

# Effect of acid buffering capacity on the remobilization of heavy metals in sewage sludge barrier for tailings

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**Abstract:** Remobilization of heavy metals from the bottom liner system due to the seepage of acid mine drainage (AMD) is an important concern in the long-term management of tailing impoundment. Titration tests were carried out to evaluate the acid buffering capacity (ABC) of sewage sludge and to investigate its effect on the remobilization of heavy metals. Test results demonstrate that the ABC increases with solid/liquid ratio and anaerobic incubation time and it is mainly attributed to the abundant organic matters contained and increasing carbonate loads. The added heavy metals (Zn, Pb, and Cu) were well immobilized during the anaerobic incubation stage but were released out dramatically during the acidification especially when pH drops below 6.0 because of dissolution of carbonates and cation exchange of clay minerals. The calculated results, from a simplified model, indicate that high levels of remobilization of heavy metals are not expected during the typical management time because of the high ABC of compacted sewage sludge barrier. These results support that sewage sludge is a suitable bottom liner material for the management of AMD from tailings.

## Introduction

Heavy metal pollutants, widely distributed in waste rock and tailings, might be discharged into the surface or ground water with seepage penetration, which possesses great threat to the nearby environment around tailing impoundment (Jung et al. 2004, Lottermoser 2010). This has become a serious problem facing the mining industries all around the world. A barrier system is conventionally used to control or to mitigate the detrimental effects of leachate by various physical and chemical processes (Manassero et al. 2000, Yeheyis et al. 2010). Tailings produced in the mining process, however, are traditionally deposited into the tailing impoundment and all the time, they are just to be simply exposed to the natural conditions. During the long-term weathering process, sulfide minerals (e.g., pyrite) left in the mine waste can be oxidized with intruded oxygen. This oxidation process results in a dramatic decrease of pH of the pore water, and with continuous infiltration of rainfall or snowmelt, Acid Mine Drainage (AMD) is formed (Waybrant et al. 1998, Johnson and Hallberg 2005).

The low pH of AMD has a potential threat to the environment. In this regard, two aspects should be mainly considered. One is that the pH of AMD is not in equilibrium with that of the surface or ground water system. Thus direct effluent of AMD can break the ecological balance and the consequence is disastrous. This problem, however, can be strategically solved by lining geotechnical barrier or liner with low hydraulic conductivity to slow down the permeation rate of AMD. Typically, the required saturated hydraulic conductivity of suitable geotechnical

materials should be less than  $1.0 \times 10^{-7}$  cm/s. The other problem is that abundant heavy metals can be leached out from the tailings during the long-term AMD permeation because of the low pH conditions. This phenomenon has been demonstrated by static leaching experiments (Doye and Duchesne 2003), column (dynamic) leaching tests (Al-Abed et al. 2008) and acid neutralization capacities tests (Saria et al. 2006). What is worse, the geotechnical barrier system would be acidified as the AMD permeates through it, and during this process those heavy metals immobilized previously in the system tend to remobilize in response to the decrease of pH condition. In this way, the barrier system would be invalid from a long time perspective. As for this problem, another essential property that a satisfactory barrier material should possess is the ability to control the pH decrease, i.e., the Acid Buffering Capacity (ABC). In other words, if the barrier system possesses sufficient ABC, the pH condition of the barrier system would be maintained and the remobilization of heavy metals would not be anticipated. Obviously, ABC is an important index in evaluating the feasibility of barrier material for tailings.

Sewage sludge barrier, as an innovative approach, has been widely reported being feasible for tailings both in controlling AMD permeation and strong retardation of heavy metals (Waybrant et al. 1998, Nason et al. 2013, Rozada et al. 2008, Costa et al. 2008, Peppas et al. 2000, Wang et al. 2010, Zhang et al. 2014, Zhang et al. 2016). Available literature data indicate that the saturated hydraulic conductivity of compacted sewage sludge with a dry density of  $0.79 \text{ g/cm}^3$  is  $3.0 \times 10^{-8}$  cm/s to  $8.0 \times 10^{-8}$  cm/s, which met with the requirement of the barrier system (Wang et al.

2010, Zhang et al. 2016). Additionally, sewage sludge contains abundant organic substances and microorganisms. Not only does this benefit the strong absorption of heavy metals presented in the leachate, but also it induces weak alkaline and reduced condition that mediates the process of sulfate reduction (Zhang et al. 2014, Tuttle et al. 1969, Kamon et al. 2002). Furthermore, sewage sludge is a cost-effective and easy-to-access material and its reuse might be of significant advance in the consideration of sustainability.

ABC of sewage sludge barrier and its impacts on the remobilization of heavy metals, however, has not been evaluated. Actually, there are some contradictory results regarding this question. For instance, laboratory test on the saturated hydraulic conductivity of compacted sewage sludge permeated with simulated AMD (pH=6.0) by Wang et al. (2010) showed that the pH of effluent varied from 7.0 to 7.9 and the heavy metals (Zn and Cd) were well immobilized in the specimen. That is, the sewage sludge seems to have enough ABC to maintain the pH condition in the barrier system. Another similar test by Zhang et al. (2014) revealed that under the seepage of synthetic AMD with low pH (pH=2.1), the concentration of Zn and Cd in the leachate increased. It seems that ABC of sewage sludge could be consumed out and it loses its function under low pH conditions. As previously mentioned, any comprehensive evaluations about the feasibility of a barrier material for tailings and the impaction of heavy metal from tailing impoundment on the adjacent environment ask for a thorough understanding of the attenuation mechanisms of heavy metal pollutants within the barrier system. In this study, acid titration test was conducted on the sewage sludge suspensions to evaluate the ABC of sewage sludge barrier system and to reveal the relationship between remobilization of heavy metals and decreasing pH. A simplified model was designed to describe the depletion of ABC within the sewage sludge barrier and therefore the prediction of its failure time. The ultimate goal of this study was to make additional estimation on the feasibility of sewage sludge as a probable barrier material for management of tailings.

