INRS - GÉORESSOURCES

CENTRE DE RECHERCHES MINÉRALES

DEVELOPMENT OF A TREATMENT PROCESS FOR CONTAMINATED SEDIMENT USING MINERAL PROCESSING TECHNOLOGIES

EXECUTIVE SUMMARY

PRESENTED TO

ENVIRONMENT CANADA (QUÉBEC REGION)
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MANAGEMENT PERSPECTIVE

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Technology Demonstration Program

Environmental Protection

EXECUTIVE SUMMARY

Development of a Treatment Process for Contaminated Sediment Using Mineral Processing Technologies [1]

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[1]Bergeron M., St-Laurent H., Blackburn D. et Gosselin A. (1997). *Développement d'un procédé de traitement de sédiments contaminés par utilisation de technologies minéralurgiques.* Rapport préparé par l'INRS-Géoressources et le Centre de Recherches Minérales pour Verreault Navigation et Environnement Canada. 118 p. et annexes I à XVI.

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1. Introduction

Transportation of merchandise and industrial activity in port zones and along waterways often results in sediment contamination. A great number of contaminated sites in port zones have already been identified and characterized by Canadian governmental agencies. In general, two categories of contaminants have been identified. The first category, is comprised of organic compounds, here designated as petroleum hydrocarbons: the second includes metallic contaminants.

Continual access of ships to the wharves requires regular dredging of port sediment. Surpassing the Toxic Effect Level (TEL[2]) involves an obligation for treatment of contaminated sediment or safe confinement.

The main objective of this project was to develop a low cost and efficient treatment process applicable to river and port sediments contaminated by organic and inorganic compounds. The process was mainly developed using, as contaminated sediment samples, material (more than 5 metric tons) sampled from a particular sector of the Montreal port zone.

The proposed approach consists of considering the contaminated sediments as a low content ore. It is, therefore, necessary to use recuperation techniques which are economical and effective. The physical approaches of the mineral treatment combining gravimetric methods and flotation technologies seem pertinent. It was a question, therefore, of assessing to what extent the existing technologies could be used to decontaminate the sediments containing levels which would be considered low in the case of mining operations.

The possibility of returning the processed sediments to free water was not considered. More specifically, the aim was to reach a restoration objective which would allow an optimal ratio between treatment costs and low disposal costs of the treated sediments on land.

[2] Centre Saint-Laurent, (1992) *Interim Criteria Quality Assessment of the Saint Lawrence River Sediment.* Environment Canada and the Quebec Ministry of the Environment ISBM 0-662-19849-2

To reach the objective, the following steps have been carried out:

1. Sampling of contaminated sediments;
2. Physicochemical and mineralogical characterization of the contaminated sediments sampled;
3. Elaboration of preliminary treatments;
4. Perfecting, assessment of a treatment procedure diagram and realization of a technico-economic study for a section of the Montreal port zone.

Two sites were sampled and characterized, one located in the Quebec port zone, the other in the Montreal port zone. In both sites the concentrations of various contaminants are a lot higher than the interim criteria: the toxic effect level (TEL) for the assessment of Saint-Lawrence sediment quality defined by Environment Canada and the Quebec Ministry of the Environment and Wildlife. For both zones sampled, the restoration objective was to obtain contamination levels below those of the Quebec Ministry of the Environment and Wildlife's C[3] criteria. This restoration objective appears optimal in regards to the treatment/disposal cost ratio.

2. Characterization

2.1 Quebec port zone

The concentrations of organic compounds for the Quebec port zone are lower than the toxic effect level (TEL). Inorganic compound analyses reveal heavy copper, zinc and cadmium contamination (levels which are respectively 8, 16 and 13 times higher than TEL) for the lot-1 and lot-2 samples of the Quebec port zone. Chrome contamination is also present. Occasionally nickel, lead and arsenic contamination were found according to the size fraction. All the metallic minerals are free and potentially recoupable. That is, the metals are present as distinct mineralogical phases which are not included within other compounds. Therefore, they can be separated from the mineralogical matrix using the appropriate technology. Approximately 40% of the sampled material is inferior to 45µm. Table 1 presents the C criteria of the MEF Contaminated Land Rehabilitation Policy, the TEL and the contamination level of sediments studied.

