Merging Prevention and Treatment of acid Mine Drainage through the use of an Organic Cover: the East-Sullivan Mine Site, Québec, Canada

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Abstract

The East Sullivan mine closed in 1966, leaving 15 Mt of acid-generating tailings. An organic cover, composed of coarse bark fragments, started to be deployed in the 80's, in order to prevent sulphide oxidation. Methane in pore gases confirmed the establishment of strict anoxic conditions. Increased infiltration raised the water table and accelerated the flush of pre-cover, acidogenic groundwater. Replacing alkaline and reducing waters indicated a geochemical environment able to sustain sulphate reduction and metal precipitation.

Given the analogies with a reducing bioreactor, a system treatment was implemented, involving acid effluents collection and release over the organic cover. Groundwater, monitored at six observation wells next to the dispersal zone, kept its pH above 6, despite acid feeds at 2.5. The treatment went on until the quality of the effluent met the regulation criteria, including toxicity tests on rainbowtroutandDaphnia (1998 to 2005).

This dual prevention-treatment system is the result of special converging circumstances. Full scale replication on another site is unlikely, given the large volume of organic wastes required. However, degrading barks could play a key role in a restoration scheme, as a complement to prevention approaches that cannot reach their full theoretical possibilities due to natural limits.

Key Words: Effluent Treatment, Sulphate Reduction, Tailings Impoundment Rehabilitation.

Introduction

The East Sullivan mine (North-Western Québec, Canada) was active from 1946 to 1966, then left to abandonment. The Québec government formally inherited the site responsibility in 1980. 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 mine tailings. East Sullivan was soon recognized as one of the 28 sites posing a major threat to the environment and to public health, amongst the 341 hazardous waste deposits of all types tallied by the province on his territory during these years (GERLED, 1990).

The placement of a wood waste cover began in 1984, following early proposals that organic covers could prevent sulphide oxidation of 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-Lavalin, 1992). Effluents with near neutral pH were expected, thanks to the organic contribution of the wood waste cover, as suggested by water collected over the impoundment. However, the effluents collected around it turned out to be strongly acidic, rather than near neutral.

That outcome 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 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 several M$ required by standard, early 90's, techniques (Cyr, 2002).

The East Sullivan Mine Tailings and Organic Cover

The East Sullivan mine site 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 for the building of a coherent and integrated data base on all aspects of the tailings impoundment: topography; thickness and extent of both tailings and forestry wastes; physical and chemical properties of tailings, including porosity, permeability, grain-size, mineralogical and geochemical compositions; composition of pore gases, surface waters, and pore waters; water table elevations (Tassé *et al.* 1992; Tassé and Germain 1996). A simplified description of the site is given below, in Table 1.

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 spilled out
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, sewage sludge	barks, sawdust, and logs sewage sludge	barks partly sewage sludge
thickness:	0.2 to 6 m (pre-1990) and 2 m (post-1990)	≈2 m	≈2 m

Geochemical Processes in the Tailings

The state of the impoundment by the end of 2005 is sketched in Figure 1, after the erection of containment dikes and near the completion of the cover placement, before system shutdown. In the early 90's, tailings were exposed to air over a much larger area, including all the impoundment south of station C3, as well as a 200-300 m strip on the northern margin. Continuous core samples recovered from 7 stations gave an insight of the geochemical processes going in the cover-free tailings (Germain *et al.* 1994). Near-surface pore gases were depleted in oxygen, and pore waters were enriched in H^+, Fe^{2+}, SO_4^{2-}, and metals by sulphide oxidation (Figure 2), either by atmospheric oxygen (Reaction 1) and/or by ferric iron (Reaction 2). Hydrolysis that follows oxidation to ferric iron (Reactions 3 and 4) produced acid as well.

$$FeS_2 + {}^7/_2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (1)$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (2)$$

$$Fe^{2+} + {}^1/_4O_2 + H^+ \rightarrow Fe^{3+} + 1/_2H_2O \quad (3)$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ \quad (4)$$

Neutralization of downward migrating water by calcite ($CaCO_3$) increased both pH and pCO_2 (Figure 2). Since the kinetic of oxidation is very slow in acid conditions (Stumm and Morgan, 1996), some ferrous iron could escape from the upper oxidation zone and reach a deeper oxygen-free environment.

