

EVALUATION OF THE CHEMICAL EFFECTS OF WASTE TO
ENERGY (WTE) ASH USED FOR THE REMEDIATION OF
ABANDONED COAL MINES AND POTENTIAL FOR REMOVAL
OF CHLORINE FROM WTE FLY ASH

by

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Submitted in partial fulfillment of the requirements for the degree of M.S. in Earth Resources
Engineering

Department of Earth and Environmental Engineering

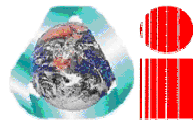
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EXECUTIVE SUMMARY

Bark Camp is the site of an abandoned coal mine in western PA that was targeted for remediation by the Pennsylvania Department of Environmental Protection (PADEP). This work was initiated by research at Penn State University on the material strength of ash-sediment mixtures and also by efforts of the Clean Ocean and Shore Trust of NY/NJ (COAST), a bi-state commission, to find beneficial uses of river sediments that could not be disposed offshore. The objective of the PADEP was to restore these hillsides, so they could support vegetation and thus return the area to a productive state within the ecosystem, by filling the gouges in the land using materials such as dredged soils and fluidized bed combustion (FBC) or municipal solid waste (MSW) ash that would otherwise be disposed in landfills.

Western PA has many abandoned coal mines such as Bark Camp, and therefore any reclamation that uses otherwise disposable material would provide tremendous environmental benefits. Three phases of mine remediation were performed at the site. The first two phases focused on FBC ash mixed with clean dredged material (mostly from the Hudson River) and was given a lime treatment. The final phase (phase III) targeted the use of MSW ash from a Waste to Energy (WTE) facility in place of FBC ash. Though fly ash was used for part of phase III, combined ash (a mixture of fly ash and bottom ash from a WTE incinerator) was used for most of this test. The location of the phase III test is referred to herein as the Bark Camp WTE site. Phase III was ultimately terminated due to high concentrations of chloride compounds observed by the PADEP.

Data was collected by the PADEP from June of 1998 through December of 2004. Many chemical species were analyzed over this time period, and all are studied and discussed herein. Typical behaviors of related compounds are identified, the most critical of which are labeled 'Category A' and 'Category B' respectively. 'Category A' species display a cyclic behavior throughout the time period. 'Category B' species display a constant increase in concentration throughout the time period. Species classified as 'Category A' or 'Category B' are discussed in detail and are compared to existing water quality parameters to determine if any are present in potentially harmful concentrations, which may require some level of pretreatment.

Chloride salts were the only compounds identified as requiring pretreatment. An existing stabilization technique for heavy metals was examined and a discussion of its potential use for the mitigation of chlorides in WTE ash is provided. Further, an existing technique specifically targeting the removal of chlorides in the fly ash component of WTE ash is introduced and discussed briefly as it is the subject of ongoing laboratory research at Columbia University. This technique has seen much success in a practical application in Hamburg, Germany. Finally, future work related to the possible pretreatment of chloride compounds is identified. A technique that can reduce the chloride levels in WTE fly ash may provide a solution to the only identified obstacle to the widespread use of WTE ash for the remediation of abandoned coal mines.

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Mr. Kent Shoemaker of the PADEP for taking time to visit the Bark Camp Site with me and share his vast knowledge of the daily operations at Bark Camp as well as relevant PADEP records and data.

Professor Nickolas J. Themelis for his role as advisor throughout my graduate studies and for initiating the Bark Camp investigation that is the subject of this report.

Michael P. Hyland, October 2005

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INTRODUCTION

1.1 Purpose of Study

The objective of this study is to provide a critical analysis of a previous full-scale test of using ash from a Waste to Energy (WTE) facility in the remediation of an abandoned coal mine in Western Pennsylvania; discuss potential problems with such a remediation; and identify suitable techniques for mitigating those problems.

1.2 Structure of Report

This report is structured as follows:

Section 2.0 - Test of Using WTE Combined Ash for the Remediation of the Bark Camp Mine Site: This section provides a background of the remediation efforts performed by the Pennsylvania Department of Environmental Protection (PADEP) at the Bark Camp Site. Existing conditions are described and the phases of mine remediation are introduced.

Section 3.0 - Chemical Effects of WTE Ash: This section analyzes a data set provided by the PADEP for many chemical species. Data was collected from three distinct monitoring locations and is classified into a number of categories.

Section 4.0 - Impact of Selected Compounds: This section provides a more detailed analysis of certain chemical species that were identified as the most critical in Section 3.0. Ultimately, the analysis arrives at those chemical species that should be targeted for pretreatment if WTE ash is to be used on a large scale basis for mine remediation.

Section 5.0 - Potential Application of the WES-PHix Process and Water Washing for Pretreatment of WTE Ash to Remove Chlorine: This section provides a detailed discussion of an existing pretreatment technology in wide-spread use for the stabilization of heavy metals and its potential for aiding in the stabilization of chlorine and chloride compounds. A brief discussion of a water-washing technique and future laboratory work to be performed at Columbia University is also provided.

Section 6.0 - Conclusion and Recommendations: This section provides a summary of the findings from the previous sections and details next steps that should be performed to arrive at a more beneficial use of WTE ash for mine remediation.

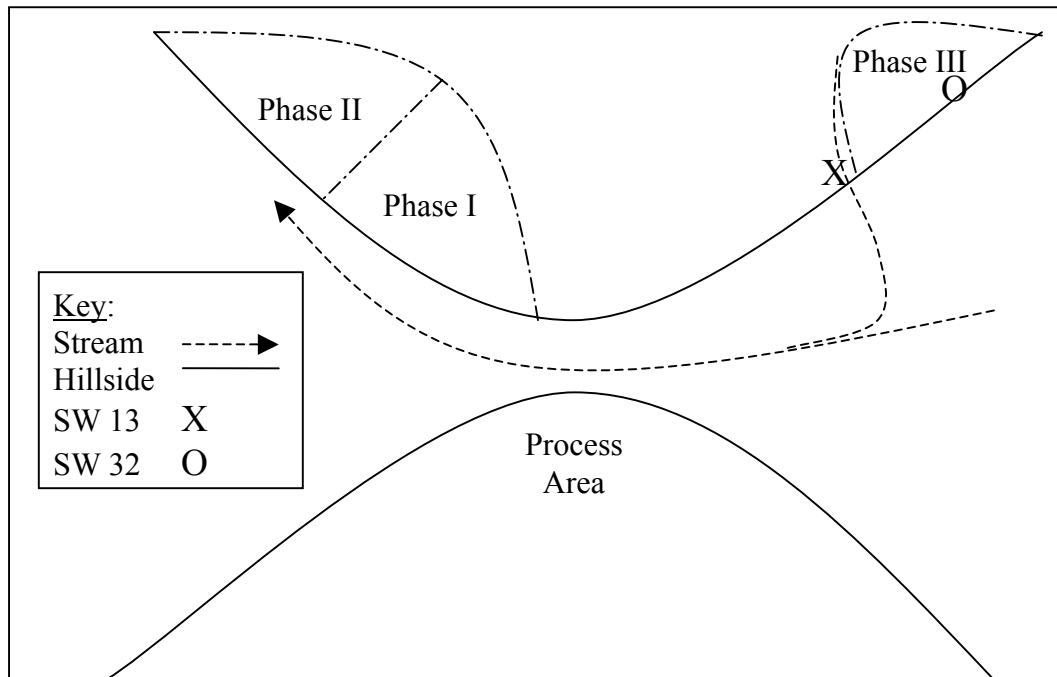
Section 7.0 - References: This section lists those references that were used in the preparation of this report.

TEST OF USING WTE COMBINED ASH FOR THE REMEDIATION OF THE BARK CAMP MINE SITE

2.1 Bark Camp Mine Site

The Bark Camp mine site is comprised of two hillsides and the valley between them, near DuBois, PA. The site visit was visited by the author in May, 2005 during which much of the history of the site and remediation to date was provided by Mr. Kent Shoemaker of the PADEP. Figure 2-1 shows the general layout of the site. The phases in this figure refer to the phase of mine remediation, described in the next section.

Figure 2-1 Bark Camp Site Plan



When the site was mined for coal, the hillsides were excavated to reveal coal seams. Overburden was dumped into the valley below. As was the case with many other coal mines, the site was abandoned when the coal was depleted, leaving the exposed hillsides. The Glen Irwin Coal Company operated these coal mines in the 1950s and 1960s. When this company became bankrupt during the 1970s, the land was left to the State of Pennsylvania. The mine remediation effort at Bark Camp was initiated by research at Penn State University on the material strength of ash-sediment mixtures and also efforts by the Clean Ocean and Shore Trust of NY/NJ (COAST), a bi-state commission, to find beneficial uses of river sediments that could not be disposed offshore.

The objective of the PADEP was to restore these hillsides to the point that they could support vegetation and thus return the area to a productive state within the ecosystem, by filling the gouges in the land using materials such as dredged soils and fluidized bed combustion (FBC) or municipal solid waste (MSW) ash that would otherwise be disposed in landfills.

Western PA has many abandoned coal mines such as Bark Camp, and therefore any reclamation that uses otherwise disposable material would provide tremendous advantages for the environment. For sites like Bark Camp, the overburden from exposing the coal seams could potentially be re-used to reclaim the hillside. Anthracite coal mines, which cover much of the similar area in eastern Pennsylvania, contain coal seams at steep angles, and accessing such mines rendered the overburden unusable. Dredged materials would have to be transported to such sites to support any major remediation effort.

2.2 Bark Camp Mine Remediation

A stream flows through the valley between the mountainsides, ultimately receiving the effluents from each of the mine remediation phases. The process area, shown in Figure 2-2, is used to prepare some of the raw materials (mixing the dredge and ash), and to add any ancillary chemicals such as lime to stabilize certain materials. It is in this process area that a potential chlorine stabilization technique, as discussed in Section 5 of this report, could be implemented, if such a treatment is not performed at the WTE facility where the ash is generated.