[3] Ministry of the Environment and Wildlife, (1996) Rehabilitation Policy for Contaminated Land. Industrial sector policy administration of the Ministry of the Environment and Wildlife. Contaminated land, ISSN 1204-2072-, ISBN 2-551-16878-3

2.2 Montreal port zone

In the sampled section of the Montreal port zone, 24,000 ppm of petroleum hydrocarbons (7 times the C criteria) were found. Samples are heavily contaminated with copper (53 times the TEL), chrome (9 times) arsenic (6 times) and nickel (6 times). Lead, mercury, zinc, cadmium and phenantrene contamination are also present according to the granulometry. All metallic minerals are free and potentially recoupable. More than 60% of the sampled material is inferior to 45 µm. Table 1 presents the contamination level of sediments studied, based on C criteria.

Table 1: C criteria level limits of the MEF Contaminated Land Rehabilitation Policy, the TEL and the contamination currently present in the sediments of Montreal and Quebec port zones.

	TEL (ppm) °	C criteria (ppm)°	Quebec harbour (ppm)*	Montreal harbour (ppm)*
Silver (Ag)		40	< 5	33
Arsenic (As)	17	**50**	14	**90**
Barium (Ba)		**2000**	493	**2135**
Cadmium (Cd)	3	20	15	6
Cobalt (Co)		300	12	15
Chrome (Cr)	100	800	134	602
Copper (Cu)	86	**500**	**557**	**2352**
Tin (Sn)		300	n.m.	< 10
Mercury (Hg)	1	10	0.3	1.23
Molybdenum (Mo)		40	< 5	<5
Nickel (Ni)	61	500	57	145
Lead (Pb)	170	1000	67	110
Selenium (Se)		**10**	< 2	**115**
Zinc (Zn)	540	**1500**	**2252**	646
Petroleum hydrocarbons C_{10} to C_{50}		**3500**	370	**24 000**

° extractable

*all these analyses represent total concentrations

- zinc and copper levels of the Quebec port zone surpass the C criteria

- the petroleum hydrocarbon, selenium, copper, barium and arsenic levels surpass the C criteria for the Montreal port zone.

3. Development of treatment procedures

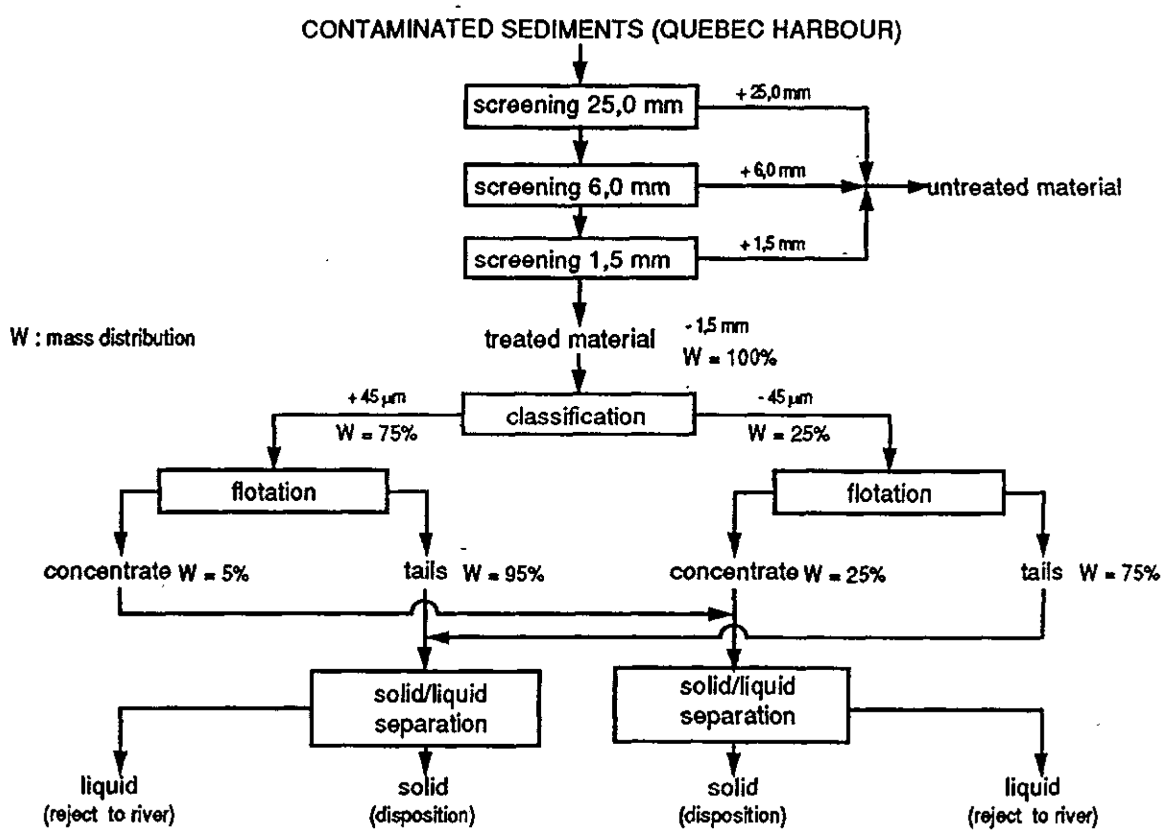
The treatment trials were aimed at 2 main objectives:

1. The elaboration of a preliminary process diagram applicable to the Quebec port zone.
2. The development, optimization and verification at the pilot level, of a process diagram applicable to the Montreal port zone; for this case, the treatment objective was fixed in the obtention of treated sediment containing contaminant levels inferior to C criteria.

3.1 Quebec port zone

A preliminary treatment diagram applicable to the Quebec port zone is presented in figure 1. The principal treatment steps involved are:

1. sieving of the sediment on a series of three sieves; the first sieve serving to protect the equipment from eventual breakage provoked by the presence of blocks or consolidated material; the two other sieves are used to remove non-contaminated coarse fractions;
2. cyclone classification of the sediment into two fractions, one being composed of particles having a diameter inferior to 45 µm, the other of particles superior to 45 µm;
3. flotation (cells or columns) of the two currents; this step enables the recuperation of metallic contaminants; based on the quantities of fines, floatation cells or columns can be used; for the moment, it is not possible to precisely choose the flotation equipment without supplementary work;
4. the solid/liquid separation of products obtained by using filter belts.



PRELIMINARY PROCESS DIAGRAM: CONTAMINATED SEDIMENTS TREATMENT (QUEBEC HARBOUR)

INRS-GÉORESSOURCES AND THE CENTRE DE RECHERCHES MINÉRALES
in collaboration with Verreault Navigation inc. and Environment Canada

Figure 1 : Preliminary treatment process diagram, Quebec harbour zone

3.1.1 Treatment results, Quebec port zone

After treatment, the zinc levels (contaminants present at the beginning having concentrations superior to C criteria were zinc and copper) were reduced from 2252 to 620 ppm while those of copper dropped from 557 to 140 ppm for respective removals of 73% and 75%. Two types of products were obtained after treatment: a treated sediment in which the contamination levels were below the C criteria and a metallic concentrate. The treated sediment can be disposed of at a modest cost (5$/Tm) in a specialized site.

The metallic concentrate obtained from the procedure can be revalued. Levels higher than 15% Zn have been found in the concentrate obtained. These levels are normally acceptable by a smelter. The next step is to produce, on an industrial scale, a sample which is representative of the zone to be treated (a concentrate) of several kilograms. The sub-samples of this concentrate will be sent to different potential buyers for final assessment. Currently it is not possible to pursue this potential development process due to a lack of a sufficient quantity of material.

The procedure could technically reach decontamination levels below TEL (allowing then, disposal in an aquatic environment) and below the B criteria (allowing then, unrestricted disposal in a land environment).