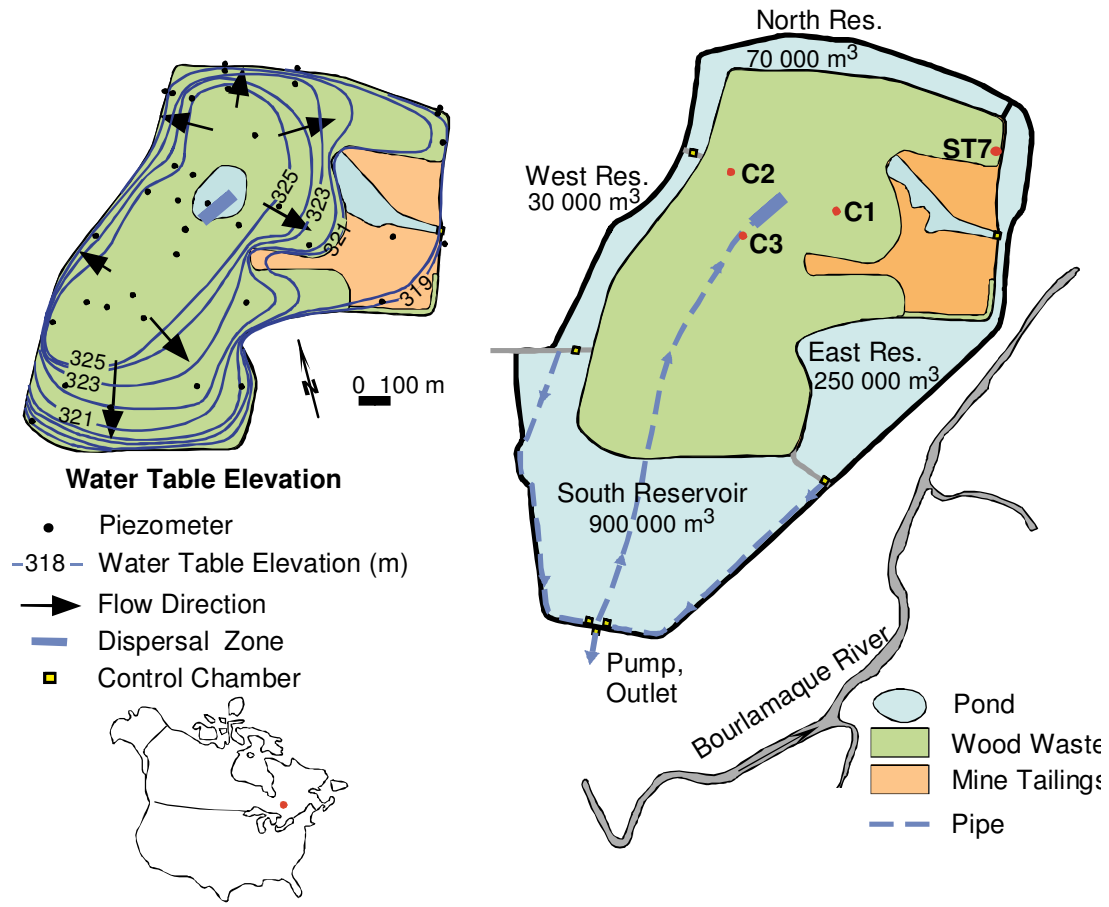

Figure 1. The East Sullivan tailings impoundment, with organic cover outline in 2005, water table elevation during recirculation, location of observation wells, and sketch of the pumping network and dispersal zone

