CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2.1 Background

2.1.1 Fly Ash Classification

The definition of fly ash used in this study follows the ASTM C 618 (1997): fly ash is a fine particle residue produced by burning coal. Currently fly ash comes primarily from coal-fired electricity generating power plants. These micron-sized compounds are captured from the exhausted gases and collected by bag house. Fly ash consists primarily of silica, alumina, and iron. It can be classified into two types by the summation of the oxides SiO_2, Fe_2O_3, and Al_2O_3.

1. Fly ash Class F

Class F fly ash is produced from the combustion of anthracite or bituminous coals, in which has the summation of the oxides SiO_2, Fe_2O_3, and Al_2O_3 is higher than 70%. Most fly ash in this type consists of low calcium (less than 10%).

2. Fly ash Class C

Class C fly ash is generated from Lignite or sub-bituminous coal combustion. Its total amount of SiO_2, Fe_2O_3, and Al_2O_3 is higher than 50% but lower than 70%. It tends to have a high calcium content (higher than 10%).

The hydration and leaching properties of fly ash are significantly influenced by the mineralogy of the fly ash, which includes the relative proportion of the glassy phase and crystalline phase materials, the size distribution of the ash, the chemical nature of glass phase, and the type of crystalline material. Thus this current criterion is not enough to classify fly ash, which has a broad chemistry range. There are many factors that influence the ash's reactivity.

2.1.2 Physical Properties of Fly Ash

Fly ash is usually in powder form and black or brown in color. The color is depended on the amount of Fe_2O_3 and carbon present in the fly ash. It is the best known, and one of the most commonly used, pozzolan in the world. The major constituents of fly ash are SiO_2, Al_2O_3, Fe_2O_3, and CaO and the minor constituents are MgO, Na_2O, K_2O, and SO_3. The particle size of fly ash collected from a power plant has a broad range from below 0.5 μm to greater than 200 μm. It is shown that the fineness of fly ash can affect the quality of the concrete. The fine-grained fly ash increases the structural strength and durability. Fly ash exhibits a continuous distribution of true particle density (TPD) <0.8 to >4.0 g.cm^{-3} (Hemmings and Berry, 1986). Most fly ashes are spherical in shape, allowing them to flow and blend freely in mixtures. That capability is one of the properties making fly ash a desirable admixture for concrete. Fly ashes are highly complex multiphase materials containing various amorphous and crystalline phases. Due to the highly heterogeneous nature of the coal utilization, as well as variations in the combustion process, the physical and chemical properties of the ashes vary on a plant by plant basis (Towler, 2002).
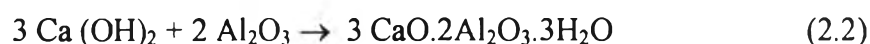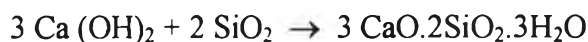
2.1.3 Chemical Reaction of Fly Ash in the Cementing Process

The definition of pozzolan is given by the ASTM C618 as a siliceous or siliceous and aluminous material which, in itself, possesses little or no cementitious value but which will, in finely divided form in the presence of moisture, react chemically with calcium hydroxide at an ordinary temperature to form compounds possessing cementitious properties. In a hydration reaction, CSH or calcium silicate hydrate ($CaO.2SiO_2.3H_2O$), which is a binding material, is produced. The cement hydration is presented in the following reaction.

$$2[3\ CaO.SiO_2] + 6H_2O \rightarrow 3\ CaO.2SiO_2.3H_2O + 3Ca\,(OH)_2$$

$$2[3\ CaO.Al_2O_3] + 6H_2O \rightarrow 3\ CaO.2Al_2O_3.3H_2O + 3Ca\,(OH)_2 \qquad (2.1)$$

The mixing of pozzolan in cement hydration can form an additional CSH gel in the mix as silica and alumina compounds released from the glassy phase of fly ash. This CSH gel reacts with calcium hydroxide which is a by-product of the hydration

reaction of cement. As it is diffusion dependent, the reaction rate is very slow. Consequently it can slowly contribute strength to the concrete. The reactivity of fly ash is depended on the presence of the glassy phase of the fly ash, hydroxide ion content, and the initial heat of the hydration reaction (Department of Civil Engineering, 2003). The reaction between fly ash and calcium hydroxide is shown below.

