

Solubility and Leaching Controls on Radionuclides in SDMP Wastes: Data Summary

Andrew R. Felmy
Dhanpat Rai
Virginia L. LeGore

FIRST DRAFT

Abstract

Samples of disposed wastes at three U.S. Nuclear Regulatory Commission (NRC) Site Decommissioning Management Plan (SDMP) sites were studied to determine 1) the key radionuclides and their concentrations present in the waste, 2) the solubility limits and solubility limiting phases for these radionuclides, 3) the rate of attainment of solubility equilibrium, 4) the observed leaching rate for radionuclides which may or may not be solubility controlled, and 5) identify, if possible, the potential for radiocolloid formation. In order to achieve these goals batch studies of ground or fractured samples were conducted over ranges of solution pH values (2 - 12), solid to solution ratio, and particle size. In addition, flow-through column studies were conducted on selected samples to help verify the mechanisms and predictive relations identified in the batch experiments. The results show that the major radionuclides present in the wastes were Th and U with their associated daughter products. Th daughters were in secular equilibrium with the parent Th-232 in all samples. U-238 daughters were in secular equilibrium in certain highly solidified non-porous samples but escape of Rn-222 had occurred from more porous samples perturbing the U-238 secular equilibrium. Analysis of solution phase concentrations and solid phase composition indicated that aqueous Th concentrations are solubility controlled, most likely by thoranite, $\text{ThO}_2(\text{c})$, which sets an upper limit on the dissolved Th concentrations. U also appears to be solubility controlled in certain waste samples (thoriated slags) high in pH and alkaline earth cations (Ca, Sr, Ba), upper limits on the observed solubilities apparently being set by the secondary formation of alkaline earth uranates. However, in samples composed predominately of depleted U, Chemetron samples, no solubility controlling phase was present and adsorption or ion-exchange processes appear to control the leachable U concentrations in these samples. Comparisons of filtered and unfiltered analyses of samples from flow-through columns did not show any evidence for the presence of radiocolloids. Maximum dissolved concentrations (solubility limits) and radionuclide leaching rates have been calculated for all three sites for use in performance assessment calculations.

Introduction:

The U.S. Nuclear Regulatory Commission (NRC) has identified 51 sites around the U.S. that have radionuclide contamination that exceeds NRC criteria for unrestricted use (NRC 1993). All of these sites require some degree of remediation before the sites can be released for unrestricted use. Two of the principal types of contaminants present at these sites are thoriated slags produced as byproducts from processing ferrocolumbium alloys or tin slag and depleted uranium (DU) produced during the processing of uranium hexafluoride. The thoriated slags or DU were then mixed with site material (i.e. soils, building rubble, or other wastes) and disposed either in unlined slag piles, over embankments, or by other means (NRC 1993). As a result, the NRC is currently in the process of conducting performance assessments of these sites to better ascertain the potential for radionuclides solubilization, leaching or migrate off site. As part of this overall effort, the Pacific Northwest National Laboratory (PNNL) was contracted to obtain selected samples from different SDMP sites and conduct batch and flow-through column leaching studies of these wastes to determine the radionuclides present in the waste, the maximum leachable concentrations (solubility limits) for important radionuclides, the time required for radionuclides to reach solubility equilibrium, the overall radionuclide leaching rates, and, if possible, identify the potential impact of colloids in transporting radionuclides.

This preliminary report presents the results of the PNNL studies for three selected SDMP sites: Molycorp Inc., Washington PA; Chemetron Corporation (Bert Ave.), Newburgh Heights OH, and Cabot Corporation, Reading PA. The radionuclide containing wastes at Molycorp and Cabot are principally thoriated slags produced from processing tin slag (Cabot) or producing ferrocolumbium alloys (Molycorp). The waste at the Chemetron site primarily consists of DU mixed with soil and other material. The following sections of this report describe the site sampling and sample selection, chemical analysis, radiological analysis, solubility and leaching studies, and investigations of radiocolloids.

Site Sampling and Sample Selection:

Samples from the Molycorp site were sent to PNNL following a site visit to the Washington PA site on September 27, 1996. Four samples of the disposed slags with the highest radionuclide content (~1200pCi/g) at the site were obtained. All of the samples were large pieces (~1-1.5kgs) of grayish slag with a rust and white coating. The samples from the Chemetron site were collected by the Oak Ridge Institute for Science and Education (ORISE). Five samples were received by PNNL. All samples consisted of a fine brown clay material with a consistent total U concentration (reported by ORISE)¹ varying from 14 to 39pCi/g. Samples from the Cabot site were obtained by both PNNL and NRC staff. A total of 21 samples from the site were obtained and shipped to PNNL. Preliminary gamma scans were performed on all samples and three of the samples with the highest radioactivity were selected for detailed study. These samples were 1) 2 kgs of slag pieces mixed with some soil (sample C-9), 2) a relatively small (280g) grayish green

¹Letter from Mr. Wade Adams (ORISE) to Dr. Andrew Felmy (PNNL) dated November 11, 1996.

(280g) grayish green sample of slag/ore (sample C-19), and 3) 1 kg of sandy soil mixed with pieces of slag (sample C-20).

Methods and Materials

The selected samples from the different sites were treated in the following manner

First, for the samples from Molycorp and Cabot that contained large pieces of slag it was necessary to fracture the material into smaller pieces in order to conduct column or batch studies. This fractured material is subsequently referred to as "coarse" ($2\text{mm} < \text{particle size} < 7\text{mm}$) material. In addition, samples of the fractured material were ground to a very fine size ($< 2\text{mm}$) for chemical analysis, radiological analysis, and for use in the solubility studies. The use of fine material in the solubility studies was necessary to speed the reaction rate and achieve, if possible, equilibrium between solid phase components of the samples and the solutions. Sample fracturization was not necessary for samples from the Chemetron site since this material was originally a fine particle soil-like material. Surface area analysis was conducted on both the coarse and fine material using a Micrometrics Model 2010 BET analyzer.

Following sample fracturization the materials were used in the following general manner. Samples of fine material were sent for chemical, radiological, particle size (selected samples only) analysis and were used in all solubility studies. In addition, selected samples were used "fine" batch studies to contrast the leaching characteristics of the fine and coarse material. Coarse material was used only in the batch and column studies. The following discussion provides more details on the analysis procedures and the sample preparation for the solubility, batch, and column studies.

Chemical Analysis Procedures

Total chemical analysis of solid materials was performed by energy dispersive x-ray fluorescence (EDXRF) with low (ppm) detection limits for most elements from Al to Ce. Chemical analysis of solutions was performed by inductively coupled plasma spectroscopy (ICP) analysis, except for samples with low concentrations of Th, U, or Nb, which were determined by inductively coupled plasma mass spectrometry (ICP-MS). Selected samples for anion analysis were also conducted using a model 4000i Dionex ion chromatograph.

Radiological Analysis

Radiological analysis of solid and solution samples were conducted using a high-efficiency intrinsic Germanium detector calibrated over the energy range 60 to 2000 keV. The following energy peaks was used to determine the radionuclide concentrations: Ac-228, 911 keV; Bi-212, 727 keV; Pb-212, 239 keV; Ra-226, 186 keV; Bi-214, 609 keV; Pb-214, 352 keV; Th-234, 62.3 keV. All analyses were performed on duplicate or triplicate samples. The Ra-226 values reported for the Molycorp site were corrected by a factor of 0.57 to account for the coincident natural U-235 peak.

Results and Discussion

Chemical Analysis

The total chemical analysis of the soil and slag samples at all three sites, Tables 1 and 2, show a bulk composition dominated by Al, Si, and Ca characteristic of aluminosilicate minerals or calcium aluminosilicate minerals with significant amounts of Fe and, with the exception of Chemetron, significant amounts of Nb. The presence of high concentrations of Nb, and to a lesser extent Ta, at least the Cabot site, being a clear indication of materials originating from the ferro-columbium smelting process. Also, of interest is the presence of significant amounts of Zr in Cabot samples which is correlated with the presence of zirconate minerals (L. Veblen personal communication) and a relatively high Mo content in slags from Molycorp.

The element in highest concentration with radioactive isotopes is Th. Th occurs in significant concentration in all samples, as high as 1.4% in Molycorp samples. The only exception being the Chemetron samples which have a higher U content than Th content. The concentration of U is fairly uniform in all samples averaging approximately 200ppm, though as we will show, the chemical form and leachability of the U differs significantly between the different materials.

Radiological Analysis

Radiological analyses of site materials yields the isotopic composition of the radioactive elements. Such analyses are important not only for more detailed analyses of possible health effects but also the relative ratios of the various isotopes yields important information on isotopic separation processes that may have occurred at the site. This information is key to understanding the site history and waste disposal practices at the site.

The ferrocolumbian slag at Molycorp contains about 1.3% Th-232 (Table 1 and 3) and is in secular equilibrium with all of its daughter products (see Table 3). The U-238 appears to be in secular equilibrium with Ra-226 but not with the Ra-226 daughters, presumably as a result of the continuous escape of Rn-222 gas since disposal. These facts indicate the slags have a certain porous structure that allows escape of the Rn-222. This fact contrasts sharply with the results for the Cabot slags, described below, where do not show such a porous structure.

The Chemetron samples showed only the Th-234 peak (first daughter of U-238) at a very low level. There are no signs at all of any other daughter products of the U-238 or U-235 decay chains. Thus this sample seems to say U was very cleanly separated from its daughters at some time in the past and only the U ended up getting mixed with the waste. This is in agreement with the site characterization report (Koh and Associates 1995) which shows that much of the U originates from depleted uranium disposed at the site. There was no signs of natural Th-232 or its daughters in this sample.

Solubility and Batch Studies

Solubility and batch studies were conducted in a controlled atmosphere chamber under an atmosphere of ultrapure argon. Solubility studies were conducted over a broad range of pH values extending from approximately 1 to 12 depending upon the specific samples examined. The batch studies were conducted at the "natural" pH of the sample which varied with reaction time as the samples dissolved. Both fine and coarse material was used in the batch experiments. All of the fine batch and solubility suspensions were prepared in the following manner. For each site sample a solid/solution suspension was prepared by placing approximately one gram of fine material in 30ml of deionized water in each 50ml centrifuge tube. Approximately 24 such suspensions were prepared for each sample in the solubility studies. Each sample was independently adjusted to a different pH value within the prescribed range using reagent grade HCl or NaOH. The batch samples were prepared in the same manner but only two suspensions (duplicates) were prepared for each site sample. All suspensions were then placed on an orbital shaker and shaken until sampling. Sampling of the solubility and batch suspensions consisted of pH measurements followed by centrifugation at 2000 x g for 7 to 10 min. A sample of the supernatant was then filtered through Amicon type F-25 Centriflo membrane cones with effective 2500-molecular-weight cutoffs and approximately 0.0018- μm pore sizes. The membrane were pretreated by washing with pH adjusted deionized water (to the approximate pH of the sample) followed by filtration of a 0.5 ml to 1.0 ml aliquot of sample to saturate any adsorption sites. The aliquot of the sample was then discarded. This pretreatment process was then followed by filtration of approximately 5ml of sample. Approximately 1ml of this sample was then withdrawn and acidified for ICP or ICP-MS and radiological analysis. The remaining unacidified sample was retained for anion analysis by IC.

The coarse batch studies were conducted in the identical manner to the fine batch studies except that approximately 6g of sample were added to 180ml of deionized water in 500ml polypropylene bottles. This procedure maintained the same solid/solution ratio as in the fine batch but allowed more particles of the larger material to be included in each sample.

Column Studies

Flow through column experiments were conducted using 32ml Savelex® teflon columns, Figure 1, connected to 3M modular infusion pumps operating at a flow rate of 0.1 ml/hr. Porous frits were placed at the top and bottom of each column to prevent any fine suspended material from passing through the column. The solutions entered the columns through the bottom and passed out the top into a sealed collection bottle. Samples from the collection bottle were taken, pH measurements made, and filtered as described for solubility and batch studies. Filtrates were split into acidified and unacidified aliquots for analysis by ICP or ICP-MS and IC. Radiological analysis was also performed on acidified samples.

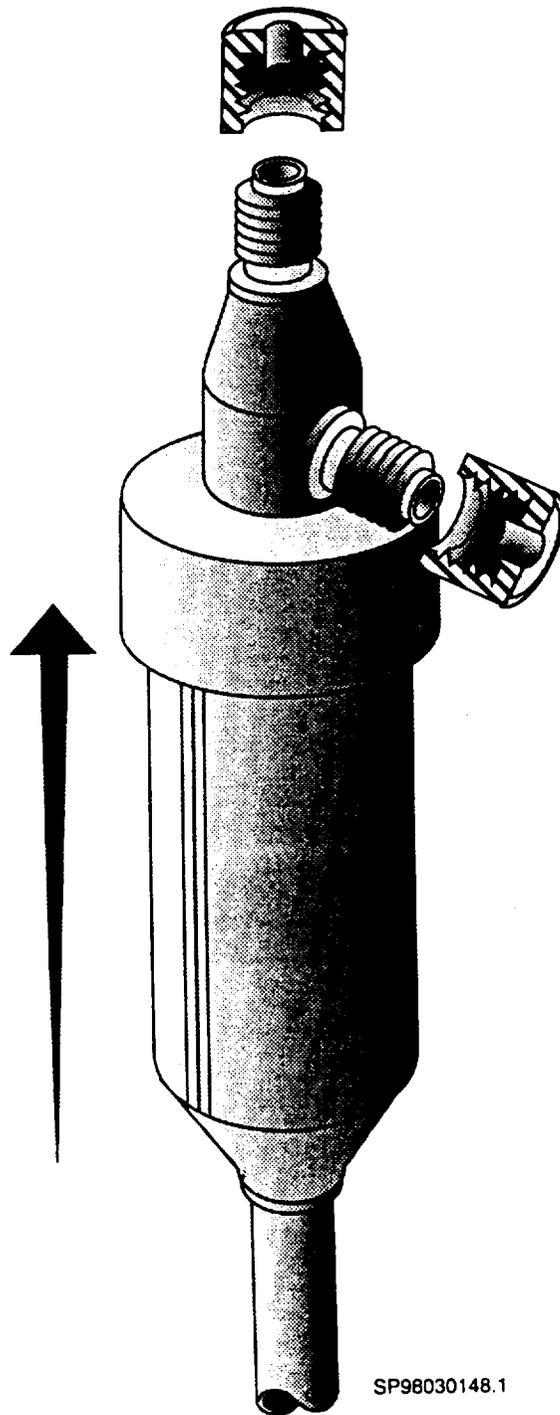


Figure 1. Schematic of Column Apparatus

Results and Discussion

Chemical Analysis

The total chemical analysis of the soil and slag samples at all three sites, Tables 1 and 2, show a bulk composition dominated by Al, Si, and Ca characteristic of aluminosilicate minerals or calcium aluminosilicate minerals with significant amounts of Fe and, with the exception of Chemetron, significant amounts of Nb. The presence of high concentrations of Nb, and to a lesser extent Ta, at least the Cabot site, being a clear indication of materials originating from the ferro-columbium smelting process. Also, of interest is the presence of significant amounts of Zr in Cabot samples which is correlated with the presence of zirconate minerals (L. Veblen personal communication) and a relatively high Mo content in slags from Molycorp.

