

# Diagenesis of FBC Ash in an Acidic Pit Lake

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**KEYWORDS:** Portland cement, longevity model, mineralogy, thermodynamic model

## **ABSTRACT**

Mineralogical evolution of placed fluidized bed combustor ash for mineland reclamation can result in the development of cementitious monolithic solids. Hydration reactions based on the early formation of ettringite and gypsum can result in unconfined compressive strengths that vary, depending on the ash source, from a few hundreds of pounds per square inch to a few thousands of pounds per square inch. Extended hydration of these cementitious elements at elevated pH values further involves the reaction with dehydroxylated clays in the ash to form an amorphous hydrous calcium silicate phase similar to that found in ordinary Portland cement. This phase commonly identified in the cement literature as C-S-H, is the 'glue' that is responsible for the mechanical and chemical properties of Portland cement concrete. Hydration products formed from the reaction of FBC ash grouts with water have been identified in the laboratory, in field specimens, and most recently confirmed by thermodynamic modeling of the pore waters associated with placed ash. The confirmation at this level allows for further modeling of placed monolithic cementitious solids using Portland cement durability as an analog.

## **INTRODUCTION**

The use of fly ash from utility power stations or from waste coal burners for unamended mineland remediation applications is both practical and offers a cost effective means of achieving the otherwise extremely costly reclamation. If practiced correctly, the use of coal combustion products [CCPs] can offer benefits that constitute a win-win situation for both the citizens and regulators for the utilities. Annually, millions of tons of CCPs are used in the reclamation of abandoned minelands [DEP, 2004] [others]. For the majority of these projects, the CCP is approached from an engineering standpoint, as a material that is routinely monitored for chemistry to ensure environmental compliance with the overseeing governance body. The most important characteristic for long-term stability of the fly ash in reclamation applications is the mineralogy and the evolution of mineralogy changes that occur with time.

The pozzolanic activity of Class F fly ashes has been discussed by Scheetz et al. [1993,1994,1995] , and the reactions with fluidized bed ashes by Fontana [1995] and Zhao [1995]. These authors addressed the progress of changes in the mineralogical compositions of the fly ash resulting from the chemical reactions of the glass and meta-clays from the ash with alkalis, either added directly to the ash or resulting from excess free lime from the ash. FBC

ashes, resulting from the burning of high sulfur-containing bituminous coals, routinely produce ettringite which has been identified by many authors Schlorholtz et al. [1987]

Cementitious behavior resulting from the hydration of the ash is similar to the hydration reactions observed in the chemical reactions in ordinary Portland cement. Loop [2003] reported the formation of these cementitious phases through thermodynamic modeling of both the pore fluids and water in contact with large-scale FBC ash placement. Analyses of the solid hydrated ashes support the theoretical modeling with visual evidence for the presence of the hydration products. Using the hydration products of Portland cement as an analog, modeling the long-term behavior of emplaced fly ash is possible.

**PARAGENESIS OF THE MINERALOGICAL ASSEMBLAGE IN ASH**

The bulk chemistry and mineralogy of ash from a co-generation facility, NEPCO, in Mcadoo, PA was quantified and reported in tables 1 and 2, respectively. This site is located in the East Central Anthracite Coal Fields of Central Pennsylvanian. The “Big Gorilla” was a pre-act water-filled surface strip mine adjacent to the NEPCO cogeneration facility. The work represents a demonstration of dry-to-wet ash placement in cooperation with the Pennsylvania Department of Environmental Protection with oversight form the Pottsville Regional Office.