$$3 \, Ca \, (OH)_2 + 2 \, SiO_2 \rightarrow 3 \, CaO.2SiO_2.3H_2O$$

$$3 \, Ca \, (OH)_2 + 2 \, Al_2O_3 \rightarrow 3 \, CaO.2Al_2O_3.3H_2O \qquad (2.2)$$

The increase of calcium silicate hydrate (CSH) formation and the reduction of calcium hydroxide affect a higher durability of concrete. Fly ash concrete is more resistant to attack from sulfate, mild acid, and chloride in seawater. Moreover the pozzolanic reaction between fly ash and lime generates less heat, resulting in lower thermal cracking when fly ash is used as a cement replacement. Thus the dependable concrete is consented for longer working time (Committee of Civil Engineering Department, 2000).

2.1.4 Fly Ash Structure

Fly ash is composed of various phase, i.e. the glassy and crystalline phases. The major glassy phase in Class F fly ash is silica or alumono-silicate, whereas the major glassy phase in Class C fly ash is calcium-alumino-silicate. During the combustion process, temperatures in the boiler may be higher than 1600°C and melt the inorganic material in the coal. In the exit chamber, the droplets cool down rapidly producing the glassy form of the fly ash. However, if it cools down slowly, the crystalline form, such as mullite, quartz, magnetite or ferrite spinel, and hermatite, is occurred (Hemmings and Berry, 1988). Glass science can be applied for fly ash study because composition of fly ash contains about 66-68% glassy phase. Since the glassy phase has a weaker structure than the crystalline phase, the reactive components in fly ash are normally contributed from the glassy phases. So fly ash which has a high glassy phase tends to be pozzolanic and contribute chemicals to the formation of hydration products when it is attacked by hydroxides released from Portland cement hydration (Dewey et al., 1996).

SiO_2 crystal consists of three-dimensional, long-range tetrahedral structures while SiO_2 glass consists of short-range order. Oxygen that forms with Si in tetrahedral is called bridging oxygen (BO).

However, most glasses are more complex than silicate glass. They are an association between silica and other oxides. These oxides including alkali and alkaline earth (e.g. Na, K), are called "network modifiers." When network modifiers are present, the Si-O networks are broken and non-bridging oxygen bonds (NBO) are formed. The separation of the network and placement of a cation in the gap reduce the strength of the glass. Therefore, these glasses are easily dissolved in water. Other oxides, with coordinated number of 3 or 4 (e.g. Si, Al, and B), are called "network formers." They are capable for repairing the broken network bonds and forming BO bonds.

Oxides other than network formers and network modifiers are classified as intermediates. In high polymerization glass, intermediates are present as network modifiers. On the other hand, in low polymerization glass, they act as network formers. Calcium oxide is always considered as an intermediate (Feng and Metzger, 1997).

The mineralogical structure of ash is a key variable determining reactivity. When the silicate phases have an amorphous structure, rather than crystalline, they tend to be pozzolanic and contribute to the formation of hydration products when they are attacked by hydroxides released from cement hydration. The increase of calcium compounds present in coals results in the production of fly ashes with an increased modification of the amorphous phases. These higher calcium fly ashes tend to be both cementitious and pozzolanic (Dewey et al., 1996).

2.1.5 Chemical durability of glasses

The chemical durability of glass is probably the most important property. It has been used to assess the resistance of glass from the attack of aqueous solutions and atmosphere agents. However it is a property that is difficult to quantify.

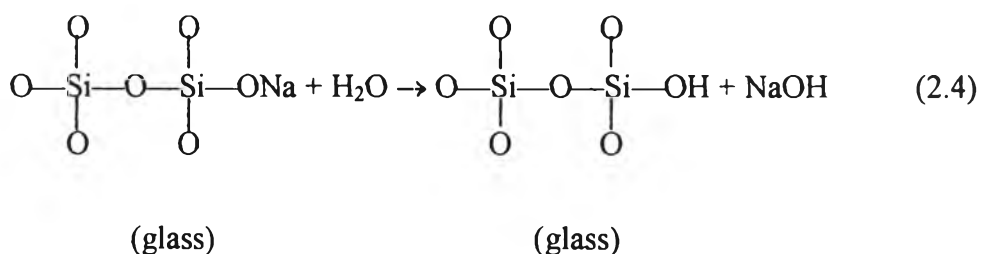### 2.1.5.1   Reaction mechanism of glasses with an aqueous solution

The leaching of glass is a heterogeneous mechanism when viewed on a molecular scale. When a piece of ordinary glass is brought into contact with an aqueous solution, three mechanisms can be occurred. These are the leaching mechanism, network dissolution, and precipitation of reaction product (Adams, 1988; Barkatt, 1988; Doremus, 1988; and Hench, 1988).

