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#### FOREWORD

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The following selection of papers on ENVIRONMENTAL ENGINEERING has recently been published in the Proceedings of the Joint CSCE-ASCE National Conference on Environmental Engineering held in Montreal, Quebec - July 1993.

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1993 CONFÉRENCE CONJOINTE DE LA SCGC-ASCE SUR LE GÉNIE ENVIRONNEMENTAL

1993 JOINT CSCE-ASCE NATIONAL CONFERENCE ON ENVIRONMENTAL ENGINEERING

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LE CONCEPT DE LA POLICE VERTE COMME REMÈDE VISANT À CONTRÔLER LA GESTION ENVIRONNEMENTALE DANS LES RÉGIONS MÉTROPOLITAINES

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## <u>Résumé</u>

La plupart des municipalités au Québec emploient des inspecteurs pour l'aménagement de leur territoire. Leur mandat recouvre une vaste catégorie de responsabilités (permis de construction. de démolition et de protection de l'environnement, etc).

L'établissement du concept de Police Verte, et la restauration de l'inspection du domaine publique, peuvent représenter le commencement d'une nouvelle période de protection de l'environnement des territoires des régions métropolitains.

Cette article décrit les paramètres, les étapes, les volets, les réglementations et les restructurations nécessaires pour adapter ce nouveau concept aux régions métropolitaines.

## <u>Abstract</u>

Most municipalities have inspectors for their territories. Their mandate covers a wide spectrum of responsibilities (construction permits, demolition permits, environmental protection, etc). The establishment of the Green Police concept and the reorganisation of the public service inspection represent a new era of environmental protection in the territory of the metropolitan urban centres. This paper summarizes the steps, parameters, restructuring actions and necessary changes of regulation which have to be introduced in the effort to adapt and apply the new concept to the territories of the metropolitan regions.

## **Introduction**

Les questions environnementales préoccupent, sans cesse, un nombre croissant de citoyens dans toutes les villes nord-américaines. La surveillance environnementale du territoire d'une ville est de plus en plus une nécessité, et plusieurs municipalités sont maintenant convaincues que le temps est venu de poser des gestes concrets. Parmi les priorités dans une ville il y a: - l'incinération, - l'enfouissement des déchets, - les dépôts sauvages, - la localisation des installations de traitement des déchets solides, - l'implantation d'une nouvelle réglementation municipale dans le domaine de l'environnement, - l'étude approfondie de l'établissement du concept de POLICE VERTE.

## <u>Historique</u>

Au cours des derniers années la prise de conscience des citoyens vis à vis les problèmes environnementaux a radicalement augmenté.

En même temps, on se préoccupe continuellement problèmes existants et de leur magnitude. Des études récentes, menées pour la Ville de Montréal, ont indiqué les difficultés inhérentes à la protection et au contrôle de la détérioration de l'environnement, et elles ont aussi demontré la nécessité d'adapter et d'appliquer, le plutôt possible, une nouvelle réglementation des nouvelles technologies et des concepts ainsi que des nouvelles stratégies a la gestion de l'environnement.

## **Problématique**

Dans une municipalité, et en particulier dans la Ville de Montréal, les inspecteurs jouent traditionnellement un rôle assez complexe. Ils ont des heures normales de bureau (de 9 h à 17 h, et ne travaillent pas en fin de semaine). Chaque jour, ils exécutent une patrouille de routine, et distribuent des avis d'infraction quand ils constatent un infraction à un règlement municipal. Environ 20% de leur temps est consacré à la patrouille environnementale. Le formation des inspecteurs-visant à leur faire connaître les différents impacts environnementaux sur les terrains publiques et privés, est presque nulle.

Dans le système actuel la réception de plaintes, utilisée par les inspecteurs n'est pas informatisée et leurs efforts ne sont pas reconnus. Les inspecteurs ne peuvent pas répondre à tous les besoins. La restructuration et la réorganisation de l'inspection du domaine publique deviennent une nécessité.

La réglementation municipale actuelle est assez spécifique en ce qui concerne les nuisances, la neige, la voirie, la voie publique, les excavations; cependant, elle ne tient pas compte des remblayages illicites, des dépôts sauvages et d'autres aspects environnementaux. La réglementation est aussi peu explicite, et requiert une réadaptation et une réévaluation.

La première application du nouveau concept, appelé POLICE VERTE, eut lieu dans les années 70 en Scandinavie. Un peu plus tard, le Mouvement Vert en Allemagne suggéra (sans succès) au parlement une série de mesures pratiques afin de protéger efficacement l'environnement des grandes agglomérations urbaines.

Dans les années 80, les différentes villes d'Europe commencèrent à introduire l'idée d'un service municipal spécial qui, initialement serait à l'écoute des citoyens, soit pour répondre à leurs questions soit pour recevoir leurs plaintes (Paris. Lyon, Amsterdam, Bruxelles, Genève, Vienne, etc). Le mandat de ces services différait selon les pays, mais ces services devaient affronter d'énormes problèmes juridiques et essayer de faire reconnaître leur autorité.

Au cours des cinq dernières années, différentes services spéciaux en Europe ont été transformés en patrouilles de surveillance environnementale, avec une grande variété de mandats et de priorités. Sans aucun doute, leur rôle est maintenant beaucoup plus déterminé par les besoins spécifiques de chaque ville. L'introduction d'une nouvelle réglementation municipale est l'un des moyens employés pour obtenir une action concrète et immédiate.

Aux États-Unis, le système municipal est très différent et variable. Les autorités municipales ont le droit d'introduire de nouveaux concepts et méthodologies de protection de l'environnement; cependant, l'expertise et les lignes directrice de l'EPA sont la plupart du temps respectées.

Au Québec, la plupart des municipalités ont des inspecteurs pour l'aménagement de leur territoire. Seule La Salle a joué un rôle de pionnier se dotant en 1990 d'un service de patrouille de surveillance environnementale. Cette patrouille a pour mandat de veiller à l'application de la réglementation en matière d'environnement et d'hygiène publiques.

Cette patrouille de la Ville La Salle compte actuellement des agents qui assurent un service minimal de 65 heure par semaine. D'avril à mai, période considérée comme la plus active, la patrouille est renforcée par la présence d'un troisième agent. Ces agents, aisément identifiables à leur uniforme de couleur verte et à une vignette apposée sur leur voiture patrouille, sillonnent le territoire sept jours sur sept, et ça à des horaires variables, afin de maximiser les chances d'intervenir contre les fautifs. La cela surveille le territoire afin de dépister:

- 1. tout déversement illégal de déchets ou rebuts,
- 2. le contrôle des animaux et l'hygiène publique,
- 3. les sources de bruit dérogeants aux normes prescrites par la réglementation municipale,
- 4. la cueillette des rebuts en vrac,
- 5. la cueillette de matériaux secs (tarification raisonnable),
- 6. la cueillette de déchets encombrants,
- 7. tout déversement de produits domestiques dangereux dans les égouts ou sur des terrains vacants.

Réorganiser l'inspection du domaine publique, introduire de nouveaux concepts et réglementer la protection de l'environnement sont une nécessité.

La nouvelle réglementation, la POLICE VERTE et la restructuration de l'inspection du domaine publique peuvent représenter le commencement d'une nouvelle période de protection de l'environnement pour les régions métropolitaines, ainsi que les premières étapes du plan général de gestion intégrée des déchets solides.

## Méthodologie

Les paramètres considérés pour établir le nouveau concept comprennent:

- 1. le rôle et le mandat de la police,
- 2. le système de pointage,
- 3. le rôle et le mandat des inspecteurs,
- 4. la nouvelle réglementation,
- 5. l'introduction de billets spéciaux d'infraction,
- 6. le système d'alarme,
- 7. la réorganisation du service municipal,
- 8. l'adaptation, vérification et démonstration du nouveau concept.

L'évaluation de ces paramètres comprend trois parties:

- 1. analyse (historique, bibliographie, inventaire, rôle traditionnel, responsabilités, plaintes, formation, etc).
- 2. synthèse (restructuration, réorganisation, revitalisation, suggestions, recommandations, etc),
- 3. vérification, démonstration, application.

Chaque partie comprend un nombre de volets plus particuliers.

#### Inventaire préliminaire pour la ville de Montréal

La réglementation municipale de la Ville de Montréal est explicite et ne traite pas spécifiquement ni des dépôts sauvages, ni des remblayages illicites de terrain, ni des patrouilles environnementales. Certains règlements peuvent s'appliquer indirectement à ces activités. Nous avons:

Règle. 47 (art 20); Règle. 270 (art 17; art 17A; art 17B arte 17C; art 17D; art 17E; art 18; art 35A; art 52; art 54; art 54C); Règle. 3189 (art 2); Règle. 5359 (art 2; art 5); Règle 5360 (art 5; art 8A art 16A; art 16B; art 16C; art 16F; art 16G); Règle. 7018.

Parmi les règlements les plus pertinents il faut noter les règlements 5359, 5360 et 7018. Les inspecteurs visitent des endroits - s'ils y constatent une infraction à un des règlements mentionnés, ils émettent alors un avis mettant le propriétaire en demeure de remédier à la situation dans le plus bref délai possible, et de voir à ce quelle celle-ci ne se répète pas. La réglementation de la Ville de Montréal est beaucoup plus élaborée que celle d'autres municipalités plus petites (i.e. Ville LaSalle: règlement 1203 - en révision - et règlement sur le zonage). La réglementation est très spécifique en ce qui concerne les nuisances, la neige, la voirie, les animaux, la voie publique, les clos de voirie, les excavations, mais en ce qui concerne la patrouille environnementale.

La plupart des dépôts illicites se font sur des terrains vagues et industriels, pendant la nuit et en fin de semaine, pour épargner de l'argent en échappant aux sanctions et en exploitant le système d'inspection et de contrôle. Le territoire de la Ville de Montréal se divise en trois régions d'inspection:

- 1. la région Est (2150, ave Dickson) avec des arrondissements: Pointe aux Trembles/Rivière des Prairies. Mercier/Hochelaga-Maisonneuve, Mont Royal/Centre sud;
- 2. la région Ouest (6000, rue Notre-Dame ouest ) avec arrondissements Côte de Neiges/Notre-dame de Grâce, Centre ville, Sud ouest;
- 3. la région Nord (1400, rue des Carrières). Arrondissements: Cartierville/Ahuntsic, Villeray/St Michel, Rosemont/Petite Patrie.

Chaque région est dotée d'un chef et d'un certain nombre d'inspecteurs. Les responsabilités et le mandat des inspecteurs sont trop lourds par rapport à leur nombre. Bien que chaque arrondissement possède son inspecteur, la plupart des arrondissements de la Ville de Montréal sont plus grands que les municipalisés avoisinantes. Cela signifie, qu'en comparaison, chaque inspecteur à Montréal contrôle une région équivalent à une petite municipalité. Le rôle des inspecteurs est complexe, et seulement 20% de leur temps est consacré à la patrouille environnementale.

Le système de plaintes utilisé par les inspecteurs n'est pas informatisé. En comparaison, le Service de l'aménagement du territoire de la Ville LaSalle, ouvre un dossier pour chaque plainte, c'est a dire un rapport de plainte informatisé, comprenant tous les renseignements pertinents et les actions correctives prises pour remédier à la situation. Sans un tel système , on ne peut pas conserver l'histoire du terrain, et l'on doit se fier uniquement à l'expérience personnelle des inspecteurs quand les plus âgés prennent leur retraite, une grande partie de l'expérience acquise et de la connaissance du territoire sont perdues. Une réévaluation du rôle et du mandat des inspecteurs est donc nécessaire. Sous le présent système, les efforts des inspecteurs ne sont pas reconnus. Ils ne peuvent pas répondre a tous les besoins.

La coopération des inspecteurs avec les municipalités d'Anjou, de Montréal Nord, de Montréal Est et de Laval, où l'on retrouve des problèmes similaires, est très importante, afin de coordonner les actions correctives pour toute la région. Un moyen d'exprimer cette coopération serait d'organiser de réunions régulières pour échanger l'information, pour établir des stratégies communes, pour régler des problèmes inter-municipaux et pour uniformiser différentes parties de la réglementation municipale.

A la direction régionale du MENVIQ, il existe un Service municipal s'occupant des plaintes écrites ou téléphoniques des citoyens, et concernant les déversements de déchets sauvages. Dès qu'une plainte est formulée, le Service d'inspection est informé du dossier et, si nécessaire, un avis est expédié au contrevenant. Si le terrain relié à la plainte appartient au territoire de la Ville de Montréal, le dossier est alors transmis au Service des travaux publics de la Ville de Montréal. Aucune surveillance de routine des déversement de dépôts sauvages n'est effectuée par le MENVIQ.

Un système de pointage a été développé pour fournir un outil plus pratique aux inspecteurs effectuant la patrouille environnementale de routine sur des sites affectés. Le tableau suivant démontré ce système de pointage

<ol> <li>Présence et qualité de l'eau de surface (fossés, petits lacs, marécages).</li> <li>1a. couleur de l'eau</li> <li>1b. niveau de l'eau</li> </ol>	Points 30 20
2. Odeur	50
3. Lixiviat	30
4. Potentiel de la contamination de la nappe	50
<ol> <li>Présence des produits toxiques (hydrocarbures, métaux, etc)</li> </ol>	50
6. Présence des produits toxiques (hydrocarbures, métaux, etc)	50
7. Assèchement de la végétation (buissons et arbres)	20
<ul> <li>8. Histoire de la contamination du site</li> <li>8a. Dépotoir actif</li> <li>8b. Contamination récente</li> <li>8c. Contamination passée</li> </ul>	50 30 50
<ol> <li>Identification du site, inventaire des lieux d'élimination des déchets dangereux au Québec</li> </ol>	70
Total	500 '

Il est évident que pour connaître le degré précis de contamination de chaque terrain visité des études plus approfondies sont absolument nécessaires.

Les inspecteurs peuvent regrouper les sites visités selon les catégories suivantes:

- a) Sites d'intervention prioritaire (très contaminés) [de 300 à 500 points]
- b) Sites d'intervention secondaire (assez contaminés) [de 200 à 300 points]
- c) Sites d'intervention non-prioritaire (présentement sans indications de contamination) [de 0 à 200 points]

L'établissement du concept de patrouille environnementale permanente (Police Verte), avec responsabilités et mandat définis avec précision par la nouvelle réglementation municipale comprend divers étapes, incluant: la recherche préliminaire, l'adaptation aux conditions locales, la vérification, l'application à court terme, et finalement, l'introduction de façonpermanente du concept général.

## Suggestions préliminaires

i) Concernant la "POLICE VERTE" et le rôle des inspecteurs.

Les expériences en Éurope et à Ville LaSalle, nous ont amenés à faire des recommandations précises pour l'introduction du concept de Police Verte sur le territoire de la Ville de Montréal, une région métropolitaine de l'Amérique du nord typique.

- 1. Augmenter le nombre d'inspecteurs,
- 2. Former et sensibiliser les inspecteurs à la protection de l'environnement,
- 3. Élaborer un mandat précis pour les patrouilles environnementales,
- 4. Former des patrouilles environnementales à plein temps parmi les inspecteurs.
- Développer un échéancier des activités pendant les deux premières années du programme,
- Trouver une réglementation municipale donnant plus d'autorité et de responsabilités aux patrouilleurs (billet d'infraction, etc).
- 7. Évaluer la structure, la performance, et les problèmes des patrouilles de surveillance environnementale.
- 8. Ajuster, développer et optimiser le concept de POLICE VERTE, en l'adaptant aux besoins particuliers, comprenant la surveillance après 17h et en fin de semaine, ainsi qu'un système d'alarme fonctionnant de minuit à 6 h du matin.
- ii) Concernant le nouveau règlement municipal

Les points principaux à considérer pour le nouveau règlement sont:

- 1. Un mandat clair et précis pour la POLICE VERTE,
- 2. La formation de la POLICE VERTE,
- 3. L'introduction de billets d'infraction,
- Les amendes et les pénalités pour infractions effectuées par les individus, les contracteurs, et les compagnies,
- 5. Les frais d'enlèvement des déchets,
- Les frais de la contamination du terrain.
- 7. Les dispositions particulières
- iii) Concernant le rôle de la Police

Surtout au cours des premiers années de la mise en oeuvre du concept de la POLICE VERTE, la coopération des inspecteurs avec la Police et les Services locaux de l'environnement est absolument indisipensable.