**Table 1. Bulk chemistry for FBC ash from NEPCO contrasted to an average composition from 5 similar facilities in the anthracite coal fields.**

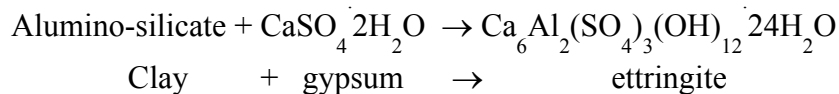
Oxide	NEPCO ash composition [wt %]	Average composition of 5 culm-derived ash analyses
SiO <sub>2</sub>	64.47	60.69
Al <sub>2</sub> O <sub>3</sub>	18.82	23.11
Fe <sub>2</sub> O <sub>3</sub>	5.74	5.08
CaO	5.45	5.44
MgO	1.48	1.15
K <sub>2</sub> O	3.77	2.90
SO <sub>3</sub>	0.26	1.60

**Table 2. Bulk mineralogical analyses of the NEPCO fly ash obtained by multiple analytical methods.**

<i>Mineral</i>	<i>Formula</i>	<i>Analytical method</i>	<i>Wt. %</i>
Quartz	SiO <sub>2</sub>	QXRD, wet chem	20.0
Mullite	Al <sub>6</sub> Si <sub>2</sub> O <sub>13</sub>	QXRD	7.0
Hematite	Fe <sub>2</sub> O <sub>3</sub>	QXRD	2.0
Portlandite	Ca(OH) <sub>2</sub>	DTA, QXRD, wet chem	6.5
Calcite	CaCO <sub>3</sub>	QXRD, wet chem	0.4
Gypsum	CaSO <sub>4</sub> .2H <sub>2</sub> O	QXRD	0.5
Meta-clays		QXRD	63.6
<i>Total</i>			100

Some of the mineralogical constituents of the ash remain inert with respect to the chemical reactions that take place within the ash fill and can be ignored in subsequent discussions. Quartz, mullite, and hematite which constitute about 30% of the ash minerals from the NEPCO fall into this category and act essentially as fillers. The meta-clays, which constitute the bulk of the sample, interact with the portlandite to produce the cementitious behavior.

The pore fluids were sampled and determined to have a pH of 12. Loop et al. [2003] demonstrated, with the use of PHREEQC a thermodynamic equilibrium code, that this pH was in part a result of the fluids approach to a pH of 12.45, the equilibrium value for water saturated with portlandite. Reaction of Ca(OH)<sub>2</sub> with atmospheric carbon dioxide in an open system precipitated the observed calcite. The high pH and the presence of both gypsum and sulfates in the mine water are responsible for the reaction of the thermally altered clays to form ettringite and possibly gismondine.



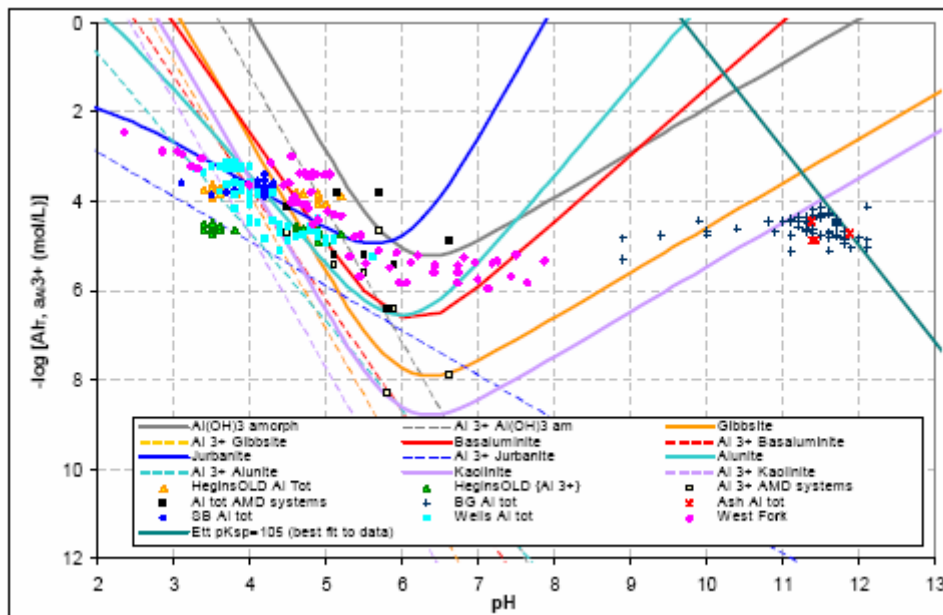
It has been thermodynamically demonstrated that ettringite is controlling the solubility of aluminum in the mine-pit lake waters at high pH (Loop (003). Ettringite is also an important component in cementitious reactions and a control for arsenic sequestration. Scanning electron microscopic (SEM) characterization of placed ash has visually predicted the development of ettringite (Fig. 3).