The element in highest concentration with radioactive isotopes is Th. Th occurs in significant concentration in all samples, as high as 1.4% in Molycorp samples. The only exception being the Chemetron samples which have a higher U content than Th content. The concentration of U is fairly uniform in all samples averaging approximately 200ppm, though as we will show, the chemical form and leachability of the U differs significantly between the different materials.

Radiological Analysis

Radiological analyses of site materials yields the isotopic composition of the radioactive elements. Such analyses are important not only for more detailed analyses of possible health effects but also the relative ratios of the various isotopes yields important information on isotopic separation processes that may have occurred at the site. This information is key to understanding the site history and waste disposal practices at the site.

The ferrocolumbian slag at Molycorp contains about 1.3% Th-232 (Table 1 and 3) and is in secular equilibrium with all of its daughter products (see Table 3). The U-238 appears to be in secular equilibrium with Ra-226 but not with the Ra-226 daughters, presumably as a result of the continuous escape of Rn-222 gas since disposal. These facts indicate the slags have a certain porous structure that allows escape of the Rn-222. This fact contrasts sharply with the results for the Cabot slags, described below, which do not show such a porous structure.

The Chemetron samples showed only the Th-234 peak (first daughter of U-238) at a very low level. There are no signs at all of any other daughter products of the U-238 or U-235 decay chains. Thus this sample seems to say U was very cleanly separated from its daughters at some time in the past and only the U ended up getting mixed with the waste. This is in agreement with the site characterization report (Koh and Associates 1995) which shows that much of the U originates from depleted uranium disposed at the site. There was no signs of natural Th-232 or its daughters in this sample.

Table 1. Chemical composition of slags at Molycorp and the highest activity sample at Chemetron

Element (ppm)	Molycorp Slag 1	Molycorp Slag 2	Molycorp Slag 3	Molycorp Slag 4	Chemetron Slag 1
Al	200000±17000	192000±17000	234000±19000	229000±1800	56100±6200
Si	88800±7400	928000±7900	86100±7500	90400±7600	258000±1,000
K	1110±160	1450±180	1050±170	1130±160	20000±1400
Ca	75700±5300	85100±6000	85100±6000	82200±5800	13970±1000
Mn	840±160	950±180	690±170	660±160	460±71
Fe	27300±1900	31200±2200	26000±1900	26700±1900	42700±3000
Ni	<57±57	<64±64	<64±64	<57±57	608±52
Cu	218±34	250±39	223±36	436±47	177±20
Zn	66±20	84±23	<38±38	103±20	241±22
Ga	<32±32	<34±34	<35±35	<32±32	214±57
Hg	<23±23	<24±24	<21±21	<22±22	<73±73
Se	<35±35	<33±33	<35±35	<33±33	<55±55
Br	<18±18	<17±17	<17±17	<17±17	<57±57
Rb	<19±19	<18±18	<18±18	<18±18	1009±91
U	248±22	218±20	230±21	262±23	65.2±8.5
Sr	169±28	330±25	382±28	372±28	118.4±9.4
Y	68±11	67.3±10	64±10	76±11	31±3.9
Nb	27500±1900	23600±1700	26900±1900	26800±1900	75.6±6.5
Mo	2980±210	3530±250	2260±160	2460±170	21.5±1.1
Th	13290±940	12060±850	14190±1000	13760±970	28±10

Table 2. Chemical composition of Slag A (96T-C-9), Grayish Green Ore (96T-C-19), and Soil site B5 (96T-C-20) at Cabot.

Element (ppm)	Cabot Slag A	Cabot Ore	Cabot Soil B5	Cabot Ore 96-T-C-21
Al	45000±3900	315000±23000	543000±5000	95200±7400
Si	337000±24000	119400±8700	281000±20000	164000±12000
P	<1500±1500	<2900±2900	<2600±2600	
Cl	<110±110	<250±250	<190±190	<260±260
K	6500±460	3640±270	6200±450	1510±140
Ca	26500±1900	137500±9600	98900±6900	217000±15000
Ti	8270±580	19800±1400	25700±1800	66000±4600
Mn	2420±180	2270±190	5600±410	5070±380
Fe	59400±4200	26500±1900	91700±6400	13730±970
Ni	71±15	82±24	77±32	<53±53
Ta	1230±100	5070±360	7750±560	12130±860
Pb	461±34	28100±2000	1600±110	<28±28
As	280±22	1062±92	616±48	
U	75.8±6	243±18	213±16	26400
Th	364±27	2240±160	1108±79	76±11
Sr	125±9	144±11	165±12	26800±1900
Y	274±19	1312±92	849±60	2460±190
Zr	4070±290	15600±1100	11740±820	23600±1600
Nb	3860±270	7120±500	13290±930	8050±560
Mo	<7.0±7	<16±16	<28.7±7.3	<18±18
W	803±67	191±63	2330±190	1970±150
S	1290±200	2060±610	1110±33	
Cd	26±10	66.9±9	<17±8.2	<8.7±8.7
Sn	1059±76	1490±110	1970±140	205±12
Sb	<23±23	931±66	183±16	<11±11
Ba	402±41	197±28	243±31	<48±48
La	598±61	2690±200	1600±120	3220±170
Ce	1540±130	6340±450	3970±290	7370±380

Table 3. Radiological analysis of slags at Molycorp and the highest activity soil sample at Chemetron. All analyses represent the average of three subsamples of each slag. Values in pCi/g.

Nuclide	Molycorp Slag 1	Molycorp Slag 2	Molycorp Slag 3	Molycorp Slag 4	Chemetron Soil 1
Th Series	(1460)	(1330)	(1560)	(1510)	
Ac-228	1,270	1,100	1,360	1,250	
Bi-212	1,530	1,310	1,610	1,510	
Pb-212	1,390	1,200	1,490	1,370	
Ra-224	1,440	1,300	1,500	1,390	
Th-228	1,190	980	1,200	1,200	
U-238 Series	(80)	(70)	(75)	(85)	(20)
Ra-226	90	75	90	80	
Bi-214	40	45	35	40	
Pb-214	45	45	40	45	
Th-234					30 ± 10
U-235 Series	**				

** Uranium values are close to detection limit and because of interferences are hard to quantify with the counting system. Values in parenthesis are calculated from the XRF data for thorium and uranium assuming all of the Th is Th-232 and all of the U is U-238.

In the case of Cabot samples (Table 4), all four samples have Th-232 and U-238 in secular equilibrium with all their daughter products. Apparently the processing conditions at the Cabot site did not result in the separation of the U-238 daughters. In addition, unlike at Molycorp, the Ra-226 daughters are in secular equilibrium, indicating only negligible escape of Rn-222 has occurred since disposal. This is apparently related to the refractory nature and low permeability of the Cabot slag samples.

Solubility, Batch Leaching, and Column Studies

Molycorp-Th

The solubility data for Th at Molycorp show very low solubilities except at low pH values (< 5) where the solubilities increase rapidly (Figure 2). A comparison of these solubility data with the calculated solubilities for possible Th solid phases, solid and dashed lines in figure 1, show that the aqueous Th concentrations are most likely controlled by thorianite ($\text{ThO}_2(\text{c})$) or possibly, at very low pH a Th-silicate (i.e. $\text{ThSiO}_4(\text{gl})$). Mineralogical analysis of these samples, L. Veblen personal communication, show the presence of some thorianite. The presence of this phase lends credence to the possibility that this phase is the primary solubility control. If a $\text{ThSiO}_4(\text{gl})$ phase does form it is most likely a secondary phase precipitated as a result of the dissolution of large concentrations (> 200mg/l) of Si at low pH. The difference in observed solubility between the thorianite solubility at the somewhat higher observed solubilities between pH 4 and 5 also indicates the presence of a small amount of amorphous $\text{ThO}_2(\text{am})$. In any event, the Th concentrations in Molycorp samples appear to be solubility limited, either by $\text{ThSiO}_4(\text{gl})$ at very low pH, $\text{ThO}_2(\text{c})$, or by trace amounts of $\text{ThO}_2(\text{am})$, and show very low solubilities over a broad range of pH values.

The batch leaching data for Molycorp samples show that the slag materials tend to buffer the solution pH values in the alkaline region (> 10, see Table 5). Although we cannot be sure, these high pH values are most likely related to the dissolution of alkaline earth compounds containing either Ca or Ba that are present in these samples. As seen from the solubility data, these high pH values are expected to maintain the dissolved Th concentrations at very low levels. The observed Th concentrations in the batch leaching studies, Figure 3, follow this expected trend. Th concentrations are uniformly low in both the coarse and fine material with maximum concentrations about $10^{-7.5}\text{M}$ ($3.2 \times 10^{-8}\text{M}$). As expected, if a solubility controlling solid was present, there is no clear differences between coarse and fine material (i.e. no surface area or particle size effect).

The pH values in the column experiments, Table 6, show a trend of much lower values than in the batch experiments. This results from the leakage of small amounts of atmospheric CO_2 into the sampling bottle during the duration of the column study. However these pH values also fall

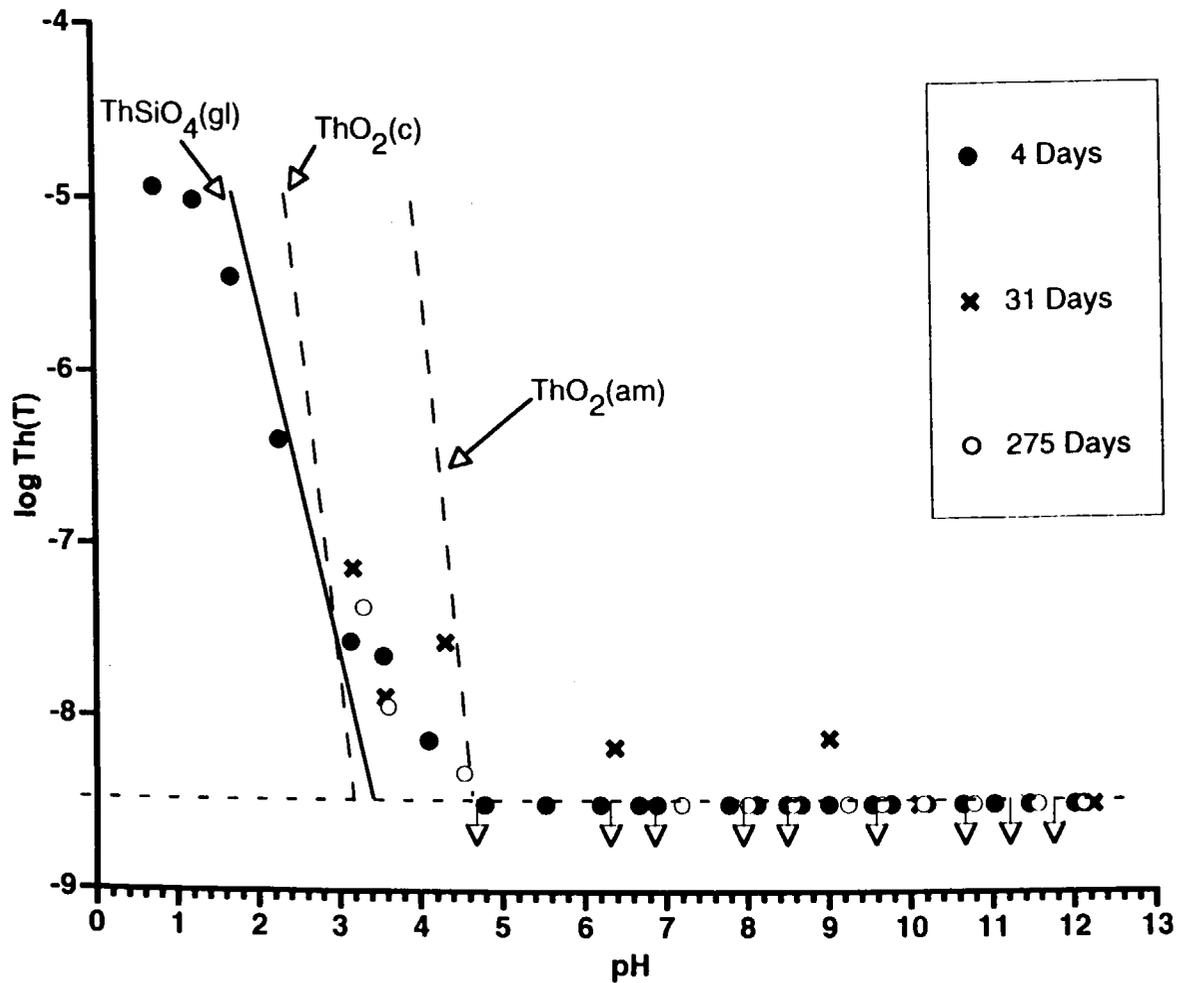


Figure 2. Th concentrations in Molycorp Solubility Studies.

Table 4. Radiological analysis of Cabot samples. Slag A(96T-C-9), Grayish Green Ore(96T-C-19). Soil Site B5(96T-C-20), and Ore (96T-C-21). Results in pCi/g.

Nuclide	Cabot Slag A	Cabot Ore	Cabot Soil B5	Cabot 96T-C-21 Ore
Th Series	(40)	(246)	(120)	(262)
Ac-228	43	176	97	246
Bi-212	49	197	112	266
Pb-212	42	160	100	238
U-238 Series	(25)	(80)	(70)	(123)
Ra-226	33	121	78	180
Bi-214	27	101	63	192
Pb-214	29	111	70	210
Th-234				140
U-235 Series	**			

** Uranium values are close to detection limit and because of interferences are hard to quantify with the counting system. Values in parenthesis are calculated from the XRF data for thorium and uranium assuming all of the Th is Th-232 and all of the U is U-238.

