THE EAST-SULLIVAN MINE SITE : FROM ABANDONMENT TO RESTORATION

Normand Tassé, INRS-Eau, Terre et Environnement, Québec, Canada.
Diane Germain, Hydrogéochem Environnement Inc., Québec, Canada.

ABSTRACT
The East Sullivan mine was closed in 1966, leaving 15 Mt of acid-generating tailings free to contaminate the environment. An experimental wood waste cover was implemented in the early 80's in order to prevent sulphide oxidation. Contaminant production and dispersion were investigated in the 90's to validate that concept and guide later actions. Ligneous wastes stop oxygen, and also favour infiltration, rise the water table and allow a rapid flushing of pre-cover, acid-prone, groundwater. These are replaced by reducing and alkaline waters that favour sulphate reduction and base metal precipitation. The initial restoration strategy was modified to take advantage of these properties. An innovative treatment of acid effluents, based on the recirculation of water discharging around the impoundment through the organic cover, was implemented in 1998. Thanks to these unconventional approaches, the restoration budget could be cut by several M$, compare to the amounts required by standard, early 90's, techniques.

RÉSUMÉ
La fermeture de la mine East Sullivan en 1966 laissait 15 Mt de résidus miniers acides libres de contaminer l'environnement. Les premières mesures de restauration, au début des années 1980, visaient l'interruption de l'oxydation des sulfures avec une couverture ligneuse. Des études de mobilisation et dispersion des contaminants ont été réalisées pour valider ce concept et orienter les interventions. La couverture bloque l'oxygène, mais augmente aussi l'infiltration, rehaussant la nappe et purgeant les eaux acidogènes pré-couverture. L'eau en remplacement, alcaline et réductrice, favorise la réduction des sulfates et la précipitation des métaux. La stratégie initiale de restauration a été modifiée pour en profiter. Depuis 1998, l'eau collectée autour des résidus miniers est traitée en la pompant sur le couvert ligneux. Grâce à cette approche non-conventionnelle, le budget de restauration a pu être coupé de plusieurs M$, par rapport aux montant requis par les techniques courantes du début des années 1990.

1. INTRODUCTION

East Sullivan is an orphan mine site that was active from 1946 to 1966 in Abitibi, QC, Canada. The Quebec government took over the site responsibility in 1980. Contrary to modern standards, nothing had been done, either during exploitation or after closure, to mitigate the site's impact on the surrounding environment and to insure the long term chemical and physical stability of the acid-producing mining wastes. East Sullivan was soon recognized as one of the 28 sites posing a potential threat to the environment and public health, with its acid mine drainage (AMD), amongst the 341 hazardous waste deposits of all types tallied by the Ministère de l'Environnement in the 80's (GERLED, 1990).

The placement of a wood waste cover began in 1984, following early proposals that organic covers can prevent oxidation of sulphidic mine tailings (Reardon and Poscente, 1984, and references therein). In this type of cover, atmospheric oxygen is consumed by the oxidation of carbon, hence its absence in the interstitial gases coming in contact with the sulphides. A restoration scheme putting forward seepage collection around the impoundment followed by passive treatment of the effluents started to be implemented in the early 1990's (SNC, 1992). Effluents with near neutral pH, thanks to the organic contribution of the wood waste cover, were expected, based on the quality of water sampled over the impoundment. However, the effluents collected around it turned out to be strongly acidic, rather than near neutral.

That finding brought forward the necessity to have a good understanding of the hydrogeological and hydrogeochemical processes going on in that peculiar set up, in order to anticipate the general properties of the seepage waters that would be collected around the impoundment over the mid- and long- terms. Studies carried thereafter not only answered to these concerns, but further allowed the recognition of specific properties of the wood waste cover that could be put at work for the site restoration. The wood waste cover, a prevention-only device, was turned into a dual prevention plus treatment system, allowing a cutback of restoration expenses, down to 9.5 M$ by 2002, from the 50 M$ required by standard, early 90's, techniques (Cyr, 2002).

2. THE EAST SULLIVAN MINE TAILINGS

The East Sullivan mine tailings is located 6 km east of Val d’Or, in north-western Québec. An extensive survey of the site in the early 90's allowed to build a coherent and integrated data base on all aspects of the tailings pile: topography, thickness and extent of both tailings and forestry wastes; physical and chemical properties of tailings (porosity, permeability, grain-size, mineralogy, composition); composition of pore gases, surface waters, and pore waters (vadose and saturated zones, organic and inorganic parameters); water table elevations. Methods and details appear in Tassé *et al.* (1992) and Tassé and Germain (1996).

