ATTACHMENT B

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WHITE PAPER

EVALUATION AND SELECTION OF A PROCESS TO REMOVE PLUTONIUM FROM WEST VALLEY HIGH-LEVEL WASTE SLUDGE WASH WATER

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DISCLAIMER

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EXECUTIVE SUMMARY

Three methods for the removal of plutonium from the West Valley Demonstration Project (WVDP) sludge wash are discussed in this paper. The sludge at the bottom of tank 8D-2 must be washed to remove the soluble sulfate salts because the sulfate ion in the sludge in the West Valley tanks is incompatible with the type of vitrification chemistry which will be used to incorporate high-level radioactive waste into a stable borosilicate glass form. This wash will be performed prior to mixing the sludge with the acidic THOREX waste from tank 8D-4 and the ion exchange media (IE-96)(1) coated with radioactive cesium (^{137}Cs) from tank 8D-1.

During laboratory modeling experiments, a substantial quantity of the plutonium and uranium compounds in the sludge were released into solution. If the wash supernatant with these increased levels of plutonium and uranium were processed through the Supernatant Treatment System (STS) and concentrated in the Liquid Waste Treatment System (LWTS) evaporator, the plutonium would change the solid waste form classification from a low-level radioactive waste (LLRW) to a transuranic waste (TRU). This is not consistent with the processing, environmental, or economic plans of the WVDP.

Three technologies that met the West Valley requirements were identified and tested in the laboratory to reduce the concentration of plutonium in the wash water. A combination of two, pH control of the sludge wash water and use of titanium coated IE-96 ion exchange media in the STS, have demonstrated very positive results. The third technology, the addition of potassium ferrate to pH adjusted sludge wash water, yielded no significant decrease of plutonium or uranium in the laboratory sludge wash water.

The exact chemical reaction which occurs in the pH controlled wash water is not known; controlling the pH of sludge wash water either prevents the plutonium and uranium compounds from disolving into the sludge wash water or precipitates the uranium and plutonium as hydroxides. The titanium coated IE-96 was effective for removing plutonium but not uranium while retaining the zeolite's activity as an ion exchanger for cesium. Both these technologies are compatible with chemistry of the existing Integrated Radwaste Treatment System (IRTS); however, some minor parameters need further investigation before they could be implemented. At this time, all current knowledge of these technologies strongly indicates that they can be implemented successfully at WVDP. Present information also suggests there should be no significant delay in solidifying the high-level waste in tanks 8D-1, 8D-2, and 8D-4 as a result of using these methods. Therefore, West Valley is planning to use the combination of high pH sludge wash water and titanium coated zeolite ion exchange media to remove plutonium from the sludge wash water.

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(1) Ionsiv IE-96 is a registered trademark of UOP, Des Plains, Illinois.

I. BACKGROUND

Nuclear Fuel Services, Incorporated (NFS), the original plant operator, reprocessed spent nuclear fuel at the West Valley site from 1966 to 1972. They employed the PUREX process to extract uranium and plutonium from commercial and government spent nuclear fuels and generated about 2 million liters (560,000 gallons) of highly radioactive waste which is stored in an underground steel tank on-site. The high-level waste generated in the PUREX extraction process is stored in tank 8D-2, and it has formed two layers in this tank. The bottom or sludge layer (about 1.5 feet) contains insoluble hydroxides and precipitated salts; the top or supernatant layer (about 20 feet) is a concentrated salt solution.

WVDP started processing the supernatant from tank 8D-2 in 1988. The processing is taking place in the IRTS which consists of four separate processing facilities: STS, LWTS, Cement Solidification System (CSS), and the Drum Cell. In the STS, the supernatant is run through three or four ion exchange columns and the ^{137}Cs is removed. In the LWTS the supernatant is evaporated to 39 weight percent; and in the CSS the concentrated waste is mixed with cement to form a stable waste form. These waste drums are transported to the Drum Cell where they are stored.

Table 1 (the attachment section at the end of the paper contains the tables and figures in numerical order) presents the chemical composition, and table 2 presents the radiochemical composition of tank 8D-2 supernatant prior to the start of processing through the STS. Table 3 gives the average values for the plutonium in this sample in more commonly used units.

The cement waste form generated from this decontaminated solution is classified as Class C waste, not TRU waste. To achieve this classification, the amount of waste to be added to each drum of cement was first calculated and then verified by laboratory tests at Battelle - Pacific Northwest Laboratories (PNL) and at West Valley Nuclear Services Company, Incorporated (WVNS). For the past two years, tank 8D-2 supernatant has been processed and the concentrate incorporated into a Class C cement waste form confirming the calculations and the laboratory tests.

The completion of this supernatant processing phase had been planned for April 1991; however, because a buildup of plutonium appears to be occurring in the LWTS evaporator, supernatant processing has been discontinued for a few months until the safety of the process can be re-assessed. An acceleration in the sludge washing activities could occur if the decision is made to process the rest of the supernatant by the same method that will be used for the sludge wash. Therefore, it is important to formulate this decision as soon as all the required testing is complete.

II. PLANNED TREATMENT OF WEST VALLEY SLUDGE

After the supernatant is processed, the next planned phase in the disposal of the high-level waste at West Valley is washing the sludge now at the bottom of tank 8D-2. The wash water from the sludge wash will be processed like the tank 8D-2 supernatant. The wash, itself, is necessary to remove the high concentration of soluble sulfate salts in the sludge, because the solubility of sulfate in the glass produced in the slurry fed ceramic melter (SFCM) is 0.3 weight percent. Any sulfate ion concentration in the feed slurry to the SFCM which exceeds the 0.3 weight percent solubility in the glass will form a molten salt layer on the surface of the melt. This layer will interfere with the melting process and result in unacceptable borosilicate glass. The amount of sludge that can be put in the glass will be much less than planned and the number of glass logs necessary for solidifying the West Valley high-level waste would be substantally increased.

WVNS-1 Experiment

The first experiment performed on the sludge samples at the West Valley site was called WVNS-1. Since WVDP intended to wash tank 8D-2 sludge with plant process water to remove the soluble sulfate salts, this first experiment modeled sludge washing with plant water. To model this action in the laboratory, sludge samples that had been taken from tank 8D-2 in 1987 and the composite of the four additional sludge samples taken in 1989 were used. The 1987 sample was sent to PNL, and composit samples from 1989 were submitted to both PNL and the WVNS Analytical and Process Chemistry Laboratories.

Table 4 lists the physical parameters of the laboratory scale tank 8D-2 sludge wash experiment at pH 10.0 using process water. This experiment was performed like the proposed process using the same ratio of sludge to wash water and the same number washes (four). In this experiment, washing the sludge with plant process water caused much of the plutonium and nearly all the uranium in the sludge to go into solution. Table 5 lists the concentrations of major radionuclides and major ions found in the four laboratory wash waters. The values in table 6 are the product of the water soluble ion and radionuclide concentrations multiplied by the volume of each wash solution to give the grams or Curies of each species removed by each wash. Thus the sum of the water soluble ions removed by the four washes can be determined. The analyses of the washed, dried sludge are also tabulated. Using these values in table 6, the weight percent of any ion which is solibilized by each wash can be calculated.

Table 7 is a list of the calculated concentrations of various radionuclides which would be present in each of the wash waters when they are concentrated to a total solid content of 39 weight percent. Table 8 lists the volumes of distillates and concentrates which would be produced when each wash is concentrated to a total solid content of

39 weight percent. Table 8 also shows the number of drums of waste which would be produced. However, the higher levels of plutonium shown in the sludge wash water would have undesirable effects on the cement waste form. The increased plutonium concentration would increase the levels of transuranic elements in the cement waste above 100 nanocuries per gram. This would change the status of the cement waste from a LLRW to a transuranic/greater than Class C (TRU/GTCC) waste. TRU/GTCC waste storage requirements would change the storage requirements at West Valley from near surface disposal to long-term storage in a repository. Since a repository is not currently available, this would require the TRU/GTCC waste be stored at the WVDP site until one is approved. Table 9 contains the radionuclide limits for class C low-level radioactive wastes.

Maintenance in the CSS and the Drum Cell facilities requires hands-on operation. WVDP is committed to maintain worker exposure at a minimum level in keeping with ALARA goals. To achieve this, the majority of the radionuclides in tank 8D-2 sludge must be retained as insoluble material in the sludge throughout the sludge washing, thus allowing the solidification of these radionuclides in glass rather than in cement. Processing wash water with increased levels of soluble actinides (alpha emitters above uranium on the periodic table) also poses an increased occupational exposure for both normal operations and postulated accident situations. It is advantageous in all aspects of this process to implement technology that reduces this potential hazard; therefore, the criteria for the technologies to remove the uranium and plutonium from the final cement product were established as listed in section III below.

III. TECHNICAL REQUIREMENTS

After the initial WVNS-1 experiment was performed, evaluating technologies that could be used to prevent the uranium and plutonium from disolving in the sludge wash was started. There were several technical requirements which had to be met by any process to be considered for use at WVDP. The technologies considered had to meet the following criteria:

1. Prevent plutonium and uranium compounds in the sludge from disolving during the sludge washing cycles or removal of plutonium from the sludge wash water before it is incorporated in a cement waste form to avoid generating large amounts of TRU/GTCC waste.

2. Be easily integrated into the present IRTS system. Excessive delays would increase the cost of solidfying the high-level waste in tank 8D-2; therefore, major mechanical modifications are to be avoided. The technology or process selected should not impact the operation of any of the IRTS subsystems. After processing supernatant, the IRTS will have to be evaluated to see if it is mechanically and structurally sound. If any problem areas are found, a refurbishment period will be needed to correct these situations. A short time period (approximately three months) is presently planned between the end of processing supernatant and the beginning of processing sludge wash. Therefore, it is desirable to be able to modify equipment, instrumentation, and software, during this time frame. Modifications that are invisioned for this time frame are procedural, process parameters (changes in flows, temperatures, densities) that can be easily facilitated by the existing systems, and software/programming (to compensate for different process parameters). If additional systems are needed, such as chemical batch tanks, process controls, etc., delays may be necessary.

3. Minimize any extraordinary demands on existing project resources, notably engineering labor, since the process may be engineered while IRTS supernatant processing and the Vitrification design continue in parallel. The technology selected must be implemented and available to support a mid CY-1991 start of sludge washing.

4. Must be capable of encompassing up to four successive 250,000 gallon additions of wash water to the sludge in the bottom of tank 8D-2. Four dilutions of the sludge constituents are currently planned and the solubilities of the various compounds may vary from wash to successive wash. This may lead to a wide range of constituents that may have to be handled by the process as well as the CSS.

5. Can not adversely affect the solubility of sulfate in the wash water or cause the precipitation of sulfates in tank 8D-2. Lower sulfate solubility would increase the number of sludge washes needed to reduce the sulfate ion to acceptable levels and increase the amount of low-level waste generated.

6. Have chemistry compatible with existing technologies employed by WVNS---the borosilicate glass waste form, cement formula, tanks 8D-1 and 8D-2, and the process system. If special chemicals are added to the contents of tank 8D-2, they must be compatible with the Vitrification process. Special chemical additions could delay approval of the technology or the cement waste form, or cause potential delays in the Vitrification schedule.

7. Not create any hazardous or mixed wastes.

8. Prevent the cement waste form from being classified as TRU/GTCC waste. The maximum concentration of all alpha emitting transuranic nuclides with half-lives greater than five years must be less than 100 nanocuries per gram (DOE Order 5820.2A defines TRU waste as 100 nanocuries per gram). The existing cement waste form being produced from decontaminated supernatant contains about 30 nanocuries per gram of TRU/GTCC constituents. It is highly desirable that the new technology will be equal to or less than this current level. This requirement will also serve to limit the cesium and strontium concentrations well below the regulatory requirements (4,600 and 7,000 Ci/m^3 respectively).

9. Maintain the limitations on other radionuclides in the cement waste form consistent with the maximum requirements for Class C, low-level waste per 10CFR61 as shown in table 9.

10. Have no impact on the STS ion exchange decontamination factor of 1000 for cesium removal (no limitation on uranium is required by 10CFR61).

11. Make use of existing systems and processes to the maximum extent practicable. The sludge wash water will be processed in the STS ion exchange columns to remove the cesium. The decontaminated wash water will be concentrated in the LWTS to an approximate 39 weight percent total solids content. The concentrate will be blended with a Portland cement in the CSS and poured into 300 liter (71 gallon) square drums. These drums will be transported from the CSS facility to the Drum Cell by a shielded drum transport, where they will be stored with the decontaminated supernatant cement drums until the final disposition of these waste forms is determined.

The technologies discussed in section IV are the ones that are in compliance with these criteria.

IV. TECHNOLOGIES UNDER CONSIDERATION

Two technologies have been under investigation to remove plutonium and uranium compounds during the sludge washing process; a third alternative would remove plutonium in the STS before it is incorporated into the cement in the CSS. It is important that the plutonium and uranium end up in the Vitrification waste, and the technologies used to contain the plutonium and uranium must not interfere with cesium removal from sludge wash waters. The processes under consideration include: A) use of titanium coated IE-96 in STS ion exchange columns to remove solubilized plutonium compounds, B) adjustment of the pH of sludge wash waters to prevent solubilization of plutonium and uranium compounds, C) a combination of technologies A and B, and D) the addition of potassium ferrate (K_2FeO_4) to the sludge wash supernatant at an elevated pH to oxidize the plutonium and uranium to a more insoluble oxidation state and subsequent co-precipitation with ferric hydroxide.

A) Titanium Coated Zeolite

The use of titanium compounds to decontaminate radioactive aqueous solutions has been documented in the chemical literature (1,2). Although the primary function of the titanates was to remove ^{90}Sr from high-level waste, researchers noted that these compounds were also very efficient at removing specific actinides. PNL has recently developed an improved method to coat IE-96 with titanium (PNL Invention Report Number E-882). PNL has demonstrated this material can remove plutonium from solutions such as tank 8D-2 supernatant and sludge wash waters.

The results of the PNL experiments comparing IE-96 with titanium coated IE-96 are summarized below.

Cesium Ion Exchange:
- slightly reduced by coating IE-96 with titanium.
- slightly reduced by increasing the pH from 10.0 to 12.5.
- reduced by increasing the temperature from 6°C to 25°C.
- not affected by drying of the titanium coated IE-96 at 93°C.

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(1) Decontamination of Hanford Plutonium Reclamation Facility Salt Waste Solution, W.W. Schulz, RHO-SA-23, June 1978.

(2) The Scandia Solidification Process - A Broad Range Aqueous Waste Solidification Method, R.W. Lynch, R.G. Dosch, B.T. Kenna, J.K. Johnstone, E.J. Nowak, Scandia Laboratories, Albuquerque, New Mexico, IAEA-SM-207/75.

Strontium Ion Exchange:

- o greatly increased by coating IE-96 with titanium.
- o greatly increased by increasing pH from 10.0 to 12.5.
- o moderately increased by increasing the temperature from 6°C to 25°C.
- o not affected by drying of the titanium coated IE-96 at 93°C.

Plutonium Ion Exchange:

- o greatly increased by coating IE-96 with titanium.
- o greatly increased by increasing the pH from 10.0 to 12.5.
- o increased by increasing the temperature from 6°C to 25°C.
- o reduced by drying of the titanium coated IE-96 at 93°C.

The effectiveness of the PNL titanium coated zeolite is shown in table 10 which lists the R_d values for cesium, strontium, and plutonium for titanium coated IE-96. The values were measured at 6°C and 25°C, at an initial pH of 10.0 and 12.5 and with coated zeolite that was dried at 93°C. Data for uncoated IE-96 is also presented in this table.

The measured R_d for cesium adsorption on IE-96 has been tested and verified to be able to predict the loading capacity of cesium on this material. However, these tests were made using a well defined solution, matrix, and at a specific temperature, not under actual field conditions.

For titanium coated IE-96, the measured R_d values for plutonium are usually very large, because the titanium coated IE-96 has a significant affinity for plutonium. Usually, the R_d for plutonium is measured using plutonium concentration between 0.2 and 0.5 μCi/ml. This concentration is low and unless a very large volume of plutonium solution is used, the equilibrium plutonium concentration is much less than the initial and in fact approaches zero. Thus normal analytical errors in the plutonium analysis cause a significant variance in the measured plutonium R_d value. However, because of the afinity of the titanium coated IE-96 for plutonium, the plutonium R_d value is a good predictive tool. This test should make a useful screening device for comparison of different titanium coated IE-96 production batches.

Several laboratory methods were developed by PNL to coat IE-96 with 1.3 to 5.3 percent titanium (as TiO_2). Table 11 lists R_d values for cesium and plutonium as a function of temperature, pH, heat treatment, and titanium coating concentration. The results are in the following list.

Cesium Ion Exchange:

- o decreased slightly with increasing titanium concentration in the coated layer on IE-96.
- o reduced slightly by increasing the pH from 10.0 to 12.5 for all titanium coating concentrations.
- o reduced by increasing the temperature from 6°C to 25°C for all titanium coating concentrations.
- o not affected by drying the titanium coated IE-96 for all titanium coating concentrations.

Plutonium Exchange:

- increased with increasing titanium concentration in the coated layer on IE-96.
- greatly increased by increasing the pH from 10.0 to 12.5 for all titanium coating concentrations.
- increased by increasing the temperature from 6°C to 25°C for all titanium coating concentrations.
- reduced by drying of the titanium coated IE-96 for all titanium coating concentrations.

