**Pacific Northwest
National Laboratory**

Operated by Battelle for the
U.S. Department of Energy

**K Basin Sludge Conditioning
Process Testing**

**Partitioning of PCBs in Dissolver
Solution After Neutralization/
Precipitation (Caustic Adjustment)**

A. J. Schmidt
G. M. Mong
E. W. Hoppe

S. O. Slate
K. L. Silvers
B. M. Thornton

RECEIVED
FEB 17 1999
OSTI

September 1998

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor Battelle Memorial Institute, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or Battelle Memorial Institute. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

PACIFIC NORTHWEST NATIONAL LABORATORY

operated by

BATTELLE

for the

UNITED STATES DEPARTMENT OF ENERGY

under Contract DE-AC06-76RLO 1830

Printed in the United States of America

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831;
prices available from (615) 576-8401.

Available to the public from the National Technical Information Service,
U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161

This document was printed on recycled paper.

(9/97)

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

K Basin Sludge Conditioning Process Testing

Partitioning of PCBs in Dissolver Solution After Neutralization/Precipitation (Caustic Adjustment)

A. J. Schmidt
G. M. Mong
E. W. Hoppe
S. O. Slate
K. L. Silvers
B. M. Thornton

September 1998

Prepared for
Numatec Hanford Corporation

Work Supported by
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest National Laboratory
Richland, Washington 99352

Summary

The purpose of the work described in this report was to gain a better understanding of how PCB congeners present in a simulated K Basin sludge dissolver solution will partition upon neutralization and precipitation (i.e., caustic adjustment). In a previous study (Mong et al. 1998¹), the entire series of sludge conditioning steps (acid dissolution, filtration, and caustic adjustment) were examined during integrated testing. In the work described here, the caustic adjustment step was isolated to examine the fate of PCBs in more detail within this processing step.

For this testing, solutions of dissolver simulant (containing no solids) with a known initial concentration of PCB congeners were neutralized with caustic to generate a clarified supernatant and a settled sludge phase. PCBs were quantified in each phase (including the PCBs associated with the test vessel rinsates), and material balance information was collected. The data from the testing support the following conclusions:

- Ninety to ninety-eight percent of the tetrachlorobiphenyl and hexachlorobiphenyl PCB congeners (i.e., congeners most representative of Aroclor 1254, the predominant Aroclor in the sludge) were removed from the dissolver solution by caustic adjustment. A similar level of removal was achieved for the octachlorobiphenyl congener. These results are very consistent with the results previously obtained by Mong et al. (1998). In a similar test, Mong et al. (1998) calculated that 91% to 99% of the PCBs in the dissolver solution partitioned to the settled sludge after caustic adjustment.
- After caustic adjustment, the congener concentrations in the supernatant were still above the Toxic Substances Control Act (TSCA) PCB limit for aqueous liquid streams, which is 0.5 ppb. However, in the actual K Basin Sludge Conditioning Process, the dissolver solution will pass through a filter before caustic adjustment. Based on engineering studies and Mong et al. (1998), filtration is expected to remove about 95% of the PCB in the dissolver solution.
- The concentrations of PCB congeners in settled sludge generated from caustic adjustment of the dissolver solution, which was saturated with the PCB congeners, were well below the TSCA criterion (2 ppm PCB) for solids/sludge.
- The majority of the recovered PCB congeners (70% to 90%) were associated with the settled sludge phase. About 6% to 20% were recovered in the solvent used to rinse the test vessels. The PCB congeners associated with the neutralized dissolver solution ranged from less than 1% to 15%. The fraction remaining with the dissolver solution decreased with increasing levels of chlorination on the PCB congeners. With respect to the dissolver solution, these results are very consistent with those obtained by Mong et al. (1998). However, they found that 35% to 99% of the recovered PCB congeners were associated with the vessel rinse solutions.

¹ Mong, G. M., E. W. Hoppe, K. H. Pool, A. J. Schmidt, K. L. Silvers, and B. M. Thornton. 1998. "K Basin Sludge Conditioning Process Testing: Fate of PCB During K Basin Sludge Dissolution in Nitric Acid and with Hydrogen Peroxide Addition." PNNL-11998, Pacific Northwest National Laboratory, Richland, Washington.

