Effect of cementitious amendment on the geochemical behavior of a surface paste tailings disposal

Hadimi I, Benzaazoua M, Maqsoud A. & Bussière B. Institut de recherche en mines et en environnement; Université du Québec en Abitibi-Témiscamingue, Rouyn-Noranda, Québec, Canada

ABSTRACT

Laboratory study of the long term geochemical behavior of paste sulfidic tailings (SPD) and the cement amendment used to the control acid mine drainage (AMD), was performed using an instrumented physical model test. This model was filled initially with nine layers of paste tailings. After 27 months, a 10th layer of cemented tailings (with 2wt.% of cement) was deposited on top of the tailings stack. The tailings were submitted to wetting/drying cycles until the 34th cycle. The collected water during each cycle was analysed for its chemistry and its volume measured. Investigation results showed that the pH of leached collected water remained around neutrality. The evolution of the concentration of metals in the leachates did not change much after the addition of the 10th layer. While the calcium concentrations increased slightly. The projection of the oxidation-neutralization curve of the physical model has shown that the uncemented paste in time becomes AMD generator however the behaviour of the cemented paste is uncertain.

RÉSUMÉ

L'étude au laboratoire du comportement géochimique à long terme d'un dépôt de résidus en pâte sulfureux (SPD) et d'amendement du ciment pour limiter la génération du drainage minier acide (DMA), a été réalisée en utilisant un modèle physique instrumenté. Ce modèle a été rempli en premier lieu avec neuf couches de résidus en pâte. Après 27 mois environ, une 10^{ème} couche de résidus cimentés (avec 2wt.% de ciment) a été déposée au-dessus de la pile des résidus. Les résidus ont été soumis à des cycles de mouillage/séchage jusqu'au 34^{ème} cycle. Durant chaque cycle, le volume des lixiviations recueillies a été mesuré et les eaux récupérées ont été analysées. Les résultats de cette étude ont montré que le pH des eaux de lixiviations est resté autour de la neutralité. L'évolution de la concentration des métaux dans les lixiviats n'a pas beaucoup changé après l'addition de la 10^{ème} couche. Cependant, Les concentrations de calcium ont légèrement augmenté. La projection de la courbe d'oxydation-neutralisation du modèle physique a montré que la pâte non cimentée dans le temps devient génératrice du DMA; cependant, le comportement de la pâte cémentée est incertain.

1 INTRODUCTION

The extraction of mineral resources plays an important role in the Canadian economy. However, ore extraction generates large amount of liquid and solid wastes. These solid wastes include overburden; mine water treatment sludge, fine-grained mill tailings produced by the ore processing plant and waste rock extracted to reach the ore body. Mine wastes have the potential to adversely impact the environment if not properly managed during the mine site exploitation and especially after its closure. In this regard, special attention is required when they contain iron sulphide minerals, such as pyrite and pyrrhotite. The oxidation of sulphides by atmospheric oxygen tends to acidify meteoric waters (Singer and Stumm, 1970; Kleinmann et al. 1981; Marcus, 1997; Aubertin et al. 2002); this phenomenon is known as Acid Mine Drainage (AMD) or Acid Rock Drainage (ARD). If the mine wastes also contain carbonate minerals, a partial or complete neutralization of the acidic water will be possible (in Aubertin et al. 2002). However, when the acid neutralization potential is not sufficient or has been exhausted, AMD occurs and can mobilize some of the elements contained in the wastes due to the drop of the leachate pH (in Aubertin et al. 2002). In these situations,

actions must be taken at the mine site to prevent environmental impacts due to AMD.

Despite the efforts of underground waste management there remains a significant amount of tailings that must be stored on the surface around the mine site (tailings impoundment). Mill tailings are commonly stored as pulp where their solid contents are less than 50%, such way of tailings management is called conventional technique. This stored area requires the construction of important dams that are often costly and difficult to manage in the long term. The conventional technique could be replaced by an alternative method which corresponds to surface past disposal technique (SPD). This later requires thickening, and filtering processes applied to the mill tailings to reach a solid content of approximately 70-80%. A small percentage of cement (optionally with about 75 solid % pulp) can be added (Deschamps et al., 2011).

The SPD allows water recycling and renders the construction of dikes unnecessary since that free water is too limited, or even non-existent. It also facilitates the mine site reclamation.

To evaluate the hydrogeological and geochemical behavior of the SPD technique, laboratory tests were performed using a physical model developed by Benzaazoua et al. (2004). This model was filled in a first



stage with 9 layers of tailing. Only the first two layers located in the model bottom were cemented with 2wt.% (by dry solid mass of total wastes) of the cement type CP10. The tailings were then rinsed every 4 weeks with 40 L of tap water. After 14 wetting/drying cycles, results of hydrogeological and hydrochemical behavior were published by Deschamps et al., (2011).