Table 4. Radiological analysis of Cabot samples. Slag A(96T-C-9), Grayish Green Ore(96T-C-19), Soil Site B5(96T-C-20), and Ore (96T-C-21). Results in pCi/g.

Nuclide	Cabot Slag A	Cabot Ore	Cabot Soil B5	Cabot 96T-C-21 Ore
Th Series	(40)	(246)	(120)	(262)
Ac-228	43	176	97	246
Bi-212	49	197	112	266
Pb-212	42	160	100	238
U-238 Series	(25)	(80)	(70)	(123)
Ra-226	33	121	78	180
Bi-214	27	101	63	192
Pb-214	29	111	70	210
Th-234				140
U-235 Series	**			

** Uranium values are close to detection limit and because of interferences are hard to quantify with the counting system. Values in parenthesis are calculated from the XRF data for thorium and uranium assuming all of the Th is Th-232 and all of the U is U-238.

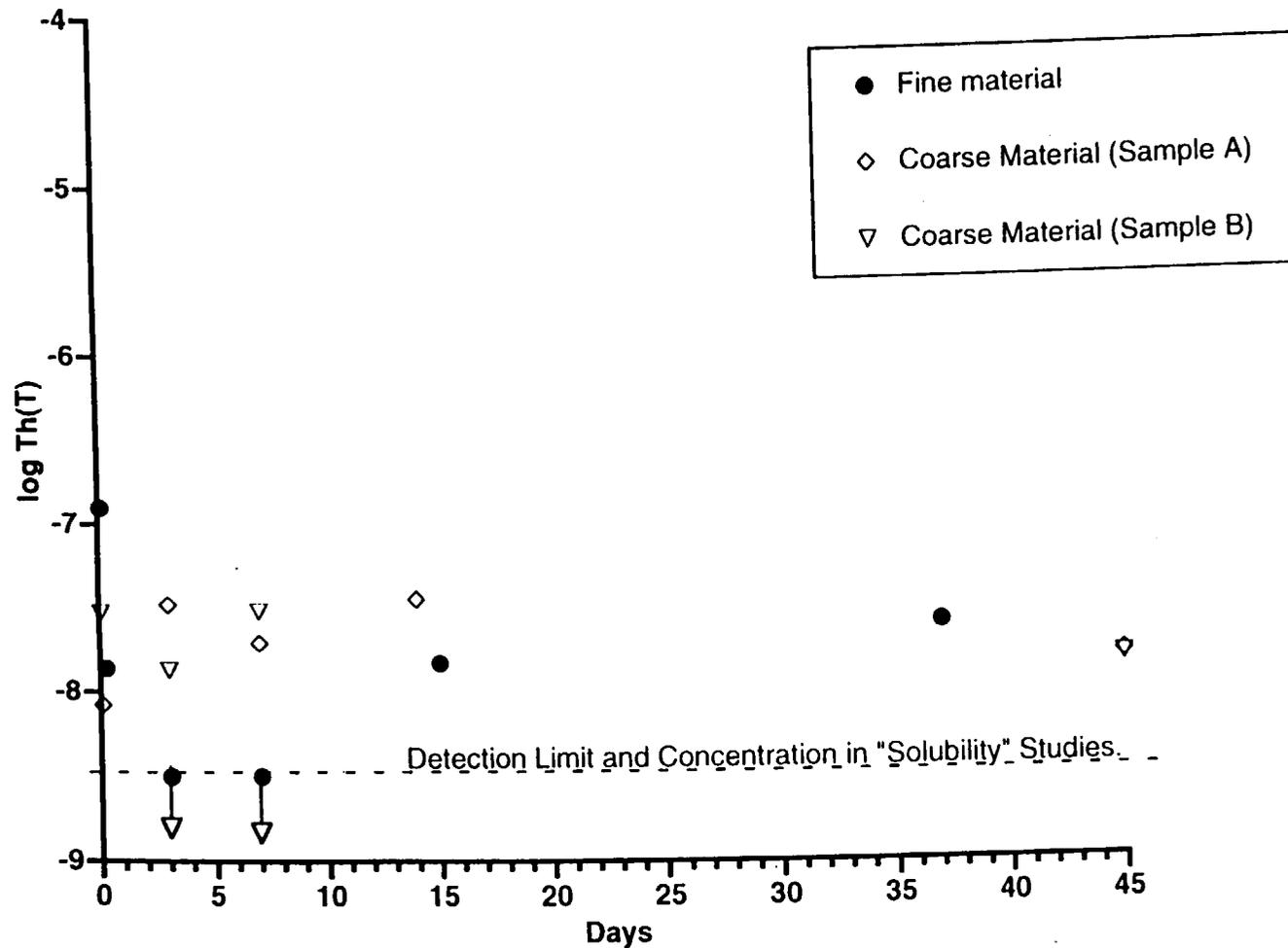


Figure 3. Th Concentrations in Molycorp Batch Leaching Studies.

Table 5. Measured pH values in batch leaching studies as a function of time.

Leaching Time	Molycorp Fine Material	Molycorp Coarse Material	Chemetron
2 hrs.	9.39	7.62	8.57
6 hrs.	9.75		8.57
3 days	10.15	10.33	8.53
7 days	10.45	10.33	8.81
15 days	10.31	9.84	8.57
37 days	10.23		8.55
45 days		10.66	

Table 6. Measured pH values in column studies as a function of time.

Leaching Time	Molycorp	Chemetron
4 days	7.96	
5 days		8.23
8 days		8.21
11 days	7.64	
30 days	8.22	8.43
72 days	8.38	
78 days		8.29

in the low solubility region, see Figure 2. The observed Th concentrations in the column experiments, Figure 4, follow this expected trend with all of the Th concentrations all at or below the analytical detection limit of approximately $10^{-8.5}$ M.

In summary, the aqueous Th concentrations in the Molycorp samples are solubility controlled either by $\text{ThO}_2(\text{c})$, $\text{ThO}_2(\text{am})$, or at very low pH, ThSiO_4 . The presence of a solubility limiting phase results in the leachable Th concentrations being independent of total sample particle size or surface area. The apparent rapid dissolution of the solubility limiting phase(s) results in consistent results between the solubility, batch, and column studies. The solubility controlling solid phases for Th are all very insoluble at pH values > 5 .

Molycorp - U

Uranium, even if present as insoluble U(IV) solid phases, is easily oxidized in solution to U(VI). The majority of U(VI) containing solid phases (Krupka and Serne) are highly soluble ($> 10^{-6}$ M). One of the major exceptions to this rule of insoluble U(VI) phases is in solutions of high pH, low carbonate, and high concentrations of alkaline earth cations. These solutions result in the precipitation of insoluble alkaline earth uranates {i.e. strontium uranate ($\text{SrUO}_4(\text{c})$), or becquerelite ($\text{CaU}_6\text{O}_{19} \cdot 11\text{H}_2\text{O}$)}. These are precisely the conditions found for the Molycorp samples, Table 5 and Figure 5. As a result, such phases, particularly the calcium uranates could limit U(VI) solubilities at the Molycorp site. Unfortunately, experimental data on the solubility of these phases is very limited. As a result, in another task of this project, the solubility of becquerelite was measured over a broad range of pH values and dissolved Ca concentrations. Details on these studies will be reported in a subsequent report, however a summary of the results is presented in Figure 6. Interestingly, these data show that solid phases such as becquerelite can maintain quite low (10^{-7} M) dissolved U(VI) concentrations at the high pH and dissolved Ca concentrations that could occur at the Molycorp site. The actual solubility data for U in samples from the Molycorp site, Figure 7, show quite low solubilities across the entire pH range. Although these concentrations are obviously not limited by becquerelite at low pH values, the solubilities at higher pH (>8) could be limited by the solubility of such phases.

The batch leaching data for U also show low dissolved concentrations (Figure 8) with some difference between fine and coarse material. The "solubility" data at the same pH appearing to be intermediate between the fine and coarse batch results. The differences do not appear to be due to differences in Ca concentrations which are very consistent between the coarse batch, fine batch, and solubility studies (i.e. 100 - 120mg/l as Ca). The results for the column studies, Figure 9, also show quite low solubilities and are in excellent agreement with the coarse batch studies.

In summary, although the solubility controlling mechanism for U in the Molycorp samples is not precisely known, the fact that the U concentrations are relatively low is not entirely unexpected for these high pH, low carbonate, high alkaline earth solutions. The solubilities can be limited by becquerelite at high pH values. The dissolved concentrations of U are consistent between the coarse batch and the column studies which allows useful calculations to be made on solubility and leaching rates (see below).

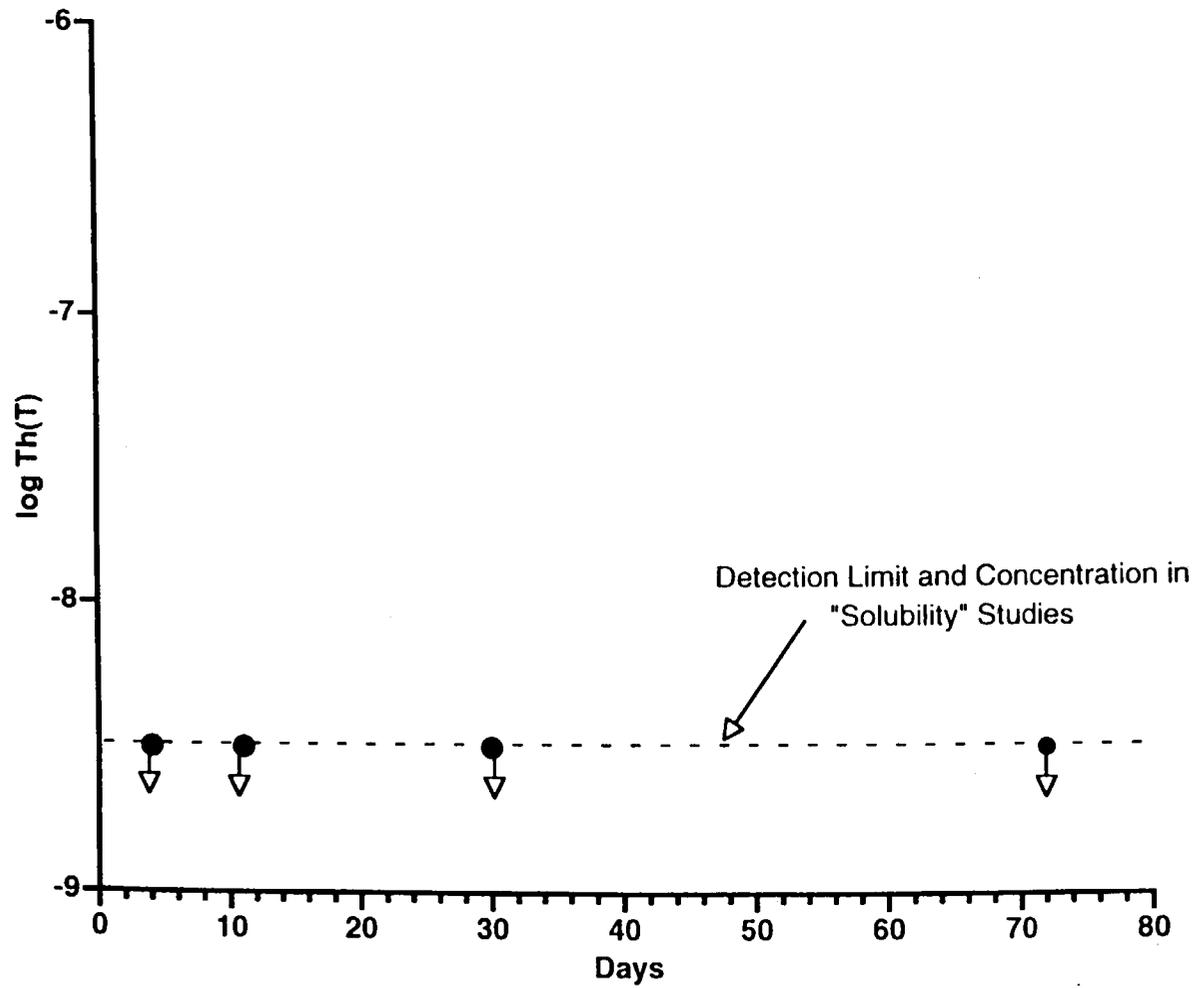


Figure 4. Th Concentrations in Molycorp Column Studies.