La Police doit être informée au sujet:

- 1. Du nouveau règlement municipale,
- 2. Des coordonnées des patrouilleurs environnementaux pour chaque région et

arrondissement de la région métropolitaine,

- 3. Des limites de l'autorité des patrouilleurs environnementaux,
- 4. Du système d'alarme pour les heures de minuit à l'aube.

La Police doit assister ces patrouilles spéciales pour faire connaître, le plus tôt possible au public les conséquences du nouveau règlement, et freiner la continuation des déversements de déchets sauvages et illicites.

# <u>Conclusion</u>

Les besoins de l'inspection environnementale et de la surveillance des terrains métropolitains ont donné naissance a l'idée de créer un nouveau type de contrôle environnemental appelé "la police verte". Pourtant, la mise au point de cette solution dépend des autorités locales ainsi que de la coopération inter-juridique et de leur coordination afin d'établir les moyens et les conditions requis pour la nouvelle réglementation, pour la réorganisation de la procédure d'inspection et pour encourager le rôle de l'inspection publique.

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## Chemical Interaction and Cyclic Freeze-Thaw Effects on the Integrity of the Soil Cover For Waite Amulet Tailings

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#### Abstract

In this study program, two cases regarding water availability during freezing were investigated. The first case adopts a positive water head to accelerate the process of ice lense growth within the clay layer during freezing, representing the worst case scenario. The second case deals with the application of a negative water head during freezing, which simulates field conditions during the fall season at Waite Amulet site.

Using the hydraulic conductivity as the measure of the changes in clay integrity, the experimental results have shown that the integrity of the clay cover is considerably reduced due to the induced water head during freezing. For the case of negative water head, the integrity of the clay cover is slightly reduced due to the limited amount of water intake during freezing.

## Introduction

The Waite Amulet tailing site near Rouyn-Noranda, Quebec consists of sulphide rich tailings deposited in an elevated 41 hectare dam. Sulphide minerals contained in these tailings oxidize when exposed to air and water, subsequently leading to the formation of acid mine drainage (AMD) which release from the impoundments. At Waite Amulet, sulphide oxidation

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and acid generation has been occurring for the last 50 years, resulting in a low-pH seepage containing high concentrations of sulphate and iron. The acidic water is collected in ditches and treated by lime neutralization before being discharged into neighbouring surface water bodies. The hydrogeochemistry studies of the Waite Amulet site (Siwik et al. 1987; Yanful and St-Arnaud, 1991) indicated that acidic pore water generated in the shallow unsaturated zone have been pushed downwards into the shallow saturated zone by infiltrating waters.

To minimize oxidation of sulphide tailings, a soil cover system is designed. The cover designs rely on the slow rate of oxygen diffusion through water-filled pores and therefore are based on the hydraulic principles and characteristics of partially saturated porous media. In regions where substantial freezing occurs during winter periods, the effects of freeze-thaw cycles on high clay content materials can be deleterious (Yong and Mohamed, 1992). Because of the interactive forces in the clay material, pore-space readjustment occurs after a few cycles of freeze-thaw, creating large pore spaces with a high degree of continuity. In essence, destroying the design considerations of low permeable material requirements (Yong et al. 1985).

In this study, a multi-layer system consisting of tailing, sand, clay and gravel was used during freeze/thaw experiments. Regarding water availability during freezing, samples were allowed to absorb water under two different water heads. The chemical migrations, in the proposed multi-layer system during freezing, were measured. Changes in clay hydraulic conductivity as a function of cyclic freeze/thaw were also calculated.

#### Material and Methods

The tested soil consisted of samples of fine grained sand designated as Ansil S-1, light brown silty clay designated as bulk varved clay, and unoxidized mine tailings designated as WA-17. The mineralogical analysis of the clay shows that it consists mainly of the following minerals in decreasing order: feldspar, quartz, kaolinite, illite, chlorite and amphibole. The following minerals are shown to exist in Ansil S-1 in decreasing order: feldspar, illite, chlorite, amphibole, and mica. The clay has a natural water content ranging from 37% to 40%.

Fig. 1 shows the proposed clay cover in the field. The actual thickness of the layers in the proposed clay cover are 0.3, 0.5, and 0.3 m for gravel, clay, and sand layers respectively. To determine the thickness of each layer in the laboratory experiments a ratio of 1 to 10 is used. Therefore, the following thickness were used: 0.03, 0.05, and 0.03 m of gravel, clay, sand layers respectively. The remainder of the acrylic tube, plexiglass, approximately 0.02 m, was tailings, giving a total sample height of 0.13 m. Fig. 2 illustrates a schematic diagram of the test apparatus indicating the dimensions of the sand layer, the location of thermocouples along the height of the sample and the cooling cap on the top of the gravel layer. The diameter of the apparatus is 0.10m.

The calculated dry densities of the placed material were 1.12 to 1.29  $Mg/m^3$  for the tailings. 1.37 to 1.73  $Mg/m^3$  for the sand and 1.48 to 1.59  $Mg/m^3$  for the clay. Based on the height of the clay layer, and the inner diameter of the plexiglass cylinder, the volume of void was calculated. With an assumed specific gravity of 2.65, one pore volume corresponds to 156 cm<sup>3</sup> of leachate.

#### Test Procedures

Initially the acrylic plexiglass cylinder was coated with a thin film of vaseline to lessen friction during freezing, and to facilitate sample extrusion. Following placement of a Whatman Grade 1 filter paper over the porous stone at the bottom of the cell, the tailings and sand were each compacted by hand in three equal lifts. The clay was statically compacted in three lifts using an Instron Tension Testing machine calibrated for compression. The approximate load placed on each lift was in the range from 5.34 kN to 5.57 kN. The gravel was then hand compacted in two lifts. Before placement of the soil, and after compaction of each material, the apparatus was weighed.

Once all the four materials were compacted in the cell, thermocouples were inserted. The four thermocouples were located at the mid-point of each material layer. The cell was then wrapped with plastic seal and two layers of fibreglass insulation. Tubing was attached from the bottom outlet to a burette filled with water, thereby allowing for water intake during the freezing cycle. Two cases were simulated regarding the water height in the burette. In the first case, the water height was 0.08 m from the top of the unoxidized tailings. This in turn induced maximum ice lense formation in the clay layer during freezing and hence simulates the worst case scenario. In the second case, the tailing layer was saturated and then the water level in the barrette was dropped to 0.13 m below the top of the unoxidized tailing layer. This condition simulates the actual water level in the field. The cooling cap was placed on the sample, and freezing commenced. It should be noted that the temperatures of the room, supply, and bath varied from -2.8 to -4.5°C, -11.0 to -14.5°C, and -16.0 to -19.5°C, respectively as shown in Fig. 2.

Following complete freezing of the sample, the leaching test was undertaken. A reservoir with acidified water, with a pH range from 3.8 to 4.5, was attached via tubing to the top inlet valve. As thawing occurred, one pore volume of leachate was collected. Permeability measurements were recorded at this time, under a head of approximately 1.50 m. Following leaching, the freezing cycle was continued or the sample was extruded, upon the test requirements. At the end of each test, the specimen was extruded, cut into slices, and then analyzed for soluble ions using the batch equilibrium test (ASTM 1984). Cations and heavy metal concentrations were determined using atomic absorption spectrophotometry (AAS). Sulphate was determined using titration with  $AgNO_3$ . The pH was measured using a standard pH meter.

#### **Physical Analysis**

The physical analysis described in this section includes: (1) water intake during freezing: (2) initial water content; (3) initial dry density of the clay (4) change in permeability, and (5) visual observations.

## **Positive Water Head**

The water height in this case was 0.08 m from the top of the unoxidized tailings. The number of tests and their conditions are shown in Table 1. Visual observations of all the tests have indicated that horizontal as well as vertical cracks were formed. Also, it is noticed that some ice lensing occurred. To be specific, for example Test No. 3, it was observed that after the first cycle, mostly horizontal cracks formed. A large horizontal crack in middle of the clay layer has been observed. Furthermore, after the second cycle, smaller horizontal cracks but, no large fractures were noticed. It should be noted that formation of ice lenses were observed at the clay/sand interface. These descriptions are shown in Table 1.

Variations in clay permeability as a function of the number of freeze/thaw cycles are shown Fig. 3. The first set of data was obtained from (Yong et al. 1991) for the clay layer only without any interactions between the clay and the chemicals leached out from the tailings. In other words, the tests were performed on one clay layer with the availability of distilled water during freezing and thawing. The second set of data is calculated in this study. For the first set of data, it was observed that an increase in permeability by 23 times after 3 cycles of freeze/thaw occurred. This is attributed to: (1) formation of microcracks in both vertical and horizonal directions, and (2) clay aggregation during freezing, hence a decrease in surface area and an increase in pore size geometry (Yong and Mohamed, 1992).

For the second series of data, it is observed that after the first cycle of freeze/thaw the permeability increased by 625 times. This is attributed to: (1) formation of microcracks in both vertical and horizontal directions; (2) reduction in the thickness of the diffused double layer due to repliceability of major cations in the clay by the inducing heavy metals in the leachate, and (3) clay aggregation during freezing. Furthermore, after the second freeze/thaw cycle, the permeability decreases by 2.9 times from the value noted after the first freeze/thaw cycle. This is attributed to compression of clay particles in an aggregated form; hence a reduction in water content and specific surface area. It is anticipated that the permeability will not show any further decrease after the second cycle and will level off. This conclusion is based on a similar behaviour of clay under freeze/thaw cycles reported by Yong and Mohamed (1992).

In addition, the variation between the 1990 data and the current permeability data, prior to the freeze/thaw is due to: (1) initial molding water content; (2) initial dry density, and (3) size of the tested samples.

#### Negative Water Head

The water height in this case was 0.13 m below the top of the unoxidized tailing layer. Test No. 6 as shown in Table 1 was conducted for this case study. Visual observations demonstrated that horizontal and vertical cracks formed in the clay layer. Due to the negative water head on the clay laver, the water intake was approximately 30 times less than the case for positive water head. The reduction in the amount of water intake reduces the effect of the chemical attack on the clay layer. However, for a long period of time, chemicals will continue to migrate in the unfrozen layer around the clay particles (Mohamed et al. 1993a and b); hence affecting the integrity of the clay layer. As usual a permeability test was preformed after thawing in the freeze/thaw cell. It was noted that the permeability was 487 times higher than the permeability without the freeze/thaw cycles. This is attributed to the formation of cracks and possible compression of clav due to formation of aggregates; hence more free path along the side walls. By performing a falling head permeability test on the same clay layer in consolidation cell, the calculated permeability was only 2 times higher than the original permeability without freeze/thaw cycles. The question is which is the representative permeability value?

To answer this question, one has to re-evaluate the 1990 permeability data reported in Fig. 1. An increase in permeability by 23 times due to 3 cycles of freeze/thaw under a positive water head was reported. Therefore, the only factor which causes the maximum change is the positive water head associated with cyclic freeze/thaw. There was no induced chemical effects on the clay during freeze/thaw cycles. In the current situation, the clay is allowed to freeze under a negative water head; hence the amount of water intake as well as the effect of chemical attack is minimal. Therefore, the effect on permeability should be less than that of the 1990 data. On the other hand, due to extrusion of the sample and the performing of the permeability test in a consolidation cell there may have been a small effect of disturbance which attributed to the lower calculated permeability value.

Last but not least, the negative water head used in this test was of a high enough degree, that will prevent the clay layer from being saturated under all weathering conditions; hence reduction in oxygen diffusion and leachate generation.

# Chemical Analysis

The chemical analysis described in this section includes: (1) migration of cations; (2) migration of heavy metals and pH changes, and (3) migration of anion.

## **Positive Water Head**

Migration of Cations: The migration profiles for Na<sup>+</sup> pore fluid concentrations versus height of the clay cover are shown in Fig. 4a. The migration profiles depict how a particular species migrate or move through the clay cover with increasing permeation due to freezing. The initial concentration of Na<sup>+</sup> in the clay was 10 ppm. After freezing period in the first cvcle, Na<sup>-</sup> concentration, in the pore fluid of the bottom layer of the clay, increases while, it decreases in the middle and top layers of the clay. After thawing, Na<sup>+</sup> concentration decreases along the clay layer. For more cyclic freeze/thaw, Na<sup>+</sup> concentration continues to decrease. On the contrary, the concentrations of  $K^+$ ,  $Ca^{2+}$ , and  $Mg^{2+}$  are increased with increasing cyclic freeze/thaw as shown in Figs. 4b to 4d. This behaviour is attributed to cation exchange or replacement by  $Fe^{2+}$  and  $Zn^{2+}$  in the bottom layer of the clay. Whilst, at the top section of the clay layer, the interaction mechanism is due to the cation exchange process between calcium, magnesium, sodium and potassium. That is, the replacement of sodium and potassium ions in the exchangeable sites by calcium and magnesium to balance the charge deficit that occurs by the elusion of sodium and potassium.

Migration of Heavy Metals: Before embarking into a discussion regarding migration of heavy metals, pH variations along the clay cover will be addressed. The variations in pH along the clay cover are shown in Fig. 5a. It can be noted that the clay has initially a pH value of about 7. Due to the generated acidic leachate from the tailings during freezing, the soil pH increases as demonstrated in the case of freezing phase during the first cycle. The pH reduced from 7 to about 4.5 in the bottom layer of the clay. Further freeze/thaw cycles attributed to further decrease in pH along the clay layer. This decrease in pH enhances the movement of heavy metals (i.e.  $Zn^{2+}$  and  $Fe^{2+}$ ) as illustrated in Figs. 5b and 5c. The results have shown that significant amount of heavy metals were retained in the top section of the clay layer. Due to the low pH in the bottom part of the clay layer, it is expected that the retention capacity of the clay in the bottom section is reduced. However, this depends on the buffering capacity of the clay to any change in pH. It is known that heavy metals would generally precipitated out of solution if the solution pHs are high. Since clay pH was initially about 7 therefore,  $Zn^{2+}$  and  $Fe^{2+}$ precipitates at the start of freezing. Further freezing decreases clay pH and enhances the mobility of  $Zn^{2+}$  and  $Fe^{2+}$  in solution. The amount of  $Zn^{2+}$ retained in the soil is less than the amount of  $Fe^{2+}$  retained. This can be

explained by the ease of exchange or the strength with which cations of equal charge are generally held is inversely proportional to the hydrated radii or proportional to the unhydrated radii (Bohn, 1979). Therefore, the predicted order of soil retention based on unhydrated radii is  $Fe^{2+}$  (0.082 nm) >  $Zn^{2+}$  (0.074 nm). Similar results were reported by Mohamed et al. (1992).

Migration of Anion: The migration profiles of so<sup>2</sup> concentration along the height of the clay cover are shown in Fig. 5d. It can be seen that the concentration of  $so_4^{2}$  in the pore fluid increased as a function of pH and freeze/thaw cycles. Therefore, the  $so_4^{3}$  attenuation by the clay cover is very low and with time this high concentration will eventually be released to the environment. Since so<sup>3-</sup> ions are generally considered as non-specific ions (Yong, Mohamed and Warkentin, 1992), i.e. only exist on the outer coating of the double layer, attenuation is generally not a function of the type or amount of clay mineral present. Chemical analysis of the sectioned clay cover showing low accumulation and retention of the  $so_4^3$  ion can be attributed to physical dispersion in the clay with perhaps a small amount of interaction at anion exchange sites on the clay edges, or to other chemical reactions. The exchange between  $so_4^{2-}$  ions and other ions with negative charges which are part of the lattice is not likely because the sulphate ion is significantly bigger than the oxygen ion, i.e., it is too large to replace or coordinate with oxygen and hydroxyl ions.

