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Solubility of Plutonium in Alkaline Salt Solutions (U)

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by

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T. B. Edwards

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SOLUBILITY OF PLUTONIUM IN ALKALINE SALT SOLUTIONS (U)

by

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1.0 Summary

Plutonium solubility data from several studies have been evaluated. For each data set, a predictive model has been developed where appropriate. In addition, a statistical model and corresponding prediction intervals for plutonium solubility as a quadratic function of the hydroxide concentration have been developed. The expression for the predicted plutonium concentration, expressed in base 10 logarithms, is

$$\mathrm{Log_{10}[Pu]} \quad = \quad -6.493 + 1.270 \times \mathrm{Log_{10}[OH]} + 0.505 \times \left\{\mathrm{Log_{10}[OH]}\right\}^2$$

where [Pu] is the plutonium concentration in mole/liter (M) and [OH] is the free hydroxide concentration in M. The model is valid only for solutions which contain a free hydroxide concentration of between 7.24×10^{-3} and 10.5 M and which consist of components in the salt solution comparable to those used to develop the model.

Because of the wide range of solution compositions, the solubility of plutonium can vary by as much as three orders of magnitude for any given hydroxide concentration and still remain within the prediction interval. Any nuclear safety assessments that depend on the maximum amount of plutonium dissolved in alkaline salt solutions should use concentrations at least as great as the upper prediction limits developed in this study. To increase the confidence in the prediction model, it is recommended that additional solubility tests be conducted at low hydroxide concentrations and with all of the other solution components involved. To validate the model for application to actual waste solutions, it is recommended that the plutonium solubilities in actual waste solutions be determined and compared to the values predicted by the quadratic model.

2.0 Introduction

Nuclear safety assessments of the interim storage and processing of high-level wastes at the Savannah River Site require information as to the solubilities of plutonium and uranium in alkaline waste solutions. The solubility of plutonium in alkaline salt solutions has been reported in several different studies [1-5]. Because of different objectives in each of these studies, the selected parameters and ranges were not consistent for all of the tests. However, there is overlap among the tests, and all tests were conducted with a free hydroxide concentration greater than 1×10^{-7} M. An effort was made to determine if the data sets could be analyzed collectively to provide a consistent model for the prediction of plutonium solubility in alkaline salt solutions. Such alkaline salt solutions are currently handled in tank farm facilities and are to be processed through the In-tank Precipitation and Extended Sludge processing operations for permanent disposal.

3.0 Data

The data from these various studies are presented in Tables 1-6 of Appendix 7.1. The unit of measure for each constituent concentration and for the Pu concentration is moles/liter (M). In addition, the concentration of Pu in milligrams/liter (mg/L) was calculated assuming all of the plutonium is present as Pu-239. The analysis of each of these data sets is discussed below.

4.0 Results

Each data set was analyzed to determine a model which fits the plutonium concentration to a function of the parameter concentrations. The results are presented below.

4.1 Data Set #1

The salt solutions in Data Set #1 from reference [1] involved only hydroxide, nitrate, and nitrite. A multiple regression analysis for these data is provided in Exhibit 1 of Appendix 7.2. The model fitted to the data is

$$Log_{10}[Pu] = -8.198 + 0.421\,[OH] + 0.231\,[NO3] + 0.100\,[NO2]$$

where [NO3] is the concentration of nitrate and [NO2] is the concentration of nitrite, both in moles/L.

Thus, all three species included in the salt solution enhance plutonium solubility as their concentrations are increased over the range of values of this study.

4.2 Data Set #2

Data Set #2 is discussed in reference [2]. These salt solutions covered a range of hydroxide, aluminate, and nitrate concentrations while holding the following species at a constant concentration: carbonate, nitrite, and sulfate. The analysis of the model fitted to these data is presented in Exhibit 2 of Appendix 7.2. The estimated model is

$$Log_{10}[Pu] = -5.912 + 1.083\,Log_{10}[OH] + 0.231\,Log_{10}[NO3] + 0.100\,Log_{10}[Al]$$

where [Al] is the concentration of aluminate in moles/L.

The estimated coefficients indicate that all three of these species increase Pu solubility over the range of values of this study.

4.3 Data Set #3

The make-up of the salt solutions of Data Set #3 was the result of a statistically designed experiment that was conducted at SRTC [3]. Parameters investigated included temperature and the concentration of nitrate, nitrite, hydroxide, aluminate, carbonate, and sulfate. Exhibits 3 and 4 in Appendix 7.2 provide the analyses of these data. Exhibit 3 shows a very extensive model fit and Exhibit 4 a reduced model with only the significant factors and interactions. The reduced model is

$$Log_{10}[Pu] = -7.474 + 0.227\,[OH] + 1.065\,[Al] + 1.740\,[CO3] + 0.098\,[NO3] - 1.299\,[SO4] + 1.687\,([SO4] * [OH])$$

where [CO3] is the concentration of carbonate in moles/L and [SO4] is the concentration of sulfate in moles/L.

Increases in the concentrations of hydroxide, aluminate, carbonate, and nitrate lead to increases in plutonium solubility over the range of values studied. The involvement of sulfate is complicated by an interaction between sulfate and hydroxide. The estimated coefficients for these terms indicate that increases in sulfate lead to increases in plutonium solubility for hydroxide concentrations greater than

$$\frac{1.299}{1.687} = 0.77 \text{ M.}$$

For hydroxide concentrations less than 0.77 M, increases in sulfate concentrations lead to decreases in plutonium solubility.

4.4 Data Set #4

Data Set #4 is from reference [4]. These salt solutions covered the low range of hydroxide concentrations with nitrate held constant at 1 M. Exhibit 5 in Appendix 7.2 is a scatter plot of these data for Log_{10}[Pu] versus Log_{10}[OH]. The scatter appears to be random. Exhibit 6 in Appendix 7.2 presents a histogram of these data. A test for normality for this distribution reveals that the data appear to come from a normal distribution. Thus, no significant model could be determined to relate the plutonium solubility with the corresponding hydroxide concentration for these salt solutions.

4.5 Data Set #5

Reference [5] is the source of Data Set #5. This study involved salt solutions which also covered a low range of hydroxide concentrations, but which varied nitrate and nitrite concentrations. However, since the experimental design was such that nitrate and nitrite were changed simultaneously, it would be impossible to distinguish between their effects. Exhibit 7 provides a scatter plot of Log_{10}[Pu] versus Log_{10}[OH]. No significant model could be determined for these data.

4.6 Determination of a Pu Solubility Model

A plot of all the solubility data is presented in Exhibit 8 of Appendix 7.2. This plot shows the natural log of plutonium molar concentrations versus the natural log of the hydroxide molar concentration. Two additional points (Data Set #6) from [3] which are provided in Table 6 of Appendix 7.2 are also included in this plot. A model of the plutonium solubility was developed using the data having hydroxide concentrations from 7.24×10^{-3} to 10.5 M (Log_{10}[OH] from -2.14 to 1.02). The lower hydroxide concentration is just below the minimum hydroxide concentration of 0.01M expected to occur during waste removal and processing operations [6]. The maximum hydroxide concentration is near the maximum hydroxide concentration currently present in the waste tanks [7].

Exhibit 9 in Appendix 7.2 provides a scatter plot of Log_{10}[Pu] versus Log_{10}[OH] over the data for which Log_{10}[OH] was within the range of -2.14 to 1.02. A fitted model which is quadratic in $Log_{10}[OH]$ is also presented in this exhibit. The equation of the model is given by

$$Log_{10}[Pu] = -6.493 + 1.270\ Log_{10}[OH] + 0.505\ (Log_{10}[OH])^2$$

Exhibit 10 in Appendix 7.2 provides a plot of the same data with the fitted quadratic model and a 99% prediction interval for the plutonium solubility. The prediction interval provides a 99% confidence interval for the plutonium solubility, a single response, for a salt solution with a known hydroxide concentration. Exhibits 11 and 12 in Appendix 7.2 provide the same results with the plutonium solubility expressed in mg/L. The details of the prediction interval calculation are presented in Appendix 7.3.

The hydroxide concentration which provides the minimum predicted plutonium solubility for the fitted, quadratic model is determined to be 0.0553 M. This value was determined by taking the derivative of the quadratic equation, setting it equal to zero, solving for the log of the hydroxide concentration, and then taking the antilog to determine the hydroxide concentration in moles/liter. A 95% confidence interval for this hydroxide concentration is given by (0.0236, 0.1293) in M. The derivation of this confidence interval is given in Appendix 7.4.

Besides hydroxide, nitrate is the only other common solution component for all of the data sets. The addition of a nitrate term to the model for plutonium solubility was investigated. Exhibit 13 in Appendix 7.2 provides a plot of the $Log_{10}[Pu]$ values versus the $Log_{10}[NO3]$ values. No evidence of a relationship between these variables is seen. Exhibit 14 provides a multiple regression which includes a $Log_{10}[NO3]$ term, and Exhibit 15 adds a second term, an interaction term between $Log_{10}[NO3]$ and $Log_{10}[OH]$. Each of these fitted models show no indication of a significant term involving $Log_{10}[NO3]$.

5.0 Discussion

Previous studies have shown that the solubility of plutonium in alkaline salt solutions is dependent on the concentration of species such as nitrate, nitrite, aluminate, carbonate, and sulfate [1-3]. However, the data from these previous tests can be fitted to a simpler prediction model based only on the hydroxide concentration. A prediction interval about the fitted curve allows one to estimate bounds on a new, independent observation of the plutonium solubility for an alkaline salt solution for which the hydroxide concentration is known.

Clearly, plutonium concentrations can span a wide range of values at similar hydroxide concentrations. The wide range of plutonium values are determined by the redox potential of the solution and the presence of complexing agents such as carbonate and sulfate.

Simplifying the plutonium solubility to a function of a single factor results in a much lower prediction accuracy for a given solution, as compared to models containing multiple parameters. This is evidenced by comparisons of the root sum square error values for the models. The root sum square error value for the quadratic model (from Exhibit 9) is 0.5787; the value for the reduced model fitted to Data Set #3 (from Exhibit 4) is 0.2246.

Thus, the scatter about the fitted model is more than 2.5 times greater for the quadratic model than the model developed specifically for Data Set #3.

This is also evidenced by a comparison of prediction intervals for the two models. Table 7 in Appendix 7.1 provides a 99% prediction interval for $Log_{10}[Pu]$ for the reduced model of Exhibit 4 (see section 4.3). Row ID #22 identifies a new salt solution with a hydroxide concentration of 1.0M and the other constituents at the midpoints of their ranges. The 99% prediction interval for the plutonium concentration corresponding to this salt solution is given in the table as (-7.125, -5.754). For a salt solution with an hydroxide concentration of 1.0 molar, the 99% prediction interval from the quadratic model (see Appendix 7.3 for formula) is given by (-8.028, -4.955). This second interval is more than twice the size of the former.

With the exception of one data point at low hydroxide concentration, all of the data in Exhibit 10 lie within the 99% prediction interval. With 102 data points used in the determination of the model, it is not unexpected to have 1 data point outside of the 99% prediction interval. Therefore, it is concluded that the quadratic model and equations for the prediction limits can be useful in predicting plutonium solubilities over the range of hydroxide concentrations from 7.24×10^{-3} to 10.5 M for alkaline salt solutions comparable to those included in this study.