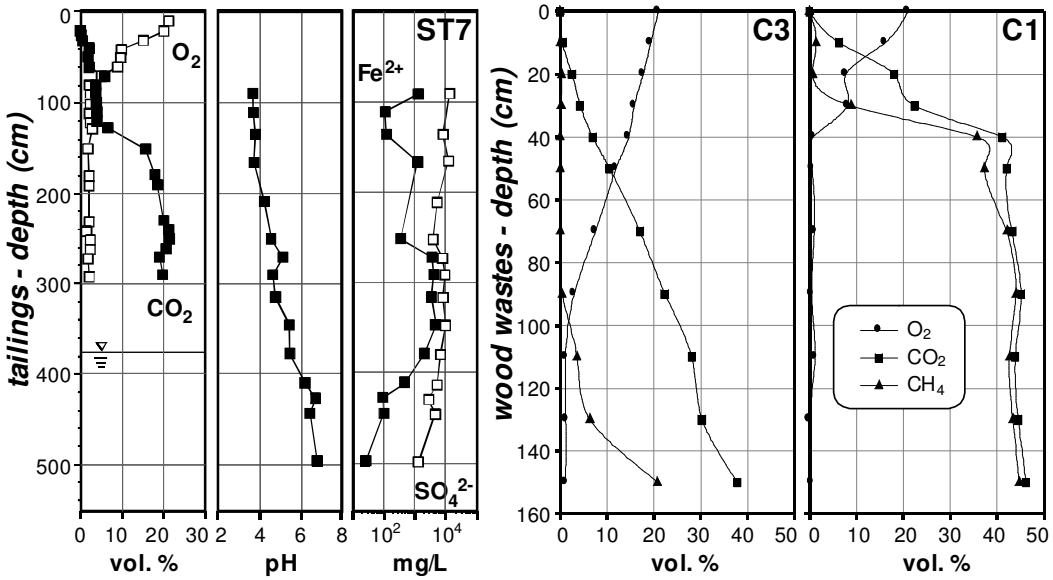

Figure 2. Typical gas and pore water profiles in tailings (ST7, prior cover placement), and typical gas profiles in forestry wastes (C3 and C1) (modified from Germain *etal.* 2009; stations localized in Fig. 1)

Geochemical Processes in the Wood Waste Cover

The cover functionality in terms of oxygen consumption was demonstrated repeatedly (Tassé *et al.* 1994; Tassé, 2000). CO_2 is produced in stoichiometric proportion to the consumption of oxygen during carbon oxidation and varies generally in inverse proportion to that of O_2 (Reaction 5). The expected mirror image was observed, but also, commonly, over-representation of CO_2 (Figure 2). That implies fermentation, releasing both CO_2 and CH_4 from organic substrates (Reaction 6). Methane is the best evidence that strongly anaerobic conditions can be reached and maintained within the forestry wastes. On the other hand, many variables can affect the degradation processes (tree species and part; waste age; degree of water saturation, *etc*.), as Tassé (2000) found after examination of several wood waste piles.

Oxidation: $CH_2O + O_2 \rightarrow CO_2 + H_2O$ (5)

where CH_2O represents a simple organic molecule

Fermentation: $CH_3COOH \rightarrow CH_4 + CO_2$ (6)

These reactions and the insulating properties of the wood wastes concur to minimize the effects of open air temperatures in the vertical profiles. For instance, freezing hardly reached the depth of 60 cm in the surveyed year, despite severe winter conditions, with average monthly temperature of -17 and -15°C in January and February (see Figure 6 in Germain *et al.* 2009). This suggests that year-long bacterial activities can take place within the cover.

The distribution of alkalinity in the saturated zone below the covered areas showed the beneficial effects associated with the forestry wastes in tailings (Figure 3). Values exceeding 2000 mg/L-$CaCO_3$ have been recorded, in contrast to 500 mg/L or less in coverless sectors. The larger alkalinity is explained by the availability of abundant dissolved organic compounds in the former setting, whereas the latter relies on mineral alkalinity only.