## Materials and methods

### Material

Sewage sludge sampled from the bottom of a settling tank in Yanerwan municipal sewage water treatment plant, located in Lanzhou, China, was used for the experiment as the barrier material in this study. The physical and chemical properties of the sewage sludge are shown in Table 1. Sampled sewage sludge was air-dried for at least 30 days before any testing procedures because it was over-saturated under natural conditions. Firstly, the water content of natural and air-dried sludge was determined. Then the air-dried sample was ground and passed through 0.5 mm sieve for other tests. In this study, the water content is defined as the mass quantity of water in a totally dry material, which can be expressed as a ratio of the weight of water to the dry weight of sludge (often presented in percentage). Dry weight of sludge was measured with oven-drying method at the temperature of 60°C instead of the standard temperature of 105°C to prevent any mass loss of contained organic substances due to charring. The difference value in water content between natural and air-dried sludge can be as large as 302.33%, which indicates good water holding capacity of the sampled sewage sludge. The liquid limit and plastic limit were measured following cone penetrometer method, which was often used in previous studies (Zhang et al. 2016). The specific gravity, whose value is equivalent to the

particle density in the unit of g/cm<sup>3</sup>, was measured following the modified pycnometer method with kerosene, instead of distilled water to prevent possible decomposition of sludge samples (O'Kelly 2005). Maximum dry density and optimum moisture water content was characterized following the standard protector compaction method proposed by ASTM (ASTM D698). The pH of sewage sludge was measured by dispersing the dried solid powder into distilled water, with a mass ratio of 1:1, and then determined by an electrometric pH meter (720 SM). Total organic carbon was determined by an automatic TOC analyzismeter (LiquiTOC/TNb). Originally enriched heavy metals of Zn, Pb and Cu were tested with acid digestion of sewage sludge powder and determined by automatic adsorption spectrometer (AAS) (SPSIC 4530F) of the solution. The leaching heavy metals (Zn, Pb and Cu) were determined as follows: 25 grams of sewage sludge powder was dispersed into 250 mL distilled water; the suspension was then vibrated for 12 hours and followed by 6 hours' standing. After that, supernatant liquid was extracted and centrifuged, and then AAS was used to determine the concentration of leaching heavy metals. The major oxides of sewage sludge sample were also characterized by X-ray fluorescence (XRF) and the results have been presented in Table 1.

**Table 1.** Properties of sewage sludge used

Properties	Results
Water content	
Natural (%)	308.74
Air-dried (%)	6.41
Liquid limit (%)	128.43
Plastic limit (%)	51.87
Specific gravity	1.85
Maximum dry density (g/cm <sup>3</sup> )	0.79
Optimum moisture content (%)	57.25
pH (Sewage sludge: distilled water = 1:1)	7.36
TOC (%)	67.62
Total Zn (mg/kg)	706.20
Total Cu (mg/kg)	120.60
Total Ni (mg/kg)	43.21
Total Cd (mg/kg)	9.10
Total Pb (mg/kg)	74.4
Total Hg (mg/kg)	2.16
Total Cr (mg/kg)	53.32
Leaching Zn (mg/L)	0.67
Leaching Cu (mg/L)	n.d.
Leaching Ni (mg/L)	n.d.
Leaching Cd (mg/L)	n.d.
Leaching Pb (mg/L)	n.d.
Leaching Hg (mg/L)	n.d.
Leaching Cr (mg/L)	n.d.
Major oxides (%)	
SiO <sub>2</sub>	37.47
Al <sub>2</sub> O <sub>3</sub>	11.52
Fe <sub>2</sub> O <sub>3</sub>	6.86
CaO	7.14
K <sub>2</sub> O, MgO and Na <sub>2</sub> O	5.25

n.d. = not detected

**Acid titration tests on sewage sludge suspensions**

Sewage sludge suspensions with different solid/liquid ratio and incubation time were prepared for acid titration tests, as indicated in Table 2. In this study, dried sewage sludge powder was dispersed in distilled water with different mass ratios of 1:20, 1:10, and 1:5; then these suspensions were named as Q1, Q2 and Q3, respectively.

Sodium acetate ( $\text{CH}_3\text{COONa}$ ) and ammonium dihydrogenphosphate ( $\text{NH}_4\text{H}_2\text{PO}_3$ ) were added into all the suspensions as nutrients for reproduction and growth of micro organisms, with concentration of 1000 mg/L and 100 mg/L, respectively, following the advice given by the US EPA (Environmental Protection Agency). Trace elements of heavy metals, Zn, Pb, and Cu, were chosen as target pollutants because they were typically found in the metallic mine waste and AMD and possess biological toxicity. The designed concentration of heavy metals was set as 500 mg/L by dissolving  $\text{ZnCl}_2$ ,  $\text{Pb}(\text{NO}_3)_2$  and  $\text{CuCl}_2$  in all of the suspensions, which is higher than the actual AMD according to available literature (Gulec et al. 2005). After the preparation, all sewage sludge suspensions were bubbled with nitrogen gas to induce a reducing respiration and they were vibrated continuously for 24 hours in a sealed tumbler to ensure sufficient contact between solid and liquid phase. Then these suspensions were transferred to an anaerobic incubator (885-AC Anaerobic Chambers, PLAS&LABS) and sealed. The temperature was controlled at 25°C by water bath method.

After certain incubation duration time of 5 days, 25 days and 50 days, 120 mL suspension was extracted from each of the prepared sewage sludge suspensions for the titration tests. The sub-sampled suspensions were then identified with a digit following the suspension number to indicate its incubation time, namely, in the form of Qi-5, Qi-25 and Qi-50, respectively ( $i = 1, 2, 3$ ). The pH and redox potential (Eh) of each suspensions were measured immediately to characterize their initial state. Acid titration tests were then conducted with 0.2 mol/L chloride acid (HCl) at a constant rate (0.3 mL/min) by an automatic titration device (702 SM Titrino, Metrohm). As soon as the pH was reduced to a designed value, the Eh was immediately recorded and 10 mL of suspension was withdrawn with an airtight syringe, centrifuged for 20 min at 4500 rpm and filtered through a syringe filter with 0.45  $\mu\text{m}$  pore size. Filtered solutions were then analyzed for heavy metals (Zn, Pb, and Cu) by AAS (SPSIC 4530F) and for the concentration of calcium ions by the ion chromatography system (ICS-2500,

Diones) to evaluate the effect of acidification on the mobility of heavy metals and the ABC of sewage sludge material. The analytical errors of AAS for all elements were below 5%, and that of ICS was less than 3% in this study.