# Negative Water Head

Migration of Cations: The migration profiles for pore fluid concentration of Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> versus clay height are shown in Figs. 6a to 6d respectively. It can be seen that the concentration of Na<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> in the clay pore fluid decrease after 3 cycles of freeze/thaw. It should be noted that during thawing in the first and second cycles there were no permeability measurements; hence, no rain condition was simulated. The migration of cations in the first and second cycles was due to the expelled water during thawing. During the thawing period of the third cycle a falling head permeability test was performed. During this phase, cations were leached from the clay hence, a reduction in the cation concentrations in the clay pore fluid was measured. The increase in the K<sup>+</sup> pore fluid concentration as shown in Fig. 6b could be attributed to cation exchange.

Migration of Heavy Metals: The migration of heavy metals could be explained on the basis of pH variations along the depth of the clay cover. Due to the limited amount of water taken in by the clay cover, the soil pH does not show a dramatic change. The soil pHs after 3 cycles of freeze/thaw were greater than 6. Therefore, the heavy metals are precipitated in the pore fluid of the clay layer. This is shown in Figs. 7b and 7c. The concentrations of  $Zn^{2+}$  and  $Fe^{2+}$  in the clay pore fluid were 0.1 ppm.

Migration of Anion: The migration profiles of  $so_4^{2*}$  are shown in Fig. 7d. Due to leaching of the clay layer, the  $so_4^{2*}$  concentration in the soil or fluid was reduced.

## Comparison between Positive and Negative Water Heads

The integrity of the clay cover was considerably reduced due to the induced positive water head during freezing which resulted in sulphide oxidation and acid generation in the tailings. Due to the low pHs, heavy metals were released and maximum interaction with the major cations resident in the clay pore fluid was obtained. This is in turn affects the integrity of the clay layer during the freeze/thaw cycles. Permeability increased by a 2.6 order of magnitude due to chemical attacks and aggregation of clay during freezing.

However, the integrity of the clay cover was slightly affected during the use of the negative water head during freeze/thaw cycles. This is mainly attributed to the limited amount of water intake during freezing and acid generation from the tailings. Nevertheless, the negative water head is far beyond the air entry value of the clay; hence, the clay layer will be unsaturated. This in turn will lead to oxygen diffusion through the clay cover. With water availability, sulphide oxidation and acid generation will be enhanced and increasing the potential of groundwater contaminants.

#### Conclusion

In this study, two cases regarding water availability during freezing were investigated. The first case adopts a positive water head to assess the maximum alteration to the clay cover during cyclic freeze/thaw. The second case adopts a negative water head during cyclic freeze/thaw to simulate field conditions during the fall season at the Waite Amulet site. For each case, physical as well as chemical analysis were performed to characterize the effect of cyclic freeze/thaw on the integrity of the proposed clay cover. It was demonstrated that the integrity of the clay cover was considerably reduced due to the induced positive water head during cyclic freeze/thaw. This is attributed to: (1) aggregation of clay particles; (2) chemical interactions between the generated acidic solutions and heavy metals from the tailings and the clay residence pore fluid. This in turn results in a reduction of the thickness of the double layer and increases the tendency of flocculation of the clay particles; hence an increase in permeability; and (3) reduction in the buffering capacity of the clay due to reduction in pHs.

For the case of the negative water head, the integrity of the clay cover is slightly reduced due to: (1) limited amount of water intake during freezing; and (2) limited amount of chemical interaction. However, due to further leaching, the residence pore fluid cations in the clay will be reduced. Hence, the thickness of the double layer will be increased and the clay tendency for dispersion will be increased. This in turn will reduce the permeability of the clay cover to water.

Nevertheless, the negative water head used in this study was less than the air entry value of the clay obtained from soil suction experiments (Yong et al. 1991). Therefore, the clay layer will remain unsaturated. This is not recommended for the decomissioning of the site (i.e. protection against oxygen and water infiltrations).

#### Acknowledgements

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Test No.	Conditions	Water Intoke during Freezing (cm <sup>2</sup> )	Initial W/C Cary (%)	Initial T <sub>d</sub> Clay (Mg/m <sup>1</sup> )	К (п/з)	Visual Observations
1	One cycle freezing/thewing	117.4	27.7	1.59	-	Many crecks, horizontal and vertical. Scree ice lenses.
2	One cycle freezing only -no leaching	172.8	-	1.53	-	Many cracks, horizontal and vertical. Some ice iceuses
3	Two cycles freezing/thawing	186.0	34.1	1.49	5.0 z 10 <sup>-7</sup> (1st) 1.7 z 10 <sup>-7</sup> (2nd)	After lat cycle, mostly horizonial cracks, large horizonial crack in middle of clay. After 2nd cycle, smaller horizonial cracks, no large fractures.
4	One cycle freezing/hawing-mo tailings	121.5	39.9	1.45	1.9 x 10"	Some horizonial crecking, visible ice lesses. One large horizonial creck at 1.5 and from bottom of cisy/sand interface.
2	Repcat Test 4 - there for 4 days	331.0	37.6	1.45	8.0 x 10 <sup>10</sup>	Horizontal crectury, ice trues at clay/ward interface. One large horizontal creck (0.8 cm) at 1.7 cm from bottom of clay/sand interface.
6	3 cycles + leaching tailings + sand	66	36.6	1.48	(1) 1.3 ± 10* (2) 3.9 ± 10*	Some horizontal crecks in the upper layers and some vertical crecks in the third layer (bottom)

# Table 1 Summary of Cyclic Freeze/Thaw Tests

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\* soil was not completely frozen when permeability was run.

soil was completely trones when permeability was run.

(1) permeability were perfromed in comolidation cell (2) permeability were performed in fromtaAbaw cell



Fig. 1 Cross Section of the Field Clay Cover



Fig. 2 Schematic diagram of test opparatus















Fig. 4b Variation of Concentration with Height for K



Fig. 4d Variation of Concentration with Height for Mg.















Neagative Water Head During Freezing



Fig. 7a Variation of pH with Height

**Negative Water Head During Freezing** Height mm m den meine in (brd ..... 0.01 0.1 Fe Concentration ppm

Fig. 7c Variation of Concentration with Height for Fe

Height mm a (Ini a 0.01 0.1 Zn Concentration ppm

Fig. 7b Variation of Concentration with Height for Zn











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# ENVIRONMENTAL IMPACT OF ANIMAL WASTE MANAGEMENT IN SMALL WATERSHEDS

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Key words: animal waste, leaching, runoff, ammonia, nitrate, potassium, phosphorous, water contamination, watershed

# <u>Abstract</u>

In areas with very intensive production of cattle, the quality of inland waters an groundwater is decreasing permanently. The management of animal wastes and its disposal without any protection directly on the soil creates environmental impact. The cattle manure pile being rich in phosphorus, potassium, and nitrogen is subjected to leaching, runoff, infiltration, and vaporisation. The evaluation of the impact of manure pile for water quality was the objective of studies. The measurements, performed on three dairy farms, show the fluctuation of stream loads on nitrate, ammonia, phosphorous and potassium. The results are presented in function of climatic, physiographic and agriculture factors influenced leaching and runoff in small drainage basin of barn yard.

# **Introduction**

In agriculture drainage basins, particularly when the cattle production is very intensive, the surface water quality is often quite low. In the province of Quebec, the cattle population is over a million heads. Some 46% of this population consists of 558 000 dairy cows and 242 500 heifers (1989). Among 16 000 Quebec dairy farms, 67.2% do not have protected places for manure disposal and 22.3% have constructions in soil. Only 10.5% of these farms have concrete structures for all disposal forms of manure including solid, semi-solid and liquid; the liquid form presents 5.6% of the total disposed manure (1989).

In spite of provincial governmental funds for improvement of the manure disposal system of manure, the farmers still dispose of the manure directly on barn yard soil using conventional conveyor systems. This type of manure management exerts serious environmental impact when no protective measures are applied.

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## Study Objectives and Methodology

The manure pile may constitute a source of serious contamination for groundwaters and for inland waters. The evaluation of the impact of improperly managed manure piles on surface water quality is the objective of this paper. This evaluation has been based on case studies performed on three Quebec dairy farms with extremely intensive production of cattle.

Three dairy farms with the same system of classic conveyor waste disposal were chosen. Each had a slightly different cattle populations and each had different physiographic factors.

Every site was equipped with an electronic rain gauge, including an automatic detector of events (precipitation). This kind of equipment permitted the evaluation of the quantity, the intensity, and the frequency of rainfalls in the tested area. For each farm the drainage basin in which the pile of manure was situated was mapped by surveying works. Ditches collected runoff from these basins. Every basin outlet was equipped with a V-notch and a water level recorder to permit the detection of flow through the basin area. The quality of surface water was measured usually once a month, except when special measurements were performed to evaluate the relationship between storm intensity and surface water concentrations. The sampling was done in the ditches before the V-notch. The sampled waters were analyzed for phosphorus, potassium, ammonia, nitrates, and total organic nitrogen. Quality of groundwaters, was evaluated through a series of sampling done in controlling wells at every site. This work will be reported in a separate paper.

#### Description of Study Areas

Three dairy farms called "J", "S", "M" were selected to perform the studies. All three are situated south of Montreal, near tributaries of the St. Lawrence River.

The farm called "J" was situated on sandy soil (parameters in Table 1). The waste is disposed on the top of a sandy hill; the base of this hill is composed of silty soil. The topographic measurements show the average slope of the drainage basin equal to 5%. This area is covered from May to November by very dense grass. The drainage area was closed by the system of ditches which discharged their waters to one outlet when the water level recorder was installed. The frequency of manure discharge is 90 times in winter, 72 times in spring, 45 times in summer, and 56 times in fall. The farmer uses 800 bundles of straw per year. Usually, the spreading of manure is done in September.

The yard of farm "S" is adjacent to the tributary directly, but the manure pile itself is situated 200 meters from its waterside. A circumferential ditch surrounds the manure disposal area and discharges directly to the river. The pile is disposed on clayey soil further described in Table 1. The topographic on site work, demonstrates that the drainage basin is a flat area (0.1 m is maximal difference of levels). The terrain is not covered by a vegetative filter in any season; however, the ditch is filled with vegetation in the summer. In this ditch a water level recorder was placed to detect runoff from the basin. The manure of all animals is discharged with the daily frequency during seven and a half months. During the other three and a half months of summer, the discharged manure concerns the cows and calves only. The spreading of manure was in October.

The next farm called "M" is situated on a flat area among a net of agriculture channels. A distance from the closest inland water is 800 m. The animal waste is disposed directly on clayey soil described in Table 1. The surface of the basin is 80% covered by grass. The base of the manure pile is directly connected to an agricultural ditch. In this ditch a water level recorder was placed to detect runoff from the basin. The waterside of this ditch is lightly covered by vegetation. The ditch slope was 0.3% on the length of 6 m from the pile to the water level recorder. The frequency of manure discharge is 90 times in winter, 40 times in spring and 39 times in the fall. Usually, the spreading was being done in July.

Site	.1.	5	יאי 🔪
Soil	Silty sand	Silty clay	Clay
Plasticity index		30.8%	41.4%
Liquidity index		0.18	- 0.02
Geological profile	Sand on dolomite	Uniform layer	Uniform layer
Mineralogy	dolomite quartz Illite	illite quartz chionte	illite feldspar chlorite
Permeability	2.5 x 10 <sup>4</sup>	2.5 x 10 <sup>7</sup>	8.5 x 10 <sup>4</sup>
Cation exchange capacity	40.8	57.6	58.4
Organic matter	3.9-7.5	7.1-7.9	5.3.7.9
Basin + Roof	1759m <sup>2</sup> + 103m <sup>2</sup>	$1455m^2 + 182m^2$	$1814m^2 + 143m^2$
Slope	5%	flat (slight depression)	flat (0.7%)
Cover	Grass	Partial Grass (10%)	Partial Grass (80%)
Runoff	Overland through a ravine	Oveland through a ditch	Ravine and Overland through a ditch
Distance from inland water	1.0 km agr. ditch 3 km river	200 m river	800 m stream
Cattle	70	95	48
Evacuation of manure	Conventional conveyor	Conventional conveyor	Conventional conveyor
Disposal	Pile on soil	Pile on soil	Pile on soil
Volume of manufe	500 m <sup>3</sup>	1073 m <sup>3</sup>	655 m <sup>3</sup>
Spreading	September	October	Juty

TABLE 1 SITE DESCRIPTION

## Particular problems of barn yard small drainage basin

The increase of pollutants level in the inland waters is directly related to the discharge of surface runoff and indirectly to the infiltration, as well as the groundwater runoff discharge. The runoff may consist of surface runoff, subsurface runoff, and groundwater runoff. The phenomenon of runoff consists of five phases:

1. The first phase relates to the rainless period just prior to the beginning of rainfall and after an extended dry period. During this phase, the groundwater table is low and its elevation continues to decrease gradually. In addition to the disposal of water by stream flow, water is also lost through evaporation on land and water surface and by transpiration from plants. The leaching from the manure pile has high levels of pollutants (phosphorus, potassium, and nitrogen compounds). Undiluted leachate from fresh wastes as well as from decomposed waste products flows to streams and/or percolates through the soil in the vicinity of the pile for the rainless period of summer.

2. The second phase is related to the initial period of rain. As the rain starts, its amount is divided among channel precipitation, interception by vegetation, infiltration into the soil, and temporary retention in surface depressions. The infiltrated water results in a gradual increase of water in the zone of aeration after the natural storage or field moisture capacity is satisfied. During this phase there is little overland flow except on impervious surfaces, while evaporation and transpiration are slight. For the little drainage basin as barn yard, this phase is relatively short. The manure pile absorbs the rain water. The leaking leachate from the pile of manure is slightly diluted.

3. The third phase relates to a continuation of rain at variable intensity. As rain continues, the capacities of vegetable interception and retention of surface depressions are reached; also, the excess rain becomes a source of runoff and detention storage on land surfaces and in channels. Overland flow occurs when the net rate of rain exceeds the infiltration rate; but it may or may not reach the stream channels, depending on retention and detection capacities of the land surface over which it travels. The infiltrated water will saturate the upper part of the zone of aeration which has been depleted in the previous phases and will then move down to the water table mostly in sandy areas. If rain continues, the water table will rise and the groundwater contribution to stream flow will increase. As the zone of aeration is saturated, subsurface runoff may contribute also to the stream flow. During this phase, evaporation and transpiration are slow. If the flow in the channels rises rapidly and becomes higher than the relatively slowly rising groundwater table, the streams will change from effluent streams to influent streams, contributing to the groundwater. At the same time, the leaching from the pile of manure increases. The new leachate raises the load of runoff with various compounds (Fig.1). The value of concentrations increase with the intensity of rainfall.

4. The fourth phase relates to a continuation of rainfall until all natural storage has been satisfied. The infiltration rate will approach the rate of the water transmission through the zone of aeration to both the groundwater table and the

subsurface runoff. The amount of subsurface runoff, which will join the stream flow almost as promptly as the overland runoff, apparently depends on the porosity of the material through which it is transmitted. In a large drainage basin, in flat swampy areas, as the rain continues, the water table rises constantly until the groundwater runoff balances the maximum rate of recharge possible, and all additional rain results in direct increment to runoff. The leaching is still very intensive from the manure pile during this phase of runoff. Consequently, concentrations in the runoff rise continuously (Fig. 1).



Fig.1. Increase of various compound concentration in agricultural ditches during a storm.

5. The fifth phase relates to the period between the termination of rain and the time when the first stage is to be reached. This usually involves a relatively long time for channel storage and surface retention to become depleted. Evaporation and transpiration are active and infiltration continues. Water in the zone of aeration reaches the water table or the stream channels. The stream flow is sustained by releasing stored water from stream channels, subsurface flow, and groundwater flow. The water table rises and then falls when its peak stage is over and the stored water is diminishing. The pile releases absorbed water even after the end of rainfall. The concentrations of different compounds in runoff are decreased after attaining the peak. This phase of the dilution phenomena will be continuous. The change of concentrations are in function of the tape of pollutant, and their adsorption/ desorption characteristics.

