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Valorisation of acid mine drainage treatment sludge as remediation component to control acid generation from mine wastes, part 1: Material characterization and laboratory kinetic testing



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ARTICLE INFO

Article history:
Received 28 July 2014
Revised 4 October 2014
Accepted 8 October 2014
Available online 26 November 2014

Keywords: Acid rock drainage Tailings Environmental Reclamation

ABSTRACT

In operating mines, acid mine drainage (AMD) is often treated using lime treatment. This process generates a significant amount of sludge that contains metal hydroxide precipitates, gypsum, and unreacted lime. The sludge may have interesting geotechnical and geochemical properties to be used as a part of covers (oxygen barriers) to prevent AMD generation from waste rocks and tailings. The main results of a project aiming to evaluate the use of sludge from the Doyon mine site (Canada) as a material in mine site rehabilitation are presented. The first part of the project involved detailed characterization of sludge, waste rock, and tailings samples. Then, laboratory column leaching tests were performed to evaluate the performance of the mixtures to control AMD produced by tailings and waste rocks. It was found that a sludge—waste rock mixture placed over waste rock reduces the metal loads in the column effluent, which remained acidic, as well as a mixture of sludge and tailings deposited over tailings can reduce metal content in effluents from tailings.

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1. Introduction

Acid mine drainage (AMD) is one of the most significant environmental issues related to the mining industry. It is caused by the oxidation of sulfide minerals present in the mine waste when exposed to air and precipitation, such as in mine waste storage facilities (tailings impoundments and waste rock piles). Oxidation may also be enhanced by acidophilic and neutrophilic sulphooxidans bacterial activity under optimal conditions (e.g., Silverman, 1967; Holmes and Crundwell, 2000; Blowes et al., 2003). Regulations in several jurisdiction require that AMD generating mine waste storage facilities be reclaimed upon site closure to prevent further oxidation. Several effective mine waste management methods and reclamation techniques were developed in the past decades to prevent and/or control the generation of AMD from mine wastes. In a humid climate such as in Canada, the most effective methods involve the limitation of oxygen transport towards the sulphidic tailings, thereby removing one of the three essential reagent of the oxidation reaction (sulfides, water, oxygen) which may prevent oxidation from occurring (e.g. Nicholson et al., 1989; Bussière et al., 2003).

However, during operation and/or when the reclamation method is not yet effective, acidic drainage must be treated to respect the effluent water quality criteria applied in the jurisdiction of the mine site. The most common method to treat AMD is by neutralization with an alkali (such as lime) through an active process, which raises the pH and precipitates dissolved metal ions as hydroxides (Skousen and Faulkner, 1996; Brown et al., 2002; Younger et al., 2002; Zinck and Griffith, 2012, 2013). Flocculants are usually added to promote settling of the resulting sludge and to produce a clear overflow. This process generates large quantities of low solid density sludge (high water content) which is deposited into a pond for further settling and storage. Because of the presence of excessive unreacted lime, gypsum and other sulfate and hydroxide species, the sludge can maintain an alkaline to neutral pH for several decades in the sludge pond (Zinck et al., 1997). Even if sludge ponds maintain a high pH with time, they must be reclaimed at the end of the mining operations similarly to other mine waste storage facilities. Given their fined-grained characteristics and neutralizing properties, the sludge may be a possible alternative to be used as material in AMD-generating waste reclamation methods, and would then reduce the environmental

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footprint of the reclaimed lands by combining two types of waste in an optimal fashion.

A review of different sludge disposal scenarios is provided in Zinck (2005, 2006), Zinck et al. (2010), and Zinck and Griffith (2012, 2013). The options reviewed include sludge mixture with tailings and waste rocks, sludge covers over tailings, sludge disposal in tailings ponds and with waste rock, sludge disposal in mine workings and pits, placement under a water cover, use of sludge in cemented mine backfill, disposal in a landfill, and hazardous waste disposal. The studies mention that sludge disposal with tailings and waste rocks is effective only when the mine wastes are non-acid generating and sulfide mineral oxidation is prevented, otherwise, sludge dissolution and metal remobilization may become an environmental issue. More specifically, Zinck et al. (2010) showed that a sludge cover placed over tailings was not able to control tailings oxidation, because desiccation cracks provide preferential channels for air and water flow, and alkalinity was not sufficient to reduce metal mobility from the tailings.