The exact chemical form of the titanium coating and nature of the bonding of the coating to the zeolite is not known at this time. However, from the chemistry of the coating technique and the stability of the coating at moderate temperatures (116°C), it is highly probable the coating is some sort of hydrated titanium (IV) oxide or hydroxide. UOP, formerly United Oil Production, which currently produces IE-96 has used scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX) to examine the coating. UOP stated that the coating appears uniform across the entire surface as the EDAX surface area scans of whole and fractured particles showed an even coating of titanium. EDAX spot area scans always showed the presence of silicon and aluminum indicating there are no discrete titanium particles in the coating. Figures 1 through 4 are micrographs of the PNL titanium coated IE-96; figures 5 through 9 are EDAX spectrographs of the titantium coating on IE-96.

The laboratory preparation method for the titanium coating of IE-96 appears straightforward. UOP has entered a confidentiality agreement with PNL in order to evaluate the feasability of producing this material commercially. To date all indications are that there will be only minor problems in scaling up to commercial production of this material.

IE-96 is currently being used to extract cesium from the supernatant in the STS which becomes an advantage if titanium coated IE-96 is used. Because with minor modifications the equipment in the STS and the handling procedures for IE-96 can be adapted to process sludge wash waters. Wet attrition tests were made on PNL samples of titanium coated IE-96 to determine if any titanium coating would flake off during loading and dumping of the columns in STS. The test sample of titanium coated IE-96 had 4.9 percent titanium (as TiO_2), and during the test, only 0.68 percent of the titanium coating was removed.

The next logical step was to test the titanium coated IE-96 in columns in the laboratory. Table 12 lists the experiments which were made using columns to measure the effective DF for plutonium. Figures 10 through 19 are probability plots of the plutonium removal for the lab tests made at PNL and WVNS.

Column flow rates were scaled to STS processes, and the results are extremely encouraging. Figures 10 through 13 are PNL experiments, and figures 14 through 19 are WVNS experiments. Figure 10, columns loaded with IE-96, shows a rapid breakthrough of cesium after only a minimum number of column volumes of synthetic West Valley waste solution were processed. Figures 11 and 12, using columns loaded with 1.3 and 5.3 weight percent titanium coated IE-96, shows that plutonium from the synthetic West Valley waste solution is strongly held on the columns. In figure 13, columns loaded with 5.3 weight percent titanium coated IE-96, shows that the plutonium from decontaminated supernatant is also strongly retained on the columns.

WVNS-1 sludge wash solution #1 (process water at pH 10) was decontaminated using four columns loaded with 5.3 percent titanium coated IE-96 and connected in series. The lead column was not changed during the experiment. Figures 14 through 16 are linear probability plots of percent C/C_0 (or percent breakthrough) for cesium, plutonium, and strontium. The experimental parameters are listed on the plots. At about sixty hours into the test, column 2 developed a leak and had to be removed. Column 1 was then connected to column 3, and the test was completed.

In figure 14, the linear probability plot of percent C/C_0 for cesium, shows the lead column had an 80 percent breakthrough of cesium at about 90 column volumes (cv). In figure 15, the linear probability plot of percent C/C_0 for plutonium, the percent C/C_0 at 90 cv, is about 0.05. This would correspond to a DF for plutonium of about 200. From the slopes of the lines in figure 16, the linear probability plot of percent C/C_0 for strontium, it appears the titanium coated IE-96 is also effective in removing strontium.

For WVNS-2, all four laboratory sludge washes (wash solutions about pH 12.5) were decontaminated using a four column system loaded with 5.3 percent titanium coated IE-96 and connected in series. The column system was designed to remove the lead column and add a fresh column to the end position. A pump failure occurred on the sixth day (between 115 and 130 cv) and the system was shut down for about one day until a replacement was installed. The experiment was then completed without further interruption. Figures 17 through 19 are linear probability plots of percent C/C_0 in the lead column for cesium, plutonium, and strontium for WVNS-2. The lead column in the four column system was removed when the value of the percent C/O for cesium approached 10 percent. This is shown in figure 17. The pump failure is probably responsible for the change in slope of the second line in figure 17. However, even with this pump malfunction, the slopes of the lines for the individual washes are in good agreement for wash #1 and wash #2.

The ^{137}Cs concentration decreases by about 1/3 in each of the succesive washes. Figure 17 shows the slopes of the lines for each successive wash similarly decrease by the same factor. A third observation shows that three columns were needed for cesium decontamination of wash #1, one column for wash #2, and one column for wash #3 and wash #4. All this data is reasonable and consistant with the behavior of a column loaded with IE-96. This is strong evidence that the titanium coating does not change the cesium extraction characteristics of IE-96.

Figure 18 shows plutonium breakthrough on column 1 between 120 and 140 column volumes (cv). Plutonium analysis of the second column in this series showed no plutonium breakthrough. The decontamination factor (DF) for plutonium in WVNS-2 is greater than the DF for plutonium in WVNS-1. Also, the pH of the wash waters in WVNS-1 was about 10 while the pH of the wash water in WVNS-2 was about 11.8. The column data (DF) at the two pHs correlates with the R_d values measured at both PNL and WVNS. This further indicates that although the R_d is not a number which can be mathmetically correlated with the DF, the values should be used as a tool for screening.

Figure 19 shows the strontium data for this experiment. Comparison of figure 19 with figure 16 shows that there is excellent extraction of strontium from the laboratory sludge washes. At present, there is no explanation for the apparent increase in the slope for wash #4.

The four laboratory wash solutions were analyzed for all major components before and after the solutions were passed through the titanium coated IE-96 columns was to determine which ions or elements are retained on the titanium coated IE-96. The data is presented in table 13. Plutonium, strontium, and cesium are nearly completely removed by the titanium coated IE-96. Potassium and calcium are also retained by this zeolite which is to be expected because of the similarities in their chemistries.

Two separate sludge wash experiments performed at PNL and WVNS using process water showed high levels of uranium and plutonium in the wash water. Calculations, based on these analyses, predicted that essentially all the uranium and up to 30 percent of the plutonium present in tank 8D-2 sludge would be solubilized when that sludge was washed with plant process water at a pH of about 10. The solubilization of uranium by carbonate ion is well understood(1); however, there is no explanation of the mechanism of solubilization of plutonium.(2)

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(1) The Chemistry of the Actinide Elements, Second Edition,Volume 1, edited by J.J. Katz, G.T. Seaborg and L.R. Morss, Section 5.4.3.

(2) Property of Pu(IV) Polymer of Environmental Importance, Dhen Pat Rai, J.L. Swanson, Nuclear Technology, Vol. 54, pages 112-117, July 1981.

Both WVNS and PNL have filtered a variety of plutonium solutions through 18 Å filters.(3) These solutions include sythetic supernatant, reconstituted supernatant, actual supernatant, sludge wash from WVNS-1 and sludge wash from WVNS-2. The results are presented in table 14. In all seven tests, the concentration of plutonium is the same, within experimental error, before and after the filtration. The fact that the plutonium passes through the 18 Å filters strongly suggests the plutonium is soluble at pH 10 in these concentrated salt solutions.

The positive results from column experiments at pH 10, using 5.3 percent titanium coated IE-96 led to the question of how the plutonium is loaded on the column. PNL sectioned columns from plutonium extraction tests into three parts, and WVNS sectioned one column from WVNS-1 into five parts and one column from WVNS-2 into five parts. Table 15 lists the results of plutonium analysis on the sectioned columns.

The data in table 15 clearly shows the majority of the plutonium is captured in the top most section of the first column. This fact is further evidence that titanium coated IE-96 indeed does have a strong affinity for plutonium from basic solutions.

B) High pH Sludge Wash Water

The sludge wash from WVNS-1 has a pH of about 10. Chemical analysis showed the solution contained significant concentrations of inorganic carbon. Therefore, the wash solution must contain a mixture of carbonate and bicarbonate ions. In adjusting WVNS-1 wash #1 to pH 12.5 for the ferrate experiment, a significant amount of yellow precipitate was formed. Analysis of the yellow precipitate showed a high concentration of uranium, and analysis of the supernatant showed a decrease in the concentration of plutonium.

Based on the above observations, a controlled experiment was made to determine the amount of caustic required to raise a sample of the sludge slurry to pH 12.5. A sample of tank 8D-2 sludge was mixed with decontaminated supernatant and process water and allowed to settle. After settling, the supernatant was sampled and analyzed for uranium and plutonium. A known amount of sodium hydroxide was added. The mixing, settling, sampling and analysis steps were repeated. The sodium hydroxide addition procedure was done ten times. The results are presented in table 16. Figure 20 is a plot of the uranium concentration versus sodium hydroxide addition; figure 21 is the plot of the plutonium versus the sodium hydroxide.

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(3) Centriflo Ultrafiltration Cones, CF 25, 18A, Amicon Company

Because of the high concentration of solids, the complexed metals hydroxides mixture, and the high pH of the solution, accurate pH measurements could not be made. Without buffering, one would expect the loss of uranium to be a logarithmic function of sodium hydroxide concentration. The straight line from four to ten grams per liter sodium hydroxide follows this hypothesis. From zero to four gram per liter, the bicarbonate is being converted to carbonate. Note an equimolar solution of carbonate/bicarbonate would have a pH of about 10.3. This data clearly indicates that the solubility of uranium is related to the hydroxide ion concentration.

C) Elevated pH combined with Titanium Coated IE-96

This combination of technologies proved to be the most effective in preventing the plutonium and uranuim from disolving in the wash water. One argument used against this combination was that the uranium concentration had no effect on waste classification and titanium coated IE-96 was so effective in removing plutonium from the sludge wash water that it was not necessary to used both technologies. However, both technologies are necessary because pH control not only keeps uranium in the washed sludge, but also keeps most of the plutonium in the sludge. This keeps the plutonium in a critically safe geometry and prevents accidental contamination of WVNS personnel. If the plutonium were not kept in the sludge, it would be extracted on the zeolite columns in STS and could become a potential criticality hazard. Without pH control of the sludge wash water, approximately 7.7 kg of plutonium would be disolved in the first wash. This means that about 2 kg of plutonium would load in each column.

WVNS-2 Experiment

WVNS-2 modeled this combination of technologies in the WVNS laboratory. Several new questions needed to be answered in this experiment. What was the effect of the high pH on the titanium coated IE-96 in the STS ion exchange columns? What effect would the high pH have on cesium removal? WVNS-2 answered the questions, and this combination of elevated pH and titanium coated IE-96 emerged as the best solution.

Table 17 lists the physical parameters, the concentrations of the major ions, and radionuclides found in the wash solutions from WVNS-2. The analysis of the same elements found in the composite sludge wash solutions after they have been decontaminated through a four column ion exchange system loaded with titanium coated IE-96 (TiO_2 coating is 5.3 weigh percent) are listed in table 18.

The decontaminated wash solutions were concentrated by evaporation to 33 to 37 weight percent. The analysis of the concentrated wash solution are tabulated in table 19. Table 20 is the calculated concentrations of the ions which should be present. The cesium (Cs) values agree very well with the experiment data, but plutonium (Pu) and strontium (Sr) vary condiserably. Cesium will remain in solution reguardless of pH, but Sr and Pu solubilities are very dependent on pH, carbonate concentration, phosphate ion concentration, and almost any other parameter which may be changed.

From table 14, it is apparent that the titanium coated IE-96 has a large affinity for Pu, Sr, and Cs. This is comparable data to WVNS-1 presented earlier in this document. The results of the comparison between experiments WVNS-2 and WVNS-1 are listed below:

- Like WVNS-1, the sulfate ion is effectively reduced to levels acceptable for the Vitrification process.
- Like WVNS-1, cesium is still captured on the zeolite in STS.
- Unlike WVNS-1, uranium is kept in tank 8D-2.
- Unlike WVNS-1, most of the plutonium is kept in tank 8D-2 and the small amount that is solubilized is removed on the titanium coated IE-96 in STS.
- Unlike WVNS-1, since much less plutonium is solubilized, the possibility of a criticality hazard is greatly decreased.
- In addition to preventing uranium and plutonium from entering the cement waste, titanium coated IE-96 was also found to effectively remove strontium from the sludge wash water.

Concerns about aluminum dissolving from the sludge and precipitating in the STS columns were resolved with the WVNS-2 experiment as ion exchange columns were also tested in the recirculation mode. There was no indication of aluminum precipitation. This can be explained by the pH measurements of the laboratory sludge wash waters. When the pH of the sludge wash is increased to about 12.5, the pH of the agitated sludge solution will reach equilibrium at a pH of 11.9. This decrease in pH is attributed to the dissolution of aluminum hydroxide in the sludge according to the following equation:

$$Al(OH)_3 + OH \text{ ---> } AlO_2^- + 2\ H_2O$$

The buffering effect from the dissolution of the aluminum hydroxide from the sludge is probably advantageous since the solution from the sludge wash is less likely to attack the IE-96. Laboratory observations of the column sectioned for determining the loading characteristic of plutonium, cesium, and strontium demonstrated that the dried IE-96 readily dislodged from the one inch sections.

A simulated solution of sludge wash with $Al(OH)_3$ and pH adjusted to about 11.9 is being passed through two columns loaded with titanium coated IE-96. The first column was tested, after passing through 250 cv at 1.0 cv/hr, to determine whether IE-96 has formed a monolith. Backflushing with water indicated that IE-96 was readily mobilized. The experiment with the simulated wash solution will be continued until 1000 cv are passed through the column.

D) **Potassium Ferrate Addition**

Twenty five milliliters of wash solution were adjusted to a pH of 12.5, and the supernatant divided into four separate samples. Varying amounts of potassium ferrate were added to three of the samples. The fourth sample with no potassium ferrate added was used as control sample for measuring the effect of increased pH on the solubility of plutonium and uranium.

No significant decrease was noted as the ferrate concentration was increased. Therefore, in this experiment, it was demonstrated that increasing the pH was more beneficial than the ferrate addition in preventing the solubilization of the plutonium and uranium in tank 8D-2 supernatant. The results of this experiment are tabulated in table 21.

The ferrate process is a two step process where the sludge is washed first, then the wash water is pumped to another tank for pH adjustment and ferrate treatment. This process would require extensive modifications to the existing systems; therefore, it will not be used at WVNS.

V. CONCLUSIONS

Laboratory modeling experiment WVNS-1 identified a problem with increased solubility of plutonium and uranium compounds in tank 8D-2 sludge wash waters. The increased solubility of plutonium and uranium in the sludge wash water is caused by a change in tank 8D-2 sludge chemistry due to the absorption of carbon dioxide, the addition of neutral process water, and subsequent agitation. Plutonium and uranium form insoluble hydroxides at high pH but are made soluble in the carbonate buffered sludge wash water. Therefore, a technology was needed to contain the plutonium and uranium in the sludge; this would prevent the generation of an increased number of cement waste drums with much higher waste classifications.

Two technologies were identified which can be used to keep the plutonium and uranium actinides in the sludge. They are pH control of the wash water and the use of titanium coated IE-96 in the ion exchange columns in STS. Experiment WVNS-2 showed-that a combination of both these technologies resulted in an improvement in the performance of the IRTS for sludge wash.

Tables 22 and 23 show comparison data for the four sludge washes in WVNS-1 and WVNS-2. It can be clearly seen that pH control alone retains most of the uranium and plutonium in tank 8D-2 sludge. Titanium coated IE-96 was shown to effectively remove cesium, plutonium, and strontium from the laboratory sludge wash waters. The experiments suggest the possibility that the cement waste from the tank 8D-2 sludge wash after treatment with the combined technologies could contain fewer radionuclides than the cement waste from the present supernatant treatment. At the worst, the data substantiates that the cement waste will be equivalent in radionuclides to the waste currently being generated.

Laboratory experiments (WVNS-1 and WVNS-2) demonstrated that titanium coated IE-96 offers the following benefits: 1) high DF for cesium, plutonium, and strontium; 2) straight forward production; 3) similar handling characteristics to IE-96; and 4) titanium, at the levels required to removed plutonium, will not interfere with vitrification chemistry.

Future laboratory work will address the remaining questions about this technology. Both experiments WVNS-1 and WVNS-2 were performed in the WVNS hot cells due to the high levels or radioactivity of the samples. The hot cells are at 40°C and thus there is good comparison between these two studies. Prior to actual use of titanium coated IE-96 in the STS, further experiments will be made at 6°C. The WVNS work at 40°C and the PNL work at 25°C should give a complete working profile when added to the planned experiments at 6°C. The test procedure for the testing is included in attachment A.

Laboratory experiments adding sodium hydroxide to sludge wash water have demonstrated these benefits: 1) prevents solubilization of or precipitates, nearly all the soluble uranium; 2) prevents solubilization of, or precipitation of, about 90 percent of the soluble plutonium; 3) easily implemented as sodium hydroxide readily dissolves in water; 4) has minimal impact in the STS; and 5) retards corrosion of the carbon steel tank by increasing the pH of the liquid in tank 8D-1.

The items that are needed if this technology is implemented are the addition of a chemical make-up tank to store sodium hydroxide solution (or dissolve the solid into solution) and the establishment of a piping route into tank 8D-2. These are not major issues and can be accomplished in the time frame allowed.

These technologies meet the technical requirements of WVDP. The sodium hydroxide addition will prevent the plutonium and uranium in tank 8D-2 sludge from being solubilized, and the titanium coated zeolite will further extract plutonium from the sludge-wash water. These technologies do not require major mechanical modifications. The chemistry of these technologies is compatible with the vitrification process and the CSS. Finally, these technologies could be implemented without any delay in the waste soldification schedule. Therefore, this combination of technologies will be used for treating the WVDP sludge wash water.

