Geochemical Evaluation of Cemented Paste Tailings in a Flooded Underground Mine

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Abstract

Two underground gold mines in the western United States recently received approval to use cemented paste tailings as backfill. Regulatory authorities required a rigorous evaluation of potential environmental effects of paste because of concerns about water quality after the mines flood with groundwater.

Preliminary testing of cemented paste tailings led to three important findings: 1) cemented paste must be cured prior to geochemical testing, 2) fragmenting cemented cylinders prior to testing alters their geochemical properties, and 3) conventional test methods such as static and kinetic tests do not adequately describe potential chemical releases from cemented paste. As a result of these findings, the Leaching Environmental Assessment Framework (LEAF Kosson et al. 2002) was used to evaluate cemented paste. LEAF consists of three primary testing protocols (EPA 2015a, 2015b and 2015c) to assess solubility across a range of pH (EPA 1313), chemical release by batch or column leaching (EPA 1314 and 1316), and diffusive release (EPA 1315). This testing framework originally developed in the EU for evaluating coal combustion waste has not been extensively used by the hard rock mining industry in the US (Van der Sloot and Zomeren 2012).

Geochemical tests were conducted on cemented cylinders that had cured for 56 days. Any test conducted on cylinders that had been crushed prior to testing yielded high pH values (pH 10 to 11.5), whereas tests on intact cylinders typically had pH values closer to neutral. Neutral pH is more typical of waters contacting aged cement that has undergone carbonation reactions that convert calcium-hydrate-silicates into calcium carbonate in the skin of the cemented material. Therefore, intact cemented specimens provide more representative chemical results for evaluating long-term environmental behavior of cemented paste.

Comparison of constituent levels in the various tests showed that concentrations measured by diffusive release tests were much lower than those found in leaching or pH-solubility tests. This finding indicates that diffusion limits the rate of release of constituents such as arsenic from cemented paste. Owing to the low permeability of cemented tailings, the diffusion release test was found to be provide the most representative data for evaluating releases from cemented paste. All

This paper provides details on the geochemical examination of cemented tailings and how they will interact with an alkaline groundwater. In addition, the paper suggests how LEAF can be applied to the environmental behavior of mining waste, specifically use of cemented paste for underground backfill.

Key words: Mine water, Underground mines, cemented paste, tailings, diffusion

Introduction

Cemented paste tailings are increasingly used for backfill of underground mines and open pits. Adding cement or other binders such as flyash to paste increases strength and also reduces chemical mobility of key constituents, especially metals. The unique geochemical nature of cemented materials poses a challenge to predicting the environmental behavior of cemented paste tailings. Conventional testing methods such a static and kinetic tests and simple solution batch tests fail to properly characterize the nature of water-rock interaction with cemented paste. The purposes of this study are to;

- evaluate the suitability of cemented paste tailings for use as backfill in an underground mine that will eventually flood with groundwater, and

- compare the LEAF protocol to traditional tests used for mine waste characterization.

Chemical and Physical Immobilization of Metals Using Cement

Solidification/stabilization is commonly used at metal-contaminated industrial sites to control chemical releases from contaminated soils and sediments (EPA 2000). In the US, solidification/stabilization is the second most commonly used remediation approach and has been applied to materials contaminated with lead, arsenic, cadmium, copper, nickel and other metals. Cement and flyash are among the most commonly used binders for waste remediation applications.

As cement cures, a series of chemical reactions occur that gradually lend increasing strength. The dominant minerals formed in cement, termed calcium-silicate-hydrates (CSH) are poorly crystalline but have a strongly cross-linked gel structure. CSH form at high pH levels (10 to 12) over a period of many weeks as cement cures in a process known as **hydration**. Metals become immobilized in cemented composites in a variety of ways including formation of metal oxide and hydroxides, sorption, or co-precipitation (Chen et al. 2009). Aluminum and arsenic solubility in untreated tailings, fresh and cured cemented paste (Figure 1) shows a progressive decline in ion solubility with increased hydration.

Cement forms in a strongly alkaline system with pH levels ranging from 10 to 12 SU. Soon after cement forms, the outside surface reacts with atmospheric carbon dioxide that breaks down CSH and forms a silica framework and calcite. The advance of the zone of **carbonation** is quite slow, often progressing only a few mm over many years. Two primary effects of carbonation are to reduce the pH of contact water by about 3 units from 11 to 8 (SU), and decreased permeability of the carbonation layer due to a slight volume increase where calcite plugs the pore space in the silicate matrix. Carbonation can either increase or decrease metal solubility relative to what occurs in the interior of the cemented form (Nath et al. 2012). For most metals tested in cemented paste tailings, however, the pH decrease from 11 to 8 causes a substantial reduction in metal mobility (Figure 2). When pH is decreased from 11 to 8, solubility of aluminum was reduced by a factor or a 20, 2.5-fold for arsenic, 5-fold for vanadium, and remained unchanged for copper (all copper values were below detection in this pH range). Given the importance of carbonation reactions, unbuffered tests that utilize crushed samples of cemented test forms are flawed in that they reflect the pH of the interior of the cement matrix rather than the protective layer formed by carbonation.

Mine Site and Tailings

A western US mine proposed to use cemented paste tailings as fill for primary and secondary stopes in their underground mining sequence. Tailings to be used as backfill are from an oxidized carbonate-hosted Carlin style deposit. Tailings have low levels of pyritic sulfur but are alkaline in pH, and are non acid-generating with net neutralization potential of +38.4 and a neutralization potential ratio of 6.9 (Table 1, Sobek et al. 1978). The tailings have low levels of base metals such as cadmium, copper and zinc but have elevated total and soluble arsenic and antimony. A key concern for using cemented paste for backfill at this site was the potential release of arsenic into groundwater when the mine resaturates during closure.