The Doyon-Westwood mine site in Rouyn-Noranda, Quebec, Canada, operated by IAMGOLD, has a sludge pond that was filled several years ago and would need to be reclaimed. The objectives of the project were to investigate the use of AMD treatment sludge as a component in site reclamation methods. Since it was identified to be unsuitable as cover material by itself by Zinck et al. (2010), the sludge was tested as a mixture with either waste rock or tailings. The geotechnical properties (Bouda et al., 2012) and sludge's alkalinity are expected to reduce AMD generation from the Doyon tailings and waste rocks. Experiments in the laboratory were first conducted to identify the potential mixtures that can reduce AMD generation when placed over acid-generating tailings and waste rocks. Then, the most efficient configurations were tested in situ at an intermediate scale (10–125 m³). The present paper describes and reports on material characterization and laboratory column kinetic tests, while the companion paper describes the construction of the field test cells and reports the results of the first two seasons of monitoring.

2. Materials and methods

2.1. Material sampling and mixture preparation

Different materials were required for the project. Waste rock and unoxidized tailings were sampled by IAMGOLD personnel and provided as drums. Unoxidized tailings were collected from fresh deposition and were kept saturated during transport and laboratory storage. Since the homogeneity of the sludge pond was unknown, a sludge sampling campaign was organized by Golder Associates in order to verify the spatial variability of the sludge characteristics within the pond. Seven sampling points were identified, and sampling cores reached depths between 8 and 24 feet following the initial site topography. The sampling points were selected based on information provided by the operator (IAM-GOLD) in order to cover most of the accessible surface of the pond and to ensure representativeness. Chemical analyses of core samples revealed that the chemical variability of sludge within the pond is low. For example, Fig. 1 presents Ca, Fe and S concentration in 5 sampling points (sample point P2 was planned but not accessible) and their average. These results were used to verify the variability of the sludge over the pond. Coefficients of variability (COV) below 0.14 were obtained for major elements (Ca, Mg, Fe, Al, S). Following these results, a composite sample was chosen for the remainder of the study.

Mixtures of sludge with waste rock and tailings were prepared in the laboratory from the humid state. For the sludge and waste rock mixtures, two different mixtures were prepared by manual

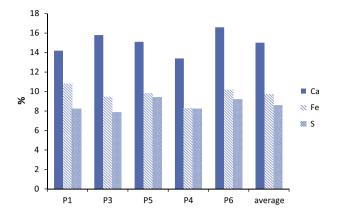


Fig. 1. Ca, Fe and S concentration in different sampling points over the surface of the sludge pond.

mixing: mix #1 with 25% sludge and 75% waste rock (by weight), and mix #2 with 10% sludge and 90% waste rock (by weight). Three mixtures of sludge and tailings were prepared using a mechanical mixer: mix #1 with 25% sludge and 75% tailings, mix #2 with 10% sludge and 90% tailings, mix #3 with 2 wt% Portland cement added to mix #2. The sludge and tailings proportions were by weight, and the initial water contents for the sludge and tailings are 120% and 26%, respectively. The selection of the sludge proportion was based on the quantity available for potential use over the site's tailings ponds; 25% sludge in a mixture was identified as the maximum sludge content according to the estimated sludge quantity at the Doyon site.

2.2. Material characterization

Different physical, chemical and mineralogical parameters were measured to characterize the materials. Specific gravity (G_s) was evaluated for sludge, waste rock, tailings, and sludge-tailings mixtures using a Micromeritics Accupyc 1330 helium pycnometer. according to ASTM D-550-06. Particle size distribution was obtained through dry screening and laser particle size analyzer (Malvern Mastersizer) for sludge and tailings. The distribution was then used to determine the D_{10} and D_{50} (diameter of 10% passing and 50% passing, respectively), and the geotechnical parameters C_U and C_C (coefficient of uniformity and conformity, respectively). Air-entry value was determined from the water retention curves evaluated for tailings and sludge-tailings mixtures using pressure plate extractor (Bouda et al., 2012). The chemical composition of sludge, waste rock and tailings was obtained by digestion in HNO₃/HCl/HF/Br followed by ICP-MS analyses. Acid generation potential was evaluated by the acid-base accounting procedure by Sobek modified by Lawrence and Scheske (1997), for sludge, waste rock and tailings samples. Mineralogical composition of the major crystallized phases was obtained through X-ray diffraction for sludge, tailings and waste rock, and quantified by the Rietveld method with the software TOPAS (Rietveld, 1993). The apparatus used is a D8 Advance by Bruker A.X.S. equipped with copper radiation.

