



Department of Energy

Washington, DC 20585

September 2, 1999

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DNF SAFETY BOARD

The Honorable John T. Conway
Chairman
Defense Nuclear Facilities Safety Board
625 Indiana Avenue, NW, Suite 700
Washington, D.C. 20004-2901

Dear Mr. Chairman:

With this letter I am pleased to report on-schedule completion of one of the commitments found in the Department's 94-1 Implementation Plan. The closure package for this commitment, as described in the Department's interface manual, *Interface with the Defense Nuclear Facilities Safety Board* (DOE M 140.1-1A), is enclosed. The following commitment is proposed for closure:

310 Stabilize high risk salts at Rocky Flats - July 1999

As discussed with your staff earlier this year, the Rocky Flats contractor completed recharacterization of IDC 413 salts as low risk concurrently with stabilizing the remaining high risk salt categories. Accordingly, that IDC is being repacked for disposal as TRU waste. Documentation of that recharacterization is also enclosed.

We continue to closely track progress on all Recommendation 94-1 commitments and will keep you and your staff apprised of our progress. If you have any questions, please contact me or have your staff call me on 202/ 586-5151.

Sincerely,

David G. Huizenga
Acting Deputy Assistant Secretary for
Nuclear Materials and Facility Stabilization
Office of Environmental Management

Enclosure

cc w/ enclosure:
M. Whitaker, S-3.1



S E P A R A T I O N

P A G E

ROCKY FLATS FIELD OFFICE WEEKLY REPORT

July 21, 1999

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DNF SAFETY BOARD**I. Schedule**

Name: Jessie Roberson
Event: Rocky Flats Closure Team meeting
Location: Washington DC
Date: July 27, 1999
Acting: To be determined.

II. Key Departmental News**III. Work on Secretarial Initiatives****Accelerated Closure of Sites**


Stabilization of High Risk Salt Residues (Rocky Flats): The Defense Nuclear Facilities Safety Board recommendation 94-1 Implementation Plan Commitment to stabilize high risk residue salts by July 1999 has been completed in Building 707.

Building 771 Decommissioning (Rocky Flats): Decommissioning work is progressing in Rooms 182A, 187 and 188. All seven gloveboxes have been removed from ventilation in Room 182A and are either awaiting size reduction or direct packaging as low level waste.

IV. Press Inquiries**V. FOIA Requests****VI. Grants, Economic Announcements and Publications****VII. Climate Change**

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VIII. Disaster Assistance


Jessie M. Roberson
Manager

SEPARATION

PAGE

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Rocky Flats Environmental Technology Site
RS-090-060

REVISION B

EVALUATION OF RISKS ASSOCIATED
WITH IMPURE SALT
FROM CELL CLEANOUT (IDC 413)

APPROVED BY:

S. J. Eberlein 5/18/99
S. J. Eberlein, Deputy Manager Date
Product Quality

Responsible Organization: Product Quality

Date: May 18, 1999

PREPARED BY:

S. J. Eberlein 5/18/99
S. J. Eberlein, Deputy Manager Date
Product Quality

RELEASED
Date 5/18/99 L. Quotin

REVIEWED FOR CLASSIFICATION
By *[Signature]* W/N
Date 5/18/99

EVALUATION OF RISKS ASSOCIATED WITH IMPURE SALT FROM CELL CLEANOUT (IDC 413)

1.0 INTRODUCTION

The Rocky Flats Environmental Technology Site (RFETS) must dispose of more than 100 metric tons of solid residue material resulting from production of plutonium weapon components. These materials are being characterized to establish a measurement basis for evaluating the nature of the hazards and the magnitude of the risks posed by the residues. Due to the chemical nature of materials used in processing mixtures containing plutonium, concerns were raised about the potential risks that might be associated with the plutonium bearing residues (Reference 1). The major concern was for the occurrence of a disruptive event that was driven by the energy release from any unstable and reactive materials that might be present in the residues. This event could possibly breach the storage/disposal container and disperse the plutonium. The source of energy release mechanisms included pyrophoricity, flammability, shock sensitivity, and reactive metals. The characterization program examined each of these phenomena as well as the dispersion potential of the residues to determine the potential presence or absence of hazards.

This paper presents the results for the Item Description Code (IDC) of IDC 413 that contained Impure Salt from Cell Cleanout. IDC 413 is from cell clean-out operations for both Electrorefining (ER) process and Molten Salt Extraction (MSE) process. The primary source of this IDC is Building 776 stationary furnaces and Building 371 tilt pour furnaces. After a pyrochemical salt run, the cell and its parts were cleaned in preparation for the next run. The residual salt from the preceding run was stored for future processing as IDC 413.

The amount of mass in this IDC is 501 kg of net bulk material. This IDC originally consisted of 32 drums and 219 other containers. The initial sampling effort obtained samples from 18 drums. Subsequently, 10 drums were processed through pyro-oxidation, including 4 that had been sampled. To obtain 95/5 confidence on the population of 22 remaining drums, 17 samples were required. Since 14 valid samples from these drums had already been obtained, four more were taken, exceeding the 95/5 confidence requirement. The data for the other four drums (which were processed) is included in the assessment as well. Sixteen other containers were sampled, providing 85/15% confidence. IDC 413 is quite similar in its characteristics to IDCs 411 (Reference 2) and 473 (Reference 3), both ER salts. Like IDC 411, IDC 413 is less air and water reactive than IDC 473. IDCs 411 and 473 were sampled to a 95-5 confidence level, providing 113 and 41 samples respectively. IDC 413 may also include residual MSE salt. The many samples of MSE salt show that it is consistently less reactive than the ER salts, so that its presence is not a concern. The consistency of data with the ER salts allows IDC 413 to be considered as part of a larger group of materials for statistical purposes. Considering the larger combined population of IDCs 413, 411 and 473 gives 188 samples taken from 2690 containers, providing a 95-2% confidence level. The objective of this paper is to establish the technical basis for handling this IDC as a "Low Risk" residue.

The electrorefining process was used at Rocky Flats to refine impure plutonium metal by removing impurities of higher electrochemical oxidation potential. The electrorefining operation was conducted in tilt pour furnaces in Building 371 and stationary furnaces in Buildings 776/779. Impure plutonium metal was cast into ingots for use as anodes in the electrorefining process. The anodes were placed in an electrolytic cell that contained a molten salt electrolyte that consisted of an equimolar mixture of NaCl-KCl and 3-mole % MgCl₂. The trivalent plutonium ions that were needed to initiate electrolysis were generated in the molten salt by magnesium chloride oxidizing the plutonium metal. When a direct current was applied to the cell, plutonium at the anode was dissolved as plutonium trichloride. The impurities remained with the anode and purer plutonium was deposited at the cathode. Droplets of purified metal collected on the cathode, ran down, dripped off and formed a pool of metal product. After the system was cooled, the plutonium product and salt were broken away from the magnesium oxide cell. The spent salt was assayed and stored for future recovery of residual plutonium. This material constitutes spent ER salt that is part of IDC 413. As a result of the process methodology, it can contain droplets of solidified plutonium, and magnesium. Owing to process phenomena, the metal was most likely coalesced as beads. This ER salt can be expected to mainly contain the metals of magnesium and plutonium and the chlorides of potassium, sodium, magnesium and plutonium. Since these processes involved molten salt solutions, the chunks and pieces of salt mixtures are quite dense and generally strongly bonded to any entrained metals.

Spent salt was generated as a secondary reaction product in the Molten Salt Extraction (MSE) process at the Rocky Flats Plant. MSE was used to separate americium from plutonium. This practice minimized impurity levels in the metal and reduced worker exposure to gamma radiation during plutonium processing. The separation was accomplished by selectively oxidizing americium metal to AmCl_3 , which then dissolves into the molten salt. Americium was removed from plutonium using magnesium chloride as a selective oxidant in a molten alkali chloride salt mixture. The salt formulation contained an equimolar mixture of potassium and sodium chloride with magnesium chloride at a range from 5-6 to 30 mole percent. The plutonium feed metal and salt mixture were added to a tantalum crucible, placed in a resistance-heated furnace and heated until molten. The molten mixture was agitated with stirrers until equilibrium was obtained. After the reaction, the rate of stirring was reduced to allow a separation of the two phases, the salt and the metal. The furnace was cooled and the salt was separated from the metal product. While the mixture was molten, the magnesium chloride oxidized most of the americium and some of the plutonium, with the actinide chlorides going into the salt phase. Several salt systems were employed. One system used a mixture of potassium and sodium chlorides with 5-6 to 30 mole % magnesium chloride in the original process. Another system consisted of 50 mole % sodium chloride, 26 mole % calcium chloride and 24 mole % magnesium chloride. Other experimental salt systems were used. Therefore, the historical data indicates that the spent MSE salts in IDC 413 consist of salt mixtures consisting of sodium chloride, potassium chloride, residual magnesium chloride, americium chloride, plutonium chloride, and calcium chloride. Since plutonium chloride can also oxidize americium, the salt can contain both trapped plutonium and magnesium metals.

2.0 CONCLUSION

As an individual entity and irrespective of its storage vessel, IDC 413, ER salts, should be considered a Low Risk material. This conclusion is based on sampling 18 of 22 drums and 16 of 219 standalone containers (plus an additional four samples from drums that were subsequently processed). For the drums, this provides the 95 percent level of confidence that not more than 5 percent of the containers have characteristics outside the established limits. For the other containers, this provides the 85-15 confidence level. IDC 413 is quite similar in its characteristics to IDCs 411 (Reference 2) and 473 (Reference 3), both ER salts. Like IDC 411, IDC 413 is less air and water reactive than IDC 473. IDCs 411 and 473 were sampled to a 95-5 confidence level, providing 113 and 41 samples respectively. IDC 413 may also include residual MSE salt. The many samples of MSE salt show that it is consistently less reactive than the ER salts, so that its presence is not a concern. The consistency of data with the ER salts allows IDC 413 to be considered as part of a larger group of materials for statistical purposes. Considering the larger combined population of IDCs 413, 411 and 473 gives 188 samples taken from 2690 containers, providing a 95-2% confidence level. All the samples have been consistent with the model of plutonium behavior in pyrochemical salts (see section 5.2 and References 4 through 9), which concludes that ignition or pyrophoricity cannot occur in these plutonium/salt mixtures. With this consistency of data, it is not necessary to take additional samples of IDC 413 to make its risk assessment of 'Low Risk.'

This IDC does not present any significant safety risk to the worker or the public when it is stored in the current configuration and during handling operations. This material in its current form does not require processing for interim or long-term, TRU waste storage and shipment.

Due to lack of definitive information, many IDCs were previously believed to consist primarily of dispersible and respirable fines. A particle size distribution test, consisting of visual observation of larger material and measurement of smaller particles, provided a qualitative assessment of particle size distribution. This information provides a better understanding of the material and supports planning for handling and disposition. However, the data are not sufficiently complete to provide a quantitative basis for safety calculations without further data collection and analysis. Thus the data are only briefly considered in this report and cannot be the total basis for evaluating the dispersion risk associated with the residue.

While particle size is an important factor in evaluating the risk of dispersion of a radiological material, two other factors have provided conclusive information that dispersion of plutonium in the residue presents no significant risk. The first factor is the lack of potential stored energy that could be the basis for a reaction leading to a disruptive event. While reactive metals are present in the residue, their configuration of a small quantity of metal in an inert

matrix does not provide the basis for the disruptive event. The second factor is the robust nature of packaging used for interim storage and final disposition. The residue, with varying quantities of fine particulates, does not present a safety risk when packed into the pipe component or an equivalent manner that reduces the potential for dispersibility of the TRU waste. (5.1 Dispersion)

The data show that there are neither pyrophoricity nor flammability phenomena associated with this IDC. Despite a small amount of reactive metals in these salts, a forced heating profile above 130°C in the Differential Thermal Analysis (DTA) unit was necessary to cause most of the exotherms. Process knowledge and the characterization data help to substantiate that a majority of the present reactive metals surrounded by salt, preventing the existence of a pyrophoric condition by protecting the metal from rapid oxidation and spontaneous ignition. Developed for assessing their risk, the model shows that mixtures of salt and reactive metal particles in the proportions encountered with these salts are not pyrophoric. In the pyrochemical salts such as IDC 413, plutonium exists in a rather low volume-percent and any reaction with air is diffusion controlled. Although a larger proportion of the cans than the drums showed exothermic reactions, none of these reactions indicated pyrophoric behavior. Material in the drums has had more exposure to air than material stored in cans in the Central Storage Vault, so the slow oxidation that occurs at room temperature has proceeded further. Material in both drums and cans will continue to oxidize without risk of ignition or pyrophoric reaction. (5.2 Pyrophoricity and Flammability)

IDC 413 is not sufficiently reactive to present a hazard. A mathematical model and corresponding reaction mechanisms were developed that assert the materials in IDC 413 will not ignite and support a self-sustained reaction under any storage and shipment conditions. The mathematical model was reviewed against the available literature for plutonium ignition characteristics. All of the Differential Thermal Analysis (DTA) data for IDC 413 is in direct agreement with the developed models.