3.2 Montreal port zone

A summary presentation of the procedure is given in figure 2. A hypothetical supply of $50m^3/h$ is proposed. First, the sediments are directed towards a series of three sieves which are used to remove non-contaminated coarse fractions. The first two sieves (2.5 and 0.6 cm) are used to protect the equipment. The procedure has not been designed to treat material having a diameter larger than 6mm. The fineness of the third sieve, currently fixed at 1.7 mm, could vary based on the results of an on-site technological demonstration. The function of the third sieve is to avoid treating uncontaminated material.

We suggest, as a hypothesis, that the material larger than 1.7 mm is not contaminated. It may be possible to find uncontaminated material smaller than 1.7 mm. In the event that this hypothesis is proven, the size of the third sieve will be adapted to the feed, that is, reduced.

The uncontaminated material is received into a container to eventually be disposed of at low cost in a sanitary landfill site (Montreal, Miron quarry). The sifted sediment (passing through the sifter) is then directed to the equipments that removes the organic contaminants. The sieved sediment is directed towards a surge tank allowing for the regularizing of the pulp flowrate (figure 3). From this tank, the sediment is sent to equipments enabling the removal of organic contaminants, being in the case of sector 103 of the Montreal port zone, petroleum hydrocarbons. These equipments consist of an attrition cell linked to a flotation unit (conditioner and column). The attrition cell enables, after addition of appropriate chemical agents, the removal of the petroleum hydrocarbons adsorbed on the surface of sedimentary particles. Conventional mechanical attriters allow for the partial removal of petroleum hydrocarbons from solid particles. The procedure diagram details the use of conventional attriters.

The mixture, including free petroleum hydrocarbons and the sediment, is then directed to the conditioner. At this stage, a collector and a foaming agent are added. The separation of petroleum hydrocarbons present in the mixture is carried out in a flotation column. The organic concentrate obtained at the top of the column, is sent to a decanter and a band filter. At the base of the column is found the partially decontaminated sediment. This is then sent to complementary equipments which allow the final removal of organics.

At this stage of the treatment, the majority of petroleum hydrocarbons have been removed from the contaminated sediment. The next step consists of removing metallic contaminants. To do this, the sediment is first classified, and then sent to metallic contaminants recuperation equipments (figure 2).

The removal of metallic contaminants is easier to carry out when the solid particles have been previously classified according to size (fine ones on one side, large ones on the other). A series of cyclones is used to carry out this work. The cyclones allow the classification of the sediment into two fractions, one inferior to 20 microns, the other larger than 20 microns.

After the classification step, the two currents of sediment are directed by means of independent circuits to flotation units. At this point, appropriate collectors and foaming agents are added at the conditioning step. The metallic contaminants are isolated from the sedimentary matrix in a flotation column. The metallic concentrate obtained at the top part of the flotation column is then filtered on a filter belt.

