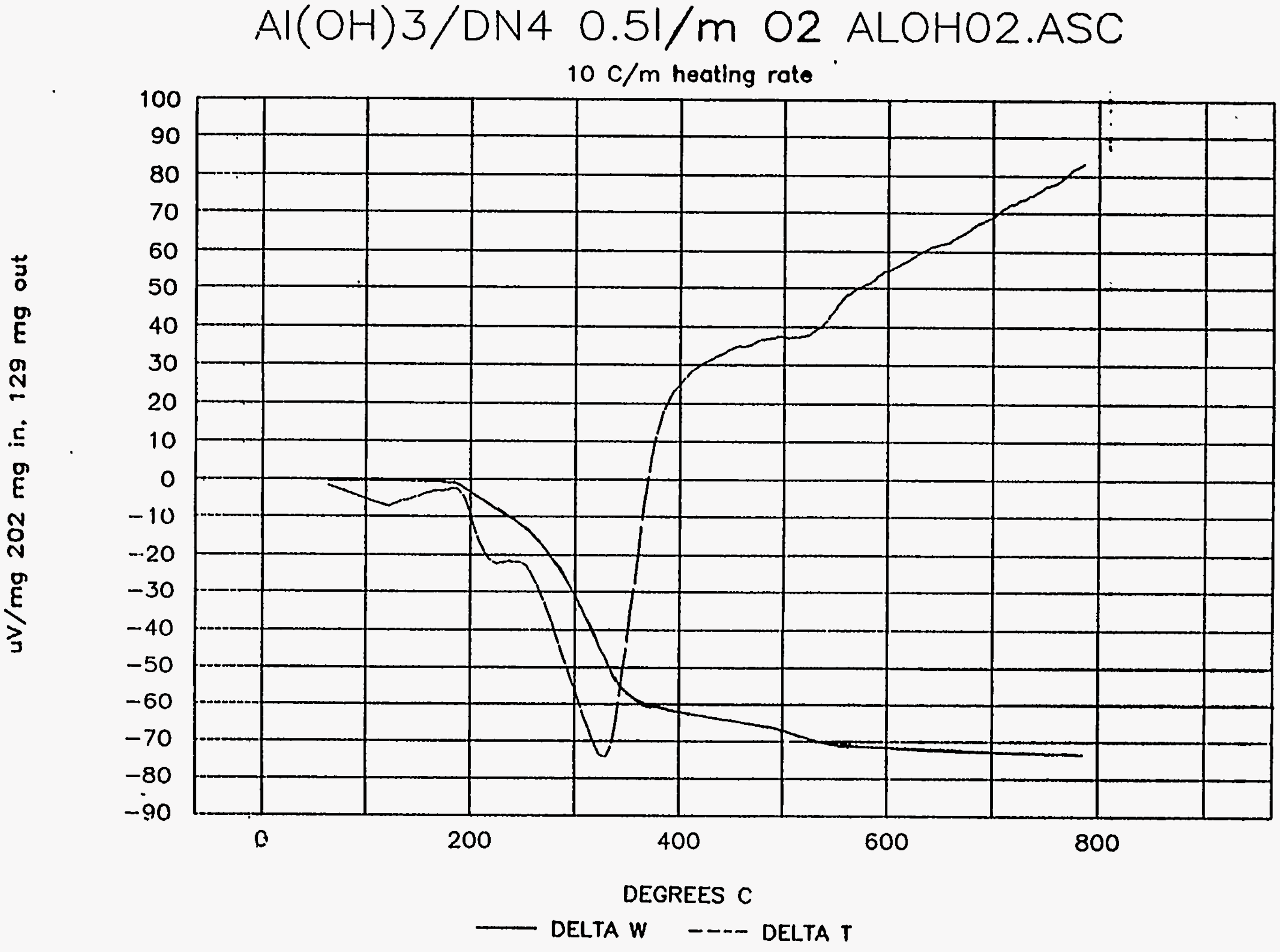
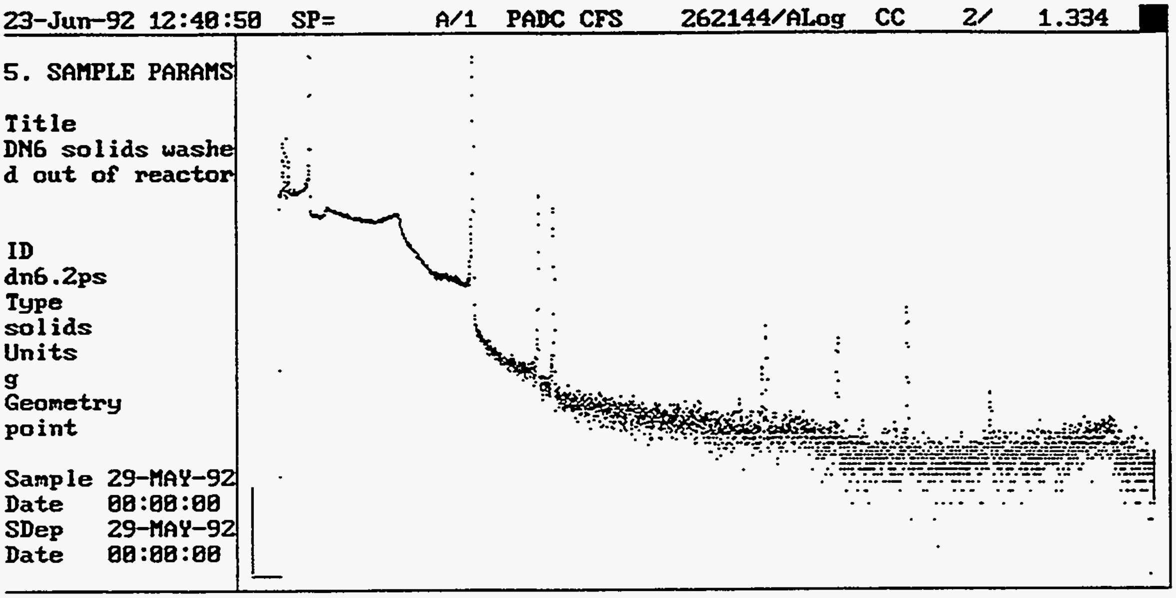


Fig. D-2. TGA and DTA analyses of DN-4 product.

APPENDIX E. RESULTS OF SURROGATE RUNS WITH RADIOACTIVE TRACERS

The samples were counted using an intrinsic germanium detector (Princeton Gammatech) and an Accuspec multichannel analyzer computer data acquisition board (Canberra) in an IBM-XT computer with AccuSpec ASAP Radionuclide Analysis Software (Canberra) for data analysis. The resulting spectra are shown, along with the peaks found and those identified according to the program criteria.



```
23-Jun-92 12:40:50  SP=       A/1  PADC CFS    262144/ALog  CC    2/    1.334

5. SAMPLE PARAMS

Title
DN6 solids washe
d out of reactor


ID
dn6.2ps
Type
solids
Units
g
Geometry
point

Sample  29-MAY-92
Date    00:00:00
SDep    29-MAY-92
Date    00:00:00
```

```
                ENERGY WINDOW       .83 TO   2048.74

PK IT  ENERGY   AREA   BKGND   FWHM  CHANNEL  LEFT  PW  CTS/SEC %ERR      FIT

 1  0   76.27 132916. 190058.  6.26   151.84   135  29 3.60E+01  1.0
 2  0   85.10  32152.  93203.  1.29   169.49   164  14 8.70E+00  2.1
 3  0   99.66   1912.  57118.  1.09   198.60   196   8 5.17E-01 21.8
 4  0  121.71   2960.  63169.  1.23   242.70   240   8 8.01E-01 14.8
 5  0  133.05 613091. 141465.  1.23   265.38   254  22 1.66E+02   .2
 6  0  513.46 684392.  16994.  1.49  1026.05  1010  27 1.85E+02   .1
 7  0  661.18  24353.   2036.  1.61  1321.42  1303  29 6.59E+00   .8
 8  0  696.02  17586.   1328.  1.60  1391.09  1373  28 4.76E+00   .9
 9  0 1117.06    193.    481.  2.26  2233.01  2218  30 5.22E-02 27.0
10  0 1163.08    329.    339.  2.00  2325.02  2316  18 8.91E-02 11.7
11  0 1173.37    902.    565.  1.65  2345.60  2338  33 2.44E-01  7.2
12  0 1331.93    871.    374.  2.04  2662.66  2645  34 2.36E-01  6.4
13  0 1461.43     41.    158.  3.75  2921.60  2912  18 1.11E-02 53.5
14  0 1488.78   1785.    274.  2.11  2976.30  2960  31 4.83E-01  3.1
15  0 1674.30    261.    267.  3.10  3347.26  3333  26 7.06E-02 13.7

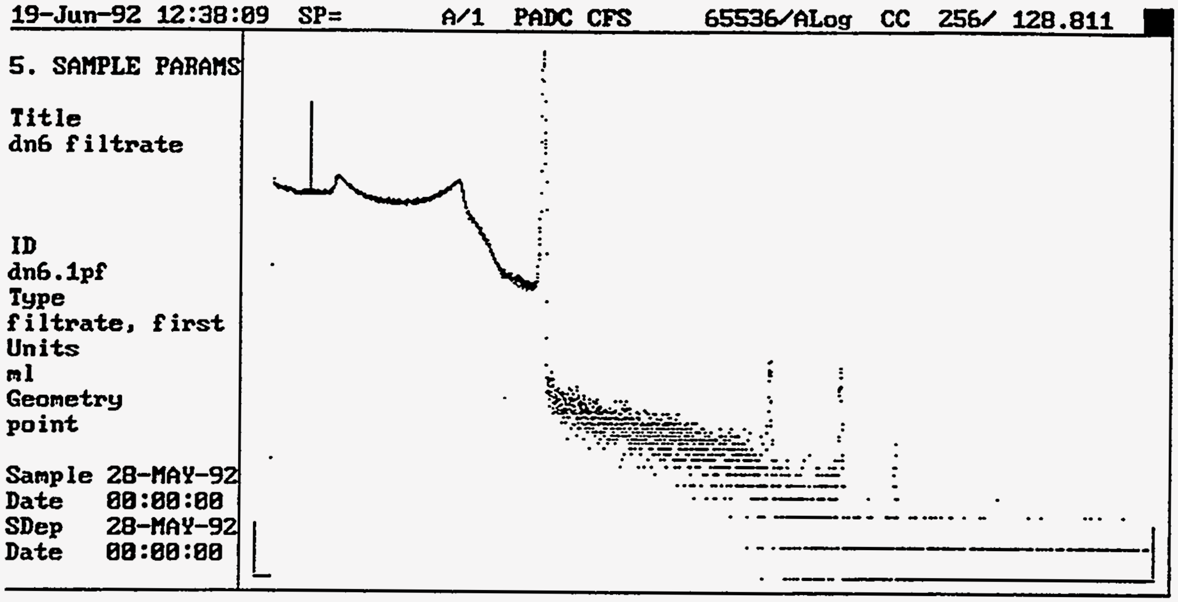
          PEAK SEARCH COMPLETED  (REV 15.8 - ND PC VERSION   MAR 90)

ACTIVATION PRODUCT
                                                       1-SIGMA
NUCLIDE  SBHR    HLIFE    DECAY     UCI/g              ERROR       %ERR
CO-60     AP      5.26Y   1.001     3.744E -5          2.382E -6    6.36
ZN-65     AP    244.00D   1.010     1.416E -5          3.828E -6   27.03


FISSION PRODUCT
                                                       1-SIGMA
NUCLIDE  SBHR    HLIFE    DECAY     UCI/g              ERROR       %ERR
CO-57     FP    270.00D   1.009     3.073E -5          4.562E -6   14.85
SR-85     FP     65.20D   1.039     2.288E -2          2.931E -5     .13
CS-137    FP     30.17Y   1.000     1.088E -3          8.596E -6     .79
CE-144    FP    284.20D   1.009     5.011E -2          1.012E -4     .20


NATURAL PRODUCT
                                                       1-SIGMA
NUCLIDE  SBHR    HLIFE    DECAY     UCI/g              ERROR       %ERR
K-40      NP  1.28E+09Y   1.000     1.826E -5          9.764E -6   53.46
```

Fig. E-1. DN-6 solids washed from the reaction after filtration.



19-Jun-92 12:38:09 SP= A/1 PADC CFS 65536/ALog CC 256/ 128.811

5. SAMPLE PARAMS

Title
dn6 filtrate

ID
dn6.1pf
Type
filtrate, first
Units
ml
Geometry
point

Sample 28-MAY-92
Date 00:00:00
SDep 28-MAY-92
Date 00:00:00

```
                    ENERGY WINDOW      .83 TO  2048.74

PK IT  ENERGY    AREA   BKGND   FWHM  CHANNEL  LEFT  PW  CTS/SEC %ERR     FIT

 1  0  661.83 607481.  11626.  5.17  1322.72  1304  41 1.69E+02   .1
 2  0 1173.61    651.    150.  5.09  2346.08  2327  40 1.81E-01  6.1
 3  0 1333.43    534.     70.  5.42  2665.66  2651  31 1.48E-01  5.5

         PEAK SEARCH COMPLETED  (REV 15.8 - ND PC VERSION   MAR 90)



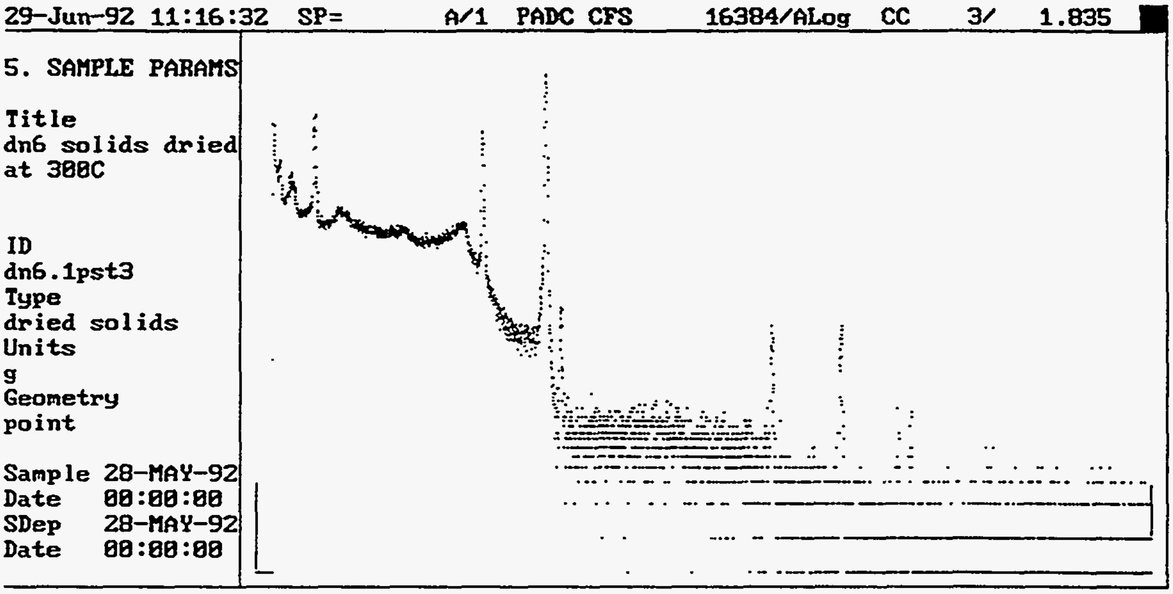
NUCLIDE IDENTIFICATION SYSTEM    (ND PC VERSION   DEC 88)
SUMMARY OF NUCLIDE ACTIVITY                                  PAGE  3

TOTAL LINES IN SPECTRUM          3
UNIDENTIFIED PEAKS               0
IDENTIFIED IN SUMMARY REPORT     3    100.00%

ACTIVATION PRODUCT
                                                   1-SIGMA
NUCLIDE  SBHR    HLIFE    DECAY   UCI/ml           ERROR       %ERR
CO-60     AP      5.26Y   1.007     5.557E -4      3.051E -5    5.49

FISSION PRODUCT
                                                   1-SIGMA
NUCLIDE  SBHR    HLIFE    DECAY   UCI/ml           ERROR       %ERR
CS-137    FP     30.17Y   1.001     6.534E -1      8.993E -4     .14
```

