Changes in Chemical and Biological Properties of Paper Sludge Used for Revegetation of Copper Tailings

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Abstract

Paper sludge from St. Marys Paper Ltd. in Sault Ste. Marie, Ontario, was used for the revegetation of acidic (pH 3.5) copper tailings at the Pronto Tailings Management Area of Rio Algom Limited, located near Spragge, Ontario. Two field experiments were established: one with a depth of paper sludge of approximately 15 cm and the other approximately 50 cm, with both applied to limed tailings and seeded with a remediation grass mixture. With a thicker layer of sludge, the pH remained close to neutral over the first three years, while organic carbon decreased by 20% and the C/N ratio decreased from 48 to 36. However, when a thinner layer of paper sludge was applied, the pH dropped to 5.5 over the same period, organic carbon decreased by more than 30%, and the C/N ratio decreased from 47 to 23. Crop yield increased over time in the thicker sludge layer, but decreased by 35-40% in the thin layer. Microbiological activity in the original paper sludge, i.e., before application, was relatively low, with the number of culturable bacteria at 10^6-10^7 CFU/g and micro-fungi at less than 10^3 CFU/g. Actinomycetes were not found. However, at the end of the first year, the upper 15-cm layer of sludge proved to be much more enriched in bacteria (up to 2×10^8 CFU/g) and actinomycetes (10^6 CFU/g). Over time, the numbers of bacteria have gradually decreased, but fungi have increased, indicating a successional pattern typical for cellulose containing materials. Microbiological activity of the bottom layer of paper sludge differed from the upper layer. For example, in the upper layer, mycelial organisms (fungi and actinomycetes) were dominant, whereas bacteria were dominant in the bottom layer. Different moisture, temperature, and gas regimes in the upper and lower layers were, probably, responsible for the differences in composition and structure of the microbial communities.

Introduction

Attempts during the 1970-80's to establish vegetation on barren pyritic copper tailings in Pronto Tailings Management Area, near Sprague, Ontario (property of Rio Algom Limited), were only partially successful. A good vegetative cover was developed only on the coarse-grained tailings but not on the fine-grained tailings, despite several applications of limestone and fertilizer. Many factors can be identified as possible contributors to the lack of vegetation on the fine-grained tailings. These include poor chemical and physical-chemical properties of tailings such as strong acidity, low content of exchangeable Ca^{2+} and Mg^{2+}, high levels of exchangeable H^+ and Al^{3+}, a lack of organic matter; undesirable physical properties such as high moisture, low porosity of aeration and, therefore, low O_2 content in spring, and low moisture and crust formation in summer, as well as high compactness, lack of structure, and low total porosity. Phytotoxicity because of high concentrations of heavy metals and exchangeable Al^{3+} are another factors limiting normal growth and development of the vegetation on acidic copper tailings.

The poor performance of previous revegetation led to the remediation experiments on the fine-grained copper tailings at Pronto proceed through neutralization of the tailings with lime, followed by covering of ~50 cm of paper-mill sludge. This remediation scenario is expected to produce several benefits such as protection against further AMD (acid mine drainage) generation in the tailings, a reduction in the salts accumulation near the surface, a more diverse and stable vegetation community than would be obtained with local topsoil, and a reduction of water and wind erosion of barren tailings. Further cost and public

approval benefits to local industries arise from the uses of one waste material to reclaim another.

Methodology

Large-Scale Experiment

Fresh paper sludge from St. Marys Paper Ltd. (Sault Ste. Marie, Ontario) was shipped to the Pronto Tailings Management Area tailings site and applied on fine tailings during the winter of 1999. The total area of the plot was approximately 1 hectare, with the design thickness of the applied paper sludge being approximately 40 to 50 cm. Prior to sludge application, lime was spread on the tailings surface to neutralize upwardly migrating groundwater. No mineral fertilizers were applied to the plot. In May of 1999, it was hydro-seeded with a Mine Reclamation Mixture (Red Top, Creeping Red Fescue, Canada Blue Grass, Kentucky Blue Grass, Timothy, Red Clover, Birdsfoot Trefoil) at 75 kg/ha.

Semi-Operational Experiment

Approximately 300 tons of fresh sludge from St. Marys Paper Ltd. was shipped to the Pronto TMA and spread on a 20 × 100 m plot to a depth of approximately 15 cm. The plot was then divided into two sub-plots (10 × 100 m). On one sub-plot, the paper sludge was incorporated (mixed) with the top layer of tailings. Therefore, there were two types of subplots: covered with paper sludge and incorporated. No fertilizer was added to either sub-plot; the same mine reclamation grass mixture was seeded on both.

