

THE USE OF CHEMOX® TO OVERCOME THE CHALLENGES OF PHC CONTAMINATED SOIL AND GROUNDWATER AT REMOTE SITES

Jevins Waddell, P.Tech.(Eng.), Carl Davison and B.J. Min, M.Eng., P.Eng.

Trium Environmental Inc.
2207, 120-5th Avenue, West
Cochrane, AB. T4C 0A4

ABSTRACT

A major theme for working in northern remote sites is overcoming logistical and technical challenges related to short season and limited access to remediate petroleum hydrocarbon impacted soil and groundwater. Chemical oxidation remediation approaches (ChemOx®⁶) can provide solutions to the unique challenges posed by these remote sites and allow expedited remediation within limited field seasons, often with less intrusive work activities common to other traditional remediation methods.

Successful chemical oxidation remediation integrates a strong understanding of oxidant chemistry and field application experience, whether using in-situ (ISOTEC®⁷) or ex-situ (EXCO®⁸) approaches. The use of hydrogen peroxide based oxidants has been widely accepted for expedited reactions with petroleum hydrocarbon contaminated mediums. However, historically, misperceptions and unreasonable expectations have often been applied to the design of these programs. By combining a strong application approach, unique transportation and logistics solutions, such as air transport, and working within a reasonable and realizable objective, chemical oxidation is well suited to handle the uncommon challenges of remote programs.

Key Words: Chemical Oxidation, Ex-situ, Catalyzed Hydrogen Peroxide, Petroleum Hydrocarbons, Remediation, Remote Site.

INTRODUCTION

Petroleum hydrocarbon contamination of soil and groundwater resources is a challenge to many industries. In some cases the remote nature and climate of these sites requires a solution that does not allow for, or limits, the effectiveness of conventional remediation options. With increased public awareness and stakeholder involvement, many of these conventional options, such as source removal and landfilling, are losing popularity for economic, social and sustainability reasons. As the distance and access to conventional remediation solutions increases, the remediation planning for remote and/or seasonally accessible contaminated sites often shifts to alternative solutions.

The general concepts of alternative remediation strategies are well known, with most of the concepts well documented in standard environmental engineering references. However, much progress and innovation largely goes unpublished, keeping clients uninformed about the advancements and options that exist,

⁶ ChemOx® is a registered trademark for catalyzed hydrogen peroxide solutions, owned by TRIUM Environmental Inc.

⁷ ISOTEC® is a registered trademark for in-situ chemical oxidation services, owned by TRIUM Environmental Inc.

⁸ EXCO® is a registered trademark for ex-situ chemical oxidation services, owned by TRIUM Environmental Inc.

especially early in remediation planning phases when time may allow combined treatment strategies to be implemented without the pressure of last minute regulatory or external third parties. This lack of available reference material and the historical misapplication and unreasonable expectations often placed on these technologies have resulted in market hesitation and uncertainty towards adopting alternative processes. Strong applied knowledge, integrated with a qualified specialist and proactive establishment of realistic objectives can overcome these limitations.

HYDROGEN PEROXIDE CHEMISTRY AND APPLICATION MECHANISMS

Chemical oxidation is the degradation of contaminants by chemicals referred to as oxidants, such as catalyzed hydrogen peroxide (H₂O₂). Catalyzed H₂O₂ can be preferred for its oxidation potential, active/rapid destruction mechanisms (<24 hour reaction timeframes), clean (no residual ions) and pH balanced reactions, and cost effectiveness. For the reasons above, except for the destruction of the petroleum hydrocarbon parameters, any alteration of the subsurface geochemistry is quickly reversed due to the short reaction timescale and pH control, the extent of which is determined by the buffering capacity of the soil and water matrix, and the blending scenario of the catalyzed H₂O₂ (i.e., ChemOx®). A complete reaction of catalyzed H₂O₂ and petroleum hydrocarbons results in mineralization (degradation) of the contaminants to carbon dioxide (CO₂), water and heat. Catalyzed H₂O₂ also provides a post-reaction oxygenated environment, which when combined with base nutrients, encourages indigenous bacterial populations for longer term polishing of contaminants after treatment.