The high alkalinity pore water also causes a large amount of meta-clay to undergo pozzolanic reactions with the formation of hydrous calcium silicate phases. Thermodynamic modeling has indicated the existence of 14Å tobermorite. This phase is the crystalline equivalent of C-S-H, the glue in Portland cement. Although

thermodynamic calculations have been established for a phase that contains no aluminum, C-S-H forming under real world cement hydration conditions always contains a finite amount of aluminum substitution at the maximum solubility limits [Barnes and Scheetz, 1989].

Thermodynamic calculations also suggest the formation of gismondine, a calcium zeolite in the assemblage of reaction products in the ash. Although this particular zeolite has not been identified in the ash via SEM characterization, the presence of zeolites in hydrating cementitious systems is well documented [Grutzeck et al., 1997, 1999, 2003]. Finally, the thermodynamic calculations also suggest that in the presence of atmospheric carbon dioxide, common minerals of the alkaline earth elements will form, including calcite and to a lesser extent, witherite.

Although these FBC ashes are not strongly pozzolanic, the presence of large amounts of thermally altered clays in the presence of an alkalinity source that will raise the pH above 9.5 results in hydration products forming that are similar to those formed in the Portland cement system. The similarities offer an unprecedented opportunity to model the behavior of these structural ash fills.



**Figure 1. Thermodynamic control over the solubility of aluminum in AMD and the Gorilla mine-pit lake waters. Plot constructed by Dr. Charles Cravotta of the U.S. Geological Survey, with an ettringite solubility line altered by the authors to best fit the Big Gorilla data.**

The hydrated phases in the ash structure have the potential to form large quantities of C-S-H from the 63 wt% thermally altered clays. Based on a Portland cement model, suggested by thermodynamic calculations of the pore fluids, a portrait of the long-term behavior of the ash structure can be constructed. Figure 5 is a schematic representation of the resulting phase assemblage and pH.

Stage I, [T<sub>0</sub> – T<sub>1</sub>] represents a period when the pH of the ash structure is controlled by the buffer established by portlandite and C-S-H. The leachate pH will remain at a value of 12.45 until such time as all of the portlandite has been removed.