Table 1 presents the physical characterization results while Table 2 presents selected chemical parameters analyzed for the studied samples. Tailings and waste rock exhibit similar density (at 2.8) while the sludge has a lower density (2.1) due to its different mineralogical composition. Waste rock particle size distribution is biased because large rocks (i.e. >30 cm) were removed prior to shipping to the laboratory. It is expected to encounter from boulder size to micrometer particles in the waste rock pile, however for the purpose of the laboratory study, rocks larger than 5 cm were discarded because of their large size and lower

Table 1Selected physical parameters evaluated for waste rock, sludge, tailings, and sludge-tailings mixture samples.

| Material | G_s | $D_{10}\left(\mu m\right)$ | $D_{50} (\mu m)$ | C_U | C_C |
|-------------------------|-------|----------------------------|------------------|-------|-------|
| Waste rock | 2.8 | 10.4 | 1600 | 375 | 1.0 |
| Tailings | 2.8 | 3.8 | 39 | 15.0 | 1.1 |
| Sludge | 2.1 | 2.6 | 25 | 17.8 | 0.6 |
| 10% Sludge-90% tailings | 2.8 | 4.0 | 27 | 9.54 | 1.0 |
| 25% Sludge-75% tailings | 2.7 | 3.8 | 28 | 10.5 | 1.1 |

Table 2Selected chemical parameters evaluated for waste rock, sludge, and tailings.

| Parameter | Waste rock | Tailings | Sludge |
|----------------------|------------|----------|---------|
| Al (%) | 7.0 | 6.2 | 2.1 |
| As (%) | <0.003 | < 0.003 | < 0.003 |
| Cu (%) | 0.008 | 0.1025 | 0.03 |
| Fe (%) | 5.4 | 5.78 | 9.21 |
| Mg (%) | 1.7 | 0.9915 | 1.59 |
| Ni (%) | 0.0145 | 0.001 | 0.006 |
| Zn (%) | 0.004 | 0.014 | 0.01 |
| S total (%) | 1.185 | 3.43 | 7.37 |
| S sulfate (%) | 0.39 | 0.38 | 7.5 |
| Ca (%) | 2.175 | 2.875 | 18.6 |
| NP (kg $CaCO_3/t$) | 4.2 | 40.6 | >203 |
| NNP (kg $CaCO_3/t$) | -21.5 | -55.7 | >203 |

reactivity (Price and Kwong, 1997). Tailings present a typical particle size distribution for hard rock mine tailings (Bussière, 2007). Sludge is finer than tailings, with a D_{50} of 25 μm . This result may also be biased because sludge particles had a tendency to agglomerate and while care was taken to separate the particles (including high attrition during measurement), some agglomerates may have remained together during the measurement. In terms of physical parameters, the sludge–tailings mixtures are very close to the tailings properties. The addition of sludge did not have much impact on particle size distribution, and reduced slightly (by 0.1) the relative density.

The chemical characterization results show that sludge possesses a strong neutralization potential (above the limit of the method used) and all of its sulfur is present as sulfates. Both the waste rock and tailings are considered acid generating because their net neutralization potential (NNP) is below -20 kg $CaCO_3/t$. Arsenic, copper, nickel and zinc concentrations are low in the three materials tested (<0.1%); whereas iron is present in significant concentrations, between 5% and 10%. Calcium occurs in high concentration in sludge (18%), because of the use of lime ($Ca(OH)_2$) in the AMD neutralization process.

Pyrite was detected by XRD in waste rock (<1%) and in tailings (3%). The main gangue minerals identified are quartz, albite, muscovite and chlorite. Sludge being mostly amorphous, its composition is not well characterized by XRD, therefore the results apply only to the crystallized fraction and cannot be extrapolated to the entire sludge mass, which may contain an important amorphous fraction. Only the crystallized fraction was analyzed, and consists of gypsum and ettringite. Metal hydroxides are expected to be present in amorphous form, as well as lime.

The tailings air-entry value (AEV) was determined to be 20 kPa for tailings and for uncemented sludge-tailings mixtures, while the sludge-tailings mixture with cement presents the highest AEV at approximately 30 kPa.

2.3. Column configuration and test procedure

Laboratory column tests are often used to evaluate the performance of cover configurations placed over AMD generating tailings (Demers et al., 2008; Bellaloui et al., 1999; Yanful et al., 1999). The

column test procedure represents one-dimensional water and gas flow through unsaturated and saturated materials by fixing the water table position and by simulation of water recharge. The performance of the cover system is evaluated by monitoring the effluent quality, the suction and water content in the cover materials. In this project, two types of column tests were performed:

- "Big" (30 cm diameter) column tests on the use of sludge-waste rock mixtures to control AMD generation from waste rock;
- "Small" (14 cm diameter) column tests on the use of sludge-tailings mixtures to control AMD generation from tailings.

