HYDROTHERMAL PREPARATION OF HIGH SURFACE AREA CALCIUM SILICATE FROM LIME AND FLY ASH IN A FLOW REACTOR

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by

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DISSERTATION

Presented to the Faculty of the Graduate School of
The University of Texas at Austin
in Partial Fulfillment
of the Requirements
for the Degree of

DOCTOR OF PHILOSOPHY

THE UNIVERSITY OF TEXAS AT AUSTIN
May, 1994

Acknowledgments

I would like Dr. Gary Rochelle for his guidance and support in doing this work. I also thank my committee members, Dr. Joel Barlow, Dr. Ramon Carrasquillo, Dr. John Ekerdt and Dr. Hugo Steinfink, for their assistance.

This work has been funded by the EPA and Texas Advanced Technology program. The EPA and Acurex have also assisted in the procurement of sample material and the performance of some analyses. I thank Carl Singer, Charles Sedman and Wojciech Josewicz for their help.

I appreciated the assistance of my fellow research group members. These included Dave, Chris, Chen, Lingbing, Mshewa, Lia, Rajesh and Renae. Tom, Harold, Shrikar and Phil also helped make some of the course work easier.

I thank the undergraduate research assistants, Liany, Amit, Darryl and Carlo. They helped me complete this work in a reasonable time by doing many of the analyses in this work.

Finally, I thank those who helped me grow personally during the course of this work. These include many of those listed above, in addition to John, Jorge and many others. I especially thank Maria for bearing with me while I finished this dissertation. I thank my family for their support and God for always being there in all I do.

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Publication No.______________

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The University of Texas at Austin, 1994

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The ADVACATE process removes sulfur dioxide from flue gases by duct injection of calcium-silicate-hydrate sorbent with high surface area prepared by slurrying calcium hydroxide with fly ash and recycled material in water at temperatures between 90 and 100° C. In this work, sorbent was prepared in bench scale batch and well-mixed flow reactors. Three low calcium ashes were studied with 1 to 8 g fly ash/g calcium hydroxide. Experiments were performed with additives including calcium sulfite hemihydrate, gypsum, calcium chloride and sodium hydroxide.

Reaction was enhanced at times through four hours by increasing hydroxide concentration to 0.1 M. Availability of calcium hydroxide to the ash reaction site was more significant than the hydroxide concentration in the bulk solution at reaction times greater than four hours. The addition of gypsum or calcium chloride to the slurry system increased the calcium concentration allowing for increased reaction rate and a maximum product surface area more than double that of ash/lime reactions. The increase in surface area occurred despite lower solution hydroxide concentration. The impact of grinding ash prior to reaction was dependent on the reactivity of the base ash.

Optimum product has a high surface area and this correlated to reacted ash silica. The product calcium to silica mole ratio was between 0.8 and 2.2 increasing with solution calcium concentration. This range is consistent with CSH, an amorphous calcium-silicate-hydrate species. Aluminum and iron in the ash reacted to a lesser extent. No significant crystalline species were noted in any reaction products.

A segregated flow model predicted product from the flow reactor in certain cases. The flow reactor provided better reaction of fly ash and calcium hydroxide due to the greater availability of fresh calcium hydroxide in the reactor. Product surface area decreased with residence time greater than ten hours in experiments with gypsum added despite additional ash reaction. Surface area of the pilot plant product material examined was predicted using the segregated flow model with CSTR residence times of less than 11 hours. Experiments at longer residence times again produced sorbent without high surface area.

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Chapter 1

Introduction

The Clean Air Act Amendments of 1990 require additional control of acid gases, sulfur dioxide and nitrogen oxides, released from coal fired electric power plants. Reductions of 10 million tons in sulfur dioxide and two million tons in nitrogen oxides emissions are required by the year 2000 (Duvale, 1991). The act is much more flexible than previous air pollution legislation, allowing utilities to take a variety of routes to meet the more restrictive emissions requirements. These include improving the efficiency of current sulfur dioxide removal systems, using lower sulfur coal, retrofitting existing plants with no current controls or trading sulfur dioxide emissions allowances.

Each of these options has its own positives and negatives. There are minor gains which may be made by increasing the efficiency of existing flue gas desulfurization (FGD) units. These existing systems generally remove greater than 90 percent of the sulfur dioxide where installed (Linciome, 1990) so additional control is limited. The trading of sulfur dioxide emissions allowances would allow the utility industry to achieve the most effective economic solution but there are questions about how efficient the market will be for trading these allowances. This uncertainty makes for considerable risk if a utility were to rely solely on this method to meet the emissions standards.

The option of switching to low sulfur coal is limited by the burner design of existing power plants. In addition, utilities are often limited to that coal available in a specific state or region. For these reasons, it is likely that retrofit of existing power plants without sulfur dioxide control will account for about 50 percent of the reduction in sulfur dioxide emissions through the end of the decade (Fink et al., 1991).

Flue gas desulfurization systems may be divided into two broad categories, wet and dry. The dry type consists of throwaway reagent and reagent recycle systems. Almost all systems utilize an alkaline calcium source, limestone for wet systems and hydrated lime for dry systems. The calcium source reacts to form calcium sulfite when exposed to sulfur dioxide. In the case of hydrated lime,

$$SO_2 + Ca(OH)_2 \rightarrow CaSO_3 + H_2O.$$

The major technology presently in use for flue gas desulfurization is limestone slurry scrubbing. This wet process scrubs the cool flue gas with an aqueous limestone slurry in a spray or tray tower. The major advantages of this technology are its potential for high sulfur dioxide removal (> 95 percent), significant operating experience and low operating costs. It is the most likely choice for new power plant construction. The high capital cost may limit its use for retrofit of existing plants, especially those used only to generate power to meet peak electrical demand.

The typical costs associated with wet and dry technologies are shown in Table 1.1. It is apparent the capital cost of a dry system can be significantly less than a wet system but the operating costs can vary widely. The spread in operating costs is due to the wider variety of systems proposed since many dry removal processes are still in the development phase and are not well defined. The systems with the lowest capital costs are the duct injection systems. These eliminate the need for a scrubber or spray dryer unit and instead remove the acid gas by spraying sorbent in the flue duct.

Table 1.1 Comparative Costs for Retrofit of Coal Burning Power Plants (Keeth et al., 1991)

technology	**capital cost $/kW**	**annualized operating cost $/ton SO_2**
wet FGD	180-260	460-620
dry FGD	50-220	410-1470

Most of the duct injection processes are still in the development stage; they usually spray a calcium based sorbent into the flue duct along with water to increase the humidity of the gas, increasing the reactivity of the sorbent towards sulfur dioxide (Peterson et al., 1989). The calcium particles have a high surface area and react with the sulfur dioxide in the flue gas forming calcium sulfite solids which are collected by a particulate collection device. The efficiency of these processes, as measured by the removal of sulfur dioxide at any given calcium to sulfur operating ratio, is not as high as for slurry scrubbers. This factor along with the higher raw material cost (lime rather than limestone) accounts for the increased operating cost of these systems.

There are several duct injection systems being developed, among them the ADVACATE (ADVAnced siliCATE) system which uses fly ash or other silica material as a carrier for the calcium. The calcium silicate material has a high surface area and is capable of carrying significant moisture without problems associated with lime alone (such as caking on the duct walls in a high humidity environment). This work is concerned with specific aspects of this ADVACATE process for flue gas desulfurization.

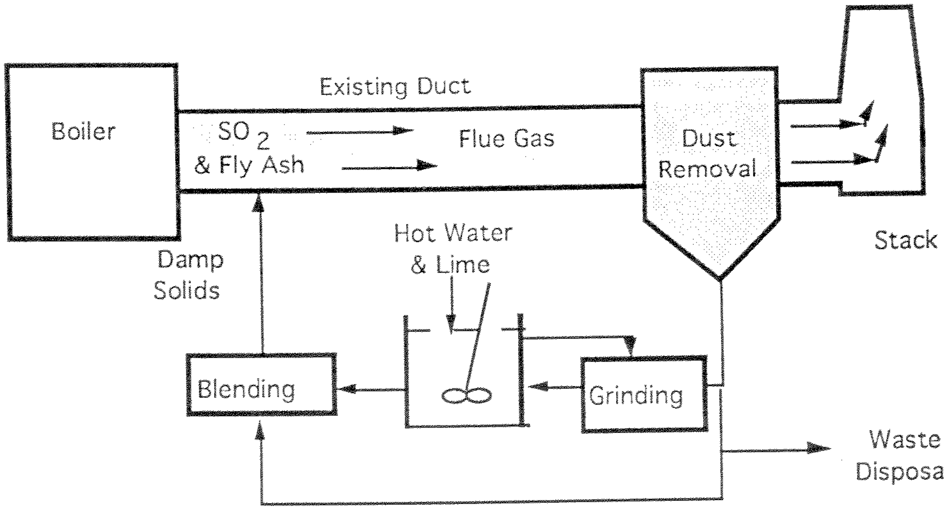

Figure 1.1 Simplified ADVACATE process

A simplified diagram of the process is shown in Figure 1.1. Fly ash is collected from the particulate collection device and is reacted with lime or hydrated lime in a slurry reactor at a temperature between 90 and 100° C. The reaction product has a high surface area, is reactive with sulfur dioxide and can retain moisture while flowing as a solid. The reacted fly ash/lime material is mixed with a dry recycle stream from the particulate collection device to lower the moisture fraction of the stream and allow the material to flow as a solid. The combined stream is sprayed into the duct with a high fraction of water to increase the reactivity of the sorbent.

The sorbent reacts with the sulfur dioxide in the duct during the approximately 2 seconds before the solids are captured by the particulate collection device (electrostatic precipitator (ESP) or baghouse). Additional reaction may take place as the flue gas passes over or through the collected solids. The amount of additional reaction can be significant if a bag filter is used as all exiting gas must pass through rather than over the collected sorbent in this case.

A fraction of the collected sorbent and fresh fly ash from the burner is collected and recycled back to the reactor. The remaining material is directed to a waste stream or a dry recycle used to increase calcium utilization in the process. The recycle and waste streams are set to maximize calcium utilization without degrading the efficiency of the particulate collection device below required emissions standards. Aspects of this process have been examined in detail by previous researchers (Chapter 3) and limited testing has been done on the pilot scale (Lepovitz et al., 1993). This work focuses on the aqueous activation reaction between fly ash and calcium hydroxide to form the calcium silicate sorbent in a bench scale flow reactor.

The aqueous hydration reaction is basically a two step mechanism. The fly ash dissolves in the basic, elevated temperature environment of the reactor. The dissolved ash, composed of primarily silicate and aluminate components, will react with the available dissolved calcium, forming calcium silicates and aluminates. The calcium silicates are amorphous, high surface area materials that are very reactive towards sulfur dioxide (Peterson and Rochelle, 1990). Every fly ash will have different fractions of silica and alumina along with other elements which will impact the reaction. The previous research in this area of the ADVACATE process is covered in more detail in the next two chapters.

Chapter 2

Fly Ash and Concrete

The hydration reaction of silica and alumina to form cement has been studied extensively. This reaction is different from the reaction to form the ADVACATE sorbent in several respects. First, the solution is much more concentrated so that the ionic strength is significantly greater in a hydrating cement. Secondly, the time scale is longer; a typical cement will continue to set over a period of many days (Mehta, 1983) as opposed to hours for the reaction in the ADVACATE system. There is also little mixing or temperature control in a cement system.

Even with these limitations, however, it is useful to examine the cement literature because it is extensive and there are strong similarities in the reactions involved in the two systems. The nature of fly ash must also be understood as it is not a pure component and will differ depending on the coal and burner design and will even vary from particle to particle. The composition and characterization of fly ashes is discussed first in this chapter. Selected equilibrium solution data is presented to discuss the impact of solution composition on the ash concrete and ADVACATE reactions. A discussion of applicable concrete research into the reaction products formed with fly ash and lime completes the chapter.

2.1 FLY ASH

Fly ash may be divided into two general classes - high and low calcium. It is made up of primarily silica and alumina components with calcium oxide varying from a few percent for low calcium ashes to about 30 percent for high calcium ashes. There are usually smaller amounts of iron, potassium and sodium oxides found in the ash. The composition of fly ashes is illustrated on a simplified ternary phase diagram in Figure 2.1. The class F ashes have significantly less calcium oxide and all ashes contain significant fractions of alumina. Other common aluminosilicate materials are shown for comparison.

The major coal minerals, aluminosilicates, carbonates, sulfides and chlorides are melted and largely decomposed (with the exception of silica) in the 1600° C temperature of the boiler (Hemmings and Berry, 1987). As the particles exit in the gas stream, they are quenched at the lower temperature so the phases formed are largely glassy as there is insufficient time for crystal formation. The larger particles will have a higher fraction of crystalline material as they cool more slowly due to their larger diameter. Fly ash is generally from 50 to 95 percent amorphous with the crystalline phases being quartz, mullite, spinel and hematite. A more detailed ternary phase diagram is provided in Figure 2.2. This shows some of the major phases at this gross ash composition but may not show all possible phases due to the heterogeneous nature of the ash.

As the molten ash cools, it may absorb gases from the air exiting the furnace. This may impact the glassy phase composition and also can lead to hollow spheres. Smaller, irregular particles may be present due to carbon (char) from incomplete burning in the boiler. The ash particles are usually close to perfect spheres and have a size that can vary between about 1 and 100 microns. A typical particle size distribution range is provided in Figure 2.3. As this figure shows, the size of ash particles varies significantly within an ash sample and from ash to ash.

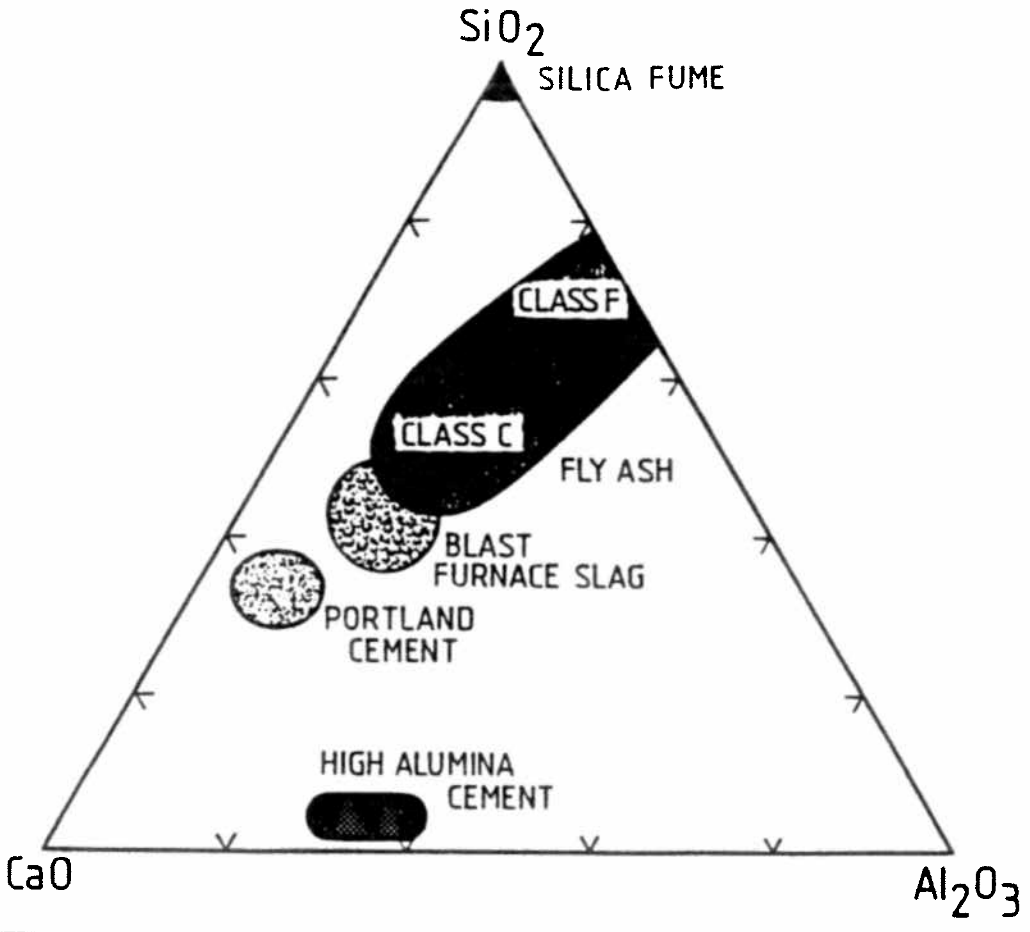

Figure 2.1 Simplified ternary phase diagram for silica-alumina-lime solid system (Tohidian and Laguros, 1987)

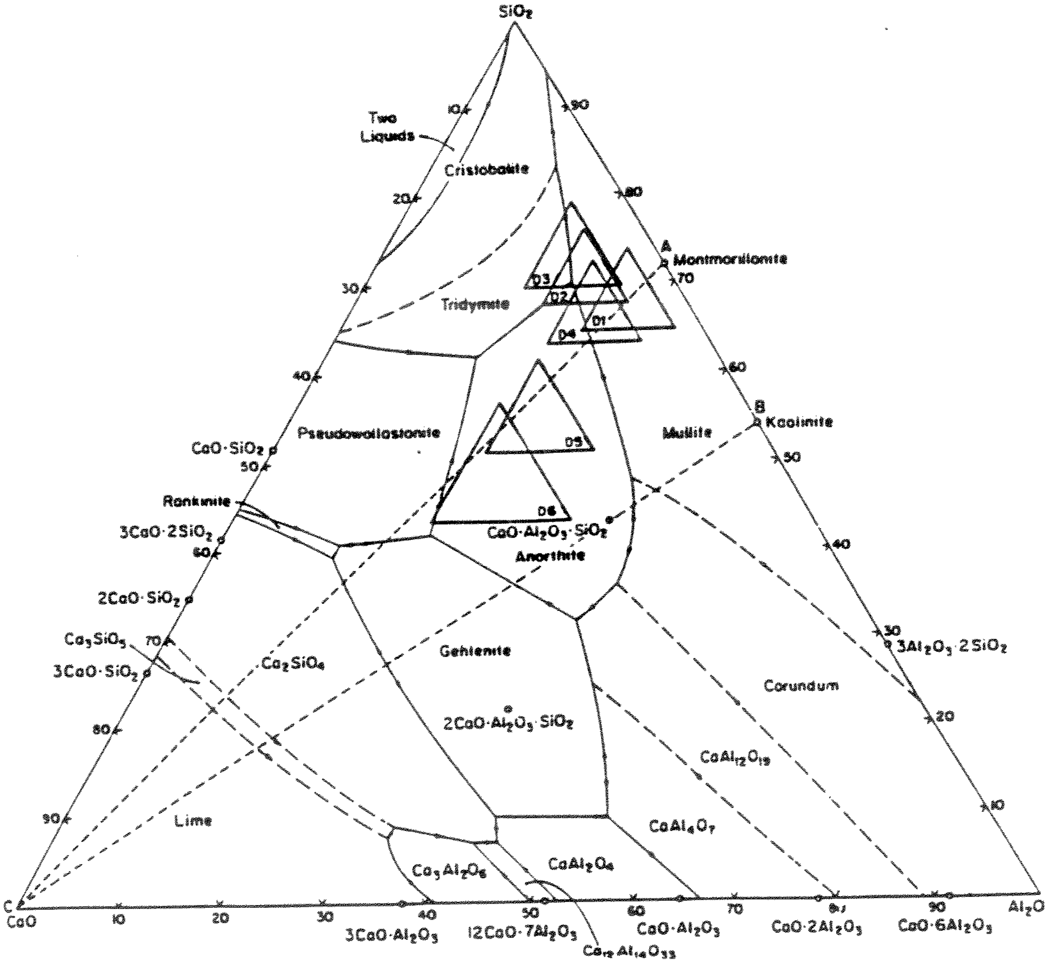

Figure 2.2 Detailed ternary phase diagram for silica-alumina-lime solid system

Triangles represent gross compositions from size fractionated samples taken from a particular ash. (Hemmings and Berry, 1986)

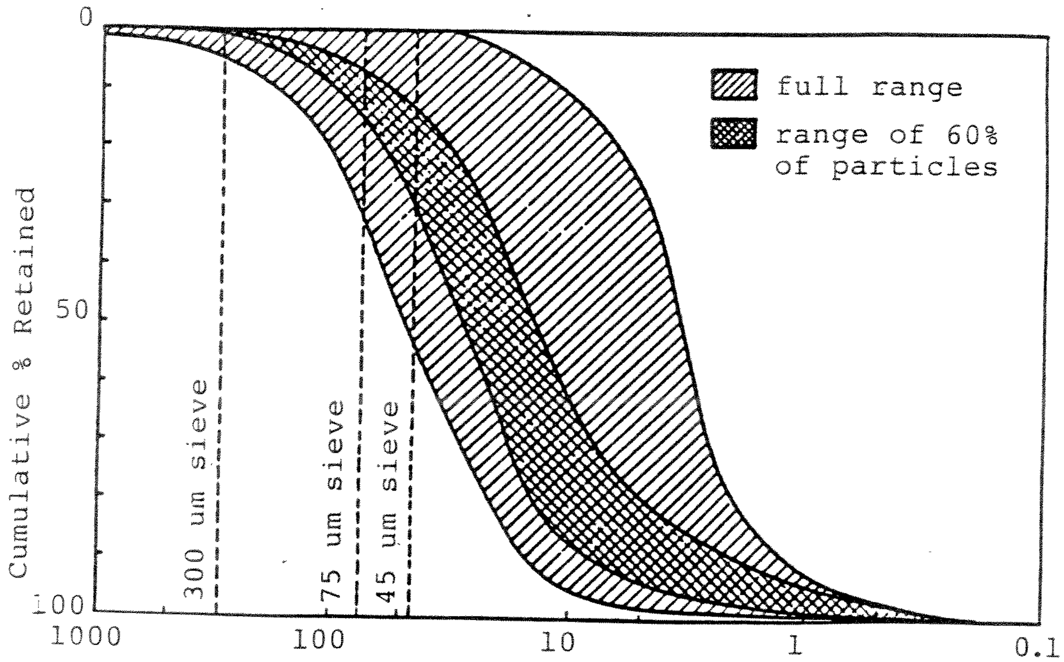

Figure 2.3 Particle size distribution range for selected fly ashes (Roy et al., 1984)

The composition of an ash can differ from particle to particle and from particle size fraction to size fraction. The differences in composition are more exaggerated on a particle to particle basis. This degree of heterogeneity is seldom observed in inorganic systems (Hemmings and Berry, 1987) and significantly impacts the way the system may be modeled. Figure 2.4 shows a schematic cut away of an ash particle and some of the possible causes for the heterogeneity within an ash particle. The phases formed are dependent on the bulk composition of the drop, the cooling rate, the location and number of nucleation sites in addition to other factors.

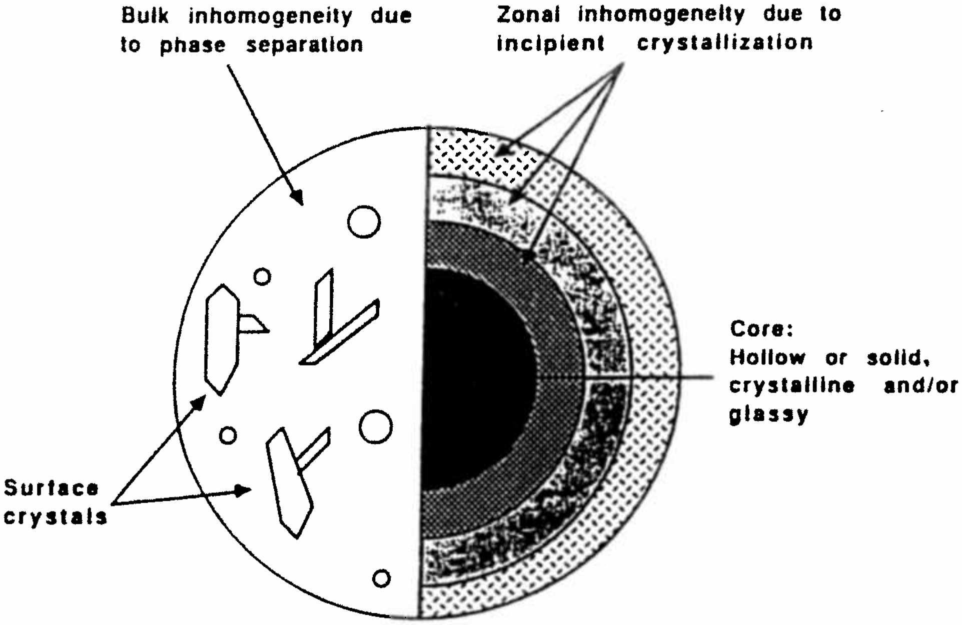

Figure 2.4 Sources of fly ash heterogeneity
(Hemmings and Berry, 1987)

It is necessary to examine the structure of the major phases in the ash particles to understand how they might react or behave in a concrete or ADVACATE hydration reaction. The major phase in any ash is composed largely of silica. The glassy phase may be further modified by positive ions such as potassium and sodium which are present in the ash. The glassy phase is usually more complicated than this, however, as other oxides with coordination numbers of 3 or 4 may substitute for silica in the network. The component most likely to do so is alumina; iron may also be present to a lesser extent. Each aluminum atom in the structure requires one positive cation (potassium or sodium) to maintain local electroneutrality.

The typical Si/Al ratio in aluminosilicate glasses is approximately 3. Class F ashes (low calcium) tend to concentrate aluminum in the glass phase relative to the bulk composition but reject Fe_2O_3 (Qian and Glasser 1987). The presence of ions such as sodium, potassium and calcium may also serve to depolymerize the network to some extent. Typical composition of this phase is provided in Table 2.1 along with the compositions of silica from other glasses for comparison. The fraction and composition of the glassy phase of the ash particle is important because it is that phase that is most reactive and susceptible to dissolution in an alkaline environment.

The activity of fly ash in cement hydration is due to the heat evolved and alkali released during the reaction (Kaushal et al., 1987). Typically, the fly ash in a cement will not react immediately but will react after a period of up to two weeks (Pietersen et al., 1990). This period is believed to be necessary to build up the alkalinity of the pore water to allow for ash dissolution at the cement temperature. This latent period may be reduced if the temperature of the cement is increased. The dissolution of class F ashes in an alkaline solution (NaOH) has been shown to be a strong function of hydroxide concentration and temperature (through 40°C) under stagnant conditions similar to those in a cement system (Pietersen et al., 1990).

Table 2.1 Glass phase composition of various materials
Numbers provided are weight percents. (Hemmings and Berry, 1987)

Host Material	Network Formers ($SiO_2+Al_2O_3+Fe_2O_3$)	Network Modifiers ($Na_2O+K_2O+CaO+MgO$)
Silica Fume	>90	<10
Bituminous Ash	84-90	10-16
Sub-bituminous Ash	81-84	16-19
Lignite Ash	72	28
Blast Furnace Slag	47	52
Window Glass	74	26
Pyrex Glass	96	4

2.2 SOLUTION CHEMISTRY

Solution composition not only has an impact on ash dissolution rate but on the product formed. The solution composition in the fly ash/hydrated lime system is complicated and is not necessarily at equilibrium if the reaction between ash and lime is rapid. The solution conditions observed in the cement reactions are more extreme than in the ADVACATE reaction system. This is due to a greater solids content and the fly ash requiring a higher hydroxide level prior to reaction due to the moderate temperature. Simple solution equilibrium data is presented here to allow for qualitative discussion of the ADVACATE reaction behavior observed in the experimental work.

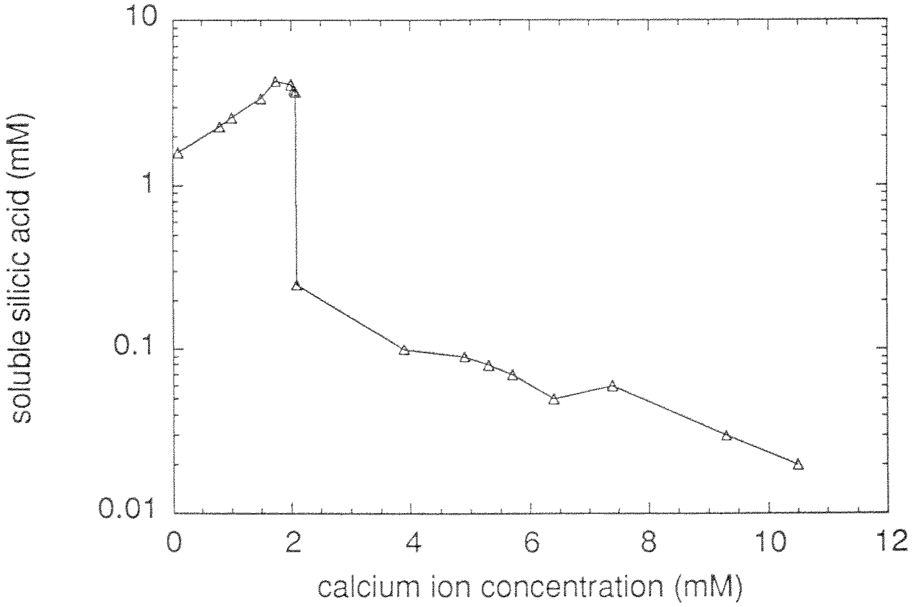

Figure 2.5 Silica solubility as a function of calcium in solution (Greenburg and Chang, 1965)

The most basic reaction is that between dissolved calcium and silica to form a calcium silicate precipitate. Solubility data for this simple system is presented in Figure 2.5. The silica solubility increases rapidly with increasing lime addition as the hydroxide level increases. After reaching a maximum solubility of over 4 mM, the equilibrium level again drops as a precipitate is formed. The rapid drop occurs at about 2 mM calcium and the silica concentration drops slowly but is still measurable at calcium levels up to 10 mM. This behavior implies that a certain minimum dissolved calcium level (2 mM) is required to prevent significant silica solubility in a reaction system.

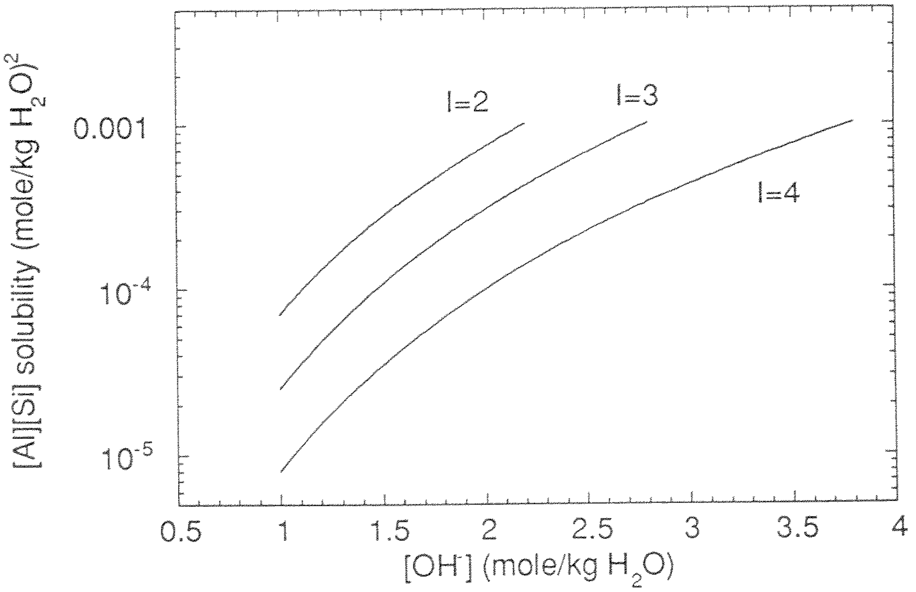

Figure 2.6 Aluminosilicate solubility behavior with hydroxide concentration

Sodium hydroxide and sodium chloride were used to set hydroxide level and ionic strength of the solution. The temperature was 95° C. (Gasteiger et al., 1992)

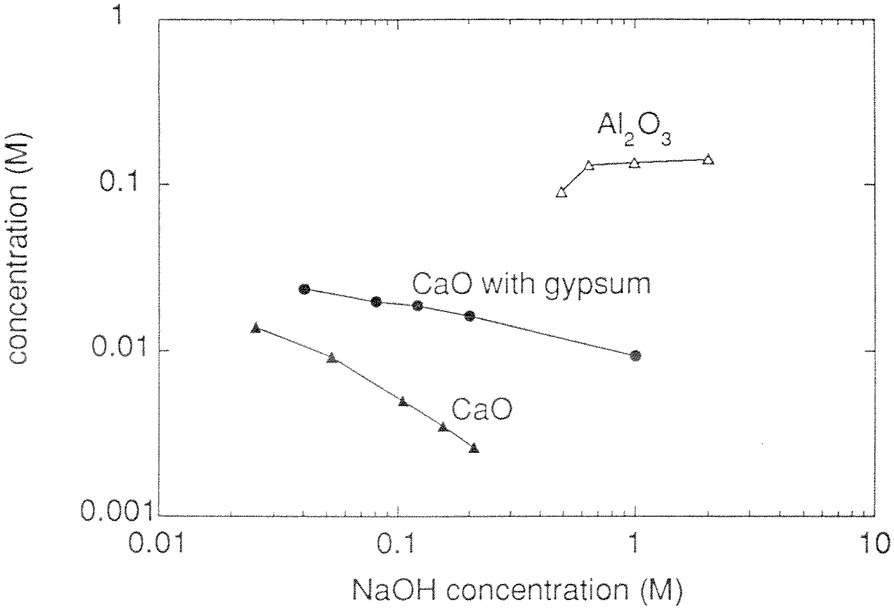

Figure 2.7 Calcium and aluminum solubility with hydroxide

CaO/gypsum data from Hansen and Pressler at 25° C, CaO data from Fratini at 20° C and Al_2O_3 data from Fricke and Juctigis at 30° C. (Linke, 1958)

The increasing solubility of silica and alumina with increasing hydroxide level is illustrated in Figure 2.6. The lines show a significant increase in silica and alumina solubility as hydroxide concentration increases. The solubility of lime on the other hand decreases with increasing hydroxide concentration (Figure 2.7). This behavior allows for high silica and low calcium concentrations at high hydroxide concentration. The effect is more significant at high temperatures as the solubility of silica and alumina increases with increasing temperature while the calcium oxide solubility decreases. Figure 2.7 also shows the effect of additives such as gypsum to the system. The addition of gypsum allows for a greater calcium concentration at a given level of sodium hydroxide.

2.3 PRODUCT FORMATION

The reaction between silica and calcium hydroxide is referred to as a pozzolanic reaction. The cement industry has a standard method of determining the pozzolanic activity of a fly ash that consists of adding a specified amount of fly ash and lime to a container and allowing it to react for a period of days. The activity is determined by measuring the fraction of free lime remaining (ASTM C 311). The loss on ignition (weight fraction char or unburned carbon in the ash), surface area, chemical composition, glass fraction and particle size distribution are considered to have some impact on pozzolanic activity of the ash. None of these, however, has proved to be a consistently good indicator of activity (Joshi and Marsh, 1987). There may be a general trend, for example, activity increasing with increasing surface area or decreasing particle size but the data scatter is too significant to use the correlation for one ash.

The Ca/Si ratio in the solid formed under mild conditions can range from about 1 to 2 depending upon the calcium concentration in solution (Figure 2.8) (Taylor 1964). This product is formed within a specific dissolved calcium window from about 1 to 20 mM. The material is referred to as calcium-silicate-hydrate (CSH) and may be divided in to two categories, CSH(I) and CSH(II) depending on the calcium to silica ratio in the solid. The calcium silicate material formed at 90 to 100° C is primarily CSH(I), a semicrystalline material with a surface area of about 200 m^2/g (Regourd, 1987). The CSH developed from fly ash hydration may be more amorphous than the cement product.

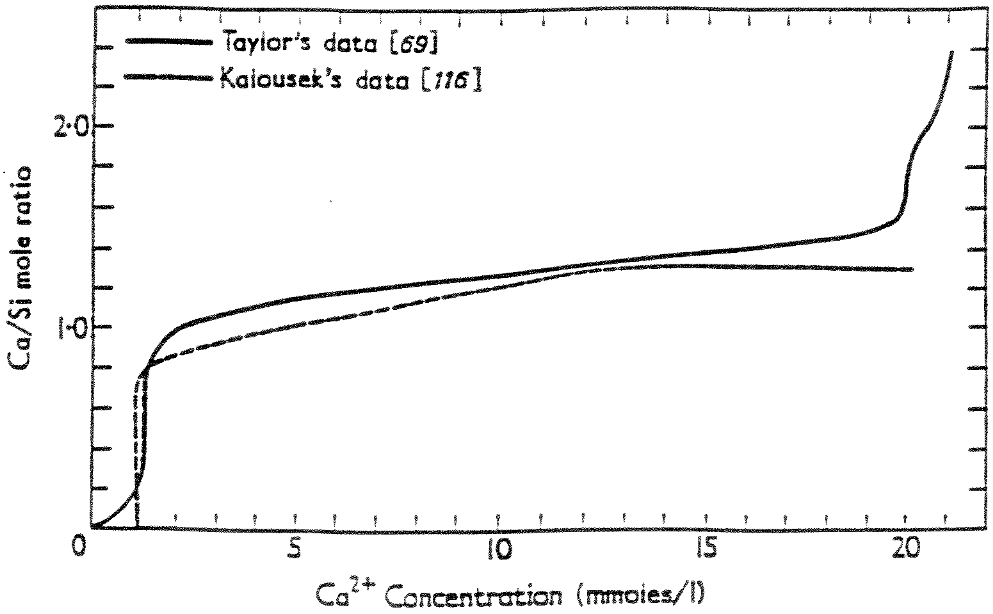

Figure 2.8 Solid/solution equilibrium for CSH

(Taylor, 1964)

The reaction product of alumina with calcium hydroxide is generally an ill crystallized solid with low surface area (Peterson, 1990). The calcium to alumina ratio of the product is similar to that in the silica product. The product of this

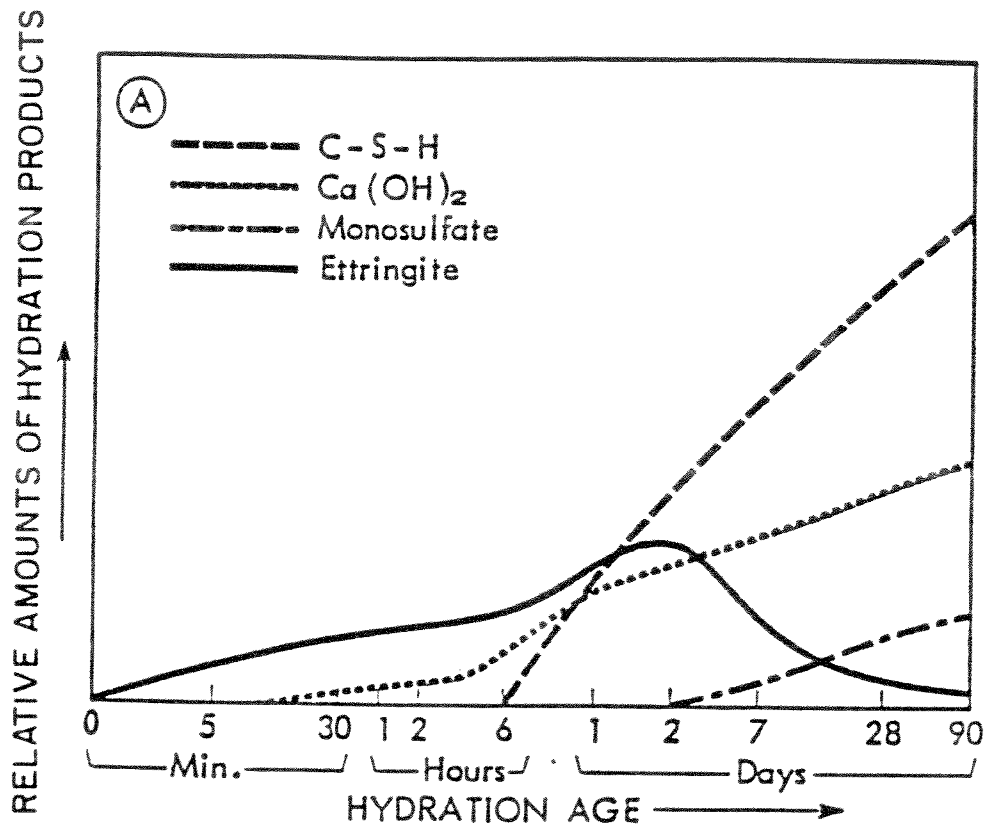

Figure 2.9 Cement hydration as a function of time

The aluminum species ettringite reacts to form a monosulfate species over time. (Mehta, 1983)

reaction will change with the addition of gypsum to the reaction system. The product formed in this case is ettringite which has a very large surface area. This species continues to react and forms a lower surface area aluminum monosulfate species (Figure 2.9). This transformation occurs over a period of days in cement and will be accelerated at higher reaction temperatures. The formation of ettringite may be inhibited at temperatures greater than 90° C (Tamura and Ibuki, 1984).

Chapter 3

ADVACATE Research Review

There has been significant previous work in the manufacture and characterization of ADVACATE solids for use in flue gas desulfurization. Jozewicz and Rochelle (1986) measured the reactivity of fly ash/lime sorbents prepared in a slurry, batch reaction at various temperatures and compared the reactivities of these materials towards sulfur dioxide in a sandbed reactor. This initial research lead to detailed examination of many aspects of the reaction system and operating parameters over the ensuing years. A chronological listing of the major research efforts is provided in Table 3.1.

The reaction product of fly ash and lime in an aqueous slurry is an amorphous, high surface area, highly hydrated material formed on the surface of the fly ash particles (Peterson and Rochelle, 1990; Peterson, 1990). The chemistry of the ADVACATE hydration reaction is similar to cement hydration reactions, the main differences being due to the impurities found in the ash, the relative reactivities of the materials, the presence of sulfate and temperature.

The research review is divided into four major areas - sorbent reactivity with sulfur dioxide, basic fly ash/hydrated lime reaction, effect of additives to the slurry reaction, and the impact of ash grinding. Each of these areas is covered with emphasis placed on the aspects of the work that impacted this research effort.

The research is evaluated at the end of this chapter to point to research needs that are examined in this dissertation.

Table 3.1 ADVACATE Research

Researcher	**Scope/Conclusions**	**Location/ Work**	**Date**
Jozewicz (Jozewicz and Rochelle, 1986)	• noted reactivity of fly ash slurried with calcium hydroxide at temperatures above 65° C • used sandbed reactor to show reaction with sulfur dioxide increased with humidity	UT various papers	1986
Chu (1986)	• SO_2/NO_x removal measured with sandbed • added NaOH and sulfite to lime/fly ash hydration reaction, hydrated at 65° C • determined optimal temperature for SO_2 and NO_x removal	UT Thesis	8/86
Peterson (1987)	• explored the impact of NaOH, fly ash type, temperature and sulfite on the hydration reaction	UT Thesis	8/87
Petersen (Petersen et al., 1988)	• fly ash grinding prior to hydration	Lund paper	10/88
Beaudoin (1990)	• developed model for quantifying the effect of moisture on the sulfur dioxide reaction with the hydrated sorbent	UT Thesis	8/90
Peterson (1990)	• found fly ash dissolution was approximately first order in hydroxide concentration • determined calcium aluminates formed were low surface area and unreactive and also inhibited the reaction with silica • gypsum promoted surface area generation in the high calcium fly ash studied	UT Dissertation	12/90

Researcher	Scope/Conclusions	Location/ Work	Date
Stroud (1991)	• developed critical moisture measurement to quantify the agglomeration of damp fly ash sorbents, correlating it with surface area and porosity	UT Thesis	8/91
Jozewicz (Josewicz et al., 1988A; Acurex, 1990)	• work performed with numerous ashes includes: - high temperature hydration of fly ash/lime - recycle of reacted sorbent on pilot scale - short time sulfur dioxide-sorbent reaction	Acurex various papers and reports	continuing
Johnson (1992)	• modification of Beaudoin model	UT Thesis	8/92
Wasserman (1992)	• effect of additives to the solids activation reaction on the reactivity of the sorbent	UT Thesis	8/92
Various-EPA, Radian, TVA (Lepovitz et al., 1993)	• 10 MW pilot plant testing • testing limited due to operational difficulties	TVA Shawnee facility paper	8/93

3.1 REACTIVITY WITH SULFUR DIOXIDE

The bulk of bench scale work examining the reactivity of calcium silicate sorbent with sulfur dioxide has been performed using a sandbed reactor. The sandbed reactor exposes the sorbent, mixed in a packed sand media, to a gas stream typical of flue gas in a coal fired power plant. The solids are exposed to a dilute sulfur dioxide gas stream for a one hour period and the conversion of the calcium hydroxide in the sorbent over that time is taken as a measure of the sorbent reactivity towards sulfur dioxide.

Josewicz and Rochelle (1986) first used this method with ADVACATE sorbent and noted that the fly ash/hydrated lime sorbents had higher reactivity than calcium hydroxide alone and reactivity increased as sorbent preparation time and slurry temperature were increased (Figure 3.1). The reaction rate with sulfur dioxide also increased with increasing gas stream humidity.

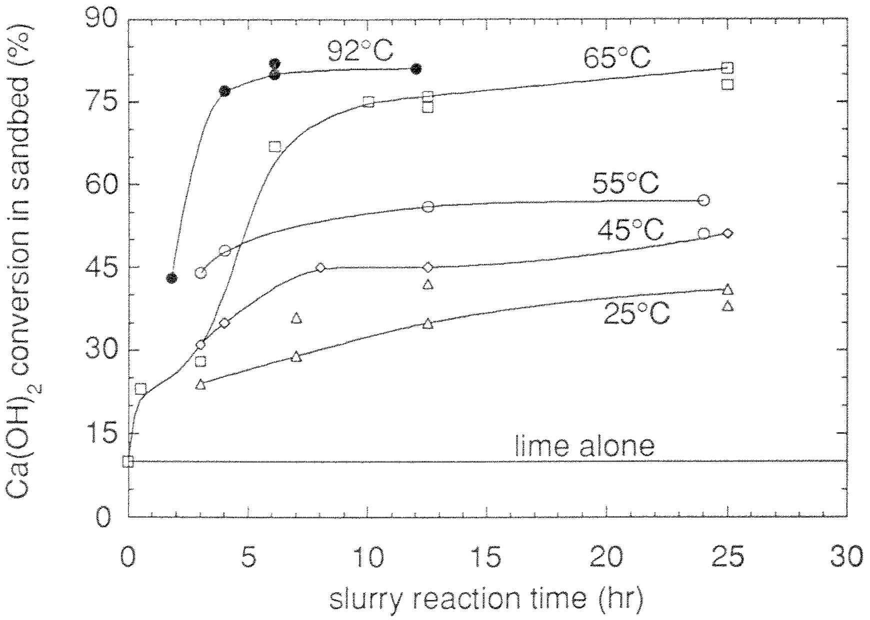

Figure 3.1 Effect of hydration temperature on sorbent reactivity with SO_2

The temperatures provided are those of the reaction of San Miguel fly ash with calcium hydroxide in 16:1 weight ratio to form ADVACATE sorbent. A 500 ppm sulfur dioxide concentration stream at 54 percent humidity was passed through the sandbed reactor. (Josewicz and Rochelle, 1986)

This reaction was examined further by varying the amount of initial moisture on the sorbent prior to reaction with sulfur dioxide. This simulated sorbent leaving the preparation reactor (reacting fly ash with calcium hydroxide) and being injected into the flue duct with entrained moisture from the reactor. The reactivity of these samples increased with increasing moisture up to about 30 weight percent water (Josewicz et al., 1991). After this point, the solids agglomerated, limiting the surface area exposed for reaction.

Attempts were made to model the gas-solid reaction by obtaining experimental data using a differential reactor system similar to the sandbed apparatus discussed earlier. In this case, a small amount of solids were used so that the sulfur dioxide concentration in the reactor was assumed constant during the reaction time. The reaction time was shorter than in the sandbed reactor (as short as 2 seconds). These efforts had mixed results as experimental reproducibility was poor (considerable data scatter). A mixed model, assuming a combination of adiabatic and isothermal characteristics in the pores of the ash best fit the data obtained (Johnson, 1992).

The increased reactivity with increased moisture retention led to an examination of solids reacted with deliquescent salts present. These solids would have increased moisture retention and therefore increased reactivity (Wasserman, 1992). Solids produced with deliquescent salts such as calcium chloride showed a much increased reactivity with sulfur dioxide. They exhibited high reactivity even if the sorbent had a low surface area.

Pilot scale work has been performed to examine this reaction using batch reacted material and injecting it into a small duct (Josewicz et al., 1988) and as part of a pilot operation of the entire process (Lepovitz et al., 1993). These experiments gave results similar to the bench scale experiments but also showed that the air flow pattern in a flue duct can have a significant impact on the sulfur dioxide removal capabilities of the sorbent. Unlike experiments in the sandbed, the duct removal is more dependent on the size and weight of the sorbent particles and the method and point of injection into the air stream.

Sorbent surface area of samples without deliquescent salts present generally correlates well with reactivity up until a surface area of about 35 m^2/g (Figure 3.2), at which point further increases in surface area have little impact on the reactivity of the material as measured by the sandbed reactor (Jozewicz et al., 1988A; Hall et al., 1991). This smaller increase in reactivity may be characteristic of the sandbed analysis method, however, as the conversion of calcium hydroxide is limited to a maximum of 1 and more highly reactive material may be more apparent at lower reaction times (exposing the sample to sulfur dioxide for less than one hour). The one hour time period results in measuring how reactive the least reactive sorbent is in the sample rather than measuring the overall reactivity of the sample. The least reactive sorbent is likely to be calcium hydroxide that has not reacted to form the calcium silicate product. These considerations help explain the leveling of reactivity at surface areas greater than 35 m^2/g.

This discussion highlights the limitations of measuring sorbent reactivity with the sandbed reactor. The sandbed measurement simulates the environment in a flue duct with a baghouse present. It does not do an adequate job in simulating the situation if there is an ESP used to remove fly ash because the time the sorbent is exposed to sulfur dioxide is on the order of seconds.