Essential information on the site are summarized in Table 1 and sketched in Figure 1. That map and other data in this paper depict the site as it was before 1994, prior any disruption of the hydrogeologic cycle. Thickness, composition and grain-size of 1 m thick intervals, sampled at every 2 m from 0.5 m depth, were determined at each control point pictured, for a total of 199 samples.

Table 1. Main characteristics of the mining and forestry wastes.

Mine tailings:

metals extracted:	Cu, Zn (Au, Ag)	accumulation:	1949-66
sulphide concentration:	3.6% S	tonnage:	15 Mt
sulphide mineralogy:	FeS_2 ($Fe_{1-x}S$, $CuFeS_2$, ZnS)	area:	1.36 km^2 (+0.68 km^2 of spreading)
acid generating potential:	108.9 kg $CaCO_3$/t	morphology:	4-5 m plateau
acid neutralizing potential:	4.1 kg $CaCO_3$/t	thickness:	2-14 m

Organic wastes:

	northwest	south	northeast
accumulation:	1984-92, then at low pace	since 1992	since 1999
species:	deciduous dominant over conifers	mainly conifers	conifers and deciduous
types of waste:	barks, logs, presswood waste, mostly overlain by sewage sludge	barks, sawdust, and logs	barks
thickness:	0.2 to 6 m (pre-1990) and 2 m (post-1990)	≈ 2 m	≈ 2 m

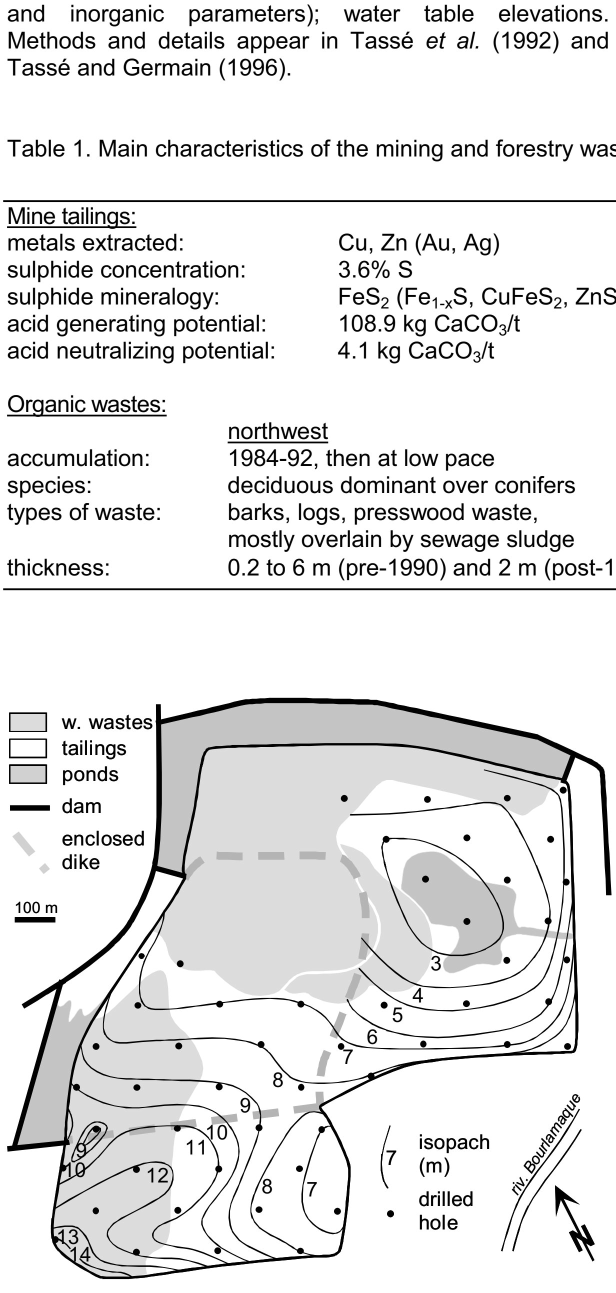

Figure 1. Map of the East Sullivan tailings impoundment in 1994

The initial impoundment, to the south, features coarse grained (d_{50} = 44 µm), sulphurous (3.96 % S), and thick tailings (av. 10.1 m). Tailings are getting finer (d_{50} = 36 and 27 µm), less sulphurous (3.15 and 2.10 % S), and thinner (av. 8.1 and 5.1 m) in the later northern (mid-50's) and north-eastern (early 60's) enlargements. In a vertical profile, coarse (d_{50} ~62-107 µm) and fine (~8-9 µm) material alternates in layers 1-17 cm thick (av. 5-7 cm), in coarse/fine proportions that vary from 0.3 in impoundment centres to 3.1 at the margins. The tailings overly an impermeable substratum composed of clayey sediments and bedrock.