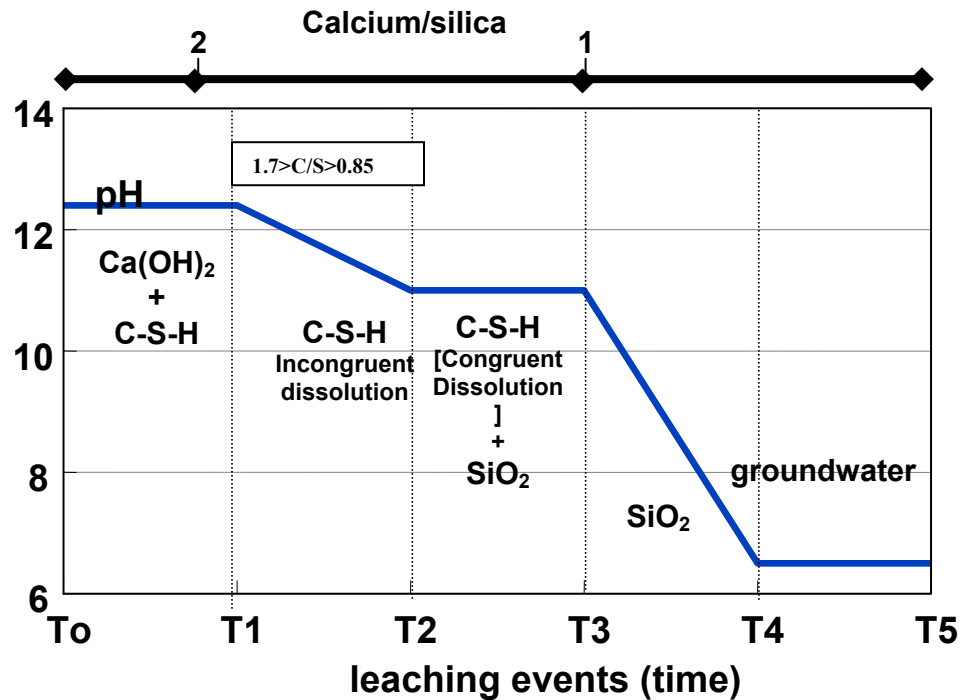
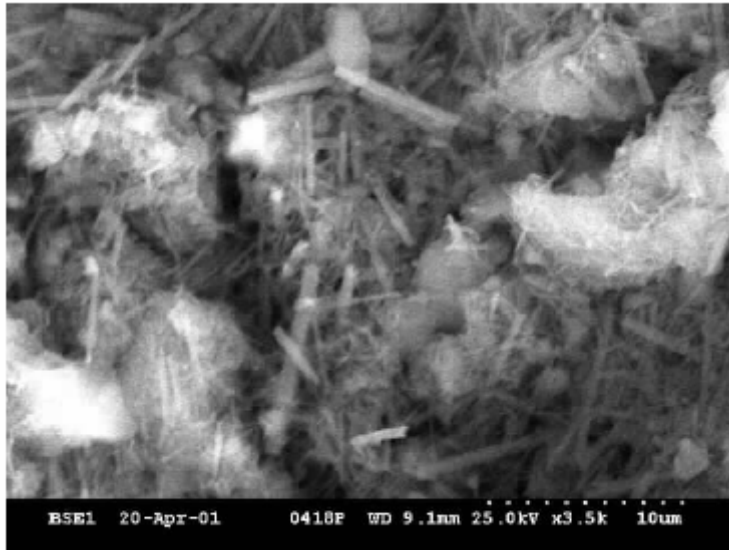
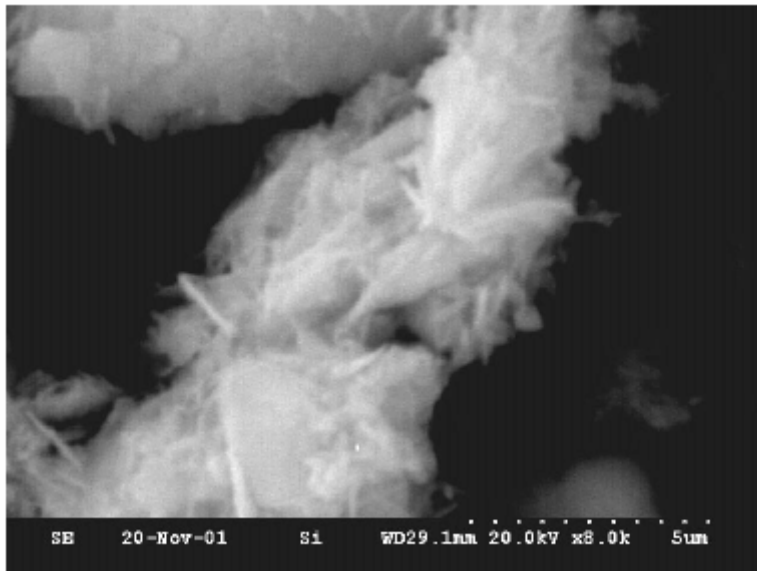


Figure 5 Effects of leaching on pH of C-S-H-portlandite-silica system as a function of continued leaching. [after Atkinson, 1985]