Shock sensitivity was a concern that was associated with these materials. The corresponding test procedure was conducted and all test results were negative. (5.3 Shock Sensitivity)

Almost all the sampled drums contained reactive metals in an inert matrix of salt that is inherently not pyrophoric. The average rate of hydrogen generation for the first hour was 2.86 liters (2.11 liters at Standard Temperature and Pressure (STP)) per kilogram of salt for 35 tests. The rate of hydrogen generation declined to 1.23 liters (0.905 liters at STP) per kilogram of salt for the second hour. However, the model shows that this level of reactive metal will not ignite at conditions in storage and shipment. This level of reactive metal does not influence the interim safe storage of the material. The water reactivity test is an indicator of the amount of reactive metals that are present. The reactive metal magnesium contributes to hydrogen in the tests but it is not pyrophoric as it normally exists. (5.4 Reactive Metals)

The process history indicates that no volatile or flammable organic compounds came into contact with these IDCs, so testing was not performed for the presence of organic compounds. (5.5 Volatile and Semi-volatile Compounds)

The storage containers that held the salts were all in acceptable conditions. They all held their material without any corrosion that breached the first level of containment. None of the filters showed signs of degradation or corrosion. (5.6 Condition of Storage Cans)

While IDC 413 was initially categorized a potential 'High Risk' material, the data demonstrate that this IDC should be reclassified a 'Low Risk' residue.

3.0 PROCEDURES

A sampling and characterization plan (Reference 10) was initially developed to obtain analytical data that would give an adequate understanding of the residues to permit handling and disposal decisions with respect to safety hazards and concerns. One objective for the sampling and characterization program was to collect sufficient data for determining the level of safety of the residues in their present state. If additional safety measures were needed, then the program would define the issues that needed to be resolved to achieve a sufficiently

safe storage condition until the residues could be processed to a more stable state. The program also gathered sufficient information to assure safe processing of the residues and provide basic information to facilitate the efficiency of their processing. During the sampling process, it became evident that the hazardous nature of this residue was significantly less than the suspected range of hazards and the residue did not require processing.

The pyrochemical salts have been selectively sampled. For the total metal analysis, DTA and x-ray diffraction (XRD) tests, representative samples were taken. For the water reactivity tests and particle size analysis, samples were taken of material that would readily fit into the test configuration (Reference 11).

Particle size measurements were made with a qualitative technique using a two stage, characterization process. The first stage was done by a classification of materials using sieves. Only 5-10 grams of material was added to a set of sieves with an 8-inch diameter. The sieves were shaken on an automatic sieve shaker for five minutes. The finest sieve was 325-mesh (45 microns). In the second characterization stage, the material passing through the 325-mesh sieve was analyzed with a Quantimet 500+ Analyzer optical microscope. This computer-based methodology systematically examined the sieved sample of particulate matter. It developed a histogram of particle size for the material that was less than 45 microns and had passed through the finest sieve. It defined the fraction of the population that was within six individual particle size ranges. The Quantimet determines the distribution of particles based on strictly the measured diameters.

The technique for particle size measurement in the characterization tests does not necessarily give the absolute particle size of the measured material. The technique uses vibratory motion to induce particles to pass through sieve openings. The classification in the sieves attempts to use the mechanical action of a small sample size passing over the sieve's wire mesh to break down the cohesive forces that exist in a fine powder mixture, causing it to pass through each screen. This method allows only a portion of the smallest, individual particles and agglomerates to pass through the finest sieves for closer scrutiny in the Quantimet Analyses unit.

Pyrophoricity is defined as the spontaneous ignition of a material in ambient air conditions. For characterization purposes, the possibility of spontaneous ignition at temperature up to 150°C was considered (Reference 10). Samples were examined using a specialized DTA unit that heated relatively large sizes of residue samples from 25 to approximately 350°C and monitored for the presence of an endothermic or exothermic event. All events were examined and exotherms that occurred below 150°C were specifically flagged for closer examination and evaluation. Since the DTA unit can monitor the occurrence of small temperature departures from the norm, it is a very conservative test that helps to evaluate a sample's responses to heating. A sample can respond by both chemical reactions such as an acid being neutralized by a base and physical changes such as a liquid evaporating, which may or may not represent any potential hazard.

Flammability was not originally considered a primary hazard. Flammability is defined as the ignition of a material at temperatures below 60°C. The presence of a flammability hazard in IDC 413 was also examined with the use of the DTA unit over the temperature range of 25 to 350°C. Specific exothermic events below 60°C were specially flagged for closer evaluation. The response of a flammable material to its environment depends upon the mechanism of ignition and the type of the ignition source. The DTA unit represents strictly a hot surface ignition source. When an organic solvent in the residue is evaporating at its boiling point, the temperature of the hot surface is merely the boiling point of the organic compound.

The potential for shock sensitivity was originally attributable to this IDC. This perception was based on the materials process history and the specific materials that were involved. In the shock tests, a 6-kg weight was dropped from a height of 50 cm onto a sample with a strike surface of 0.304 inch. The test was repeated ten times on the same sample.

Since there was the potential for reactive metals (Mg and Pu) in IDC 413, a method to quantify the amount of reactive metals was needed. There was no direct measurement technique for evaluating this condition that would help evaluate safety status. The Department of Transportation (DOT) test for "Dangerous When Wet" conditions was adapted for interpreting hazards associated with reactive metals. In this test a sample is added to water and the amount of hydrogen is measured each hour for a seven-hour duration. The actual amount of hydrogen produced in

the water reaction can be used to estimate the quantity of reactive metals that are present in the sample. For a given metal, the quantity of generated hydrogen is stoichiometrically related to the quantity of metal that reacted with the water. In the test, samples of 10 grams material were reacted with water in a 500-ml flask. The gas was pumped to a combustible gas sensor and a calibrated reading was registered on the monitor.

A method for estimating the relative amounts of the crystalline constituents in the residues is XRD. The technique employed used a powder pattern that is formed and measured using a Rigaku Model RU200 horizontal x-ray diffractometer. For this technique, the residue must be ground to a fine powder. A mortar and pestle was used to accomplish this action. The powder is mounted on a non-crystalline substrate (combination of packing tape and teflon) in a thin layer. The x-rays that are diffracted from the sample are detected with a proportional counter and recorded on strip chart. The patterns that are created are characteristic of the crystalline structure of the material on the substrate. From the patterns, it is possible to define the crystal structure and lattice parameters, and subsequently identify the materials. From the relative intensity of the diffracted x-rays, it is possible to estimate the relative amounts of the material in the sample on the substrate.

The method for determining the amount of moisture in the salt residue measures the weight loss at elevated temperature. The moisture content of salt residues is measured using an automated moisture balance (Denver Instrument Model IR-10Q or equivalent) and a two-step drying sequence (Procedure L4160-A). A sample size of 2-5 grams is used. After the initial sample weighing, the heating chamber is rapidly brought to the temperature for the first measurement (105°C); the temperature is controlled with a platinum temperature sensor to $\pm 1^\circ\text{C}$. The sample is held at 105°C until the sample reaches a constant weight. This is determined as a loss of weight of less than 0.05% of its initial weight in a one-minute period. The sample is then heated to 210°C and held at the second temperature until a constant weight is reached. The reported moisture content is based on the total weight loss of the sample at 210°C.

Total metal content of the residues is determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Twenty two metals are determined by this method which include aluminum, antimony, arsenic, barium, beryllium, cadmium, calcium, chromium, cobalt, copper, iron, lead, magnesium, manganese, molybdenum, nickel, phosphorus, selenium, silver, strontium, thallium, titanium, vanadium and zinc. Prior to analysis, solid samples of salt residues (~ 1-2 grams) must be solubilized or digested using acid digestion sample preparation methods. The preparation method used is SW846 Method 3050B Acid Digestion of Sediments, Sludges and Soils. This analytical method provides for multi-element determinations by using simultaneous optical systems and radial viewing of the plasma. The instrument measures characteristic emission spectra for each metallic element by optical spectrometry. Samples in the form of liquid solutions are nebulized and the resulting aerosol is transported to a plasma torch. Elemental-specific emission spectra are produced by a radio-frequency inductively couple plasma. The intensity of the emitted spectra is proportional to the concentration of the metal in solution. The limit of detection of each element is dependent on the emission characteristics for the spectral lines used for the determination and the sensitivity of the instrument for these spectral lines.

Process history for IDC 413 did not indicate the presence of organic compounds. Therefore, Gas Chromatography/Mass Spectrometry Analysis was not conducted. The presence of organic compounds was also evaluated in the DTA unit by monitoring exotherms for the burning of flammable organic compounds and endotherms for the evaporation of these organic compounds.

4.0 RESULTS

Table 1 provides the summary of information and characterization data for the specific tests that were required by the characterization plan (Reference 10) for the safety evaluation for IDC 413. Thirty-eight samples were taken and analyzed. All drums are listed in the table with a D prefix. The other containers do not have the D prefix.

When contact dose rate measurements were performed, a pass indicated that the total surface reading was less than 200 mRem/hr. This measurement was taken on either the drum or the individual package containing the primary container and the salt. A passing designation on the visual inspection indicated that the primary container with the salt was intact and had not been breached. For evaluating pyrophoricity, the temperature at which an exotherm

initiated was considered important. If an exotherm initiated below 150°C, it potentially represented an energy release of concern. The temperature of the initiation of the exotherm was recorded (see Table 1), and the nature of the reaction causing the energy release was more thoroughly examined. Temperatures at which endotherms initiated were also recorded since they were often indicators of mechanism that would stimulate a release of energy. The water reactivity test measures the amount of reactive metals that are present in the pyrochemical salts. The total volume of hydrogen produced per kilogram of material in the seven-hour period is included in Table 1.

With respect to dispersibility, the majority of the material was the size of one sixteenth to three inches, crushed pieces from the breakout procedure for removing the product. Possibly as many as 18 of the 38 samples of this IDC had been through a jaw crusher. When the production mixture solidified during cool-down, a dense solid mixture was generated. During the breakout operation, the majority of the salt was freed from the vessel. The breakout process would have contributed to a micro-cracking of the salt, yielding pieces and a collection of fines from the fractured salt. The dispersibility issue is mitigated because much of the salt is in large pieces. The test results show that intimate mixtures such as salt, reactive metal and metal oxides were also collectively bonded together, thereby altering the rate of dissolution in water reactivity tests. This intimate mixture is a composite material, and its reactivity is substantially curtailed by the overall properties of the whole unit. As a rule, the salt residue consists of an inner core of metal surrounded by its own metal oxide and encased in a layer of salt. Its reactions are governed by this structure. Salt is tenaciously bonded to the constituents in pyrochemical salts. Its mode of fracture under stress permits thin layers of salt to remain on foreign particles. Even grinding the pyrochemical salts will not readily separate the salt from the metal particles.

IDC 413 did not show any potential risks associated with either pyrophoricity or flammability. An accurate description of a compilation of the DTA curves is very important. Without a single exception, the DTA data supports the developed model. The DTA model will be presented in the discussion section.

None of the samples shows any exotherms when heated to 60°C. Sixty-eight percent of the samples exhibited exotherms when they were heated above 100°C to 350°C. Lacking the presence of exotherms, 24% of the tests displayed only endotherms that were typical of the loss of the waters of hydration for magnesium chloride. One of the key characteristics of the exotherms in DTAs is an endotherm immediately preceding the exotherm. Frequently, an exotherm is preceded by a very small and brief endotherm. Forty eight percent of the exotherms were immediately preceded by an endotherm.

The model shows that water causing the endotherm helps contribute to the subsequent onset of an exotherm. Forty percent of the IDC 413 tests with exotherms had exotherms without the presence of endotherms. Forty-one percent of the tests had both the presences of endotherms and exotherms. Fourteen percent of the IDC 413 tests had the combination of multiple exotherms that occurred over a prolonged period of time. Multiple exotherms show that plutonium is not rapidly consumed in a self-sustaining ignition. Sixty percent of the exotherms are considered to be small and insignificant with a total delta T of less than about 10°C.