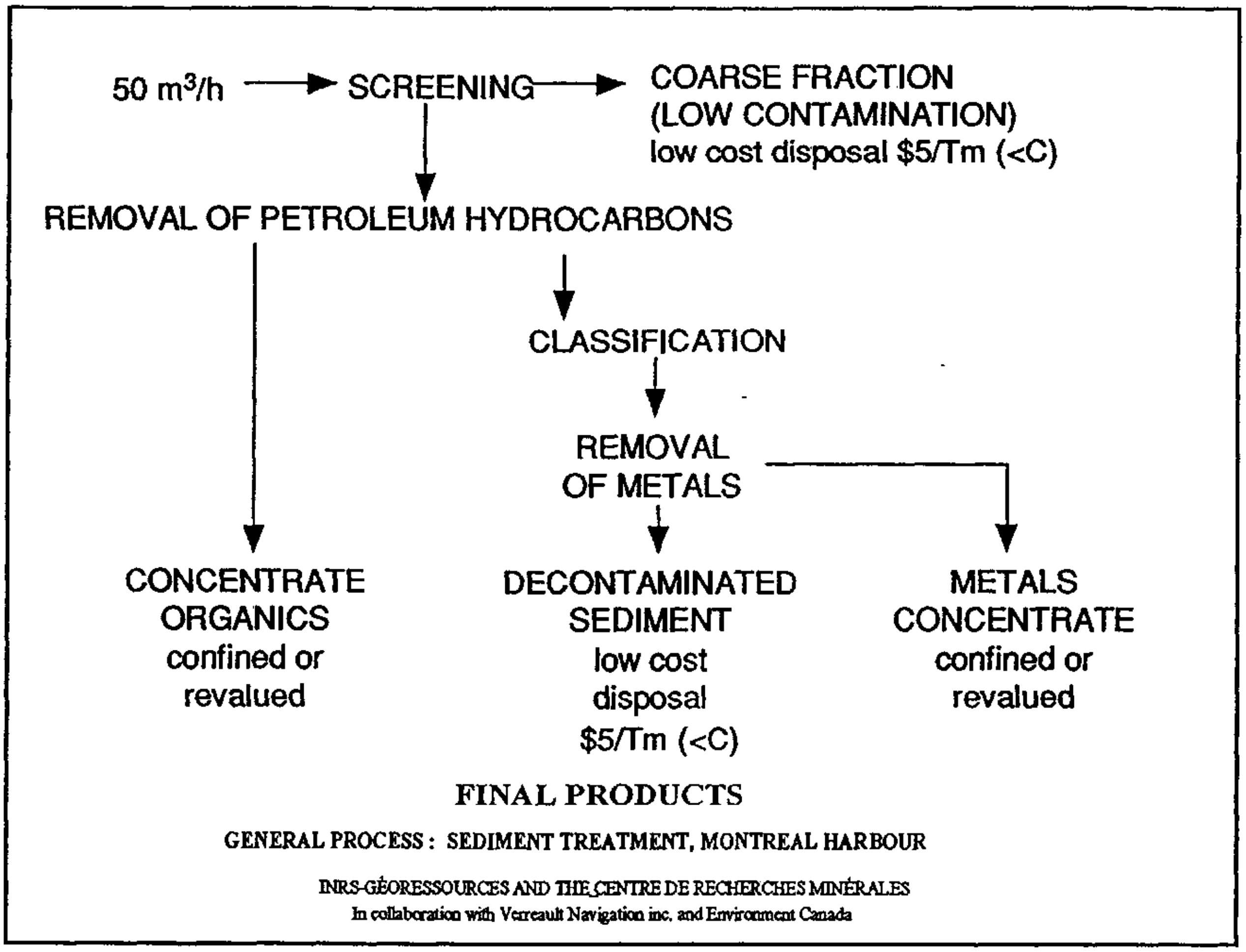


Figure 2 : General treatment process : Montreal port zone

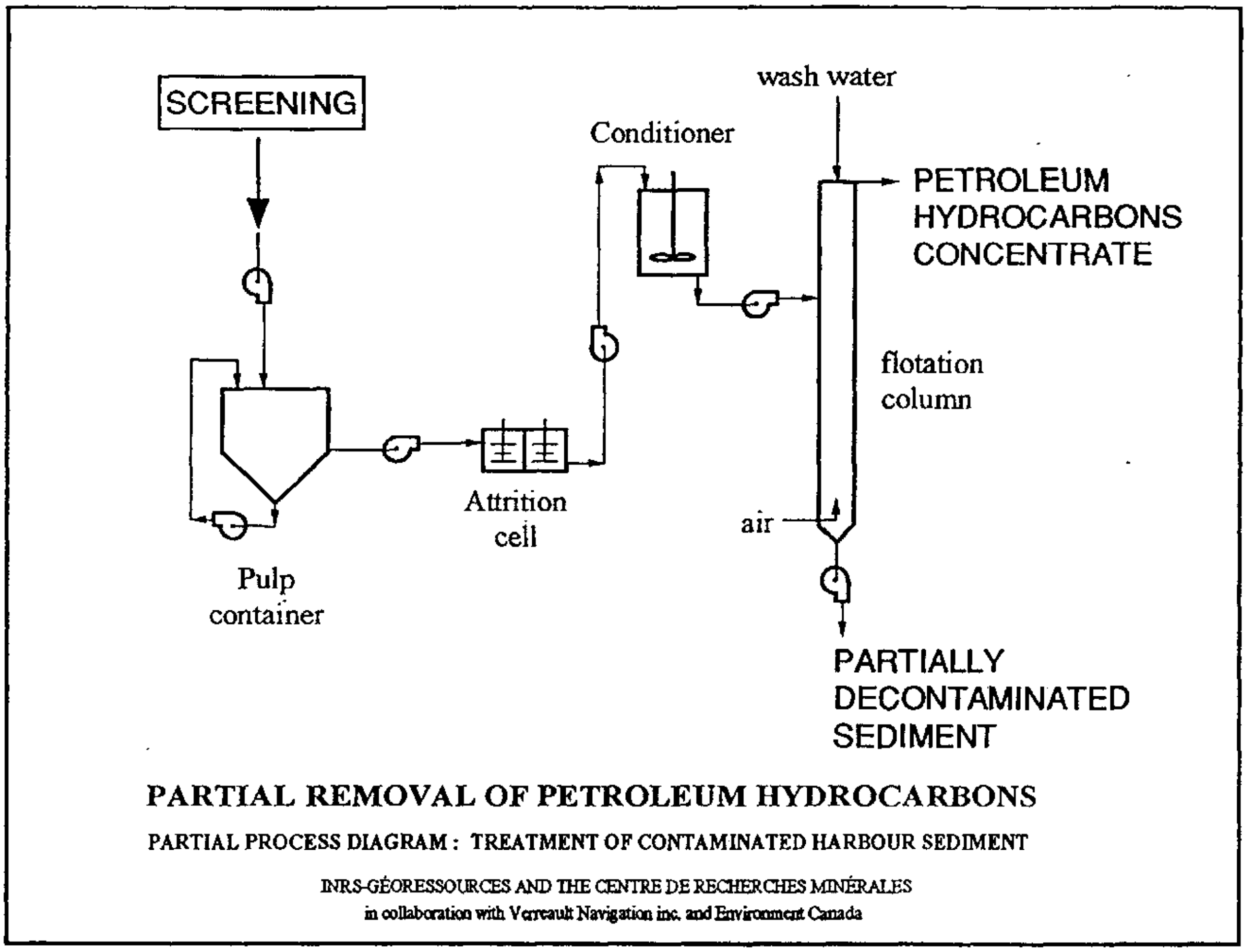


Figure 3 : Partial removal of petroleum hydrocarbons, Montreal port zone

As with the petroleum hydrocarbon flotation, the partially decontaminated sediment is found at the base of the column. This is then sent to complementary equipments (not presented) which finalize the metallic contaminant removal. The last step of the treatment involves the filtering of the sediment through a band filter. The levels of contaminants in the treated sediment are under the ones defined by the C criteria.

3.2.1 Treatment results, Montreal port zone

The results of the optimal trials are presented in table 2. The procedure enables the metal and organic compound levels to be lowered below C criteria. For the petroleum hydrocarbons, of which pre-treatment levels are 24,000 ppm, the flotation treatment lowers their value to 2500 ppm, (percentage of removal, 89%). The inorganic compounds present removal percentages of 54% for Ba, 56% for As, 79% for Cu and 99% for Se.