Test Protocols

A geotechnical testing program was conducted to determine the strength of cemented paste at different rates of binder addition. To evaluate potential environmental effects of cemented paste, numerous tests were conducted on the 15 cm diameter cemented test cylinders used for strength tests. Cylinders were cured for 56-days prior to testing. For tests requiring granular samples, the cylinders were crushed to less than 5 mm fragments.

Humidity cell tests (ASTM 2007a) were conducted on a crushed sample and an intact cemented cylinder. A Meteoric Water Mobility Procedure (MWMP, ASTM 2007b) extraction was performed on a crushed specimen. EPA 1313, 1314 and 1315 tests were also conducted (EPA 2015a, 2015b and 2015c). The leaching and diffusion tests were modified to reflect the nature of groundwater that will flood the underground mines. The diffusion test protocol was also based in part on an ASTM test (C-1308) for cemented radioactive waste (ASTM 2008). The chemical nature of the leachant is an important consideration when evaluating cemented materials because groundwater may chemically attack the cement (Baker and Bishop 1996). Groundwater in the vicinity of this carbonate-hosted

deposit is strongly alkaline with a well-head pH of around 6.5 to 7 owing to elevated carbon dioxide partial pressure. Groundwater chemistry was approximated by creating a synthetic groundwater into which a mixture of air and carbon dioxide was bubbled to maintain near neutral pH. Although the local groundwater contains 0.12 mg/L arsenic in addition to other metals, the synthetic groundwater did not include added metals so that metal release from cemented paste could be more easily detected. The highly alkaline groundwater is not expected to degrade the cement.

Results

Humidity Cell and MWMP Tests

Humidity cell tests on intact versus crushed samples gave widely different results. Arsenic in the intact cylinder was 0.01 to 0.03 mg/L through most of the test, increasing to 0.09 mg/L in the final week. The pH of the unbuffered test began at 10 SU, but decreased after about 3 weeks to 8 SU. This relatively rapid change in pH reflects the initially rapid development of a carbonation zone that decreases the pH of contact water to equilibrium with calcite. Continuous aeration of the humidity cell provides ample carbon dioxide for the carbonation reaction. Crushed samples had much higher arsenic from 0.15 to 0.37 mg/L but similar pH. Both tests tended to increase in arsenic through time. This change is attributed to corrosion of the outside surface of the cemented grains by distilled water added each week to flush the humidity cell. The addition of large amount of water (water weight equivalent to 0.6 times the mass of the sample each week) may have removed calcite from the zone of carbonation, increasing the permeability of the outside layer of the sample leading to more rapid chemical exchange.

The MWMP extraction had 0.08 mg/L arsenic at a pH of 11.4 which was intermediate between the intact and crushed sample HCT results for week 1. The high pH of the MWMP test indicates that it reflects the interior of the cement sample rather than the protective layer.

pH-Solubility Tests

EPA 1313 tests (EPA 2015a, Figure 4) were conducted on tailings, cemented paste tailings (5 % binder) and on a composite of wall rock collected from the underground mine void. Metal levels were measured in a series of 10:1 extracts with synthetic groundwater. All samples exhibited minimum arsenic levels at near neutral pH levels with higher arsenic release at pH below 6 or above 9. Solution pH levels of 5.5 to 7 are near optimum for sorption of arsenate from solution by metal oxyhdroxides (Dzombak and Morel 1990). Arsenic solubility in cemented paste was about one order of magnitude lower than in untreated tailings across the entire gamut of pH values tested. This overall reduction in arsenic release was attributed to chemical reactions of arsenic with binder. Cemented paste had similar arsenic releases as wall rock so would have little net effect on dissolved arsenic during underground mine flooding.

Leaching Tests

EPA 1314 leaching tests (EPA 2015b, Figure 5 and 6) were also conducted on tailings, cemented tailings (5% binder) and mine wall rock. For soluble constituents such as sodium (Figure 5), the leaching test followed a traditional model of advective-dispersive solute transport. Advection displaces the majority of a soluble constituent within the first few pore volume of solution displacement in a column test with dispersion causing a gradual shift from the concentration of the interstitial solution to that of the eluent solution, giving the classical S-shaped breakthrough curve. Tests conducted on untreated tailings showed that sodium was mostly removed before an LS ratio of 8. Leaching results for arsenic were unlike sodium in that elevated arsenic persisted even after leaching 100 weight equivalents of synthetic groundwater. The persistent release of arsenic is typical of constituents with a high solid:liquid partitioning coefficient (Kd) and whose concentration in solution is more strongly controlled by equilibrium reactions that are pH-dependent (Kosson et al. 2002)

During early stages of leaching, cemented paste had much lower soluble arsenic (about 0.1 mg/L) than untreated tailings (about 0.5 mg/L), but above an LS ratio of 30, arsenic values for the two samples tended to converge at about 0.2 mg/L (Figure 6).

The gradual decrease in arsenic with increased leaching from the untreated tailings was attributed either to removal of a more soluble phase of arsenic or due to leaching the soluble sulfate which can compete with arsenate for limited sorption sites in the tailings solids. As the sulfate was removed, remaining arsenic became more strongly sorbed.

Arsenic levels in cemented paste were initially lower (0.1 mg/L) during the first 10 weight equivalents of synthetic groundwater leaching, but then increased to around 0.2 to 0.25 mg/L. During initial leaching steps, most bicarbonate was also removed from synthetic groundwater (bicarbonate reduced from 200 mg/L to less than 20 mg/L). The decreased bicarbonate was attributed to carbonation reactions on the fresh surfaces of cemented grains. The secondary calcite that would have formed as a result of these reactions may have reduced soluble arsenic through co-precipitation (Schafer et al. 2006). After leaching by about 30 weight equivalents of synthetic groundwater, the tailings and cemented tailings had similar arsenic results.