Fig. E-2. DN-6 filtrate from solids poured from the reactor before any washing.



```
29-Jun-92 11:16:32  SP=        A/1  PADC CFS    16384/ALog  CC    3/   1.835

5. SAMPLE PARAMS

Title
dn6 solids dried
at 300C


ID
dn6.1pst3
Type
dried solids
Units
g
Geometry
point

Sample 28-MAY-92
Date    00:00:00
SDep    28-MAY-92
Date    00:00:00
```

```
                    ENERGY WINDOW      .83 TO  2048.74

PK IT  ENERGY    AREA   BKGND   FWHM  CHANNEL  LEFT  PW  CTS/SEC %ERR     FIT

 1  0   56.14    6945.  19033.  3.83   111.58   102  20 1.93E+00  5.1
 2  0   83.23    9103.  26875. 10.99   165.76   149  36 2.53E+00  5.8
 3  0  133.09   30505.  18862.  4.11   265.46   253  32 8.47E+00  1.5
 4  0  513.61   26185.   6958.  4.36  1026.34  1009  35 7.27E+00  1.0
 5  0  661.44   81313.   3617.  4.24  1321.95  1305  39 2.26E+01   .4
 6  0  696.47     772.    283.  4.19  1391.98  1378  30 2.14E-01  6.8
 7  0 1173.69     584.     85.  4.56  2346.24  2334  33 1.62E-01  5.6
 8  0 1332.73     545.     89.  4.55  2664.26  2646  36 1.51E-01  5.9

        PEAK SEARCH COMPLETED  (REV 15.8 - ND PC VERSION   MAR 90)
```

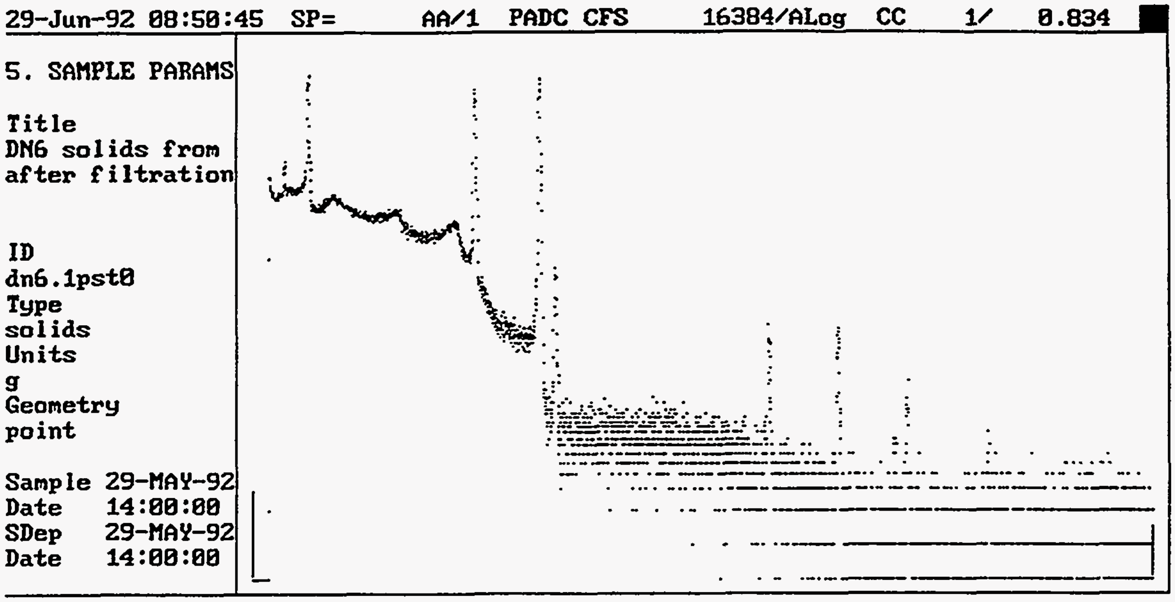
```
NUCLIDE IDENTIFICATION SYSTEM    (ND PC VERSION    DEC 88)
SUMMARY OF NUCLIDE ACTIVITY                                  PAGE  3

TOTAL LINES IN SPECTRUM          8
UNIDENTIFIED PEAKS               3
IDENTIFIED IN SUMMARY REPORT     5      62.50%

ACTIVATION PRODUCT
                                                     1-SIGMA
NUCLIDE  SBHR    HLIFE    DECAY   UCI/g              ERROR       %ERR
CO-60     AP      5.26Y   1.012     3.794E -3        2.246E -4    5.92

FISSION PRODUCT
                                                     1-SIGMA
NUCLIDE  SBHR    HLIFE    DECAY   UCI/g              ERROR       %ERR
SR-85     FP     65.20D   1.412     1.906E -1        1.994E -3    1.05
CS-137    FP     30.17Y   1.002     5.835E -1        2.362E -3     .40
CE-144    FP    284.20D   1.082     4.287E -1        6.348E -3    1.48
```

Fig. E-3. DN-6 product solids dried at 300°C.



```
29-Jun-92 08:50:45  SP=      AA/1  PADC CFS      16384/ALog  CC     1/   0.834

5. SAMPLE PARAMS

Title
DN6 solids from
after filtration


ID
dn6.1pst0
Type
solids
Units
g
Geometry
point

Sample 29-MAY-92
Date    14:00:00
SDep   29-MAY-92
Date    14:00:00
```

```
                    ENERGY WINDOW    25.34 TO  2048.74

PK IT  ENERGY    AREA   BKGND   FWHM  CHANNEL  LEFT  PW  CTS/SEC %ERR       FIT

 1  0   79.50    5331.  16967.  4.08   158.31   151  17 1.48E+00  5.7
 2  0  133.22   75840.  29731.  4.25   265.72   253  32 2.11E+01   .8
 3  0  513.80   65256.   9207.  4.36  1026.73  1009  44 1.81E+01   .6
 4  0  661.54   84136.   2107.  4.45  1322.15  1304  40 2.34E+01   .4
 5  0  696.53    1845.    355.  3.81  1392.11  1378  31 5.13E-01  3.5
 6  0 1173.52     533.    157.  3.54  2345.89  2334  29 1.48E-01  6.8
 7  0 1333.02     624.     86.  4.88  2664.83  2648  35 1.73E-01  5.5
 8  0 1459.69      31.     47.  3.86  2918.13  2901  28 8.58E-03 50.4
 9  0 1489.16     171.     55.  3.65  2977.06  2956  40 4.76E-02 12.8

          PEAK SEARCH COMPLETED  (REV 15.8 - ND PC VERSION   MAR 90)

  NUCLIDE IDENTIFICATION SYSTEM    (ND PC VERSION   DEC 88)
  SUMMARY OF NUCLIDE ACTIVITY                                  PAGE  3

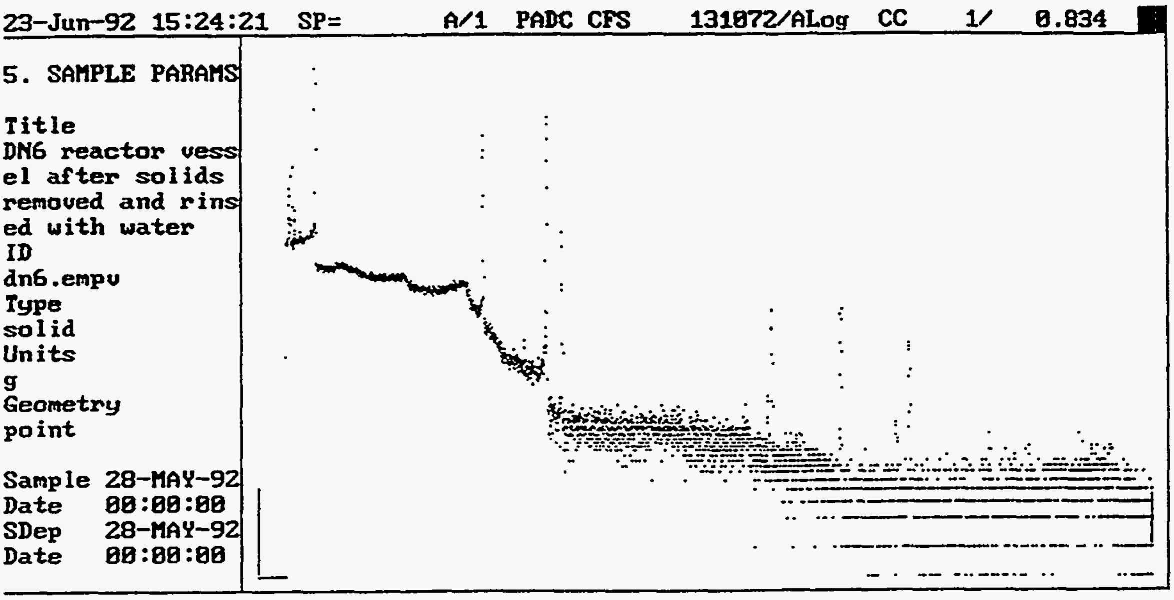
  TOTAL LINES IN SPECTRUM           9
  UNIDENTIFIED PEAKS                2
  IDENTIFIED IN SUMMARY REPORT      7     77.78%


  ACTIVATION PRODUCT
                                                      1-SIGMA
  NUCLIDE  SBHR    HLIFE    DECAY    UCI/g            ERROR       %ERR
  CO-60     AP      5.26Y   1.010     1.067E -3       5.851E -5    5.48


  FISSION PRODUCT
                                                      1-SIGMA
  NUCLIDE  SBHR    HLIFE    DECAY    UCI/g            ERROR       %ERR
  SR-85     FP     65.20D   1.347     1.115E -1       6.545E -4     .59
  CS-137    FP     30.17Y   1.002     1.484E -1       5.581E -4     .38
  CE-144    FP    284.20D   1.071     2.593E -1       2.035E -3     .78


  NATURAL PRODUCT
                                                      1-SIGMA
  NUCLIDE  SBHR    HLIFE    DECAY    UCI/g            ERROR       %ERR
  K-40      NP  1.28E+09Y   1.000     5.394E -4       2.719E -4   50.41
  AN-511    NP   1000.00Y   1.000     8.279E -2       4.861E -4     .59
```

Fig. E-4. DN-6 product solids dried at room temperature.



23-Jun-92 15:24:21 SP= A/1 PADC CFS 131072/ALog CC 1/ 0.834

5. SAMPLE PARAMS

Title
DN6 reactor vessel after solids removed and rinsed with water
ID
dn6.empv
Type
solid
Units
g
Geometry
point

Sample 28-MAY-92
Date 00:00:00
SDep 28-MAY-92
Date 00:00:00

```
                          ENERGY WINDOW      .83 TO  2048.74

PK IT  ENERGY    AREA   BKGND   FWHM  CHANNEL  LEFT  PW  CTS/SEC %ERR      FIT

 1  0    73.67  12865.  23319.  2.83   146.65   137  17 2.58E+00  2.9
 2  0    79.68  15291.  11954.  1.05   158.66   155   9 3.06E+00  1.5
 3  0    84.80   5227.  18779.  1.20   168.90   164  14 1.05E+00  5.7
 4  0    99.75    737.  13168.   .86   198.80   195   9 1.48E-01 28.3
 5  0   132.97 188155.  23365.  1.06   265.21   255  16 3.77E+01   .3
 6  0   513.34  48158.   4975.  1.35  1025.80  1011  21 9.65E+00   .5
 7  0   661.07  82822.   1305.  1.44  1321.21  1307  28 1.66E+01   .4
 8  0   695.94   5405.    350.  1.50  1390.93  1379  18 1.08E+00  1.5
 9  0  1171.96   1231.    357.  1.84  2342.77  2312  45 2.47E-01  4.9
10  0  1331.97   1107.     96.  1.77  2662.74  2648  27 2.22E-01  3.5
11  0  1460.20     75.     39.  2.26  2919.15  2913  15 1.50E-02 18.0
12  0  1488.69    533.     91.  1.88  2976.12  2958  31 1.07E-01  5.6

               PEAK SEARCH COMPLETED  (REV 15.8 - ND PC VERSION   MAR 90)

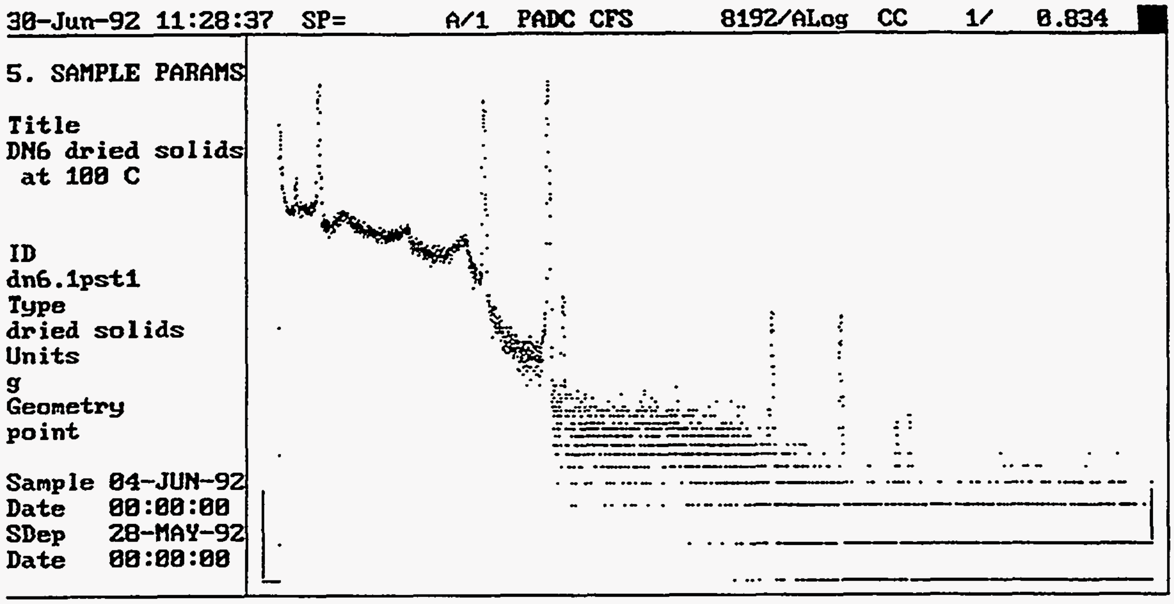
  TOTAL LINES IN SPECTRUM          12
  UNIDENTIFIED PEAKS                5
  IDENTIFIED IN SUMMARY REPORT      7     58.33%


  ACTIVATION PRODUCT
                                                        1-SIGMA
  NUCLIDE  SBHR    HLIFE    DECAY    UCI/g              ERROR        %ERR
  CO-60     AP      5.26Y   1.000     4.125E -6         1.459E -7     3.54


  FISSION PRODUCT
                                                        1-SIGMA
  NUCLIDE  SBHR    HLIFE    DECAY    UCI/g              ERROR        %ERR
  SR-85     FP     65.20D   1.006     1.351E -4         7.417E -7      .55
  CS-137    FP     30.17Y   1.000     3.210E -4         1.167E -6      .36
  CE-144    FP    284.20D   1.001     1.324E -3         3.844E -6      .29


  NATURAL PRODUCT
                                                        1-SIGMA
  NUCLIDE  SBHR    HLIFE    DECAY    UCI/g              ERROR        %ERR
  K-40      NP  1.28E+09Y   1.000     2.883E -6         5.179E -7    17.96
```