**Results and discussion****Acid Buffering Capacity (ABC) of sewage sludge suspensions**

Alkalinity or acid neutralizing capacity is traditionally used to describe the acid buffering capacity of the ground water system (Stumm and Morgan 1996). In most cases, the ending point of the titration test was set up to pH=4.3. This is because the alkalinity of the aqueous system is mainly attributable to the bicarbonate ( $\text{HCO}_3^-$ ) and carbonate ( $\text{CO}_3^{2-}$ ). In soil-water system, however, large quantities of non-carbonate substances contained in the soil particles can also accept protons, such as hydroxide precipitate of metals, dissolved organic matters and silicate (Stumm and Morgan 1996). In consideration of the fact that sewage sludge used in this study was rich in organic matters and larger amount of mineral oxides (Table 1), the ending point of pH 3.0 was therefore employed in this study. The ABC of sewage sludge suspensions ( $\beta$ ) can be calculated as follows:

$$\beta = -\frac{dc_A}{dpH} \quad (1)$$

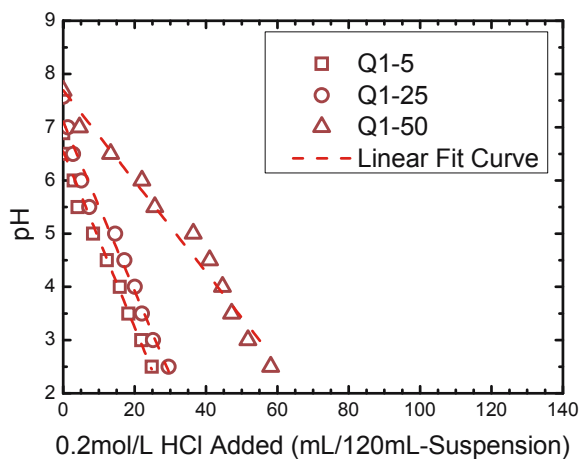
Where  $c_A$  is the consumed acid amount when pH of per litter suspension drops by one unit. It shows the ability of the sewage sludge suspension to inhibit the acidification. The titration test curves of sample group Q1, Q2 and Q3 are presented in Fig. 1, Fig. 2 and Fig. 3, respectively. It can be found that the pH value drops with the added hydrochloric acid in a generally linear pattern. Then the ABC of each sewage sludge suspension can be calculated from the slope of its corresponding titration curve, and the calculated results are shown in Table 4. Test results show that the ABC of suspension increases with incubation time when the soil/liquid ratio is constant and also increases with the increasing solid/liquid ratio while the incubation time is the same. It can be derived from the test results that the ABC of a real compacted sewage sludge barrier would be larger because of a bigger solid/liquid ratio (Table 2).

**Table 2.** Preparation of sewage sludge suspensions with different solid/liquid ratio and their incubated conditions

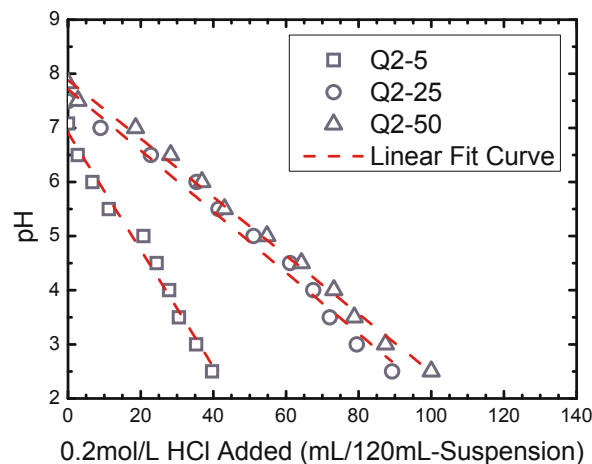
Suspension number	Q1	Q2	Q3
Solid/Liquid ratio (by mass)	1:20	1:10	1:5
Nutrients	$\text{CH}_3\text{COONa}$ : 1000 mg/L $\text{NH}_4\text{H}_2\text{PO}_3$ : 100 mg/L		
Added concentration of heavy metals	$\text{Zn}^{2+}$ : 500 mg/L $\text{Pb}^{2+}$ : 500 mg/L $\text{Cu}^{2+}$ : 500 mg/L		

**Table 3.** Sewage sludge suspensions sub-sampled for acid titration tests after incubation

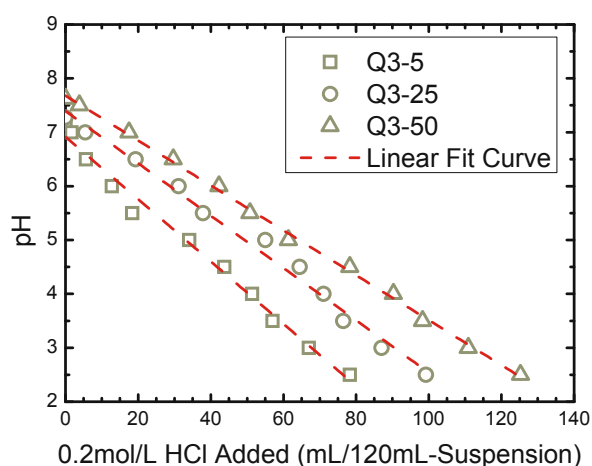
Sub-sampled suspension number	Q1-5	Q1-25	Q1-50	Q2-5	Q2-25	Q2-50	Q3-5	Q3-25	Q3-50
Incubation time (days)	5	25	50	5	25	50	5	25	50
Initial pH	7.00	7.36	7.61	7.08	7.49	7.68	7.17	7.57	7.82
Initial Eh (mV)	162	-57	-289	-12	-292	-425	-44	-295	-431



**Fig. 1.** Acid titration curve for sample Q1 with different incubation time



**Fig. 2.** Acid titration curve for sample Q2 with different incubation time



**Fig. 3.** Acid titration curve for sample Q3 with different incubation time

**Table 4.** ABC of sewage sludge suspensions calculated from the titration test curves

Sample number	ABC (mol/L)	Squared error of linear fit curve
Q1-5	0.00992	0.98168
Q1-25	0.01025	0.97462
Q1-50	0.01913	0.97774
Q2-5	0.01517	0.98281
Q2-25	0.02911	0.98414
Q2-50	0.03071	0.99465
Q3-5	0.02849	0.98686
Q3-25	0.03400	0.98943
Q3-50	0.03993	0.99803

A possible explanation for this phenomenon is that the initial pH and Eh conditions of different sewage sludge suspension change with incubation time and solid/liquid ratio. Fig 4 and Fig 5 illustrate the initial pH and Eh conditions of each sample group, respectively. Generally, for the same incubation time, the initial pH value increases slightly with

the solid/liquid ratio. This is because increasing solid-liquid ratios means increasing solid phase, correspondingly with the increasing content of acid buffer substances in sewage sludge. Besides, the initial pH value rises linearly with incubation time. This is because the redox potentials of different sample group (Fig. 5) decrease with incubating time so that the initial degree

of reduction was deepened. In general, alkalinity and pH value tend to increase during reduction, since oxidized components are more acidic or less basic than their reduced counterparts (Bourg et al. 1995). Moreover, with increasing incubated time, microbiologically mediated degradation of organic matter has been reported to induce an increase in increased alkalinity values and in total inorganic carbon, which could also improve the ABC of sewage sludge suspensions to some extent (Lazzaretti-Ulmer and Hanselmann 1999). The initial Eh value decreases linearly with the incubation time but it appears to be little related to the solid/liquid ratio. This is probably because the activity of the contained microorganism reaches its peak when the solid/liquid ratio is beyond a certain range. Thus in a real sewage sludge barrier, a satisfactory initial pH and Eh conditions could be expected.