**Figure 2. Scanning electron micrograph of ettringite growth in FBC ash.**

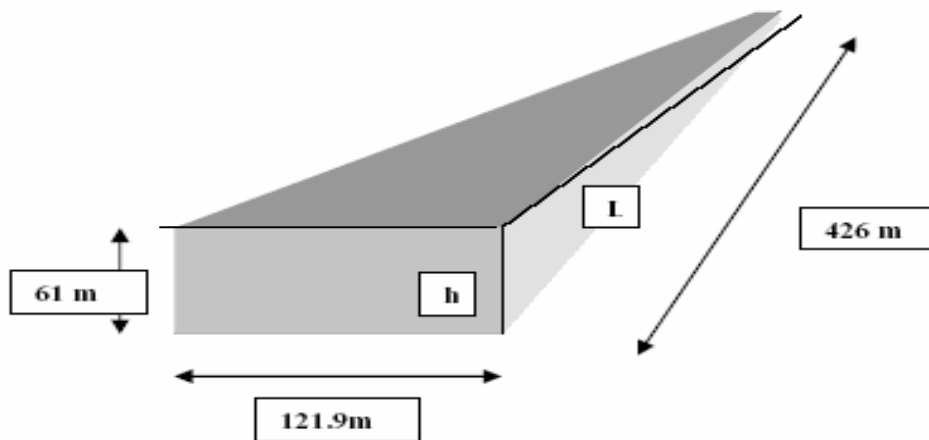


**Figure 3. Development of C-S-H in ash.**

### **LONGEVITY OF THE ASH FILL**

The most commonly asked question of a structural fill concerns the timescale of stability. This is a fair question that can be addressed in several ways. Subsequent calculations will attempt to provide bounding calculations that will bracket the anticipated longevity based upon several different approaches describing the ash fill.

**Case I – Darcy’s Law Approximation.** During the course of the ash placement, both compaction measurements on the ash fill and hydraulic conductivity measurements were made. It was determined that the hydraulic conductivity of the ash was  $1 \times 10^{-6}$  cm/sec, a value not atypical of others reported for ash monofills [Ghosh and Subbarao, 1998]. The structural fill can be represented as a homogeneous body in which water movement will remain in a laminar flow condition. With these assumptions, Darcy’s law can be used to describe the time it would take for a given volume of water to flow through the mass. Figure 4 provides details for the dimensions of this model calculation.



**Figure 4. Model for calculation of hydraulic conductivity.**

$$Q = KIA$$

Where:

Q = flow rate (vol/time)

K = hydraulic conductivity ( $1 \times 10^{-6}$  cm/sec)

I = hydraulic head (h/L)

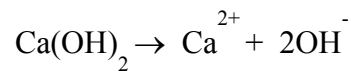
A = cross sectional area of the pile (cm<sup>2</sup>)

The compacted ash in the Gorilla represents approximately 1.7 million m<sup>3</sup> of ash. If the porosity is approximately twenty percent, the volume of ash contains about 12 million cubic feet or about 90 million gallons (0.34 million m<sup>3</sup>) of pore water. Using Darcy’s Law, one can determine the time required for a single gallon of this 90 million gallons of pore water to flow through this modeled system based on the conservative assumptions that the hydraulic head is the complete thickness of the fill. Using the stated assumptions and the dimensions of the Big Gorilla pit and assuming a rectangular parallelepiped as shown in Figure 4, an estimated 3,000,000 years is calculated for that one gallon of pore water to move through the entire ash body. It must also be recognized that as this water

moves through the fill, it will become alkaline with the fill acting as a large alkaline reservoir.

The initial calculations were conservative, based on a hydraulic head of ~15% compared to the more commonly encountered 1% head. The corresponding time interval for the smaller gradient is well in excess of 10,000,000 years.

**Case II – Shrinking Core Model for Portlandite Dissolution.** Bounding calculations can be conducted for the leach interval  $T_0$ - $T_1$  based upon a) ash structure control of the leaching and b) the contacting geologic control of the leaching.