ATTACHMENTS

Table 1(1). Chemical Composition of Tank 8D-2 Supernatant (1987) - pH = 10

Compound	Wt. % Wet Basis	Wt. % Dry Basis	Total Kg in Supernatant
$NaNO_3$	21.10000	53.3800	602,659
$NaNO_2$	10.90000	27.5700	311,326
Na_2SO_4	2.67000	6.7600	76,261
$NaHCO_3$	1.49000	3.7700	42,557
KNO_3	1.27000	3.2100	36,274
Na_2CO_3	0.88400	2.2400	25,249
NaOH	0.61400	1.5500	17,537
K_2CrO_4	0.17900	0.4500	5,113
NaCl	0.16400	0.4200	4,684
Na_3PO_4	0.13300	0.3400	3,799
Na_2MoO_4	0.02420	0.0600	691
Na_3BO_3	0.02090	0.0500	597
$CsNO_3$	0.01870	0.0500	534
NaF	0.01760	0.0400	503
$Sn(NO_3)_4$	0.00859	0.0200	245
$Na_2U_2O_7$	0.00808	0.0200	231
$Si(NO_3)_4$	0.00806	0.0200	230
$NaTcO_4$	0.00620	0.0200	177
$RbNO_3$	0.00416	0.0100	119
Na_2TeO_4	0.00287	0.0070	82
AlF_3	0.00271	0.0070	77
$Fe(NO_3)_3$	0.00152	0.0040	43
Na_2SeO_4	0.00054	0.0010	15
$LiNO_3$	0.00048	0.0010	14
H_2CO_3	0.00032	0.0008	9
$Cu(NO_3)_2$	0.00022	0.0005	6
$Sr(NO_3)_2$	0.00013	0.0004	4
$Mg(NO_3)_2$	0.00008	0.0002	2
TOTAL	39.53000	100.0000	1,129,038
H_2O (by difference)	60.47		1,727,164

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(1) High Level Waste Characterization at West Valley, Larry E. Rykken, DOE/NE/44139-14 (DE87005887), Page 12.

Table 2(1). Radiochemical Composition of Tank 8D-2 Supernatant Prior to STS Startup

Isotope	1 ft.	5 ft.	15 ft.
	mCi/g		
Rare Earth B	2.1-E4	1.5-E4	2.7-E4
^{90}Sr	1.14-E3	1.13-E3	1.12-E3
^{106}Ru	<1.5-E5	<1.5-E5	<1.5-E5
^{125}Sb	5.7-E5	5.5-E5	5.4-E5
^{134}Cs	2.36-E2	2.32-E2	2.35-E2
^{137}Cs	2.86 E0	2.80 E0	2.84 E0
^{144}Ce	<7.6-E7	<7.6-E7	<7.6-E7
^{241}Am	<1.5-E5	<1.5-E7	<1.5-E7
^{243}Am	<2-37	<2-E7	<2-E7
^{244}Cm	<6-E8	<6-E8	<6-E8
	µg/g		
^{238}Pu	0.0024	0.0031	0.0027
^{239}Pu	0.1302	0.1545	0.1461
^{240}Pu	0.0251	0.0307	0.0301
^{241}Pu	0.0051	0.0066	0.0060
^{242}Pu	0.0021	0.0025	0.0024
^{233}U	0.0170	0.0190	0.0180
^{234}U	0.0140	0.0170	0.0160
^{235}U	0.9670	1.1010	1.0440
^{236}U	0.0970	0.1080	0.1050
^{238}U	55.1450	63.1820	59.8650

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(1) Cement Waste Qualification Report - WVDP Purex Decontaminated Supernatant, C. W. McVay, J. R. Stimmel and S. Marchetti, DOE/NE/44139-49 (DE89009019), Page 23.

Table 3. Radiochemical Composition of Tank 8D-2 Supernatant Prior to STS Startup

Isotope	Mass %	µg/u	µg/mL	µCi/g	µCi/mL
^{238}Pu	1.49	0.0027	0.0036	0.04679	0.06177
^{239}Pu	78.4	0.1436	0.1896	0.00891	0.01178
^{240}Pu	15.6	0.0286	0.0378	0.00650	0.00858
^{241}Pu	3.2	0.0059	0.0078	0.60829	0.80294
^{242}Pu	1.27	0.0023	0.0031	0.00001	0.00001
Alpha Pu*		0.1773	0.2340	0.06221	0.08212

* ^{241}Pu decays by Beta Emission

Table 4. Physical Data for WVNS-1 at pH 10.0

Wash Parameter	1st Wash	2nd Wash	3rd Wash	4th Wash
Supernatant Weight(g)	427.600	519.400	539.600	533.200
Supernatant Volume (mL)	383.800	500.800	534.800	532.100
Supernatant in Sludge (mL)	198.000	198.000	198.000	198.000
Total Liquid Volume (mL)	581.800	698.800	732.800	730.100
Supernatant pH	10.050	10.160	10.060	9.760
Density (g/mL)	1.114	1.037	1.009	1.002
Supernatant TDS (wt%)	16.800	4.920	1.400	0.490

Table 5. Chemical and Radionuclide Analysis of WVNS-1

Major Ion Concentrations in mg/mL

Ion	1st Wash	2nd Wash	3rd Wash	4th Wash
Nitrite	28.60	8.59	2.26	0.68
Nitrate	34.20	9.15	2.33	0.61
Sulfate	27.20	8.60	2.06	0.58
Sodium	46.30	32.30	4.45	1.78
Uranium	5.01	1.44	0.44	0.13

Isotope Concentrations in μCi/mL

Nuclide	1st Wash	2nd Wash	3rd Wash	4th Wash
Gross Alpha	2.970	0.769	0.153	0.056
Gross Beta	341.000	106.000	27.100	8.960
^{60}Co	<0.014	<0.007	<0.002	ND
^{90}Sr	1.020	0.280	0.095	0.079
^{99}Tc	0.144	0.057	0.015	0.004
^{125}Sb	<0.300	<0.010	<0.030	<0.007
^{137}Cs	300.000	89.000	26.000	7.750
^{154}Eu	<0.064	<0.024	<0.007	<0.002
^{155}Eu	<0.078	<0.023	<0.009	<0.002
^{238}Pu	1.870	0.507	0.118	0.034
$^{239/240}\text{Pu}$	0.875	0.232	0.052	0.015

ND = Not Detected

Table 6. Weights of Radioisotopes and Ions

Radioisotope	1st Wash	2nd Wash	3rd Wash	4th Wash	Washed Dried Sludge
Wt or Vol of Sample	383.8mL	500.8mL	534.8mL	532.1mL	57.4g
^{125}Sb (μCi/sample)					
^{137}Cs (μCi/sample)	1.15E+05	4.46E+04	1.39E+04	4.10E+03	1.35E+04
^{241}Am (μCi/sample)	N.D.	N.D.	N.D.	N.D.	N.D.
^{57}Co (μCi/sample)	N.D.	N.D.	N.D.	N.D.	1.96E+04
^{60}Co (μCi/sample)	N.D.	N.D.	N.D.	N.D.	1.15E+03
^{154}Eu (μCi/sample)	N.D.	N.D.	N.D.	N.D.	4.14E+04
^{155}Eu (μCi/sample)	N.D.	N.D.	N.D.	N.D.	6.95E+03
^{99}Tc (μCi/sample)	5.53E+01	2.85E+01	8.08E+00	1.90E+00	
^{90}Sr (μCi/sample)	3.91E+02	1.39E+02	5.10E+01	4.21E+01	2.66E+06
Total Pu *	1.05E+03	3.70E+02	9.09E+01	2.61E+01	4.91E+03
^{238}Pu (μCi/sample)	7.18E+02	2.54E+02	6.31E+01	1.80E+01	3.39E+03
$^{239/240}$Pu (μCi/sa)	3.36E+02	1.16E+02	2.78E+01	8.09E+00	1.53E+03
Ion Analysis					
U (μg/sample)	1.92E+06	7.21E+05	2.35E+05	6.90E+04	1.29E+05
Fe (μg/sample)					2.74E+07
Na (μg/sample)	1.78E+07	6.61E+06	2.38E+06	9.47E+05	3.82E+06
Nitrite (μg/sample)	1.10E+07	4.30E+06	1.21E+06	3.61E+05	**
Nitrite (μg/sample)	1.31E+07	4.58E+06	1.25E+06	3.25E+05	**
Sulfate (μg/sample)	1.04E+07	4.31E+06	1.10E+06	3.08E+05	2.42E+05

* Total Pu is the alpha emitting Pu only

** The laboratory does not have a method for analyzing ions on dried sludge.

Table 7. Calculated Values of Radioisotopes in WVNS-1 Sludge Wash if the Wash Solutions are Concentrated to 39 wt%

Concentration in $\mu Ci/mL$

Isotope	1st Wash	2nd Wash	3rd Wash	4th Wash
Total Pu *	6.3	6.3	5.2	4.8
^{90}Sr	2.36	2.37	2.91	7.74
^{99}Tc	0.33	0.48	0.46	0.39

* Total Pu is the sum of the alpha emitting isotopes only.

NOTE: If the Pu is not removed from the wash solutions, the average concentration of the alpha emitting Pu is 5,600 nanocuries per gram. The cement waste form would far exceed the 100 nanocuries per gram limit of TRU waste.

Table 8. Distillate and Concentrate Volumes from WVNS-1

Total Solid Content is 39 weight percent

Each Sludge Wash = 1,000,000 litres

Volumes	1st Wash	2nd Wash	3rd Wash	4th Wash
Distillate	603,000	911,000	973,000	989,400
Concentrate	212,000	89,000	27,000	10,600
Estimated Drums (Cement Waste)	1,600	650	200	80

Table 9. Radionuclide Limits for Class C Low-Level Radioactive Waste

Nuclide	Amount	Unit
^{241}Pu	3,500	Nanocuries per gram
^{99}Tc	3	Curies per cubic meter
^{90}Sr	7,000	Curies per cubic meter
^{137}Cs	4,600	Curies per cubic meter

Table 10. Cesium, Strontium, and Plutonium R_d Values

					Unheated				93°C - 2 hours			
			Ionsiv^{o} IE-96		Batch A		Batch B - Dried		Batch A		Batch B - Dried	
Isotope	Temp °C	Initial pH	R_d	Final pH	R_d	Final pH	R_d	Final pH	R_d	Final pH	R_d	Final pH
Cesium	6	10.0	315	9.1	256	9.0	256	9.0	255	9.0	212	9.0
Cesium	6	12.5	274	12.3	222	12.3	234	12.2	214	12.3	231	12.3
Strontium	6	10.0	6	9.2	152	9.1	137	9.1	108	9.1	79	9.1
Strontium	6	12.5	76	12.2	1144	11.1	889	10.7	2797	12.2	3722	12.4
Plutonium	6	10.0	8	9.2	117	9.1	140	9.1	105	9.1	97	9.1
Plutonium	6	12.5	402	12.3	1949	11.1	2323	10.7	1704	12.2	2812	12.2
Cesium	25	10.0	182	9.1	153	9.1	153	9.0	154	9.1	157	9.0
Cesium	25	12.5	157	12.6	131	12.4	134	12.2	135	12.6	137	12.5
Strontium	25	10.0	9	9.1	279	9.1	235	9.1	189	9.1	148	9.1
Strontium	25	12.5	808	12.4	1958	11.1	1381	10.7	3937	12.5	3297	12.4
Plutonium	25	10.0	22	9.1	1364	9.1	1090	9.1	477	9.1	530	9.0
Plutonium	25	12.5	1152	12.4	6913	11.1	6460	10.7	3870	12.4	3942	12.4

Batch A = 2.0% Ti as TiO_2
Batch B = 2.2% Ti as TiO_2

Table 11. Cesium and Plutonium R_d Values as a Function of Titanium Loading

% Ti	Temp	Type	Pu R_d	pH	Cs R_d	pH	Pu R_d	pH	Cs R_d	pH
0	6	---	8	9.2	315	9.1	757	12.5	306	12.4
0	6	---	---	---	---	---	402	12.3	274	12.3
0	25	---	22	9.1	182	9.1	1075	12.5	193	12.3
0	25	---	---	---	---	---	1152	12.4	157	12.6
1.6	6	OD	58	9.1	313	9.1	(543)	12.4	250	12.5
1.6	6	AD	44	9.1	288	9.1	3123	12.4	228	12.5
1.6	25	OD	264	9.1	189	9.2	2665	12.4	174	12.5
1.6	25	AD	44	9.1	288	9.1	3523	12.4	180	12.5
2.7	6	OD	93	9.2	278	9.2	2688	12.3	248	12.5
2.7	6	AD	73	9.2	274	9.2	3250	12.3	227	12.5
2.7	25	OD	403	9.1	178	9.1	4009	12.4	168	12.5
2.7	25	AD	300	9.1	167	9.1	3332	12.4	142	12.5
3.9	6	OD	123	9.1	270	9.2	2203	12.4	160	12.5
3.9	6	AD	100	9.2	252	9.2	4003	12.4	161	12.5
3.9	25	OD	533	9.1	168	9.2	4151	12.4	149	12.4
3.9	25	AD	386	9.1	155	9.1	4819	12.4	127	12.4
4.7	6	OD	154	9.1	246	9.1	3099	12.3	185	12.5
4.7	6	AD	140	9.1	233	9.1	4895	12.3	183	12.5
4.7	25	OD	804	9.1	143	9.1	3692	12.3	116	12.4
4.7	25	AD	787	9.1	143	9.1	5041	12.3	131	12.4

OD = oven dried at 116_{o}C
AD = air dried at RT

Table 12. Types of Column Studies made with Titanium Coated IE-96

Lab	%Ti	Columns	Temp	pH	Solution
PNL	0.0	3	25	10.0	Synthetic West Valley Waste
PNL	1.3	3	25	10.0	Synthetic West Valley Waste
PNL	5.3	3	25	10.0	Synthetic West Valley Waste
PNL	5.3	3	25	10.0	Decontaminated Supernatant
WVNS	5.3	4*	40	10.0	WVNS-#1
WVNS	5.3	4	40	12.5	WVNS2-#1,#2, #3 & #4

* One column leaked during test and had to be removed.

Table 13. Ratio of Ions Before and After Column
The Values are DF of the Titanium Coated Zeolite

Measured Parameters or Laboratory Analysis	First Wash	Second Wash	Third Wash	Fourth Wash
Density	1.01	1.00	1.00	1.00
pH	1.02	0.99	0.98	0.98
Nitrite	0.99	0.92	1.09	1.14
Nitrate	1.10	0.94	1.08	1.08
Sulfate	1.21	1.03	1.30	1.19
Chloride	———	———	———	———
Phosphate	———	———	———	———
Sodium	1.01	0.70	1.00	1.01
Potassium	38.78	33.81	———	———
Uranium	2.88	1.20	1.88	1.33
Chromium	1.94	0.85	1.43	1.04
Calcium	3.35	7.70	———	———
Aluminum	1.22	0.72	0.83	0.78
^{239}Pu				
Total Pu	37436	13172	2991	151
^{90}Sr	14611	651	169	28
^{137}Cs	6624	59296	711340	3156

Table 14. Plutonium Chemistry Studies
Pu concentrations in μCi/mL

	Pu Source	Pre 18 A	Post 18 Å
WVNS	WVNS1 #1 (pre col.)	2.15000	2.29000
	WVNS1 #1 (post col.)*	0.00460	0.00420
	WVNS2 #1 (pre col.)	0.29800	0.30300
	Tank 8D-2 Supernatant	0.08800	0.10900
PNL	PNL Synthetic	0.03500	0.02900
	8D-2 Supernatant	0.01000	0.00700
	8D-2 Supernatant (post col.)	0.00064	0.00045

* Post column sample passed through 0.45 um filter to prevent any zeolite particles from interfering with this analysis.

Table 15. PNL Column Analysis - % Plutonium in Column Sections

Section	1st Column	2nd Column	3rd Column
Top	77.1	1.7	0.25
Middle	15.1	0.7	0.15
Bottom	4.5	0.3	0.10
Total	96.7	2.7	0.50

	Section	^{137}Cs	Total Pu
Top	0 to 1"	16.9%	96.7%
	1 to 2"	19.3%	1.8%
	2 to 4"	13.4%	0.4%
	4 to 5"	18.2%	0.4%
Bottom	5 to 6"	18.8%	0.3%

This column was loaded to >80 percent breakthrough of cesium.

Table 16. Plutonium and Uranium Concentrations in Sludge Wash Water as a Function of Sodium Hydroxide Added

Measurements made 16 hours after hydroxide addition.

g/l NaOH Added	μCi/g ^{238}Pu	μCi/g $^{239/240}$Pu	μCi/g Pu Total	μCi/g Uranium
0.00	2.03	0.93	2.96	3860.0
1.29	2.03	0.87	2.90	3370.0
2.54	1.54	0.70	2.23	2670.0
3.74	1.26	0.60	1.86	1260.0
4.91	1.13	0.50	1.63	880.0
6.04	0.67	0.42	0.97	410.0
7.14	0.30	0.19	0.62	205.0
8.20			0.59	152.0
9.22			0.40	65.0
9.22*			0.26	6.4

* The slurry was agitated an additional 72 hours without adding more NaOH to determine if the Pu and U had completely precipated during the first 16 hours of agitation.