The first three columns (diameter of 30 cm) were installed to test the use of sludge–waste rock mixtures to control AMD generation from waste rock with the following configuration:

CO#1: 35 cm waste rock (control column).

CO#2: 35 cm of 25% sludge-75% waste rock mixture placed over 35 cm waste rock.

CO#3: 35 cm of 10% sludge–90% waste rock mixture placed over 35 cm waste rock.

Volumetric water content in the sludge-waste rock cover layer was monitored using ECH₂O probes set to record measurements every 12 h at mid-height of the cover (17.5 cm from the surface). Suction was measured once per month with tensiometers positioned also 17.5 cm in the cover layer from the top surface of the column. Water recharge was added to the top of the column every month, and allowed to drain by the bottom outlet. The volume of flushing water added was sufficient to completely flood the material in the column, in order to capture the secondary mineral precipitates that would have formed on the waste rock surfaces as a result of sulfide oxidation and acid neutralization. The effluent was analyzed for pH, Eh, conductivity by probe readings, acidity and alkalinity by titration, and metal content by ICP-AES.

The second set of columns (diameter of 14 cm) installed to evaluate the use of sludge-tailings mixtures to control AMD generation from tailings, comprises four columns with the following configurations:

CO#4: 35 cm tailings (control column).

CO#5: 35 cm of 25% sludge-75% tailings mixture (porosity (n) of approximately 0.44) placed over 35 cm tailings (n = 0.5).

CO#6: 35 cm of 10% sludge–90% tailings mixture ($n \approx 0.44$) placed over 35 cm tailings (n = 0.5).

CO#7: 35 cm of 10% sludge–90% tailings mixture with 2% cement ($n\approx0.44$) placed over 35 cm tailings (n=0.5).

These columns are also equipped with volumetric water content sensors and tensiometers to measure suction placed at midheight of the cover (17.5 cm from the top). Monthly leaching was done by adding 2 L of deionized water to the top of the column. The chosen leaching volume is based on two considerations: (i) to displace most of the pore water volume of the acid-generating tailings (approximately 2 L), and (ii) to simulate realistic precipitation (approximately 130 mm/month). The leachate collected at the bottom was analyzed for the same parameters as the waste rock columns.

3. Results

3.1. Use of sludge-waste rock mixtures to control AMD generation from waste rock

The results related to the column tests on the use of sludge—waste rock mixtures are presented first in terms of volumetric

water content and suction, and then geochemical results are presented. Volumetric water content measurements showed that the sludge-waste rock mixtures were not able to maintain a high degree of saturation. Indeed, the volumetric water content stayed between 2% and 5% for mixtures 25% sludge-75% waste rock and 10% sludge-90% waste rock, while it stayed somewhat higher between 6% and 10% for the mixture 10% sludge-90% waste rock with cement. The exact porosity of the mixtures was not determined; however these values of volumetric water content represent a low degree of saturation. Visually, the sludge-waste rock mixture appeared as a thin sludge coating over the waste rock particles, with minimal cohesion between waste rock particles. Measured suction values were generally between 1.5 and 10 kPa, which are probably above the AEV of the sludge-waste rock mixtures. An estimate using the modified MK model (Aubertin et al., 1998, 2003) indicated that the AEV of the waste rock would be around 0.6 kPa. The mixtures as cover are not expected to be efficient as an oxygen barrier due to the low water content. However, the high alkalinity of the sludge may provide neutralization of the acidity produced by sulfide oxidation. This hypothesis was verified by monitoring the effluent quality for a period of one year. The evolution of pH over the course of the test is presented in Fig. 2a. The effluent of the control column remained low, at pH values of approximately 2.5, whereas the covered columns maintained a slightly higher pH (between 2.8 and 3.3 depending on the configuration). However, the increase in pH with the application of the cover was not sufficient to reach neutral values, perhaps due to the relatively low amount of sludge added compared to the total mass of the mixture. Furthermore, the sludge did not prevent sulfide oxidation from the waste rock, and the sludge neutralization