### 1.   Diffusion mechanism or ion exchange

The initial mechanism is the ion exchange process, in which alkaline or alkaline earth ions from the glass are replaced by hydrogen ions from the solution. Silanols are formed but the remaining constituents of the glass are not changed during this process. This can result in the formation of a hydrated silica-rich layer on the surface of the glass. Ion exchange reactions are diffusion controlled. Thus, the rate of this reaction varies with the square root of time as shown in Equation 2.3 (Adams, 1998).

$$r = a * t^{1/2} \qquad (2.3)$$

An alkaline-hydrogen ion exchange occurs in only a short period depending on the glass structure. The rapid leaching of alkaline affects the thickness of hydrated silica layer. The leaching rate increases with a higher alkaline content. The ion exchange reaction is shown in the Equation 2.4 (Hench, 1988).

$$O{-}\underset{\underset{O}{|}}{\overset{\overset{O}{\|}}{Si}}{-}O{-}\underset{\underset{O}{|}}{\overset{\overset{O}{\|}}{Si}}{-}ONa + H_2O \rightarrow O{-}\underset{\underset{O}{|}}{\overset{\overset{O}{\|}}{Si}}{-}O{-}\underset{\underset{O}{|}}{\overset{\overset{O}{\|}}{Si}}{-}OH + NaOH \qquad (2.4)$$

(glass)   (glass)

Within the subsurface layer of glass, two hydroxyl groups recombine to form bridging oxygen ($\equiv$Si-O-Si$\equiv$) and an interstitial water molecule. The former one leads to improving the resistance of the leached layer towards dissolution, the latter one enhances mobility within the ion exchange layer. The repolymerization of hydroxyl groups or the silanol form is shown in Equation 2.5 (Hench, 1988).

$$\equiv Si-OH \quad + \quad OH-Si\equiv \quad \rightarrow \quad \equiv Si-O-Si\equiv \quad + \quad H_2O \quad (2.5)$$
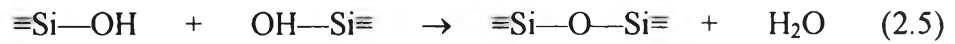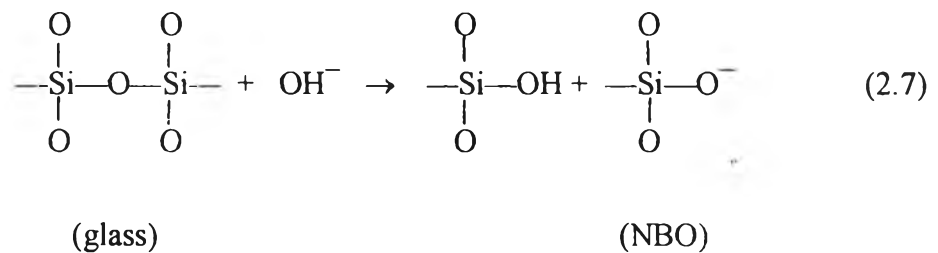
Silanols form   Silanols form   Silicate form

2. Network dissolution or etching mechanism

Network dissolution is a mechanism that breaks down of the silica structure. The reaction rate of this stage is shown as the following equation (Adams, 1998).

$$r = b * t \qquad\qquad\qquad (2.6)$$

The etching reaction is shown in Equation 2.7 (Hench, 1988). The addition of the alkaline ion, such as Na or K, tends to raise the ion exchange rate, which affects the dissolution rate that also increases.

$$
\begin{array}{ccc}
O & O & O & O \\
| & | & | & | \\
-Si-O-Si- + OH^- & \rightarrow & -Si-OH + & -Si-O^- \\
| & | & | & | \\
O & O & O & O
\end{array}
\qquad (2.7)
$$

(glass)   (NBO)

The non-bridging oxygen (NBO) formed in the above reaction was attacked further by a molecule of another water-producing hydroxyl ion, which then attacked the structure as shown in Equation 2.7. OH^- was the catalysis of the reaction (Geasee, 1993).