Fig. E-5. DN-6 empty reactor vessel after the solids were removed and vessel rinsed.



```
30-Jun-92 11:28:37  SP=        A/1  PADC CFS      8192/ALog  CC    1/   0.834

5. SAMPLE PARAMS

Title
DN6 dried solids
 at 100 C


ID
dn6.1pst1
Type
dried solids
Units
g
Geometry
point

Sample 04-JUN-92
Date   00:00:00
SDep   28-MAY-92
Date   00:00:00
```

```
                    ENERGY WINDOW      .83 TO  2048.74

PK IT  ENERGY    AREA   BKGND   FWHM  CHANNEL  LEFT  PW  CTS/SEC %ERR      FIT

 1  0   79.45   2061.   7048.  3.73   158.20    150  15 5.73E-01  9.3
 2  0  133.21  35044.  13279.  4.42   265.70    251  31 9.73E+00  1.1
 3  0  513.72  28535.   3703.  4.43  1026.57   1009  36 7.93E+00   .8
 4  0  661.56  41904.   1053.  4.44  1322.18   1304  60 1.16E+01   .6
 5  0  696.20    876.    220.  4.87  1391.46   1379  33 2.43E-01  5.9
 6  0 1173.53    599.     90.  3.95  2345.93   2333  33 1.66E-01  5.6
 7  0 1332.63    551.     50.  4.15  2664.06   2647  32 1.53E-01  4.8
 8  0 1488.78     52.     26.  3.60  2976.29   2965  23 1.46E-02 21.4


NUCLIDE IDENTIFICATION SYSTEM    (ND PC VERSION    DEC 88)
SUMMARY OF NUCLIDE ACTIVITY                                      PAGE  3

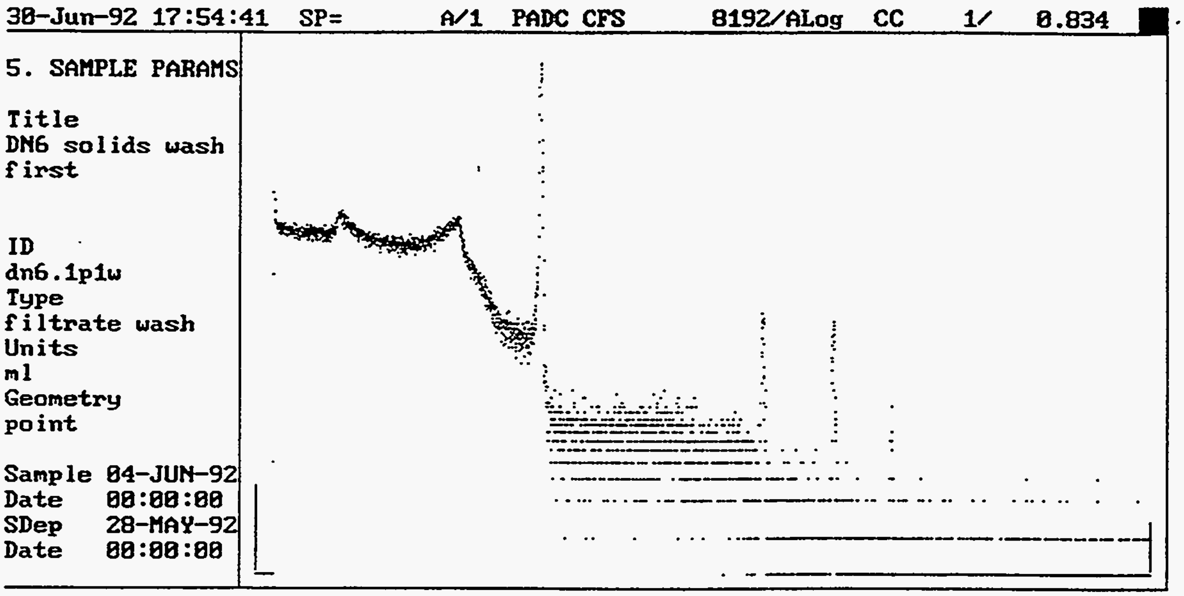
TOTAL LINES IN SPECTRUM           8
UNIDENTIFIED PEAKS                2
IDENTIFIED IN SUMMARY REPORT      6     75.00%


ACTIVATION PRODUCT
                                                        1-SIGMA
NUCLIDE  SBHR    HLIFE    DECAY    UCI/g                ERROR      %ERR
CO-60     AP     5.26Y   1.010     3.193E -3            1.547E -4   4.84


FISSION PRODUCT
                                                        1-SIGMA
NUCLIDE  SBHR    HLIFE    DECAY    UCI/g                ERROR      %ERR
SR-85     FP    65.20D   1.324     1.624E -1            1.336E -3    .82
CS-137    FP    30.17Y   1.002     2.505E -1            1.449E -3    .58
CE-144    FP   284.20D   1.067     4.045E -1            4.554E -3   1.13


NATURAL PRODUCT
                                                        1-SIGMA
NUCLIDE  SBHR    HLIFE    DECAY    UCI/g                ERROR      %ERR
AN-511    NP  1000.00Y   1.000     1.227E -1            1.009E -3    .82
```

Fig. E-6. DN-6 product solids dried at 100°C.



```
30-Jun-92 17:54:41   SP=        A/1  PADC CFS      8192/ALog   CC    1/    0.834

5. SAMPLE PARAMS

Title
DN6 solids wash
first


ID
dn6.1p1w
Type
filtrate wash
Units
ml
Geometry
point

Sample 04-JUN-92
Date   00:00:00
SDep   28-MAY-92
Date   00:00:00
```

```
                    ENERGY WINDOW      .83 TO  2048.74

PK IT  ENERGY   AREA   BKGND   FWHM  CHANNEL  LEFT  PW  CTS/SEC %ERR     FIT

 1  0  661.65  59185.   2154.  4.79  1322.36  1305  40 1.64E+01   .5
 2  0 1173.86    636.     69.  4.51  2346.59  2329  36 1.77E-01  5.4
 3  0 1332.90    503.     73.  4.61  2664.60  2645  37 1.40E-01  5.8
 4  0 1461.91     62.      0.  4.40  2922.56  2908  31 1.72E-02 14.5

         PEAK SEARCH COMPLETED  (REV 15.8 - ND PC VERSION   MAR 90)

  NUCLIDE IDENTIFICATION SYSTEM   (ND PC VERSION   DEC 88)
  SUMMARY OF NUCLIDE ACTIVITY                                 PAGE  3

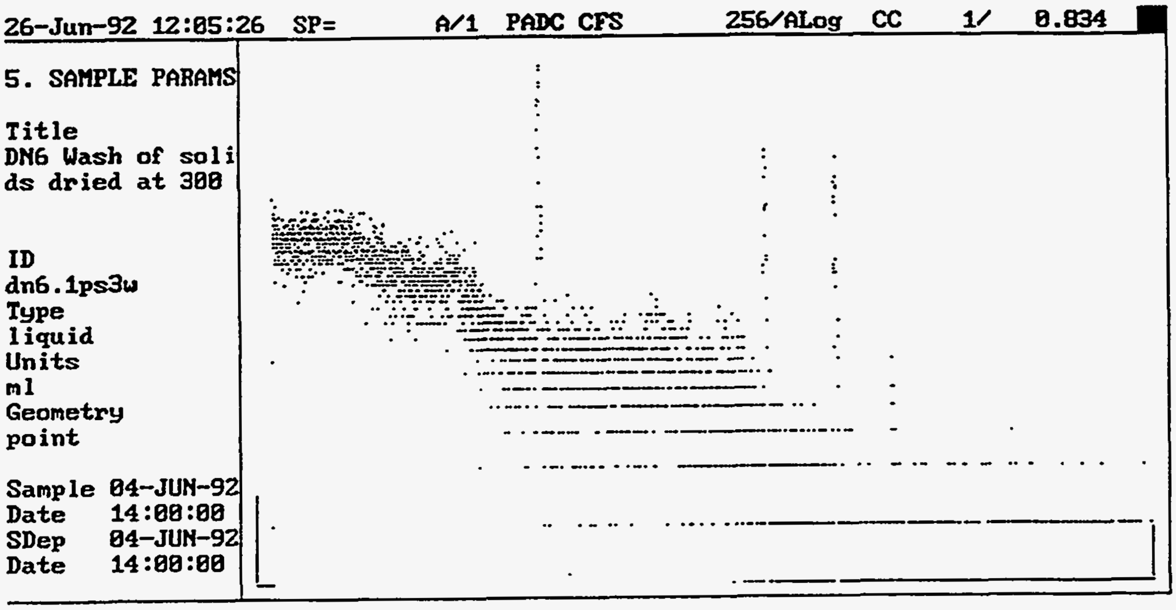
  TOTAL LINES IN SPECTRUM         4
  UNIDENTIFIED PEAKS              0
  IDENTIFIED IN SUMMARY REPORT    4    100.00%


  ACTIVATION PRODUCT
                                                     1-SIGMA
  NUCLIDE  SBHR    HLIFE    DECAY   UCI/ml            ERROR        %ERR
  CO-60     AP      5.26Y   1.010     5.250E -4       3.048E -5     5.81


  FISSION PRODUCT
                                                     1-SIGMA
  NUCLIDE  SBHR    HLIFE    DECAY   UCI/ml            ERROR        %ERR
  CS-137    FP     30.17Y   1.002     6.368E -2       2.982E -4      .47


  NATURAL PRODUCT
                                                     1-SIGMA
  NUCLIDE  SBHR    HLIFE    DECAY   UCI/ml            ERROR        %ERR
  K-40      NP  1.28E+09Y   1.000     6.616E -4       9.618E -5    14.54
```

Fig. E-7. DN-6 wash of room temperature dried solids.



```
26-Jun-92 12:05:26  SP=        A/1  PADC CFS        256/ALog  CC     1/   0.834
5. SAMPLE PARAMS

Title
DN6 Wash of soli
ds dried at 300


ID
dn6.1ps3w
Type
liquid
Units
ml
Geometry
point

Sample 04-JUN-92
Date    14:00:00
SDep   04-JUN-92
Date    14:00:00
```

```
                ENERGY WINDOW       .83 TO  2048.74

PK IT  ENERGY    AREA    BKGND   FWHM  CHANNEL  LEFT  PW  CTS/SEC %ERR     FIT

 1  0  661.20   2035.     217.   4.50  1321.47  1303  36 5.65E-01  3.1
 2  0 1173.02    644.      45.   2.49  2344.89  2329  33 1.79E-01  5.0
 3  0 1332.45    617.      19.   4.16  2663.69  2647  34 1.71E-01  4.3

         PEAK SEARCH COMPLETED  (REV 15.8 - ND PC VERSION   MAR 90)
```

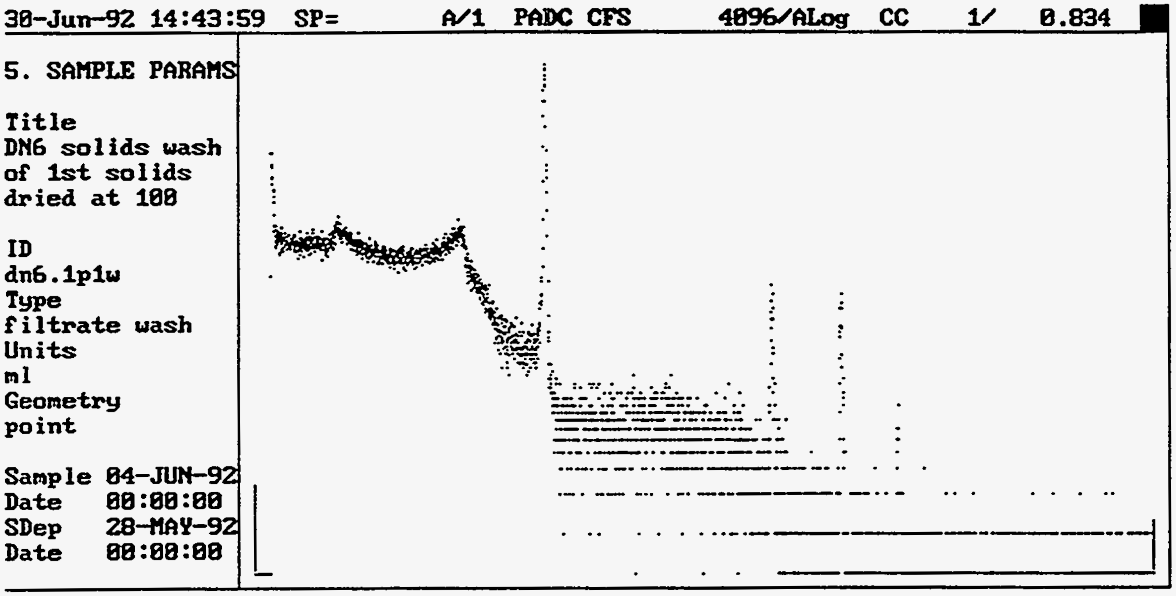
```
NUCLIDE IDENTIFICATION SYSTEM   (ND PC VERSION    DEC 88)
SUMMARY OF NUCLIDE ACTIVITY                                     PAGE  3

TOTAL LINES IN SPECTRUM          3
UNIDENTIFIED PEAKS               0
IDENTIFIED IN SUMMARY REPORT     3    100.00%

ACTIVATION PRODUCT
                                                     1-SIGMA
NUCLIDE  SBHR    HLIFE    DECAY    UCI/ml            ERROR        %ERR
CO-60     AP      5.26Y   1.008     6.417E -4        2.734E -5     4.26

FISSION PRODUCT
                                                     1-SIGMA
NUCLIDE  SBHR    HLIFE    DECAY    UCI/ml            ERROR        %ERR
CS-137    FP     30.17Y   1.001     2.189E -3        6.816E -5     3.11
```

