

STABILIZATION/SOLIDIFICATION TREATMENTS FOR FILTER CAKE,  
A BY-PRODUCT OF ASPHALTENE GASIFICATION

By

CHARLES BOWER

B.Sc., Queens University, 1995

A thesis submitted in partial fulfillment of  
the requirements for the degree of

MASTER OF SCIENCE  
in  
ENVIRONMENT AND MANAGEMENT

We accept this thesis as conforming  
to the required standard

.....  
Dr. Matt Dodd, Thesis Supervisor  
Royal Roads University

.....  
Thesis Coordinator  
School of Environment and Sustainability

.....  
Michael-Anne Noble, Director  
School of Environment and Sustainability

ROYAL ROADS UNIVERSITY

February 2012

© Charles Bower, 2012

**Abstract**

Filter Cake, which contains leachable nickel and vanadium above the criteria in the Alberta Waste Control Regulation, is produced at an oil sands facility operated by Nexen Inc. and is currently being disposed in a landfill. Bench scale and field tests were performed with stabilization/solidification (S/S) treatment reagents such as Portland cement, fly ash, elemental sulphur, and CETCO Oilfield Service's proprietary reagents to assess their efficacy at reducing leachable metals in Filter Cake. The CETCO reagents were the most effective treatment for reducing leachable nickel and vanadium in Filter Cake. Treatments with Portland cement were successful in bench scale tests, but inconsistent in field tests. The inconsistent results obtained for Portland cement may have been due to interferences of the cement reactions from factors such as fine particulates. S/S treatments of Filter Cake present a viable waste management option. However, the associated reduced cost and environmental impacts were not substantial.

**Acknowledgments**

I would like to acknowledge my wife, Vicky Ren, my son, Timothy Hu, my father in law, Fei Ren, my mother in law, Guizhen Wang, and my parents, Peter and Susan Bower, for their endless support through the development and completion of my Master's thesis. In addition, I would like to thank my Thesis Supervisor, Dr. Matt Dodd, for his guidance and direction, Al Ross with CETCO Oilfield Services for his assistance, Stan McBride for encouraging me to study an issue that would reduce environmental impact, and Jim MacPherson for his support and suggestions throughout this project. Finally, I would like to acknowledge Nexen Inc. for their support of this project and my Master's degree.

## Table of Contents

1.0	Introduction.....	7
1.1	Background .....	7
1.2	Research Objective.....	9
1.3	Research Question.....	9
1.4	Significance of Proposed Study .....	9
2.0	Literature Review.....	10
2.1	Leaching Tests.....	10
2.2	Waste Handling Options .....	10
2.3	Stabilization/Solidification (S/S) Treatments.....	11
	2.3.1 Portland cement .....	12
	2.3.2 Portland cement and pozzolanic materials.....	14
	2.3.3 Other additives with Portland cement.....	15
	2.3.4 Sulphur.....	16
2.4	S/S Treatment Reagents to be Used in this Study .....	18
3.0	Methodology .....	18
3.1	Field Tests by Hazco .....	19
3.2	Field Tests by CETCO .....	20
3.3	Field Testing by Nexen .....	22
3.4	Bench Scale Testing by Nexen.....	24
4.0	Results.....	26
4.1	Characterization of Untreated Filter Cake .....	26
4.2	Hazco Field Test.....	31
4.3	CETCO Field Test.....	35
4.4	Nexen Field Test .....	39
4.5	Bench Scale Tests.....	53

	5
5.0 Discussion .....	58
5.1 Bench Tests .....	58
5.2 Field Tests .....	59
5.3 Sustainable Development.....	61
6.0 Conclusion .....	61
7.0 References.....	63

## List of Figures

Figure 1. Untreated Filter Cake .....	27
Figure 2. Treated Filter Cake from Hazco Field Tests .....	31
Figure 3. Treated Filter Cake from CETCO Field Tests .....	36

## List of Tables

Table 1_Percent of Portland Cement Added for Each Batch for the Field Tests by Hazco .....	19
Table 2_Percent and Weights of S/S Treatment Reagents for Blends used by CETCO for Field Tests .....	21
Table 3_Percent of Portland Cement Added for Each Blend for the Field Tests by Nexen.....	22
Table 4_Results of Analysis for Regulated Parameters for Untreated Filter Cake Samples Collected Between July 2010 and July 2011 .....	28
Table 5_Total Metals and Carbon in Untreated Filter Cake Samples Collected Between July 2010 and July 2011 .....	30
Table 6_Leachable Nickel Results for the Different Batches Tested by Hazco.....	32
Table 7_Leachable Vanadium Results for the Different Batches Tested by Hazco.....	33
Table 8_TCLP Pretest pH Results for the Different Batches Tested by Hazco .....	34
Table 9_pH Results for the Different Batches Tested by Hazco .....	34
Table 10_Leachable Nickel Results for the Different Blends tested by CETCO.....	37
Table 11_Leachable Vanadium Results for the Different Blends tested by CETCO.....	37
Table 12_TCLP Pretest pH Results for the Different Blends tested by CETCO .....	38
Table 13_pH Results for the Different Blends tested by CETCO.....	38
Table 14_Leachable Nickel for Different Time Periods after Mixing for the Field Tests by Nexen	40
Table 15_Leachable Vanadium for Different Time Periods after Mixing for the Field Tests by Nexen .....	42
Table 16_TCLP Pretest pH Results for Different Time Periods after Mixing for the Blends Tested in the Field by Nexen .....	44
Table 17_pH Results for Different Time Periods after Mixing for the Field Tests by Nexen .....	45
Table 18_Total Nickel for Different Time Periods after Mixing for the Field Tests by Nexen....	46
Table 19_Total Vanadium for Different Time Periods after Mixing for the Field Tests by Nexen	47
Table 20_Bulk Density and Percent Moisture for Different Time Periods after Mixing for the Blends Tested in the Field by Nexen .....	49
Table 21_TCLP and pH Results for the Different Blends from Bench Scale Tests.....	54
Table 22_RPD and RSD for Duplicates for Bench Scale Tests .....	57

## 1.0 Introduction

### 1.1 Background

The Global Reporting Initiative (GRI) defines sustainable development as follows: what should be sustained is reduced use of materials and emissions, and what should be developed are employment, profitability, and health and safety, diversity, and dignity of workers (Kates, Parris, & Leiserowitz, 2005). As an operating company supporting the GRI, Nexen Inc. (Nexen) together with its partner CNOOC Canada Inc. (“CNOOC”) has developed an integrated Steam Assisted Gravity Drainage (SAGD) and Upgrader facility for producing and upgrading oil sands or bitumen production south of Fort McMurray, Alberta. One of the initiatives to minimize the environmental impact associated with waste from this facility is to find the best waste management option for Filter Cake, which is a by-product of asphaltene gasification.

As part of the process for upgrading bitumen produced from SAGD, asphaltenes, which are the fractions of crude oils that are insoluble in n-Pentane or n-Heptane (Speight, 1999), are used to make Synthetic Gas or Syngas in the Asphaltene Gasification Unit (AGU). The asphaltene is produced at the Nexen operated SAGD and Upgrader facility through a proprietary process. The AGU utilizes 99% of the carbon in the asphaltene to produce Syngas. The remaining 1% is converted to carbon or soot, which coats the ash particles to protect downstream equipment from erosion (Nexen, 2010). The raw Syngas is washed with water in order to remove the soot and ash from the Syngas. A membrane filter press is then used to separate the soot and ash from the wash water. The separated soot and ash is called Filter Cake, which contains 85% water and 15% solids by design (Nexen, 2010). The Filter Cake that was being produced at the time of the Nexen (2010) report contained 72-85% water. The dry portion of

Filter Cake consisted of 80% soot and 20% ash; the ash contained 34.7% vanadium and 12.5% nickel (Nexen, 2010).

The limit for non-hazardous waste for leachable nickel and vanadium is 5.0 mg/L and 100 mg/L, respectively, in Section 1 of Schedule 1 of the Alberta Waste Control Regulation (WCR) (Alberta Environmental Protection [AEP], 1996). The leachable values for nickel and vanadium in the Filter Cake exceed these limits, and, therefore, the Filter Cake has been classified as a hazardous waste. Currently, Filter Cake is transported via covered trucks and disposed in a Class I landfill in Riley, Alberta, which is over 400 km away from the oil sands facility. Due to the high carbon and metal content of the Filter Cake and the volumes that are produced, there is a significant opportunity to find waste handling or recycling options for this Filter Cake that reduce the costs of handling as well as the environmental and social impacts.

One of the recycling options for the Filter Cake that was developed during the construction of the Nexen/CNOOC Upgrader in 2006 was the Zimpro® wet air oxidation unit from Siemens Water Technologies (Rettger, Arnold, Brandenburg, & Felch, 2006). The Zimpro® wet air oxidation unit was developed for burning off the remaining carbon in order to concentrate and recover the metals in the Filter Cake (Rettger et al., 2006). However, the Zimpro® wet air oxidation unit was never completed.

In 2010, Nexen reviewed a number of technologies that could be used to handle Filter Cake (Nexen, 2010). These included technologies, such as the Zimpro® wet air oxidation unit, that concentrate the metals in the Filter Cake by burning off excess carbon (see Section 2.2). In addition, Nexen (2010) considered selling the Filter Cake as a source fuel and chemically fixing the metals in the Filter Cake. Chemically fixing the metals in the Filter Cake is generally referred to as stabilization/solidification (S/S) technologies, which can be used to bind or fix

hazardous contaminants in wastes to prevent them from leaching out. This study focuses on the technical feasibility of using S/S technologies to reduce the leachable properties of Filter Cake to allow for its disposal in a Class II landfill in Janvier, Alberta. The Class II landfill is only 80 km away from the oils sands facility compared to over 400 km for the currently used Class I landfill. Disposing treated Filter Cake in the Class II landfill is expected to reduce the costs as well as the environmental and social impacts associated with handling the waste.

## **1.2 Research Objective**

The objective of this research project is to determine which S/S treatment reagents will be most effective at reducing the leachable nickel and vanadium concentrations in the Filter Cake to levels below the criteria listed in Section 1 of Schedule 1 of the Alberta WCR. In addition, this study will evaluate the economic and environmental impacts for the effective S/S treatment reagents.

## **1.3 Research Question**

My research questions are as follows:

- 1) Are there S/S treatment reagents and processes that can effectively reduce leachable nickel and vanadium in Filter Cake to levels below the criteria in Section 1 of Schedule 1 of Alberta's WCR?
- 2) What is the best S/S treatment reagent or combination of treatment reagents that can be used to treat the Filter Cake so the treated Filter Cake will comply with non-hazardous waste criteria?

## **1.4 Significance of Proposed Study**

If the S/S treatments can effectively reduce the leachable nickel and vanadium in the Filter Cake to concentrations below the non-hazardous waste criteria, the treated Filter Cake can

be disposed in a Class II landfill. Since there is a Class II landfill only 80 km away from the oil sands facility, disposing the treated Filter Cake in a Class II landfill instead of a Class I landfill would be expected to reduce the costs as well as the social and environmental impacts associated with disposal. It is also possible that the treated Filter Cake could be used as construction material during the warmer months, which would allow for the recycling of some of the waste resulting in less waste going to a landfill. The results of this research project will provide recommendations to industry on the best S/S treatment reagents for Filter Cake and whether this waste management option meets the requirements of sustainable development.

## **2.0 Literature Review**

The literature review was conducted on leaching tests, different waste handling or recycling options for the Filter Cake produced at the oil sands facility, and S/S technologies that can be used for reducing the leachable properties of the waste.

### **2.1 Leaching Tests**

The Method 1311 Toxicity Characteristic Leaching Procedure (TCLP) (U.S. Environmental Protection Agency [EPA], 1992) as described in US EPA Regulation 40CFR261 is the recommended procedure for leachability (AEP, 1996) and is the most widely accepted test (Cullinane, Jones, & Malone, 1986). However, the TCLP test does not adequately predict the leachable properties of a waste over the long term (U.S. EPA, 1993). Instead, leaching tests provide relative results for the success of S/S treatments with different reagents (U.S. EPA, 1993).

### **2.2 Waste Handling Options**

Research on different waste handling or recycling options for Filter Cake has been conducted by Nexen (2010). These included the possibility of building facilities, such as the

Zimpro® wet air oxidation unit as discussed above, which could concentrate the metals in the Filter Cake in order to sell the ash to a metals reclaimer and, in one case, use the heating value of the Filter Cake. These facilities would be very expensive to build and would require significant process development. Other options that were investigated included selling the Filter Cake to potential users, since the heating value of the Filter Cake is similar to low grade petroleum coke or coal. There was limited interest in this option due to the high water content of the Filter Cake; the amount of energy in the Filter Cake was roughly equivalent to the energy that would be required to dry the Filter Cake. The last waste handling option for the Filter Cake that was investigated by Nexen (2010) was S/S technologies to chemically bind the metals in the Filter Cake so the waste could be disposed in the Class II landfill in Janvier. This waste handling option was one of the most economic options investigated by Nexen (2010).

### **2.3 Stabilization/Solidification (S/S) Treatments**

Stabilization treatments involve chemical reactions that reduce the solubility and immobilize hazardous contaminants such as metals (Cullinane et al., 1986; U.S. EPA, 2000; U.S. EPA, 2009). Solidification treatments solidify a waste material by encapsulating the waste or incorporating it into a solid mass. This process reduces the surface area of the waste exposed to leaching or isolates the waste from the environment (Cullinane et al., 1986; U.S. EPA, 2000; U.S. EPA, 2009). Various chemicals and processes have been used for S/S treatments including:

- Sorbents such as activated carbon, gypsum, and clays which remove free liquid through either chemical reactions or capillary action;
- Pozzolanic materials, such as fly ash from coal-fired plants, which are materials that contain silicic acid and can be mixed with hydrated lime ( $\text{Ca(OH)}_2$ ) to form cementitious compounds;

- Portland cement and Portland cement with pozzolanic materials;
- Thermoplastic microencapsulation which uses materials such as asphalt, polyethylene, or elemental sulphur to encapsulate fine grained waste materials; and,
- Macroencapsulation which uses materials such as polybutadiene or polyethylene to form a jacket around the solidified waste (Cullinane et al., 1986; Jones, 1990).