Sewage sludge suspension is consisted of two phases, i.e., the fluid and solid phase. The ABC of fluid phase is governed by amphoteric organics, strongly alkaline and weakly acidic salts etc. The ABC of solids phase is attributed to alkaline clay minerals, metallic oxide, hydroxide and carbonates contained in soil particles (Yong et al. 1992). What's more, the sewage sludge suspension contains abundant organics (Table 1), such as protein and volatile fatty acids. These organic matters would also contribute greatly to the ABC of the suspension (Moosbrugger et al. 1993, Zhao and Men 2008). The neutral points of these acidic

buffer substances, however, are different. Acid (protons) would firstly react with alkaline substances in the system with higher neutral points when added. As shown in Table 5, the buffering reactions in sewage sludge suspension can be understood as follows: the added protons are firstly consumed by dissolution reactions with carbonates ( $pH > 6.2$ ), once the carbonates are exhausted, additional protons replace base cations ( $Ca^{2+}$ ,  $Mg^{2+}$ ,  $K^+$  and  $Na^+$ ) at exchangeable sites of clay minerals ( $5.5 \leq pH < 6.2$ ). This means reaction of cation exchange can also consume dissolved hydrogen ions, representing certain ABC of the system. The unceasingly added protons will then react with organic substances ( $4.2 \leq pH < 5.5$ ). Ultimately, further addition of acid induces dissolution of aluminum oxides in the system ( $3.8 \leq pH < 4.2$ ), and finally leads to the dissolution of Ferric oxides ( $pH < 3.8$ ) (Bozkurt et al. 2000).

According to the pH ranges of unique buffering reactions mentioned above, acid buffering mechanism in the sewage sludge suspension can be therefore divided into five patterns: carbonates dissolution, cation exchange, organics buffering, aluminum hydroxide dissolution, and ferric hydroxide dissolution. The proportion of each mechanism shared can be then evaluated, which is presented in Table 6. It can be found that the ABC of the sewage sludge suspension is mainly attributed to the organic buffering, which accounts for more than 30% in all tested samples, especially in the samples with

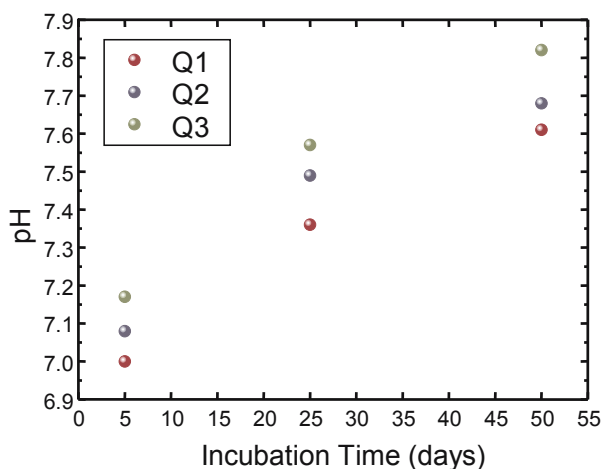


Fig. 4. Initial pH conditions of different sample groups before titration test

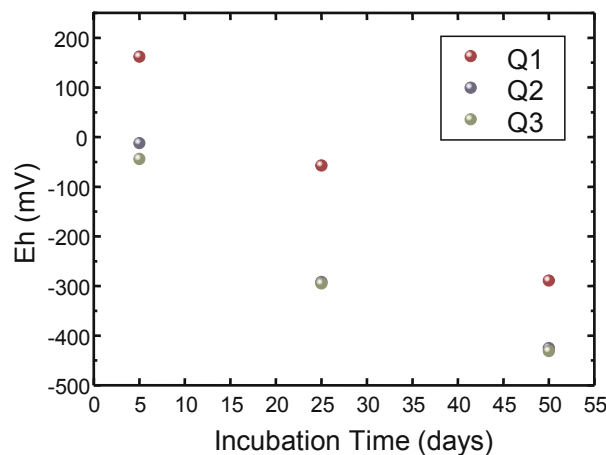


Fig. 5. Initial Eh conditions of different sample groups before titration test

Table 5. Acid producing and acid buffering reactions in tailing impoundment-sewage sludge barrier system (Bozkurt et al. 2000)

Type	Reactions
Acid producing:	
Sulfides	$FeS + 9/4O_2 + 3/2H_2O \rightarrow FeOOH + SO_4^{2-} + 2H^+$
	$FeS_2 + 15/4O_2 + 5/2H_2O \rightarrow Fe(OH)_{3(s)} + 2SO_4^{2-} + 4H^+$
Acid Consuming:	
Carbonate minerals	$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + H_2O + CO_2$
Cation exchange	$SO:Me + 2H^+ \rightarrow SO:H_2 + Me^{2+}$
Aluminum	$Al_2O_3 + 6H^+ \rightarrow 2Al^{3+} + 3H_2O$
	$Al(OH)_3 + 3H^+ \rightarrow Al^{3+} + 3H_2O$
Iron	$Fe_2O_3 + 6H^+ \rightarrow 2Fe^{3+} + 3H_2O$

5 day incubation time (more than 40%). What is remarkable is that the portion contributed by the carbonate dissolution increases dramatically with the incubation time for each sample group. Meanwhile, the proportion of organic buffering shows a decreasing trend, ending with a proportion similar to the carbonate dissolution. This is explained by the fact that a higher initial pH value means a wider buffering reaction range of carbonate dissolution. Therefore, the proportion of carbonate dissolution increases with incubation time (Table 6). A lower Eh condition indicates a stronger anaerobic respiration of microorganisms, which expands the organic matters contained in the sewage sludge. In this way, the proportion of organic buffering shows a decreasing tendency.

Figure 6 shows the changes of concentration of calcium ion during the titration test for samples Q1-50, Q2-50 and Q3-50, respectively. It can be found that the concentration of calcium ion increases with decreasing pH, indicating the increase of carbonate dissolution. This clearly supports that carbonate dissolution contributes greater to the ABC of sewage sludge suspensions with increasing solid/liquid ratio. In addition, with a larger solid/liquid ratio, the concentration of the calcium ion is higher. This might be a reason for that initial pH value increases with solid/liquid ratio (Fig. 4).