Table 2 : Metal contaminants and organic concentrations for TEL, criteria B criteria C and concentration of contaminants before and after treatment, Montreal port zone.

Parameters	**TEL**	**Montreal port zone**	**Criteria B**	**Objectif**	**Montreal port zone**	**Removal**
	(ppm)	**before (ppm)***	**(ppm)**	**Criteria C**	**end (ppm)+**	**% ++**
Silver (Ag)		33	20	40	20	
Arsenic (As)	17	90	30	50	40	56%
Barium (Ba)		2135	500	2000	980	54%
Cadmium (Cd)	3	6	5	20	4.5	
Cobalt (Co)		15	50	300	n.m.	
Chrome (Cr)	100	602	250	800	434	
Copper (Cu)	86	2352	100	500	490	79%
Tin (Sn)		< 10	50	300	< 10	
Mercury (Hg)	1	1.23	2	10	1	
Molybdenum (Mo)		< 5	10	40	< 5	
Nickel (Ni)	61	145	100	500	142	
lead (Pb)	170	110	500	1000	108	
Selenium (Se)		115	3	10	< 1	99%
Zinc (Zn)	540	646	500	1500	442	
PCB	1	< 0,5	1	10	n.m.	
C10 to C50		24 000	700	3500	2500	90%
(petroleum hydrocarbons)						

n.m.: not-measured

*: represents total concentrations

+: Value obtained by combination of the results according to grain-sizes distribution