Leaching tests may overestimate actual arsenic release. The protective layer formed by carbonation is disrupted when a sample is crushed so that the high pH interior of the cemented material is exposed during leaching. Surface area is also greatly increased as a result of sample fragmentation. Diffusion tests, described below, provide a more representative means of testing release from intact cemented materials

Diffusion Tests

EPA 1315 diffusion tests (EPA 2015c, Figure 7 and 8) are fundamentally different than other analytical tests used for mine waste characterization. The test consists of sequentially placing an intact, cured cemented specimen into a series of batch solutions. The contact duration in each subsequent batch solution is carefully controlled so that the rate of mass release from the cylinder into the solution by diffusion can be determined. The primary purpose of the diffusion test is two-fold. Firstly, the test identifies whether the release of a constituent is diffusion-limited or not. Secondly, if constituent release is diffusion limited, the analytical data can be used to calculate the effective diffusivity of an ion in the cemented specimen. If apparent diffusivity is more than 100X slower than ion diffusion in water (e.g. about 4.4×10^{-6} cm^2/s for arsenate), the ion is considered diffusion-limited. Since the amount of a constituent measured in each batch solution depends on the batch duration and on the sequence of the test, the constituent concentration measured in solution is less important than the diffusion rate calculated from the results.

The equation for calculating effective diffusivity assumes that the test cylinder is a semi-infinite solid for which the cumulative fraction of any constituent leached (CFL) is a function of diffusivity, test duration and cylinder geometry from equation [1]. The CFL curve is fit to experimental data by varying the value of effective diffusivity (De) to minimize the mean square error in measured versus predicted CFL using an iterative solver.

$$CFL = \sum \frac{a_n}{A_0} = \sum IFL = 2\frac{S}{V}\left[\frac{D_e t}{\pi}\right]^{1/2}$$
[1]

Where a_n is the mass of constituent in the nth batch solution (mg)
A_o is the total constituent mass in the cylinder (mg)
S is the cylinder surface area (cm^2)
V is the cylinder volume (cm^3)
D_e is the effective diffusivity cm^2/s
t is time in s

Diffusion test results (Figure 7) for paste cemented with varying binder amounts show a progressive reduction in arsenic release as binder is increased from 3 to 12%. For all binder levels, the effective diffusivity was more than 5 orders of magnitude slower than diffusion of arsenate in water.

Comparing all geochemical test results for a cemented paste (Figure 8), diffusion test results yielded much lower arsenic concentrations than leaching tests, pH-solubility tests, or humidity cells at a

similar pH level suggesting that all other tests would overestimate constituent release for a diffusion-limited constituent such as arsenic.

Test Interpretation

Suitability of Cemented Paste as Backfill

Geochemical tests results showed that addition of as little as 3% binder to an oxidized tailing significantly reduced the mobility of all constituents evaluated. Owing to the low permeability of the cemented paste tailings matrix, release of all metal ions tested was controlled by diffusion. Extrapolation of test results to the flooded conditions after mining indicated that cemented paste used as backfill would have no adverse or measurable effect on water quality. Regulatory approval was received for the proposed use of cemented paste.

Applicability of LEAF Protocol for Mine Waste Evaluations

The LEAF series of tests provides a broad spectrum of information about mine waste that facilitates an in depth understanding of the nature of water-rock interactions. At least three fundamentally different categories of water-rock interactions are addressed by the suite of tests. Constituents can be categorized according to the factor that controls release from solid to aqueous phase (Kosson et al. 2009, Van der Sloot and Zomeren 2012)

•   **Advection-Controlled** – This release mechanism includes more soluble constituents such sodium, chloride, nitrate and boron that are readily leached out of the solid phase (e.g. have a low Kd) with progressive rinsing. The leach test (EPA 1314, EPA 2015b) best describes the release of these constituents.

•   **pH Dependent Control** – Constituents with high Kd values, which is the case for many metals in alkaline waters, are often not readily leached from a system because the constituent is very slowly depleted. Ions that form low-solubility solids or that are strongly sorbed onto mineral surfaces are included in this category. Determining the apparent solubility of these constituents is complex because small changes in pH or counter-ion concentrations can have large effects on constituent release. Where pH of the contact water is the primary factor affecting constituent release, EPA method 1313 provides insight into ion mobility.

•   **Diffusion Controlled** – The concept of flow in granular porous media is the basis for much of the theoretical development of groundwater and transport models. In a homogeneous granular porous media, water contacts all mineral grains, so chemical equilibrium reactions can occur rapidly relative to the flow dynamics. In reality many systems exhibit two regions of flow: a rapid flow region and an immobile region where chemical flux is controlled by diffusion (van Genuchten and Wierenga 1976). Examples of two-region flow include preferred flow in waste rock, copper and gold leaching, fracture flow groundwater systems, and cemented paste tailings used as backfill. EPA test method 1315 (EPA 2015c) and related tests such as ASTM C-1308 (ASTM 2008) provide a basis for evaluating and quantifying the diffusive rate of release from monolithic waste fills or systems with preferred flow paths around large clasts.

The LEAF series of tests proved to be superior to conventional mine waste characterization tests such as static, humidity cell and simple batch tests (e.g. MWMP, ASTM 2007b) for evaluating the performance of cemented paste tailings backfill in an underground mine.

Tables

Table 1. Static tests, total and soluble metals in tailings.