Figure 2-2 Process Area at Bark Camp



2.3 Phases I and II

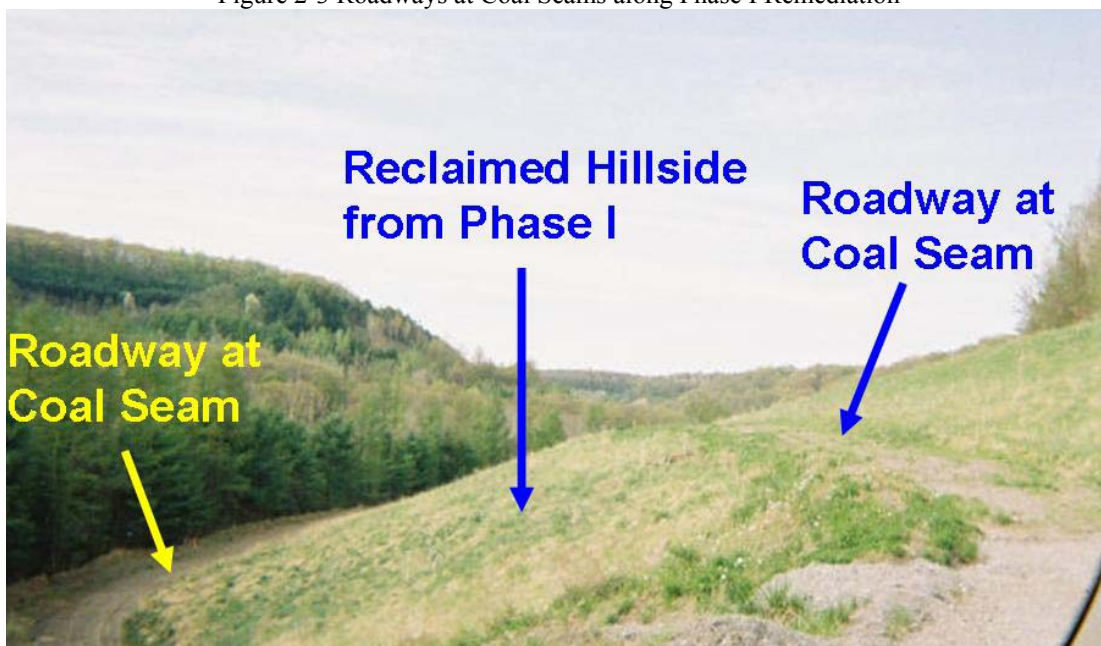
The Phase I site is regulated by monitoring wells 4, 5 and 6 (MW4, MW5 and MW6). This phase did not receive ash from a WTE Facility. Ash generated from the FBC of coal wastes, in power plants located in Pennsylvania, was used in mixture with dredged material from New York Harbor. In this case, FBC ash is defined as ash resulting from the combustion of ‘clean’ coal, like that which was mined from the Bark Camp site

originally. Lime was also added to the ash-sediment mixture to effect consolidation after placement in the old mine.

The Phase II site is regulated by monitoring wells 7, 8 and 9 (MW7, MW8 and MW9). Though neither FBC nor combined WTE ash was used for the remediation of this hillside, there was a WTE fly ash component added to the mixture of FBC ash, dredged material and lime for the latter part of the Phase II remediation.

Together, Phase I and II represent a restoration of approximately 11,000 linear feet (LF) of high wall. Two existing coal seams, now used as roadways, act as endpoints for the hillside as shown in Figure 2-3. As the seams run roughly parallel, each seam is approximately 5,500 LF; therefore, the far end of the Phase II remediation is slightly beyond one mile from the process area location.

Figure 2-3 Roadways at Coal Seams along Phase I Remediation



The groundwater monitoring wells range in depth from 40-feet to 120-feet below ground surface (40-120 fbs). Dredged material used for Phases I and II was initially provided from Perth Amboy in New Jersey. However the bulk of the dredged material was taken from the Hudson River.

2.4 Bark Camp WTE Site

On the basis of the successful remediation of the Phase I and II tests, a pilot test was performed on the 'west side' of the mountain, which targeted using WTE ash in place of FBC ash. During the pilot study, fly ash from a WTE facility was initially used in conjunction with FBC ash, same as was done near the end of the Phase II remediation. After the pilot test results were analyzed and deemed to be satisfactory, a permit was granted to perform a full-scale test at the same location. This third full-scale test is referred to as Phase III and extended from about June of 1998 through December of 2004.

During Phase III, combined ash from the same WTE facility that provided ash for the pilot test was substituted for the fly ash. Combined ash is defined as the mixture of bottom and fly ash generated in a WTE facility and consists approximately of 90% of bottom ash and 10% fly ash. i.e., ash collected in the gas control system of the plant. The WTE ash used during the pilot study and Phase III remediation was provided by the Essex County Facility of American Ref-fuel (Essex Facility), currently a division of Covanta Energy Corp.; dredged material was mostly received from an ongoing dredging project at the Parker Dam State Park, located in Pennsylvania's Moshannon State Forest.

2.5 Observations from Phases II and III

Phase III was ultimately terminated due to the detection by PADEP of abnormally high chloride concentrations. The high level of chlorides was driving down the pH of the stream at Bark Camp, causing fatal conditions for the naturally occurring fish and other wildlife, as far as two to three miles downstream of the Bark Camp site. Such high levels are not unexpected. The total input of chlorine in U.S. WTE facilities amounts to about 0.5% of the municipal solid wastes (MSW) feed, i.e. about 5,000 short tons for the Essex County WTE that is combusting about one million tons of MSW per year, nearly half of which is generated in Manhattan (Themelis, 2005). Although there was a fly ash component from a WTE facility added during Phase II and in the pilot test at the Bark Camp WTE site that led to the Phase III test, the impact was not noted at these times presumably because the amount of WTE fly ash added to the conventional FBC ash was relatively small. In effect, the high chlorine content of the WTE ash was diluted by cleaner ash. Apart from the aforementioned occurrence of chlorine, at this time the Phase III hillside appears to be in as good a condition as the hillsides from the Phase I and II remediation efforts. Figure 2-4 shows the condition of the Phase III hillside, as of the May 2005 site visit.

Figure 2-4 Reclaimed Hillside at Phase III Bark Camp WTE Site



The remainder of this report focuses on the results of regular monitoring of the Phase III remediation.

CHEMICAL EFFECTS OF WTE ASH

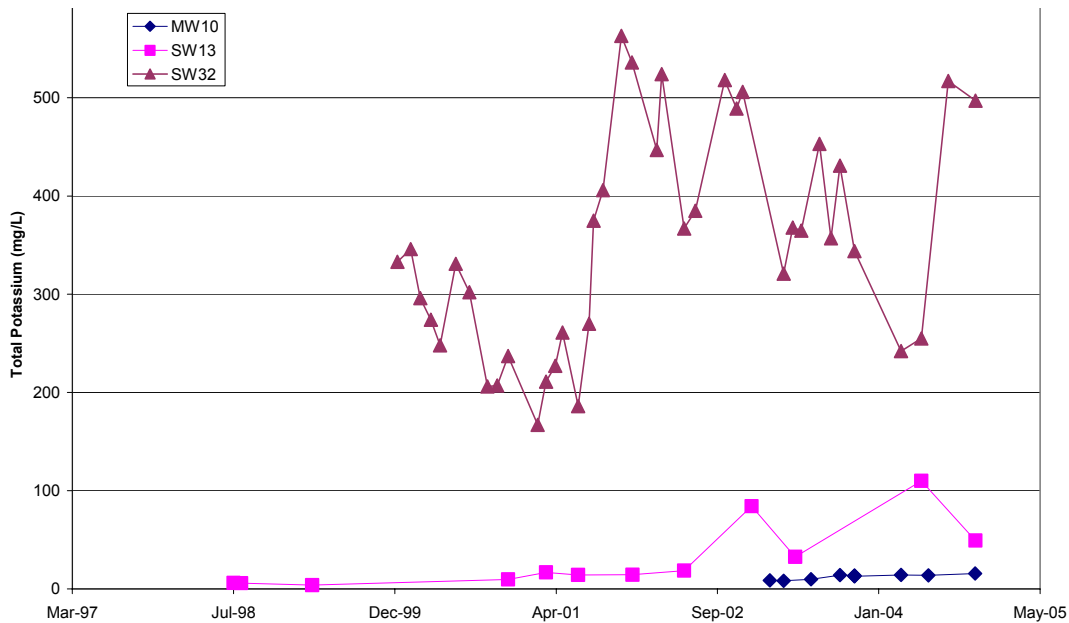
3.1 General Trends of Time Series Analyses

The data analyzed in this report were provided by the PADEP to COAST. These data were collected from the three sampling locations at the Bark Camp WTE site (Phase III), adjacent to the Bark Camp Phase I and II locations, as discussed in Section 2, from roughly June of 1998 through December 2004. In total, 325 separate elements, compounds, or indicators (collectively referred to as ‘species’) were analyzed on multiple dates (sampling events) throughout the time period. They are classified into seven categories, as described below. An alphabetical listing of all laboratory analyses performed, a corresponding sequential listing, and the full time series analyses for all species are provided in Appendix A. This appendix is presented in sequential test code order.

Whereas some literature in this field defines Total X vs. Dissolved X as the amount of X present in the solid ash vs. the amount of X present in the leachate, only the leachate was sampled at the Bark Camp WTE site. Therefore Total X refers to the total amount of element X present in the leachate at the Bark Camp WTE site in all of its compounds. The data presented herein were used to identify those species that are most prevalent in the WTE ash supplied by the Essex Facility.

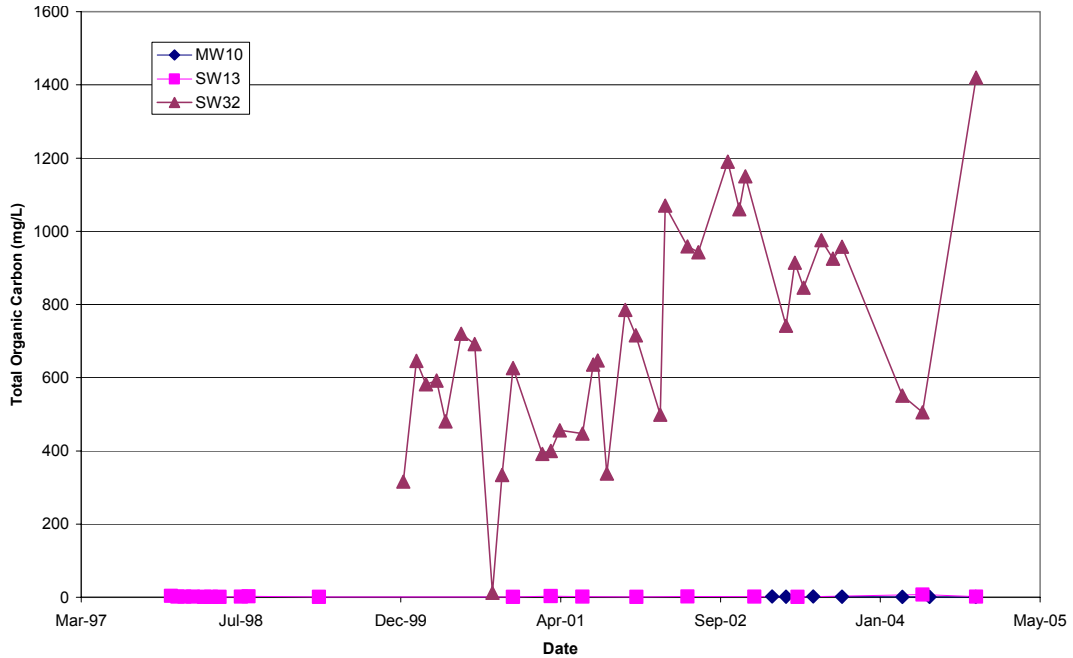
Category A species display cyclic behavior in concentration at the Surface Water 32 (SW32) sampling location; and either constant or late-increasing (after September of 2002) behavior in concentration at the Surface Water 13 (SW13) and Monitoring Well 10 (MW10) sampling locations. This typical behavior is shown in Figure 3-1 below:

Figure 3-1: Typical Behavior of Category A Species (Total Potassium data provided by PADEP)



Category B species display a consistent rise in concentrations at the SW32 sampling location, as shown in Figure 3-2 below. Some species also show increases in the concentrations seen at the SW13 and MW10 sampling locations. Category B species are discussed in detail in Section 4.2.