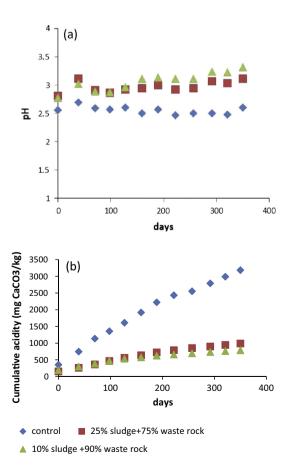


Fig. 2. Evolution of pH (a) and normalized cumulative acidity (b) in the effluent of the column tests on waste rock.

potential may be depleted rapidly. Eh values, not presented here, varied between 515 mV and 860 mV, with an average of approximately 730 mV for all columns. These values represent and oxidizing environment, which support the assumption that sulfide oxidation occurred. The increase in pH was accompanied by a decrease in acidity for the covered configurations, as shown in Fig. 2b, where acidity for covered columns was more than half of that of the control column. Acidity was expressed as cumulative acidity normalized for the total mass of waste rock in each column (35 kg in control, 70 kg in waste rock covered with sludge-waste rock mixtures) to better illustrate the influence of the waste rock-sludge mixtures to reduce AMD generation. From 70 days on, the acidity produced by the control column is approximately three times that of the covered columns, which indicates that the waste rock-sludge mixture indeed provides neutralization of acidity produced by the waste rock, but not sufficiently enough to generate a neutral effluent.

The beneficial effect of the sludge–waste rock mixture cover is also seen by the concentration of metal species in the effluents. Fig. 3 presents the evolution of zinc and copper, expressed as mg metal per kg of waste rock in the column (including the cover). The presence of the cover reduces the concentration of zinc and copper in the effluent, the most significant reduction occurring with the 10% sludge–90% waste rock mixture, with values stabilized at 0.1 mg Zn/kg and 0.4 mg Cu/kg, from values approximately of 0.25 mg Zn/kg and 1.5 mg Cu/kg in the uncovered configuration.

In typical column tests, the evolution of sulfur and calcium loads in the effluents can also indicate the extent of inhibition of oxidation by the cover because it is generally assumed that most sulfur (most probably as sulfates) is released by sulfide mineral oxidation, and that calcium is released during dissolution of neutralizing minerals to counteract the acidity produced by sulfide oxidation (Benzaazoua et al., 2004). However, in the present project, the dissolution of the sludge, which is rich in calcium sulfate minerals, may also contribute to the overall amounts of Ca and S found in the effluents. Indeed, the graphs of cumulative calcium and sulfur release (Fig. 4) show that more Ca is released in the covered column effluents, while more S is released in the control

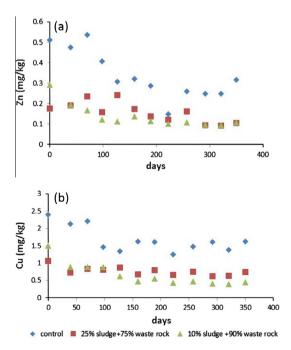


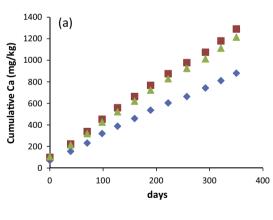
Fig. 3. Evolution of Zn (a) and Cu (b) normalized load in the effluent of the column tests on waste rock.

column. The reduction of S in the covered columns effluents can be explained in part by a reduction in sulfide oxidation rate caused by the addition of the sludge–waste rock cover, and in part by the precipitation of sulfur-bearing minerals during acid neutralization. Part of the S may also come from the partial dissolution of sludge, so it is not possible with only S release data to quantify the real reduction in sulfide oxidation caused by the sludge–waste rock mixture. The sludge dissolution is confirmed by the difference in Ca release between the covered columns and the control column. Further verifications were done using thermochemical modeling (Visual MINTEQ). Simulations confirmed that gypsum and ettringite (among others) are unsaturated and may dissolve, while other minerals containing sulfate, such as jarosite, are oversaturated and may precipitate.

To summarize, the sludge–waste rock mixtures, when placed on waste rock, were not able to completely prevent the generation of AMD. The low AEV of the mixture resulted in a low volumetric water content, sulfide oxidation in the waste rock was not sufficiently reduced, and the sludge neutralization potential was not enough to yield a neutral leachate. However, the sludge–waste rock mixture reduced the metal loading in the effluent. These results correspond well with work performed by Coleman et al. (1997), where waste rock covered by sludge was tested in barrels. They also found that the sludge layer provided limited neutralization of the acid generating waste rock, reduced the metal concentrations, and suspected dissolution of part of the calcium sulfate present in the sludge.