As mentioned above, the sewage sludge suspension is consisted of solid and liquid phase. In order to investigate

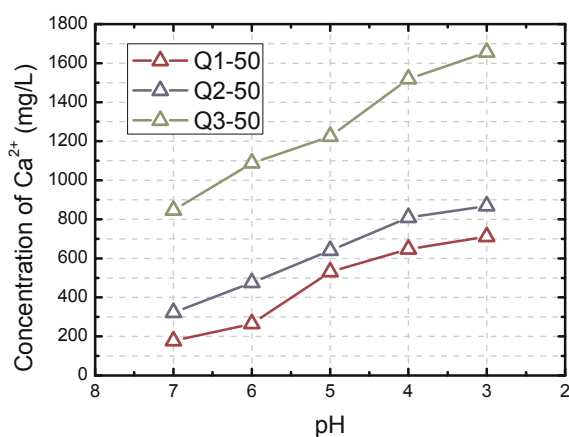
how much ABC is consumed regarding the dry sewage sludge powder, the apparent ABC of sewage sludge powder contained in the suspension was calculated as follows,

$$(ABC)_a = \frac{c_A}{m_s} \quad (2)$$

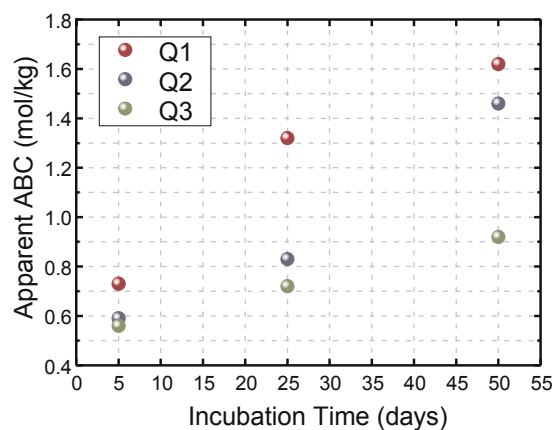
Where  $c_A$  is the molar mass of consumed protons when pH= 3.0 (mol);  $m_s$  is the dry weight of sewage sludge powder contained in the suspensions (kg). The calculated results are shown in Fig 7. The larger apparent ABC of sewage sludge powder indicates smaller potential reserves to inhibit the acidification. It can be found that the apparent ABC of sewage sludge powder increases with incubation time but decreases with the solid/liquid ratio. The former is due to the anaerobic inspiration of microorganisms and decreasing initial Eh conditions, which would develop the potential reserves of dry sewage sludge powders. The latter is because that increasing solid/liquid ratio means more solid substances; the surface of solid particles cannot be fully exposed in the suspension. There are a lot of buffering substances to consume out the added protons, and thus the apparent ABC decreases with solid/liquid ratio. For a real compacted sewage sludge barrier, the solid/liquid ratio is large enough and the potential reserve of its ABC is rather considerable from this viewpoint.

**Table 6.** Proportion of different acid buffer mechanisms contributed to ABC of sewage sludge suspension (%)

Sample number	Carbonates Dissolution (pH≥6.2)	Cation Exchange (5.5≤pH<6.2)	Organics Buffering (4.2≤pH<5.5)	Aluminum Hydroxide Dissolution (3.8≤pH<4.2)	Ferric Hydroxide Dissolution (pH<3.8)
Q1-5	9.48	8.72	48.05	11.62	22.19
Q1-25	16.41	13.57	45.02	7.85	17.17
Q1-50	35.66	13.56	34.21	4.86	11.77
Q2-5	14.50	16.95	44.04	6.88	17.54
Q2-25	38.27	14.21	29.55	5.49	12.78
Q2-50	38.28	12.24	29.14	6.72	13.53
Q3-5	14.97	13.05	43.91	8.25	19.94
Q3-25	30.29	12.96	35.37	5.82	15.56
Q3-50	33.84	12.03	31.52	7.31	15.30



**Fig. 6.** Changes in the concentration of  $Ca^{2+}$  during the acid titration tests for sample Q1-50, Q2-50 and Q3-50



**Fig. 7.** Apparent ABC of sewage sludge powder for different tested samples to indicate their potential reserves

### Remobilization of heavy metals during acidification of sewage sludge

The added concentration of selected heavy metals (Zn, Pb, Cu) is as high as 500 mg/L in all tested samples. There were, however, no soluble heavy metals detected before titration tests began. It indicates that the sewage sludge has a beneficial effect on the immobilization of heavy metals. This is due to the effect of precipitation from carbonate mineral, oxide and hydroxide, co-precipitation from Fe-Mn oxide and adsorption from soil organic particles. However, during the acidification, those heavy metals immobilized previously become remobilized, which is as shown in Fig. 8 and Fig. 9.

Figure 8 shows the evolution of soluble heavy metals (Zn, Pb and Cu) as a function of pH value for sample group Q1 to investigate the effect of incubation time. The amount of soluble heavy metals increases with decreasing pH value. And when pH drops below 6.0, all of soluble heavy metals increase dramatically, especially Q1-5, with only 5 days of incubation time. It can be also found that soluble Zn, Pb and Cu gradually decrease with the longer incubated time. Figure 9 illustrates the effect of different solid/liquid ratio on the remobilization of heavy metals in sewage sludge suspensions. It can be found that soluble heavy metals decrease with increasing solid/liquid ratio. What is interesting is that when pH drops below 6.0, soluble heavy metals also rise rapidly.

The immobilized heavy metals in the sewage sludge suspension are generally classified into five chemical

speciations on the basis of different activities: exchangeable, binding to carbonates, binding to Fe-Mn oxides, binding to organic matter and residual state (Zhang et al. 2014, Tessier et al. 1979). Releasing rate of particulate heavy metals is linked to their chemical speciation in sediments. Available literature indicates that mechanisms for heavy metals releasing are dissolution, ion exchange and desorption (Calmano et al. 1993). The heavy metal specification immobilized in the sewage sludge barrier conducted by Zhang et al. (2014) indicates that most of the heavy metals immobilized are in the state of organic and residual fraction, which has stronger stability and would not be easily released into the environment (Alloway and Jackson 1991). The exchangeable fraction and carbonate fraction, however, are easier to be affected by the acidification, as shown in Table 5. When pH value drops below 6.2, dissolution of carbonate increases sharply with decreasing pH conditions. Those heavy metals immobilized in the form of the carbonate fraction and exchangeable fraction would then become remobilized. This is why the concentration of heavy metals increases faster after pH drops below 6.0.