Contents

Summary	iii
1.0 Introduction	1
2.0 Description of the Experiments	3
2.1 Test Material	3
2.2 Test Procedure	4
2.3 Sampling and Analysis	5
2.3.1 Extraction	5
2.3.2 Analysis	6
3.0 Results and Discussion	7
3.1 Fate of PCB Congeners in Liquid Phase	7
3.2 Fate of PCB Congeners in Precipitated Sludge Phase	8
3.3 Final Distribution of PCB Congeners	9
3.4 Discussion of Mass/Volume Data	10
4.0 References	13
Appendix -- Analytical Data for PCB Congeners	A1

Tables

1	PCB Congener Concentrations Added to and Measured in Dissolver Solution	4
2	Description of Test Matrix	5
3	PCB Concentration and Percent Removal in Liquid Phase	7
4	PCB Concentration in the Sludge	8
5	Distribution of PCBs in Vessel 3 (V3)	9
6	Distribution of PCBs in Vessel 4 (V4)	10
7	Mass/Volume Balance Table	11

1.0 Introduction

Two water-filled concrete pools (basins) in the 100K Area of the Hanford Site contain over 2100 metric tons of N Reactor fuel elements stored in aluminum or stainless steel canisters. During the time the fuel has been stored, approximately 52 m³ of heterogeneous solid material have accumulated at the bottom of the K Basins. This sludge is a mixture of spent fuel element corrosion products, ion exchange materials (organic and inorganic), graphite-based gasket materials, iron and aluminum metal corrosion products, sand, and debris (Makenas et al. 1996, 1997). In addition, small amounts of polychlorinated biphenyls (PCBs) have been found, which are significant from a regulatory standpoint.

The predominant congener group of PCBs in the sludge has been identified as Aroclor 1254. The maximum concentration of PCBs in the sludge, which was found in the K East (KE) Weasel Pit sludge, is 140 ppm (settled sludge basis) (Schmidt 1997). However, the distribution of the PCBs is non-uniform throughout the sludge (i.e., regions of high and low concentrations and places where no PCBs are present). Low concentrations of Aroclors 1016/1242, 1221, 1248, 1254, and 1260 have been identified and quantified in K West (KW) Canister sludge (Makenas et al. 1998). In some of these samples, the concentration of 1260 is higher than that of 1254.

Ultimately, it is planned to transfer the K Basin sludge to the Hanford double shell tanks. Before the sludge can be transferred, however, chemical pretreatment (i.e., K Basin Sludge Conditioning Process) is required to address criticality issues, and the destruction or removal of PCBs may be necessary.

Under the direction of Duke Engineering & Services Hanford and Numatec Hanford Corporation, Pacific Northwest National Laboratory (PNNL) performed tests to determine the chemical fate of polychlorinated biphenyls (PCBs) in potential processing steps within the K Basin Sludge Conditioning Process (Mong et al. 1998). One set of tests examined the effect of hydrogen peroxide on the disposition of PCBs in a 0.5 M nitric acid/1 M Fe(NO₃)₃ solution, contacting the PCBs to an environment similar to "Fenton Reagent." A second series of tests examined the disposition of PCBs in a much stronger (~10 M) nitric acid solution, similar to that likely to be encountered in actual sludge processing. From this testing, the PCB congeners most representative of Aroclor 1254 do not appear to be appreciably chemically altered by solutions of nitric acid or hydrogen peroxide at reflux temperatures. Reflux temperature nitric acid (~110°C) caused some volatilization of less chlorinated PCB congeners, to an extent, into the vapor phase. The majority of PCB congeners that did not escape into the vapor phase remained associated with the solids in the reaction flask or with the surface of the reaction flask and associated components (condenser, thermometer), and were chemically unchanged. After caustic adjustment of the dissolver solution, 91% to 99% of the PCBs partitioned to the precipitate. These results were obtained in tests conducted without filtration of the dissolver solution or the final supernatant. Filtration (0.45-μm PVDF filter) removed 88% to 97% of the dissolved PCBs in spiked water.