Static test Results		Constituent	Total (mg/kg)	Soluble MWMP (mg/L)
Paste pH	7.71	Arsenic	821	0.56
Total Sulfur (%)	0.22	Barium	1970	0.024
Sulfate Sulfur (%)	0.01	Cadmium	1.36	<0.001
Non-extractable Sulfur (%)	0.056	Copper	62.4	<0.05
Acid Neutralizing Potential (kg/t as CaCO₃)	45	Iron	21100	<0.01
Acid Generating Potential (kg/t as CaCO₃)	6.6	Antimony	106.5	0.078
Net Neutralizing Potential (kg/t as CaCO₃)	38.4	Zinc	131	<0.01
Neutralizing Potential Ratio (ANP/AGP)	6.9			

Figures
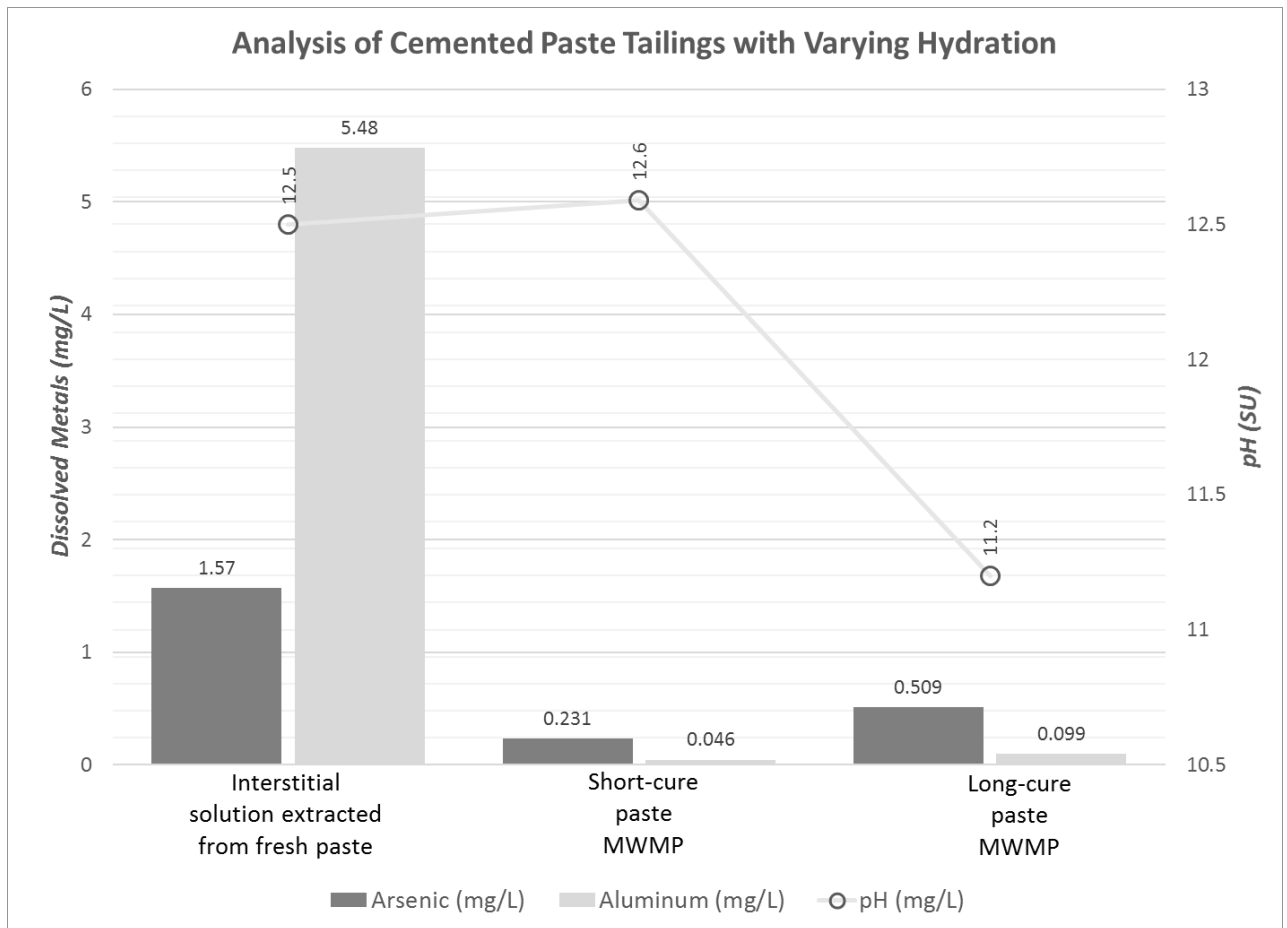
Figure 1. *Solubility of arsenic and aluminum in groundwater, untreated tailings and in cemented paste tailings with increasing time for hydration.*
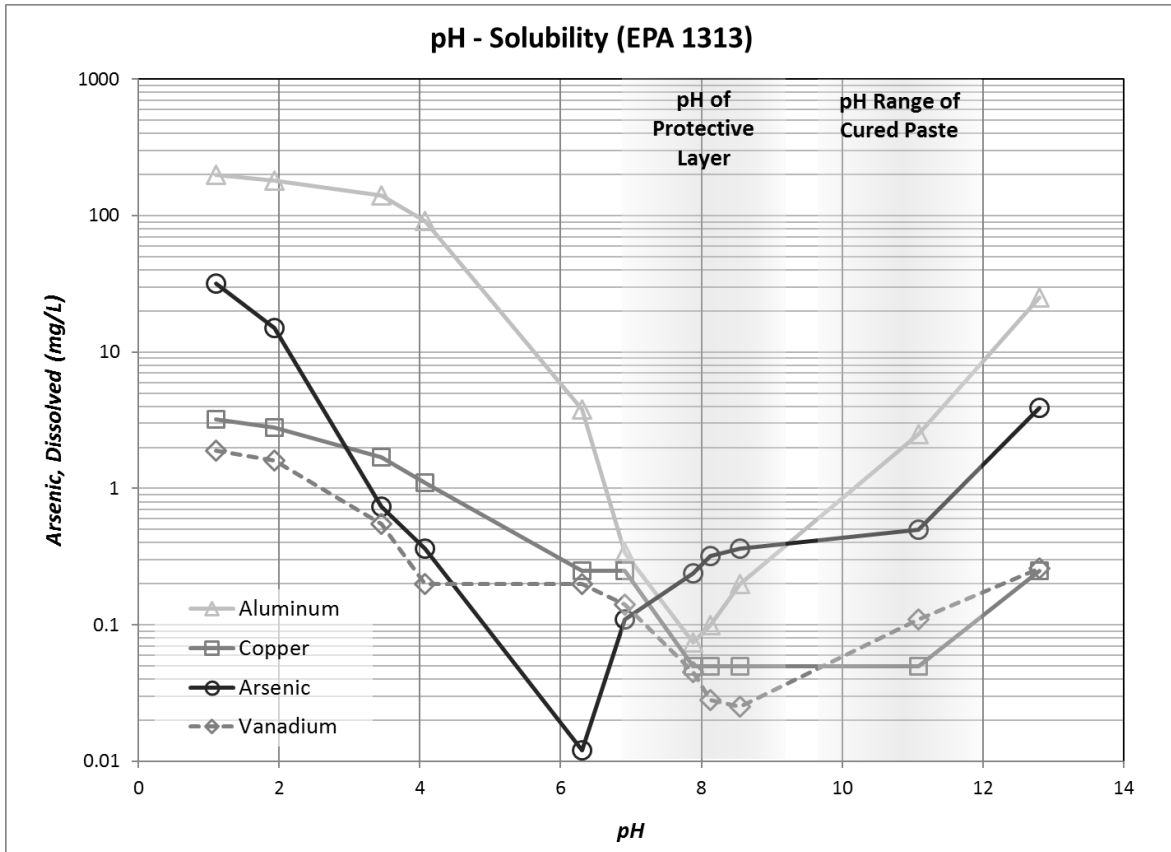
Figure 2. *Solubility of aluminum, copper, arsenic and vanadium in samples of 56-day cured cemented paste tailings at varying pH.*
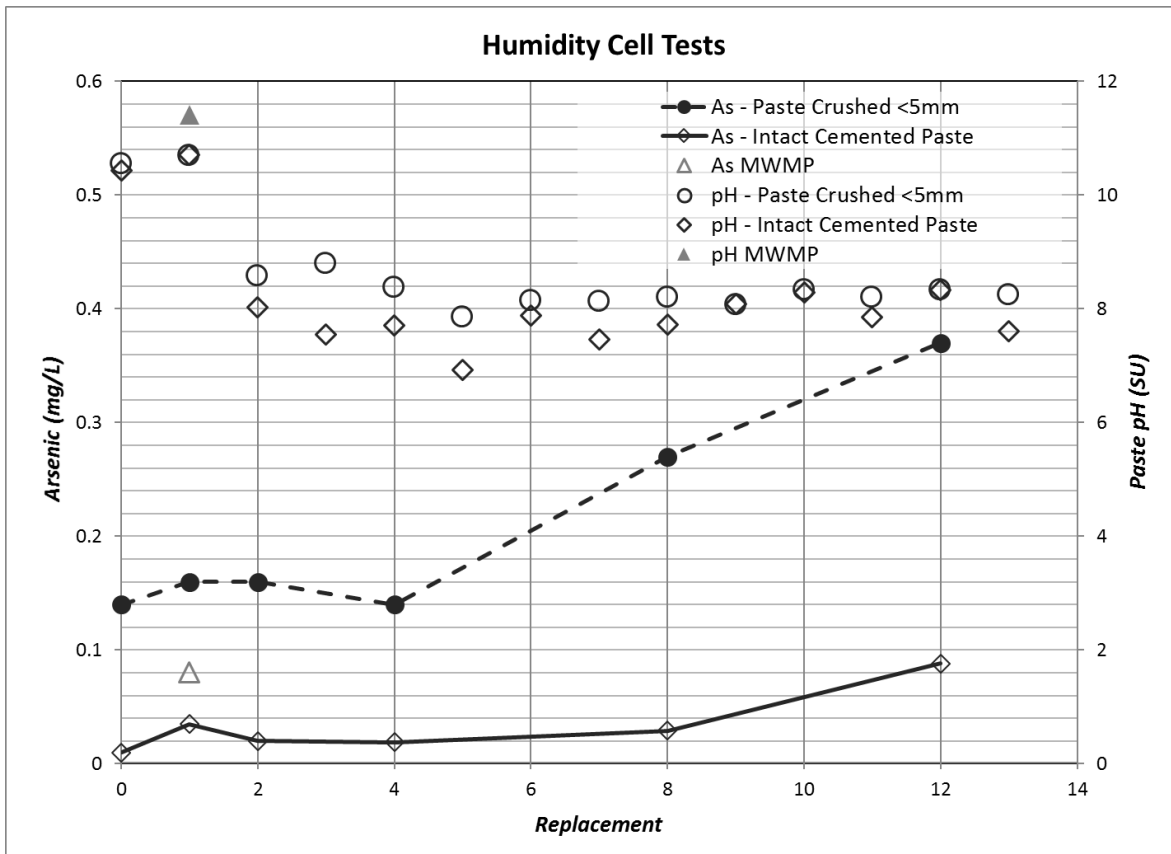