Because of the wide range of solution compositions, the solubility of plutonium can vary by as much as three orders of magnitude for any given hydroxide concentration and still remain within the prediction interval. For more accurate prediction of the plutonium solubility, the more extensive models developed for each data set should be used. Any nuclear safety assessments that depend on the maximum amount of plutonium dissolved in alkaline salt solutions should use concentrations at least as great as the upper prediction limits developed in this study.

Far fewer data points exist for hydroxide concentrations less than 0.5M than for higher hydroxide concentrations. Thus, there is greater uncertainty in the ability of the model to accurately predict the plutonium solubilities corresponding to these lower hydroxide salt solutions. To increase the confidence in the prediction model, it is recommended that additional solubility tests be conducted at low hydroxide concentrations and with all of the other solution components involved.

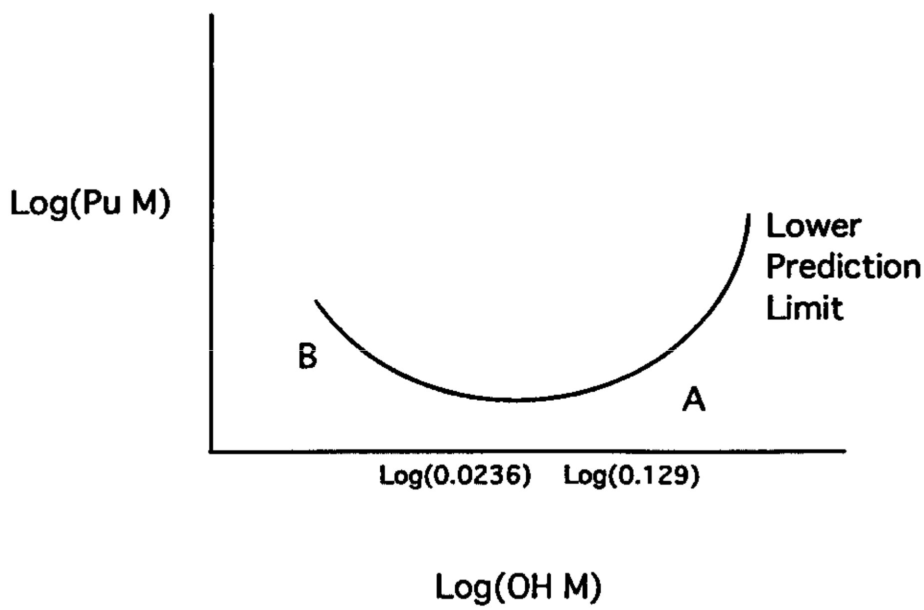
The studies cited here reported plutonium concentrations for alkaline salt solutions saturated in plutonium. A new alkaline salt solution whose plutonium concentration is below the lower prediction limit corresponding to its hydroxide concentration may signal one of two events:

(1) the salt solution is not saturated in plutonium, or

(2) the salt solution is saturated in plutonium and an improbable event has occurred.

For alkaline salt solutions falling into category (1) and having hydroxide concentrations greater than the upper confidence limit, 0.129 M, for the hydroxide value which is expected to minimize plutonium solubility, evaporation is not expected to crystallize plutonium. This situation is represented by data point A in the chart below. For example, if a solution 0.2M in free hydroxide and containing 1×10^{-9} M plutonium were evaporated to a free hydroxide concentration of 0.8M, no plutonium would be expected to crystallize because the plutonium concentration after evaporation, $4x10^{-9}$ M, is below the minimum predicted solubility of $7.1x10^{-9}$ M.

However, for solutions falling into category (1) and having hydroxide concentrations below the lower confidence limit, 0.0236 M, for the hydroxide value which is expected to minimize plutonium solubility, evaporation of the solution may result in some crystallization of plutonium from solution. This situation is represented by data point B in the chart below. For example, if a solution 0.01M in free hydroxide and containing $1x10^{-9}$ M plutonium were evaporated to a free hydroxide concentration of 0.1M, some plutonium may crystallize, because the minimum predicted curve would be intersected. After evaporation the plutonium concentration would be $1x10^{-8}$ M, which is above the minimum predicted solubility of $1.4x10^{-9}$ M. Note however, that the plutonium may not crystallize since the evaporated concentration is still below the maximum predicted solubility of $2.1x10^{-6}$ M.



The quadratic model has not been evaluated against actual waste solutions which contain not only the components used in the solubility studies, but also contain smaller amounts of many other chemical species. Some of these species such as the halides, oxalate, and phosphate, could form complexes with plutonium, and thereby, increase the plutonium solubility above that predicted by the quadratic model. To validate the model for application to actual waste solutions, it is recommended that the plutonium solubilities in actual waste solutions be determined and compared to the values predicted by the quadratic model. The waste solutions selected for the determination of plutonium solubility should span as wide a range of hydroxide concentrations as possible.

6.0 References

[1] Delegard, C. H., "Solubility of $PuO_2 \cdot H_2O$ in Alkaline Hanford High-Level Waste Solution," RHO-RE-SA-75P, May 2, 1985.

[2] Delegard, C.H. and S. A. Gallagler, "Effects of Hanford High-Level Waste Components on the Solubility of Cobalt, Strontium, Neptunium, Plutonium and Americium," RHO-RE-ST-3P, 1983.

[3] Hobbs, D. T., T. B. Edwards, and S. D. Fleischman, "Solubility of Plutonium and Uranium in Alkaline Salt Solutions (U), WSRC-TR-93-056, February 12, 1993.

[4] "Bedrock Waste Storage: Technical Progress Report, February-April, 1972," DPST-72-122-2, July, 1972.

[5] Marine, I. W., "Bedrock Waste Storage: Technical Progress Report, September 1972 - June 1973," DPST-73-122-1, October, 1973.

[6] Personal Communication with M. Hay, February 25, 1993.

[7] Pike, J. A., "Tank Chemistry Report, December 1992 (U)," WER-HLE-930221, January 18, 1993.

[8] Coleman, H. W. and W. G. Steele, **Experimentation and Uncertainty Analysis for Engineers**, John Wiley & Sons, New York, 1989.

7.0 Appendices

7.1 Tables

Table 1: Plutonium Solubility Study: Data Set # 1

Reference: Delegard, C. H., "Solubility of $PuO_2 \cdot H_2O$ in Alkaline Hanford High-Level Waste Solution," RHO-RE-SA-75P, May 2, 1985.

Data Set	[NaOH]M	[NaAlO2]M	[Na2CO3]M	[NaNO3]M	[NaNO2]M	[Na2SO4]M	[Pu]M	[Pu]mg/L
1	4.00E+00			4.00E+00			1.26E-06	3.01E-01
1	5.00E+00			1.00E+00			1.34E-06	3.20E-01
1	5.00E+00			1.50E+00			1.58E-06	3.78E-01
1	5.00E+00			2.00E+00			1.68E-06	4.02E-01
1	5.00E+00			3.00E+00			2.48E-06	5.93E-01
1	5.00E+00			3.00E+00			1.92E-06	4.59E-01
1	5.00E+00			4.00E+00			3.00E-06	7.17E-01
1	6.00E+00			2.00E+00			4.74E-06	1.13E+00
1	7.00E+00			1.00E+00			7.93E-06	1.90E+00
1	4.00E+00				4.00E+00		4.00E-07	9.63E-02
1	5.00E+00				1.00E+00		1.17E-06	2.80E-01
1	5.00E+00				1.50E+00		9.20E-07	2.20E-01
1	5.00E+00				2.00E+00		5.50E-07	1.33E-01
1	5.00E+00				3.00E+00		1.12E-06	2.68E-01
1	5.00E+00				3.00E+00		7.00E-07	1.67E-01
1	5.00E+00				4.00E+00		7.80E-07	1.85E-01
1	6.00E+00				2.00E+00		5.54E-06	1.32E+00
1	7.00E+00				1.00E+00		5.09E-06	1.22E+00
1	1.00E+00			1.00E+00	1.00E+00		3.00E-08	8.29E-03
1	2.00E+00			1.00E+00	1.00E+00		1.20E-07	2.94E-02
1	3.00E+00			1.00E+00	1.00E+00		3.20E-07	7.58E-02
1	4.00E+00			1.00E+00	1.00E+00		7.70E-07	1.83E-01
1	5.00E+00			2.50E-01	2.50E-01		2.01E-06	4.80E-01
1	5.00E+00			5.00E-01	5.00E-01		2.85E-06	6.81E-01
1	5.00E+00			1.00E+00	1.00E+00		3.86E-06	9.23E-01
1	5.00E+00			1.00E+00	1.00E+00		2.09E-06	5.00E-01
1	5.00E+00			1.50E+00	1.50E+00		6.49E-06	1.55E+00
1	5.00E+00			2.00E+00	2.00E+00		8.71E-06	2.08E+00
1	5.00E+00			2.50E+00	2.50E+00		8.47E-06	2.02E+00
1	5.00E+00			3.00E+00	3.00E+00		1.48E-05	3.54E+00
1	5.00E+00			3.00E+00	3.00E+00		1.48E-05	3.54E+00
1	6.00E+00			1.00E+00	1.00E+00		4.60E-06	1.10E+00
1	6.00E+00			2.50E+00	2.50E+00		3.82E-05	9.13E+00
1	7.00E+00			1.00E+00	1.00E+00		1.03E-05	2.46E+00
1	7.00E+00			2.00E+00	2.00E+00		9.41E-06	2.25E+00
1	8.00E+00			1.00E+00	1.00E+00		2.99E-05	7.15E+00
1	8.00E+00			1.50E+00	1.50E+00		8.44E-05	2.02E+01
1	9.00E+00			1.00E+00	1.00E+00		1.07E-04	2.56E+01
1	9.00E+00			1.00E+00	1.00E+00		6.67E-05	1.59E+01
1	1.00E+01			5.00E-01	5.00E-01		2.69E-04	6.43E+01
1	1.00E+01			1.00E+00	1.00E+00		1.45E-04	3.47E+01
1	1.05E+01			2.50E-01	2.50E-01		1.84E-04	4.40E+01

Table 2: Plutonium Solubility Study: Data Set # 2

Reference: Delegard, C.H. and S. A. Gallagler, "Effects of Hanford High-Level Waste Components on the Solubility of Cobalt, Strontium, Neptunium, Plutonium and Americium," RHO-RE-ST-3P, 1983.