Based on the PNNL tests (Mong et al. 1998) and engineering evaluations, the baseline plan for addressing PCBs within the K Basin Sludge Conditioning Process is to partition most of the PCBs to the acid insoluble solids (during sludge dissolution) and filter the dissolver solution (collecting some PCBs on the filter). The filtered dissolver solution will next be caustically adjusted to a pH of greater than 12 to meet Tank Waste Remediation System (TWRS) Double Shell Tank waste acceptance criteria. During the caustic adjustment step, it is anticipated that the majority of any trace quantities of PCBs will

partition to the resulting sludge, creating a liquid supernatant stream that contains less than 0.5 ppb PCB (Toxic Substances Control Act, TSCA, limit for aqueous liquid streams), and a final sludge stream with less than 2 ppm PCB (TSCA limit for solids/sludge). The bulk of the PCBs, which will be associated with the acid insoluble residuals, will be dispositioned to the Environmental Restoration Disposal Facility (ERDF), which can accept wastes containing PCBs.

The purpose of the work described in this report was to further evaluate how PCB congeners present in a simulated K Basin dissolver solution will partition upon neutralization and precipitation (i.e., caustic adjustment). In the previous study (Mong et al. 1998), the entire series of processing steps (acid dissolution, filtration, and caustic adjustment) were examined during integrated testing. In the work described here, the caustic adjustment step was isolated and the fate of PCBs in this step was examined in much greater detail. Solutions of dissolver simulant (containing no solids) with a known initial concentration of PCB congeners were neutralized with caustic to generate a clarified supernatant and a settled sludge phase. PCBs were measured in each phase, and material balance information was collected.

This report contains a description of the experiments, including the materials and reagents used in the tests, procedures followed, and sampling and analysis methods. The results and discussion section provides an evaluation of the fate of PCB congeners in the liquid and settled sludge phases, a final distribution of congeners, and mass/volume material balance data.

2.0 Description of the Experiments

The testing described in this report was conducted in accordance with Test Instruction TI-28510-13: "Partitioning of PCB in Dissolver Solution After Neutralization/Precipitation" (Schmidt 1998).

2.1 Test Material

Approximately 500 ml of a master solution were prepared to simulate the solution (dissolver solution) that will leave the K Basin Sludge Conditioning System dissolver. The master solution was prepared by adding 50 g/L $\text{Fe}(\text{NO}_3)_3$ [i.e., 0.21 M Fe added as $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$] to a 3 M HNO_3 solution. This iron concentration is close to the maximum expected to be found in the dissolver solution from dissolution of KE Floor and Weasel Pit Sludge (i.e., where the highest concentrations of PCBs have been found).

Four PCB congeners were added to the master solution at the levels shown in Table 1. Three of these congeners, 2,2',4,4' tetrachlorobiphenyl; 2,2', 4,4', 6,6' hexachlorobiphenyl; and 2,2',3,3',4,4',5,5' octachlorobiphenyl, were added at levels well above their solubility limits. The fourth congener, 2,4 dichlorobiphenyl, a less chlorinated PCB not present in the Aroclors identified in the K Basin sludge, was added to the master solution at a level below its solubility limit. After the solution components were added [i.e., 3 M HNO_3 , 50 g/L $\text{Fe}(\text{NO}_3)_3$, and PCB congeners in Table 1], the master solution was heated on a hot plate at 52°C for 20 min and then allowed to equilibrate for 2 hr to ensure the dissolver solution was saturated with the three higher chlorinated PCB congeners.

The mixture of PCB congeners in Table 1 represented PCBs that bracket the chlorine content of Aroclor mixtures (e.g., Aroclor 1254, 1242), without the need to analyze the entire Aroclor PCB pattern in the data. The exceptionally clean chromatographic patterns provided simple quantification and ready identification of any major extra components appearing in the chromatograms. The relative amounts per congener chosen were meant to create a mix in which all analyses would fall within the dynamic range of the detector for each run, so that quantification could be done on a single dilution of each sample. In this mixture, the PCB congeners most representative of Aroclor 1254 are 2,2',4,4' tetrachlorobiphenyl and 2,2', 4,4', 6,6' hexachlorobiphenyl. [Note: Aroclor 1254 contains essentially no dichlorobiphenyl; it is composed of 1% tri-, 15% tetra-, 53% penta-, 26% hexa-, and 4% heptachlorobiphenyl.]