Often, the most important components to implementation of a catalyzed H₂O₂ remediation program are the expediency of the reaction and flexibility of application. However, the inherent limitation of chemical oxidation is the stoichiometric demands of high concentrations of the contaminants. This stoichiometric demand – combined with the depth, location, and extent of the contaminant impacts in the soil/groundwater mediums at each site – dictate the appropriate application method, whether in-situ or ex-situ. The general criteria for selection of an in-situ or ex-situ method are presented in Table 1.

Table 7. General Application Technique Selection Criteria

In-situ	Ex-situ
✓ Groundwater Bearing Zone	✓ Vadose/Unsaturated Soils
✓ Dissolved Phase/Down gradient Plumes	✓ Less than 4 metres below grade
✓ Greater than 4 metres below grade	✓ Low Permeability Unconsolidated Soils
✓ Permeable Unconsolidated Soils	✓ Aged/Weathered Mediums (i.e. Bio-Piles)
✓ Fractured Bedrock	✓ Single Events/Rapid Closure
✓ Multiple Events	

As indicated above, when impacted material exists primarily as dissolved phase and in the saturated groundwater zone, TRIUM will apply our in-situ chemical oxidation (ISOTEC®) approach. This approach involves installation of dedicated injection wells and multiple treatment events. Injection wells allow greater flexibility and lower costs for setting up an effective multi-event treatment program. Multiple events are necessary to capture the occurrence of “rebounding”, which is a common concern of

in-situ processes. Rebounding should be expected in most programs and is actually an indicator of success of the process, as contaminants must desorb from the soil to become available/contactable by the oxidant, which occurs in an aqueous phase reaction. Several reaction processes occur during an oxidation program that govern desorption of the contaminants including soil/water partitioning coefficients, and partial oxidization intermediates. Therefore, in-situ programs should always be considered on a longer time frame and with awareness of the required natural processes that must occur to support the treatment method.

When unsaturated conditions or low permeability soils are treated, TRIUM applies our ex-situ chemical oxidation approach (EXCO®). EXCO® is effective as it allows enhanced contact (i.e., mechanical mixing) between the oxidant and the soil in its original location, and also allows for optimization of the soil conditions prior to application. EXCO® applications can target either treatment in established treatment cells/pads or employ an in-place mixing method. The processes also allow the treatment to progress discretely with only the required volume of soil for treatment being open/exposed at any given time. This reduces equipment requirements, volatilization, cross contamination and other regulatory concerns, while ensuring that optimal treatment conditions are achieved in very short timeframes.

As the timeframe of treatment using the EXCO® approach with catalyzed H₂O₂ is measured in days, closure sampling of treated soils can occur within 72 hours, providing a rapid turnaround and higher degree of treatment certainty. In addition to economic advantages, by treating the material on site, the inherent safety risks and carbon offset associated with transporting impacted soils is greatly reduced. Many clients consider this reduced health and safety risk and sustainability measure a value add to the process, and will incorporate these soft costs in selecting a remediation technique.

CASE STUDY – REMOTE SITE

The advantages of the ChemOx® approach were evaluated through a technology matrix evaluation conducted by the client for a remote, air access only, site. The outcome of the review indicated that the logistics and expediency of the EXCO® process would be best suited to achieve the objectives of the program. Specific details and concentrations have been altered in this paper for client disclosure however the outline of the process remains consistent.

Project Logistics

Among many logistical considerations, the program was limited by a short field season and fly-in only access. On-site facilities and equipment requirements were addressed by the client that would allow the on-site operation to run safely, however a primary challenge of transporting the oxidant to site had to be overcome. As the EXCO® program would require several thousand kilograms of 50% catalyzed H₂O₂, an air transportation exemption was required. Under the Transportation of Dangerous Goods Regulation (TDG), the allowable air transportation of hydrogen peroxide was limited to 20% concentration in 5 litre containers. Working with the client, a review was completed with Transport Canada, which resulted in approval and issuance of an equivalency certificate allowing handling and transportation of the oxidants by air at between 20% and 60% concentration in 200 L drums (with over-packs).

Baseline Conditions of Impacted Soil

The impacted soil targeted for treatment at the site comprised a coarse-grained soil, in an alluvial area. Based on laboratory analytical results from early assessment programs at the site, light extractable petroleum hydrocarbons (LEPH) and heavy extractable hydrocarbons (HEPH) were reported at <3,000 parts per million (ppm). Upon further investigation once heavy equipment resources were available, LEPH and HEPH concentrations were encountered ranging from non-detect to one order of magnitude higher than anticipated.