The runoff, from the hydrological point of view, is influenced by climatic and physiographic factors. The barn yard, where the manure is disposed, is a very small drainage basin, consequently, some factors affect runoff quality and quantity more than others. The quality of runoff is influenced by:

1. Climatic factors: precipitation (type, forme, frequency, intensity, duration, time distribution, areal distribution, and previous precipitation), interception

(vegetation species, age, composition and density, season of the year, and size of storm), evaporation (wind, temperature, atmospheric pressure, nature and shape of evaporation surface), transpiration (solar radiation, temperature, humidity, wind, soil moisture, and type of vegetation);

2. Physiographic factors: drainage basin geometric factors (size, shape, slope, orientation, hydrographic net), physical factors (land use, land cover, topographical conditions, surface infiltration conditions, soil mineralogy, permeability, groundwater conditions);

3. Agriculture factors: type of stored animal wastes (kind of animals, humidity of wastes, straw quantity added), age of manure pile (stage of compost decomposition), method of manure evacuation and disposal, volume of manure and its spatial distribution.

#### **Results and Discussion**

Rainfalls are only one form of precipitation considered in this study. The measurements of precipitation were taken from April to November during three years. The freezing period and the thawing period were avoided. In 1990, during this period, the cumulative value of precipitation for site "S" was 651 mm, for site "J" 647 mm, and for site "M" 885 mm.

All three sites are characterized by a high intensity rainfall even though the frequency is low. A daily storm is often a half or a third of monthly precipitation. This phenomenon was valuable for summer as well as for spring and fall. An example: on site "M", on May 27, 1991 daily precipitation was 29.4 mm. In other cases: on July 20, 1990, daily precipitation was 71 mm, when monthly precipitation was 222 mm. A similar situation was observed on site "S".

The intensity of storms was also high; an example: on site "M", rainfall intensity in August 1989 was 5 mm per 15 min. On the same site, in another year, the intensity of rainfall was 4 mm per 5 min on July 20, 1990, or 3 mm per 5 min in September 1990. The intensity of rain in site "J" was similarly high.

In these specific climatic conditions, runoff is mainly influenced by the intensity of precipitation. The relation between the rainfall and runoff may be intuitively simple, nevertheless, field measurements in outlet from drainage basin demonstrate contrary conclusion. The surface runoff peak follows precipitation; however, the cumulative value of runoff is bigger than the cumulative value of precipitation for the same period of time. For ex.: in April - May 1991, the runoff from the drainage basin in site "M" was more than two times bigger than the precipitation on this area: rainfall was 120 mm and runoff was 270 mm.

A pile of manure situated in a drainage basin changed the conditions of the runoff phenomena. The volume of this pile has risen since the spreading moment with daily discharge. Cattle manure has variable humidity dependent on feeding products and manure management (hay quantity, maintenance of solid and liquid manure). However, in every case, a pile still has a capacity to absorb some quantity of precipitation as a sponge. In favourable conditions the pile may release absorbed water. In the specific condition of very intensive rain, it releases more water including liquid contained in manure. The pile manages the retention time of a small basin. This retention is time variable and dependent of manure pile characteristics. The following factors influence absorption of the pile: volume, method of disposal (occupied area), manure humidity, and quantity of straw applied.

During heavy rainfalls, leaching from the pile intensifies. The surface runoff is carrying the pollutants mobilized by the leaching process. In the clayey sites, the surface runoff is the principal overflow in the basin. The runoff reaches its peak at the same time as the peak of precipitation. Values of different pollutant concentrations rise in the same rhythm as the runoff; however, the pollutants have different sensitivity to leaching and dissolution in rainwater. An example concerns the influence of a one and a half hour storm on surface water quality in the tested ditch, at site "M" (Fig. 1). During the second 30 min period of the storm, the concentration of phosphorus rose from 49 mg/L to 440 mg/L, and during the following 15 min, it fell to 47 mg/L; the concentration of ammonia rose from 7 mg/L to 165 mg/L then fell to 5 mg/L; the concentration of nitrate rose from 3 mg/L to 11 mg/L then, during the following 15 minutes, fell to 2 mg/L, and during the next 135 minutes, decreased to 0.5 mg/L. This example shows the variability of concentrations during rainfalls.

During a typical intensive storm, near the St.Louis Lake shore, the discharge from the manure pile was very intensive and concentration of phosphorus or ammonia can increase 10 to 20 times. In similar cases, only continuous sampling can present real data of runoff water quality. Contrary, the periodical measurements of inland water quality can give only general information.

The fluctuation of nitrates and ammonia loads, in three farm ditches during two years 1990 and 1991 is presented in Figs. 2 and 3.

For the clayey site, runoff from the manure pile has very important values during the dry period in summer time and during the intensive storm. On site situated on a sandy slope the surface runoff is detected only in spring and autumn. During the summer time, only subsurface runoff occurs.

If animal waste is disposed directly on the soil, leachate from the pile flows in the runoff to the inland water. The result is a remarkable increase in contamination by nitrates, nitrites, ammonia as well as phosphorus and potassium.

## **Acknowledgements**

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Fig.2. Nitrogen compounds in agricultural ditches. First year of measurements. Sites 'J', 'S', 'M'.







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# IMPACT OF WATER TABLE ON METRIBUZEN LEACHING E. Aubin<sup>1</sup>, S.O. Prasher<sup>2</sup> and R.N. Yong<sup>1</sup>

## Abstract

The primary objective of this study is to investigate the role of water table management systems in reducing environmental pollution from agricultural sources. In particular, field measurements were made in the soil and ground water zones of a potato farm near Joliette, Quebec to determine the threat to water pollution by a commonly-used herbicide metribuzen. Two water table management practices were investigated, namely subirrigation and subsurface drainage.

Only preliminary conclusions can be drawn from this study since 1992 was the first year of a three-year study. The metribuzen concentration in the ground water zone of subirrigated plots was significantly lower than in the subsurface drainage plots. From the soil measurements, it was found that metribuzen dissipation in the 0-20 cm zone was almost the same. However, it appears that the dissipation rates were different at lower depths. The herbicide appeared to be dissipating faster in subirrigated plots than in drainage drainage. It is believed that metribuzen persisted longer in drainage plots and thus it had more opportunity to leach.

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# Introduction

Installation of subsurface drainage systems is essential in many humid regions of North America to realize full agricultural potential of soils. More than 600,000 ha of agricultural land has been subsurface drained in Quebec by 1988 (Shady, 1989). However, drainage improvement works are becoming increasingly unpopular in the eyes of the general public. The systems are viewed as conduits of environmental pollution from agricultural areas as they can carry leached-out fertilizer and pesticide residues onto the regional lakes and rivers.

By controlling the water table on agricultural farms, it might be possible to reduce environmental pollution from agriculture by keeping the chemicals within the farm boundaries for extended periods. Most agricultural pesticides have a half-life ranging from a few weeks to a few months, and if we do not allow drainage water to escape farm boundaries for that time, like in a controlled drainage or subirrigation system, the water that finally leaves the farm in the fall would contain chemicals that are considerably less toxic than before. The microbial degradation process may also get accelerated by the higher moisture content caused by subirrigation and controlled drainage systems. Additionally, less nitrate-N leaching would result due to increased denitrification caused by keeping the drain pipes submerged with these systems.

Though the impact of water table management on nitrate-N leaching is well documented, its role in reducing pesticide pollution is not very well understood (Kalita and Kanwar, 1990; and Fausey et al., 1990). Whereas Arjoon et al. (1993) found that subirrigation might reduce leaching of prometryn herbicide in an organic soil, Arjoon and Prasher (1993) found that subirrigation might induce leaching of metolachlor into ground water. So, further investigations are needed in this area. The environmental impact of these systems is tremendous because it may bring about reduction in the environmental pollution from agricultural chemicals without requiring any drastic changes in the current agricultural practices. If found effective, the water table management systems may become on-farm pollution control systems in the humid regions of North America.

# Site Description

Field experiments were conducted at the Laurin Farm located near Joliette, Quebec, which grows potatoes on a two-year potato, one year grain crop rotation. The soil at the farm consists of 90 to 180 cm of very fine alluvial sand, free of rocks, over a marine clay layer, 2.0 to 2.5 m deep. The subsurface drainage of the top soil is quite good but the infiltrating water tends to accumulate over the clay layer thus causing ponding problems in early Spring and late Fall (Lajoie, 1965).

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A subsurface drainage system was installed at the farm in 1977 where drains were placed at depths ranging between 90 and 150 cm and at 18 m intervals. However, to overcome problems due to excessive drainage in the summer months, a subirrigation system was installed in 1989 on a part of the farm to supplement crop water requirements during hot dry months. It is estimated that a constant water table depth of 80 to 90 cm will cause enough capillary movement to meet water requirement of potatoes in this soil. An irrigation pond was dug to provide water for subirrigation in the dry summer months.

Two water table managements are under investigation in this study, namely subirrigation and subsurface drainage system. Due to the prevailing conditions at the farm, three plots under subirrigation and one under subsurface drainage were used in this study. Three sets of water table observation pipes were installed in each test plot. Two pipes were located 1 m away on either side of the drain, while the third was placed at the midspacing. In addition, two continuous water table recorders were installed in each treatment that recorded water table heights at the midspacing at 6 h intervals throughout the summer months.

Three observation wells, 100 mm diameter and 1.40 m long, were installed at the midspacing in each test plot. These wells were used to take water samples for chemical analyses. Prior to each water sampling, the wells were completely emptied with a hand pump to remove existing water. The wells were allowed to refill for a period of a few hours before one-litre ground water samples, representing the shallow ground water, were taken. About 10 ml of dichloromethane was added to each sample to prevent any further degradation of the herbicide before they were stored at 4 °C.

Soil samples were collected at four depths, i.e. 0-200, 200-400, 400-600, and 600-800 mm from the beginning to the end of the growing season. A single bulk sample for each depth was taken with the help of a soil auger. Three random samples per water table treatment were hermetically sealed and frozen shortly after collection.

## Methods of Analysis

Both soil and water samples were analyzed for nitrate-N and herbicide residue analysis in the laboratory.

Nitrate Analysis: Between 15 and 20 g of the thawed soil were transferred into a flask where 100 ml of 1.0 N KCl solution (in water) was added. The samples were shaken for one hour, filtered and then transferred into a light-resistant glass container. They were kept in the refrigerator until they were analyzed with a colorimeter using a cadmium reducing tube (Keeney and Nelson, 1989). The soil moisture content was measured by oven-drying the samples at 105 °C. The nitrate concentration in water was measured directly using an ion-selective electrode.

**Pesticide Analysis:** About 100 g of soil was transferred into a flask and mixed with 100 ml of pesticide grade methanol. The solubility of metribuzen in methanol is 400 g/L. The contents were shaken for 90 minutes, filtered and transferred into a round-bottom flask. The mixture was evaporated using a rotary evaporator. About 10 ml of methanol was added to reconstitute the pesticide in methanol. The latter was transferred into a 20 ml glass container which was kept refrigerated until its analysis on a gas chromatograph.

The water samples were extracted with pesticide grade dichloromethane. About 300 ml of water sample was hand-mixed with 100 ml of dichloromethane in a separatory funnel. The organic phase, containing the herbicide, was collected from the bottom. This procedure was repeated twice. The organic layer was evaporated in a rotary evaporator and the residues were re-constituted in methanol. The latter solution was kept refrigerated until its analysis on a gas chromatograph.

Gas Chromatography: A Varian 3400 gas chromatograph equipped with a nitrogen-phosphorus detector, along with a megabore DB-5, 30 m long, column was used in this study. The detector and injector temperatures were 285 and 190 °C, respectively. The column had an initial temperature of 90 °C, and it was increased to 260 °C with an increment of 10 °C/min.

# **Results and Discussion**

Although both nitrate-N and metribuzen levels were measured in the soil and ground water samples, only the results on herbicide levels, as affected by the water table management practice, are described in this paper. In general, the nitrate-N levels in ground water ranged from 3 to 90 mg/L. Also, the nitrate-N concentrations under subsurface drainage tended to be higher than under subirrigation. The nitrate-N results have not been properly analyzed at this time and, therefore, they will be presented at a later date.

The measured levels of metribuzen in ground water samples ranged from 7.8 to 29.4 ug/L in both treatments. In general, higher levels were measured under subsurface drainage than under subirrigation systems. Since, the "agricultural" benefit of subirrigation is to keep water tables high during the growing season, and everything else in terms of pesticide and fertilizer inputs and other cultural and crop management practices were the same in both treatments, an attempt was made to seek a relationship between water table height and pesticide levels.
From Figure 1, we can see that, as expected, the water table was generally higher in the subirrigated plots than in the drainage plots. Initially, the difference in water table heights between the two treatments is quite big (about 30 cm), and it tends to decrease with time. However, the water table seems to have remained shallower with subirrigation. In addition, it appears from Figure 1 that the herbicide concentration in ground water is low if the water table is at a shallow depth from the soil surface and vice-versa. The metribuzen concentration is plotted in figured 2 as a function of water table depth. A straight line relationship between the log of concentration and water table depth is observed. Two distinct straight line relationships are observed, one each for drainage (r = 0.64) and subirrigation (r =0.70). Again, the line for subirrigation is lower than the line for drainage, meaning that lower herbicide concentration was observed in the subirrigation plots than in the drainage plot for the same water table level. The latter clearly shows the probable role a subirrigation system might play in reducing pesticide pollution from agricultural farms.

To further investigate the role of the two water table management practices, the rate of dissipation of metribuzen in the soil profile was studied. For the 0-200 mm depth, the rates were found to be almost identical (Figure 3). This means that the herbicide fate at that depth is almost identical in both treatments, be it leaching, microbial degradation, sorption, etc.. For the 200-400 mm depth, the rates are beginning to deviate from each other. Since 1992 was the first year of this study. a significant amount of time and human resources were expended in designing the experiment, establishing the plots, and making field installations. Therefore, there were only two sampling days for the drainage plot for the 200-400 and 400-600 mm depths. Still, we can observe that the rate of dissipation is different, as is evident from the slope of the two straight lines. It appears that the herbicide was dissipating faster in the drainage plots than in the subirrigation plots. Again, the dissipation could be leaching, sorption or degradation. On looking at the similar relationship in Figure 5 for the 400-600 mm depth, it appears that the metribuzen concentration is increasing at this depth. This means that probably leaching is occurring at the 200-400 mm depth and that it is accumulating at the 400-600 mm depth in the drainage plots. On the contrary, the metribuzen concentration in the subirrigation plots is decreasing, implying that the pesticide is dissipating at a faster rate.

The above information, coupled with the fact that the metribuzen levels were lower in the ground water zone of the subirrigation plots, can lead us to conclude, albeit not very conclusively, that our hypothesis that subirrigation systems may reduce pollution from agricultural farms appears to be correct. What appears to be happening is that with subirrigation we are maintaining a higher moisture content in the soil, and this is leading to higher adsorption of the herbicide, and thus higher microbial degradation. However, we need more data before any concrete



Figure 1. Metribuzin concentration in ground water versus the water table depth.



Figure 2. Correlation between the logarithmic value of metribuzin concentration in ground water and water table depth.



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Figure 3. Metribuzin dissipation in the upper soil horizon versus the time period after the herbicide application.



Figure 4. Metribuzin concentration in soil at a depth of 20-40 cm with time after herbicide application.



Figure 5. Metribuzin concentration in soil at a depth of 40-60 cm with respect to time after herbicide application.

conclusions can be drawn. In 1993, we are planning to make significant efforts to collect more data in our test plots. It appears though that subirrigation systems may have a grater role to play in making agriculture sustainable in the humid areas of North America.