Three drum samples and six container samples showed exotherms at or below 150°C, requiring closer examination. All of these exotherms occurred in the temperature range of 110-150°C. Only three of these exotherms showed a sharp rate of temperature rise, but all reactions declined rapidly without giving rise to an ignition, as expected from the model of Pu behavior in salt (see Section 5.2 and References 4 through 9).

IDC 413 displayed other aspects of a typical DTA for pyrochemical salts. Usually plutonium oxidation continued to 350°C and prolonged exotherms were created. Plutonium metal was usually present at the end of the DTA run at 350°C. This was as evidenced by the failure of the curve to return to the baseline. Both the prolonged oxidation and the failure of the system to return to baseline are evidence that plutonium has not ignited in a self-sustaining reaction that would completely consume the material in a brief time. One hundred percent of the tests exhibited prolonged oxidation with unoxidized plutonium left at the end of the test.

Multiple runs in the DTA were frequently required for IDC 413 to oxidize the material, showing the difficulty in completely oxidizing the metal in its present state in the salt residues. In multiple runs, endotherms are frequently observed from the continued release of the waters of hydration of magnesium chloride. This shows that the water

was not readily released from small chunks of salt, even despite the maximum DTA temperature of 350°C. Twenty-two percent of the tests required multiple runs to give a stable baseline characteristic of a thermally inert material. Three of the DTA runs showed a lack of thermal activity, i.e., 35 tests had either exotherms or endotherms or a combination of the two.

Closer examination of the characterization data permits further conclusions to be made. The tests from IDC 413 all had low rates of heat generation per time interval. These results are consistent with the metal being encased in a salt composite material with the occurrence of water-based oxidation and a very low reactivity with air.

Twenty-four percent of the DTA tests had only endotherms. These endotherms generally had the shape of the endotherm for hydrated magnesium chloride (see Reference 12). Sixteen tests showed that the samples lost about 0.56 weight percent at 110°C water and 1.08% at 210°C. This water was most likely bound as the waters of hydration of magnesium chloride. Upon heating, hydrated magnesium chloride oxidizes to the oxychloride and an accurate assessment of water content is not possible. Since this IDC consists of a limited number of materials with reasonably predictable consequences upon heating to 350°C, the endotherms can be considered as a result of water loss and the exotherms can be considered as a result of the oxidation of plutonium.

The data was averaged to make many of the conclusions in this report (however, ignition calculations are with the worst case tests). The tests showed that the material is sufficiently heterogeneous that the data for a particular sample cannot always be correlated within its own set of test results. For a homogeneous sample, the water reactivity, DTA, total metals and moisture content data could be correlated to make definitive statements. The tests for IDC 413 show that this is not actually practical. For example, D22458 showed an exotherm with a temperature differential of 19°C in the DTA despite the fact that its water reactivity test generated only 0.29 liters of hydrogen per kilogram of salt. In contrast, D11918 showed an exotherm with a temperature differential of only 2°C despite the fact that its water reactivity test generated 11.32 liters of hydrogen per kilogram of salt. One possibility is that all the reactive metal was magnesium. Another possibility is that the plutonium particle was sufficient in size and lacked a sufficient moisture level in its salt coating to encounter oxidation in the temperature range of the DTA. Another possibility was that the material was sufficiently heterogeneous that the container readily yielded samples that had reactive metals present and ones that did not have them present. Therefore, to best summarize the state of this IDC, the data was averaged. Still, individual sample summaries are made to better help understand the data.

The average total hydrogen generated in the water reactivity tests was 5.96 liters of gas per kilogram of sample for seven hours. Unless otherwise stated in this report, all values for hydrogen generation are at the laboratory conditions in Building 559 that are approximately 25°C and 610 torr. The values for the total amount of hydrogen evolved for the seven-hour test ranged from a high of 21.98 liters (16.18 liters at STP) to a low of 0.29 liters. These high and low rates are quite similar to both IDC 411 and IDC 473. Tests with hydrogen generation rates for any one hour that were greater than one liter per kilogram per hour were flagged in this study and more closely evaluated. Sixty-six percent of the samples had at least one hour in which the rate was greater than 1 liter of gas per kilogram of sample per hour. The average rate of hydrogen generation for the first hour was 2.86 liters (2.11 liters at STP) per kilogram of salt for 35 tests. The rate of hydrogen generation declined to 1.23 liters (0.905 liters at STP) per kilogram of salt for the second hour. However, the average hourly rate for hydrogen generation was 0.851 liters per kilogram of salt. Correcting the average hourly rate to STP gives a value of 0.626 liters per kilogram of salt.

IDC 413 averaged 0.626 liters per kilogram of salt per hour at STP. IDC 411 averaged 0.682 liters per kilogram per hour. Therefore, IDC 413 is similar in its content of water reactive metals to IDC 411. IDC 413 has a lower content of water reactive metals than IDC 473.

Total metal analysis was conducted on all 38 samples. Of the tests performed in the characterization program, the total metal analysis is the best indicator to distinguish between MSE and ER salts. Even with the presence of the total metal analysis, it is sometimes difficult to distinguish between the ER and MSE salts. The data appeared to fall into three subsets based on the magnesium content. In subset A, sixteen tests for total metal analysis showed that the samples averaged 12.38% magnesium by weight with a total possible magnesium chloride content of 48.71% by weight. Subset A was more likely to consist of MSE salt. In subset B, seventeen tests showed that the samples averaged 4.688% magnesium by weight with a total possible magnesium chloride content of 18.45% by weight.

Subset B was more likely to consist of more ER salt than MSE salt. In subset C, five tests averaged 7.022% magnesium and 4.204% calcium by weight with a total possible magnesium chloride content of 27.63% by weight. The XRD tests frequently showed magnesium oxide from the ceramic crucibles as a contaminant in this IDC. This fact probably was the main influence for raising the magnesium content in this IDC above the ranges that were expected. As would be expected, this IDC is a rather simple mixture with a rather limited range of chemicals. The composition of the salts was rather constant, showing only slight amounts of impurities. Common impurities were iron and nickel, materials that would have been introduced by the reaction of plutonium with containment vessels. Zinc and aluminum or their inorganic compounds were occasionally present in these residues.

The process history indicated that this IDC did not contact any organic compounds in its normal handling. Therefore, these materials were not tested for the presence of volatile and semi-volatile organic compounds (VOCs and semi-VOCs). IDC 413 should not demonstrate the characteristic of flammability. The DTA tests confirmed this fact. There were no exotherms below 60°C. All the endotherms can be associated with the evaporation of hydrated water from magnesium chloride and were not from the evaporation of organics.

There was a concern that shock sensitive materials were formed over time with the storage of this IDC. However, all shock sensitive tests were negative.

The XRD data presented an estimated average of the weight percent content of the major constituents. This average was done without the use of standards to calibrate the reading of mixtures. The average for IDC 413 was 19% KCl, 27% NaCl, and 28% plutonium oxide. All the samples were generally gray. Samples were notably more gray with fewer signs of green material than IDC 411. Since the ER and MSE processes were conducted at elevated temperature in an inert atmosphere, the plutonium oxide must be a result of long-term corrosion or oxidation of the plutonium.

This IDC frequently consisted of large chunks ranging from one to three inches in diameter. A large proportion of the material was as pieces in the 1/16- to 1-inch range. The remaining material was generally present as coarse fines. It did appear that some of the material had been passed through a jaw crusher. None of the material had been passed through a hammermill. The color of the material was consistent with ER salts. The color was predominantly gray. The cumulative data implies that this IDC is a straight-forward mixture that contains the materials that one would expect in ER and MSE salts. The containment vessels were usually in acceptable condition with no signs of corrosion. These facts help permit an evaluation of this IDC with a high level of confidence.

Most of the containers were evaluated for their contact dose rate measurement. With the exception of fourteen drums, all these containers passed the established criterion and had values for gamma radiation that were less than 200 mRem/hour. The explanation for these high dose rates has a two-fold nature. The IDC had a higher plutonium assay and most likely a higher americium content. Poor packing techniques lead to discoloration of polyvinylchloride (PVC) and probably created internal system contamination. This condition led to a higher dose rate.

The salts were stored in 8801 volrath cans and bagged. These bagged cans were stored in 8802 cans. Poor packing techniques led to salt particles throughout this system. The salt contamination obviously led to deterioration of PVC materials. Brown to black PVC was noted. The outsides of storage cans had PVC stains on their surfaces. All the sample containers were in acceptable condition with no sign of rusting. The original condition of the storage containers is uncertain. The salt mixtures were sufficiently dry to be readily removed from their containers. As a rule, the salts acted like granules and not as masses bonded together by their deliquescent nature. Clumping of the salts was not noted and a pasty, fluid salt mass was never observed. There were never any signs of free water in the drums or containers. Therefore, there were never sufficient water levels to cause salt-water based corrosion of their containers. With its lower water content, rusting of the cans was not observed. Rust penetrations through the containment can were not noted. No signs of corroded drums were noted.

In the filter test program, only one IDC 413 drum was sampled. Neither this drum nor any of the sampled drums showed filters with signs of degradation or corrosion.

5.0 DISCUSSION

In 1993, the level of detailed information for the chemical and physical characteristics of IDC 413 was very limited. Based on the nature of pyrochemical salts and their process history, concerns were noted that the material might contain finely divided plutonium that could be dispersible and pyrophoric. For these reasons, this IDC was conservatively categorized as a High Risk residue in the 94-1 Implementation Plan (Reference 1).

The following discussions present the interpretation of the characterization data as it relates to storage of the material in its current form. The characterization data indicates that this IDC can be considered Low Risk and does not require treatment.

5.1 DISPERSION

Due to lack of definitive information, many IDCs were previously believed to consist primarily of dispersible and respirable fines. A particle size distribution test, consisting of visual observation of larger material and measurement of smaller particles, provided a qualitative assessment of particle size distribution. This information provides a better understanding of the material and supports planning for handling and disposition. However, the data are not sufficiently complete to provide a quantitative basis for safety calculations without further data collection and analysis. Thus the data are only briefly considered in this report and cannot be the total basis for evaluating the dispersion risk associated with the residue.

While particle size is an important factor in evaluating the risk of dispersion of a radiological material, two other factors have provided conclusive information that dispersion of plutonium in the residue presents no significant risk. The first factor is the lack of potential stored energy that could be the basis for a reaction leading to a disruptive event. While reactive metals are present in the residue, their configuration of a small quantity of metal in an inert matrix does not provide the basis for the disruptive event. The second factor is the robust nature of packaging used for interim storage and final disposition. The residue, with varying quantities of fine particulates, does not present a safety risk when packed into the pipe component or an equivalent manner that reduces the potential for dispersibility of the TRU waste.

5.2 PYROPHORICITY AND FLAMMABILITY

The residues were produced by a process involving a number of metallic elements that, if present in the elemental form, could be considered pyrophoric in nature. The elements that generally fall in this category are Na, K, Mg, Ca and Pu. The issue is whether these metals are present in the residues and if they constitute a pyrophoric hazard.

Sodium and potassium are not considered an issue at this time because they are highly reactive with oxygen or moisture in the ambient environment. These elements, if present as metals, should have long since oxidized to other chemical forms; there has been no evidence of these elements through the large series of measurements made on the residues. Magnesium and calcium are not of concern because of their high ignition temperature. Magnesium's ignition temperature is about 510°C. Apparently, calcium does not have an ignition temperature since it was not possible to find one designated during an extensive literature search. Differential Thermal Analysis of both magnesium metal in ribbon and powdered form and calcium in a similar form did not demonstrate any exotherms in the temperature range up to 150°C. Both of these elements will oxidize in an autothermic reaction at temperatures significantly above the upper ignition temperature limit of 150°C that is of concern for the residue program.

For plutonium metal, measurements of temperature for ignition have shown that bulk quantities of powdered Pu metal can ignite in air at a temperature as low as 110°C. The issue is whether exotherms for a residue, exhibited below 150°C, are indicators of a potential for comparable autothermic ignition of the Pu metal in particulate form in the salt matrix. The exotherms exhibited in the DTA test for residues at temperatures below 200°C are not indicators of the initiation of an autothermic reaction. This position is applicable for residues with plutonium content up to 80 weight percent. This conclusion is based on 1) the intrinsic oxidation characteristic of Pu metal and 2) the diffusion control of the oxygen supply required for the autothermic reaction in a situation where Pu metal is diluted in an inert matrix such as salt.