The presence of network modifiers of high electric field strength in the glass, such as Ca^{+2} or Al^{+3}, greatly decreases the thickness of the silica-rich films, and increases the film density and glass durability. Moreover, the addition of phosphate, calcium or aluminium can generate secondary films, such as the $CaO-P_2O_5$ or $Al_2O_3-SiO_2$ layers. These dual layers will be formed on top of the silica rich layer film after a rapid ion exchange reaction. These dual layers effectively restrains corrosion from the hydrated silica layer (Hench, 1988).

The mechanisms of leaching and network dissolution are show in the figure below (Geasee, 1993).
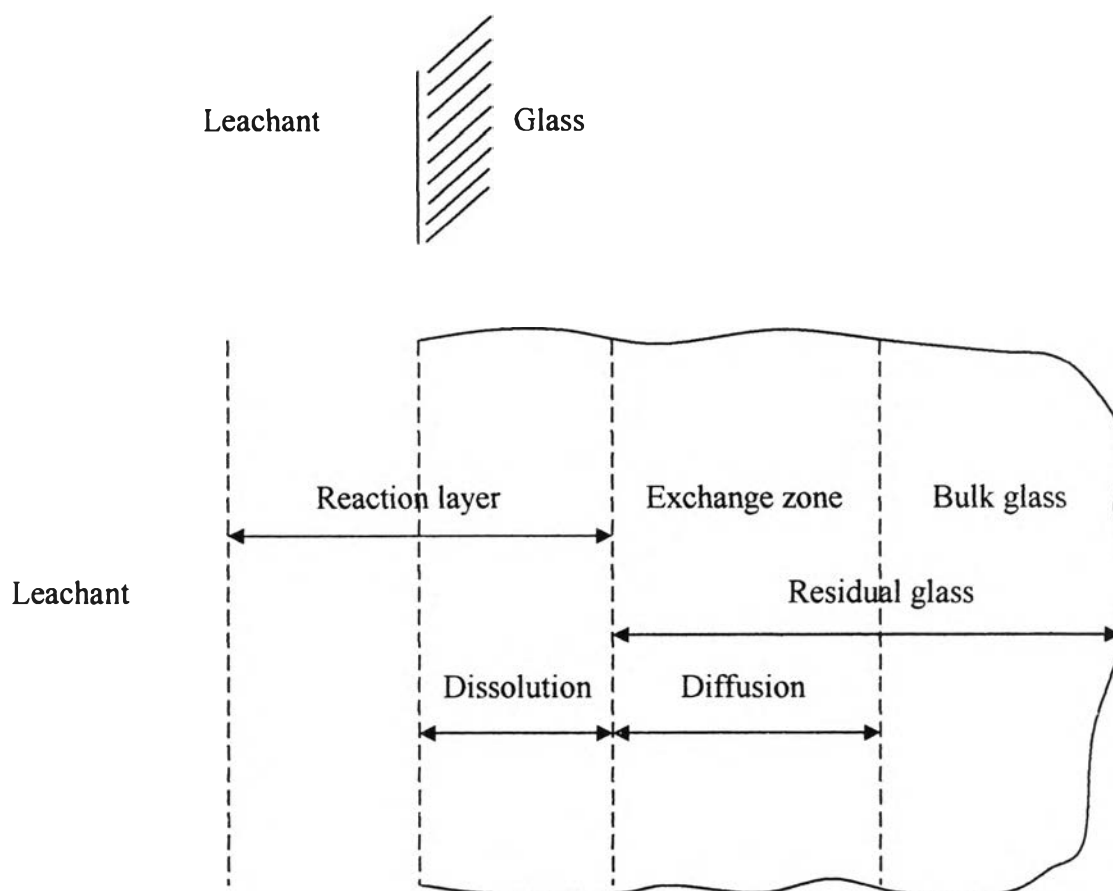
Figure 2.1: Reaction mechanisms: Leaching and network dissolution of glass in an aqueous solution.

3. Precipitation of the reaction product

The leached or dissolved species from the glass accumulates in the solution and changes their activities. If their solubility limit is reached, then compound formation and precipitation will occur, preferentially in the vicinity of the glass surface.

The formation of the precipitated phases does not necessarily result in complete retardation of the glass dissolution process. When the crystalline phase is formed by precipitation in the solution, the corrosion process continues even through

the aqueous phase has approached saturation with respect to the glass. This mechanism would cause the corrosion rate to resume its increase with time after a temporary slowdown (Barkatt, 1988).