Data Set	[NaOH]M	[NaAlO2]M	[Na2CO3]M	[NaNO3]M	[NaNO2]M	[Na2SO4]M	[Pu]M	[Pu]mg/L
2	4.00E+00	5.00E-05	2.50E-02	2.00E+00	1.00E+00	5.00E-03	4.58E-06	1.09E+00
2	1.00E+00	5.00E-05	2.50E-02	2.00E+00	1.00E+00	5.00E-03	1.04E-06	2.49E-01
2	4.00E+00	5.00E-05	2.50E-02	2.00E-08	1.00E+00	5.00E-03	2.07E-06	4.95E-01
2	*1.00E+00*	*5.00E-05*	*2.50E-02*	*2.00E-08*	*1.00E+00*	*5.00E-03*	*4.80E-07*	*1.14E-01*
2	2.00E+00	5.00E-01	2.50E-02	2.00E+00	1.00E+00	5.00E-03	3.39E-06	8.10E-01
2	2.00E+00	5.00E-09	2.50E-02	2.00E+00	1.00E+00	5.00E-03	1.29E-06	3.08E-01
2	2.00E+00	5.00E-01	2.50E-02	2.00E-08	1.00E+00	5.00E-03	1.24E-06	2.96E-01
2	2.00E+00	5.00E-09	2.50E-02	2.00E-08	1.00E+00	5.00E-03	5.70E-07	1.36E-01
2	4.00E+00	5.00E-01	2.50E-02	2.00E-04	1.00E+00	5.00E-03	3.31E-06	7.91E-01
2	*4.00E+00*	*5.00E-09*	*2.50E-02*	*2.00E-04*	*1.00E+00*	*5.00E-03*	*2.34E-06*	5.59E-01
2	1.00E+00	5.00E-01	2.50E-02	2.00E-04	1.00E+00	5.00E-03	1.00E-06	2.38E-01
2	1.00E+00	5.00E-09	2.50E-02	2.00E-04	1.00E+00	5.00E-03	3.70E-07	8.77E-02
2	2.00E+00	5.00E-05	2.50E-02	2.00E-04	1.00E+00	5.00E-03	5.70E-07	1.37E-01
2	2.00E+00	5.00E-05	2.50E-02	2.00E-04	1.00E+00	5.00E-03	5.10E-07	1.21E-01
2	2.00E+00	5.00E-05	2.50E-02	2.00E-04	1.00E+00	5.00E-03	7.40E-07	1.78E-01

Table 3: Plutonium Solubility Study: Data Set # 3

Reference: Hobbs, D. T., T. B. Edwards, and S. D. Fleischman, "Solubility of Plutonium and Uranium in Alkaline Salt Solutions (U), WSRC-TR-93-056, February 12, 1993.

Data Set	[NaOH]M	[NaAlO2]M	[Na2CO3]M	[NaNO3]M	[NaNO2]M	[Na2SO4]M	[Pu]M	[Pu]mg/L
3	2.00E+00	5.00E-02	2.00E-02	1.00E+00	2.00E+00	4.00E-01	1.58E-06	3.78E-01
3	1.25E+00	1.90E-01	1.60E-01	2.50E+00	1.05E+00	2.10E-01	2.70E-07	6.52E-02
3	1.25E+00	1.90E-01	1.60E-01	2.50E+00	1.05E+00	2.10E-01	2.90E-07	6.86E-02
3	1.25E+00	1.90E-01	1.60E-01	2.50E+00	1.05E+00	2.10E-01	5.00E-07	1.19E-01
3	5.00E-01	3.30E-01	3.00E-01	4.00E+00	1.00E-01	2.00E-02	1.22E-06	2.92E-01
3	7.50E-01	3.63E-01	2.00E-02	4.00E+00	2.00E+00	2.00E-02	3.50E-07	8.46E-02
3	2.00E+00	3.30E-01	2.00E-02	1.00E+00	1.00E-01	4.00E-01	3.07E-06	7.34E-01
3	2.00E+00	3.30E-01	3.00E-01	1.00E+00	2.00E+00	2.00E-02	1.30E-06	3.11E-01
3	2.00E+00	5.00E-02	3.00E-01	1.00E+00	1.00E-01	2.00E-02	5.30E-07	1.27E-01
3	5.00E-01	3.30E-01	2.00E-02	4.00E+00	2.00E+00	4.00E-01	2.60E-07	6.14E-02
3	2.00E+00	3.30E-01	2.00E-02	4.00E+00	1.00E-01	2.00E-02	6.70E-07	1.61E-01
3	5.00E-01	5.00E-02	2.00E-02	1.00E+00	1.00E-01	2.00E-02	7.00E-08	1.72E-02
3	1.25E+00	1.90E-01	1.60E-01	2.50E+00	1.05E+00	2.10E-01	4.30E-07	1.04E-01
3	1.40E+00	2.30E-01	2.10E-01	2.80E+00	1.40E+00	2.80E-01	6.70E-07	1.60E-01
3	5.00E-01	5.00E-02	3.00E-01	4.00E+00	2.00E+00	2.00E-02	6.10E-07	1.47E-01
3	5.00E-01	5.00E-02	2.00E-02	4.00E+00	1.00E-01	4.00E-01	8.00E-08	1.90E-02
3	5.00E-01	3.30E-01	2.00E-02	1.00E+00	2.00E+00	2.00E-02	7.00E-08	1.63E-02
3	5.00E-01	5.00E-02	3.00E-01	1.00E+00	2.00E+00	4.00E-01	1.80E-07	4.18E-02
3	5.00E-01	3.30E-01	3.00E-01	1.00E+00	1.00E-01	4.00E-01	5.30E-07	1.28E-01
3	2.00E+00	5.00E-02	3.00E-01	4.00E+00	1.00E-01	4.00E-01	4.09E-06	9.78E-01
3	5.00E-01	3.30E-01	3.00E-01	1.00E+00	1.00E-01	4.00E-01	1.20E-07	2.92E-02

Table 4: Plutonium Solubility Study: Data Set # 4

Reference: "Bedrock Waste Storage: Technical Progress Report, February-April, 1972," DPST-72-122-2, July, 1972.

Data Set	[NaOH]M	[NaAlO2]M	[Na2CO3]M	[NaNO3]M	[NaNO2]M	[Na2SO4]M	[Pu]M	[Pu]mg/L
4	4.10E-07			1.00E+00			1.30E-07	3.18E-02
4	7.20E-07			1.00E+00			1.40E-07	3.30E-02
4	1.05E-06			1.00E+00			5.00E-07	1.20E-01
4	6.17E-06			1.00E+00			1.00E-07	2.41E-02
4	1.23E-05			1.00E+00			8.00E-08	1.90E-02
4	1.74E-05			1.00E+00			1.40E-07	3.42E-02
4	1.74E-05			1.00E+00			1.10E-07	2.58E-02
4	2.51E-05			1.00E+00			7.00E-08	1.71E-02
4	3.80E-05			1.00E+00			4.00E-07	9.51E-02
4	3.98E-05			1.00E+00			1.70E-07	4.06E-02
4	5.37E-05			1.00E+00			4.00E-08	8.63E-03
4	7.94E-05			1.00E+00			3.00E-07	7.24E-02
4	1.48E-04			1.00E+00			1.90E-07	4.61E-02
4	3.39E-04			1.00E+00			2.20E-07	5.38E-02
4	3.47E-04			1.00E+00			3.00E-08	6.60E-03
4	4.68E-04			1.00E+00			4.00E-08	8.63E-03
4	6.17E-04			1.00E+00			6.00E-08	1.42E-02
4	7.41E-04			1.00E+00			2.00E-08	4.06E-03
4	2.75E-03			1.00E+00			8.00E-08	1.93E-02
4	7.24E-03			1.00E+00			3.70E-07	8.89E-02
4	7.41E-03			1.00E+00			7.00E-08	1.73E-02
4	1.02E-02			1.00E+00			1.50E-07	3.49E-02
4	1.32E-02			1.00E+00			1.40E-07	3.25E-02
4	1.32E-02			1.00E+00			1.60E-07	3.92E-02
4	4.27E-02			1.00E+00			2.00E-07	4.78E-02
4	7.59E-02			1.00E+00			7.00E-07	1.67E-01
4	8.71E-02			1.00E+00			1.50E-07	3.70E-02
4	8.91E-02			1.00E+00			1.00E-07	2.44E-02
4	1.02E-01			1.00E+00			2.00E-08	4.45E-03
4	1.10E-01			1.00E+00			3.30E-07	7.98E-02
4	2.88E-01			1.00E+00			7.00E-08	1.71E-02
4	4.79E-01			1.00E+00			3.00E-08	7.10E-03
4	5.01E-01			1.00E+00			1.00E-07	2.41E-02
4	5.75E-01			1.00E+00			4.00E-08	8.89E-03
4	5.89E-01			1.00E+00			1.90E-07	4.45E-02
4	6.46E-01			1.00E+00			5.00E-08	1.20E-02

Table 5: Plutonium Solubility Study: Data Set # 5

Reference: Marine, I. W., "Bedrock Waste Storage: Technical Progress Report, September 1972 - June 1973," DPST-73-122-1, October, 1973.

Data Set	[NaOH]M	[NaAlO2]M	[Na2CO3]M	[NaNO3]M	[NaNO2]M	[Na2SO4]M	[Pu]M	[Pu]mg/L
5	2.60E-07			8.75E-01	1.25E-01		4.00E-08	8.60E-03
5	5.00E-07			8.75E-01	1.25E-01		9.30E-09	2.22E-03
5	2.69E-06			8.75E-01	1.25E-01		6.10E-09	1.46E-03
5	7.24E-03			8.75E-01	1.25E-01		4.50E-09	1.08E-03
5	1.17E-01			8.75E-01	1.25E-01		5.20E-09	1.24E-03
5	2.24E-01			8.75E-01	1.25E-01		5.00E-08	1.09E-02
5	2.00E-07			3.50E+00	5.00E-01		3.90E-09	9.32E-04
5	8.91E-06			3.50E+00	5.00E-01		3.00E-08	5.98E-03
5	7.41E-04			3.50E+00	5.00E-01		3.70E-09	8.84E-04
5	1.17E-02			3.50E+00	5.00E-01		1.80E-09	4.30E-04
5	1.66E-01			3.50E+00	5.00E-01		2.00E-08	5.02E-03

Table 6: Plutonium Solubility Study: Data Set # 6

Reference: Hobbs, D. T., T. B. Edwards, and S. D. Fleischman, "Solubility of Plutonium and Uranium in Alkaline Salt Solutions (U), WSRC-TR-93-056, February 12, 1993.