Plutonium metal exhibits dual mechanisms for oxidation with moisture and oxygen. Figure 1 shows the two curves for the rate of oxidation under the moisture dependent regime and the moisture independent regime. The high rate of reaction at low temperature (room temperature to 150°C) is driven by reaction in the presence of moisture and not with reaction with oxygen in the air. Above 110°C, this reaction rate decreased with increasing temperature. For an autothermic reaction to proceed, the rate of reactions must continually increase with increasing temperature. The effect of the decreasing rate of reaction with increasing temperature associated with reactions stimulated by moisture cannot proceed as an autothermic reaction. Exothermic reactions with significant differential temperature increases that occur at temperatures below 150°C are driven by Pu particulate reacting with moisture and it is clear that these reactions cannot continue as autothermic reactions.

For an autothermic reaction initiated by reaction with moisture to proceed, it must be capable of maintaining the reaction rate when the reaction is supported only with oxygen in the air. Reactions initiating above 60°C have little chance of making the transition because of the reaction rate curve does not generate sufficient energy to increase the temperature above 200°C. Only reactions initiating below 60°C have the potential for releasing sufficient energy to achieve the reaction rates for reaction in air that will maintain the energy release to support the autothermic reaction.

The situation is further limited by the fact that plutonium metal is dispersed within a matrix of inert salt with limited porosity. This condition, in effect, establishes oxygen diffusion control for reactions of Pu metal; the supply of oxygen cannot meet the demand to support the autothermic reaction. It has been demonstrated by a physical model represented by mathematical relationships that this condition is in effect for conditions to 80 weight percent Pu metal in salt.

The minimum temperature at which the available data and analysis indicates pyrophoricity in residues with Pu metal is 200°C. Therefore, DTA data that demonstrates exotherms below 150°C, reflect the dominant reaction of the Pu in the residues with available moisture in the environment. While they may show apparent rapid and substantial differential temperature increases, they are not indicators of a potential autothermic reaction.

The technical justification for the above position is outlined in a variety of technical analyses presented in references 4 through 9.

All the DTA tests that showed a significant exotherm below 150°C were "flagged" for more detailed examination by an individual familiar with this type of data. All detailed examination of the exotherms indicated that none of the thermal excursions for this IDC constituted an ignition of an exothermic reaction.

The characterization data makes a strong case that IDC 413 shows no indication of a pyrophoric or flammable nature. The DTA tests are consistent throughout the entire test matrix. The water reactivity tests showed that reactive metals were consistently present in the samples. The DTA tests frequently produced exotherms. The data shows that the resultant exotherms are protracted in length. The exotherms have a low average heat release over their duration. Most of the exotherms have a relatively slow rate of heat rise at their onset and a slow recovery by the unit to the baseline curve. These indications are all examples of a *non-hazardous and relatively low reactivity* material, which is gradually oxidizing, in a forced heating profile. Since the reactive metals reacted gradually with water in the water reactive tests, the particle size of the reactive metal is sufficient that there would be a marked reduction on their reactivity in air, thereby markedly reducing any potential for a pyrophoric nature.

The reactive metals gradually oxidize in the DTA tests. Metal pieces were encapsulated in salt matrices and have coatings of dense salt and their own oxide. Since oxygen must diffuse through fissures in the salt and the metal oxide layers to oxidize the metal, this state markedly reduces any tendency towards a pyrophoric condition. Oxygen must also diffuse through the loosely packed powders to react with any available metal. The salt and any plutonium oxide that was formed also serves as a diluent to help prevent the sustainment of a flame, absorb and subsequently dissipate any heat of reaction from air oxidation, and smother any reactive metal by reducing the availability of air. The model is not dependent on a salt coating on metal particles to reach this risk assessment. In the proportion of metal particles to salt particles in the pyrochemical salt matrix, the salt matrix effectively prevents an ignition by

reducing the rate of oxygen diffusion to the sites of metal oxidation. Therefore, operations such as grinding the salt will not alter the conclusions in this report.

The need for a forced oxidation of reactive metals in DTA tests is a clear indicator of the lack of metal pyrophoricity at normal storage conditions. Lacking the need for auxiliary aids such as a spark source or catalyst to stimulate a spontaneous reaction, a pyrophoric material readily self-ignites at ambient conditions. The burning of a pyrophoric material in a self-sustaining reaction yields a product with a negative free energy of formation and the accompanying reaction must attain its energy of activation so that its kinetic properties favor an extremely high rate of reaction. All DTA tests constituted slow oxidation rates of any metal present. The characteristic of pyrophoricity is an extremely rapid oxidation of a material by definition of the hazard. The salts can be considered inert materials.

For IDC 413, all the DTA test results were consistent with and readily explained by the model. For pyrochemical salts, the DTA tests now principally serve to support the model.

Two tests were flagged for closer evaluation because their DTAs showed low temperature exotherms. These samples were taken from containers 5800071 and 7569620. In certain cases the raw data must be evaluated to accurately interpret the data. For this report the raw data was evaluated for each test. For producing a DTA, at least two consecutive runs are made with the DTA unit. In some cases, the material changes too much between thermal runs and a highly accurate DTA was not obtained. The DTA then contains minor errors that contribute to a misinterpretation of the onset temperature. For 756920, the sample contains all six waters of hydration that produced an endotherm at 120°C. It probably also contained a small amount of water that was physically adsorbed on its surface. This condition produced another endotherm at about 40°C. This amount of water probably slightly altered both its thermal conductivity and specific heat. This fact produced an artifact of an exotherm in the DTA that had a temperature differential of only about 2°C. Closer examination of the data leads the observer to the conclusion that the sample did not produce an exotherm at all. Like MSE salts, samples with higher hygroscopic salts content would have a higher chance of producing this result. The total metal analysis for this sample showed both a high magnesium and calcium content and helps to confirm the conclusion.

The sample from 5800071 represents a different situation than 7569620. The DTA indicated that sample 5800071 had a large percentage of plutonium metal in it. The plutonium assay showed plutonium content of 44%. Neither the first or second run of the DTA unit was satisfactory for converting all of the metal to the oxide. The DTA curve for this sample showed a low temperature exotherm that is obviously an artifact of the unit's calculation technique. This is readily seen in a close evaluation of the raw data and its associated curves. The raw data clearly show smooth curves characteristic of a thermally inert material until about 150°C. At this temperature an exotherm begins. This conclusion is based on the knowledge of the highly reproducible shape of a thermally inert substance that is heated in the DTA. The difference between the baseline and sample curves that produced the artifact is once again the product of material differences. The salt with plutonium metal and the later salt with plutonium oxide have slightly different thermal conductivities, specific heats and possibly even particle sizes. These differences produced the low temperature artifact in the DTA curve.

It is also noted that samples 76002071 and D16072 had the only two low temperature exotherms in this IDC that are considered significant exotherms. These exotherms occurred at respectively 130°C and 110°C. The exotherm for D16072 had a temperature differential of only about 8°C as compared to only 15°C for 76002071. The curves conformed to the model and they do not indicate a hazard.

A bounding calculation takes the largest exotherm from a DTA test and calculates the impact on the pipe component. The largest exotherm for the entire test matrix was from the sample for 3915920 (Figure 2). This was not typical of a significant exotherm for IDC413. A significant exotherm has a characteristic shape and usually occurs in the 130-150°C temperature range. A calculation is made assuming the entire pipe contains 2500 g of a salt mixture which is equivalent in composition to this sample. Therefore, the pipe contains 2500 g of ER salt with a potential heat of reaction of 284 Joules per gram. (In contrast, the largest exotherms for IDC 473 and 411 had heats of reactions of 544 and 391 Joules per gram, respectively, References 2 and 3.) The potential heat of reaction for this example is -710,000 Joules/pipe. This is equivalent to the pipe containing 160 grams of plutonium. Therefore, the pipe can contain its entire charge of 2500 grams.

If the pipe component had its maximum charge of plutonium as the metal and it completely reacted with air to form plutonium dioxide, then 885,464 joules would be released by the oxidation reaction (References 13 and 14).

The calculation assumed all the heat was transferred to the pipe component used for packaging the material, and determined the effects on the integrity of the package. For calculation of heat transfer to the package, it is assumed that the material is packaged in a 12-inch steel pipe (see Reference 15 for a description). The pipe component has a mass of 79.45 kg with a heat capacity of 0.50 joules per gram per °C. Since the DTA data showed that magnesium is not significantly oxidized to temperatures of about 350 °C, oxidation of any magnesium is not considered in this calculation. If all the ΔH_{RXN} is transferred to the pipe, the heat input corresponds to a 22.2°C rise in the temperature of the steel pipe component. This temperature spike raises the temperature of the pipe to 47.2°C. The potential temperature rise must be compared to the limits of the containment package. The allowable temperature increase for the pipe component is 128°C. This rise is the difference between 21°C, room temperature, and 149°C. This higher temperature is the limit at which the life expectancy of the ethylene propylene o-ring in the pipe component is limited to 1000 hours.

The above calculation is based on three assumptions. These are 1) the material can ignite, 2) the material has a sufficient source of oxygen available to it for complete conversion of plutonium to plutonium oxide and 3) the reaction goes to completion. This risk assessment contends that the material cannot ignite as demonstrated by the model and supported by the DTA results. It also contends that the oxidation reaction is oxygen limited as regulated by a fixed air volume in the pipe. The movement of a fresh supply of air to the reaction front is diffusion controlled through the pipe filter. On a localized basis, the reaction mixture within the pipe is also oxygen limited. Oxygen cannot diffuse rapidly enough into the salt mass to sustain an ignition. This paper also stresses that the material is in a form that prevents the reaction from readily going to completion, i.e., reactive metals are coated with salt.

The mechanism for ignition of the metal is a self-heating action. The internal heat generated by a reaction in the bulk material must raise the mass temperature sufficiently to cause an ignition of the material. Oxygen must diffuse into the reaction front and heat is dissipated outward to the environment.

The exotherms in the DTA tests constitute a condition of more rapid oxidation from water brought on by forced heating. The exotherms in the DTA tests are not indicators of ignitions of the reactive metals. The mathematical model shows that the material cannot ignite and this condition is independent of sample geometry. The plutonium in the salt residue has been oxidizing slowly over time (hence the material in drums is even less reactive than the material in cans, which have had less exposure to oxygen). This slow oxidation will continue in repackaged salt, without risk of ignition, leading to a completely stable and unreactive material. An additional consideration is that salt residue will be repackaged into a much more robust configuration (e.g. a pipe component) than the current storage containers. The anticipated slow oxidation will have no impact on the integrity or heat capacity of this robust package. Even a worst case reaction does not affect the packaging integrity, as shown in the calculation above.

The position is taken that this IDC is Low Risk and does not require 95-5 sampling. The drums were sampled to 95-5 and do not require additional sampling to rate them as a Low Risk material. All the data from the drums conforms to the model. The samples from drums in IDC 413 are quite similar to material from other IDCs of pyrochemical salts. The issue is whether the stand-alone-containers need to be sampled to a 95-5 confidence level. The containers showed slightly greater water reactivity than the drums. The containers generated 7.08 liters of hydrogen per kilogram of salt for the seven hours test. The drums generated 5.14 liters of hydrogen per kilogram of salt for the seven hours tests. Both values are consistent with other IDCs and less than the values experienced for IDC 473. Therefore, this IDC was typical of the entire pyrochemical salt residue inventory. It is important to realize that set production processes and controlled experimental conditions produced the pyrochemical residues. Set processes produced a highly consistent residue form. The experimental data for all pyrochemical salts confirms this fact. When viewed as a collective whole, the pyrochemical salts are considered Low Risk. If the ER salts are considered as a single category, the characterization results confirm this Low Risk designation at the 95-2% confidence level. It is neither necessary nor cost effective to perform additional tests on the stand-alone-containers.

Additional testing will not add new information to the present data base. As a result, the whole IDC is considered Low Risk.

5.3 SHOCK SENSITIVITY

The primary constituents for IDC 413 are the chlorides of potassium, sodium, and magnesium. These materials are all thermally stable in the temperature range of 25-350°C and have relatively low chemical reactivity. These salts contain plutonium chloride and possibly plutonium, and magnesium metals. It was originally conjectured that a shock sensitive material could be formed from residual potassium and sodium metals. However, the condition of shock sensitive was shown not to be a credible hazard. All samples passed the shock sensitive tests. Any potassium and sodium oxide has probably been converted to a more stable carbonate or hydroxycarbonate. Since a shock sensitive material would readily release its store of potential energy in a strong heating profile, the lack of significant exotherms in the DTA tests confirmed that these IDCs were not shock sensitive.

Since no indication of shock sensitivity has been shown with any ER salts, then the current level of sampling for the containers is adequate for making IDC 413 a Low Risk material.