3.2. Use of sludge-tailings mixtures to control AMD generation from tailings

The sludge-tailings mixtures were placed on non-oxidized tailings as described above. Suctions measured in the sludge-tailings



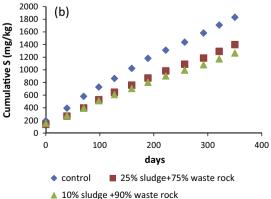


Fig. 4. Cumulative Ca (a) and S (b) load for the effluents of the column tests on waste rock.

layers of the two mixtures tested are presented in Fig. 5. Most of the measurements for the uncemented mixtures are located between 6 and 10 kPa, while the cemented mixture showed suctions of approximately 20 kPa early in the test which then decreased to 12 kPa. The higher suction measured in the cemented mixture may be related to the cement hydration process which induces water suction. The AEV of the mixtures were determined to be around 20–30 kPa, thus the measured suctions are only slightly below the AEV of the cover mixtures. The measured suctions correspond relatively well to the hydrostatic equilibrium suction, which is approximately 7 kPa in this study.

Fig. 6 presents the volumetric water content measured on the 20th day of each cycle in the middle of the sludge-tailings mixture cover. The 20th day was chosen because the volumetric water contents were found to be stabilized for several days at this time. From the sixth cycle on, the volumetric water contents are relatively stable, with values near 30% for uncemented mixtures, and 24% for the cemented mixture. The initial porosity of the mixture cover was calculated to be approximately 0.44, therefore the measured volumetric water contents are quite low, corresponding to a degree of saturation below 70%.

The performance of the mixtures as cover to control AMD generation was evaluated by geochemical monitoring of the column effluents, and by comparison with a control (uncovered) column. The column testing period was established initially at one year (12 leaching cycles). However after 12 cycles, the uncovered column still did not produce acidic drainage. Previous work also observed a delay before AMD generation from Doyon tailings in laboratory conditions (Benzaazoua et al., 2008; Demers et al., 2008); indeed the tailings have a high water retention capacity because of their phyllosilicate content that slows water flow. The Doyon tailings are nevertheless acid generating based on the static tests results, and on field observations. The main drawback for laboratory testing is that it is difficult to state on the performance of sludge-tailings mixtures as cover to limit oxygen transport based on geochemical results, but these results still give clues on the cover performance that will eventually be validated by field tests.

Fig. 7a presents the pH values measured in the column leachates. All values remained neutral, around pH 8, for the duration of the test for all configurations. Acidity was low in all leachates, with values generally below 20 mg CaCO₃/L. There is still some oxidation within the tailings, indeed, Eh values, not presented here, average near 500 mV for all columns, indicating that the systems are oxidizing. Fig. 7b presents the normalized cumulative acidity and demonstrates that acidity is reduced for columns covered with the sludge–tailings mixture, the cemented mixture cover provided the most noticeable reduction. The calculated reduction ratio provided by the uncemented mixtures is 3 for the entire test period,

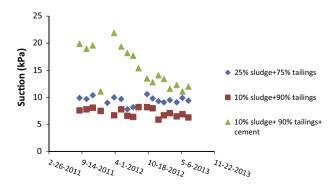


Fig. 5. Suction measurements in the sludge-tailings mixture placed as a cover over tailings.

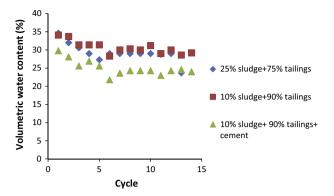
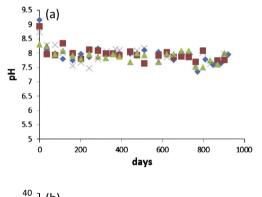


Fig. 6. Volumetric water content in the sludge-tailings mixture placed as cover over tailings.



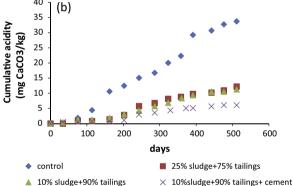


Fig. 7. Evolution of pH (a) and normalized cumulative acidity (b) in the effluent of the column tests on tailings.

which corresponds to the same reduction ratio observed with the placement of the sludge-waste rock mixtures on waste rock.