The U.S. EPA (2000) reported that the most common S/S treatment technologies used at U.S. Superfund remedial sites were cement treatment systems, followed by proprietary reagents, phosphate, pH controls, and fly ash and lime. The following sections provide the chemical compounds and processes that are most likely to be effective at reducing the leachable properties of the Filter Cake produced at the oil sands facility.

### ***2.3.1 Portland cement***

Wastes treated with Portland cement with or without pozzolanic substances have been shown to be very effective at reducing leachable properties (Cullinane et al., 1986). However, the success of S/S treatments with Portland cement depends on the waste, the type of contaminants, and other compounds and factors that can interfere with cement reactions (Conner, 1997; U.S EPA, 1993).

Conner (1997) discussed the success of using Portland cement for stabilizing different metals and reported that nickel contaminated waste can usually be stabilized with Portland cement. However, there are few studies on the use of S/S treatments for vanadium contaminated wastes. Conner (1997) described a study where electric arc furnace dust which was spiked with vanadium was successfully stabilized with Portland cement. No information on either the concentration or chemical species of vanadium in the waste or other properties of the waste such as organic content and particle size were provided.

One of the challenges of using Portland cement is that the high alkalinity of Portland cement can affect the performance of S/S treatments (Cullinane et al., 1986). Shi and Spence (2004) reported that the pore solution of cements has a pH greater than 12.5. However, most metals including nickel are least soluble when the pH is between 9.5 and 11 (Cullinane et al., 1986). Shi and Spence (2004) also indicated most metals are least soluble at a pH of 10, and as a result, S/S treatments of metal contaminated wastes with reagents such as Portland cement should generally strive for a pH of 10. U.S. EPA (1993) described how most metal hydroxides have minimal solubility within a pH range of 7.5 to 11 and at particular oxidation states.

As discussed above, there is a lack of studies for stabilizing wastes contaminated with vanadium, and, as a result, it is difficult to know what range of pH and what oxidation state of vanadium would render the vanadium least soluble. Kunz, Giannelli, & Stensel (1976) provided solubility curves for tetravalent and pentavalent vanadium ( $V^{4+}$  and  $V^{5+}$ , respectively) versus pH, which showed that  $V^{4+}$  and  $V^{5+}$  are least soluble within a pH of 7.5 to 9. As a result, S/S treatments for wastes with vanadium may be more effective at reducing the leachability of vanadium if the pH of the treated waste is in this range. Kunz et al. (1976) suggested only  $V^{4+}$  and  $V^{5+}$  are likely to be soluble in water.

One method for reducing the pH of waste treated with Portland cement is through the use of low alkali Portland cement (Shi & Spence, 2004). Typical ASTM Type I, II, and III cements have an alkali content as high as 0.91-0.94% by weight (Shi & Spence, 2004). Low alkali ASTM Type I, II, and III cements have an alkali content of 0.43 to 0.45% (Shi & Spence, 2004). As a result, low alkali cements may reduce the leachability of some metals in S/S treatments (Shi & Spence, 2004).

It has been documented that some substances and factors can interfere with Portland cement reactions (Cullinane et al., 1986; U.S. EPA 1993; Conner, 1997). For example, large volumes of fine, soft wastes can interfere with the bonding of Portland cement and particles of waste (Cullinane et al., 1986). The U.S. EPA (1993) described how fine particulates and organic compounds can interfere with cement reactions. As the Filter Cake contains fine particulates, the fine particulates may interfere with cement reactions when the Filter Cake is treated with Portland cement.

Another substance that can interfere with cement based S/S treatments is sulfate (U.S. EPA, 1993; Jones, 1990). Sulfate causes the formation of ettringite, which expands and increases the porosity of the stabilized waste and may also cause the waste to breakdown (U.S. EPA, 1993). Sulfides and sulfites can also oxidize to sulfates, which can then form ettringite (U.S. EPA, 1993). Filter Cake contains a small amount of sulphur compounds, which may interfere with cement reactions.

Finally, another drawback of using Portland cement is chemical incompatibilities (U.S. EPA, 1993). For example, the high alkalinity of Portland cement can cause ammonia gas to be released if ammonium ions are present in the waste (Cullinane et al., 1986; U.S. EPA, 1993).

### ***2.3.2 Portland cement and pozzolanic materials***

Pozzolanic materials can be mixed with lime to form cementitious compounds for S/S treatments (Cullinane et al., 1986). Pozzolanic materials such as coal fly ash, silica fume, and blast furnace slag can also be added with Portland cement to reduce the pH of the pore solution in cements by reducing the calcium to silicate ratio (Shi & Spence, 2004). The calcium silicate hydrate (C-S-H) is the key hydration product in most cements (Shi & Spence, 2004). By using additives such as fly ash, excess  $\text{Ca(OH)}_2$  will be consumed, which will lower the pH and

precipitate more metals (Shi & Spence, 2004). Cullinane et al. (1986) also discussed how natural pozzolana, such as fly ash have silicic acid, which will react with any free calcium hydroxide from the Portland cement. Blast furnace slag can also act as a reducer to reduce the oxidation state of metal contaminants (Shi & Spence, 2004). In addition, using blast furnace slag may precipitate some metals as sulphides, which are less soluble than hydroxides (Shi & Spence, 2004).

The advantage of using pozzolanic substances such as fly ash is that a waste product from another industry such as the electricity industry can be recycled, which reduces the environmental impact associated with harvesting and processing virgin materials to produce Portland cement (Canada Green Building Council [CaGBC], 2004). In addition, using fly ash in S/S treatments allows this waste product to be used to treat hazardous waste instead of just sending the fly ash to a landfill. Finally, the cost for fly ash is significantly less than the cost of Portland cement (Cullinane et al., 1986).

Some S/S treatments have used bentonite with solidification treatments (Cullinane et al., 1986; U.S. EPA, 1999). Bentonite can significantly reduce the amount of fly ash required for S/S applications with fly ash and lime (Cullinane et al., 1986).

### ***2.3.3 Other additives with Portland cement***

Conner (1997) provided a list of various additives that can be added with Portland cement to improve S/S of hazardous wastes. For example, ferrous sulphate can be added as a reducing agent to reduce the oxidation state of metal contaminants such as hexavalent chromium ( $\text{Cr}^{+6}$ ). This stabilization process requires a large amount of chemical use since three treatment reagents must be used. The pH of the waste is initially reduced below 3, ferrous sulphate is then added,

followed by treatment with Portland cement (Conner, 1997). Reducing the oxidation state of metals by adding ferrous sulphate occurs at a slower rate when the pH is above 3 (Conner, 1997).

Conner (1997) also discussed additives that can be used to control pH and increase the buffering capacity of stabilized wastes. For example, CaO can be added to increase pH and provide an additional source of calcium, while MgO is an additive that will act as a buffering agent.

#### ***2.3.4 Sulphur***

One of the most important mechanisms for stabilization of metals is precipitation of metals as insoluble hydroxides, silicates, or sulphides (Conner, 1997). Precipitation of metal hydroxides by adding treatment reagents such as Portland cement or pozzolanic materials is the most common mechanism (Conner, 1997). Sulphide precipitation is likely the second most common mechanism as sulphides are typically less soluble than hydroxides under alkaline conditions (Conner, 1997). Various sulphur species can be used for precipitation including iron sulphide and elemental sulphur which minimize the risk of H<sub>2</sub>S production by allowing only a small amount of unused sulphide to be present at any one time (Conner, 1997). Portland cement will need to be added either after or at the same time that these sulphur compounds are added according to Conner (1997).

Lin, Cross, Chian, Lai, Giabbai, & Hung (1996) and Lin (1995) described how real world lead contaminated soils as well as simulated lead contaminated soils were successfully solidified and stabilized with sulphur and sodium sulphite (Na<sub>2</sub>SO<sub>3</sub>). It is important to note that the sulphur and sodium sulphite stabilization was achieved without Portland cement treatment. The real world lead contaminated soils were successfully treated with 33 weight percent sulphur and 2.0 weight percent sodium sulphite. The simulated lead contaminated soils which were

essentially sand with lead contamination were stabilized with as little as 5.3 weight percent sulphur and 0.16 weight percent sodium sulphite. Real world lead contaminated soils spiked with lubricating oil were also successfully stabilized with 15 weight percent sulphur and 3 weight percent sodium sulphite (Lin et al., 1996). Lin et al. (1996) suggested that the real world lead contaminated soils had more fine particles and therefore, required additional sulphur. Lead contaminated soils treated with sulphur alone were not successfully stabilized (Lin et al., 1996). Lin et al. (1996) indicated the mechanism of stabilization with sulphur and sodium sulphite is microencapsulation and chemical reactions of lead with polysulphide. They suggested that lead contaminated soils stabilized with sulphur and sodium sulphite could be used in road construction due to the high unconfined compressive strength, low permeability, and resistance to freezing and thawing.

As large amounts of liquid elemental sulphur are produced at the oil sands facility, using sulphur for S/S treatments with the Filter Cake may reduce the environmental impact and cost of treating the Filter Cake through reduced use of purchased chemicals.

One of the drawbacks of using thermoplastic microencapsulation treatment reagents such as elemental sulphur is the waste may not be compatible with these treatment reagents (Cullinane et al., 1986). Sulphur or asphaltene are reduced compounds that may start burning when mixed with oxidizing compounds (Cullinane et al., 1986). Also, ammonium and cyanides in the waste can act as complexing or chelating agents, which will decrease the effectiveness of this S/S treatment at reducing the leachable properties of wastes with heavy metals (Cullinane et al., 1986). Pretreating the wastes to destroy oxidizers or chelating compounds prior to thermoplastic microencapsulation treatments may be more effective at reducing the leachable properties of waste than S/S treatments with Portland cement or pozzolanic substances (Cullinane et al., 1986).

## 2.4 S/S Treatment Reagents to be Used in this Study

Based on the literature review, the following S/S treatment reagents were used in bench tests and field tests:

1. Portland cement (Type I)
2. Low alkali Portland cement (Type I)
3. Portland cement (Type I) with fly ash (type F)
4. CETCO Oilfield Services (CETCO) Sorbond LPC II and Sorbond Briquetting with CETCO LR 2000 (wetting agent). These treatment reagents are proprietary chemicals and the exact proportions of the different substances are not known. CETCO Sorbond LPC II and Sorbond Briquetting contain bentonite, Portland cement, and calcium oxide based on the Material Safety Data Sheets (MSDS). Sorbond Briquetting contains a higher proportion of bentonite than Sorbond LPC II, while LR 2000 contains water and silicates (A. Ross, personal communication, December 8, 2011).
5. Elemental sulphur with sodium sulphite.

## 3.0 Methodology

Two contractors, Hazco Environmental Services (Hazco), a division of CCS Corporation, and CETCO elected to conduct bench tests and field tests for S/S treatments with the Filter Cake. Nexen collected samples from the field tests performed by these contractors and the results are provided in Section 4.1, 4.2, and 4.3. Subsequent to these field tests, Nexen conducted independent field tests using reagents similar to the ones used by Hazco and monitored the leachable characteristics over a period of one year. Additional bench tests were also undertaken to determine if there were any other treatment reagents that might be more successful at reducing

the leachable properties of the Filter Cake. The methodology for these field tests, bench tests, and sampling techniques are provided in the sections below.

### 3.1 Field Tests by Hazco

Hazco tested three different proportions of Portland cement in their S/S field tests with Filter Cake (Table 1). The Filter Cake was collected and treated on July 9<sup>th</sup> and 10<sup>th</sup>, 2010.

Table 1

*Percent of Portland Cement Added for Each Batch for the Field Tests by Hazco*

Batch	Portland Cement by Weight (%) <sup>a</sup>
1, 4	25
2, 5	20
3, 6	15

<sup>a</sup>Percent Portland cement by weight of the Filter Cake

Ten tonnes of Filter Cake per batch was mixed with Portland cement in three large bins measuring 12 m long by 3 m wide by 2.7 m high using an excavator. The Filter Cake and Portland cement were first mixed together. Potable water from the city of Fort McMurray was then added to the mixture via a small pump and hose while the excavator continued with the mixing. The regular excavator bucket was replaced with an Allu bucket, which was then used for further mixing. The total mixing time averaged from 1 hour to 1.5 hours for each batch.

One composite sample was collected for each batch of Filter Cake before treatment and 0 hours, 24 hours, 48 hours, and 12-13 days after treatment. Samples were placed into one 500 mL and two 120 mL clear glass jars with no head space. The jars were placed in a cooler with ice and shipped to Maxxam Analytics (Maxxam) for a Basic Class II Landfill Package, which included TCLP, flash point, pH, and free liquid tests. Duplicate samples were also collected and stored in a fridge. On October 25, 2010, 3.5 months after treatment, the duplicate untreated samples for Batch 1 and 4 were homogenized and, then, split into duplicates and shipped to two different commercial laboratories, Maxxam and AGAT Laboratories (AGAT) for analysis.