Figure 3-2: Typical Behavior of Category B Species (Total Organic Carbon data provided by PADEP)



Category C species display no change in concentration at any of the three sampling locations over time, as shown in Figure 3-3 below:

Figure 3-3: Typical Behavior of Category C Species (Total Boron data provided by PADEP)

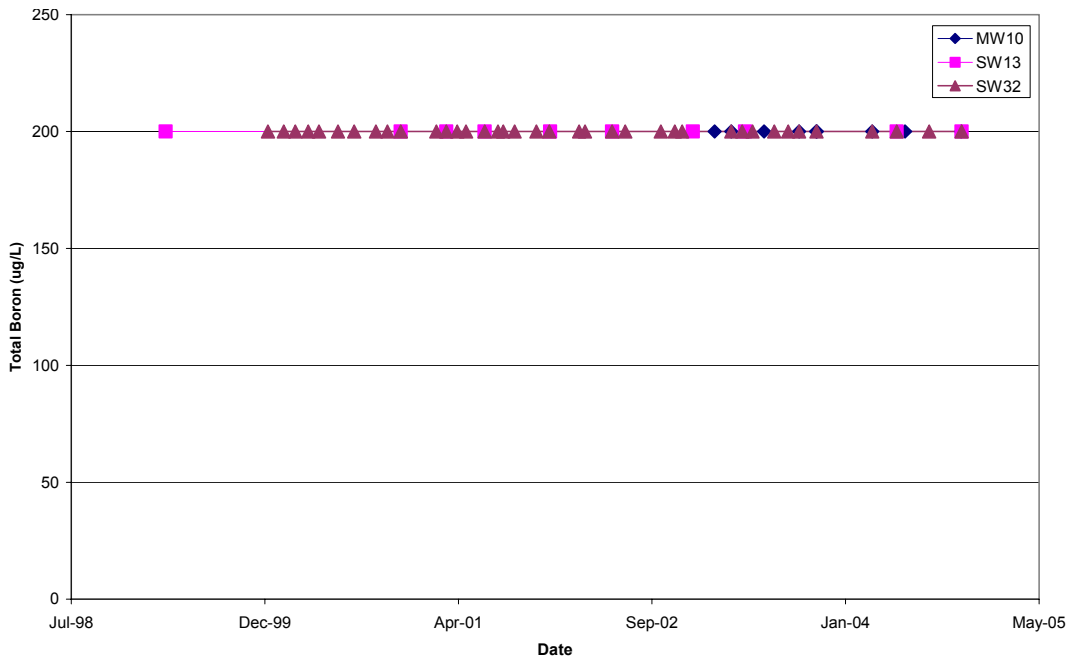


Table 3-1 lists the species that have been labeled as Category C and indicates the constant concentrations that were observed at each of the sampling locations:

Table 3-1: Concentrations of Category C Species at SW32, SW13 and MW10

Species	Conc. (ug/L)	Species	Conc. (ug/L)	Species	Conc. (ug/L)
Total Mercury	1.0	Total Cadmium	10.0	Total Chromium	50.0
Dissolved Mercury	1.0 *	Dissolved Boron	200 *	Dissolved Chromium	50.0 *
Dissolved Silver	10.0 *	Total Boron	200	Total Thallium	2.0 **

Notes: * indicates MW10 and SW32 sampling locations only; ** indicates SW13 sampling location only; all data adapted from PADEP data

Category D species display fairly constant concentrations over time at all sampling locations, with some spikes seen at SW32 near April of 2001, as shown in Figure 3-4 below. The relevance of this date is discussed later in this section.

Figure 3-4: Typical Behavior of Category D Species (Total Manganese data provided by PADEP)

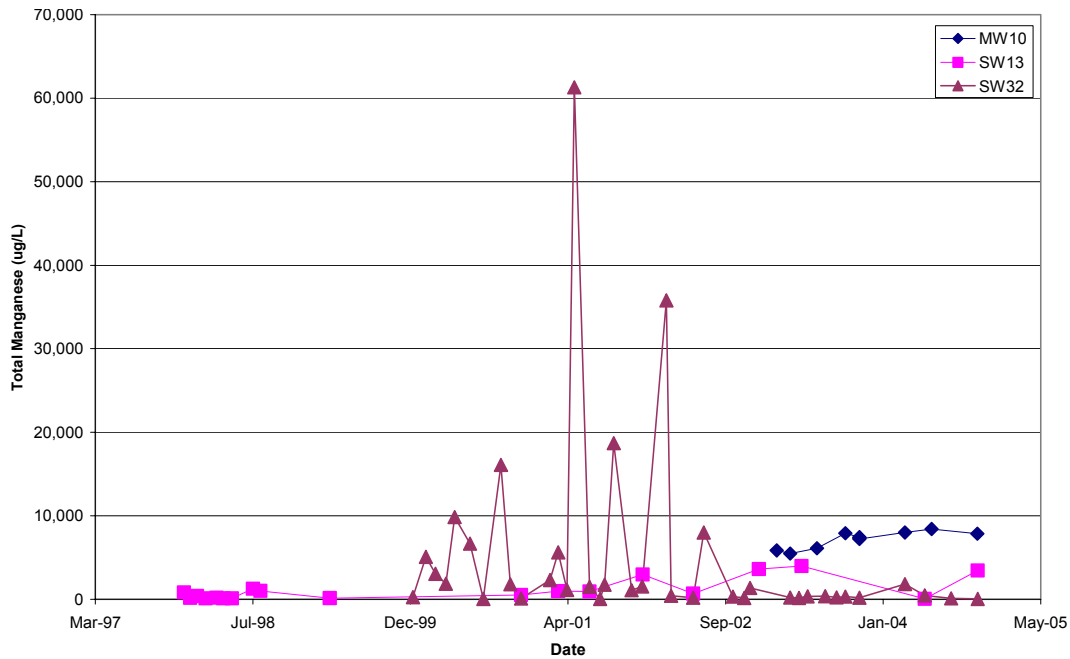


Table 3-2 lists the species that have been labeled as Category D, the constant value for that location (majority of sampling events), and the peak value, observed near April, 2001:

Table 3-2: Average and Peak Concentrations ($\mu\text{g/L}$) of Category D Species at SW32

Species	Average	Peak	Species	Average	Peak
Total Silver	10	50	Total Iron	2,000	81,600
Total Manganese	200	61,300	Total Arsenic	65	359
Total Lead	10	79.8	Total Cobalt	50	200
Sulfate	17 *	578 *	Total Selenium	70	394

Notes: * indicates concentration in mg/L; all data adapted from PADEP data

Category E species display similar behavior over time for the concentrations at the SW32 and MW10 sampling locations, with MW10 lagging in both magnitude and time, as shown in Figure 3-5 below:

Figure 3-5: Typical Behavior of Category E Species (Dissolved Zinc data provided by PADEP)

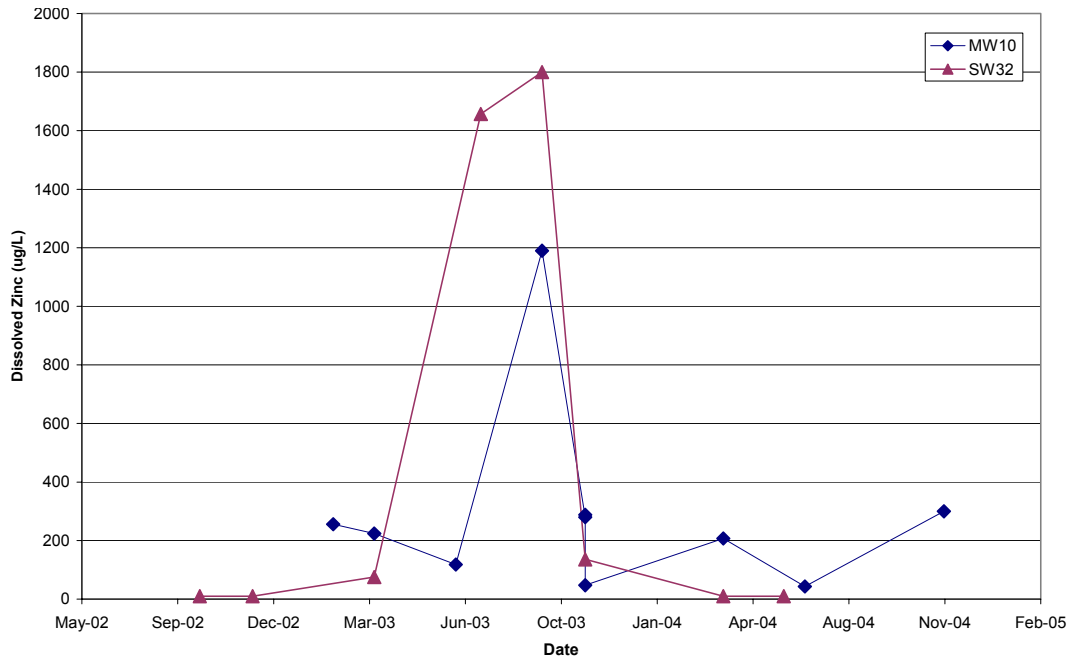


Table 3-3 lists the species that have been labeled as Category E and indicates the peak concentration reached for sampling locations SW32 and MW10 respectively:

Table 3-3: Peak Concentrations (µg/L) of Category E Species at SW32

Species	SW32	MW10	Species	SW32	MW10
Dissolved Arsenic	125	40	Dissolved Nickel	921	261
Dissolved Zinc	1,800	1,190	Dissolved Selenium	70	70
Dissolved Sodium	1,390 *	292 *	Dissolved Potassium	505 *	50 *

Notes: * indicates concentration in mg/L; all data adapted from PADEP data

Category F species are those for which there were insufficient data to examine the behavior of the concentration. A listing of these elements, along with the specific reason for their exclusion is provided in Appendix B.