More specifically, the main objective of this work is to better understand the long-term geochemical behavior of the SPD technique and to evaluate the effect of the addition of small amounts of binder to reduce sulfide oxidation and to avoid or delay the AMD production. The specific objectives of this research project are:

- to evaluate the long term geochemical behavior of the existing instrumented physical model. The focus here is to better characterize the oxidation of sulphides by following the evolution of leachates chemical quality over the time;
- To assess the influence of the addition of a surface cemented layer and to study its effect on the geochemical behavior of paste.

This paper presents a section related to materials and methods description, then the main results on the geochemical behavior are presented. Finally this paper ends by a discussion and conclusion.

2 MATERIAL AND METHODS

2.1 Chemical analysis

The elemental composition of paste samples was analyzed by ICP-AES (Perkin Elmer Optima 3100RL). Prior to elemental analyses, paste samples were digested (complete digestion by HNO3, Br2, HF, and HCI).

2.2 Physical model description

The physical model (a Lexan transparent plastic box), reinforced by a metal frame, is 200 cm (length) by 50 cm (width) by 100 cm (height) (figure 1). The box mounted on a plate at the bottom, is equipped with a draining system covered by geotextile to prevent the loss of solid particles. Water percolation is allowed at the bottom of the model to collect leachate for geochemical analyses. More information can be found in Deschamps et al. (2011).

Paste tailings used in the physical model test have been prepared from the filtered tailings mixed with tap water to obtain the desired paste consistency. Based on the work of Theriault et al., (2003), a 250 mm slump was targeted. This slump value corresponds to a solid content of 74%. The chemical characteristics of the tailings are summarized in Table 1. The tailings pore water (collected in the filter cake) contained 865 mg/L of sulfur (as sulphate) and its pH was 8.17; more detail can be found in Deschamps (2009).



Figure 1. Physical model used in experimental tests

In a first stage, nine layers were deposited inside the box of the physical model. Just the first two layers contain 2wt.% of cement Portland (CP10). In a second stage, and just before the 28th cycle, a tenth cemented layer (with 2wt.% of cement CP10) was added as cover at the top of the layers stack. Tailings used for the preparation of the tenth cemented layer paste were the same as those used for the first nine layers. Each layer is approximately 4 cm thick. The second layer was deposited inside the model 7 days after the first one. Subsequently, the frequency of addition of other layers was two to three days. Finally, and after completing 27 wetting/drying cycles a last layer (tenth) was added to the layers stack already deposited inside the model.

Table 1. Main chemical characteristics of the tailings and pore water (from Deschamps 2009).

Parameter	Value
Chemical parameters	
Sulfur content (wt.%)	6.1
Zn content (wt.%)	0.05
Cu content (wt.%)	0.04
Ca content (wt.%)	3.34
Acidification potential (kg CaCO3/t)	190
Neutralization potential. (kg CaCO3/t)	64
Pore water parameters	
рН	8.17
Eh (mV)	397
Conductivity (Imho)	4150
Sulfur content (as SO4) (mg/L)	865
Ca content (mg/L)	596

2.3 Monitoring of the physical model test: wetting/drying tests

After four weeks following the ninth layer deposit, wetting/drying cycles were performed (Deschamps 2009). The wetting period was performed during two days (first day and second day of wetting) then drying period starts. Drying periods was longer and usually about 26 days in order to allow i) water percolation until hydrogeological equilibrium of the physical model is reached and ii) to favor a maximum reactivity of SPD. The average period of a wetting/drying cycle is about 4 weeks.

During the wetting/drying cycles, the percolated water from the physical model was collected and its volume was measured. Also, chemical analysis were performed on collected water. Just after the 14th wetting period it was decided to extend the drying period by two additional weeks, in order to simulate the influence of a longer drying period on the behavior of the SPD tailings in the physical model.

3 MAIN RESULTS

The leachate collected at the bottom of the physical model after each wetting/drying cycle was analyzed in

terms of pH, electrical conductivity (EC), redox potential (Eh) and chemical composition by ICP-AES. In following, the results of the above analyses during the test period (34 cycles) are presented with emphasis on the effect of the 10th cemented layer addition.

3.1 pH, EC and Eh

In general, since the beginning of the test, the pH remained around the neutrality (pH between 6.6 and 8.2). The addition of the cemented layer on the top of the physical model has kept the pH neutral as shown in figure 2a (pH between 6.8 and 7.3).