5.4 REACTIVE METALS

The water reactivity test is conducted for the purpose of determining the quantity of residue that is present as reactive metal. The total amount of plutonium is determined by NDA techniques but plutonium is present in numerous chemical forms, e.g., PuO₂, PuCl₃, and Pu metal. While not capable of determining the amount of a specific specie of a metallic element, this test provides an alternative means of estimating the amount of Pu metal.

Although this measurement is derived from DOT requirements, it was executed for information purposes and not the purpose of determining the nature of a placard that a transport vehicle must post while carrying such material. Based on the DOT requirements, the levels of reactivity exhibited by these salt materials would only induce a minor upgrade in the packaging requirements as a basis for shipment. The packaging method used for the residue salts far exceeds those specified in the DOT requirements for safety purposes.

Based on the process that created these pyrochemical salts, the reasonable candidates for reactive metals are magnesium and plutonium. Total metal analysis confirmed the presence of magnesium at an average level of about 8.24% by weight. It is either present as the metal, its oxide or a chloride. In the total metal analysis, neither potassium nor sodium was analyzed for their presence in the salt.

The water reactivity tests did show the presence of reactive metals in almost all the samples. These reactive metals reacted slowly with water as would large, spherical particles or pieces of magnesium and plutonium. All the observed slow reactions extended over the entire seven hours of the reactivity tests. These observations confirm the presence of reactive metals in a form that have a reduced level of hazard. Spherical particles are observed in the sampling observations.

During sampling, several pieces of material appeared to be metal and special water reactivity tests were run with these small, individual pieces. A 0.5863 gram sample of 5800071 produced a total of 99.59 liters of hydrogen per kilogram of salt for the seven hours (Figure 3). A 0.0693 gram sample of 76002354 produced a total of 281.84 liters of hydrogen per kilogram of salt for the seven hours (Figure 4). If the two samples were strictly plutonium, they could have individually produced 64 liters of hydrogen per kilogram of salt for the seven hours. If the two samples were magnesium, they could have individually produced 1260 liters of hydrogen per kilogram of salt for the seven hours. Assuming that the samples are simply one metal, then the gas generation is caused by magnesium. Then 580071 consists of 7.9% metal and 76002354 consists of 22.4% metal.

Magnesium has a much lower reactivity rate in water. Its reaction rate is significantly increased by salt solution. It is most likely concluded that the pieces were agglomerates of metal spheres and salt. The 5800071 sample would have contained 0.0463 grams of magnesium metal. If it had been one particle in the sample, the diameter would have been 3.7 mm. If it had been ten particles of equal size in the salt agglomerated sample, the particle size would

have been 1.7 mm. Figure 3 for 5800071 implies that the sample consisted of small spheres that decayed rapidly. The decay rate readily fits an exponential curve. The sample for 76002354 had a non-uniform rate of decay (Figure 2). This sample probably consisted of only one to several particles of metal. The 0.0155 gram of metal in one spherical particle would have had a diameter of 3.7 mm.

The total metal analysis confirms that both MSE and ER salts are present in IDC 413 with the MSE salts generally having higher magnesium content than the ER salts. However, the water reactivity data implies that the MSE salts have a slightly higher water reactivity than previously examined MSE salts such as IDC 405 that generated a total quantity of hydrogen of 3.25 liters per kilogram of sample for the seven hours test.

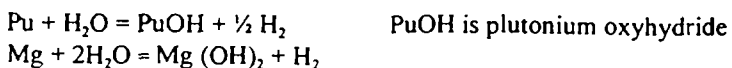
The hydrogen generation data represents a kinetic study. The majority of water reactivity tests fit a definite pattern of water-based corrosion. These tests fit the shape of an exponential equation. It is conjectured that the reactive metal particles are mainly spherical in shape. For a sphere, the surface area to volume ratio doubles as the diameter is halved. For a sphere, as the diameter is halved, the volume and the mass of the material are reduced by 1/8. These geometric considerations lead to an exponential decay rate for the reactive metal particles. The data is plotted with liters of hydrogen on the ordinate and hours on the abscissa. Figure 5 for D16068 and Figure 6 for 76002175 show the exponential equations and curves that best fit the data. There is an excellent fit between equation and curve. Clearly particles of similar diameters were rapidly corroding in the tests. The differences in the two equations may represent two different metals.

Using the data from D69148 in Figure 7, the particle size of the reactive metal was calculated. The water reactivity test curve for D69148 has a good exponential fit. Therefore, the curve can be considered representative of several particles of metal of the same diameter corroding in water. At seven hours, the curve approaches quite closely to a zero hydrogen generation rate, showing that the metal was mostly consumed in the test. The total amount of generated hydrogen is directly related to the original mass of the metal. For this calculation, the reactive metal was assumed to be plutonium. However, the size of the reactive metal would be similar if it had been a magnesium piece. If one particle of plutonium had been present in the D69148 sample, then it would have had a diameter of about 6.0 mm. If several particles of plutonium of equal size had been present in the D69148 sample, then the number of particles can be calculated as a function of their diameter. The possible combinations are 5 particles at 3.5 mm, 10 particles at 2.8 mm, 20 particles at 2.2 mm, 40 particles at 1.8 mm and 80 particles at 1.4 mm. Clearly, these are rather large pieces of plutonium that do not represent a hazard. The surface area to volume ratio for a sphere declines as the diameter increases. As this ratio declines for an air reactive metal, the potential for a lower temperature exotherm declines. These pieces of plutonium are well within the boundaries of the model. The metal was well disguised under its layer of colored salt and was not visually obvious to the sampling team.

Since it helps to add another layer of defense to the model for predicting the pyrophoric potential of plutonium-containing salt residues, a separate model was developed to estimate the particle sizes of plutonium beads in ER salts (Reference 4). This model predicts an average original particle size for beads of 1.8 mm. Over time in storage, the average bead size has been reduced to approximately 1 mm.

Occasionally, there was a sharp break in the curve and a departure from exponential decay. Figure 8 for D19622 illustrates this fact. Possibly, the sample consisted of several very small particles and several larger particles. The smaller particles were mostly corroded in the first hour and the larger particles continued to decay at a defined exponential rate for the remaining six hours.

For the tests, the average total quantity of generated hydrogen is 5.96 liters per kilogram of sample in the seven-hour tests. In contrast, the averages for IDCs 473 and 411 were 11.0 and 6.50 liters per kilogram of sample, respectively. Tests were conducted at approximately 20-25°C and about 550-610 torr. At 25°C, one gram of plutonium (0.0042 mole) will react with water to produce 0.00209 mole of hydrogen or 0.064 liter of gas at 610 torr; one gram of magnesium (0.0412 mole) will react with water to produce 0.0412 mole of hydrogen or 1.26 liters of gas (References 16 and 17).



This calculation assumes that plutonium goes to the trivalent Oxidation State in aqueous solution (Reference 18). Assuming all the reactive metal was plutonium, a kilogram of sample contained 93.1 grams of plutonium metal that is 9.31% plutonium by weight. Assuming all the reactive metal was magnesium, a kilogram of sample contained 4.73 grams of magnesium or 0.473% by weight. It must be recognized that the reactive metals are largely encased in a salt, metal oxide matrix that must dissolve or spall for the metals to react with water in the water reactivity tests. This salt, metal oxide matrix significantly reduces the rate of oxidation of the metals in air, sharply reducing any tendency to be pyrophoric. Again, magnesium metal is not pyrophoric.

For purposes of evaluating the potential for exothermic events, the reaction of interest is not the reaction of metal with water, but the reaction of metal with oxygen to generate metal oxide with a concomitant release of heat. The generation of heat and the resultant potential for breach of containment was considered.

A bounding calculation was based on the worst case test for water reactivity. The hydrogen generated in the worst case test is first assumed to be from the reaction of water with plutonium. Then, this content of plutonium is assumed to be representative of the entire salt mixture that is packed into the pipe component. Even though a large fraction of the hydrogen could have originated from the reaction of magnesium with salt water, it is assumed all of hydrogen was caused by the reaction of plutonium. This premise forms the basis of the first part of the worst case calculation. The calculation then assumes all of the metal oxidizes spontaneously in air. Container 7569620 produced a total of 21.98 liters of hydrogen per kilogram of salt. This is equivalent to a plutonium assay of 35 weight percent. Once again, plutonium is the only present metal that has accelerated oxidation in the temperature regime of concern. The pipe is limited to a plutonium assay of 10% by weight. Therefore, the pipe is restricted to accepting about 575 grams of this salt. Other low plutonium content salt can be mixed with this material to produce a final mixture containing 2500 grams of salt as long as the plutonium content does not exceed 200 grams. This means that the pipe has its full charge of plutonium as the metal. This calculation then becomes equivalent to the bounding case described in section 5.2.

For IDCs 473, 411, and 413, the worst case, water reactivity tests are 27.2, 19.0 and 21.98 liters of hydrogen per kilogram per seven hours, respectively. This consistency in data for the three IDCs is also noted for the worst case exotherms and the average total liters of hydrogen generated in the water reactivity tests. Clearly, the three IDCs are quite similar with IDC 473 having the most air and water reactive metal content.

As run, the water reactivity tests give a good estimate of the total metal content. The salts mostly contain spheres of metal that completely react in the water reactivity tests. Using a distinctive test procedure, the water reactive tests accurately define the amount of water reactive metal that is present. However, it does not define the amount of water reactive metal that is also air reactive. The amount of air reactive metal will be less than or equal to the amount of metal as indicated by the water reactive tests. Therefore, the above calculation explicitly defines a worst case situation.

The pyrochemical salts have been selectively sampled. For the total metal analysis, DTA and XRD tests, representative samples were taken. For the water reactivity tests and particle size analysis, samples were taken of material that would readily fit into the test configuration. Since the large chunks were never suspected of representing an ignition hazard, this technique represented a worst case test with respect to pyrophoricity. Since plutonium was still shown to be present in the fines, it helps show that dense, intact salt layers are still protecting plutonium particles from air oxidation. Therefore, slower, water-based oxidation of plutonium particles is occurring. Since water has equilibrated throughout the sample's large and small pieces, the metal content should be similar in both the chunks and the smaller pieces. Therefore, the sampling technique has not skewed the water reactivity data. The IDC has large pieces but is mainly less than one inch in diameter. Since a 1/2-inch chunk of salt will erode away about 1/2 its weight in 50 minutes, the large 3-inch chunks will more gradually release their metal to attack over several hours' duration. Therefore, the rate of plutonium reaction from attack by water in solution will be slowed with the larger chunks.

Since the level of water reactive metals in this IDC is very consistent with the quantities seen in the other IDCs of pyrochemical salts, there is no need to conduct further sampling of IDC 413.

This level of reactive metal in the salts will not represent a hazard in the interim safe storage of these materials.

5.5 VOLATILE AND SEMI-VOLATILE COMPOUNDS

The history of the ER process shows that the salts and the resulting residues were not contacted with any organic compounds. The temperature of processing, 800-900°C, was sufficiently high to prevent the existence of organic compounds in residues. The DTA tests did not show any endotherms that could be associated with the evaporation or boiling of an organic compound. It was clearly obvious that all endotherms were associated with the release of the waters of hydration of magnesium chloride.

5.6 CONDITION OF THE STORAGE CONTAINERS

The storage containers that held the pyrochemical salts were all in acceptable condition. They all successfully held their material without any corrosion that breached the first level of containment. Since the condition of the containers that held IDC 413 is consistent with the conditions of all containers that held pyrochemical salts, there is no need to conduct further sampling of this IDC.

6.0 SUMMARY

As an individual entity and irrespective of its storage vessel, IDC 413 should be considered a Low Risk material. This IDC does not present any significant safety risk to the worker or the public when it is stored in the current configuration and during handling operations. This IDC satisfies the requirements of the interim safe storage plan. IDC 413 was sampled to a 95-5 confidence level for drums and an 85-15 confidence level for other containers. Since this IDC is so similar to IDCs 411 and 473 that were sampled to a 95-5 confidence level, it does not require further characterization for this risk assessment of 'Low Risk.'