++: % of removal were calculated only for contaminants showing initial concentrations above criteria C

The treated sediments have contaminant levels inferior to C criteria, which allows them to be disposed of at low cost. The contemplated scenario for disposal of the decontaminated sediments requires filtering the treated sediments (in order to make them "pellatable") and transporting them to the Miron quarry, a landfill facility.

Presently, we anticipate dispatching the petroleum hydrocarbon concentrates to a specialized recuperator after the filtration step. This would serve to limit the volume of concentrate. Potential revalue of the concentrate is being considered.

For the Montreal port zone, interesting levels of Au, Ag and Cu are present in the metallic concentrates. The highest levels found in the concentrates are 1.5% Cu, 4g/t Au. 120g/t Ag. These levels are normally treatable, according to the regulations in effect in the mining industry, by a concentrator (flotation plant). This concentrate can also be dispatched to a foundry (smelter). In both cases, the next step is the production, on an industrial scale, of a representative sample of the zone to be treated (a concentrate) of several hundred kilograms.

3.2.2 Costs of treatment, Montreal port zone

The global operating costs of a treatment unit (including treatment equipment rental, dredging, treatment and disposal and/or enhancement of treated material and metallic or petroleum hydrocarbon concentrates) can vary between $55/t to $220/t depending on the volume to be treated (table 3).

As demonstrated in table 3, these costs are comparable to those reported in the literature, notably those incurred with the Bergmann commercial treatment technology applicable to contaminated soil and sediments, a treatment which was developed using mineral processing equipments. The efficiency of the Bergmann technology was demonstrated within the context of several sediment treatment projects, both in Europe and North America. The estimated costs of application of the Bergmann technology treatment procedure, which was prepared by the US-EPA Superfund Innovative Technology Evaluation (SITE) Program, have been taken from the Remediation Guidance Document (ARCS) Program[4]. The Bergmann technology does not apply to treatment of sediment containing more than 30% of material inferior to 45 microns (Traver, 1996)[5]. The section studied in the Montreal port zone is comprised of sediments of which 60% present particle diameters inferior to 45 microns and for which, a priori, the Bergmann treatment is not applicable.

[4] U.S. Environmental Portection Agency. 1994. "ARCS Remediation guidance document" EPA 905-B94-003. Great Lakes National Program Office, Chicago, Il.
[5] Traver R.P. (1996). *Conditioning sediment and soil for site remediation.* Presentation at cleaning contaminated sediment. Bergmann USA.

Table 3. Cost estimates based on volumes of sediment to be treated

Volume	Total costs	
	$ Can/mT	
metric ton	Bergmann	INRS/CRM
14 560	225 $	220 $
45 000	185 $ [(a)]	160 $
89 180	120 $	100 $
222 950	85 $	70 $
1 490 580	60 $	55 $

(a) estimate obtained by a graphical interpolation

As with most treatment technologies, operating costs vary mainly according to:

1. type of contaminants present (organic, inorganic or mixed contaminants)
2. level of contamination
3. volume to be treated as well as type of matrix
4. criteria of desired restoration
5. methods of disposal or treatment of metallic or petroleum hydrocarbon concentrates obtained during treatment

The preceding costs are presented as examples and will be valided only after carrying out a technological demonstration project on land bearing on the whole treatment procedure, from dredging the sediments to treatment and disposal, or enhancement, of the waste and treated sediments.