Due to the depositional setting, it was suspected that the coarse-grained soils could maintain elevated natural total organic carbon (TOC) in the water phase. Elevated TOC often results from naturally occurring phytogenic interferences, and can act as a scavenger of the oxidant, which is referred to as Natural Oxidant Demand (NOD). High carbon contents also sequester petroleum hydrocarbons making them less “available”. This can be an important consideration in determining plume migration and contaminant transport.

A background TOC assessment was conducted at this site, and an analytical interference of phytogenic compounds was observed to cause bias to standard analytical methods and analysis. Most jurisdictions have protocols for determining “background” concentrations including methods for making the distinction between naturally occurring phytogenic hydrocarbons and petrogenic petroleum hydrocarbons. These methods begin with taking background soil samples that are representative of the area in contest, and requesting additional laboratory preparation, sample cleanup or analysis. For phytogenic hydrocarbons a silica gel cleanup is one laboratory method that can be applied, and is not necessarily automatically included in the standard method for analyzing petroleum hydrocarbons. For example, in British Columbia, this silica gel cleanup procedure is referred to as a Method 10 cleanup. Soil samples were collected from the area surrounding the site to characterize the background concentrations/interferences and for consideration in adjusting remediation guideline endpoints. Additionally a background cell was selected to determine if the catalyzed H₂O₂ could introduce interference to the analytical method by reacting with the phytogenic compounds.

The results of the phytogenic and oxidant interference testing indicated that interference was observed for HEPH parameters, ranging between 300 ppm and 500 ppm. These “Background Correction” values could then be used to adjust HEPH concentrations when evaluating the chemical oxidation process performance.

Series of Tests

The program was conducted as a series of tests, which consisted of i) preliminary bench-scale test, ii) field pilot application, and iii) secondary bench-scale test. The field pilot application program was conducted following the preliminary bench-scale test, and was based on the limited sample and analytical data available at that time. Once mobilized to site for the pilot application, concentrations of LEPH/HEPH in the main treatment area were found to be higher than the concentrations used in the preliminary bench-scale program. This was a limiting factor for the pilot application program as the stoichiometric oxidant demand to address these higher concentrations exceeded the amount of catalyzed H₂O₂ mobilized to the site. The objective of the pilot application was shifted to focus on a demonstration

of potential reductions at these higher concentrations and a secondary bench-scale test was conducted following the pilot program. The secondary bench-scale test would prove out the oxidant's ability to achieve the required endpoints and provide projections for financial thresholds and technology optimization factors.

1st Bench-scale Test

Prior to commencing the field pilot a bench-scale test was conducted on the initial soils collected from the site. The oxidant loading from the bench-scale program that performed best was then used to design the field pilot program. In the first bench-scale testing program, reductions of between 60% and 80% were reliably reproduced, indicating that the catalyzed H₂O₂ could achieve the preliminary program objectives. Based on the results of the 1st bench-scale, an oxidant loading of >100 kg/m³ (50% catalyzed hydrogen peroxide) was deemed most effective to overcome the elevated TOC and petroleum hydrocarbon concentrations.

Field Pilot Scale Test

The oxidant loading and design parameters from the bench-scale were carried out in the field over a two week period. Two pilot cells of 50 m³ each were prepared at the site, and each cell was treated with >100 kg/m³ of the catalyzed H₂O₂. Mixing was achieved using an excavator equipped with a standard digging bucket. As the soils were found to be at optimum moisture conditions, the catalyzed H₂O₂ could be applied directly to the soil aliquots with dilution occurring from the moisture already present in the soil.

As the actual LEPH/HEPH concentrations were higher than the concentrations used in the first bench-scale program, the expectations of the oxidant performance were adjusted to determine the maximum reductions that could be achieved. Throughout the program, composite and discrete samples were collected to track reductions throughout the program and validate the effectiveness of each sampling technique.

Petroleum hydrocarbon samples were collected on Day 1 (representing pre-treatment concentrations), on Day 3 of treatment (to capture assumed homogenous soil concentrations due to mixing) and at the completion of the program.

The petroleum hydrocarbon levels in the homogenized samples were reduced on average by 33% compared to the pre-treatment (unhomogenized) samples. The petroleum hydrocarbon levels in the post-treatment samples from Cell 1 and Cell 2 had an average reduction of 36% and 23% respectively, compared to the homogenized concentrations.