Samples of the potable water used were collected prior to and after the treatments. The water samples were also shipped to Maxxam for the analysis for routine water quality parameters, benzene, toluene, ethylbenzene, and xylene (BTEX), F1-F2 hydrocarbons, total organic carbon (TOC), dissolved organic carbon (DOC), total and dissolved regulated metals, total suspended solids (TSS), phenols, naphthenic acids, glycols, sulphide, oil and grease, and total coliforms.

### **3.2 Field Tests by CETCO**

CETCO used a different mixing procedure for S/S field tests. Instead of using an excavator to mix the Filter Cake with treatment reagents in large bins, the Filter Cake was mixed in a small Crown Construction Equipment mortar mixer, model 6-SR. The proportions and weights of S/S treatment reagents used for each blend are shown in Table 2. Filter Cake was collected and treated on July 28<sup>th</sup>, 2010.

Table 2

*Percent and Weights of S/S Treatment Reagents for Blends used by CETCO for Field Tests*

Blend Description	S/S Treatment Reagent by Weight (%) <sup>a</sup>	Weight per Batch (kg)	Number of Batches	Total Weight per Blend (kg)
Blend 1				
Filter Cake		32	10	318
Water	50	16	10	159
CETCO Sorbond LPC II	15	5	10	50
Total		53	10	526
Blend 2				
Filter Cake		32	8	254
Water	50	16	8	127
CETCO Sorbond Briquetting	15	5	8	40
Total		53	8	421
Blend 3				
Filter Cake		32	8	254
CETCO LR 2000 <sup>b</sup>	35	12	8	98
CETCO Sorbond Briquetting	15	5	8	40
Total		49	8	392
Blend 4				
Filter Cake		32	7	222
CETCO LR 2000 <sup>b</sup>	35	12	7	86
CETCO Sorbond LPC II	15	5	7	35
Total		49	7	343

<sup>a</sup>Approximate percent S/S treatment reagent by weight of the Filter Cake; <sup>b</sup>CETCO LR 2000 is diluted with water at a ratio of 8 parts water to 1 part LR 2000.

For the treatments with CETCO treatment reagents, Filter Cake and CETCO Sorbond LPC II or Sorbond Briquetting were mixed in the mortar mixer without any water until a homogeneous mix had been obtained, which took approximately 6-7 minutes (A. Ross, personal communication, July 28, 2010). It was determined that a homogenous mix had been obtained when the treatment reagents, which were light in colour, were no longer visible. Mixing these treatment reagents into the Filter Cake without any water allowed the treatment reagents to be more evenly distributed. After mixing the Filter Cake and Sorbond LPC II or Sorbond Briquetting, potable water from the city of Fort McMurray or LR 2000 diluted with potable water was added to the mixture. Then, this mixture was mixed in the mortar mixer until the

water was absorbed and a moist granular material was obtained. This took approximately another 5 minutes.

Two composite samples of Filter Cake were collected for each blend before treatment and immediately after mixing with the reagents. Composite samples were also collected 24 hours, 48 hours, and 7 days after mixing. A sample of the potable water used was also obtained just prior to treatment.

### 3.3 Field Testing by Nexen

After the two contractors had performed field testing as described above, Nexen determined that the treatment reagents used by Hazco should be retested using the mixing technique used by CETCO. The proportions of Portland cement added for each blend are provided in Table 3. Filter Cake for these treatments was collected on November 2<sup>nd</sup>, 2010.

Table 3

*Percent of Portland Cement Added for Each Blend for the Field Tests by Nexen*

Blend	Portland Cement by Weight (%) <sup>a</sup>
1	25
2	20
3	15

<sup>a</sup>Percent Portland cement by weight of the Filter Cake.

The mixing was performed in a large tent with a concrete floor with a Crown Construction Equipment mortar mixer, model C9-C. Filter Cake was added to the mortar mixer, and while the mortar mixer was turning at low speed, Portland cement was slowly added. The Filter Cake and Portland cement were first mixed for 15 minutes without any water at the maximum speed of the mortar mixer. Samples were collected and placed on paper plates to ensure all the Portland cement had been thoroughly mixed into the Filter Cake. Then, water was added slowly while the mortar mixer was turning at low speed. Finally, the Filter Cake, Portland cement, and water were mixed for another 5 minutes at the maximum speed of the mortar mixer.

The treated Filter Cake was allowed to cure in 20 L plastic buckets in a tent that was heated throughout the colder months.

The samples of Filter Cake before and after treatment were collected using the same methodology as the samples collected for the Hazco and CETCO field tests with the exceptions noted below. One composite sample of Filter Cake was collected for each blend before treatment, immediately after treatment, and 24 hours, 48 hours, 72 hours, 96 hours, 120 hours, 144 hours, 168 hours, 1 month, 3 months, 6 months, and 12 months after treatment.

Duplicate samples were collected for every fourth sample starting with the untreated sample for Blend 1. Odd numbered duplicate samples were sent to AGAT, while even numbered duplicate samples were sent to Maxxam. Starting with the 1 Month after treatment samples, a duplicate of each sample was sent to Maxxam and AGAT due to concerns with the inconsistent results obtained from the two commercial laboratories. In addition, for every fourth sample, four duplicate samples were collected and two were sent to each laboratory.

The parameters tested by the commercial laboratories included the Basic Class II Landfill Package (as described above), total metals, pH, and bulk density for samples from untreated to 168 hours after treatment. Starting with the 1 month after treatment samples, the parameters tested were reduced to TCLP metals, pH, and bulk density, since these parameters were the only changing parameters. For the samples analyzed by Maxxam, bulk density was conducted using the methodology described by McKeague (1978), which specifies the sample must be packed tightly for bulk density measurements. The Blake and Hartge (1986) method for bulk density, which specifies the sample must be packed as lightly as possible, was used by AGAT. The Blake and Hartge (1986) method is a more useful measure for waste management, because

landfill tipping fees are based on mass and this measure of bulk density can be used to estimate tipping fees using the total volume of the waste.

### **3.4 Bench Scale Testing by Nexen**

Due to the inconsistent results obtained from the field tests for some reagents such as Portland cement, bench scale tests were performed to determine if other treatment reagents might be more effective. These were conducted at the laboratory at the Nexen/CNOOC Oil Sands facility using the following reagents:

1. Low alkali Portland cement (Type I) at various concentrations (15%, 20%, and 25%)
2. Low alkali Portland cement (Type I) with fly ash (type F) at various concentrations:
  - a. PC at 20%, FA at 5%, 15%, and 25%
  - b. PC at 15%, FA at 10%
  - c. PC at 10%, FA at 15%
  - d. PC at 5%, FA at 20%
3. CETCO Sorbond LPC II at 15% with CETCO LR 2000 at 35%
4. Elemental sulphur at various concentrations (5%, 10%, 15%, 20%, 25%, 30%, 35%, 40%, and 45%) with sodium sulphite at 3%

The low alkali Portland cement (Type I) and fly ash (Type F) were obtained from Lafarge North America Inc. (Lafarge). Based on the mill certifications, the low alkali Portland cement had 0.53 to 0.55% alkalis, while the fly ash had 3.66% total alkalis. The Portland cement was produced at the Exshaw Plant in Exshaw, Alberta, while the fly ash was collected from the Sundance Power Plant, west of Edmonton, Alberta. The Sorbond LPC II and LR 2000 were obtained from CETCO. Liquid sulphur was collected in a metal bucket from the rail car loading

area at the Nexen/CNOOC SAGD and Upgrader facility, while sodium sulphite was ordered from Fisher Scientific.

Representative samples of Filter Cake were collected on July 28, 2011 from a semi-trailer truck used to transport the Filter Cake to the landfill. These samples were mixed in a barrel in order to obtain a homogenous sample. Sub-samples were collected from the homogenous sample and analyzed at Maxxam for the Basic Class II Landfill Package, total metals, total carbon, particle size, wet bulk density, dry bulk density, and percentage moisture. Bulk density was tested using the methodology described by Blake and Hartge (1986).

For the S/S treatments of Filter Cake in bench scale tests, mixing was performed using an Arrow Engineering mixer, model 850, and 1000 mL beakers. A Denver electronic scale, model TP 3101, with a precision of 0.1 g was used to measure the correct amount of Filter Cake, treatment reagents, and water.

The general strategy for bench scale tests was a two-step procedure. The first step was to treat 100 grams of Filter Cake with different proportions of treatment reagents to determine, based on visual observations, what would likely be the best formulations. The next step was to increase the bench scale tests to 300 grams of Filter Cake using the best formulations determined in Step 1. Testing was performed with greater amounts of Filter Cake in Step 2 to ensure visual observations were consistent between 100 grams and 300 grams and to ensure there was adequate material for laboratory analysis. For treating Filter Cake with sulphur and sodium sulphite, the methodology described by Lin (1995) was used with minor modifications.

It was generally thought that a certain amount of water was needed to provide a homogenous mixture for the Filter Cake and Portland cement mixture. A lot of resistance was noted when less than 15% water was added to the mixture with the resistance increasing with

mixing. This suggested that if the larger scale field or pilot tests involved high shear mixers, the resistance and heat generated from mixing would likely be too high. When either 30%, 35% or 40% water was added, the material agglomerated into large clumps. Based on these observations, it was determined that the optimal amount of water required was in the range of 15% to 25%. Therefore, 20% water was added for most of the bench scale tests using Portland cement.

After mixing, the treated Filter Cake samples were cured for three days at room temperature while the samples were exposed to air. After curing, a composite sample was collected in a 500 mL clear glass jar and sent to Maxxam for TCLP metals, pH, and percent moisture analyses. Duplicate samples were collected for 10% of the samples.

## **4.0 Results**

The results of field and bench scale treatments of Filter Cake with different S/S treatment reagents are provided in the following sections. Samples of untreated Filter Cake were collected prior to field and bench scale tests and the results of different tests to characterize the Filter Cake are reported in Section 4.1. The results of field tests by Hazco, CETCO, and Nexen are provided in Section, 4.2, 4.3, and 4.4, respectively. Finally, the results of additional bench scale tests are provided in Section 4.5.

### **4.1 Characterization of Untreated Filter Cake**

The Filter Cake appeared to be similar to petroleum coke or coal. The main differences between petroleum coke or coal and Filter Cake were the higher amounts of moisture (75-82%) and very fine particles (Table 4). Untreated Filter Cake is shown in Figure 1.

Figure 1. Untreated Filter Cake Being Sampled from a Semi-Trailer Truck



For untreated Filter Cake samples, the concentrations of metals and volatile organic compounds (VOCs) in the TCLP leachate were all below detection except for nickel, vanadium, selenium, iron and cobalt (Table 4). Leachable selenium, iron, and cobalt levels were significantly less than the limit of 1, 1000, and 100 mg/L, respectively, while leachable nickel and vanadium exceeded the limit of 5.0 and 100 mg/L, respectively. The flash points for all the samples were greater than 61 °C, and all untreated samples passed the free liquid test. The pH ranged from 5.6 to 7.2. The wet bulk density results using the methodology described by McKeague (1978) ranged from 0.90 to 1.06 g/cm<sup>3</sup>, while the wet bulk density results using Blake and Hartge (1986) ranged from 0.70 to 0.80 g/cm<sup>3</sup>. The moisture content of the Filter Cake

ranged from 75 to 82%, and the particle size test indicated almost all of the Filter Cake particles were less than 0.075 mm in diameter.

Table 4

*Results of Analysis for Regulated Parameters for Untreated Filter Cake Samples Collected Between July 2010 and July 2011*

Parameter	Alberta Environment Limit	Average Values for Untreated Filter Cake Samples			
		Hazco Field Test - Produced July 9-10, 2010	CETCO Field Test - Produced July 28, 2010	Nexen Field Test - Produced Nov. 2, 2010	Nexen Bench Test - Produced July 27-28, 2011
Leachable Volatiles (mg/L)	various	ND	ND	ND	ND <sup>a</sup>
Leachable Nickel (mg/L)	5	165	254	219	172
Leachable Vanadium (mg/L)	100	390	646	428	188
Leachable Selenium (mg/L)	1	0.1 <sup>b</sup>	0.2	0.1 <sup>c</sup>	0.1 <sup>d</sup>
Leachable Iron (mg/L)	1000	2 <sup>e</sup>	1 <sup>f</sup>	ND	ND
Leachable Cobalt (mg/L)	100	ND	1 <sup>g</sup>	ND	ND
Free Liquid	None	Pass	Pass	Pass	Pass <sup>a</sup>
Flash Point	<61 °C	>75 °C	>75 °C	>61 °C	>61 °C <sup>a</sup>
pH	<2, >12.5	5.58	5.78	7.15	6.69
Wet Bulk Density (g/cm <sup>3</sup> ) <sup>h</sup>	NA	0.97	0.90	1.06	0.98 <sup>a</sup>
Wet Bulk Density (g/cm <sup>3</sup> ) <sup>i</sup>	NA	0.80	-	0.70	0.72
Dry Bulk Density (g/cm <sup>3</sup> )	NA	0.23	-	0.20	0.13
Moisture (%)	NA	75	-	79	82
Particle Size - Sieve Pan (%)	NA	-	-	-	100 <sup>a</sup>
Particle Size - Sieve #200 (>0.075 mm) (%)	NA	-	-	-	0.4 <sup>a</sup>
Particle Size - Grain Size	NA	-	-	-	FINE <sup>a</sup>

Note. ND = not detected; NA = not applicable; dash indicates value was not available; regulated parameters not listed were below the detection limit.