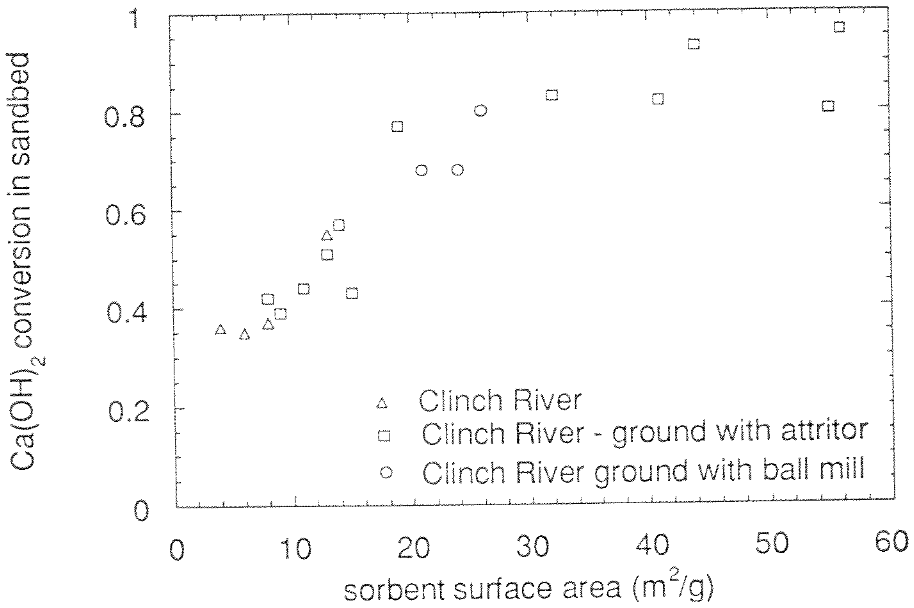

Figure 3.2 Sorbent surface area impact on reactivity with sulfur dioxide

Sorbent samples were reacted in slurry reactor for 1 to 6 hours at temperatures from 60 to 90° C at a fly ash to calcium hydroxide weight ratio of 3:1. The sandbed reactor was at 60° C with 1000 ppm sulfur dioxide in the gas. (Hall et al., 1993)

The surface area of the material has also been correlated with the ability of the sorbent to carry moisture as a free flowing solid (Stroud, 1991). The increased surface area allows the sorbent to carry the high fraction of water necessary to increase the reaction rate while still existing as a free flowing solid. These observations (increasing reactivity with sulfur dioxide and increased ability to retain moisture which also enhances reactivity with sulfur dioxide) indicate that sorbent surface area is a good indicator to track as a measure of overall sorbent reactivity towards sulfur dioxide in a flue duct.

3.2 BASIC SORBENT PREPARATION

There are two major species in the ash available for reaction - silica and alumina. As the fly ash and lime react, calcium hydroxide is consumed and surface area is generated (Figure 3.3). This plot presents data from an experiment using ground Clinch River fly ash at a temperature (90° C) typical of previous work. The reaction product of ash and lime under these conditions has little crystallinity as determined by X-ray diffraction (Peterson, 1990). It forms as a product on the surface of the ash particles (Jozewicz and Rochelle, 1986). Work similar to this, using both reactivity towards sulfur dioxide and surface area as measures of extent of reaction, has been performed on a number of ashes. High calcium fly ashes generally react quickly to form a solid of moderate surface area but do not continue to react over a long time period (high calcium ashes are not examined in this study).

Experiments were performed with pure forms of silica and alumina to determine which species formed the high surface area material observed in the fly ash/hydrated lime reaction system. Silica fume reacted to create high surface area material at a rate greater than in the case of reactions performed with fly ash and calcium hydroxide. The alumina reacted with the available calcium hydroxide to form low surface area calcium aluminates that were unreactive towards sulfur dioxide (Peterson, 1990). The calcium silicate material formed in these experiments was consistent with CSH, the amorphous, high surface area material observed under similar conditions in concrete hydration.

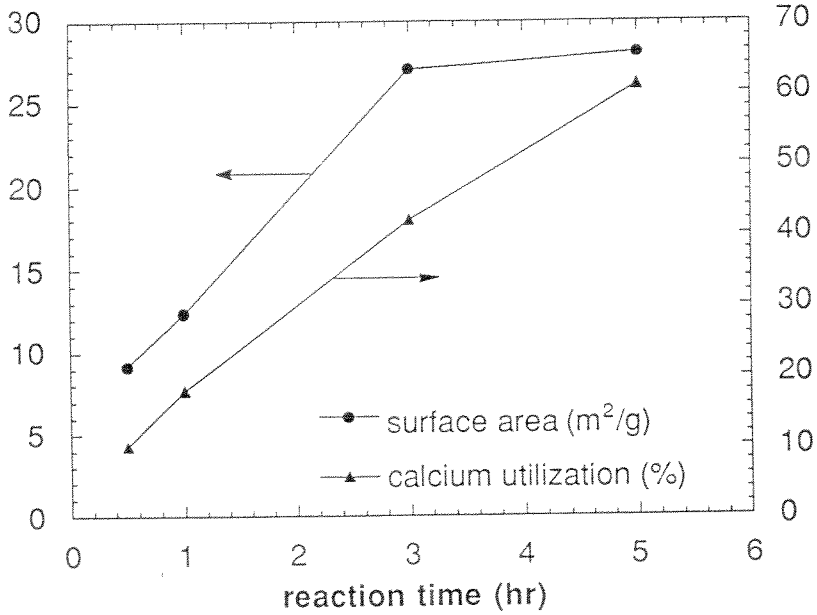

Figure 3.3 Typical ADVACATE slurry reaction indicators

Reaction of ground Clinch River fly ash with calcium hydroxide (3:1 weight ratio) at 90° C. (Peterson, 1990)

Preliminary investigations were made into examining possible rate limiting steps in the reaction process. Since calcium hydroxide dissolves within minutes in water (Eitel, 1966), the major focus of this effort was to examine the dissolution of ash in an alkaline environment typical of that observed in this reaction. The equilibrium dissolution of silica,

$$(SiO_2)_x + 2H_2O \rightarrow (SiO_2)_{x-1} + Si(OH)_4$$

is promoted by increasing solution pH (Iler, 1979). Peterson (1990) performed fly ash dissolution measurements, finding the rate of silica dissolution from fly ash without a product layer.

Fly ash dissolution was first order in hydroxide concentration in the case of low calcium fly ashes while the reaction order was approximately second for high calcium ashes. A comparison of the dissolution rate to the rate of silica reaction during the ash reaction with calcium hydroxide showed the dissolution rate was initially higher in the ash dissolution experiments than in the reaction with calcium hydroxide for the ash studied.

Early studies showed the reaction between fly ash and calcium hydroxide was accelerated by increasing temperature and this behavior was examined in greater detail by performing experiments at high temperature and pressure conditions. The reactivity of the solids produced towards sulfur dioxide is provided in Figure 3.4. These experiments show a unique behavior of reactivity with sorbent preparation time. While reactivity is increased in a much shorter time than is typical at lower reaction temperatures in these type of reactions, the reactivity actually decreases after a certain sorbent preparation time. This effect is more dramatic with increased temperature and may be indicative of another solid phase being formed at the more extreme reaction conditions. An optimum temperature of approximately 150° C was found where the reaction rate was much greater than that achievable at atmospheric pressure (Jozewicz et al., 1988).

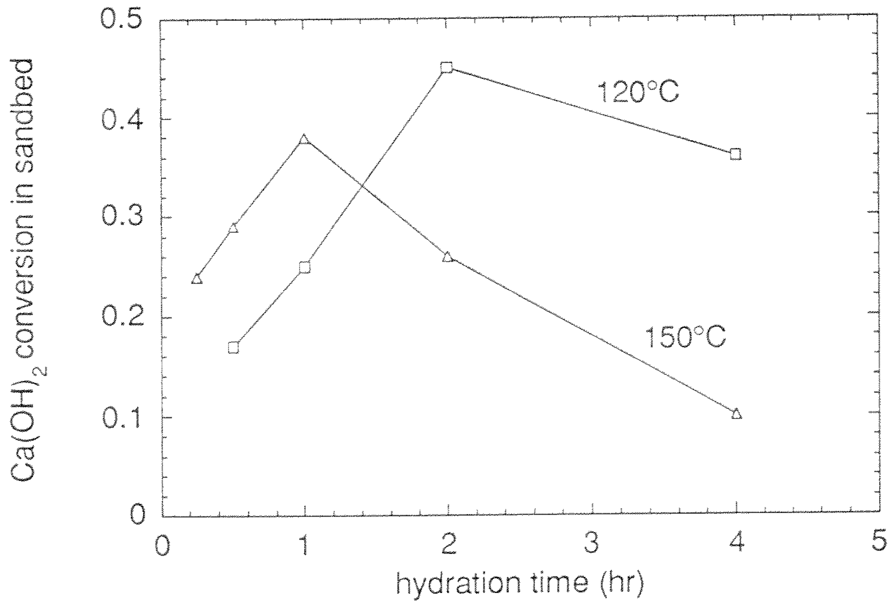

Figure 3.4 Reactivity of pressure hydrated sorbent towards sulfur dioxide

Fly ash and calcium hydroxide (1:1 weight ratio) reacted at the temperatures indicated. Sandbed reactor at 60 percent humidity, 64° C and sulfur dioxide concentration 500 ppm. (Josewicz et al., 1988)

The impact of solution chemistry on the reaction has been explored to a lesser extent. Significant changes in solution chemistry have been noted as the ash dissolved during the reaction. Sampling techniques used to analyze the solution chemistry have largely measured equilibrium ion concentrations at room temperature or concentrations in dilute reaction systems. Peterson noted dissolved calcium concentration was at an intermediate level when the higher reactivity sorbent was prepared in batch reactions (Peterson and Rochelle, 1988).

All work reviewed above was performed in batch reactions on the bench scale. A limited number of runs were performed with a flow reactor on the pilot scale in the summer of 1992 (Lepovitz, 1993). These results are discussed more fully in Chapter 7.

3.3 IMPACT OF ADDITIVES

Efforts to examine the impact of additives to the fly ash/hydrated lime reaction have been concentrated in two major areas - the addition of sodium hydroxide to increase the rate of ash dissolution and the addition of calcium sulfite hemihydrate and calcium sulfate dihydrate (gypsum) to approximate the material collected in the flue gas particulate collection device and recycled to the reactor for reactivation and injection into the duct. If gypsum is added to the system, ettringite (a calcium aluminum sulfate species with high surface area) might be formed at high sulfate concentrations (Jones, 1944). Gypsum also increases the dissolved calcium level and minimizes the impact that potassium and sodium ions have on the pH of the solution.

Peterson (1990) did work using gypsum, ash and pure components (silica and alumina sources) to determine the impact of gypsum on the reaction. He found that gypsum promoted the production of calcium silicates in high calcium ashes for reaction times through 8 hours. He did not note a significant impact for the low calcium ash studied. He believed the positive impact observed in the case of high calcium ash was due to the gypsum reacting with the alumina phases in the ash, encapsulating them so that they did not react with calcium hydroxide. This behavior was observed in the pure component reactions performed. The presence of sulfite had little impact on surface area generation but improved solids reactivity to a small extent (Peterson, 1990).

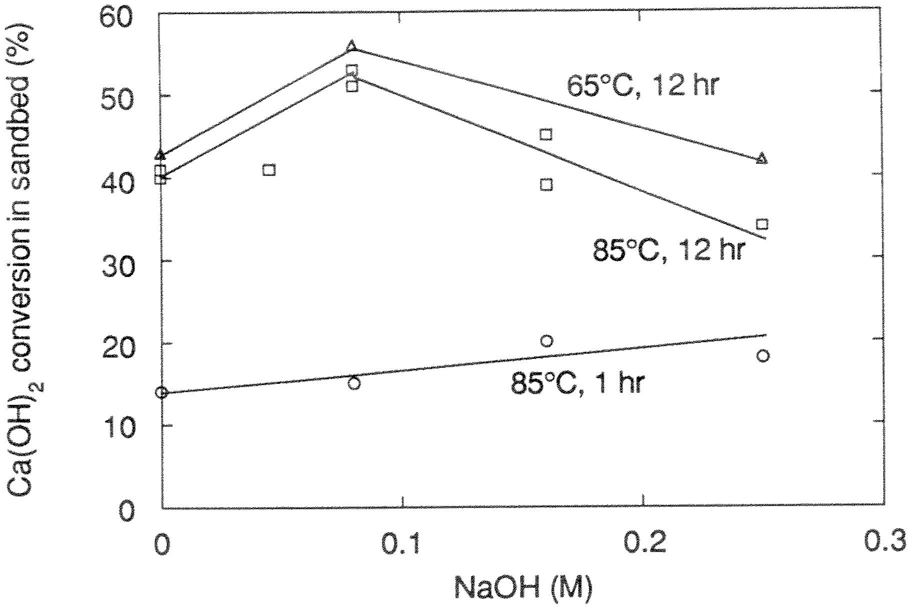

Figure 3.5 Impact of adding sodium hydroxide to fly ash/hydrated lime reaction

Fly ash and hydrated lime at 4:1 weight ratio reacted at the times and temperatures indicated. Sandbed reactor at 55 percent relative humidity, 66° C and 450 ppm sulfur dioxide. (Peterson, 1988)

The addition of sodium hydroxide was found to increase the reaction with a maximum rate observed at 0.08 N under certain conditions for Clinch River ash

(Figure 3.5) (Peterson, 1988). The impact of sodium hydroxide was dependent on the sorbent preparation time and temperature in this case. Testing the reactivity of the sorbent in this manner did not separate the effect of the sorbent preparation and the impact of the sodium hydroxide as a hygroscopic agent in the sandbed reactor. Other work has shown an increase in reactivity as sodium hydroxide level was increased through 0.25 N (Josewicz et al., 1988A).

The impact of calcium chloride on the reaction was examined in a study performed concurrently with this one. Calcium chloride was added to reactions with gypsum and calcium sulfite in addition to the fly ash and hydrated lime. There was a small positive impact on the generation of surface area and a large increase in reactivity with sulfur dioxide. The effect was observed with calcium chloride levels of 0.2 N with little additional benefit observed at greater concentrations of calcium chloride (Wasserman, 1992).

3.4 IMPACT OF GRINDING

Another technique used to increase the reaction rate involves grinding the ash to increase the surface area available for reaction, thereby increasing the reaction rate (Petersen et al., 1988; Peterson, 1990). An example of this is shown in Figure 3.6. Grinding had a positive impact in this case but the increase in reactivity was not proportional to the surface area. Additional examples of the impact of grinding are provided in Figure 3.7. In some cases, grinding actually had a negative impact on the reactivity of the sorbent towards sulfur dioxide. Grinding was used in the full operation pilot plant study performed in the summer of 1992 (Lepovitz et al., 1993).

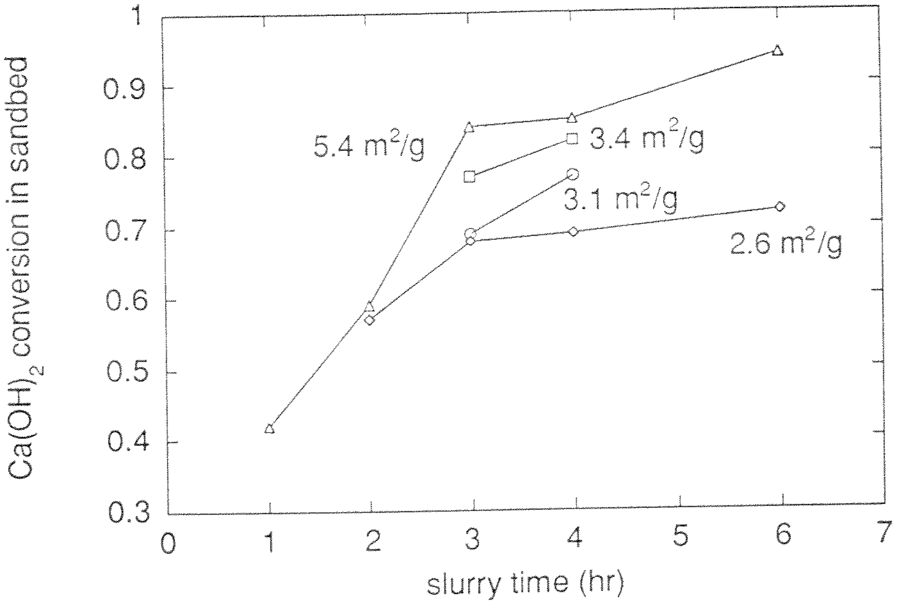

Figure 3.6 Impact of grinding on the reactivity of Clinch River fly ash

Clinch River ash ground to the surface area indicated prior to hydration reacted with hydrated lime at 90° C. (Acurex , 1990)

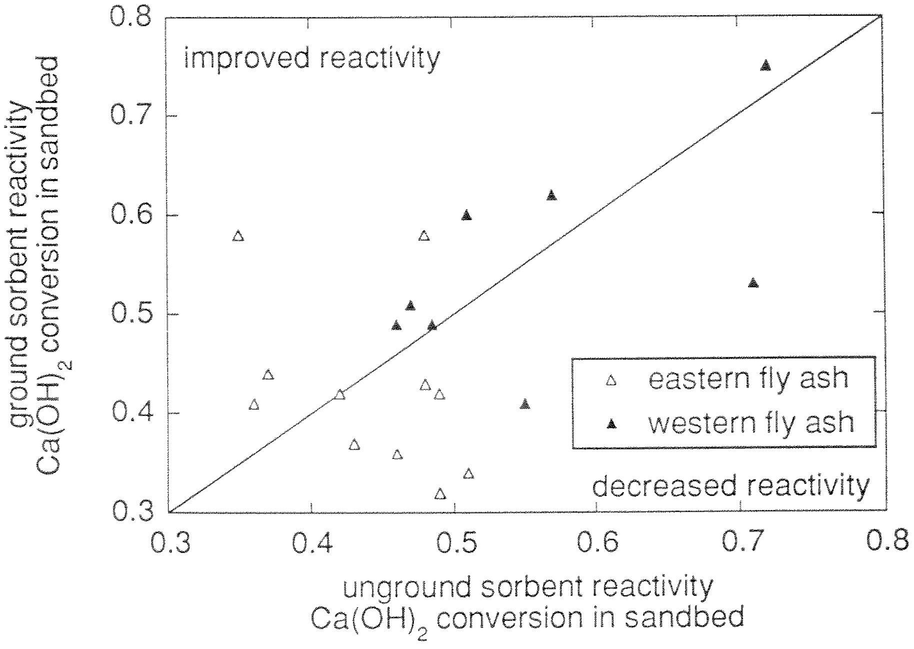

Figure 3.7 Effect of ash grinding on a variety of fly ash sorbents

Ashes reacted with calcium hydroxide at a 3:1 weight ratio for 3 hours at 90° C. The sandbed reactor was at a relative humidity of 60 percent, temperature of 64° C and 1000 ppm sulfur dioxide. (Singer et al., 1991)

3.5 RESEARCH EVALUATION

The research performed to this point has concentrated on the effect of ash type and reaction rate as measured by reactivity towards sulfur dioxide in the sandbed reactor. There has been little work performed to examine the impact of solution chemistry on the reaction between fly ash and hydrated lime to determine if the impact of additives is due to the effect they have on solution composition or the effect they may have on the product formed by the reaction. This behavior can be examined by more detailed studies of reactions with sodium hydroxide and calcium chloride present while monitoring all ions in solution. The extent of reaction between calcium hydroxide and fly ash may be tracked by a measure of reacted ash, calcium hydroxide or surface area which correlates with reactivity of the sorbent with sulfur dioxide. These measures exclude the effect of deliquescent salts.

Batch reaction studies may permit a better understanding of what might occur in the CSTR. The CSTR will have a solution chemistry significantly different from the constantly changing composition in batch reactions. The impact of gypsum on the reaction of low calcium ashes at long reaction times has not been explored. This information is useful because gypsum and calcium sulfite will be present in any operating system and the use of a CSTR will result in some material being exposed to the reaction environment for extended time periods. There has been no work performed with a CSTR prior to the pilot plant work performed concurrently with this study.

The CSTR allows for the study of the system with constant solution composition so that its effect on the reaction to form calcium silicates may be more clearly measured. The solid particle history in the CSTR is distributed and this might also impact the reaction. A detailed study of reaction variables in both the batch and flow reactors will provide a better understanding of the basic reaction and provide information for system scale up.

Chapter 4

Experimental Procedures and Methods

This chapter provides an overview of the reactants used in this study, the experimental equipment and procedures, and the techniques used to analyze and characterize the product formed.

4.1 REACTANTS

The reactants used for this research may be divided into three categories - silica sources, lime sources and additives to the reaction system. The silica sources were largely low calcium fly ashes from several coal-fired power plants. The lime source was usually a commercial grade hydrated lime used by previous researchers. The additives were from varied sources. Each of these materials is described in some detail below.

4.1.1 Silica Sources

The silica sources included three low calcium fly ashes collected from two different power plants. Reacted material (ADVACATE) from a pilot plant run at the Shawnee test facility was also used. In addition, experiments were run with silica fume, a by-product from the manufacture of silicon metal. The source and composition of each is provided in Table 4.1. The Clinch River fly ash was from a sample taken at the Appalachian Power Company's Clinch River Plant. It is from a Virginia bituminous coal and had been used previously by Peterson (1988, 1990), Stroud (1991), Wassserman (1992) and Singer et al. (1991).

Table 4.1 Composition of Silica Sources

	Clinch River[1]	Shawnee[2]	Martwick[3]	Silica Fume[1]	ADVACATE[3]
Collection point & date	ESP 10/86	bag house 7/91	mechanical precollector 5/92	1989	ESP 9/92
Loss on Ignition	-	†	7%	-	-
BET surface area (m^2/g)	3	10	5.4	20	7.6
Component (wt %)					
silica, SiO_2	57	51	47.6	92	18.1
alumina, Al_2O_3	27	19	19.5	3	7.8
iron oxide, Fe_2O_3	8	20	20	2	6.7
potassium oxide, K_2O	3.1*	2.4	2.1	-	0.7
sodium oxide, Na_2O	0.6*	0.4	0.3	-	1
lime, CaO	4	3	4.1	0.1	21.3@

* - from American Electric Power Service Corporation Ash Utilization & Research Section, 10-4-84 sample.

† - not measured but visible

@ - total Ca expressed as CaO; this sample included a large fraction of $CaCO_3$

[1] - from Peterson (1990)

[2] - X-ray fluorescence of coal on ignited basis from Peabody Coal Company through Acurex.

[3] - X-ray fluorescence of material by Acurex/EPA

The Shawnee ash was from a sample received in July 1991 from TVA's Shawnee Power Plant test facility. The ash was from a West Virginia bituminous coal and was collected from an ESP that followed a cyclone separation earlier in the flue duct. The Martwick ash was from a sample taken in May 1992 from the Shawnee test facility. It was taken from the mechanical precollector and resulted from burning a bituminous coal from the Martwick mine. The Shawnee and Martwick fly ashes are from the same burner and have significant amounts of unburned carbon, or char, in the sample. This char may cause measured BET surface area to over predict the surface area of the ash sample available for reaction.

The major difference in ash compositions was a larger amount of aluminum and a lower fraction of iron in the Clinch River ash than the other ashes. Ground fractions of the Shawnee and Martwick ashes were also used in this study. These ashes were ground with a Union Process batch attritor at Acurex, RTP, North Carolina. The compositions of the ground materials are assumed to be the same as the original ashes. The measured surface areas are 9 and 20.2 m^2/g for the ground Martwick and Shawnee ashes respectively.

The silica fume, a highly reactive form of amorphous silica, was obtained through the University of Texas' Ferguson Structural Engineering Laboratory and is the same as that used by Peterson (1990) and Stroud (1991). The ADVACATE material is sorbent collected from a pilot scale ADVACATE process and is described more fully in Chapter 7.

4.1.2 Lime Sources

The calcium hydroxide used in most experiments was commercial Mississippi Rotary Hydrated Lime (Code MR200) from the Mississippi Lime Company. It was purchased in 1990 and had a measured BET surface area of 7 m^2/g. It was approximately 90 percent calcium hydroxide as measured by hydrochloric acid titration to a phenolphthalein endpoint. This was consistent with the alkalinity as measured by sugar dissolution (technique described later in this chapter). The remaining 10 percent was inert and calcium hydroxide that had been carbonated due to exposure to the atmosphere. This material was used in all experiments unless otherwise noted.

Two other sources were also used. The first was a reagent grade lime obtained from Spectrum Chemical and opened in October, 1992. The second was a pebble lime obtained from the Shawnee test facility through Acurex. It was from a sample taken at the ADVACATE pilot facility on 7/15/92. These materials also had approximately 90 percent calcium hydroxide as measured by acid titration. These were used in a limited number of experiments and their use is identified when the data is presented.

4.1.3 Additives

Additives to the fly ash and lime reaction system included calcium sulfite hemihydrate, calcium sulfate dihydrate (gypsum), anhydrous calcium chloride, sodium hydroxide, potassium hydroxide, sodium sulfate and potassium sulfate. Each of these was reagent grade (Table 4.2) with the exception of the calcium sulfite hemihydrate. Laboratory produced calcium sulfite hemihydrate was used in experiments performed through February, 1991. This material was made by adding 1 M $CaCl_2$ to 1 M Na_2SO_3 with the precipitate gravity filtered and washed. It was then vacuum dried at 60° C.

Table 4.2 Reagent grade additives to the experiments

Chemical	**Manufacturer**	**surface area (m^2/g)**
$CaSO_4 \cdot 2H_2O$	Aldrich	2*
$CaCl_2$ (anhydrous)	Spectrum	nm
NaOH 2 N and 5 N	Fisher	nm
NaOH (solid)	Spectrum	nm
KOH (solid)	EM Science	nm
Na_2SO_4	MCB Reagents	nm
K_2SO_4	MCB Reagents	nm

nm - not measured
* - from Stroud (1991)

There were two problems associated with this material. First, it could only be produced in small quantities so that the same batch of material was not used for all experiments. Second, it had a high residual sodium content as observed in the solution chemistry of the batch reactions in which the material was used. These problems were alleviated by obtaining calcium sulfite from a slurry scrubber at EPRI's high sulfur test facility. This sample was taken in January 1991 from a scrubber using thiosulfate as an oxidation inhibitor. This calcium sulfite hemihydrate had a BET surface area of 9 m^2/g and was verified to be 86 percent calcium sulfite hemihydrate by an iodometric titration (Tseng, 1984) of the dried solid material.

4.2 REACTOR SYSTEM

4.2.1 Batch Reactor

The batch reaction took place in a 600 ml glass, jacketed reactor (6 in high, 3 in id). A plexiglass cover was placed on top of the reactor to minimize water loss during the experiment. Temperature was monitored with a mercury thermometer or thermocouple and the reactor was stirred at approximately 1000 RPM with a Fisher Scientific Steadfast Stirrer Model SL 600. Temperature was maintained using a Lauda M3 water bath with a water/ethylene glycol mixture circulating through the reactor jacket.

The water and soluble additives to the reaction (such as sodium hydroxide, potassium hydroxide or calcium chloride) were added to the reactor first. The liquid temperature was increased to within 10° C of the desired final temperature and the remaining reactants (the silica source, calcium hydroxide, gypsum and/or calcium sulfite hemihydrate) were added. The reactor was at the operating temperature within 5 minutes of the final reactants being added. The solids fraction in the reactor was usually around 20 percent by weight but this fraction was varied for certain experiments and is specified in the data in Appendix B. Samples were obtained while the stirrer was operating by inserting a 60 ml syringe with a tube attached through a hole in the top of the reactor and into the slurry.

4.2.2 CSTR

The CSTR equipment is illustrated in Figure 4.1 with typical operating parameters provided. The same 600 ml glass reactor was used as in the batch reaction with temperature controlled manually by adjusting the temperature of the water bath (water/ethylene glycol) as required to maintain a constant reactor temperature. The reactor was again stirred at approximately 1000 RPM. The solids fraction in the reactor was generally maintained at about 20 percent as this allowed for the best pumping of the product slurry.

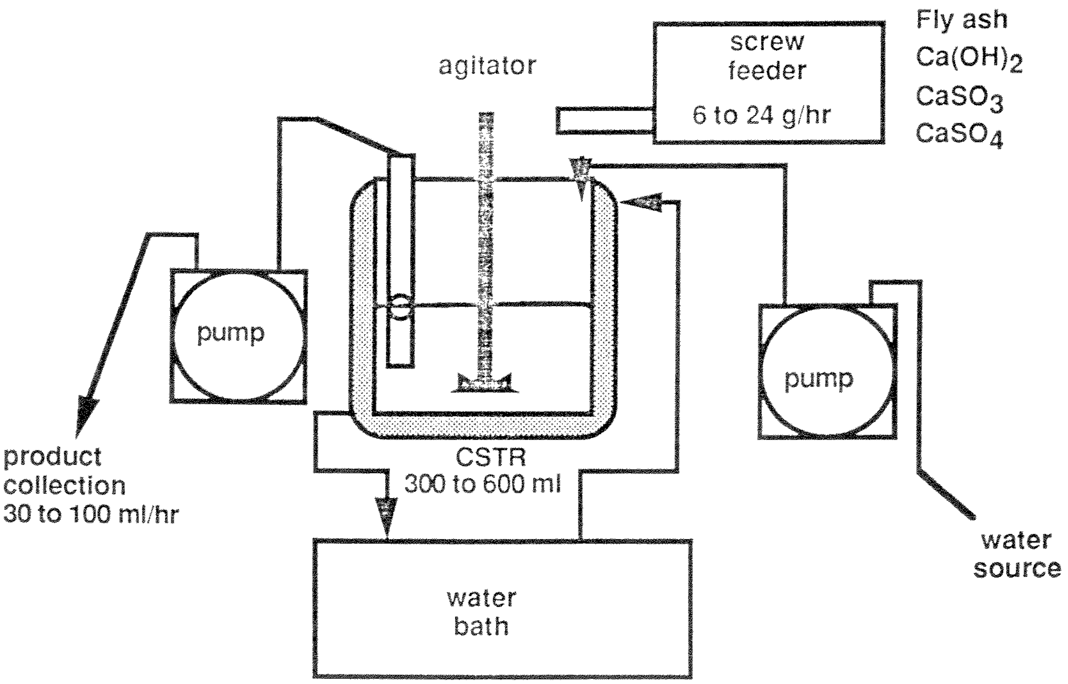

Figure 4.1 Bench scale CSTR system

The solid reactants were combined and shaken prior to being placed in the solids feeder so that a thoroughly mixed feed was obtained. The calcium hydroxide and calcium sulfite hemihydrate were sieved through an 80 mesh sieve prior to mixing to ensure a homogeneous mixture was obtained. The solid reactants were mixed so as to minimize the non-ash fraction (if possible) since the feeder performance was better with a high ash fraction. The calcium solids agglomerated due to high humidity above the open reactor causing the feeder to partially plug and the feed rate to degrade over the course of the experiment. This behavior required more frequent adjustments to the feeder to maintain the desired solids feed rate.

This mixture was added to an Accurate 102 volumetric solids feeder (serial number 100-91-0379) which fed into the open reactor. This was a screw-type feeder (1/8 in screw, 1/25 Hp) with a bin (0.1 cu ft) that was mechanically agitated to ensure that the solids did not bridge the screw. The initial Clinch River ash CSTR runs were performed with a center rod helix screw. This was changed to an open helix for the rest of the experiments because the open helix showed better feed characteristics over the long CSTR operating times. The solids feed rate was obtained by taking one minute samples from the outlet of the feeder and weighing them on a Sartorius balance. Samples were obtained periodically throughout the run and any adjustments to the feed rate were made by changing the feeder screw speed. Solids were added manually at times during some very long residence time reactions (greater than 16 hours). In these cases, the solids were added at periods of less than 7 percent of the CSTR residence time.

Water was added to the reactor from a hold tank with a variable speed Cole-Parmer peristaltic pump (Model No. 7520-35 with 0.064 in id tubing). Calcium chloride, if used, was added to the reactor by mixing it with the water feed. The products were removed by another peristaltic pump (Model No. 7553-10 with 0.123 in id tubing) that pumped slurry intermittently so as to maintain a constant level in the reactor. The residence time of the reactor was defined as the slurry volume in the reactor divided by the outlet flow rate. The outlet flow rate was adjusted by increasing or decreasing the inlet pump speed. Level was maintained constant with a hole punched into the 1/4 in id outlet tube. It allowed for the pumping of liquid when the level covered the punched hole; otherwise, air was pumped to the collection device. The outlet flow rate was monitored periodically and adjusted as necessary to maintain a constant residence time in the reactor.

Table 4.3 CSTR system operating ranges

Parameter	High	Low
outlet flow (ml/hr)	165	25
Solids in (g/hr)	77	6
reactor volume (ml)	600	340
slurry depth (in)	3	5
residence time (hr)	24	2.1
slurry density (wt % solids)	37	16

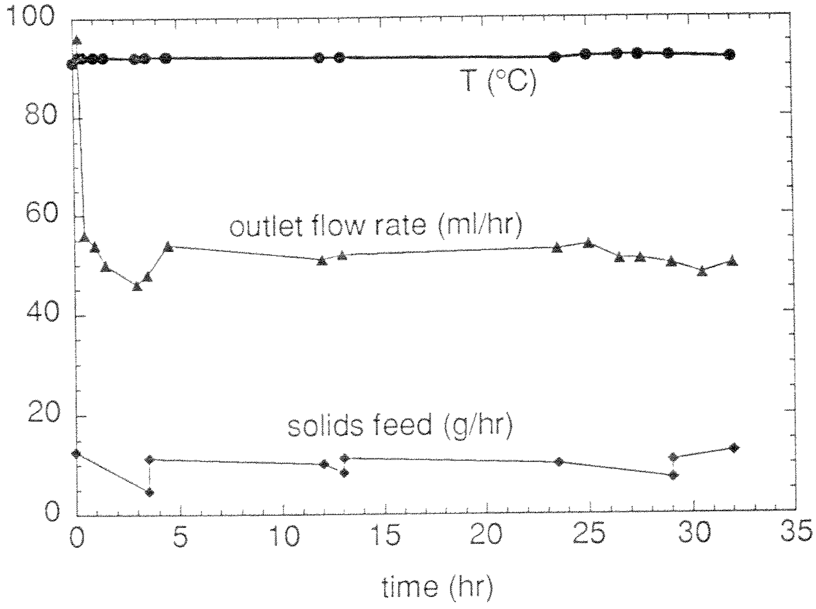

Figure 4.2 Variation in system parameters for a typical CSTR experiment

A continuous run with 8.7 hour residence time performed with Shawnee ash. The reactor operation was started at time zero.

Hydrated lime/Shawnee ash	1:1 weight ratio
Calcium chloride	0.3 N
20 wt % solids	92° C

Samples were taken from the outlet of the reactor during the run. This involved collecting sample over a period of one-half to two hours, depending on the outlet flow rate. The high agitation rate helped to ensure that a representative sample was obtained from the reactor. This was also checked by obtaining a large volume sample from the reactor at the end of the CSTR run and comparing it to the samples obtained during the run. There was generally no noticeable trend in these samples (other than that due to solution temperature differences). The ranges of the operating parameters are given in Table 4.3 while the data from a typical experiment is presented in Figure 4.2.

4.2.3 Sample Handling

Slurry samples were taken as described previously with CSTR operating samples taken at room temperature while batch reaction and CSTR end point samples were filtered immediately (hot) unless otherwise noted. The slurry sample was vacuum were filtered through 9 cm medium porosity filter paper and the liquid portion of the sample was filtered again through a 45 micron 25 mm Supor 450 membrane syringe filter. The filtering was performed as rapidly as possible to limit sample temperature change during the process. The liquid was stored in an air tight 60 ml polyethylene or polypropylene sample bottle.

The solids were dried using the following techniques. The method used in experiments through July, 1992 was to dry the solids without gypsum in an atmospheric oven at 100° C and to dry those with gypsum in a vacuum oven at about 60° C. These methods were consistent with those used by previous researchers (Peterson, 1990; Stroud, 1991; Wasserman, 1992). The drying methods were examined in more detail (Appendix D) and it was determined that vacuum drying at 100° C allowed for minimal reaction during the drying period. This was the method used to dry all samples after September 1992. The dried solids were sieved through a 80 mesh sieve. Those solids that did not go through the sieve were ground slightly and added to the rest of the sample. The solids were stored in 60 ml sample bottle.

4.3 SAMPLE ANALYSIS

Solid and liquid samples were characterized by several analyses. BET surface area and sugar dissolution to determine calcium hydroxide were performed on all solid samples while selective dissolution, X-ray diffraction and various thermal analyses were performed on selected samples. Atomic absorbance and pH measurements were performed to determine ion concentrations in solution for the liquid samples. The ions measured included calcium, potassium, sodium, aluminum, silicon, iron and hydroxide. Ion chromatography was used to measure sulfate and chloride on selected sample solutions. Each of these analyses is discussed in some detail below.

4.3.1 Solids Analyses

4.3.1.1 BET Surface Area

BET (Brunauer-Emmett-Teller) surface area was measured with nitrogen adsorption using a Micromeritics Accusorb 2100E Physical Adsorption Analyzer. The BET method measures physical adsorption of nitrogen (in this case) at liquid nitrogen temperature. Following evacuation of the solid sample to remove all gases from the sample, gas adsorption occurs first in a monolayer on the sample due to van der Waal's forces. Any additional adsorption beyond the initial layer is largely due to condensation forces as liquid builds on liquid. The BET equation may be written as follows:

$$\frac{P}{V(P^s-P)} = \frac{1}{V_mC} + \frac{(C-1)P}{V_mP^s}$$

where P = pressure
P_s = N_2 saturation P
V_m = volume of N_2 monolayer
C = constant determined by isotherm

BET theory assumes that evaporation may only occur from an exposed surface and does not permit lateral interaction between molecules. A plot of $P/V(P^s-P)$ versus P/P^s will be linear (especially at low P/P^s) and can be used to obtain V_m which may used to obtain the surface area of the sample (Hines and Mattox, 1985; Micromeritics, 1979).

For this study, the sample was evacuated overnight at 100° C (or 25° C to prevent the loss of waters of hydration if the sample included gypsum, calcium sulfite or calcium chloride). The gas volume of the sample manifold and tubes was then measured using helium. The surface area was obtained by admitting nitrogen to the sample chamber to obtain the data to use in fitting the equation above. Three to five points were used to develop the line. There was no difference in accuracy with the smaller number of points. A carbon standard was tested periodically to verify the accuracy of the device. The reproducibility of the analysis is discussed in Appendix A.

4.3.1.2 Calcium Hydroxide by Sugar Dissolution

The measurement of free calcium hydroxide by sugar dissolution has been used by several others in ADVACATE research (Wasserman, 1992; Stroud, 1991; Peterson, 1990). It is a technique used by the cement industry. An excess amount of sucrose reacts with calcium hydroxide so that all solid calcium hydroxide is solubilized and may be measured in an acid titration. The reaction between calcium hydroxide and sugar may be simplified as,

$$\mathrm{Ca(OH)_2\ (s) + 2\ sucrose^{-}H^{+} \rightarrow Ca^{2+} + 2\ sucrose^{-} + 2H_2O.}$$

This reaction will deplete all the available calcium hydroxide if an excess of sucrose is used. The liquid may be titrated with hydrochloric acid to lower the pH and measure the amount of free calcium hydroxide,

$$\mathrm{Ca^{2+} + 2\ sucrose^{-} + 2HCl \rightarrow 2\ sucrose^{-}H^{+} + CaCl_2.}$$

This method may measure calcium hydroxide loosely associated with calcium silicates but has given consistent results for this and other studies.

In this study, a solid sample equivalent to 0.25 g of calcium hydroxide as a reactant was slurried with 100 ml 15 percent sugar solution in a covered 250 ml beaker for ten minutes. For example, if the reactants were one part calcium hydroxide and three parts fly ash, one gram of material would be used. The effect of slurry time was examined by Peterson (1990) and ten minutes was determined to be sufficient to react all available hydrated lime from the sample. The slurry was vacuum filtered through 9 cm medium porosity filter paper and phenolphthalein added to the liquid portion. The liquid was titrated with 0.2 N HCl to the phenolphthalein end point. The sample weight was recorded to four decimal places while the buret was readable to 0.03 ml.

The calcium hydroxide remaining in the sample was obtained from this titration and the calcium utilization was determined by subtracting this from the weight of calcium hydroxide added to that sample (reactant calcium hydroxide fraction times sample weight). This measure was sensitive to slurry solid composition, as decreasing the solids fraction decreased the capability of obtaining a representative sample from the reactor. This caused increased variability in this measure at low solids concentrations. This measure was also extremely sensitive to the drying method. Moderate drying techniques increased calcium hydroxide utilization as the calcium hydroxide reacted during the drying time (Appendix D).

4.3.1.3 Selective Dissolution

Selective dissolution is a technique used to measure the amount of acid soluble material reacted from the fly ash and incorporated into the solid product phase. A measured amount of solid is dissolved in a mildly acidic solution and the solution is filtered to remove the insoluble ash and other material. The ash is insoluble in HCl solutions up through 0.5 N and will not be measured in the solution. The filtrate ion concentration may be measured for silicon, aluminum or iron to determine the amount of material that has reacted from the ash. The method was developed by Dagerholt (1988) and used by Peterson (1990).

In this study, about 0.2 g of solid sample was weighed out and slurried with 50 ml of 0.1 N HCl as measured by pipette. This was stirred for 10 minutes and then was syringe filtered through a 45 micron 25 mm Supor 450 membrane syringe filter into a 60 ml polyethylene sample bottle. The samples were then analyzed for aluminum, silicon, iron or calcium by atomic absorbance (see section 4.3.2 for details). The weight fraction of solids dissolved in the solution was greater than in previous studies to allow for increased accuracy in the atomic absorbance measurement of aluminum and silicon ions.

4.3.1.4 X-ray Diffraction

Powder X-ray diffraction is a common technique used to identify crystalline phases in a material by measuring the diffraction of X-rays from the crystal planes in the material (McKie and McKie, 1986). Powder samples were mounted on a glass slide using ethanol or amyl acetate and checked at a 2-theta from 5 to 60 degrees using a Cu K_α source. Two systems were used: a Philips X-ray generator with IBM Series 1 control system and a Philips APD 3520 X-ray generator, Philips APD 3520 and IBM PC control system. Identification of species was generally made by comparing the results of the X-ray to JCPDS references (1993). This data is summarized in Appendix C.

4.3.1.5 Thermal Analyses

Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) were performed on selected solids samples. TGA involved heating the sample at a constant rate and noting the change in sample weight (due to water loss in this case) during heating. TGA was used to examine calcium silicate water loss in addition to that due to calcium hydroxide and gypsum. It was used as a measure of calcium silicate hydration in certain cases. Samples were run on a Perkin Elmer TGA 7 instrument. A nitrogen purge gas was used as the sample was heated unless otherwise noted.

DSC was used to attempt to differentiate solid samples. This analysis heats up the sample at a specified rate and measures the heat input required to maintain the heating rate. In this study, it is a measure of the amount and how tightly the waters of hydration are held by the calcium silicates and other solid phases in the system. Two instruments were used to collect this data, a Perkin Elmer DSC 7 and a DSC-2. The output from the TGA and DSC was analyzed by a Perkin Elmer 2500 Professional Computer or 3600 Data Station in the case of the DSC-2.

4.3.1.6 Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) was performed using a Jeol JSM-35 Scanning Microscope to attempt to visually differentiate some of the solids formed. The samples were sputtered with gold to make them visible by SEM. Other details are specific to the samples viewed and are provided with the photographs presented.

4.3.1.7 Ash Dissolution

Ash dissolution was carried out by adding 0.3 g of ash to 225 ml of solution. The hydroxide level was controlled by adding 5 M NaOH to the water to set the concentration desired. Disodium EDTA (1.2 g) was added as a chelating agent to keep the ash clean of any product. The slurry was stirred and heated at 92° C. At the completion of the run, the sample was vacuum filtered through a medium porosity filter paper. The liquid was again filtered through a 0.45 micron syringe filter. The liquid was analyzed for silicon or aluminum using the atomic absorbance technique.

4.3.2 Solution Analyses

4.3.2.1 Atomic Absorbance

Flame atomic absorbance (AA) was used to measure the concentration of calcium, potassium, sodium, silicon, aluminum and iron in solution. This technique involves heating an aspirated liquid sample to 2000 to 3000° K in an acetylene flame. The intense heat causes the sample to be atomized so that the atoms within the solution may be measured by an absorption technique. This is done by transmitting a wavelength of light specific to that element through the flame by using a hallow cathode lamp containing the same element being analyzed. This allows a very element specific wavelength to be generated. The fraction of the light absorbed is then detected and may be converted to a concentration in the sample by comparing it to that measured with known standards containing the same element. Some alkali elements may ionize in the flame and this phenomenon can be reduced by adding a more easily ionized element to act as an ionization suppressant (Harris, 1987).

The analysis was performed with a Varian model AA-1475-AB spectrophotometer. The wave length, concentration ranges and any ion suppressants used are shown in Table 4.4. Samples were diluted to match the concentration range listed. Samples were bracketed within the standards used for the analysis to ensure an accurate reading was obtained. The standards were made from 1000 ppm commercial standard solutions except in the case of sodium which was made from reagent grade sodium chloride. The suppressants were made from reagent grade chemicals. The reproducibility of this analysis is examined in Appendix A.

Table 4.4 Atomic absorbance analysis operating parameters

Ion	Range (ppm)	Wavelength (nm)	Suppressant
Ca	1-4	422.7	2000 ppm Na (NaCl)
Na	0.5-2	589.0	2000 ppm K (KCl)
K	0.5-2	766.5	2000 ppm Cs ($CsNO_3$)
Si	10-200	250.7	none
Al	10-200	309.3	2000 ppm K (KCl)
Fe	2.5-10	248.3	none

4.3.2.2 Ion Chromatography

Ion chromatography was used to measure the concentration of sulfate and chloride in solution. This technique involves injecting a sample solution into a series of ion exchange columns and measuring the conductivity of the solution exiting the columns as a function of time. The injected ion will come to equilibrium with the resin and be held up until displaced by the eluant. The holdup time is a function of the affinity of the measured ion for the resin while the measured conductivity is proportional to the ion concentration (Dionex, 1983).

The instrument used was a Dionex model 2000i/SP with a Hewlett-Packard 3390A reporting integrator. The guard and separator columns used were a Dionex HPIC-AG4A and a HPIC-AS4A respectively. A Dionex Anion micro membrane suppresser was used as a cation suppresser module and 5 mM sulfuric acid was used as a cation suppresser solution. The eluant was a 0.75 mM $NaHCO_3$ and 2.0 mM Na_2CO_3 solution. The eluant used for chloride was half this strength to ensure good peak separation. The standards were made with reagent grade chemicals (0.01 to 0.05 mM for sulfate and 0.02 to 0.1 mM for chloride). Calcium and sodium were added to the standards to approximate the sample matrix to be injected into the analyzer.

4.3.2.3 pH

The pH was measured at room temperature using a Corning 125 pH meter with a ceramic junction and single probe (Corning 476182 combination electrode). The pH was used primarily for qualitative comparison of trends within an experiment. It was not a useful measure of hydroxide when comparing experiment to experiment.

4.4 TYPICAL EXPERIMENT

Data presented and discussed in Chapters 5 through 9 is often taken from several different experiments and is organized to facilitate the discussion of results. The procedure and data from a typical batch experiment is presented here so that a comprehensive view of one such batch experiment is obtained.

4.4.1 Reaction and Sample Collection

The experiment was performed on September 9, 1992 with Shawnee fly ash, hydrated lime and 0.2 N $CaCl_2$. Four hundred ml water was added to the batch reactor and the water bath was set 101° C to heat up the water to the reaction temperature of 92° C. Anhydrous calcium chloride (4.44 g) was added as the water was heating. The fly ash (53.33 g) and calcium hydroxide (26.67 g) were added to the reactor when the temperature was approximately 80° C. The reactor was then covered and the stirrer started. The water bath temperature was lowered to 93.5° C. The reactor temperature reached 92° C about five minutes after the addition of the ash and calcium hydroxide.

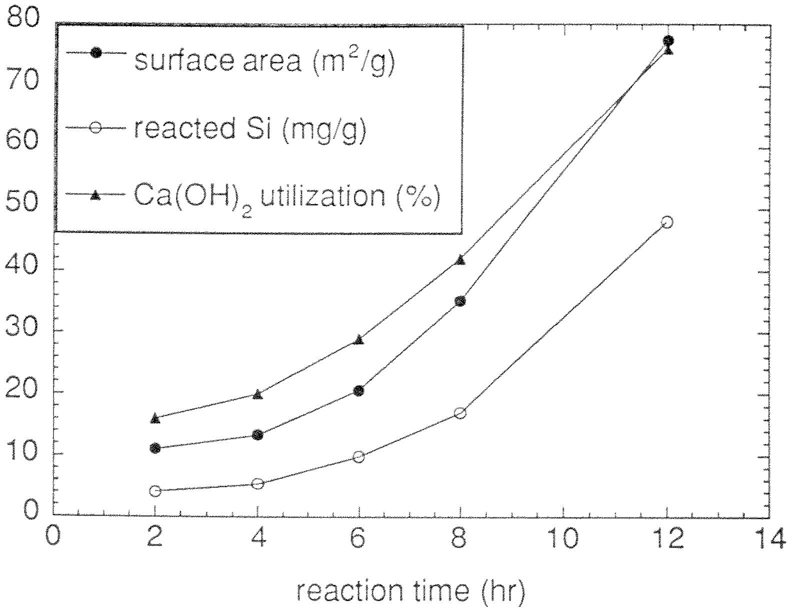

Figure 4.3 Solids analyses for Shawnee ash, 0.2 N $CaCl_2$, batch reaction product

Hydrated lime/Shawnee ash	1:2 weight ratio
Calcium chloride	0.2 N
20 wt % solids	92° C

Samples were taken at 2, 4, 6, 8 and 12 hours of reaction. Each 50 ml sample (except for the 12 hour, large volume end sample) was taken by syringe through a hole in the reactor cover. It was immediately filtered through the vacuum filter. The liquid was then filtered through a syringe filter and stored in a polyethylene sample bottle. The solids were vacuum dried at 200° F over night. The solids were sieved following drying and stored in sample bottles.

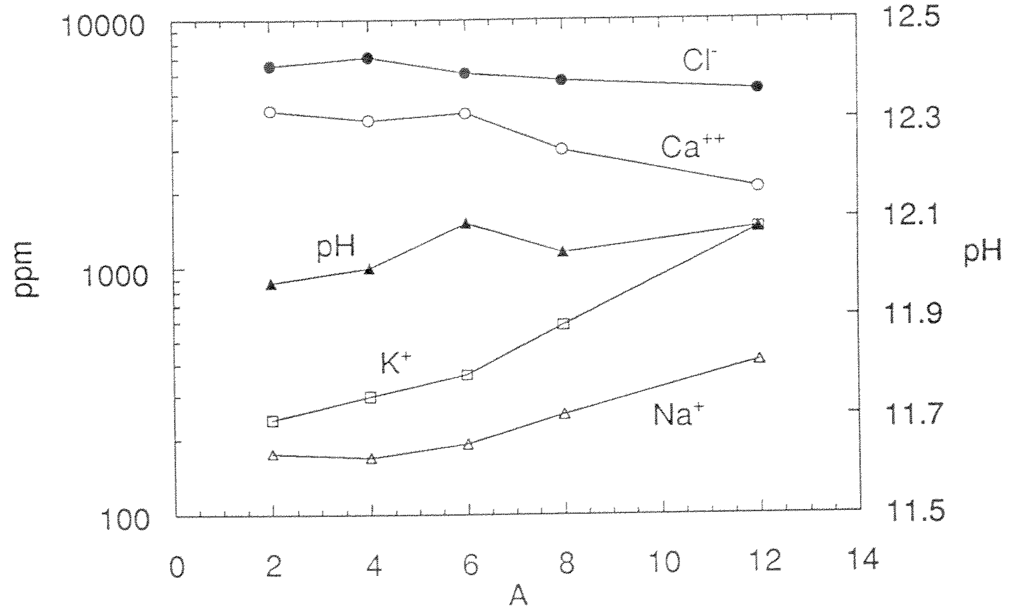

Figure 4.4 Solution analyses for Shawnee ash, 0.2 N $CaCl_2$ batch reaction product

Hydrated lime/Shawnee ash	1:2 weight ratio
Calcium chloride	0.2 N
20 wt % solids	92° C

4.4.2 Solids Analyses

The solids were analyzed for BET surface area (4.3.1.1), calcium hydroxide utilization and reacted silica. Calcium hydroxide utilization was obtained through the sugar dissolution analysis (4.3.1.2) and the reacted silica with the selective dissolution analysis (4.3.1.3). The results from each of these is presented in Figure 4.3. Each increases with reaction time as expected.