The percentages described above, can be further expressed by the overall reduction of each relative to the oxidant performance expectations for the oxidant loading that was applied to the site. In Cell 1, the overall reductions achieved were 1.3 to 2.3 times greater than the theoretical reductions. In Cell 2, the overall reductions achieved were -2 to 1.1 times greater than the theoretical reductions. The sample point representing the -2 times reduction is considered to be a result of sample homogeneity and process interference (other activities that were being conducted at the time).

Secondary Bench-scale

Following the field pilot program, a secondary bench-scale test was conducted with soil selected from an area of high impact at the site (remaining after the field pilot). The purpose of the secondary bench-scale test was to demonstrate the oxidant performance to achieve the required endpoints and provide projections for financial thresholds and technology optimization. One of the important variables arising from the field program was the timeframe between applications to allow equilibrium between soil and water due to the elevated TOC. The secondary bench-scale dosing strategy was modified to include a 5 to 7 day pause between ChemOx® applications to determine the effect of the equilibrium “stall”.

Three applications of the catalyzed H₂O₂ were completed, observing the 5 to 7 days between treatments. At the completion of the bench-scale, all three sets of samples achieved the regulatory guideline objective. The average reduction of petroleum hydrocarbon concentrations in all three sets of samples was >90%, and was able to demonstrate that catalyzed H₂O₂ could achieve the program endpoints.

During the second bench-scale program, the reductions observed in the field were plotted against the theoretical oxidant demand. It was observed that the oxidant demand to achieve the reductions noted was trending in a non-linear curve, and the oxidant was “outperforming” the theoretical stoichiometric oxidant demand. This is believed to occur as a result of the amount of “available” petroleum hydrocarbons being greater as the concentration increased. The performance of the second bench-scale program was then plotted after the field data points on this curve to determine how the efficiencies of the catalyzed H₂O₂ would be affected as the concentrations decreased. Figure 1 illustrates this non-linear curve and demonstrates the program performance to illustrate the actual oxidant demand required to achieve the program objectives.

Although, the findings indicate that an oxidant dosing slightly greater than the theoretical oxidant demand would be required, the efficiencies of the delayed treatment timeframes (5 to 7 days between dosing) could overcome the scavenging and sequestering effects of the high TOC. The blue line represents the laboratory reported values, with the red line showing the adjusted values based on the phytogenic interference caused by the elevated TOC. Actual values cannot be presented, however the trend of the graph remains accurate.

DISCUSSIONS AND CONCLUSIONS

Throughout the sequence of tests, the application of TRIUM’s EXCO® process using catalyzed H₂O₂ demonstrated that a chemical oxidation approach could achieve the safety and technical endpoints established for the program. The field pilot EXCO® program was conducted efficiently and demonstrated that high concentration hydrogen peroxide could be transported safely by air. Actual site conditions revealed that petroleum hydrocarbon concentrations were greater than estimated and therefore reductions to achieve the regulatory guidelines were not achieved during the field pilot given the