Fig. E-8. DN-6 wash of product solids dried at 300°C.



```
30-Jun-92 14:43:59  SP=        A/1  PADC CFS      4096/ALog  CC     1/   0.834

5. SAMPLE PARAMS

Title
DN6 solids wash
of 1st solids
dried at 100

ID
dn6.1p1w
Type
filtrate wash
Units
ml
Geometry
point

Sample 04-JUN-92
Date   00:00:00
SDep   28-MAY-92
Date   00:00:00
```

```
                     ENERGY WINDOW      .83 TO  2048.74

PK IT  ENERGY    AREA   BKGND   FWHM  CHANNEL  LEFT  PW  CTS/SEC %ERR     FIT

 1  0  661.62  29079.   1227.  4.76  1322.30  1304  44 8.08E+00   .7
 2  0 1173.69    605.     90.  4.49  2346.24  2330  31 1.68E-01  5.4
 3  0 1332.85    546.     37.  4.81  2664.49  2645  37 1.52E-01  4.8
 4  0 1460.43     54.     14.  4.52  2919.61  2902  27 1.49E-02 18.4
```

```
NUCLIDE IDENTIFICATION SYSTEM    (ND PC VERSION   DEC 88)
SUMMARY OF NUCLIDE ACTIVITY                                  PAGE  3

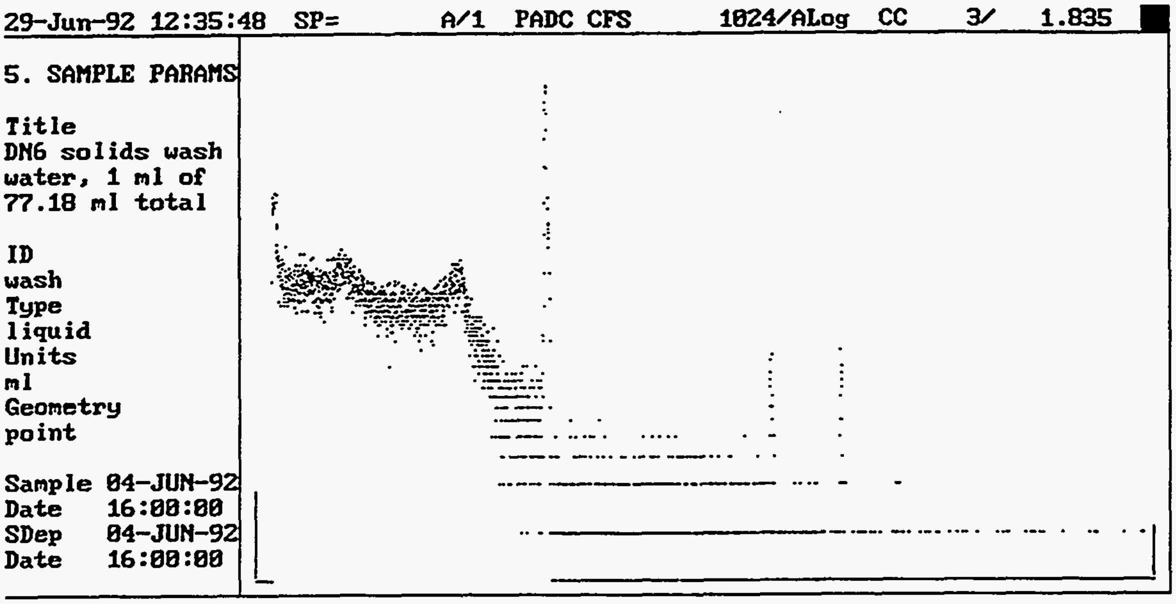
TOTAL LINES IN SPECTRUM          4
UNIDENTIFIED PEAKS               0
IDENTIFIED IN SUMMARY REPORT     4     100.00%

ACTIVATION PRODUCT
                                                          1-SIGMA
NUCLIDE  SBHR     HLIFE    DECAY   UCI/ml                 ERROR        %ERR
CO-60     AP       5.26Y   1.010      5.695E -4           2.740E -5     4.81

FISSION PRODUCT
                                                          1-SIGMA
NUCLIDE  SBHR     HLIFE    DECAY   UCI/ml                 ERROR        %ERR
CS-137    FP      30.17Y   1.002      3.129E -2           2.140E -4      .68

NATURAL PRODUCT
                                                          1-SIGMA
NUCLIDE  SBHR     HLIFE    DECAY   UCI/ml                 ERROR        %ERR
K-40      NP  1.28E+09Y    1.000      5.711E -4           1.050E -4    18.39
```

Fig. E-9. DN-6 wash of product solids dried at 100°C.



```
29-Jun-92 12:35:48  SP=        A/1  PADC CFS      1024/ALog  CC    3/   1.835

5. SAMPLE PARAMS

Title
DN6 solids wash
water, 1 ml of
77.18 ml total

ID
wash
Type
liquid
Units
ml
Geometry
point

Sample 04-JUN-92
Date   16:00:00
SDep   04-JUN-92
Date   16:00:00
```

```
                    ENERGY WINDOW      .83 TO  2048.74

PK IT  ENERGY   AREA   BKGND   FWHM  CHANNEL  LEFT  PW  CTS/SEC %ERR    FIT

 1  0  661.50   6540.    187.  4.98  1322.07  1306  37 1.09E+01  1.4
 2  0 1172.88     93.     18.  3.85  2344.63  2328  28 1.56E-01 15.9
 3  0 1331.74     62.     26.  2.88  2662.29  2650  21 1.04E-01 18.8

           PEAK SEARCH COMPLETED  (REV 15.8 - ND PC VERSION   MAR 90)
```

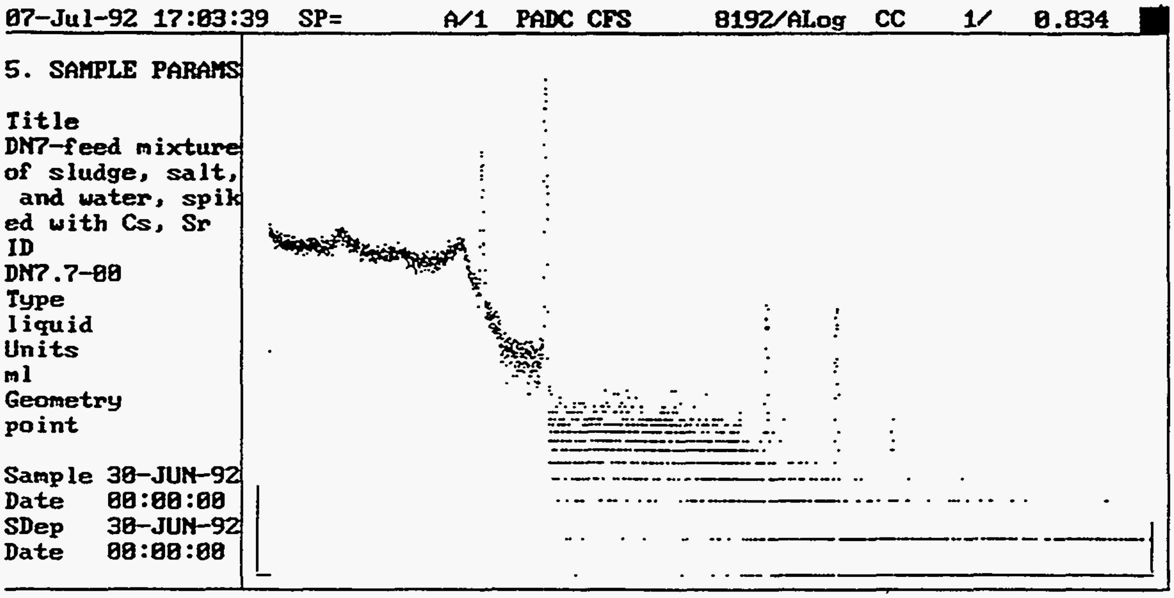
```
NUCLIDE IDENTIFICATION SYSTEM   (ND PC VERSION   DEC 88)
SUMMARY OF NUCLIDE ACTIVITY                                PAGE  3

TOTAL LINES IN SPECTRUM        3
UNIDENTIFIED PEAKS             0
IDENTIFIED IN SUMMARY REPORT   3    100.00%

ACTIVATION PRODUCT
                                                   1-SIGMA
NUCLIDE  SBHR   HLIFE   DECAY   UCI/ml             ERROR      %ERR
CO-60    AP      5.26Y  1.000     3.852E -4        7.227E -5  18.76

FISSION PRODUCT
                                                   1-SIGMA
NUCLIDE  SBHR   HLIFE   DECAY   UCI/ml             ERROR      %ERR
CS-137   FP     30.17Y  1.000     4.215E -2        5.840E -4   1.39
```

Fig. E-10. DN-6 filtrate from wash of reactor and product washed from reactor.



```
07-Jul-92 17:03:39  SP=        A/1  PADC CFS     8192/ALog  CC    1/   0.834

5. SAMPLE PARAMS

Title
DN7-feed mixture
of sludge, salt,
 and water, spik
ed with Cs, Sr
ID
DN7.7-00
Type
liquid
Units
ml
Geometry
point

Sample 30-JUN-92
Date   00:00:00
SDep   30-JUN-92
Date   00:00:00
```

```
                     ENERGY WINDOW      .83 TO  2048.74

PK IT  ENERGY    AREA    BKGND   FWHM  CHANNEL  LEFT  PW  CTS/SEC %ERR      FIT

 1  0  513.68    9870.    2306.  4.13  1026.50  1012  29 2.74E+00  1.6
 2  0  661.47   39041.     650.  3.97  1322.00  1305  35 1.08E+01   .5
 3  0 1173.16     587.      92.  4.05  2345.19  2325  40 1.63E-01  5.7
 4  0 1332.71     571.      32.  3.48  2664.22  2645  34 1.59E-01  4.6
 5  0 1461.23      55.      13.  4.35  2921.21  2909  25 1.52E-02 17.6

           PEAK SEARCH COMPLETED  (REV 15.8 - ND PC VERSION   MAR 90)

     NUCLIDE IDENTIFICATION SYSTEM    (ND PC VERSION    DEC 88)
     SUMMARY OF NUCLIDE ACTIVITY                                  PAGE  3

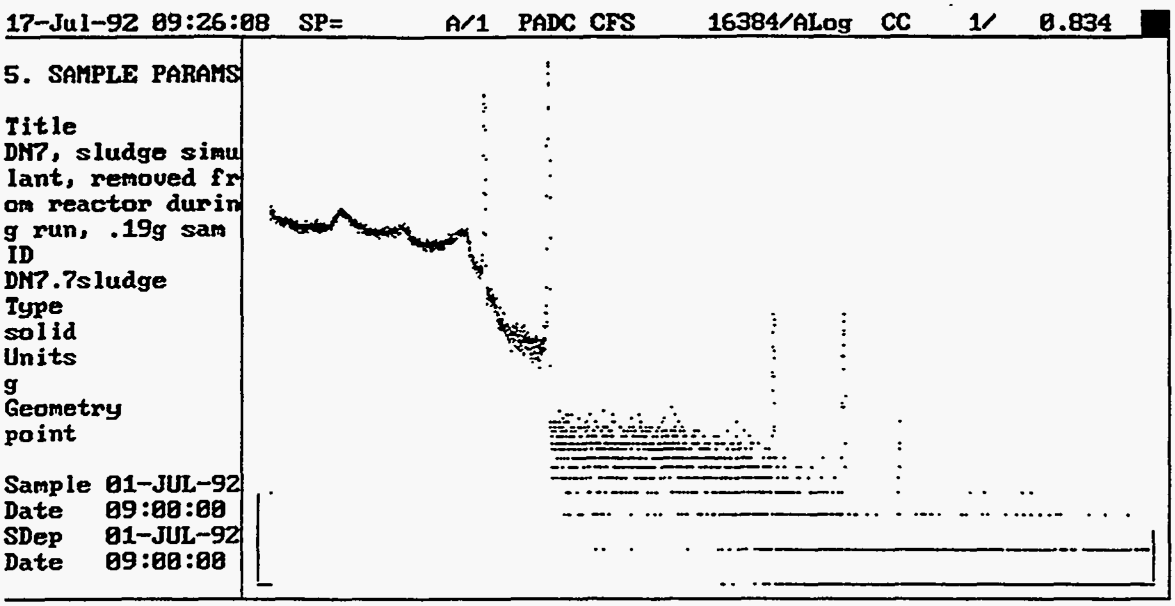
     TOTAL LINES IN SPECTRUM          5
     UNIDENTIFIED PEAKS               0
     IDENTIFIED IN SUMMARY REPORT     5     100.00%

     ACTIVATION PRODUCT
                                                          1-SIGMA
     NUCLIDE  SBHR    HLIFE    DECAY   UCI/ml             ERROR        %ERR
     CO-60     AP      5.26Y   1.003     5.912E -3        2.691E -4    4.55

     FISSION PRODUCT
                                                          1-SIGMA
     NUCLIDE  SBHR    HLIFE    DECAY   UCI/ml             ERROR        %ERR
     SR-85     FP     65.20D   1.082     8.263E -2        1.311E -3    1.59
     CS-137    FP     30.17Y   1.000     4.196E -1        2.242E -3     .53

     NATURAL PRODUCT
                                                          1-SIGMA
     NUCLIDE  SBHR    HLIFE    DECAY   UCI/ml             ERROR        %ERR
     K-40      NP  1.28E+09Y   1.000     5.829E -3        1.028E -3   17.65
```