4.4.3 Solution Analyses

The solution was analyzed for pH (4.3.2.3), sodium, potassium, calcium, and chloride. Sodium, potassium and calcium were determined by AA (4.3.2.1) while calcium was determined by IC (4.3.2.2). They are illustrated in Figure 4.4.

Chapter 5

Batch Reaction System

Batch reactions are examined first to give insight into the basic reaction characteristics and how this behavior may change in a flow system. The batch experiments are divided into three reaction systems - fly ash-hydrated lime, simulated recycle, and reaction with calcium chloride present. Each of these systems has unique characteristics and behaves differently in the batch reaction. The impact of changing hydroxide concentration in the solution is also examined. The systems are compared in the last section of this chapter. Clinch River fly ash, Shawnee fly ash and silica fume were used to generate the batch reaction data in this chapter. All data from the experiments performed is presented in tabular form in Appendix B.

5.1 REACTION OF FLY ASH AND HYDRATED LIME

The fly ash-hydrated lime system is the simplest in terms of the number of species present but is probably the most difficult to study in the batch reaction due to the extreme changes in solution composition over the course of the reaction. The reaction will be examined first by reviewing the solution changes as the ash particle reacts in the slurry. These changes can impact the generation of surface area as the ash reaction is dependent on the fraction of calcium hydroxide, solids concentration and reaction time. Each of these is examined by comparing the generation of surface area in reactions with Shawnee and Clinch River fly ashes and silica fume.

5.1.1 Solution Chemistry

The dissolution and reaction of ash results not only in the formation of calcium silicates and calcium aluminates but also in the release of soluble ions from the ash. The dissolved aluminum and silicon are normally undetectable (<5 ppm) using the analysis techniques described in Chapter 4. This is due to high calcium concentration in solution so that any silicon or aluminum in solution will react with the calcium forming insoluble product material. The solubility of these calcium silicates and aluminates is also limited by the moderate solution pH. These concentrations become measurable at high hydroxide levels (near 0.1 M).

Figure 5.1 illustrates the changes in reactor solution chemistry for a reaction with 0.25 g calcium hydroxide/g Clinch River ash. Potassium and sodium concentration increase throughout the reaction as fly ash dissolution releases potassium and sodium impurities from the fly ash particles. The hydroxide concentration (as measured by pH) increases in a similar manner. The calcium concentration decreases significantly throughout the eight hours of reaction as the product surface area is built up. The significance of this may be explained by examining a simplified reaction sequence.

<u>Silica Reactions</u>

$$(SiO_2)_X + 2H_2O + OH^- \rightarrow (SiO_2)_{X-1} + Si(OH)_5^-$$

$$Ca(OH)_2 \rightarrow Ca^{++} + 2OH^-$$

$$Ca^{++} + Si(OH)_5^- \rightarrow \text{calcium silicates}$$

The relative ratio of calcium to silicate in solution may impact where the calcium silicate product precipitates. Under normal reaction conditions, the solution is high in dissolved calcium and the product precipitates on the ash surface.

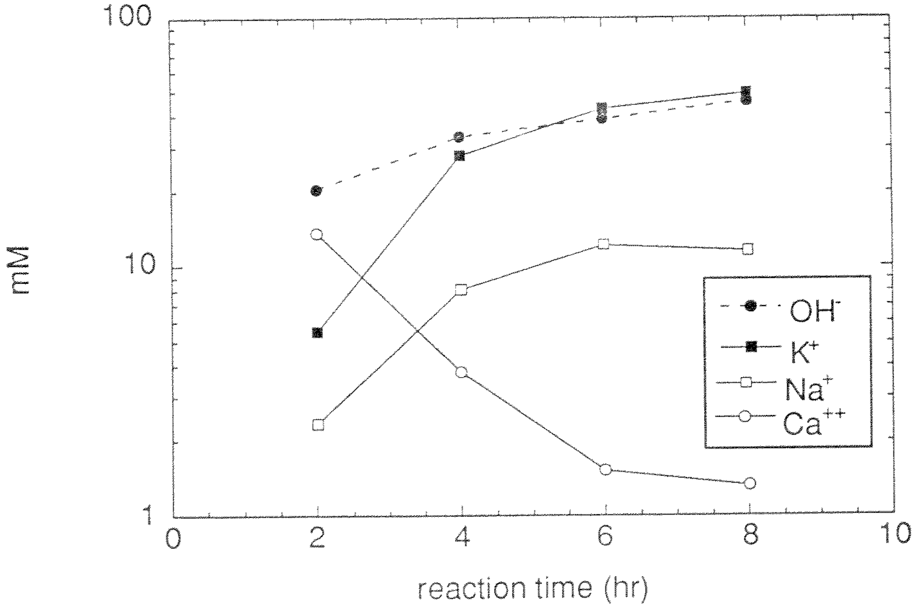

Figure 5.1 Solution chemistry changes for a typical fly ash/hydrated lime reaction

Hydrated lime/Clinch River fly ash	1:4 weight ratio
35 wt % solids	98° C

The other major component in the ashes studied is alumina which can react with calcium hydroxide in a similar manner. It may also react with any sulfate in solution to form a hydrated calcium sulfate aluminate material with composition determined by the solution composition and temperature.

Alumina Reactions

$$Al(OH)_3 + Ca(OH)_2 \rightarrow Ca_3Al_2(OH)_{12}$$

$$x(CaSO_4) + y(Al(OH)_3) + z(Ca(OH)_2) \rightarrow \text{hydrated complex}$$

Each of the above reaction sequences can be impacted by the slurry solution composition. The iron in the fly ash also reacts in this system but the product species is less well defined.

In a reaction system with sufficient calcium hydroxide, the major factor impacting solution composition is the dissolution of alkali metals from the ash. The increasing alkali metals in solution effectively lower the dissolved calcium concentration and increase the hydroxide in the solution as charge balance is maintained. The impact of potassium and sodium in solution may be reduced by the presence of gypsum or calcium chloride which act as buffers to limit the change in hydroxide concentration.

Solution Reactions

$$H_2O + K_2O\ (Na_2O) + Ca^{2+} + 2OH^- \rightarrow Ca(OH)_2 + 2K^+\ (Na^+) + 2OH^-$$

$$CaSO_4 \rightarrow Ca^{2+} + SO_4^{2-}$$

$$CaCl_2 \rightarrow Ca^{2+} + 2Cl^-$$

The first reaction sequence listed (silica reactions) is the probable mechanism for calcium silicate product formation (Peterson, 1990) and may be used to explore possible rate limiting processes. It has been assumed the dissolution of ash is the rate limiting step in the formation of calcium silicates and the dissolution has been shown to be first order in hydroxide in the case of low calcium ashes. But the existence of a product layer can impact the diffusion of hydroxide to the ash surface and also the diffusion and precipitation of the product away from the surface. In addition, as the ash dissolves, the release of alkali ions increases hydroxide concentration, limiting the calcium solubility.

The limited solubility of the calcium may also impact the reaction rate and this will be discussed in detail when examining surface area generation in the batch reaction. The change in solution chemistry is a strong function of the ash used and the ash fraction in the reactor. Clinch River and Shawnee ashes are compared in Figure 5.2. Clinch River ash has a larger fraction released of potassium and sodium at early reaction times so that the solution hydroxide level is higher and the corresponding equilibrium calcium concentration lower. A decrease in ash fraction in the slurry results in lower ion concentration as expected.

The dissolution of calcium hydroxide may also be the rate limiting step in the reaction sequence. While this is not likely to be true in batch reactions with a high calcium hydroxide reactant fraction, it may come into play at longer reaction times when there is less calcium hydroxide available to dissolve and provide calcium for reaction. In a clean system (no other ions present), calcium hydroxide may be expected to dissolve in a matter of minutes (Eitel, 1966) and this is observed in the batch reaction system at short times with the calcium concentration in solution being close to saturation for calcium hydroxide. At longer reaction times, the dissolved calcium level decreases below that expected based on the change in hydroxide level. This effect is explored more fully when examining the reactions of Shawnee ash with sodium hydroxide added to maintain a constant hydroxide level during the reaction.

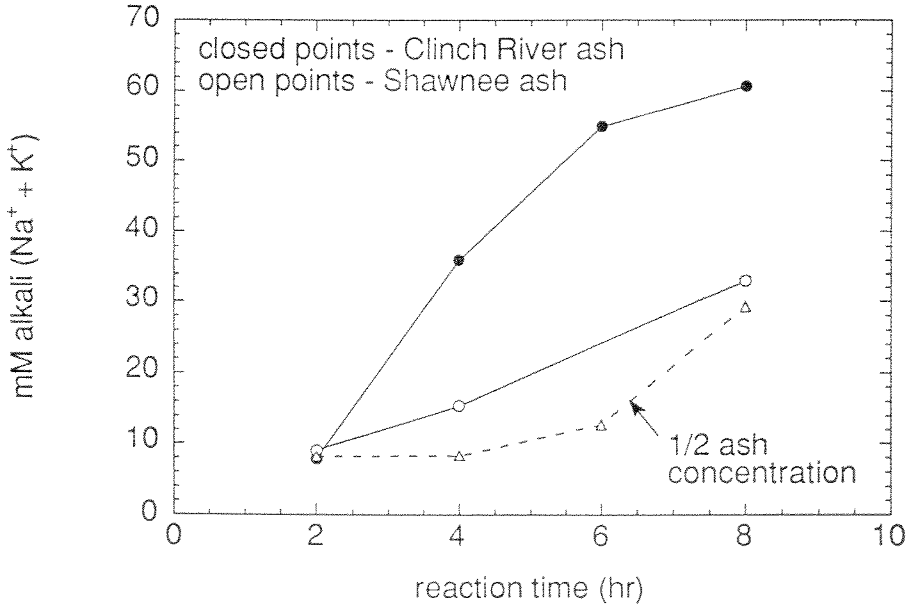

Figure 5.2 Dissolution of alkali metals from two fly ashes

Hydrated lime/Clinch River fly ash Shawnee fly ash	1:4 weight ratio
17 to 35 wt % solids	92 and 98° C

5.1.2 Surface Area

A comprehensive view of the product surface area for the fly ash/hydrated lime system is presented in Figure 5.3. The surface area generation in most cases is approximately linear with time. Clinch River ash does not generate surface area for as long a time as the Shawnee ash but the rates are comparable at short reaction times within the significant data scatter. The lower ultimate surface area for Clinch River ash could be due to three factors. First, the particle size of the Shawnee ash is smaller as the BET surface area of the material is three times greater. If there is a maximum depth that the reaction can penetrate into the ash, one would expect the Clinch River ash to have a lower surface area. In addition,

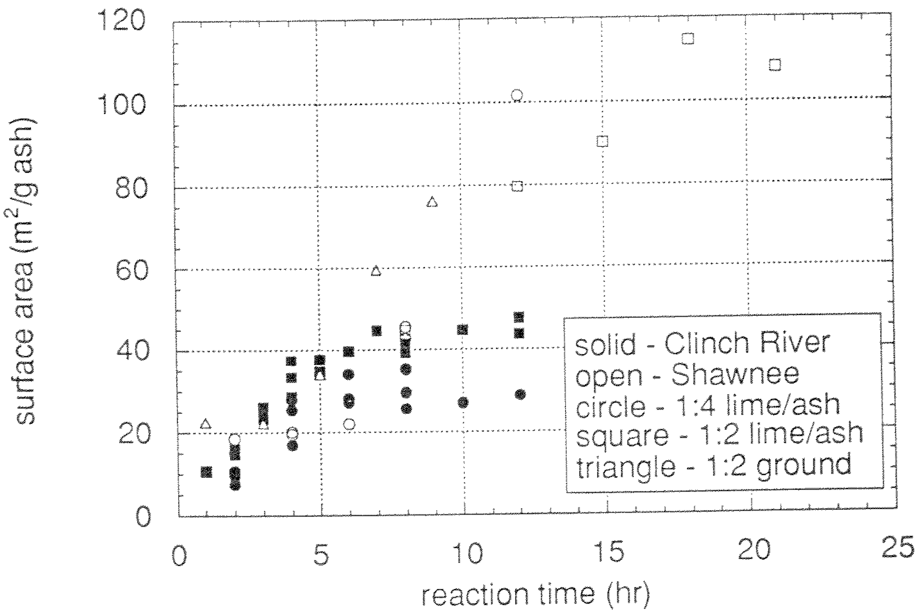

Figure 5.3 Surface area generation in fly ash/hydrated lime reactions

Hydrated lime/Clinch River fly ash 1:4 to 1:2 weight ratios
Shawnee fly ash
ground Shawnee fly ash
17 to 35 wt % solids 92 and 98° C

the ash structure and composition is different so that the Clinch River ash may have a higher fraction of the unreactive crystalline silica phase or a greater fraction of silicon in the unreactive alumina phase limiting the surface area (Chapter 8). Finally, the greater fraction of potassium and sodium in the Clinch River ash inhibits calcium hydroxide dissolution and final product surface area. This effect is quantified in the next section.

5.1.3 Calcium Hydroxide Utilization

The impact of calcium concentration in solution on the reaction is apparent in the calcium hydroxide utilization for the fly ash/hydrated lime reaction. A reaction with a greater calcium hydroxide to ash ratio will have a higher relative lime reactivity. The decrease in ash fraction at a constant solids weight fraction in the reactor will also limit the change in solution composition over the reaction time. This effect is seen when comparing reactions of Clinch River ash with 0.25 g calcium hydroxide/g ash and the 0.5 g calcium hydroxide/g ash reactions (Figure 5.4).

As a larger fraction of calcium hydroxide is added to the batch reaction, the amount of calcium hydroxide reacted (as measured by the sugar dissolution technique), increases at any point in the reaction. The reaction of calcium hydroxide and generation of surface area ceases by 6 hours of reaction in both cases. The lower calcium hydroxide case has lower surface area and this area roughly corresponds to the lower calcium hydroxide utilization for this case. Increasing the calcium hydroxide available allowed for increased surface area. If there was no solution effect on calcium hydroxide dissolution, the surface area generation should be independent of calcium hydroxide fraction (if there is unreacted calcium hydroxide available as in this case) as its dissolution would be much greater than that of fly ash.

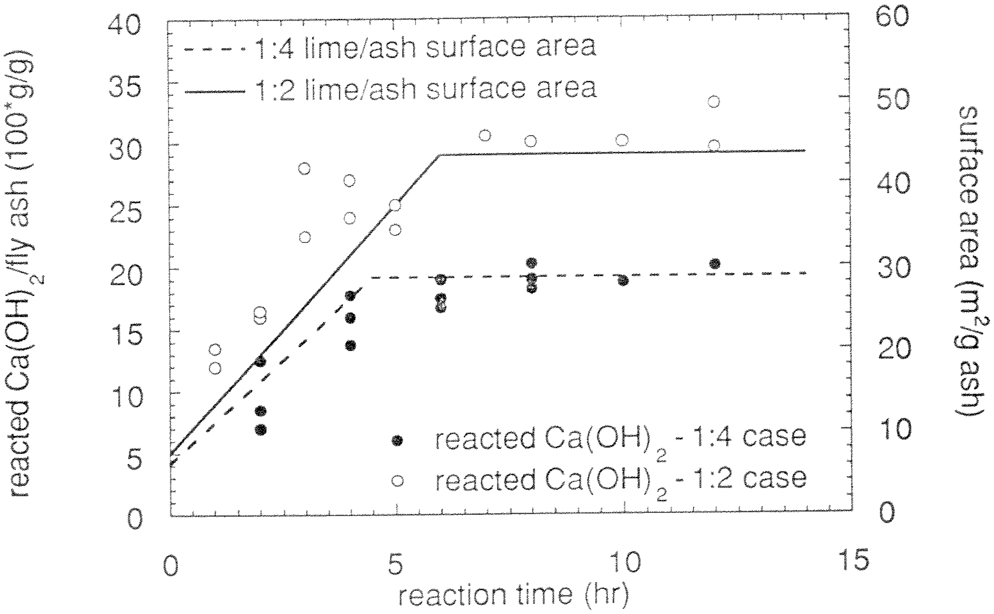

Figure 5.4 Calcium utilization - Clinch River fly ash/hydrated lime reactions (I)

The lines shown are a fit of the surface area data shown in Figure 5.3.

Hydrated lime/Clinch River fly ash	1:4 to 1:2 weight ratios
17 to 35 wt % solids	98° C

The increase in calcium hydroxide added to the reaction allows a greater fraction to dissolve and form a high calcium silicate at short reaction times. The reaction is, in effect, limited by calcium hydroxide dissolution. The reaction ended by about 6 hours and this is most likely due to the low solution calcium concentration at this point. The low concentration is due in part to the higher solution hydroxide level and also due to the lower calcium hydroxide activity at this time. This effect is also observed in the CSTR experiments (Chapter 6).

There is scatter in the calcium hydroxide utilization data due in part to the batch reaction sampling and drying technique (Appendix D). This was avoided by running a of series reactions where the entire batch was analyzed to ensure a representative solids sample was obtained (Figure 5.5). In this case, the plot is corrected to account for the calcium hydroxide used being only 90 percent calcium hydroxide by acid titration. This allows for a more accurate plot, especially at low calcium hydroxide conversions. This data highlights the increased reaction with increased calcium hydroxide fraction. There is a rapid dissolution (approximately 0.008 g/g of the initial increase is due to saturating the solution) and reaction at times less than five minutes followed by increased difference in calcium hydroxide utilization throughout the two hours of reaction.

The effect of calcium hydroxide solution concentration was examined further in a semi-batch reaction with Clinch River fly ash where additional calcium hydroxide was added to the reactor every three hours during a 12 hour experiment. In this case, reaction continued over a much longer time period (significant surface area growth over 9 hours) and the end product had a surface area of 73 m^2/g ash, 30 m^2/g greater than the other Clinch River ash experiments. This surface area was still less than the experiments performed with gypsum and calcium chloride present (to be detailed in the next sections). It also provided an indication that the CSTR is likely to be more effective than the batch reactor for this reaction.

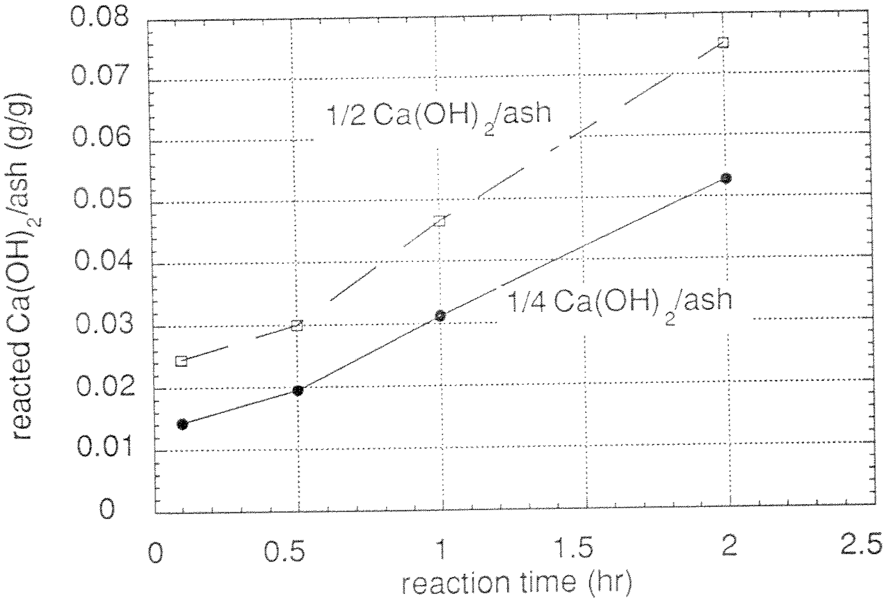

Figure 5.5 Calcium utilization - Clinch River fly ash/hydrated lime reactions (II)

Each point represents data from one experiment. Bulk samples were taken to minimize inaccuracies in sampling technique. Data was corrected for effective initial calcium hydroxide fraction.

Hydrated lime/Clinch River fly ash	1:4 to 1:2 weight ratios
20 wt % solids	100° C

5.1.4 Silica Fume/Lime Reaction

This behavior implies that the type of lime used in experiments with calcium hydroxide to ash ratios of less than 0.5 may have a significant impact on the reaction rate. If the calcium hydroxide had an increased surface area, it would dissolve more rapidly, allowing the reaction rate to increase. A series of experiments was performed with silica fume, a highly reactive form of amorphous silica, to investigate this possibility. Silica fume is unique because its reactivity is much greater than ash and there are fewer impurities such as sodium and potassium in the material so the change in solution hydroxide level over the course of reaction is less extreme than for fly ashes. Silica fume was chosen because as a relatively pure, reactive form of silica, it would highlight the impact of lime dissolution on the reaction. These experiments represent the extreme case of highly reactive silica and lower activity lime. The silica fume may be made even more reactive by adding sodium hydroxide to the solution because the increased hydroxide should dissolve the silica fume more rapidly, freeing it for reaction.

The behavior of silica fume and calcium hydroxide with increasing solution hydroxide concentration is shown in Figure 5.6. As hydroxide concentration was increased, the rate of surface area growth actually decreased despite the increased silica fume dissolution rate. Calcium hydroxide utilization shows a somewhat different behavior. At one-half hour of reaction, there is more than 60 percent utilization in the 0.1 N sodium hydroxide case compared to 35 percent in the base case. This is due to the high dissolution rate of the silica fume; its increased activity may be observed in the solution compositions. In the base case, calcium concentration is 18.8 mM while silicon concentration is less than 0.4 mM. In the 0.1 N sodium hydroxide case, calcium concentration is 0.05 mM while silicon concentration is 1.3 mM.

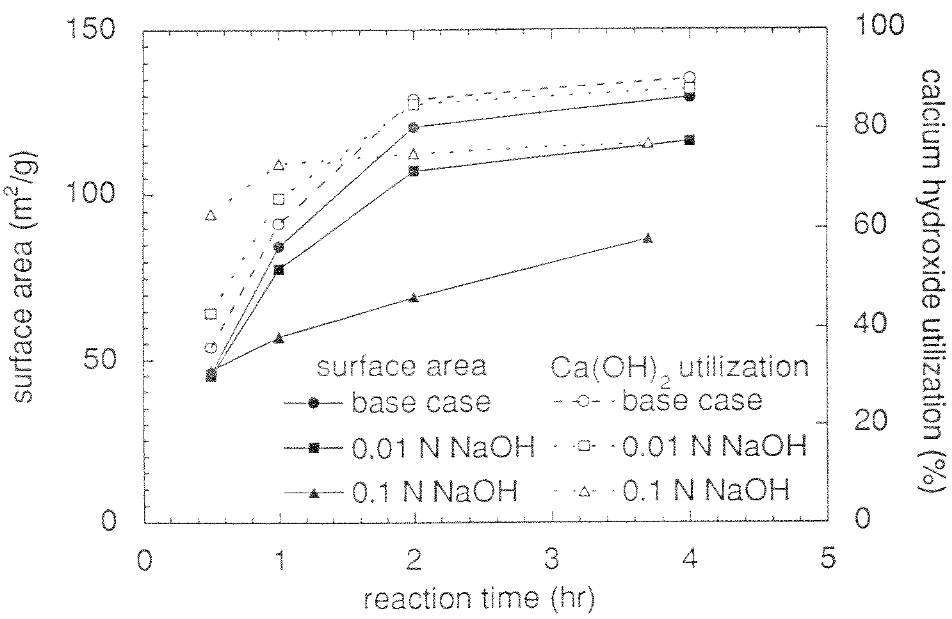

Figure 5.6 Effect of silica fume reactivity on the hydration reaction

Sodium hydroxide was added to increase the silica fume reactivity. The surface area generated decreased as the hydroxide concentration was increased.

Hydrated lime/Silica fume	1:1 weight ratio
9 wt % solids	92° C

The calcium hydroxide utilization in the 0.1 N sodium hydroxide experiment quickly levels at less than 80 percent and is the lowest conversion of the three reactions shown at four hours of reaction. The reaction differs from the ash/hydrated lime reactions shown earlier as generation of surface area occurs after the calcium hydroxide utilization levels. The lower calcium hydroxide utilization and product surface area is consistent with the hypothesis that as silica reactivity is increased, the reaction between the silica and calcium hydroxide may take place on the calcium hydroxide rather than on the surface of the ash. The 0.1 N hydroxide level allows the silica to be present in solution at levels greater than the calcium, essentially making the silica fume more reactive than the calcium hydroxide.

The ultimate surface area in the high hydroxide reactions is lower than expected based on the amount of reacted calcium hydroxide. This may be due to a lower surface area product being formed at high hydroxide concentrations so as the silica reacts at the calcium hydroxide surface, a different calcium silicate is formed with a lower surface area per gram of reacted calcium hydroxide. In addition, the product might also coat the calcium hydroxide particle, making the inside of the particle unavailable for measurement by the sugar dissolution method. This would result in an artificially high calcium hydroxide utilization.

The impact of the type of lime used is examined in Figure 5.7. Three types of lime were used in these experiments - hydrated, newly purchased reagent grade and pebble limes. The hydrated lime had a BET surface area of 7 m^2/g while the reagent grade and pebble limes, slaked at 100° C, had a surface areas of 34 and 31 m^2/g respectively. The lime sources were preslaked for one hour in the experiments shown. An experiment was performed with pebble lime and 0.1 N NaOH with no lime preslake to determine if preslake increased the lime reactivity. The results were similar to the reaction with preslake even in this extreme case so preslaking appeared to have little effect on the reaction rate. If lime dissolution were a factor in determining the reaction rate, the reactions with high surface area hydrates should generate surface area at a greater rate.

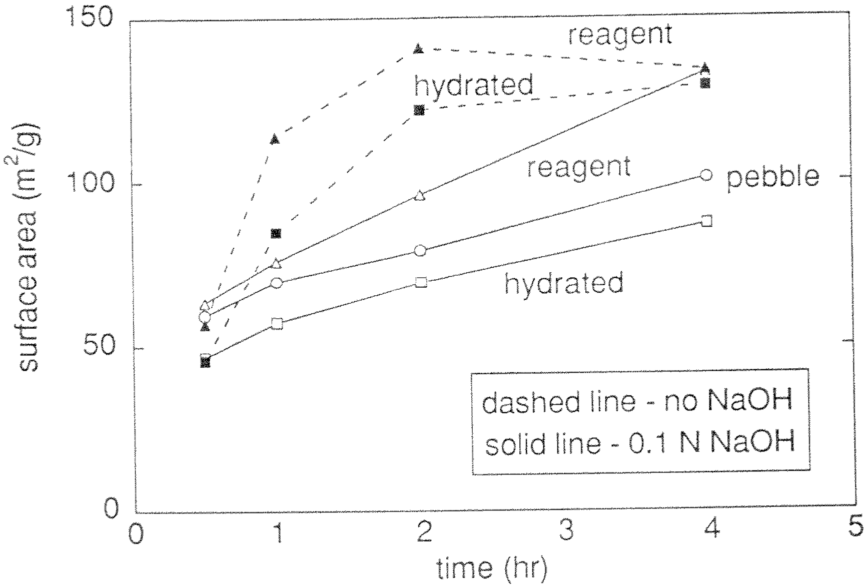

Figure 5.7 Impact of lime type on surface area in reactions with silica fume

Hydrated lime/Silica fume	1:1 hydrated weight ratio
Reagent lime	
Pebble lime	
9 wt % solids	92° C

The reagent lime allowed for a greater reaction rate at reaction times between 0.5 and 1 hour if no sodium hydroxide was added to the reaction. Reactions performed with 0.1 N hydroxide present to increase silica reactivity showed a similar behavior. In this case, surface area generation was lower for all the sources of lime at all times. Only the reagent grade lime was able to match the surface area at four hours of reaction. The pebble lime reaction, while performing better than the hydrated lime, was significantly slower than the reagent grade lime reaction.

5.1.5 Fly Ash/Hydrated Lime/NaOH Reactions

The impact of solution hydroxide concentration on the reaction between fly ash and hydrated lime was examined through a series of Shawnee ash batch experiments at low solids concentrations. Sodium hydroxide was added to each solution to maintain a constant hydroxide level in solution during the reaction. The solids concentration was controlled such that the increase in sodium, potassium and hydroxide was less than 20 percent over the course of the reaction. Shawnee fly ash was used to examine this behavior as it reacted over a much longer time period, forming a higher surface area material, enhancing any differences in the reactions. Figure 5.8 illustrates the behavior of this ash with varying sodium hydroxide concentration. The points shown are from multiple experiments with solid fractions less than 5 percent by weight. The data for the short reaction times are cross plotted on Figure 5.9.

The calcium ion concentration is less than 0.025 mM at all reaction times for experiments with hydroxide concentration greater than 0.2 N. At very short reaction times, the beneficial effect of the high hydroxide level to dissolve ash outweighs the limited calcium availability as the surface area of the high hydroxide products is greater than in the low hydroxide/high calcium cases studied. The impact of high hydroxide concentration (greater than 0.2 M) and therefore low calcium concentration is apparent at reaction times greater than 5 hours. The high solution silicate and aluminate levels (greater than 9 mM, Table 5.1) indicate that there is little calcium available for reaction and this results in minimal surface area generation at longer reaction times.

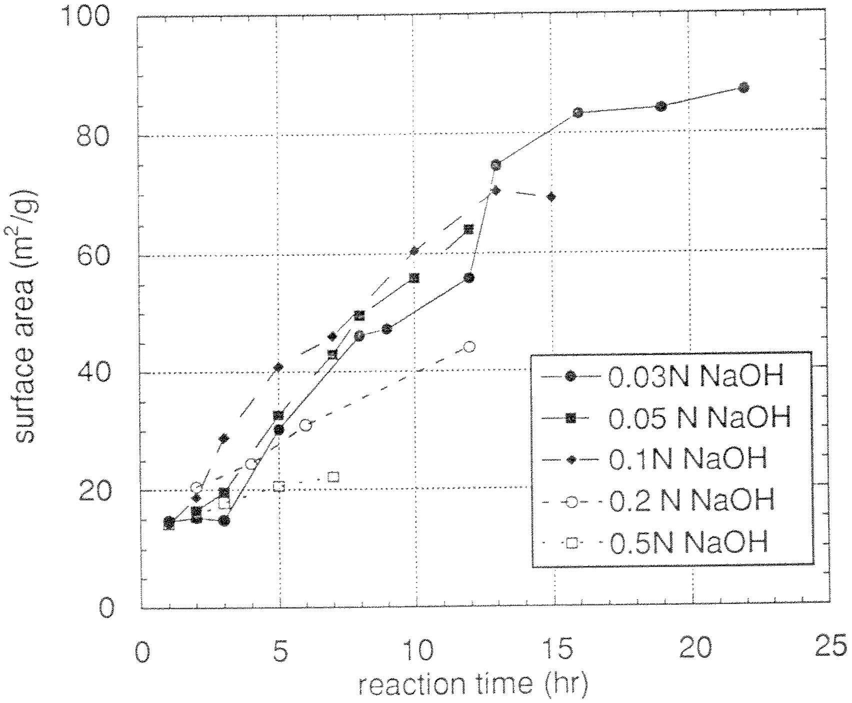

Figure 5.8 Impact of hydroxide level on Shawnee ash surface area generation

Surface area development at a constant hydroxide level. Data shown is from multiple experiments at each hydroxide concentration.

Hydrated lime/Shawnee fly ash	1:4 weight ratio
2.5 to 5 wt % solids	92° C

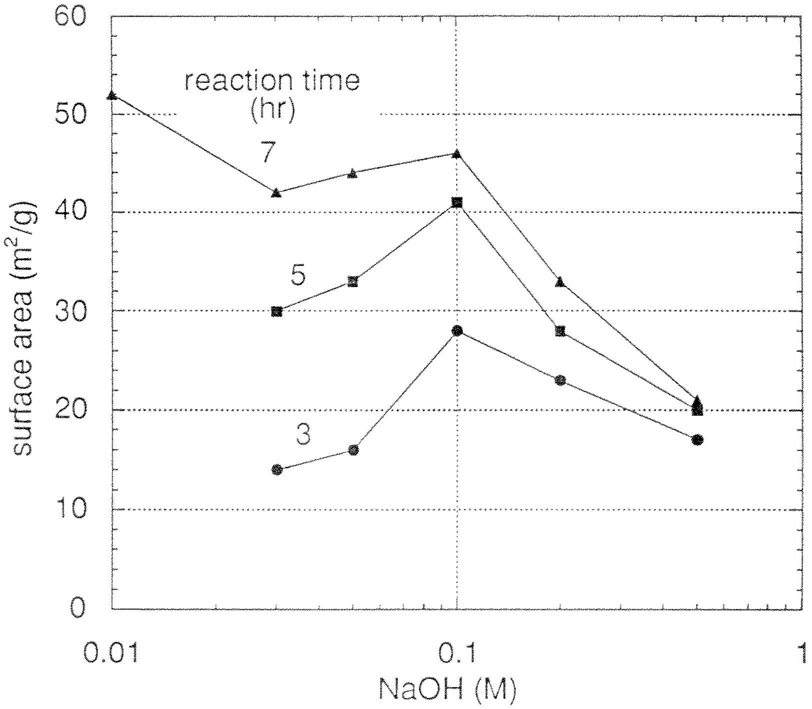

Figure 5.9 Cross plot of surface area and hydroxide level - Shawnee ash

Conditions are the same as those for Figure 5.8

The calcium concentration decreases throughout the reaction time for the low hydroxide reactions despite the approximately constant hydroxide concentration. In the 0.03 M sodium hydroxide case, the dissolved calcium ranged from 20 mM at one hour of reaction to less than 1 mM at eight hours. This occurs despite calcium hydroxide still being present in the system. An experiment performed with potassium hydroxide rather than sodium hydroxide (this species more closely matches the dissolution of the ash species studied) showed similar behavior.

Table 5.1 Solution silicate and aluminate at various hydroxide concentrations

NaOH concentration (M)	**reaction time (hr)**	**aluminum concentration (mM)**	**silicon concentration (mM)**
0.05	7	2.1	-
0.1	5	3.3	-
0.1	7	-	3.8
0.2	6	9.3	-
0.2	12	9.9	9.7
0.5	7	10	20.7

All reactions were performed with a 1:4 calcium hydroxide to Shawnee ash weight fraction at 92° C. Solids concentration varied from 3.3 to 5 wt %.

The other observation that may be made from this data is the insensitivity of the surface area generation rate to hydroxide concentration (for sodium hydroxide less than 0.2 N) at reaction times greater than 5 hours. The reaction was carried out until no further area generation was observed for several of these cases and the generation of area continued until through 14 hours at comparable rates for the cases with less than or equal to 0.1 N hydroxide. This insensitivity to solution hydroxide concentration was also observed in the Clinch River experiments where the solids concentration was changed by a factor of two thereby changing the hydroxide concentration by about two (since hydroxide concentration was largely a function of potassium and sodium dissolved from the ash in those experiments).

The difference in surface area at short reaction times may be attributed to the increased ash dissolution due the higher bulk solution hydroxide concentration causing increased reaction rate as proposed by Peterson (1990). The subsequent behavior is not as clear. The maximum surface area produced was also dependent on the hydroxide level with a lower final surface area in the higher hydroxide cases. This difference is due in part to a lower calcium hydroxide utilization at high hydroxide concentrations (about 40 percent for the 0.5 N NaOH experiment as compared to 98 percent for the 0.01 N experiment).

5.2 RECYCLE - GYPSUM AND CALCIUM SULFITE

Calcium sulfite hemihydrate and gypsum (calcium sulfate dihydrate) were added to the reaction to better represent a system with recycle of product material from the ESP to the slurry reactor. This is likely to be the case in an operating system. The fraction of sulfur materials used in the batch experiments performed were representative of those expected to be encountered in an operating system with about 25 percent oxidation of sulfite to sulfate. These experiments were performed with Clinch River and Shawnee fly ashes.

5.2.1 Solution Chemistry

The reaction of fly ash and hydrated lime with calcium sulfite and gypsum present (recycle materials) is quite different from the fly ash/hydrated lime case. A comparison of the solution compositions is provided for Clinch River fly ash in Figure 5.10. Sodium and potassium concentration increase throughout the reaction period; the levels are lower than in the fly ash/hydrated lime reaction because the ash fraction in solution is lower - 0.16 g ash/g water as opposed to

0.28 g ash/g water in the fly ash/hydrated lime reaction. The addition of calcium sulfite and sulfate maintains the hydroxide concentration at an almost constant level throughout eight hours of reaction. Calcium concentration again decreases with reaction time but is always much higher than the fly ash/hydrated lime experiment due to the high solubility product of calcium sulfate in aqueous solution. This reaction system can utilize all the calcium hydroxide added to the reaction as the hydroxide concentration decreases after eight hours due to a lack of calcium hydroxide. The same trends are observed for Shawnee fly ash.

The new species present in solution are sulfite and sulfate ions. The sulfite ion was not measured since it has a low solubility product in water and did not impact the reaction significantly in previous studies (Peterson, 1990). In addition, it is difficult to prevent the oxidation of sulfite (and therefore biasing the measurement) while attempting to measure it. The impact of calcium sulfite on the reaction was checked and is shown later in this section (Figure 5.15). Sulfate is tracked and generally built up in solution as the reaction proceeds and potassium and sodium are released into the solution. The calcium concentration declines by as much as one third during the same time period.

The sulfate trend for the typical experiment is provided in Figure 5.11 (solids points). This is contrasted with an experiment performed with a lower fraction of gypsum where the sulfate concentration decreases between 16 and 18 hours of reaction and dissolved calcium shows an even more significant drop. This drop is most likely due to the depletion of the gypsum added to the batch reactor. The incorporation of gypsum into an aluminum compound is described more fully in Chapter 8. This illustrates the impact sulfate has in maintaining a high calcium concentration at long reaction times and also indicates that the gypsum may be incorporated into a reaction product. The amount of gypsum added to the reactor far exceeded the solubility so that sulfate concentration would not be expected to decline unless no more solid phase gypsum exists.

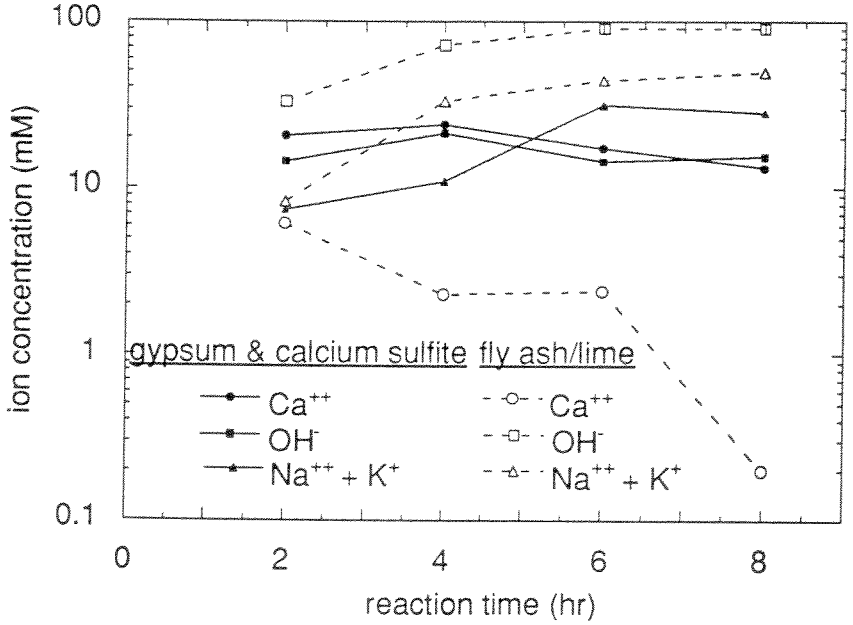

Figure 5.10 Effect of recycle materials on solution chemistry - Clinch River ash

Hydrated lime/Clinch River fly ash	1:4 weight ratio
Hydrated lime/Clinch River ash/ calcium sulfite/gypsum	1:4:3:1 weight ratio
35 wt % solids	98° C

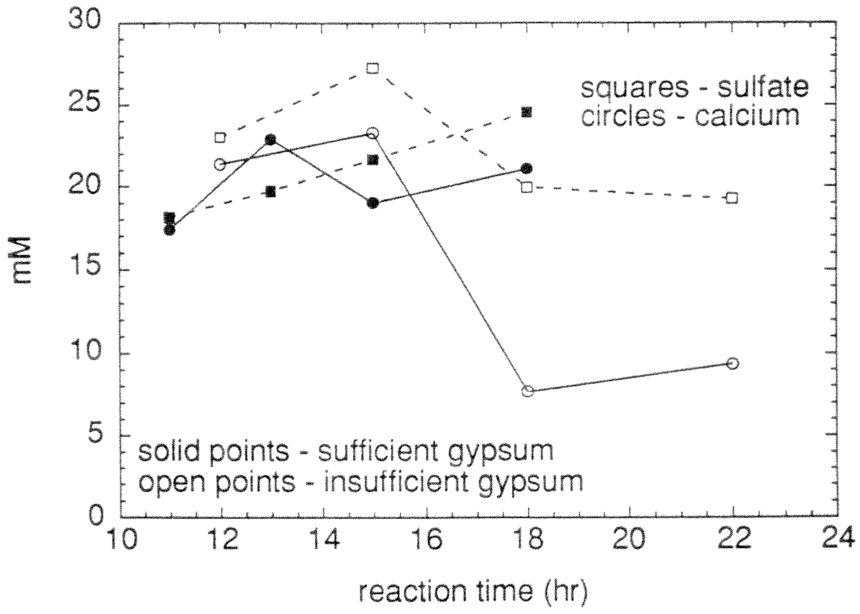

Figure 5.11 Gypsum depletion in a batch reaction - Clinch River ash

Hydrated lime/Clinch River ash/ calcium sulfite/gypsum	4:4:1:4 and 4.8:4:3:1 weight ratios
22 to 35 wt % solids	98° C

5.2.2 Surface Area

Product surface area generation in Clinch River ash experiments containing gypsum and calcium sulfite hemihydrate is illustrated in Figure 5.12. The fly ash/hydrated lime data is provided for comparison. In this plot, the surface area is shown in terms of area per gram of ash rather than area per gram of total material. This corrects for the large excess of reactants used in some of the batch experiments so that the points for various ratios of reactants may be plotted on the same graph and meaningful comparisons made. All data points are shown with the exception of those where surface area was limited by the amount of hydrated lime added (as indicated by decreasing hydroxide concentration and a calcium hydroxide utilization greater than 90 percent - Table 5.2). As calcium hydroxide was depleted, there was insufficient hydroxide and calcium available to the reaction site and this was observed in the surface area generation and the solution hydroxide level. At least one part lime to two parts ash was required to obtain the highest surface area material.

Table 5.2 System behavior with calcium hydroxide limited batch reaction

Ash	**pH**	**Calcium Utilization (%)**	**Surface Area (m^2/g ash)**
Clinch River - low $Ca(OH)_2$ (25% of ash)	11.8	94	96.3
Clinch River - high $Ca(OH)_2$ (120% of ash)	11.84	46	130.6
Shawnee - low $Ca(OH)_2$ (25% of ash)	11.51	93	93
Shawnee - high $Ca(OH)_2$ (100% of ash)	12.5*	47	118.5

*- All samples taken at 12 hours except for the Shawnee high calcium case when pH was taken at 14 hours. Reaction contained gypsum in addition to the ash and hydrated lime.

The points show the same general trend as the fly ash/hydrated lime data; the scatter at lower reaction times is due in part to plotting the surface area in terms of ash. At lower reaction times with low ash concentration, all surface area is attributed to the ash. Surface area of product from experiments with high additive fractions is then biased high at low reaction times since much surface

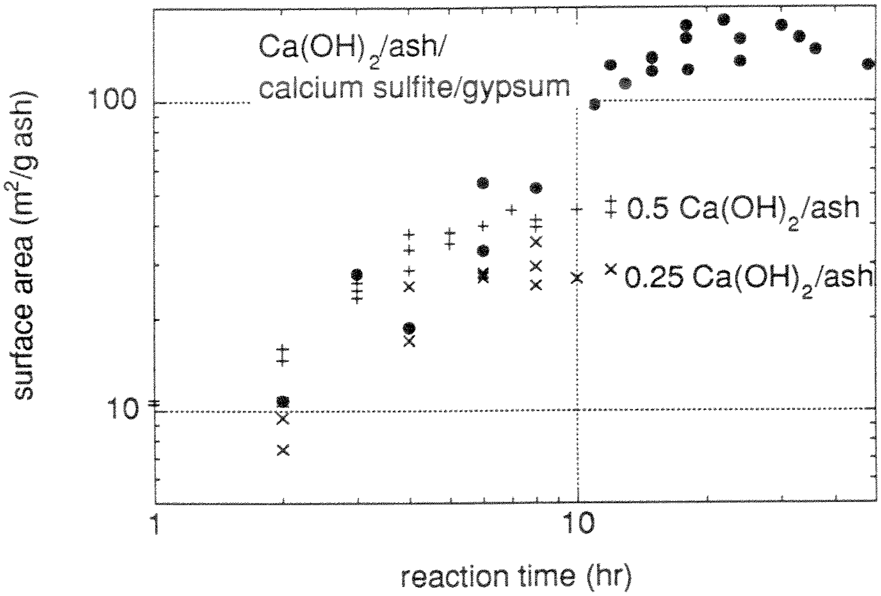

Figure 5.12 Clinch River ash surface area generation with recycle materials

Circles indicate surface area from multiple experiments with calcium sulfite and gypsum present. Fly ash/hydrated lime experiments as described in Figure 5.4

Hydrated lime/Clinch River ash/ calcium sulfite/gypsum	hydrated lime 11 - 36 wt % ash 29 - 44 wt % calcium sulfite 13 - 33 wt % gypsum 9 - 29 wt %
22 to 35 wt % solids	98° C

area is not due to calcium silicates. This effect becomes smaller as the reaction proceeds. The surface area generation continues for about twenty hours until a steady surface area is observed. The duration of reaction is due in part to the buffering effect the gypsum has on the solution. The pH is lower than in the fly ash/hydrated lime reactions and does not change as significantly with reaction time. If potassium or sodium levels in solution are used as measures of ash dissolution, ash dissolution is much greater in the recycle case for reaction times greater than eight hours while the opposite is true at shorter times.

Potassium dissolution data from Clinch River ash in the recycle system is provided in Figure 5.13. The solution potassium level was corrected for the ash fraction and percent dissolution was obtained using the ash analysis from Table 4.1. Potassium dissolution continues for a somewhat longer period than surface area generation but shows the same trend.

The batch reaction surface area as a function of reaction time for Shawnee ash is presented in Figure 5.14. It includes data from multiple experiments where the calcium hydroxide fraction was increased for experiments with long reaction times to ensure that the reaction was not limited by calcium availability. In this system, there is a latent period of about five hours before any surface area generation. This may be characteristic of the ash, requiring a higher hydroxide concentration to initially etch the ash surface to start the reaction sequence. It might also be due to the high amount of char in the ash.

Surface area generation again is linear with time before leveling off at about 250 m^2/g ash. The difference in ultimate surface area between this and Clinch River ash may be characteristic of the ashes as solid phase compositions and microstructure could determine the ultimate reactivity of the silica in the ash (Hemmings and Berry, 1987). The Shawnee ash silica conversion at the end of the reaction is greater than 80 percent as measured by the selective dissolution technique. This could represent the maximum possible reaction as only the silica present in the glassy phase will be reactive. The larger particle size of the Clinch River ash may also limit the surface area.

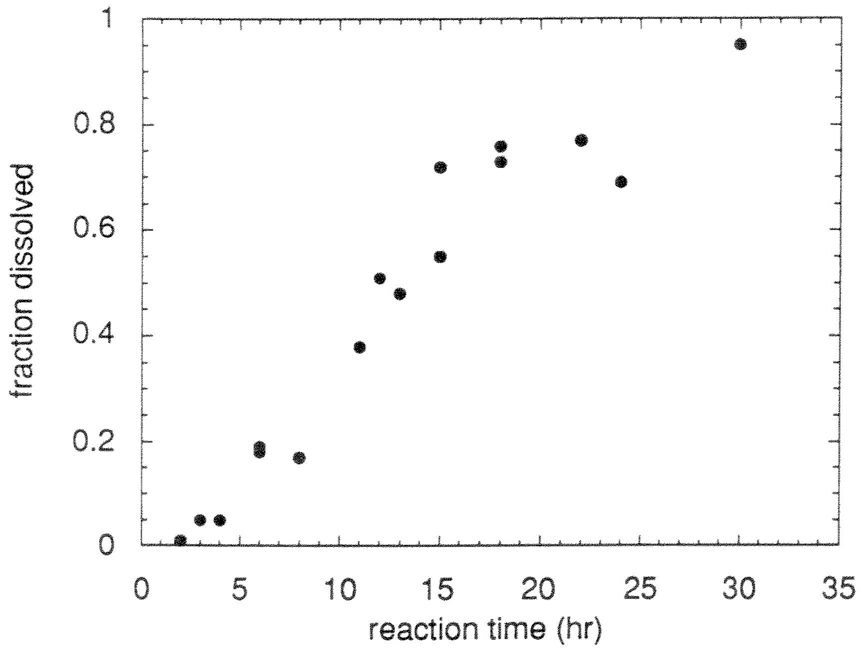

Figure 5.13 Potassium dissolution from Clinch River ash with recycle materials

Fraction of potassium dissolved determined by measuring potassium in solution and comparing it to the ash potassium concentration in Table 4.1.

Conditions the same as those in Figure 5.12.