Once the master solution was prepared, an aliquot was collected and analyzed for PCBs. The results of this analysis are shown in Table 1. These results show the concentration of 2,4 dichlorobiphenyl is significantly less than what would be predicted based on its solubility limit. Some of the added 2,4 dichlorobiphenyl may have been lost from the test system. As shown in Table 1, the vapor pressure for 2,4 dichlorobiphenyl is significantly higher than that of the other congeners. Erickson (1992) notes that during sulfuric acid cleanup of pigment samples, losses of mono- through trichlorobiphenyls were reported when the samples were heated with sulfuric acid for at least 15 min at 40°C to 50°C. Also, Mong (1997) provides a good description of the propensity of PCBs to escape from water.

The measured concentration of 2,2',4,4' tetrachlorobiphenyl in the master solution is near the solubility limit, as expected, while the measured concentrations for the 2,2', 4,4', 6,6' hexachlorobiphenyl and the 2,2',3,3',4,4',5,5' octachlorobiphenyl are 115 times and 7.5 times greater (respectively) than their solubility limits in pure water at 25°C. However, the solubility limits in Table 1 are for pure water, and

Table 1. PCB Congener Concentrations Added to and Measured in Dissolver Solution

PCB Congener	PCB Congener Concentrations, ng/ml		Physical Properties of Congeners ⁽¹⁾	
	Calculated from Quantity Added to Master Dissolver Solution	Measured in Master Solution,	Solubility in H ₂ O, ppb ⁽²⁾	Vapor Pressure (mm Hg, 25°C)
2,4 dichlorobiphenyl	73	2.16	1400	1 x 10E-3
2,2',4,4' tetrachlorobiphenyl	168	56	68	8.6 x 10E-5
2,2', 4,4', 6,6' hexachlorobiphenyl	169	104	0.9	1.3 x 10E-5
2,2',3,3',4,4',5,5' octachlorobiphenyl	12	10.4	1.4	--

(1) Taken from Erickson (1992).

(2) Solubility in parts per billion, approximately equal to ng/ml.

are probably not applicable to the high ionic strength master solution. The higher-than-expected measured concentrations may be the result of coordination or complexation of the congeners with iron. The PCB congeners were added to the master solution (500 ml) in a 100- μ l methanol aliquot and, though remote, there is a possibility that a co-solvency effect with the trace quantity of methanol increased their solubilities. A study on the effects of solution pH during liquid/liquid extraction of PCBs from water samples found that pH has an effect, but the trend was confounding (i.e., various Aroclor mixtures were affected differently by pH) (Erickson 1992).

Surrogates, tetrachloroxylene (TCX) and decachlorobiphenyl (DCB), were added to the master solution sample prior to the extraction. The TCX and DCB recoveries were excellent, 106% and 99%, respectively.

2.2 Test Procedure

Five 100-ml glass graduated cylinders (test vessels) were cleaned, tared and labeled V1 through V5. The function of each test vessel is described in Table 2. Approximately 83 ml of the master acid dissolver solution were added to each vessel. Next, 19 M sodium hydroxide (i.e., caustic adjustment) was added to adjust the solution pH to 12.9 +/- 0.1 in V3, V4, and V5, and the neutralized solutions/slurries were well mixed. The caustic additions increased the solution volumes in these vessels to 102 - 103 ml. Immediately after the caustic addition, a very fine iron hydroxide precipitate formed. This precipitate was allowed to settle for 18 hr. After settling, a clarified supernatant and a settled sludge phase was formed. The supernatant from V3 and V4 was sampled, extracted, and analyzed for PCB. When all of the supernatant was decanted, the settled sludge from these two vessels was re-acidified (to redissolve

the precipitate), and extracted and analyzed for PCB. The sludge in V5 was centrifuged and dried at 105°C to provide mass and volume data on centrifuged and dry sludge.

A 3 M HNO₃ solution was added to the contents of V1 and V2 to increase the volume in these two vessels to 103 ml (i.e., same final volume as in V3, V4, and V5). The volumes in V1 and V2 were adjusted to keep a constant ratio of liquid to surface area for the solutions in all five graduated cylinders. To maintain quality control, all tests were conducted concurrently to ensure that all solutions were in contact with test vessels for the same period of time. Weights and volumes of V1 - V5 were measured during each step in the testing to provide comprehensive mass balances.