The reason for that soluble heavy metals decrease with increasing incubation time and solid/liquid ratio is probably because the chemical speciation of heavy metals has been amended since the initial Eh values become smaller with increasing incubated time and solid/liquid ratio (Fig. 5). Once the Eh value drops below -150 mV, reduction reaction of sulfate would happen, consequently, insoluble metal sulfide

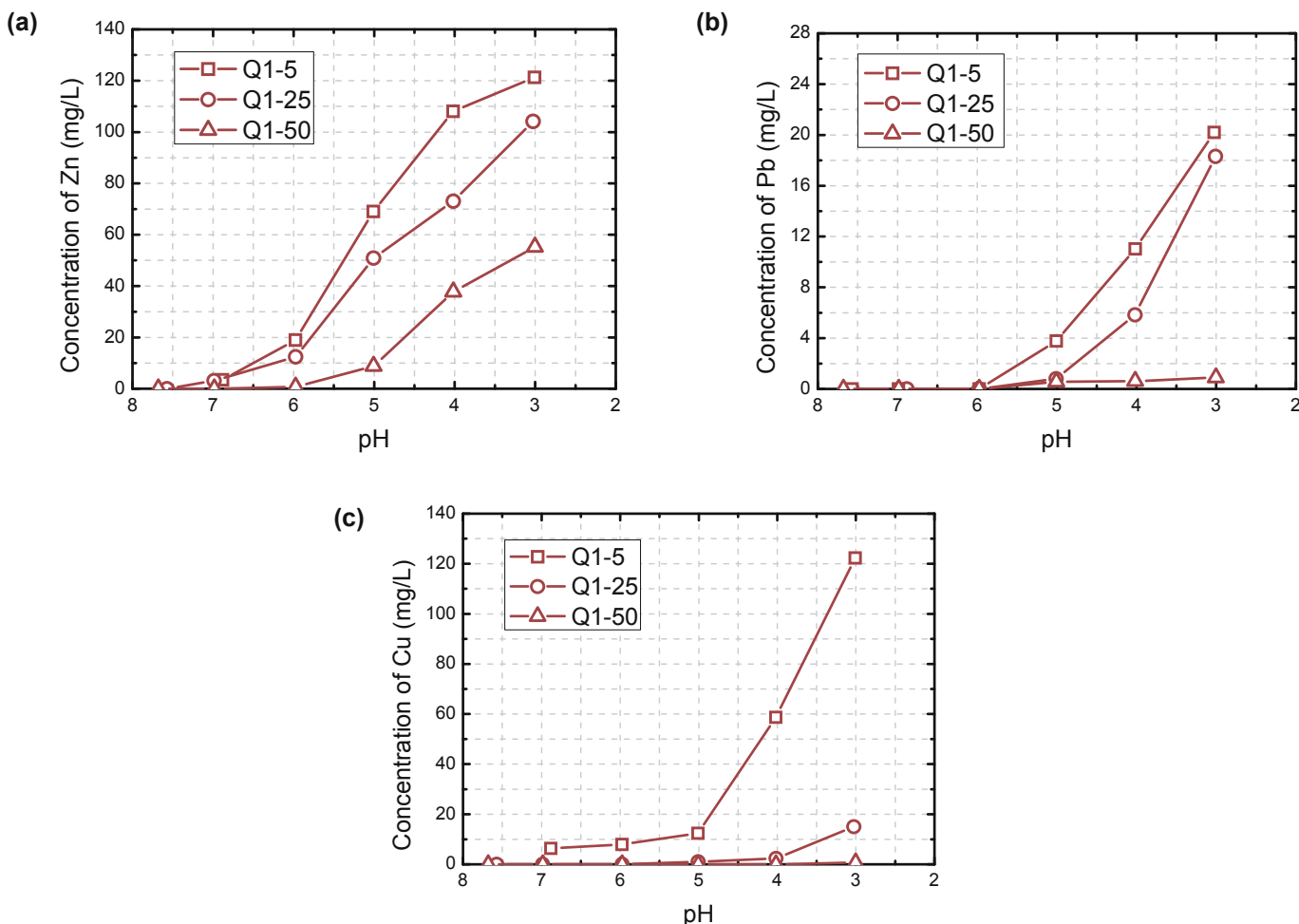
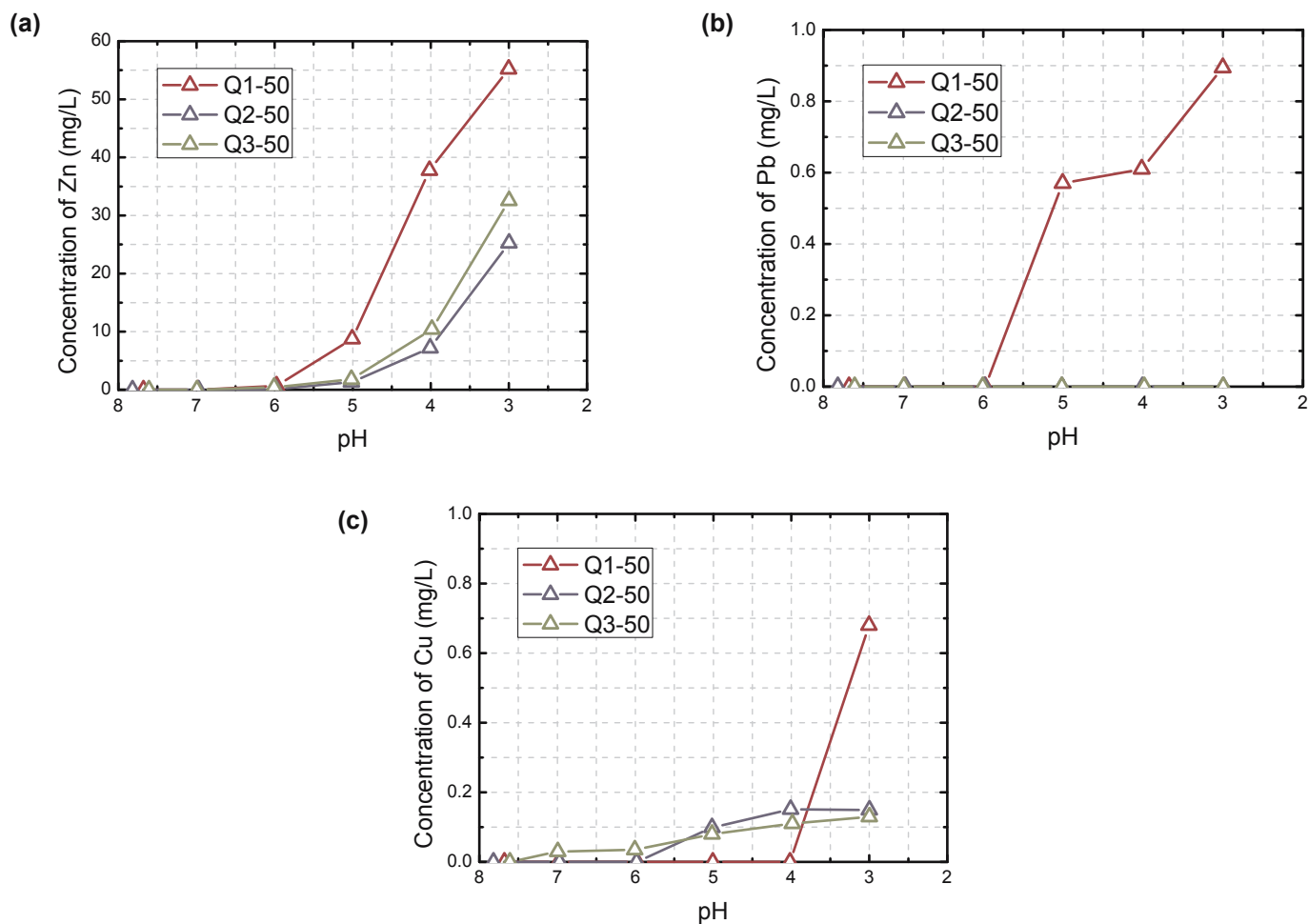