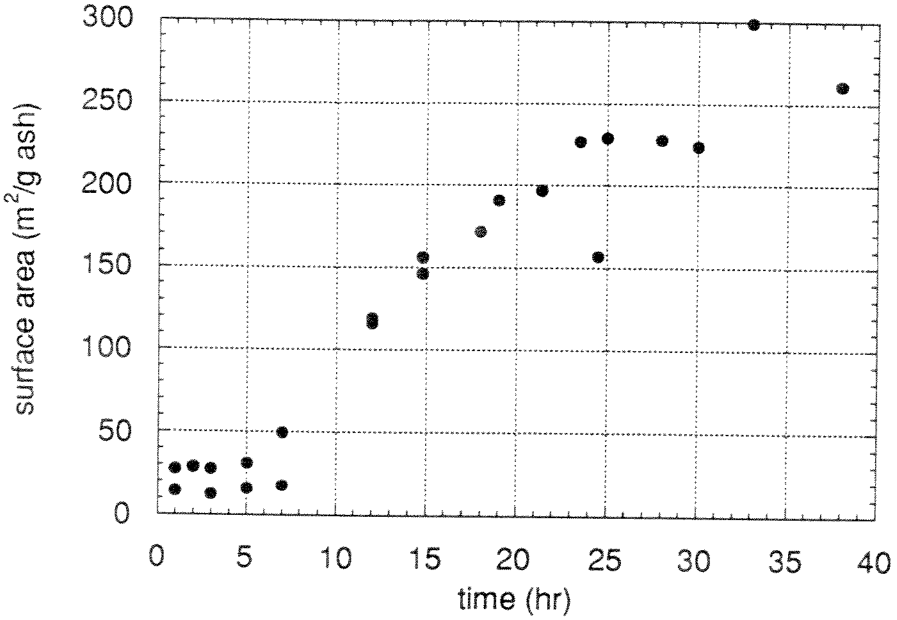

Figure 5.14 Shawnee ash surface area generation with recycle materials

Hydrated lime/Shawnee ash/ calcium sulfite/gypsum

18 wt % solids

Hydrated lime 20 - 40 wt %
ash 33 - 44 wt %
calcium sulfite 0 - 30 wt %
gypsum 8 - 20 wt %
92° C

5.2.3 Calcium Sulfite and Gypsum

Peterson (1990) observed that calcium sulfite had little impact on the reaction between Clinch River fly ash and hydrated lime at reaction times through 8 hours. This observation is consistent with the hypothesis that the major impact of added sulfur species on the reaction is through changing the solution chemistry and not due to any change in product forming the surface area. The calcium sulfite has little impact on solution composition due to its limited solubility. There is evidence that sulfate is incorporated into the solid product but does not impact surface area (Chapter 8).

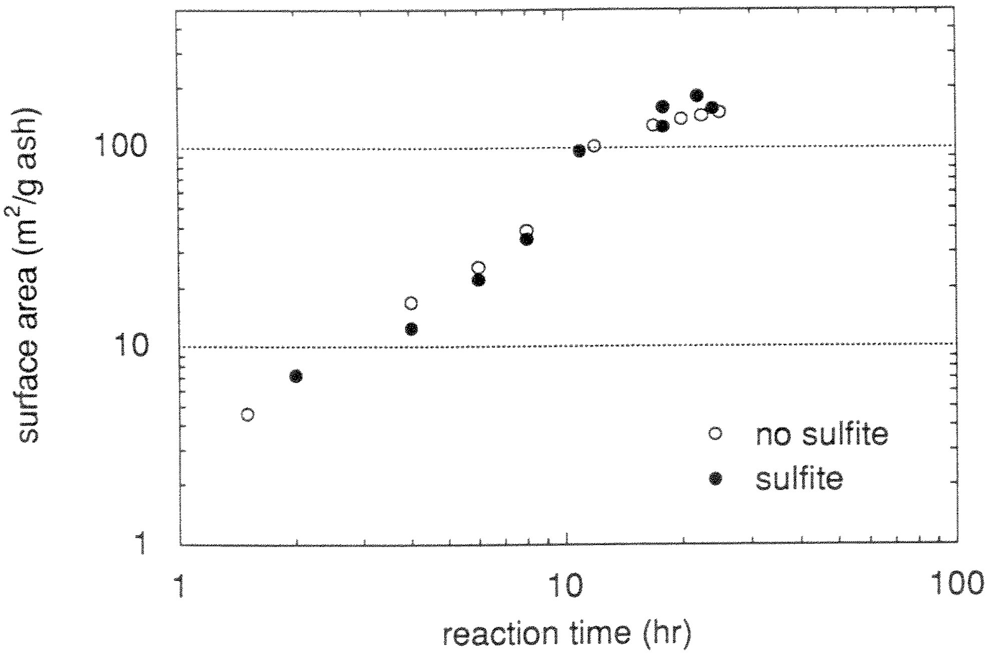

Figure 5.15 Calcium sulfite impact on surface area generation - Clinch River ash

Hydrated lime/Clinch River ash/ calcium sulfite/gypsum	hydrated lime 9 - 33 wt % ash 32 - 67 wt % calcium sulfite 0 - 33 wt % gypsum 9 - 33 wt %
22 to 35 wt % solids	98° C

The impact of sulfate incorporation into the product is discussed in Chapter 8. The impact of sulfite on the reaction was further examined by comparing experiments with only gypsum as an additive to experiments with gypsum and calcium sulfite present (Figure 5.15). There is little difference between the experiments with any difference within the reproducibility possible for the experiments (Appendix A). Solution chemistry was also comparable for the experiments.

5.3 REACTIONS WITH FLY ASH/HYDRATED LIME/CALCIUM CHLORIDE

The experiments performed with calcium chloride present primarily utilized Shawnee fly ash; Clinch River ash was used to determine if trends held from ash to ash. The concentrations of calcium chloride used in the study are several times greater than that expected if the coal was the only source of chloride (combustion freeing the chloride to be captured by the sorbent in the flue duct). This reaction system also allows the reaction to be studied at high calcium concentrations and moderate hydroxide levels.

5.3.1 Solution Chemistry

The reaction with calcium chloride present best approximates a batch reaction with constant solution chemistry. Typical solution chemistry changes over time are illustrated by a Shawnee fly ash experiment with 0.6 N calcium chloride in Figure 5.16. The calcium chloride provides a much increased calcium concentration in solution over the fly ash/lime case and also serves to buffer the hydroxide increase that would otherwise take place due to the dissolution of sodium and potassium from the ash. There are changes in calcium and hydroxide concentration during the reaction period but these are small compared to the changes observed in the fly ash/hydrated lime reaction. The significant increase in potassium and sodium concentration would not appear to impact surface area generation since these are released from the ash and are not incorporated into the product.

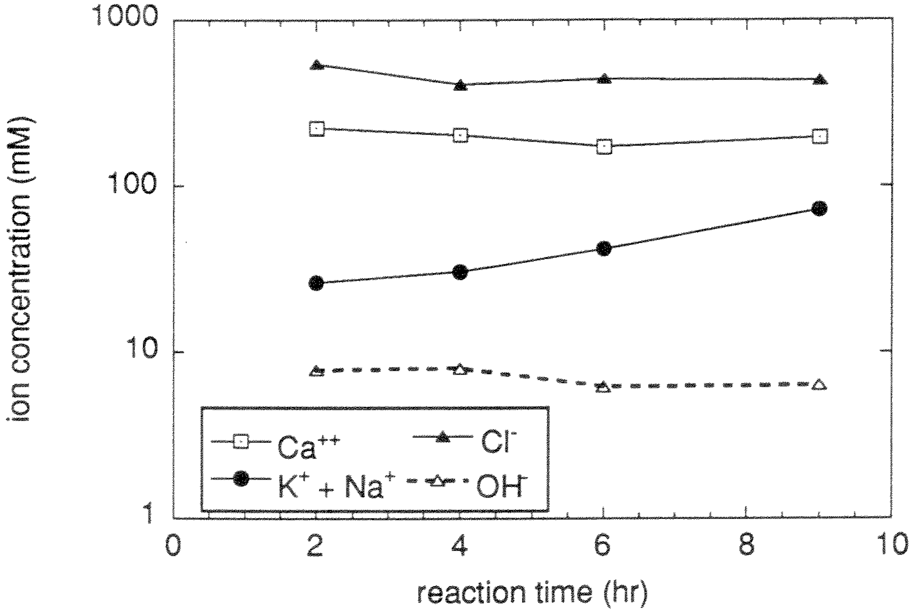

Figure 5.16 Solution chemistry in a reaction with calcium chloride present

Hydrated lime/Shawnee ash	1:2 weight ratio
Calcium chloride	0.6 N
17 wt % solids	92° C

The changes in calcium solution concentration seen in the 0.2 N calcium chloride case are more significant. This is especially true for Clinch River ash. For example, the calcium concentration decreased from 99 mM at 2.7 hours to 36.5 mM at 12 hours of reaction in one experiment. This change may be sufficient to impact the surface area generation in that experiment. There is some incorporation of chloride into the product as the chloride concentration typically decreases from 20 to 40 percent over the first 10 hours of reaction. The effect this has on the product material composition is examined in Chapter 8.

5.3.2 Surface Area

The product surface area generated in Shawnee fly ash calcium chloride batch reactions is presented in Figure 5.17. The points represent multiple batch reactions performed at varying hydrated lime to fly ash weight ratios (0.5 to 1) to ensure that calcium hydroxide was not exhausted, limiting the reaction. The surface area growth is exponential for the two calcium chloride concentrations examined with surface area growth proportional to the surface area. This type of behavior is only observed in reactions with high solution calcium concentration. It is seen to a limited extent for recycle (calcium sulfite and gypsum present) experiments at reaction times less than 12 hours.

The behavior may be due to the product surface area on the ash limiting the diffusion of the reactants to the reacting ash surface. Another possibility is that the product layer allows for the precipitation of the product species following reaction and that this controls the reaction rate. The higher calcium concentration system generates surface area more rapidly indicating that the availability of calcium to the reaction site can play a factor in the reaction rate even at these high calcium levels. The maximum surface area is 250 m^2/g ash regardless of the calcium chloride level; the reacted silica at this time was equivalent to 83 percent of the available silica as measured by x-ray fluorescence on the ignited coal. It is likely that all the silica in the amorphous phase had been reacted.

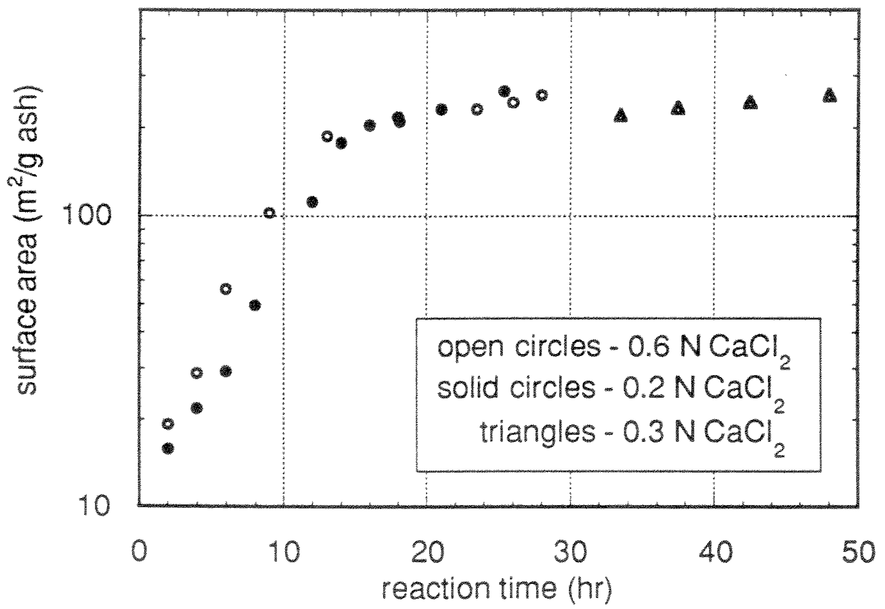

Figure 5.17 Surface area generation with calcium chloride present - Shawnee ash

Hydrated lime/Shawnee ash	1:2 to 1:1 weight ratio
Calcium chloride	0.2 to 0.6 N
17 wt % solids	92° C

The reaction rate at any given product surface area is independent of the solution calcium concentration after four hours of reaction time as the slopes of the two data sets are equal. The higher calcium concentration apparently accelerates the early reaction but after a product layer is developed on the ash, the reaction rate is limited by a step that is independent of dissolved calcium at these levels. It should also be noted that these rates, especially at the longer reaction times, are much greater than would be expected based on fly ash dissolution with no product layer at an equivalent bulk solution hydroxide level. Rates of the magnitude observed at 10 hours are typical of ash dissolutions at 0.1 M hydroxide, about ten times the level measured for this system. Comparisons to ash dissolution are examined more fully in the next section.

The behavior of Clinch River fly ash under similar conditions is provided in Figure 5.18. In this case, surface area development is linear over moderate reaction times. There is some exponential nature at low reaction times but it is not as consistent as for the Shawnee ash. The 12 hour 0.2 N calcium chloride point is lower than expected based on the trend as calcium hydroxide has been depleted at this time. The rates are again comparable after the short reaction times so that the main impact of high calcium chloride concentration is at short reaction times and is not a factor once surface area has been developed.

5.4 SYSTEM COMPARISON

The system comparison is subdivided into two major areas - comparison of the ADVACATE reaction rate with that of fly ash dissolution and comparison of ash product surface area generation rates and maximum surface areas in the experiments discussed thus far.

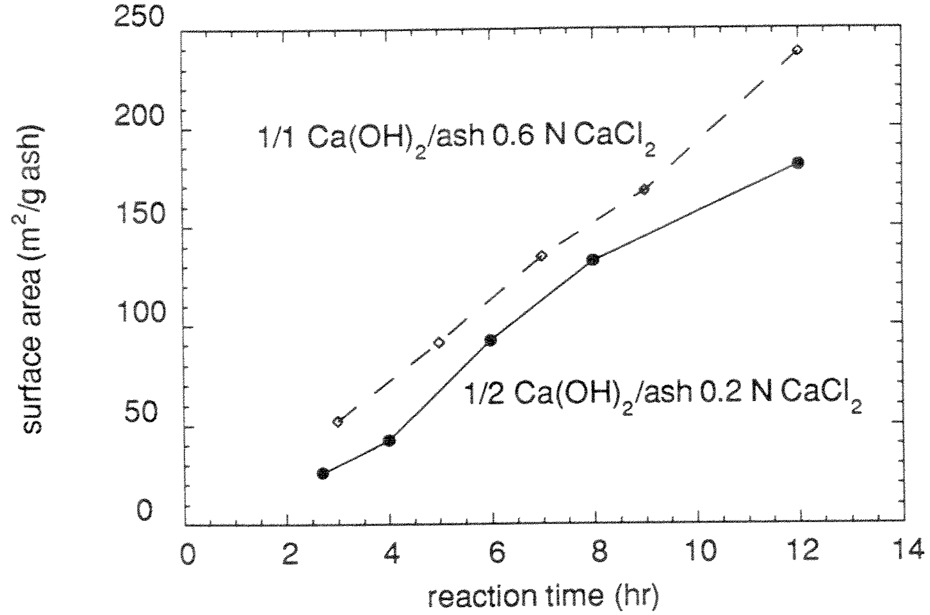

Figure 5.18 Surface area generation with calcium chloride - Clinch River ash

Hydrated lime/Clinch River ash	1:2 to 1:1 weight ratio
Calcium chloride	0.2 to 0.6 N
14 to 17 wt % solids	98° C

5.4.1 Comparison to Fly Ash Dissolution

The proposed reaction path for the formation of high surface area calcium silicate material has been the dissolution of ash due to high hydroxide concentration followed by reaction with calcium and subsequent precipitation as a solid phase. The simplest model of this reaction sequence assumes the hydroxide concentration at the dissolving ash surface is the same as that in the bulk solution and that ash dissolution controls the reaction rate since calcium hydroxide can dissolve in minutes. This model may be checked by comparing the rate of silicon dissolution and reaction with calcium hydroxide to the dissolution rate of the ash in a high hydroxide environment. The ash dissolution and data analysis performed (described in Chapter 4) was done in a manner similar to Peterson (1990).

A small amount of ash was slurried in water and sodium hydroxide added to set the hydroxide level. Disodium EDTA was added as a chelating agent to prevent any product formation on the ash that might inhibit dissolution or tie up the dissolving silicon in a solid phase. The results from a series of Shawnee fly ash dissolutions are provided in Figure 5.19. The data is plotted assuming a shrinking core sphere model (the reaction rate is proportional to exposed unreacted surface area) so if the data fit that model perfectly, a linear fit would result. This model does not precisely match the fly ash which is heterogeneous and has a distributed particle size but it provides an adequate fit except at very short reaction times.

There is a rapid dissolution over the first one-half hour (more pronounced at higher hydroxide concentrations) that is not typical of subsequent behavior. The rate drops off as the reaction time increases and the particle size decreases. Peterson found low calcium ash dissolution was first order in hydroxide and this ash behaves in a similar manner. The char does not appear to impact the ash dissolution rate (when compared to Peterson's work performed with other ashes).

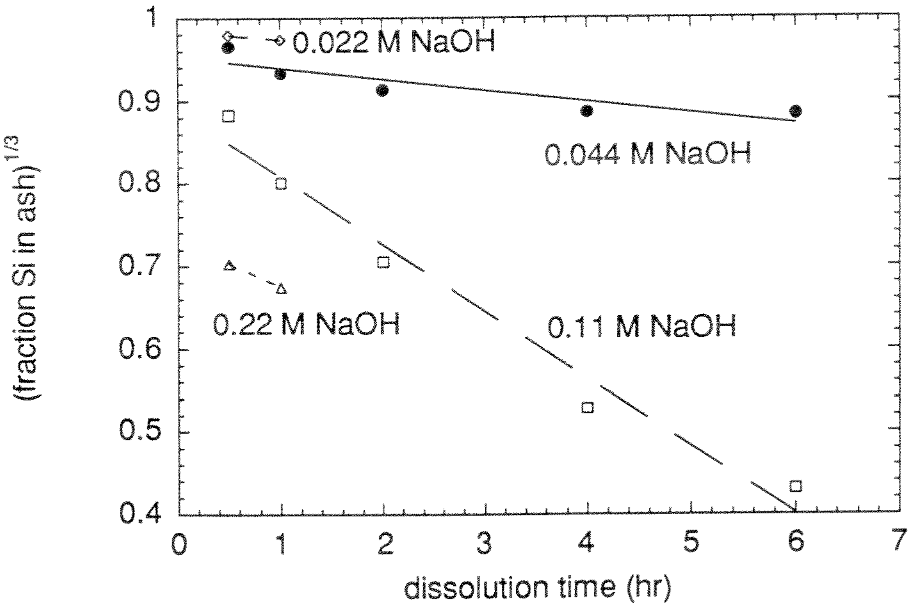

Figure 5.19 Shawnee fly ash dissolution under basic conditions

Shawnee ash dissolution at varying sodium hydroxide concentrations plotted so that a shrinking core model would be linear. Experiments took place in 225 ml water at 92° C with 0.3 g ash and 1.2 g EDTA.

An approximation of the reaction rate may be obtained by using the data on the plot to provide a reaction rate at the mean between any two points. This approximation can provide a comparison to the rates observed in the ash/lime reaction systems (calculated in a similar manner). The ash dissolution rates are shown in Figure 5.20 plotted against available silicon to the two-thirds power. This again should give a linear fit for a shrinking core model. The ash dissolution rate behaves as expected with the reaction rate decreasing with less exposed surface area as the ash dissolves. The ratio of the slopes of the two fitted lines should give an indication of the reaction order. If the order is assumed to be first, the ratio of the slopes is within 10 percent of that expected based on the hydroxide ratios. The y-intercepts of the lines are not close to 0; this illustrates the limitations of the model.

A Shawnee fly ash experiment with 0.2 N calcium chloride is also shown on the plot. The calcium chloride reaction exhibits an extreme behavior. The hydroxide concentration for this reaction is about 0.03 M. The dissolution or reaction rate is much greater than expected based on ash dissolution except at short reaction times and actually increases with extent of reaction (as was the case for the surface area). Fly ash/hydrated lime experiments with sodium hydroxide added exhibited a dissolution rate independent of hydroxide concentration or calcium hydroxide fraction.

For example, Shawnee fly ash experiments with 0.1 M sodium hydroxide fell far below the rate expected based on the ash dissolution experiments. These reactions showed a dissolution rate of about 10 mg Si/g ash-hr independent of extent of reaction over the reaction period. Fly ash/hydrated lime and simulated recycle experiments show an ash reaction unrelated (again approximately 10 mg Si/g ash-hr) to the solution hydroxide and do not follow a shrinking core reaction model as the reaction rate is constant with product formation rather than decreasing. These results show that bulk solution hydroxide concentration has little impact on the reaction rate once a product layer has formed on the ash particle.

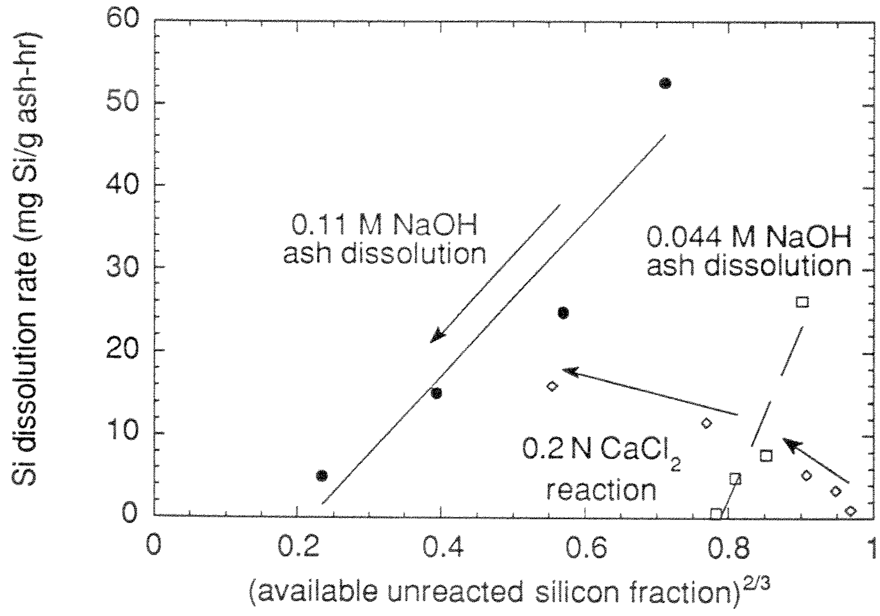

Figure 5.20 Comparison of Shawnee ash dissolution and reaction rates

Reaction rates obtained by the difference in reacted silicon over two samples and plotted at the average time of the interval. The plot allows for a linear fit of a shrinking core reaction model. Ash dissolution data taken from Figure 5.19. Reaction data from reactions with 0.2 N calcium chloride and a 1:2 to 1:1 hydrated lime to ash weight ratio at 92° C.

5.4.2 Maximum Surface Areas and Rates

The reaction systems examined (fly ash/hydrated lime, recycle and calcium chloride) exhibited considerably different solution chemistry over the course of the batch reactions. The two ions of major importance, calcium and hydroxide, showed only a general relationship to surface area generation. High calcium-low hydroxide reactions generally had lower surface area generation at short reaction times but far exceeded that of high hydroxide/low calcium reactions at reaction times greater than 10 hours.

The generation of surface area over any time period was not related to solution composition alone. For example, the calcium concentration varied from 200 mM in the 0.6 N calcium chloride case to less than 3 mM in the fly ash/hydrated lime case at comparable reaction times and rates. Hydroxide concentration ranged from about 0.01 to 0.05 N. Quantities such as calcium hydroxide activity (approximated by concentrations) also showed little relationship to surface area generation. Solution composition was dependent on the reaction history as calcium hydroxide reactivity declined with time in the fly ash/hydrated lime reactions. The only generalization immediately apparent is that when the calcium concentration was less than 2 mM, significant surface area generation did not occur.

Product surface area generation may be compared in two ways, the rate and the maximum achievable surface area. Maximum surface area products achieved for each of the systems studied is provided in Figure 5.21. The higher surface area Shawnee ash created a higher surface area product in all the systems studied despite the greater fraction of silica in Clinch River ash. This apparent anomaly is not unexpected since the pozzolanic reactivity of fly ash at low temperatures has not been well correlated with silica fraction or consistently with surface area (Joshi and Marsh, 1987).

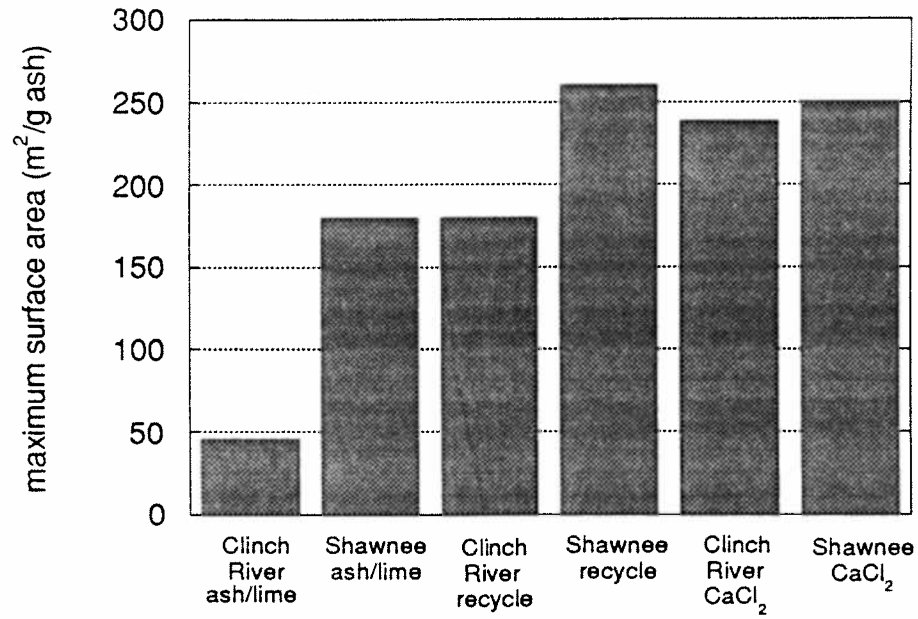

Figure 5.21 Maximum batch reaction surface area obtained for ashes studied

Maximum surface areas generated per g ash for each ash and additive studied. The Clinch River calcium chloride reaction represents the surface area at 12 hours of reaction.

Shawnee ash systems with gypsum and calcium chloride present create surface area of about the same magnitude and utilize over 80 percent of the silica as measured by selective dissolution and X-ray fluorescence analysis performed on the ignited coal. A comparison of the ultimate surface areas of the recycle and fly ash/hydrated lime system products indicate that solution chemistry might be limiting surface area growth for Clinch River ash as the surface area in this case is one quarter the recycle surface area while for the Shawnee ash, it is about 70 percent.

Table 5.3 Surface area generation values for batch reaction systems

System	**Time of area generation (hr)**	**Surface area generation rate (m^2/g ash hr)**
Clinch River fly ash/lime	6	6.5
Shawnee fly ash/lime	18	10
Clinch River recycle	18	10
Shawnee recycle	25	10
Clinch River $CaCl_2$	12	20
Shawnee $CaCl_2$	12-14	18-21

The average rates of surface area growth from ash to ash are similar (Table 5.3). Surface area formation continues in a linear manner at about 10 m^2/g-hr for both ashes in the fly ash/hydrated lime and recycle reaction systems. The calcium chloride system generates area at more than twice the rate and the growth is much larger at longer reaction times. The behavior of these systems indicate that the additives provide no advantage unless batch reaction times are expected to be greater than six hours. Higher product surface areas require longer reaction times and in this case, the additives studied would be beneficial.

Chapter 6

CSTR Reaction System

The Continuous-flow Stirred Tank Reactor (CSTR) allows for a reaction environment considerably different than the batch reactor. The solution chemistry in the flow system is approximately constant when steady-state has been reached while the solid reactants have a dispersed reaction history. These significant differences limit the use of batch reaction experiments to predict the performance of the CSTR. The first section of this chapter discusses using batch reaction data to predict CSTR product and presents a segregated flow model that is useful under certain conditions. The bulk of the chapter is dedicated to experimental results for CSTR experiments performed with Clinch River and Shawnee ashes. The results are compared to each other and with the segregated flow prediction.

6.1 APPROXIMATION FROM BATCH REACTION

The simplest approximation of the flow reactor from the batch reaction would be to treat the reaction as a simple homogeneous reaction and use the kinetic data generated from the batch reaction in the CSTR design equation. This simple method is inadequate, however, not only because of the different possible rate limiting processes described in the previous chapter but because of the nature of the batch reaction data. In all cases, the reaction rate is constant or actually increasing with reaction time until the reaction almost ceases. A method that treated the reaction system as homogeneous would not accurately represent the system and would predict greater conversion than would be the case in the operating system. A better approach would consider the slowest step in the reaction process that limited the rate. In most cases this would be the dissolution of fly ash and this would lead to the examination of individual ash particles. Each ash particle could be treated as a separate entity with a residence time in the reactor provided by the ideal CSTR residence time distribution (Figure 6.1).

6.1.1 Segregated Flow Model

A segregated flow model may be used for slurry systems where the reaction takes place on the solid phase. The reaction is not homogeneous but each solid particle is segregated such that the reaction on each is independent of the others in the reactor. The reaction to form calcium silicates does not always match the requirements necessary for this model but this model approximates the behavior in this system as well as any simple model.

6.1.1.1 Justification

SEM photographs of the sorbent have shown that product is formed on the surface of the ash (Jozewicz and Rochelle, 1986, Izquierdo, 1992). Examples of this are shown in Figures 6.2 and 6.3 for the Clinch River recycle and fly ash/hydrated lime CSTR experiments. Fresh unreacted ash is seen adjacent to reacted ash. The product appears as the white porous material on the surface of the ash particle. A batch reaction product is shown in Figure 6.4. In this case, all the ash shows evidence of reaction since all particles have the same time history in the reactor.

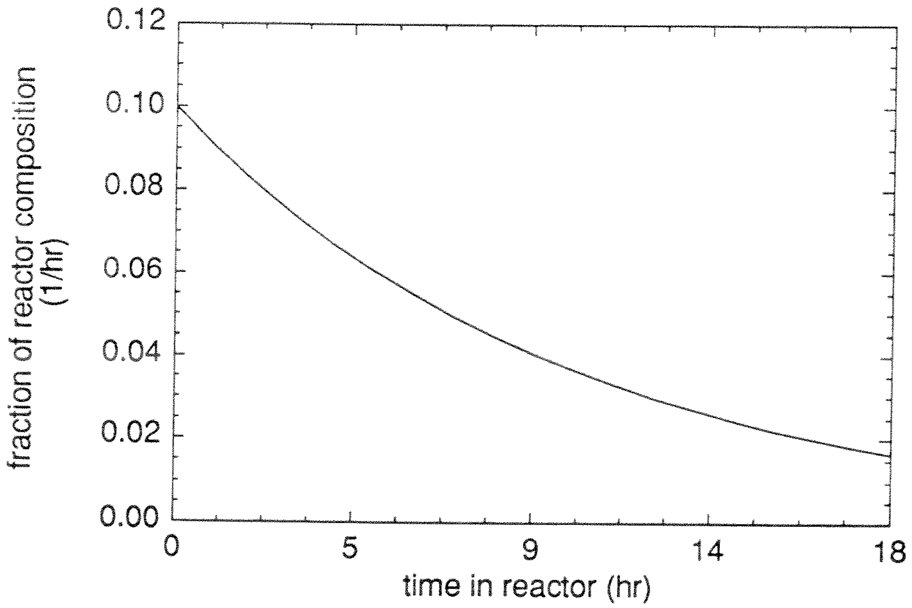

Figure 6.1 Reactor time history of the product stream from an ideal CSTR

Curve assumes ideal CSTR behavior with a 10 hour residence time. The total outlet flow is obtained by integrating the curve from time zero to infinity.

The dissolution of the fly ash particle has been assumed to be the rate determining step in the reaction to form surface area. If this holds true, the ash particles could be treated as being segregated from each other with dissolution and reaction taking place on the ash surface. In addition, the batch reaction system should be insensitive to the fraction of calcium hydroxide added to the reaction. This was the case for batch reactions performed with gypsum and calcium chloride present for the ratio of reactants examined. This was not the case for the fly ash/hydrated lime system so it is clear that certain assumptions must be met prior to using a segregated flow model to predict CSTR performance.

Figure 6.2 SEM photograph of product from a fly ash/hydrated lime CSTR

The material shown is from a Clinch River CSTR with 9.8 hour residence time. The reaction was performed at 98° C with a solids feed of one part hydrated lime to four parts ash.

This approximation requires that the CSTR have perfect mixing and that a representative product stream is taken from the reactor. The bench scale CSTR was verified to be a well mixed slurry visually and was checked through the use of mixing correlations (Gates et al., 1976). A final check was performed by taking a large volume sample from the reactor and comparing it to the last flow sample results (Chapter 4). These showed the reactor to be well mixed.

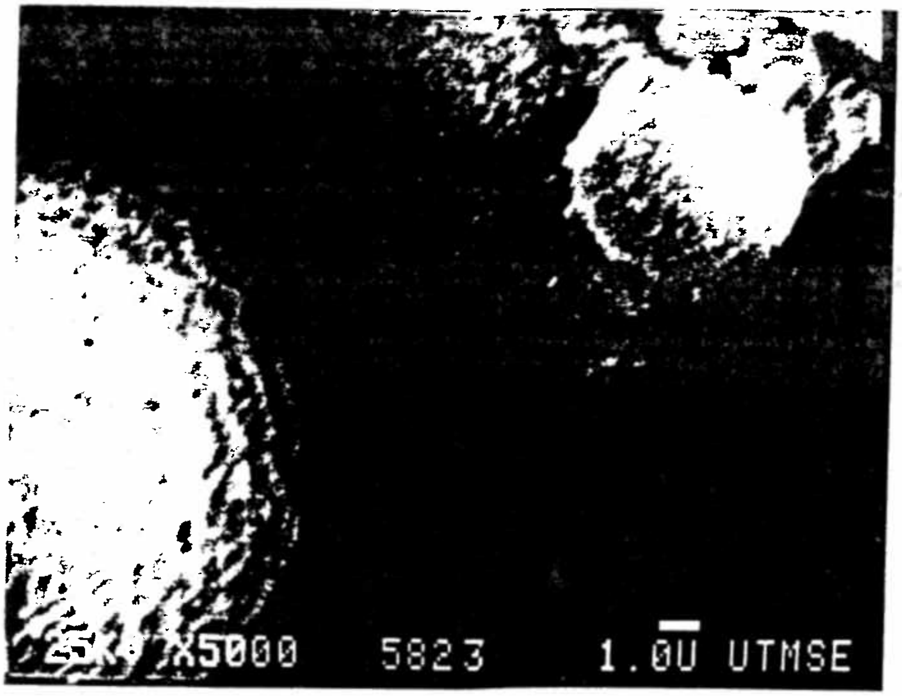

Figure 6.3 SEM photograph of product from a CSTR with recycle materials

The material shown is from a Clinch River CSTR with 5 hour residence time. The reaction was performed at 98° C with a solids feed of hydrated lime/ash/calcium sulfite/gypsum in a 2:8:1:1 weight ratio.

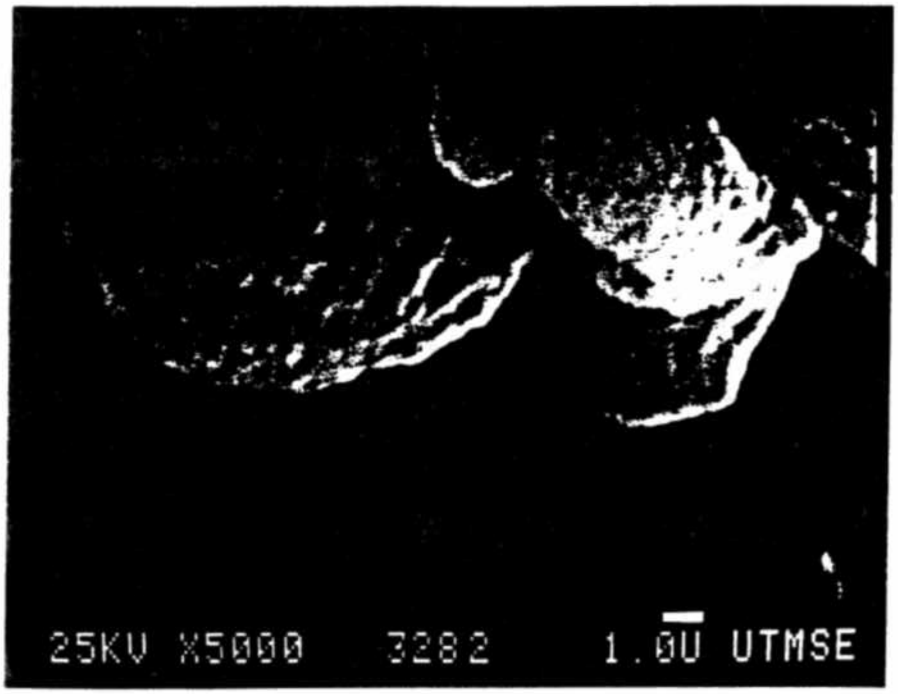

Figure 6.4 SEM photograph of product from batch reaction with recycle materials

The material shown is from a Clinch River batch reactor after 22 hours of reaction time. The reaction was performed at 98° C with hydrated lime/ash/calcium sulfite/gypsum in a 4.8:4:3:1 weight ratio.

6.1.1.2 Assumptions

Two requirements are necessary for the segregated flow model to hold in the calcium silicate reaction. First, the dissolution and reaction at the surface of the ash particle must be limiting the reaction rate throughout the reaction period. If the dissolution of calcium hydroxide should limit the area generation late in the reaction, the batch system may not act the same as the CSTR where only one mechanism will limit the reaction producing surface area.

Secondly, reaction solution chemistry must be similar throughout the batch reaction and in the CSTR. This does not require that all ions in solution be constant but that the reaction rate be insensitive to any changes that occur. This is only true when there is sufficient calcium hydroxide to supply calcium to the reaction site as both calcium and hydroxide concentrations can impact the reaction behavior. If there is constant solution chemistry, the CSTR product surface area may be predicted from the batch results. Each ash particle will act as a batch reactor in the CSTR environment with the particle reaction time set by the residence time distribution for the CSTR.

6.1.1.3 Method

The expected CSTR product surface area (or other indicator of reaction product) is the result of integrating over the reactor product outlet stream containing the ash particles. This is done by taking the surface area as a function of time from the batch reaction multiplied by the residence time distribution (for that residence time) from time zero to infinity to account for all possible ash particles. The reactor is well mixed and is assumed to have an ideal residence time distribution. In equation form,

$$P(\tau) = \int_0^\infty \frac{p(t)\exp(-t/\tau)}{\tau}\,dt$$

where

τ = residence time

$p(t)$ = product from batch reaction at time t

$P(\tau)$ = product from CSTR at residence time τ

$\frac{\exp(-t/\tau)}{\tau}$ = residence time distribution curve for an ideal CSTR

The complex reaction may be reduced to a relatively simple form with the assumptions presented. This relationship will not hold if there is a significant difference in the solution chemistry between the batch reaction used to determine the rate data and the CSTR. Solution chemistry may be impacted by the dissolution of potassium and sodium from the ash. The batch reaction may be impacted significantly by the concentration of several ions such as calcium and hydroxide (Peterson and Rochelle, 1988). If the concentration of these ions varies during the batch reaction, the rate data may not be used in this manner. The same analysis is also used with other measures of reaction such as reacted silicon.

6.1.1.4 Examples

The batch data was fit to a simple linear or exponential function to facilitate the use of the data in the expression above to generate a curve of predicted CSTR product with residence time. Figure 6.5 shows how the reacted silicon was fit for the Shawnee ash calcium chloride experiments. An exponential fit was used through the first 12 to 14 hours followed by a linear fit. In this case, the exact linear fit was not used but a horizontal line was used as little reaction occurred beyond 14 hours. Similar fits for surface area were used for the rest of the systems and ashes studied and these are provided in Table 6.1.

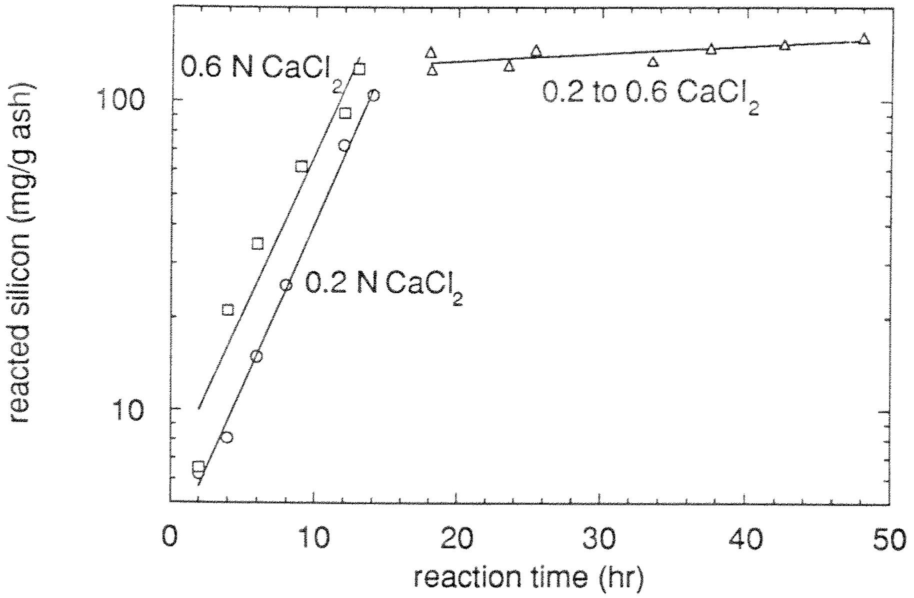

Figure 6.5 Fit of Shawnee batch reaction with calcium chloride reacted silicon

Hydrated lime/Shawnee ash	1:2 to 1:1 weight ratio
Calcium chloride	0.2 to 0.6 N
17 wt % solids	92° C

The CSTR product prediction differs significantly from the surface area obtained in a batch reaction for the same residence time. In the case of fly ash/hydrated lime or recycle systems, the model predicts a lower surface area for any given residence time. In the case of the calcium chloride system, the opposite is true. The calcium chloride batch reaction surface area as a function of time was fit with an exponential curve fit during the period of area growth, leveling at 250

m^2/g ash similar to that for the reacted silicon. The prediction is shown along with a portion of the batch reaction data in Figure 6.6. The increasing surface area growth results in a much higher product surface area from the CSTR than in the batch reaction at residence times between 4 to 8 hours. For example, at six hours with 0.2 N calcium chloride, the batch reaction provides a product with a surface area of 29 m^2/g ash whereas the CSTR prediction is 53 m^2/g ash.

Table 6.1 Data fits of batch reaction surface area data

Clinch River		
1/4 fly ash/hydrated lime	$t < 4.6$ hr	Area = $6.3t + 5$
	$t > 4.6$ hr	Area = 29
1/2 fly ash/hydrated lime	$t < 6$ hr	Area = $6.5t + 5$
	$t > 6$ hr	Area = 44
recycle materials	$t < 18$ hr	Area = $8.9t$
	$t > 18$ hr	Area = 160

Shawnee		
recycle materials	$t < 5$ hr	Area = 20
	$5\text{ hr} < t < 25$ hr	Area = $11.5t + 20$
	$t > 25$ hr	Area = 250
0.2 N calcium chloride	$t < 16.3$ hr	Area = $9.6\exp(0.2t)$
	$t > 16.3$ hr	Area = 250
0.6 N calcium chloride	$t < 13.9$ hr	Area = $13.5\exp(0.21t)$
	$t > 13.9$ hr	Area = 250

All surface areas in terms of m^2/g ash.

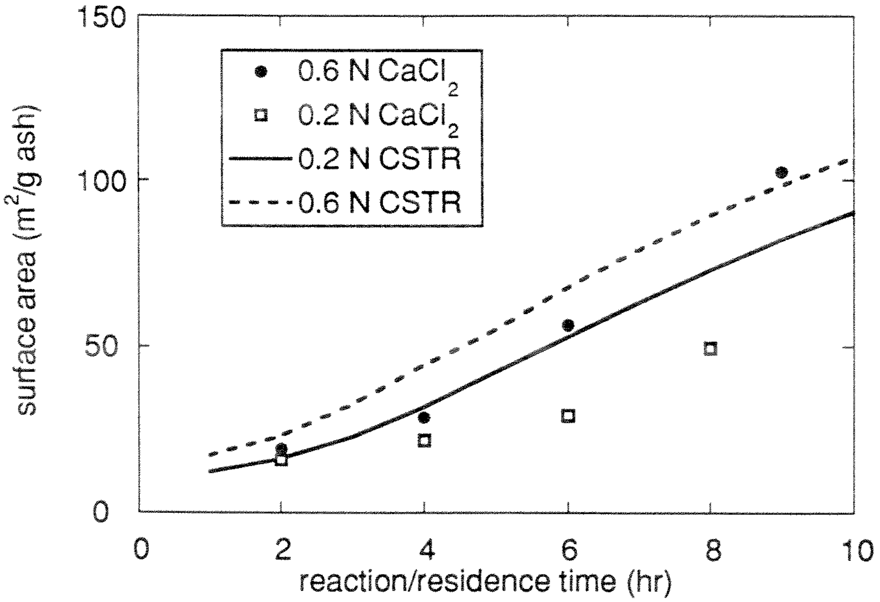

Figure 6.6 Comparison of batch data to CSTR model for calcium chloride system

Batch data is the same as that shown on Figure 5.17. The CSTR curves are obtained by using the batch reaction data in the CSTR product prediction expression.

The CSTR apparatus required manual control of water bath temperature, inlet water feed rate and inlet solids feed rate to maintain a constant temperature, solids concentration and residence time throughout the reaction period. The manual control and length of the runs required to reach a steady state resulted in some variation in these parameters over the course of the reaction. This effect is described more fully in Chapter 4.

While there were variations about the average for each control variable, there was not a trend for any and therefore any variations have little effect on the CSTR product. The CSTR was generally sampled at least three times following three residence times of operation and if any trend or large variations were observed, it will be noted. The last sample was typically a large volume sample of the reactor to ensure that the outlet flow was representative of the composition of the CSTR. This sample was filtered hot while the outlet samples cooled during the collection time so the solution composition of these two types of samples will not be the same.

6.2 CSTR EXPERIMENTS

The CSTR experimental results are discussed in the following sections. They are divided into the three major reactions systems, calcium chloride, simulated recycle (gypsum) and fly ash/hydrated lime, and are presented from those best fit by the model approximation to the worst fit. A data summary of CSTR results is presented in Table 6.2. The complete experimental results are provided in Appendix B.

6.2.1 Reaction with Calcium Chloride Present

The calcium chloride system best approximates the batch reaction with constant solution chemistry and therefore is most likely to be fit by the segregated flow model. CSTR reactions were studied with Shawnee ash and are compared with the predictions at two calcium chloride concentrations, 0.2 and 0.6 N. Two indicators of reaction, surface area and reacted silicon, are examined.

Table 6.2 CSTR Data Summary

Experiment[1]	Residence Time (hr)	Surface area (m^2/g)	% $Ca(OH)_2$ Reacted	pH	Na^+ + K^+ (mM)	Ca^{++} (mM)	$SO4^=$ or Cl^- (mM)
Clinch River Fly Ash							
1/4	6.0	19.7	65	12.46	33.7	2.3	-
1/4	9.8	22.2	84	12.58	29.9	8.1	-
Calcium Chloride							
2.5/4 0.25 N	16.9	77.8	88	12.16	79.1	69.0	-
Gypsum & Calcium Sulfite							
1/4/0.5/0.5	5.0	27.1	76	11.95	16.9	25.9	16.3
1/4/0.5/0.5	8.6	32.8	93	11.88	19.0	13.3	20.1
1/4/0.5/0.5	8.6	52.5	93	11.62	21.4	16.0	21.5
1/4/0.6/0.4	12.6	40.7	97	11.28	17.9	11.1	19.7
1.8/4/0.5/0.5	12.3	46.1	88	11.93	32.7	10.3	15.1
3/4/0.7/0.7	17.5	26.6	83	11.94	41.7	21.9	15.3
1/8/1/1	5.1	13.2	78	11.24	11.0	24.0	12.5
3/4/0.7/0.7	17.5	27.4	80	12.51	64.8	5.8	15.7
2.8/4/0.7/1.2	16.8	20.2	81	12.43	35.3	24.2	18.1
Shawnee Fly Ash							
1/4	3.0	15.7	33	12.48	5.3	24.9	-
1/4	6.4	38.8	82	12.53	15.7	13.8	-
1/4	9.2	36.5	92	12.43	16.3	8.7	-
1/2	5.9	50.0	60	12.57	19.1	11.7	-
1/2	8.8	45.7	66	12.60	38.0	9.9	-
1/2 ground	3.8	21.1	34	12.53	6.5	19.6	-
1/2 ground	6.5	52.3	67	12.56	20.5	11.4	-
1/4	2.1	14.5	22	12.53	7.3	35.9	-
1/1	5.4	49.4	42	12.69	28.3	11.3	-
1/1	10.0	55.2	48	12.73	38.4	9.6	-
Calcium Chloride							
1/2 0.21 N	3.9	23.4	33	12.16	13.3	110	206
1/2 0.22 N	8.8	71.1	80	12.05	33.4	62.9	195
1/1 0.3 N	8.7	52.0	54	12.28	24.8	85.5	224
1/4 0.2 N	5.9	35.1	66	12.13	19.0	89.5	172
1/2 0.2 N	5.7	33.9	59	12.18	26.7	101	180
1/2 0.2 N	5.9	37.6	65	12.30	30.4	105	196
1/1 0.28 N	15.9	76.5	62	12.26	39.2*	78.5	-

Experiment[1]	Residence Time (hr)	Surface area (m^2/g)	% $Ca(OH)_2$ Reacted	pH	Na^+ + K^+ (mM)	Ca^{++} (mM)	$SO4^=$ or Cl^- (mM)
Gypsum							
2/4/0/1.5	5.6	33.9	60	12.42	11.5	22.7	14.3
3/4/0/1.2	9.0	31.8	57	12.44	13.6	25.2	14.7
4/4/0/1	12.9	58.7	62	12.52	15.5*	21.9	-
3/4/0/1	8.7	58.6	55	12.49	-	26.0	-
4/4/0/1	15.0	57.4	64	12.45	-	-	-
4/4/0/1	18.4	57.4	74	12.09	-	-	-

* - does not include Na^+

[1] - reactant weight ratio hydrated lime/fly ash/calcium sulfite/gypsum

6.2.1.1 Surface Area

The predicted surface area for the CSTR is plotted on Figure 6.7 with the results of CSTR experiments using Shawnee fly ash. The CSTR experiments were performed at three different hydrated lime to fly ash weight ratios (0.25, 0.5, and 1.0) and at approximately four residence times from 4 to 16 hours. The calcium chloride concentration for the CSTR reactions was between 0.2 and 0.3 N as calculated by a mass balance around the reactor. The arrows on the plot indicate the trend of the reaction product with time if a trend was noted. The reactions with a trend were not confirmed to be at steady state based on the sample analysis.

One would expect the CSTR results to lie between the two predicted curves if the CSTR model were valid. This is the case for the experiments of less than 6 hours residence time as only the 0.25 g calcium hydroxide/g ash, 6 hour residence time experiment did not match the lower curve. This was likely due to not achieving steady state or having insufficient calcium hydroxide available for

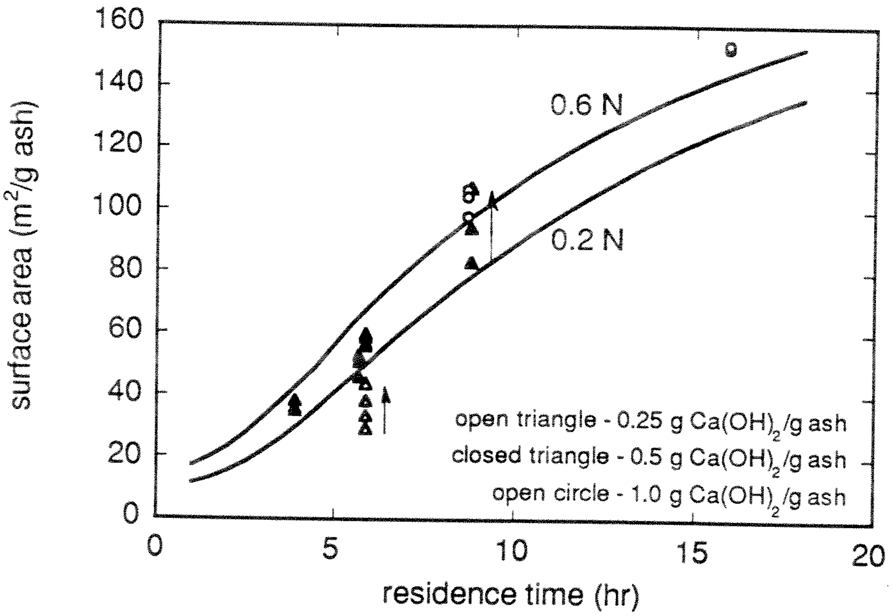

Figure 6.7 CSTR product surface area - Shawnee ash with calcium chloride

All samples taken after three residence times of reactor operation after startup are shown. Any trend in the data with reactor operating time is indicated by the arrows. The curves are the predicted performance from the segregated flow model.