The flux is calculated from:

$$\text{Flux} = -D_i [(C_t - C_{gw})/X]$$

$$dX/dt = [D_i/X][C_t - C_{gw}/C_s]$$

Walton et al. [1990] have developed an approach for the depth of leaching of portlandite from a cementitious body that takes the form:

$$x = [2D_i(C_p - C_{gw})/C_s t]^{1/2}$$

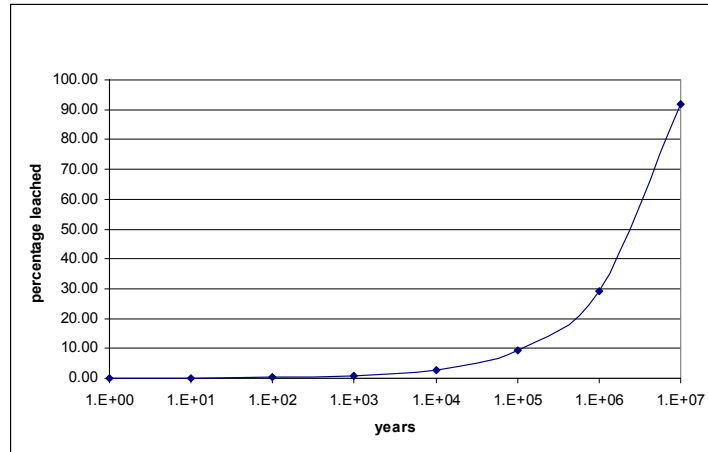
Where:

X	distance	cm
$D_i$	intrinsic diffusivity	$\text{cm}^2/\text{sec}$
$C_p$	concrete pore	$\text{moles}/\text{cm}^3$
$C_{gw}$	groundwater	$\text{moles}/\text{cm}^3$
$C_s$	solids	$\text{moles}/\text{cm}^3$
t	time	sec

The shrinking core model assumes that the removal of calcium from the exterior surface of the concrete is rapid relative to the movement through the concrete. This relationship takes the inventory of Ca-ions in the pore fluids of the ash structure minus the leaching water concentration and ratios it to the total available in the solids. By multiplying against the intrinsic diffusivity for calcium in the ash as a function of the square root of time (diffusion controls the leaching), a depth of penetration into the structure can be calculated. Because concrete is less permeable than the surrounding bed rock, the dominant flow direction will rarely be normal to the concrete (structural fill) surface.



Based on 61 m, the smallest dimension of the filled Gorilla pit and assuming diffusion through both sides toward the middle of the structure, a time (t) can be calculated when both diffusion surfaces meet. The results of this calculation, based on a conservative intrinsic diffusivity of  $3 \times 10^{-6} \text{ cm}^2/\text{sec}$ , yielded a time frame for  $T_0-T_1$  on the order of 10,000,000 years. Figure 6 summarizes this calculation release as percentage portlandite leached from the smallest dimension of the Gorilla ash fill as a function of time based on an ash structure-controlled leaching model.



**Figure 6. Percentage leached of the smallest dimension of the Gorilla ash fill as a function of time based on an ash structure-controlled leaching model.**

**Case III – Diffusion Model for the Dissolution of Portlandite.** The alternative approach suggested by Walton et al. [1990] [after Atkinson and Hearne, 1984] was to allow the surrounding geology to control the diffusion of calcium from portlandite in the ash fill to diffuse into the surrounding geology. In this approach, the concentrations are described by an error function:

$$\left[ \frac{C - C_{gw}}{C_l - C_{gw}} \right] = \text{erfc} \left[ \frac{X}{(4D_e t/R_d)^{1/2}} \right]$$

The total material leached in a given time period is obtained by integrating with respect to time:

$$M_t = \Phi C_l - C_{gw} (4R_d D_e t/\pi)^{1/2}$$

The total amount of calcium hydroxide removed can be related to the inventory in the fill as:

$$M_t = X C_{\text{bulk}}$$

Following a similar approach, Walton presented the following equation in which he calculated the depth of leaching in the ash fill:

$$x=2\Phi[Cp-Cgw/Cs](RdDeT/\pi)^{0.5}$$

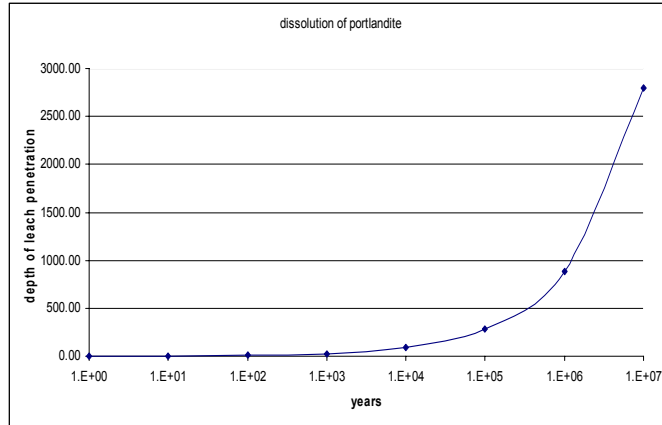
where:

X	distance	cm
Cp	concrete pore	moles/cm <sup>3</sup>
Cgw	ground water	moles/cm <sup>3</sup>
Cs	solids	moles/cm <sup>3</sup>
Rd	retardation	
De	effective diffusivity	cm <sup>2</sup> /sec
Φ	porosity	
t	time	sec

In this analysis he also utilizes the percentage of the total inventory of calcium in the ash released but controlled by the effective diffusivity of the geologic media as well as the retardation of the geologic media. Assuming conservative values for  $R_d$  and  $D_e$ , the estimated time that the leaching process took to diffuse through parallel sides of the ash structure 61 m thick was on the order of 255,000 years (Fig. 7).

Although the length of time to accomplish the total removal of portlandite from the ash structure in the Gorilla ranges over two-orders of magnitude, the bounding calculations suggest that for the leaching interval  $T_0$ - $T_1$ , times in excess of a quarter of a million years will transpire. It is noteworthy to point out that during this time interval a slow release of alkalinity in the form of calcium hydroxide will be taking place. Only after the total removal will the pH begin to drop.

Stage II [ $T_1$ - $T_2$ ] is represented by the stability of a single phase and described by the incongruent dissolution of C-S-H from a calcium to silica ratio of 1.7 to a value of 0.85 and will proceed until pH 10.7 is reached. All of the excess calcium in the structure is removed and C-S-H begins to undergo congruent dissolution. Estimates of the length of time involved in this stage of leaching of the fill are difficult to make since they depend on the amount of C-S-H formed during the hydration of the ash components. In Portland cement concrete as a point of reference, this stage typically is calculated to require approximately 1,000,000 years to reach the onset of congruent dissolution of the C-S-H [Atkinson, 1985].



**Figure 7. Percentage leached of the smallest dimension of the Gorilla ash fill as a function of time based on a geology-controlled leaching model.**

The transition marks the onset of Stage III [T<sub>2</sub>-T<sub>3</sub>] in which the phase rule dictates the coexistence of two phases, C-S-H and SiO<sub>2</sub>. Dissolution follows at a constant pH until all of the C-S-H is removed. Following a similar argument, direct estimates of the durability are not possible. However, by analogy with concrete Atkinson [1985] calculates about 500,000 years to achieve complete dissolution of the C-S-H. Stage IV represents the stability of only a single phase, SiO<sub>2</sub>, thus allowing, by the Gibbs Phase Rule, the pH to drop to the controlling groundwater pH, Stage V.

## CONCLUSIONS

The above exercises were conducted in order to provide some sense of the long-term stability that may be anticipated from the structural fill in the Big Gorilla Pit. The calculations were conducted based upon our recognition that the changing mineralogy of the fill materials could be modeled using phase relationships for calcium silicate in Portland cement as an analog. The approach presented a stepped four stage dissolution of the portlandite and hydrous calcium silicate. Furthermore, the calculations were conducted with conservative input data to the model. Reasonable but aggressive parameters were chosen that would ‘hasten’ the leaching of the fill and in this manner provide a more conservative interpretation of the data. The calculations for Case II and Case III followed the dissolution of portlandite and made the assumption that when the portlandite was removed, the cementitious element was compromised.

These results suggest that the structural fill will be stable for a period of time most probably in excess of 100,000 years and likely well in excess of 1,000,000 years. During the period of time in which it is altering, the pH of the leachates released from the fill will be above a value of 10.7 for the vast majority of that time. In an environment where the ground waters are impacted by acid mine drainage, it is anticipated that projects such as these can have profound long-term environmental benefits.

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