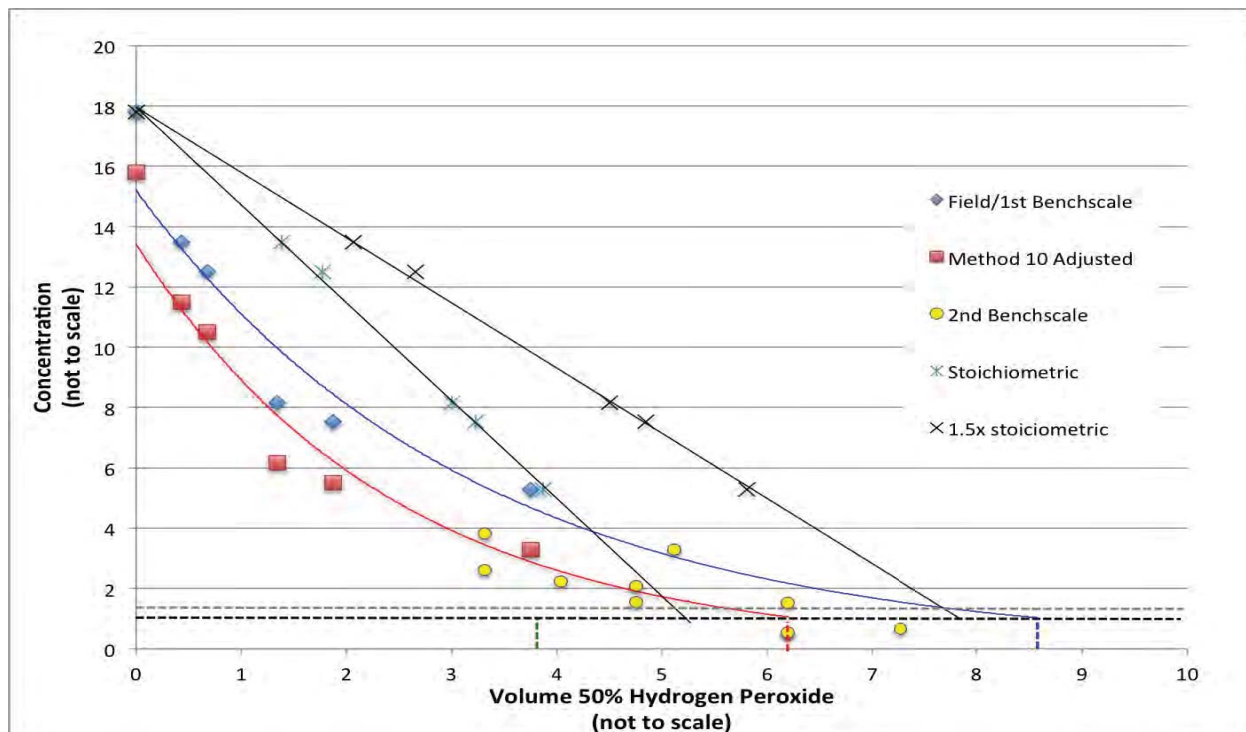


Figure 10. Field/Benchscale Performance vs. Theoretical Oxidant Demand

theoretical oxidant demand relative to the volume of catalyzed H₂O₂ delivered to the site. The follow-up second benchscale program proved that a modified application strategy using the catalyzed H₂O₂ could achieve the regulatory guideline objective, and provided the client the required parameters and estimations for consideration of full-scale treatment.

Given the difference in actual site conditions relative to the benchscale design parameters, the chemical oxidation approach exceeded the original design expectations, and the program was able to demonstrate the ability of chemical oxidation remediation strategies to overcome many of the unexpected challenges presented by remote sites.

Overcoming Northern Challenges

Proceedings of the 2013 Northern Latitudes Mining Reclamation Workshop and
38th Annual Meeting of the Canadian Land Reclamation Association