<sup>a</sup>Sample collected on Aug. 8, 2011 only; <sup>b</sup>Batch 3 and 6 only as other results were below the detection limit; <sup>c</sup>samples analyzed by Maxxam only as result from AGAT was below the detection limit; <sup>d</sup>samples collected on Jan. 31, 2012 only as other results were below the detection limit; <sup>e</sup>Batch 4-6 only as other results were below the detection limit; <sup>f</sup>all samples except Blend 2, Sample 1 and Blend 3, Sample 2, which were below the detection limit; <sup>g</sup>all samples except Blend 1, Sample 1 and 2 and Blend 4, Sample 1, which were below the detection limit; <sup>h</sup>analyzed using reference method by McKeague (1978); <sup>i</sup>analyzed using reference method by Blake and Hartge (1986).

The total metals concentrations for untreated Filter Cake samples collected between July 2010 and July 2011 are provided in Table 5. Total metals are not available for the untreated Filter Cake used for the field tests with CETCO treatment reagents. Additional elements including total carbon were analyzed for samples of Filter Cake produced on December 7, 2010

and July 27-28, 2011 (Table 5). For many of these Filter Cake samples, a duplicate sample was sent to a separate lab.

The results of total metals and carbon show there is a high level of variability in the concentration of different metals and carbon in samples collected during this time period. This heterogeneity is mainly due to the operation of the gasification trains. The gasification trains are designed to produce Filter Cake with carbon to ash ratio of 5 to 1 (Rettger et al., 2006).

However, it has been observed that individual trains have been producing Filter Cake with carbon ratios either as low as 2.5 to 1 or as high as 20 to 1. Due to equipment reliability issues, the four gasification trains have been operational at different times resulting in Filter Cake with different concentrations of metals and carbon as well as variable leachable nickel and vanadium.

For the untreated Filter Cake collected for bench scale tests on July 27-28, 2011, only Gasifier Train #4 was running, and this train was running on a carbon to ash ratio of 5 to 1. As a result, the Filter Cake produced on July 27-28, 2011 should be close to design specifications. Both the leachable nickel and vanadium results and total metal concentrations for the Filter Cake produced on July 27-28, 2011 were lower than Filter Cake produced and sampled for previous tests.

Table 5

*Total Metals and Carbon in Untreated Filter Cake Samples Collected Between July 2010 and July 2011*

Elements	Untreated Filter Cake Samples (mg/Kg)					
	Hazco Field Test - Produced July 9-10, 2010 <sup>a</sup>		Nexen Field Test - Produced Nov. 2, 2010 <sup>b</sup>		Produced Dec. 7, 2010 <sup>c</sup>	Nexen Bench Test - Produced July 27-28, 2011 <sup>d</sup>
	Maxxam	AGAT	Maxxam	AGAT	Maxxam	Maxxam
Soluble Boron	4.2	-	6	-	8	-
Hex. Chromium	150	-	550	-	240	-
Total Antimony	ND	4.2	20	18.8	ND	2
Total Arsenic	20	31.4	31	32.9	16	12
Total Barium	ND	9.6	ND	9.9	ND	ND
Total Beryllium	ND	1.3	ND	1.2	ND	ND
Total Bismuth	-	ND	-	ND	-	-
Total Cadmium	0.9	4.2	2	4.0	1	0.7
Total Chromium	58	88.8	90	96.3	39	35
Total Cobalt	50	95	98	113	38	43
Total Copper	ND	2.4	ND	3.2	ND	ND
Total Lead	ND	1.7	ND	1.8	ND	ND
Total Mercury	ND	ND	0.2	ND	ND	ND
Total Molybdenum	2,000	2,870	3,567	2,880	1,650	1,200
Total Nickel	11,000	21,800	22,333	27,400	8,600	7,700
Total Selenium	11	24.2	16	22.2	9	4.2
Total Silver	ND	ND	ND	ND	ND	ND
Total Thallium	ND	ND	ND	ND	ND	ND
Total Tin	ND	1.1	ND	1.1	ND	ND
Total Titanium	-	590	-	653	-	-
Total Uranium	ND	ND	ND	ND	ND	ND
Total Vanadium	39,000	52,000	66,000	69,800	32,000	23,000
Total Zinc	ND	36.1	43 <sup>e</sup>	52.3	ND	19
Total Aluminum	-	ND	-	278	74	46
Total Boron	-	ND	-	7.1	ND	5
Total Calcium	-	-	-	-	940	390
Total Iron	-	780	-	930	315	380
Total Lithium	-	0.7	-	ND	ND	ND
Total Magnesium	-	-	-	-	ND	30
Total Manganese	-	88.3	-	135	ND	42
Total Phosphorus	-	-	-	-	ND	66
Total Potassium	-	-	-	-	ND	64
Total Sodium	-	-	-	-	845	67
Total Strontium	-	29	-	25.4	ND	ND
Total Sulphur	-	-	-	-	7,650	8,000
Total Carbon	-	-	-	-	785,000	705,000

Note. ND = not detected; dash indicates value was not available.

<sup>a</sup>Duplicate Batch 1 and 4 untreated Filter Cake samples stored in a fridge were blended on Oct. 25, 2010, and, then, duplicate samples were sent to Maxxam and AGAT; <sup>b</sup>duplicate samples were sent to Maxxam and AGAT; values for Maxxam were an average of results for Blend 1, 2 and 3, while values for AGAT were Blend 1 only; <sup>c</sup>values are an average from 2 samples; <sup>d</sup>value for total carbon is an average of 4 lab duplicates; <sup>e</sup>value for Blend 1 was below the detection limit; value provided is an average of Blend 2 and 3.

## 4.2 Hazco Field Test

The treated Filter Cake in the Hazco field test visually appeared to be similar to the untreated Filter Cake (Figure 2). Figure 2 shows the treated Filter Cake on the shovel.

Figure 2. Treated Filter Cake from Hazco Field Tests



The results of field tests performed by Hazco are provided in Tables 6 to 9. Treating the Filter Cake with Portland cement was very effective at reducing leachable nickel as all the values were well below 5 mg/L, with the exception of Batch 3, 48 hours after treatment (Table 6). This value may be either due to the heterogeneity of the treated Filter Cake or an outlier since the concentration for Batch 3, 12-13 days after treatment was below the detection limit. In addition, all the leachable nickel concentrations for Batch 6, which were treated with the same percentage

of Portland cement, were well under the limit. The results in Table 6 show that leachable nickel results were generally consistent across the different time periods when the treated Filter Cake was tested.

Table 6

*Leachable Nickel Results for the Different Batches Tested by Hazco*

Sample	% Portland Cement <sup>a</sup>	Leachable Nickel (mg/L)					
		Untreated	Immediately After Mixing	24 Hr. After Mixing	48 Hr. After Mixing	12-13 Days After Mixing	27 Days After Mixing <sup>b</sup>
Batch 1	25%	140	1.5	0.7	ND	ND	ND
Batch 1 – Lab. Dup.	25%	140					
Batch 2	20%	140	1.3	ND	ND	ND	-
Batch 3	15%	160	0.7	ND	<b>10</b>	ND	-
Batch 4	25%	160	ND	ND	ND	ND	-
Batch 5	20%	190	ND	ND	ND	ND	-
Batch 6	15%	200	1.7	0.5	ND	0.8	-

Note. ND = not detected; results over Alberta Environment limit are in boldface.

<sup>a</sup>Percent Portland cement by weight of the Filter Cake; <sup>b</sup>TCLP results for 27 days after mixing were only tested for Batch 1; the results shown for 27 days after mixing are an average of the values from samples collect from 0-15, 30-45, and 60-75 cm from the top of the pile.

The leachable results for vanadium for field tests performed by Hazco are provided in Table 7. In contrast to the data for leachable nickel, some of the concentrations were well above the limit. For Batches 3 and 6, which were the treatments that received 15% Portland cement, the leachable vanadium results were well over the limit. For the batches treated with 20% Portland cement, the leachable vanadium results were initially under the limit, but increased with time resulting in all the concentrations after 12-13 days of curing exceeding the limit. For batches treated with 25% Portland cement, the leachable vanadium concentrations peaked around 24 to 48 hours after treatment, where they exceeded the limit. Then, the leachable vanadium values decreased to well below the limit. The one sample collected 27 days after treatment was for Batch 1, which was treated with 25% Portland cement. The leachable vanadium for this sample was well below the limit.

Table 7

*Leachable Vanadium Results for the Different Batches Tested by Hazco*

Sample	% Portland Cement <sup>a</sup>	Leachable Vanadium (mg/L)					
		Untreated	Immediately After Mixing	24 Hr. After Mixing	48 Hr. After Mixing	12-13 Days After Mixing	27 Days After Mixing <sup>b</sup>
Batch 1	25%	<b>270</b>	44	100	<b>130</b>	9	6
Batch 1 – Lab. Dup.	25%	<b>220</b>					
Batch 2	20%	<b>320</b>	38	45	53	<b>110</b>	
Batch 3	15%	<b>370</b>	<b>410</b>	<b>380</b>	<b>230</b>	<b>520</b>	
Batch 4	25%	<b>400</b>	<b>160</b>	<b>190</b>	11	11	
Batch 5	20%	<b>460</b>	18	<b>160</b>	94	<b>170</b>	
Batch 6	15%	<b>520</b>	<b>250</b>	<b>380</b>	<b>280</b>	<b>330</b>	

Note. Results over Alberta Environment limit are in boldface.

<sup>a</sup>Percent Portland cement by weight of the Filter Cake; <sup>b</sup>TCLP results for 27 days after mixing were only tested for Batch 1; the results shown for 27 days after mixing are an average of the values from samples collected from 0-15, 30-45, and 60-75 cm from the top of the pile.

The variability in the leachable vanadium results for Batches 1 and 4 may be due to differences in the TCLP pretest pH results (Table 8). For the TCLP test, the pH of the material is tested prior to leachate extraction in order to determine whether Fluid #1, which has a pH of 4.93, or Fluid #2, which has a pH of 2.88, will be used for the extraction (U.S. EPA, 1992). If the initial pH is above 5, HCl is added and the sample is heated. If the pH is still greater than 5 after the addition of HCl, Fluid #2 is used, otherwise Fluid #1 is used for the extraction.

From Table 8, some of the second pH values for the TCLP pH pretest for Batches 1 and 4 were above 5 and as a result Fluid #2 was used for the extraction. For the time period up to 48 hours for Batch 1 and up to 24 hours for Batch 4, Fluid #2 was used, while after these time periods, Fluid #1 was used. The leachable vanadium was well over the limit when Fluid #2 was used, but dropped below the limit when Fluid #1 was used.

Table 8

*TCLP Pretest pH Results for the Different Batches Tested by Hazco*

Sample	% Portland Cement <sup>a</sup>	TCLP Pretest pH Results					
		Untreated	Immediately After Mixing	24 Hr. After Mixing	48 Hr. After Mixing	12-13 Days After Mixing	27 Days After Mixing <sup>b</sup>
Batch 1	25%	6/2	<b>12/6</b>	<b>12/6</b>	<b>12/6</b>	10/3	11/4
Batch 2	20%	6/2	12/4	12/4	12/4	10/3	
Batch 3	15%	6/2	12/3	12/2	8/2	8/3	
Batch 4	25%	6/2	<b>12/7</b>	<b>12/6</b>	12/4	10/3	
Batch 5	20%	6/2	12/4	12/3	12/3	10/3	
Batch 6	15%	6/3	12/3	12/3	12/3	9/3	

Note. The first value is the initial TCLP pretest pH result, and the second value is the pH after HCl has been added; TCLP tests required to use Fluid #2 for the extraction are in boldface.

<sup>a</sup>Percent Portland cement by weight of the Filter Cake; <sup>b</sup>TCLP results for 27 days after mixing were only tested for Batch 1; the results shown for 27 days after mixing are an average of the values from samples collected from 0-15, 30-45, and 60-75 cm from the top of the pile.

The Waste Control Regulation (AEP, 1996) specifies that the pH of the waste must not be greater than 12.5. Table 9 shows that the pH of the treated waste is just under this limit for most of the samples collected for the batches treated by Hazco.

Table 9

*pH Results for the Different Batches Tested by Hazco*

Sample	% Portland Cement <sup>a</sup>	pH (1:1 water to waste)					
		Untreated	Immediately After Mixing	24 Hr. After Mixing	48 Hr. After Mixing	12-13 Days After Mixing	27 Days After Mixing <sup>b</sup>
Batch 1	25%	6.06	<b>12.7</b>	12.5	12.5	12.3	12.2
Batch 2	20%	5.97	12.4	12.4	12.4	11.9	
Batch 3	15%	5.63	11.7	11.4	10.6	10.4	
Batch 4	25%	5.49	<b>12.7</b>	12.3	<b>12.6</b>	12.4	
Batch 5	20%	5.22	<b>12.6</b>	12.1	12.4	12	
Batch 6	15%	5.1	12.1	11.1	11.6	11.2	

Note. Results over Alberta Environment limit are in boldface.

<sup>a</sup>Percent Portland cement by weight of the Filter Cake; <sup>b</sup>TCLP results for 27 days after mixing were only tested for Batch 1; the results shown for 27 days after mixing are an average of the values from samples collected from 0-15, 30-45, and 60-75 cm from the top of the pile.

The other parameters that were tested for the treated Filter Cake samples included free liquid, flash point, leachable volatiles, and the remaining leachable metals. All the samples passed the free liquid and flash point tests. Leachable VOCs such as benzene, toluene, and

ethylbenzene were below detection, while leachable selenium was detected in a few of the treated samples (in the range of 0.1 to 0.2 mg/L). Leachable iron (up to 32 mg/L) was generally higher in the treated samples compared to the untreated Filter Cake samples. The increase in leachable iron was likely due to the iron in the Portland cement.

As mentioned previously, the potable water added to the Filter Cake and Portland cement mixture was sent to Maxxam to test for various parameters. The analysis of the potable water indicated there were no contaminants in the potable water that would interfere with the cement reactions.