Fig. E-11. DN-7 Hanford surrogate feed mixture of sludge, salt, and water.



```
17-Jul-92 09:26:08  SP=        A/1  PADC CFS     16384/ALog  CC    1/   0.834

5. SAMPLE PARAMS

Title
DN7, sludge simu
lant, removed fr
om reactor durin
g run, .19g sam
ID
DN7.7sludge
Type
solid
Units
g
Geometry
point

Sample 01-JUL-92
Date   09:00:00
SDep   01-JUL-92
Date   09:00:00
```

```
                  ENERGY WINDOW      .83 TO  2048.74

PK IT  ENERGY   AREA    BKGND   FWHM  CHANNEL  LEFT  PW  CTS/SEC %ERR     FIT

 1  0  514.08  44956.   5536.  3.02  1027.29  1013  29 1.25E+01    .6
 2  0  661.87  87813.   1134.  3.13  1322.81  1304  34 2.44E+01    .4
 3  0 1173.89    621.     67.  2.55  2346.64  2331  32 1.72E-01   5.1
 4  0 1333.29    589.     17.  2.63  2665.38  2649  29 1.64E-01   4.4
 5  0 1461.03     43.     17.  1.89  2920.80  2909  21 1.20E-02  20.3

        PEAK SEARCH COMPLETED  (REV 15.8 - ND PC VERSION   MAR 90)


    NUCLIDE IDENTIFICATION SYSTEM   (ND PC VERSION   DEC 88)
    SUMMARY OF NUCLIDE ACTIVITY                                 PAGE  3

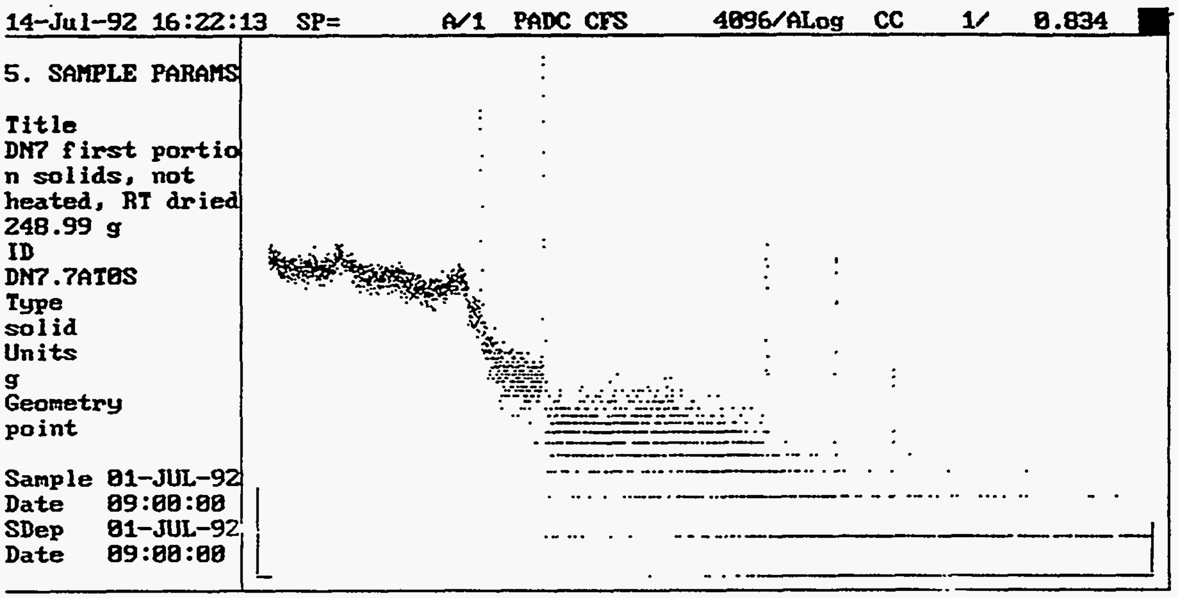
    TOTAL LINES IN SPECTRUM         5
    UNIDENTIFIED PEAKS              0
    IDENTIFIED IN SUMMARY REPORT    5     100.00%

    ACTIVATION PRODUCT
                                                       1-SIGMA
    NUCLIDE  SBHR     HLIFE    DECAY    UCI/g          ERROR        %ERR
    CO-60     AP      5.26Y    1.006     3.220E -3     1.404E -4     4.36

    FISSION PRODUCT
                                                       1-SIGMA
    NUCLIDE  SBHR     HLIFE    DECAY    UCI/g          ERROR        %ERR
    SR-85     FP     65.20D    1.177    .2.156E -1     1.331E -3      .62
    CS-137    FP     30.17Y    1.001     4.969E -1     1.745E -3      .35

    NATURAL PRODUCT
                                                       1-SIGMA
    NUCLIDE  SBHR     HLIFE    DECAY    UCI/g          ERROR        %ERR
    K-40      NP  1.28E+09Y    1.000     2.431E -3     4.945E -4    20.35
```

Fig. E-12. DN-7 sludge simulant removed during experiment.



```
14-Jul-92 16:22:13  SP=        A/1  PADC CFS       4096/ALog  CC    1/   0.834

5. SAMPLE PARAMS

Title
DN7 first portio
n solids, not
heated, RT dried
248.99 g
ID
DN7.7AT0S
Type
solid
Units
g
Geometry
point

Sample 01-JUL-92
Date   09:00:00
SDep   01-JUL-92
Date   09:00:00
```

```
                ENERGY WINDOW      .83 TO  2048.74

PK IT  ENERGY    AREA   BKGND   FWHM  CHANNEL  LEFT  PW  CTS/SEC %ERR      FIT

 1  0  514.05    5300.    620.  1.70  1027.24  1018  17 1.47E+00  1.6
 2  0  661.88   13927.    245.  1.78  1322.83  1310  25 3.87E+00   .9
 3  0 1173.94     589.     51.  2.01  2346.74  2333  22 1.64E-01  4.8
 4  0 1333.24     542.     53.  2.36  2665.29  2652  20 1.50E-01  4.7
 5  0 1461.81      69.     17.  2.09  2922.36  2909  21 1.91E-02 15.4

           PEAK SEARCH COMPLETED  (REV 15.8 - ND PC VERSION   MAR 90)
```

```
NUCLIDE IDENTIFICATION SYSTEM   (ND PC VERSION   DEC 88)
SUMMARY OF NUCLIDE ACTIVITY                                PAGE  3

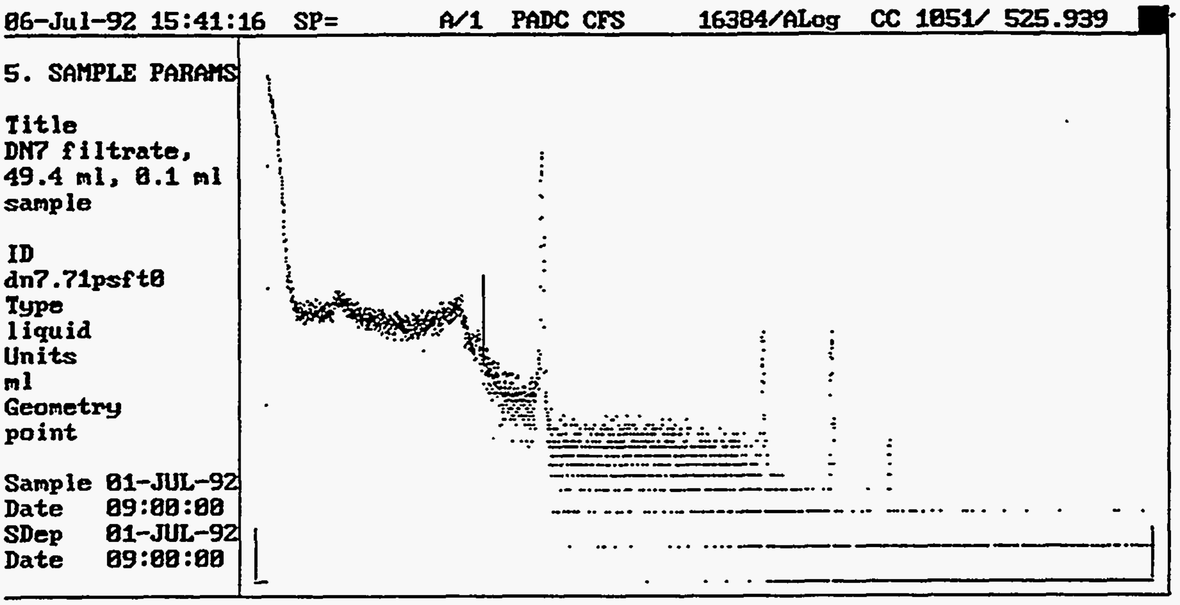
TOTAL LINES IN SPECTRUM          5
UNIDENTIFIED PEAKS               0
IDENTIFIED IN SUMMARY REPORT     5     100.00%

ACTIVATION PRODUCT
                                                     1-SIGMA
NUCLIDE  SBHR    HLIFE     DECAY   UCI/g             ERROR       %ERR
CO-60     AP       5.26Y   1.004     5.620E -3       2.649E -4    4.71

FISSION PRODUCT
                                                     1-SIGMA
NUCLIDE  SBHR    HLIFE     DECAY   UCI/g             ERROR       %ERR
SR-85     FP     65.20D    1.139     4.671E -2       7.671E -4    1.64
CS-137    FP     30.17Y    1.001     1.497E -1       1.333E -3     .89

NATURAL PRODUCT
                                                     1-SIGMA
NUCLIDE  SBHR    HLIFE     DECAY   UCI/g             ERROR       %ERR
K-40      NP  1.28E+09Y    1.000     7.355E -3       1.132E -3   15.39
```

Fig. E-13. DN-7 first product solids dried at room temperature.



```
06-Jul-92 15:41:16  SP=        A/1  PADC CFS      16384/ALog  CC 1051/ 525.939

5. SAMPLE PARAMS

Title
DN7 filtrate,
49.4 ml, 0.1 ml
sample

ID
dn7.71psft0
Type
liquid
Units
ml
Geometry
point

Sample 01-JUL-92
Date   09:00:00
SDep   01-JUL-92
Date   09:00:00
```

```
                    ENERGY WINDOW      .83 TO  2048.74

PK IT  ENERGY    AREA    BKGND    FWHM  CHANNEL   LEFT  PW  CTS/SEC %ERR      FIT

 1  0   57.51     618.   11171.   1.40   114.34    113   5 1.72E-01 26.1
 2  0  661.60   18781.     841.   4.16  1322.26   1304  36 5.22E+00   .8
 3  0 1173.62     583.      65.   4.42  2346.10   2330  33 1.62E-01  5.4
 4  0 1332.89     555.      44.   3.97  2664.58   2647  32 1.54E-01  4.9
 5  0 1460.88      39.      30.   5.04  2920.51   2907  22 1.09E-02 24.5

         PEAK SEARCH COMPLETED  (REV 15.8 - ND PC VERSION   MAR 90)


  NUCLIDE IDENTIFICATION SYSTEM   (ND PC VERSION   DEC 88)
  SUMMARY OF NUCLIDE ACTIVITY                                PAGE  3

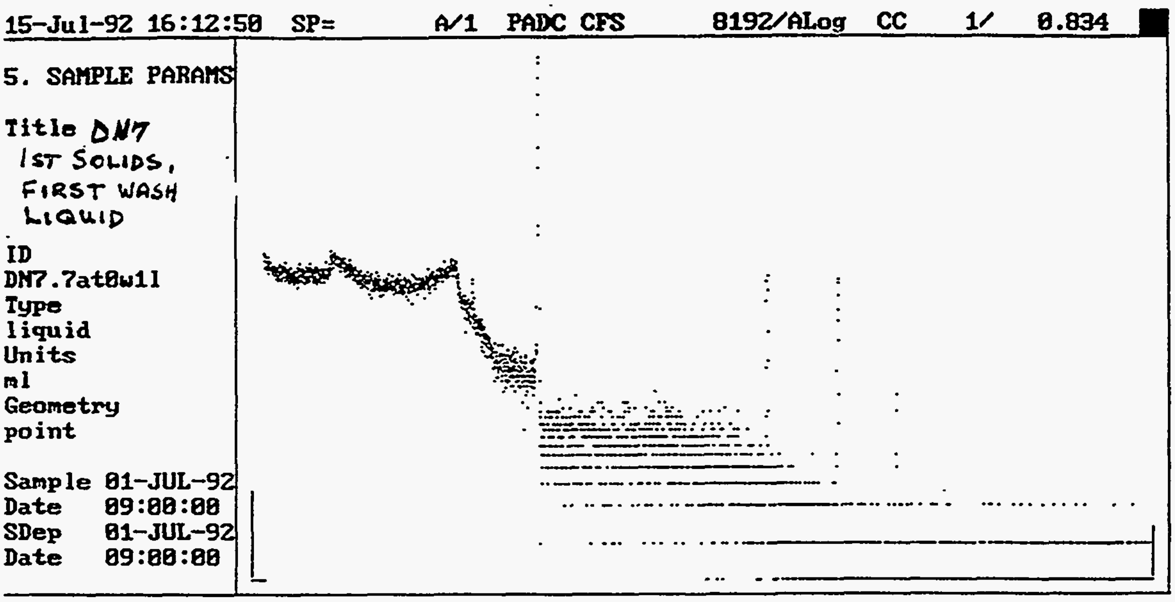
  TOTAL LINES IN SPECTRUM          5
  UNIDENTIFIED PEAKS               1
  IDENTIFIED IN SUMMARY REPORT     4      80.00%


  ACTIVATION PRODUCT
                                                     1-SIGMA
  NUCLIDE   SBHR    HLIFE     DECAY   UCI/ml          ERROR        %ERR
  CO-60      AP      5.26Y    1.002     5.749E -3     2.821E -4     4.91


  FISSION PRODUCT
                                                     1-SIGMA
  NUCLIDE   SBHR    HLIFE     DECAY   UCI/ml          ERROR        %ERR
  CS-137     FP     30.17Y    1.000     2.018E -1     1.691E -3      .84


  NATURAL PRODUCT
                                                     1-SIGMA
  NUCLIDE   SBHR    HLIFE     DECAY   UCI/ml          ERROR        %ERR
  K-40       NP  1.28E+09Y    1.000     4.194E -3     1.029E -3    24.54
```