Table 17. Chemical Analysis of Laboratory Scale Sludge Washes Before Decontamination with Titanium Coated Zeolite

Measured Parameters or Laboratory Analysis	1st Wash	2nd Wash	3rd Wash	4th Wash
Wt Super (gram)				
Density (g/mL)	1.109	1.032	1.0090	1.0020
Vol Super (mL)	422.000	444.000	402.0000	483.0000
Liq Vol in Sludge (mL)	175.000	175.000	175.0000	175.0000
Total Liquid Vol (mL)	597.000	619.000	577.0000	658.0000
pH	11.870	11.580	11.6300	11.5900
Nitrite (μg/g soln)	21100.000	6080.000	2070.0000	580.0000
Nitrate (μg/g)	20600.000	5680.000	1830.0000	399.0000
Sulfate (μg/g)	25400.000	6620.000	2340.0000	593.0000
Chloride (μg/g)	978.000	614.000	22.0000	14.0000
Phosphate (μg/g)				
Sodium (μg/g) AA	44880.000	11510.000	4190.0000	1710.0000
Potassium (μg/g) AA	1900.000	710.000	230.0000	(.5300)?
Uranium (μg/g) Fluorimeter	150.000	36.000	3.2000	1.6000
Cr (μg/g) AA Tot	157.000	23.000	11.0000	2.4000
Ca (μg/g) AA	12.400	9.240	3.0800	0.5700
Al (μg/g)	1000.000	180.000	100.0000	60.0000
^{239}Pu (μCi/g)	0.198	0.0260	0.00732	0.00120
Total Pu (μCi/g)	0.292	0.0382	0.01050	0.00160
^{90}Sr (μCi/g)	0.282	0.0963	0.00203	0.00909
^{137}Cs (μCi/g)	418.000	118.0000	41.40000	11.90000

Table 18. Chemical Analysis of Sludge Wash - After Decontamination with Titanium Coated Zeolite (5.3 wt% TiO_2) Columns

Measured Parameters or Laboratory Analysis	1st Wash	2nd Wash	3rd Wash	4th Wash
Wt Super (gram)				
Density (g/mL)	1.102	1.032	1.009	1.002
Vol Super (mL)				
Liq Vol in Sludge (mL)				
Total Liquid Vol (mL)				
pH	11	11.67	11.9	11.81
Nitrite (µg/g soln)	21300	6600	1900	510
Nitrate (µg/g)	18700	6070	1700	370
Sulfate (µg/g)	21000	6400	1800	500
Chloride (µg/g)				
Phosphate (µg/g)				
Sodium (µg/g) AA	44300	16400	4200	1700
Potassium (µg/g) AA	49	21	71	28
Uranium (µg/g) Fluorimeter	52	30	17.2	1.2
Cr (µg/g) AA Tot	81	27	7.7	2.3
Ca (µg/g) AA	3	1	20	0.7
Al (µg/g)	820	250	120	77
^{239}Pu (µCi/g)	1.86E-06	1.65E-06	2.38E-06	6.94E-06
Total Pu (µCi/g)	7.80E-06	2.90E-06	3.51E-06	1.06E-05
^{90}Sr (µCi/g)	1.93E-05	1.48E-04	1.20E-05	3.24E-04
^{137}Cs (µCi/g)	6.31E-02	1.99E-03	5.82E-05	3.77E-03

Table 19. Experimental Chemical Analysis After Concentration of the Decontaminated Wash Solution to wt% Determined

Concentrated SW #	SW # 1	SW # 2	SW # 3 (2.92)	SW # 4 (6.46)
Nitrite (µg/g soln)	61800	48200	48500	25600
Nitrate (µg/g)	64600	50600	46400	34000
Sulfate (µg/g)	44700	50400	51100	33800
Chloride (µg/g)				
Phosphate (µg/g)				
Sodium (µg/g) AA	104400	101000	111000	95800
Potassium (µg/g) AA	1600	1500	1600	1450
Uranium (µg/g) Fluorimeter				
Cr (µg/g) AA Tot	262	200	150	111
Ca (µg/g) AA	8.2	9	14	4
Al (µg/g)	2100	1470	<280	<70
^{239}Pu (µCi/g)	1.64E-05	4.08E-05	6.98E-06	2.30E-05
Total Pu (µCi/g)	2.76E-06	2.88E-04	5.02E-05	6.04E-05
^{90}Sr	1.22E-01	1.17E-02	1.43E-03	1.78E-01
^{137}Cs (µCi/g)				
Density	1.297	1.265	1.26 *	1.26 *
	37.5	33.6	33.0 wt% *	33.0 wt% *

* The product from SW # 3 and # 4 were diluted with water so that the product can be removed from the distillation vessel.

Table 20. Calculated Ion Concentration at 33 to 37.5 wt% TDS

Concentration Factor	3.16	9.60	30.00	96.00
Concentrated SW #	SW # 1	SW # 2	SW # 3	SW # 4
Nitrite (μg/g soln)	67308	49632	58900	40290
Nitrate (μg/g)	59092	45646	52700	29230
Sulfate (μg/g)	66360	48128	55800	39500
Chloride (μg/g)				
Phosphate (μg/g)				
Sodium (μg/g) AA	139988	123328	130200	134300
Potassium (μg/g) AA	154	137	2201	2212
Uranium (μg/g) Fluorimeter	164	225	527	94
Cr (μg/g) AA Tot	255	203	238	181
Ca (μg/g) AA	11	9	620	55
Al (μg/g)	2591	1880	3720	6083
Total Pu (μCi/g)	2.46E-05	2.18E-05	1.09E-04	8.37E-04
^{90}Sr (μCi/g)	6.10E-05	1.11E-03	3.72E-04	2.56E-02
^{137}Cs (μCi/g)	1.99E-01	1.50E-02	1.80E-03	2.98E-01

Table 21. Activity of Plutonium and Uranium as a Function of Potassium Ferrate Concentration of Potassium Ferrate

	0.0 mg/L	80 mg/L	400 mg/L	2000 mg/L
Gross Alpha	$<4.40 \times 10^{-4}$	$<4.10 \times 10^{-2}$	$<2.80 \times 10^{-2}$	$<4.20 \times 10^{-2}$
Gross Beta	3.58×10^{-2}	3.36×10^{-2}	3.11×10^{-2}	3.33×10^{-2}
Total Pu*	6.50×10^{-4}	8.70×10^{-4}	8.30×10^{-4}	2.60×10^{-4}

* The reported activity values are in μCi/ml

Table 22. Radiochemical Analysis for WVNS1 and WVNS2

WVNS1

Isotope Concentrations in µCi/mL

Nuclide	1st Wash	2nd Wash	3rd Wash	4th Wash
Gross Alpha	2.970	0.769	0.153	0.056
Gross Beta	341.000	106.000	27.100	8.960
^{60}Co	<0.014	<0.007	<0.002	ND
^{90}Sr	1.020	0.280	0.095	0.079
^{99}Tc	0.144	0.057	0.015	0.004
^{125}Sb	<0.300	<0.010	<0.030	<0.007
^{137}Cs	300.000	89.000	26.000	7.750
^{154}Eu	<0.064	<0.024	<0.007	<0.002
^{155}Eu	<0.078	<0.023	<0.009	<0.002
^{238}Pu	1.870	0.507	0.118	0.034
$^{239/240}$Pu	0.875	0.232	0.052	0.015

Table 23. Chemical Analysis of WVNS1 and WVNS2

WVNS1

Ion Concentrations in mg/mL

Ion	1st Wash	2nd Wash	3rd Wash	4th Wash
Nitrite	28.60	8.59	2.26	0.68
Nitrate	34.20	9.15	7.33	0.61
Sulfate	27.20	8.60	2.06	0.58
Sodium	46.30	32.30	4.45	1.78
Uranium	5.01	1.44	0.44	0.13

WVNS2

Nitrite	23.40	6.270	2.0400	0.5800
Nitrate	22.80	5.860	1.8500	0.4000
Sulfate	28.20	6.830	2.3600	0.5900
Sodium	49.80	11.900	4.2300	1.7100
Uranium	0.17	0.037	0.0032	0.0016

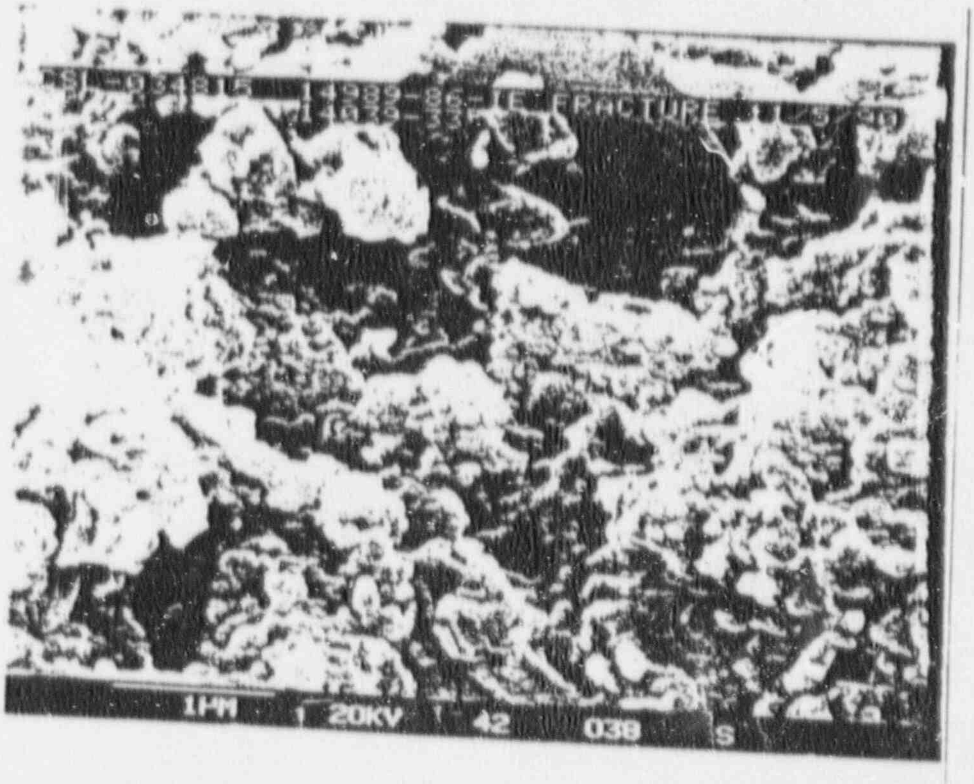

Figure 1. Scanning Electron Micrograph of Titanium Coated IE-96 (at magnification of 1 μm)

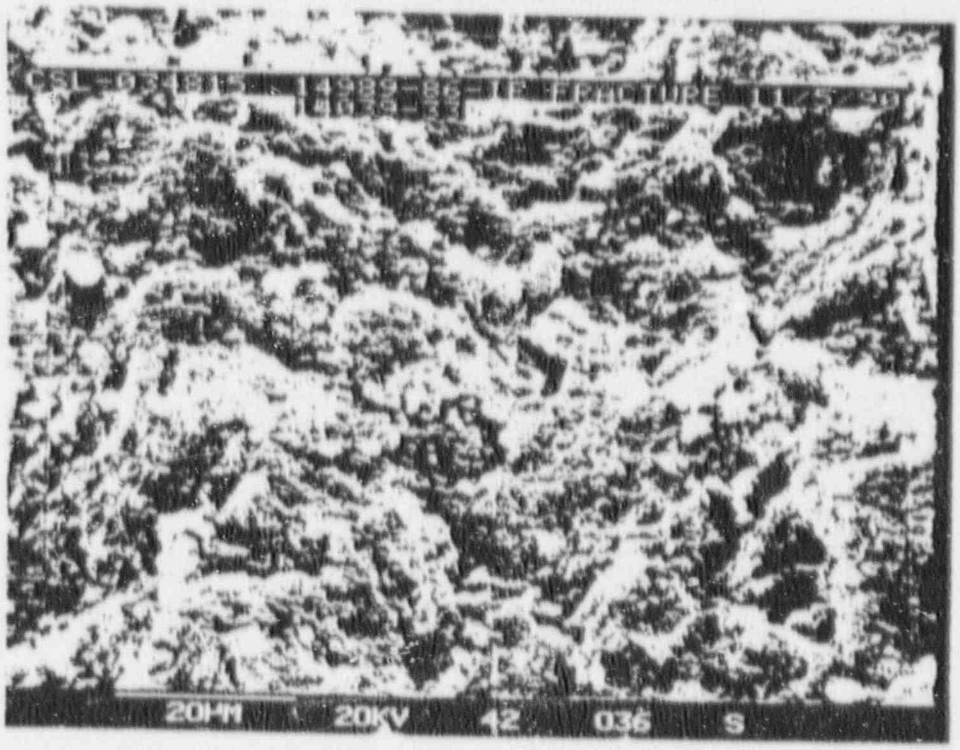

Figure 2. Scanning Electron Micrograph of Titanium Coated IE-96 (at magnification of 20 μm)

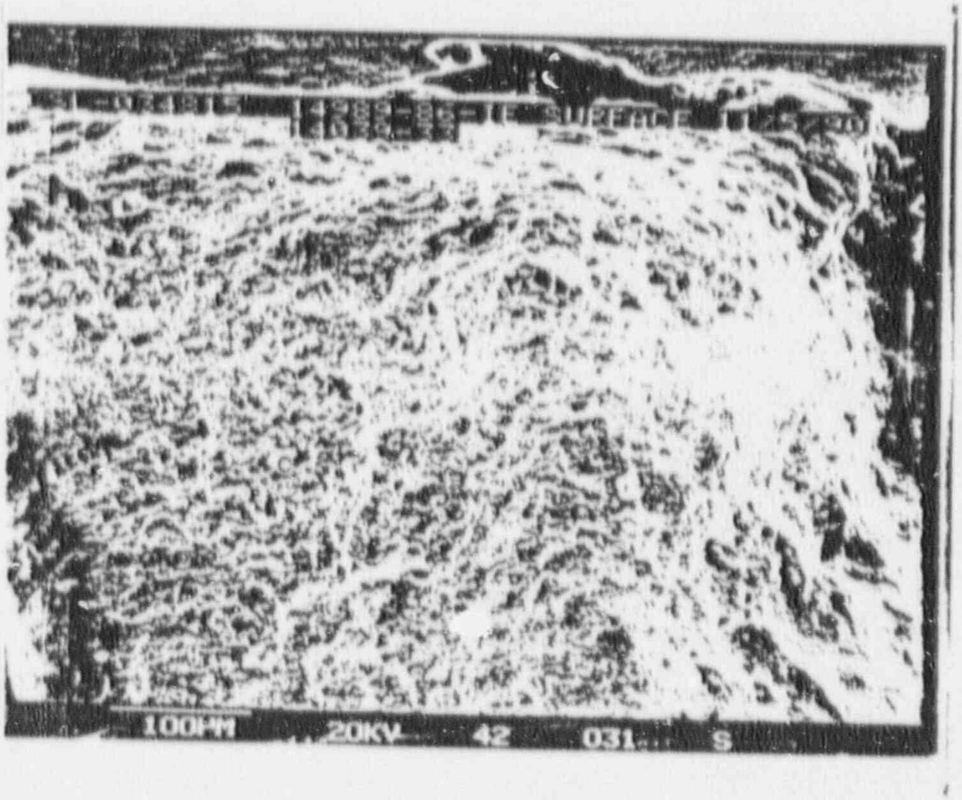

Figure 3. Scanning Electron Micrograph of Titanium Coated IE-96 (at magnification of 100 μm)

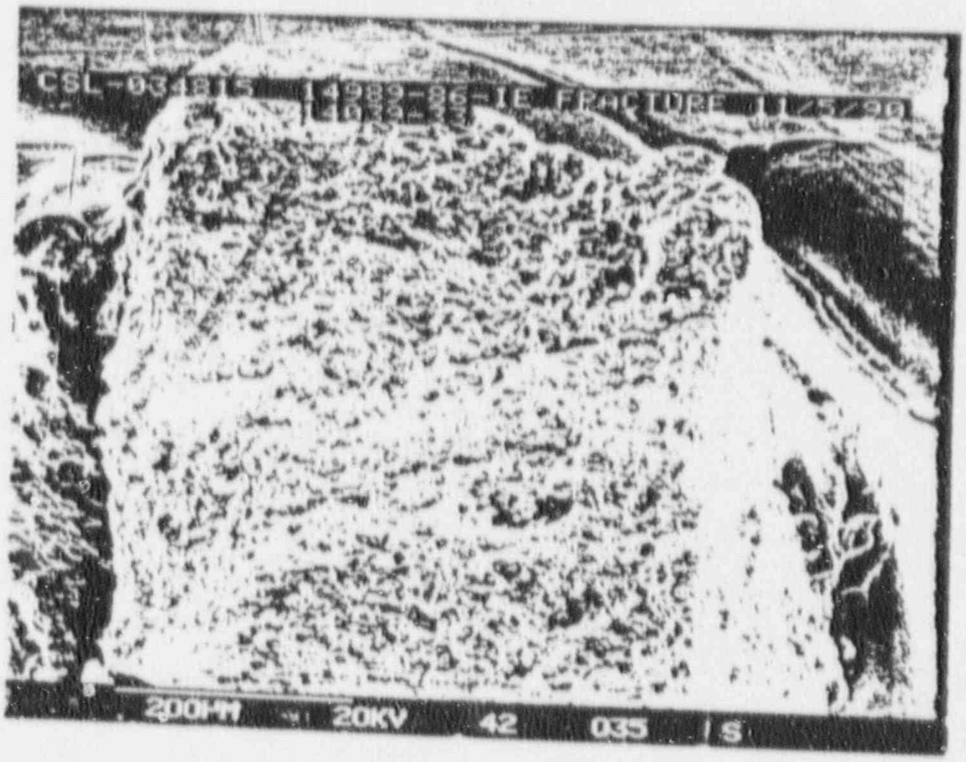

Figure 4. Scanning Electron Micrograph of Titanium Coated IE-96 (at magnification of 200 μm)