### **4.3 CETCO Field Test**

The treated Filter Cake from the CETCO field tests is shown in Figure 3. As with the Hazco field tests, the treated Filter Cake from CETCO field tests was similar in appearance to the untreated Filter Cake.

Figure 3. Treated Filter Cake from CETCO Field Tests



The results of the field tests performed by CETCO are provided in Tables 10 to 13. Blend 1 and 4 were approximately 15% CETCO Sorbond LPC II and 50% water or 35% CETCO LR 2000, respectively. Blend 2 and 3 were approximately 15% CETCO Sorbond Briquetting with 50% water or 35% CETCO LR 2000, respectively. The effectiveness of the blends used by CETCO for reducing leachable nickel below the limit was inconsistent with the exception of Blend 4 (Table 10).

Table 10

*Leachable Nickel Results for the Different Blends tested by CETCO*

	Leachable Nickel (mg/L)				
	Untreated	Immediately After Mixing	24 Hr. After Mixing	48 Hr. After Mixing	1 Week After Mixing
Blend 1, Sample 1	<b>240</b>	2.9	ND	ND	<b>79</b>
Blend 1, Sample 2	<b>220</b>	3.5	ND	ND	1.6
Blend 2, Sample 1	<b>290</b>	<b>5.1</b>	1.3	0.6	1.7
Blend 2, Sample 2	<b>260</b>	4.8	0.9	<b>7.9</b>	<b>110</b>
Blend 3, Sample 1	<b>260</b>	0.6	<b>120</b>	1.7	2.4
Blend 3, Sample 2	<b>280</b>	3.2	<b>120</b>	0.8	ND
Blend 4, Sample 1	<b>200</b>	4	1.5	ND	ND
Blend 4, Sample 2	<b>280</b>	1.4	ND	ND	ND

Note. ND = not detected; results over Alberta Environment limit are in boldface.

The CETCO blends were also inconsistent for reducing leachable vanadium below the limit with the exception of Blend 4 (Table 11). Blend 4 was consistent at reducing leachable vanadium below the limit from 24 hours after mixing through to 1 week after mixing, which is an improvement over the trials with Portland cement shown in Section 4.2.

Table 11

*Leachable Vanadium Results for the Different Blends tested by CETCO*

	Leachable Vanadium (mg/L)				
	Untreated	Immediately After Mixing	24 Hr. After Mixing	48 Hr. After Mixing	1 Week After Mixing
Blend 1, Sample 1	<b>640</b>	8	79	56	<b>420</b>
Blend 1, Sample 2	<b>660</b>	<b>130</b>	74	<b>190</b>	ND
Blend 2, Sample 1	<b>630</b>	<b>280</b>	<b>600</b>	<b>500</b>	<b>640</b>
Blend 2, Sample 2	<b>690</b>	<b>470</b>	<b>580</b>	<b>630</b>	<b>280</b>
Blend 3, Sample 1	<b>580</b>	<b>570</b>	<b>270</b>	<b>610</b>	<b>640</b>
Blend 3, Sample 2	<b>600</b>	<b>630</b>	<b>270</b>	<b>540</b>	<b>530</b>
Blend 4, Sample 1	<b>760</b>	<b>560</b>	33	30	5
Blend 4, Sample 2	<b>610</b>	<b>370</b>	28	52	5

Note. ND = not detected; results over Alberta Environment limit are in boldface.

The TCLP pretest pH results indicated that Fluid #1 was used for most of the TCLP extractions (Table 12). However, for Blend 4, 1 week after mixing, Fluid #2 was used and despite using the extraction fluid with a lower pH, the leachable vanadium and nickel results were well below the limit. Fluid #2 was also used for Blend 1, Sample 1 for 1 week after mixing,

and the leachable nickel and vanadium results were well above the limit. As a result, the combination of Sorbond LPC II and LR 2000 provided superior performance over LPC II and water for reducing leachable nickel and vanadium below the Alberta Environment limits.

Table 12

*TCLP Pretest pH Results for the Different Blends tested by CETCO*

Sample	TCLP Pretest pH Results				
	Pre Treatment	Immediately After Mixing	24 Hr. After Mixing	48 Hr. After Mixing	1 Week After Mixing
Blend 1, Sample 1	5/3	9/3	11/3	11/2	<b>10/8</b>
Blend 1, Sample 2	5/3	9/3	11/3	11/2	10/4
Blend 2, Sample 1	5/3	9/3	11/2	10/2	9/4
Blend 2, Sample 2	5/2	9/3	11/2	10/2	<b>10/7</b>
Blend 3, Sample 1	5/3	9/4	<b>11/6</b>	10/2	9/4
Blend 3, Sample 2	5/4	9/3	<b>11/6</b>	10/2	9/4
Blend 4, Sample 1	5/3	<b>9/6</b>	11/2	11/3	<b>10/7</b>
Blend 4, Sample 2	5/3	<b>9/8</b>	11/2	11/3	<b>10/7</b>

Note. The first value is the initial TCLP pretest pH result, and the second value is the pH after HCl has been added; TCLP tests required to use Fluid #2 for the extraction are in boldface.

In general, the pH values of the Filter Cake treated with CETCO reagents were lower than the values for the treatments with Portland cement (Table 13).

Table 13

*pH Results for the Different Blends tested by CETCO*

	pH (1:1 water to waste)				
	Untreated	Immediately After Mixing	24 Hr. After Mixing	48 Hr. After Mixing	1 Week After Mixing
Blend 1, Sample 1	5.97	12.5	12.3	12.4	11.9
Blend 1, Sample 2	5.74	11.1	12.2	12.0	12.1
Blend 2, Sample 1	5.45	11.9	10.8	10.9	9.49
Blend 2, Sample 2	5.57	11.2	10.7	10.6	10.7
Blend 3, Sample 1	5.87	11.1	10.9	10.9	10.7
Blend 3, Sample 2	5.76	11.1	10.5	10.7	10.6
Blend 4, Sample 1	5.94	<b>12.6</b>	12.5	12.2	12.2
Blend 4, Sample 2	5.96	<b>12.6</b>	12.5	12.4	12.1

Note. Results over Alberta Environment limit are in boldface.

Most of the treated samples passed the free liquid and flash point tests; however, the flash point for Blend 2, Sample 1 for the time period immediately after mixing was 42 °C, which

was less than the requirement for flash point to be greater than 61 °C. Leachable VOCs such as benzene, toluene, and ethylbenzene were below detection. There were a few treated samples that contained leachable selenium in the range of 0.1 to 0.3 mg/L. The range of leachable iron in the treated Filter Cake samples was from non-detectable to 30 mg/L, which was higher than the untreated Filter Cake samples. The higher values of leachable iron in the treated Filter Cake compared to the untreated Filter Cake were likely due to the iron in the CETCO Sorbond LPC II, which also contained Portland cement.

#### **4.4 Nexen Field Test**

Due to the inconsistent results obtained in the field tests with Portland cement as presented in Section 4.2, a retest was performed using a mortar mixer to mix the Filter Cake and Portland cement. It was anticipated that the mortar mixer would provide a more thorough mix. In addition, the treated Filter Cake was tested for TCLP metals and other tests at different time periods up to one year after treatment, which was a much longer period than the previous field tests.

Similar to the results obtained in previous field tests with Portland cement, this treatment reagent was effective in reducing leachable nickel below the Alberta Environment limit of 5 mg/L (Table 14). The only leachable nickel result over this limit was a duplicate for the sample collected twelve months after treatment for the trials with 15% Portland cement.

Table 14

*Leachable Nickel for Different Time Periods after Mixing for the Field Tests by Nexen*

	Leachable Nickel (mg/L)												
	Un- treated	0 Hr.	24 Hr.	48 Hr.	72 Hr.	96 Hr.	120 Hr.	144 Hr.	168 Hr.	1 Mo.	3 Mo.	6 Mo.	12 Mo.
Blend 1 – 25% Portland Cement													
Analyzed by Maxxam													
Blend 1	<b>220</b>	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.1
Dup.					ND								1.4
Batch 1 <sup>a</sup>		ND											
Analyzed by AGAT													
Dup.	<b>214</b>								ND	ND	ND	0.7	2.5
2 <sup>nd</sup> Dup.												0.9	
QA/QC													
RPD (%)	3				NC				NC	NC	NC		<b>78<sup>b</sup></b>
RSD (%)												NC	
Blend 2 – 20% Portland Cement													
Analyzed by Maxxam													
Blend 2	<b>220</b>	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.1
Dup.		ND								ND			1.4
Analyzed by AGAT													
Dup.						ND				ND	ND	0.9	3.4
2 <sup>nd</sup> Dup.										ND			3.1
QA/QC													
RPD (%)		NC				NC					NC	NC	
RSD (%)									NC				<b>52<sup>b</sup></b>
Blend 3 – 15% Portland Cement													
Analyzed by Maxxam													
Blend 3	<b>220</b>	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.1	3.3
Dup.							ND				ND		
Analyzed by AGAT													
Dup.			ND							ND	1.9	1.5	<b>6.7</b>
2 <sup>nd</sup> Dup.											4.9		
QA/QC													
RPD (%)			NC				NC			NC		<b>31<sup>b</sup></b>	<b>68</b>
RSD (%)											NC		
Control													
Analyzed by Maxxam													
Control										<b>190</b>	<b>200</b>	<b>260</b>	<b>450</b>
Analyzed by AGAT													
Dup.										<b>248</b>	<b>250</b>	<b>314</b>	<b>515</b>
QA/QC													
RPD (%)										26	22	19	13

Note. ND = not detected; results over Alberta Environment limit are in boldface; RPD = relative percent difference; RSD = relative standard deviation; RPD was used when there were two duplicates, while RSD was used when there were four duplicates; NC = not calculable; for duplicate results where one or more of the values was ND, the RPD or RSD was NC; RPD and RSD values above 30% are in boldface.

<sup>a</sup>Sample was collected from Blend 1, Batch 1 only; each blend consisted of three batches; <sup>b</sup>duplicate results were less than five times the reported detection limit (RDL).

The duplicate samples tested either by the same laboratory, Maxxam, or a different laboratory, AGAT, indicated there was good agreement between duplicates. If there were two duplicates, the relative percent difference (RPD) was calculated for the two duplicates. If there were four duplicates, the relative standard deviation (RSD) was calculated for the four duplicates. For most of the duplicate samples tested, the leachable nickel results were below the detection limit, and as a result, the RPD or RSD could not be calculated. For some of the duplicates, the RPD or RSD could be calculated but the leachable nickel results were not five times the reported detection limit (RDL). In this case, the RPD or RSD was calculated and it was noted in Table 14 that the results were not five times the RDL. For the remaining duplicates, leachable nickel results were at least five times the RDL and the RPD values were less than 30% with one exception: Blend 3, 12 months after treatment.

The leachable vanadium results were inconsistent (Table 15). Some of the leachable vanadium results were well under the limit of 100 mg/L, while other values were well above this limit. Initially, it appeared that the longer the Filter Cake was cured, the lower the leachable vanadium results as all the samples collected one month after treatment were under the limit. However, the samples collected three months after treatment and especially the samples collected six and twelve months after treatment had leachable results that were well over the limit.

The leachable vanadium results for the Filter Cake treated with 15% Portland cement in this trial were lower than the leachable vanadium results in field tests performed by Hazco. For the Hazco field test with 15% Portland cement, the leachable vanadium was well over the limit for all time periods. For the Nexen field test with 15% Portland cement, the leachable vanadium was under the limit for some of the time periods.

Table 15

*Leachable Vanadium for Different Time Periods after Mixing for the Field Tests by Nexen*

		Leachable Vanadium (mg/L)												
		Un- treated	0 Hr.	24 Hr.	48 Hr.	72 Hr.	96 Hr.	120 Hr.	144 Hr.	168 Hr.	1 Mo.	3 Mo.	6 Mo.	12 Mo.
Blend 1 – 25% Portland Cement														
Analyzed by Maxxam														
Blend 1	<b>390</b>	ND	1	8	<b>190</b>	<b>210</b>	<b>200</b>	<b>160</b>	<b>190</b>	4	12	<b>300</b>	<b>340</b>	
Dup.					<b>160</b>							<b>300</b>		
Batch 1 <sup>a</sup>		2												
Analyzed by AGAT														
Dup.	<b>513</b>								2.7	4.5	<b>201</b>	<b>369</b>	<b>437</b>	
2 <sup>nd</sup> Dup.												<b>423</b>		
QA/QC														
RPD (%)	27				17 <sup>b</sup>				<b>194<sup>b</sup></b>	12 <sup>b</sup>	<b>177</b>		25	
RSD (%)												17		
Blend 2 – 20% Portland Cement														
Analyzed by Maxxam														
Blend 2	<b>410</b>	1	4	10	7	12	26	12	<b>160</b>	5	8	<b>300</b>	<b>460</b>	
Dup.		3								5			<b>440</b>	
Analyzed by AGAT														
Dup.						7.7				6.9	<b>247</b>	<b>384</b>	<b>516</b>	
2 <sup>nd</sup> Dup.										6.5			<b>495</b>	
QA/QC														
RPD (%)		<b>100<sup>b</sup></b>				<b>44<sup>b</sup></b>					<b>187</b>	25		
RSD (%)										17			7 <sup>b</sup>	
Blend 3 – 15% Portland Cement														
Analyzed by Maxxam														
Blend 3	<b>400</b>	57	74	<b>120</b>	<b>140</b>	<b>120</b>	99	47	52	33	61	<b>370</b>	<b>510</b>	
Dup.							<b>120</b>				68			
Analyzed by AGAT														
Dup.			61							62	<b>372</b>	<b>450</b>	<b>636</b>	
2 <sup>nd</sup> Dup.											<b>405</b>			
QA/QC														
RPD (%)			19 <sup>b</sup>				19 <sup>b</sup>			<b>60</b>		20	22	
RSD (%)											<b>83</b>			
Control														
Analyzed by Maxxam														
Control										<b>280</b>	<b>260</b>	<b>380</b>	<b>410</b>	
Analyzed by AGAT														
Dup.										<b>352</b>	<b>382</b>	<b>418</b>	<b>517</b>	
QA/QC														
RPD (%)										23	<b>38</b>	10	23	

Note. ND = not detected; results over Alberta Environment limit are in boldface; RPD = relative percent difference; RSD = relative standard deviation; RPD was used when there were two duplicates, while RSD was used when there were four duplicates; RPD and RSD values above 30% are in boldface.