Whitehorse, Yukon September 9 – 12, 2013

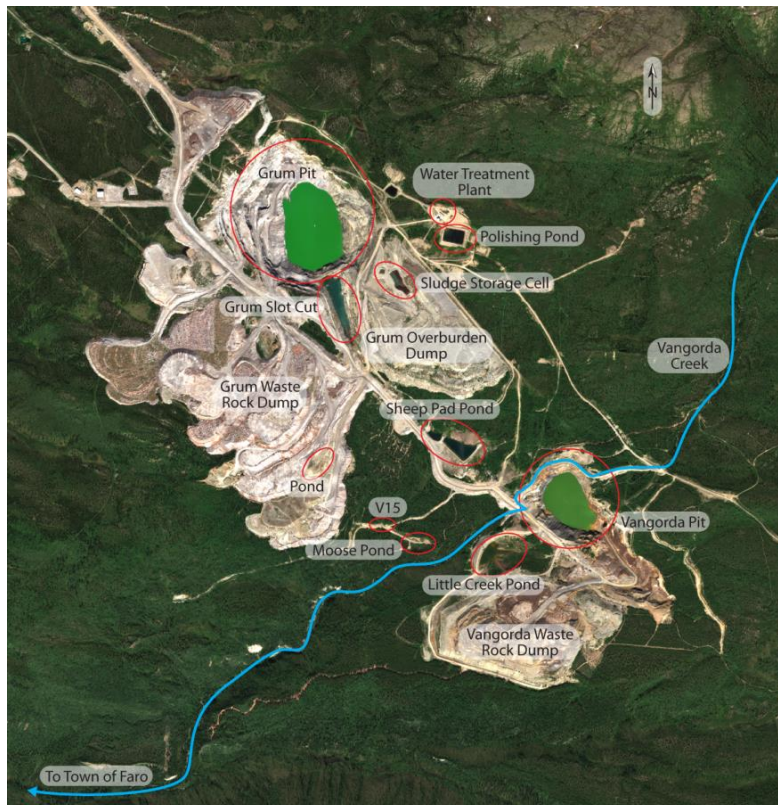


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Stewart, Karpenin, and Siciliano	Northern Biochar for Northern Remediation and Restoration
Petelina	Biochar application for revegetation purposes in Northern Saskatchewan
Chang	Bioremediation in Northern Climates
Geddes	Management of Canada's Radium and Uranium Mining Legacies on the Historic Northern Transportation Route
Hewitt, McPherson and Tokarek	Bioengineering Techniques for Re-vegetation of Riparian Areas at Colomac Mine, Northwest Territories
Bossy, Kwong, Beauchemin, Thibault	Potential As ₂ O ₃ Dust conversion at Giant Mine (paper not included)
Waddell, Spiller and Davison,	The use of ChemOx to overcome the challenges of PHC contaminated soil and groundwater at contaminated sites
Douheret,	Physico-Chemical treatment with Geotube® filtration: Underground Mine Desludging in winter TTS, Iron (Fe) and Zinc treatment
Coulombe, Cote, Paridis, Straub	Field Assessment of Sulphide Oxidation Rate - Raglan Mine
Smirnova et al	Results of vegetation survey as a part of neutralizing lime sludge valorization assessment
Baker, Humbert, Boyd	Dominion Gurney Minesite Rehabilitation (paper not included)
Martínez, Borstad, Brown, Ersahin, Henley	Remote sensing in reclamation monitoring: What can it do for you?

Wednesday:

Eary, Russell, Johnson,
Davidson and Harrington

Knight

Polster

Dustin

Kempenaar, Marques
and McClure

Smreciu, Gould, and
Wood

Keefer

Pedlar-Hobbs, Ludgate and
Luchinski

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Stewart and Siciliano

Nadeau and Huggard

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NORTHERN LATITUDES MINING RECLAMATION WORKSHOP

The Northern Latitudes Mining Reclamation Workshop is an international workshop on mining, land and urban reclamation and restoration methods. The objective of the workshop is to share information and experiences among governments, industry, consultants, Alaska Natives, northern First Nations and Inuit groups which undertake reclamation and restoration projects, or are involved in land management in the north or in comparable environments.

The first Workshop was held in Whitehorse, Yukon Territory, Canada in 2001 and it has been held every two years since, alternating between Canada and Alaska. The primary sponsors of the Workshop include the Yukon Geological Survey, Indian and Northern Affairs Canada, Natural Resources Canada, US Department of the Interior Bureau of Land Management, and the State of Alaska Department of Natural Resources.

CANADIAN LAND RECLAMATION ASSOCIATION

The CLRA/ACRSD is a non-profit organization incorporated in Canada with corresponding members throughout North America and other countries. The main objectives of CLRA/ACRSD are:

- To further knowledge and encourage investigation of problems and solutions in land reclamation.
- To provide opportunities for those interested in and concerned with land reclamation to meet and exchange information, ideas and experience.
- To incorporate the advances from research and practical experience into land reclamation planning and practice.
- To collect information relating to land reclamation and publish periodicals, books and leaflets which the Association may think desirable.
- To encourage education in the field of land reclamation.
- To provide awards for noteworthy achievements in the field of land reclamation.

ACKNOWLEDGEMENTS

The sponsoring organizations wish to acknowledge the work and support of all the people who made this conference a success, including:

- The Conference Organizing Committee: Alissa Sampson, Andrea Granger, Bill Price, David Polster, Diane Lister, Justin Ireys, Linda Jones, Mike Muller, Neil Salvin and Samantha Hudson.
- The Conference Papers and Posters Committee: Andy Etmanski, Bill Price, Chris Powter, David Polster, Diane Lister and Scott Davidson
- The Conference Sponsors (see next page)
- The Conference paper and poster presenters
- Dustin Rainey, Jocelyn Douheret and Brian Geddes for permission to use their photos on the Cover, Papers and Posters pages, respectively

CITATION

This report may be cited as:

Polster, D.F. and C.B. Powter (Compilers), 2013. Overcoming Northern Challenges. Proceedings of the 2013 Northern Latitudes Mining Reclamation Workshop and 38th Annual Meeting of the Canadian Land Reclamation Association. Whitehorse, Yukon September 9 – 12, 2013. 264 pp.