Category G species are those for which there are identical data sets for multiple laboratory analyses. Furthermore, there is a discrepancy in the data, falling into one of the following two sub-categories:

- Inconsistent Measurements: Multiple analyses were performed on the same sample (or two samples were taken on the same day) and the measurements do not agree.
- Inconsistent Sampling Periods: Samples were generally only taken from one location during a given sampling event, and significant time passes between sampling events such that the long-term behavior of the concentrations are not identifiable.

3.2 Additional Fill Material Placement

Eight laboratory species exhibit a cyclic behavior wherein there is a relatively constant decrease in concentration for sampling location SW32 from December of 1999 until just before April of 2001. This is followed by a sharp spike in concentration during April of 2001 and another, more gradual, decrease in concentration through the remainder of the overall sampling time period.

The presence of distinct cycles suggests that there was some defining event that either triggered the release of stored elemental deposits, or resulted in an increase in the available chemicals in the fill material. It was later verified with PADEP that different fill material was placed on the Bark Camp WTE site in April of 2001. While the original fill material was a mixture of WTE ash, FBC ash and clean dredged material, as discussed in Section 2, the fill material placed in April of 2001 contained no FBC ash and it is unknown what amount of dredged material, if any, was included.

As the second cycle did not contain any amount of FBC ash in the fill material, this cycle more directly reflects the long-term leaching behavior of WTE ash taken from the Essex Facility. It also implies that WTE ash takes longer to degrade than FBC ash, as discussed in the next section. The composition of the dredged material should not impact the chemical effects of the fill material as clean dredged material was used at this site.

IMPACT OF SELECTED COMPOUNDS

4.1 Cyclic Behavior of Category A Species

Table 4-1 lists the species that have been labeled as Category A and includes local minima and maxima for each of the sampling locations:

Table 4-1: Concentrations of Category A Species

Species	Concentrations ($\mu\text{g/L}$ except as otherwise noted)					
	<u>SW32</u> max	<u>SW32</u> min	<u>SW13</u> max	<u>SW13</u> min	<u>MW10</u> max	<u>MW10</u> min
Specific Conductivity	20,700 *	9,820 *	3,740 *	180 *	5,220 *	2,660 *
Chloride	7,494 **	1,315 **	1,265 **	4.23 **	1,456 **	240 **
Total Potassium	563 **	167 **	110 **	3.81 **	15.6 **	8.24 **
Total Sodium	2,040 **	76.5 **	376 **	27.2 **	263 **	155**
Total Barium	5,600	1,510	174	27	56	22
Total Copper	1,800	10	40	10	19	10
Total Molybdenum	281	70	70	70	70	70
Nitrate	1.6 **	0.04 **	1.86 **	0.04 **	0.2 **	0.04 **

Notes: * indicates units of $\mu\text{mhos/cm}$; ** indicates concentration units of mg/L ; all data adapted from PADEP data

Figures 4-1 through 4-8 show the individual time series for each of these eight species:

Figure 4-1: Specific Conductivity ($\mu\text{mhos/cm}$) vs. Time (data provided by PADEP)

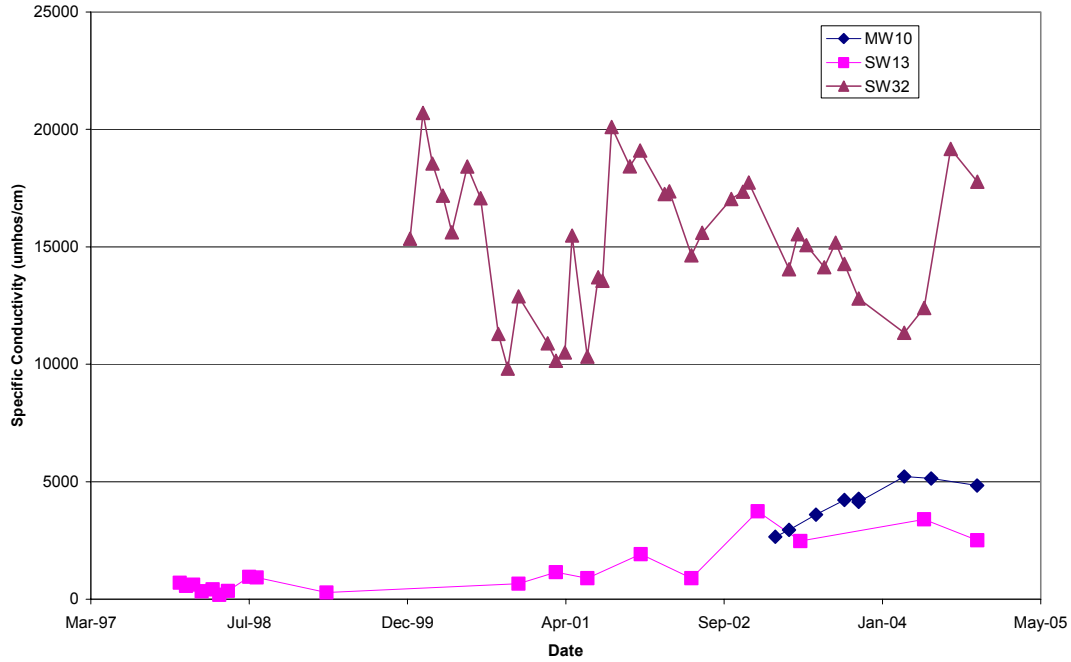


Figure 4-2: Chloride Concentration (mg/L) vs. Time (data provided by PADEP)

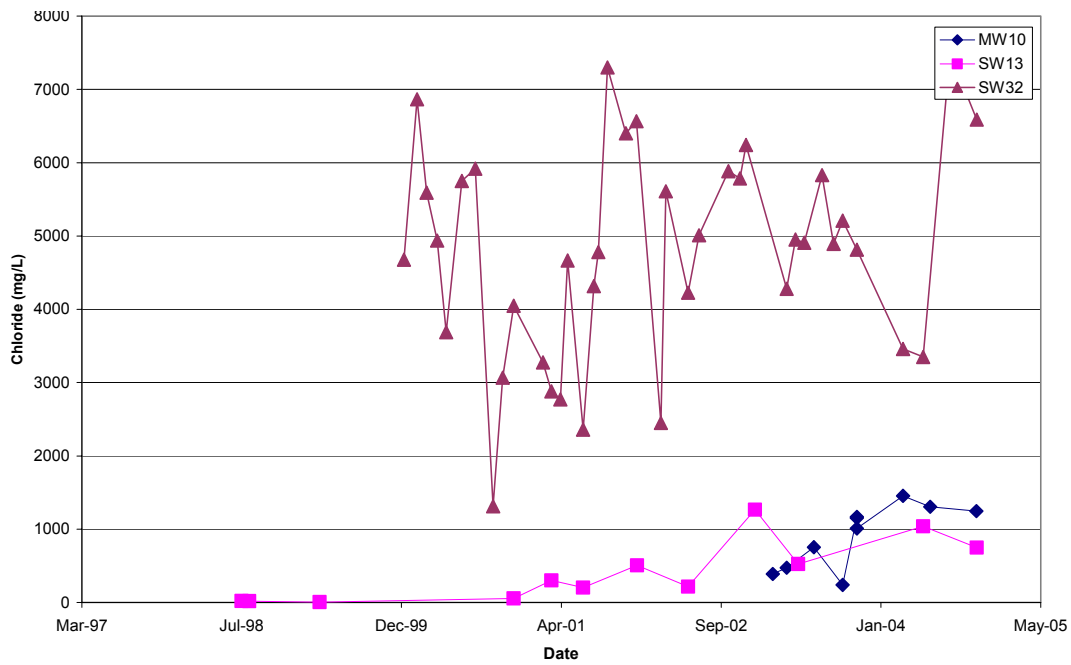


Figure 4-3: Total Potassium Concentration (mg/L) vs. Time (data provided by PADEP)

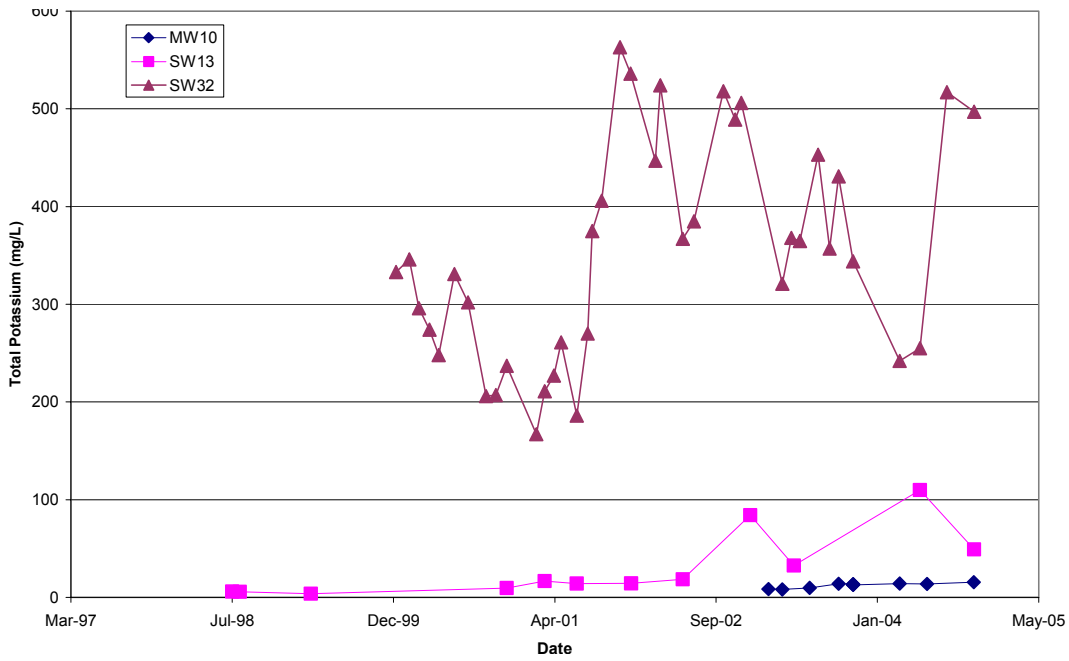


Figure 4-4: Total Sodium Concentration (mg/L) vs. Time (data provided by PADEP)