<sup>a</sup>Sample was collected from Blend 1, Batch 1 only; each blend consisted of three batches; <sup>b</sup>duplicate results were less than five times the reported detection limit (RDL).

The analysis of leachable vanadium duplicates revealed there were inconsistencies between some of the duplicates. There were a number of RPDs and RSDs where the leachable vanadium results were not five times the RDL. For some of the samples, the RPD or RSD was not five times the RDL, because Maxxam increased the RDL for the analysis. However, for a number of the analyses where the results were not five times the RDL, the RPD or RSD was less than 30%. For the samples where the results were at least five times the RDL, the RPD or RSD values were less than 30% except for Blend 3, 1 month after treatment and Blend 1, 2 and 3 and Control, 3 months after treatment.

The higher leachable vanadium results can be partially explained by the TCLP pretest pH results and the pH of the fluid that was used for the extraction (Table 16). For Blends 1 and 2, leachable vanadium was well under the limit when Fluid #1 was used and well over the limit when Fluid #2 was used. For Blend 3, similar results were obtained. However, most of the samples from 48 to 120 hours after treatment had leachable vanadium results just over the limit and Fluid #1 was used.

The TCLP pretest pH results were fairly similar for most of the duplicates. As a result, the pH of the fluid used for the extraction for the TCLP tests was the same for most duplicates. However, there were large differences between duplicates for the TCLP pretest pH results for Blend 1, 168 hours after treatment, and Blend 1, 2 and 3, 3 months after treatment. As a result, the pH of the fluid used for extraction for the TCLP tests were different between duplicates for these samples, which explains why the RPD and RSD results for leachable vanadium for these samples were also very high.

Table 16

*TCLP Pretest pH Results for Different Time Periods after Mixing for the Blends Tested in the Field by Nexen*

		TCLP Pretest pH Values											
	Un-treated	0 Hr.	24 Hr.	48 Hr.	72 Hr.	96 Hr.	120 Hr.	144 Hr.	168 Hr.	1 Mo.	3 Mo.	6 Mo.	12 Mo.
Blend 1 – 25% Portland Cement													
Analyzed by Maxxam													
Blend 1	6/2	10/4	10/4	10/4	<b>11/6</b>	<b>11/6</b>	<b>11/6</b>	<b>10/5</b>	<b>10/5</b>	11/4	11/4	<b>10/7</b>	<b>9/7</b>
Dup.					<b>11/7</b>							<b>10/7</b>	
Batch 1 <sup>a</sup>		10/4											
Analyzed by AGAT													
Dup.	6/2								10/2	12/4	<b>12/10</b>	<b>11/9</b>	<b>11/7</b>
2 <sup>nd</sup> Dup.												<b>12/10</b>	
Blend 2 – 20% Portland Cement													
Analyzed by Maxxam													
Blend 2	6/3	10/4	10/4	11/4	11/4	11/4	10/4	10/3	<b>10/5</b>	11/4	11/4	<b>10/6</b>	<b>9/7</b>
Dup.		10/4								11/4			<b>9/7</b>
Analyzed by AGAT													
Dup.						11/2				12/2	<b>12/10</b>	<b>11/10</b>	<b>11/8</b>
2 <sup>nd</sup> Dup.										12/3			<b>11/7</b>
Blend 3 – 15% Portland Cement													
Analyzed by Maxxam													
Blend 3	6/3	11/4	11/4	11/4	10/4	10/4	10/3	11/2	11/3	11/4	11/4	<b>10/6</b>	<b>9/7</b>
Dup.							10/4				11/4		
Analyzed by AGAT													
Dup.			11/2							11/3	<b>12/9</b>	<b>12/9</b>	<b>10/7</b>
2 <sup>nd</sup> Dup.											<b>12/9</b>		
Control													
Analyzed by Maxxam													
Control										6/3	6/2	6/2	6/2
Analyzed by AGAT													
Dup.										7/2	7/1	7/2	7/2

Note. The first value is the initial TCLP pretest pH result, and the second value is the pH after HCl has been added; TCLP tests required to use Fluid #2 for the extraction are in boldface

<sup>a</sup>Sample was collected from Blend 1, Batch 1 only; each blend consisted of three batches.

The pH of the treated Filter Cake was under the limit of 12.5 for most of the samples with the exception of two duplicate samples analyzed by AGAT: Blend 1, 3 months after treatment and Blend 2, 96 hours after treatment (Table 17). All of the RPD and RSD values for duplicates were well below 30%, except for the Control, 1 month after treatment. The pH analyzed by AGAT for the Control, 1 month after treatment was very high and is an outlier.

Table 17

*pH Results for Different Time Periods after Mixing for the Field Tests by Nexen*

		pH (1:1 water to waste)												
		Un- treated	0 Hr.	24 Hr.	48 Hr.	72 Hr.	96 Hr.	120 Hr.	144 Hr.	168 Hr.	1 Mo.	3 Mo.	6 Mo.	12 Mo.
Blend 1 – 25% Portland Cement														
Analyzed by Maxxam														
Blend 1	7.0	8.3	12.0	12.4	12.4	12.5	12.0	12.3	12.3	12.2	12.1	11.8	11.0	
Dup.					12.4							11.9		
Batch 1a		12.2												
Analyzed by AGAT														
Dup.	6.4								12.5	12.3	<b>12.6</b>	11.7	9.8	
2nd Dup.												11.7		
QA/QC														
RPD (%)	9				0				2	1	4		12	
RSD (%)												1		
Blend 2 – 20% Portland Cement														
Analyzed by Maxxam														
Blend 2	6.5	12.4	12.3	12.4	12.4	12.5	12.1	12.1	12.3	12.2	12.2	12.1	10.9	
Lab Dup.					12.3			12.2						
Dup.		12.5								12.2			10.9	
Analyzed by AGAT														
Dup.						<b>12.7</b>				12.1	12.5	11.9	10.4	
2nd Dup.										12.0			10.8	
QA/QC														
RPD (%)		1			1	2		1			2	2		
RSD (%)										1				2
Blend 3 – 15% Portland Cement														
Analyzed by Maxxam														
Blend 3	6.9	12.4	12.3	12.2	12.1	12.1	12.2	12.0	12.1	12.2	11.9	11.9	9.2	
Lab Dup.		12.4												
Dup.							12.0				11.9			
Analyzed by AGAT														
Dup.			12.5							11.9	12.2	11.7	9.1	
2nd Dup.											12.2			
QA/QC														
RPD (%)		0	2					2		2		2	1	
RSD (%)											1			
Control														
Analyzed by Maxxam														
Control										6.8	6.5	6.3	6.2	
Analyzed by AGAT														
Dup.										12.0	6.3	6.4	5.8	
QA/QC														
RPD (%)										<b>55</b>	2	2	7	

Note. Results over Alberta Environment limit are in boldface; RPD = relative percent difference; RSD = relative standard deviation; RPD was used when there were two duplicates, while RSD was used when there were four duplicates; there were no reported detection limits (RDLs); RPD and RSD values above 30% are in boldface.

<sup>a</sup>Sample was collected from Blend 1, Batch 1 only; each blend consisted of three batches.

The total nickel and vanadium in the untreated Filter Cake and treated Filter Cake samples is provided in Tables 18 and 19, respectively. The concentrations of nickel and vanadium in the untreated Filter Cake for the field tests performed by Nexen were higher than the concentrations in the other field and bench scale tests (see Table 5). The concentrations of nickel and vanadium in the treated Filter Cake were fairly consistent across the different time periods of sampling.

Table 18

*Total Nickel for Different Time Periods after Mixing for the Field Tests by Nexen*

	Total Nickel (mg/kg)								
	Un-treated	0 Hr.	24 Hr.	48 Hr.	72 Hr.	96 Hr.	120 Hr.	144 Hr.	168 Hr.
Blend 1 – 25% Portland Cement									
Analyzed by Maxxam									
Blend 1	18,000	8,700	9,800	9,600	9,100	9,400	8,400	9,800	9,300
Dup.					8,100				
Batch 1 <sup>a</sup>		9,500							
Analyzed by AGAT									
Dup.	27,400								9,270
QA/QC									
RPD (%)	<b>41</b>				12				0
Blend 2 – 20% Portland Cement									
Analyzed by Maxxam									
Blend 2	25,000	11,000	11,000	8,900	9,200	9,900	11,000	11,000	6,100
Dup.		11,000							
Analyzed by AGAT									
Dup.						9,820			
QA/QC									
RPD (%)		0				1			
Blend 3 – 15% Portland Cement									
Analyzed by Maxxam									
Blend 3	24,000	11,000	12,000	12,000	11,000	12,000	6,200	9,700	11,000
Dup.							6,900		
Analyzed by AGAT									
Dup.			12,100						
QA/QC									
RPD (%)			1				11		

Note. RPD = relative percent difference; all of the duplicates were more than five times the reported detection limit (RDL); RPD values above 30% are in boldface.

<sup>a</sup>Sample was collected from Blend 1, Batch 1 only; each blend consisted of three batches.

The concentration of nickel and vanadium was fairly similar between duplicates (Table 18 & 19). All of the RPD values were less than 30% except for the nickel concentration in the untreated sample for Blend 1.

Table 19

*Total Vanadium for Different Time Periods after Mixing for the Field Tests by Nexen*

	Total Vanadium (mg/kg)								
	Un-treated	0 Hr.	24 Hr.	48 Hr.	72 Hr.	96 Hr.	120 Hr.	144 Hr.	168 Hr.
Blend 1 – 25% Portland Cement									
Analyzed by Maxxam									
Blend 1	56,000	26,000	28,000	30,000	29,000	29,000	29,000	34,000	31,000
Dup.					27,000				
Batch 1 <sup>a</sup>		29,000							
Analyzed by AGAT									
Dup.	69,800								31,800
QA/QC									
RPD (%)	22				7				3
Blend 2 – 20% Portland Cement									
Analyzed by Maxxam									
Blend 2	71,000	32,000	36,000	29,000	29,000	33,000	40,000	36,000	19,000
Dup.		33,000							
Analyzed by AGAT									
Dup.						29,100			
QA/QC									
RPD (%)		3				13			
Blend 3 – 15% Portland Cement									
Analyzed by Maxxam									
Blend 3	71,000	35,000	36,000	57,000	38,000	41,000	20,000	29,000	35,000
Dup.							22,000		
Analyzed by AGAT									
Dup.			33,600						
QA/QC									
RPD (%)			7				10		

Note. RPD = relative percent difference; all of the duplicates were more than five times the reported detection limit (RDL); RPD and RSD values above 30% are in boldface.

<sup>a</sup>Sample was collected from Blend 1, Batch 1 only; each blend consisted of three batches.

Table 20 provides the wet and dry bulk density and percent moisture for the untreated and treated Filter Cake samples collected at different time periods after mixing. For wet and dry density, Maxxam used McKeague (1978) as a reference method, while AGAT used Blake and Hartge (1986) as a reference method as discussed in Section 3.3. As a result, the bulk density

values obtained by Maxxam were higher than AGAT. The percent moisture in the treated Filter Cake decreased over the twelve months of the experiment, because the buckets where the treated Filter Cake was left to cure were left open to the air in a heated tent.

The wet and dry bulk density and percent moisture values were consistent between duplicates (Table 20). All of the RPD and RSD values were less than 30% except for the percent moisture for Blend 2, 96 hours after treatment and Blend 3, 24 hours after treatment. The only AGAT results that were used in the calculation of RPD and RSD values were the percent moisture results, because Maxxam and AGAT used different procedures for bulk density tests. All of the wet and dry bulk density and percent moisture results were more than five times the RDL, and as a result, all the calculated RPD and RSD values were valid.