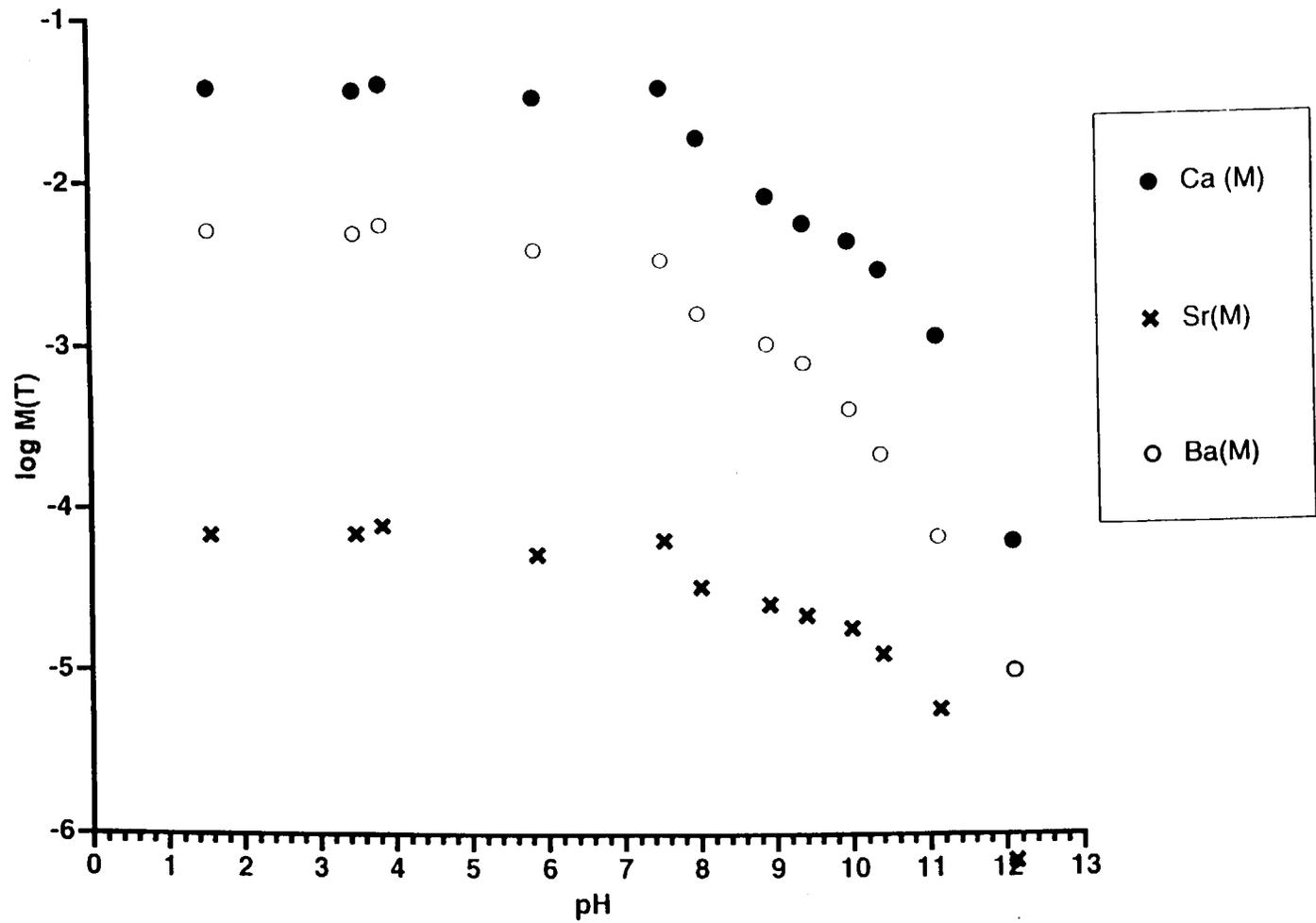


Figure 5. Alkaline Earth Cation Solubilities in Molycorp Samples.

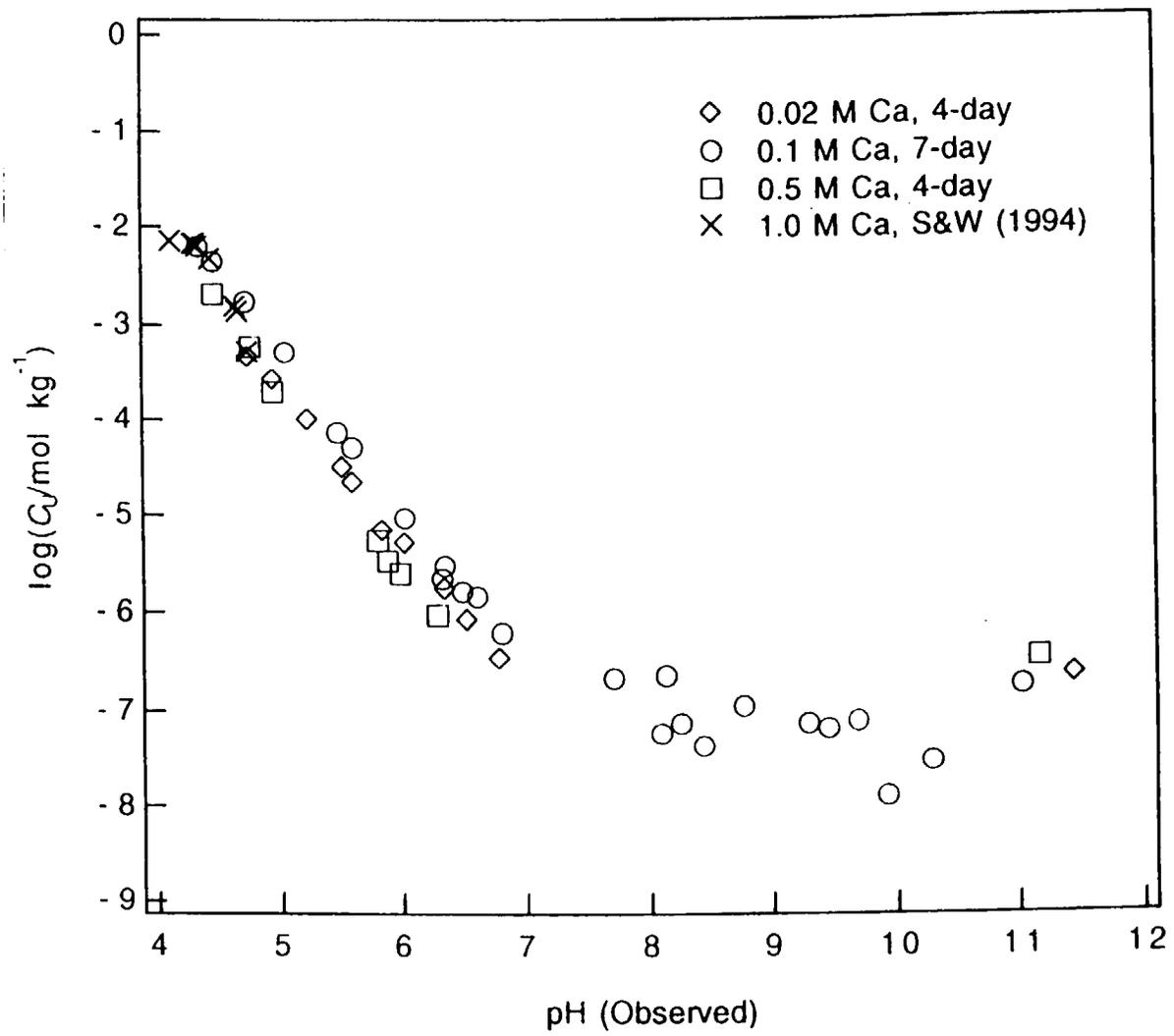


Figure 6. Becquerelite Solubility Data.

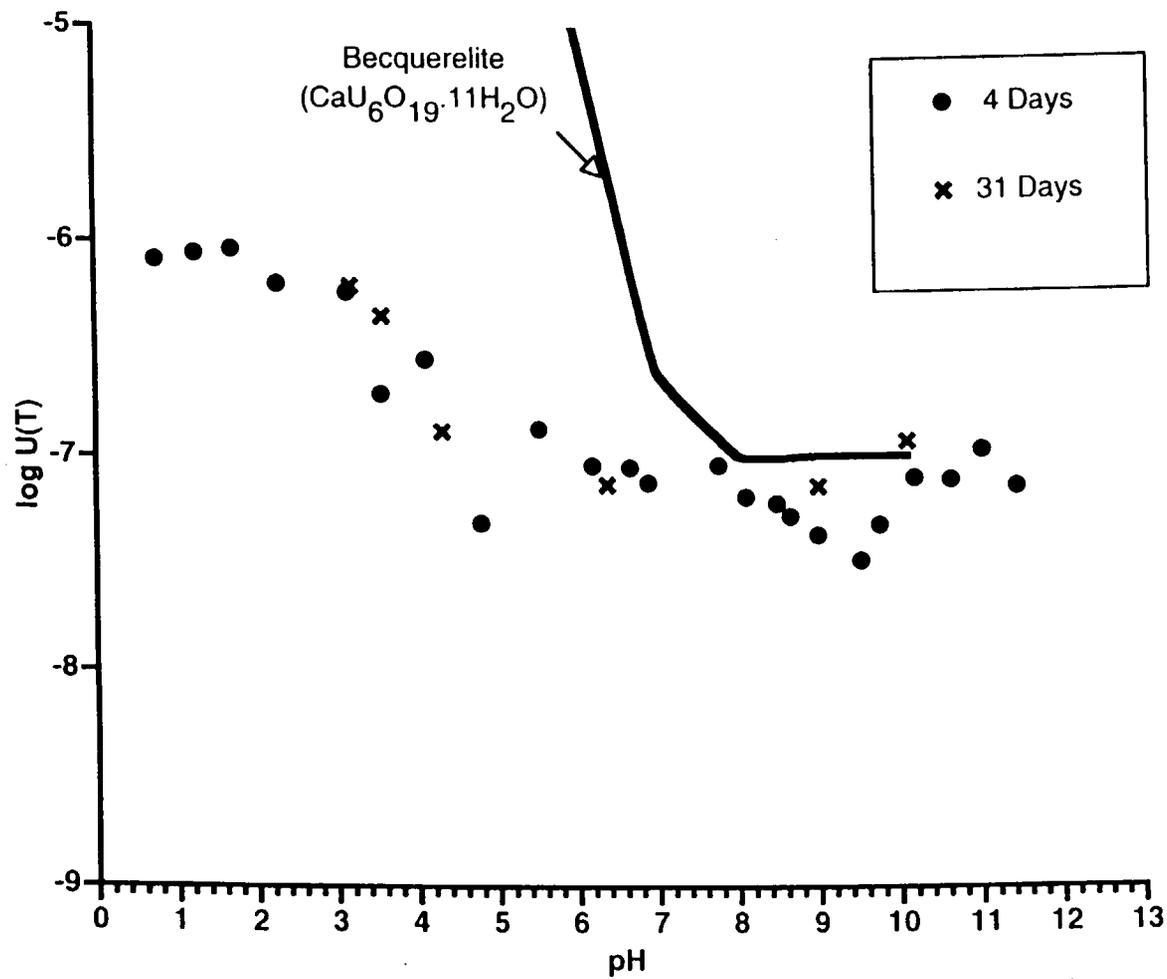


Figure 7. U Concentrations in Molycorp Solubility Studies.

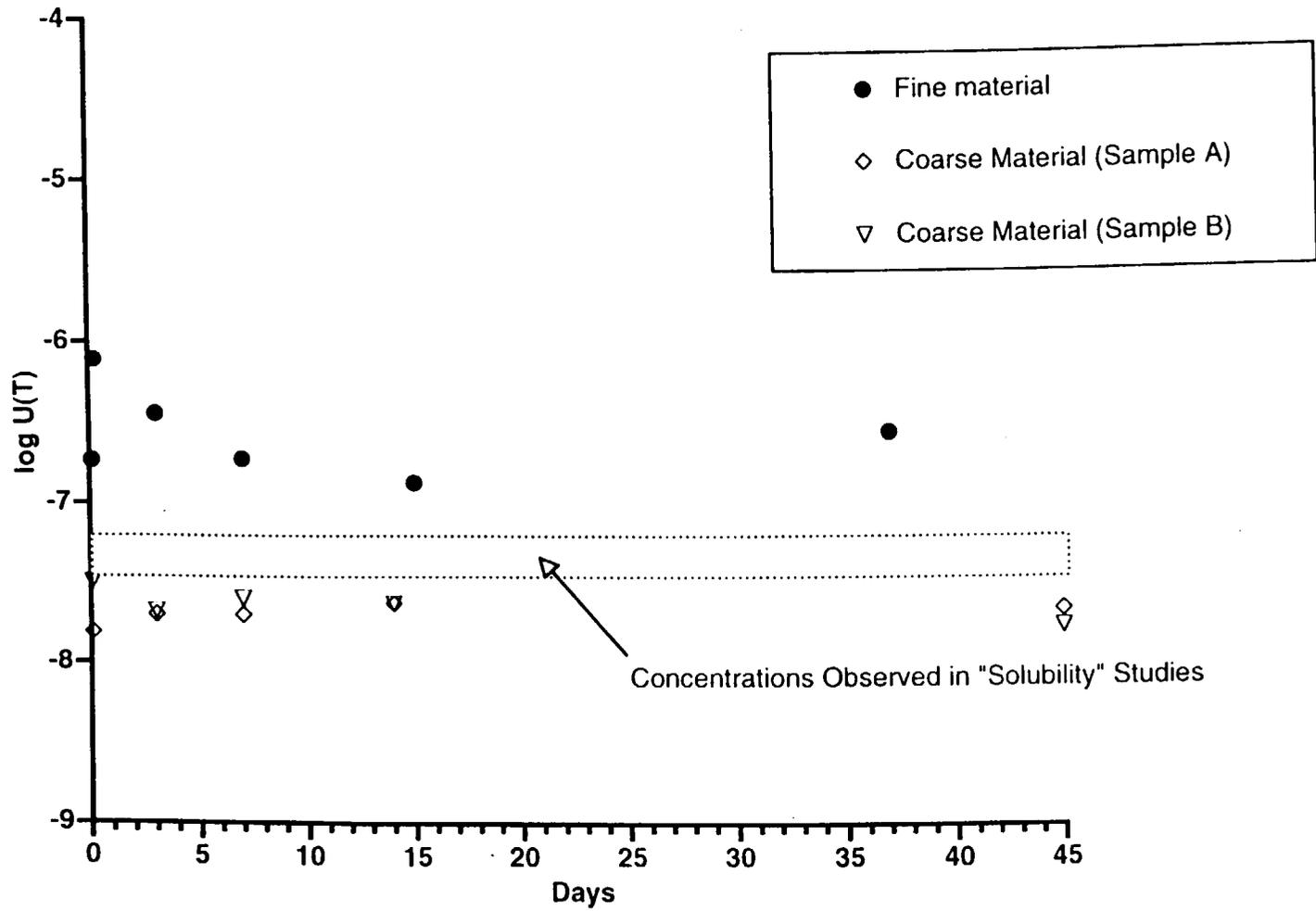


Figure 8. U Concentrations in Molycorp Batch Leaching Studies.