Figure 3. *Solubility of arsenic and solution pH for humidity cell tests of crushed and intact cylinders.*
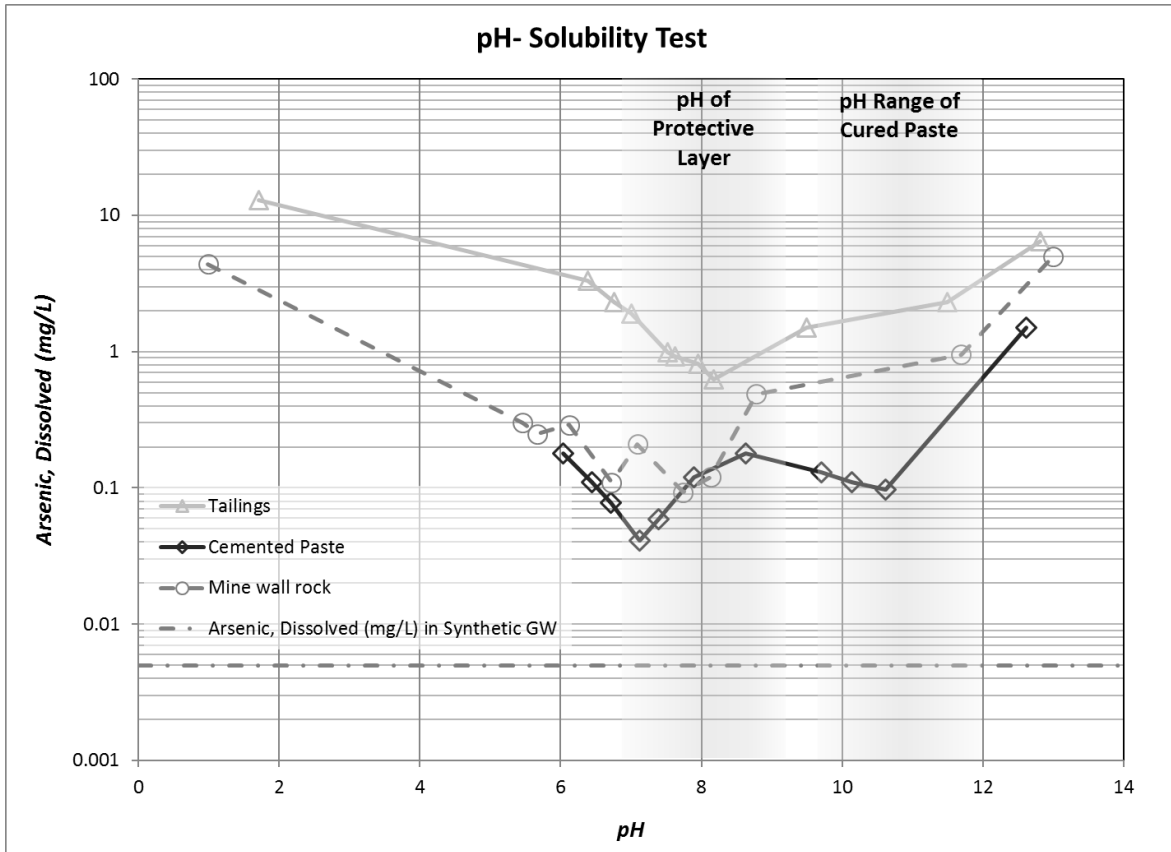
Figure 4. *Solubility of arsenic in tailings, cemented paste tailings and in mine wall rock as a function of pH.*
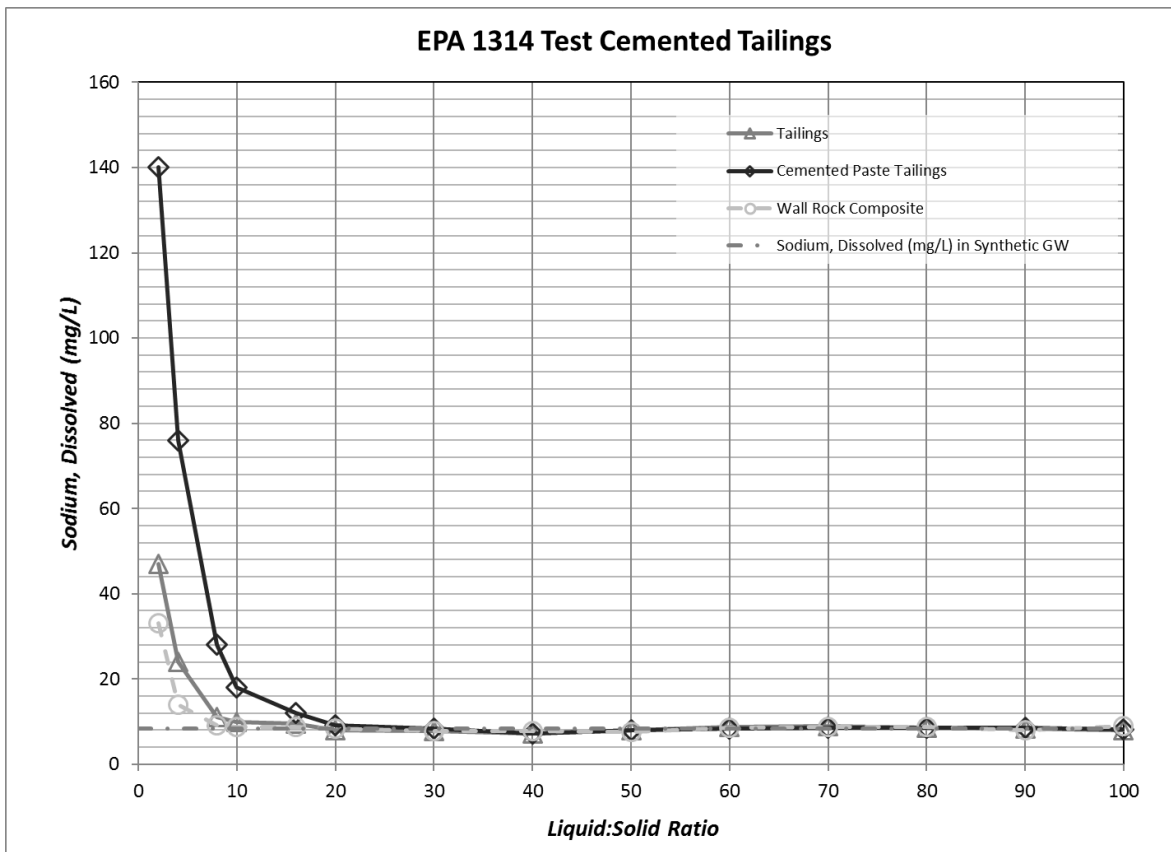