Table 2. Description of Test Matrix

Test Vessel ID	Purpose/Function for Content of Test Vessel
V1	used to provide a sample of initial acid dissolver solution (i.e., before caustic adjustment) from a system identical to that used for the precipitation test
V2	duplicate of V1
V3	acid dissolver solution was caustic adjusted, samples of neutralized dissolver solution and settled sludge provided
V4	duplicate of V3
V5	duplicate of V3 and V4; however, only used to collect data on mass and volume of centrifuged sludge and mass of dried sludge

2.3 Sampling and Analysis

2.3.1 Extraction

TCX and DCB were added as surrogate compounds to all samples just prior to the extraction process. Recovery of these compounds was used as a measure of efficiency of the extraction process. The surrogate recoveries represent the optimum recovery possible without the chemical treatment test variables included. The volatility of the surrogate compounds bracket the range represented by the PCBs chosen for these tests and for almost all of the possible PCB congeners. Recoveries ranging from 54% to 106% were obtained for the surrogates, which were spiked at 0.02 µg per sample (liquid samples) (see appendix).

Following the addition of the surrogate compounds, the liquid samples were processed using liquid/liquid extractions in separatory funnels with methylene chloride. The sample extracts were then concentrated and exchanged into hexane.

2.3.2 Analysis

After sample extraction and preparation, analyses were performed using a gas chromatograph (GC) with two electron capture detectors (ECD). Response factors for the ECDs were obtained on dilutions of a PCB congener spike solution. ECD allows detectability limits below the ng/ml range. GC conditions were a single 2-microliter injection made on-column onto a 5M fused silica retention gap split between two analytical columns: a 0.32 mm x 30 mm DB-17 (0.25-micron phase) and a 0.32 mm x 30 mm DB-1701 (0.25-micron phase). The oven-programmed temperature was 68°C for 0.5 min, then 20°C/min to 200°C, 3°C/min to 250°C, and 20°C/min to 280°C; held at 280°C for 15 min. ECD temperature was 300°C with a purified nitrogen make-up gas.

3.0 Results and Discussion

This section provides an evaluation of the PCB congener data and the mass balance information. The raw PCB analytical data are included in the appendix.

3.1 Fate of PCB Congeners in Liquid Phase

The concentrations of PCB congeners in the dissolver solution before and after caustic adjustment were determined in duplicate. The results from the duplicate tests were used to calculate relative percent differences (RPDs). The concentrations (averages of duplicates) and RPDs are provided in Table 3, which also shows the percent removal of each congener from the caustic adjustment step. For the congeners of most interest (i.e., most representative of Aroclor 1254), tetrachloro- and hexachlorobiphenyl, 90% to 98% removal was achieved. A similar level of removal was achieved for the octachlorobiphenyl congener. These results are very consistent with the result previously obtained by Mong et al. (1998). In a similar test, they calculated that after caustic addition, 91% to 99% of the PCBs in the dissolver solution partitioned to the precipitated sludge. [Note: in the study conducted by Mong et al. (1998), the PCB congener concentration in the dissolver solution before caustic adjustment was not measured, but calculated by difference.]

Table 3 shows that the concentration of dichlorobiphenyl increased after the caustic adjustment step. As noted in Section 2.1, unexpected results were obtained when determining the dichlorobiphenyl concentration in the master solution (i.e., measured concentration was low by a factor of about 30, based on how much was added and its solubility in water). If the predicted concentration of dichlorobiphenyl (73 µg/ml - see Table 1) is used as the initial concentration in the dissolver solution before caustic adjustment, then a 93% removal is calculated for this congener.

Table 3. PCB Concentration and Percent Removal in Liquid Phase

PCB Congener	Dissolver Solution Before Caustic Adjustment		Dissolver Solution After Caustic Adjustment		% PCB Removal from Dissolver Solution by Caustic Adjustment
	PCB, µg/L	RPD, %	PCB, µg/L	RPD, %	
2,4 dichlorobiphenyl	2.30	29.9	5.0	23.2	-117%
2,2',4,4' tetrachlorobiphenyl	35.8	7.82	3.42	35.4	90.4 %
2,2', 4,4', 6,6' hexachlorobiphenyl	59.0	16.3	1.15	36.5	98.1 %
2,2',3,3',4,4',5,5' octachlorobiphenyl	5.91	8.12	0.08	25.0	98.6 %

The loss of 2,4 dichlorobiphenyl from the dissolver solution both before (Table 1) and after caustic adjustment may be related to the increased fugacity of this less chlorinated congener from water solutions at low concentrations (Mong 1997). The more highly chlorinated congeners with lower solubilities and lower vapor pressures apparently do not exhibit this effect.