EDAX Spectrograph of Titanium Coating or IE-96

UNION CARBIDE CORP. CSL LAB MON 05-NOV-90 11:20
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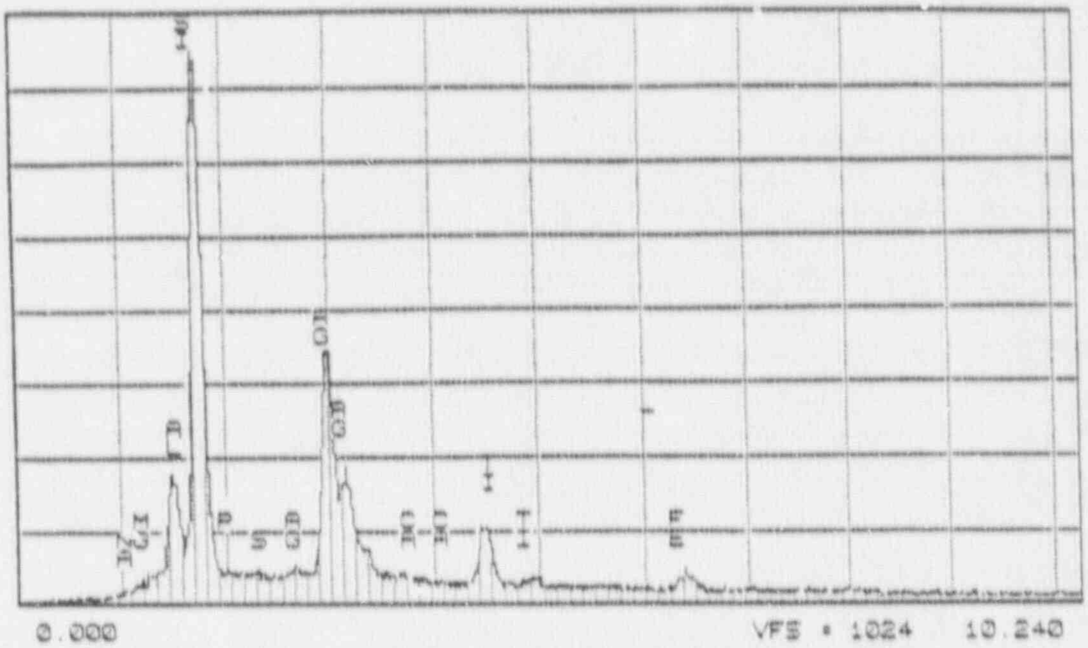

96 SAMPLE# 14039-33 . AREA SCAN OF # 035 20KV (FRACTURE)

UNION CARBIDE CORP. CSL LAB MON 05-NOV-90 11:23
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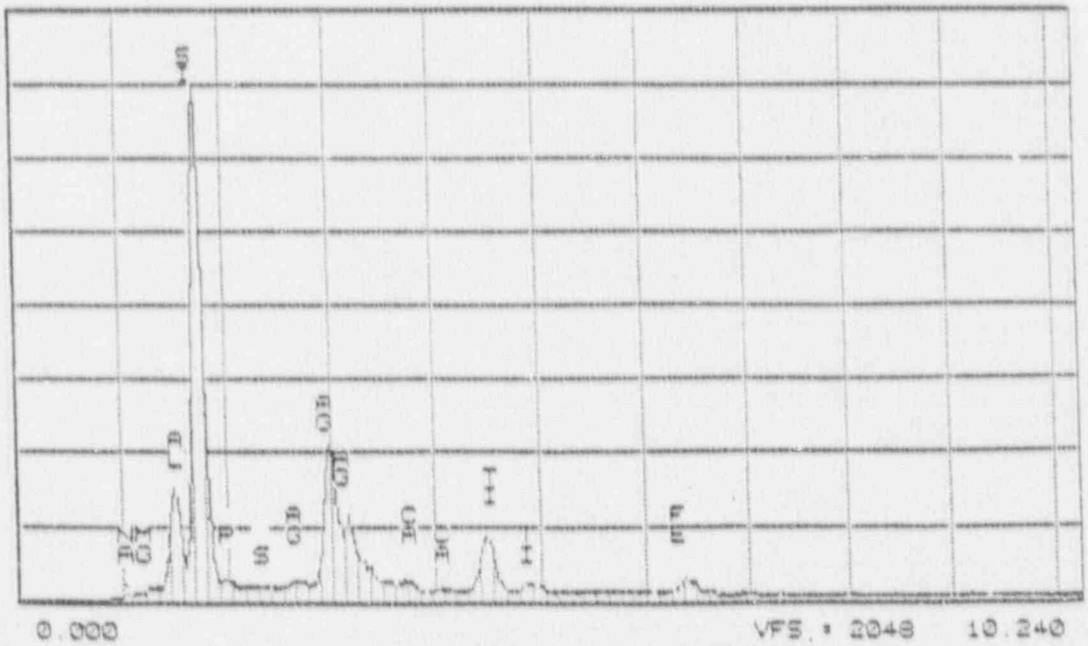


114 SAMPLE# 14039-33 AREA SCAN OF # 036 20KV (FRACTURE)

Figure 5

EDAX Spectrograph of Titanium Coating or IE-96

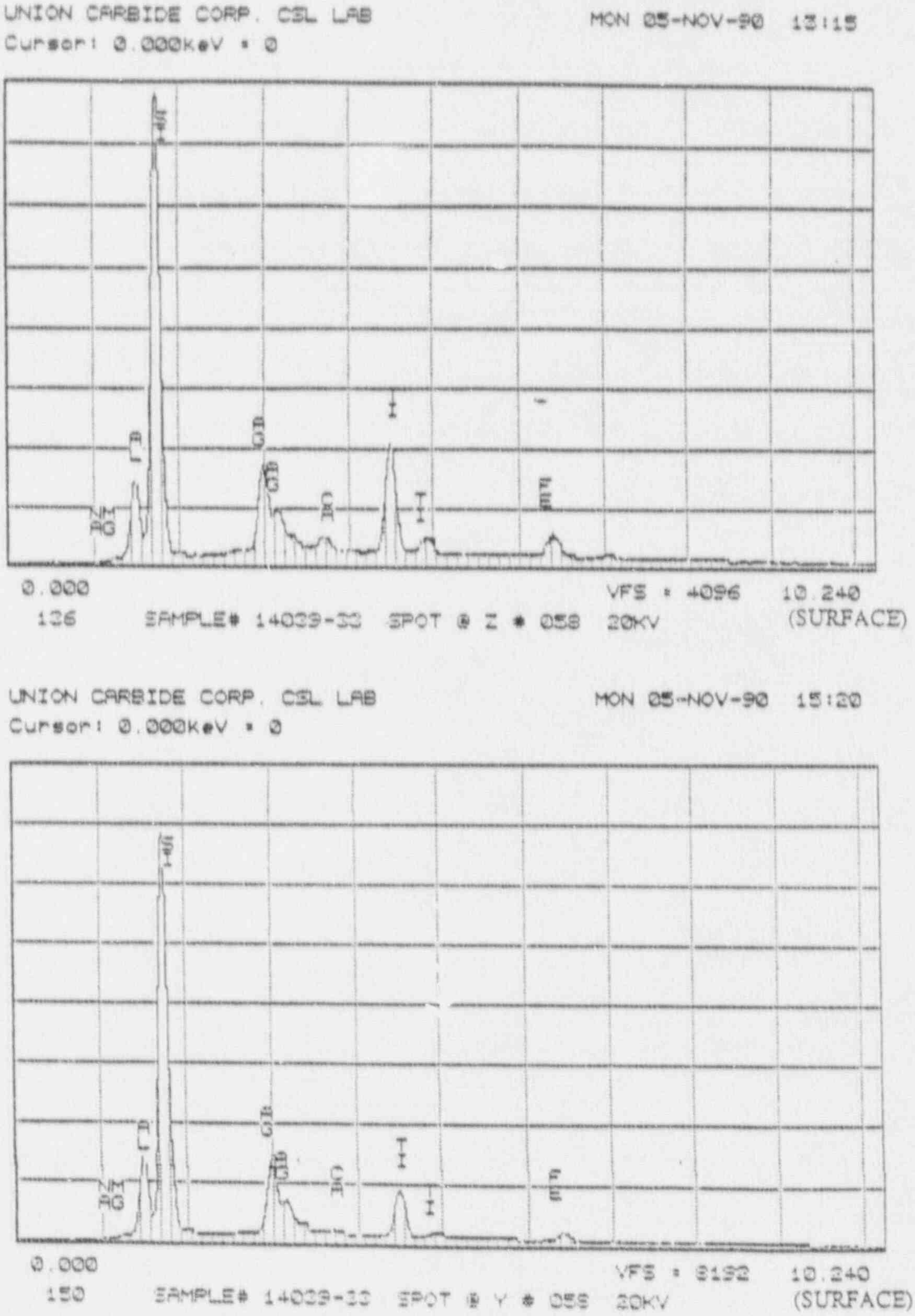
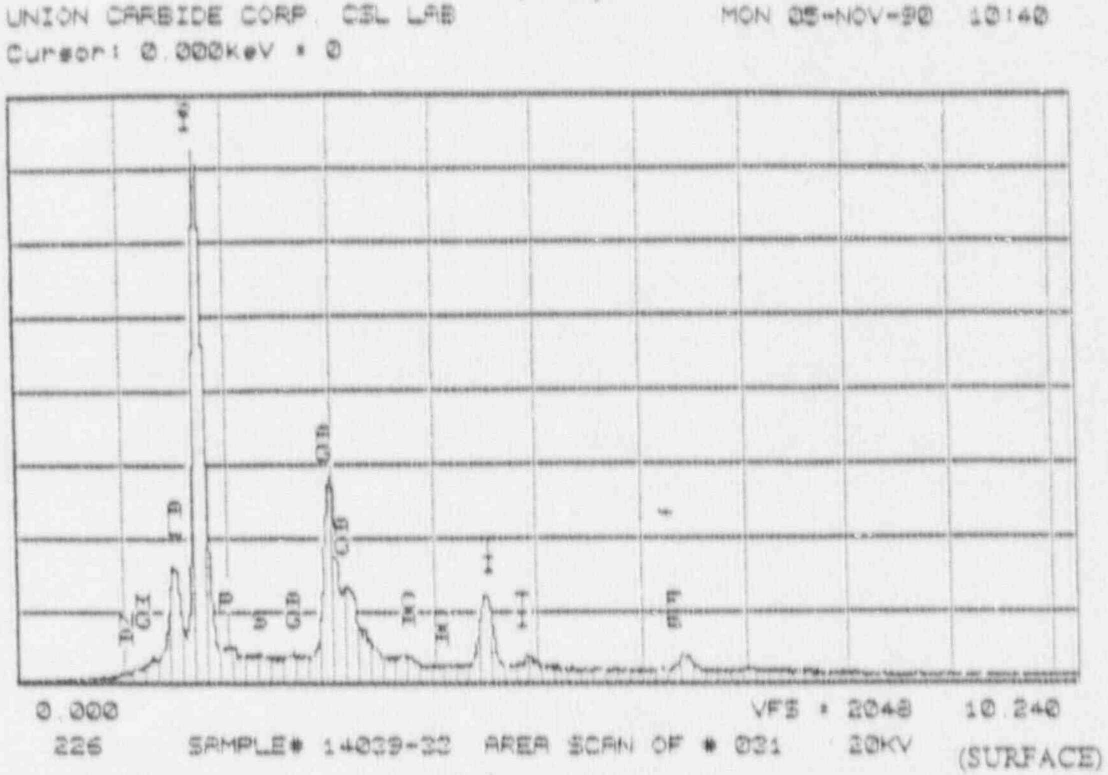


Figure 6

EDAX Spectrograph of Titanium Coating or IE-96



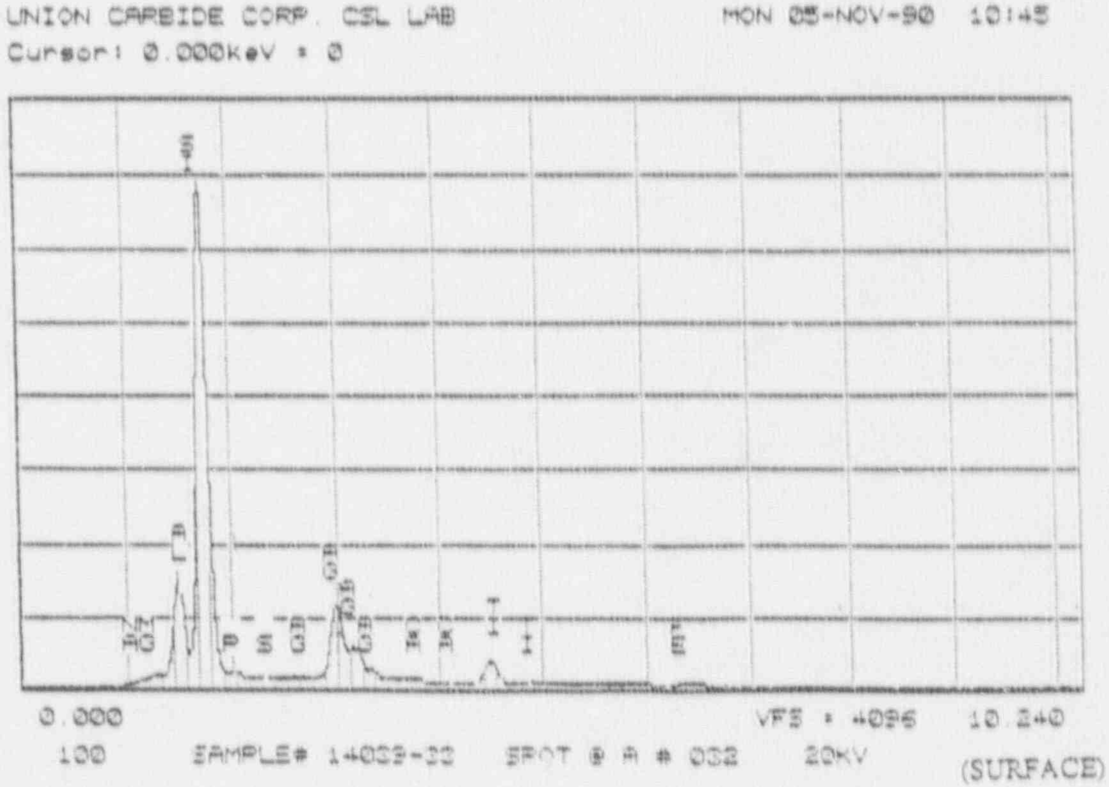
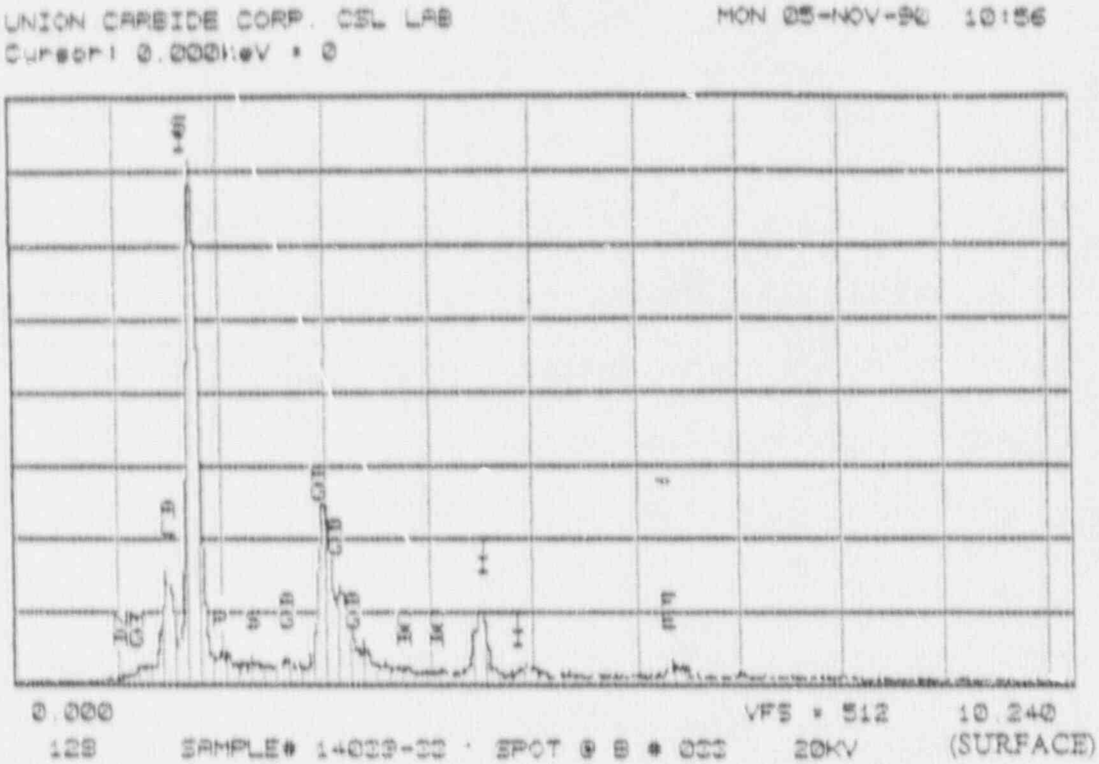