The monitoring program includes the following facets characteristic of both agricultural and environmental research monitoring programs:

- the determination of the effect of paper sludge on the establishment and growth of vegetation on fine copper mine tailings materials;
- nutritional, water, and temperature regimes of organic cover;
- chemical and physical properties of both the organic cover and tailings materials;
- chemical properties of groundwater;
- behavior of some potentially toxic elements within the sludge-tailings-groundwater-vegetation system.

Each mixed paper sludge and tailings sample was combined from 5-7 individual samples. In the laboratory, all debris such as stones, tree branches, bark, and wood chips, were removed. In these fresh samples, soil moisture, hygroscopic coefficient, pH, electrical conductivity, and redox-potential were determined. After this, samples were dried at room temperature, ground, and prepared for chemical analyses.

Various plant species were collected for analyses. Each mixed sample was collected from 50 to 150 individual samples. In the laboratory, both wet and dry weight of 1000 stems was determined. In addition, the aboveground biomass from 1 × 1 m quadrants was cut to determine the output per square meter, and to perform chemical analyses on it. In the laboratory, both wet and dry weight (g/m^2) was determined. After drying, all samples were ground. Representative portions were taken from these "macro-samples" for chemical analyses.

Piezometers were installed on the both control and covered tailings sites to enable monitoring of the pore-water chemistry. The piezometers were installed with screens at different depth to collect water at 0-31 cm, 31-62 cm, 62-93 cm, and 93-124 cm. Samples of pore-water were taken in October and November of 1999. The following year all the piezometers were empty because the water table was lower due to the construction of a system of drainage ditches throughout the fine tailings area.

Results and Discussion

Soil Moisture

Initial paper sludge moisture was equal to ~ 250%. Over time, on both the large-scale and semi-operational experimental plots, a clear gradual reduction of the sludge moisture was found (Table 1), which was caused by intensive evapotranspiration. On tailings with a thinner organic layer and less abundant vegetation (semi-operational plot), sludge moisture content stabilized at approximately 80%. The establishment of more abundant vegetation on the 1-ha plot resulted in drying out the upper layer of paper sludge even more with moisture levels dropping to 40%. Hygroscopic moisture levels increased over time (Table 2) showing thus that

the level of non-available water in paper sludge slightly increased.

Covered tailings had some small areas where vegetation was not well developed. Measurements showed that paper sludge from these areas was characterized with much higher moisture levels. Therefore, it may be concluded that development of too abundant vegetation on paper sludge causes significant drying the sludge, and in the future, vegetation developed on paper sludge can suffer from the lack of available water.

There is a tendency for moisture levels of revegetated tailings (under paper sludge) to be lower than barren untreated tailings (control).

Table 1: Paper sludge and tailings moisture (%)

Material	Large-scale plot		Semi-operational plot		
	1st year	2nd year	1st year	2nd year	3rd year
Paper sludge	202 / 87*	40	182	106	81
Mineral tailings	35	31	30	29	28

*July and August, respectively

Table 2: Paper sludge and tailings hygroscopic moisture (%)

Material	Large-scale plot		Semi-operational plot		
	1st year	2nd year	1st year	2nd year	3rd year
Paper sludge	6.0 / 6.7*	10.4	n.a.	6.8	9.9
Mineral tailings	1.6	2.4	n.a.	2.2	2.7

*July and August, respectively

Soil reaction (pH)

Original paper sludge had a neutral reaction. When a thick layer of the sludge was applied (50 cm in the large-scale experimental plot), no paper sludge acidification was found over time. However, after the application of a relatively thin layer of this organic amendment (15 cm, semi-operational plot), gradual sludge acidification did occur (Table 3). Therefore, to prevent this process, more lime has to be spread on the tailings prior to the sludge application. On our opinion, the use of 3-4 cm layer of lime on the acidic copper tailings could be sufficient to keep the pH of the organic amendment within the neutral level.

Table 3: pH of paper sludge and tailings

Material	Large-scale plot		Semi-operational plot		
	1st year	2nd year	1st year	2nd year	3rd year
Paper sludge	6.6	6.9	6.3	6.1	5.5
Mineral tailings	3.6	4.2	3.8	4.2	4.2

Temperature Regime of Paper Sludge and Tailings

The temperature of a soil greatly affects the rate of chemical, physical, and biological processes. Biodegradation in soil can come to a near standstill, thereby limiting the rate at which nutrients (N, P, S, Ca) are made available. In addition, absorption and transport of water and nutrients by higher plants are adversely affected by low temperature.