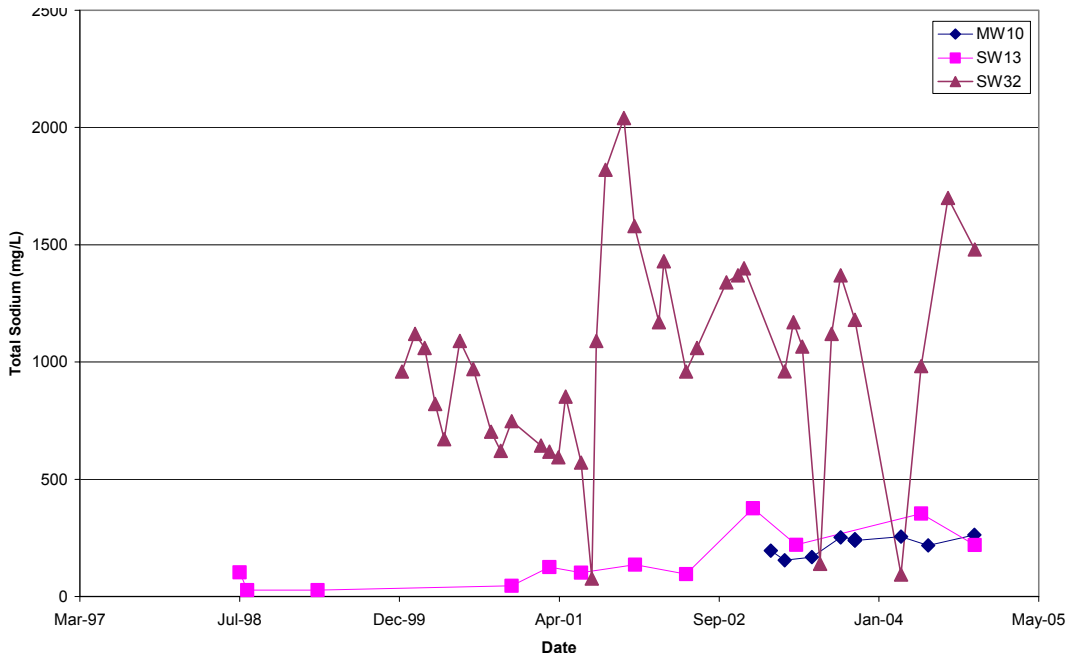


Figure 4-5: Total Barium Concentration ($\mu\text{g/L}$) vs. Time (data provided by PADEP)

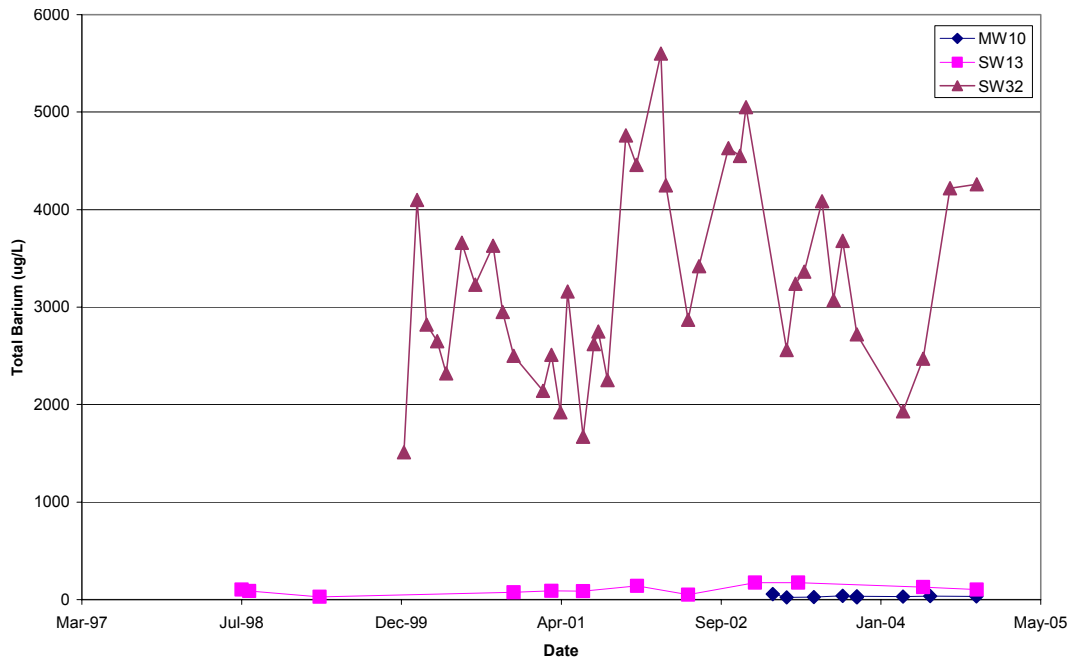


Figure 4-6: Total Copper Concentration ($\mu\text{g/L}$) vs. Time (data provided by PADEP)

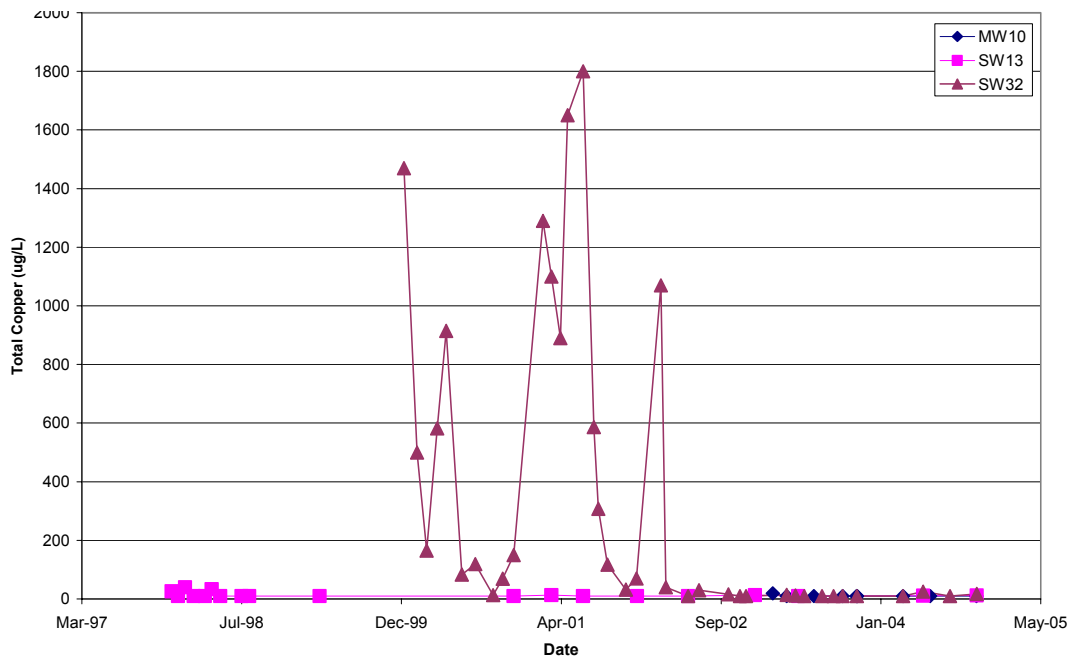


Figure 4-7: Total Molybdenum Concentration ($\mu\text{g/L}$) vs. Time (data provided by PADEP)

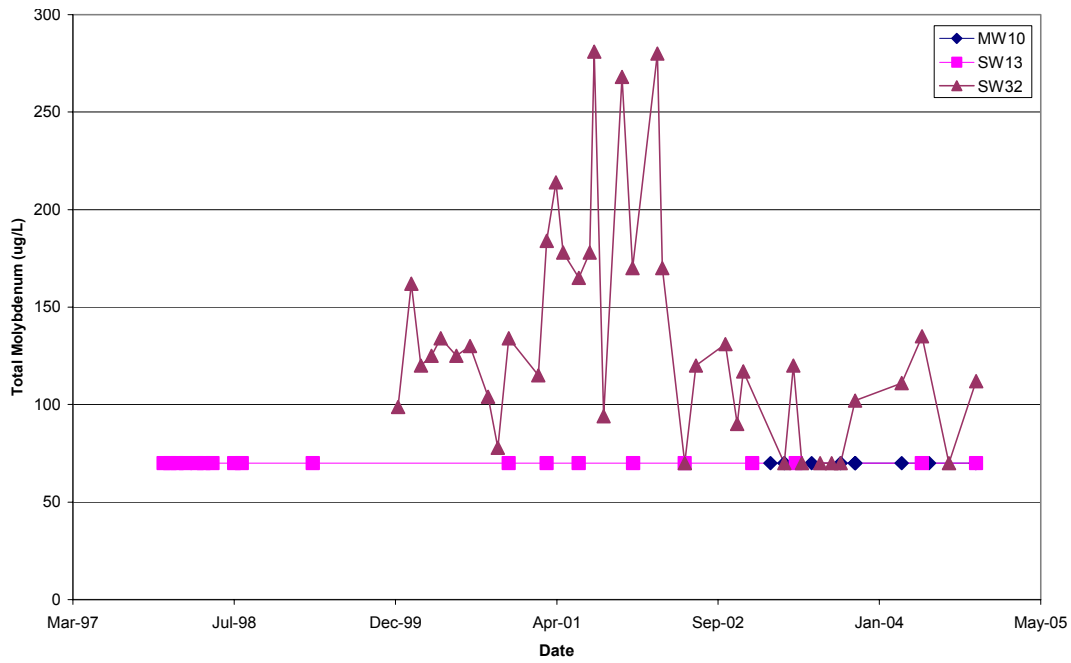
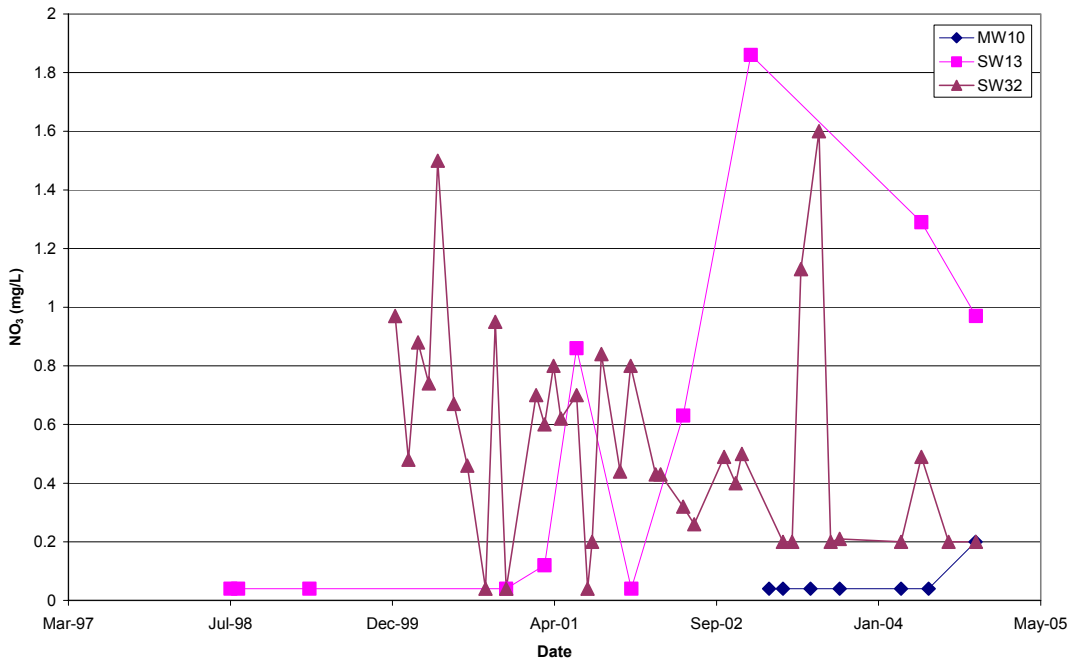