7.0 REFERENCES

1. Defense Nuclear Facilities Safety Board 94-1 Implementation Plan.
2. A. G. Phillips, "Evaluation of Risks Associated with Electrorefining Salt - Final Disposition (IDC 411)," RS-090-040, Rev. C, January 7, 1999.
3. A. G. Phillips, S. J. Eberlein, and D. L. Vieth, "Evaluation of Risks Associated with Electrorefined Salt Packaged for LANL (IDC 473)," RS-090-047, March 30, 1999.
4. J. M. Haschke, et al, "Analysis and Characterization of Plutonium in Pyrochemical Salt Residues," pending journal publication, February 1999.
5. Fauske & Associates, "Assessment of the Pyrophoricity Potential for Plutonium Containing Salt Residues," December 1998.
6. J. M. Haschke, "A Technical Review of the Assessment Report on Pyrophoricity of Plutonium Containing Salt Residues," RS-090-038, November 1998.
7. J. M. Haschke, et al, "A Mechanism for Plutonium Pyrophoricity," Journal of Nuclear Materials, 210 (1994) 130-142.
8. J. M. Haschke et al, "Reaction Kinetics of Plutonium with Oxygen, Water, and Humid Air: Moisture Enhancement of the Corrosion Rate," Journal of Alloys and Compounds, 243 (1996) 23.
9. D.L. Vieth, "Potential Pyrophoricity in Salt Residues," Safe Sites of Colorado Document RS-090-037, February 12, 1999.

10. K. A. Phillips, "Project Plan for Inspection, Sampling and Characterization of Solid Residues," Rocky Flats Document SRM-012-002, Revision E, February 27, 1998.
11. K. A. Phillips, Memorandum to S. J. Eberlein, "Sampling Technique for Pyrochemical Salts," KAP-007-99, March 22, 1999.
12. A.G. Phillips, "Water Studies of Salts Used in Pyrochemical Processes," Safe Sites of Colorado Document 96-RC-003, November 1, 1996.
13. D. T. Thorp, Memorandum to J. M. Ball, "Use of the Pipe Component for Stabilization of Residues; Cost Saving Proposal," DTT-002-97, February 17, 1997.
14. J. B. Schlierloh, "Thermal Analysis of Pipe Component, 6-inch and 12-inch," Rocky Flats Engineering Calculation CALC-000-T-000225, October 1, 1997.
15. D. F. Dustin, "Technical Basis for the Implementation of the Pipe Component for Accelerated Removal of Residues from Rocky Flats," RFETS Document RS-090-028, Issue A, December 5, 1997.
16. A.G. Phillips, "Analytical Methods for Determining the Hazardous Characteristics of Ignitability and Reactivity for Pyrochemical Salt," EG&G Rocky Flats, RFP-94-001, January 25, 1994.
17. A.G. Phillips, "Developing a Method for Evaluating the Ignitability of Pyrochemical Salts," Safe Sites of Colorado Document 96-I&E-001, May 22, 1996.
18. J. M. Haschke, et al., "The Reaction of Plutonium with Water, Kinetic and Equilibrium Behavior of Binary and Ternary Phases in the PU+O+H System," RFPD-3416, February 3, 1983.

Table 1. IDC 413 Results

| Container | Contact Dose Rate, (mRem/hour) | Visual of Primary Container | Pyrophoricity | Temperature of Endotherm (degrees centigrade) | Temperature of First Exotherm (degrees centigrade) | Temperature of Second Exotherm (degrees centigrade) | Water Reactivity (total liters of hydrogen per kilogram of salt) | Shock Sensitivity |
|-----------------------------|--------------------------------|-----------------------------|---------------|---|--|---|--|-------------------|
| 3915920 | pass | pass | pass | 175 | 180 | NA | 8 1 | pass |
| 5800071 | pass | pass | FLAG | NA | 150 | NA | 5.90, SW 99.59 | pass |
| 7569620 | pass | pass | FLAG | NA | NA | NA | 21.98 | pass |
| 76002044 | 230 | pass | pass | 155 | 265 | NA | 8.63 | pass |
| 76002071 | pass | pass | FLAG | 185 | 130 | 250 | 18.85 | pass |
| 76002353 | pass | pass | FLAG | NA | 135 | NA | 1.82 | pass |
| 76002354 | pass | pass | FLAG | NA | 130 | NA | 3 45, SW281.75 | pass |
| 76002401 | pass | pass | pass | 140 | NA | NA | 3.05 | pass |
| 76002402 | pass | pass | pass | NA | NA | NA | 3 01 | pass |
| 0302808 | 200 | pass | pass | 150 | NA | NA | 0 47 | pass |
| 76002175C06359 | N/A | pass | FLAG | NA | 150 | NA | 9 65 | pass |
| 76002178C06546 | N/A | pass | pass | 135 | 205 | NA | 5.39 | pass |
| 76002825 | pass | pass | FLAG | 160 | 110 | 240 | 4.95 | pass |
| 76002845 | pass | pass | pass | 150 | NA | NA | 2.24 | pass |
| BL77-2 | 360 | pass | pass | 150 | 245 | NA | 6 | pass |
| C06094 | N/A | pass | pass | 130 | 190 | NA | 9 86 | pass |
| D09695 | pass | pass | pass | 140 | 244 | NA | 1 21 | pass |
| D10618 | 470 | pass | pass | 155 | NA | NA | 6 48 | pass |
| D11918 | 250 | pass | pass | NA | 200 | NA | 11 32 | pass |
| D12240 | 240 | pass | pass | 100 | NA | NA | 0.84 | pass |
| D12385 | 250 | pass | pass | 130 | 210 | NA | 1 45 | pass |
| D13151 | pass | pass | pass | 135 | 220 | NA | 4.29 | pass |
| D13259 | pass | pass | pass | 150 | 170 | 245 | 7.84 | pass |
| D13561 | 380 | pass | pass | 140 | 200 | NA | 12 22 | pass |
| D13968 | 310 | pass | FLAG | NA | 140 | NA | 6.06 | pass |
| D14711 | pass | pass | pass | 110 | NA | NA | 2 9 | pass |
| D15979 | EXCEEDS RWP LIMIT | | | | | | | |
| D16060 | pass | pass | pass | NA | NA | NA | 2 44 | pass |
| D16068 | pass | pass | pass | NA | 180 | NA | 12 24 | pass |
| D16070 | 210 | pass | pass | NA | 195 | NA | 6 28 | pass |
| D16072 | pass | pass | FLAG | NA | 110 | 210 | 7 13 | pass |
| D16073 | 200 | pass | pass | 140 | 215 | NA | 8 45 | pass |
| D19622 | pass | FAIL [1] | pass | 115 | NA | NA | 5 28 | pass |
| D21249 | 330 | pass | pass | 140 | 240 | NA | 0 72 | pass |
| D21267 | 210 | pass | pass | 150 | NA | NA | 2 14 | pass |
| D22458 | 230 | pass | pass | 145 | 220 | NA | 0 29 | pass |
| D23814 | pass | pass | pass | NA | NA | NA | 0 41 | pass |
| D48815 | pass | pass | pass | 47 | NA | NA | 0 29 | pass |
| D69148 | pass | pass | FLAG | NA | 135 | 200 | 12 69 | pass |
| NA is not applicable | | | | | | | | |
| Note 1 lid not secured well | | | | | | | | |
| SW is special work | | | | | | | | |