# Conclusions

Only preliminary conclusions can be drawn at this time since this is the first year of a three-year study. It appears that water table management may play a key role in reducing pollution from agricultural farms in humid areas. It was found that, in general, higher water tables during subirrigation resulted in lesser metribuzen levels in shallow ground water. Also, for any given water table depth, there was lesser herbicide in the ground water zone of a subirrigated plot than in the drainage plot. This was attributed to the faster rate of microbial degradation in the subirrigation plots. The latter was thought to be caused by higher adsorption and consequently higher degradation. However, more field measurements are needed before any concrete conclusions can be drawn.

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### THE GEOCHEMICAL DISTRIBUTION OF HEAVY METALS AND INORGANIC LIGANDS AS A CRITICAL FACTOR IN THE CLEAN-UP OF CONTAMINATED SEDIMENTS

Rosa Galvez-Cloutier<sup>1</sup>, Raymond N. Yong<sup>1</sup> and Hugh A.B. Potter<sup>1</sup>

### <u>ABSTRACT</u>

In contrast to Europe and the United States, it is only very recently that the Canadian government has announced a program for the restoration of harbours involving the clean-up of contaminated sediments. This brings an urgent need for scientific support to assist the emerging Canadian sediment treatment technologies to remain competitive in today's market.

In the search for that support, the GRC conducted a full geochemical and geotechnical characterization study and metal speciation analysis on the highly contaminated superficial sediments from the Lachine Canal. This study included: (1) the assessment of the type and distribution of contaminants and (2) the evaluation of the chemical stability given physico-chemical changes.

### **1. INTRODUCTION**

The present critical contamination of marine and river sediments is the inevitable consequence of a past irresponsible industrial production practice which allowed the legal and illegal discharge of contaminated liquids and residues into rivers and oceans. One local example of this scenario is the Lachine Canal in Montreal City. Since the beginning of its construction in 1821 until 1978 when the canal was closed, industries on both shores discharged solid and liquid wastes which accumulated at the bottom of the canal. Up to now, very little has been known about how contaminants were retained by the sediments nor for how long they will remain there. We believe that it is mainly for this reason that only encapsulation and/or solidification techniques have been proposed as solutions. This study aims to improve our understanding of the forms in which heavy metals are retained by sediments, and to determine the key parameters that control this retention. Clarification of these retention mechanisms will allow efficient metal washing or extracting techniques to be proposed or developed.

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### 2. METHODS AND MATERIALS

### 2.1 Sediment Sampling and Analysis program

Following a study conducted by Dessau&Lemieux and Roy&Associés in 1985, 44 sampling points were identified along the Lachine Basin and Canal. This study determined that the contaminated volume requiring clean-up was approximately 230,000 m3 in the basin and 225,000 m3 in the canal. Both zones were divided into transepts of 100 m in the basin and 150 m in the canal.

The sediments were collected from a boat using an Ekman grab sampler, this type of grab falls by gravity into the sediments, thus collecting mostly superficial sediments. A mother sample of 20 L was collected for every sampling point, each sample was subdivided into portions before being sent for analysis. Exposure to atmospheric air was minimised.

Two types of analysis were performed: (1) a characterization study which included the measurement of 14 descriptive parameters, 19 contaminant parameters and 4 geotechnical properties and (2) a geochemical metal speciation analysis which was performed on a composite sample of those individual samples that contained the highest metal concentrations.

Standard (ASTM, EPA, MEC or MENVIQ) testing procedures for the assay of sediment properties and characteristics were used when available. For the geochemical speciation analysis two approaches were used: the Tessier et al. (1979) sequential extraction analytical procedure, and 3 numerical models MINTEQA2 (EPA), PHREEQM (USGS) and GEOCHEM (UofC) for metal equilibrium speciation.

### 3. RESULTS

The results for the characterization study are summarized in Table 1 and Figures 1 to 5. The analytical approach for speciation was performed on a previously mixed sample which included only the most heavily contaminated samples, a summary of these results is presented in figure 6. Some of the results of the sensitivity analysis run with the 3 models are shown in figure 7.

### 4. DISCUSSION AND CONCLUSIONS

The characterization study revealed that the sediments contained very high concentrations of certain heavy metals. Zn, Pb, Cu, Cd, Hg and As, generally exceeded the available quality criteria (based on total metal concentrations) thus supporting the need for clean-up. The sediments are composed primarily of silt, clay and colloidal size particles which include a wide range of highly reactive surface materials: oxides and hydroxides, high specific surface area clay minerals (chlorite, illite) and high concentrations of organic colloids. The specific affinity that each of these materials exhibited for specific metals was revealed by the results of the analytical speciation. As a consequence of the presence of these reactive materials, interstitial water is held strongly as is shown in the water holding capacity curve in figure 4 and thus is very difficult to remove by physical means.

The presence of Pyrite (crystalline  $\text{FeS}_2$ ), as revealed in the mineralogical analysis and the high Amorphous Content (high amorphous  $\text{Fe}_2O_3$ ), agrees with both the pH dependency of the CEC - AEC and with the Fe speciation. The exchangeable fraction of the analytical procedure includes the metals associated with the Fe oxides and the clay minerals.

Under the conditions of non-surface reactive models (which account for the exchangeable and organic fraction of the analytical procedure) and input of 23 compounds (cations and anions) from the characterization analysis, the numerical speciation model predicted the great tendency of Pb, Zn, Cr, Cd and Cu to precipitate and form hydroxides (i.e. Zn(OH)2, Pb(OH)2), carbonates (i.e. ZnCO3, PbCO3) and sulfates (i.e.  $ZnSO_4$ ). The analytical procedure confirmed that the oxide/hydroxide and the carbonate fraction are important forms in which heavy metals are retained. The sulfate fraction is not included in the Tessier speciation scheme.

The Iron sulfate formation/dissolution is a pE dependent reaction while heavy metal oxide precipitation/dissolution is pH dependent. These 2 parameters control the release and retention of heavy metals in the oxides/hydroxide/carbonate and sulfate forms which is equivalent to 20-50 % of the total metal content. The prevalence of an almost neutral pH at those high levels of contamination reveals the high buffer capacity of the natural sediments. An example of pE and pH dependency of the metal species is shown in Fig. 7.

Even though heavy metals are more strongly attached to organic matter, the results show that there is a preference to fill exchangeable sites and to precipitate as hydroxides, carbonates and sulfates. These fractions are considered potentially bioavailable and so should be the target for extraction during clean-up. At this point it is pertinent to mention that some solidification processes provoke the shift from the exchangeable form to oxide/hydroxide, carbonate, or sulfate metal form which still remains potentially bioavailable.

Physico-chemical	Range	Geotechnical	Range		
рН	5.5 - 6.8	Grain Size Distribution	Figure 5		
ምር	13.4 - 22.5	Water Content (%)	35 - 298		
Conductivity (meq/L)	1.8 - 5.5	*Permeability (opt. water content) (m/s)	1.48 x 10 <sup>-7</sup> 4.06 x 10 <sup>-9</sup>		
Organic Matter (%)	4.3 - 27.8	*Compression Strength (MP2)	1.9 - 5		

Table No 1 Sediment Descriptive Parameters

Tot. Na (mg/Kg)	204 - 705	•Mineralogy		
Tot. K (mg/Kg) 1600 - 3900		Quartz, Feldspar, Dolom. Amphiboles, Pyrite,	Chlorite, Illite, Kaolinite	
Tot. Ca (mg/Kg)	254 - 472	*Special parameters		
Tot. Fe (%)	2-6	pH dep. CEC & AEC	Figures 2, 3	
Sol. HCO, (mg/L)	12 - 164	Water Holding Capacity	Figure 4	
Sol. SO₄ (mg/L)	0.6 - 91.5	Amorphous Fe, Si, Al %	2 - 4	
Sol. CI (mg/L)	6 - 61			

\* Measured in selected samples

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# Figure 1: Heavy Metal Contamination Profile

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Figure 6 Sequential Selective Metal Extraction Initial Original pH 6.8













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# COUPLED HEAT AND MOISTURE FLOW IN UNSATURATED EXPANSIVE CLAY BARRIERS

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# ABSTRACT

The main thermodynamic forces active in the near-field of a nuclear fuelwaste multiple-barrier system during the unsaturated stage are the gradients of temperature, fluid pressure and chemical potential. The processes that have a direct impact on transport mechanism of heat and moisture within the clay-based compacted buffer material are coupled. The major problems in describing coupled heat and mass flows in unsaturated clay-based materials are the lack of experimental data and the lack of a method to estimate coupled transport parameters.

The paper presents the experimental procedures, the analysis of experimental data and a method of determining the diffusivity parameters used to estimate the coupled heat and water flows in unsaturated clay-based materials. Several series of of one-dimensional tests were performed to examine the transient temperature and moisture flow in buffer material compacted at a dry density of 1.67 Mg/m<sup>3</sup> and optimum moisture content, volumetric moisture content of 0.28 cm<sup>3</sup>/cm<sup>3</sup>. Diffusivity parameters were calculated using the measured temperature and moisture distribution combined with an analytical solution of the coupled heat and mass flow equation and a square-root time technique.

### INTRODUCTION

The Canadian concept for the disposal of nuclear fuel wastes focuses on the deep burial of the material in hard rock formations. The sealed-waste containers will be emplaced in a deep vault system. A clay-based compacted buffer material will be used to separate the waste container from the host rock. Bentonite clay-based buffer have been selected since they could fulfill the following requirements:

- (1) serve as a geochemical filter for radionuclides;
- (2) act as a medium for heat conduction for the heat produced by radioactive decay of the waste in the container;
- (3) provide sufficient strength to support the weight of the container;
- (4) accommodate any detrimental effects of rock movement;
- (5) be capable of swelling under fluid flux in order to:
  - (a) seal gaps and cavities that may be present during emplacement,
  - (b) accommodate the shrinkage and cracks developing because of heat-induced moisture movement away from the container during the presaturation period.

When the heat-generating wastes are disposed, the bentonite-sand buffer will be unsaturated with water. The ability of the buffer material to fulfill the requirements may be influenced by the changes in its physical condition as heat transfer and moisture movement occur in the unsaturated material. These changes are being examined. This paper describes the results of research to evaluate the performance of buffer material when subject to temperature and moisture gradients.

The methodologies used to predict the coupled heat and water flows in unsaturated clay-based materials generally involve the development of a transport model and an evaluation of its associated flow coefficients or diffusivity parameters. A number of models have been developed (e.g. Smith, 1943; Philip and de Vries, 1957; Taylor and Cary, 1960; Boersma et al., 1972). None of the models are entirely satisfactory. Many of the difficulties are related to (a) the way the driving forces are expressed, and (b) the uncertainties with regard to the transport coefficients associated with the models. For buffer materials swelling pressure is developed locally as the water content is redistributed. A technique that uses experimental data and a theoretical formulation to calculate the diffusivity parameters in the coupled process is being developed to reflect these processes.

Yong and Xu (1988), Yong et al. (1990), and Mohamed et al. (1990) used an identification technique based on the measured moisture and temperature distributions as functions of space and time to calculate the diffusivity parameters in a coupled heat and moisture transport processes. The basic principle of the identification technique relied on matching experimentally obtained values of temperature and volumetric water content at various times in the controlled test with the predicted diffusivity parameters. The technique uses a nondimensional analysis to calculate the nondimensional diffusivity parameters. In order to transform the nondimensional diffusivity parameters into dimensional parameters, it is necessary to identify the final steady state time,  $t_{f}$ , for volumetric water content distributions.

This paper describes a study to evaluate the material parameters that govern the process of coupled heat and mass flow in the buffer material. A onedimensional test configuration has been used to examine the transient temperature and moisture flow in a buffer material compacted at maximum dry density and optimum moisture content. Several series of one-dimensional tests were used to investigate the nature of the transient process. The diffusivity parameters were calculated using the measured transient temperature and moisture distributions combined with an analytical solution of the coupled heat and mass flow equation (Yong et al., 1992) and a proposed square-root time technique.

# EXPERIMENTAL INVESTIGATION Apparatus

A scheme drawing of the test equipment is given in Figure 1. Each end of the specimen is in contact with a controlled-temperature warming plate to provide heat; pressure cell to measure changes in the reaction pressure arising from the redistribution of water with time. The specimen is insulated around its perimeters by a rigid PVC liner which also minimizes volume change in the specimen. The specimen and PVC liner are encased within a rigid support of concrete and steel around the perimeters and steel end plates. A cooling system is installed inside the concrete and bottom end plates to control the temperature around the perimeter, and hence the temperature gradient. A ring-type heater is installed in the heating plate to control the temperature input. The heating temperature is monitored and controlled by the thermalogic control unit. This unit enhances the ability to calculate the total input heat quality. A temperature monitoring unit is used to read the various thermocouples by amplifying and converting the thermocouple readings from millivolts to degrees Celsius and displaying them on a digital voltmeter. Mohamed et al. (1993) describe the experimental apparatus and its associated components in detail,

### **Experimental Procedures**

### Buffer material

The buffer material selected for this investigation was a laboratoryprepared mixture of sodium bentonite (Avonseal) and graded Indusmin silica sand at a proportion of 50/50 by dry weight. Quigley (1984) reported the detailed composition of the bentonite. The mixing solution used a "reference" synthetic granite groundwater (GGW) whose recipe is given by Abry et al. (1982). The liquid limit of the Avonseal clay tested was 284% and the plastic limit was 41%; the grain size distribution was 3% sand, 12% silt, and 85% clay. The specific proportions of the mixture were chosen because of their potentially attractive physical, chemical and mechanical properties for the required performance criteria adopted in the Canadian nuclear fuel waste disposal program.

### Specimen preparation

The buffer material specified above was mixed with a known amount of granitic groundwater. Samples were stored in a humid room for one week to reach equilibrium. To achieve a constant dry density of 1.67 Mg/m<sup>3</sup>, samples were divided into five layers and a known quantity of wet material was compacted statically in each layer. Thermocouples were placed after compaction inside the soil specimen at different positions along its length. Specimens were left for a period of 24 hours to reach equilibrium after the installation procedures were completed. To check the uniformity of the initial volumetric water content and dry density, one specimen was taken out and sectioned into portions. The distributions of volumetric water content and dry density were uniform to within 1%. Once this procedure had been completed, specimens were heated at one end at a predetermined temperature which was maintained. The temperature at perimeter of the specimens, i.e., the concrete section, was set by using a cooling system to cool it to a known value. Temperature measurements as a function of space and time were taken to determine the temperature profiles along the specimens during heating. The tests were ended at different times and the specimens were sectioned into 9 portions to determine the moisture distribution along their length.

### EXPERIMENTAL RESULTS

Five tests were performed. The initial and boundary conditions and the duration of each test are shown in Table 1. All tests were performed at the same initial and boundary conditions with the exception of the temperature at the cooler end of the specimen that varied between 15.5 and 31.5 °C. The test duration, i.e. the time at which a test was stopped and the samples were sectioned to measure their volumetric water content, used in this study was 2, 5, 10, 14 and 31 days. The differences in temperature at the cooling system did not considerably affect the observed thermal performance of the buffer material during testing (Mohamed et al. 1993). The main objectives of these experiments were: (1) to investigate the thermal and moisture distribution within the buffer material subjected to thermal gradient; (2) to investigate the time required for moisture to reach a local equilibrium within the buffer material, and (3) to provide the necessary experimental data to calculate the diffusivity parameters.