Figure 4-8: Nitrate Concentration (mg/L) vs. Time (data provided by PADEP)



Specific conductivity, chloride and those elements that easily form chloride compounds (sodium and potassium) track each other very closely. This is expected because conductivity is often used to approximate the salinity of a solution, as it is a measure of the ability of a solution to conduct electrical current, which is transported by ions (Metcalf & Eddy, 1991). In this respect, conductivity is an indicator of the presence of other elements and compounds, and its presence is neither harmful nor beneficial to the performance of the fill material.

For chloride, sodium and potassium, the first cycle is the most distinguishable. Examining the SW32 sampling location, the first cycle occurs between the January 24, 2000 and June 26, 2001 sampling events. The concentration of each of these species was decreased by roughly 50% over this time period. The second cycle begins prior to the November 7, 2001 sampling event and continues until approximately March of 2004. The concentration is again decreased by approximately 50%, though the rate of decrease is significantly lower as the cycle period is substantially longer for the second cycle than for the first. A summary of the two cycles for these species is provided in Tables 4-2 and 4-3, below. The extreme minimum that occurs on July 30, 2001 for total sodium and the extreme maximum that occurs on September 11, 2001 for chloride are excluded from these summary tables to facilitate a more direct comparison.

Table 4-2: Summary of Cycle 1 Activity for Selected Category A Species

	Chloride	Sodium	Potassium
Start Date	1/24/2000	1/24/2000	1/24/2000
End Date	6/26/2001	6/26/2001	6/26/2001
Duration (mos.)	18	18	18
Start Conc. (mg/L)	6,865	1,120	346
End Conc. (mg/L)	2,358	571	186
% Decrease in Conc.	66%	49%	46%
Rate of Decrease *	3.7% per month	2.7% per month	2.6% per month

Notes: * rate of decrease assumed to be linear over the time period; all data adapted from PADEP data\

Table 4-3: Summary of Cycle 2 Activity for Selected Category A Species

	Chloride	Sodium	Potassium
Start Date	11/7/2001	11/7/2001	11/7/2001
End Date	3/23/2004	5/25/2004	3/23/2004
Duration (mos.)	28	30	28
Start Conc. (mg/L)	6,400	2,040	563
End Conc. (mg/L)	3,458	983	242
% Decrease in Conc.	46%	52%	57%
Rate of Decrease *	1.6% per month	1.7% per month	2.0% per month

Notes: * indicates units of $\mu\text{mhos/cm}$; ** indicates concentration units of mg/L; all data adapted from PADEP data

It should be noted that the concentrations of sodium and potassium are nearly twice as high at the beginning of the second cycle as they were at the beginning of the first cycle. However, the concentration of chlorides does not change appreciably. Because of the high levels of chlorine typical for WTE ash, it is assumed that cations such as sodium and potassium will readily form their corresponding chloride compounds, and it is these chloride compounds that account for the majority of the form in which these species are detected. Since the chloride concentration remains approximately equal, and sodium and potassium have doubled in initial concentration, this implies that other elements that readily form chloride compounds are less prevalent in the WTE ash used for the fill material placed in April of 2001.

The concentrations of chlorides, potassium and sodium are increasing at sampling location SW13 and MW10, located further away from the Bark Camp WTE site and liner material. One possible reason for this is that these chloride compounds are migrating extremely slowly to the downstream sampling locations.

4.2 Increasing Concentrations of Category B Species

Four laboratory analyses exhibit increases in the concentration at all sampling locations throughout the overall sampling period. Table 4-4 lists the species that have been labeled Category B and includes local minima and maxima for each of the sampling locations:

Table 4-4: Concentration of Category B Species

Species	Concentrations ($\mu\text{g/L}$ except as otherwise noted)					
	<u>SW32</u> max	<u>SW32</u> min	<u>SW13</u> max	<u>SW13</u> min	<u>MW10</u> max	<u>MW10</u> min
Total Nickel	1,310	111	51	50	334	101
Total Distilled Phenols	5,924	110	31	5	6.76	5
Total Dissolved Solids (TDS)	18,810 *	76 *	2,870 *	88 *	5,500 *	2,300 *
Total Organic Carbon	1,420 *	12.5 *	7.2 *	1.0*	2.0 *	1.0 *

Notes: * indicates concentration units of mg/L; adapted from PADEP data

Figures 4-9 through 4-12 show the individual time series for each of these four species.

Figure 4-9: Nickel Concentration ($\mu\text{g/L}$) vs. Time (data provided by PADEP)

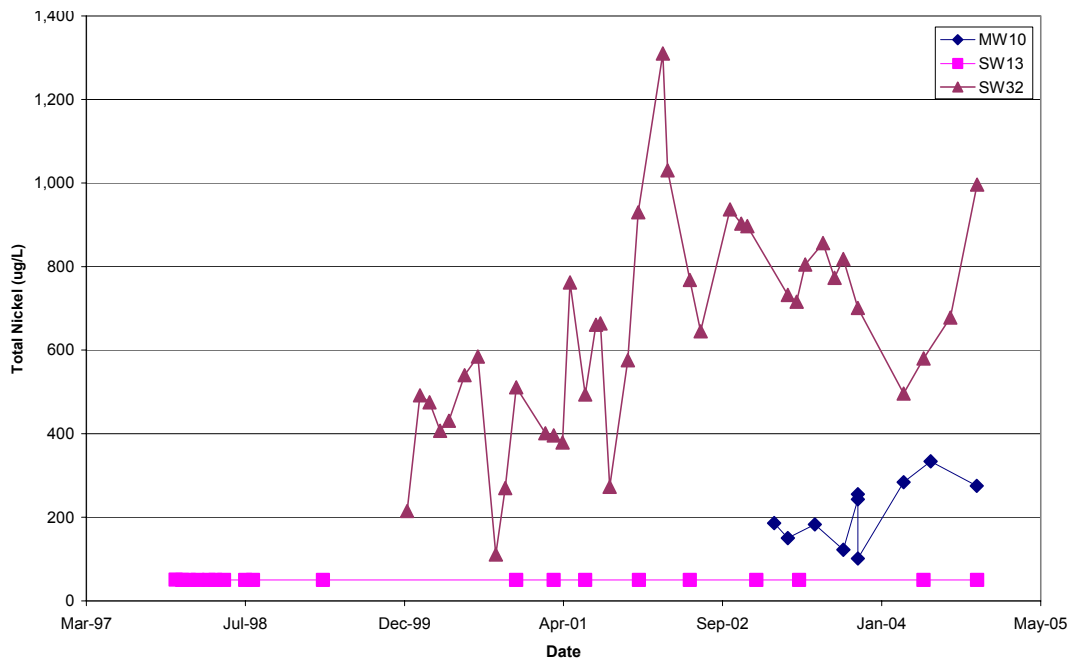


Figure 4-10: Total Distilled Phenols Concentration (µg/L) vs. Time (data provided by PADEP)

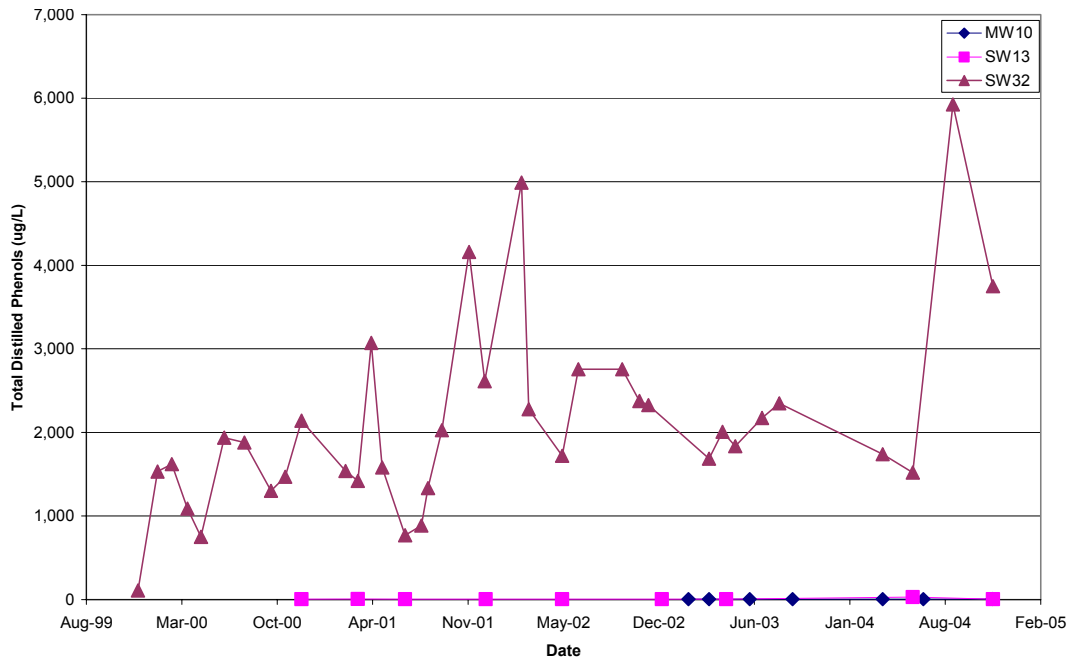


Figure 4-11: Total Dissolved Solids Concentration (mg/L) vs. Time (data provided by PADEP)