In neutral leachates, many metal ions theoretically precipitate and are not likely to remain in solution, such as Fe, and were often measured near or below the detection limit of the analytical method. Other elements, such as Cu and Zn, are more soluble at neutral pH and were found in measurable concentrations in the columns leachates. Fig. 8 shows that the copper and zinc loads are lower in covered columns and demonstrate a low rate of increase compared to the control case. For copper and zinc, the column covered with the 10% sludge–90% tailings with cement presents the overall best performance to limit metal release.

The evolution of calcium and sulfur concentrations in the leachates can also provide hints on the oxidation processes occurring in the tailings, since S is produced by sulfide oxidation and Ca by acid neutralization by neutralizing minerals (mostly silicates), assuming that there are no other sources for these elements. As

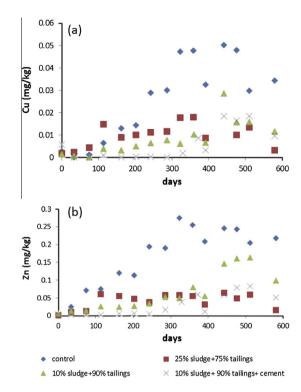


Fig. 8. Evolution of Cu(a) and Zn(b) normalized load in the effluent of the column tests on tailings.

mentioned in the previous section, the sludge used in the mixture may also contribute to release significant amounts of sulfate and calcium. To isolate each of the contributions (pyrite oxidation and sludge dissolution), the possible dissolution of sludge was evaluated by comparison between the covered and control columns, and by thermodynamic modeling (Visual Minteg). Fig. 9 shows that less Ca and S are released in the covered columns compared to the control case, indicating either a dampening of the sulfide oxidation process, or an increase in sulfate mineral precipitation, or a combination of both. The Ca reduction factor is 2.3 for the entire test period, while the reduction factor for S is 2.2. Modeling indicated that gypsum is near equilibrium (saturation index of -0.008) therefore it is less likely to dissolve than in the condition of the waste rock column tests, and no secondary sulfate mineral is oversaturated and would precipitate. The results demonstrate that in neutral conditions prevailing in the column tests on tailings, sludge is unlikely to dissolve.

To verify that calcium release is indeed associated with neutralization of acidity caused by sulfide oxidation, the column test results for the control condition can be used to evaluate the long-term acid generation potential of mine wastes by a method called "oxidation-neutralization curves" (Benzaazoua et al., 2004). When calcium dissolution (and other elements related to the neutralizing minerals, such as Mg and Mn) is caused by acid neutralization reactions, then a plot of Ca + Mg + Mn versus S cumulative release is linear (see Fig. 10a). This linear curve can be extrapolated, and the initial content in the tailings can be positioned on the graph, as presented in Fig. 10b. If the initial content in the tailings is below the curve, the neutralizing minerals content will be depleted before the sulfide minerals, assuming constant reaction rates, therefore the tailings will be considered acid generating in the long term. This method was applied to the control column, which did not generate acid throughout the testing period, although these tailings are known to be AMD generating from ABA testing. The initial composition being below the curve, this

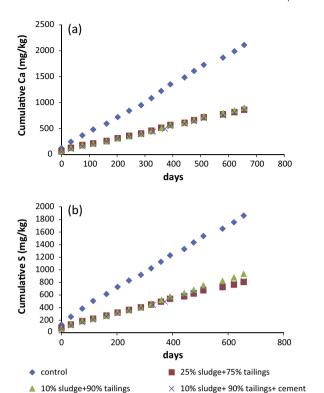


Fig. 9. Cumulative Ca (a) and S (b) load for the effluents of the column tests on tailings.

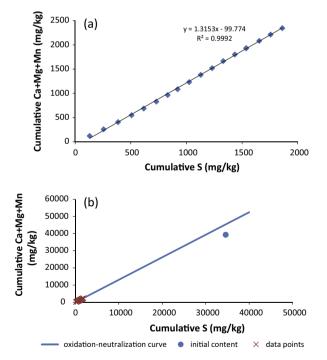


Fig. 10. Oxidation–neutralization curve for the tailings column test, data points and linear regression (a), and extrapolation (b).

material is considered AMD generating in the long term. Because of the possible (however unlikely) contribution of sludge dissolution to the overall calcium and sulfur concentrations in the column leachates, the oxidation–neutralization curves cannot be used for configurations where sludge is present. Overall, the covers made of sludge and tailings mixture were able to reduce the generation of copper, zinc, calcium and sulfur in the effluents from the Doyon tailings column tests. Acidic conditions were not observed for any test, including the control condition (uncovered tailings). However, extrapolation of the reaction rates indicated that the uncovered tailings will eventually generate AMD in the long term which is consistent with previous studies (Demers et al., 2008). Even if the suction measured in the covers were slightly below the AEV of the mixtures, the volumetric water content was somewhat low, and allowed oxygen transport through the cover. With a better control over the volumetric water content of the cover, such as by preventing evaporation with a coarsegrained layer, the oxygen flux would be reduced and the leaching of copper and zinc should be reduced.