The study of the tailings temperature is important, because the rate of pyrite oxidation is strongly temperature dependant. This is logical since the rate is related to the Arrhenius equation in which the rate is an exponential function of temperature. This relationship predicts a 4-5-fold increase of the rate for a 10-degree increase, still quite significant.

Barren and vegetated sludge-covered tailings had various temperature profiles. The surface of

barren sites was characterized by higher temperature values than vegetated areas (Table 4).

Table 4. Air, surface, and soil temperature

	August, 1999		October, 1999		November, 1999	
	Barren	Vegetated	Barren	Vegetated	Barren	Vegetated
Air	28.4	28.1	10.3	10.1	-0.6	-0.7
Surface	36.0	30.0	12.4	10.8	2.3	0.2
Sludge (top)	26.9	32.0	9.2	14.0	7.7	9.2
Sludge (bottom)	22.8	31.9	13.2	18.1	12.2	14.4
Tailings (top)	20.3	27.7	n.a.	n.a.	13.6	15.8
*Tailings (top)	n.a.				1.5	n.a.
*Tailings (bottom)	n.a.				4.4	n.a.

* Control (no paper sludge applied)

On the contrary, the temperature of sludge (both top and bottom layers) and tailings (top) on vegetated sites was higher than on barren areas. The highest difference (9 ºC in August) between these sites was found in the bottom layer. In October and November, the differences became less significant, but these tendencies did remain. Most probably, higher temperature is caused by higher microbiological activity on the vegetated areas. Most likely, the cellulose-breaking thermophilic bacteria *Clostridium thermocellum* and *C. thermosaccharolyticum* were responsible for the decomposition of paper sludge cellulose and the accompanying heat release. In addition, plant cover of vegetated sites may play a role as a thermo-barrier, decreasing heat irradiation from the sludge to atmosphere.

Chemical reaction rates, particularly for pyrite oxidation, became different on barren and covered tailings, so comparative monitoring of both types of tailings is recommended in further research to evaluate qualitatively and quantitatively biogeochemical processes occurring in both situations, and reveal the influence and role of organic cover in these processes.

Nutrients in paper sludge and tailings

Results on the levels of organic carbon and total Kjeldahl nitrogen show significant mineralization of paper sludge (Tables 5 and 6). Interestingly, higher losses of organic carbon were found in the semi-operational plot, where thinner layer of the sludge was applied. Levels of nitrogen in the organic amendment in both experiments were similar. At the same time, C/N ratio was slightly more favorable in the sludge from the semi-operational plot (28 during the first three years and 23 on the third year) than in the large-scale experiment (30-31).

Table 5: Nitrogen levels (TKN, g/kg) in paper sludge and tailings

Material	Large-scale plot		Semi-operational plot		
	1st year	2nd year	1st year	2nd year	3rd year
Paper sludge	10.9	9.0	11.9	7.2	9.1
Mineral tailings	0.14	0.25	n.a.	n.a.	0.10

Table 6: Organic carbon levels (%) in paper sludge and tailings

Material	Large-scale plot		Semi-operational plot		
	1st year	2nd year	1st year	2nd year	3rd year
Paper sludge	33	28	33	20	21
Mineral tailings	0.5	n.a.	n.a.	0.2	<0.1

*C level in the initial paper sludge was 38%

In the large-scale experiment, levels of phosphorus were around 1.3 g/kg during the first two years. In the semi-operational experiment, it was gradually decreasing from 1.2 to 0.7-0.8 g/kg from 1st to 3rd year after the sludge application. Significant bioremoval of this nutrient by abundant vegetation growing on paper sludge could be one of the main reasons for this.

Two to three years after sludge application, plants contained levels of nitrogen, phosphorus, and potassium similar to the vegetation from the tailings revegetated 30 years ago without paper sludge application. However, because of the higher crop yield of the covered plots, the bioremoval of macro-nutrients (g/m^2) was higher. However, there was an obvious tendency for N, P, and K bioremoval to be reduced on these plots. Most likely, in the future the difference in macro-nutrients bioaccumulation between covered plots and naturally vegetated tailings will be insignificant.

The Influence of Paper Sludge on Plant Growth

Over time, on both the large-scale and semi-operational experimental plots, timothy became the dominant grass. The dry weight of 1000 timothy stems stabilized during the 2nd and 3rd year at approximately 2.0 kg. On both covered plots, the dry weight of 1000 stems of the other grasses (grass mixture of rye-grass, blue-grass, squirrel-grass, and other) decreased over time.