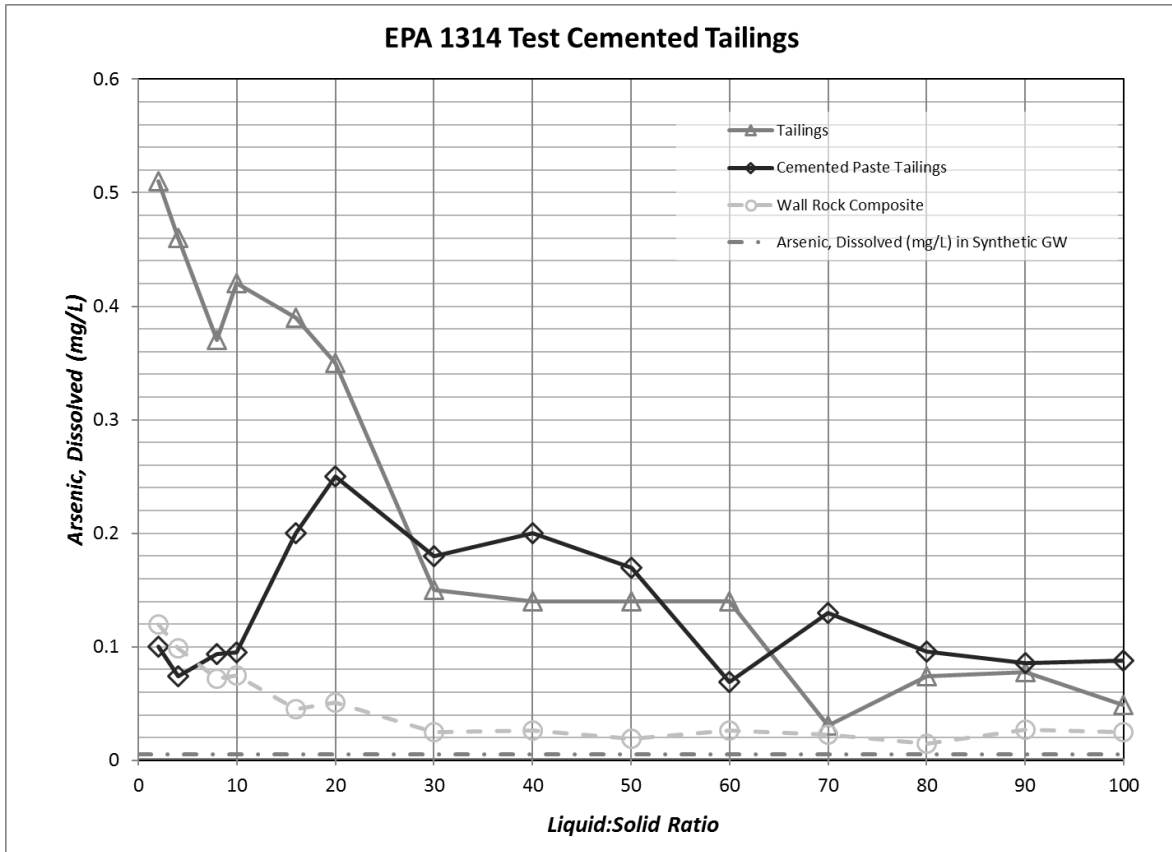**Figure 5.** *Sodium leaching tests for tailings, cemented tailings and mine wall rock.*