Figure 7

EDAX Spectrograph of Titanium Coating or IE-96



UNION CARBIDE CORP. CSL LAB MON 05-NOV-90 10:56
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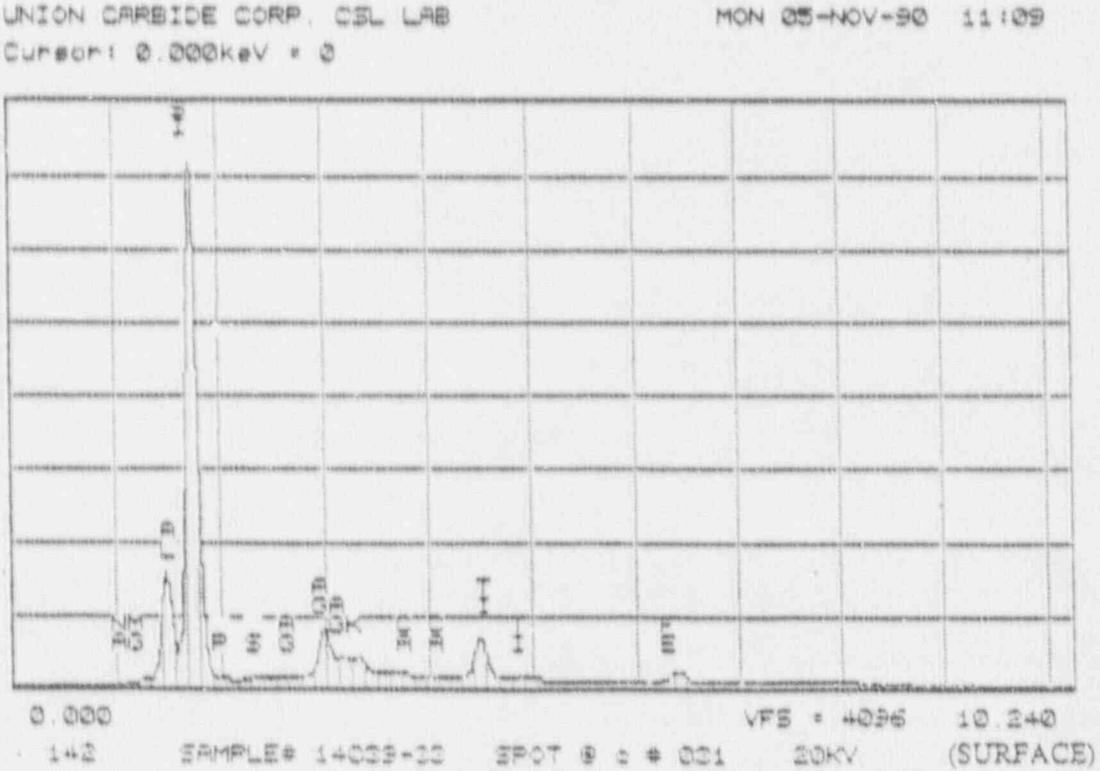
128 SAMPLE# 14039-33 · SPOT @ B # 003 20KV (SURFACE)

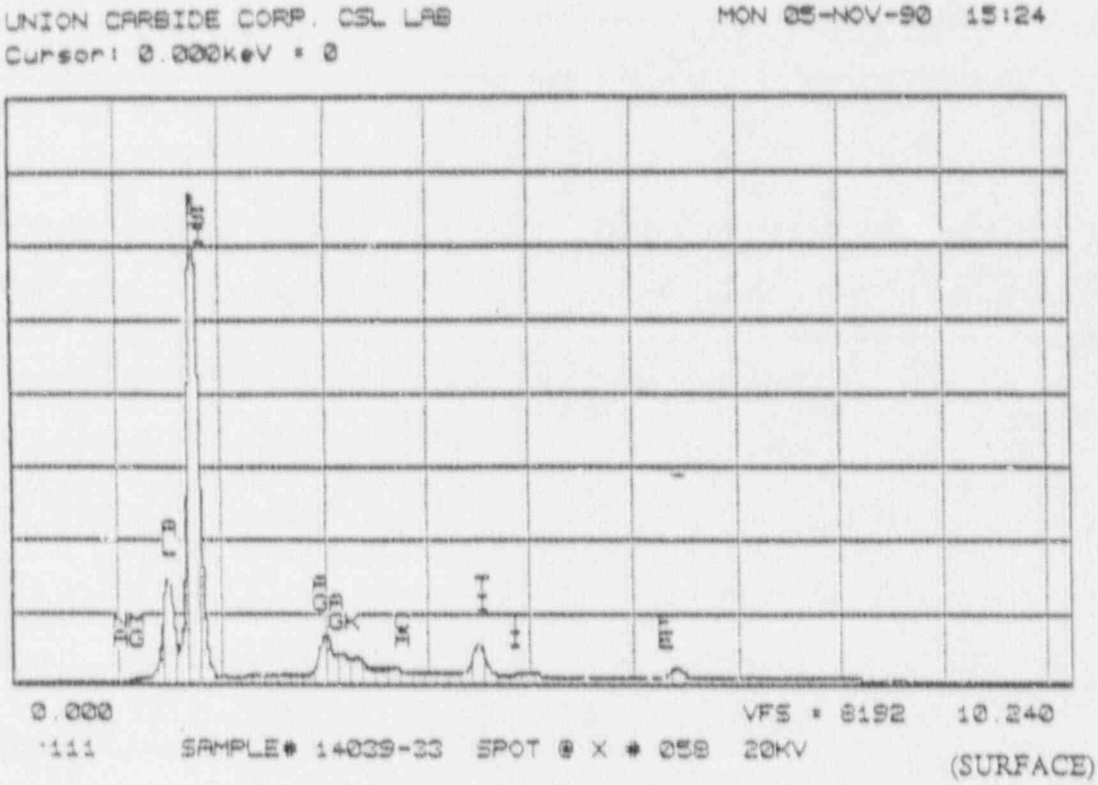


UNION CARBIDE CORP. CSL LAB MON 05-NOV-90 11:09
Cursor: 0.000keV = 0

142 SAMPLE# 14039-33 SPOT @ c # 001 20KV (SURFACE)

Figure 8

EDAX Spectrograph of Titanium Coating or IE-96



UNION CARBIDE CORP. CSL LAB MON 05-NOV-90 15:24
Cursor: 0.000KeV = 0

VFS = 8192
·111 SAMPLE# 14039-33 SPOT @ X # 058 20KV
(SURFACE)

Figure 9

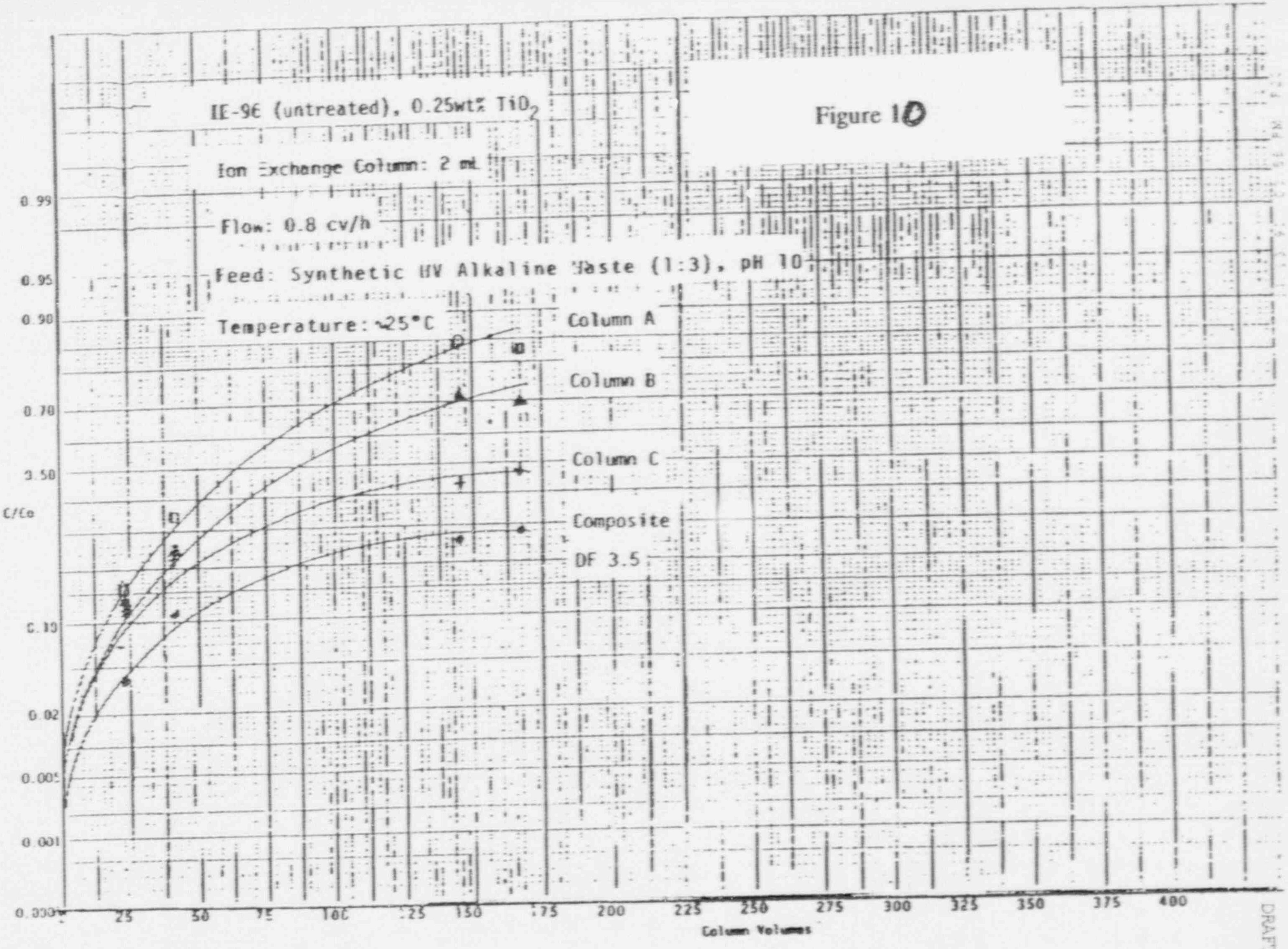
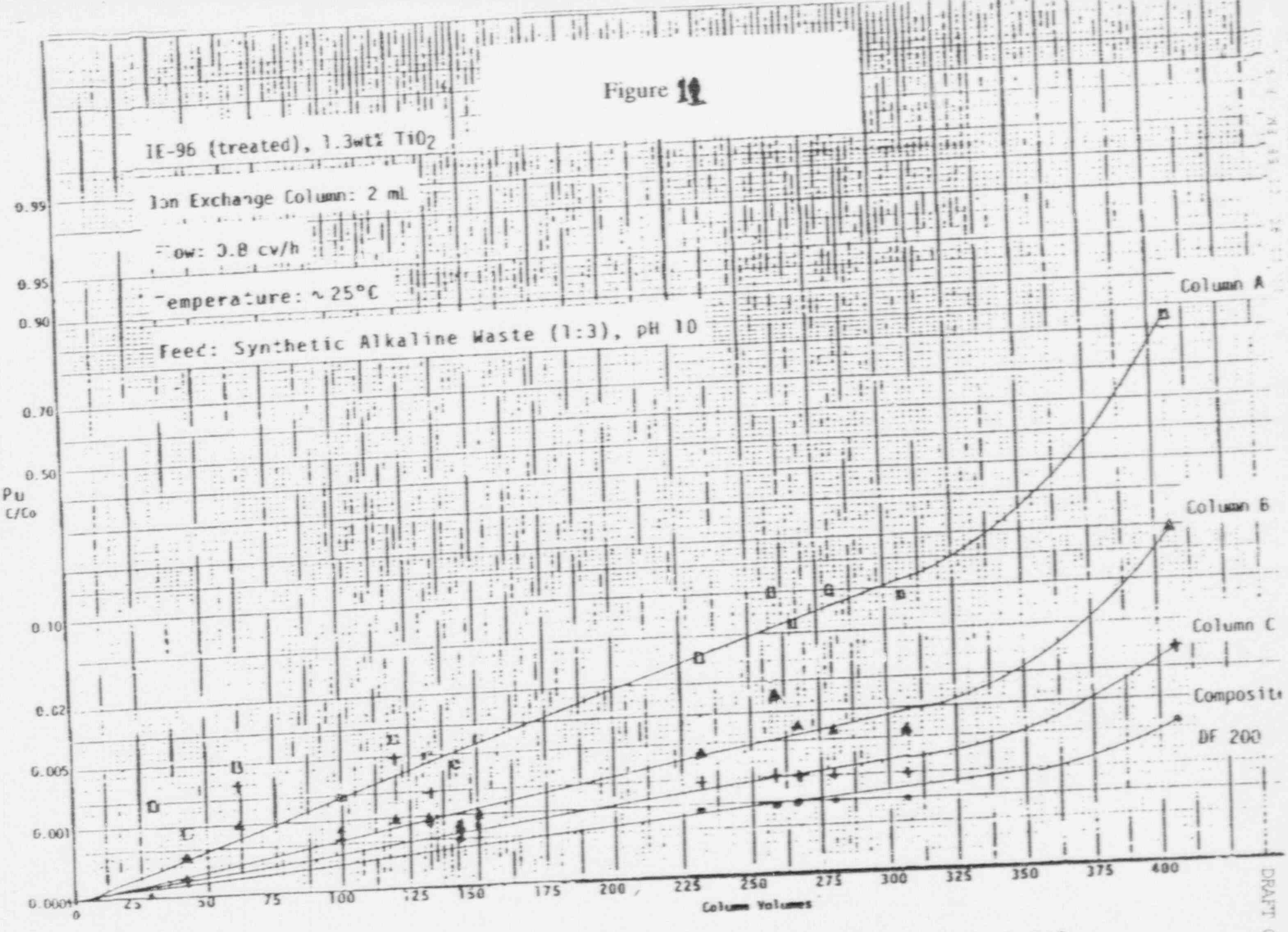


Figure 1D

Recovery of Plutonium From Synthetic Alkaline Waste - IE-96

DRAFT C

Figure 11



Recovery of Plutonium From Synthetic WV Alkaline Waste - 1.3wt% TiO_2

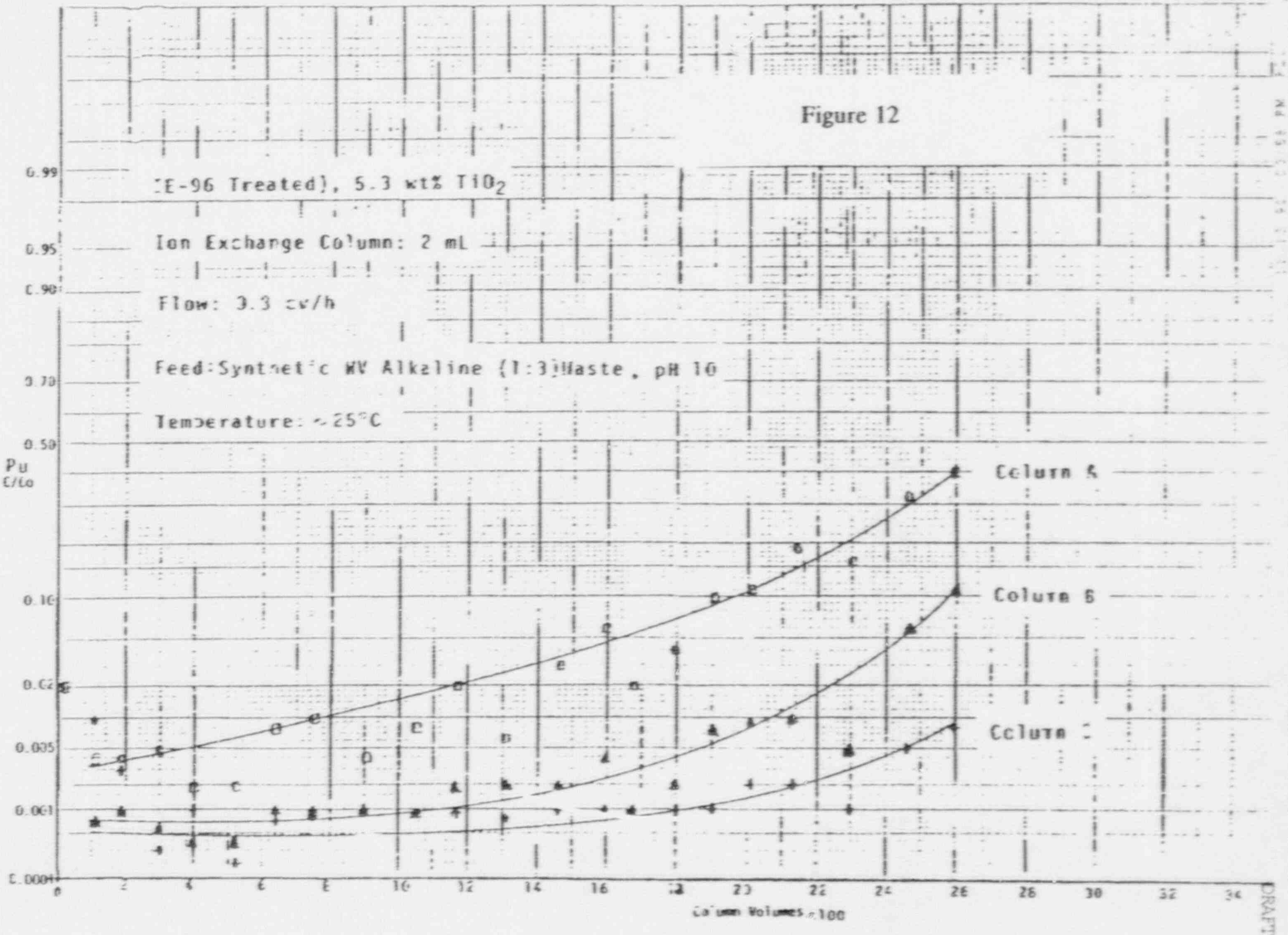
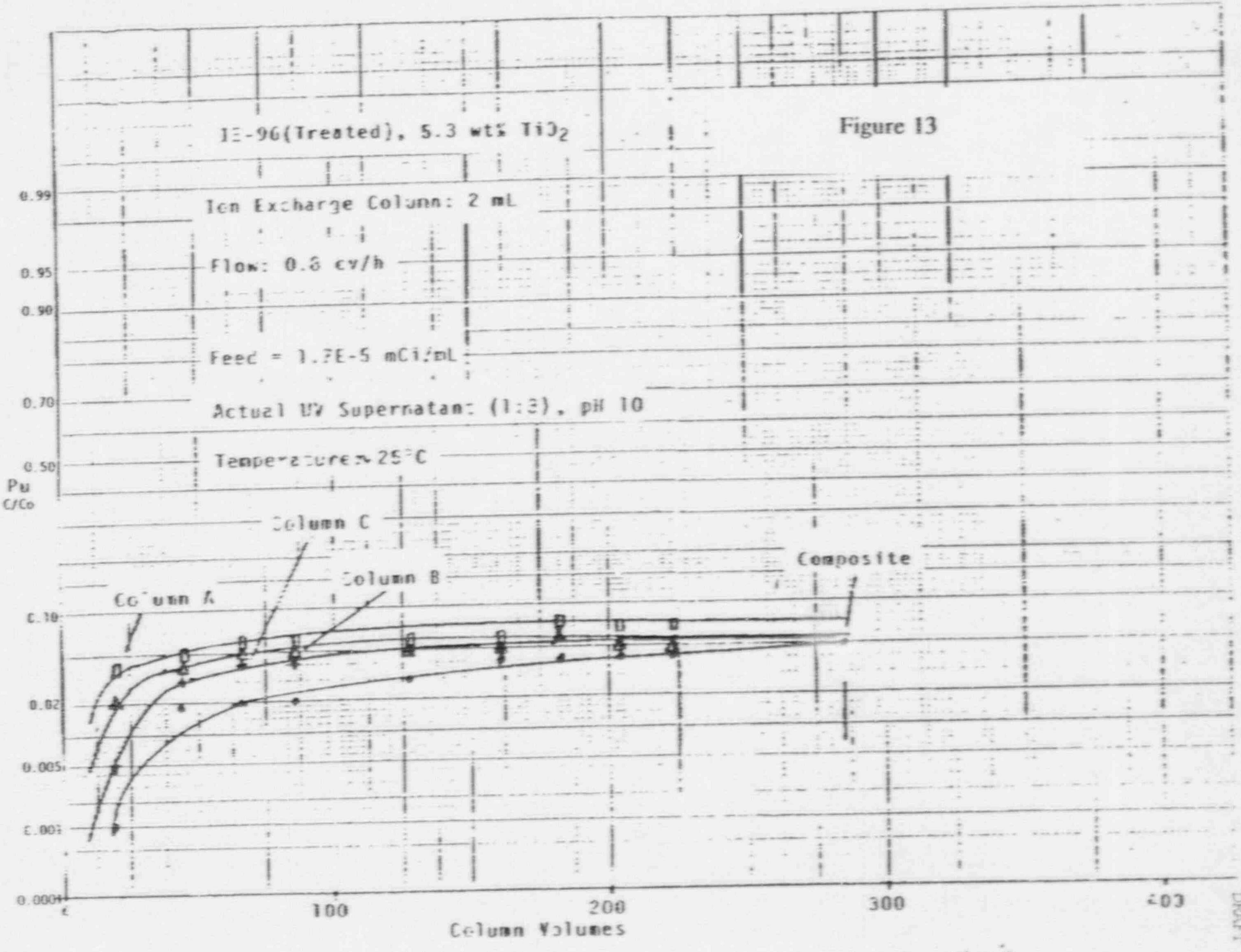