The congener concentrations in the dissolver solution after caustic adjustment are above the TSCA limit (i.e., 0.5 ppb) for aqueous liquid streams; however, in the actual K Basin Sludge Conditioning Process, the dissolver solution will pass through a filter before caustic adjustment. Based on engineering studies and Mong et al. (1998), about 95% of the PCB in the dissolver solution is expected to be removed by filtration.

3.2 Fate of PCB Congeners in Precipitated Sludge Phase

Upon caustic adjustment of the acid dissolution stream, a fine iron hydroxide particulate formed and was allowed to settle for 18 hr. After settling, about 50% of the vessel volumes were occupied with sludge, while the remaining vessel volumes contained clarified neutralized dissolver solution supernatant. The supernatant was decanted, and the entire sludge volume was extracted (after re-acidification) and analyzed for PCB. Table 4 shows the results of the PCB analyses. The results in Table 4 show that concentrations of PCB congeners in settled sludge generated from caustic adjustment of a dissolver stream, which was saturated with the PCB congeners, is well below the TSCA criterion for solids/sludge (2 ppm PCB). The results are reported on a wet settled sludge basis since this is the form in which the sludge will exist when transferred to TWRS. The PCB sludge concentration data can be converted to a "dry sludge" basis using the mass/volume data provided in Section 3.4.

The RPDs for the concentrations in the sludge phase are somewhat higher than those obtained from the analysis of the liquid phases (Table 3). The higher RPDs may have partially been caused by differences in the volumes of settled sludges obtained between the duplicate tests.

Table 4. PCB Concentration in the Sludge

PCB Congener	PCB Concentration in Settled Sludge	
	PCB, ng/g	RPD, %
2,4 dichlorobiphenyl	15.7	44.5
2,2',4,4' tetrachlorobiphenyl	66.6	30.9
2,2', 4,4', 6,6' hexachlorobiphenyl	66.6	20.7
2,2',3,3',4,4',5,5' octachlorobiphenyl	6.9	17.4

3.3 Final Distribution of PCB Congeners

Tables 5 and 6 show the distribution of the PCB congeners among the various phases (settled solids, neutralized dissolver solution, and vessel rinsate) for the tests conducted in V3 and V4 (see Table 2 for test conditions). These tables also include information on total PCB congener recovery.

In general, the majority of the congeners (70% to 90%) become associated with the settled sludge phase. About 6% to 20% were recovered in the solvent used to rinse the vessel. The PCB congeners associated with the neutralized dissolver solution ranged from less than 1% to 15%. The fraction remaining with the dissolver solution decreased with increasing levels of chlorination.

With respect to the dissolver solution, these results are very consistent with those obtained by Mong et al. (1998). However, Mong et al. (1998) found that 35% to 99% of the recovered PCB congeners were associated with the vessel rinse solutions. Their tests were conducted in the vessels for 8 hr at boiling temperatures, while the tests described in this report were conducted at ambient temperatures.

The "overall PCB mass recovery values %" were calculated by dividing the sum of the PCBs recovered in the three fractions by the quantities measured in the acidified dissolver solution (Table 1). The recoveries are reasonable for all congeners, except for dichlorobiphenyl. This is another strong indication that the measured concentrations of dichlorobiphenyl in the initial dissolver solution are low (by a factor of 8 to 10).

Table 5. Distribution of PCBs in Vessel 3 (V3)

PCB Congener	Percent of Total Recovered PCB in Stream			Overall PCB Mass Recovery ⁽¹⁾ , %
	Settled Solids	Neutralized Dissolver Solution	Vessel Rinse Solution	
2,4 dichlorobiphenyl	80	14	6.4	960
2,2',4,4' tetrachlorobiphenyl	86	2.7	12	140
2,2', 4,4', 6,6' hexachlorobiphenyl	88	0.99	11	69
2,2',3,3',4,4',5,5' octachlorobiphenyl	92	0.69	7.1	67

(1) % recovery = 100 x (total congener mass recovered)/(congener mass measured in starting solution).