FIGURE ONE

RATE-TEMPERATURE RELATIONSHIPS
OF PLUTONIUM OXIDATION

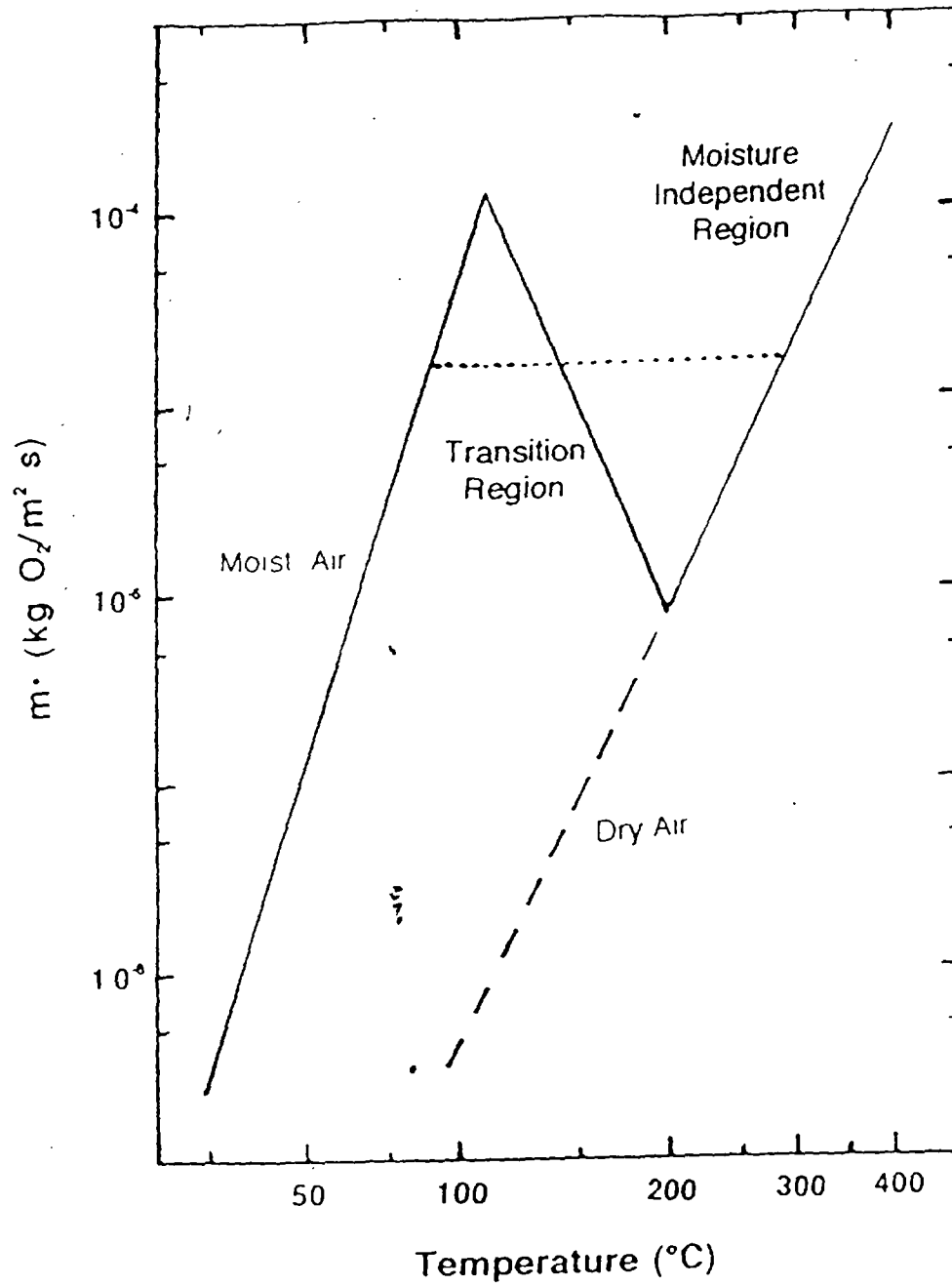
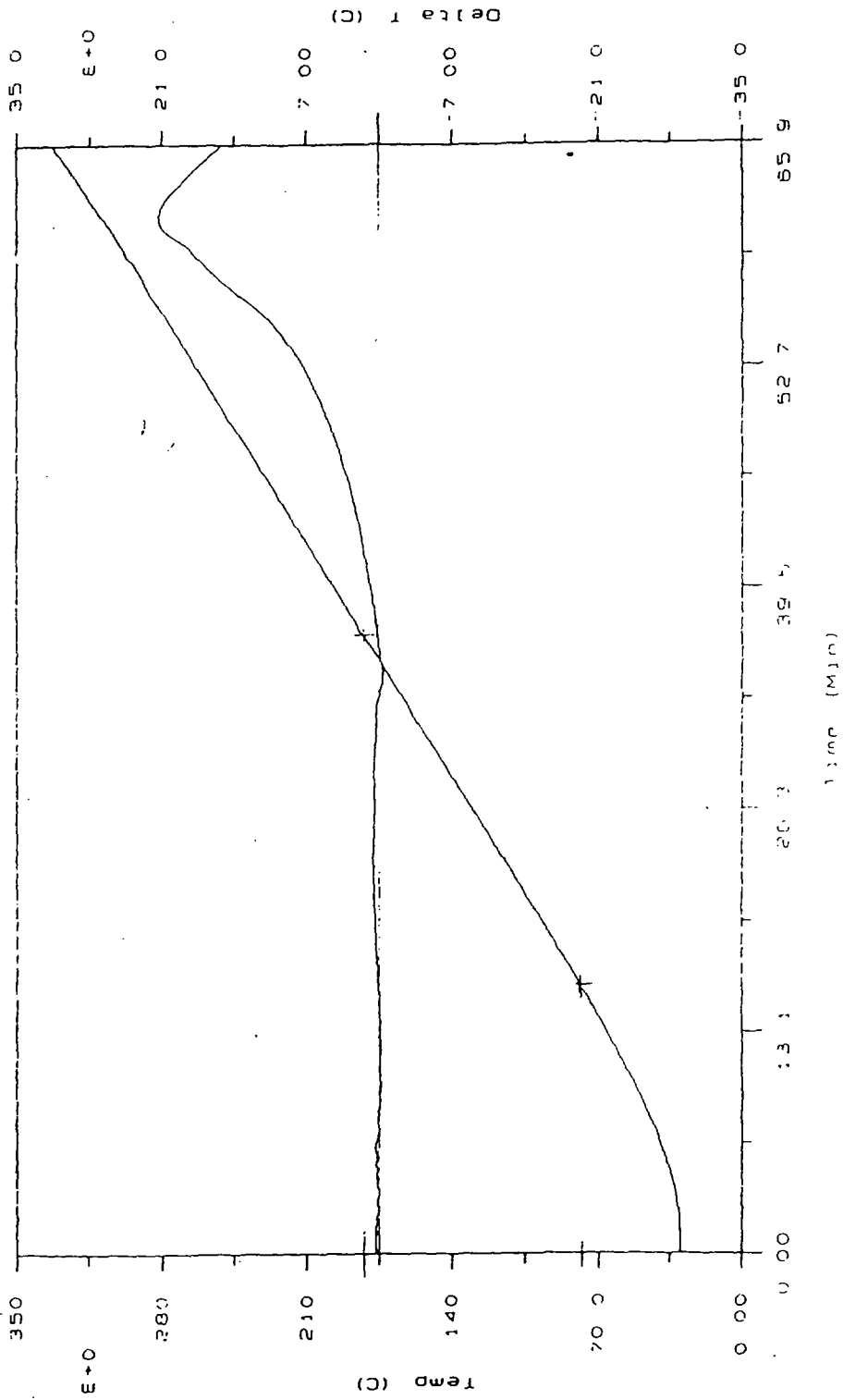
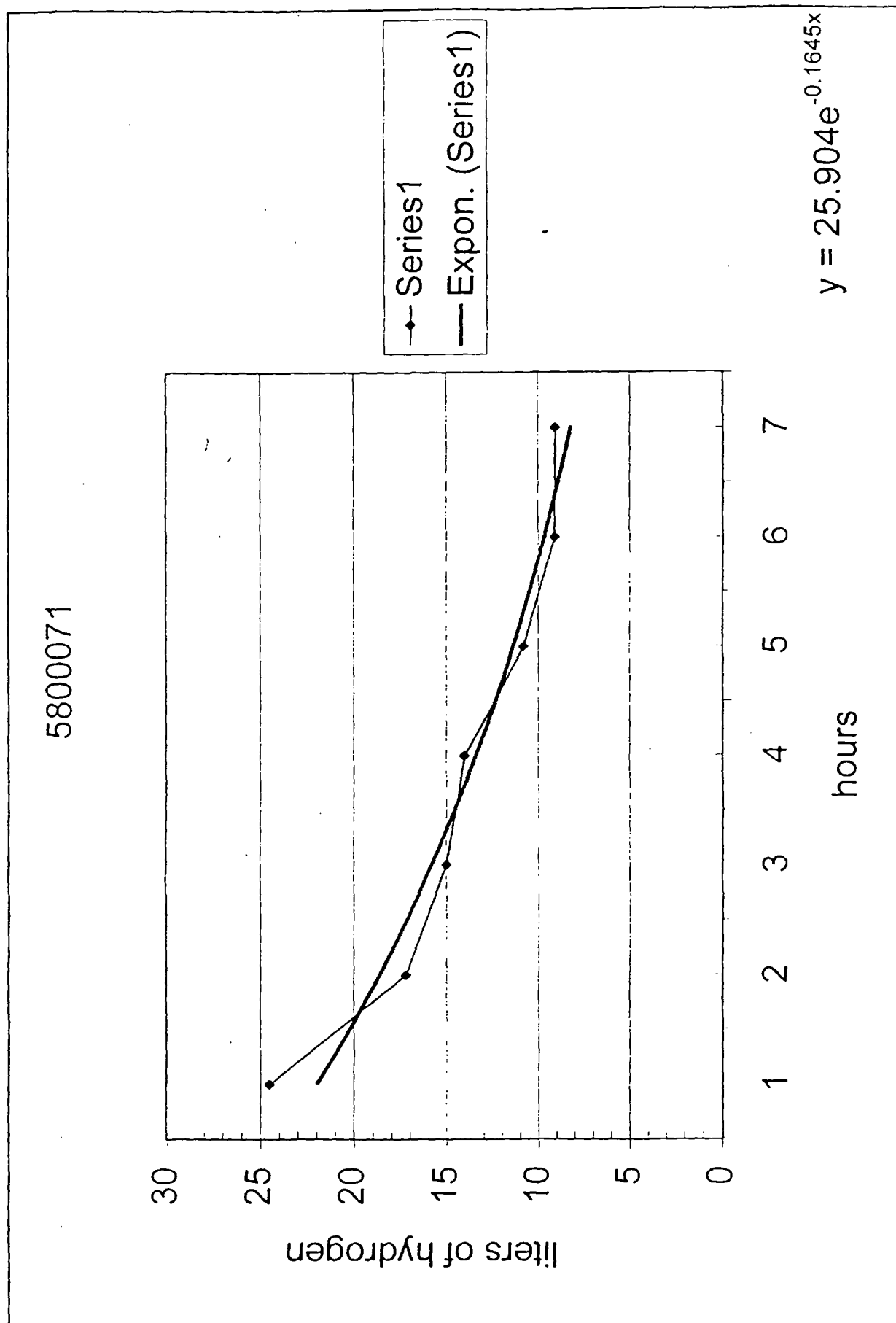