Figure 2. Measured values of the :(a) pH, (b) electrical conductivity and (c) Eh of the leached collected from the physical model after each wetting/drying cycle. The red line indicates the time of the 10th cemented layer deposit

The electrical conductivity of the leachates (EC) showed a general increase tendency until the 23rd cycle

(EC was 7110 µmho/cm at approximately 656 days) then the EC decreased gradually (see Figure 2b). Following the 10th layer deposit (red line – see Figure 2.b), the EC value has stabilized during the first two wetting/drying cycles (about 5800 μ mho/cm), thereafter it declined steadily to reach 4750 μ mho/cm at the end of test. The EC decrease indicates a net reduction of the leachate mineralisation. This effect is probably attributed to the impact of the Layer 10 that can play an important role against the reactivity of the tailings.

The measured values of the Eh are presented in figure 2c, where one can observe that the overall parameter haves a similar evolution than that of the EC.

3.2 The chemical leachates quality results

The analysis results of the main elements concentration in the leachate collected after each wetting during the test period are presented in figures 3 to 5. However, the concentration of Al, As, Ba, Bi, Cd, Pb, Sb, Se and Ti were very low (below the detection limit of the used equipment) throughout the test period (34 months) and therefore these results are not presented here.

Metal concentration has increased slightly due to prolonged drying period (after cycle 14 – see Figure 3). And following the 10^{th} cemented layer deposit, the metal concentration decreased. This could be due to the dissolution of cement and the increased alkalinity in the tailing. The iron concentration until the 27^{th} cycle was low (0.62 mg/L to 0.728 mg/L). After the addition of the 10^{th}

layer, the amount of iron decreased again to reach 0.075 mg/L after 34 wetting. This could be explained by the iron precipitation as iron hydroxides in the paste.

The copper concentration was low (<0.025 mg/l). The amount of nickel and zinc in leachate was also very low (<0.5 mg/L), they have shown a tendency to decline after the 10^{th} cemented layer deposit.

The silica concentration was low and less than 16.5 mg/L.

The 10th cemented layer deposit has promoted a slight increase in the concentration of sulphates during the first two cycles following the last layer addition to reach 4200 mg/L. Thereafter, and until the end of the test, the amount of sulphate in the leachate decreased gradually to a concentration of 2950 mg/L in the last cycle. On the other side, the 10th cemented layer deposit produced a slight increase of the calcium concentration (maximum 592 mg/L in the last cycle). But the magnesium concentration decreased continuously after the addition of the layer 10. The manganese concentration was also decreased after the addition of the last layer 10. However, the cumulative concentration of Ca+Mg+Mn and SO₄ increased more following the 10th cemented deposit. This is due to the change of the total amount of cement and the total sulfidic tailings in the physical model. In the others words, there was an oxidation and alkalinity contribution due to the 10th cemented layer deposit.



Figure 3. The concentration evolution of (a) Fe, (b) Cu, (c) and Zn (d) Ni, in the leachate collected after each wetting (1st to 34th). The horizontal red line shows the maximum acceptable concentration by Directive 019, and the vertical red line indicates the time of the 10th cemented layer deposit.

3.3 Reactivity of the compact tailings into the physical model

The oxidation-neutralization curve designed to evaluate the long term AMD generation potential of the material of the tailings, based on the results of a kinetic test (Benzaazoua et al., 2004). The method aims to establish the link between the release of sulfur (as sulphate) product of sulfide oxidation and the release of chemical elements from the neutralization reactions. The oxidationneutralization curve developed for the tailings into the physical model during the entire test period are presented in the figure 6a and 6b respectively before and after the 10^{Th} cemented layer deposit. In these figures, the fitted curve using linear model show that the obtained slope value is about 0.33 (and R² = 0.9879) for the entire period. This slope value is similar to those found in tailings (Benzaazoua et al., 2004c; Villeneuve 2004; Bouzahzah 2013), and slightly more elevated than that obtained value for the release of the model from the beginning of the test until the 27th cycle (just before the 10th layer - 0.32). The slight variation in the slope value may be due to decreased oxidation of the sulphides and dissolution of the cement, which implies an increase in the neutralizing capacity of cemented layer.



Figure 4. The instant concentration evolution of : (a) Ca, (c) Mg, and (e) Mn, and the cumulative concentration of : (b) Ca, (d) Mg and (f) Mn in the leachate collected after each wetting $(1^{st} to 34^{th})$. The vertical red line indicates the time of the 10th cemented layer deposit.