		Time Period After Mixing												
		Un- treated	0 Hr.	24 Hr.	48 Hr.	72 Hr.	96 Hr.	120 Hr.	144 Hr.	168 Hr.	1 Mo.	3 Mo.	6 Mo.	12 Mo.
		Blend 2 – 20% Portland Cement												
Analyzed by Maxxam														
Blend 2	Wet Bulk Density (g/cm3)	1.1	1.2	1.1	1.2	1.2	1.1	1.0	1.0	1.0	0.80	0.80	0.74	0.62
Blend 2	Dry Bulk Density (g/cm3)	0.22	0.37	0.34	0.38	0.39	0.39	0.33	0.37	0.36	0.30	0.32	0.36	0.39
Blend 2	Moisture (%)	79	68	66	68	64	68	68	68	67	63	60	46	36
Lab. Dup.	Wet Bulk Density (g/cm3)						1.1	1.0						
Lab. Dup.	Dry Bulk Density (g/cm3)						0.37	0.35						
Dup.	Wet Bulk Density (g/cm3)		1.3								0.74			0.62
Dup.	Dry Bulk Density (g/cm3)		0.4								0.28			0.4
Dup.	Moisture (%)		69								63			36
Analyzed by AGAT														
Dup.	Wet Bulk Density (g/cm3)						0.6				0.78	0.78	0.67	0.62
Dup.	Dry Bulk Density (g/cm3)						0.30				0.30	0.32	0.33	0.4
Dup.	Moisture (%)						50				61	60	51	36
2nd Dup.	Wet Bulk Density (g/cm3)										0.75			0.61
2nd Dup.	Dry Bulk Density (g/cm3)										0.29			0.39
2nd Dup.	Moisture (%)										61			36
QA/QC														
RPD (%)	Wet Bulk Density (g/cm3)		8				0	0			8			0
RPD (%)	Dry Bulk Density (g/cm3)		8				5	6			7			3
RPD (%)	Moisture (%)		1				31					0	10	
RSD (%)	Moisture (%)										2			1

		Time Period After Mixing												
		Un- treated	0 Hr.	24 Hr.	48 Hr.	72 Hr.	96 Hr.	120 Hr.	144 Hr.	168 Hr.	1 Mo.	3 Mo.	6 Mo.	12 Mo.
		Blend 3 – 15% Portland Cement												
Analyzed by Maxxam														
Blend 3	Wet Bulk Density (g/cm3)	0.99	1.2	1.1	1.1	0.96	1.0	1.0	0.99	0.98	0.93	0.86	0.77	0.59
Blend 3	Dry Bulk Density (g/cm3)	0.2	0.34	0.33	0.33	0.30	0.34	0.31	0.30	0.30	0.29	0.29	0.31	0.35
Blend 3	Moisture (%)	79	71	70	73	71	71	71	71	70	69	66	54	40
Lab. Dup.	Wet Bulk Density (g/cm3)		1.2											
Lab. Dup.	Dry Bulk Density (g/cm3)		0.34											
Lab. Dup.	Moisture (%)		71											
Dup.	Wet Bulk Density (g/cm3)							1.0				0.89		
Dup.	Dry Bulk Density (g/cm3)							0.34				0.3		
Dup.	Moisture (%)							70				66		
Analyzed by AGAT														
Dup.	Wet Bulk Density (g/cm3)			0.5							0.78	0.8	0.71	0.5
Dup.	Dry Bulk Density (g/cm3)			0.24							0.25	0.27	0.29	0.31
Dup.	Moisture (%)			51							68	66	59	39
2nd Dup.	Wet Bulk Density (g/cm3)											0.82		
2nd Dup.	Dry Bulk Density (g/cm3)											0.27		
2nd Dup.	Moisture (%)											67		
QA/QC														
RPD (%)	Wet Bulk Density (g/cm3)		0					0				3		
RPD (%)	Dry Bulk Density (g/cm3)		0					9				3		
RPD (%)	Moisture (%)		0	<b>31</b>				1			2		9	2
RSD (%)	Moisture (%)											1		

		Time Period After Mixing												
		Un- treated	0 Hr.	24 Hr.	48 Hr.	72 Hr.	96 Hr.	120 Hr.	144 Hr.	168 Hr.	1 Mo.	3 Mo.	6 Mo.	12 Mo.
		Control												
Analyzed by Maxxam														
Control	Wet Bulk Density (g/cm3)										0.80	0.82	0.57	0.43
Control	Dry Bulk Density (g/cm3)										0.18	0.21	0.2	0.23
Control	Moisture (%)										78	75	53	47
Lab. Dup.	Wet Bulk Density (g/cm3)												0.57	0.43
Lab. Dup.	Dry Bulk Density (g/cm3)												0.19	0.22
Lab. Dup.	Moisture (%)									78				
Analyzed by AGAT														
Dup.	Wet Bulk Density (g/cm3)										0.74	0.69	0.48	0.39
Dup.	Dry Bulk Density (g/cm3)										0.17	0.17	0.17	0.21
Dup.	Moisture (%)										78	75	65	47
QA/QC														
RPD (%)	Wet Bulk Density (g/cm3)												0	0
RPD (%)	Dry Bulk Density (g/cm3)												5	4
RPD (%)	Moisture (%)										1	0	21	0

Note. RPD = relative percent difference; RSD = relative standard deviation; RPD was used when there were two duplicates, while RSD was used when there were four duplicates; only AGAT percent moisture data was used in calculation of RPDs and RSDs, because AGAT bulk density data was analyzed using Blake and Hartge (1986), while Maxxam bulk density data was analyzed using McKeague (1978); if there were both field duplicates and lab duplicates for a sample, RPDs provided are for field duplicates only; RPD and RSD values above 30% are in boldface.

<sup>a</sup>Sample was collected from Blend 1, Batch 1 only; each blend consisted of three batches.

For the samples from immediately after mixing until 1 month after mixing, other parameters that were tested included free liquid, flash point, leachable volatiles, and the remaining leachable metals. All the samples passed the free liquid and flash point tests, while leachable VOCs were below detection. The range of leachable iron in the treated Filter Cake samples was from non-detectable to 40 mg/L, which was higher than the untreated Filter Cake samples.

#### **4.5 Bench Scale Tests**

Due to the unsatisfactory results of many of the field tests, additional treatment reagents were investigated through bench scale experiments. The treatment reagents investigated included low alkali Portland cement, low alkali Portland cement and fly ash, and elemental sulphur. In addition, CETCO's Sorbond LPC II and LR 2000 were tested for comparison, as these treatment reagents provided the best results in the field.

For trials with low alkali Portland cement, the same ratios that were tested in the field were repeated in bench scale tests for comparison (Table 21). Interestingly, all the treatments with 25%, 20%, and 15% Portland cement and 20% water were effective at reducing leachable nickel and vanadium below the limit. Leachable nickel and vanadium were below the limit even when the amount of water added was 0% or 40%. However, the highest leachable vanadium concentration was obtained with 15% Portland cement.

The greater success achieved in bench scale tests compared with field tests was likely due to the more homogeneous mix that was obtained in bench scale tests. The mixer used in bench scale tests was able to grind up the clumps of Filter Cake and more thoroughly distribute the treatment reagents throughout the Filter Cake. In addition, the leachable nickel and vanadium in the raw Filter Cake used for bench scale tests were generally less than the leachable nickel and vanadium in the raw Filter Cake used for field tests (see Section 4.1).

Table 21

*TCLP and pH Results for the Different Blends from Bench Scale Tests*

Sample #	Treatments	TCLP Pretest pH <sup>a</sup>	Fluid # Used <sup>b</sup>	Leachable Nickel (mg/L)	Leachable Vanadium (mg/L)	pH <sup>c</sup>	Moisture (%)
Untreated Samples							
	Sampled Aug. 7, 2011	7/2	1	<b>160</b>	<b>170</b>	6.46	82
	Sampled Dec. 12, 2011 <sup>d</sup>	7/2	1	<b>180</b>	<b>217</b>	6.59	83
	Sampled Jan. 31, 2012 <sup>d</sup>	7/2	1	<b>177</b>	<b>177</b>	7.01	82
Trials with Portland Cement (PC)							
1	25% PC, 20% H <sub>2</sub> O	10/2	1	ND	3	12.3	
2	20% PC, 20% H <sub>2</sub> O	10/2	1	ND	11	12.1	
3	15% PC, 20% H <sub>2</sub> O	10/2	1	ND	67	12	
4	25% PC, 40% H <sub>2</sub> O	10/2	1	ND	5	12.4	
5	25% PC, 0% H <sub>2</sub> O	10/2	1	ND	3	12.3	
Trials with Portland Cement and Fly Ash (FA)							
6	20% PC, 5% FA, 20% H <sub>2</sub> O	7/2	1	ND	18	12.4	
7	20% PC, 15% FA, 20% H <sub>2</sub> O	7/2	1	ND	20	12.2	
8	20% PC, 25% FA, 20% H <sub>2</sub> O	11/2	1	ND	16	12	
9	15% PC, 10% FA, 20% H <sub>2</sub> O	11/2	1	ND	63	12	
10	10% PC, 15% FA, 20% H <sub>2</sub> O	9/2	1	ND	<b>220</b>	10.9	
11	5% PC, 20% FA, 20% H <sub>2</sub> O	8/2	1	<b>9.3</b>	<b>340</b>	9.64	
Trials with CETCO Sorbond LPC II and LR 2000 <sup>e</sup>							
12	15% LPC II, 35% LR 2000	11/3	1	ND	22	11.9	
12	15% LPC II, 35% LR 2000 - Lab. Dup.					12.0	
12	15% LPC II, 35% LR 2000 - Dup.	11/2	1	ND	17	12.0	
13	15% LPC II, 35% LR 2000	11/2	1	ND	14	12.0	
14	15% LPC II, 35% LR 2000	11/3	1	ND	12	11.9	
Trials with Sulphur (S)							
15	5% S, 3% NaSO <sub>3</sub> <sup>f</sup>	7/2	1	<b>670</b>	<b>650</b>	4.15	13
15	5% S, 3% NaSO <sub>3</sub> - Lab. Dup.	7/2	1				13
16	5% S, 3% NaSO <sub>3</sub>	7/2	1	<b>500</b>	<b>520</b>	4.54	25
17	15% S, 3% NaSO <sub>3</sub>	7/2	1	<b>360</b>	<b>420</b>	3.38	13
18	25% S, 3% NaSO <sub>3</sub>	7/2	1	<b>260</b>	<b>490</b>	4.33	19
19	35% S, 3% NaSO <sub>3</sub>	7/1	1	<b>180</b>	<b>490</b>	5.72	23
19	35% S, 3% NaSO <sub>3</sub> - Lab. Dup.	7/1	1			5.7	21
20	45% S, 3% NaSO <sub>3</sub>	7/2	1	<b>180</b>	<b>460</b>	5.46	21
20	45% S, 3% NaSO <sub>3</sub> - Dup.	7/2	1	<b>160</b>	<b>420</b>	5.25	20

Note. ND = not detected; results over Alberta Environment limit are in boldface.

<sup>a</sup>The first value is the initial TCLP pretest pH result, and the second value is the pH after HCl has been added; <sup>b</sup>fluid used for TCLP extraction; <sup>c</sup>pH using a 1:1 water to sample ratio; <sup>d</sup>values are an average of three duplicate samples; <sup>e</sup>CETCO LR 2000 is diluted with water at a ratio of 6 parts water to 1 part LR 2000; <sup>f</sup>sample was heated for a longer period of time to increase the temperature, but the sample started burning after treatment and water was added to stop the burning.

From both the field tests and bench scale tests, 20% Portland cement was more effective at reducing leachable vanadium, and as a result, further bench scale tests were performed using 20% low alkali Portland cement. Bench scale tests with low alkali Portland cement and fly ash were designed for answering two questions. First, will the addition of fly ash reduce the pH of the treated Filter Cake and as a result, be more effective at reducing leachable vanadium? Second, will the replacement of some of the Portland cement with fly ash be just as effective or more effective at reducing leachable vanadium?

By keeping the proportion of low alkali Portland cement constant at 20% and increasing the proportion of fly ash from 5 to 25%, it was determined that adding more fly ash had minimal effect on the pH of the treated Filter Cake. In addition, leachable vanadium was slightly higher with the addition of fly ash than with Portland cement alone. By comparing 25% Portland cement and no fly ash with samples where increasing amounts of Portland cement were replaced with fly ash, it was determined that partial replacement of Portland cement with fly ash reduced the pH of the treated Filter Cake. For example, with 10% Portland cement and 15% fly ash, the pH was 10.9 and with 5% Portland cement and 20% fly ash, the pH was 9.64. With increasing the amount of replacement of Portland cement with fly ash up to 10% Portland cement and 15% fly ash, leachable nickel was not detected in TCLP tests. However, leachable vanadium started to increase with 15% Portland cement and 10% fly ash.

For treatments with CETCO Sorbond LPC II and LR 2000, three bench scale tests were performed using proportions of treatment reagents that were similar to the proportions used in the field by CETCO. For all samples tested with CETCO treatment reagents in bench scale tests, the leachable nickel and vanadium were well under the limit.

Bench scale tests with elemental sulphur and sodium sulphite were not effective at reducing leachable nickel or vanadium. By adding increasing amounts of elemental sulphur to

the Filter Cake, there was little change in the leachable vanadium results. However, with increasing amounts of elemental sulphur, there was a decrease in leachable nickel.

The leachable nickel and vanadium, pH, and percent moisture results for bench scale tests were consistent between duplicates (Table 22).

Table 22

*RPD and RSD for Duplicates for Bench Scale Tests*

Treatments	TCLP Pretest pH <sup>a</sup>	Leachable Nickel (mg/L)	Leachable Vanadium (mg/L)	pH <sup>b</sup>	Wet Bulk Density (g/cm <sup>3</sup> ) <sup>c</sup>	Dry Bulk Density (g/cm <sup>3</sup> ) <sup>c</sup>	Moisture (%)
Untreated, Sampled Dec. 12, 2011							
Duplicate 1	7/2	180	190	6.61	0.62	0.12	83
Duplicate 2	7/2	180	220	6.59	0.66	0.11	83
Duplicate 3	7/2	180	240	6.57	0.67	0.12	83
RSD (%)	0	0	12 <sup>d</sup>	0	4	5	0
Untreated, Sampled Jan. 31, 2012							
Duplicate 1	7/2	180	180	7.07	0.78	0.14	82
Duplicate 2	7/2	170	180	6.99	0.78	0.14	82
Duplicate 3	7/2	180	170	6.98	0.78	0.14	82
RSD (%)	0	3	3	1	0	0	0
Sample 12							
15% LPC II, 35% LR 2000 <sup>e</sup>	11/3	ND	22	11.9			
15% LPC II, 35% LR 2000 - Dup. <sup>e</sup>	11/2	ND	17	12.0			
RPD (%)	<b>40</b>	NC	26 <sup>d</sup>	1			
Sample 15							
5% S, 3% NaSO <sub>3</sub>							13
5% S, 3% NaSO <sub>3</sub> - Lab. Dup.							13
RPD (%)							0
Sample 19							
35% S, 3% NaSO <sub>3</sub>				5.72			23
35% S, 3% NaSO <sub>3</sub> - Lab. Dup.				5.7			21
RPD (%)				0			9
Sample 20							
45% S, 3% NaSO <sub>3</sub>	7/2	180	460	5.46			21
45% S, 3% NaSO <sub>3</sub> - Dup.	7/2	160	420	5.25			20
RPD (%)	0	12 <sup>d</sup>	9 <sup>d</sup>	4			5

Note. RPD = relative percent difference; RSD = relative standard deviation; RPD or RSD were used when there were two and three duplicates, respectively; NC = not calculable; RPD and RSD values above 30% are in boldface.