Data Set	[NaOH]M	[NaAlO2]M	[Na2CO3]M	[NaNO3]M	[NaNO2]M	[Na2SO4]M	[Pu]M	[Pu]mg/L
6	5.10E-02	5.00E-02	3.00E-01	1.00E+00	1.00E-01	4.00E-01	1.24E-06	2.96E-01
6	5.10E-02	5.00E-02	3.00E-01	1.00E+00	1.00E-01	4.00E-01	1.67E-06	3.99E-01

Table 7: 99% Prediction Interval for Reduced Model Fitted to Data Set #5

Row ID	[NaOH]M	[NaAlO2]M	[Na2CO3]M	[NaNO3]M	[NaNO2]M	[Na2SO4]M	[Pu]M
1	2	0.05	0.02	1	2	0.4	1.58E-06
2	1.25	0.19	0.16	2.5	1.05	0.21	2.70E-07
3	1.25	0.19	0.16	2.5	1.05	0.21	2.90E-07
4	1.25	0.19	0.16	2.5	1.05	0.21	5.00E-07
5	0.5	0.33	0.3	4	0.1	0.02	1.22E-06
6	0.75	0.363	0.02	4	2	0.02	3.50E-07
7	2	0.33	0.02	1	0.1	0.4	3.07E-06
8	2	0.33	0.3	1	2	0.02	1.30E-06
9	2	0.05	0.3	1	0.1	0.02	5.30E-07
10	0.5	0.33	0.02	4	2	0.4	2.60E-07
11	2	0.33	0.02	4	0.1	0.02	6.70E-07
12	0.5	0.05	0.02	1	0.1	0.02	7.00E-08
13	1.25	0.19	0.16	2.5	1.05	0.21	4.30E-07
14	1.4	0.23	0.21	2.8	1.4	0.28	6.70E-07
15	0.5	0.05	0.3	4	2	0.02	6.10E-07
16	0.5	0.05	0.02	4	0.1	0.4	8.00E-08
17	0.5	0.33	0.02	1	2	0.02	7.00E-08
18	0.5	0.05	0.3	1	2	0.4	1.80E-07
19	0.5	0.33	0.3	1	0.1	0.4	5.30E-07
20	2	0.05	0.3	4	0.1	0.4	4.09E-06
21	0.5	0.33	0.3	1	0.1	0.4	1.20E-07
22	1	0.19	0.16	2.5	1.05	0.21	•

Row ID	Pred [logPu]	S.E. Pred	L99%PI	U99%PI
1	-6.0047	0.2676	-6.8013	-5.2080
2	-6.2942	0.2303	-6.9797	-5.6088
3	-6.2942	0.2303	-6.9797	-5.6088
4	-6.2942	0.2303	-6.9797	-5.6088
5	-6.1032	0.2677	-6.9002	-5.3062
6	-6.4902	0.2545	-7.2480	-5.7325
7	-5.7063	0.2726	-6.5179	-4.8948
8	-6.0074	0.2668	-6.8017	-5.2131
9	-6.3057	0.2729	-7.1181	-5.4933
10	-6.7635	0.2639	-7.5491	-5.9778
11	-6.2000	0.2759	-7.0213	-5.3787
12	-7.1836	0.2735	-7.9976	-6.3695
13	-6.2942	0.2303	-6.9797	-5.6088
14	-5.9736	0.2349	-6.6730	-5.2743
15	-6.4015	0.2671	-7.1967	-5.6063
16	-7.0618	0.2745	-7.8788	-6.2448
17	-6.8852	0.2648	-7.6736	-6.0969
18	-6.8692	0.2602	-7.6439	-6.0946
19	-6.5709	0.2589	-7.3417	-5.8000
20	-5.2226	0.2793	-6.0538	-4.3913
21	-6.5709	0.2589	-7.3417	-5.8000
22	-6.4394	0.2303	-7.1249	-5.7540

7.2 Exhibits

Exhibit 1: Multiple Regression Analysis for Data Set # 1

Response: Log(PuM)

Summary of Fit

Rsquare	0.917475
Root Mean Square Error	0.255614
Mean of Response	-5.38004
Observations (or Sum Wgts)	42

Lack of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack of Fit	33	2.3990465	0.072698	4.3363
Pure Error	5	0.0838249	0.016765	Prob>F
Total Error	38	2.4828714		0.0536

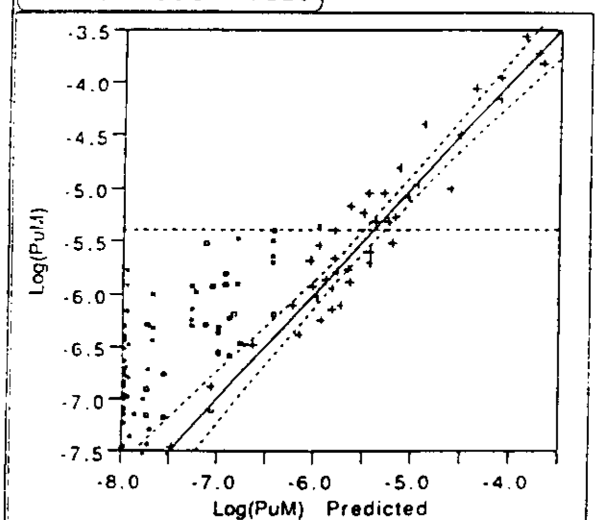
Parameter Estimates

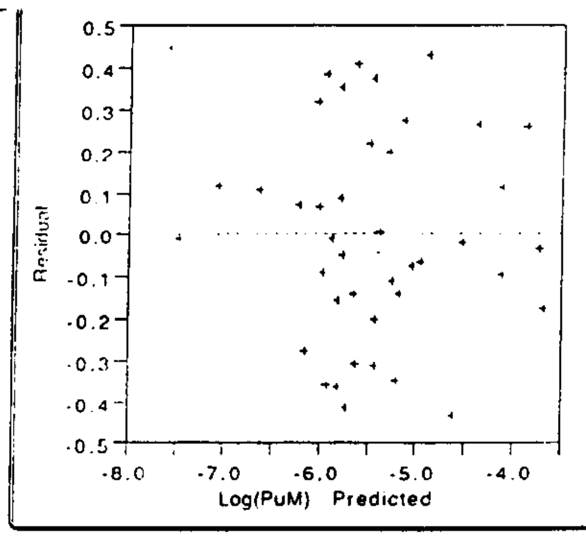
Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	-8.197946	0.15865	-51.67	0.0000
[NaOH]M	0.4209096	0.0207	20.34	0.0000
[NaNO3]M	0.230704	0.03735	6.18	0.0000
[NaNO2]M	0.1003163	0.03735	2.69	0.0107

Effect Test

Source	Nparm	DF	Sum of Squares	F Ratio	Prob>F
[NaOH]M	1	1	27.027978	413.6594	0.0000
[NaNO3]M	1	1	2.492425	38.1462	0.0000
[NaNO2]M	1	1	0.471254	7.2125	0.0107

Whole-Model Test





Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	3	27.603267	9.20109	140.8214
Error	38	2.482871	0.06534	Prob>F
C Total	41	30.086138		0.0000

Exhibit 2: Multiple Regression Analysis for Data Set # 2

Response: Log(PuM)

Summary of Fit

Rsquare	0.792367
Root Mean Square Error	0.179081
Mean of Response	-5.93665
Observations (or Sum Wgts)	15

Lack of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack of Fit	9	0.33832373	0.037592	5.2039
Pure Error	2	0.01444735	0.007224	Prob>F
Total Error	11	0.35277108		0.1715

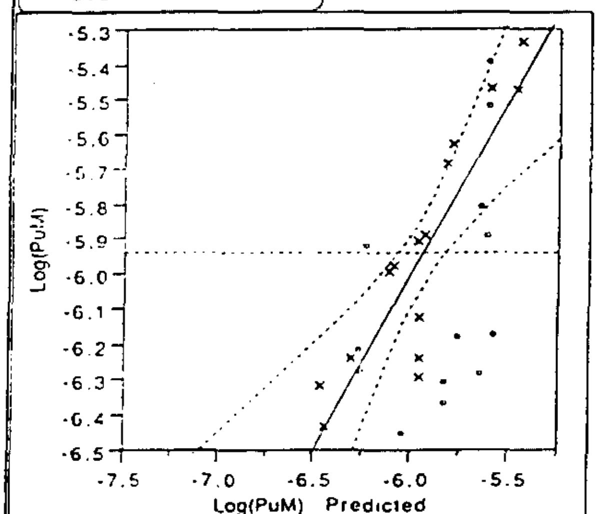
Parameter Estimates

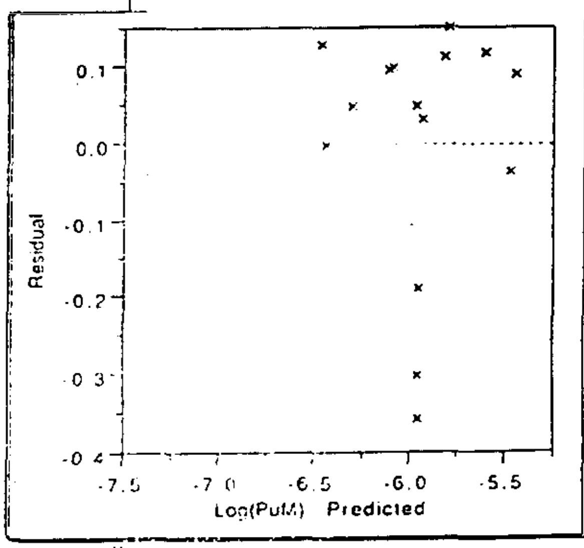
Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	-5.912101	0.1192	-49.60	0.0000
Log(OH)	1.0828816	0.21033	5.15	0.0003
Log(Al)	0.0418801	0.01583	2.65	0.0228
Log(NO3)	0.0460669	0.01583	2.91	0.0142

Effect Test

Source	Nparm	DF	Sum of Squares	F Ratio	Prob>F
Log(OH)	1	1	0.85010291	26.5076	0.0003
Log(Al)	1	1	0.22450518	7.0005	0.0228
Log(NO3)	1	1	0.27163672	8.4701	0.0142

Whole-Model Test





Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	3	1.3462448	0.448748	13.9927
Error	11	0.3527711	0.032070	Prob>F
C Total	14	1.6990159		0.0005

Exhibit 3: Full Model Fit for Data Set # 3

Response: Log(PuM)

Summary of Fit

Rsquare	0.93039
Root Mean Square Error	0.221084
Mean of Response	-6.35701
Observations (or Sum Wgts)	21

Lack of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack of Fit	3	0.08585922	0.028620	0.4467
Pure Error	4	0.25628687	0.064072	Prob>F
Total Error	7	0.34214608		0.7330

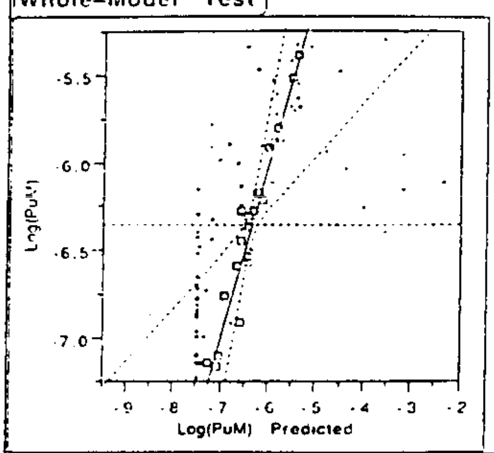
Parameter Estimates

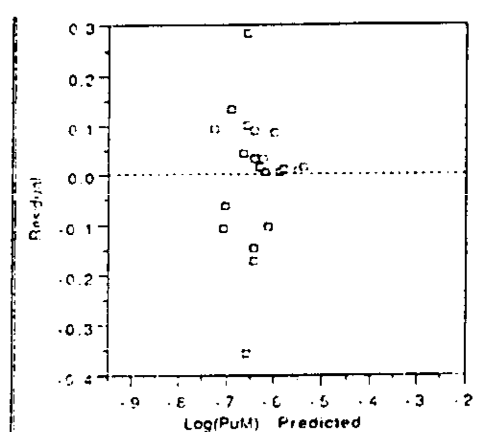
Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	-7.634784	0.39151	-19.50	0.0000
[NaOH]M	0.4036466	0.32144	1.26	0.2495
[NaAlO2]M	0.8006055	0.73467	1.09	0.3119
[Na2CO3]M	2.45347	0.75561	3.25	0.0141
[NaNO3]M	0.1439941	0.09971	1.44	0.1919
[NaNO2]M	-0.178531	0.20883	-0.85	0.4209
[Na2SO4]M	-1.309344	0.5563	-2.35	0.0508
[NaAlO2]*[NaOH]M	0.2199041	0.62337	0.35	0.7346
[Na2CO3]*[NaOH]M	-0.604407	0.6343	-0.95	0.3724
[NaNO3]M*[NaOH]M	-0.04311	0.07107	-0.61	0.5633
[NaNO2]M*[NaOH]M	0.199996	0.16628	1.20	0.2682
[Na2SO4]*[NaOH]M	1.6709172	0.46736	3.58	0.0090
[NaOH]M*[NaNO3]M*[NaNO2]M	-0.155536	0.09572	-1.62	0.1482
[NaNO3]M*[NaNO2]M	0.1169912	0.08353	1.40	0.2041