Hydrated lime/Shawnee ash	1:4 to 1:1 weight ratio
Calcium chloride	0.2 to 0.3 N
16 to 21 wt % solids	92° C

reaction. There is no apparent benefit in adding excess hydrated lime to the CSTR feed as seen in the nine hour residence time experiments, except that it may decrease the time necessary for the reactor to achieve steady state. This again is consistent with the model assumption of the ash dissolution and reaction being rate determining. The 9 and 16 hour experiments both outperformed the predicted value for product surface area by a small amount. This deviation may be caused by an increase in product hydration due to some incorporation of calcium chloride into the product at longer reaction times biasing the surface area data at long reaction times. It might also be due to errors associated with the determination of CSTR residence time.

6.2.1.2 Reacted Silicon

This behavior was examined further by checking another indicator of reaction - acid soluble silicon measured by selective dissolution to determine the amount of silica reacted from the ash. The batch reaction data for this indicator exhibited behavior similar to the surface area with exponential growth over about 12 hours (Figure 6.5). This data was fit and used to generate the predicted CSTR product silicon shown in Figure 6.8. The differences between the two plotted curves is again due to the differences in calcium concentration. The experiment results behave much like the surface area points, with the 9 and 16 hour experiments slightly exceeding the predicted value.

6.2.2 Reaction with Recycle (Gypsum and Calcium Sulfite) Present

The recycle reaction is designed to most closely approximate the behavior of an operating system. This system has fairly constant batch solution chemistry and the CSTR behavior is similar to that predicted by the model at CSTR residence times less than 12 hours. Experiments were performed with Clinch River and Shawnee ashes. There was unusual behavior noted for Clinch River ash in the CSTR for residence times greater than 16 hours. This behavior is examined in some detail with the CSTR experimental results while the resulting product material is discussed more fully in Chapter 8.

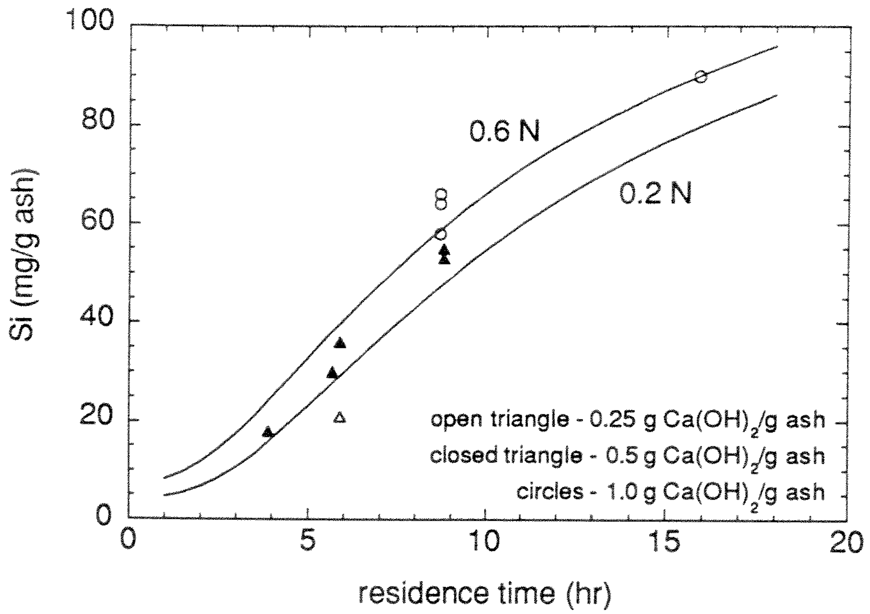

Figure 6.8 CSTR product silicon - Shawnee ash with calcium chloride

All samples taken after three residence times of reactor operation following startup are shown. The curves are the predicted performance from the segregated flow model. Conditions are the same as those for Figure 6.7.

6.2.2.1 Surface Area

The gypsum or recycle system includes calcium sulfate dihydrate (gypsum) in addition to fly ash and hydrated lime as reactants. The gypsum serves to buffer the solution, minimizing the hydroxide ion concentration change during the reaction period. This maintains the dissolved calcium concentration at about 20 mM although it may decrease by as much as a third during the batch reaction period. There may be a similar increase in hydroxide concentration. This moderately stable solution chemistry may allow a prediction from batch results similar to that used in the calcium chloride case.

The prediction and CSTR experimental results are shown in Figure 6.9 for Shawnee fly ash. CSTR experiments performed with Shawnee fly ash contained no calcium sulfite hemihydrate. This procedure was used to minimize feeder problems with the small particle size and high fraction of calcium material in the feed (as discussed in Chapter 4). The impact of sulfite on the reaction was shown to be minimal in the batch reaction (Chapter 5).

There is a significant variation in the CSTR experimental results, especially in the experiments performed at a residence time of about 9 hours. The CSTR results follow the prediction trend except for the variation at this time. There is also scatter within each run which may be due to difficulties in feeding the low particle size material despite the precautions taken to minimize feeder problems. The change in product surface area as residence time is increased from 13 to 18 hours is minimal.

A similar set of experiments were performed with Clinch River fly ash and the CSTR experimental points are provided on Figure 6.10. There were two experiments performed at low calcium hydroxide fractions with this ash (10 and 17 weight percent for the 5 and 12 hour residence times respectively) and they are indicated by the boxes on the plot. Additional calcium hydroxide was added to the solids feed in each of the two cases when the experiments were repeated. The product surface area matched the surface area predicted by the model in the new experiments. This behavior is the same as that of the calcium chloride system

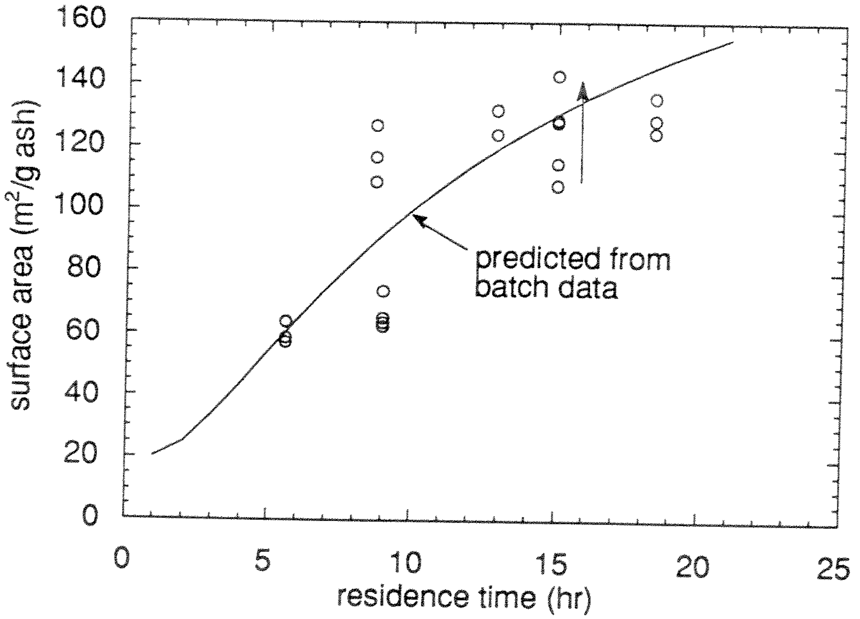

Figure 6.9 CSTR product surface area - Shawnee ash with recycle materials

All samples taken after three residence times of reactor operation after reactor startup are shown. The curves are the predicted performance from the segregated flow model. The arrow shows the trend of the 15 hour reaction product with time.

Hydrated lime/Shawnee ash/ gypsum	hydrated lime 27 to 44 wt % ash 44 to 53 wt % gypsum 11 to 20 wt %
16 to 21 wt % solids	92 and 98° C

where once a sufficient fraction of calcium hydroxide was available, the reaction product matched the predicted surface area.

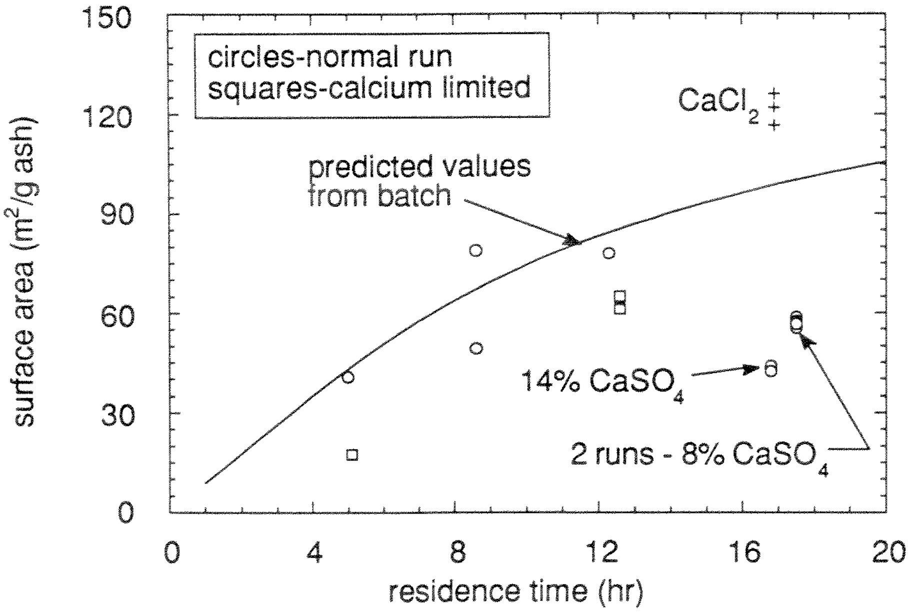

Figure 6.10 CSTR product surface area - Clinch River ash with recycle materials

All samples taken after three residence times of reactor operation following reactor startup are shown. The curves are the predicted performance from the segregated flow model. The squares indicate results from experiments limited by calcium hydroxide available for reaction. Pluses indicate data from an experiment performed with calcium chloride rather than recycle materials.

Hydrated lime/Clinch River ash/ gypsum/calcium sulfite	hydrated lime 9 to 36 wt % ash 46 to 73 wt % calcium sulfite 8 to 10 wt % gypsum 8 to 14 wt %
Calcium chloride	0.25 N
18 to 24 wt % solids	98° C

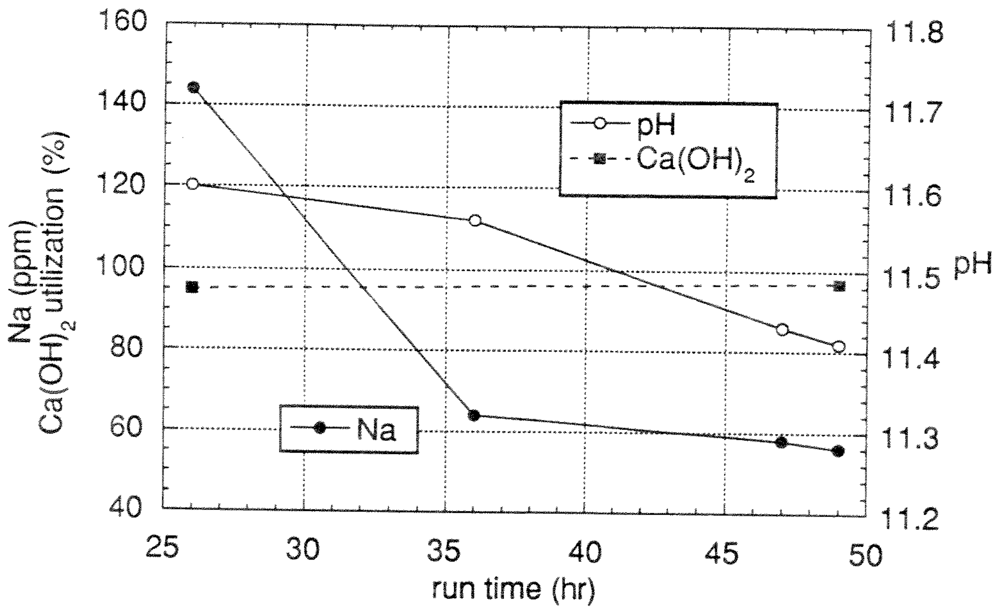

Figure 6.11 Solution behavior in a calcium hydroxide limited CSTR

Clinch River fly ash CSTR with 12.6 hour residence time started at time zero.

Hydrated lime/Clinch River ash/ calcium sulfite/gypsum	1:4:0.6:0.4 weight ratio
21 wt % solids	98° C

The behavior of the CSTR under calcium hydroxide limiting conditions is illustrated in Figure 6.11. The dissolution of calcium hydroxide is as high as possible as indicated by the constant calcium hydroxide utilization over the operating time of the CSTR. The hydroxide level, as measured by pH, and sodium level decreases over time because there is insufficient calcium hydroxide available to maintain hydroxide concentration and therefore ash dissolution. This is not observed until later in the CSTR run because at time zero, there is fresh ash and calcium hydroxide in the reactor. Only when the reactor approaches steady state does calcium hydroxide concentration become low enough to limit the reaction rate.

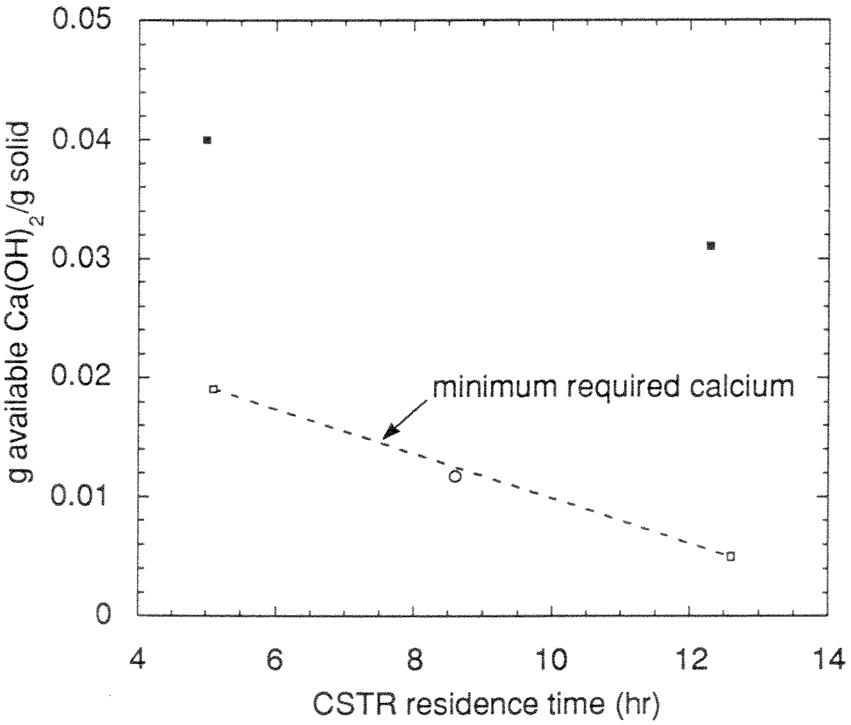

Figure 6.12 Calcium hydroxide fraction required for optimum recycle CSTR

The open squares represent CSTR experiments with insufficient calcium hydroxide. The samples are the same as those from Figure 6.10 except the experiments with a residence time greater than 13 hours are excluded.

This behavior can be used to obtain a curve indicating the minimum required calcium hydroxide to prevent its dissolution from being reaction rate controlling. Figure 6.12 is an example of such a plot, showing the calcium hydroxide available for dissolution as a function of residence time for the Clinch River fly ash reactions. The Shawnee ash experiments were performed at a higher ratio of calcium hydroxide to ash and are not shown. The line connects the two results from the two experiments performed with a low calcium hydroxide fraction. Product surface area from these two experiments fell well below the predicted value. Since the calcium hydroxide dissolution limits the reaction in these cases, a normal surface area product point should not fall below the line.

The experiments were also performed at a greater calcium fraction and the calcium hydroxide available for dissolution was much higher as shown. The 8.6 hour residence experiment that had significant variation in product surface area also fell on this line, indicating that the experiment may have been starved for calcium hydroxide at times so any small variation in solids feed could have a significant impact on the product. This may be causing the product variation observed in that experiment.

Clinch River ash CSTR product surface area falls off at residence times of about 16 hours (Figure 6.10). Two separate CSTR experiments were performed with a 16 hour residence time and these gave almost identical results. An experiment was performed with calcium chloride to determine if this system had the same qualitative behavior as the Shawnee ash and the surface area was again verified to be high at this residence time (as indicated by the +). The lower surface area with long residence time was unique to the recycle system.

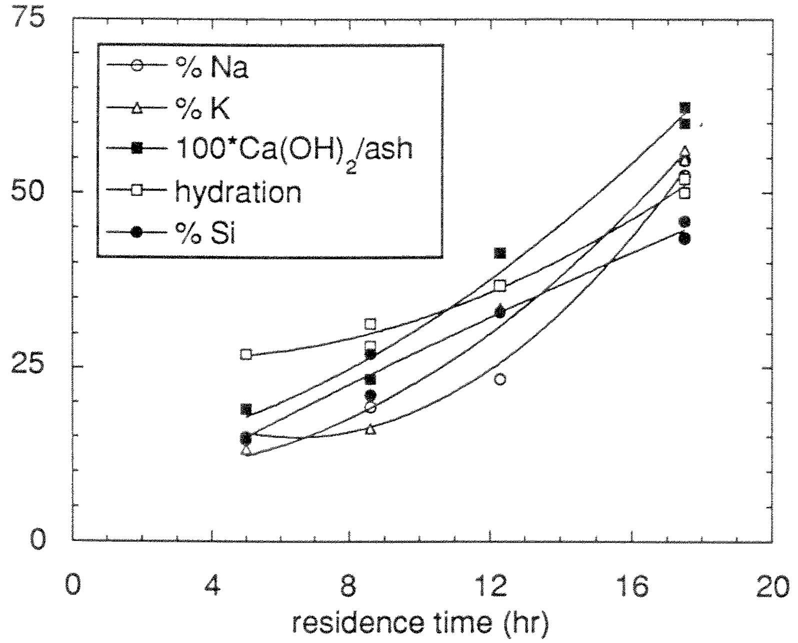

Figure 6.13 CSTR reaction indicators - Clinch River recycle system

CSTR conditions are the same as though on Figure 6.10. The percentages are based on the ash composition provided in Chapter 4. The reacted $Ca(OH)_2$ is based on a weight fraction and the hydration is 1000 times the weight fraction lost between 150 and 350° C by TGA.

6.2.2.2 Long Residence Time Factors

The reason for this behavior was investigated further by first repeating the experiment with a higher gypsum fraction present. This run is indicated by the triangles on the plot (Figure 6.10) and showed a lower surface area, indicating that sulfate may be the species causing the reduction in surface area. Another check was done with other indicators of reaction: sodium and potassium in solution from ash dissolution, reacted calcium hydroxide as determined by the sugar dissolution technique, and reacted silica from the ash as determined by selective dissolution. All of these measurements are shown in Figure 6.13. The increase in reacted silica is almost linear with residence time because silica continued to react in the batch system at times beyond 30 hours so that a tapering off of the reacted silica will not be apparent until longer residence times are achieved. This additional silica reaction did not result in greater surface area. The same general trend is observed in the other reaction indicators.

The material was also examined by SEM and X-ray diffraction to look for any morphological changes that might be causing the decrease in surface area despite the reaction of the ash. There was no significant difference noted between these and samples from other experiments. This indicates that a low surface area amorphous or ill-crystallized sulfate species may be forming and inhibiting area formation or plugging pores. These material analyses are discussed in more detail in Chapter 8.

6.2.2.3 Silicon comparison

The silicon reacted from the ash in the CSTR does not correlate with the batch reaction as well as the surface area does. Reacted silicon for Shawnee and Clinch River ash reactions is shown in Figures 6.14 and 6.15. The CSTR points are generally higher than the batch reaction for a given reaction time and reacted silicon is therefore greater than would be predicted by the segregated flow model.

The calcium chloride points are shown for the Clinch River ash to illustrate that despite comparable silicon reaction, the surface areas of the two products differ.

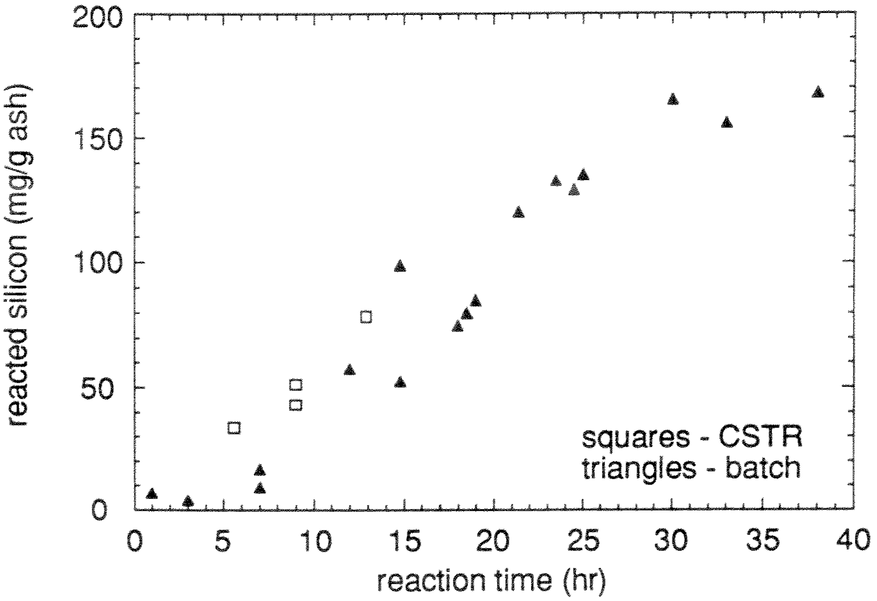

Figure 6.14 Comparison of ash reaction in batch and CSTR - Shawnee

The conditions for the batch reactions are described in Figure 5.14 and the conditions for CSTR experiments are described in Figure 6.9. The reacted silicon was determined by the selective dissolution method.

6.2.3 Fly Ash - Hydrated Lime Reactions

The fly ash/hydrated lime system behaves quite differently from the two systems examined previously. The changes in solution chemistry are significant and the assumptions necessary for the segregated flow model are not met. Clinch

River fly ash is examined briefly and Shawnee ash (ground in addition to the unground) is covered in more detail.

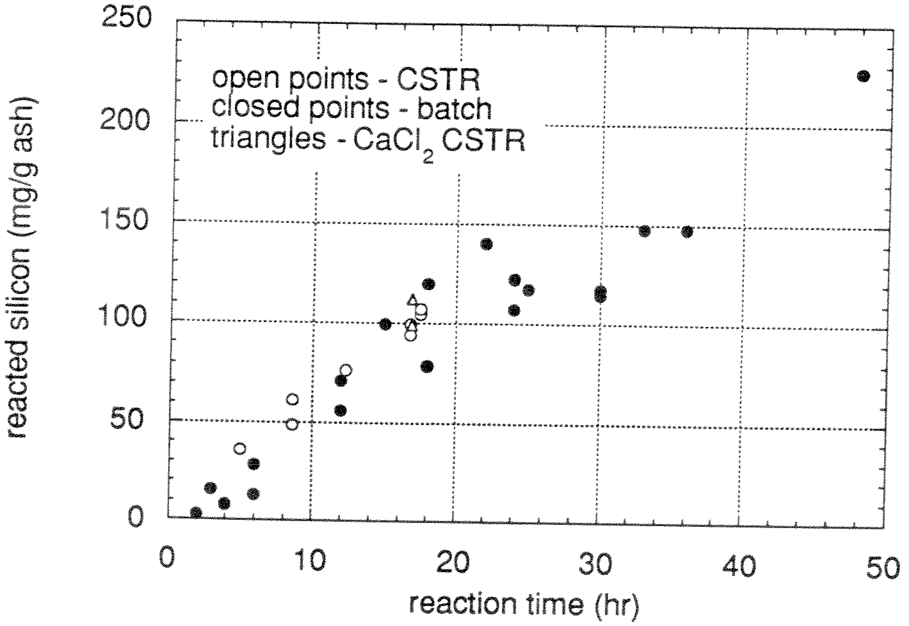

Figure 6.15 Comparison of ash reaction in batch and CSTR - Clinch River

The conditions for the batch reactions are described in Figure 5.12 and the conditions for CSTR experiments are described in Figure 6.10. The reacted silicon was determined by the selective dissolution method.

6.2.3.1 *Solution Composition*

Typical batch and CSTR solution chemistry for Shawnee ash experiments is shown in Figure 6.16. The lines illustrate the CSTR calcium and alkalinity (potassium and sodium) in solution for an 8.8 hour residence time experiment while the points provide the values for a batch reaction at the same calcium hydroxide fraction (0.5 g/g ash) as the CSTR. Both systems have comparable alkalinity levels over the reaction times considered. Despite this, the CSTR has considerably higher dissolved calcium levels (at least 10 times as much for most of the times shown) than the batch reactor.

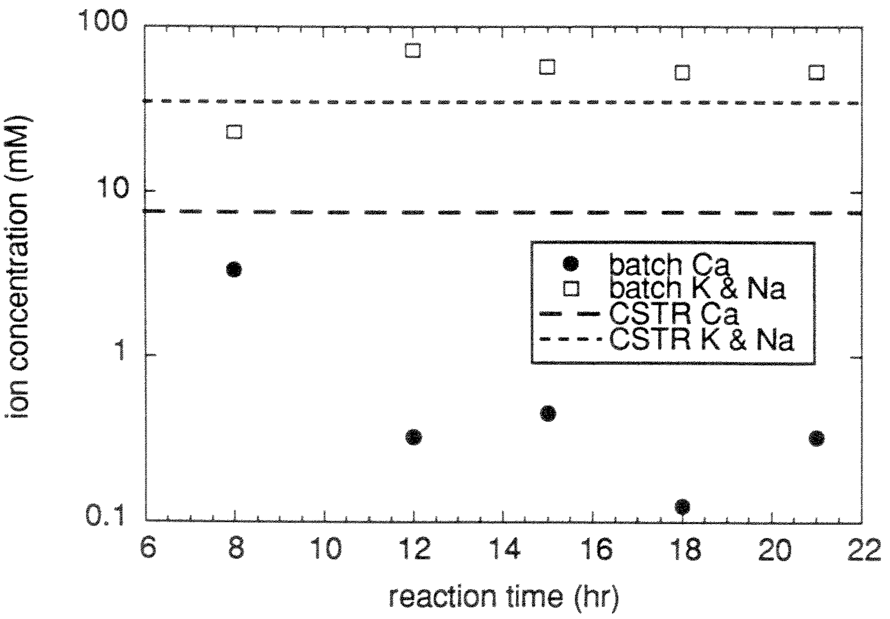

Figure 6.16 Batch and CSTR solution chemistry for ash/lime system - Shawnee

Hydrated lime/Shawnee ash	1:2 weight ratio
CSTR 8.8 hr residence time	21 % solids
batch reaction - 18 wt % solids	92° C

A particle in the batch reactor would be exposed to as high as 20 mM calcium in solution at short reaction times with a low hydroxide level and then be exposed to a much lower calcium level (<1 mM) with higher hydroxide concentration at moderate and long reaction times. The particle in the CSTR, on the other hand, would be exposed to a high hydroxide, high calcium environment for its entire residence time in the reactor. The high calcium, high hydroxide system should provide a better surface area product for any given residence time in the reactor.

6.2.3.2 Surface Area

The reason for the difference in calcium concentration between the batch reactor and the CSTR at a given alkalinity may be better explained by examining data from the CSTR reactions performed with Shawnee ash (Figure 6.17). There are two factors that may affect the dissolved calcium concentration. First, the equilibrium concentration can be changed by the solution hydroxide concentration, but in this case, the hydroxide levels are comparable due to the alkalinity being the same. However, it is possible that the equilibrium concentration of calcium hydroxide in solution decreases with calcium hydroxide exposure to the reaction environment. The second factor is the rate of dissolution of the calcium hydroxide compared to the rate of the reaction on the surface of the ash particle. This dissolution is a function of the activity of the calcium hydroxide, the particle size at any point in time and may be dependent on the history of the particle in solution.

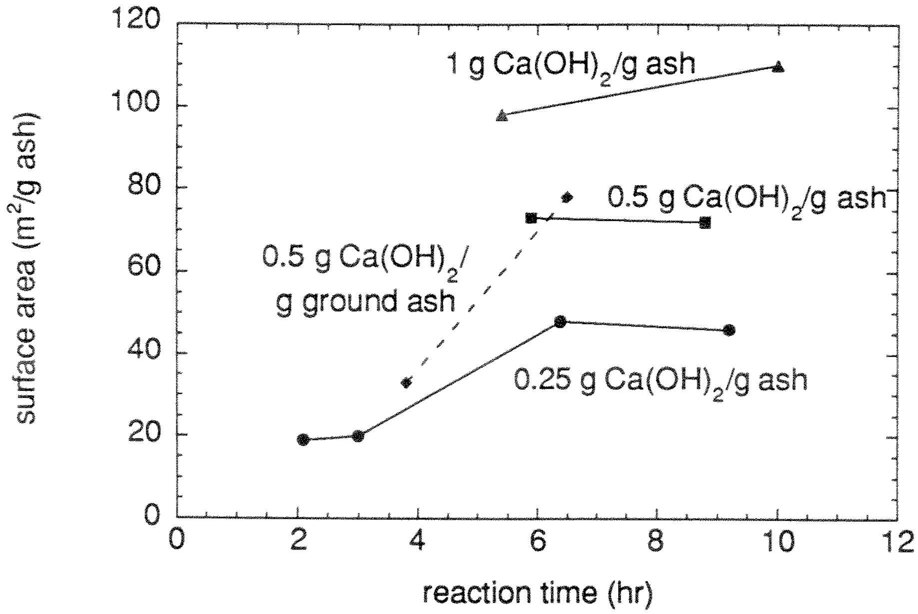

Figure 6.17 CSTR surface area generation for Shawnee ash/lime system

Surface areas shown are the average of the samples taken from the reactor at steady state.

Hydrated lime/Shawnee ash	1:4 to 1:1 weight ratios
/ground Shawnee ash	1:2 weight ratio
17 to 37 wt % solids	92° C

Under reaction conditions with a high dissolved calcium concentration, as was the case with the two reaction systems examined previously, there is little opportunity for the reaction between calcium hydroxide and silicate to take place anywhere but on the ash particle. In the fly ash/hydrated lime system, however, the fraction of calcium hydroxide and dissolved calcium decreases with reaction time as hydroxide concentration increases. This provides an environment where the reaction between the two species may occur at the calcium hydroxide particle, forming a product layer that could inhibit dissolution. This type of behavior is consistent with batch reactions that have been performed at high hydroxide levels (Chapter 5).

This hypothesis would explain the behavior of the CSTR experiments as additional calcium hydroxide was added to the system. The surface area per gram ash increases at any given residence time as additional calcium hydroxide is added. The surface area of the CSTR product was greater than that from comparable batch reactions where duplicate residence times were examined. This increase over batch reaction was greatest for the intermediate residence time of about six hours. The results were comparable at the longer residence times studied.

The experiments show dissolution of calcium hydroxide may be limiting the reaction rate in the CSTR. Grinding exposes additional surface area on the ash, allowing reaction on a greater surface area of ash (in this case approximately doubling the measured BET surface area of the base ash). If ash dissolution was the limiting reaction mechanism, one would expect to see a greater surface area from the ground ash CSTR. This does not occur as the surface area of the 0.5 g calcium hydroxide/g ash case is about the same as that for the unground ash at the two residence times examined. The reacted silica from selective dissolution for these reactions shows the same behavior. The fly ash/hydrated lime reaction also creates higher surface area product than reactions with gypsum or calcium chloride present at short residence times.

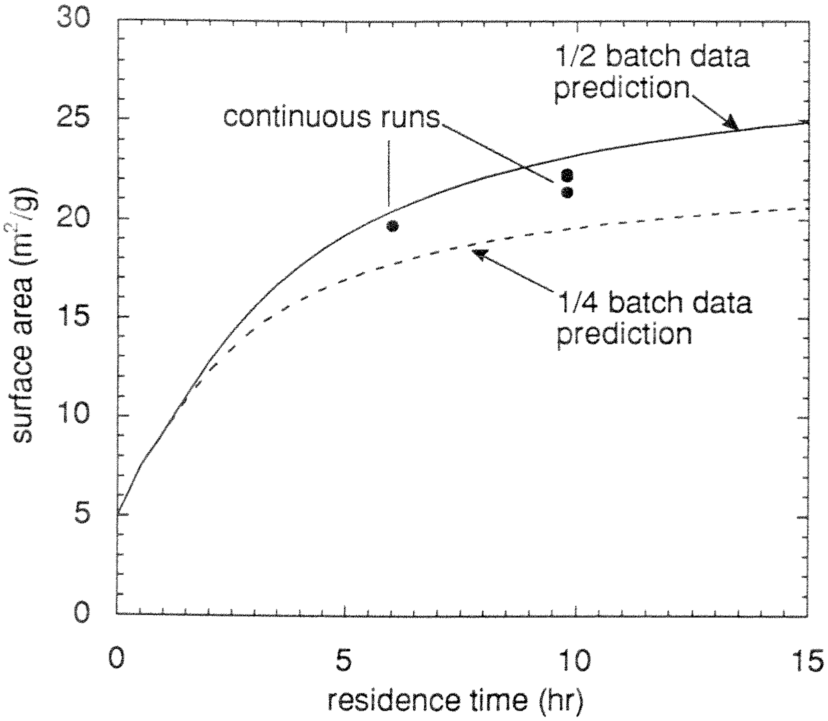

Figure 6.18 CSTR surface area generation for Clinch River ash/lime system

Surface areas shown are the samples taken from the reactor at steady state (three residence times of reactor operation).

Hydrated lime/Clinch River ash	1:4 weight ratio
19 to 33 wt % solids	98° C

The lack of additional surface area growth at long residence times may be explained by changes in the solution chemistry as the residence time increased. The equilibrium effect of the increased hydroxide concentration limits the calcium solubility as additional ash reacts at the longer residence times. Secondly, as the residence time increases for any given fly ash to hydrated lime ratio, the fraction of unreacted lime in the reactor goes down and the length of time it has been exposed to the solution increases so the calcium hydroxide becomes less reactive and is less likely to dissolve. Both of these factors tend to limit the calcium concentration in solution, limiting the reaction rate and product surface area.

Similar behavior was observed in the Clinch River fly ash system (Figure 6.18). In this case, the batch reaction data at two fly ash/hydrated lime ratios was used to predict the CSTR behavior. The 0.25 g $Ca(OH)_2$/g ash CSTR feed exceeded the prediction for that range from the batch data, performing almost as well as a 0.5 g $Ca(OH)_2$/g ash system would predict. This behavior is consistent with the Shawnee ash experiments where CSTR product surface area is greater than that expected based on the segregated flow model.

6.3 SYSTEM COMPARISON

An overview of surface area generated for a given residence time for each of the reaction systems studied is useful for determining the optimum solution chemistry and the benefits of promoting the oxidation of species such as sulfite to enhance the reaction rate. The experimental results are plotted together on Figure 6.19. The Shawnee ash forms a higher surface area solid for each system studied at comparable residence times.

The Shawnee ash/lime CSTR is optimum for CSTR residence times less than six hours at calcium hydroxide to ash ratios of 0.5 or greater. A calcium hydroxide to fly ash ratio of 1 or more is likely for an operating system. While calcium hydroxide availability appears to limit the fly ash/hydrated lime reaction, the other systems with more moderate hydroxide levels are limited by ash dissolution so that the addition of more calcium hydroxide does not impact the reaction rate. At residence times beyond eight hours, the calcium chloride system is optimum and the recycle system is superior to the fly ash/hydrated reaction.

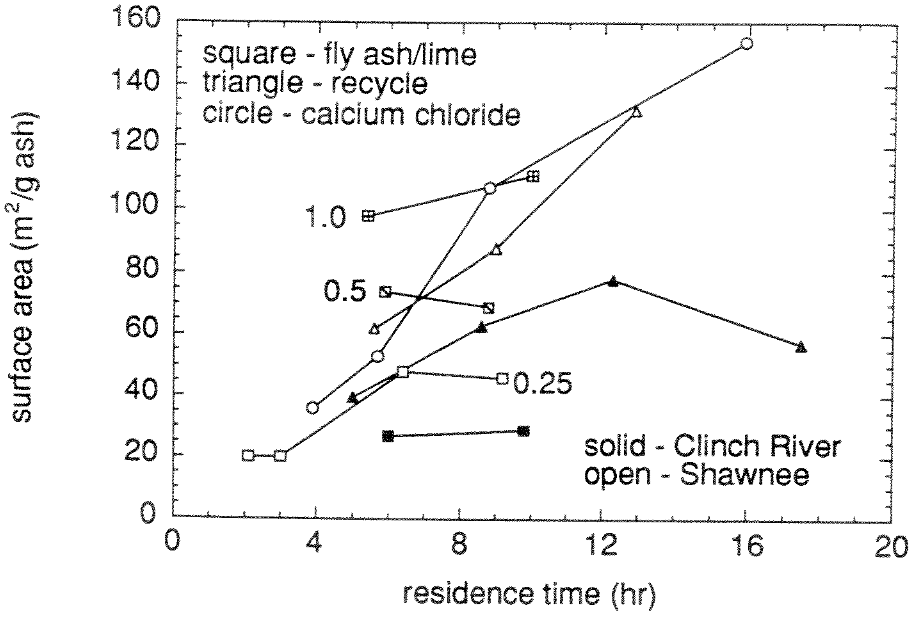

Figure 6.19 Comparison of product surface area from all systems/ashes

The average surface area of the product produced from each CSTR experiment at a given residence time. Conditions for each experiment are provided in the system specific plots earlier in the chapter. The numbers labeling the fly ash/hydrated lime experiments are the hydrated lime to ash weight ratio.

Chapter 7

CSTR with Field Material

Previous research efforts (Peterson, 1990, Stroud, 1991, Wasserman, 1992, Johnson, 1992) have approximated field conditions on the bench scale by adding calcium sulfite hemihydrate and gypsum to the fly ash/hydrated lime reaction. It was assumed that this approximation could be used to determine which variables affect the reaction rate and how the reaction might be optimized. The limited pilot scale duct injection work did not provide large enough quantities of reacted sorbent for further experimental study. Pilot plant operations at the Shawnee test facility in Paducah, Kentucky in the summer of 1992 made reacted material available and allowed for comparison of the bench work to the process on the pilot scale. This chapter first compares bench scale work performed with the ash (Martwick) and simulated recycle (gypsum and calcium sulfite added) to that performed with material collected from the pilot facility (referred to as ADVACATE). The bench scale runs are then compared to the available pilot plant data. This comparison is limited due to limited pilot data obtained during the testing. Detailed data tables for these experimental results are provided in Appendix B.

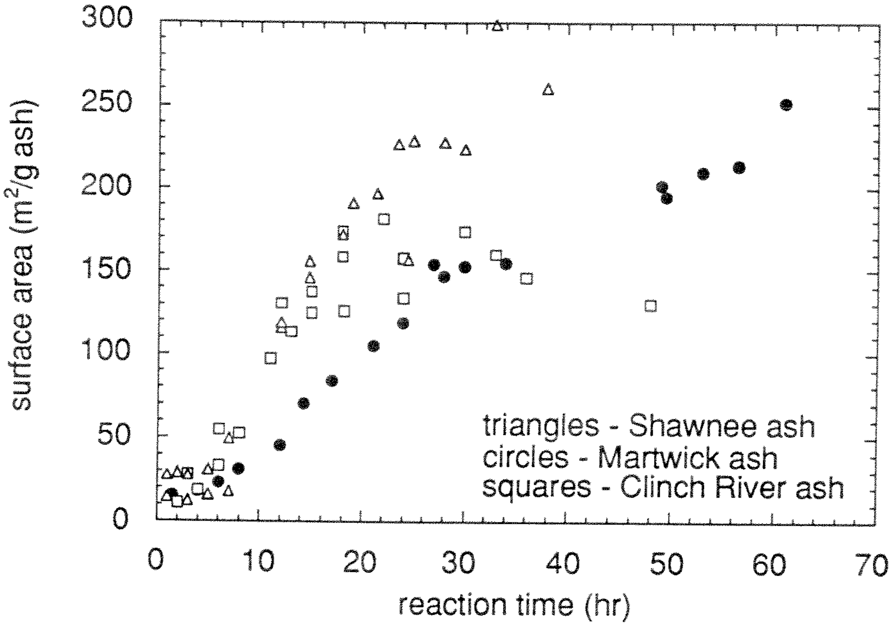

Figure 7.1 Comparison of recycle fly ash reactions

Hydrated lime/Martwick ash/
calcium sulfite/gypsum

18 wt % solids

hydrated lime 25 to 36 wt %
ash 36 to 50 wt %
calcium sulfite 9 to 13 wt %
gypsum 13 to 20 wt %
92° C

Conditions provided for Shawnee and Clinch River experiments in Chapter 5.

7.1 MARTWICK ASH

Martwick ash generally has a lower reaction rate with calcium hydroxide than the other low calcium ashes studied. The surface area resulting from the batch reaction of fly ash, calcium hydroxide, calcium sulfite hemihydrate and gypsum for the Martwick, Shawnee and Clinch River ashes is illustrated in Figure 7.1. The graph presents data from multiple batch reactions with each of the ashes. The surface area is again normalized per gram ash to allow for experiments with varying ratios of reactants to be plotted together for comparison. The surface area growth in all cases is approximately linear over the region of surface area generation and the ultimate surface areas of the Shawnee and Martwick products are comparable; however, the rate of growth is much lower in the case of Martwick ash. The reaction of the ash continues until over 85 percent of the silica in the ash, as measured by selective dissolution, has been reacted.

In the case of highly reactive silica sources, the availability of calcium hydroxide to the reacting ash surface may limit the reaction rate (Chapter 5). The Martwick fly ash systems studied here do not exhibit this characteristic due to the low reactivity of the ash, the presence of gypsum to buffer the solution chemistry, and the large fraction of calcium hydroxide added to the experiments to simulate the chemistry in the operating pilot plant. The low reactivity of this ash makes it an ideal candidate for grinding so particle size of the ash may be reduced and greater surface area exposed for reaction with the calcium hydroxide in solution.

The recycle (calcium sulfite and gypsum present in addition to the fly ash and hydrated lime) system is compared to the fly ash/hydrated lime and ground recycle systems in Figure 7.2. Surface area generation rate is comparable for the two unground ash systems at short reaction times but the unbuffered fly ash/hydrated lime system stops generating surface area at about 14 hours of reaction whereas the recycle system continues to create surface area through 60 hours of reaction.

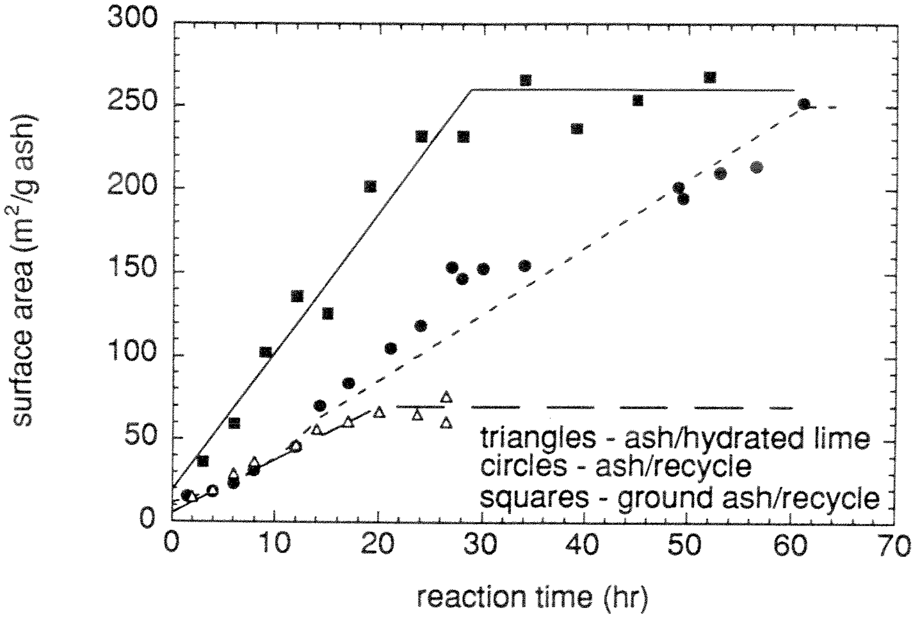

Figure 7.2 Surface area generation in Martwick ash reactions

Hydrated lime/Martwick ash	1:2 weight ratio
Hydrated lime/Martwick ash/ calcium sulfite/gypsum	hydrated lime 25 to 36 wt % ash 36 to 50 wt % calcium sulfite 9 to 13 wt % gypsum 13 to 20 wt %
Hydrated lime/ground Martwick ash/ calcium sulfite/gypsum	2:2:1:1 weight ratio
18 wt % solids	92° C

There are two likely causes for this difference. First, as the dissolution of the ash continues, the concentration of potassium and sodium in solution increase causing a corresponding increase in hydroxide level. This can lower the activity of calcium hydroxide in solution, limiting its solubility, especially at long reaction times. In this ash/hydrated lime reaction, calcium hydroxide utilization increases from 65 percent at 14 hours to 78 percent at 26.5 hours, a rate much lower than at the start of the reaction. This is despite a silicon dissolution rate comparable to that at the start of the reaction. The dissolution occurs without the generation of significant surface area. The reason for the reaction with no creation of surface area might be attributed to the higher solution hydroxide and low calcium concentrations. The lack of surface area at low calcium concentrations was observed previously in Shawnee ash experiments with sodium hydroxide present (Chapter 5).

The reaction with ground ash behaves as expected. The added surface area resulted in surface area growth almost twice as fast as with unground ash. A direct comparison between rate and increased ash surface area is not possible due to the nonreactive char in the ash contributing to the measured ash surface area. The behavior confirms ash dissolution as being the rate determining step in the reaction forming surface area for this fly ash. The lines on the plot approximate the batch reaction rate data and are used to obtain predictions for CSTR behavior using the method presented in Chapter 6.

The predictions and experimental surface areas obtained in CSTR experiments are shown in Figure 7.3. The fly ash/hydrated lime system was only examined at one residence time and does not match the predicted value. This is consistent with Shawnee and Clinch River ashes examined earlier (Chapter 6), however, since the fly ash/hydrated lime batch reaction does not exhibit the

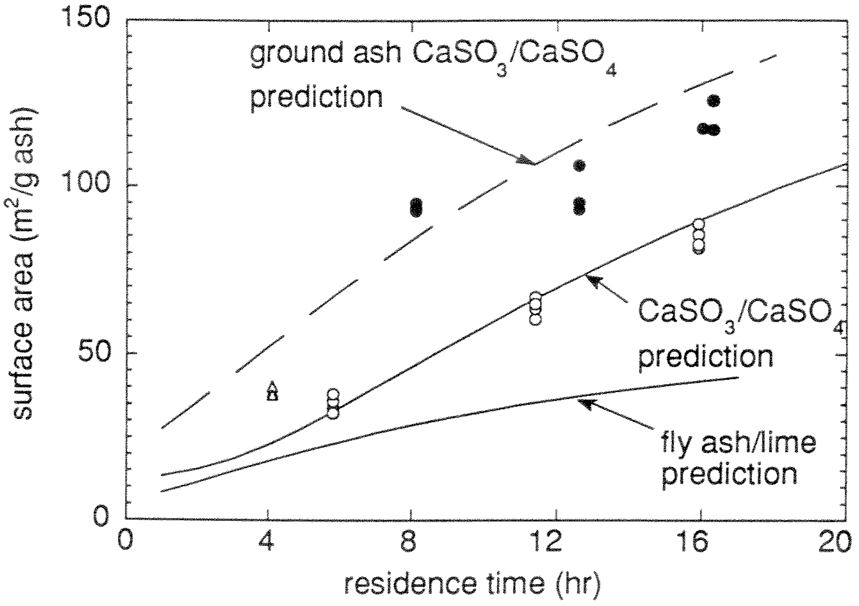

Figure 7.3 Product surface area from Martwick ash CSTR

All samples taken following three residence times of reactor operation are shown. The open circles are for reactions using unground ash while the solid circles are those for ground ash experiments. The triangles are from ash/hydrated lime reactions.

Hydrated lime/Martwick ash/ calcium sulfite/gypsum	hydrated lime 25 to 37 wt % ash 33 to 67 wt % calcium sulfite 0 to 17 wt % gypsum 0 to 17 wt %
15 to 21 wt % solids	92° C

constant solution chemistry assumed in the CSTR model (described in Chapter 6). The addition of calcium sulfite and sulfate at short residence times actually has a negative impact on the CSTR as the 4 hour residence time fly ash/hydrated lime experiment outperforms the 6 hour recycle experiment. This behavior is due to the high dissolved calcium concentration in the CSTR as compared with the batch reaction for the hydrated lime/ash system. This again is similar to results obtained with Shawnee ash (Chapter 6).

The recycle experiments match the predicted values well. There is more variation in the ground ash results and this might be caused by difficulties in providing a consistent feed rate of the ground material to the reactor. The advantage of grinding material is most apparent at the low residence times. This advantage would be less obvious in the case of an ash with higher reactivity towards calcium hydroxide.

7.2 COMPARISON WITH PILOT PLANT

7.2.1 Recycle Material

The pilot plant recycle material or ADVACATE was collected from the electrostatic precipitator (ESP) at the Shawnee test facility so it consisted of unreacted ash as well as the material that had reacted with sulfur dioxide in the duct (Figure 7.4). The pilot facility had an attritor in recirculation with the reactor so the reacted material has been ground to a surface area as high as 20 m^2/g. The ADVACATE material collected had a surface area of 7.6 m^2/g, considerably lower than the material exiting the slurry reactor. This was due in part to the high dry recycle that was run in the pilot plant (>10 times the stream into the reactor).

It was also due to pore plugging caused by the sorbent reaction with sulfur dioxide in the flue duct.