Fig. 8. Release of heavy metals vs pH during titration tests for Q1 with different incubated time: (a) Zn; (b) Pb; (c) Cu



**Fig. 9.** Release of heavy metals vs pH during titration tests for Q1-50, Q2-50 and Q3-50 with different solid/liquid ratio: (a) Zn; (b) Pb; (c) Cu

would generate and subsequently subside (Connell and Patrick 1968). The amount of released Zn is much larger than that of Pb and Cu during acidification, which means Pb and Cu were more effectively immobilized with a long period of anaerobic incubation. The release of heavy metals in sewage sludge suspension is not only related to activities of heavy metals, but also is linked with the physical, chemical and mineral characteristics of soil particles. As shown in Figure 10, there are obvious differences in pH value for each heavy metal starting to be released. For instance, concentration of dissolved Zn increases dramatically when pH value drops below 6.0, while obvious rise for that of dissolved Pb and Cu occurs when pH value drops below 5.0, approximately. It seems that the amount of released heavy metals takes the order of  $Zn > Cu > Pb$  during the process of acidification. And the results presented by Coz et al. (2004) and Singh et al. (2000) are in agreement with these findings in this study. With regard to the management of heavy metal pollution from mine waste, following the safety-first principle, a criterion for heavy metal releasing from sewage sludge barrier can be established: heavy metals would start to be released out rapidly when the sewage sludge is acidified to the pH value of 6.0, in other words, the sewage sludge barrier would be invalidated. In this context, effective ABC of sewage sludge barrier is defined as the molar mass of acid consumed by per liter of sewage sludge suspension

until  $pH=6.0$  (in unit mol/L). The decreasing soluble heavy metals with increasing solid/liquid ratio indicates that the more potential reserve of ABC which sewage sludge barrier possesses, the smaller the risk of heavy metal remobilization is. That is, a larger solid/liquid ratio means a smaller apparent ABC (Fig 7), which in turn, means more potential reserve of acid buffering substances.

#### **Modelling long-term consumption of ABC in sewage sludge barrier**

The AMD, produced by oxidation of sulfide minerals in tailings can induce acidification of sewage sludge barrier when permeating downward to the bottom. This process can be illustrated with a simple model as shown in Figure 11. Acidification of sewage sludge barrier would engage potential release of heavy metals that are initially immobilized in the barrier under reducing condition, which implies that the ABC of sewage sludge barrier plays an important role during its long-term service. Testing results of acid titration on sludge suspensions suggest that heavy metals would not be significantly released unless pH dropped below 6.0. On the basis of acid-base neutralization theory, only after the effective ABC of sewage sludge barrier is consumed out, the pH of transudation liquid drops below 6.2, resulting in corresponding leachate of heavy metals.



Taking a column in the compacted sewage sludge barrier, with a unit section perpendicular to the direction of flow line, the critical condition for ABC failure can be described as:

$$\sum (ABC)_{act} = \sum Acidity \quad (3)$$

Where  $\sum (ABC)_{act}$  is the summation of effectively apparent ABC possessed by the column;  $\sum Acidity$  is the total amount of acid contained in the AMD penetrating through the column.

The value of effectively apparent ABC, as mentioned previously, is estimated by acid titration tests for sewage sludge suspensions, under which condition the solid particles are fully dispersed so that the ABC of sewage sludge shows its extreme potency. While in the compacted sewage sludge barrier, the ABC can be only exerted by those particles exposed to the permeating liquid. With respect to this difference, porosity of compacted sewage sludge barrier should be introduced to amend the effective ABC from tests for suspensions. This leads to the distribution:

$$\sum (ABC)_{act} = S\gamma_d h n (ABC)_{act} \quad (4)$$

Where  $(ABC)_{act}$  is the effective ABC of sewage sludge suspension (mol/kg);  $\gamma_d$  (kg/m<sup>3</sup>),  $h$  (m) and  $n$  stand for the dry density, thickness and porosity of compacted sewage sludge barrier, respectively;  $S$  is the area of a unit section (m<sup>2</sup>). The total amount of acid in the AMD permeating through the sewage sludge barrier can be described as:

$$\sum Acidity = qStc_0 \quad (5)$$

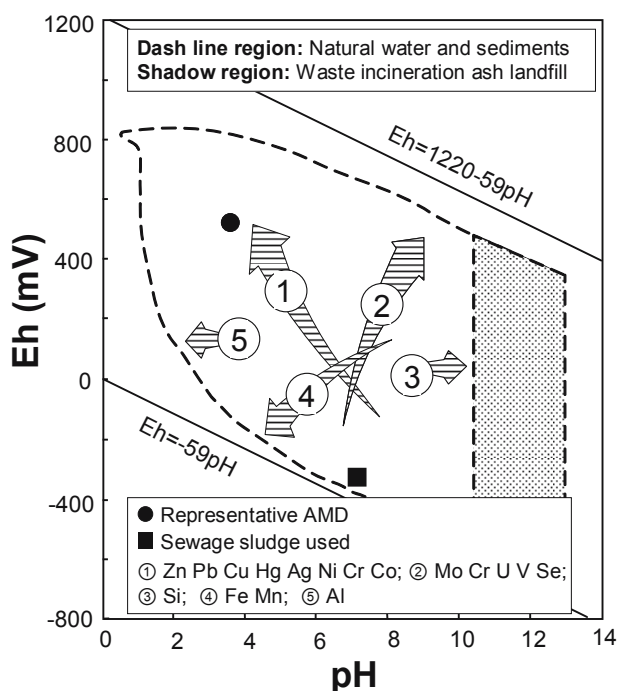


Fig. 10. Dissolvability of different oxide minerals in response to the changes of Eh and pH conditions