Figure 12

Recovery of Plutonium From Synthetic Alkaline Waste - 5.3wt% TiO$_2$

DRAFT C

Figure 13



Recovery of Plutonium from Actual WV Alkaline Waste - 5.3 wt% TiO2

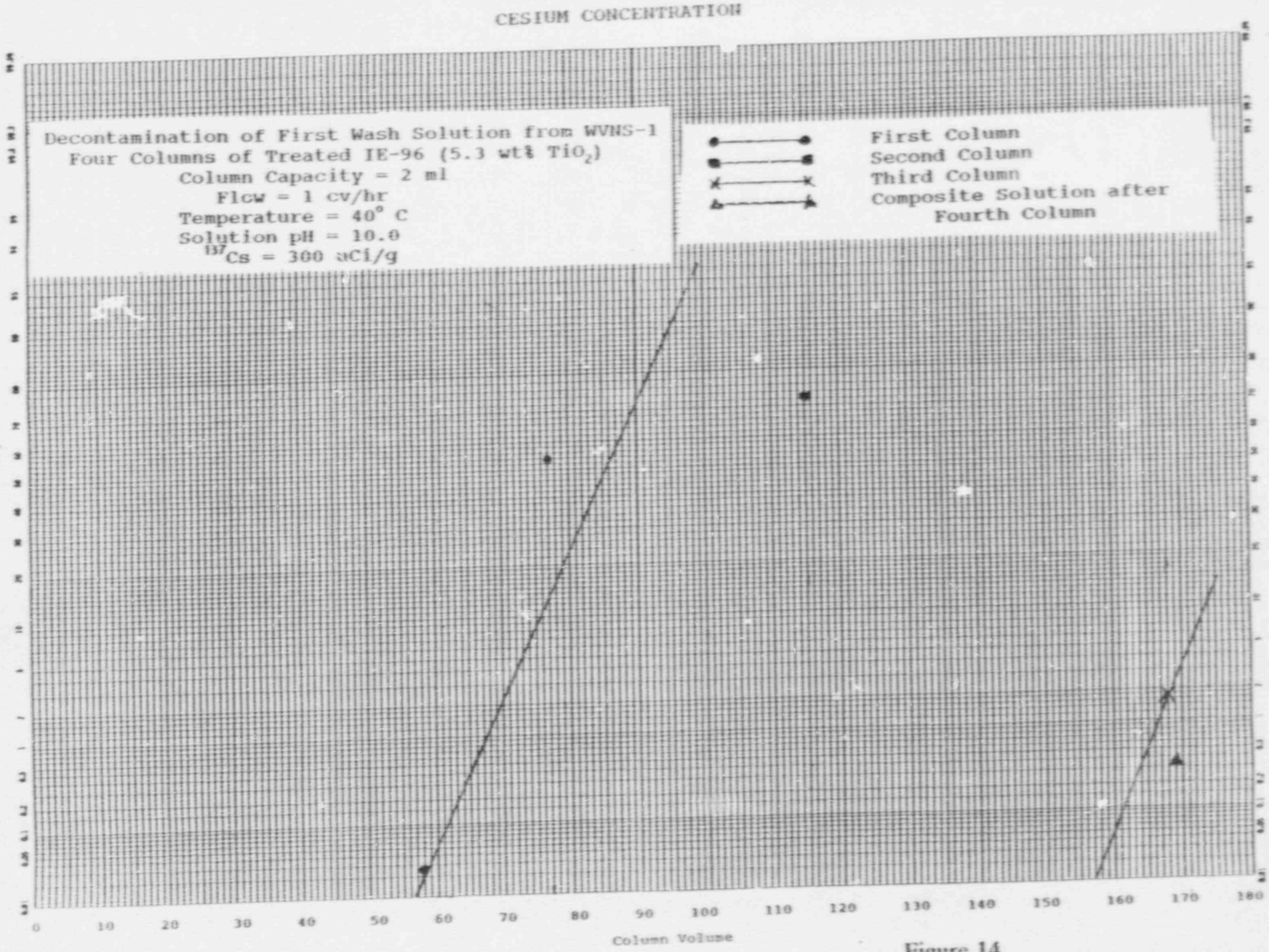

CESIUM CONCENTRATION
Decontamination of First Wash Solution from WVNS-1
Four Columns of Treated IE-96 (5.3 wt% TiO2)
Column Capacity = 2 ml
Flow = 1 cv/hr
Temperature = 40° C
Solution pH = 10.0
137Cs = 300 uCi/g
First Column
Second Column
Third Column
Composite Solution after Fourth Column
% C/C0
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
Column Volume

Figure 14

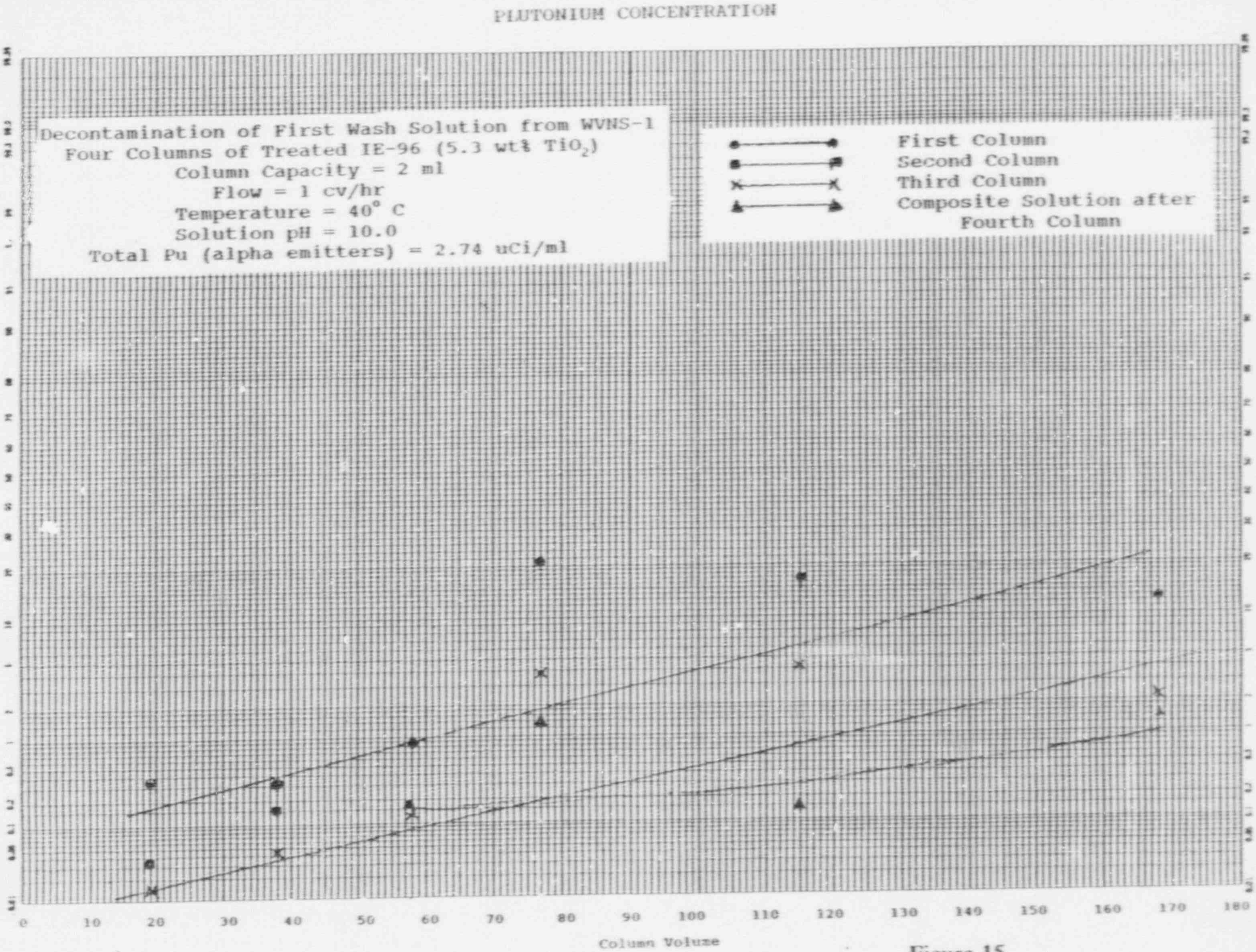

PLUTONIUM CONCENTRATION
Decontamination of First Wash Solution from WVNS-1
Four Columns of Treated IE-96 (5.3 wt% TiO2)
Column Capacity = 2 ml
Flow = 1 cv/hr
Temperature = 40° C
Solution pH = 10.0
Total Pu (alpha emitters) = 2.74 uCi/ml
First Column
Second Column
Third Column
Composite Solution after Fourth Column
% C/C0
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
Column Volume

Figure 15

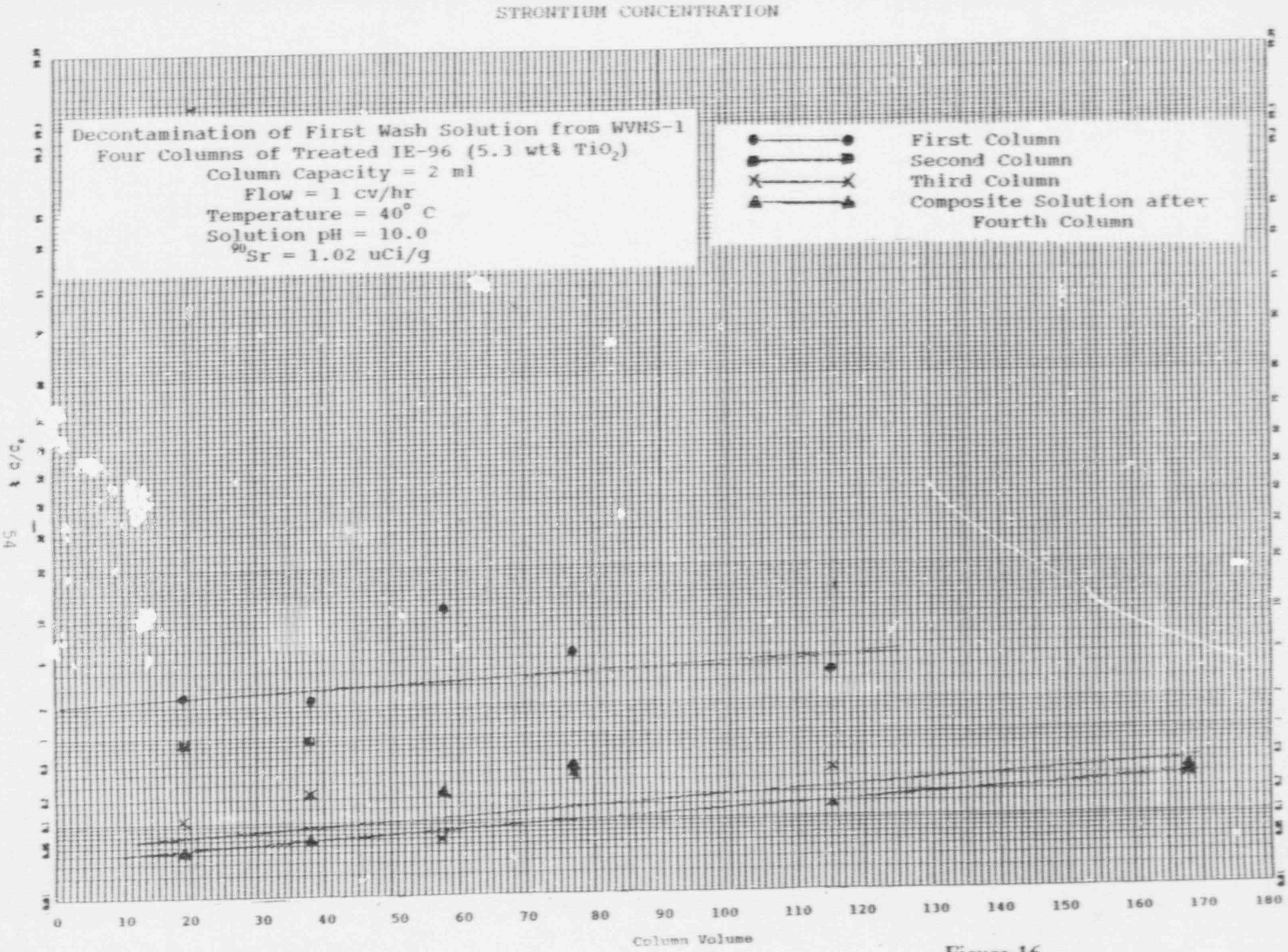

STRONTIUM CONCENTRATION
Decontamination of First Wash Solution from WVNS-1
Four Columns of Treated IE-96 (5.3 wt% TiO2)
Column Capacity = 2 ml
Flow = 1 cv/hr
Temperature = 40° C
Solution pH = 10.0
90Sr = 1.02 uCi/g
First Column
Second Column
Third Column
Composite Solution after Fourth Column
% C/C₀
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
Column Volume