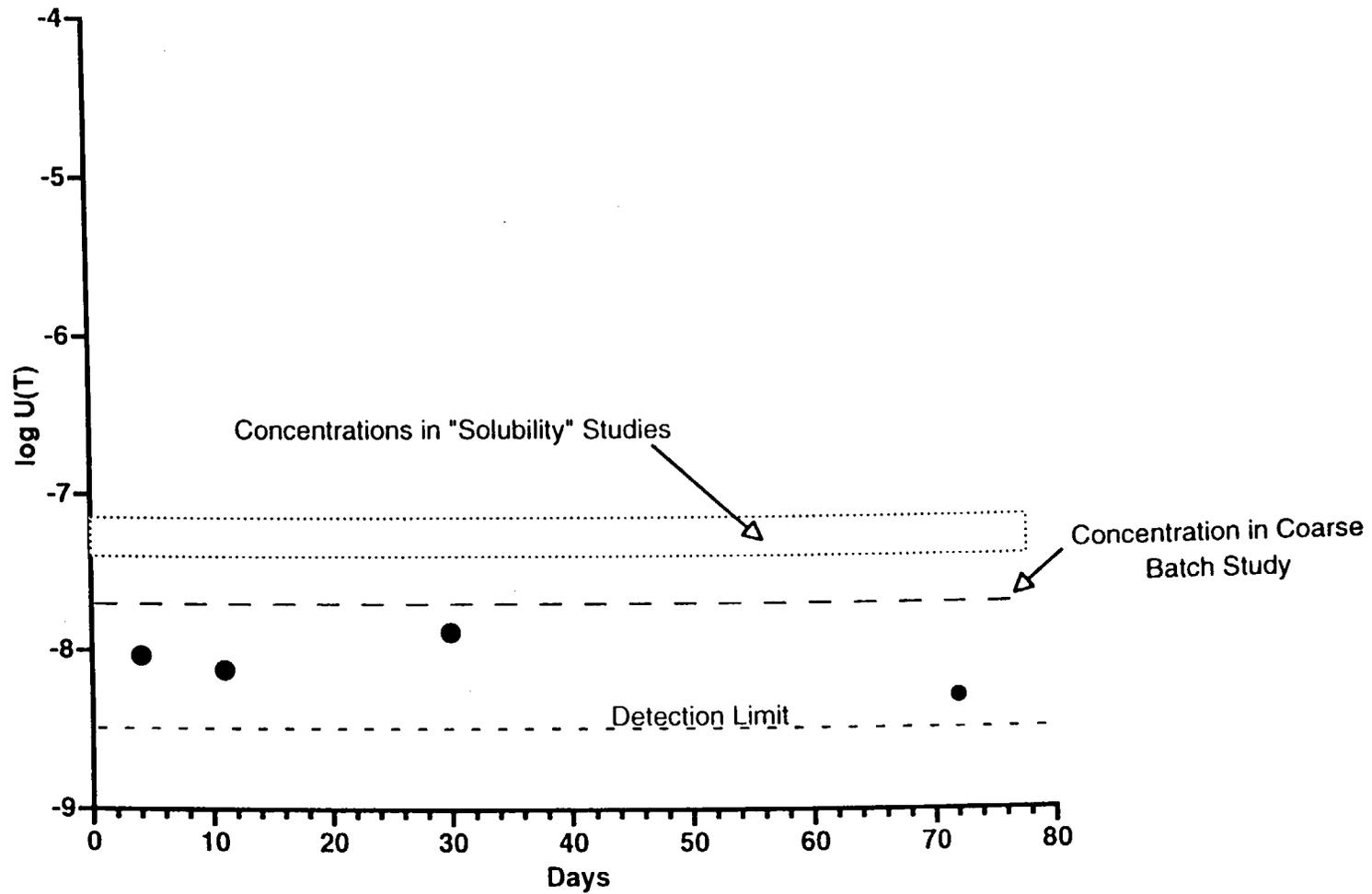


Figure 9. U Concentrations in Molycorp Column Studies.

Molycorp - Other radionuclides

Only very low concentrations of other radionuclides were detected in the solubility studies, batch studies or column studies. All Th-232 or U-238 daughters were either completely undetectable or found to be very low, typically <2pCi/ml. The only exceptions were the 14 pCi/ml of Bi-212 and 11pCi/ml of Pb-212 were found in the most acid solubility point analyzed (pH = 3.5) and Ra-226 which showed soluble concentrations in the solubility studies as high as 16pCi/ml. There was also evidence for some Pb-210, but the uncertainties of these analyses were so high as to prevent quantitation, and Cs-137 from fallout at concentrations <2pCi/ml.

Chemetron - Th

The total Th concentrations in the Chemetron samples, Table 1, was very low relative to the other sites sampled. This very low Th concentration is reflected in very low observed Th solubilities, Figure 10, which seldom exceeded 10^{-8} M even at very low pH values. This result agrees with the batch leaching data that shows maximum Th concentrations of $10^{-7.5}$ M. Even all dissolved Th concentrations in the column studies were at or below the analytical detection limit of approximately $10^{-8.5}$ M.

Table 7. Th concentrations in batch leaching studies of Chemetron samples.

Leaching Time	Chemetron -log [Th]
2 hrs.	-8.29
6 hrs.	< -8.50
3 days	-7.45
7 days	< -8.50
15 days	< -8.50
37 days	-7.54

Chemetron - U

The total U concentration in Chemetron samples, Table 1, is also less than that found at other sites. However, the chemical form of the U is quite different. The chemetron process resulted in the conversion of depleted UF_6 to depleted U_3O_8 . This difference in chemical form results in quite different observed U solubilities, Figure 11, than those observed at Molycorp where the U was relatively insoluble even at very low pH. The U in the chemetron samples is relatively easily solubilized by acid with essentially 100% of the U soluble at low pH values. The observed U concentrations in solution also do not appear to correspond to any known solubility controlling solid phase for a U(VI) solid. The dramatically reduced soluble U concentrations over the pH range 3 to 5 seem to correspond more to adsorption edges for U(VI) on aluminum

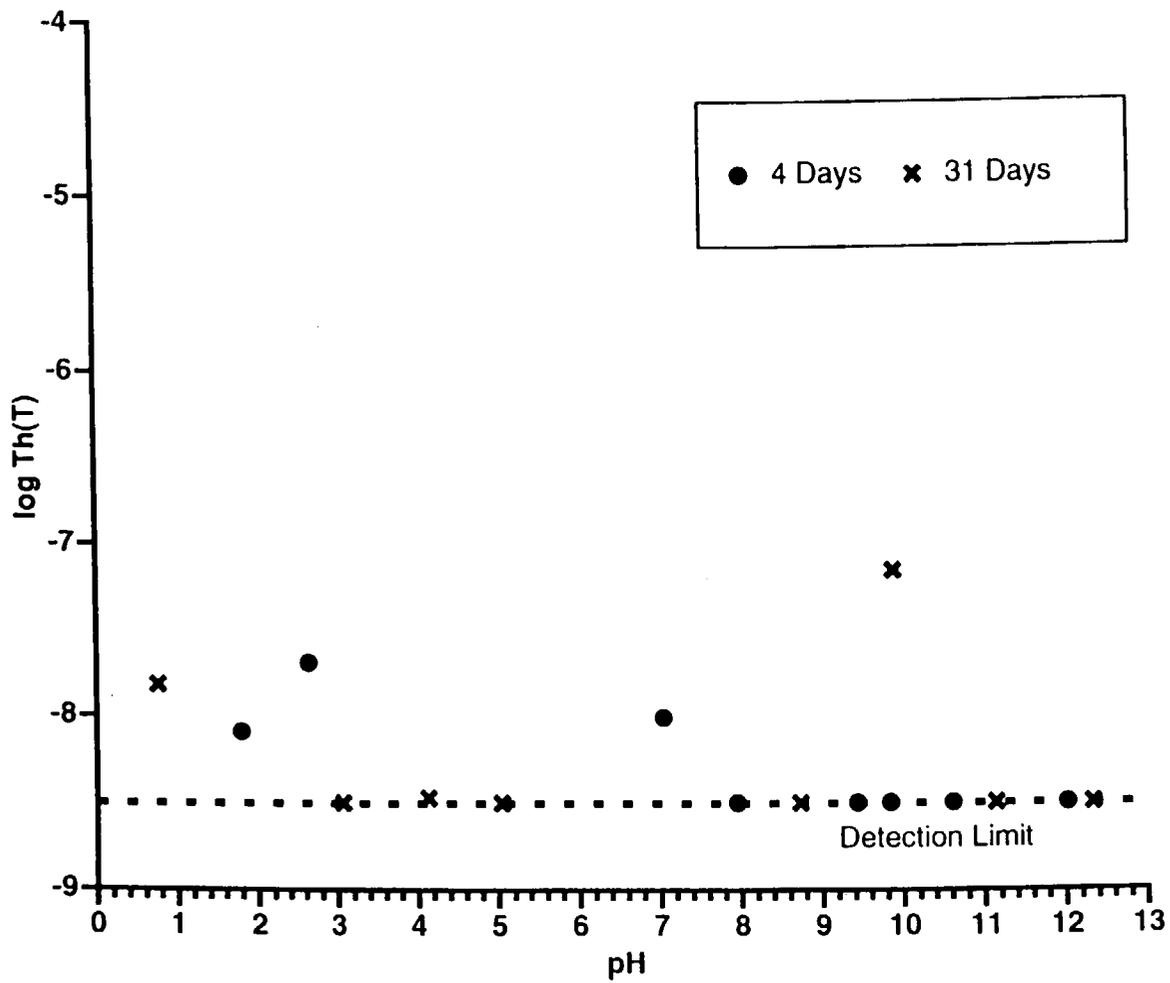


Figure 10. Th Concentrations in Chemetron Solubility Studies.

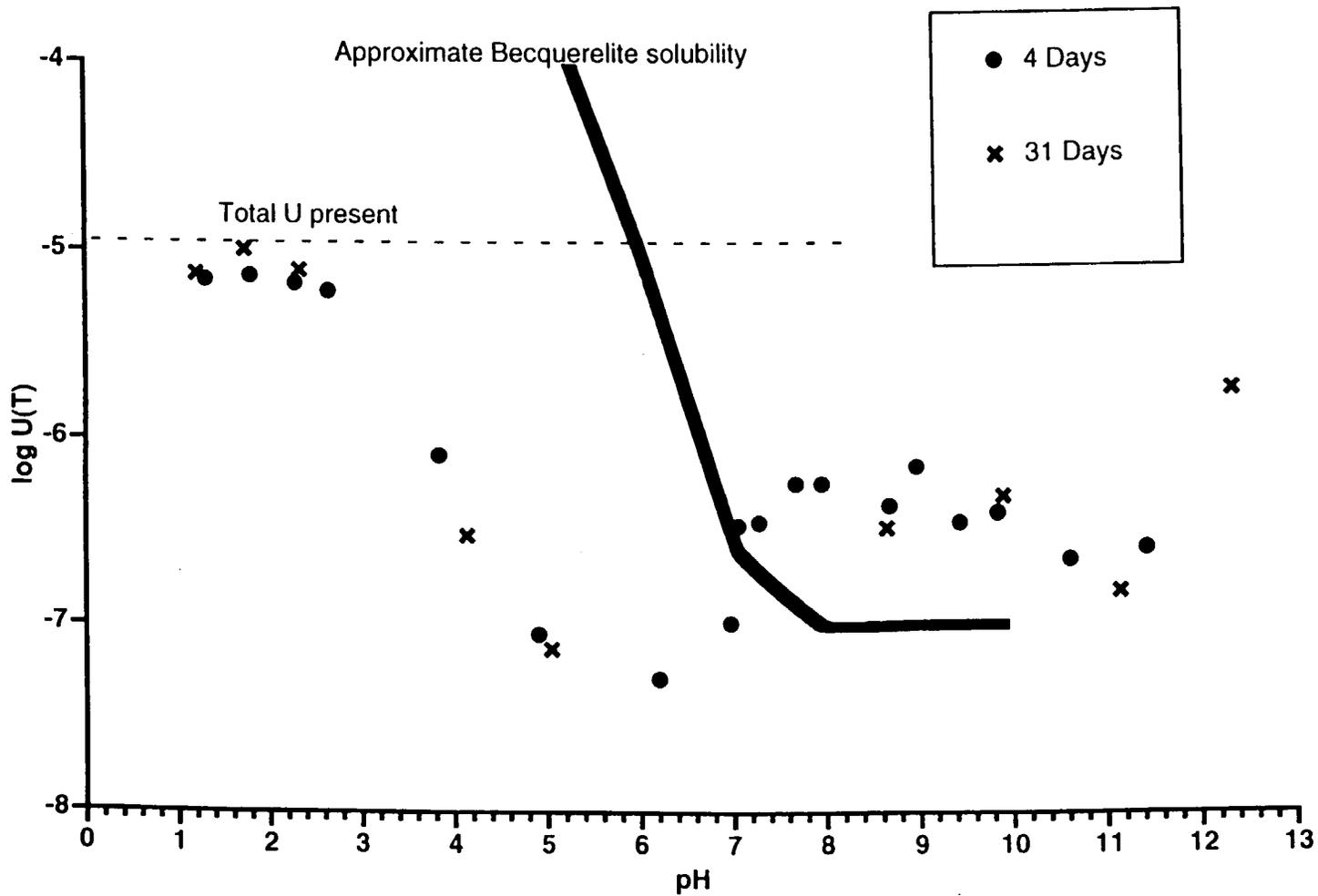


Figure 11. U Concentrations in Chemetron Solubility Studies. Solid Line Represents a Curve Fit to the Experimental Data In Figure 6.

oxide or silica oxide surfaces (McKinley et al. 1995) than to expected solubility trends. This is also reasonable given the clayey nature of the chemetron samples. The observed U concentrations in the batch leaching studies, Figure 12, show very similar trends to the solubility studies at the same pH values. This is expected. The chemetron samples were all a fine clayey soil. No fracturization of "coarse" batch studies were conducted. These studies therefore closely mimic the solubility studies except that no pH adjustments were made in the batch studies. The results for the column studies were however dramatically different, Figure 13. These data show very high dissolved U concentrations. These increases in concentration are clearly related to the much higher solid/solution ratio in the column studies as opposed to the solubility or batch studies. Clearly, the U in chemetron samples is highly reactive and not controlled by solubility phenomena. It appears likely that the observed U concentrations in solution are controlled by adsorption or ion exchange processes on the soil minerals. X-ray absorption fine structure (XAFS) studies are planned to help further define the chemical form of the U in these leached soils. Never-the-less, as described in subsequent sections, the more soluble form of U in chemetron samples results in significantly increased leaching rates and higher upper bounds on soluble U than for the Molycorp or Cabot slag type materials.