Where  $q$  is the flow velocity of AMD (m/s);  $c_0$  is the concentration of acid in AMD (mol/L); and  $t$  is the time of seepage (s). Since the flow velocity of AMD is very small in the compacted sewage sludge barrier, it should be in agreement with the Darcy's law, which can be expressed by the equation:

$$q=ki=kH/h \quad (6)$$

Where  $i$  is the hydraulic gradient;  $k$  is the hydraulic conductivity of saturated sewage sludge barrier, which depends on physical properties of the material (m/s);  $H$  is the head of AMD (m);  $h$  is the thickness of the sewage sludge barrier (m). Combining equations (3)~(6), then yields:

$$t = \frac{\gamma_d n (ABC)_{act} h^2}{k C_0 H} \quad (7)$$

The equation (7) reveals the relationship between the consumed effective ABC and the time, with which the service life-time of sewage sludge barrier for tailings can be estimated. Geotechnical tests on sewage sludge show that the dry density, porosity, and hydraulic conductivity of compacted sewage sludge is equal to 1.05g/cm<sup>3</sup>, 0.47, and 6.34×10<sup>-9</sup>cm/s, respectively. The acid concentration in AMD, according to the results reported by Benner et al. (1997), is taken as an empirical value of 4.6×10<sup>-2</sup> mol/L.  $(ABC)_{act}$  is selected as the minimum value from the results of titration tests for suspension samples. The service life-time is obviously varied with the thickness of the barrier and the water head of AMD. As illustrated in Fig. 12, it is significantly shortened with the increasing water head and decreasing thickness, both of which depend on the designed parameters for tailing piles. Hereon base, three conditions for engineering practice are briefly discussed.

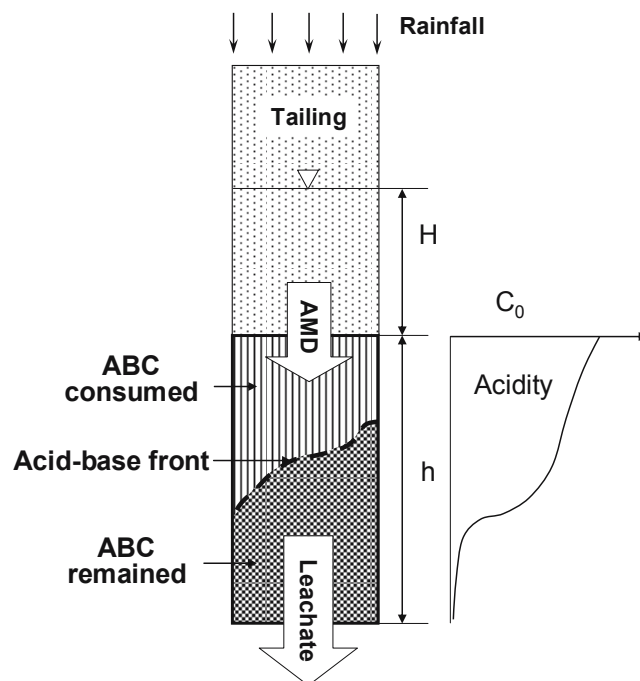


Fig. 11. Schematic illustration of the acidification process of a unit sewage sludge barrier by AMD penetration in tailing impoundment

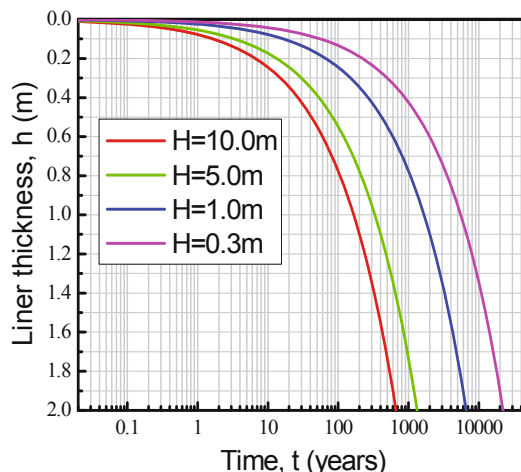


Fig. 12. Depletion time of effective ABC in a sewage sludge barrier as functions of its thickness and the hydraulic head of AMD

Followed by the principles of a landfill for municipal solid waste, there should be an ultimate cover on the top of tailing piles and the thickness of the liner at the bottom should be larger than 2 meters. Moreover, the maximum water head should be no more than 0.3 m, which meets the standard proposed by U.S. Environmental Protection Agency. In this condition, tailing piles are strictly encapsulated. If there is no designed cover on the top, i.e., the normal condition, raining water can directly penetrate through the tailing piles, leading to a dramatic increase of water head. For this instance, the thickness is assumed to be unchanged and the water head is set up to a constant value of 10 meters. In most cases, however, the mine waste is just simply disposed, under which condition the thickness is reduced and its value is supposed to be 0.5 m with water head unchanged ( $H=10$  m). Calculations on these three conditions show that the time required to exhaust the effective ABC of sewage sludge barrier is 22184, 666 and 42 years, and 42 years, respectively. The calculated results are far beyond the duration of management of a typical tailing impoundment. That is to say, the sewage sludge is a satisfactory material to act as a barrier for tailings in the viewpoint of acid buffering capacity and the remobilization of heavy metals due to acidification by AMD is not expected even in a long time perspective.

## Conclusions

The results from this study support that sewage sludge is a suitable material acting as a bottom liner material regarding the remobilization of heavy metals due to acidification in the long-term management of tailing impoundment. Sewage sludge has a high acid buffering capacity because of abundant organic matters and carbonate loads contained. Increasing solid/liquid ration and anaerobic incubation time contribute to the development of acid buffering capacity due to higher initial pH and lower initial Eh conditions, which are induced by increasing buffering substance and respiration of microorganisms. Remobilization of heavy metals is ascribed to the dissolution of contained carbonates during the acidification and it develops fast when pH drops below 6.0. It seems that, however, the compacted sewage sludge barrier has enough acid buffering capacity to inhibit the acidification by AMD seepage

within typical management duration of tailing impoundment. Elevated levels of remobilization of heavy metals would be therefore not expected during this period. Nevertheless, the sewage sludge used in this study was only collected in one sludge water treatment. The acid buffering capacity of sewage sludge, however, depends on its composition, such as initial pH, contents of metals and organic substances, etc. And the composition depends on numerous factors, inter alia, on the land development, region and economic development. Sewage sludge from other treatment plants should be therefore employed to make comparisons for further researches.

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