3. GEOCHEMICAL PROCESSES IN THE TAILINGS

Continuous core samples recovered from 7 stations (Figure 2) give an insight of the geochemical processes going on in the tailings (Germain *et al.* 1994). Typical results are shown in Figure 3 for st 7, located close to the north-eastern corner of the impoundment. Near-surface pore waters are enriched in H^+, Fe^{2+}, SO_4^{2-} and metals by sulphide oxidation, either by atmospheric oxygen (Eq. 1) or by ferric iron (Eq. 2). Hydrolysis that follows oxidation of iron (Eq. 3 and 4) produces acid as well. Since the kinetic of oxidation is very slow in acid conditions (Stumm and Morgan, 1996), ferrous iron is allowed to migrate downward in an oxygen-free underground environment.

$$FeS_2 + {}^{7}/_{2}O_2 + H_2O \longrightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad [1]$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \longrightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad [2]$$

$$Fe^{2+} + {}^{1}/_{4}O_2 + H^+ \longrightarrow Fe^{3+} + 1/_{2}H_2O \qquad [3]$$

$$Fe^{3+} + 3H_2O \longrightarrow Fe(OH)_3 + 3H^+ \qquad [4]$$

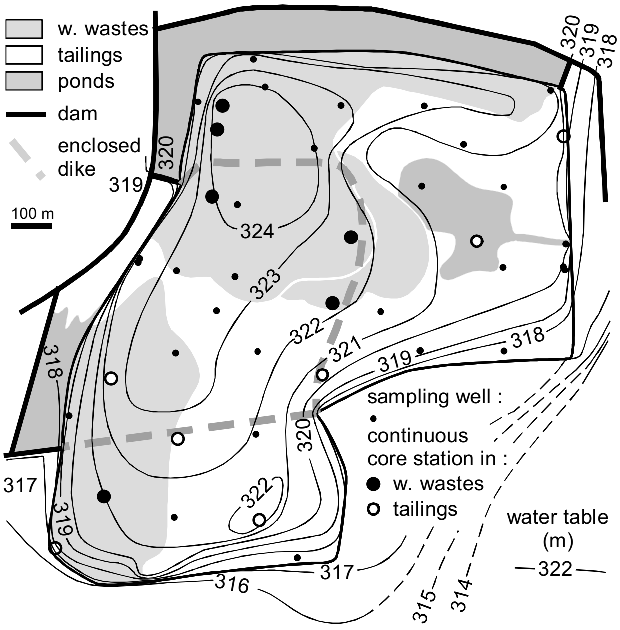

Figure 2. Localization of sampling wells and continuous core stations used in hydrogeochemical groundwater studies

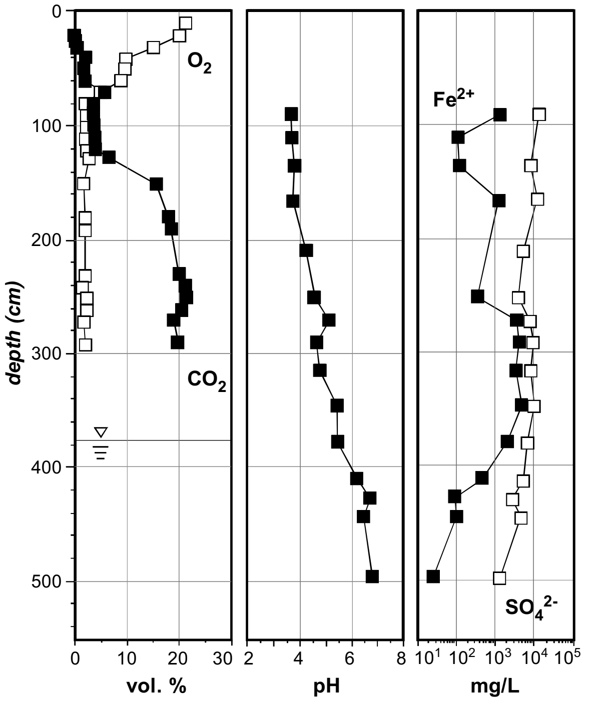

Figure 3. Geochemical profiles at near-margin station st 7

As the pore waters percolate downwards, calcite dissolution releases CO_2 to pore gases and increases pH and Ca^{2+}, easing adsorption and bringing the pore water in the stability field of siderite ($FeCO_3$) and gypsum ($CaSO_4 \cdot 2H_2O$). This decreases Fe^{2+}, SO_4^{2-}, and heavy metals concentrations. For instance, concentration of dissolved iron is reduced from 18 000 ppm in the vadose zone to less than 100 ppm in the saturated zone of st 7 (Figure 3). Residual Fe^{2+} is carried to the edge of the tailings pile where it seeps. Oxidation occurs under atmospheric oxygen and hydrolysis can proceed, thanks to the higher pH acquired upon migration. Alkalinity gained from solid-groundwater interactions cannot always overcome the acid produced this way, especially near margins, where the travel lengths and times are short. Seepage is thus acid, and that this acid is only indirectly related to sulphide weathering at the surface of the tailings. In that scheme, acid production around the impoundment can goes on a long time after the placement of an oxygen barrier, since acidity is stored in groundwater as Fe^{2+}, and kept until emergence.