Effect Test

Source	Nparm	DF	Sum of Squares	F Ratio	Prob>F
[NaOH]M	1	1	0.07707398	1.5769	0.2495
[NaAlO2]M	1	1	0.05804526	1.1876	0.3119
[Na2CO3]M	1	1	0.51614857	10.5599	0.0141
[NaNO3]M	1	1	0.10193207	2.0854	0.1919
[NaNO2]M	1	1	0.03572393	0.7309	0.4209
[Na2SO4]M	1	1	0.27076991	5.5397	0.0508
[NaAlO2]*[NaOH]M	1	1	0.00608257	0.1244	0.7346
[Na2CO3]*[NaOH]M	1	1	0.04438019	0.9080	0.3724
[NaNO3]M*[NaOH]M	1	1	0.01798549	0.3680	0.5633
[NaNO2]M*[NaOH]M	1	1	0.07071147	1.4467	0.2682
[Na2SO4]*[NaOH]M	1	1	0.62476108	12.7820	0.0090
[NaOH]M*[NaNO3]M*[NaNO2]M	1	1	0.12906235	2.6405	0.1482
[NaNO3]M*[NaNO2]M	1	1	0.09568823	1.9616	0.2041

Whole-Model Test





Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	13	4.5730389	0.351772	7.1969
Error	7	0.3421461	0.048878	Prob>F
C Total	20	4.9151850		0.0071

Exhibit 4: Reduced Model Fit for Data Set # 3

Response: Log(Pu)

Summary of Fit

Rsquare	0.85631
Root Mean Square Error	0.224605
Mean of Response	-6.35701
Observations (or Sum Wgts)	21

Lack of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack of Fit	10	0.44997476	0.044997	0.7023
Pure Error	4	0.25628687	0.064072	Prob>F
Total Error	14	0.70626163		0.7045

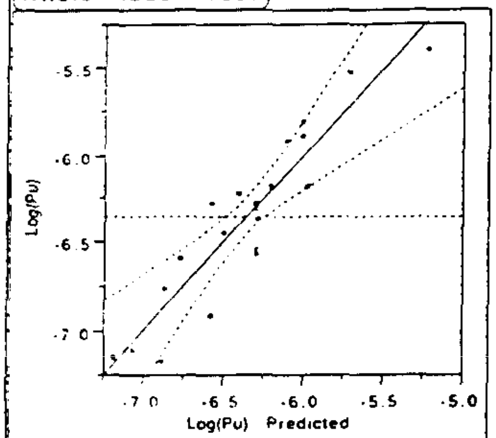
Parameter Estimates

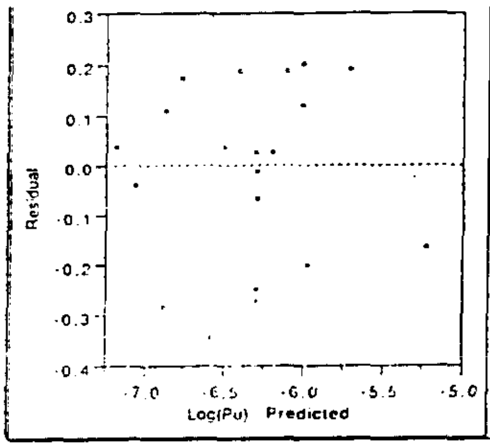
Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	-7.474104	0.22259	-33.58	0.0000
[NaOH]M	0.226612	0.12154	1.86	0.0834
[NaAlO2]M	1.0654283	0.41542	2.56	0.0225
[Na2CO3]M	1.7404752	0.42039	4.14	0.0010
[NaNO3]M	0.0982531	0.0385	2.55	0.0230
[Na2SO4]M	-1.298512	0.55204	-2.35	0.0338
[Na2SO4]*[NaOH]M	1.6866183	0.43444	3.88	0.0017

Effect Test

Source	Nparm	DF	Sum of Squares	F Ratio	Prob>F
[NaOH]M	1	1	0.17537312	3.4764	0.0834
[NaAlO2]M	1	1	0.33183030	6.5776	0.0225
[Na2CO3]M	1	1	0.86470624	17.1408	0.0010
[NaNO3]M	1	1	0.32859101	6.5136	0.0230
[Na2SO4]M	1	1	0.27911764	5.5329	0.0338
[Na2SO4]*[NaOH]M	1	1	0.76033119	15.0718	0.0017

Whole-Model Test

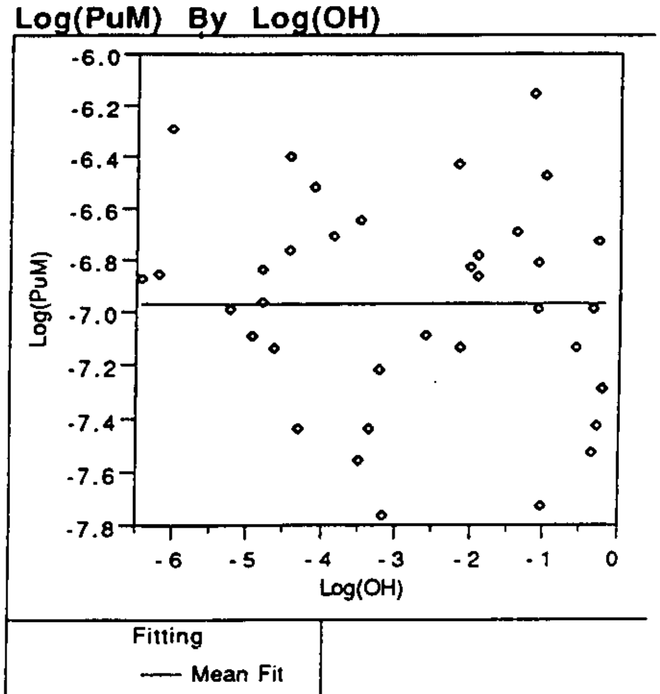




Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	6	4.2089233	0.701487	13.9054
Error	14	0.7062616	0.050447	Prob>F
C Total	20	4.9151850		0.0000

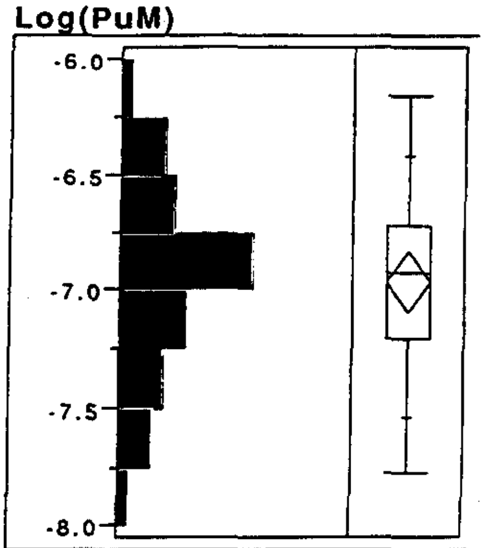
Exhibit 5: Scatter Plot for Data Set # 4



Mean Fit

Mean	-6.96422
Std Dev [RMSE]	0.395492
Std Error	0.065915
SSE	5.474476

Exhibit 6: Histogram of Plutonium Solubilities for Data Set # 4



Quantiles

maximum	100.0%	-6.1549
	99.5%	-6.1549
	97.5%	-6.1549
	90.0%	-6.4207
quartile	75.0%	-6.7185
median	50.0%	-6.9214
quartile	25.0%	-7.2052
	10.0%	-7.5368
	2.5%	-7.7696
	0.5%	-7.7696
minimum	0.0%	-7.7696

Moments

Mean	-6.96422
Std Dev	0.39549
Std Err Mean	0.06592
upper 95% Mean	-6.83040
lower 95% Mean	-7.09803
N	36.00000
Sum Wgts	36.00000

Test for Normality

Shapiro-Wilk W Test

W	Prob<W
0.979292	0.7897

Exhibit 7: Scatter Plot for Data Set # 5

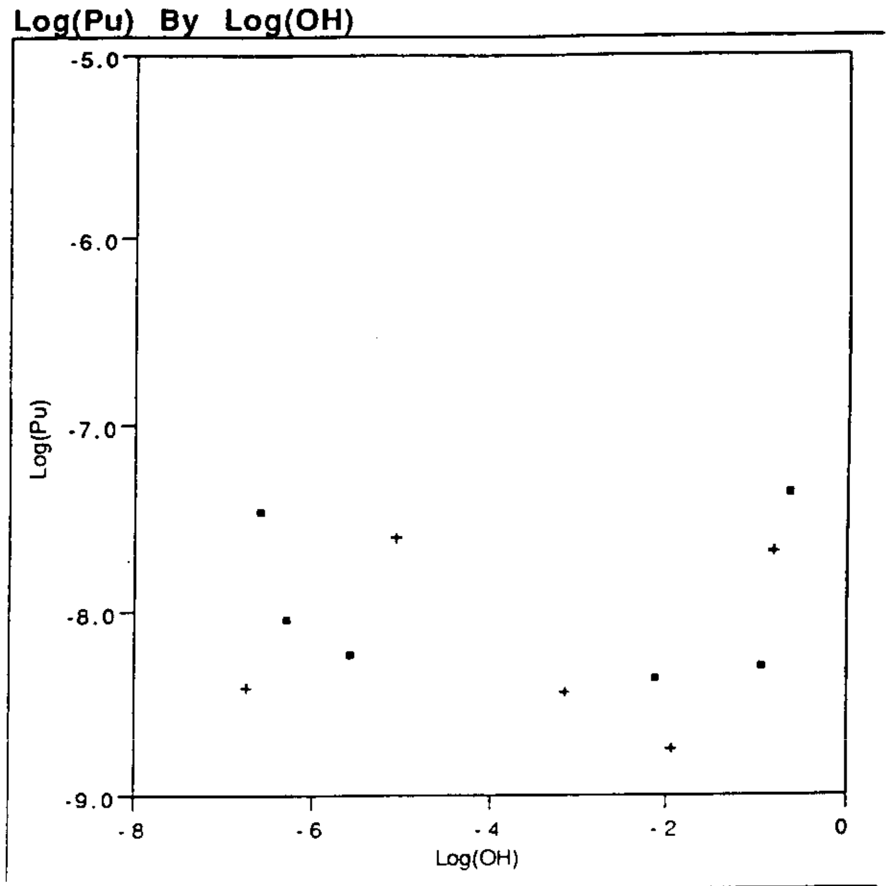


Exhibit 8: Plot of Plutonium Solubility Data

SYMBOLS: Data Set #1 - pluses #4 - diamonds
#2 - x's #5 - triangles
#3 - boxes #6 - y's