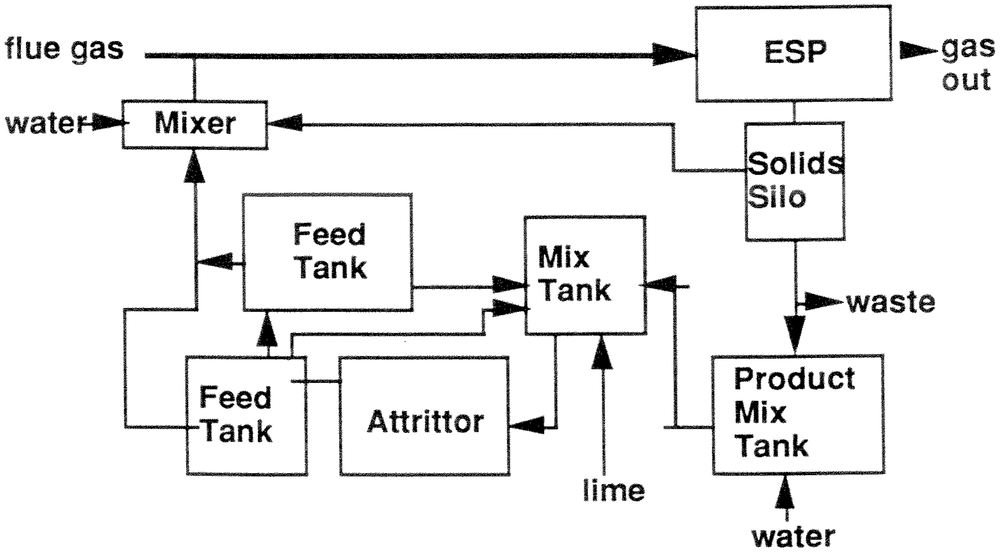

Figure 7.4 Shawnee 10-MW ADVACATE pilot plant process flow diagram

This reduction in surface area is similar to that observed in an earlier bench scale reaction where Clinch River product was reacted with sulfurous acid in aqueous solution (Figure 7.5). Clinch River fly ash was reacted with calcium hydroxide for 4 hours with the surface area generated shown on the plot. After the

the sulfurous acid was added to react with all the available calcium (simulating the sulfur dioxide - sorbent reaction), the surface area dropped to about 10 m^2/g and was only restored over the next 3 hours after new calcium hydroxide was added to the reactor. The restoration of surface area from previously reacted silica took

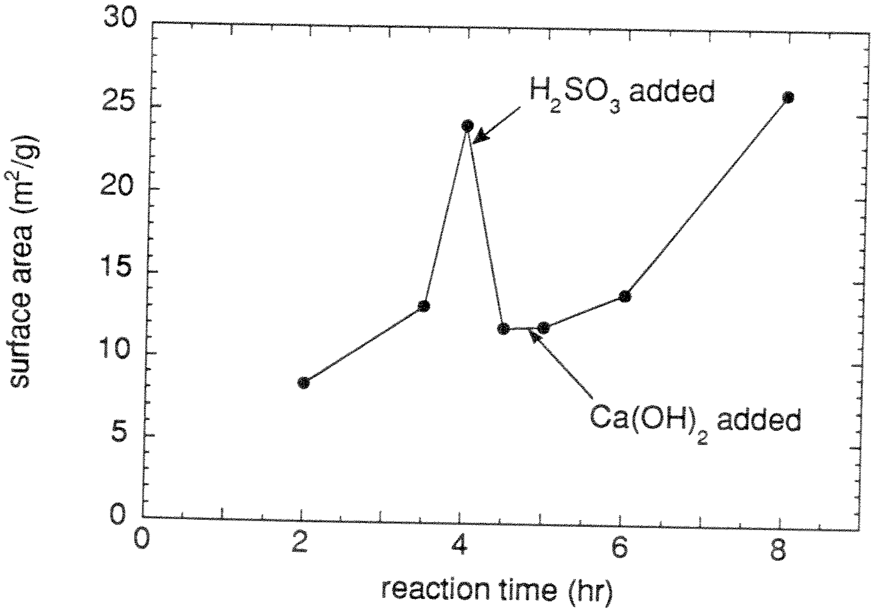

Figure 7.5 Surface area change in an aqueous sorbent-sulfur dioxide reaction

A hydrated lime/Clinch River fly ash batch reaction was performed at 98° C. Sulfurous acid was added after the 4 hour sample to react with all available calcium silicates and calcium hydroxide. Additional calcium hydroxide was added at 4.5 hours and the resulting surface area growth was tracked. The reaction with sulfur dioxide significantly lowered the sorbent surface area which was only recovered following several hours of additional reaction.

about 3 hours; this time period is significant to an operating system as a large fraction of the ash going to the reactor has been reacted previously. The sulfate level in solution after the reaction with sulfurous acid was less than 0.5 mM, lower than observed in reactions with ADVACATE material. This indicates some oxidation of sulfite in the pilot plant.

7.2.2 Batch Reaction

The recycle systems may now be compared to the ADVACATE, or pilot plant, material. The solution chemistry from reactions with the two materials is compared in Figure 7.6. The high gypsum fraction in the Martwick system provides a much higher sulfate level than in the ADVACATE case. This also allows a greater calcium concentration in the Martwick experiment. The potassium concentration is greater at the start of the reaction in the ADVACATE case because there has been previous reaction in the pilot plant due to the continuous recycle. In addition, there may be some contamination in the lime source. The reaction rate of the ADVACATE material is also likely to be greater causing potassium concentration to increase at greater rate as some of the ash has been ground. This should also cause its surface area to lie above the Martwick recycle system if the addition of calcium sulfite and gypsum provide a good approximation of the recycle system.

The surface area of the ADVACATE material is compared with that of the ash in Figure 7.7. The ADVACATE ash fraction was determined using the X-ray fluorescence data for the material (Table 4.1). The ADVACATE material is more reactive than the unground ash as expected and also lies below the ground material at longer reaction times due to the unground fraction in the ADVACATE material taking longer to react. This behavior further reinforces the assumption that each ash particle reacts individually and it is the ash dissolution that determines the reaction rate for this fly ash. While there is considerable scatter at

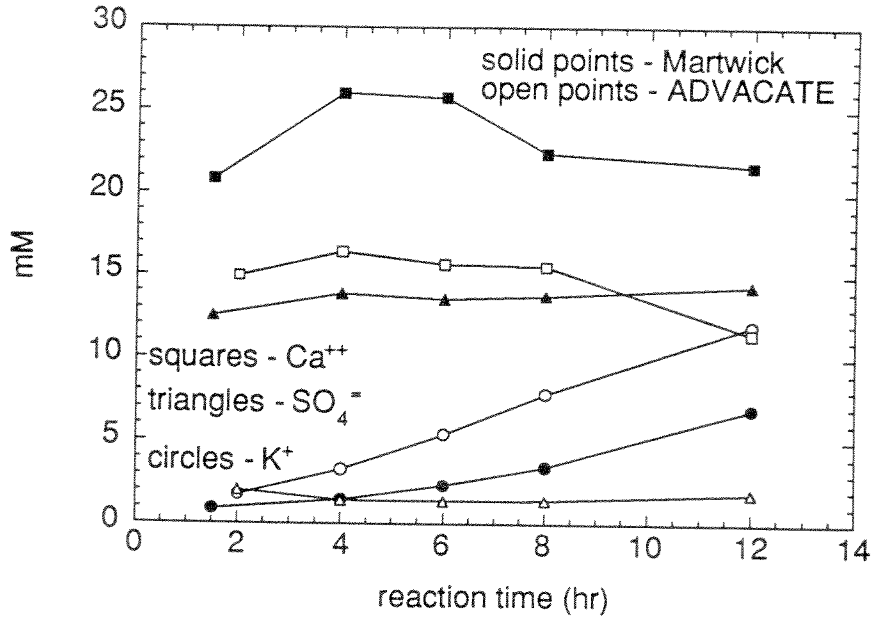

Figure 7.6 Solution chemistry for Martwick and ADVACATE batch reactions

Hydrated lime/Martwick ash/ calcium sulfite/gypsum	2:4:1:1 weight ratio
Hydrated lime/ADVACATE material	1:2 weight ratio
18 wt % solids	92° C

long reaction times, all the materials generate about the same ultimate surface area. The simulated recycle reaction system compares fairly well to the actual material.

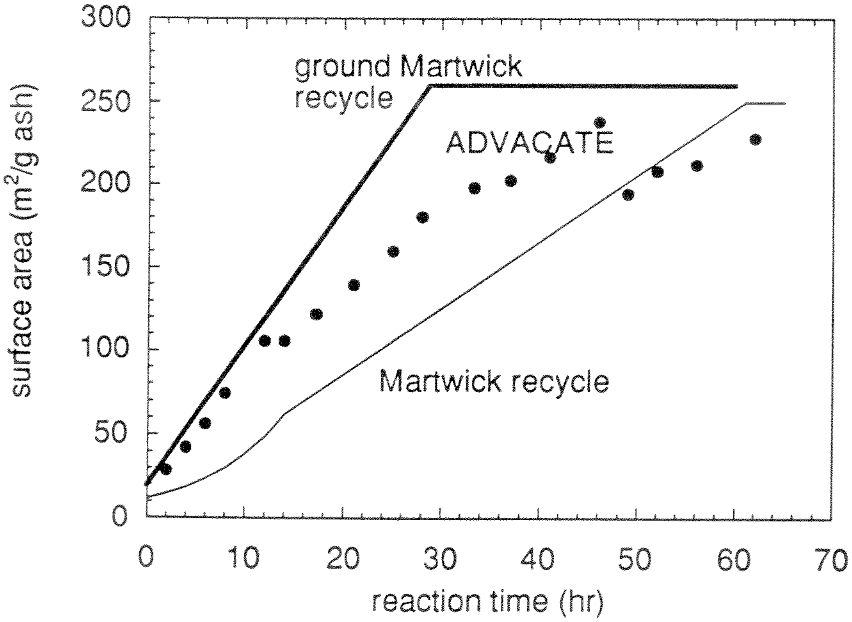

Figure 7.7 Comparison of ADVACATE and Martwick ash area generation

Hydrated lime/ADVACATE material 1:2 weight ratio
18 wt % solids 92° C

Martwick ash data shown is the fit of the batch reaction data in Figure 7.2.

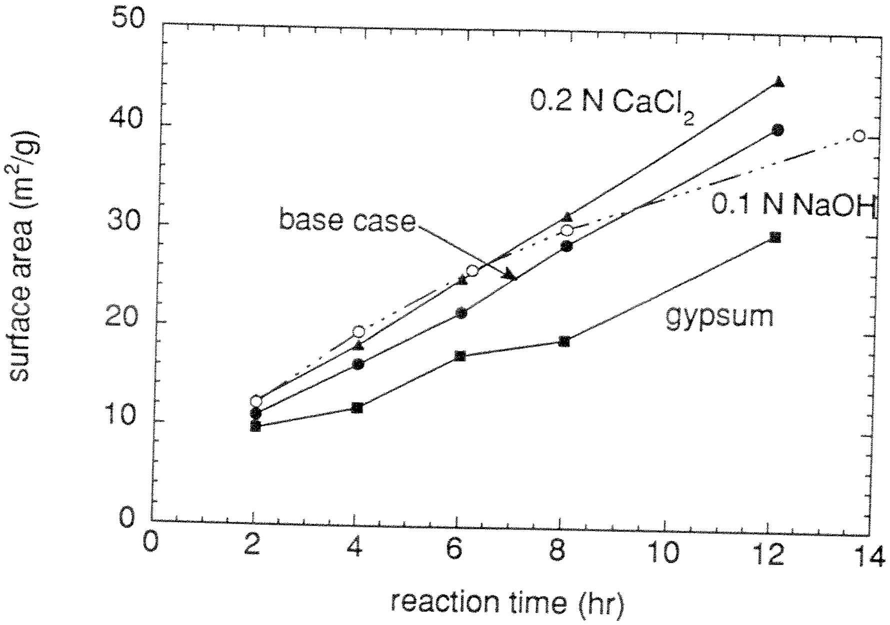

Figure 7.8 Impact of additives on the hydrated lime/ADVACATE batch reaction

The surface area of the product from the experiment performed with gypsum is corrected for the presence of an additional inert.

Hydrated lime/ADVACATE material 1:2 weight ratio
Additives: $CaCl_2$ 0.2 N
NaOH 0.1 N
gypsum 2:4:1 hydrated lime/ADVACATE/gypsum weight ratio
18 wt % solids 92° C

7.2.3 Impact of Additives on the System

The ADVACATE material is only about one third ash with a high fraction of calcium materials. Experiments were performed with three additives, sodium hydroxide, calcium chloride and gypsum, to determine the impact these materials might have on an operating system with a high recycle level (Figure 7.8). Each of these additives have had a positive effect on fly ash/hydrated lime reactions (Chapter 5). In the reaction with ADVACATE material, the impact of calcium chloride was positive but much less than observed earlier. The same is true of the reaction with sodium hydroxide present. The impact of the additives was dampened by the recycle reaction products and high ratio of calcium hydroxide to ash in the ADVACATE experiments.

The addition of gypsum actually had a negative impact on the reaction rate. The positive effect of gypsum is due to the increased dissolved calcium concentration at longer reaction times. In this case, calcium concentration is high with the base material as a small fraction of gypsum is present in the material along with the calcium sulfite. The net result is that the addition of more gypsum does not increase dissolved calcium greatly but causes a decrease in hydroxide concentration. The lower hydroxide concentration can cause a lower reaction rate due to slower ash dissolution.

7.2.4 CSTR

The ADVACATE material was run in the CSTR at four residence times (Figure 7.9). The product surface area matched the predicted value (using batch data to obtain the predicted performance as shown in Chapter 5) at residence times through 10 hours. The increase in surface area was minimal as residence time was increased from 10 to 24 hours. The lack of increased surface area with increased residence time was observed previously with Clinch River ash, but in that case the product surface area actually declined at a residence time beyond 12 hours. That system also had more gypsum present and a higher sulfate concentration in solution.

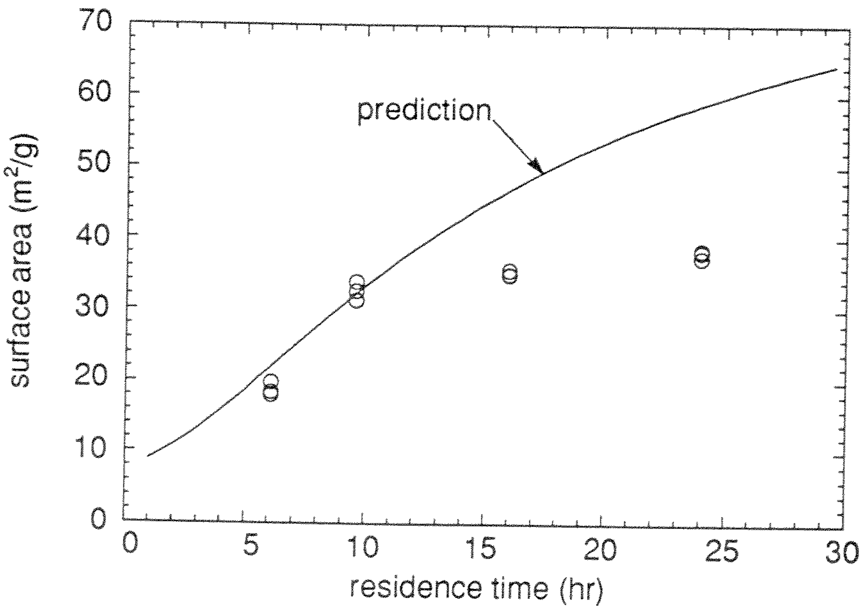

Figure 7.9 CSTR surface area generation - ADVACATE material

Surface area of all samples following three residence times of reactor operation are shown.

Hydrated lime/ADVACATE material 1:2 weight ratio
17 to 23 wt % solids 92° C

In both cases, the increase in residence time did not impact the reaction of the fly ash (as measured by reacted silicon) but only the generation of surface area. The reacted calcium hydroxide as measured by the sugar dissolution technique and the reacted silica by selective dissolution continued to increase with residence time as did dissolved potassium, another measure of ash dissolution (Figure 7.10). This again is consistent with the Clinch River ash behavior.

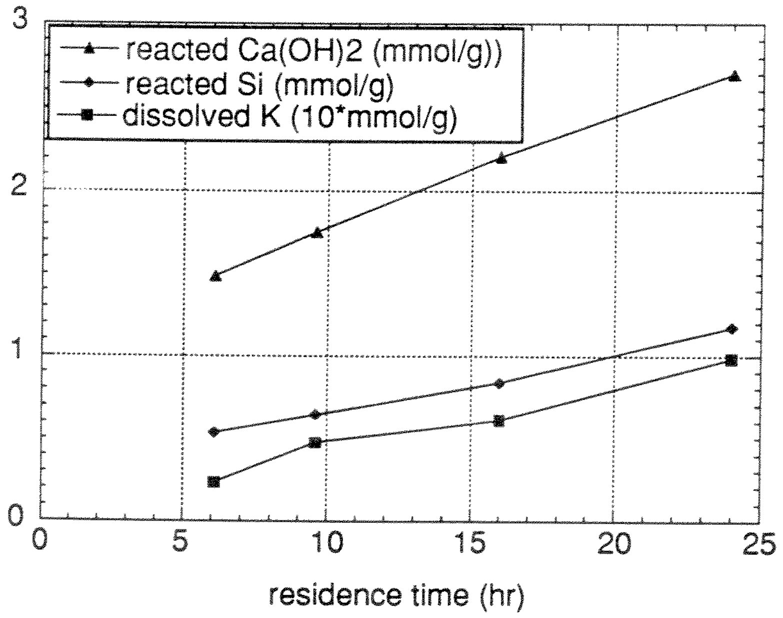

Figure 7.10 Indicators of reaction with residence time in an ADVACATE CSTR

Experiment conditions are provided in Figure 7.9. Reacted calcium hydroxide determined by sugar dissolution method and the reacted silicon by selective dissolution method.

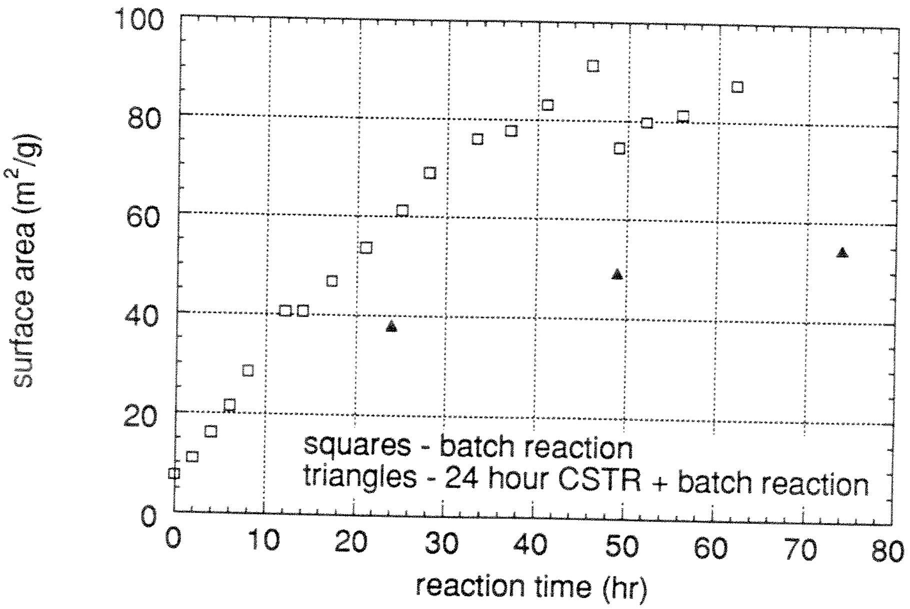

Figure 7.11 Reaction of long CSTR residence time ADVACATE material

CSTR product was reacted for an additional 50 hours in a batch reactor. The ADVACATE batch reaction points are shown for comparison.

24 hour residence time CSTR product	see Figure 7.9
9 wt % solids	92° C

This unusual behavior was examined further by reacting the product material from the 24 hour experiment in a batch reactor for an additional period of time (Figure 7.11). The batch reaction data is shown on the plot for comparison with the CSTR material. The product of the CSTR is shown at 24 hours with the additional reaction times of 26 and 50 hours in the batch reactor. It is apparent that the loss in surface area is not totally recoverable and that the ultimate surface area achievable has been limited. All the silica in the fly ash had been reacted in the material with the 74 hour total reactor residence time.

7.3 FIELD COMPARISON

A simplified schematic of the pilot plant was shown in Figure 7.4. There are a series of mix and feed tanks in addition to the main reaction tank so that the system may show some characteristics of a plug flow reactor. In addition, the tanks were not well mixed so are not likely to show the characteristics of an ideal CSTR. The pilot plant was limited to nine full system runs at basically two reactor residence times - approximately 3 and 12 hours. Additional test variables were checked in the other tests performed (lime/sulfur dioxide mole ratio, impact of fly ash, reaction temperature). There were also two pilot scale batch reactions performed.

7.3.1 Batch Reaction

Two batch reactions were performed at the pilot facility (Figure 7.12). The first, referred to as semi-batch, involved operating the system in the continuous mode then stopping the feed to the reaction tanks and to the duct. The material was recirculated through the attritor, feed tank and mix tank during the test. The second, referred to as batch, involved slaking lime for one hour, then adding the ADVACATE product slurry from a previous run to the product mix tank. This slurry was recirculated through the reaction system for 4 hours then reacted in the batch reactor. Both runs had an ADVACATE to lime ratio of about 1.5:1 (as compared to 2:1 for the bench scale experiments). The fraction of ash in the ADVACATE material was not reported. In each of these experiments, surface area increased through 12 hours to a maximum of about 60 m^2/g material.

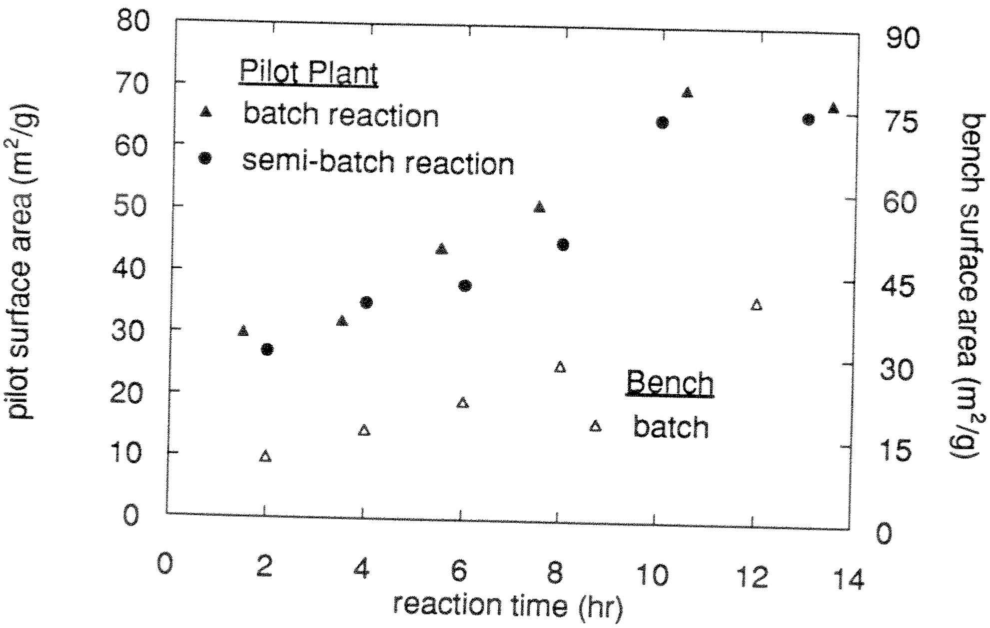

Figure 7.12 Pilot plant batch reaction surface area generation

Pilot plant experiments at 200 to 205° F with hydrated lime/ADVACATE material in a 2/3 weight ratio (Lepovitz et al., 1993). The bench scale experimental conditions were described in Figure 7.2.

Direct comparisons of product surface area from the bench scale to the pilot plant are not possible because the composition of the ADVACATE material used in the pilot runs is not known; however, qualitative comparison of certain aspects may be made. The bench scale batch reaction data is shown on Figure 7.12 for comparison. The initial surface area is lower since there was no grinding prior to reaction. This difference is maintained throughout the reaction time as the surface area generation rate in the pilot plant reaction is greater than the bench scale experiment after scaling the axes for the fraction of ADVACATE material. The final pilot plant product surface area of 70 m^2/g is less than seen on the bench scale with this material but that is due to the larger excess of calcium hydroxide in pilot scale reaction. The reaction time when area growth stops is apparently shorter in the pilot scale reaction (12 versus 50 hours).

One factor contributing to this is the method used to conduct the experiment. The ADVACATE material used had a reaction time equal to the reactor residence time when the reaction was commenced whereas the bench scale reaction used dry material from the ESP. A larger factor is the extent of grinding in the pilot plant. Pilot plant material was ground to about 20 m^2/g as is seen in the plot of surface area against reaction time. This exposed additional surface area for reaction, decreasing reaction time as was seen in the case of ground Martwick fly ash. That Martwick ash was ground to about 9 m^2/g and generated surface area over 25 to 30 hours. These observations support the importance of grinding in a system with a low reactivity ash and a high calcium hydroxide to ash ratio.

7.3.2 CSTR

A summary of the pilot plant CSTR results is provided in Figure 7.13. In this plot, reactivity of the sorbent produced is measured by reporting sulfur dioxide removed in the duct. This is a measure of the reactivity of both the reacted material stream and the dry recycle stream. The data does not account for differences such as recycle ratios, temperature differences and lime to ash variances. The reactions performed with residence times between 3 and 6 hours are lumped together but the two reactions performed with residence times greater than 10 hours are indicated.

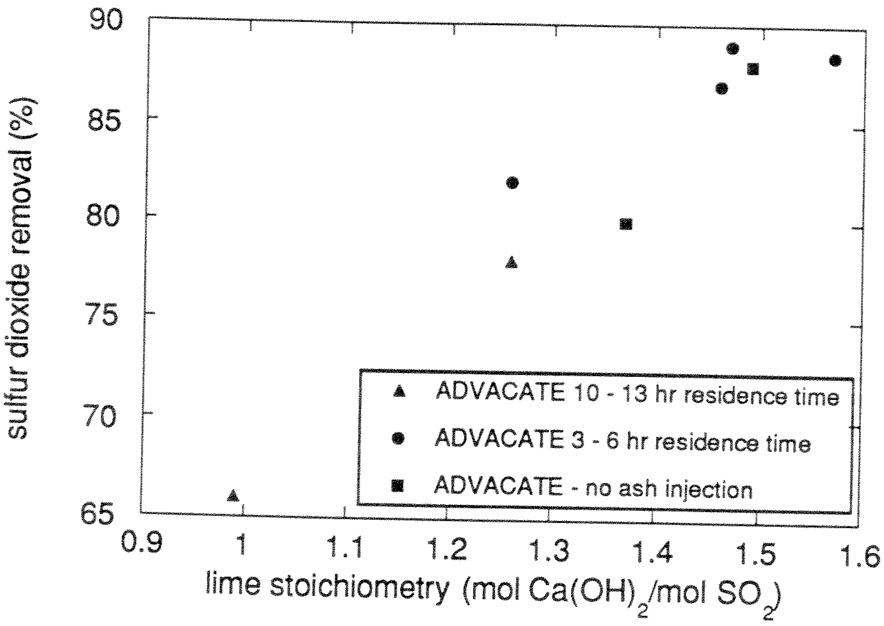

Figure 7.13 Effect of CSTR residence time on pilot plant sulfur dioxide removal

Experiments performed at 20° F approach to saturation in duct with an ESP used for particulate control. The temperature of the CSTR was controlled between about 190 and 200° F but temperature excursions did occur during some of the runs. The sulfur dioxide removal is determined by measuring the change in sulfur dioxide concentration across the control device.

These runs (10-13 hour residence time) produced lower sulfur dioxide removal and also produced significantly lower surface area sorbent. The surface area of these sorbents ranged from 13 to 19 m^2/g material as opposed to 22 to 40 m^2/g for the lower residence times. This exact behavior was not reproduced on the bench scale but a leveling of surface area with residence time did occur. The pilot plant behavior is like that observed with Clinch River ash. The low surface area material at the pilot plant may be due a slightly higher temperature similar to that of the Clinch River reactions since the temperature was difficult to maintain at the pilot facility. Another difference between the bench scale and the pilot plant experiments is that there was grinding with reaction at the pilot plant. The examination of this CSTR behavior is summarized in Chapter 8.

Chapter 8

Material Characterization

The reaction product composition is examined in detail in this chapter. The bulk composition of the product layer is examined first by presenting the bulk product composition of the ash systems studied and comparing product development with reaction time, reactants and reactor type. The second half of the chapter attempts to characterize the material by several different techniques including X-ray diffraction, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), scanning electron microscopy (SEM) and infrared spectrophotometry (IR). The low surface area product observed in the Clinch River and ADVACATE CSTR reactions at long residence times with gypsum present is compared with other product material throughout the discussion. The possible causes for this low surface area product at long CSTR residence time (noted in Chapters 6 and 7) are summarized at the end of this chapter.

8.1 SORBENT COMPOSITION

The elemental composition of the reaction product is determined chemically by the selective dissolution method. This technique dissolves the product layer in a mildly acidic solution (0.1 M HCl). The acid dissolves the reacted silica, alumina and iron oxides into the solution but the unreacted ash does not dissolve (Chapter 4). The technique provides a quantitative measurement of silicon, aluminum and iron. The other technique used to determine product composition is sugar dissolution; it measures available calcium hydroxide by a pH titration technique. These analyses do not provide an exact composition of the products formed but provide a gross composition of all products. Each of these major product components is examined below. The data used to generate the plots is presented in Appendix B.

8.1.1 Calcium Hydroxide

The behavior of reacted calcium hydroxide with surface area development is shown in Figures 8.1 through 8.4. Figure 8.1 illustrates the behavior of the product from various batch experiments. The surface area generated per gram of calcium hydroxide generally increases with extent of reaction. Much of this behavior may be attributed to the difference in reaction rate between silicon and aluminum with calcium hydroxide (and iron to a lesser extent) as the reaction continues. A greater fraction of calcium hydroxide reacts with the alumina at the shorter reaction times so there is a lower surface area per gram reacted calcium hydroxide (discussed later in the chapter).

There is not a strong difference between the ashes examined but the small differences are more clearly differentiated in the figures later in the chapter. The Shawnee ash experiments with calcium chloride and sodium hydroxide generally form product with lower surface area per gram of reacted calcium hydroxide. This may be due to gypsum in the other experiments being available for reaction with aluminum in the ash, lowering the calcium hydroxide conversion at any point in the reaction. It was noted that gypsum is depleted in the reaction and a calcium aluminum sulfate species is formed (described more fully later in the chapter). This could substitute for a calcium aluminum product.

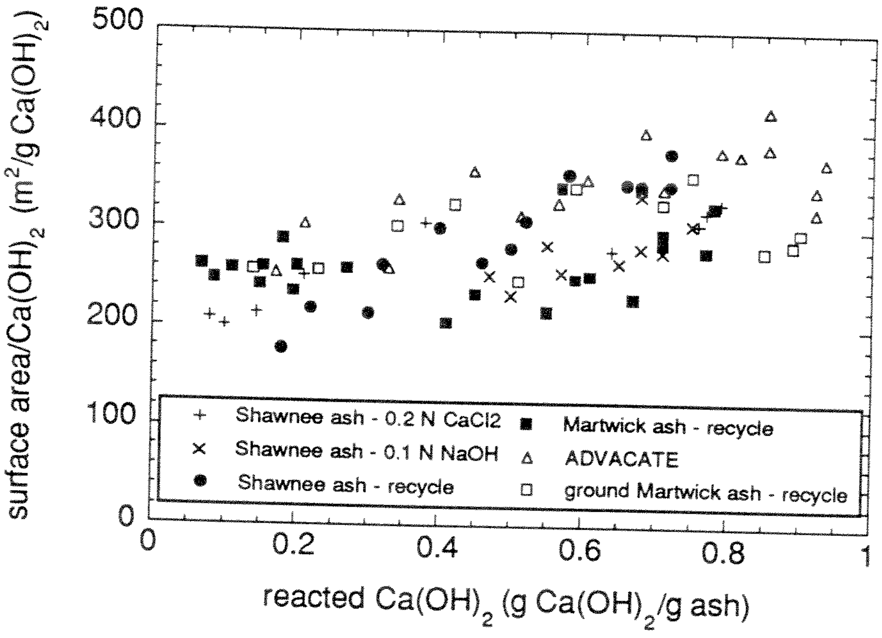

Figure 8.1 Surface area generation with calcium hydroxide reaction - various

The reacted calcium hydroxide was determined by sugar dissolution. The analysis was performed on samples from the batch experiments described in Chapters 5 and 7.

This data is compared to that from CSTR reactions with recycle materials present in Figure 8.2. The CSTR product generally has a greater calcium fraction for a given surface area. The greater calcium to surface area ratio for the CSTR points is due in part to the high fraction of material in the CSTR for a short reaction time (a function of the particle residence time distribution).

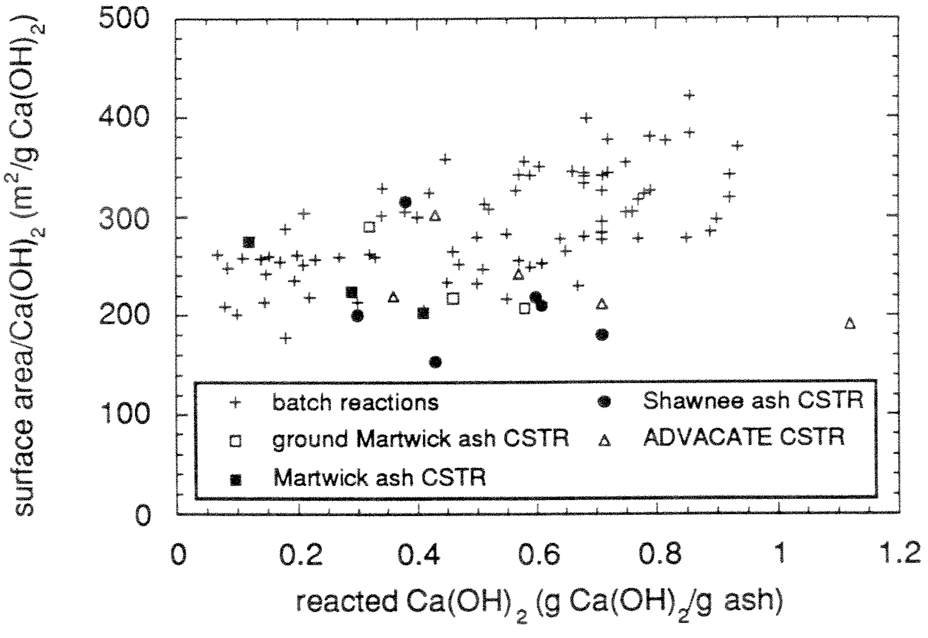

Figure 8.2 Surface area generation with calcium hydroxide reaction - CSTR

The reacted calcium hydroxide was determined by sugar dissolution. CSTR results are compared with the batch reaction results presented in Figure 8.1. The analysis was performed on samples from the CSTR experiments described in Chapters 6 and 7.

This material had a lower surface area per gram reacted calcium hydroxide than seen in Figure 8.1. There again are no strong differences between the ashes presented. Surface area per gram calcium hydroxide does not increase with increasing extent of reaction in these experiments which may indicate that the reactivity of the calcium hydroxide or solution composition may be causing this behavior in the batch reaction (as these are the two major differences between the two systems). The ADVACATE point with a reacted calcium hydroxide greater than 1 is from a long residence time CSTR and had low surface area development. This behavior is consistent with that observed in reactions with sulfate present at long residence times.

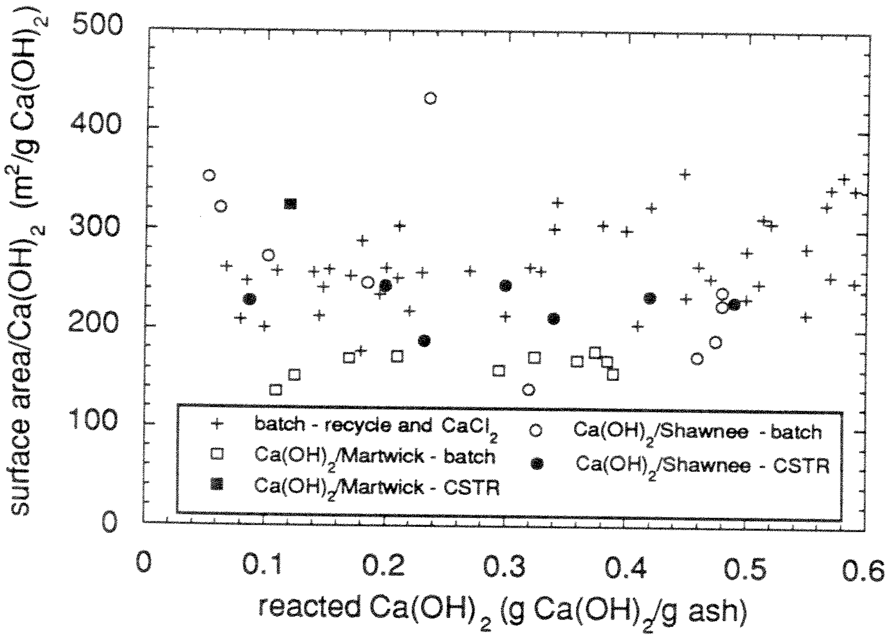

Figure 8.3 Surface area generation with calcium hydroxide reaction - ash/lime

The reacted calcium hydroxide was determined by sugar dissolution. Fly ash/hydrated lime results are compared with the batch reaction results presented in Figure 8.1. The analysis was performed on samples from the experiments described in Chapters 5, 6 and 7.

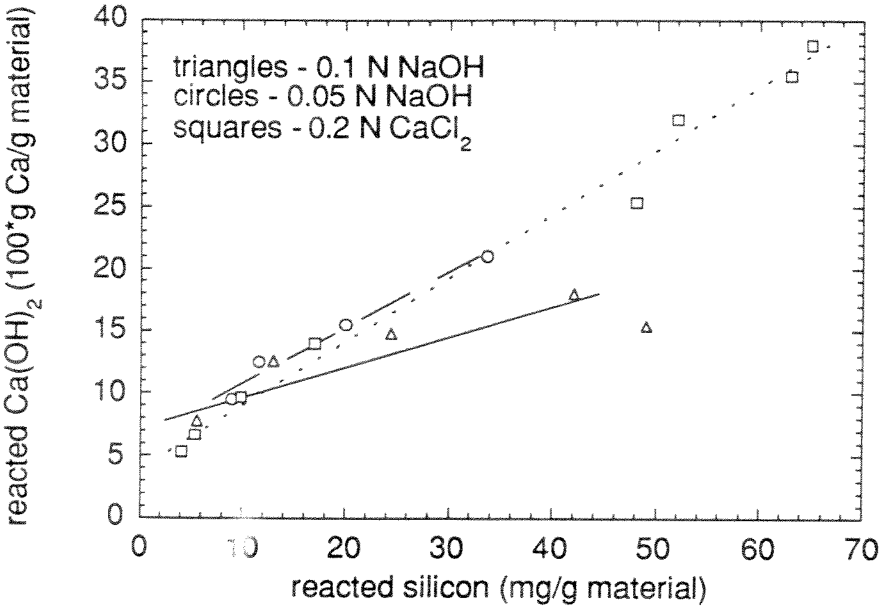

Figure 8.4 Determination of product calcium to silicon ratio in 3 reaction systems

The reacted silicon was determined by selective dissolution and the reacted calcium by sugar dissolution. The batch reactions were performed with Shawnee fly ash at 92° C and are described more fully in Chapter 5. The slopes of the lines fit to the data provide a measure of the product Ca/Si ratio.

The fly ash-hydrated lime reactions are compared in Figure 8.3. The same trend is again observed as was noted with the Shawnee calcium chloride and sodium hydroxide experiments in Figure 8.1 (a lower surface area per gram reacted calcium hydroxide in the ash/lime reactions). The low surface area per gram of reacted calcium hydroxide may also be due to the reaction rate and the surface area generation rate at short reaction times for the ash-lime system. At short reaction times with excess calcium hydroxide present, the reaction between calcium hydroxide and ash is rapid (due to high dissolved calcium and hydroxide) and the generation of surface area proceeds at a lower rate. This causes a greater calcium to surface area ratio in the product at short and intermediate reaction times.

Calcium hydroxide utilization may also be correlated with reacted silica from the ash. An example of this correlation is in Figure 8.4. The reacted calcium hydroxide is plotted against the reacted silicon to provide a calcium to silicon ratio over a given time period. This ratio will be biased by the reacted aluminum but may corrected for this effect (the impact of aluminum is detailed in section 8.1.3). The ratio of calcium to silicon was obtained for three systems on the plot - Shawnee ash with 0.1 and 0.05 N NaOH, and 0.2 N $CaCl_2$. The recycle and fly ash/hydrated lime systems behaved in a manner similar to the 0.05 M NaOH system. In all cases the y-intercept is greater than zero. This is due to the reaction of aluminum with the calcium hydroxide. The slope may be used to obtain the calcium to silica mole ratio in the product. This ratio, after correction for aluminum, is 1.8, 0.8 and 2.2 for the 0.05 M NaOH, 0.1 M NaOH and 0.2 N $CaCl_2$ systems respectively. These ratios indicate there is a higher fraction of calcium to silica in systems with a higher dissolved calcium concentration and that a higher calcium solid may have a greater surface area for a given reacted silica.

8.1.2 Silica

The surface area correlation with reacted silicon for several ash/lime systems is provided in Figure 8.5. There is a fair amount of scatter in the data but the line fit through all the points provides a slope which indicates the surface area generated per gram of reacted silicon. The surface area was calculated through the slope of the line to provide surface area per gram reacted silicon. All silicon was assumed to form CSH with typical CSH molecular structure. This was used with the fraction of silicon in the material to determine a product surface area of about 200 m^2/g CSH for the reaction. This value is similar to that from literature (Regourd, 1987). The deviation of the data from the line is consistent with that

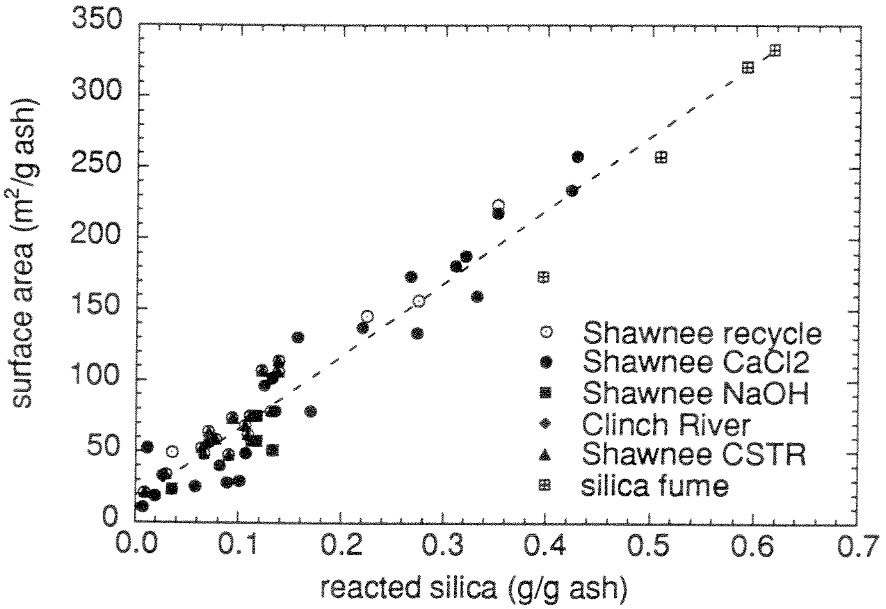

Figure 8.5 Surface area generation per gram of reacted silicon

Samples were taken from various Clinch River and Shawnee ash experiments (Chapters 5 and 6) and analyzed for surface area and reacted silicon. Batch reaction data was used unless otherwise indicated. The line plotted is a fit of all the data points shown.

observed in the surface area per gram of reacted calcium hydroxide. The product from experiments performed with silica fume also agrees with the correlation.

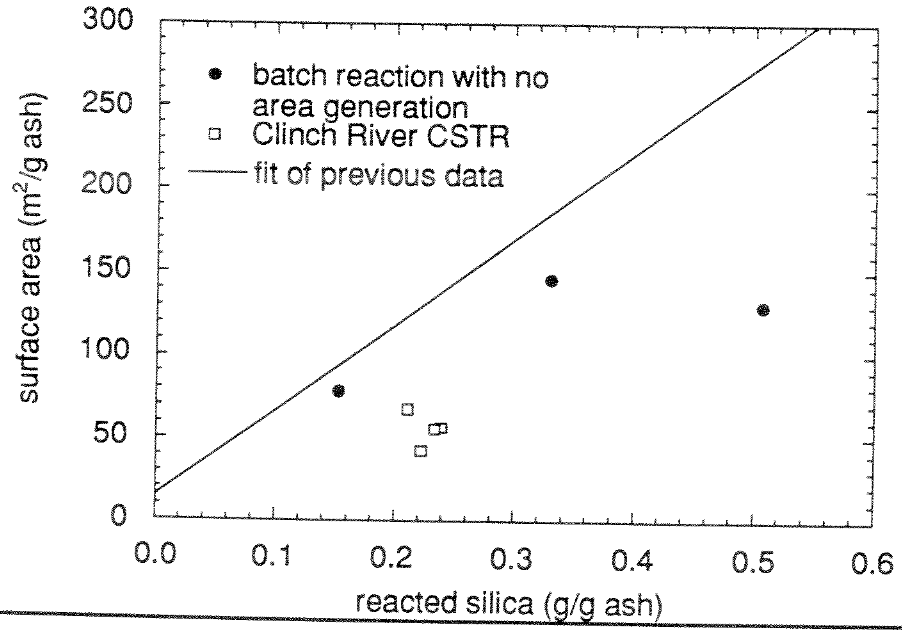

Figure 8.6 Surface area generation per gram of reacted silicon - low area cases

The line shown is a fit of the points from Figure 8.5. The points are from Clinch River batch and CSTR samples taken after no further surface area generation was observed.

Figure 8.6 compares the fit of the previous data with samples taken from experiments at long reaction times where no additional surface area generation was observed. The CSTR experiments that under performed the predicted surface area results based upon batch reaction data are also included. This comparison showed reaction of silica could occur under certain conditions where surface area was not generated. The points lie below and to the right of the line indicating that silica reacted but formed a product with lower surface area. There was not a significant difference in the calcium to silicon ratio for these samples.

8.1.3 Alumina

Another major species present in the ash is alumina. Its behavior is critical because it has the potential to react with the calcium hydroxide forming a low surface area material. In addition, there have been experiments performed with pure alumina indicating that under certain conditions, the reaction of alumina with calcium hydroxide terminates before either species is exhausted. This was presumably because the alumina was encapsulated by a product layer, limiting the extent of reaction (Peterson, 1990). The reaction of aluminum is tracked for experiments with Shawnee and Clinch River ashes in Figures 8.7 and 8.8.

The silicon to aluminum ratio in the product is plotted against the extent of reaction as measured by reacted silicon in each of these figures. The silicon to aluminum ratio in the base ash is provided on each plot for comparison. The reaction of the two species starts at approximately the same rate but the silica soon reacts preferentially so that the silicon to aluminum product ratio increases to about 4 for Shawnee ash and 5 for Clinch River ash. These ratios are greater than those seen in the base ashes indicating that the aluminum phases in the ash may be encapsulated, limiting their reaction. Another possible cause for this behavior is that a greater fraction of the aluminum in the ashes is present in an unreactive crystalline phase. The same trend is seen in the pilot plant ash but there is more scatter in the data.

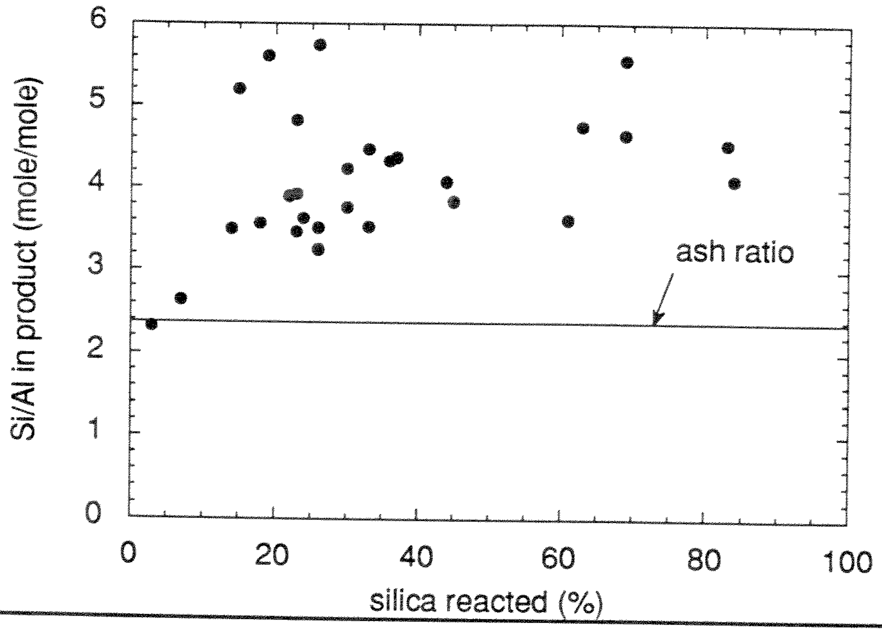

Figure 8.7 Changes in Si/Al product ratio with extent of reaction - Shawnee ash

Selected data taken from Figure 8.5 is divided by the reacted aluminum as determined by selective dissolution. The line shows the relative ratio of silicon to aluminum in the ash. The reaction with aluminum is inhibited as compared to the reaction with silicon as the reaction proceeds.

The points include data from experiments performed with various additives and both types of reactors. There was generally not a noticeable difference in the product ratio caused by the additives. The exception to this generalization was in the case of reactions with a high hydroxide concentration (greater than 0.1 M NaOH). These experiments are represented by points on the Shawnee plot with a silicon to aluminum ratio of greater than 5 at low reacted silica. This shift was caused by the high solubility of aluminum in the high hydroxide solution. If the aluminum and silicon in solution were accounted for, these points would follow the same general trend as the rest of the points on the graph. The effect is illustrated in Table 8.1.