Fig. E-14. DN-7 first filtrate liquid from the reactor.



```
15-Jul-92 16:12:50  SP=       A/1  PADC CFS      8192/ALog  CC    1/   0.834

5. SAMPLE PARAMS
Title DN7
 1st Solids,
 First Wash
 Liquid
ID
DN7.7at0w11
Type
liquid
Units
ml
Geometry
point

Sample 01-JUL-92
Date   09:00:00
SDep   01-JUL-92
Date   09:00:00
```

```
                    ENERGY WINDOW      .83 TO  2048.74

 PK IT  ENERGY    AREA   BKGND   FWHM  CHANNEL  LEFT  PW  CTS/SEC %ERR      FIT

 1  0  514.05     314.   1164.  1.83  1027.23  1018  20 8.73E-02 24.1
 2  0  661.86   28247.    485.  1.80  1322.79  1304  29 7.85E+00   .6
 3  0 1173.91     565.     60.  1.95  2346.69  2334  28 1.57E-01  5.0
 4  0 1333.23     545.     29.  1.96  2665.27  2652  21 1.51E-01  4.5
 5  0 1461.19      34.     18.   .98  2921.12  2904  23 9.52E-03 23.1

          PEAK SEARCH COMPLETED  (REV 15.8 - ND PC VERSION   MAR 90)


NUCLIDE IDENTIFICATION SYSTEM   (ND PC VERSION   DEC 88)
SUMMARY OF NUCLIDE ACTIVITY                              PAGE  3

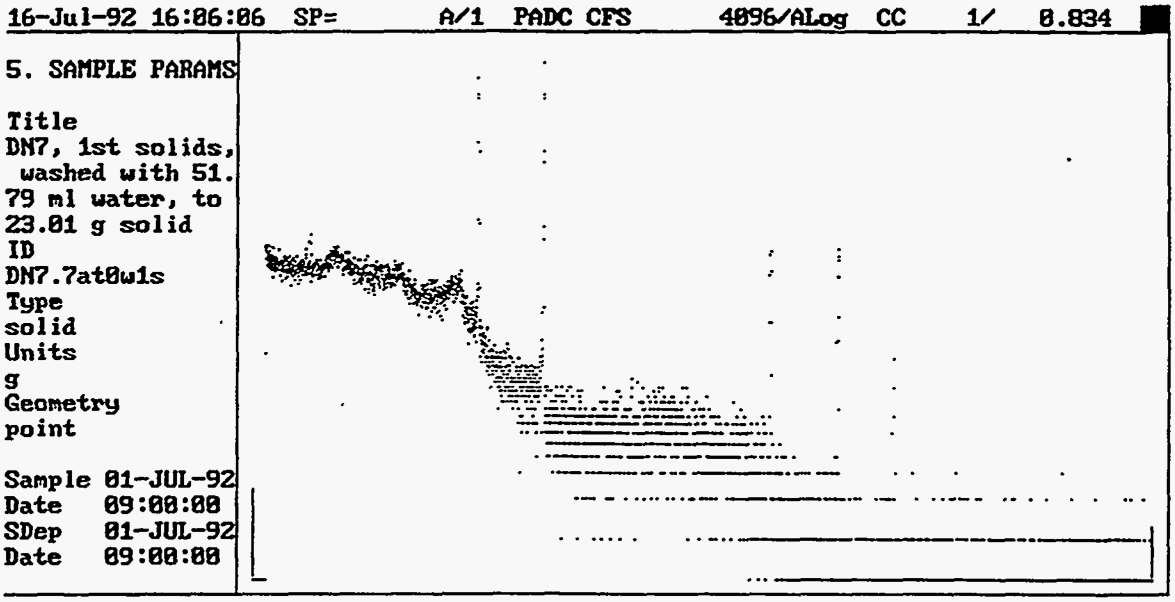
TOTAL LINES IN SPECTRUM          5
UNIDENTIFIED PEAKS               0
IDENTIFIED IN SUMMARY REPORT     5    100.00%


ACTIVATION PRODUCT
                                                    1-SIGMA
NUCLIDE  SBHR    HLIFE    DECAY   UCI/ml            ERROR      %ERR
CO-60     AP      5.26Y   1.004     5.659E -4       2.546E -5   4.50


FISSION PRODUCT
                                                    1-SIGMA
NUCLIDE  SBHR    HLIFE    DECAY   UCI/ml            ERROR      %ERR
SR-85     FP     65.20D   1.139     2.771E -4       6.678E -5  24.10
CS-137    FP     30.17Y   1.001     3.037E -2       1.887E -4    .62


NATURAL PRODUCT
                                                    1-SIGMA
NUCLIDE  SBHR    HLIFE    DECAY   UCI/ml            ERROR      %ERR
K-40      NP  1.28E+09Y   1.000     3.655E -4       8.436E -5  23.08
```

Fig. E-15. DN-7 first solids wash liquid.



```
16-Jul-92 16:06:06  SP=        A/1  PADC CFS       4096/ALog  CC     1/   0.834

5. SAMPLE PARAMS

Title
DN7, 1st solids,
 washed with 51.
79 ml water, to
23.01 g solid
ID
DN7.7at0w1s
Type
solid
Units
g
Geometry
point

Sample 01-JUL-92
Date    09:00:00
SDep    01-JUL-92
Date    09:00:00
```

```
                      ENERGY WINDOW       .83 TO  2048.74

        PK IT  ENERGY   AREA    BKGND   FWHM  CHANNEL  LEFT  PW  CTS/SEC %ERR      FIT

         1  0  121.65    128.    915.  1.38    242.57   239  10 3.56E-02 45.8
         2  0  132.68    149.    892.  1.29    264.64   262   9 4.13E-02 37.6
         3  0  513.84   7858.    654.  1.56   1026.81  1014  21 2.18E+00  1.3
         4  0  661.72  11291.    211.  1.65   1322.50  1311  22 3.14E+00  1.0
         5  0 1173.82    528.     65.  1.94   2346.50  2333  26 1.47E-01  5.4
         6  0 1333.22    561.     18.  1.97   2665.24  2653  20 1.56E-01  4.5
         7  0 1461.09     45.     28.  1.30   2920.92  2912  15 1.26E-02 20.2

               PEAK SEARCH COMPLETED  (REV 15.8 - ND PC VERSION   MAR 90)

          NUCLIDE IDENTIFICATION SYSTEM    (ND PC VERSION   DEC 88)
          SUMMARY OF NUCLIDE ACTIVITY                                  PAGE  3

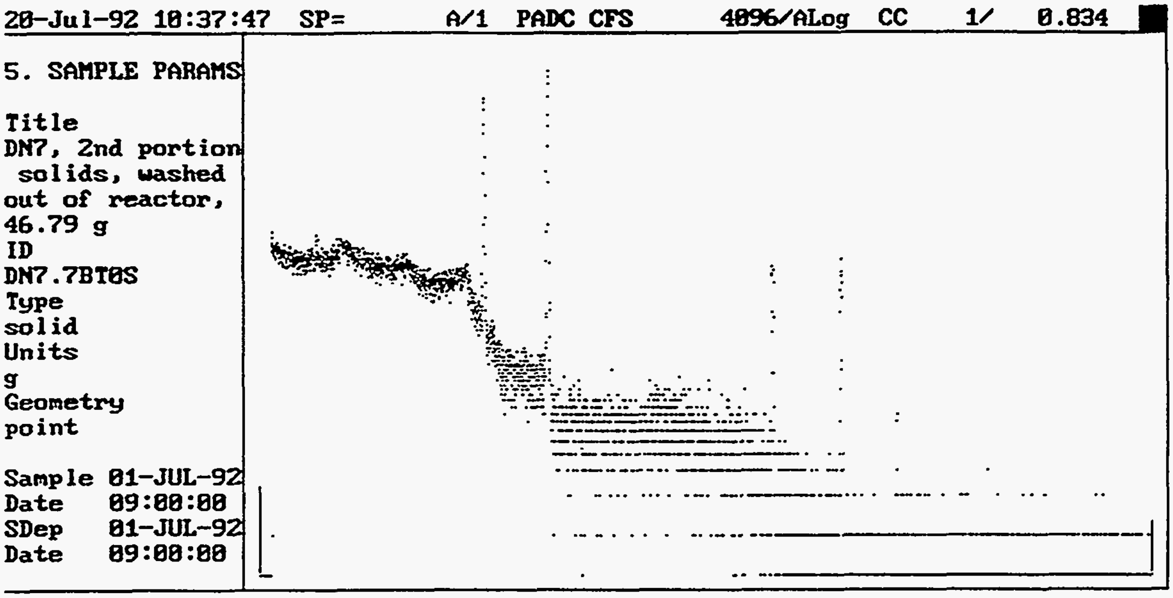
          TOTAL LINES IN SPECTRUM          7
          UNIDENTIFIED PEAKS               0
          IDENTIFIED IN SUMMARY REPORT     7    100.00%

          ACTIVATION PRODUCT
                                                           1-SIGMA
          NUCLIDE  SBHR    HLIFE    DECAY    UCI/g         ERROR       %ERR
          CO-60     AP      5.26Y   1.005     7.275E -3    3.255E -4    4.47

          FISSION PRODUCT
                                                           1-SIGMA
          NUCLIDE  SBHR    HLIFE    DECAY    UCI/g         ERROR       %ERR
          CO-57     FP    270.00D   1.034     4.091E -4    1.876E -4   45.84
          SR-85     FP     65.20D   1.148     8.727E -2    1.157E -3    1.33
          CS-137    FP     30.17Y   1.001     1.517E -1    1.496E -3     .99
          CE-144    FP    284.20D   1.032     3.733E -3    1.403E -3   37.59

          NATURAL PRODUCT
                                                           1-SIGMA
          NUCLIDE  SBHR    HLIFE    DECAY    UCI/g         ERROR       %ERR
          K-40      NP  1.28E+09Y   1.000     6.044E -3    1.223E -3   20.24
```

Fig. E-16. DN-7 first solids after washing.



```
20-Jul-92 10:37:47  SP=      A/1  PADC CFS      4096/ALog  CC    1/   0.834

5. SAMPLE PARAMS

Title
DN7, 2nd portion
 solids, washed
out of reactor,
46.79 g
ID
DN7.7BT0S
Type
solid
Units
g
Geometry
point

Sample 01-JUL-92
Date   09:00:00
SDep   01-JUL-92
Date   09:00:00
```

```
                    ENERGY WINDOW      .83 TO  2048.74

PK IT  ENERGY    AREA    BKGND   FWHM  CHANNEL  LEFT  PW  CTS/SEC %ERR     FIT

 1  0  132.86     224.   1208.  1.93   265.01    261  11 6.23E-02 31.1
 2  0  513.59    8678.    958.  2.32  1026.30   1011  29 2.41E+00   .4
 3  0  661.40   13840.    351.  2.26  1321.87   1304  41 3.84E+00  1.0
 4  0 1173.42     589.     73.  2.81  2345.70   2330  29 1.64E-01  5.2
 5  0 1332.61     557.     49.  2.77  2664.02   2647  25 1.55E-01  4.8
 6  0 1460.27      37.     14.  2.63  2919.29   2907  20 1.04E-02 21.3

          PEAK SEARCH COMPLETED  (REV 15.8 - ND PC VERSION   MAR 90)

   NUCLIDE IDENTIFICATION SYSTEM   (ND PC VERSION   DEC 88)
   SUMMARY OF NUCLIDE ACTIVITY                                PAGE  3

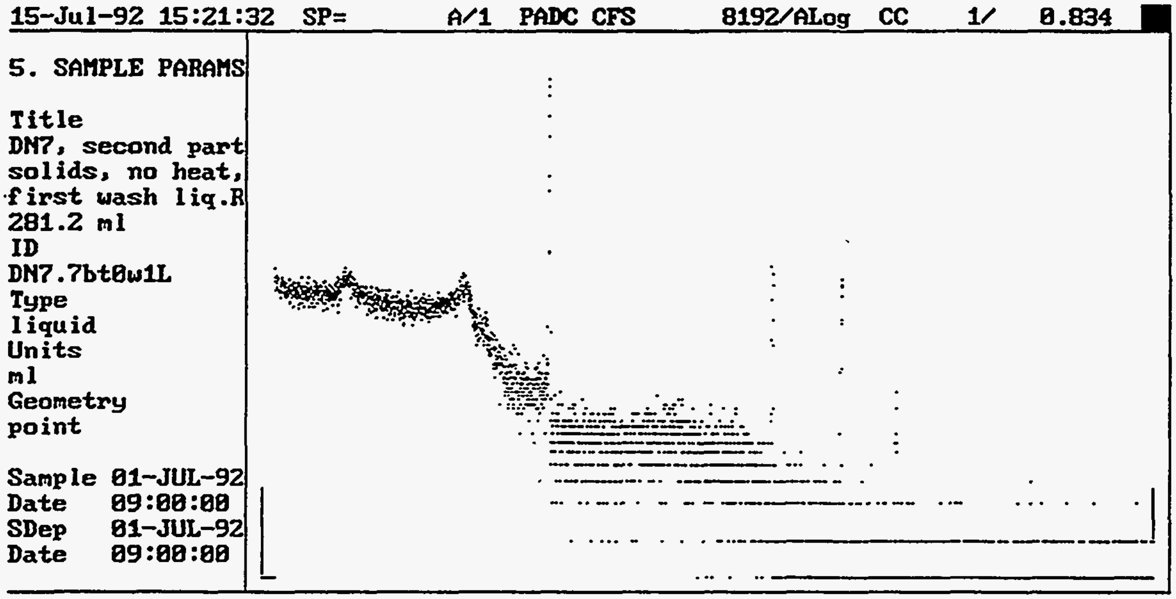
   TOTAL LINES IN SPECTRUM          6
   UNIDENTIFIED PEAKS               0
   IDENTIFIED IN SUMMARY REPORT     6     100.00%

   ACTIVATION PRODUCT
                                                      1-SIGMA
   NUCLIDE  SBHR    HLIFE    DECAY   UCI/g            ERROR       %ERR
   CO-60     AP      5.26Y   1.007     4.452E -3      2.122E -4    4.77

   FISSION PRODUCT
                                                      1-SIGMA
   NUCLIDE  SBHR    HLIFE    DECAY   UCI/g            ERROR       %ERR
   SR-85     FP     65.20D   1.224     6.319E -2      8.810E -4    1.39
   CS-137    FP     30.17Y   1.001     1.145E -1      1.095E -3     .96
   CE-144    FP    284.20D   1.047     3.520E -3      1.096E -3   31.13

   NATURAL PRODUCT
                                                      1-SIGMA
   NUCLIDE  SBHR    HLIFE    DECAY   UCI/g            ERROR       %ERR
   K-40      NP  1.28E+09Y   1.000     3.060E -3      6.506E -4   21.26
```