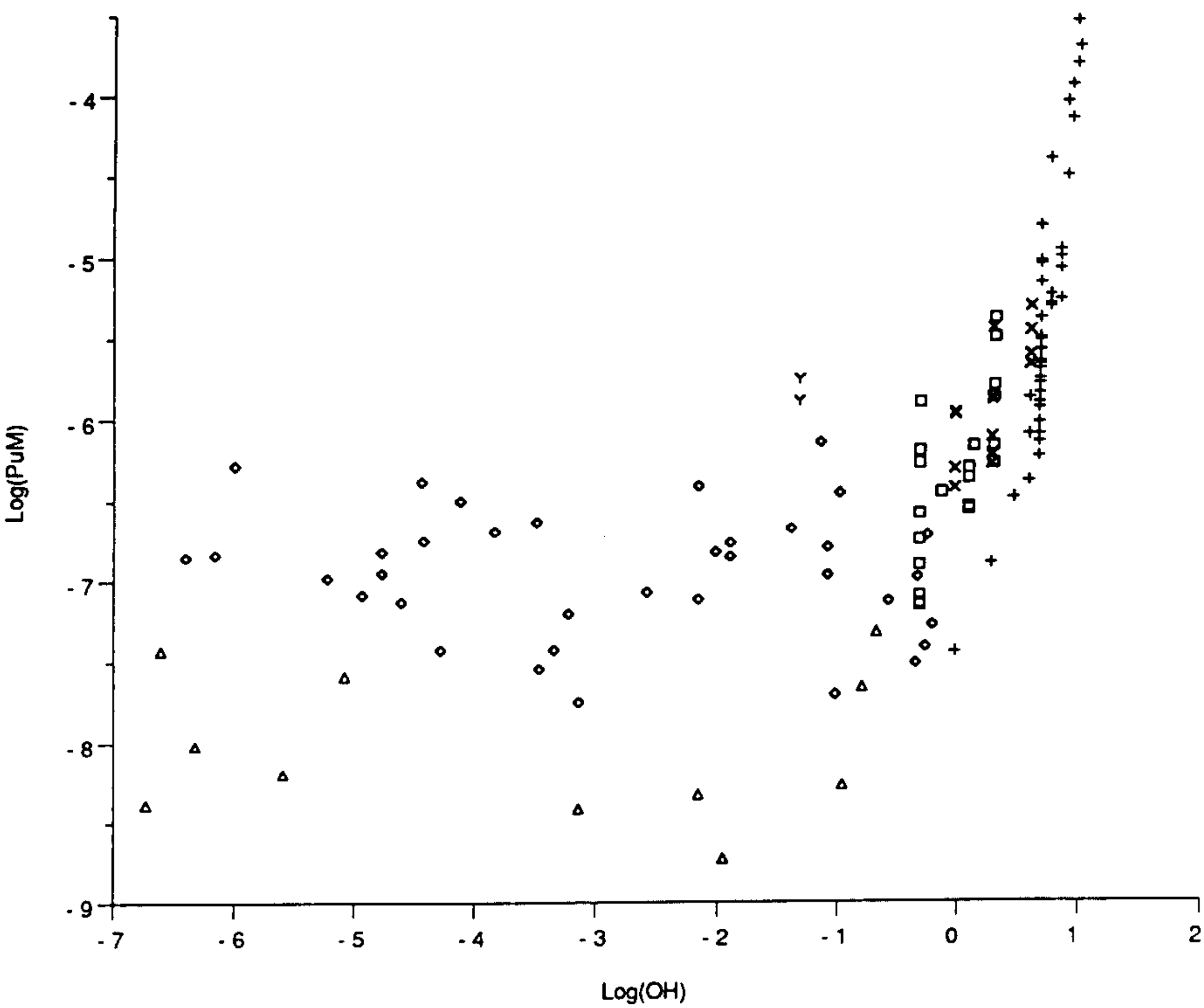
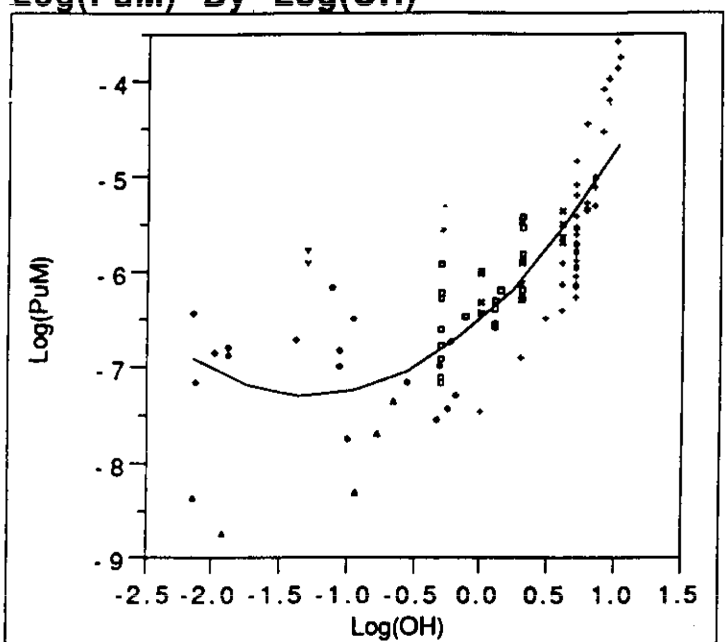


Exhibit 9: Scatter Plot and Quadratic Fit of Log_{10}[Pu M] versus Log_{10}[OH]

Log(PuM) By Log(OH)



Fitting

—— Polynomial Fit, degree=2

Polynomial Fit, degree=2

Summary of Fit

Rsquare	0.654311
Root Mean Square Error	0.578681
Mean of Response	-6.06504
Observations (or Sum Wgts)	102

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	2	62.749892	31.3749	93.6924
Error	99	33.152318	0.3349	Prob>F
C Total	101	95.902210		0.0000

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	-6.493019	0.08093	-80.23	0.0000
Log(OH)	1.2704822	0.09599	13.24	0.0000
Log(OH)^2	0.5051876	0.07794	6.48	0.0000

Exhibit 10: Quadratic Model with Prediction Limit for Plutonium Solubility for Pu Concentrations Expressed in Molar

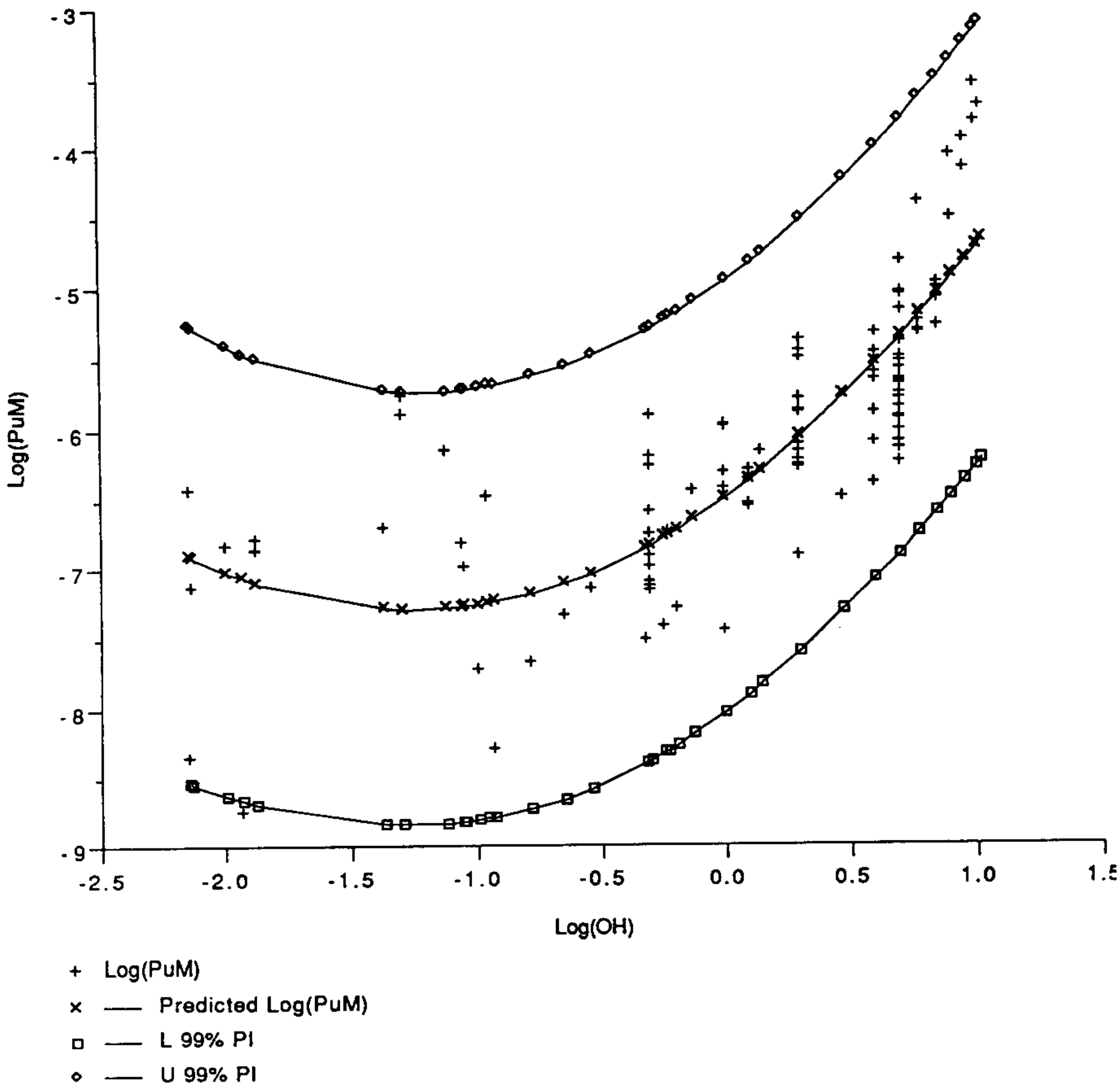
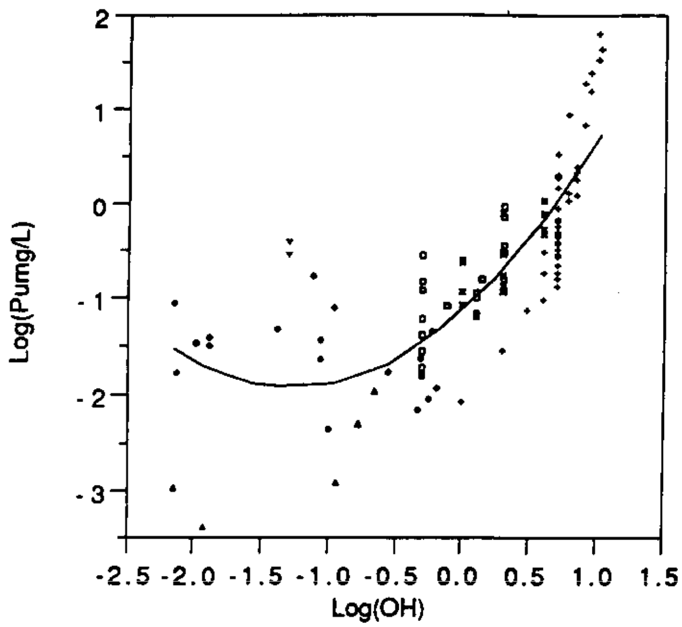