Chemetron - other radionuclides

The radiological analysis of the solubility and column data did not show significant concentrations of any Th-232 or U-238 daughter. Bi-212 and Pb-212 were detected in a few samples, but the concentrations were so low and the uncertainty of the analysis so high that any quantification of concentration was impossible. Such low concentrations are consistent with the radiological analysis of the solid chemetron samples, Table 2.

Th - Cabot

The solubility data for Th in three samples from the Cabot site, Figure 14, show a very consistent trend of very low solubilities, except at the very lowest pH values. Sample C-19, the greyish green slag showed the highest solubilities consistent with the total analyzed Th concentrations in these samples. Interestingly, the observed Th solubilities for the Cabot samples are in general even lower than for the Molycorp slag, with only the solubility in the C-19 sample apparently limited by thorianite, $\text{ThO}_2(\text{c})$.

In the case of the batch leaching experiments, the solution pH values were generally basic but highly variable, Table 8. This variability is apparently related to the changing nature of the solutions as a result of a very slow dissolution rate. The slow dissolution rate is apparent from the dissolved Ca concentrations, the dominant cation, which increase only very slowly with time. The fact that the solutions are so poorly buffered may also impact the pH meter readings. In any event, the pH values are in general between 8 and 10. The corresponding Th concentrations in these batch leaching samples, Figure 15, show quite low solubilities and bracket the range of Th concentrations expected from the solubility studies.

The column studies, Figure 16, also show very low dissolved concentrations with the majority of the samples at the analytical detection limit of $10^{-8.5}\text{M}$. As was true in the previous column studies of the Molycorp and Chemetron samples, the measured pH values varied only over a

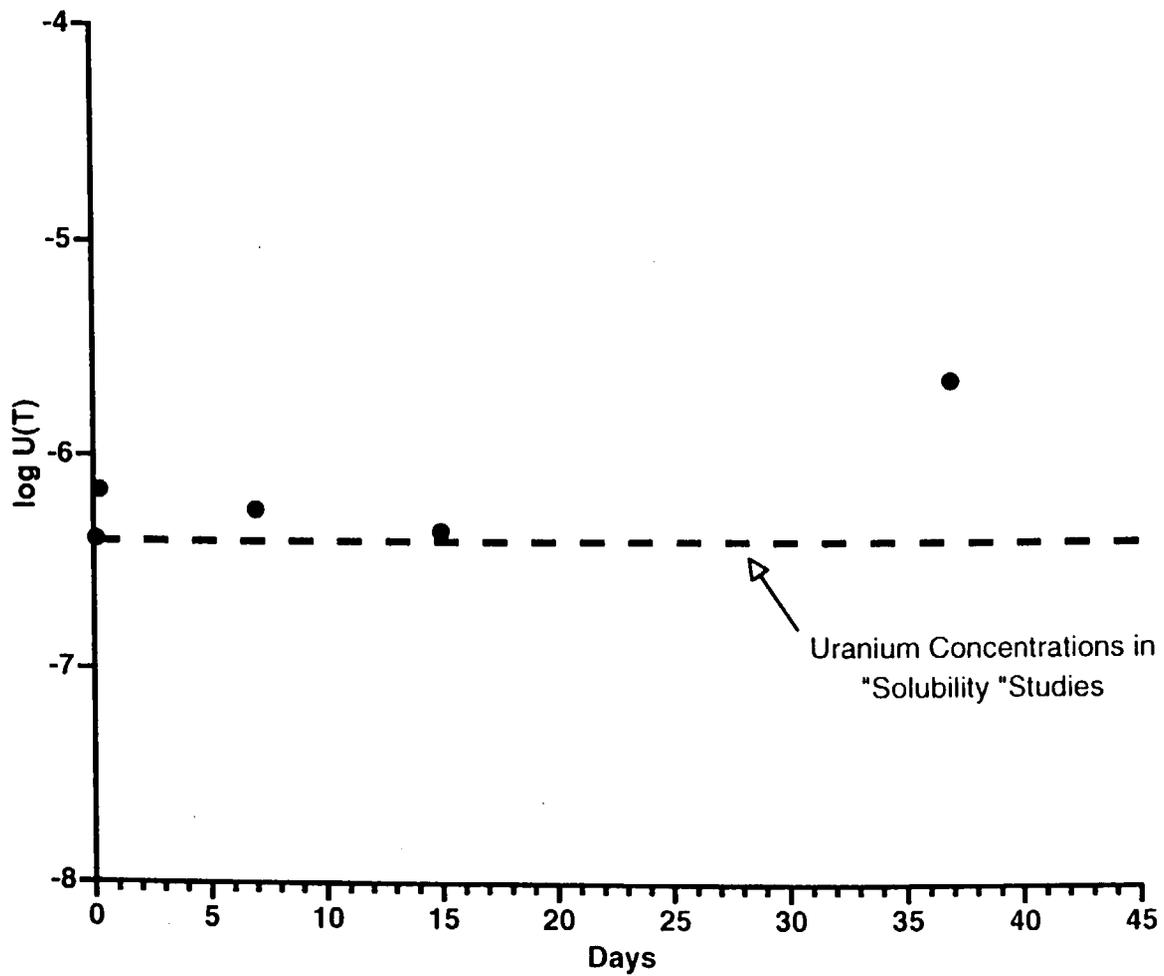


Figure 12. U Concentrations in Chemetron Batch Leaching Studies.

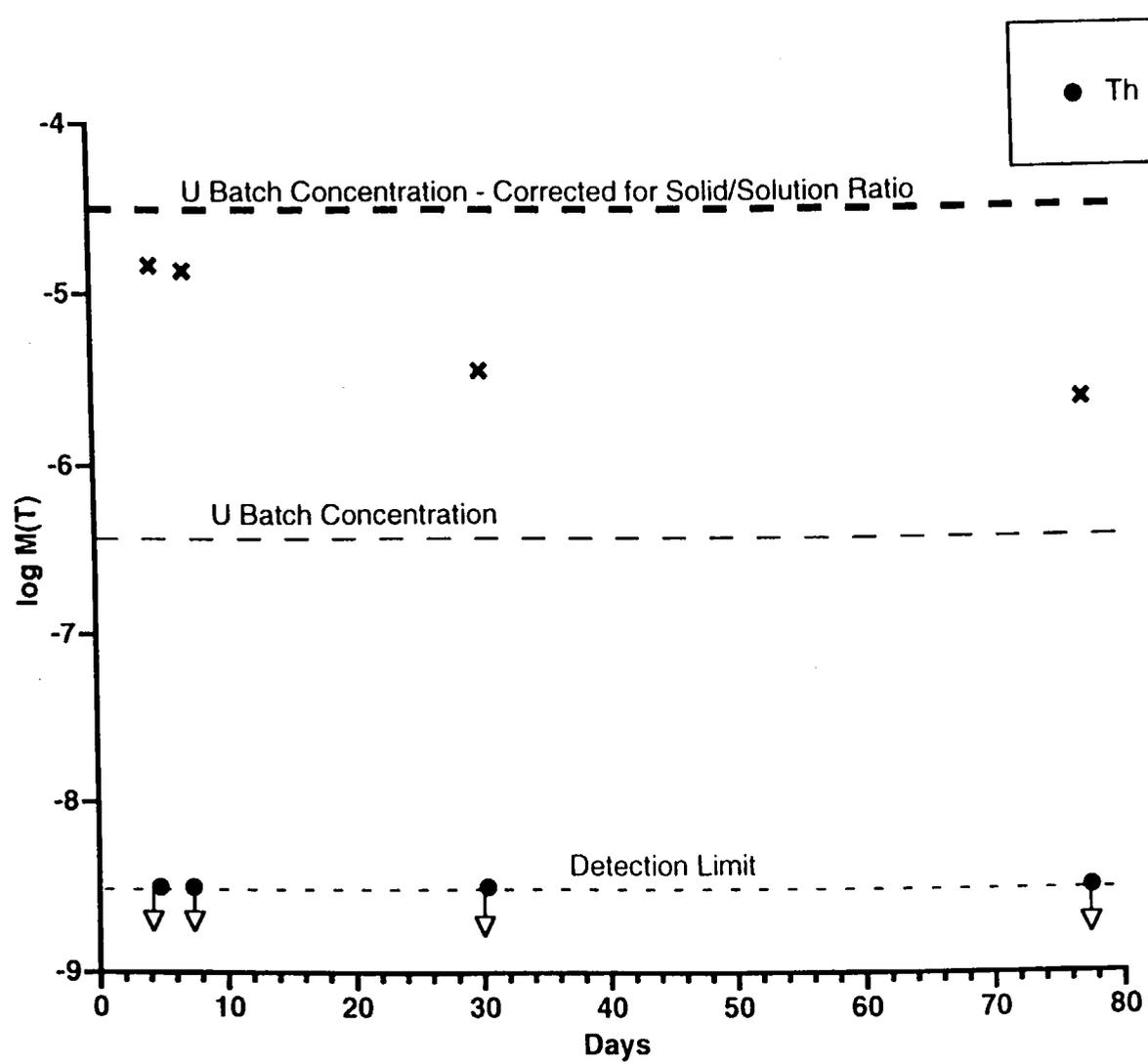


Figure 13. Th and U Concentrations in Chemetron Column Studies.

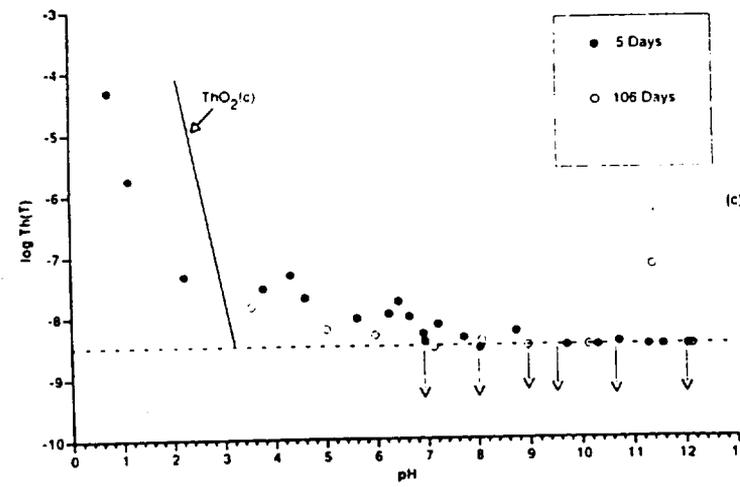
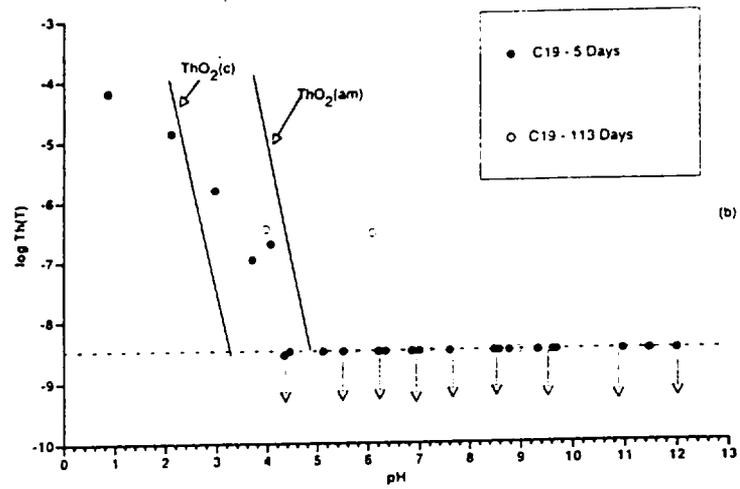
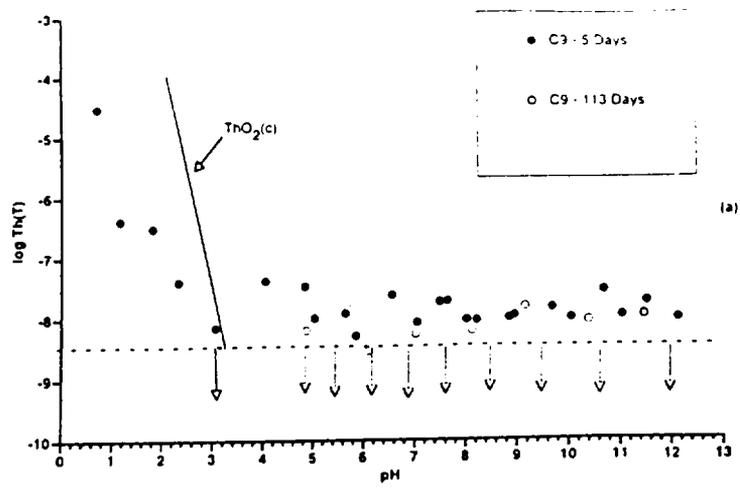


Figure 14. Th Concentrations in Cabot Solubility Studies. (a) C-9, (b) C-19, (c) C-20.