Neutralizing capacities are locally exceeded in the vicinity of enclosed dikes, where coarse grained-tailings favours air infiltration and act as a drain for groundwater (Germain *et al.* 1994). That deterioration represents the long term fate of the impoundment, in the absence of any mitigation, given the acid/neutralizing potentials evaluated from the tailings composition (Table 1).

4. GEOCHEMICAL PROCESSES IN THE WOOD WASTE COVER

The cover functionality in term of oxygen consumption was demonstrated repeatedly (Tassé *et al.* 1994; Tassé, 2000). CO_2 is produced in stoechiometric proportion to the consumption of oxygen during carbon oxidation and varies generally in inverse proportion to that of O_2, giving a mirror image (Eq. 5; Figure 4).

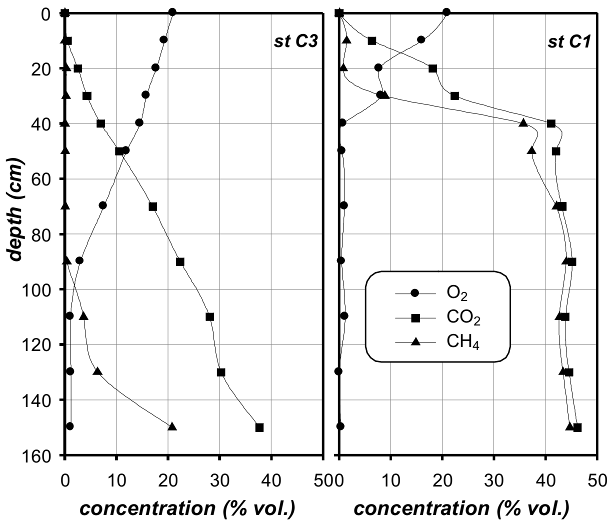

Figure 4. Typical O_2, CO_2 and CH_4 profiles in East Sullivan forestry wastes (from Tassé, 2000)

Over-representation of CO_2 happens and implies fermentation, releasing both CO_2 and CH_4 from organic substrates (Eq. 6). Methane is the best evidence of strongly anaerobic conditions within the forestry wastes. Tassé (2000) expands on the variables (tree species and part; ages; degree of water saturation, etc.) that can affect the degradation processes over the short and long term.

$CH_2O + O_2 \longrightarrow CO_2 + H_2O$ [5]
where CH_2O represents a simple organic molecule

$CH_3COOH \longrightarrow CH_4 + CO_2$ [6]

Temperature profiles throughout the cover are influenced by surface temperatures (Figure 5). Freezing did not go below 60 cm in the surveyed year, despite severe winter conditions (average monthly temperature of -17.0 and -15.1°C for January and February). This suggests year-long bacterial activity within the cover. Low temperatures at depth in late April and early May are due to cold water infiltration that follows snow cover melting.

The distribution of alkalinity in the saturated zone below the covered areas shows the beneficial effects associated with the forestry wastes in tailings (Figure 6). Values exceeding 2000 ppm $CaCO_3$ have been recorded, in contrast to 500 ppm or less in the sectors dependent on mineral alkalinity only. Some of this alkalinity is associated to dissolved organic compounds, and some to dissolved inorganic carbon, thanks to high (20-40%) partial CO_2 pressures associated to carbon oxidation and near neutral pHs of groundwater. In tailings, similar CO_2 concentrations in the vadose zone result from acid dissolution of calcite. The acid conditions prevent any build-up of comparable alkalinity in the underlying saturated zone.