Figure 6. *Arsenic leaching tests for tailings, cemented tailings and mine wall rock.*
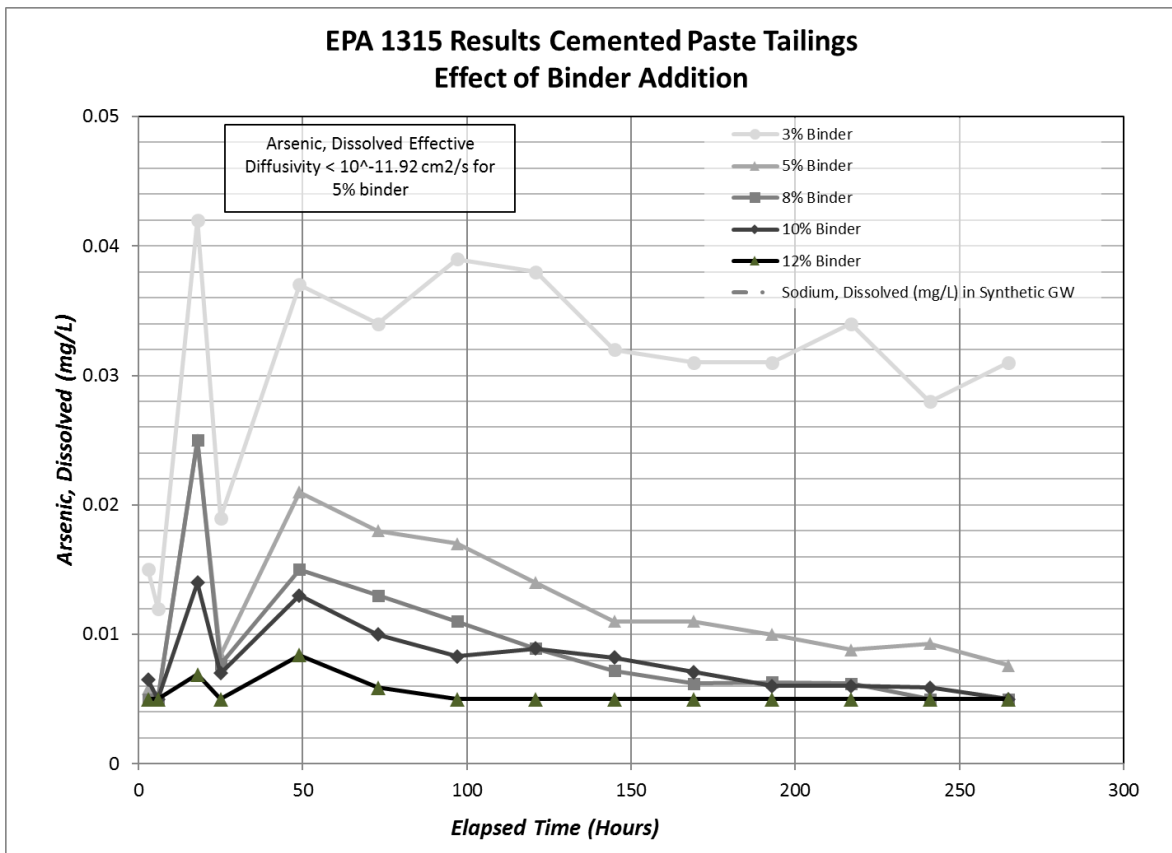

Figure 7. *Arsenic diffusion tests for cemented tailings with varying binder addition (50 % Portland Cement and 50 % flyash).*
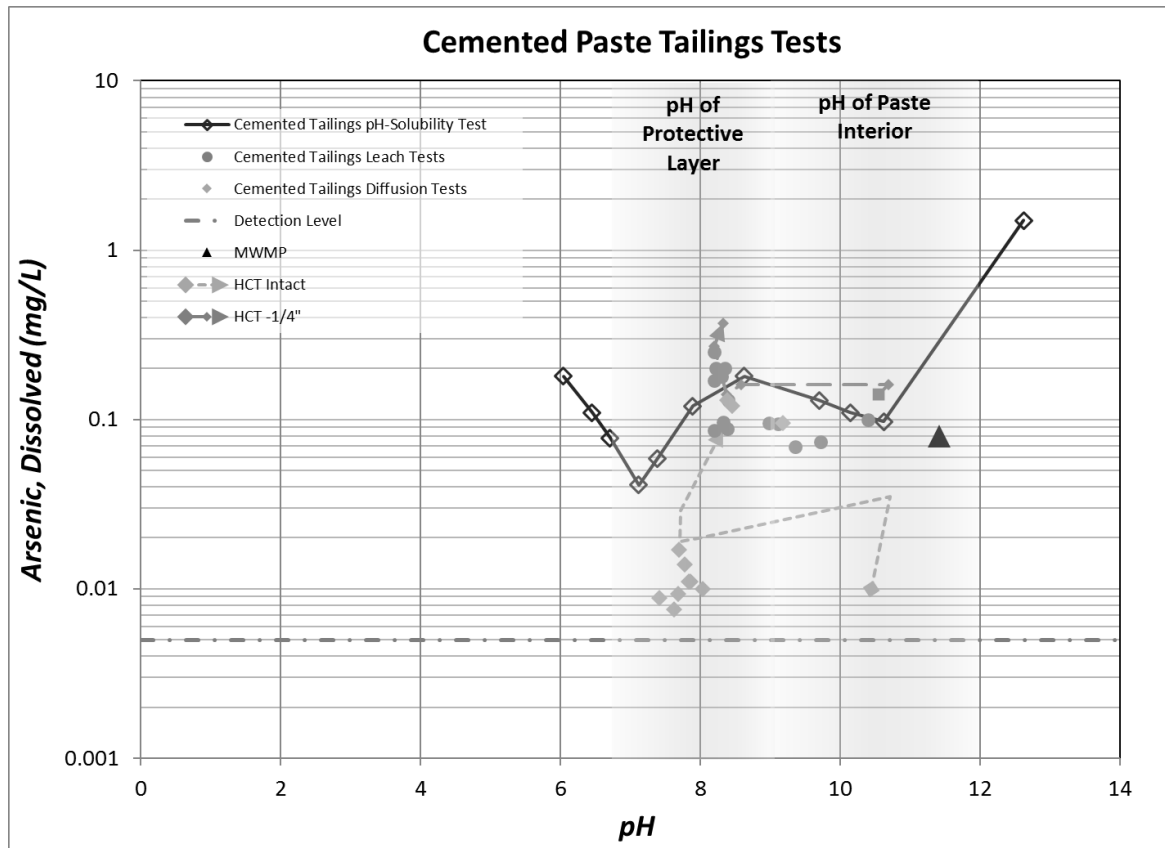
***Figure 8**: Results of various tests for evaluating the environmental effects of cemented paste tailings.*

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