In the long term, mechanisms controlling corrosion is a combination of matrix dissolution followed by incongruent dissolution and solution/precipitation reactions (Hence, 1988). When a species reaches the saturation condition, there is no longer any driving force for that species to leave. Consequently the species continuously accumulate on the glass solution interface as the matrix dissolves (Hence, 1988).

Ion exchange dissolution commonly occurs in most glass. In the unstable or reactive glass, the kinetics of ion exchange and dissolution is so fast that precipitation cannot occur. The most controlling factor determining whether the predominant mechanism will be ion exchange or dissolution is the pH of the contact solution. Ion exchange dominates in the acid range whereas network dissolution dominates in the alkaline regime, increasing dramatically as pH increases.

2.1.5.2 Factors influencing glass durability (Hench, 1988)

The factors affecting the reactivity or dissolution rate of glass during the Single pass flow through (SPFT) test are shown as follows:

1. Bulk glass composition
2. Temperature
3. Exposure time
4. Solution pH and solution concentration
5. Surface area to volume (S/V)
6. Crystallization percentage
7. Corrosion behavior of powdered glass
8. Surface feature

2.1.6 Kinetic Rate

Glass leaching can be modeled as a combination of diffusion and dissolution reactions. The leaching kinetics of silicate glass can be typically expressed in terms of the equation below (Holland, 1966).

$$F(t) = k_1 t^{0.5} + k_2 t \tag{2.8}$$

Where $F(t)$ is the leaching as a function of time t and $k1$ and $k2$ are diffusion and dissolution coefficients respectively. Much research has been done to determine mechanisms for controlling the leaching of glass. The factors influencing the leaching of glass can be separated by their region: imposed test condition and glass composition. The test parameters are pH and solution composition; $Si(OH)^-_4$, H_4SiO_4, $Al(OH)_4$, $Ca(OH)_2$, temperature, and surface area (Hench, 1988). The pH of the alkali solution affects the dissolution rate because of the ionization of silicic acid formed in the ion diffusion of water. At pH <8, the effect of pH on the dissolution rate is not significant as long as the pH is maintained constant. Above a pH of 8, the surface of glass rapidly dissolves and no ion diffusion occurs.

2.2 Literature Review

ASTM-618 classifies fly ash into two types, Class C and Class F, by the sum of oxides SiO_2, Al_2O_3, and Fe_2O_3. However it does not directly relate to pozzolanic activity. The most important factors are the quantity of reactive materials present and the rate at which the reactive components enter into the hydration reaction (Bumrongjaroen and Livingston, 2004). The reactive components for pozzolanic activity of fly ash are silica and alumina. However, the leaching rate of these components depends on the durability of the ash, which is influenced by a network modifier or alkali and alkali earth. They create non-bridging oxygen (NBO) and reduce the strength of the fly ash. Varshneya (1997) states that the creation of NBO decreases the connectivity of the glass network, so fluidity increases. Increasing fluidity makes it easier for a melt to rearrange the structure.

Since fly ash is mainly composed of glassy phase, the techniques commonly used to characterize its reactivity are Scan Electron Microscope (SEM), X-Ray diffraction (XRD), and chemical methods. The XRD can be used to quantify both the glassy phase and crystalline phase. The typical crystalline phases found in fly ash are quartz, mullite, magnetite, ferrite spinel, and hematite (Hemmings and Berry, 1988).

The effects of a network modifier on glass characteristic were investigated by Mauro (2000). The results showed that a greater network modifier increased the density of glass. Furthermore, it also affected the refractive index. The refractive index reduced when tetrahedral bonds were formed but it rose when NBO was created. High alkalis content influenced a decreasing of the band gap of energy as well. The energy that an electron required to reach the exciting state was reduced with more alkalis content. Moreover alkalis influent to the leaching rate of sodium silicate glass was rapidly increased. Thus, the presences of alkalis caused low chemical durability of glass.

To assess the leaching rate of chemical composition from fly ash, the analysis of the leachate that is typically used for glass can be applied to fly ash. The ASTM (1994) specification C1285-94, the Product Consistency Test (PCT), is commonly used to assess the leaching rate from different types of glass. This test method is static and can evaluate the chemical durability of homogeneous and devitrified glasses by measuring the concentrations of the chemical species released from a crushed glass to a test solution.