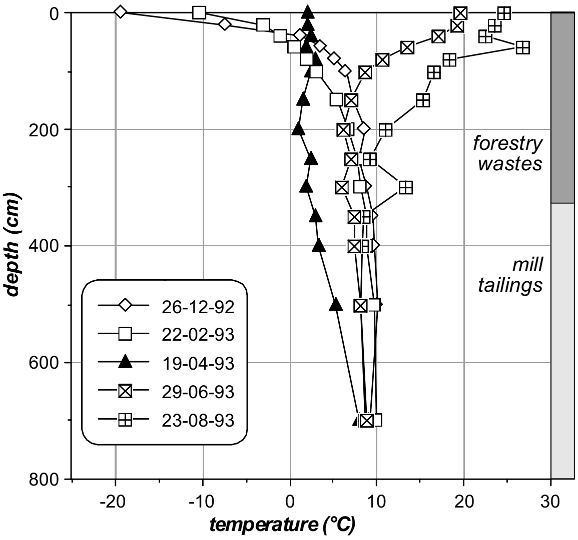

Figure 5. Selected temperature profiles in forestry wastes (from Tassé *et al.* 1997)

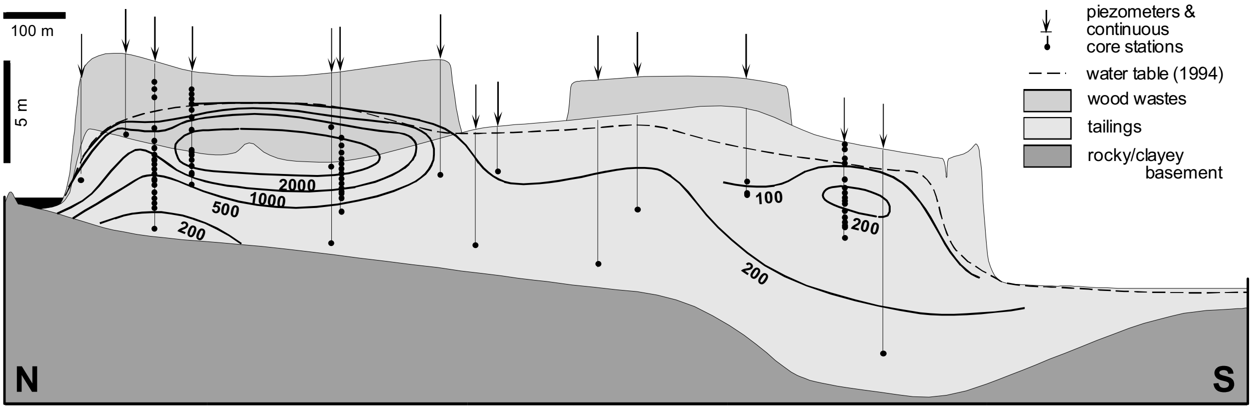

Figure 6. Distribution of alkalinity (in ppm $CaCO_3$) along a N-S section across the tailings pile (from Tassé *et al.* 1997)

5. COVER PLACEMENT AND REDUCTION OF AMD

The interruption of sulphide weathering, either by an organic barrier or by some other oxygen-proof cover, does not mean an immediate cessation of AMD. As previously stated, acidity is stored in groundwater as Fe^{2+}, and acid-prone waters generated prior cover placement must first be flushed out from the tailings. Acidity/alkalinity balance allows some predictions about the pH of a given pore water that will be eventually discharged around the impoundment (Figure 7). The problematic samples are those for which alkalinity will be totally exhausted, at a ratio of 1.8 ppm $CaCO_3$ for each 1 ppm Fe^{2+}. Samples collected under the oldest parts of the cover (pre-1992, north sector) generally present no threat, with high alkalinity and low Fe^{2+}. Elsewhere, most acid prone samples are located next to the dikes, including former dikes, now enclosed in finer tailings. They can also be located in more central parts, in tailings directly poured out from the mouth of carrying pipes. These locations correspond to zones of high hydraulic conductivity, where O_2 diffusion favours or has favoured high rates of alteration. Alteration and acid generation is also enhanced near margins, because the vadose zones are deeper than within the impoundment, allowing deeper weathering.