Exhibit 11: **Scatter Plot and Quadratic Fit of Log_{10}(Pu mg/L) versus Log_{10}[OH]**

Log(Pumg/L) By Log(OH)



Fitting

—— Polynomial Fit, degree=2

Polynomial Fit, degree=2

Summary of Fit

Rsquare	0.654311
Root Mean Square Error	0.578681
Mean of Response	-0.68664
Observations (or Sum Wgts)	102

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	2	62.749892	31.3749	93.6924
Error	99	33.152318	0.3349	Prob>F
C Total	101	95.902210		0.0000

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	-1.114621	0.08093	-13.77	0.0000
Log(OH)	1.2704822	0.09599	13.24	0.0000
Log(OH)^2	0.5051876	0.07794	6.48	0.0000

Exhibit 12: **Quadratic Model with Prediction Limit for Plutonium Solubility for Pu Concentrations Expressed in mg/L**

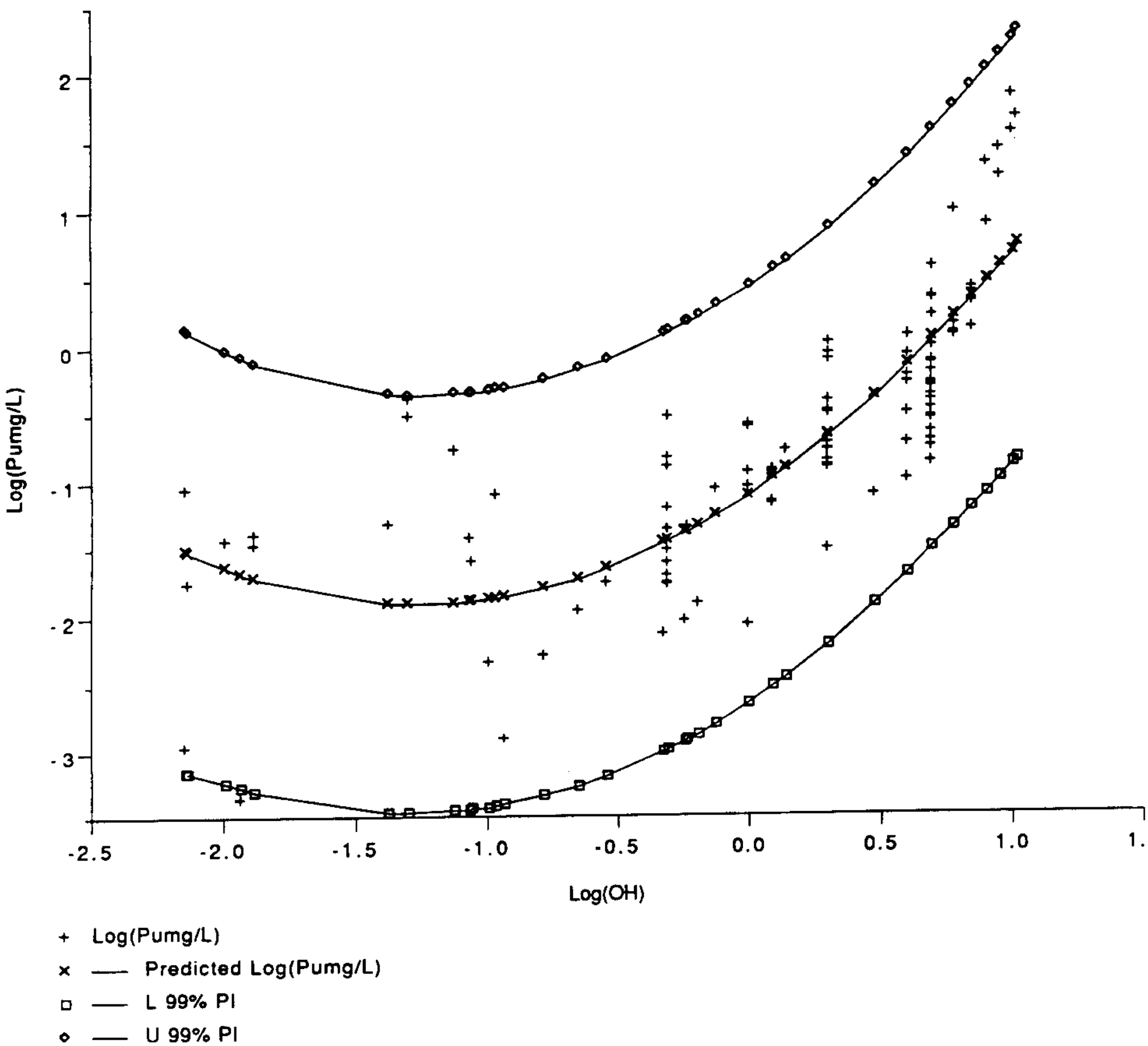


Exhibit 13: Scatter Plot of Log_{10}[Pu] versus Log_{10}[NO3]

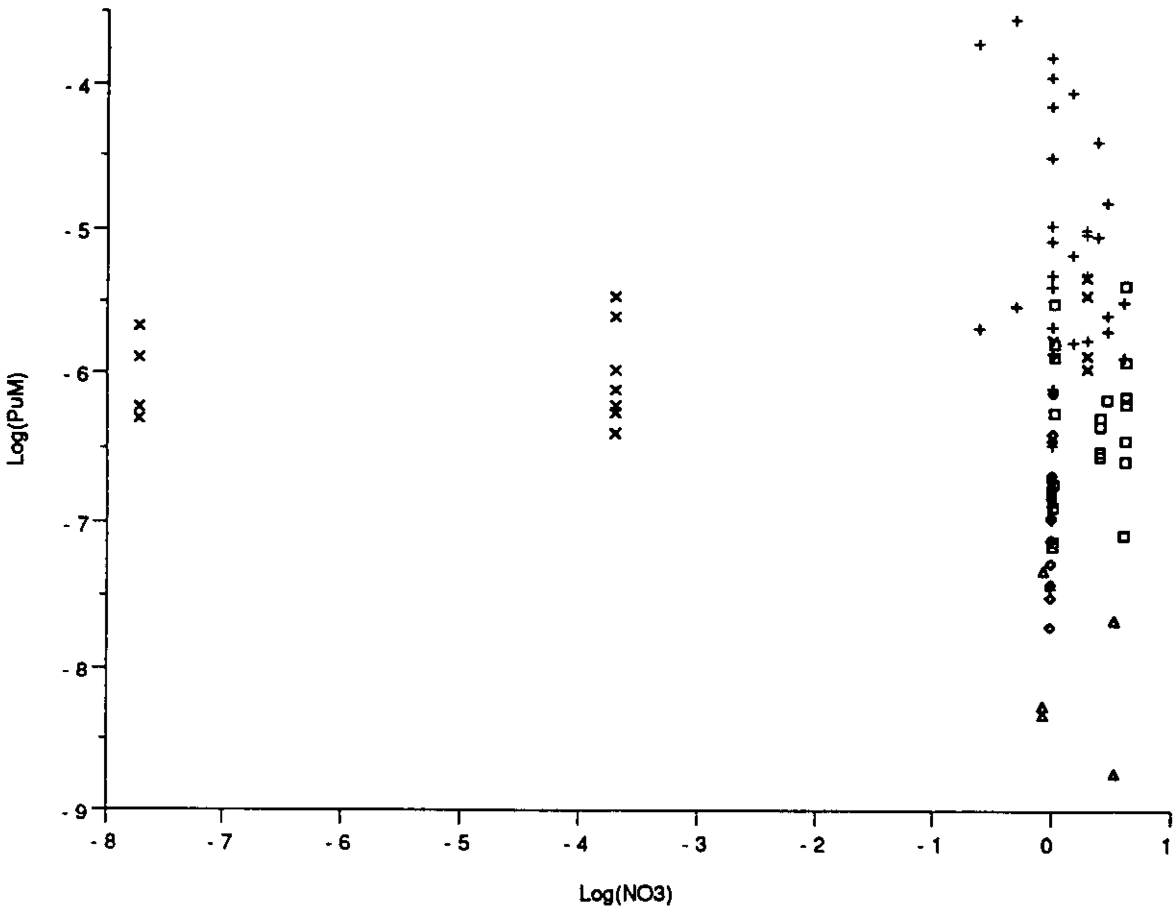


Exhibit 14: Multiple Regression Analysis With Additional Log_{10}[NO3] Term

Response: Log(PuM)

Summary of Fit

Rsquare	0.697485
Root Mean Square Error	0.566605
Mean of Response	-6.07793
Observations (or Sum Wgts)	93

Lack of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack of Fit	57	24.182616	0.424256	3.0925
Pure Error	32	4.390013	0.137188	Prob>F
Total Error	89	28.572629		0.0005

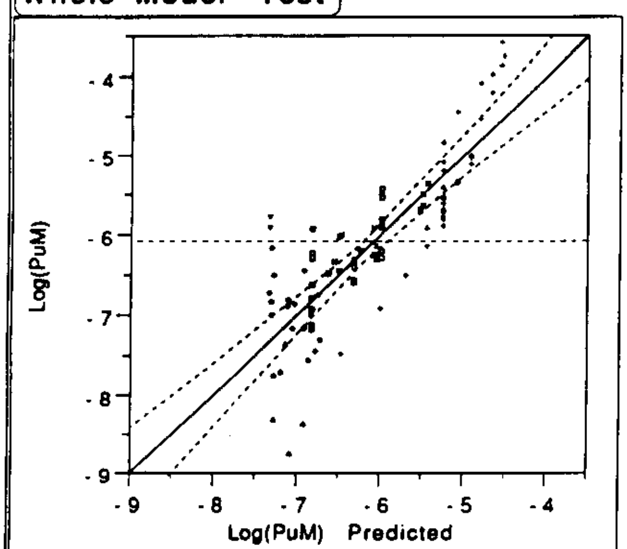
Parameter Estimates

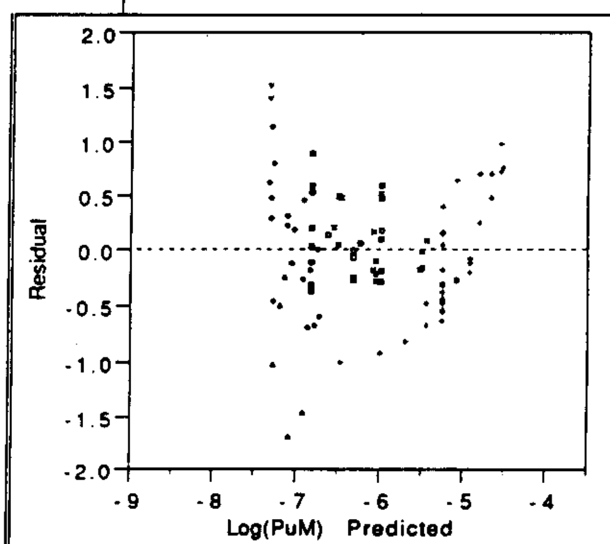
Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	-6.456402	0.08234	-78.41	0.0000
Log(NO3)	0.0098962	0.03206	0.31	0.7583
Log(OH)^1	1.364097	0.09837	13.87	0.0000
Log(OH)^2	0.5428204	0.07794	6.96	0.0000