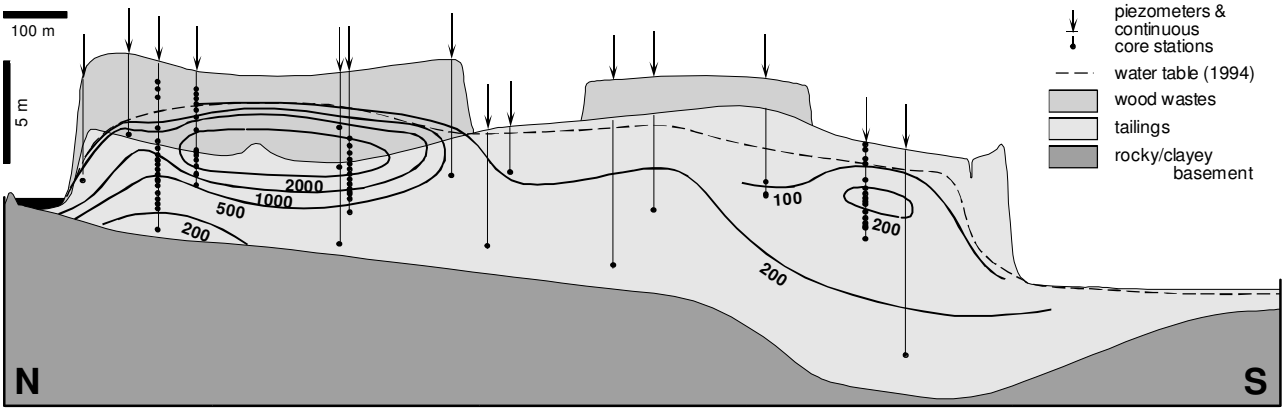

Figure 3. Alkalinity (mg/L-$CaCO_3$) along a N-S vertical section, in 1994 (Tassé *et al.* 1997)

Time to AMDInterruption

The interruption of sulphide oxidation, either by an organic barrier or by some other oxygen-proof cover, does not turn AMD into neutral drainage instantaneously. Acidity can be stored in oxygen-free groundwater as Fe^{2+}, and acidification resumes as soon as O_2 becomes available. It follows that the seeping acid-prone waters generated prior cover placement will deliver their load of acid as long as the bulk of that groundwater is not flushed out from the tailings and that a neutral acidity/alkalinity balance is reached.

Vertical profiles shows that transport time and length matter in the loss of Fe^{2+} and acidity, and in the gain of pH and alkalinity (Figure 2). Fluxes have been investigated with a numerical groundwater flow model (SEEP) in order to estimate the time required to evacuate the Fe^{2+} derived from sulphide oxidation (Tassé *et al.* 2004). Residence timesaccording to the particle tracking technique (CTRANS)are depicted in Tassé *et al.* (1997) for various cross-sections through the impoundment. Simulations lead to the conclusions that: 1) flow was relatively rapid within the forestry wastes, above the interface with the tailings; 2) flow was much slower in the tailings, except in the coarser-grained southern part and along the spigotted margins, where the deeper reach of O_2 allowed the massive production of contaminated groundwater; 3) flushing times should range from 5 to 10 years for that specific sector, decreasing to a few months next to the margins. Elsewhere, most samples with an unfavourable acidity/alkalinity balance were isolated and apparently not connected to zones of high hydraulic conductivity. It was assumed that the long transport distances and times would allow these waters to pick up alkalinity through mineral interactions, loose acidity by Fe^{2+} precipitation, and thus become on the long run inoffensive, *i.e.* able to keep near neutral pH upon seepage and oxidation.

Treatment of AMD

In many adverse environments, specialized bacteria can live and fulfil their energy needs by mediating reactions involving either organic or inorganic compounds. A “bioreactor” emerges from that principle when optimum conditions are brought together to drive the reactions in a desired direction. If sulphate, sulphate reducing bacteria (SRB) and suitable organic substrates are available, the SRB will secure their energy needs by oxidizing the organic compounds, using the sulphur of sulphate as the terminal electron acceptor (Reaction 7), and available metals such as Fe, Ni, Cu, Co, Zn, Cd, *etc*. will be precipitated by reduced sulphur as mostly insoluble sulphide minerals (Reaction 8).

$$SO_4^{2-} + 2CH_2O \rightarrow H_2S + 2HCO_3^- \quad (7)$$

$$Me^{2+} + H_2S \rightarrow MeS + 2H^+ \quad (8)$$

where Me represents Fe, Ni, Cu, Co, Zn, Cd, *etc*.

Actually, SRB are used in many varieties of bioreactors, from constructed wetlands (Wildeman *et al.* 1992) to reactive walls (Benner *et al.* 2000). At East Sullivan, the breakdown of the forestry wastes provides organic compounds, the "Acid" of "AMD" is sulphuric acid, and SO_4^{2-} is actually involved in redox reaction, as evidenced by the typical smell of H_2S noted at some sampling locations. Laboratory tests on various types of bark fragments also showed their ability to support sulphate reduction, despite some differences in residence time (Tassé and Germain 2002).