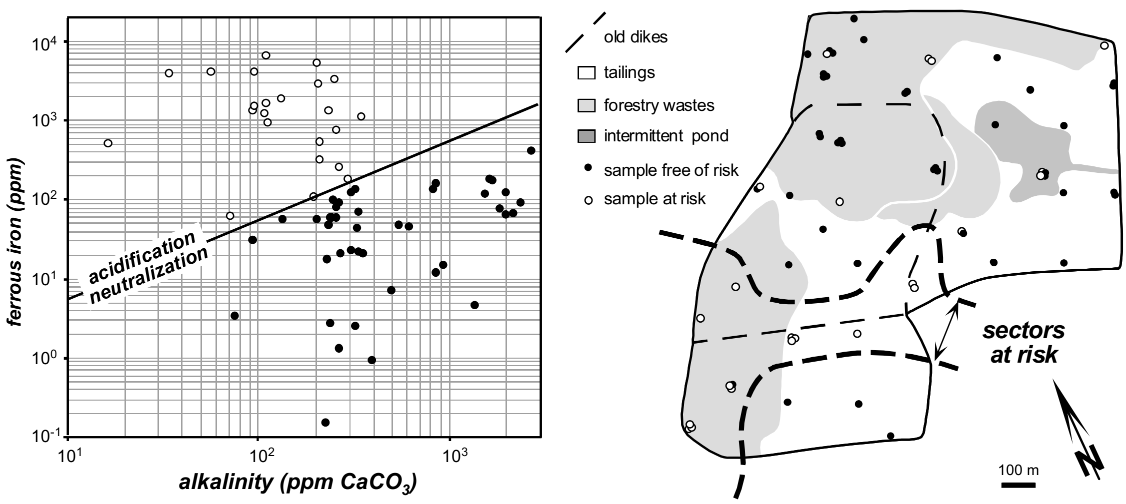

Figure 7. Ferrous iron *vs* alkalinity diagram for samples from the saturated zone

Given the importance of transport time and length in neutralization and gain of alkalinity, groundwater flow was modelized in order to estimate the flushing time of acid-prone waters, that is the time required to evacuate Fe^{2+} derived from sulphide oxidation. Two cross-sections, across the entire tailings pile and through the north-eastern margin (Figure 8), were analysed with the codes SEEP/W and CTRAN/W (GEOSLOPE, 1994 a, b).

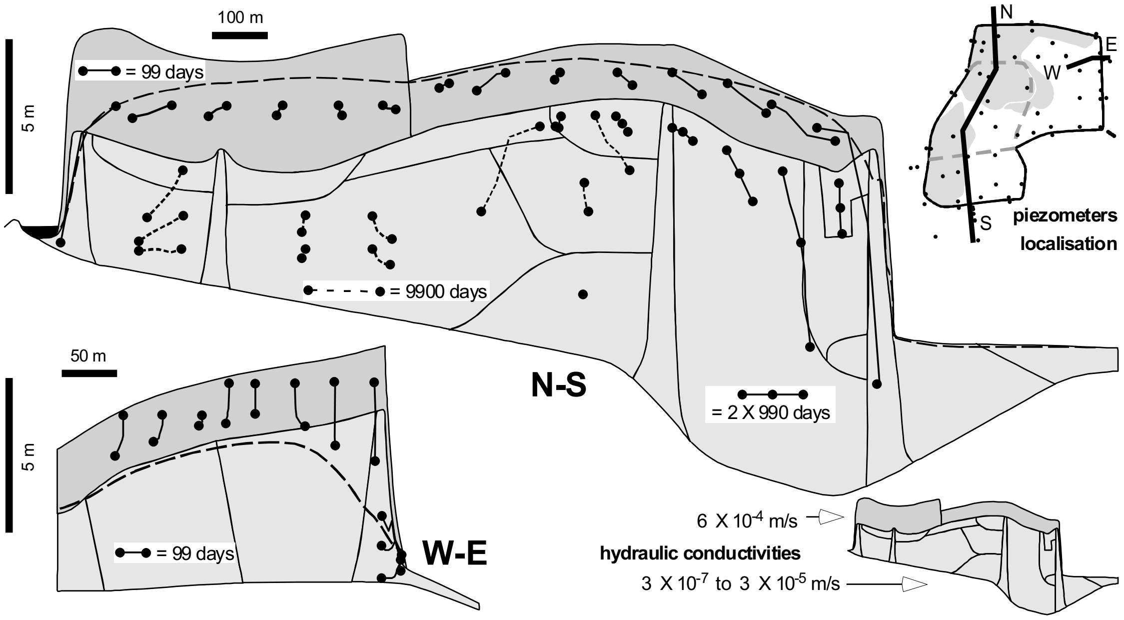

Figure 8. Trace of modelized particles within the ligneous cover and the mine tailings along two cross-sections (from Tassé *et al.* 1997; modelization assumes a complete coverage of the tailings by wood wastes)

The particle tracking simulations show that flow is relatively rapid within the forestry wastes, above the interface with the mill tailings. It is much slower in the tailings, except in the southern part, i.e., the zone containing, overall, the most critical groundwater. Flushing times are expected to be in the order of 5 to 10 years, for the internal parts of that sector, and a matter of a few months, next to the margins. Elsewhere, samples identified as “at risk” are more isolated, and unrelated to zones of high hydraulic conductivity. The transport distances and times for these waters, therefore, could be long, with the possibility that they may acquire additional alkalinity through interactions with the mineral medium, and become potentially inoffensive, i.e. able to keep near neutral pH upon seepage oxidation.