Effect Test

Source	Nparm	DF	Sum of Squares	F Ratio	Prob>F
Log(NO3)	1	1	0.030582	0.0953	0.7583
Poly(Log(OH),2)	2	2	65.843856	102.5475	0.0000

Whole-Model Test





Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	3	65.877751	21.9593	68.4002
Error	89	28.572629	0.3210	Prob>F
C Total	92	94.450380		0.0000

Exhibit 15: Multiple Regression Analysis With Additional $Log_{10}[NO3]$ and Interaction Terms

Response: Log(PuM)

Summary of Fit

Rsquare	0.701585
Root Mean Square Error	0.56594
Mean of Response	-6.07793
Observations (or Sum Wgts)	93

Lack of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack of Fit	56	23.795372	0.424917	3.0973
Pure Error	32	4.390013	0.137188	Prob>F
Total Error	88	28.185385		0.0005

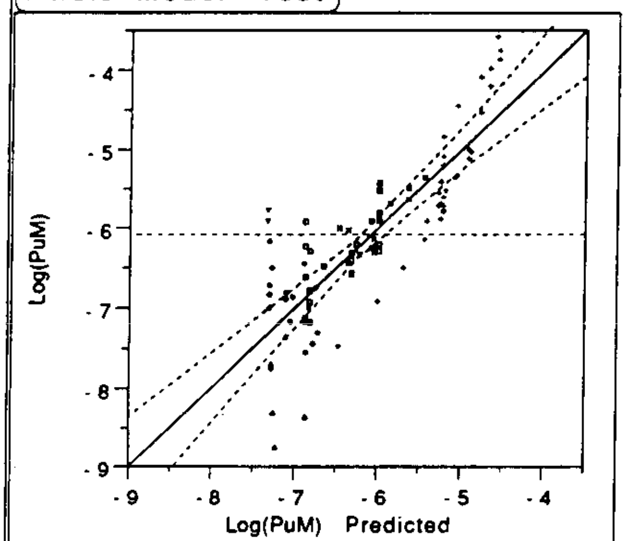
Parameter Estimates

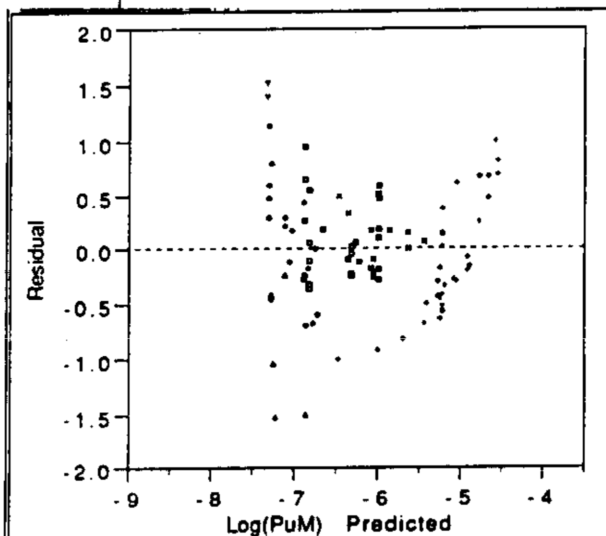
Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	-6.458377	0.08226	-78.51	0.0000
Log(OH)	1.3693884	0.09837	13.92	0.0000
Log(OH)*Log(OH)	0.5511262	0.07821	7.05	0.0000
Log(OH)*Log(NO3)	0.1441625	0.13111	1.10	0.2745
Log(NO3)	-0.033118	0.05056	-0.66	0.5141

Effect Test

Source	Nparm	DF	Sum of Squares	F Ratio	Prob>F
Log(OH)	1	1	62.067804	193.7872	0.0000
Log(OH)*Log(OH)	1	1	15.903820	49.6547	0.0000
Log(OH)*Log(NO3)	1	1	0.387244	1.2090	0.2745
Log(NO3)	1	1	0.137440	0.4291	0.5141

Whole-Model Test





Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	4	66.264995	16.5662	51.7229
Error	88	28.185385	0.3203	Prob>F
C Total	92	94.450380		0.0000

Exhibit 16: SAS Output for Quadratic Fit of $Log_{10}[Pu]$ versus $Log_{10}[OH]$

Model: MODEL1

X'X Inverse, Parameter Estimates, and SSE

	INTERCEPT	LOGOH	LOGOH2	LOGPUM
INTERCEP	0.0195567	-0.0121642	-0.0132518	6.4930190
LOGOH	-0.0121642	0.0275146	0.0152492	1.2704823
LOGOH2	-0.0132518	0.0152492	0.0181387	0.5051876
LOGPUM	-6.4930190	1.2704823	0.5051876	33.152318

Dependent Variable: LOGPUM

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Prob>F
Model	2	62.74989	31.37495	93.692	0.0001
Error	99	33.15232	0.33487		
C Total	101	95.90221			

Root MSE	0.57868	R-square	0.6543
Dep Mean	-6.06504	Adj R-sq	0.6473
C.V.	-9.54127		

Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	T for H0: Parameter=0	Prob > |T|
INTERCEP	1	-6.493019	0.08092574	-80.234	0.0001
LOGOH	1	1.270482	0.09598886	13.236	0.0001
LOGOH2	1	0.505188	0.07793679	6.482	0.0001

Covariance of Estimates

COVB	INTERCEP	LOGOH	LOGOH2
INTERCEP	0.0065489753	-0.004073432	-0.004437642
LOGOH	-0.004073432	0.0092138618	0.0051065259
LOGOH2	-0.004437642	0.0051065259	0.0060741426

7.3 Determination of Prediction Intervals

Let $\hat{y}$ represent the predicted value of $Log_{10}[Pu]$ in either M or mg/L. A 100 $(1-\alpha)$% prediction interval for $Log_{10}[Pu]$ for a given value of $Log_{10}[OH]$, say x, is given by

$$\hat{y} \quad \pm \quad t_{n-p,\alpha/2}\ s\sqrt{\left[\ 1 + (\ 1 \quad x \quad x^2\ )\ (\mathbf{X'X})^{-1} \begin{pmatrix} 1 \\ x \\ x^2 \end{pmatrix}\right]}$$

where

$t_{n-p,\alpha/2}$ is the upper $\alpha/2$ percentile of the Student's t distribution with n-p degrees of freedom where n is the number of observations (102) and p is the number of parameters in the fitted model including the intercept term (3),

s is the root mean square error term from the fitted model,

x is the salt solution's value of $Log_{10}[OH]$ for which the plutonium solubility is being predicted, and

$(\mathbf{X'X})^{-1}$ represents the inverse of the $\mathbf{X'X}$ matrix where $\mathbf{X}$ is the design matrix used in the multiple regression.

Exhibit 16 of Appendix 7.2 is an analysis similar to that of Exhibit 9 except it was completed using the SAS statistical package for the IBM/PC. The results from that analysis are used to determine the following prediction interval for $Log_{10}[Pu]$ where $\hat{y}$ is expressed in M or mg/L as desired:

$$\hat{y} \pm t_{99,\alpha/2}\ 0.5787\ \sqrt{1.0196 - 0.0122\ x + 0.0010\ x^2 - 0.0265\ x^3 + 0.0181\ x^4}$$

$$\hat{y} \pm t_{99,\alpha/2}\ \sqrt{0.3414 - 0.0081\ x + 0.0003\ x^2 - 0.0089\ x^3 + 0.0061\ x^4}$$

For $\alpha = 0.01$ with $t_{99,0.995} = 2.6264$, that is a 99% prediction interval, we have

$$\hat{y} \pm \sqrt{2.3550 - 0.0559\ x + 0.0021\ x^2 - 0.0614\ x^3 + 0.0421\ x^4}$$

7.4 Determination of Confidence Interval for Hydroxide Concentration Which Minimizes Predicted Plutonium Solubility

Let $y = Log_{10}[Pu]$ and $X = Log_{10}[OH]$. Assuming that the quadratic equation is an appropriate model over the range of hydroxide under investigate, the equation for the expected value of y, denoted by E[y], may be written as

$$E[y] = \beta_0 + \beta_1 X + \beta_2 X^2 \qquad (1)$$

Let X_{min} = the value of X which minimizes E[y]. Thus, taking the derivative of (1), setting it equal to zero, and solving for x gives

$$X_{min} = \frac{-\beta_1}{2\beta_2} \qquad (2)$$

The parameters β_1 and β_2 are unknowns which are estimated using the multiple regression approach of Exhibit 9 or Exhibit 16. Let b_1 and b_2 be the estimates for β_1 and β_2, respectively. Then X_{min} is estimated by the random variable, x_{min}, which is a function of b_1 and b_2, $f(b_1,b_2)$, given by

$$x_{min} = f(b_1,b_2) = \frac{-b_1}{2b_2} \qquad (3)$$

The variance of x_{min} is estimated using the propagation of variance technique based on the Taylor Series expansion of the function $f(b_1,b_2)$ (as described in [8]). Let the estimates of variances and covariances be denoted as follows (the values are from Exhibit 16):

Term	Description	Value
$var(x_{min})$	= estimated variance of x_{min}	(to be estimated)
$var(b_1)$	= variance of b_1	(0.00921)
$var(b_2)$	= variance of b_2	(0.00607)
$cov(b_1,b_2)$	= covariance between b_1 and b_2	(0.00511)

The estimate of the variance of x_{min} is given by

$$var(x_{min}) = \left(\frac{\partial f(b_1,b_2)}{\partial b_1}\right)^2 var(b_1) + \left(\frac{\partial f(b_1,b_2)}{\partial b_2}\right)^2 var(b_2)$$

$$+ \left(\frac{\partial f(b_1,b_2)}{\partial b_1}\right)\left(\frac{\partial f(b_1,b_2)}{\partial b_2}\right) cov(b_1,b_2)$$

where $\frac{\partial f(b_1,b_2)}{\partial b_t}$ is the partial derivative of $f(b_1,b_2)$ with respect to b_t for t=1 and 2.

Taking the partial derivations and evaluating them at the estimated parameter values of $b_1 = 1.2705$ and $b_2 = 0.5052$, yields the following equations

$$var(x_{min}) = \left(\frac{-1}{2b_2}\right)^2 var(b_1) + \left(\frac{b_1}{2b_2^2}\right)^2 var(b_2) + \left(\frac{-1}{2b_2}\right)\left(\frac{b_1}{2b_2^2}\right) cov(b_1,b_2)$$

$$var(x_{min}) = \left(\frac{-1}{1.0104}\right)^2 0.009214 + \left(\frac{1.27048}{0.51042}\right)^2 0.006074 + \left(\frac{-1}{1.0104}\right)\left(\frac{1.27048}{0.51042}\right) 0.005107$$

$$var(x_{min}) = 0.0341$$

Thus, the standard deviation of x_{min} is given by $\sqrt{0.0341} = 0.1846$ and a 2-sigma (approximately 95%) confidence interval for x_{min} is given by

$$x_{min} \pm 2\sqrt{var(x_{min})}$$

$$-1.2574 \pm 2\sqrt{0.0341}$$

$$(-1.6266, \quad -0.8882)$$

Since this is a confidence interval on $Log_{10}[OH]$, the corresponding 95% confidence interval on the value of hydroxide, in M, which minimizes the plutonium solubility is obtained by taking the antilog of the end points and is given by

$$(0.0236, \quad 0.1293)$$

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