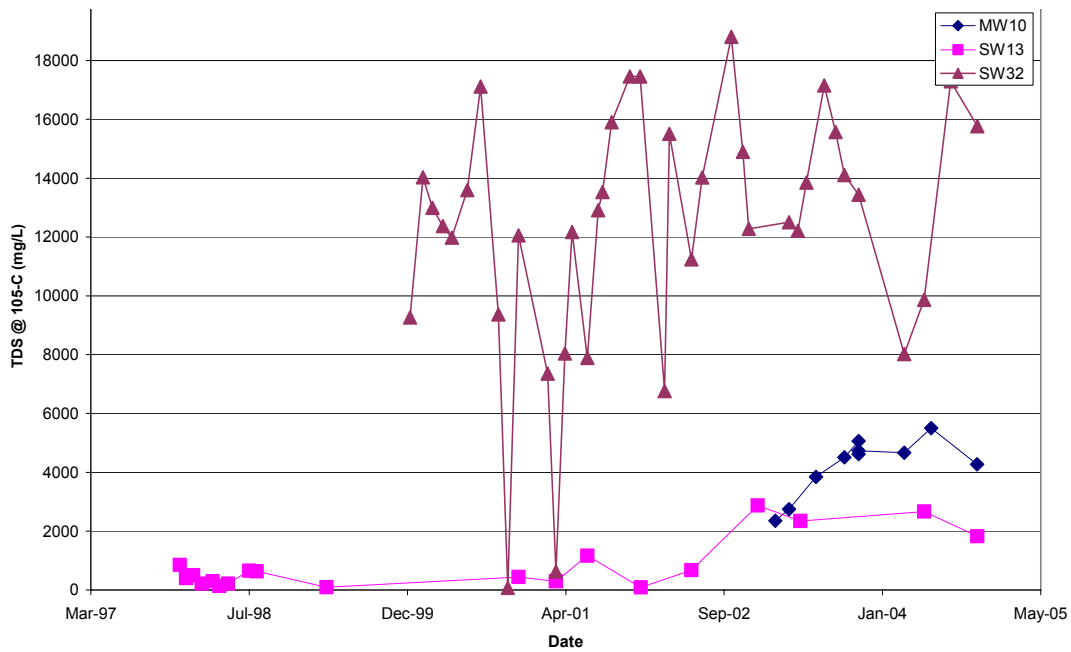
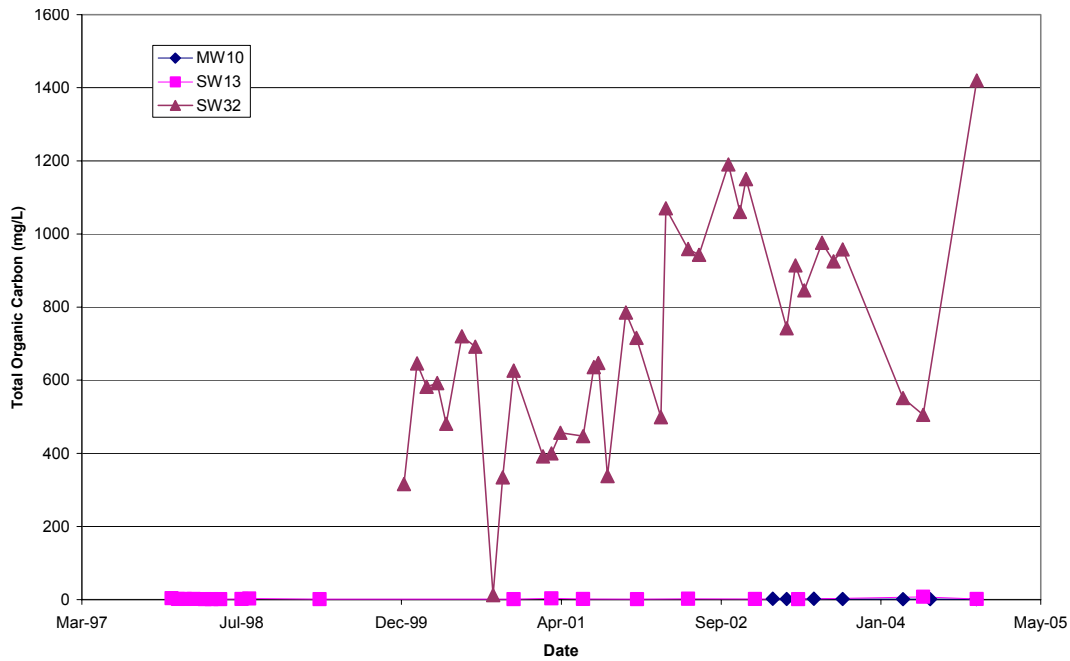


Figure 4-12: Total Organic Carbon Concentration (mg/L) vs. Time (data provided by PADEP)



With the exception of nickel, these species are indicators of broader phenomena. Aquatic life is sensitive to drastic increases in Total Organic Carbon and Nickel, but neither is particularly harmful at these concentrations. Total Dissolved Solids is another indicator of electrical conductivity. However, since the conductivity was cyclic, following the behavior of chloride, potassium and sodium discussed above, another source of TDS must be accounting for the continuous rise.

4.3 EPA Established Acceptable Levels/Exposure Limits

A partial listing of metals and pesticides included in the US Environmental Protection Agency (EPA) Toxicity Characteristics Rule 55FR 11798 (March 29, 1990) is presented in Table 4-5 along with the corresponding peak concentrations observed at the Bark Camp WTE site:

Table 4-5: Comparison of Leachate Threshold Concentrations with Observed Concentrations

<u>Species</u>	<u>TCR Regulatory Level (mg/L) *</u>	<u>Bark Camp WTE peak concentration (µg/L) **</u>
Arsenic	5.0	359
Barium ***	100.0	5,100
Cadmium	1.0	15
Chromium	5.0	50
Endrin	0.02	50
Lead	5.0	80

Lindane	0.4	50
Mercury	0.2	8
Methoxychlor	10.0	50
Selenium	1.0	394
Silver	5.0	10
Toxaphene	0.5	25

Notes: * data adapted from 'Highlight 2' Table US EPA Publication 9234 2-08/FS (May, 1990); ** indicates data adapted from PADEP; *** indicates element previously identified as Category 'A' element/compound

Toxicity Characteristics published by the EPA are guidelines used to identify hazardous wastes. In some areas, local regulations are stricter than these national guidelines and hence the local regulations govern. No corresponding leachate concentration thresholds were located for the state of Pennsylvania, and therefore it is assumed that these national standards govern. The peak concentrations at the Bark Camp WTE site are orders of magnitude below the threshold concentrations, for all species listed.

Table 4-6 summarizes the available threshold concentration regulations for those species previously identified as Category A and Category B, excluding the indicator species:

Table 4-6: Category A and B Threshold Concentrations and Observed Concentrations

<u>Species</u>	<u>Relevant Threshold Concentration</u>	<u>Source</u>	<u>Bark Camp WTE peak concentration (µg/L) *</u>
Chloride	1,470 mg/L	EPA – 1998 **	7,494 mg/L
Barium	100 mg/L	EPA - TCR	5.6 mg/L
Nitrate	10 mg/L	EPA – PDWS ***	1.6 mg/L
Copper	1.3 mg/L	EPA – NRWC ****	1.8 mg/L
Nickel	4,600 µg/L	EPA – NRWC ****	1,310 µg/L
Potassium	None		563 mg/L
Molybdenum	None		281 µg/L
Sodium	None		2,040 mg/L

Notes: * indicates data adapted from PADEP; ** US EPA Ambient Water Quality Criteria for Chloride Publication 440/5-88-001 (February, 1988); *** EPA Primary Drinking Water Standards; **** EPA – Priority Pollutant National Recommended Water Quality Criteria

Of the eight species, one element (Barium) is covered by the national Toxicity Characteristics regulations, two (copper and nickel) are covered by EPA National

Recommended Water Quality Criteria, included in full as Appendix C, which addresses sensitivity of aquatic life and includes human sensitivities as well, one species (Nitrate) is covered only by the EPA Primary Drinking Water Guidelines, which are difficult to relate to concentrations of fill material leachate, and the remaining three have no published threshold concentration levels, and are thus assumed to be of no consequence at the concentrations listed. Table 4-6 shows that of all the Category A and Category B elements and compounds, only chlorides are present in excess of the relevant guidelines available at this time.

4.4 Identification of Candidate Compounds for Pretreatment

Based on the data above and the measurements taken at the Bark Camp WTE site, chlorides have been identified as the sole family of compounds that are present in the leachate at unacceptable levels and therefore should be investigated for pretreatment and stabilization. Section 5 discusses an existing stabilization technique for heavy metals and its possible application to chlorides along with a unique water-washing technique currently in use in Europe.

POTENTIAL APPLICATION OF THE WES-PHIX PROCESS AND WATER WASHING FOR PRETREATMENT OF WTE ASH TO REMOVE CHLORINE

5.1 Literature

Wheelabrator Technologies, Inc. (WTI), holding multiple patents on the WES-PHix technology, was requested by Prof. Nickolas Themelis, Director, Earth Engineering Center of Columbia University to provide information on their process. The following documents were provided by Wheelabrator, Inc.:

- United States Patent No. 4,737,356 dated April 12, 1988.
- United States Patent No. 5,245,114 dated September 14, 1993.
- ‘Heavy Metal Stabilization in Municipal Solid Waste Combustion Dry Scrubber Residue Using Soluble Phosphate’ by Eighmy et al, Environmental Science Technology 31 No. 11, dated 1997.
- ‘Characterization and Phosphate Stabilization of Dusts from the Vitrification of MSW Combustion Residues’ by Eighmy et al, Waste Management 18, dated 1998.
- ‘The Use of the WES-PHix Process to Stabilize Municipal Waste Combustion Ash’ by Mark Lyons dated October 1999.
- ‘Final Report of the Field Lysimeter Leaching Experiments: WES-PHix Amended CASR’ by Crannell and Eighmy dated August 2004.

5.2 Description

The WES-PHix process is a method of ash stabilization to mitigate the leaching of heavy metals, specifically lead. The process was developed for use in the pretreatment of ash generated during the combustion of MSW. When MSW is combusted and the byproducts are captured for reuse, the process is known as a WTE process. As MSW is combusted in incinerators, the solid ash that is left behind is called bottom ash. Air, exhausted during combustion, must be treated before ultimately being discharged to atmosphere. The combustion gases are cleaned using scrubbers (dry and/or wet), baghouses, etc. Ash collected from the Air Pollution Control equipment is referred to as fly ash. Combined ash is the blending of bottom ash and fly ash, a process undertaken to create a homogenous waste product that can safely be disposed of without qualifying as a hazardous material under local and federal regulations.