Lasaga (1995) constructed a model from the leaching tests. The results had shown that many models were problematic because they were based on the results of batch leaching tests. Since the glass leaching rate is typically high, it is difficult to maintain far from saturation condition. For more accurate prediction on the glass leachability, McGrail et al. (2000) studied on single-pass flow-through tests (SPFT), which is designed to continuous flow and to establish steady-state conditions. In the experiment, pH and temperature were varied to investigate the effect of they had on the leaching rate. The flow-through rate for experiments at 23°C were relatively slow (20 ml/d) and at 90°C were as fast as 100 ml/d. The results have been concluded that when the flow rate per surface area ratio increased, the leaching rate increased and then reached a constant value. The effect of pH was also investigated and it was

found that when the pH increased, the leaching rate increased with a constant value. Furthermore, the result showed that temperature had a positive effect on the leaching rate.

In addition to above studies, Abraitis et al. (2000) studied the influence of dissolved Si and Al on the leaching rate. The rate-influencing effect of dissolved Al is far more significant than Si. These findings indicate that processes which moderate Al solubility are likely to influence the leaching rate of glass. Jiricka and Helebrant (1998) is also studied the SPFT test and compared it with the static test. The experiment concluded that the solution pH in unbuffered static tests changed rapidly during the first 24 h, while in SPFT tests, the pH changed was not significant. The activation energy of the leaching rate based on the normalized Si release was 47.4±4 kJ/mol for soda-lime glass. Jantzen (1988) also studied the effect of pH on the glass durability. It was found that at pH values of greater than 9.5, the solubility of silica increased rapidly due to dissociation of silicic acid. To determine the glass durability, both the glass composition and pH of the environment should be taken into account.

For glasses, the overall leaching process is irreversible and no overall equilibrium is attainable. The leaching of silica polymorphs is governed by the siloxane hydrolysis reaction (Abraitis et al., 2000) and the rates of leaching are catalyzed by an aqueous cation such as Na (Berger et al., 1993) and inhibited by a variety of metals including Al, Fe, Zn, Cu, Be, and Ga. The factors affecting glass durability are the (1) exposed surface area of the glass sample, (2) temperature of leaching, (3) pH of the leaching solution, and (4) glass composition (Doremus, 1994).

Paul (1982) conducted a study on how the surface area of glass to the volume of the leaching solution influenced the quantity of material extracted from silicate glass. The result showed that the higher surface area per volume ratio affected an increasing of the pH in the solution. The network dissolution rate was raised along with pH. By contrast, the accumulated reaction products were able to slow down the dissolution rate in a closed system to almost zero.

Mauro (2000) compared the effects of network formers and network modifiers on the properties of glass. The samples were prepared by using various alkali concentrations to determine how alkali content affected glass properties. The results are interpreted that adding alkali modifiers to SiO_2 glass created NBO sites throughout the glass network. However, if an alkali was added into B_2O_3 glass, it didn't always create NBO as in silicates glass. The alkali may instead convert boron from a 3-coordination to a 4-coordination state, thereby making it tetrahedrally coordinated that increases the connectivity of the network. The fraction of boron atoms in tetrahedral coordination increases until about 35-40 mole % alkali. The formation of NBO becomes apparent at greater alkali concentrations.

Since fly ash is composed of various compounds, a graphical presentation of the data is problematic. Therefore, cement chemistry typically uses the ternary system $CaO-Al_2O_3-SiO_2$. However, this omits several important elements to glass science (Doremus, 1994). Hence, Bumrongjaroen and Livingston (2004) interpreted the fly ash characterization using a triaxial diagram of fly ash composition. However, the experiment used triaxial plots of the data with the axes: $Al_2O_3+SiO_2+Fe_2O_3$, Na_2O+K_2O, and CaO, known as glass network formers, network modifiers, and intermediates, respectively. This can also be very useful for studying the reactivity of glassy phases because a high Na_2O+K_2O content favors leaching in an aqueous solution.

Oelkers and Gislason (2001), estimated the overall uncertainties to be on the order of 30%. However, at least 10% come from uncertainties in the estimate of the surface area and its change over the course of the experiment. Moreover, McGrail et al. (2000) also stated that the uncertainty of the leaching rate may be much greater than the typical 35 %.