Fig. E-17. DN-7 second solids, washed from the reactor during cleanup.



```
15-Jul-92 15:21:32  SP=        A/1  PADC CFS      8192/ALog  CC    1/   0.834

5. SAMPLE PARAMS

Title
DN7, second part
solids, no heat,
first wash liq.R
281.2 ml
ID
DN7.7bt0w1L
Type
liquid
Units
ml
Geometry
point

Sample 01-JUL-92
Date   09:00:00
SDep   01-JUL-92
Date   09:00:00
```

```
                    ENERGY WINDOW      .83 TO  2048.74

PK IT  ENERGY   AREA   BKGND  FWHM  CHANNEL  LEFT  PW  CTS/SEC %ERR     FIT

 1  0  661.88  17190.   285.  1.82  1322.83  1307  27 4.78E+00   .8
 2  0 1173.94    622.    22.  1.86  2346.74  2340  16 1.73E-01  4.2
 3  0 1333.22    587.    15.  2.35  2665.24  2650  23 1.63E-01  4.3
 4  0 1462.25     78.     0.  1.64  2923.26  2900  59 2.17E-02 13.6

         PEAK SEARCH COMPLETED  (REV 15.8 - ND PC VERSION   MAR 90)


    NUCLIDE IDENTIFICATION SYSTEM   (ND PC VERSION   DEC 88)
    SUMMARY OF NUCLIDE ACTIVITY                            PAGE  3

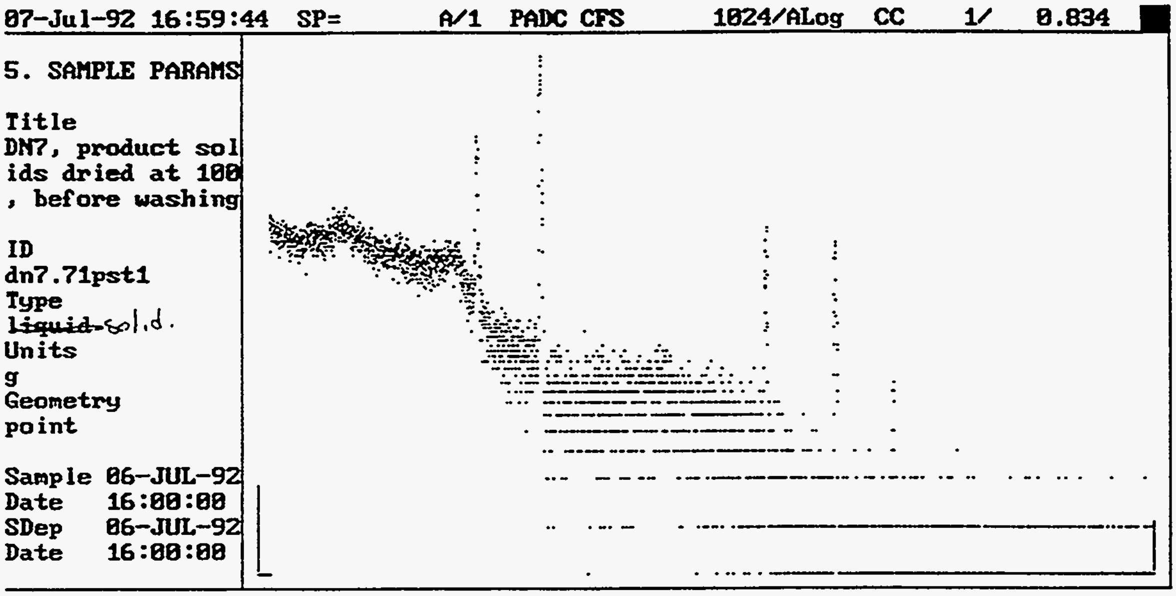
    TOTAL LINES IN SPECTRUM        4
    UNIDENTIFIED PEAKS             0
    IDENTIFIED IN SUMMARY REPORT   4    100.00%


    ACTIVATION PRODUCT
                                                    1-SIGMA
    NUCLIDE  SBHR    HLIFE    DECAY   UCI/ml        ERROR       %ERR
    CO-60     AP      5.26Y   1.004     6.096E -4   2.616E -5    4.29


    FISSION PRODUCT
                                                    1-SIGMA
    NUCLIDE  SBHR    HLIFE    DECAY   UCI/ml        ERROR       %ERR
    CS-137    FP     30.17Y   1.001     1.848E -2   1.477E -4     .80


    NATURAL PRODUCT
                                                    1-SIGMA
    NUCLIDE  SBHR    HLIFE    DECAY   UCI/ml        ERROR       %ERR
    K-40      NP  1.28E+09Y   1.000     8.327E -4   1.134E -4   13.62
```

Fig. E-18. DN-7 second solids, wash liquid from reactor cleanup.



07-Jul-92 16:59:44 SP= A/1 PADC CFS 1024/ALog CC 1/ 0.834

5. SAMPLE PARAMS

Title
DN7, product sol
ids dried at 100
, before washing

ID
dn7.71pst1
Type
~~liquid~~ solid.
Units
g
Geometry
point

Sample 06-JUL-92
Date 16:00:00
SDep 06-JUL-92
Date 16:00:00

```
                    ENERGY WINDOW      .83 TO  2048.74

PK IT  ENERGY   AREA   BKGND   FWHM  CHANNEL  LEFT  PW  CTS/SEC %ERR     FIT

 1  0  513.77   2364.    870.  4.44  1026.67  1010  34 6.57E-01  3.9
 2  0  661.73   7862.    268.  4.45  1322.52  1305  36 2.18E+00  1.3
 3  0 1174.05    610.     66.  3.57  2346.96  2331  36 1.69E-01  5.3
 4  0 1333.20    597.      0.  3.65  2665.20  2646  39 1.66E-01  4.3
 5  0 1461.19     54.     20.  3.60  2921.13  2907  26 1.49E-02 19.4

          PEAK SEARCH COMPLETED  (REV 15.8 - ND PC VERSION   MAR 90)

 NUCLIDE IDENTIFICATION SYSTEM   (ND PC VERSION   DEC 88)
 SUMMARY OF NUCLIDE ACTIVITY                                 PAGE  3

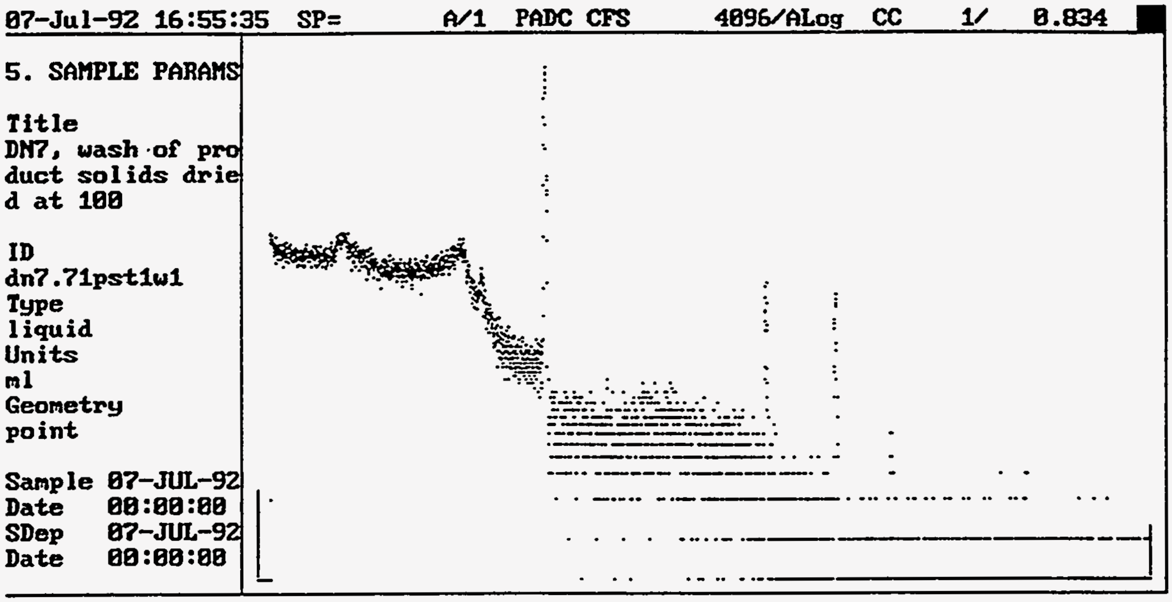
 TOTAL LINES IN SPECTRUM         5
 UNIDENTIFIED PEAKS              0
 IDENTIFIED IN SUMMARY REPORT    5    100.00%

 ACTIVATION PRODUCT
                                                   1-SIGMA
 NUCLIDE  SBHR    HLIFE    DECAY   UCI/g           ERROR        %ERR
 CO-60     AP      5.26Y   1.000     1.234E -2     5.249E -4     4.25

 FISSION PRODUCT
                                                   1-SIGMA
 NUCLIDE  SBHR    HLIFE    DECAY   UCI/g           ERROR        %ERR
 SR-85     FP     65.20D   1.010     3.698E -2     1.434E -3     3.88
 CS-137    FP     30.17Y   1.000     1.689E -1     2.114E -3     1.25

 NATURAL PRODUCT
                                                   1-SIGMA
 NUCLIDE  SBHR    HLIFE    DECAY   UCI/g           ERROR        %ERR
 K-40      NP  1.28E+09Y   1.000     1.144E -2     2.215E -3    19.36
```

Fig. E-19. DN-7 product solids dried at 100°C, before washing.



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07-Jul-92 16:55:35  SP=        A/1  PADC CFS       4096/ALog  CC     1/    0.834

5. SAMPLE PARAMS

Title
DN7, wash of pro
duct solids drie
d at 100

ID
dn7.71pst1w1
Type
liquid
Units
ml
Geometry
point

Sample 07-JUL-92
Date   00:00:00
SDep   07-JUL-92
Date   00:00:00
```

```
                    ENERGY WINDOW      .83 TO  2048.74

 PK IT  ENERGY    AREA    BKGND   FWHM  CHANNEL  LEFT  PW  CTS/SEC %ERR     FIT

  1  0  661.56  24101.     443.   4.10  1322.18  1305  35 6.69E+00   .7
  2  0 1173.59    602.      73.   3.48  2346.04  2324  39 1.67E-01  5.5
  3  0 1332.77    522.      40.   4.01  2664.34  2650  28 1.45E-01  5.0

         PEAK SEARCH COMPLETED  (REV 15.8 - ND PC VERSION   MAR 90)

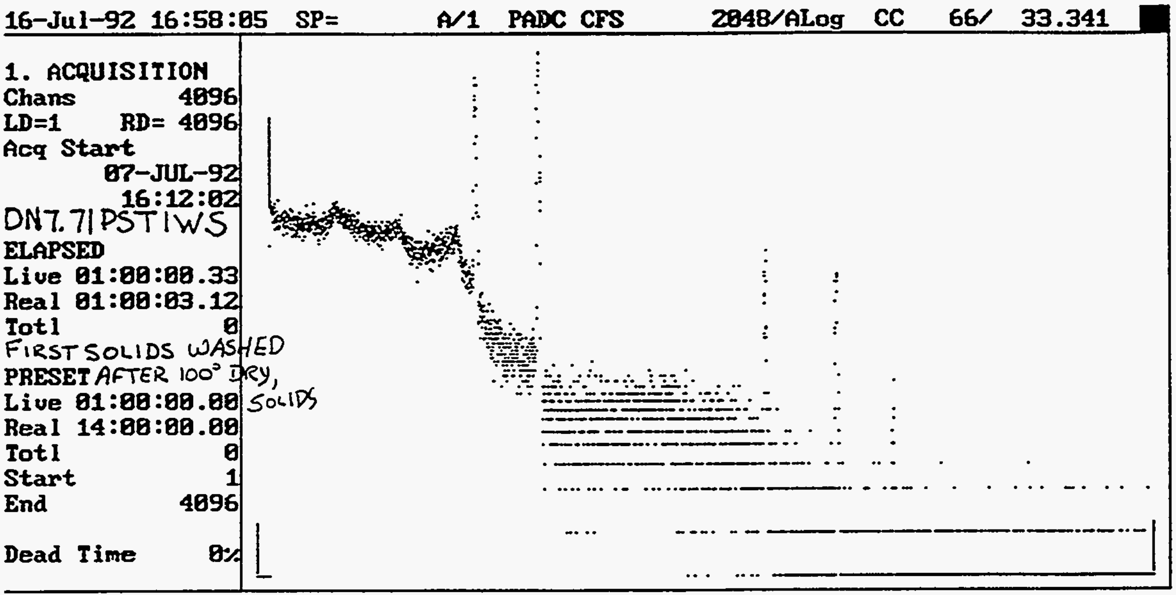

    NUCLIDE IDENTIFICATION SYSTEM    (ND PC VERSION   DEC 88)
    SUMMARY OF NUCLIDE ACTIVITY                                  PAGE  3

    TOTAL LINES IN SPECTRUM           3
    UNIDENTIFIED PEAKS                0
    IDENTIFIED IN SUMMARY REPORT      3    100.00%

    ACTIVATION PRODUCT
                                                       1-SIGMA
    NUCLIDE  SBHR    HLIFE    DECAY   UCI/ml           ERROR       %ERR
    CO-60     AP      5.26Y   1.000     5.395E -4      2.679E -5    4.96

    FISSION PRODUCT
                                                       1-SIGMA
    NUCLIDE  SBHR    HLIFE    DECAY   UCI/ml           ERROR       %ERR
    CS-137    FP     30.17Y   1.000     2.589E -2      1.769E -4     .68
```

Fig. E-20. DN-7 wash of product solids dried at 100°C.



```
16-Jul-92 16:58:05  SP=        A/1  PADC CFS       2048/ALog  CC    66/  33.341

1. ACQUISITION
Chans         4096
LD=1     RD= 4096
Acq Start
       07-JUL-92
        16:12:02
DN7.71PSTIWS
ELAPSED
Live 01:00:00.33
Real 01:00:03.12
Totl            0
FIRST SOLIDS WASHED
PRESET AFTER 100° DRY,
Live 01:00:00.00 SOLIDS
Real 14:00:00.00
Totl            0
Start           1
End          4096

Dead Time      0%
```

```
                  ENERGY WINDOW      .83 TO  2048.74

PK IT  ENERGY   AREA   BKGND   FWHM  CHANNEL  LEFT  PW  CTS/SEC %ERR      FIT

 1  0   513.93  10532.   1413.  4.35  1026.99  1010  34 2.93E+00  1.4
 2  0   661.73  16912.    334.  4.31  1322.53  1306  34 4.70E+00   .8
 3  0  1173.79    552.    123.  2.56  2346.45  2330  34 1.53E-01  6.3
 4  0  1333.10    566.     40.  4.33  2664.99  2647  33 1.57E-01  4.8
 5  0  1461.67     54.     13.  1.37  2922.09  2906  29 1.50E-02 18.5

         PEAK SEARCH COMPLETED  (REV 15.8 - ND PC VERSION   MAR 90)


NUCLIDE IDENTIFICATION SYSTEM   (ND PC VERSION   DEC 88)
SUMMARY OF NUCLIDE ACTIVITY                                PAGE  3