6. TREATMENT OF AMD

The geochemical environment below the wood wastes cover is reducing and alkaline (Figure 6). In organic-rich anoxic environments, specialized bacteria can live and fulfil their energy needs by mediating redox reactions between organic and inorganic compounds. Manganese oxide, nitrate, iron oxide and sulphate are reduced, while organic compounds are oxidized. Reduction occurs in that order, according to the Gibbs free energy involved in the reactions, in environment allowing for segregation of bacterial communities (e.g. deep sea; Froelich *et al.* 1979). If SO_4 and sulphate reducing bacteria (SRB) are available, and if the environment is reducing enough to allow H_2S production, metals such as Fe, Ni, Cu, Co, Zn, Cd, etc. are precipitated as insoluble sulphide minerals. At East Sullivan, the breakdown of the forestry wastes provides organic compounds easy to metabolise. The "acid", in "AMD", is sulphuric acid, and SO_4^{2-} can be involved in the above redox reaction. Actually, the rotten eggs smell of H_2S can be noted at some sampling sites, pointing that this reaction is going on.

Tassé *et al.* (1997) believed that the alkaline and reducing milieu underlying the wood waste could be put at work for the site rehabilitation, simply by driving the acid residual waters trough it. A side effect of recirculation would be the increase water infiltration, raising the water table, and allowing a faster purge of acid-prone groundwater generated prior to organic cover placement. SRB are used in many varieties of bioreactors, from constructed wetlands (Wildeman *et al.* 1992) to reactive walls (Benner *et al.* 2000). Conceptually, a wood waste cover allowing prevention and treatment of AMD has several advantages over these “classic” alternatives:

- the system is a priori less sensitive to the hydrogeologic and vegetative cycles that affect purifying wetlands, because anaerobic conditions in an oversized organic cover can persist despite strong irregularities in influent discharge and climatic conditions;
- the insulating capacity of the forestry wastes keeps the temperature almost constant and above the freezing point at shallow depths all year round, providing an effectiveness over an extended season, a factor of importance in a nordic region;
- the extent of the cover is directly proportional to the volume of tailings to be covered, so that the volume of “reagents” poses no problem of space management;
- contact time can be long relative to a constructed wetland, and, despite increased infiltration, levels of supersaturation are likely to be attained more easily.

Nevertheless, some uncertainties had to be faced. A reactive cover is a bioreactor, and as such, will perform well as long as its bacterial flora is fed with the proper reactive material, in a suitable geochemical environment. The feed is less a concern. The carbon reservoir can be replenished if showing any weakness on the long term. However, the impact of the acid pH on the bacteria and the organic quality of the effluents were more worrying:

- anaerobic and aerobic oxidation that contribute to establish an adequate environment for SRB are controlled by bacteria; their collective resistance to acid pHs could not be defined; nevertheless, SRB are most functional at pH’s between 5 and 9, but can tolerate pH’s as low as 2.6 (Bolis *et al.* 1991, in Eger and Wagner, 1995); actually, SRB could overcome pH 1.6 conditions and rise the pH to 6 in closed vessel experiments with tree barks and artificial AMD (Tassé and Germain, 2002);
- organic leachates can be associated with the presence of undesirable substances, such as phenols or chelating complexes; actually, phenols and phytotoxic substances are released by humification and composting of forestry wastes, but significant attenuation occurs within only a few weeks, if the mass of organic waste is not fed with new reactive products (Solbraa *et al.* 1983).

Recirculation was implemented in 1998, and the effects on pH and metal content monitored (Germain *et al.,* these proceedings).

7. CONCLUSION

A cover of forestry wastes features several qualities with respect with other types of cover: possible substitute in the absence of suitable inorganic material; no disturbance of the natural environment (industrial waste rather than natural material); sturdy and simple to erect; less reactive than many other organic covers, prone to impair the environment with effluents with high biochemical oxygen demand, and undesirable concentrations of nutrients and micro-organisms. Moreover, it can be used for the purge and treatment of acid and acidogenic groundwater. Since the placement of such a cover may require several years, disposal should first target the margin, where contaminant production and dispersion are at their maximum.

8. ACKNOWLEDGEMENTS

Many thanks are expresses to all the people who helped us on the field at various time, over the years. Officers of Ressources naturelles, faune et parcs – Québec, and especially Robert Tremblay, Claude Dufour and Johanne Cyr, are thanked for their long term collaboration, discussion, understanding, etc. Financial support for the various legs of this project was provided by the Ministère des Ressources naturelles, Faune et Parcs du Québec and Ressources naturelles Canada.