The mechanism utilized by the WES-PHix process is to transform highly-soluble compounds containing lead and other trace metals into more insoluble compounds, which incorporate the added phosphate. Phosphate was selected after testing a variety of potential chemical agents. In addition to its ability to form more insoluble compounds, it also has minimal effects on the physical properties of the ash. This was an important factor because the physical nature of the solid ash allows for easy transport and handling, keeping costs at a minimum. (Lyons 1999).

WTI’s US patents cover soluble phosphate treatment of just bottom ash, as well as the combination of soluble phosphate and lime treatment for fly ash (lime is provided naturally through the scrubbing process or is added separately) and combined ash. In both cases, soluble phosphate can be added to the ash as a wet application (injected into the quench bath make-up water at the bottom of incinerator vessels that cools the bottom ash) or as a dry application (sprayed on in solution or sponge applied to the ash mixtures).

Additionally, under the protection of these patents are all forms of soluble phosphate such as phosphoric acid and salts, as they are all recognized as an equivalent process. The application point is not distinguished in these documents since the WES-PHix process can be applied at any point of the ash treatment train.

5.3 Laboratory and Field Tests

The documents provided by WTI include results of three tests (two laboratory and one field) that specifically examined the behavior of ash treated with soluble phosphate. A consortium of universities, led by University of New Hampshire (UNH) performed extensive ash pretreatment testing, including soluble phosphate pretreatment with the WES-PHix process. An independent study was conducted by the EPA that compared multiple pretreatment alternatives including portland cement, and the WES-PHix process specifically. UNH also led a companion 18-year long field test that was intended to bridge the gap between the laboratory data and results based on field condition long-term leaching. (Crannell and Eighmy, 2004). Table 5-1 summarizes the results of these tests:

Table 5-1: WES-PHix Reduction in Leaching of Selected Elements using Dutch Total Availability Test

Species	% Reduction in Leaching by Treatment with WES-PHix		
	1993 EPA Test	1996 UNH Test	Field Test*
Cadmium	32	38	**
Copper	51	58	43.5
Lead	99.7	99	90.2
Zinc	36	28	37.1
Aluminum	--	75	68
Chromium	100	--	--
Chlorine	--	--	-19%

Notes: *field test conducted from 1980 through 2004; ** indicates all values were below detection limit; data adapted from Crannell and Eighmy (1998) and Eighmy et al (1997)

All three tests confirm that WES-Phix is very effective in reducing lead leaching. The WES-PHix process is also effective in reducing Aluminum and Copper leaching and moderately effective in reducing Cadmium and Zinc leaching. Metals other than lead were more effectively stabilized by lime pretreatment in conjunction with soluble phosphate pretreatment. However, the field test demonstrated that it has the opposite effect on chlorine leaching - treatment with soluble phosphate promoted chlorine leaching. This is of significance for the Bark Camp WTE site, as discussed below.

5.4 Application for the Bark Camp WTE Site

A process such as WES-Phix is not directly applicable to the pretreatment of the ash used at the Bark Camp WTE site, because the level of metals is fairly low, while chlorides are in abundance and have been identified as the target compounds for pretreatment. Table

5-2 displays concentrations from one of the laboratory tests, the field test and the Bark Camp WTE site:

Table 5-2: Initial Concentrations in Ash Leachate for Selected Species

<u>Species</u>	<u>1996 UNH Test</u>	<u>Field Test</u>	<u>Bark Camp WTE*</u>
Cadmium	195 mg/Kg	47 mg/Kg	15 µg/L
Copper	2,169 mg/Kg	370 mg/Kg	1,800 µg/L
Lead	8,900 mg/Kg	1,350 mg/Kg	79.8 µg/L
Zinc	23,500 mg/Kg	4,100 mg/Kg	1,820 µg/L
Aluminum	<1,800 mg/Kg	33,500 mg/Kg	11,700 µg/L
Chromium	9.13 mg/Kg	--	50 µg/L
Chlorine	326,700 mg/Kg	22,500 mg/Kg	7,300 mg/L **

Notes: * Initial concentrations assumed to be peak values near April 2001; ** reported value is total Chlorides; data adapted from Crannell and Eighmy (1998), Lyons (1999) and PADEP

Leachate concentrations from the 1996 UNH test and the associated field test are provided in mg constituent per Kg of leachate. Initial concentrations provided in Table 5-2 represent the initial leachate concentration of ash material that was untreated, which provides a basis for why pretreatment is necessary at all, and a platform to compare the initial concentrations with those from the Bark Camp WTE site, which did not receive any pretreatment. Leachate is water based, hence 1 Kg of leachate is the equivalent of 1 L of leachate (assuming 4-degrees C) and therefore the initial concentrations listed are the equivalent of mg/L concentrations. With the exception of chlorine, represented as mg/L of chlorides, the Bark Camp WTE site initial concentrations for these species are orders of magnitude lower than the corresponding initial concentrations from the laboratory and field tests.

Lead, the target of the WES-PHix process, is at substantially lower levels in the Bark Camp WTE site leachate. The state of New Hampshire requires the lead concentration in waste leachate be at or below 5 mg/L (or mg/Kg) to be considered a standard waste, and not be subject to hazardous waste transport and handling criteria. The peak concentration, without any pretreatment, of the Bark Camp WTE site leachate was 79.8 µg/L, which occurred in April of 2001 when fresh fill material was placed, containing no coal ash. Though copper and aluminum appear to be in abundance in the Bark Camp WTE site leachate, and are removed somewhat effectively by the WES-PHix process, neither species is harmful at the listed concentrations and the capital cost of a WES-PHix treatment train is not warranted for a field observed 43.5% and 68% reduction in leaching respectively for these species. Therefore ash used at the Bark Camp WTE site, if it continues to be of similar composition as the Essex Facility ash, is not a candidate for the WES-PHix process.

5.5 Development of Pretreatment Alternatives

The principles used in the development of the WES-PHix process may provide some insight into possible pretreatment alternatives that target all chlorides or simply chlorine specifically. The goals of pretreatment of the Bark Camp WTE site ash would be very similar to the goals of the original chemical agent testing for lead stabilization: maintain the physical properties of the ash, and transform highly soluble chlorides into more stable, less soluble compounds.

Laboratory experiments are being conducted at Columbia University to attempt to identify an appropriate process. Multiple methods for chloride stabilization will be examined. The following analyses should be performed for each method to provide a basis with which to select a cost effective pretreatment process:

- Initial particle size distribution of ash prior to treatment – Similar to the analysis described in the Lyons, 1999 paper. This can be a physical test using standard sieve sizes and a laboratory scale, and need not involve any volatilization or advanced analytical techniques.
- Final particle size distribution of ash after treatment – Same as above.
- Classification of initial chlorine compounds – Through spectroscopy or other means, a breakdown of how much chlorine is present in the ash, and in what form it leaches, is needed to begin to address means of stabilizing the compounds.
- Solubility of initial chlorine compounds – This can likely be estimated through laboratory techniques for any compounds whose solubility has not yet been studied in detail and corresponding data made available to the public.
- Classification and solubility of final chlorine compounds – A repeat of the analyses performed on the initial, untreated material, necessary to evaluate the effectiveness of any chemical pretreatment to form very insoluble complex compounds in the leachate that take the place of the highly soluble chlorides.

Combustion of MSW ash, treatment of exhaust gases, chemical addition to the respective ashes, and varying ratios of fly ash:bottom ash in combined ash mixtures, all contribute to a large fluctuation in the overall pH of the ash that is targeted for disposal or reuse. Two of the articles provided by Wheelabrator focus on the ability of soluble phosphate pretreatment to immobilize heavy metals across the widest possible pH range. They identify which less-soluble compounds are formed by the addition of soluble phosphate, and at what pH ranges. Similar studies could be undertaken if a chemical pretreatment alternative for chlorides is identified through the above laboratory testing.

Additionally, a chloride washing technique is currently used in Hamburg, Germany wherein the fly ash component of WTE ash is subjected to a cold water wash. This water-washing has been very successful to date in removing chlorides from the fly ash component. As was stated in the 2005 Themelis paper: chlorine volatilization and subsequent capture of chlorine in the form of calcium chloride result in the fly ash component of MSW ash retaining the majority of the chlorides (Themelis, 2005). Therefore, a simple technique such as water-washing applied directly to the fly ash component could significantly reduce the chlorides leaching from the Bark Camp WTE site. As this technique is relatively simple and inexpensive, its application could be easily incorporated.

Mr. Adam Penque, of the Department of Earth Environmental Engineering at Columbia University, will be performing the laboratory experiments described herein as part of ongoing PHD research in the field of ash recovery and reuse. Columbia University has obtained samples of WTE ash (both bottom ash and fly ash) from the same facility that provided WTE ash for the Phase II remediation at the Bark Camp WTE site. Therefore these laboratory experiments will be directly applicable to the results described in this paper. Details of the laboratory experiments and results will be provided under separate cover.

CONCLUSION AND RECOMMENDATIONS

6.1 Bark Camp WTE Site

Sections 3 and 4 of this paper show that WTE ash, of similar composition to that provided by the Essex Facility, may potentially be used as fill material for mine remediation efforts, if it is pretreated to eliminate the chloride leaching problem. As described in Section 5, the most promising technique is already in use in Hamburg, Germany and requires only a simple cold water-wash of the fly ash component. Such a process will be relatively inexpensive, particularly if it is provided at the production site (i.e. the Essex Facility), where treatment trains are already in place and can be adapted to supply the cold water-wash.

Laboratory work is being performed at Columbia University related to the pretreatment of WTE ash will determine if the water-washing technique is effective for removal of chlorides from the WTE ash used at the Bark Camp WTE site. If this technique is ineffective, further laboratory work, outlined in Section 5, can be performed to potentially identify an alternate chemical pretreatment alternative, akin to the addition of soluble phosphate in the WES-PHix process. However, it is recognized that any such chemical pretreatment alternative would necessarily be more expensive and therefore more cumbersome to implement than a cold water-washing technique.

If multiple alternatives are discovered to be effective in isolating and removing the chloride compounds, a cost-benefit analysis should be performed to determine which, if any, of the proposed alternatives would be the most advantageous. If chloride compounds can be removed from the WTE ash, there appears to be no further obstacle to its widespread use as fill material in the remediation of abandoned coal mines.

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APPENDICES

The Appendices to this report, as well as the Report itself, are available in pdf file at the web page of the Waste-to-Energy Research and Technology Council (www.columbia.edu/cu/wtert)