4. Discussion

The objective of the research project was to investigate the potential valorization of lime neutralization sludge as part of mine site reclamation. The conventional management of sludge involves mainly deposition in a settling pond and final reclamation at the end of the operations, when the site must be closed. Most of time, sludge is removed and re-deposited in tailings ponds. But given the neutralization properties of the sludge, and its favorable physical properties, sludge management may be engineered to maximize reuse of material and reduce contamination from acid-generating materials. The tests on the use of sludge-waste rock mixtures demonstrate the capacity of the sludge to neutralize part of acid generated by waste rocks. Although the sludge-waste rock mixtures were unable to yield a neutral effluent when placed over acid-generating waste rock, it still reduced significantly the metal loads in the effluents. So the disposal of sludge on waste rock could be an interesting option to reduce the dissolved metal concentrations of an effluent to regulate the feed to a water treatment plant, at least temporarily. This option should not be considered an alternative to an adequate reclamation of the waste rock pile, since the experiments identified the possible re-dissolution of sludge which could eventually re-solubilize precipitated metal ions and affect the effluent quality. Indeed, the risk associated with sludge dissolution was highlighted by Zinck (2005) and Zinck et al. (2010) where she identified several factors that can affect sludge stability, including leachant pH. With a low leachant pH, metal leaching is expected, and the metal concentrations reached may exceed the regulatory limits.

The tests on the use of sludge-tailings mixture were not yet conclusive on the ability of the mixture to prevent acid generation. However, using acidity and metal loads as clues, mixtures proved to be able to reduce the rate of sulfide oxidation from the tailings. Therefore, sludge deposition with tailings, particularly towards the end of the tailings storage pond useful life, may be an interesting option to reduce metal content in the effluents, and possibly to reduce acid generation.

The tests were conducted in controlled laboratory conditions. To further evaluate the valorization potential of the sludge to reduce acid mine drainage generation from waste rock and tailings, intermediate scale field tests (10 to 125 $\rm m^3)$ were initiated. Results from the first two seasons of monitoring are presented in the companion paper.

5. Conclusions

Lime neutralization sludge management is often considered a simple and straightforward task: deposition in a settling pond and final reclamation or re-deposition in tailings pond at the end of operations. However, the sludge presents interesting properties

which can be taken advantage of, particularly in terms of reduction of acid mine drainage from mine wastes. Column experiments in the laboratory were conducted to identify the potential mixtures that can reduce acid generation when placed over acid-generating tailings and waste rock. Sludge-waste rock mixtures, when placed on waste rock, were not able to limit the transport of gaseous oxygen. The low AEV of the mixture resulted in a low volumetric water content, and acid neutralization in the waste rock was not sufficient to yield a neutral leachate. However, the sludge-waste rock mixtures reduced metal loading in the effluent. Covers made of sludge and tailings mixture were able to reduce the generation of copper, zinc, calcium and sulfur from the Doyon tailings. Acidic conditions were not observed for any test, including the control condition. However, extrapolation of the reaction rates indicated that the uncovered tailings will eventually generate AMD in the long term. Even if the suction measured in the covers were slightly below the AEV of the mixtures, the volumetric water content was somewhat low, and allowed oxygen transport through the cover. With a better control over the volumetric water content of the cover, such as by preventing evaporation with a coarse-grained layer, the oxygen flux would be reduced and metal leaching should be reduced. Further testing is now being conducted in intermediate field tests on the Doyon mine site to verify the results obtained in the laboratory, and to evaluate the influence of climatic conditions on the performance of the sludge-waste rock and sludge-tailings mixtures to reduce acid mine drainage generation from waste rock and tailings.

Acknowledgements

The authors would like to acknowledge the contribution of their partners, the Ministère du Développement Économique, Innovation et Exportation (MDEIE) du Québec, IAMGOLD, Division Doyon – Mouska – Westwood, the MISA group, URSTM-UQAT, Golder & Associates, and ACCORD Abitibi-Témiscamingue. Also, the authors acknowledge Lafarge for providing the cement.

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