On these bases, 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 through it. Several conceptual advantages contributed to the decision to go ahead with that suggestion. A wood waste cover allowing prevention and treatment of AMD can be preferred to “classic” bioreactor for several reasons:

- the extent of the cover is directly proportional to the volume of tailings to be covered, so that the volume of reactive material poses no problem of space management;
- the size of an organic cover is such that anaerobic conditions can persist despite irregularities in influent discharge and climatic conditions, which is not the case, for instance, for purifying wetlands and their vegetative cycles;
- 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;
- contact time can be long relative to a constructed wetland;

- increased water infiltration raises the water table, allowing a faster purge of acid-prone groundwater generated prior to organic cover placement.

Nevertheless, some uncertainties had to be faced, mainly about the impact of the acid water on the bacteria and on the organic quality of the effluents:

- the collective resistance of bacteria to acid water could not be defined; 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);
- phenols and phytotoxic substances are released by humification and composting of forestry wastes; however, 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).

Some controlled tests were performed to determine if these concerns were substantiated. Lab tests involved wood waste fragments of various composition (coniferous and mixed coniferous-deciduous barks, saw dust and planar shave), age (1965 to recent), inoculate of sulphate reducing bacteria (from sediments or sewage sludge), with and without dolostone a neutralizing agent, all in closed vessels with a synthetic solution of acid mine drainage. The pH, alkalinity, and $Fe^{2+}$and SO_4^{2-}concentrations were measured at intervals, over 70 days. Best performances were provided by deciduous bark over all other types, and dolostoneenhanced acid neutralisation, in the early stages (Tassé and Germain 2002). Field tests involved two anoxic bioreactor filled with bark fragments from deciduous trees, with and without dolomite. The results (unpublished) confirmed that sulphate reduction could be triggered and go on without any neutralizing agent.

Collection and recirculation systems

Effluents from the impoundment were collected in four reservoirs built around it in 1998 and 1999. The North reservoir drained into the West reservoir, and the waters of the East and West reservoirs could be either released in the South reservoir or sent to a pumping station/outlet at its southern end through pipes (Figure 1). Reservoirs capacities and recharge rates calculated from hydrogeological simulation were: North, 70 000 m^3 and 1 170 m^3/d; West, 30 000 m^3 and 430 m^3/d; East, 250 000 m^3 and 6 600 m^3/d; South, 900 000 m^3. Recharge data for the South reservoir were irrelevant and ignored, since the inflow from the East and West reservoirs could vary, as well as the outflow to the natural environment or to recirculation. During recirculation, water was pumped back over the organic cover to a 120 m long dispersal zone located over the oldest wood wastes, dating back to the mid-80's. The freeze-free period, in North-Western Québec, allowed recirculation to proceed from the beginning of May to the end of October.

The mean pumping rates and volumes of water treated from 1998 to 2005 are 4 888 m^3/d and 636 608. In 2006, the recirculation was no longer required, since the alkalinity present in the North, West and South reservoirs was higher than the acidity still present in the East reservoir. Therefore, since 2006, the acid water from the East reservoir is discharged directly into the South reservoir, where it is naturally neutralised.

Performance of the water treatment system

The performance of the treatment applied to the problematic waters over the years and during each year can be visualized in Figure 4. This figure allows a direct comparison of the composition of recirculated waters before and after its infiltration and transit over a few tens of meters, thanks to an observation well close to the dispersal zone (C3-p4, at 3.1 m depth; Figure 1).

Composition of feed-water varied widely, according to which reservoir was tapped, the time of the year and the year itself. Initial recirculation involved the East reservoir, until its quality meet the criteria listed

in Table 2. Then, feed-water was pumped either from the West or South reservoirs. During the eight years of its operation, the system was fed with water with iron as high as 500 mg/L, and pH most often in the 3.0 to 3.5 range. Over this time, pore water quality improved steadily in observation well C3-p4. The average Fe^{2+} concentration decreased from 28.2 mg/L in 1998 to less than 2 mg/L from 2000 to 2005, except on one occasion, on May 12, 2005 (5 mg/L). The pH of pore water was always near neutral during these years, despite the low pH feed.

Table 2. Water quality criteriafor final mining effluents (Ministère du Développement durable, de l'Environnement et des Parcs du Québec)

Inorganic parameters	**Mean conc.** (mg/L)	**Max. conc.** (mg/L)
Cu	0.3	0.6
Ni		