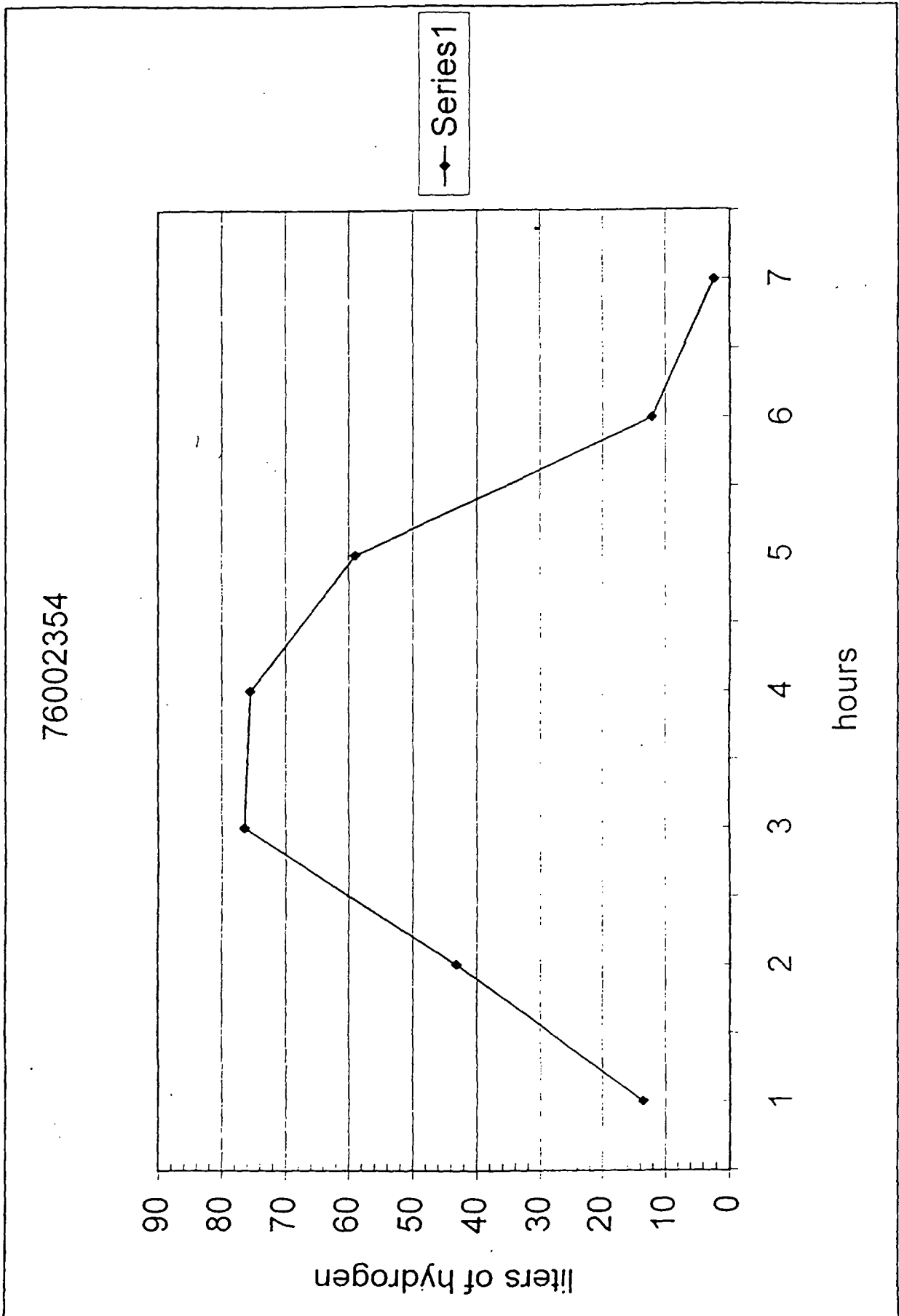
FIGURE TWO

3915920



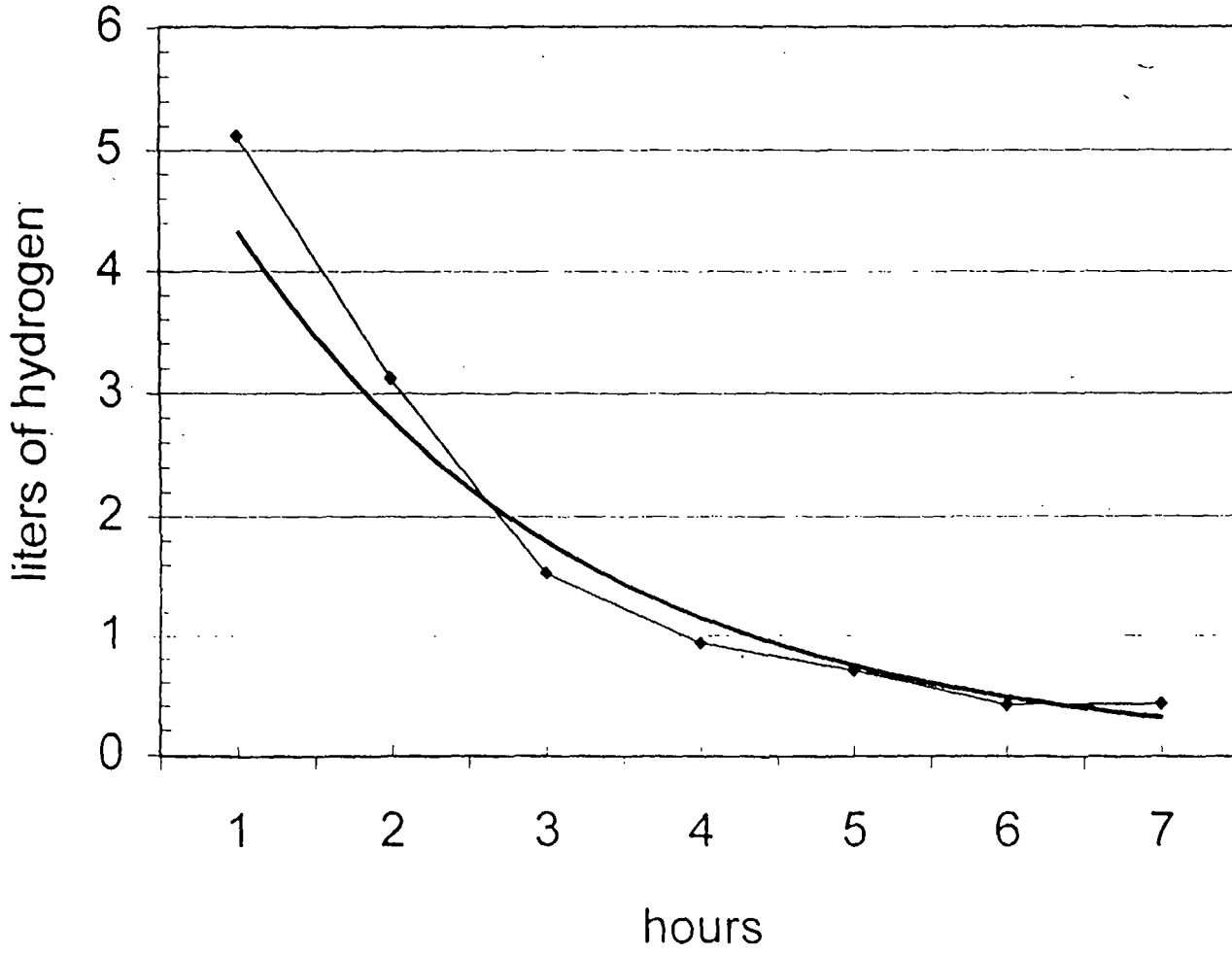


5800071



76002354

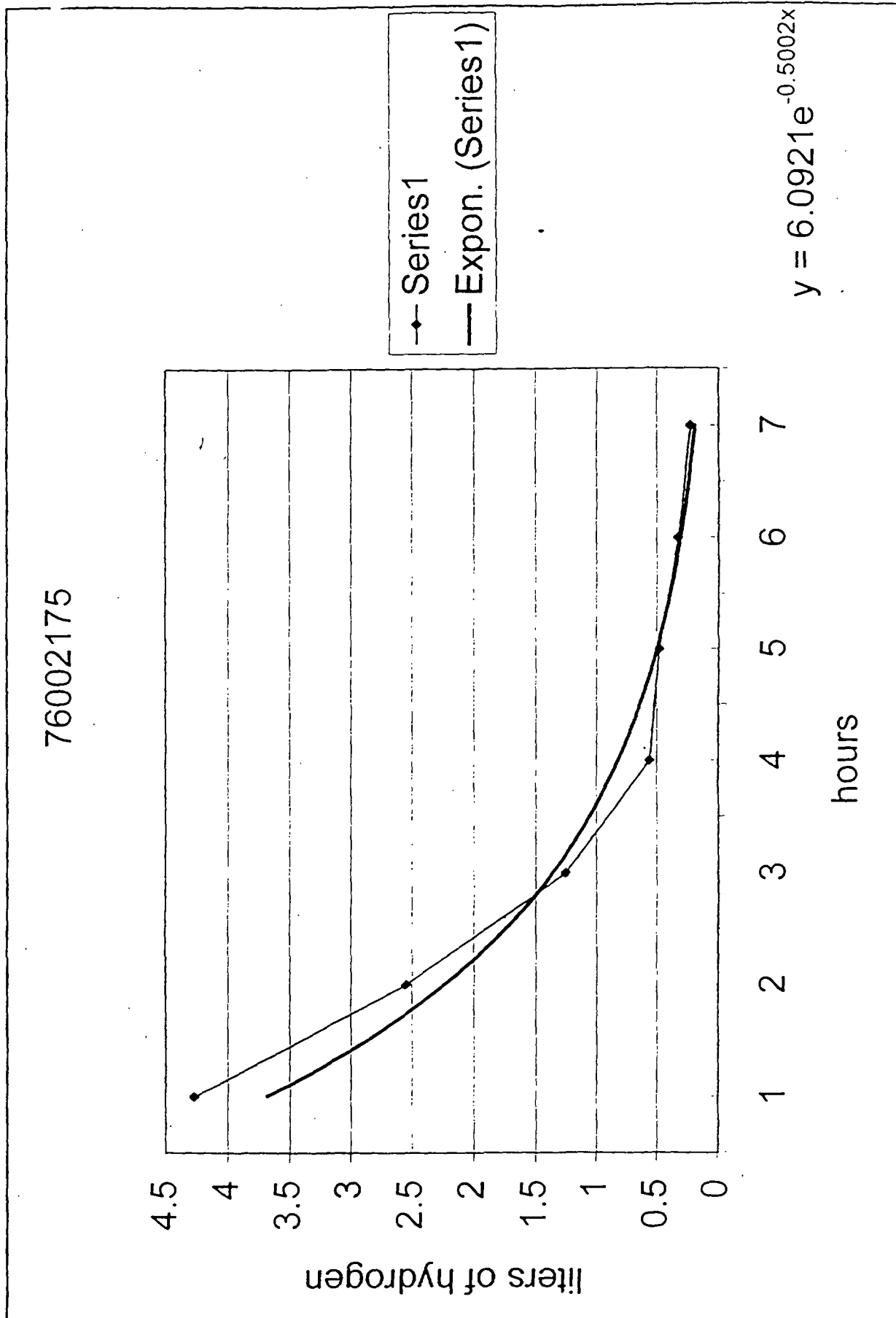
D16068

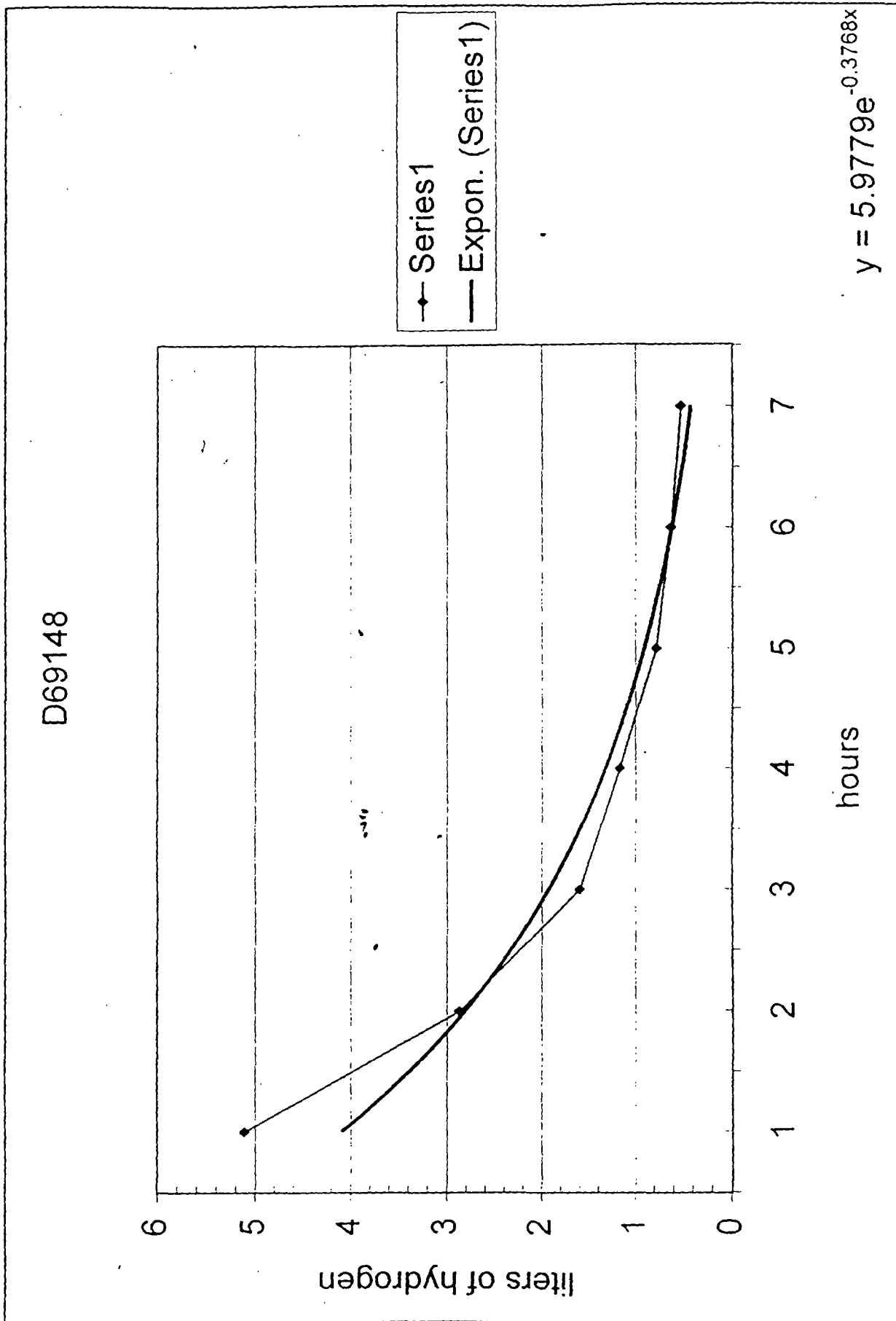


$$y = 6.7448e^{-0.4408x}$$

FIGURE SIX

76002175



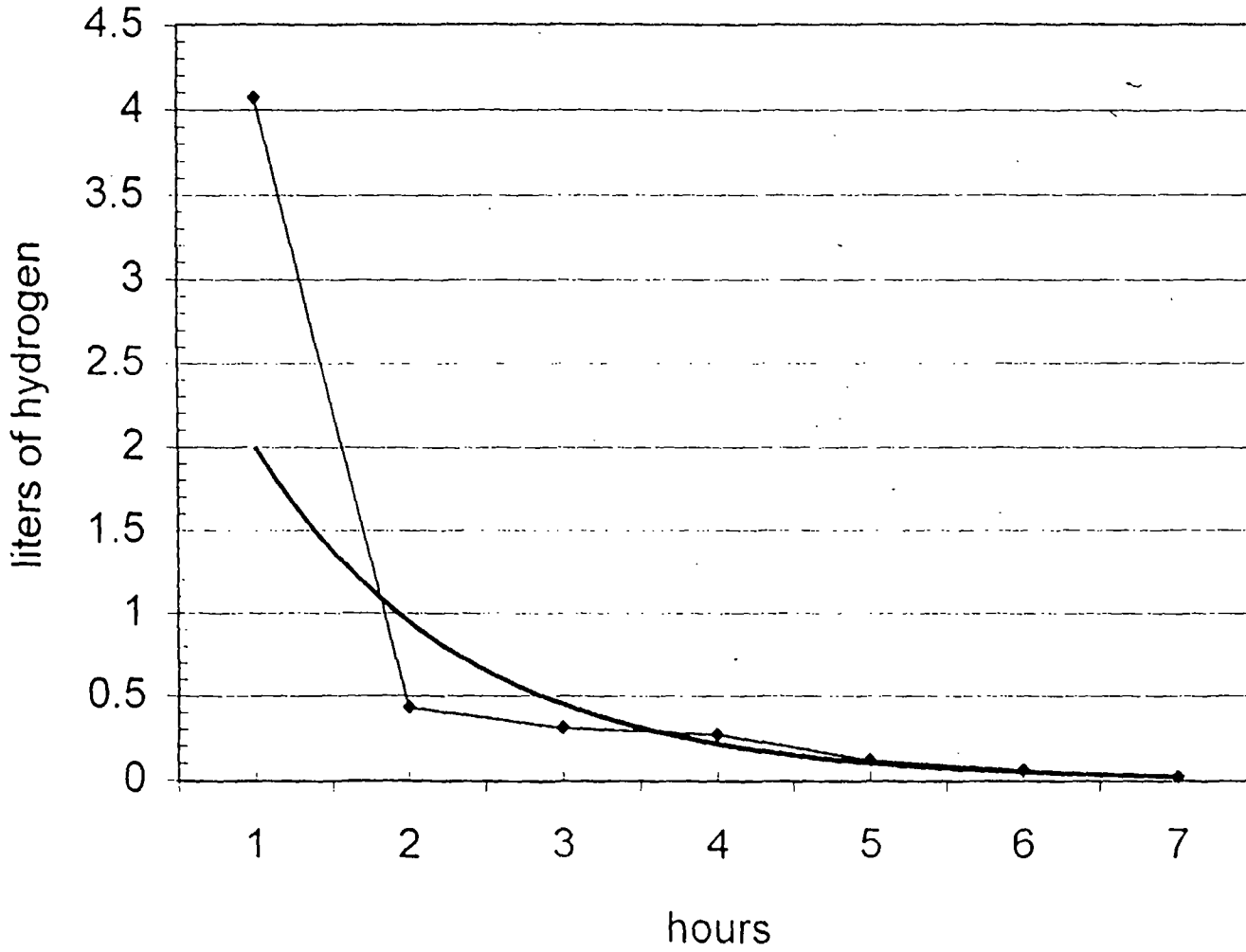


D69148

D19622

RS-090-060

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◆ Series1
— Expon. (Series1)

$$y = 4.2137e^{-0.7441x}$$