Table 6. Distribution of PCBs in Vessel 4 (V4)

PCB Congener	Percent of Total Recovered PCB in Stream			Overall PCB Mass Recovery ⁽¹⁾ , %
	Settled Solids	Neutralized Dissolver Solution	Vessel Rinse Solution	
2,4 dichlorobiphenyl	68	15	17	760
2,2',4,4' tetrachlorobiphenyl	76	2.3	22	120
2,2', 4,4', 6,6' hexachlorobiphenyl	84	0.81	16	63
2,2',3,3',4,4',5,5' octachlorobiphenyl	92	0.59	7.6	60

(1) % recovery = $100 \times (\text{total congener mass recovered})/(\text{congener mass measured in starting solution})$.

3.4 Discussion of Mass/Volume Data

Mass and volume data were collected during each step within this testing to provide comprehensive mass balance information (Table 7). This information was used to convert PCB congener data from a mass to concentration basis. In addition, information was also provided on the mass and volume of settled sludge, centrifuged sludge, and dried sludge. Table 7 shows that there is considerable variability in the mass and volume of settled sludge obtained after an 18-hr settling period.

The settled sludge obtained from V5 was centrifuged (2000 rpm HN-S centrifuge x 10 min, 3X) and dried. Centrifuging resulted in sludge that was 34% (weight) solids. In comparison, the settled sludge from V5 was 13% (wt) solids. If it is assumed that V3, V4, and V5 contained equal masses of dry solids, the settled sludge from V3 and V4 were 10% and 12% (wt) solids. Consequently, to convert the settled sludge PCB congener concentration data (Table 4) to a dry solids basis, the data could be multiplied by a factor of ~10 (after subtracting out the PCBs associated with the interstitial liquid). Even when neglecting to subtract out the PCBs associated with the interstitial liquid, the total PCB concentration on a dry sludge basis is less than the 2 ppm PCB TSCA criterion.

Table 7. Mass/Volume Balance Table

Vessel Number	Acid Dissolver Solution Used		After Caustic (or Acid Addition) ⁽¹⁾		Settled Sludge (18 hr settling time)		Centrifuged Sludge ⁽²⁾		Dried Sludge ⁽²⁾
	Mass, g	Volume, ml	Mass, g	Volume, ml	Mass, g	Volume, ml	Mass, g	Volume, ml	Mass, g
V1	94.82	83.5	113.28	103	--	--	--	--	--
V2	94.16	83.5	112.3	103	--	--	--	--	--
V3	93.06	82.5	119.22	103	70.96	60	--	--	--
V4	91.00	82	177.00	102	64.72	55	--	--	--
V5	93.04	82.5	119.5	103	54.82	46	20.8	16	7.16

⁽¹⁾ For V3, V4, and V5, a 19 M NaOH solution was added to neutralize the acid dissolver solution and raise the pH to 12.9±0.1. A similar volume of HNO₃ was added to V1 and V2 to keep the ratio of liquid to surface area constant for all five vessels.

⁽²⁾ The contents of V5 were not analyzed for PCB. The purpose of V5 was to obtain data on the mass and volume of centrifuged sludge and the mass of dried (105°C) sludge.

4.0 References

Erickson, M. D. 1992. *Analytical Chemistry of PCBs*. Lewis Publishers, Boca Raton, Florida.

Makenas, B. J., T. L. Welsh, R. B. Baker, D. R. Hansen, and G. R. Golcar. 1996. "Analysis of Sludge from Hanford K East Basin Floor and Weasel Pit." WHC-SP-1182, Westinghouse Hanford Company, Richland, Washington.

Makenas, B. J., T. L. Welsh, R. B. Baker, E. W. Hoppe, A. J. Schmidt, J. Abrefah, J. M. Tingey, P. R. Bredt, and G. R. Golcar. 1997. "Analysis of Sludge from Hanford K East Basin Canisters." HNF-SP-1201, Duke Engineering & Services Hanford, Richland, Washington.