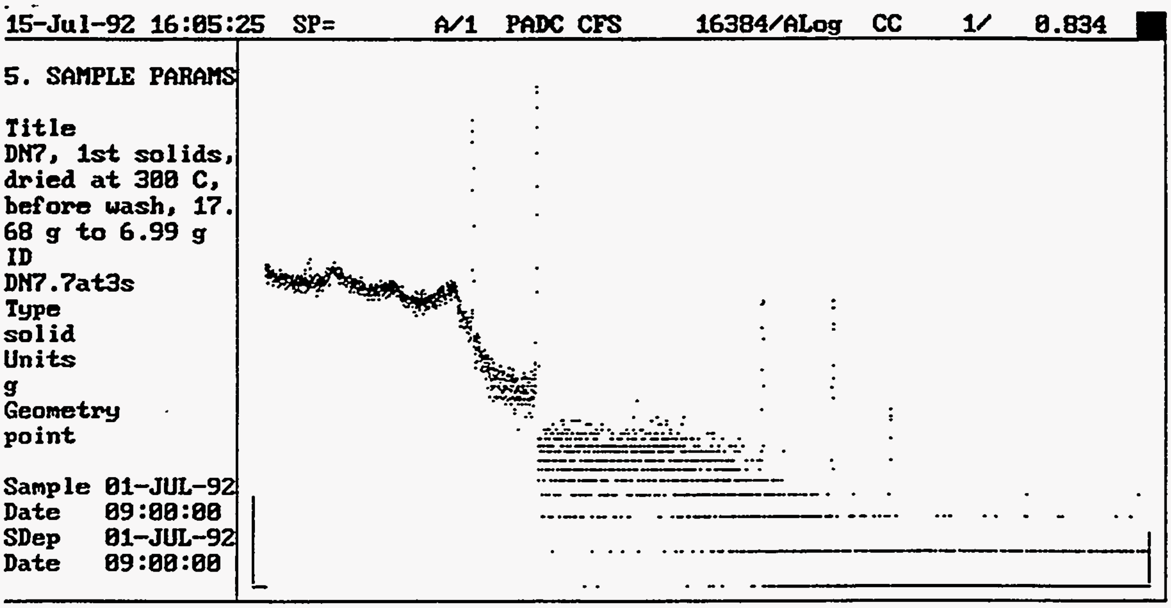
TOTAL LINES IN SPECTRUM          5
UNIDENTIFIED PEAKS               0
IDENTIFIED IN SUMMARY REPORT     5    100.00%


ACTIVATION PRODUCT
                                                  1-SIGMA
NUCLIDE  SBHR    HLIFE    DECAY   UCI/g           ERROR       %ERR
CO-60     AP     5.26Y   1.002     5.324E -3      2.535E -4    4.76


FISSION PRODUCT
                                                  1-SIGMA
NUCLIDE  SBHR    HLIFE    DECAY   UCI/g           ERROR       %ERR
SR-85     FP    65.20D   1.070     7.925E -2      1.073E -3    1.35
CS-137    FP    30.17Y   1.000     1.652E -1      1.357E -3     .82


NATURAL PRODUCT
                                                  1-SIGMA
NUCLIDE  SBHR    HLIFE    DECAY   UCI/g           ERROR       %ERR
K-40      NP  1.28E+09Y  1.000     5.246E -3      9.730E -4   18.55
```

Fig. E-21. DN-7 product solids dried at 100°C, after washing.



```
15-Jul-92 16:05:25  SP=        A/1  PADC CFS     16384/ALog  CC    1/   0.834

5. SAMPLE PARAMS

Title
DN7, 1st solids,
dried at 300 C,
before wash, 17.
68 g to 6.99 g
ID
DN7.7at3s
Type
solid
Units
g
Geometry
point

Sample 01-JUL-92
Date   09:00:00
SDep   01-JUL-92
Date   09:00:00
```

```
                    ENERGY WINDOW       .83 TO  2048.74

 PK IT  ENERGY    AREA    BKGND   FWHM  CHANNEL  LEFT  PW  CTS/SEC %ERR      FIT

  1  0  121.89     185.    1464.  1.29   243.07   240   8 5.14E-02 37.1
  2  0  133.04     235.    1788.  1.20   265.36   262   9 6.53E-02 33.1
  3  0  514.05   14531.    1529.  1.57  1027.22  1015  24 4.04E+00  1.0
  4  0  661.85   30080.     370.  1.66  1322.77  1309  24 8.36E+00   .6
  5  0 1173.98     617.      57.  2.07  2346.81  2332  23 1.71E-01  4.7
  6  0 1333.35     528.      19.  1.77  2665.50  2655  19 1.47E-01  4.6
  7  0 1461.77      68.       4.  1.92  2922.28  2912  21 1.89E-02 13.9

          PEAK SEARCH COMPLETED  (REV 15.8 - ND PC VERSION   MAR 90)

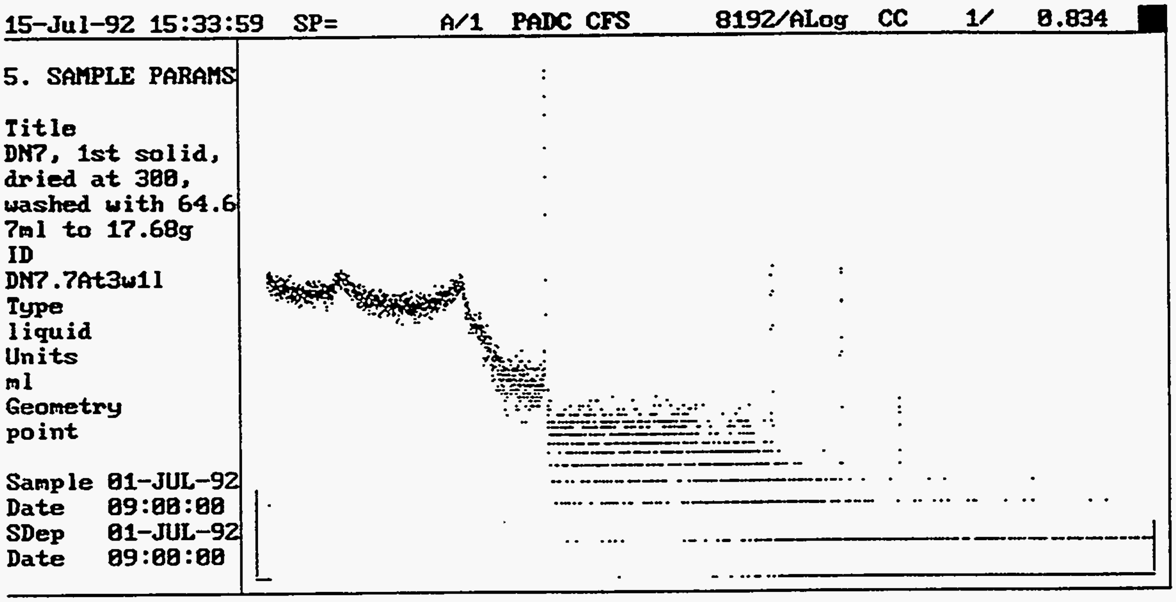
 TOTAL LINES IN SPECTRUM          7
 UNIDENTIFIED PEAKS               0
 IDENTIFIED IN SUMMARY REPORT     7    100.00%

 ACTIVATION PRODUCT
                                                       1-SIGMA
 NUCLIDE  SBHR    HLIFE    DECAY   UCI/g               ERROR        %ERR
 CO-60     AP       5.26Y  1.005      1.097E -2        5.029E -4    4.59

 FISSION PRODUCT
                                                       1-SIGMA
 NUCLIDE  SBHR    HLIFE    DECAY   UCI/g               ERROR        %ERR
 CO-57     FP    270.00D   1.034      9.466E -4        3.516E -4   37.15
 SR-85     FP     65.20D   1.150      2.587E -1        2.672E -3    1.03
 CS-137    FP     30.17Y   1.001      6.468E -1        3.845E -3     .59
 CE-144    FP    284.20D   1.033      9.460E -3        3.133E -3   33.12

 NATURAL PRODUCT
                                                       1-SIGMA
 NUCLIDE  SBHR    HLIFE    DECAY   UCI/g               ERROR        %ERR
 K-40      NP  1.28E+09Y   1.000      1.451E -2        2.021E -3   13.92
```

Fig. E-22. DN-7 product solids dried at 300°C, before washing.



```
15-Jul-92 15:33:59  SP=        A/1  PADC CFS       8192/ALog  CC     1/   0.834

5. SAMPLE PARAMS

Title
DN7, 1st solid,
dried at 300,
washed with 64.6
7ml to 17.68g
ID
DN7.7At3w11
Type
liquid
Units
ml
Geometry
point

Sample 01-JUL-92
Date   09:00:00
SDep   01-JUL-92
Date   09:00:00
```

```
                  ENERGY WINDOW      .83 TO  2048.74

PK IT  ENERGY   AREA   BKGND  FWHM  CHANNEL  LEFT  PW  CTS/SEC %ERR    FIT

 1  0  661.82  19253.    371.  1.60  1322.70  1307  30 5.35E+00   .8
 2  0 1173.85    604.     39.  1.85  2346.57  2334  20 1.68E-01  4.5
 3  0 1333.26    564.      7.  1.62  2665.33  2654  21 1.57E-01  4.3
 4  0 1461.34     41.     16.  2.20  2921.42  2912  16 1.13E-02 19.7

         PEAK SEARCH COMPLETED  (REV 15.8 - ND PC VERSION   MAR 90)
```

```
NUCLIDE IDENTIFICATION SYSTEM   (ND PC VERSION   DEC 88)
SUMMARY OF NUCLIDE ACTIVITY                                  PAGE  3

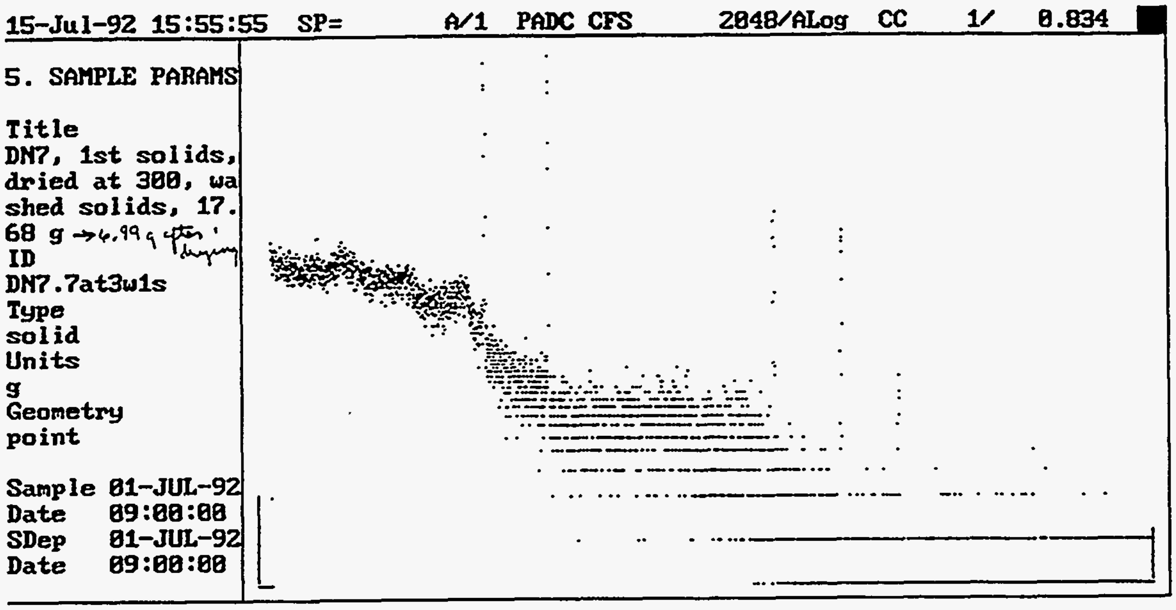
TOTAL LINES IN SPECTRUM          4
UNIDENTIFIED PEAKS               0
IDENTIFIED IN SUMMARY REPORT     4    100.00%

ACTIVATION PRODUCT
                                                  1-SIGMA
NUCLIDE  SBHR    HLIFE    DECAY   UCI/ml          ERROR      %ERR
CO-60     AP      5.26Y   1.005     5.859E -4     2.496E -5    4.26

FISSION PRODUCT
                                                  1-SIGMA
NUCLIDE  SBHR    HLIFE    DECAY   UCI/ml          ERROR      %ERR
CS-137    FP     30.17Y   1.001     2.070E -2     1.579E -4     .76

NATURAL PRODUCT
                                                  1-SIGMA
NUCLIDE  SBHR    HLIFE    DECAY   UCI/ml          ERROR      %ERR
K-40      NP  1.28E+09Y   1.000     4.349E -4     8.578E -5   19.72
```

Fig. E-23. DN-7 wash of product solids dried at 300°C.



15-Jul-92 15:55:55 SP= A/1 PADC CFS 2048/ALog CC 1/ 0.834

5. SAMPLE PARAMS

Title
DN7, 1st solids,
dried at 300, wa
shed solids, 17.
68 g →4.99 g after drying
ID
DN7.7at3w1s
Type
solid
Units
g
Geometry
point

Sample 01-JUL-92
Date 09:00:00
SDep 01-JUL-92
Date 09:00:00

```
                  ENERGY WINDOW      .83 TO  2048.74

 PK IT  ENERGY   AREA   BKGND  FWHM  CHANNEL  LEFT  PW CTS/SEC %ERR    FIT

  1  0  133.07    89.    740.  1.13   265.42   262  10 2.49E-02 58.5
  2  0  513.98  5087.    646.  1.47  1027.08  1014  28 1.41E+00  1.9
  3  0  661.80  6910.    193.  1.71  1322.66  1314  19 1.92E+00  1.3
  4  0 1173.93   627.     62.  1.78  2346.71  2335  25 1.74E-01  4.8
  5  0 1333.06   540.     25.  2.17  2664.92  2648  24 1.50E-01  4.5
  6  0 1460.98    37.     18.  1.41  2920.72  2916  11 1.04E-02 20.9

          PEAK SEARCH COMPLETED  (REV 15.8 - ND PC VERSION   MAR 90)

    NUCLIDE IDENTIFICATION SYSTEM   (ND PC VERSION   DEC 88)
    SUMMARY OF NUCLIDE ACTIVITY                                PAGE  3

    TOTAL LINES IN SPECTRUM     .      6
    UNIDENTIFIED PEAKS                 0
    IDENTIFIED IN SUMMARY REPORT       6    100.00%


    ACTIVATION PRODUCT
                                                      1-SIGMA
    NUCLIDE  SBHR    HLIFE   DECAY    UCI/g           ERROR      %ERR
    CO-60     AP     5.26Y   1.005    1.121E -2       5.051E -4   4.51


    FISSION PRODUCT
                                                      1-SIGMA
    NUCLIDE  SBHR    HLIFE   DECAY    UCI/g           ERROR      %ERR
    SR-85     FP    65.20D   1.149    9.045E -2       1.687E -3   1.87
    CS-137    FP    30.17Y   1.001    1.486E -1       1.895E -3   1.28
    CE-144    FP   284.20D   1.032    3.598E -3       2.105E -3  58.52


    NATURAL PRODUCT
                                                      1-SIGMA
    NUCLIDE  SBHR    HLIFE   DECAY    UCI/g           ERROR      %ERR
    K-40      NP  1.28E+09Y  1.000    7.959E -3       1.666E -3  20.93
```

Fig. E-24. DN-7 product solids dried at 300°C, after washing.

ORNL/TM-12245

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