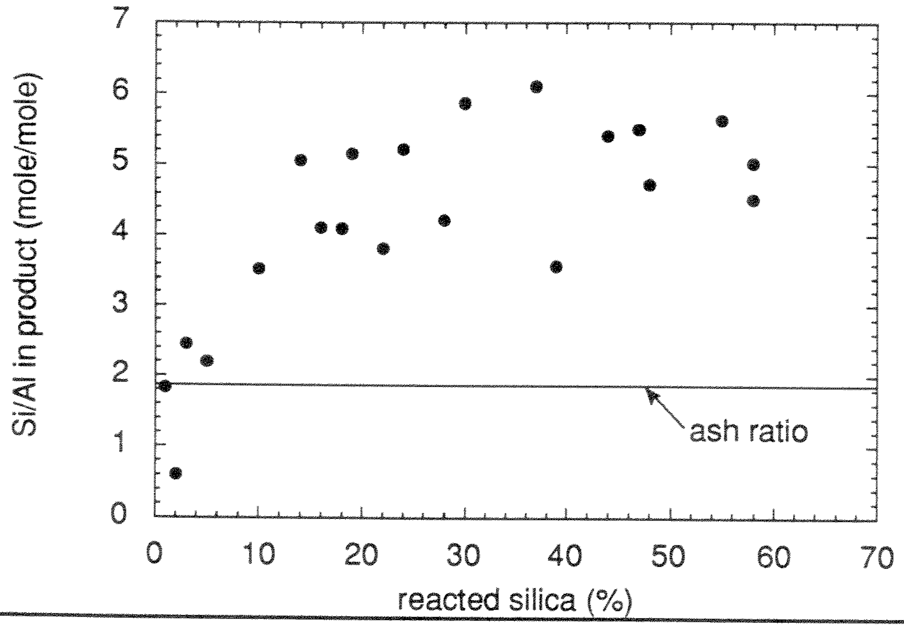

Figure 8.8 Changes in Si/Al product ratio with extent of reaction - Clinch River

Selected data taken from Figure 8.5 is divided by the reacted aluminum as determined by selective dissolution. The line shows the relative ratio of silicon to aluminum in the ash. The reaction with aluminum is inhibited as compared to the reaction with silicon as the reaction proceeds.

Table 8.1 Effect of solution hydroxide concentration on product Si/Al

Experiment	Reacted silicon (%)	Product Si/Al (mol/mol)	Si Fraction in Solution	Al Fraction in Solution	Corrected Reacted Si (%)	Corrected Product Si/Al (mol/mol)
0.5 M NaOH	19.3	5.7	0.23	0.47	25	3.9
0.2 M NaOH	15	5.1	0.17	0.52	18.2	2.9

8.1.4 Grinding and Pilot Plant Material

Changes in product surface area with reacted silicon are plotted with a linear fit of all the Shawnee fly ash points in Figure 8.9. The grinding of the ash (both at the pilot plant and of the raw ash) allowed for a greater surface area per gram of reacted silicon than unground material from any of the original fly ashes. This bias is due in part to the grinding and increase in surface area of the inerts (in the case of the pilot plant material). The Martwick ash product generally lies about the line as expected. The exceptions are several points that lie well below and to the right of the line. These points are again from batch reaction products taken when little surface area generation took place at long reaction times in a fly ash/hydrated lime reaction system. The ADVACATE points that lie below the line are product from those long residence time CSTR experiments that did not form surface area as predicted.

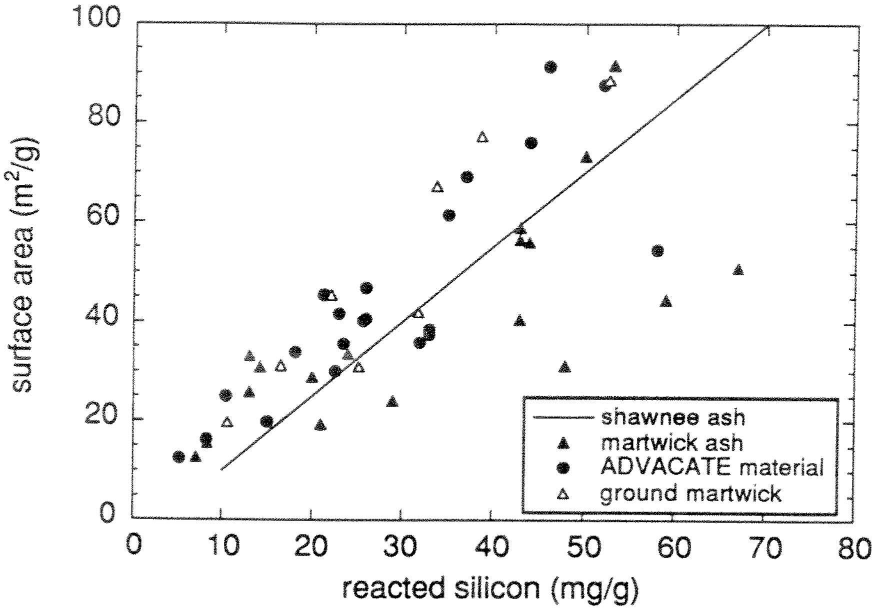

Figure 8.9 Surface area generation per gram of reacted silicon - pilot plant ashes

Samples were taken from various pilot plant ash experiments (Chapter 7) and analyzed for surface area and reacted silicon. The line plotted is a fit of the Shawnee data from Figure 8.5 for comparison.

8.1.5 Iron Oxide

Iron oxide is the other major species in the ash that may react with calcium hydroxide. It reacts at a lower rate than silica (similar to aluminum). A greater fraction of the Clinch River ash iron reacts but the iron level in the product is greater in the ashes which have larger initial iron fractions. These trends are illustrated in Figure 8.10.

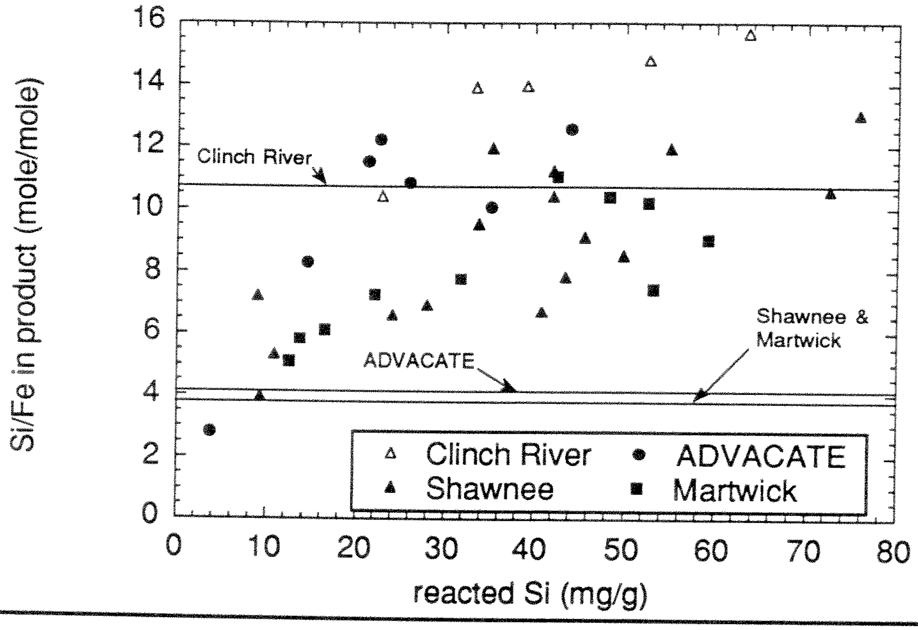

Figure 8.10 Changes in Si/Fe product ratio with extent of reaction - all ashes

Reacted silica is divided by the reacted iron as determined by selective dissolution. The line shows the relative ratio of silicon to aluminum in the ash. The reaction with iron is inhibited as compared to the reaction with silicon.

8.2 SORBENT CHARACTERIZATION

One of the main objectives of this chapter is to better explain the behavior of the CSTR at long residence times with gypsum present. The experiments performed to attempt to explain this behavior have been explored in Chapters 6 and 7. The behavior of these systems and the investigation is summarized here along with the material characterization methods used to attempt to differentiate the material formed. The behavior of CSTR systems with calcium sulfate present is summarized in Table 8.2. While this unexpected behavior was not observed with all ashes, it has been observed in two cases on the bench scale and in the pilot plant.

Table 8.2 Long residence time CSTR behavior - simulated recycle

Material	**Behavior**
Clinch River ash	area drops between 12 & 17 hr
Shawnee ash	to 18 hr - inconclusive
Martwick ash	to 16 hour - meets predicted
ADVACATE material	area steady between 10 & 24 hr

The lack of increased surface area with increased residence time in the reactor may be due to one of two causes. The first is the creation of a new phase other than the CSH believed to produce the high surface area product. The quantity of new material required to be formed can be estimated by noting the surface area expected per gram of reacted silicon (as illustrated earlier in this chapter) and comparing it to the actual reacted silicon. This comparison is made for Clinch River ash and ADVACATE material in Figure 8.11. If a new bulk product is being formed, the material would need to react with as much as 60 percent of the silica in the ash and form a solid phase with no surface area. This quantity of material should be readily identifiable by the techniques described later unless the low surface area product is almost identical to CSH. The other possible cause for the low surface area is that new material is formed and closes or blocks pores in the product. In this case, the amount of material may be small and might not be detectable.

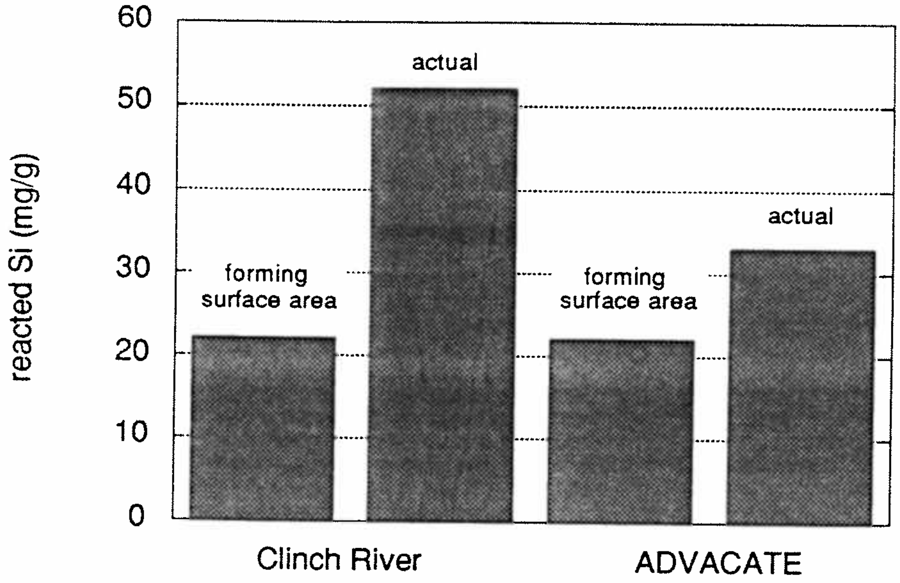

Figure 8.11 Low surface area silica fraction in CSTR experiments with gypsum

The actual silicon is determined by selective dissolution of samples from the long residence time CSTR that simulated a recycle system. Each had a lower surface area than expected. The fraction forming surface area is determined by assuming the line generated in Figure 8.5 can be used to predict how much silica is forming CSH, the high surface area calcium silicate material.

A series of tests including TGA, DSC, X-ray diffraction and IR were performed to characterize the product and test the first hypothesis. These did not show a conclusive difference between the materials with the unexpectedly low surface area and other materials. The results are described more fully below.

8.2.1 Thermogravimetric Analysis (TGA)

TGA provides information on the extent of sorbent hydration and can be used to help identify the type of material if water of hydration is lost over a specified temperature. An example of a TGA performed on a product sample is provided in Figure 8.12. This solids sample was taken from a Clinch River fly ash reaction with hydrated lime after three hours of reaction. There is a continuing loss of water over the temperature range between 100 and 430° C as the hydrated calcium silicates and aluminates lost water. The weight loss between 430 and 470° C is primarily from the unreacted calcium hydroxide losing water and forming lime ($Ca(OH)_2 \rightarrow CaO + H_2O$). The calcium silicates formed lose water over the entire temperature range examined and there is no readily identifiable trend in water loss.

Figure 8.13 shows the water loss of a sample obtained from a Clinch River experiment (12.3 hour residence time) with gypsum present. There is a greater water loss over the temperature range and this result is typical of experiments performed with calcium sulfite and gypsum present. In these cases, the reactants included additional hydrated material, and this was incorporated into the product. The total hydration of the reactants and the final product formed in each of the two reaction systems were comparable so no net hydration occurred over the reaction period. Figure 8.14 more clearly illustrates the water loss from gypsum between 130 and 150° C as the sample was heated. This sample was from a batch reaction with gypsum present after three hours of reaction time. Comparing the results from the two figures makes it apparent that the gypsum is incorporated into the product material over the reaction period.

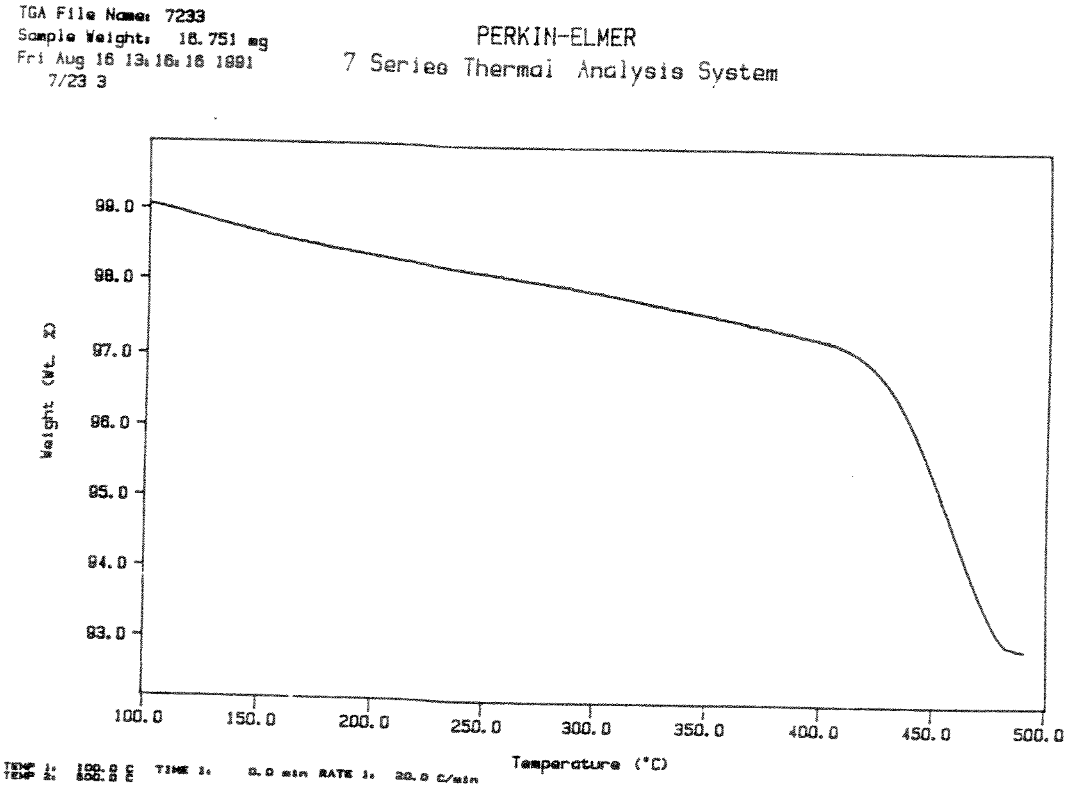

Figure 8.12 TGA of a Clinch River fly ash/hydrated lime 3 hour reaction sample

Water loss from a Clinch River hydrated lime/fly ash reaction sample (1/2 weight ratio). The early loss is from calcium silicates while the drop at 450° C is due to the unreacted calcium hydroxide.

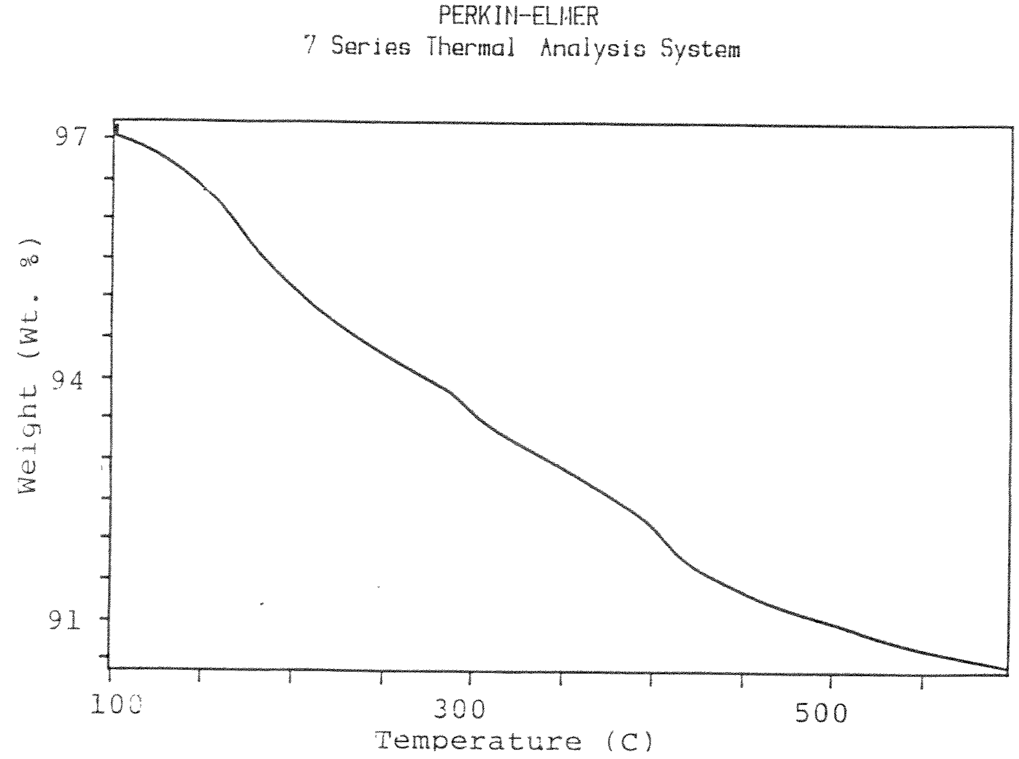

Figure 8.13 TGA of Clinch River recycle CSTR sample (12.3 hour residence time)

Water loss from a Clinch River hydrated lime/ash/calcium sulfite/gypsum CSTR reaction sample (1.8/4/0.5/0.5 weight ratio). The water loss is largely from calcium silicates and aluminates.

Batch reactions with gypsum present (Figure 8.15) show the same trends as the CSTR case. In both cases, the only clearly identifiable feature is a dip at about 280° C. The difference in hydration between the two samples is due to the difference in the extent of reaction. Figure 8.16 provides the curve for the long residence time CSTR experiment where surface area was lower than expected. The hydration of the product is consistent with a greater extent of reaction than indicated by the surface area. There is not a great difference in the shape of the curve and the others; although the dip at 280° C appears to be somewhat more pronounced. In all samples examined, the loss of waters of hydration from the calcium sulfite hemihydrate added to the reaction was not readily identified.

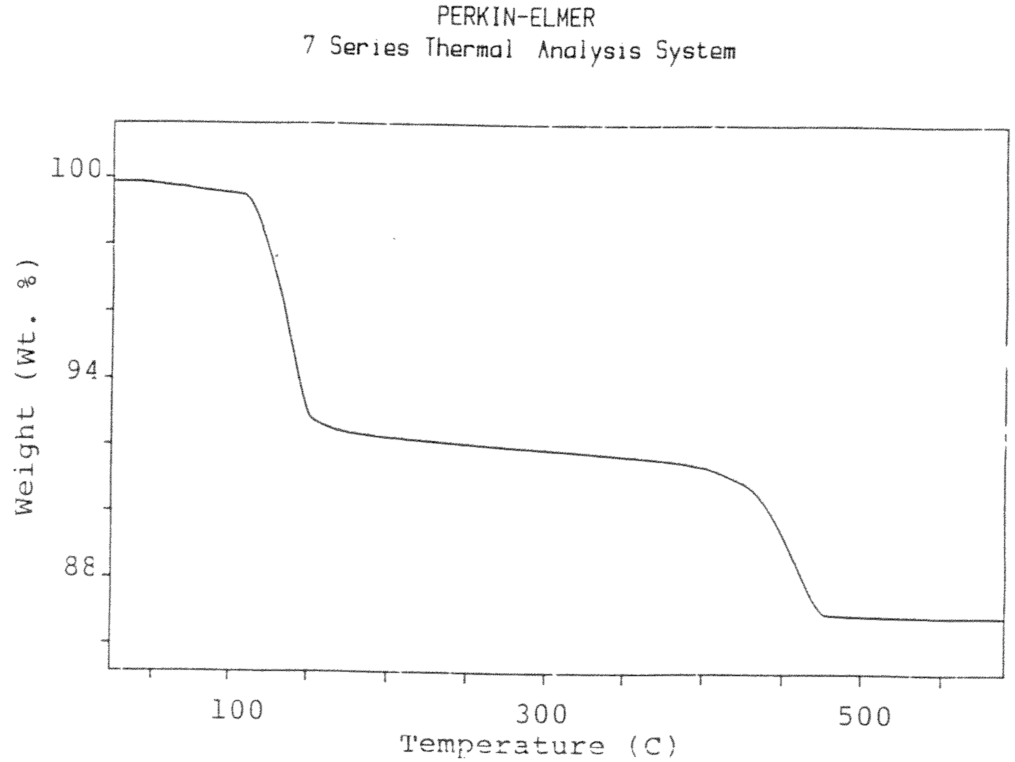

Figure 8.14 TGA of a Clinch River recycle 3 hour batch reaction sample

Water loss from a Clinch River hydrated lime/ash/calcium sulfite/gypsum batch reaction sample (4/4/1/4 weight ratio). The major water losses are due to gypsum and calcium hydroxide.

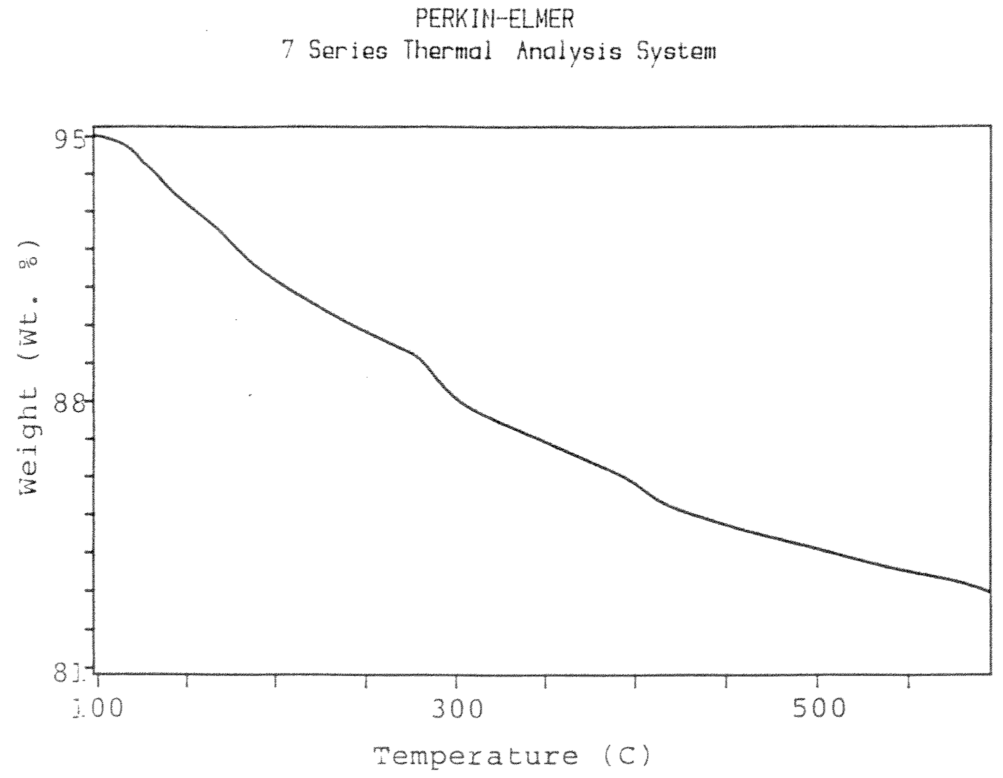

Figure 8.15 TGA of a Clinch River recycle 48 hour batch reaction sample

Water loss from a Clinch River hydrated lime/ash/calcium sulfite/gypsum batch reaction sample (4/4/1/2 weight ratio - reaction time was 48 hours). The water loss is largely from calcium silicates.

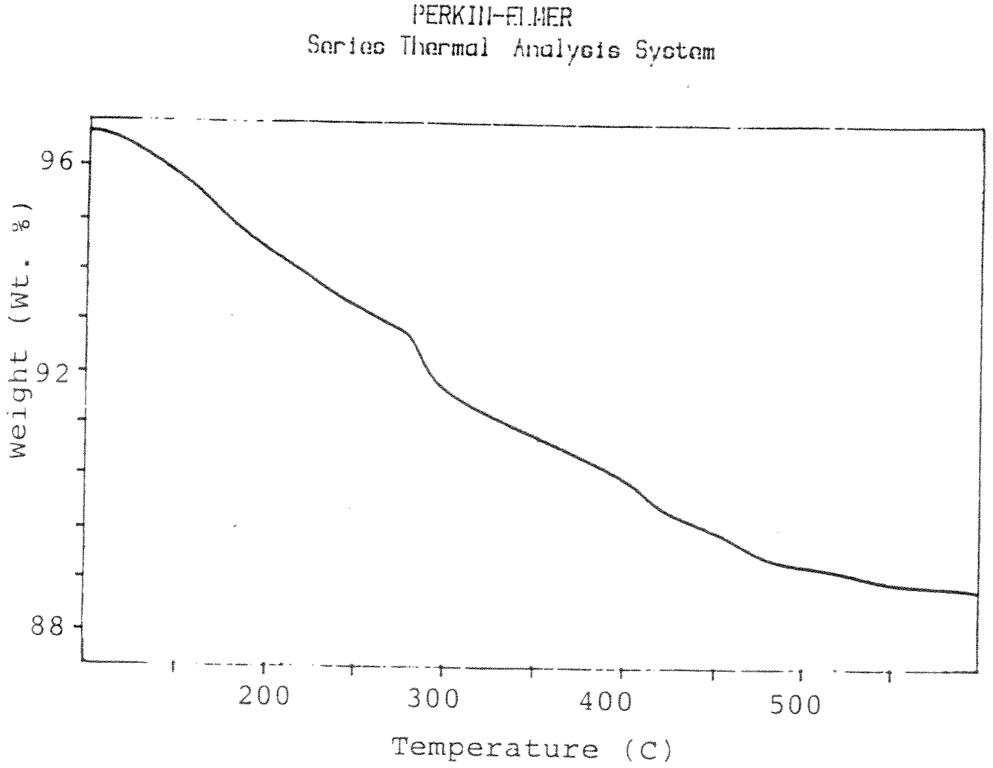

Figure 8.16 TGA of a Clinch River recycle low surface area CSTR sample

Water loss from a Clinch River hydrated lime/ash/calcium sulfite/gypsum CSTR reaction sample with low surface area (3/4/0.7/0.7 weight ratio - residence time was 17.5 hours). The water loss is largely from calcium silicates.

TGAs on the samples from ashes with a significant amount of char did not provide useful information as the char clouded the weight loss due to hydration and also caused problems in maintaining a constant temperature rise over the analysis (a nitrogen purge was not available for the analyses performed on these samples). An example of this behavior is shown in Figure 8.17. A summary of the weight losses of all the samples analyzed over the general regions for gypsum, calcium silicates and calcium hydroxide is provided in Table 8.3.

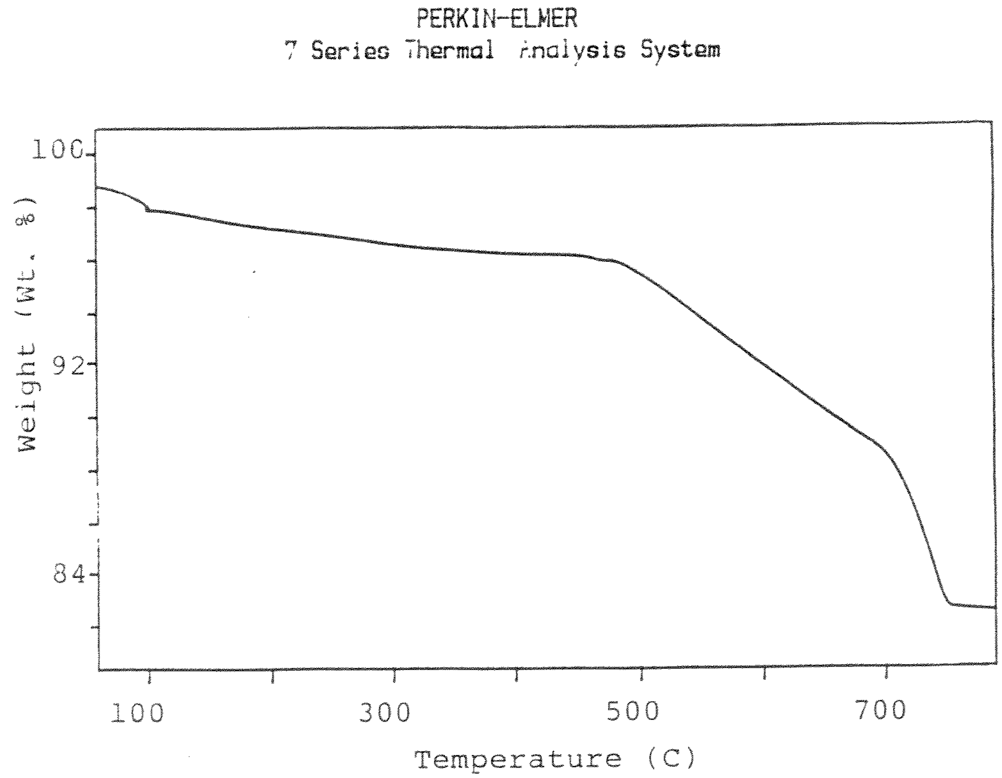

Figure 8.17 TGA of a Shawnee fly ash batch reaction product

Water loss from a hydrated lime/Shawnee fly ash batch reaction sample with 0.1 N NaOH. Reaction time was three hours. The weight loss is similar to other Shawnee ash samples; it was apparently biased by the char present in the ash.

Table 8.3 Summary of Clinch River fly ash TGA Results

Sample (Date, reaction time, reactant weight ratio*)	Gypsum Present (% of Added)	Ash hydration (100*g water loss/g ash)	Unreacted Calcium Hydroxide (%)	Hydration of Reactants (%)
7/23 2 1:2:0:0	-	1.2	63	8.1
6/24 3 1:2:0:0	-	2.4	17	8.1
4/2 11 4:4:1:4	58	12	47	14.2
7/2 17.5 CSTR 3:4:0.7:0.7	-	11	10	11.1
3/28 22 4.8:4:3:1	-	13	43	12.4
3/28 12 4.8:4:3:1	-	12	44	12.4
7/11 33 4:4:1:2	38	17	6	14.3
8/20 17.5 CSTR 3:4:0.7:0.7	-	11	8	11.1
5/13 8.6 CSTR 1:4:0.5:0.5	-	4.4	15	6.5
5/13 8.6 CSTR 1:4:0.5:0.5	-	4.7	15	6.5
5/8 5 CSTR 1:4:0.5:0.5	-	3.8	17	6.5

* - reaction time for CSTR experiments given as residence time (all in hours); weight ratios in calcium hydroxide/ash/calcium sulfite/gypsum ratio

8.2.2 Differential Scanning Calorimetry (DSC)

DCS provides information similar to that obtained by TGA but rather than providing the weight loss at a constant temperature rise, the required heat input to maintain that temperature rise is recorded. This analysis was restricted to comparing the long residence time ADVACATE CSTR experiment with low surface area to material from a batch reaction (Figure 8.18). Both curves show the same general trend and the small differences can be attributed to the differences in sample weight and the fraction of unreacted calcium hydroxide present in the sample. The calcium hydroxide peak occurs at a lower temperature in this analysis. This may be due to differences in the heating rates and in the different instruments used in the two analyses. These is no indication that the two product materials examined are significantly different.

8.2.3 X-ray Diffraction

X-ray diffraction provides the best available method to identify any crystalline material formed. Peterson (1990) performed X-ray diffraction on several samples, including those performed with pure components. He verified that the calcium silicate product formed was largely amorphous with most peaks on the X-rays due to unreacted calcium hydroxide or calcium carbonate. He did not analyze samples from reactions performed with gypsum present. The major peaks noted for each of the samples examined in this study is provided in Appendix C.

Figure 8.19 shows the results from an X-ray analysis performed on a sample from a batch experiment performed with Clinch River ash with gypsum present after 18 hours reaction. In addition to those species previously identified by Peterson, this X-ray shows the presence of an aluminum monosulfate species ($Ca_4Al_2SO_{10} \cdot 12H_2O$ with major peaks at 10 and 19 degrees 2-theta No. 18-275 (JCPDS, 1993)). This species is mentioned in concrete literature and is typically

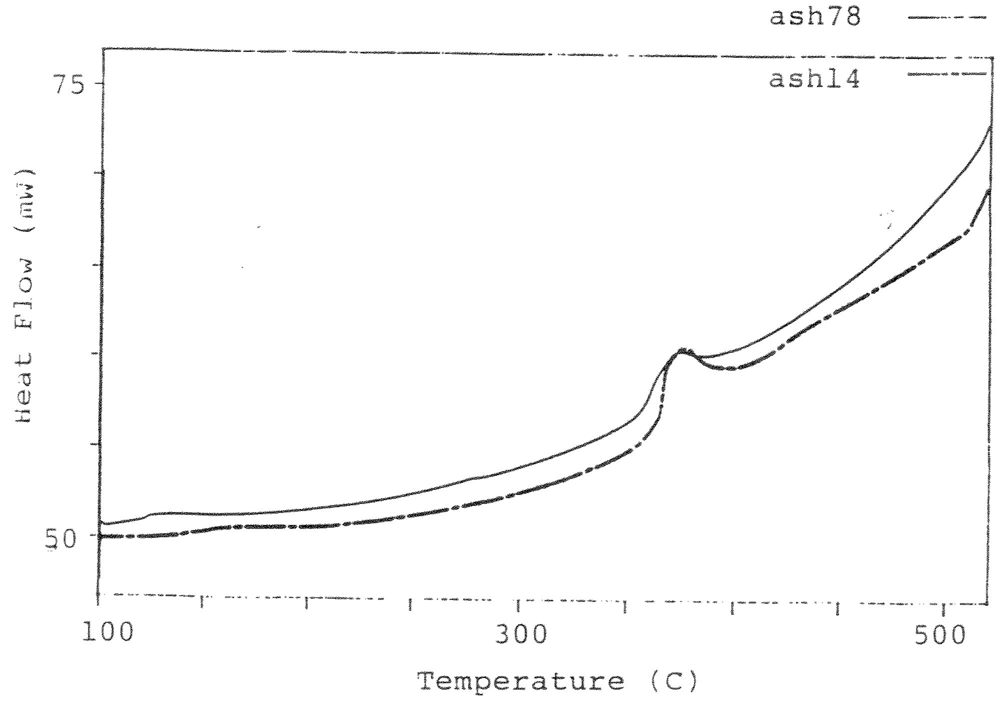

Figure 8.18 DSC comparison of low surface area to normal ADVACATE product

The 24 hour residence time CSTR product (ash78 - 37.4 m^2/g) is compared with a batch sample of comparable surface area (ash14 - 40.7 m^2/g)

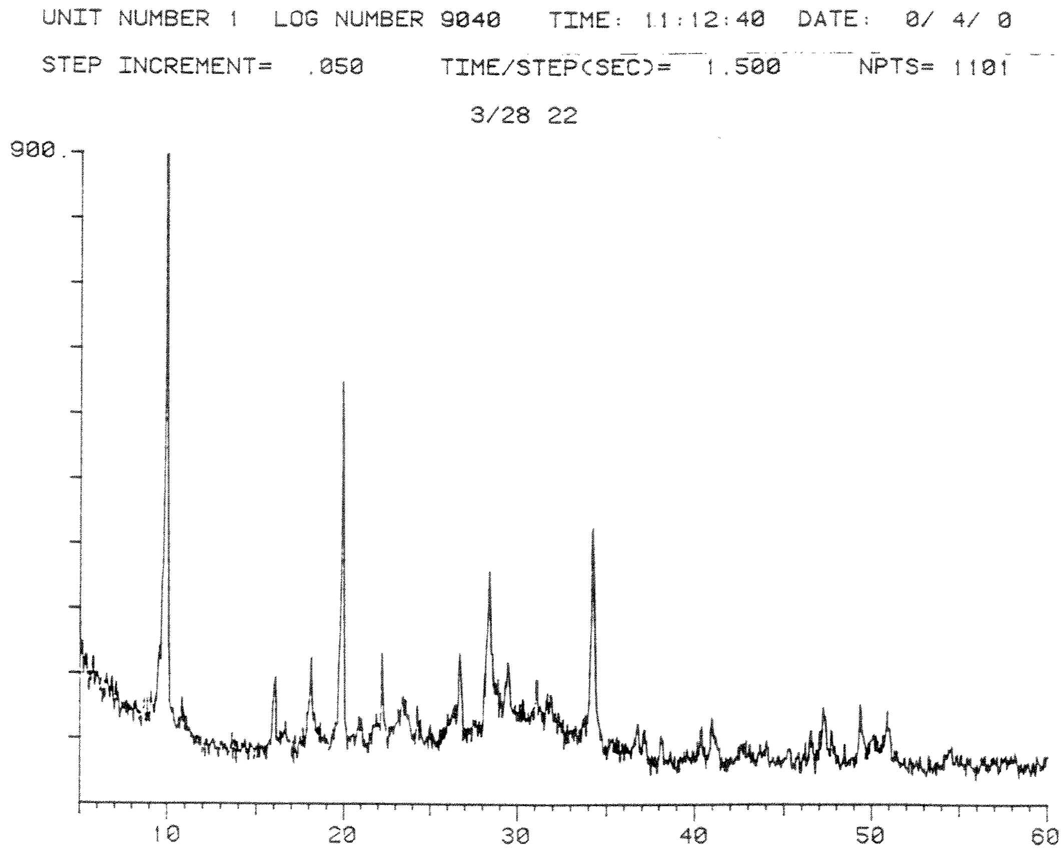

Figure 8.19 X-ray diffraction results for a Clinch River recycle batch reaction

The sample is from a batch reaction of hydrated lime/Clinch River fly ash/calcium sulfite/gypsum (4.8/4/3/1 weight ratio) reacted for 18 hours.

formed after ettringite has decomposed. Unlike ettringite, it does not have a high surface area. Figure 8.20 shows the results from an X-ray of a CSTR sample with gypsum present (12.3 hour residence time) and is consistent with the results from the batch reaction.

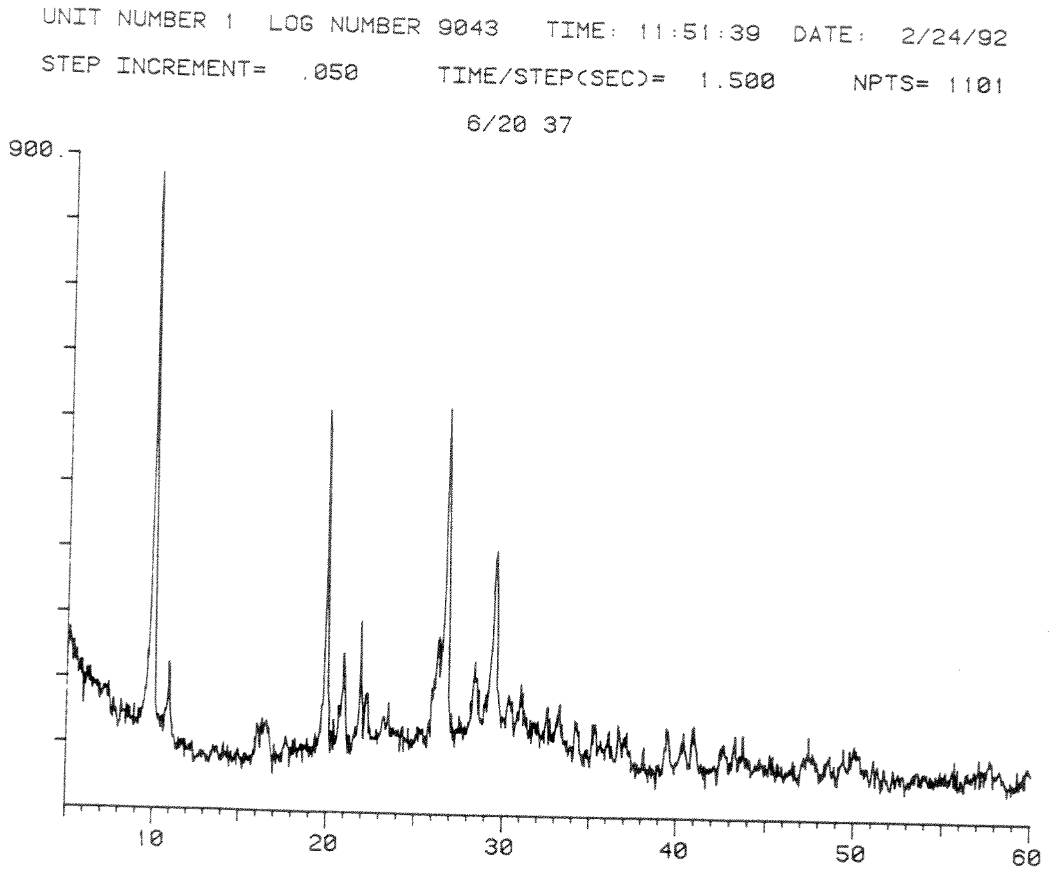

Figure 8.20 X-ray diffraction results for a Clinch River recycle CSTR reaction

The sample is from a CSTR reaction of hydrated lime/Clinch River fly ash/calcium sulfite/gypsum (4.8/4/3/1 weight ratio) with a residence time of 12.3 hours.

The long residence time CSTR, low surface area case is shown in Figure 8.21. In this case, the magnitude of the two major peaks is swapped but this is likely due to a new preferred orientation due to a difference in the moisture content of the samples. The differences in the two peaks has been noted in concrete literature (Taylor, 1964). There is no significant difference that would indicate a new product.

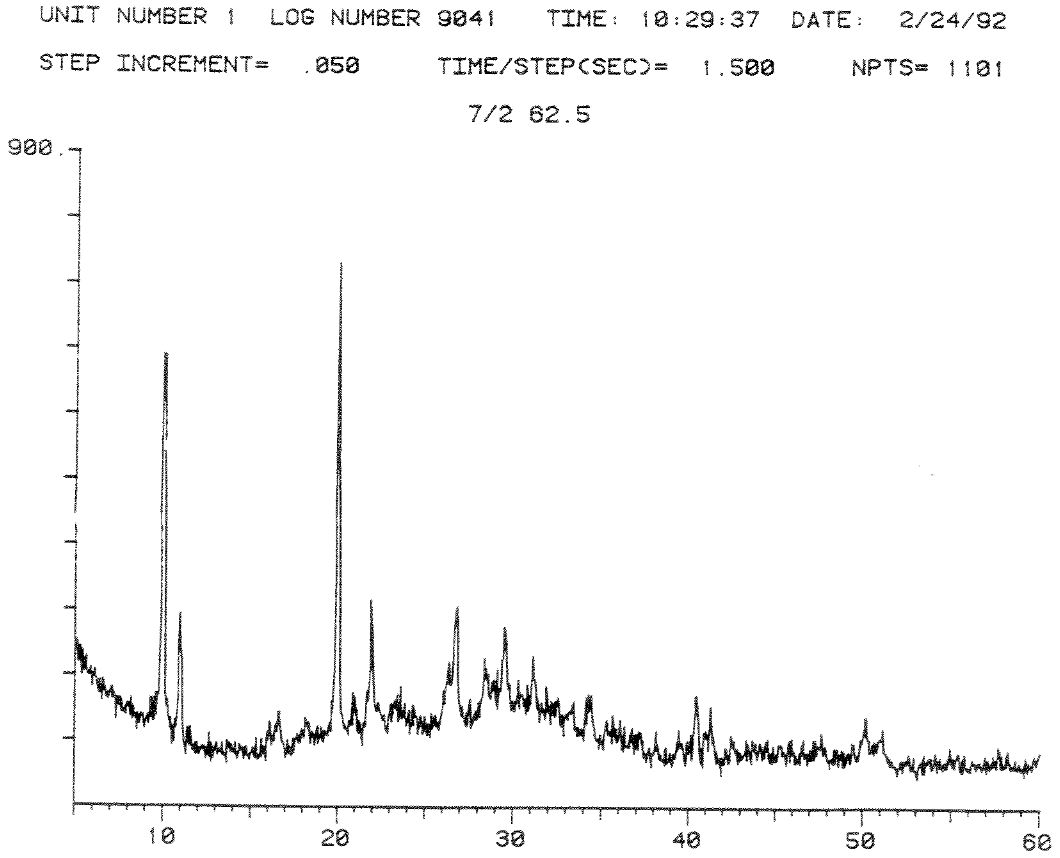

Figure 8.21 X-ray diffraction results for low surface area Clinch River CSTR

The sample is from a CSTR reaction of hydrated lime/Clinch River fly ash/calcium sulfite/gypsum (3/4/0.7/0.7 weight ratio) with a residence time of 17.5 hours. This sample had a surface area lower than expected based on reaction time and other reaction indicators.

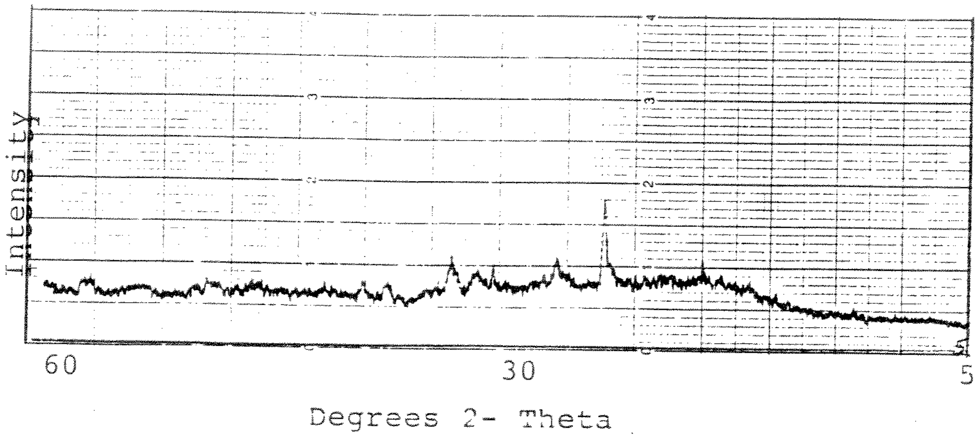

Figure 8.22 X-ray diffraction results for Shawnee ash reaction with NaOH added

The sample is from a batch reaction of hydrated lime/Shawnee fly ash (1/4 weight ratio) with 0.2 N NaOH. The reaction time was 12 hours.

X-ray diffraction analysis was performed on other samples to better understand the effect of additives on the reaction product. (Figures 8.22 and 23). The sample prepared with sodium hydroxide present exhibited very little crystallinity with a possible unique species being $Na_4Ca_8Si_5O_{20}$ (JCPDS No. 30-1174). The sample prepared with calcium chloride showed more peaks indicating the presence of β-$Ca_4Al_2O_6Cl_2 \cdot 10H_2O$ (JCPDS No. 31-245). The pilot plant product used for the ADVACATE bench scale experiments was also examined at Acurex (Figure 8.24). The reaction product exhibited little crystallinity; the peaks were due to silicon oxide from the ash, calcium carbonate from the carbonation of calcium hydroxide in the flue duct, calcium sulfite and sulfate from the reaction of sulfur dioxide with the sorbent and unreacted calcium hydroxide.

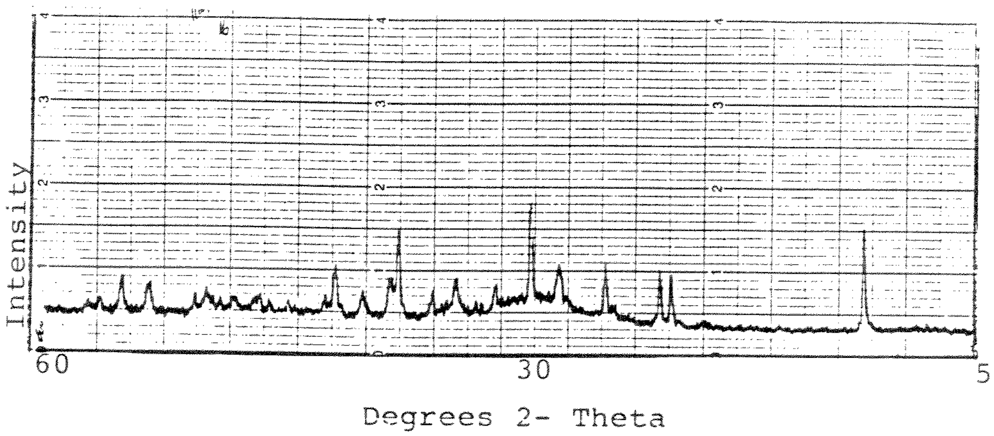

Figure 8.23 X-ray diffraction results for Shawnee ash reaction with $CaCl_2$ added

The sample is from a batch reaction of hydrated lime/Shawnee fly ash (1/1 weight ratio) with 0.6 N $CaCl_2$. The reaction time was 16 hours.

8.2.4 Infrared Spectrophotometry (IR)

Analysis by powder IR was limited to a comparison of the ADVACATE 24 hour residence time, low surface area CSTR sample to similar batch reaction material. The plots from the two samples are provided in Figures 8.25 and 26. Any differences noted in the plots were due to the differences in extent of reaction of the ash and calcium hydroxide. This analysis was limited by the large particle size and a finer powder would have been desirable. The left hand side of the plot (higher wave numbers) is depressed due to large particle size of the samples. Peaks due to hydroxide (at 3650), carbonate (1400 to 1500 and 800), sulfite (990 and 620) and small amount of sulfate (1000 to 1200) can be identified on the plot (Meserole, 1994). Again there was no significant difference in the reaction products.

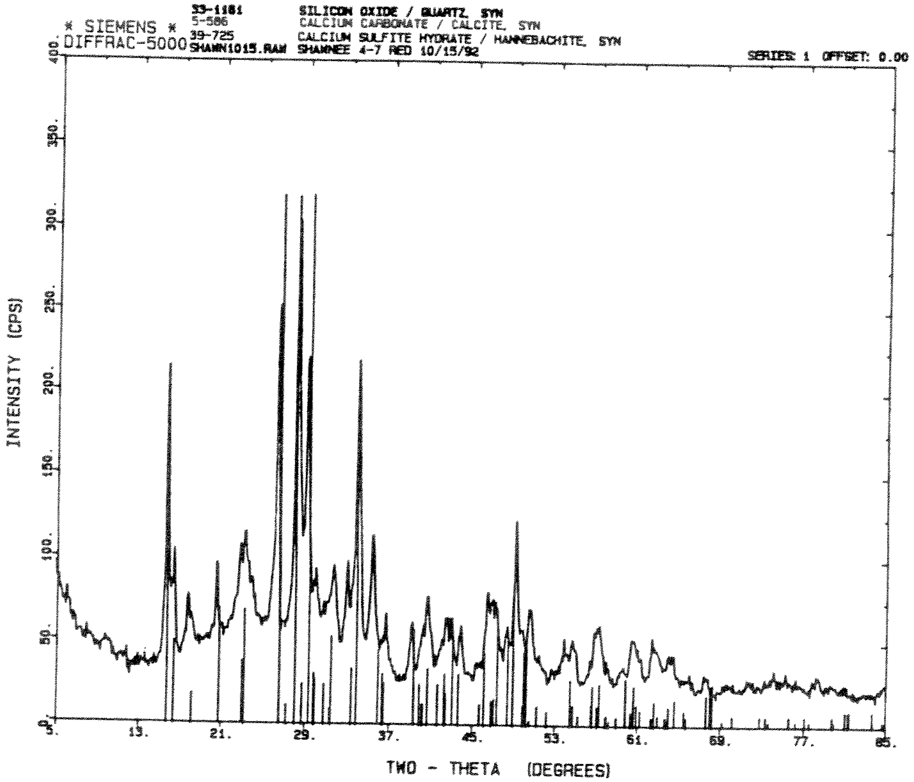

Figure 8.24 X-ray diffraction results for ADVACATE material

The sample is from the Shawnee pilot plant ESP and was analyzed by Acurex.