Figure 16

CESIUM BREAKTHROUGH FROM THE LEAD COLUMN

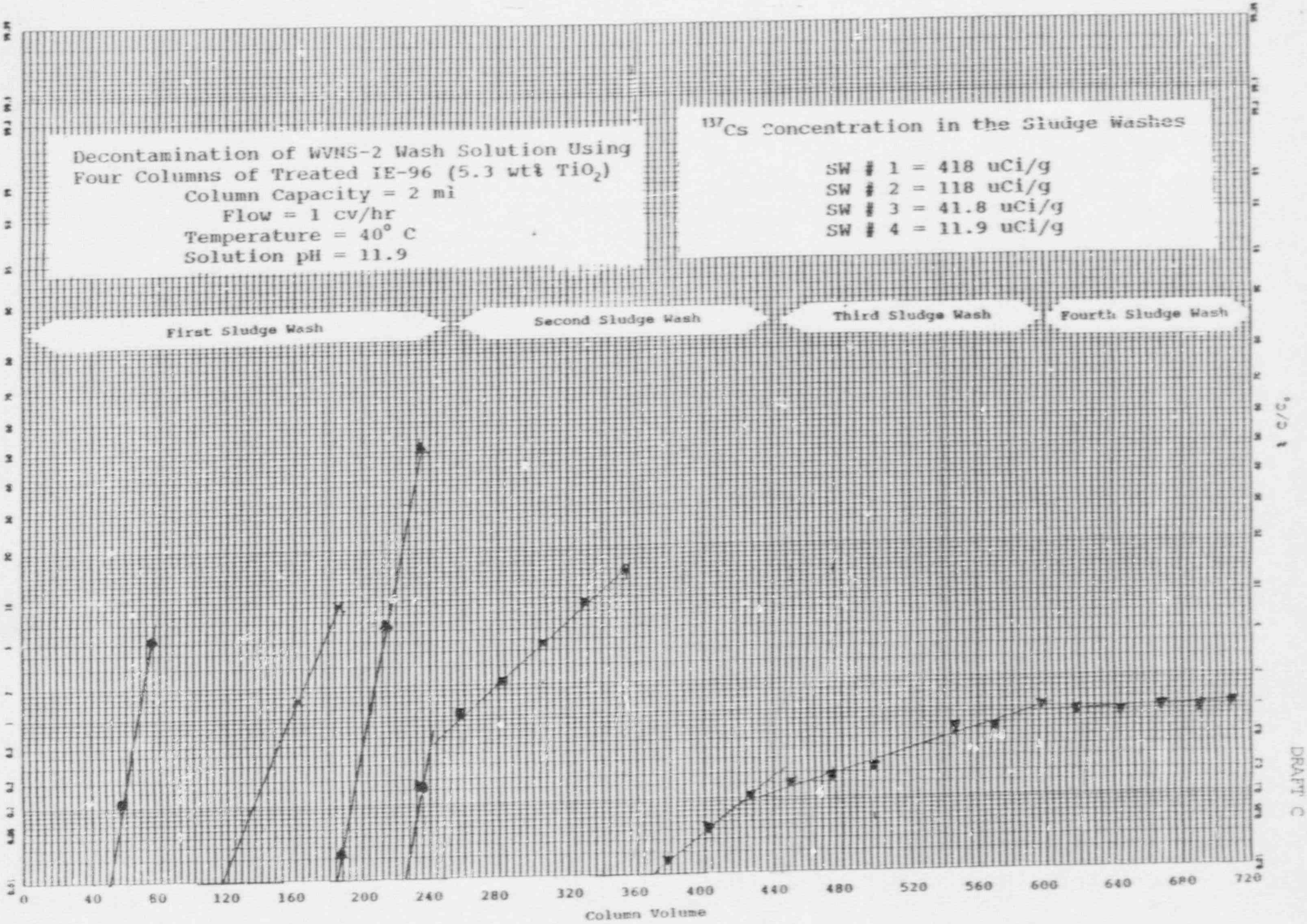


Figure 17

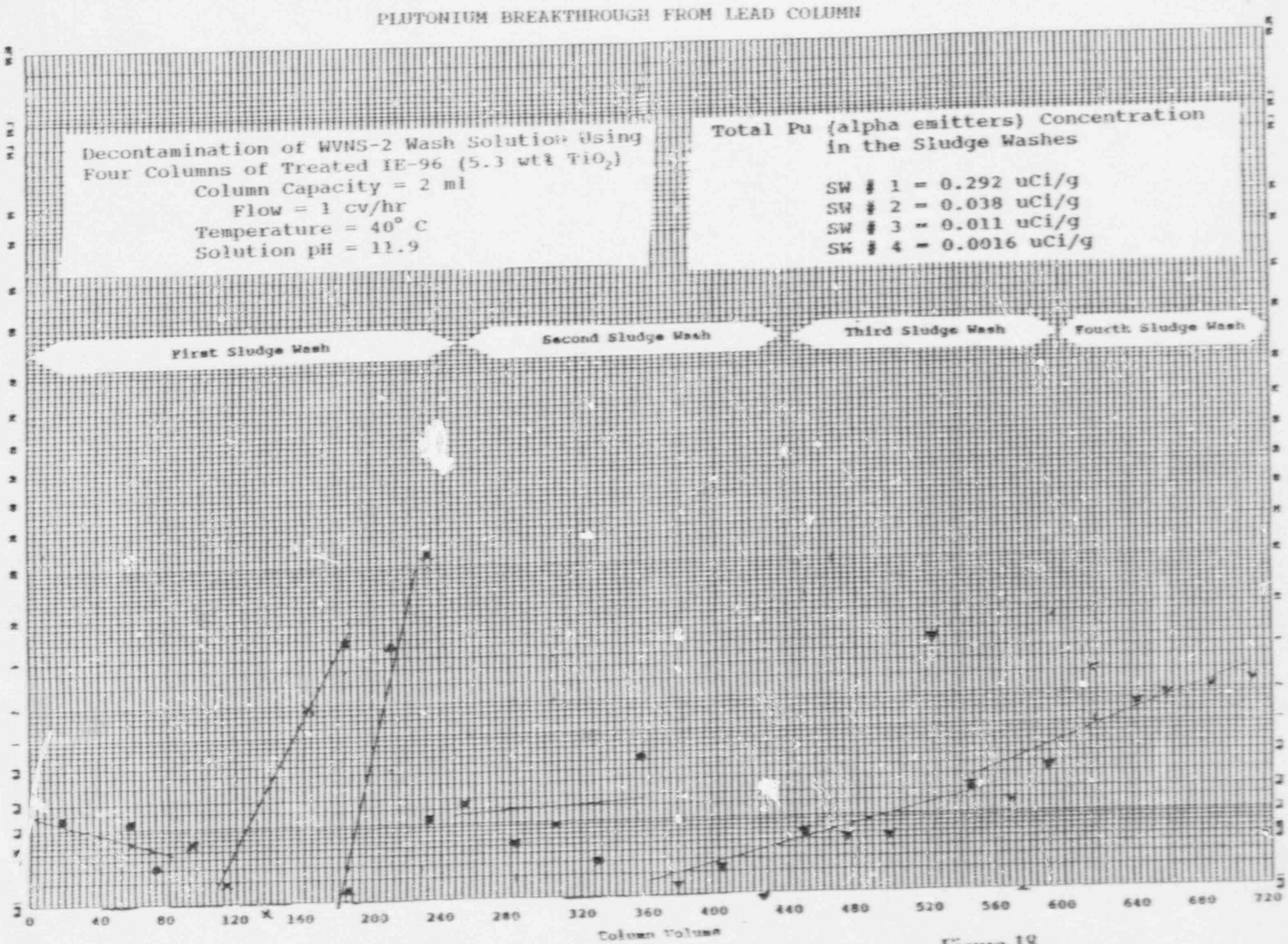


Figure 18

DRAFT C

STRONTIUM BREAKTHROUGH FROM THE LEAD COLUMN

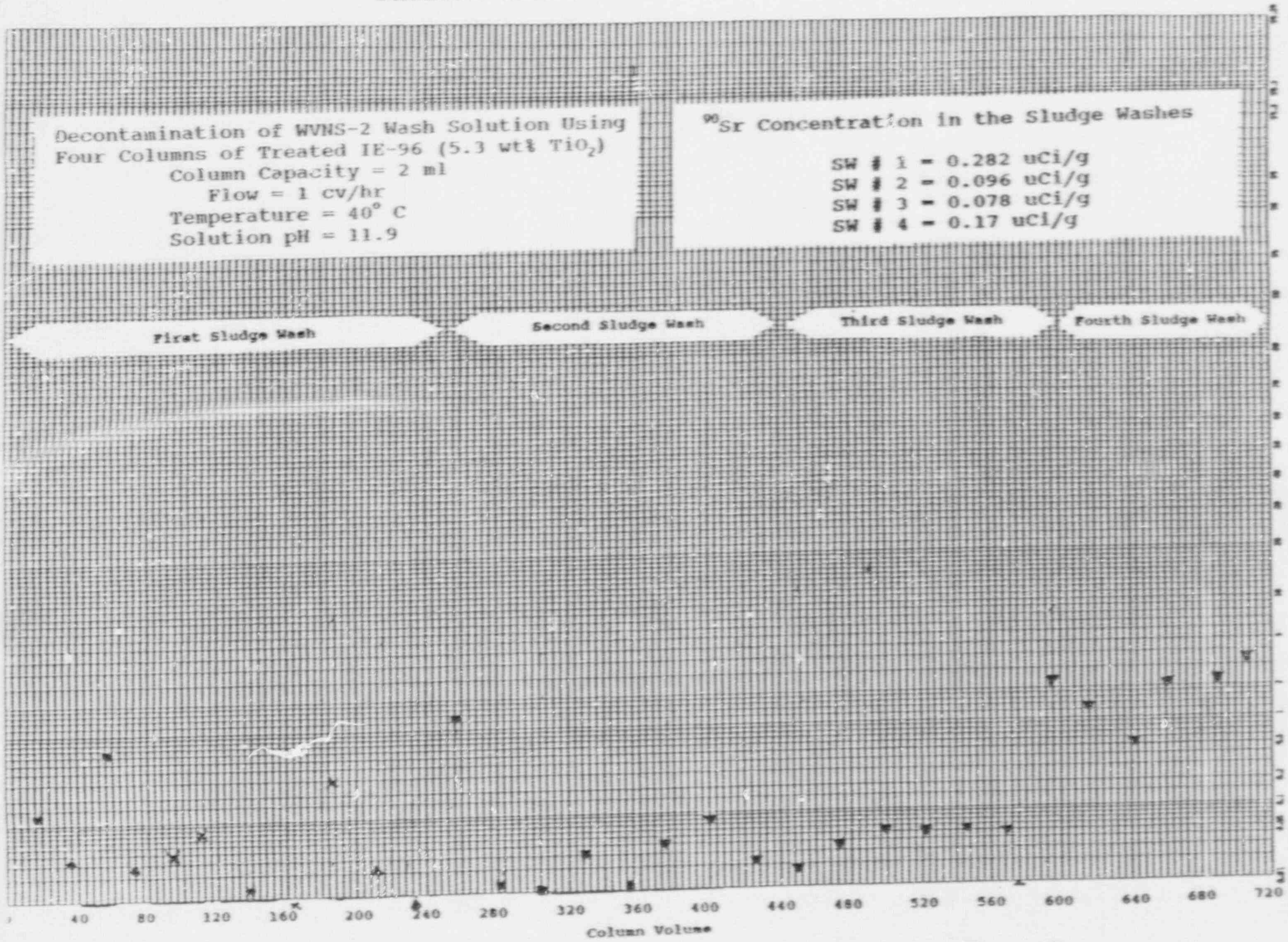
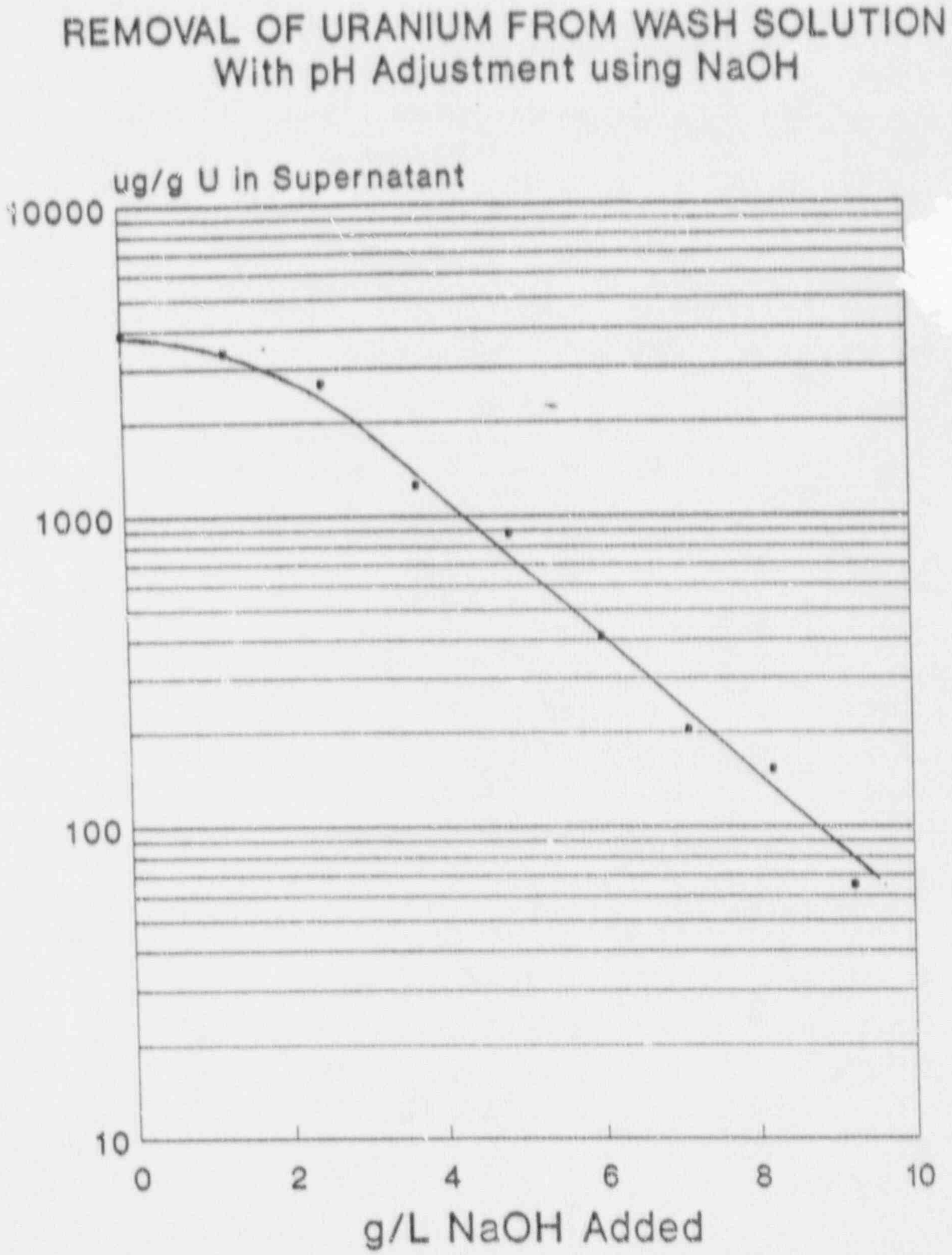


Figure 19

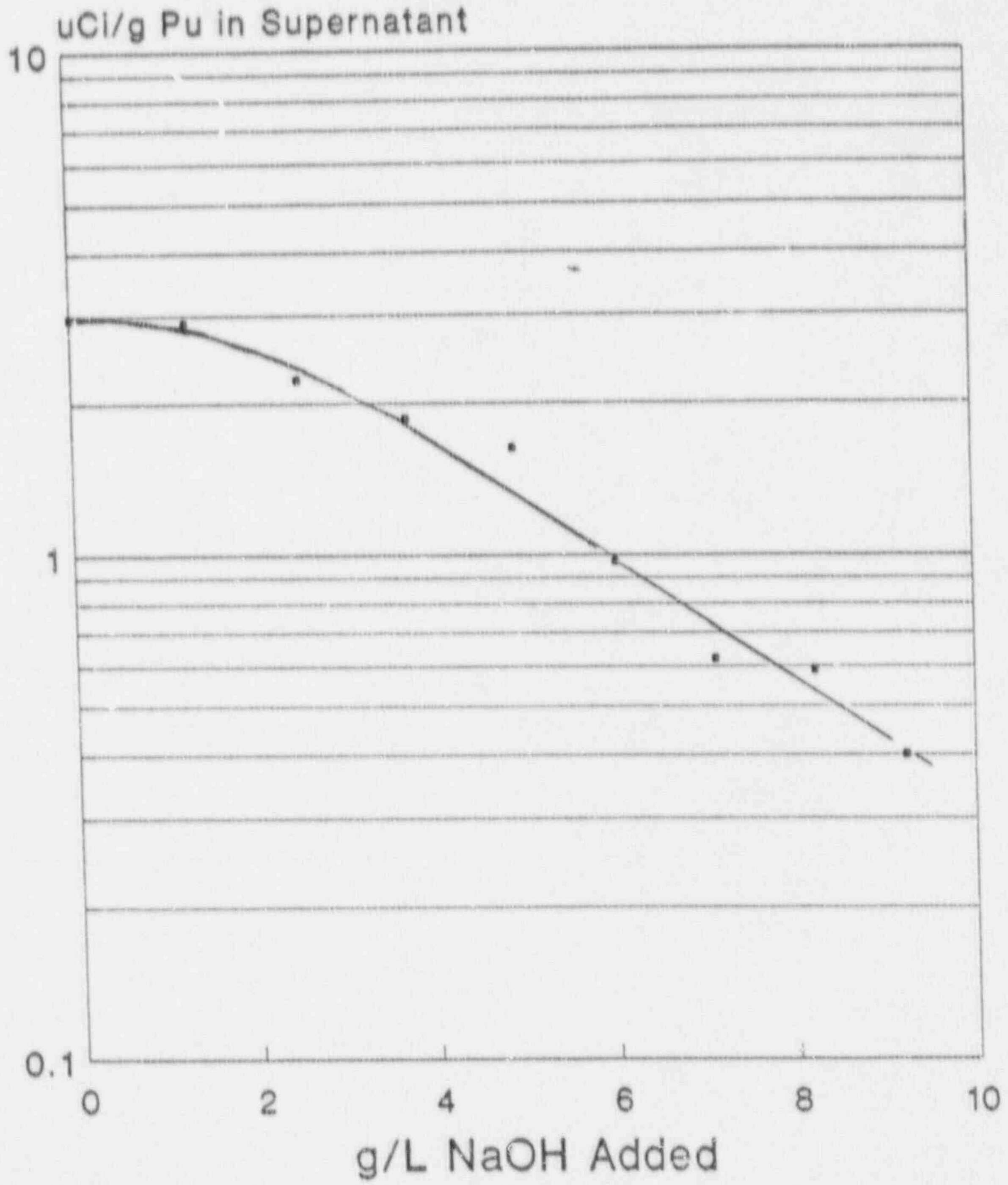
DRAFT C



8/16/90

Figure 20

REMOVAL OF PLUTONIUM FROM WASH SOLUTION
With pH Adjustment using NaOH



8/16/90

Figure 21