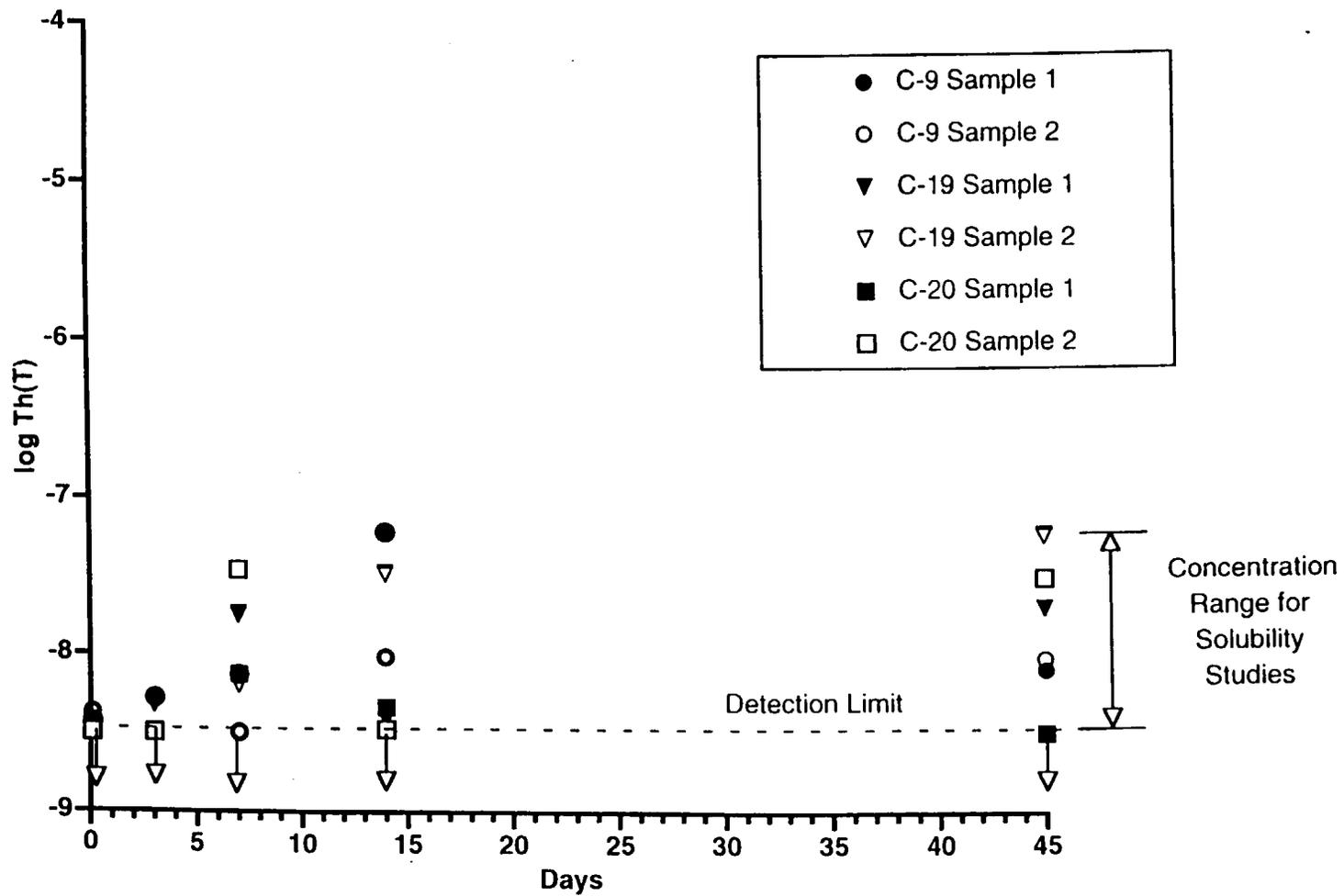


Figure 15. Th Concentrations in Cabot Batch Leaching Studies.

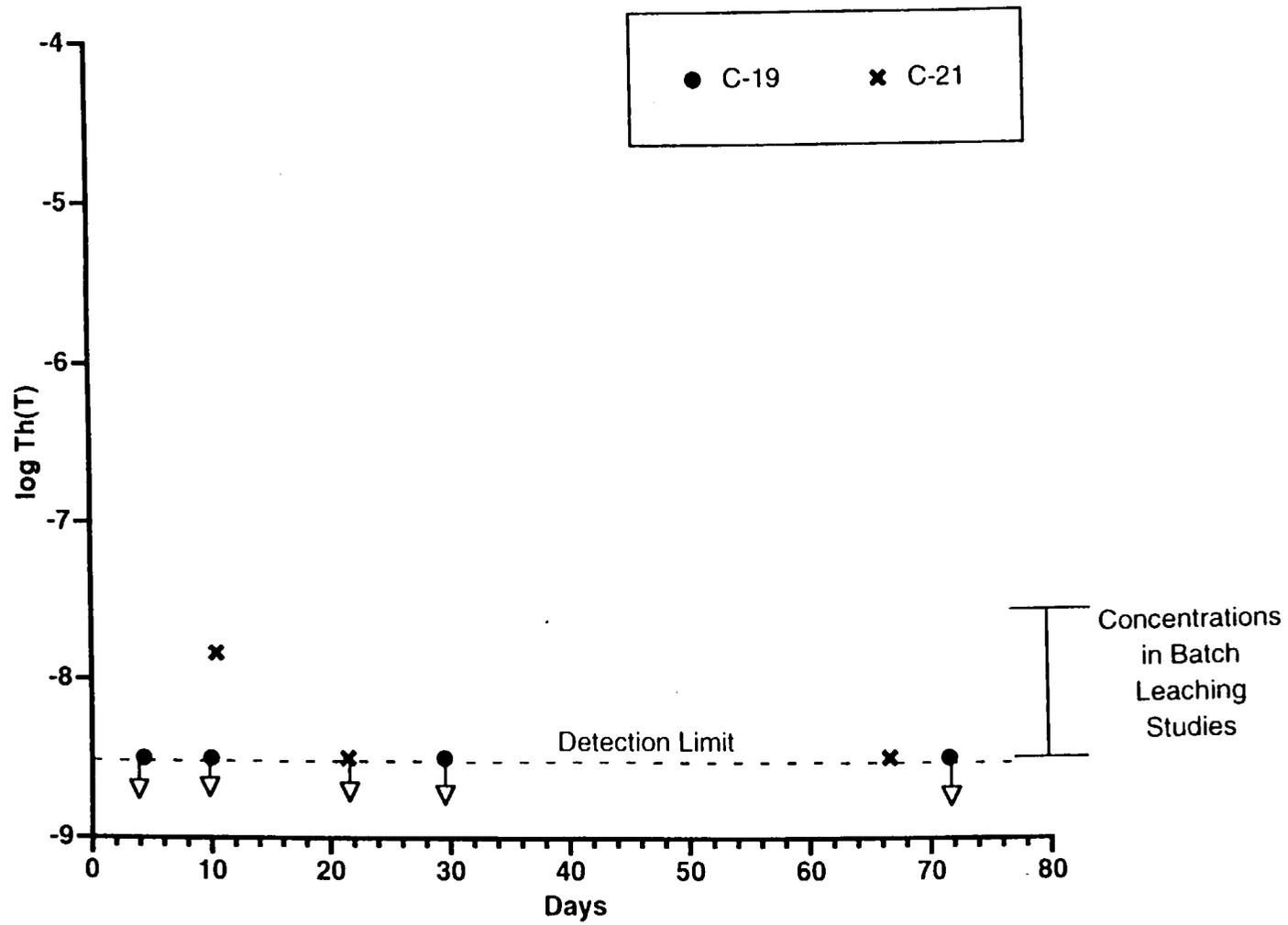


Figure 16. Th Concentrations in Cabot Column Studies.

very narrow range (i.e. 7.9 to 8.8).

Table 8. Measured pH values and Ca concentrations in batch leaching studies as a function of time for Cabot samples.

Leaching Time	C-9		C-19		C-20	
	pH	Ca(mg/l)	pH	Ca(mg/l)	pH	Ca(mg/l)
2 hrs.	7.86	1.5	7.83	1.5	7.57	2.9
3 days	9.97	4.7	10.5	5.1	9.90	6.3
7 days	9.12	6.9	9.30	8.7	8.93	8.6
14 days	8.37	14.4	8.70	11.8	8.03	9.9
45 days	9.12	14.6	9.70	24.3	8.54	13.1

Cabot - U

Uranium solubilities in Cabot samples. Figure 17, show very low solubilities in a similar fashion to the slag samples at Molycorp. At very high pH values, the solubilities could become limited by becquerelite, although the Ca concentration in these samples is about an order of magnitude lower than in the Molycorp samples (see Figure 18). The observed U concentrations in the batch leaching studies, Figure 19, also show very low dissolved U concentrations which are in good agreement with the U solubility studies. Similarly, the U concentrations in the column studies, Figure 20, correspond to the batch leaching studies. No particle size or surface area effect is seen. In summary, the concentration controlling mechanism for U in Cabot samples is not precisely known. Becquerelite could limit the solubility at high pH values, but this is less likely than in Molycorp samples owing to the lower dissolved Ca concentrations. It is possible that the U concentrations are simply controlled by slow dissolution of the solid phase material but this also appears unlikely since the dissolved concentrations in the solubility studies, which used ground, very small particle size material yielded similar results to the batch and column studies with different particle sizes and higher solid/solution ratios (column studies). It appears more likely that the U is tightly bound in either a very insoluble or refractory phase.

Cabot - other radionuclides

The very refractory nature of the Cabot samples was also reflected in the leaching of U-238 or Th-232 daughters. As was true with the chemetron samples, no Th-232 or U-238 daughters were detected at significant concentration in the solubility, leaching, or column studies. Bi-212 and Pb-212 were detected in a few samples, but the concentrations were so low and the uncertainty of the analysis so high that any quantification of concentration was impossible.

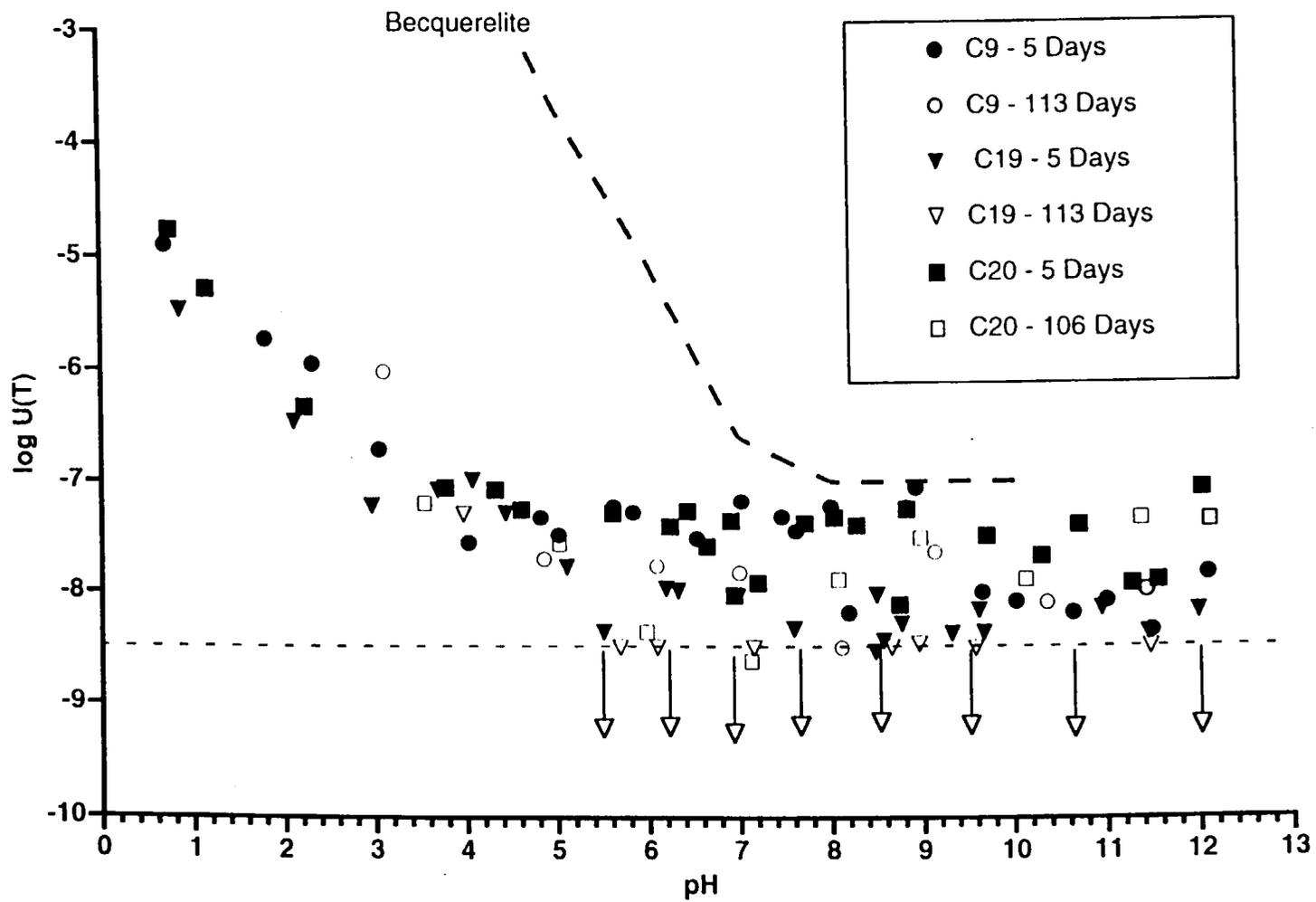


Figure 17. U Concentrations in Cabot Solubility Studies.

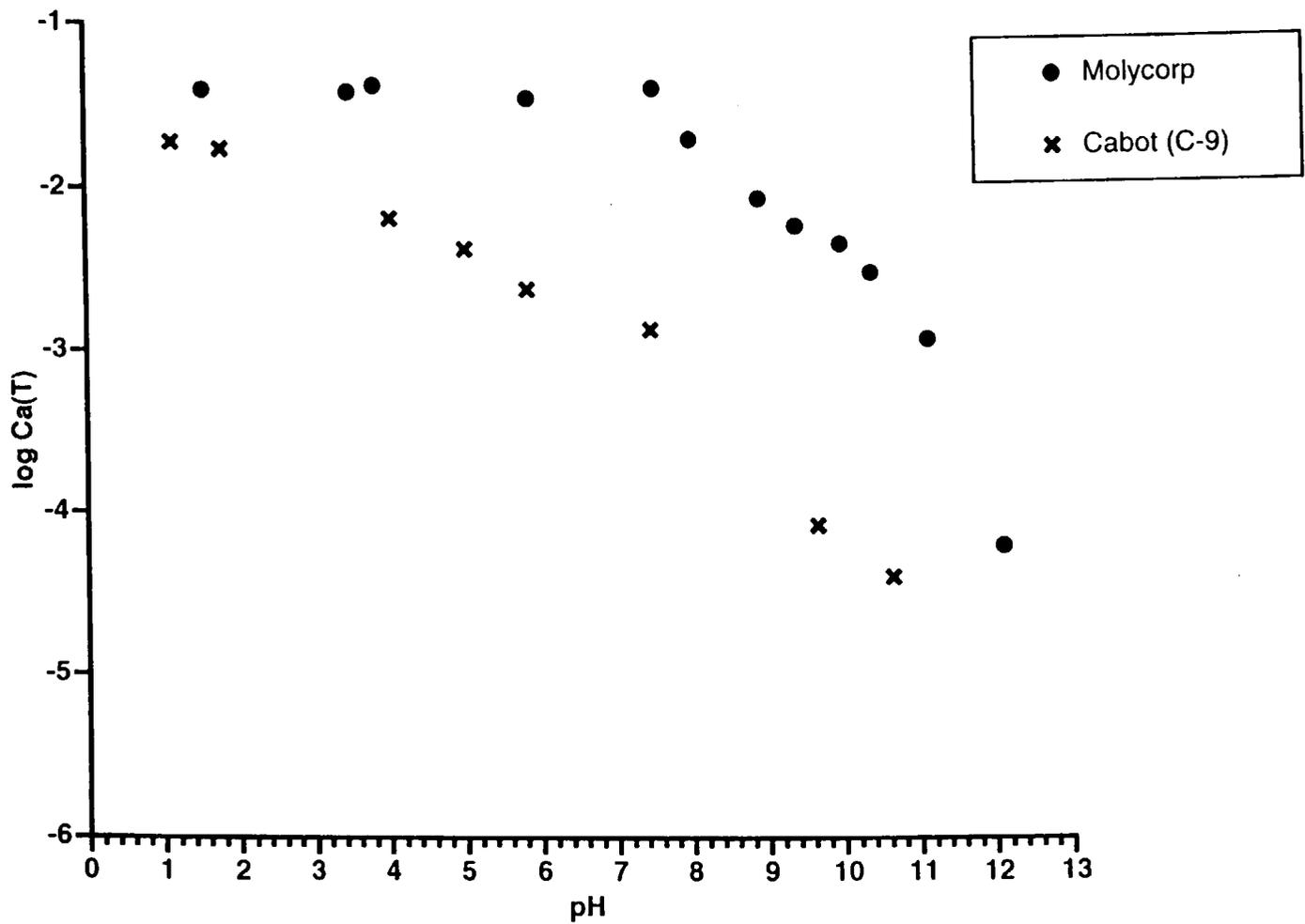


Figure 18. Calcium Concentrations in Molycorp and Cabot Solubility Studies.