	Init	Initial Conditions			Boundary Conditions		
No.	Water Content (%)	Volumetric Water Cont. (cm <sup>3</sup> /cm <sup>3</sup> )	Dry Density (Mg/m <sup>3</sup> )	Heater Temp. (°C)	Cooler Temp. (°C)	Test Duration (d)	
	16.90	0.2806	1.67	120	15.5		
	10.80	0.2800	1.07	120	15.5	2	
2	16.80	0.2806	1.67	120	23.4	5	
3	16.80	0.2806	1.67	120	33.0	10	
4	16.80	0.2806	1.67	120	31.5	14	
5	16.80	0.2806	1.67	120	24.5	31	

Table 1. Initial and boundary conditions for tested specimens

The temperature distributions were similar as a function of space and time in all the experiments. Temperature distribution profiles as functions of time in Test 3 (Figure 2) are typical for different thermocouple locations within the buffer material. For each thermocouple location, the temperature initially increased with time, attend a maximum, and, then started to decrease. The decrease in temperature is attributed to the phase change of water into vapour within the specimen. It should be noted that all the specimens were tested in a closed-system configuration. The test results show that temperature reaches steady state over a short time period of 100 to 200 min.

Figure 3 shows the volumetric water content distributions as a function of distance from the heating source and time for Tests 1 to 5. After 2 days of heating, the volumetric water content in the first 10 mm adjacent to the heater reduced from 0.28 to 0.10; at the end opposite the heater in the longitudinal direction, the volumetric water content increased from 0.28 to 0.31. This indicates a movement of moisture from the warmer side to the cooler side in the longitudinal direction of the specimen. Also, after 2 days of heating, the maximum volumetric water content within the specimen was obtained about 55 mm away from the heating element. This can be attributed to the fact that water flows from warmer areas to cooler areas during heating, but the water flow was not fast enough to increase the volumetric water content to its maximum value at

the end opposite to the heater. Therefore, the maximum volumetric water content was observed in the zone adjacent to the dry side. After a long period of time, the maximum volumetric water content was obtained at the end opposite to the heating element.

These phenomena can be noticed from the volumetric water content distribution for 2, 5, 10, 14 and 31 days of heating, as shown in Figure 3. Experimental data suggested that a heating time of 14 days is approximately enough to observe a local equilibrium in the moisture content within the specimen.

# ANALYSIS OF EXPERIMENTAL DATA

### Governing Equations

The experimental data presented in Figures 2 and 3 can be used to evaluate the diffusivity parameters governing the coupled heat and moisture movement in the buffer material. The methodology adopted in this study combines an analytical technique reported by Yong et al. (1992) with a proposed square-root time technique.

The one-dimensional coupled heat and mass flow equations take the forms:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x} \left[ L_{WW} \frac{\partial \theta}{\partial x} \right] + \frac{\partial}{\partial x} \left[ L_{WT} \frac{\partial T}{\partial x} \right]$$
(1)

$$\frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left[ \frac{L_{TT}}{C_v} \frac{\partial T}{\partial x} \right] + \frac{\partial}{\partial x} \left[ L_{TW} \frac{\partial T}{\partial x} \right]$$
(2)

where  $\theta$  = volumetric water content,  $\theta = \theta(x,t)$ ; T = temperature, T = T (x,t);  $L_{ww}$  = diffusivity coefficient for fluid flow due to a gradient of  $\theta$ ;  $L_{TT}$  = thermal conductivity coefficient for heat transfer due to a gradient of T;  $L_{wT}$  = coupling diffusivity coefficient that specifies the moisture flow under a temperature gradient;  $C_v$  = specific heat of buffer. A zero value is assigned to  $L_{TW}$ , which implies that the thermal field is not affected by the moisture distribution, and the second term on the right hand side of Eqn. 2 vanishes. It can be observed from experimental results that there is a relaxation in the temperature distributions as a result of water movement (Mohamed et al., 1993). For example, the recorded difference in the temperature before and after water movement is about 4°C at a distance of 3 mm from the heater. The difference in temperature decreased as the distance from the heater increased. This small difference in temperature should not have affect the overall thermal field within the specimen.

The boundary conditions corresponding to the experiments are given by

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$$T = T_1$$
 at  $x = 0$ ; and  $T = T_2$  at  $x = L$  (3)

$$L_{WW} \frac{\partial \theta}{\partial x} + L_{WT} \frac{\partial T}{\partial x} = 0 \text{ at } x = 0 \text{ and } x = L .$$
 (4)

The initial conditions corresponding to the experiments are given by

$$\mathbf{T} = \mathbf{T}_{\mathbf{i}} \quad \mathbf{at} \quad \mathbf{x} = \mathbf{0} \tag{5a}$$

$$T = T_2 \text{ at } 0 < x \leq L$$
 (5b)

$$\boldsymbol{\theta} = \boldsymbol{\theta}_0 \quad \text{at } \boldsymbol{0} \leq \mathbf{x} \leq \mathbf{L} \tag{5c}$$

where  $T_1$  = temperature at hot end;  $T_2$  = temperature at cooler end; L = length of the specimen;  $\theta_0$  = initial volumetric water content.

Equations (1) and (2) can be represented in a nondimensional form by using the following representations:

$$\theta^* = \frac{\theta - \theta_0}{\theta_0}; T^* = \frac{T - T_2}{T_1 - T_2}; \tau = \frac{L_{TT}}{C_v} \frac{t}{L^2}; \varsigma = \frac{x}{L}$$
 (6)

where  $\theta^{\bullet}$  = nondimensional volumetric water content;  $T^{\bullet}$  = nondimensional temperature;  $\tau$  = nondimensional time factor; and  $\zeta$  = nondimensional distance.

The governing equations for coupled heat and mass flow in nondimensional forms are

$$\frac{\partial \theta^*}{\partial \tau} = L_{WW}^* \frac{\partial^2 \theta^*}{\partial \zeta^2} + L_{WT}^* \frac{\partial^2 T^*}{\partial \zeta^2}$$
(7)

$$\frac{\partial \mathbf{T}^*}{\partial \tau} = \frac{\partial^2 \mathbf{T}}{\partial \zeta^2} \tag{8}$$

where:

$$L_{WW}^{*} = \frac{L_{WW}}{L_{TT}^{*}}; \ L_{WT}^{*} = \frac{T_{1} - T_{2}}{\theta_{0}} \frac{L_{WT}}{L_{TT}^{*}}$$
(9a)

$$L_{TT}^{*} = \frac{L_{TT}}{C_{v}}$$
 (9b)

The boundary conditions in a nondimensional form are given by

$$T^* = 1 \text{ at } \zeta = 0; \text{ and } T^* = 0 \text{ at } \zeta = 1$$
 (10a)

$$L_{WW}^{*} \frac{\partial \theta}{\partial \zeta}^{*} + L_{WT}^{*} \frac{\partial T^{*}}{\partial \zeta} = 0 \text{ at } \zeta = 0 \text{ and } \zeta = 1 .$$
 (10b)

The initial condition in a nondimensional form are given by

$$T^* = 1$$
 at  $\zeta = 0$ ; and  $T^* = 0$  at  $0 < \zeta \leq 1$  (11a)

$$\theta^* = 0 \text{ at } 0 \leq \zeta \leq 1 . \tag{11b}$$

# SOLUTIONS

### (A) Solution for Temperature:

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Using Fourier series analysis, the solution for nondimensional temperature distribution is:

$$T^{*}(\zeta,\tau) = (1-\zeta) - \sum_{h=1}^{2} \left(\frac{2}{n\pi}\right) e^{-(n\pi)^{2}\tau} \sin(n\pi\zeta) . \qquad (12)$$

For sufficiently large  $\tau$ , Equation (12) can be written as

$$T^*(\zeta, \tau) \approx (1 - \zeta) - \frac{2}{\pi} e^{-\pi^2 \tau} \sin(\pi \zeta)$$
 (13)

For  $\zeta = \frac{1}{2}$ , Equation (13) is reduced to

$$T^* (\mathfrak{H}, \pi) = \frac{1}{2} - \frac{2}{\pi} e^{-\pi^2 \tau} . \qquad (14)$$

The degree of equilibrium in temperature may be expressed as

$$T_{xQ} = \frac{T^*(\frac{1}{2}, \tau)}{t^*(\frac{1}{2}, \pi)} = 1 - \frac{4}{\pi} e^{-\pi^2 \tau}.$$
 (15)

Figure 4 shows the relationship between the degree of equilibrium in temperature,  $T_{EQ}$ , and the square-root time factor,  $\sqrt{\tau}$ , given by Equation (15).

### (B) Solution for Volumetric Water Content:

Using Fourier series analysis, the solution for nondimensional volumetric water content distribution is:

$$\theta^{\star}(\zeta,\tau) = \frac{L_{WT}^{\star}}{L_{WW}^{\star}}(\zeta-\frac{1}{2}) + \sum_{n=1}^{\infty} \frac{2L_{WT}^{\star}}{L_{WW}^{\star}} \frac{1}{(n\pi)^{2}} [1-(-1)^{n}] e^{-L_{WW}^{\star}(n\pi^{2})} \cos(n\pi\zeta).$$
(16)

For sufficiently large  $\tau$ , Equation (16) can be written as

$$\theta^{*}(\zeta,\tau) \simeq \frac{L_{WT}^{*}}{L_{WW}^{*}} \left[ \zeta - \frac{1}{2} + \frac{4}{\pi^{2}} e^{-L_{WW}^{*}(\pi^{2})\tau} \cos(\pi\zeta) \right] .$$
(17)

It is convenient to substitute

$$r_{\theta} = L_{WW}^{*} \tau \tag{18}$$

where  $\tau_0 = a$  nondimensional time factor for nondimensional volumetric water content. Equation (17) then becomes

$$\theta^*(\varsigma,\tau) \simeq \frac{L_{WT}^*}{L_{WW}^*} \left[ \varsigma - \frac{1}{2} + \frac{4}{\pi^2} e^{-\pi^2 \tau_\theta} \cos(\pi\varsigma) \right] . \tag{19}$$

For  $\zeta = 1$ , Equation (19) is reduced to

$$\theta^{*}(1,\tau) = \frac{L_{WT}^{*}}{L_{WW}^{*}} \left[ \frac{1}{2} - \frac{4}{\pi^{2}} e^{-\pi^{2} \tau_{\theta}} \right] .$$
 (20)

The degree of equilibrium in volumetric water content is expressed as

$$\theta_{\mathbf{x}Q} = \frac{\theta^{+}(1,\tau)}{\theta^{+}(1,\tau)} = 1 - \frac{8}{\pi^{2}} e^{-\pi^{2}\tau_{\theta}}.$$
 (21)

The relationship between the degree of equilibrium in volumetric water content,  $\theta_{EQ}$ , and the square-root time factor,  $\sqrt{\tau_{\theta}}$ , given by Equation (21) is shown in Figure 5.

# DETERMINATION OF DIFFUSIVITY PARAMETERS

The values of  $L_{TT}^{\bullet}$ ,  $L_{WW}$ , and  $L_{WT}$  of a particular experiment (i.e., the initial volumetric water content and heater temperature) in the one-dimensional test can be determined by comparing the characteristics of the experimental and theoretical temperature and volumetric water content curves. The characteristics of the curves are brought out clearly when test time is plotted to a square-root scale.

# The square-root time method

# (A) Temperature distribution:

Figure 6 shows the forms of the experimental curves at the hot end (i.e., near the heater) and at the cooler end (i.e., at the end opposite to the heater in

the longitudinal direction). The recorded temperatures are plotted against the square root of time in minutes. Figure 4 shows the theoretical curve of the degree of equilibrium in temperature,  $T_{EQ}$ , as a function of the square root of the temperature time factor,  $\sqrt{\tau}$ . The theoretical curve is linear up to about 70% equilibrium, and at a 90% temperature equilibrium the abscissa (AC) is 1.139 times the abscissa (AB) of the production of the linear part of the curve. This characteristic is used to determine the point on the experimental curve corresponding to  $T_{EQ} = 90\%$ .

The experimental curve usually consists of a short curve representing the initial increase in temperature at the cooler end, a linear part and a second curve. The point D corresponding to  $T_{EQ} = 0$  is obtained by extrapolating the linear part of the curve back to the ordinate at zero time. A straight line (DE) is then drawn with an abscissa 1.139 times the corresponding abscissa on the linear part of the experimental curve. The intersection of the line DE with the experimental curve locates the point  $(a_{T90})$  corresponding to  $T_{EQ} = 90\%$ , and the corresponding value  $\sqrt{t_{T90}}$  can be be obtained. For the same value of  $\sqrt{t_{T90}}$  a corresponding point  $(b_{T90})$  can be obtained from the experimental data of the temperature distribution at the heater. It should be noted that the temperature has to stabilize within the specimen to achieve an equilibrium distribution in temperature. Therefore, temperature values at the cooler end of the specimen should be used to calculate  $\sqrt{t_{T90}}$ . The value of  $\tau$  corresponding to  $T_{EQ} = 90\%$  is 0.2572, and the thermal diffusivity,  $L_{TT}^{*}$ , is given by

$$L_{TT}^{4} = \frac{0.2572L^{2}}{t_{T90}} .$$
 (22)

(B) Volumetric Water Content Distribution:

Figure 7 shows the types of the experimental curves at the hot end and at the cooler end. The measured volumetric water content values are plotted against the square root of time in days. Figure 5 shows the theoretical curve of the degree of equilibrium in volumetric water content,  $\theta_{EQ}$ , as a function of the square root of the volumetric water content time factor,  $\sqrt{\tau_{\theta}}$ . The theoretical curve is linear up to about 80% equilibrium, and at 90% equilibrium in volumetric water content the abscissa (A<sub>1</sub>, C<sub>1</sub>) is 1.167 times the abscissa (A<sub>1</sub>, B<sub>1</sub>) of the production of the linear part of the curve. This characteristic is used to determine the point on the experimental curve corresponding to  $\theta_{EQ} = 90\%$ .

The experimental curve usually consists of a linear part and a curve. The point  $D_1$  corresponding to  $\theta_{EQ} = 0$  is obtained by extrapolating the linear part of the curve back to the ordinate at zero time. A straight line  $(D_1, E_1)$  is then drawn having its abscissa 1.167 times the corresponding abscissa on the linear part of the experimental curve. The intersection of the line  $(D_1, E_1)$  with the

experimental curve locates the point  $(a_{090})$  corresponding to  $\theta_{EQ} = 90\%$  and the corresponding value  $\sqrt{t_{090}}$  is obtained. For the same value of  $\sqrt{t_{090}}$ , a corresponding point  $(b_{090})$  is obtained from the experimental data of volumetric water content distribution at a close section of the specimen close to the heater. Note that equilibrium volumetric water content values should be calculated from the volumetric water content distribution at a section near the cooler side of the specimen. The volumetric water content values at points  $(a_{090})$  and  $(b_{090})$  represents  $\theta(1, t_{090})$  and  $\theta(0, t_{090})$  respectively. The value of  $\tau_0$  corresponding to  $\theta_{EQ} = 90\%$  is 0.0473, and the nondimensional moisture diffusivity  $L_{ww}^*$  is given by

$$L_{WW}^{*} = \frac{\tau_{\theta g 0}}{\tau_{\theta g}} = \frac{0.0473}{\tau_{\theta g}}$$
(23)

The  $\tau_{ef}$  can be calculated from the following relationship of equilibrium in temperature and volumetric water content:

$$\tau_{\theta_{f}} = 0.257 \frac{t_{\theta_{90}}}{t_{\tau_{90}}} . \tag{24}$$

Hence, Equation (23) takes the following form:

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$$L_{WW}^{*} = 0.184 \frac{t_{T90}}{t_{090}} .$$
 (25)

Using Equations (9a), (22) and (25), the moisture diffusivity,  $L_{ww}$ , takes the following form:

$$L_{WW} = 0.0473 \frac{L^2}{t_{\theta gg}} .$$
 (26)

The relationship between nondimensional moisture diffusivity,  $L_{ww}^{\bullet}$ , and nondimensional thermal moisture diffusivity,  $L_{wT}^{\bullet}$ , may take the following form:

$$L_{WT}^{*} = L_{WW}^{*} \left[ \theta^{*}(1,\tau) - \theta^{*}(0,\tau) \right] .$$
 (27)

Using Equations (27) and (9a), the thermal moisture diffusivity,  $L_{WT}$ , reduces to the following form:

$$L_{WT} = \frac{L_{WW}}{(T_1 - T_2)} \left[ \theta(1, \tau) - \theta(0, \tau) \right] t_{\theta = 0}$$
 (28)

It should be noted that  $T_1$  and  $T_2$  are determined from Figure 6 and correspond to the temperature values for  $b_{T90}$  and  $a_{T90}$  respectively. Also,  $\theta(1,\tau)$  and  $\theta(0,\tau)$  are determined from Figure 7 and correspond to the volumetric water content values for  $a_{990}$  and  $b_{990}$  respectively.