Figure 5. The instant concentration evolution of : (a) Ca+Mg+Mn and (c) Sulphate and the cumulative concentration of : (b) Ca+Mg+Mn et (d) Sulphats in the leachate collected after each wetting $(1^{st} to 34^{th})$. The vertical red line indicates the time of the 10^{th} cemented layer deposit.



Figure 6. Oxidation–neutralization curve for the paste tailings tested in the physical model for: a) the period before the 10th layer addition and (b) the entire test period.

Figure 7. shows the projection of the oxidationneutralization curve and the other elements plotted as single points (uncemented paste and 2 wt.% cemented paste) for the period before the 10th cemented layer addition (Figure 7a) and for the entire test period (Figure 7b).

First, the linear regression of the curve Ca+Mg+Mn as a function of sulphates of the physical model test is extrapolated. Second, the initial concentration of total sulfur is converted to sulphates) and the initial concentrations of calcium, magnesium and manganese added (also converted in to mass g) are shown in the Figure 7.

The slight variation between figure 7a and 7b may be due to the short difference between the period tests. For figure 7a the projection of the oxidation-neutralization curve was made for the period (from the 1st cycle to the 27^{th} cycle), and for figure 7b the projection of the oxidation-neutralization curve was made for the period (from the 28^{th} cycle to the 34^{th} cycle).

In figure 7a and 7b, the point of the uncemented paste is located clearly below the extension of the regression of the oxidation-neutralization curve and indicates the material with limited neutralizing elements and did not allow to neutralize all the produced acidity by sulfide oxidation. In this case, the material will be classified as long-term acid generator. The point of the cemented paste is projected just below the oxidation-neutralization curve.



Figure 7. Projection of the oxidation-neutralization curve for: a) the period before the 10th layer addition and (b) the entire test period.

The cemented tailing has more neutralizing elements than the uncemented tailing; however its acidity generation potential is uncertain.

4 MAIN CONCLUSIONS

Investigation results showed that the pH of the collected leached water at the bottom of the physical model following the wetting cycles remained around neutrality. The evolution of the concentration of metals in the leachates did not change much after the addition of the 10th layer. On the other hand, the amount of sulphates after the first two wetting cycles decreased to a concentration of 2952 mg/L in the last cycle. This evolution was proportional to that of magnesium. While

the calcium concentrations increased slightly. This could be explained by the cement dissolution and the increase of alkalinity more generally in the tailings. Thus, the projection of the oxidation-neutralization curve of the physical model has shown that the uncemented paste in time becomes acid generator; however the cemented paste can be considered as uncertain in tem the potential acid generation.

ACKNOWLEDGEMENTS

The authors would like to thank the Canada Research Chair on Integrated Management of Sulfidic Wastes using Backfill for their financial support. The authors also would like to acknowledge the URSTM-UQAT laboratories

REFERENCES

- Aubertin, M., Bussière, B. and Bernier, L. 2002. Environnement et gestion des rejets miniers - Manual on CD-ROM.
- Benzaazoua, M., Perez, P., Belem, T. and fall, M. (2004). A laboratory study of the behaviour of surface paste disposal. In: Proceedings of the 8th Minefill 2004 sympodium, pp. 180-192, Beijing, China.
- Bouzahzah, H. 2013. Modification et amélioration des tests statiques et cinétiques pour une prédiction fiable du drainage minier acide. (Thèse du doctorat en sciences de l'environnement), Université du Québec en Abitibi-Témiscamingue.
- Deschamps, T. 2009. Étude du comportement physique et géochimique d'un dépôt de résidus miniers en pâte dans des conditions de surface. (Ph.D.), Université du Québec en Abitibi-Témiscamingue.
- Kleinmann, R.L.P., D.A. Crerar, and R.R. Pacelli, 1981. Biogeochemistry of Acid Mine Drainage and a Method to Control Acid Formation. *Mining Engineering*, pp. 300 – 305, March 1981.
- Marcus, J.J. 1997. Mining Environmental Handbook: Effect of Mining on the Environment and American Environmental Controls on Mining. Imperial College Press.
- Singer, P.C., Stumm, W., 1970. Acidic mine drainage: the rate-determining step. *Science* 167, 1121-1123.
- Theriault, J., Frostiak, J.and Welch, D. 2003. Surface disposal of paste tailings at the Bulyanhulu gold mine, Tanzania. Paper presented at the Proceedings (CD-ROM) of Sudbury mining environment conference, Sudbury, Ontario.
- Villeneuve, M. 2004. Évaluation du comportement géochimique à long terme de rejets miniers à faible potentiel de génération d'acide à l'aide d'essais cinétiques. (M.Sc.A.), École Polytechnique de Montréal, Montréal.