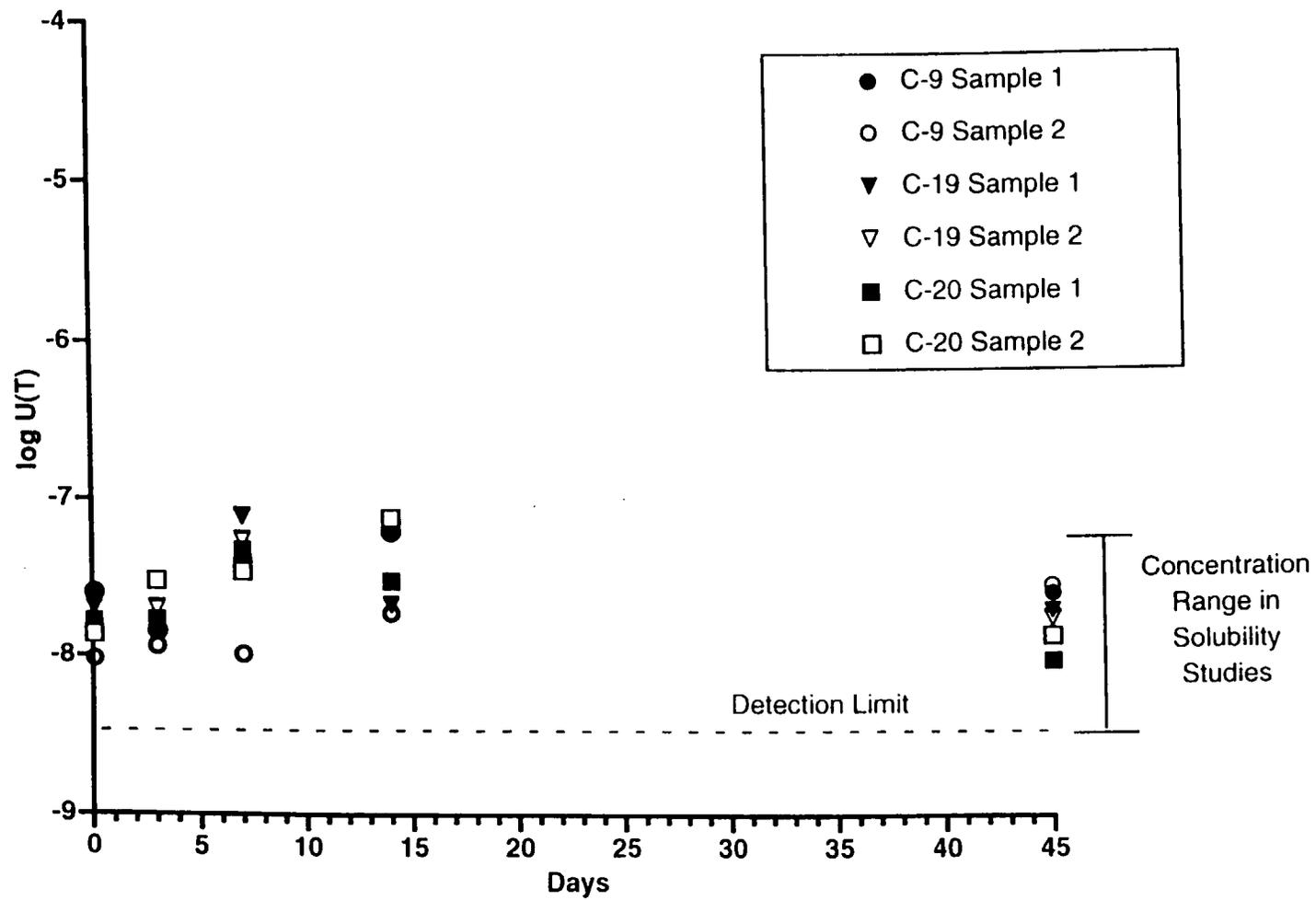


Figure 19. U Concentrations in Cabot Batch leaching Studies.

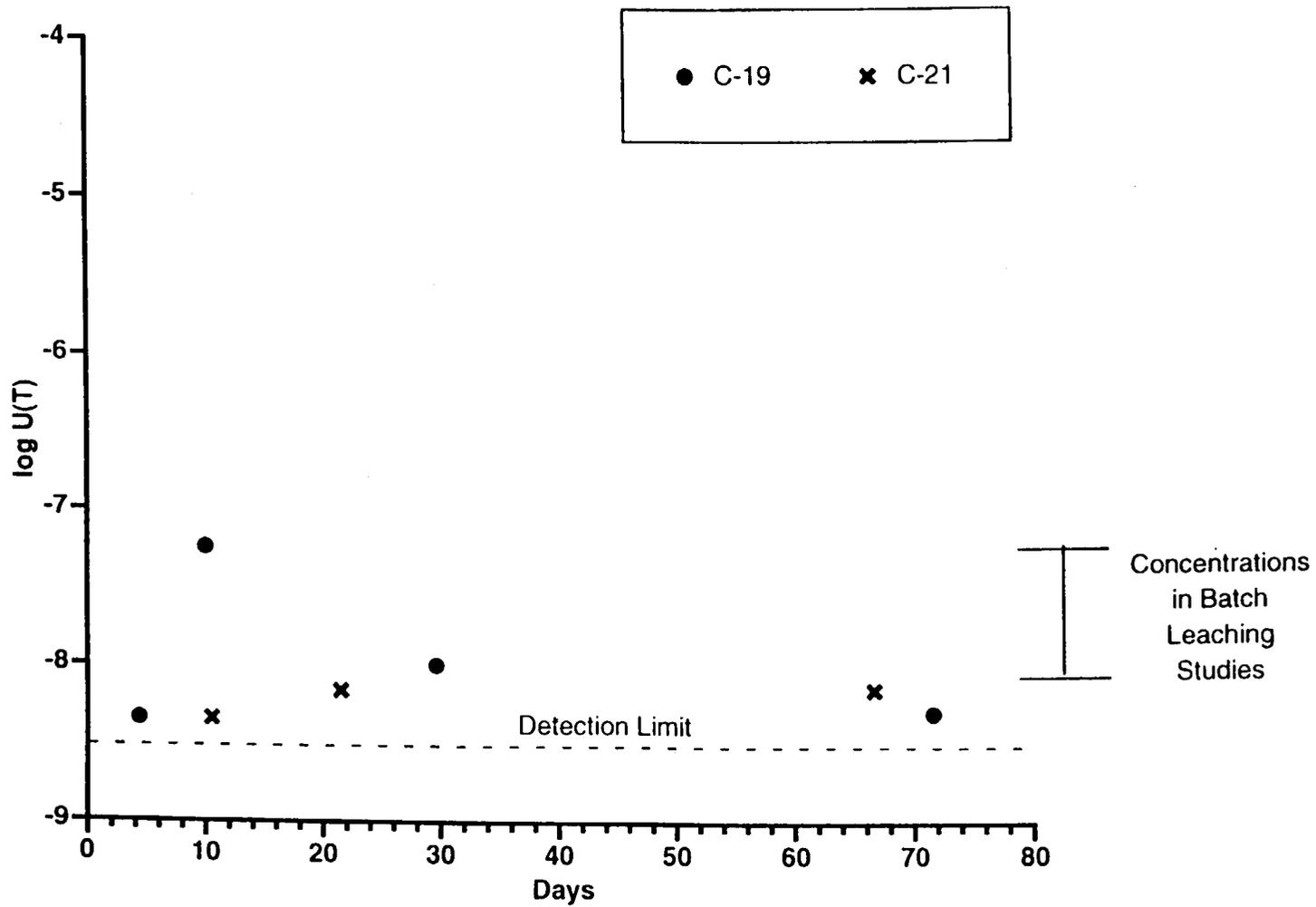


Figure 20. U Concentrations in Cabot Column Studies.

Calculations of solubility limits and leaching rates:

Molycorp: Solubility controlled for both Th and U.

Th - data from the coarse batch study were used (Figure 3). The highest solubility observed was $10^{-7.5}$ M Th after 2hrs contact time. The solution volume was 30ml. This yields the following

- maximum solubility = 3.2×10^{-8} M
- leaching rate = 1.1×10^{-7} gTh/hr²

U - data from the coarse batch study were used (Figure 8). The highest solubility observed was $10^{-7.6}$ M U after 2hrs contact time. The solution volume was 30ml. This yields the following

- maximum solubility = 2.5×10^{-8} M
- leaching rate = 8.9×10^{-8} gU/hr³

Chemetron: Solubility controlled for Th not U.

Th - data from the coarse batch study were used (Table 7). The highest solubility observed was $10^{-7.5}$ M Th after 3 days contact time. The solution volume was 30ml. This yields the following

- maximum solubility = 3.2×10^{-8} M
- leaching rate = 3.1×10^{-9} gTh/hr

U - data from the column study (Figure 13) were used to define a "solubility" limit owing to the high solid/solution ratio and U concentration. Data from the batch study (Figure 12) were used to give a maximum leaching rate. The highest U concentration observed in the column study was $10^{-4.8}$ M U after 4.7 days of leaching and this was selected as the solubility limit. The leaching rate was calculated from the batch data at 2hrs of leaching (steady state already obtained). The solution volume was 30ml and the specific surface area was $19\text{m}^2/\text{g}$. This yields the following:

- maximum solubility = 1.6×10^{-5} M
- leaching rate = 7.5×10^{-8} gU/m².hr⁴

²The leaching rates are calculated as follows:
 $(3.2 \times 10^{-8} \text{ moles Th/l}) (.031) (232 \text{ gTh/mole}) / 2 \text{ hrs.} = 1.1 \times 10^{-7} \text{ gTh/hr.}$

³The leaching rates are calculated as follows:
 $(2.5 \times 10^{-8} \text{ moles U/l}) (.031) (238 \text{ gU/mole}) / 2 \text{ hrs.} = 8.9 \times 10^{-8} \text{ gU/hr.}$

⁴The leaching rate are calculated as follows:
 $(4 \times 10^{-7} \text{ moles U/l}) (.031) (238 \text{ gU/mole}) / ((2 \text{ hrs.}) (19 \text{ m}^2/\text{gsoil}) (1 \text{ gsoil}))$
 $= 7.5 \times 10^{-8} \text{ gU/m}^2 \cdot \text{hr.}$

Cabot: Solubility controlled for both Th and U.

Th - data from the coarse batch study were used (Figure 15). The highest solubility observed was $10^{-7.4}$ M Th after 14 days contact time. The solution volume was 30ml. This yields the following:

- maximum solubility = 4×10^{-8} M
- leaching rate = 8.3×10^{-10} gTh/hr.

U - data from the coarse batch study were used (Figure 19). The highest solubility observed was $10^{-7.2}$ M U after 7 days contact time. The solution volume was 30ml. This yields the following:

- maximum solubility = 6.3×10^{-8} M
- leaching rate = 2.7×10^{-9} gU/hr.

Radiocolloids

A comparison of filtered and unfiltered Th and U concentrations in the column studies did not show any evidence for the formation or transport of radiocolloids in any of the samples studied.

Table 9. Filtered and unfiltered Th and U concentrations in column studies. UF - unfiltered, F - filtered.

Analysis	Molycorp	Chemetron	Cabot (C-19)	Cabot (C-21)
Th - UF	$< 10^{-8.5}$	$< 10^{-8.5}$	$< 10^{-8.5}$	$10^{-7.4}$
Th - F	$< 10^{-8.5}$	$< 10^{-8.5}$	$< 10^{-8.5}$	$10^{-7.4}$
U - UF	$< 10^{-8.5}$	$10^{-5.60}$	$< 10^{-8.5}$	$10^{-7.2}$
U - F	$10^{-8.5}$	$10^{-5.62}$	$10^{-8.3}$	$10^{-7.2}$

References

Koh B., and Associates (1995). Site Remediation Plan Chemetron Project Harvard Avenue and Bert Avenue Sites. Chemetron Corporation Inc., Newburgh Heights, OH.

McKinley, J.P., J.M. Zachara, S.C. Smith, and G.D. Turner (1995). The Influence of Uraiy, Hydrolysis and Multiple Site-Binding Reactions on Adsorption of U(VI) to Montmorillonite Clays and Clay Minerals, 43(5), 586-598.

U.S. Nuclear Regulatory Commission (1993). Site Decommissioning Management Plan NUREG-1444, Supplement 1.

Krupka, K.M. and R.J. Serne. Performance Assessment of Low-Level Radioactive Waste Disposal Facilities: Effects on Radionuclide Concentrations by Cement/ground-Water Interactions. DRAFT.