In summary, the moisture diffusivity and thermal moisture diffusivity can be calculated from Eqs. 26 and 28, respectively.

# **APPLICATION**

Figure 6 presents the experimentally recorded temperature distributions as a function of the square-root time for Test 3. These data were used to calculate  $t_{TNO} = 76.56 \text{ min} = 0.053 \text{ d}$ ,  $T_1 = 118^{\circ}\text{C}$  and  $T_2 = 31.11^{\circ}\text{C}$ . Using Equation (22), the thermal diffusivity was calculated

$$L_{TT}^{*} = \frac{0.2572 \times (110)^{2}}{0.053} = 587.192 \times 10^{2} \text{ mm}^{2}/\text{d} . \qquad (29)$$

The experimental data (Fig. 3) in a reduced format as shown in Figure 7, were used to estimate  $t_{990}$ ,  $\theta(1,\tau)$  and  $\theta(0,\tau)$ . The  $t_{990}$  was estimated at a value of 16 days, and the volumetric water contents at the wet side ( $\theta(1,\tau)$ ) and at the dry side ( $\theta(0,\tau)$ ) at values of 0.35 and 0.067 respectively. Finally, the moisture diffusivity and the thermal moisture diffusivity were calculated as follows:

$$L_{WW} = 0.0473 \times (110)^2 = 35.77 \text{ mm}^2/\text{d}$$
 (30)

$$L_{WT} = \frac{35.77}{(118 - 31.11)} [0.35 - 0.067] = 0.1167 \text{ mm}^2/(d^{\circ}C). \quad (31)$$

### CONCLUSION

This paper outlines an experimental technique that has been used to study the heat-induced moisture movement within an unsaturated bentonite-sand buffer material. One-dimensional tests conducted on buffer material were used to assess the time-dependent movement of moisture and temperature resulting from an externally imposed thermal gradient. An analytical technique and the squareroot time method were used successfully in conjunction with the experimental results for the time-dependent temperature and moisture distribution to calculate the heat and moisture diffusivity parameters. This technique is now sufficiently well developed to permit the determination of functional relation between each individual diffusivity parameter and the temperature and volumetric water content. This can be achieved by: (1) conducting experiments with different initial volumetric water contents and externally imposed temperature gradients;

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(2) calculating various diffusivity parameters in each case, and (3) establishing appropriate correlations between the calculated values as a function of the volumetric water content and temperature.

The proposed square-root time method can be used to determine the required steady-state time for the volumetric water content in the identification technique (Yong and Xu, 1988; Mohamed et al., 1990). The steady-state time is estimated to be equal to the  $t_{990}$  determined by square-root time method.

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# MOBILITY AND RETENTION OF Pb AND Zn IN SAND/BENTONITE

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and

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### ABSTRACT

During a compatibility study involving concentrated solutions of Pb and Zn and a mixture of 90% sand - 10% bentonite, it was observed that the coefficient of hydraulic conductivity calculated for the zinc test was one order of magnitude greater than that of a lead test having similar characteristics. This was partly explained by the occurrence of high affinity adsorption in the Stern layer. Chemical analyses performed showed that Pb was mostly found as adsorbed species, whereas Zn was mostly found in the leachate collected. The greater mobility of Zn was interpreted in terms of the lower selectivity of Zn ions for the bentonite surfaces, which can be explained based on the Gibbs free energy ( $\Delta G^{\circ}$ ) of the system.

### INTRODUCTION

The coefficient of hydraulic permeability (k) of a clay barrier is affected by several procedural aspects involving its determination (Yong et al., 1991; Yong and Cabral, 1992), as well as by numerous soil system variables, including the types of clay minerals forming the solid phase of the medium and the type(s) of contaminant(s) which will interact with it. Generally, an increase in the measured k-value of a clay soil is associated with a collapse of the diffuse double layer (DDL); in other words, a

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reduction of its thickness. The capability a species have to affect the DDL (or its thickness) can, in turn, be associated with the occurrence of high affinity adsorption (or the adsorption in the Stern layer). In the cases where high affinity adsorption occurs, the negative charges at the surface are satisfied by the ions present in the Stern layer, with less ions required in the Gouy diffuse layer (GDL) to provide electrical equilibrium. As a consequence, a collapse of the DDL occurs; therefore the potential in between particles to be overcome by the percolating fluid is lower, which facilitates the flow of the solution leading to the measurement of higher k values.

During a compatibility study described by Yong et al. (1991) and Yong and Cabral (1992), permeability tests were performed with compacted samples of a sand/bentonite mixture and concentrated solutions of lead and zinc. In the present study, the Boltzmann equation and the Gibbs free energy of the system are resorted to explain, respectively, 1) how the higher k-value for the zinc test can be associated with high affinity adsorption in the Stern layer and 2) the higher mobility, or lower selectivity of zinc ions to the bentonite surfaces.

Property	Sand/Bentonite (90%/10%)
Liquid Limit (LL)	355% (bentonite)
LL w/ 500 ppm Pb-sol	328% (bentonite)
Plastic Limit (PL)	55% (bentonite)
Unified soil classif.	СН
Specific gravity	2.66
Proctor Maximum dry density (kN/m <sup>3</sup> )	17.2
Optimum moisture content	16.0%
% clay size material (ASTM)	10.0%
Specific surface area (m <sup>2</sup> /g)	855 (Alammawi, 1988) (for bentonite only)
Diam. of sand grains (mm)	0.06 - 0.6

Table 1 - Geotechnical and Physical Properties of the Sand/Bentonite (90% / 10%)

### MATERIALS AND METHODS

The material tested was a mixture of 10% Na-bentonite and 90% fine to medium sand (Silica 40) containing negligible amounts of fines. The geotechnical properties of this soil are presented in Table 1, and the chemical properties in Table 2. X-ray diffraction analysis indicated that trace amounts of feldspar and mica were present in the bentonite obtained from Avonlea Minerals Ind. of Saskatchewan.

Property	Bentonite
soil pH (range of 3 tests)	8.6-8.8
Cation Exchange Capacity (meq/100g) :	109.0
Na*	63.7
к.	1.9
Ca	35.7
Mgʻʻ	7.5
% by mass of:	
carbonate content	0.00
organic content (Galvez, 1989)	0.00

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Table 2 - Chemical Properties of the Sand/Bentonite Mixture

Concentrated solutions of lead and zinc were used as permeants. A 2500 ppm lead solution was prepared by mixing distilled water and lead nitrate  $(Pb(NO_y)_2)$ , whereas zinc sulphate  $(ZnSO_{\bullet}, 7H_2O)$  was used to prepare a 2000 ppm zinc solution.

For this experimental program, a standard triaxial cell was modified into a flexible wall permeameter. In order to obtain a better dispersivity of the soil particles and good reproducibility, samples were statically compacted 2 % wet of the Proctor optimum (Dunn and Mitchell, 1984) into an 80 cm<sup>3</sup> compaction mold. The maximum dry density and optimum moisture content of the mixture is indicated in Table 1.

Samples were saturated by application of back pressure (BP) in steps of 34 kPa. Since the intervals between steps were long (overnight after the  $3^{rd}$  step), good equilibration of pore pressure was obtained, resulting in low final BP's (170 kPa for the Zn test and 200 kPa for the Pb test). Samples were tested under an initial hydraulic gradient of 25. The two burettes "in" and "out" were monitored to ensure that the inflow and outflow rates were equal. The pressure levels were controlled throughout the duration of the tests, with chamber pressures (triaxial cell) always kept 13.6 Kpa ( $\approx 2$  psi) higher than the pressure applied to the inlet burette. This helped maintaining the seal between the sample and the membrane and was sufficient to prevent swelling of the samples; measurements taken after their extrusion did not indicate any change in sample dimensions. This level of confining pressure does not seem to influence the measured value of the coefficient of hydraulic permeability (Boynton, 1983; in Daniel et al., 1985). The leachate in the burette "out" was collected at various intervals.

Following permeability testing, the compatibility study continued with the chemical analyses of the samples and of the leachate collected. The soil samples were washed two times with distilled water in order to recover the contaminant from the pore



Figure 1 - Variation of the coefficient of hydraulic conductivity of S/B percolated with Zn and Pb solutions in the triaxial cell

solution. The heavy metal cations adsorbed on the clay surface (*Pb* or Zn), and the remaining exchangeable cations (*Na*, *Ca*, *K*, *Mg*, and *Al*) were recovered by mixing the soil with a concentrated solution of ammonium acetate, which had its pH adjusted to 3.6. The mixture was left to shake, centrifuging followed, and the supernatant was collected in plastic bottles. This was repeated three times in order to optimize the exchange of ammonium ions for the cations of interest, the concentrations of which were measured by AAS. The concentrations of *Pb* and *Zn* in the effluent collected were also measured by AAS. Further details concerning the experimental procedures can be found in Yong et al. (1991) and Yong and Cabral (1992).

### RESULTS

As shown in Figure 1, the k value obtained for the Zn ( $k_{Zn} = 3.4 \times 10^{-6} \text{ cm/s}$ ) test is one order of magnitude higher than the k calculated for the Pb test ( $k_{Pb} = 4.5 \times 10^{-7} \text{ cm/s}$ ). In order to confirm the results, the Zn test was repeated following the same steps; a total of 4.1 pore volumes (pv) were percolated and the stabilized k was 5.7 x  $10^{-6} \text{ cm/s}$ . Other tests using Pb solutions as permeant confirmed the results presented in Figure 1 (Yong and Cabral, 1992; Yong et al., 1991).

Since most conditions involving the two tests presented in Figure 1 were practically the same, the higher permeability of S/B samples to concentrated Zn solutions can be interpreted as being a result of the adsorption of a greater proportion of Zn ions - as compared to Pb ions - very close to the bentonite surfaces, in the Stern layer (high

affinity adsorption). The occurrence of high affinity adsorption can be partly explained using the Boltzmann equation, which can be written in the following way:

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$$C_{1} = C_{2} \exp\{\frac{(E_{2} - E_{1})}{kT}\}$$
 (1)

where:

 $C_1 \equiv \text{concentration of cations in the inner Helmholtz plane (ions/m<sup>3</sup>);}$   $C_2 \equiv \text{concentration of cations in the outer Helmholtz plane<sup>(1)</sup> (ions/m<sup>3</sup>);}$   $k \equiv \text{Boltzmann constant (1.38 x 10<sup>-16</sup> erg/°K);}$   $T \equiv \text{temperature (°K);}$  kT = 0.4 x 10<sup>-20</sup> J/ion at 20°C; and $E_1, E_2 \equiv \text{the potential energies of the ions in the two planes.}$ 

(1) Note : According to Grahame (1947), the outer Helmholtz plane defines the outer boundary of the Stern layer, where the Gouy distribution of ions begins.

Alammawi (1988) calculated the difference  $(E_2 - E_1)$  for several elements, including *Pb* and *Zn*. According to his results,  $(E_2 - E_1)$  was greater for *Zn* than for *Pb*. It can be seen from the Boltzmann equation that the greater the potential energy difference, the greater the number of ions in the inner part of the Stern layer  $(C_1)$ , i.e., the inner Helmholtz plane (IHP). As stated before, this means that, out of the total quantity of cations adsorbed, more are adsorbed close to the particle surface, in the Stern layer (high affinity adsorption), and less are in the Gouy's diffuse layer of ions (low affinity adsorption), therefore leading to a DDL collapse.

Based on evidence presented by Elrashidi and O'Connor (1982), it is unlikely that the nature of the ligand, who compete with the charged surfaces for the soluble Zn (complex formation), cause measurable changes in Zn adsorption when the metal is associated with 0.005 to 0.1 M solutions of  $Cl^-$ ,  $NO_J^-$ , or  $SO_A^-$ . A 0.1 M solution of  $SO_A^+$  is equivalent to 9600 ppm, which is a much higher concentration of this ligand than the one used in this study.

Upon termination of permeability testing, chemical analyses were performed with the soil samples and the leachate collected. With the concentrations of Pb and Zn in the leachate collected, breakthrough curves were drawn. These curves are presented in Figure 2. They show very clearly that, for tests with similar characteristics, Zn ions were detected in the outflow much earlier than Pb. This can be associated mainly with the lower selectivity (or higher mobility) of Zn as compared to Pb for most clays and oxides, at various system pH (Farrah and Pickering, 1976, 1977, 1978; Phadungchewit, 1990). It is important to precise here that selectivity should not be confused with high affinity adsorption. Selectivity is however directly proportional to the total amount retained in both the Stern and Gouy layers.



Figure 2 - Breakthrough curves of the two ions investigated.

The fact that ionic Zn is more mobile than ionic Pb can be explained in terms of the greater activity of Zn and based on the standard Gibbs free energy ( $\Delta G^\circ$ ) of the system, defined as (Sawyer and McCarty, 1978; Bohn et al., 1985):

$$\Delta G^{\circ} = -RT \ln K$$
 (2)

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where:

R ≡ universal gas constant;
 T ≡ absolute temperature in °K; and
 K ≡ equilibrium constant of the reaction describing the exchange phenomena.

The negative sign means that energy is released and the system becomes more stable. The higher the absolute value, the more 'spontaneous' is the reaction (Bohn et al., 1985). If only ionized or ionizable species are involved, and assuming that only two cations are involved in the process, the exchange reaction can be written as (adapted from Schweich and Sardin, 1986):

$$wHM^{**} + 2EC^{**} - clay \rightleftharpoons 2EC^{**} + wHM^{**} - clay$$
(3)

where:  $HM^{**} \equiv \text{divalent heavy metal } (Pb \text{ or } Zn); \text{ and}$ EC = exchangeable cation of valence w. Considering the exchange of  $Pb^{++}$  (or  $Zn^{++}$ ) for  $Na^{+}$ , the equation constant (K) may be described as (Krishnamoorthy and Overstreet, 1949):

$$K = \frac{[Pb^{**}]_{ads} (Na^{*})^2}{(Pb^{**})_{ads} [Na^{*}]^2}$$
(4)

in which the brackets refer to the concentrations present in the exchange phase (adsorbed) as exchangeable ions, and the parenthesis denote the activities of the ions in the equilibrium solution. According to Schweich and Sardin (1986), the equilibrium law associated with the reaction given by Equation (3) is described by the selectivity coefficient **D**. Thus, Equation (2) can be written as follows:

$$\Delta G^{\circ} = -RT \ln D \tag{5}$$

Since the selectivity of Pb is higher than that of Zn (Farrah and Pickering, 1978; Phadungchewit, 1990):

$$\Delta G^{\circ}_{Po} < \Delta G^{\circ}_{Zo}$$
 or  $|\Delta G^{\circ}_{Po}| > |\Delta G^{\circ}_{Zo}|$ 

A positive variation of the free energy can be also related to the activity (a) of the solute according to Equation (6):

$$\Delta G = RT \ln a \tag{6}$$

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Thus,  $\mathbf{a}_{2n} > \mathbf{a}_{Pb}$  or  $(2n)_{sol} > (Pb)_{sol}$ .

Comparing the selectivity coefficients of Pb and Zn:

$$D_{Ib} = \frac{[Pb] (Na)^{2}}{(Pb) [Na]^{2}} > D_{2a} = \frac{[2n] (Na)^{2}}{(Pb) [Na]^{2}}$$
(7)

and given that the exchangeable system is the same:

$$D_{Pb} = \frac{[Pb]_{adi}}{(Pb)_{iol}} > D_{Zh} = \frac{[Zn]_{adi}}{(Zn)_{iol}}$$
(8)

It can be seen that the above relation will hold only if  $[Pb]_{sds} > [Zn]_{sds}$ , which corresponds to the results obtained in this research (see Table 3).