Data on crop yield of vegetation collected on 1 × 1 m quadrants showed that wet weight of aboveground biomass reached 1800 g/m^2, and dry weight – 500-900 g/m^2 (Table 7). From an agricultural point of view, such crop yield capacity is high, and reflects a good nutritive regime of paper sludge. Over time, the output of vegetation on each m^2 decreased on the semi-operational plot and increasing on the 1-ha plot, which related to thicker layer of sludge on the 1-haplot.

Table 7: Crop yield on 1 × 1 m quadrants (August sampling)

Parameter	1-ha plot		Semi-operational plot	
	Years after remediation/revegetation			
	1st	2nd	2nd	3rd
Wet weight, g/m^2	1844	1418	1821	1155
Dry weight, g/m^2	485	723	941	570
Dry matter, %	27	51	52	50

Heavy metals in vegetation on remediated plots

Plants growing on paper sludge contain lower amounts of some trace elements compared to the same species growing on the non-covered tailings, because root penetration into the tailings matrix was minimal, promoting thus lower translocation of metals to the vegetative material (Table 8). Vegetation from 1-ha plot contained, as a rule, lower levels of heavy metals than plants from the semi-operational plots because of the higher sludge thickness on the 1-ha plot.

Table 8. Levels of elements (mg/kg) in vegetation from the covered and non-covered copper tailings, semi-operational plot (1999)

Site type	Species	Fe	Al	Mn	Cu	Ni	Zn	Pb	Co
Paper sludge	Timothy	127	186	76	6.2	1.31	22.1	0.62	1.79
Control*		857	712	106	14.3	3.45	20.1	1.44	8.82
Paper sludge	Blue-grass	425	165	156	4.7	1.56	20.7	0.46	1.99
Control*		364	275	176	8.6	2.22	12.1	1.30	5.50

* Isolated plants growing on copper tailings where paper sludge was not applied

Microbiological activity of paper sludge

Microbiological activity in the original paper sludge, i.e., before application, was relatively low, with the number of bacteria at 10^6-10^7 CFU/g and micro-fungi at less than 10^3 CFU/g. Actinomycetes were not found. However, at the end of the first year, the upper 15-cm layer of sludge proved to be much more enriched in bacteria (up to 2×10^8 CFU/g) and actinomycetes (10^6 CFU/g). Over time, the numbers of bacteria have gradually decreased, but fungi have increased, indicating a successional pattern typical for cellulose containing materials. Microbiological activity of the bottom layer of paper sludge differed from the upper layer. For example, in the upper layer, mycelial organisms (fungi and actinomycetes) were dominant, whereas bacteria were dominant in the bottom layer. Different moisture, temperature, and gas regimes in the upper and lower layers were, probably, responsible for the differences in composition and structure of the microbial communities.

Conclusions

In semi-operational and large-scale experiments, lime and paper sludge were applied on fine copper tailings to both enhance site stabilization and promote establishment of healthy, sustainable vegetation. Application of these soil amendments prevented water and wind erosion of mineral tailings and resulted in neutralization of upward migrating porewater and tailings surface. Paper sludge placement over sulfide tailings could hinder tailings oxidation and generation of acidic mine drainage. Improved site aesthetics was an important consequence of this technology.

The nutritive regime of paper sludge becomes depleted with time. The measured contents of both organic nitrogen and carbon have decreased rapidly over the duration of the current study indicative of fast mineralization of the applied cellulose-rich organic material. However, some probable reduction of the aboveground biomass on the covered tailings cannot be considered as negative.

Vegetation plays an important role in both thermo- and water regimes of the organic soil amendment. Transpiration has been found to be a more significant factor in water losses from the soil than evaporation on vegetated sites.

No acidification of paper sludge was found on the site covered with the thick layer (50 cm) in contrast to the semi-operational plot where sludge depth was relatively small.

Plants growing on paper sludge contain lower amounts of some trace elements than the same species growing on barren tailings. At the same time, vegetation from the site with thicker layer of paper sludge (50 cm) was characterized by less bioaccumulation of heavy metals, than plants from plots with relatively thin layer of organic amendment (15 cm). This observation suggests that, at this stage of the ecosystem development, plants are deriving much of their nutrient supply from the sludge material, with minimal penetration of roots into the underlying tailings materials.

The research data obtained in this study indicates prospective ways to control and improve the processes and regimes occurring in paper sludge used for the stabilization and revegetation of barren copper tailings.