9. RÉFÉRENCES

Benner, S., Blowes, D., and Ptacek, C., 2000. Long term performance of the Nickel Rim reactive Barrier : a Summary. Proc. of the 5th International Conference on Acid Rock Drainage, Vol. 2, pp. 1221-1225.

Cyr, J., 2002. The rehabilitation of state-owned mining sites : $20 million invested. Highlights on the mines, Ressources naturelles, faunes et parcs – Québec. http://www.mrnfp.gouv.qc.ca/english/mines/quebec-mines/2002-02/rehabilitation.jsp

Eger, P. and Wagner, J., 1995. Sulfate reduction for the treatment of acid mine drainage; long term solution or short term fix? In: Hynes, T.P. and Blanchette, M.C. (eds), Proc. of Sudbury '95 - Mining and the Environment. (CANMET, Ottawa); Vol. 2, pp. 515-524.

Froelich, P.N., Klinkhammer, G.P., Bender, M.L., Luedtke, N.A., Heakth, G.R., Cullen, D., Dauphin, P., Hammond, D., Hartman, B., and Maynard, V., 1979. Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis. Geochimica et Cosmochimica Acta, Vol. 43, pp. 1075-1090.

GEO-SLOPE, 1994a. User's Guide SEEP/W, Version 3. GEO-SLOPE International Ltd., Calgary, Alberta.

GEO-SLOPE, 1994b. User's Guide CTRAN/W, Version 3. GEO-SLOPE International Ltd., Calgary, Alberta.

GERLED, 1990. Inventaire des lieux d'élimination de déchets dangereux au Québec (mise à jour des données depuis 1984). Ministère de l'Environnement et de la Faune, Envirodoq EN850255.

Germain, M.D., Tassé, N., and Bergeron, M., 1994. Limit to self-neutralization in acid mine tailings: the case of East-Sullivan, Québec, Canada. In: Blowes, D.W. and Alpers, C.N. (eds), Environmental Geochemistry of Sulfide Oxidation. American Chemical Society, Symposium Series 550, pp. 365-379.

Reardon, E.J. and Poscente, P.J., 1984. A study of gas compositions in sawmill waste deposits: evaluation of the use of wood waste in close-out of pyritic tailings. Reclamation and Revegetation Research, Vol. 3, pp. 109-128.

SNC Inc., 1992. Élaboration d'un programme de restauration du site minier East Sullivan. Rapport final présenté à la direction du développement minéral, Ministère des Ressources naturelles du Québec; 211 pages.

Solbraa, K., Sant, M.D., Selmer-Olsen, A.R., and Gislerod, H.R., 1983. Composting soft and hardwood barks. Biocycle, Vol. 24, pp. 44-59.

Stumm, W. and Morgan, J.J., 1996. Aquatic chemistry. 3rd edition. Wiley-Interscience, New York; 1022 p.

Tassé, N., 2000. Efficient Prevention of Sulphide Oxidation by an Organic Cover: For How Long a Reactive Barrier can be Reactive? Proc. of the 5th International Conference on Acid Rock Drainage, Denver, Colorado, pp. 979-986.

Tassé, N., Germain, D., and Bergeron, M., 1992. Caractérisation géochimique du parc de résidus miniers East-Sullivan. Service du développement minier, Ministère de l'Énergie et des Ressources du Québec; 124 p.

Tassé, N. and Germain, D., 1996. Qualité des eaux résiduelles au site East Sullivan: Rapport final. Service du développement minier, Ministère des Ressources naturelles du Québec; 251 p.

Tassé, N., Germain, M.D., and Bergeron, M., 1994. Composition of interstitial gases in wood chips deposited on reactive mine tailings: consequences for their uses as an oxygen barrier. In: Blowes, D.W. and Alpers, C.N. (eds), The Environmental Geochemistry of Sulfide Oxidation. American Chemical Society, Symposium Series 550, pp. 631-644.

Tassé, N., Germain, D., Dufour, C., and Tremblay, R., 1997. Organic-waste Cover Over the East Sullivan Mine Tailings: Beyond the Oxygen Barrier. Proc. of the 4th International Conference on Acid Rock Drainage, Vancouver, B.C., Vol. 4, pp. 1627-1642.

Tassé, N. and Germain, D., 2002. Performance of Forestry Wastes for the Treatment of Acid Mine Drainage Through a Reactive Barrier. Proc. of the 7th International Conference on Environmental Issues and Waste Management in Mineral and Energy Production (SWEMP 2002), Cagliari, Italy. R. Ciccu (Ed.), DIGITA, Università degli Studi di Cagliari, Italy; pp. 723-730.

Wildeman, T.R., Brodie, G.A., and Gusek, J.J., 1992. Wetland design for mining operations. Bitech Publ. Co., Vancouver, B.C.