As a cross checking of the overall procedures, and to give support to the results obtained, ion mass balances were calculated for each test. As evidenced by the results presented in Table 3, the retention patterns observed for the two tests were very different; most Zn ions were identified in the leachate (68%), whereas the majority of Pb ions were recovered from the bentonite surfaces (adsorbed form).

Test (C in ppm; final C/C <sub>0</sub> ; tot # pv`s)	Pb or Zn input (g)	Pb or Zn adsorbed (g) (% tat)	Pb or Zn in pores (g) (% tot)	Pb or Zn in leachate (g) (% tot)	Total (g)	Δ
Pb-test         i = 25 $C = 2500$ $C/C_0 = 0.70$ 16.5 pv's	0.657	0.431 (61%)	0.010 (1%)	0.268 (38%)	0.709	8%
Zn-test i = 25 $C \approx 2000$ $C/C_0 = 0.79$ 13.6 pv's	0.438	0.093 (28%)	0.015 (4%)	0.232 (68%)	0.340	225

Note: Quantities in grams were obtained by adding the amounts of each individual slice (except for Pb or  $Z\pi$  input).  $\Delta$  = discrepancy between Pb or Zn input and total identified in the system.

Table 3 - Results of mass balance calculations with sand/bentonite samples tested for Pb and Zn

Results of other *Pb* tests performed by the authors (Yong and Cabral, 1992) confirmed this trend. Significant precipitation as lead nitrate -  $Pb(NO_3)_2$  - or lead hydroxide -  $Pb(OH)_2$  - have occurred due to the high pH of the bentonite (8.6 to 8.8). The precise proportions of ions in the precipitate, physisorbed, and specifically adsorbed forms were not accessed in this study; they can be evaluated experimentally using the sequential extraction technique (Yong et al., 1993).

It is important to note that the higher advective velocities associated with the Zn test (approximately ten times higher than those of the Pb test) may have had some influence on the retention characteristics of this ion. In the present case, Zn precipitates formed may be carried out of the sample into the collection burette.

The difference in amounts of Zn introduced in the system and recuperated during chemical analysis ( $\Delta = 22\%$  in Table 3) can be partly attributed to a relative inefficiency of the concentrated ammonium acetate solution to 'extract' Zn ions adsorbed in the Stern layer. It can also be attributed to experimental errors involving

the numerous dilutions necessary to obtain the degree of accuracy needed for atomic absorption analysis.

### FINAL COMMENTS

The higher k value calculated for the Zn test, as compared to the calculated  $k_{Pb}$  obtained during a test performed under similar conditions, was associated to a comparatively higher proportion of Zn high affinity adsorbed in the Stern layer. The greater mobility of Zn, as compared to Pb, was interpreted in terms of the lower selectivity of this particular ion to bentonite surfaces. The results confirm the affinity order Pb > Znobtained by Farrah and Pickering (1978), Harter (1983), among others.

In view of the results obtained and due to the very high CEC, specific surface area, and pH of bentonite, it can be postulated that adsorption as ionic species (physisorption), precipitation, and high affinity adsorption are the prevailing retention modes for Pb. This is in agreement with observations made by Harter (1983) concerning retention of Pb by montmorillonite. In the case of Zn, a less significant proportion is physisorbed (low affinity adsorption in the GDL) and, comparatively to Pb, more ions are adsorbed in the Stern layer (high affinity adsorption).

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A Technique to Improve Bottom Ash Suitability for Utilization

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### <u>Abstract</u>

Since the bottom ash residues obtained from municipal solid waste incinerators contain considerable amounts of leachable heavy metals, problems have been encountered in deciding upon final disposal scenarios based on concerns about soil and groundwater contamination. Several alternatives, other than landfilling, have been investigated for the ultimate disposal of these residues. The basic factors influencing ash utilization scenarios include concerns of environmental impacts acceptability, technical and economical feasibility, and market availability. A physical treatment process, involving magnetic removal of metal and particle separation into different sizes by sieving, has been suggested as a means for reducing the bottom ash content in heavy metals: namely, Pb, Zn, Cd, Cu, and Cr.

### Introduction

Municipal solid waste (MSW) incineration (with energy recovery) has become a widely used alternative, especially in countries where landfill areas are scarce and difficult to site. Fortunately or unfortunately, MSW incineration is considered as a potential viable alternative in any waste management plan (Black and Cunningham, 1991; Gavasci et al., 1990; Sussman, 1989).

The incineration of solid waste produces three main types of solid residues: (1) fly ash (10 to 30% by weight of total residues), which is the fine dust collected from the flue gas by emission control devices; (2) slag (around 1% of total weight); and (3) bottom ash (70 to 90% of total residue), which is the remaining heavy material residue collected at the

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bottom of the combustion chamber. Although the incineration of the MSW provides a reduction of 70 to 80% by weight, the amount of the remaining residues to be disposed of is still substantial (Hasselriis, 1988; Sawell et al., 1989).

The bottom ash component consists of a metallic and a non-metallic fraction. The non-metallic inert material has properties very similar to sand and gravel. This fact leads to considering some useful utilization scenarios of bottom ash other than landfilling, e.g., aggregate material in construction works. Hartlen and Rogbeck (1989) presented the possibility of using "ash-gravel" in road construction and abutment fills. Some implications of such a practice would be the conservation of natural aggregate and the diversion of significant volumes of "waste material" from landfill, thus extending the operating life span of the landfill and saving on the tipping fees.

However, the environmental acceptability of such a practice is still debatable and should be addressed. The overriding concerns as to the best method of solid waste combustion ash management are the content and leachability of heavy metals (e.g., lead, cadmium, copper. zinc, etc.), salts and sulfates contained in the ash and the potential public health effects that may result from improper ash management. In addition, other concerns include the presence of trace organics and inhalation of contaminants from the dust generated by the ash.

Moreover, if ash should be beneficially reused as a raw material, e.g., structural fill for road subbases or building block materials, regulatory requirements are necessary.

The scope of this paper is to present the preliminary results of a bottom ash characterization and the basic considerations for treating MSW incinerator ash residues to improve their suitability in utilization scenarios.

#### Incinerator Description

The Montreal Des Carrières incinerator started its operations in 1969. It consists of 4 parallel mass burning incinerator units designed to handle a total of 1200 tons of municipal refuse per day.

The incinerator chamber is fed by gravity via a vibrating feeder, and the refuse moves thereof to the incineration chamber via vibrating grates. To control the formation of acid gases, lime powder is directly injected at the point where the refuse is fed. The flue gases pass through a water walled/boiler economizer heat recovery chamber, enter a multicyclone unit which is followed by a 3-stage electrostatic precipitator.

All three types of ashes are conveyed to a quench tank, then transported by a drag chain through an incline and dumped in a hauling truck.

# Sampling and Testing

Since all of the ash streams are combined in the quench tank, it was not possible to obtain a separate bottom ash sample after quenching.

The samples of bottom ash were collected off the finishing grate, just prior to entering the quench tank. Thus, by doing so, it is not known whether or not quenching alters the bottom ash characteristics.

Composite samples of bottom ash were prepared and separated into different particle size fractions; namely, greater than 2 mm (i.e., retained on sieve #10), between 2 and 0.595 mm (i.e., passing sieve #10 and retained on #30), between 0.595 and 0.297 mm (i.e., passing sieve #30 and retained on #50), and less than 0.297 mm (i.e., passing sieve #50). The total amount of lead (Pb), zinc (Zn), cadmium (Cd), chromium (Cr), and copper (Cu) present in these four particle size fractions was determined using the Aqua Regia Digestion method (Walton, 1980).

To determine the metal solubility of bottom ash under non-aggressive leaching conditions, a representative unit sample of bottom ash was crushed to pass sieve #100 before being leached out with distilled water in a batch leach test. The tests were conducted in polyethylene bottles at a liquid to solid ratio (L/S) of 10, by mixing 3 g of ash with 30 mL of distilled water. The mixture was then shaken for one day on a horizontal shaker. After the mixing period, the liquid and solid phases were separated by centrifugation and by pressure filtration using 0.45  $\mu$ m membrane filters. The remaining solids were then reexposed to fresh distilled water at the same L/S ratio and the procedure was repeated for 5 cycles. At the end of the 5<sup>th</sup> cycle, the L/S was 50. The tests were performed in triplicates and the leachate samples were analyzed for pH, and chloride content. A sub-sample of eac leachate was preserved with concentrated nitric acid to be subsequently analyzed for metal content using the Flame Atomic Absorption (FAA).

The total solids content of the bottom ash was determined by sample weight loss after 24 hour period at 104°C according to ASTM method D2216-71. The fixed solids content of each ash was based upon weight loss of a dry sample placed in a 550°C muffle furnace for one hour (APHA standard method 290E).

## Results and Discussion

The particle size distribution of the Des Carrières incinerator bottom ash is shown in Figure 1 below. It can be seen from Figure 1 that the bottom ash fraction with size smaller than 2 mm does not constitute more than 20% of the total mass.

The variation of Pb, Zn, Cd. Cr, and Cu content with the particle size of bottom ash is shown in Figure 2.

In general, the bottom ash contained low concentrations (less than 100 mg/kg) of Cd



Figure 1. Particle Size Distribution of Two Bottom Ash Samples.



Figure 2. Total Metal Concentration in Four Particle Size Fractions.

and Cr, moderate concentrations of Cu, and high concentrations of Pb and Zn.

Referring to Figure 2, it is observed that an abrupt drop in metal concentrations; especially Pb, Zn and Cu, and to a lesser extent Cd, occurs when the particle size exceeds 2 mm. Indeed, the fraction of particles with size larger than 2 mm had the lowest metal content, as compared to the smaller size fractions. The highest amounts of Pb, Zn and Cu were found in the particles with sizes between 2 and 0.297 mm. However, Cr appeared to be equally distributed among all particle sizes, whereas Cd concentration increased with decreasing particle size. Moreover, not only is the total amount of heavy metals (Pb, Zn, Cu) in bottom ash particles smaller than 2 mm greater than that found in particles with larger size, but it is also more leachable (Stegemann and Schneider, 1991; Gavasci et al., 1990).

The percentages of the various heavy metals contained in the bottom ash with particle size greater and smaller than 2 mm are presented in Table 1. The results presented in Table 1 show the interdependence between the metal content of bottom ash and its particle size. It is hence obvious that the removal of the bottom ash with particle size smaller than 2 mm, which constitutes less than 20% of the total weight, would reduce the amount of Pb by as much as 130 times, the amount of Zn by 40 times, the amount of Cd by 6 to 7 times, the amount of Cr by 3 times, the amount of Cu by 80 times.

| Particle Size | Metal Content (%) |      |         |        |      |
|---------------|-------------------|------|---------|--------|------|
|               | РЪ                | Zn   | Cd      | Сг     | Cu   |
| > 2 mm        | 0.01              | 0.03 | 0.00033 | 0.0074 | 0.01 |
| < 2 mm        | 1.4               | 1.2  | 0.0022  | 0.024  | 0.8  |

Table 1. Heavy metal content of bottom ash as a function of particle size.

Based on these results, it is suggested to discard the fraction of bottom ash with size smaller than 2 mm, when it is desired to utilize the material in a construction work. By doing so, at least 80% by weight of the total bottom ash stream would be effectively utilized while the remaining portion, which constitutes no more than 20% by weight of the total stream, would be handled with the fly ash stream.

The concentrations of cations and anions were again higher in the leachate from the smallest particle size fraction, with the same applying for the pH and buffering capacity.

The total solids content of the bottom ash was greater than 99.6%, indicating that the ashes were essentially dry.

The fixed solid content, on the other hand, was greater than 97%, indicating that the non-combusted carbon and volatile organic content of the bottom ash, reported as loss of

weight on ignition (LOI) was less than 3%.

The analyses of the extracted fluids obtained from the batch leaching test at the end of each cycle, were as follows:

- The pH of the leachate remained alkaline throughout the test. It decreased from 12.12, after cycle 1, to 11.38, at the end of cycle 5.

- The chloride dissolution was observed to occur during the first and second cycles. This fact was of course expected since, even under alkaline conditions, chlorides are known to readily dissociate in water.

- The average cumulative fractions of each metal leached out at the end of the fifth cycle were determined by dividing the mass of the contaminant measured in the leachate to the mass of that contaminant in the original sample, expressed as a percentage. Typically, less than 0.25% of Zn, less than 5.3% of Pb, and less than 1.7% of Cu were leached out during the test. It was noted that the amount of Pb and Zn leached out decreased from cycle 1 to cycle 5, i.e., decreased as the pH of the ash decreased from 12.12 to 11.38, indicating therefore the amphoteric nature of the metals. Hence, the pH (and redox potential) environment is an important parameter in that respect.

What has been presented indicates the advantage of removing the fraction of bottom ash with particle size smaller than 2 mm. Moreover, the fraction of the ash with particle size greater than 2 mm could be subjected to a process where the metallic fraction would be magnetically removed. The cost associated with this "physical treatment technique" should be minimal especially when compared to an electro-chemical treatment technique. Legiec et al. (1988) and Vehlow et al. (1989) have presented the technical possibility of operating a continuous process for heavy metal removal. The extraction studies presented by Legiec et al. (1988) revealed information on the leaching characteristics of the ashes and on the ability of some extraction solutions to separate these metals from the ash matrix. The electrochemical plating techniques was then utilized to recover the metals, in a relatively pure form, from the extraction solution. Although the results were promising, the cost of implementing such a technique on a full-scale basis, without mentioning the operating problems that are likely to occur, has yet to be addressed, and since the amount of metals present in the bottom ash is much less than that found in the fly ash, such a technique would not be warranted for bottom ash conditioning.

Thus, the preferred approach for improving the suitability of MSW incinerator bottom ash in utilization scenarios is to separate the fractions with size smaller than 2 mm.

## Conclusion and Recommendations

In order to conserve natural aggregates and reduce, or eliminate, the cost associated with MSW incinerator bottom ash disposal, it is strongly recommended to make use of this "aggregate-like" material in construction use. However, the content and leachability of some heavy metals, especially lead and zinc, present in these ashes raised concern about adverse potential effects that accompany any utilization scenario. Considering the amount of bottom ash, an expensive and laborious treatment technique, such as metal recovery by electrochemical treatment processes will not be advantageous if compared to a process which involves the magnetic removal of the bottom ash metallic fraction and its segregation into two different fractions; namely, the fraction with size greater than 2 mm and the fraction with size smaller than 2 mm.

Preliminary study showed that the fraction of bottom ash with size greater than 2 mm, which consists of around 80% by weight of the total amount; contains a much smaller level of heavy metals which are also less leachable than those contained in the fraction with size smaller than 2 mm.

It is therefore suggested to magnetically remove the metallic fraction from the ash and to discard the fraction with size smaller than 2 mm (less than 20% of total weight), while retaining the remaining part for constructive utilization.

Since the characteristics of solid waste can vary substantially over short periods of time (based upon the nature of the waste burned and the incinerator operating parameters), the remaining residue, i.e., the ash, is very heterogeneous. Consequently, in order to provide statistically valid results which will present a basis for assessing the environmental acceptability of a given ash utilization scenario, it is necessary to take daily samples on an hourly basis over a long time period (e.g., a year) and correlate the results of the ash characterization (which affect the short and long-term behaviour of the ash in the environment) with the quality of the influent waste and the operating parameters of the incinerator.

There is a need to develop some reliable and reproducible laboratory tests to predict leachate characteristics at the site where the ash is utilized in one way or another.

It is essential that the ash residue streams be handled in a well-designed closed-system to prevent the generation of fugitive air borne dust.

At this point in time, and before starting to utilize bottom ash on a large scale, it is recommended to wait for additional research and guidelines to regulate bottom ash utilization scenarios, in order not to endanger the public health nor the environment.

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