<sup>a</sup>The first value is the initial TCLP pretest pH result, and the second value is the pH after HCl has been added; the RPD or RSD was calculated using the second pH value; <sup>b</sup>pH using 1:1 water to sample ratio; <sup>c</sup>bulk density was analyzed using Blake and Hartge (1986); <sup>d</sup>duplicate results were less than five times the reported detection limit (RDL); <sup>e</sup>CETCO LR 2000 is diluted with water at a ratio of 6 parts water to 1 part LR 2000.

## 5.0 Discussion

This section discusses the results of treatments of Filter Cake with various reagents in both the bench tests and field tests. The sustainability of the most successful treatments for Filter Cake is also discussed including the economics and other issues such as greenhouse gas (GHG) emissions.

### 5.1 Bench Tests

The results of bench scale tests confirmed that the treatment reagents tested in the field, CETCO Sorbond LPC II, LR 2000 and Portland cement, were the most effective treatment reagents with Filter Cake. The other treatment reagents tested in bench scale tests, low alkali Portland cement with fly ash and elemental sulphur, were not effective at reducing leachable nickel and vanadium below the Alberta Environment limits. The results of these bench tests are discussed in the following section.

Treatments with CETCO Sorbond LPC II and LR 2000 were successful in all 3 bench scale tests. The ability of low alkali Portland cement to successfully reduce leachable nickel and vanadium to levels below the limit in bench scale tests may have been due to using a mixer that was able to pulverize the Filter Cake to yield a homogeneous mix; the mixer used in bench scale tests provided a more homogenous mix compared to the mortar mixer used in field tests.

The trials with low alkali Portland cement and fly ash were effective at reducing leachable nickel below the limit, but were not effective at reducing leachable vanadium. Partial replacement of Portland cement with fly ash only reduced the pH of the treated samples when more than half the Portland cement was replaced with fly ash. These results support the finding by Shi and Spence (2004) that fly ash can reduce the pH of treated wastes. However, leachable vanadium increased by reducing the percentage of Portland cement and increasing the percentage of fly ash.

From the research conducted by Kunz et al. (1976), the lowest solubility for tetravalent and pentavalent vanadium was at a pH of 7.5 to 9. Kunz et al. (1976) also suggested that the other valency states for vanadium were not likely soluble in water. Other authors have found most metals are least soluble, and hence, less leachable at a pH of 10 (Shi & Spence, 2004), 9.5 to 11 (Cullinane et al., 1986), and 7.5 to 11 (U.S. EPA, 1993). As a result, it was expected that using an additive such as fly ash with Portland cement would reduce the pH of the treated Filter Cake, and consequently, reduce the leachable vanadium. However, as discussed above, even though partial replacement of Portland cement with fly ash reduced the pH of the treated Filter Cake, there was an increase in leachable vanadium. A possible explanation for the failure of the combination of Portland cement and fly ash to reduce the leachable vanadium may be that the vanadium species in the Filter Cake are different than the species studied by Kunz et al. (1976) and are least soluble at a higher pH range.

Treatments with elemental sulphur and sodium sulphite were not effective at reducing the leachable properties of Filter Cake. Transition metals such as nickel react with sulphur only at high temperatures (Durrant & Durrant, 1970). The Filter Cake and sulphur mixture started to burn when it was heated to elevated temperatures. The treatments of Filter Cake with elemental sulphur and sodium sulphite may not have been successful due to the fact that it was not possible to heat the mixture to the reaction temperature required.

## **5.2 Field Tests**

The field tests with Portland cement were successful at reducing leachable nickel well below the limit. However, these field tests yielded inconsistent results for reducing leachable vanadium as some of the treated samples were well above the limit for leachable vanadium. For the field tests performed by Nexen, the leachable properties tended to increase the longer the sample was allowed to cure. For 3 months, 6 months, and 12 months after treatment, leachable

vanadium was well over the limit. Various researchers have reported results of long term studies of stabilized wastes where the leachable properties remained the same over time and other stabilized wastes where the leachable properties increased over time (U.S. EPA, 1993). In some cases, the increase in leachable properties was due to alterations of the chemical structure (U.S. EPA, 1993). For the Filter Cake treated with Portland cement in the Nexen field tests, it is possible the leachable vanadium concentrations increased over time due to alterations of the chemical structure.

The Nexen field test yielded better results for reducing leachable vanadium for the trials with 15% Portland cement compared to the Hazco field test. The improved results for leachable vanadium could be due to the better mixing technique used in the Nexen field tests. The Nexen field tests used a mortar mixer which provided a more homogeneous mix compared to the excavator employed in the Hazco field tests.

Most of the CETCO blends were not effective; however, CETCO Sorbond LPC II and LR 2000 were the most effective treatment reagents used in the field and reduced the leachable metals well below the Alberta Environment limits and also kept the pH under the Alberta Environment limit. This treatment reagent was only tested with the Filter Cake for up to 1 week after mixing. As a result, there was no opportunity to test the effectiveness of these treatment reagents over a longer period of time as was done with Portland cement.

The reason the metals in the Filter Cake were difficult to stabilize with some of the treatment reagents was likely due to interference from the very fine material that makes up the Filter Cake. The particle size analysis of the untreated Filter Cake indicated that 99.6% of the particles were less than 0.075 mm in diameter. As discussed previously, Conner (1997) and U.S. EPA (1993) reported that fine particles can interfere with the stabilization reactions of treatment reagents such as Portland cement. Nexen (2010) indicated that combustion of the asphaltenes in

the gasifiers resulted in a coating of carbon on the metals. It is possible the carbon coating on the metals also inhibited the treatment reagents. In addition, as discussed above, sulphate or sulphide can also affect cement reactions (U.S. EPA, 1993; Jones, 1990). Filter Cake contains approximately 0.8% sulphur, which may have interfered to some degree with stabilization reactions.

### **5.3 Sustainable Development**

Other considerations for the use of S/S technologies for Filter Cake are whether this waste management option is more sustainable than other alternatives. In other words, are the economic, environmental, and social impacts reduced through the use of this waste management option? The economics can be evaluated by considering the bids that were submitted by the two contractors. One of the bids submitted was more favourable than the other, but both bids did not meet the economic threshold for pursuing the project. From the evaluation of greenhouse gas (GHG) emissions, there was a relatively small net reduction in GHG emissions from treating the Filter Cake and sending the treated Filter Cake to Janvier instead of sending the untreated Filter Cake to Riley.

### **6.0 Conclusion**

The CETCO Sorbond LPC II and LR 2000 were the most successful treatment reagents for reducing leachable nickel and vanadium in the Filter Cake to levels below the limits in the Alberta WCR. Treatments of Filter Cake with Portland cement were successful in bench scale tests but inconsistent in field tests. Stabilizing the nickel and vanadium in the Filter Cake with CETCO LPC II and LR 2000 is a viable waste management option. However, this waste management option did not result in a significant reduction in waste handling costs or other environmental factors such as GHG emissions.

Recommendations include the following:

1. S/S treatments of waste should be tested for leachable properties over a long term period to ensure that the treatment is effective over the long term.
2. Treating the Filter Cake with Portland cement was not effective due to interference from factors such as fine particulates in the Filter Cake. However, Portland cement may be effective with other ash residues containing nickel and vanadium if the waste does not contain fine particulates.
3. Obtaining a homogeneous mix is essential for S/S treatments, and high shear mixers are likely to be more effective at obtaining a homogenous mix and successfully stabilizing metals in wastes.

## 7.0 References

- Alberta Environmental Protection. (1996). *Alberta user guide for waste managers*. Retrieved from <http://environment.gov.ab.ca/info/library/7423.pdf>
- Blake, G. R., & Hartge, K. H. (1986). Bulk density. In A. Klute (Eds.), *Methods of soil analysis: Part 1, physical and mineralogical methods* (Sec. ed., pp. 363-375). Madison, Wisconsin: American Society of Agronomy and Soil Science Society of America.
- Canada Green Building Council. (2004). *LEED green building rating system, reference package, for new construction and major renovations, LEED Canada-NC, Version 1*. Retrieved from [http://my.cagbc.org/documents.php?sbget=document,,880,,0,view\\_item,,10,,,main,,10,,0](http://my.cagbc.org/documents.php?sbget=document,,880,,0,view_item,,10,,,main,,10,,0)
- Conner, J. R. (1997). *Guide to improving the effectiveness of cement-based stabilization/solidification* (PCA Serial No. 2075). Retrieved from Portland Cement Association website: <http://www.cement.org/bookstore/profile.asp?id=188>
- Cullinane, M. J., Jones, L. W., & Malone, P. G. (1986). *Handbook for stabilization/solidification of hazardous waste* (EPA/540/2-86/001). Retrieved from Portland Cement Association website: <http://www.cement.org/waste/pdfs/EPAHandbook.pdf>
- Durrant, P. J., & Durrant, B. (1970). *Introduction to advanced inorganic chemistry*. London, England: Longman.
- Jones, L. W. (1990). Interference mechanisms in waste stabilization/solidification processes. *Journal of Hazardous Materials*, 24(1), 83-88. doi: 10.1016/0304-3894(90)80005-O
- Kates, R., Parris, T., & Leiserowitz, A. (2005). What is sustainable development? Goals, indicators, values, and practice. *Environment* 47(3), 8-21. Retrieved from Environment Complete database.

- Kunz, R. G., Giannelli, J. F., & Stensel, H. D. (1976). Vanadium removal from industrial wastewaters. *Journal (Water Pollution Control Federation)*, 48(4), 762-770. Retrieved from <http://www.jstor.org/pss/25038577>
- Lin, S. L. (1995). *Effectiveness of sulfur for solidification/stabilization of metal contaminated wastes* (Doctoral dissertation). Retrieved from ProQuest Dissertations and Theses. (9526121)
- Lin, S. L., Cross, W. H., Chian, E. S., Lai, J. S., Giabbai, M., & Hung, C. H. (1996). Stabilization and solidification of lead in contaminated soils. *Journal of Hazardous Materials*, 48, 95-110. doi:10.1016/0304-3894(95)00143-3
- McKeague, J. A. (Ed.). (1978). *Manual on soil sampling and methods of analysis* (Sec. ed.). Ottawa, Ontario: Canadian Society of Soil Science.
- Nexen Inc. (2010, May). *Soot processing report*. Unpublished manuscript.
- Rettger, P., Arnold, J., Brandenburg, B., & Felch, C. (2006). *Gasification technologies – 2006: The Long Lake integrated upgrading project: Status report and discussion of soot processing*. Retrieved from Siemens Global website: [http://www.water.siemens.com/en/applications/wastewater\\_treatment/Pages/opti\\_wetox\\_cs.aspx?&overrideWeb=http:%2f%2fwww.water.siemens.com%2fen%2foil-gas%2fdownstream](http://www.water.siemens.com/en/applications/wastewater_treatment/Pages/opti_wetox_cs.aspx?&overrideWeb=http:%2f%2fwww.water.siemens.com%2fen%2foil-gas%2fdownstream)
- Shi, C., & Spence, R. (2004). Designing of cement-based formula for solidification/stabilization of hazardous, radioactive, and mixed wastes. *Critical Reviews in Environmental Science and Technology*, 34, 391-417. doi:10.1080/10643380490443281
- Speight, J. G. (1999). *Chemistry and technology of petroleum* (3<sup>rd</sup> edition). New York, NY: Marcel Dekker Incorporated.

- U.S. Environmental Protection Agency. (1992). *Method 1311: Toxic characteristic leaching procedure*. Retrieved from [www.epa.gov/osw/hazard/testmethods/sw846/pdfs/1311.pdf](http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/1311.pdf)
- U.S. Environmental Protection Agency. (1993). *Technical resource document: Solidification/stabilization and its application to waste materials* (EPA/530/R-93/012). Retrieved from [http://www.cement.org/waste/wt\\_tech\\_epapubs.asp](http://www.cement.org/waste/wt_tech_epapubs.asp)
- U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Technology Innovation Office. (1999). *Solidification/stabilization resource guide* (EPA/542-B-99-002). Retrieved from <http://www.epa.gov/tio/download/remed/solidstab.pdf>
- U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. (2000). *Solidification/stabilization use at Superfund sites* (EPA-542-R-00-010). Retrieved from [http://www.cluin.org/download/remed/ss\\_sfund.pdf](http://www.cluin.org/download/remed/ss_sfund.pdf)
- U.S. Environmental Protection Agency, National Risk Management Research Laboratory, Office of Research and Development. (2009). *Technology performance review: Selecting and using solidification/stabilization treatment for site remediation* (EPA/600/R-09/148). Retrieved from <http://www.epa.gov/nrmrl/pubs/600r09148/600r09148.pdf>