4. Conclusions and recommendations

Certain sectors of the Montreal and Quebec port zones are contaminated beyond the toxic effect level (TEL). Samples collected from a section of the Quebec port zone are contaminated with metals. The copper, zinc and cadmium contamination are respectively 8, 13 and 16 times higher than the TEL. These contaminants are distributed in all grain-size fractions examined (<12 µm < 45µm <75 µm <150µm >150 µm). Less significant contamination of nickel, chrome, lead and arsenic are also present according to the grain-size distribution. Nearly 35% of the mass of these sediments have a diameter inferior to 45 µm.

Sediments taken from a section of the Montreal port zone are strongly contaminated by metals and petroleum hydrocarbons. The metallic contaminants for all the examined grain-size fractions

(<12 µm <45 µm <75µm <150 µm >150 µm), are copper, chrome, arsenic and nickel which present levels, respectively of 53, 9, 6 and 3 times higher than the TEL. More than 60% (in mass) of these sediments have a diameter less than 45 µm. All the inorganic contaminants are free and can be recovered by mineralogical procedures.

The treatment trials of these contaminated sediments have been carried out using mineral processing technology. Given the important presence of fine particles in the samples (45µm) the trials have been particularly aimed at the use of technologies adapted to the treatment of fines. These technologies being Mozley Inc.'s multiple gravity separator (MGS) and flotation technologies (cells and columns)

In regards to the contaminated sediments in the Quebec port zone, the trials with the MGS and the flotation equipments result in reaching levels below C criteria. A preliminary treatment diagram elaborated using flotation equipments has been proposed. The flotation trials indicate that zinc levels dropped from 2252 ppm (before treatment) to 620 ppm (after treatment) which corresponds to a 73% removal. A similar result was observed for copper with a 75% removal (from 557 to 140 ppm). The metallic concentrate obtained contains 15% zinc and has, in principle, revalue potential as a supply concentrate for foundries.

A verified and optimized procedure, on the semi-industrial scale, on a semi-ongoing basis, has been developped, using sediment samples from a sector of the Montreal port zone. It was decided to proceed with exhaustive trials using the material from this zone, as it contained the two main types of contaminants (metallic, petroleum hydrocarbon) most often found in river port zones. The procedure allows for the recuperation of petroleum hydrocarbons and metals. The procedure involves three main steps. In the first step the petroleum hydrocarbons are separated from the sedimentary matrix. This step also includes pre-treatment of sediment in an attrition cell. The second step implies a classification of two size fractions. The equipments used include, among other things, flotation columns.

Three treatment sub-products were obtained. First, treated sediments for which contaminant levels were reduced below those of C criteria; second, a metallic concentrate and third, a petroleum hydrocarbons concentrate.

It should be noted that the treatment reduces copper levels from 2342 ppm to 490 ppm (79% removal), while selenium levels drop from 115 ppm to levels inferior to 1ppm (> 95% removal). The concentrations of petroleum hydrocarbons fall from 24,000 ppm to 2500 ppm (89%

removal). The process mass balance indicates, after filtering, that the treated sediment represents 15% of the mass in situ, the organic concentrate 5%, the metallic concentrate 11% and water present in the sediments 68%, a low contaminated coarse fraction (1% of in situ mass) is discharged at the process entrance.

It is anticipated to dispose of, at a modest cost, the treated sediments in a landfill site. The petroleum hydrocarbon concentrate will be directed to a specialized recuperator. The metallic concentrate contains 1.5% copper, 4g/t gold, 120g/t silver is recoupable as supply for foundries.

Currently, the procedure does not permit to reach the B and TEL criteria. Nevertheless, decontamination objectives aiming at below B and TEL criteria is technically possible for the sedimentary matrix in which the particles have diameters superior to 1 micron and for which the metallic contaminants are free from the matrix. To define the technological limits of the procedure more work is needed.

The main recommendations from this report are the following. A technological demonstration of the treatment procedure developed should be carried out on the 1/100 scale, this scale allowing us to have rapid access to complementary equipment or no as anticipated.

For the port of Montreal, supplementary attrition trials, on the removal of petroleum hydrocarbons before flotation should be carried out in order to improve the effectiveness of the procedure and by so doing, to reduce equipment costs.