Makenas, B. J., T. L. Welsh, R. B. Baker, G. R. Golcar, P. R. Bredt, A. J. Schmidt, and J. M. Tingey. 1998. "Analysis of Sludge from Hanford K West Basin Canisters." HNF-1728, Fluor Daniel Hanford, Inc., Richland, Washington.

Mong, G. M. 1997. "PCB Literature Search - Destruction Technologies." Letter Report 28510, Transmitted by K. L. Silvers (PNNL) to R. J. Lodwich (DESH) on October 24, 1997, Pacific Northwest National Laboratory, Richland, Washington.

Mong, G. M., E. W. Hoppe, K. H. Pool, A. J. Schmidt, K. L. Silvers, and B. M. Thornton. 1998. "K Basin Sludge Conditioning Process Testing: Fate of PCB During K Basin Sludge Dissolution in Nitric Acid and with Hydrogen Peroxide Addition." PNNL-11998, Pacific Northwest National Laboratory, Richland, Washington.

Schmidt, A. J. 1997. "Evaluation of Polychlorinated Biphenyls (PCB) Data from K East Basin Sludge Samples." Letter to R. P. Omberg (DESH) on January 7, 1997, Pacific Northwest National Laboratory, Richland Washington. This document is to be published as an appendix to HNF-2367.

Schmidt, A. J. 1998. "Test Instruction: Partitioning of PCB in Dissolver Solution After Neutralization/Precipitation." TI-28510-13, Rev. 0, July 9, 1998, Pacific Northwest National Laboratory, Richland, Washington.

Appendix

Analytical Data for PCB Congeners

Analytical Data for PCB Congeners

Target Compounds	2,4 Dichlorobiphenyl	2,2',4,4' Tetrachlorobiphenyl	2,2',4,4',6,6' Hexachlorobiphenyl	2,2',3,3',4,4',5,5' Octachlorobiphenyl
Quantity Spiked ⁽¹⁾ , ng/ml	73.00	168.00	169.00	12.00
Quantity Spiked ⁽¹⁾ , total ng	6059.00	13,944.00	14,027.00	996.00
Original ⁽²⁾ , ng/ml	2.16	56.00	104.00	10.40
V1-DS ⁽³⁾ , ng/ml	2.45	34.40	54.20	5.67
V2-DS ⁽⁴⁾ , ng/ml	1.76	37.20	63.80	6.15
V3-NDS ⁽⁵⁾ , ng/ml	5.58	4.02	1.36	0.09
V4-NDS ⁽⁶⁾ , ng/ml	4.42	2.81	0.94	0.07
V3-Sldg ⁽⁷⁾ , total ng	1359.60	5458.00	5214.00	532.00
V4-Sldg ⁽⁸⁾ , total ng	908.00	4208.00	4460.00	469.00
V1-SW ⁽⁹⁾ , total ng	72.80	1233.80	1885.20	146.40
V2-SW ⁽⁹⁾ , total ng	45.42	861.20	1477.00	140.18
V3-SW ⁽⁹⁾ , total ng	110.02	743.20	642.80	41.04
V4-SW ⁽⁹⁾ , total ng	224.00	1229.80	835.00	39.00

Surrogate Recovery Results

Surrogate Compounds	Tetrachloroethylene	Decachlorobiphenyl
Original ⁽²⁾ , % recovery	106	99
V1-DS ⁽³⁾ , % recovery	64	104
V2-DS ⁽⁴⁾ , % recovery	67.5	109
V3-NDS ⁽⁵⁾ , % recovery	64.5	108
V4-NDS ⁽⁶⁾ , % recovery	54	109

- (1) Quantity of PCB added to the Master Solution. Note: quantity added exceeded the solubility limit for the tetrachloro, hexachloro, and octachlorobiphenyl congeners.
- (2) Quantity of PCB congeners measured in Master Solution.
- (3) Vessel 1 - dissolver solution before caustic adjustment.
- (4) Vessel 2 - dissolver solution before caustic adjustment.
- (5) Vessel 3 - neutralized (after caustic adjustment) dissolver solution.
- (6) Vessel 4 - neutralized (after caustic adjustment) dissolver solution.
- (7) Vessel 3 - settled sludge after caustic adjustment.
- (8) Vessel 4 - settled sludge after caustic adjustment.
- (9) Solvent washes for various vessels.