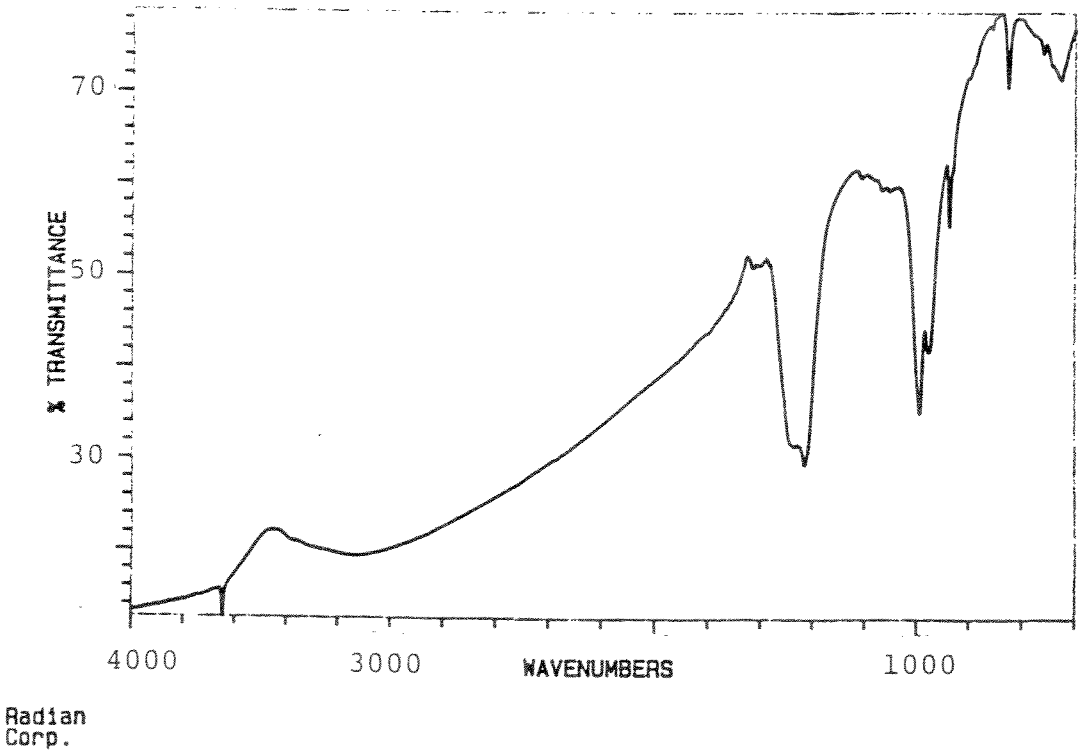

Figure 8.25 IR analysis of ADVACATE batch reaction product

This sample is from a 14 hours batch reaction of ADVACATE material with hydrated lime. It is similar to results from the CSTR (both high and low surface area - Figure 8.26).

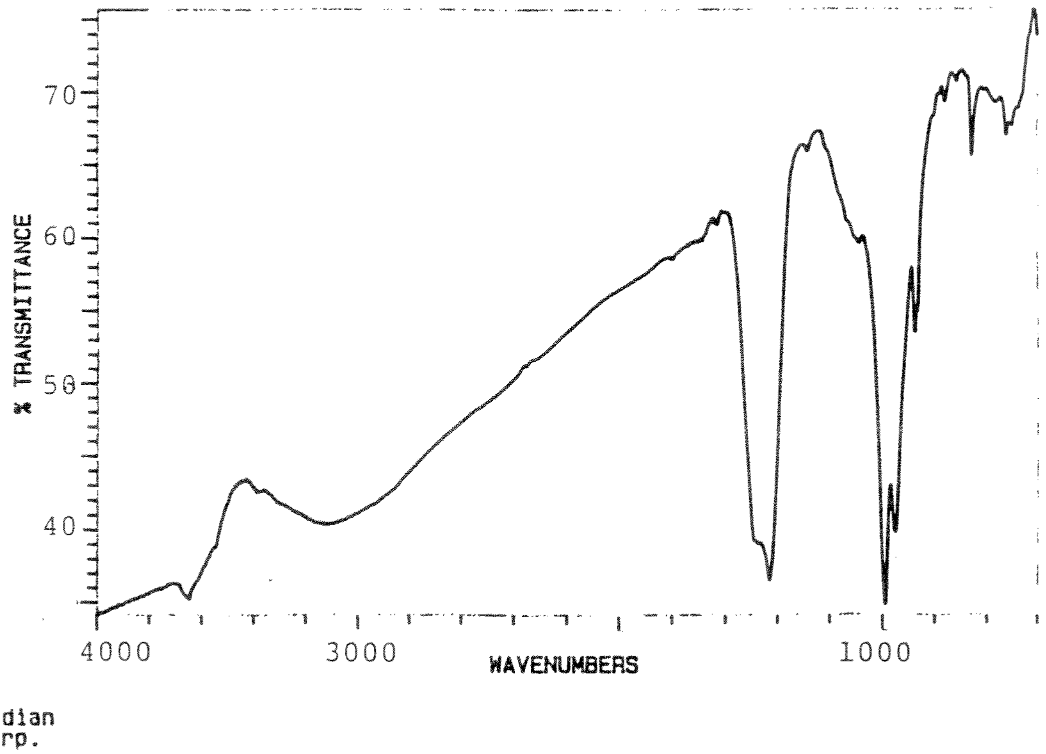

Figure 8.26 IR analysis of ADVACATE CSTR reaction product

This sample is from a 24 hour residence time CSTR reaction of ADVACATE material with hydrated lime. It is typical of results from the batch reaction (Figure 8.25).

8.3 SURFACE POROSITY

The previous examination further reinforces the conclusion that the calcium silicate product is an amorphous, hydrated calcium silicate of variable composition. There is little crystallinity present and the low surface area CSTR material is not readily distinguishable from the other calcium silicates formed. This leads to a more detailed examination of the porosity forming the surface area of the material. It is possible that in the case of the low surface area product, the lowering of surface area is not caused solely by a new bulk phase but by the blocking of pores in the calcium silicates already formed. This possibility was examined by characterizing selected samples through Scanning Electron Microscopy (SEM) and the pore size distribution. The last section of this chapter will summarize the additional experiments performed in a attempt to propose a likely cause for the low product surface area observed in the long residence time experiments.

8.3.1 Scanning Electron Microscopy (SEM)

The calcium silicate product was examined by SEM earlier in Chapter 6. An example of the product from the low surface area product is found in Figure 8.27. It has the same general appearance as the other material with the porous surface being visible but the resolution of the photograph is not good enough to note whether or not pores have been plugged with other material. This comparison is consistent with the earlier efforts to differentiate the material from the other products formed as there is no other significant bulk material identifiable.

8.3.2 Pore Size Distribution

A pore size distribution was obtained by nitrogen adsorption/desorption to determine if there was any significant difference in the distribution that might be attributed to material blocking the pores. A typical adsorption and desorption isotherm is provided in Figure 8.28. There is a wide spread of pore sizes with the mean pore size for four samples given in Table 8.4. This measurement in itself is not useful to compare the samples for pore blockage.

Figure 8.27 SEM of low surface area Clinch River CSTR product

Porosity can be normalized by sample surface area to allow direct comparison of the pore size distribution for samples with different surface areas. Cumulative porosity was compared for two samples with almost 100 percent silica

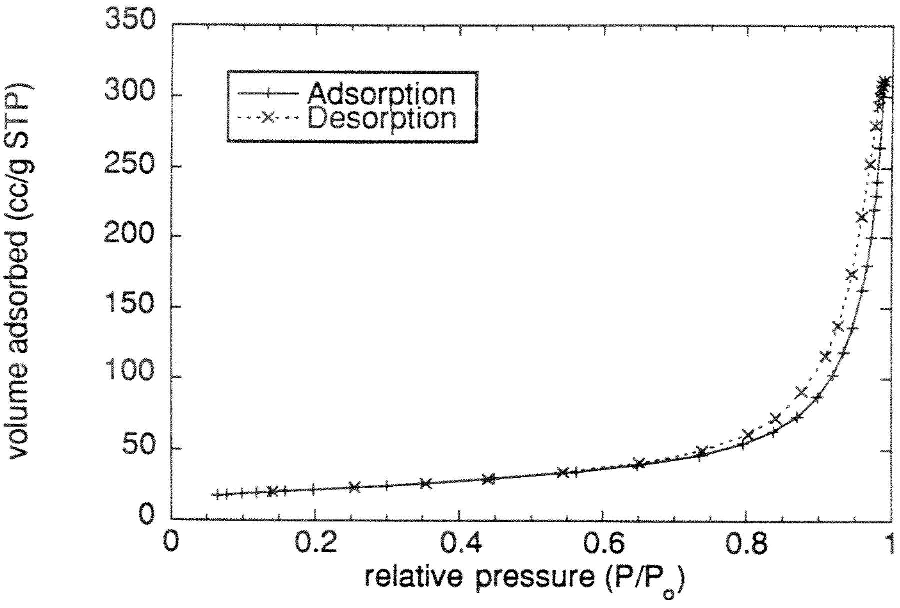

Figure 8.28 Typical nitrogen porosity isotherms for ADVACATE product

Nitrogen adsorption/desorption isotherm for the product of an ADVACATE material reaction. Hydrated lime was reacted with ADVACATE material in a 1/2 weight ratio for 62 hours.

utilization (Figure 8.29). One sample was 24 hour CSTR reaction product reacted for an additional 50 hours of batch reaction. It had lower surface area than expected based on the reaction time and the reacted silica (54.4 m^2/g). The other sample was from a batch reaction with a surface area of 87.6 m^2/g. The total adsorption porosity was 0.00545 and 0.00528 cm^3/m^2 for the CSTR/batch and batch reaction material respectively. The desorption values were 0.00556 and

0.00613 cm^3/m^2. The curves are very similar except that the fraction of pores less than 50 Å was greater in the long residence CSTR time product.

Table 8.4 ADVACATE product pore volume

Sample	**Pore Volume (cm^3/g)**
62 hr batch reaction	0.41
25 hr batch reaction	0.32
24 hr CSTR + 50 hr batch reaction	0.23
21 hr batch reaction	0.23

The low surface area case was also compared to a batch reaction sample with similar surface area and a CSTR sample with the expected surface area based on the reaction time and reacted silica. These showed the same qualitative behavior as the example shown. This behavior is not inconsistent with that which might be observed should the pores be reduced in size due to the precipitation of a new product material in the pores. Figure 8.30 shows the difference expected in the adsorption isotherm if the pore radius was reduced by 30 Å in the batch sample. This effectively increases the contribution of the small pores to the pore volume.

8.4 INVESTIGATION SUMMARY OF LOW SURFACE AREA CSTR PRODUCT

The reaction of ash and lime in the presence of calcium sulfite and calcium sulfate produced low surface area solids in three cases. The material analyses performed could not detect a significant difference in the low surface area product and other product despite calculations which showed that the product would have to comprise a significant fraction of the calcium silicate material. It is possible, however, that a smaller fraction of material may be plugging pores thereby reducing product surface area with a smaller, undetectable fraction of material.

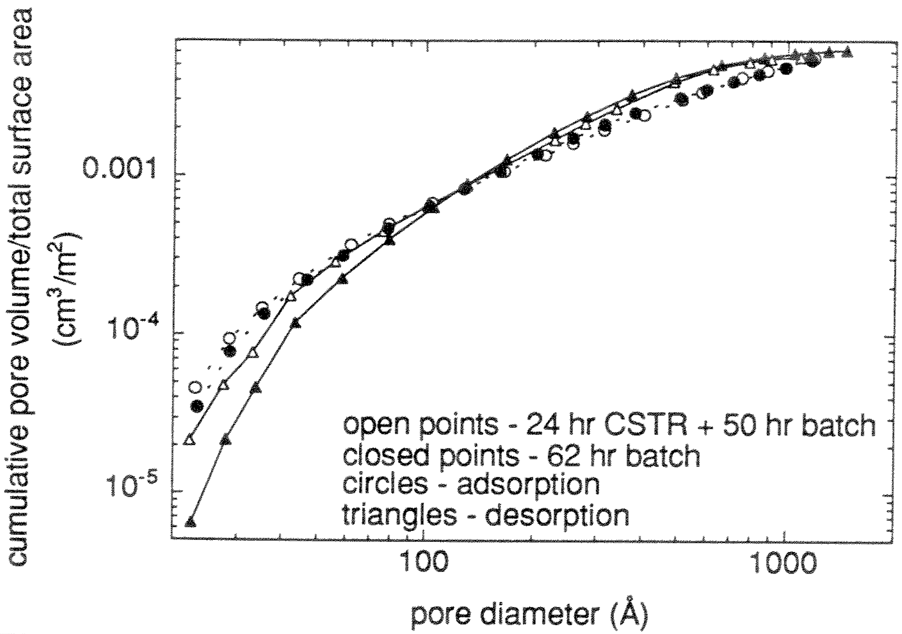

Figure 8.29 Cumulative pore size distribution comparison of two samples

The two samples shown have comparable reacted silica but the batch reaction sample had a greater surface area (54.4 versus 87.6 m^2/g). Pore diameter was obtained by using BJH (Barrett, Joyner, Halenda) method.

Experiments performed with Clinch River ash showed this behavior was promoted by the addition of more gypsum to the reaction although the behavior was also observed in reactions with ADVACATE material despite the small fraction of gypsum in the reactants (although additional oxidation of sulfite to sulfate could have taken place in the open CSTR). Experiments performed with ADVACATE material showed that the loss of product surface area was permanent and could not be restored by additional batch reaction.

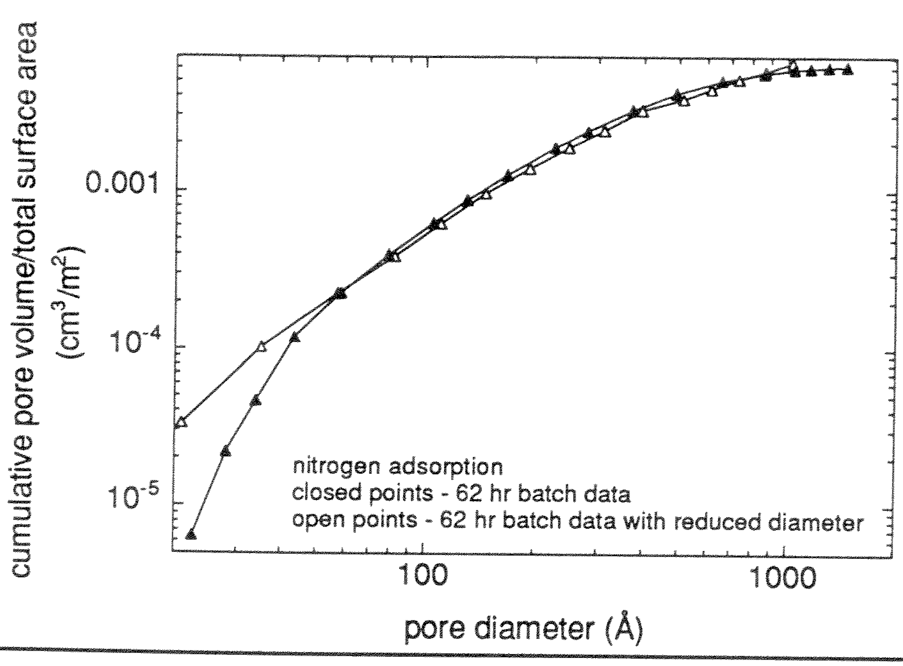

Figure 8.30 Effect of reducing pore diameter on pore size distribution

The adsorption isotherm for the 62 hour ADVACATE batch reaction with hydrated lime (1 part hydrated lime to 2 parts ash). It is compared with the result of reducing the diameter of all pores by 30 Å.

A major difference between the batch and CSTR reaction environments is the presence of particles of ash, lime and product materials in the same reactor for different reaction times. This may allow interactions between the materials that would not take place in a batch reactor. If the segregated flow model did not strictly hold, there might be interactions that could occur through the solution between fresh ash particles and older product material. For example, it was shown that there is always some level of silicate in solution. If this silicate reacted at the surface of a high calcium fraction, high surface area product particle, it might affect the large surface area of the material.

This possibility was examined by reacting ground Shawnee ash for 24 hours (surface area - 238 m^2/g ash) and then adding fresh ash over the next two hours (10 percent of the original amount). If the presence of fresh, reactive ash affected the existing product, it would be seen by a reduction in surface area. This did not occur, however, as the surface area of samples taken over the next five hours ranged from 240 to 259 m^2/g ash.

The other mechanism through which a transfer from reacted particles to fresh ash could occur is through nucleation of a new product phase. It is possible that the thermodynamically stable phase for the system under the reaction conditions is a lower surface area material. Its formation may be limited by the nucleation and growth kinetics. In a batch reaction, there would be limited time for nucleation to take place before all the available silica had been reacted to form the higher surface area CSH. The presence of highly reacted material in the CSTR could increase the formation rate of the lower surface area product if the nuclei (or silica dissolved from the ash) could be transferred from ash particle to particle.

This hypothesis was examined by performing several experiments. First, a batch reaction was performed with ADVACATE material and was continued until no further surface area growth was observed (to 62 hours - maximum surface area of 90 m^2/g at 46 hours). A second batch reaction was performed with the low surface area product from the 24 hour residence time CSTR. This material was reacted for an additional 50 hours resulting in a product with a surface area of 53 m^2/g. The resulting product surface areas are shown on Figure 8.31. There was a variance in the product surface area observed in the batch reactions performed and that is shown by the cross hatched bar. Finally, the 24 hour CSTR product was mixed with fresh ADVACATE and hydrated lime in a 1/2/1 weight ratio (that is a reaction with 3 parts raw materials and one part low surface area product).

If the batch reaction of these materials occurred so that all materials reacted independently, the resulting maximum surface area would be that shown in the third column on the figure (an arithmatic average of the maximum surface area in each of the cases). Two experiments were performed with reaction times from 54 to 62 hours and the resulting product surface areas are shown by the last bar (from 56 to 64 m^2/g). In one of the experiments, the material behaved almost exactly like the CSTR material, indicating almost complete transfer of the effect to the new material. In the other case, there is an intermediate condition where some surface area growth appears to be inhibited. The experiments support the possibility of a nucleation type of phenomenon promoting the lower surface area product.

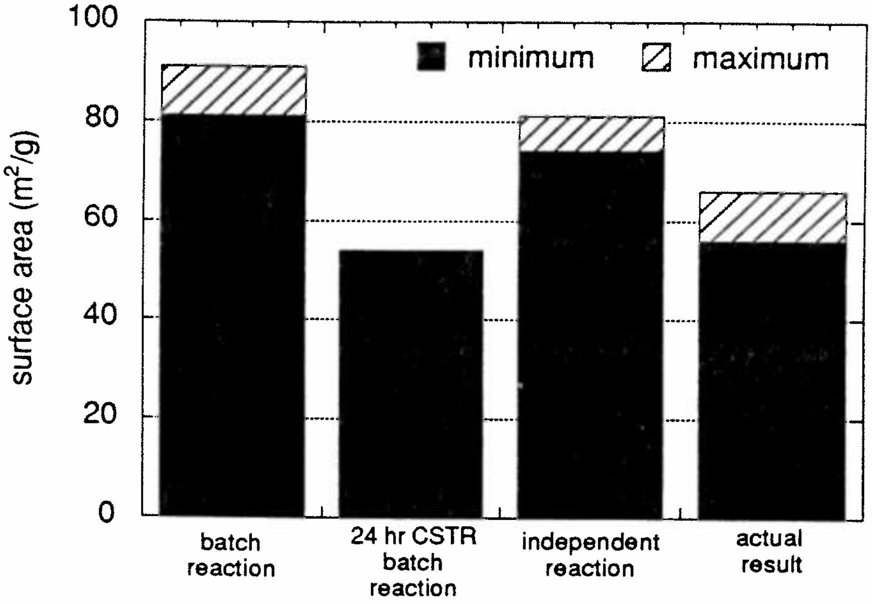

Figure 8.31 Batch reaction with added ADVACATE CSTR product material

High surface area product from the ADVACATE batch reaction and the CSTR product (first two bars) are compared to the product of a batch reaction with CSTR product and new reactants. If the materials reacted independently, the resulting surface area would be that indicated by the third bar. The two materials do not act independently in the batch reaction as seen by the final bar. The cross hatched areas indicate scatter in experiment results.

Chapter 9

Conclusions & Recommendations

This study continued the examination of the fly ash/hydrated lime reaction under more varied and prolonged reaction conditions than previous work. The major conclusions are presented in the first section of this chapter. A narrative summary of the major findings from this work is presented in the second section. The chapter concludes with recommendations for further work.

9.1 CONCLUSIONS

The following are the major conclusions from this study of the reaction of low calcium ash to create ADVACATE sorbent:

1. The reaction of fly ash with hydrated lime is accelerated by high initial hydroxide concentration as the ash is dissolved more quickly, becoming available to react with calcium hydroxide. After the initial product layer has developed on the ash, high hydroxide concentrations have a negative impact on the reaction as the dissolution of calcium hydroxide is inhibited. Reaction rate does not correlate with bulk solution hydroxide level after the product layer has been formed.
2. Hydroxide concentration increases through the course of the fly ash/hydrated lime batch reaction due to the dissolution of potassium and sodium from the ash. Additives such as gypsum and calcium chloride act

to buffer the change in hydroxide concentration over the course of the batch reaction. This allows for prolonged reaction and higher surface area product despite a lower initial reaction rate. Greater final product surface areas were noted in experiments with lower hydroxide concentrations.

3. The impact of additives is largely due to their effect on solution chemistry. Analysis of the product solids showed little difference between those solids reacted with gypsum, calcium chloride or sodium hydroxide and those without the additives. A calcium aluminum sulfate species was formed when gypsum was present but this species did not impact surface area.
4. The product surface area was correlated with reacted silicon. This was independent of the ash or additives in the experiment. The work supported the hypothesis that CSH, an amorphous hydrated calcium silicate, created the high product surface area.
5. Silicon reacted preferentially over the aluminum and iron in the ash. The silicon to aluminum ratio in the product increased with extent of reaction until leveling at about twice the ratio in the ash. This ratio was unaffected by additives to the reaction. The iron in the ash exhibited similar behavior.
6. The segregated flow CSTR model fit the experiment results in systems with calcium chloride and gypsum present. These additives allowed for a stable batch reaction solution composition so that the assumptions required for the segregated flow model were met. The exceptions to this were in several CSTR reactions with gypsum present and residence times

greater than 10 hours. The product from these experiments showed the expected calcium hydroxide reaction and ash dissolution but the surface area was less than expected.

7. The low surface area product at long CSTR residence times appeared to be due to a nucleation of low surface area product at the longer residence times. It probably plugged the pores of the high surface area calcium silicates but this species could not be identified. Similar behavior was also observed in the pilot plant.
8. CSTR experiments performed without additives present generated product with surface area highly dependent on the fraction of calcium hydroxide present in the feed to the reactor. This was also true of the batch reactions. Both of the these systems showed that the availability of calcium hydroxide could limit the reaction rate of fly ash and hydrated lime.
9. Bench scale work was compared to pilot plant results. The pilot plant results were consistent with those expected based on the bench scale work although the comparison was limited due to little pilot plant data and differences in the operation of the systems.
10. Bench scale work performed at calcium hydroxide to ash ratios of less than 1:1 may not be representative of an operating system. A high ratio of lime to ash is likely to be used in an operating system and the reaction rate can depend on this ratio.

9.2 SUMMARY

The summary is structured by reactor system - batch, CSTR and reaction of pilot plant material. Each section presents different elements of the reaction forming ADVACATE material based on conclusions reached through the experimental work performed.

9.2.1 Ash/Lime Batch Reaction and the Impact of Additives

The major areas examined in the batch reaction included the impact of the reactant weight ratios, the bulk solution chemistry and the time of reaction. The product material was also examined to determine and identify significant product phases formed in the reactions with additives (sodium hydroxide, gypsum, calcium sulfite, and calcium chloride) present.

9.2.1.1 Product Characterization

Reacted silicon correlated with surface area independent of the ash (or silica fume) studied. It was also largely independent of additives to the reaction system. The surface area also matched that expected based on literature values for the amorphous calcium-silicate-hydrate, CSH. Material characterization using X-ray diffraction, SEM, TGA, DSC and IR also supported CSH as being the primary reaction product creating the high product surface area. Additives such as gypsum were incorporated into the product but did not have a significant impact on the calcium silicates forming the surface area. The same was true of the other additives examined (calcium sulfite hemihydrate, sodium hydroxide, and calcium chloride). The calcium to silicon mole ratio in the product formed ranged from

0.8 to 2.2 depending on the calcium concentration in solution, behavior similar to that expected from CSH.

Other major products formed in the reaction of ash and hydrated lime were calcium aluminates and calcium aluminum sulfates if gypsum was present in the reaction system. Surface area generation was independent of these species. The sulfate appeared to substitute for calcium hydroxide to some extent allowing for lower calcium hydroxide utilization in reactions with gypsum present. The incorporation of sulfate into the product was noted by X-ray diffraction showing the calcium aluminum sulfate hydrate while the disappearance of gypsum was observed in solution chemistry changes and in TGA of product material. The reaction of the aluminum in the ash was not as rapid as the reaction of calcium with silicon and the product had an aluminum content approximately one half that of the ash. This behavior was again independent of any additives to the system. Iron behaved like aluminum but no product species was identifiable with X-ray diffraction.

9.2.1.2 Batch Reaction

The impact of the ratio of calcium hydroxide to fly ash in the reactor was dependent on the additives to the reaction system. Since both reactants are solids - one with extremely low solubility (ash) and the other with limited solubility (calcium hydroxide) at the reaction conditions, the effect of changing the ratio of the two solids in the reaction is dependent on the rates of dissolution of the two species in the reaction system. A high calcium hydroxide fraction promoted a greater reaction rate in experiments performed in high hydroxide solutions (fly ash/hydrated lime and experiments with sodium hydroxide added). The reaction rates in experiments with a more buffered solution hydroxide and higher dissolved calcium (reactions with gypsum or calcium chloride present) were largely independent of the ash to calcium hydroxide ratio. This disparity is explained by examining the effect of solution composition on the reaction forming calcium silicates.

SEM and solution composition analyses showed that the calcium silicate product forms on the surface of the fly ash. This requires the calcium hydroxide to dissolve, go through the bulk solution and diffuse through the product layer on the ash to the ash surface to dissolve silica from the ash. The silicate can then react with the calcium and precipitate to form the high surface area product. Initially, ash dissolution should occur much more slowly than the transport of the calcium and hydroxide ions from the calcium hydroxide particle. The ash dissolution was measured in terms of hours while calcium hydroxide can reach saturation in minutes in pure water. Even so, ash dissolution was measured for Shawnee ash without a product layer and this rate was generally greater than the reaction rate measured in the fly ash/hydrated lime system.

As the batch reaction proceeds, the dissolved calcium concentration in the bulk solution decreases below that expected for a saturated solution. This decrease may be attributed in part to a lessening of the solid calcium hydroxide activity as the particle is exposed to the reaction environment for a prolonged period. It may also be due to the dissolution of the calcium hydroxide playing a role in the reaction rate. If the reaction rate was only limited by ash dissolution, it would not be dependent on the ash to hydrated lime ratio. It is, however, in the high hydroxide reaction systems studied. Both of these reaction systems exhibit a large decrease in calcium concentration as the reaction proceeds. Adding a larger fraction of calcium hydroxide delays this decrease so that the reaction may occur at the maximum rate over a longer reaction period.

The lowering of calcium solubility is due to the high hydroxide concentration and the lowering of the solid calcium hydroxide activity with reaction time. This phenomenon was noted with all the ashes and also with silica fume. It is probably due to the formation of some product on the surface of the calcium hydroxide particle that occurs due to the limited solubility of silica and alumina in the basic solution. This effect can be minimized by lowering the bulk solution hydroxide composition and increasing the dissolved calcium concentration with additives such as gypsum and calcium chloride.

Silicate and aluminate in solution were not measurable in systems with calcium chloride or gypsum present and the dissolved calcium levels were greater and more constant. The minimum measured dissolved calcium level for sustained surface area growth was about 2 mM which corresponds to CSH solubility from literature (Taylor, 1964). The reaction rate of the two low hydroxide systems was lower at short reaction times as ash dissolution is dependent on hydroxide concentration. The bulk solution pH provides an adequate measure of reaction site hydroxide concentration at short reaction times as the ash surface had not been isolated from the bulk solution by a product layer.

After the establishment of an initial product layer, the bulk solution hydroxide level (in the range examined - 0.01 to 0.5 M) had little impact on reaction rate. This is likely due to the ash being the source of alkali metals (potassium and sodium) so that the hydroxide level at the surface of the ash could be significantly higher than that of the solution. This explains the behavior of the system with calcium chloride where the reaction rate late in the reaction was much greater than that possible based on the bulk solution hydroxide concentration. High solution hydroxide inhibited the dissolution of calcium hydroxide and had a negative impact except for reaction times less than four hours or at high calcium hydroxide to ash reactant weight ratios.

The lower hydroxide/high calcium systems also allowed for increased silica utilization forming high surface area product. The reaction utilized 80 to 90 percent of the silica in the ash; a fraction that probably accounted for all the amorphous silica in the ash. This increase in utilization was due to reaction over a longer time period in these systems. The moderate changing solution composition in these two systems also allowed for a better approximation of CSTR behavior.

9.2.2 CSTR Performance

The CSTR examination covered two general areas (system and model performance) with two ashes (Clinch River and Shawnee) and two additives to the reaction (gypsum and calcium chloride).

9.2.2.1 Model

The reaction between ash and lime involves two solids, one (ash) having multiple compounds in heterogeneous particles. The system does not lend itself to an exact, mechanistic model. Further, the batch experiments showed that there are two potential rate determining steps - ash and hydrated lime dissolution. The segregated flow model was chosen as the best for approximating the CSTR as the reaction to form the CSH took place on the ash and the model only required a straight forward assumption. The segregated flow model required batch reaction data and it was necessary to assume that the batch reaction rate could approximate that observed in the CSTR.

9.2.2.2 Reaction with Calcium Chloride Present

The segregated flow assumption was met in the case of the experiments with calcium chloride added and this system performed as predicted by the model. The CSTR produced higher surface area product than the batch reactor for moderate residence times (4 to 8 hours) due to the exponential nature of the surface area growth in the batch system.

9.2.2.3 Reaction with Gypsum Present

The recycle (gypsum and calcium sulfite added to the reaction) system had a fairly constant solution composition so that the segregated flow model could be expected to predict the system performance in the CSTR. The approximation held for CSTR residence times up to 10 to 12 hours for all ashes studied but decreased or steady product surface areas were noted for Clinch River and ADVACATE material (see section 9.2.3) with CSTR residence times beyond 15 hours. Examination of the product material showed that reaction was taking place but that surface area was not generated. The was most likely due to a crystallization phenomenon as the low surface material only occurred with the CSTR material and was not observed in batch reactions. A small quantity of unidentified material could block the pores, decreasing surface area. This behavior was also observed at the Shawnee pilot plant.

9.2.2.4 Fly Ash/Hydrated Lime Reaction

The fly ash/hydrated lime system did not meet the assumption necessary for the segregated flow model due to the significantly changing solution chemistry during the batch reaction as potassium and sodium dissolving from the ash led to an increase in hydroxide and decrease in calcium concentrations with reaction time. Due to this, the CSTR did not match the prediction made using the model and batch reaction data. The CSTR product, like the batch reactor product, was highly dependent on the ash to calcium hydroxide weight ratio, with greater reaction taking place with a high calcium hydroxide fraction. The CSTR produced product with a greater surface than the batch reaction with the same residence time. This was due to a greater dissolved calcium level in solution than in the batch reaction. The greater calcium level was likely due to fresh calcium hydroxide being added to the reactor in the flow system.

The fly ash/hydrated lime CSTR performed better than the additive systems for CSTR residence times through six hours. At longer residence times, the system with calcium chloride provided the highest surface area product. Operating a CSTR with gypsum present can provide adequate product but may not provide the surface area expected at residence times greater than ten hours.

9.2.3 Grinding/Pilot Plant System

The final portion of this research effort focused on comparing simulated recycle material with actual pilot plant material and examining the pilot plant material over a wider range of conditions than were possible on the larger scale. The impact of grinding a low reactivity ash was also studied.

9.2.3.1 Simulated Recycle Material

The actual recycle material from the Shawnee pilot plant had a lower fraction of gypsum and significantly more calcium carbonate than the simulated material. This did not significantly change the batch reaction as both the ash and the recycle material reacted for a similar time and formed a product of similar surface area. The pilot plant material also had limited surface area after reaction with sulfur dioxide which was consistent with the results from a bench scale experiment.

9.2.3.2 Grinding

Grinding greatly enhanced the reaction of the Martwick ash as expected due to the slow reaction rate of the unground ash. The ground ash examined in this study confirmed that grinding is not appropriate for all ashes (for example, Shawnee fly ash) but will accelerate the reaction rate where the ash dissolution clearly limits the rate. The ground material also had greater surface area per gram of reacted silicon.

9.2.3.3 Reaction

Additives had less of an impact on this system due to the high calcium hydroxide to ash weight ratio in the pilot plant and also due to the presence of the small gypsum fraction. The high calcium hydroxide to ash ratio is likely to be seen in operating systems and reactions performed at the high ratios are more insensitive to additives to the reaction system. The CSTR segregated flow model fit the CSTR product well except for the low surface area, long residence time experiments noted previously.

9.3 RECOMMENDATIONS

The study of the reaction to form ADVACATE sorbent has been extensive and much of the research left to be performed is in specific areas. Some of these include:

- Examine the impact of additives and the CSTR on high calcium ashes. Experiments with high calcium ash to this point have utilized less than half the silica in the ashes. The high initial dissolution of potassium, sodium and alumina in these ashes may make them more reactive in experiments with calcium chloride or a high calcium hydroxide fraction present.
- Attempt to model the system using calcium hydroxide as the base species rather than ash. This would require additional experiments on several ashes.
- Better characterize/optimize the dry recycle material from the ESP. Presently, this material has low surface area and this could have a major impact on the economics of the system design. The ideal ADVACATE material would retain a high fraction of its surface area following reaction with sulfur dioxide.
- Examine the impact of grinding and particle size on the particle flow in a flue duct. This would provide insight on the value of grinding beyond a certain particle size in the system.
- Continue the examination of different silica sources. Sources such as silica fume can generate surface area in one-tenth the time as fly ashes.
- Perform additional work at the high calcium hydroxide to fly ash ratios likely to be seen in an operating system.

APPENDICES

Appendix A

Reproducibility of Analytical Techniques

The reproducibility of experiments performed to make ADVACATE sorbent has not been examined in any detail despite the significant amount of experimental work performed previously. There is expected to be a fair amount of data scatter based on the work reviewed. The scatter is due to the variability in the reactants and the difficulties in obtaining representative samples of the slurry undergoing reaction. A limited check of experimental reproducibility was performed as part of this study. This is not meant to be a statistical quantification of the data quality but to give an indication of the data variability. The number of required experiments and time involved precluded a full statistical study. Two major areas were studied - the reproducibility of analyses and reproducibility of the experiments. The analyses are covered first by examining the solution and then the solids analyses results.

A.1 ANALYSES

The analyses are expected to be much more reproducible than the experiments as they are fairly standard laboratory analyses. They were checked by performing each analysis (usually three times) from the point of the stored solution or solid sample.

A.1.1 Solution

The reproducibility of the potassium, sodium and silicon analyses performed by AA are provided in Tables A.1 through A.3. The columns of each table are headed by the experiment date and sample time in hours. Each was checked at least two different concentrations (provided in ppm) to verify each throughout the likely concentration range. The sodium and potassium analyses are generally reproducible to within two percent. The silicon measurement is less accurate and this was due to having more difficulty analyzing this species with the AA. This was due to analyzing the ion at concentrations below that recommended by the manufacturer.

Table A.1 Potassium Reproducibility

Potassium	8/12/92 1	8/26/92 8	8/24/92 25
1	63	1380	1540
2	62	1420	1500
3	63	1380	1640
average (ppm)	63	1393	1560
standard deviation	0.9 %	1.7 %	4.6 %

Table A.2 Sodium Reproducibility

Sodium	7/8/92 24	8/31/92 10	8/26/92 1.5
1	111	415	44
2	110	415	43
3	110	418	43
average (ppm)	110	416	43
standard deviation	0.5 %	0.4 %	1.3 %

Table A.3 Silicon Reproducibility

Silicon - selective dissolutions	5/5/92 33	3/1/92 8
1	64	1.85
2	68	1.68
3	65	1.64
average (ppm)	66	1.72
standard deviation	3.2%	6.5%

The reproducibility of the sulfate and chloride analyses performed by IC are provided in Tables A.4 and A.5. Each was performed at three different concentrations to verify each throughout the likely concentration range. These are generally reproducible to within 5 percent.

Table A.4 Sulfate Reproducibility

Sulfate	9/28/92 23.4	10/4/92 30	8/12/92 1
1	2100	3140	1360
2	2070	3190	1200
3	2160	3200	1250
average (ppm)	2110	3180	1270
standard deviation	2.2 %	1 %	6.4 %

Table A.5 Chloride Reproducibility

Chloride	6/5/92 22.5	4/16/92 21	4/22/92 12
1	6640	14600	16600
2	5890	15100	17300
3	8020	14600	18100
average (ppm)	6850	14700	17300
standard deviation	16 %	2 %	4.3 %

A.1.2 Solids

Three solids analyses were checked - sugar dissolution for calcium hydroxide utilization, BET surface area and selective dissolution for reacted silicon. These again are examined over a range of values and are presented in Tables A.6 through A.8. The sugar and selective dissolution column headings provide the date of the experiment and sample time in hours. The sugar dissolution is accurate to about 1 percent. The BET surface area was checked for a number of materials and very little deviation was found from analysis to analysis. Selective dissolution was somewhat less reproducible but that is expected as the silicon AA measurement is part of the analysis.

Table A.6 Sugar Dissolution Reproducibility

Sugar Analysis	8/12/92 2	9/9/92 6	9/9/92 12
1	32.3	17.6	82.1
2	32.6	17.1	81.7
3	33.0	17.5	81.9
average (%)	32.6	17.4	81.9
standard deviation	1.1 %	1.3 %	0.2 %

Table A.7 BET Surface Area Reproducibility

BET Surface Area (2 analyses performed)	difference (m^2/g)	average surface area (m^2/g)
Sample 1	1.5	46.3
Sample 2	0.3	47.9
Sample 3	0.1	41.3
Sample 4	0.2	4.6
Sample 5	0.1	16.9
Sample 6	1.0	128.9
Sample 7	3.1	122.1
Sample 8	0.1	116.2

In addition, the carbon standard was measured 5 times and all measured surface areas were within 2 of the average surface area of 118.1 m^2/g.

Table A.8 Selective Dissolution Reproducibility

Selective Dissolution (Si)	3/1/92 8	5/5/92 33
1	3.5	51.1
2	3.2	53.9
3	3.1	51.8
average (mg/g)	3.3	52.3
standard deviation	6.1 %	2.8 %

Each analysis was generally reproducible to within 5 percent and this is sufficient for data analysis as each variable measured ranged over one to two orders of magnitude in the experiments performed. The experimental reproducibility is discussed in the next section.

A.2 EXPERIMENTS

The reproducibility of experiments was less consistent than that of the analyses. Two experiments were examined in detail, an early set using Clinch River fly ash and hydrated lime as reactants and a later set using Shawnee ash with sodium hydroxide as an additive. The Clinch River experiment was sampled at four times and performed four times. The data for each of four analyses is presented in the following data tables. The date of each experiment is provided in the left hand column.

Table A.9 Hydrated lime/Clinch River fly ash (1/4) reproducibility

2 hour sample	Surface area (m^2/g)	Calcium (ppm)	Potassium (ppm)	% Calcium reacted
2/28/91	6.0	246	230	50
8/15/91	7.6	544	215	34
8/2/91	8.6	510	268	28
8/21/92	8.4	448	198	21
average	7.7	437	228	33
std deviation	16 %	30 %	13 %	38 %

4 hour sample	Surface area (m^2/g)	Calcium (ppm)	Potassium (ppm)	% Calcium reacted
2/28/91	13.6	92	1020	71
8/15/91	20.4	151	1090	64
8/2/91	20.4	52	1130	55
8/21/92	22.4	185	1140	55
average	19.2	120	1095	61
std deviation	20 %	50 %	5 %	13 %

6 hour sample	Surface area (m^2/g)	Calcium (ppm)	Potassium (ppm)	% Calcium reacted
2/28/91	21.8	96	1360	76
8/15/91	22.4	61	1670	70
8/2/91	22.6	42	1650	67
8/21/92	27.3	33	1600	72
average	23.5	58	1570	71
std deviation	11 %	48 %	9 %	5 %

8 hour sample	Surface area (m^2/g)	Calcium (ppm)	Potassium (ppm)	% Calcium reacted
2/28/91	28.2	8	1540	81
8/15/91	23.6	53	1920	76
8/2/91	20.5	37	1880	73
8/21/92	28.1	33	1890	79
average	25	33	1810	77
std deviation	16 %	56 %	10 %	5 %

The potassium results were the most reproducible with a standard deviation of less than 13 percent for all the sample times. This is as good as might be expected based on the limited number of experiments compared. The surface area and reacted calcium numbers are less reproducible and the reasons for this behavior are in the drying technique used (see Appendix D for more information). This are improved when better drying techniques were used as seen in the Shawnee experiments explained next.

The dissolved calcium also varied significantly. This was largely due to the nature of this experiment. In these cases, the solid calcium hydroxide was probably not at equilibrium with the solution so that any delay in the final filtering step would cause an increase in concentration. In addition, any cooling of the sample would increase the calcium hydroxide solubility. For these reasons, dissolved calcium was only used as a qualitative indicator.

The Shawnee fly ash experiments have only three common sample times and these results are shown in Table A.10. In this case, the surface area and reacted calcium hydroxide numbers are much more reproducible due to the better drying technique and smaller sample size. The dissolved calcium is again highly variable as a percentage of the concentration measured. The trend is the same in all the experiments however.

Table A.10 Hydrated lime/Shawnee ash with 0.1 N NaOH reproducibility

1 hour sample	Surface area (m^2/g)	Calcium (ppm)	Potassium (ppm)	% Calcium reacted
10/18/91	14.2	44	42	39
12/11/92	14.2	48	46	27
12/17/92	16.9	12	47	34
average	15.1	35	45	33
std deviation	10 %	57 %	6 %	18 %

3 hour sample	Surface area (m^2/g)	Calcium (ppm)	Potassium (ppm)	% Calcium reacted
10/18/91	28.8	1.2	147	74
12/11/92	28.6	3	165	59
12/17/92	31.8	2	167	61
average	29.7	2.1	160	65
std deviation	6 %	44 %	7 %	13 %

5 hour sample	Surface area (m^2/g)	Calcium (ppm)	Potassium (ppm)	% Calcium reacted
10/18/91	41	< 1	188	77
12/11/92	36.7	1	226	69
12/17/92	41.5	2	228	72
average	39.7	-	214	73
std deviation	7 %	-	11 %	6 %

The system with gypsum present also behaved in a similar manner but there were insufficient duplicate experiments to determine standard deviations. This error analysis reveals that differences in results need to be consistently greater than 10 percent before additives could be said to have an impact. In addition, the calcium hydroxide utilization data used to determine material composition (in Chapter 8) was limited to that dried at a high temperature. Duplicates were generally not run for the CSTR experiments but aside from two experiments, these generally tracked as expected and those with similar residence times showed consistent behavior.

Appendix B

Experimental Data

The experimental data generated during this study is presented in the following tables. The data is organized in the following manner:

1. experiment type (batch or CSTR)
2. silica source (ash type, silica fume or ADVACATE) - these are the basis for the table titles
3. additive (none or the additive in alphabetical order)
4. sample date

The data is grouped by experiment with each row presenting data from a sample drawn at that time. The analysis results are organized by columns. The columns are always presented in the same order for each silica source but will not all be shown if an analysis was not performed on that silica source. The columns contain information as follows:

column 1	the experiment date and sample times (in hours) are provided. The CSTR experiment sample times are the time from the start of the reactor operation.
column 2	the weight ratio of the solid reactants is given in the following sequence - calcium hydroxide/silica source/calcium sulfite hemihydrate/gypsum. The normality of any liquid or

	completely soluble solid reactants is presented next. The residence time is provided for the CSTR experiments. The weight percent solids in the slurry and any other pertinent information is also listed.
column 3	specific BET surface area of the solid sample (m^2/g)
column 4	calcium hydroxide reacted (in percent of the amount added to the reaction) obtained from the sugar dissolution analysis. This was not corrected for any calcium hydroxide in the silica source (in ADVACATE material for example) or for the hydrated lime being less than 100 percent calcium hydroxide.
column 5	reacted silicon in the solid sample obtained by selective dissolution (mg Si/g sample)
column 6	reacted aluminum in the solid sample obtained by selective dissolution (mg Al/g sample)
column 7	reacted iron in the solid sample obtained by selective dissolution (mg Fe/g sample)
column 8	pH of the solution as read
column 9	sodium concentration in solution in mM (by AA)
column 10	potassium concentration in solution in mM (by AA)
column 11	calcium concentration in solution in mM (by AA)
column 12	sulfate concentration in solution in mM (by IC)
column 13	chloride concentration in solution in mM (by IC)
column 14	silicon concentration in solution in mM (by AA)
column 15	aluminum concentration in solution in mM (by AA)

ADVACATE - batch

		area	% Ca	Si	Al	Fe	pH	Na^+	K^+	Ca^{++}	$SO_4^=$	Si	Al
4/28/93	1/2/0/0												
49	20% solids	74.5	64	-	-	-	12.43	5.2	19.1	8.4	-	-	-
52		79.8	64	-	-	-	12.42	5.4	23.1	7.3	-	-	-
56		81.4	-	-	-	-	12.43	5.5	21.4	7.0	-	-	-
62		87.6	65	52.0	8.7	-	12.52	5.8	22.7	11.4	-	<0.2	-
5/2/93	1/2/0/0												
25	3/18/93 79 hr sample - 10% solids	49.2	74	-	-	-	-	-	7.8	15.3	-	-	-
50		54.4	79	58.0	13.0	-	-	-	5.1	12.3	-	<0.2	<0.2
5/8/93	1/2/0/0.3												
26.5	3/18/93 79 hr sample - 10% solids	52.1	72	-	-	-	-	-	5.4	23.5	-	-	-
7/25/93	1/2/0/0												
56.1	started with 25% 7/18/93 sample	65.5	72	-	-	-	-	-	-	-	-	-	-
8/4/93	1/2/0/0												
54.8	started with 25% 7/18/93 sample	55.8	66	-	-	-	12.34	-	-	-	-	-	-
61.5		58.8	65	-	-	-	12.31	-	-	-	-	-	-

ADVACATE - batch		area	% Ca	Si	Al	Fe	pH	Na+	K+	Ca++	SO4=	Si	Al
12/9/92	1/2/0/0												
2	20% solids	11.0	7	-	-	-	12.41	0.7	1.7	15.0	2.00	-	-
4		16.2	10	8.2	2.6	-	12.37	1.0	3.3	16.4	1.43	-	-
6		21.6	19	-	-	-	12.39	1.5	5.4	15.7	1.36	-	-
8		28.5	20	-	-	-	12.45	2.1	7.8	15.6	1.41	-	-
12		40.6	28	26.0	4.4	4.8	12.45	-	11.9	11.5	1.85	<0.2	-
12/30/92	2/4/0/1												
2	20% solids	8.3	6	-	-	-	12.35	0.5	1.3	31.8	12.71	-	-
4		10.1	12	-	-	-	12.39	0.9	2.1	27.5	17.92	-	-
6		14.7	10	-	-	-	12.04	0.9	3.1	20.3	-	-	-
8		16.2	15	-	-	-	12.21	1.1	4.0	23.4	11.77	-	-
12		25.5	21	-	-	-	12.30	2.0	6.9	25.0	13.54	-	-
2/8/93	1/2/0/0												
14	20% solids	40.7	33	-	-	-	12.41	-	15.6	4.6	-	-	-
17.2		46.8	37	26.0	4.4	-	12.46	-	18.0	9.6	-	-	-
21		53.7	40	-	-	-	12.49	-	21.4	9.9	-	-	-
25		61.4	48	35.0	5.2	7.0	12.52	-	24.4	8.3	-	-	-
28		69.2	46	37.0	5.4	-	12.50	-	24.6	8.1	-	<0.2	-
3/23/93	1/2/0/0												
33.3	20% solids	76.0	54	44.0	10.1	7.0	12.52	-	32.8	9.8	-	-	-
37		77.7	56	-	-	-	12.43	-	27.2	6.6	-	-	-
41		83.2	59	-	-	-	12.50	-	21.0	10.6	-	-	-
46		91.3	59	46.0	10.4	-	12.45	-	20.5	7.5	-	-	-

ADVACATE - batch		area	% Ca	Si	Al	Fe	pH	Na+	K+	Ca++	SO4=	Si	Al
Additives - Calcium Chloride													
2/26/93	1/2/0/0												
2	0.2 N CaCl2	12.4	7	5.2	-	-	12.15	-	6.3	96.3	-	-	-
4	20% solids	18.2	12	-	-	-	12.03	-	7.8	92.8	-	-	-
6		25.0	10	10.4	-	-	12.11	-	-	104.3	-	-	-
8		31.5	22	-	-	-	12.11	-	13.1	84.0	-	-	-
12		45.4	31	21.3	-	3.7	12.06	-	16.7	92.8	-	-	-
Additives - Sodium Hydroxide													
3/5/93	1/2/0/0												
2	0.1 N NaOH	12.2	1	-	-	-	12.79	-	1.8	1.8	-	-	-
4	10% solids	19.5	8	-	-	-	12.75	-	3.4	0.6	-	-	-
6.2		25.9	16	-	-	-	12.76	-	5.2	1.9	-	-	-
8		30.1	20	22.6	-	3.7	12.75	-	7.3	3.2	-	-	-
13.6		40.2	29	25.7	-	-	12.70	-	10.1	4.4	-	<0.2	<0.2

Clinch River-Batch		area	% Ca	Si	Al	Fe	pH	Na+	K+	Ca++	SO4=	Al
2/28/91	1/4/0/0											
2	34% solids	6.0	50	-	-	-	12.52	2.4	5.9	6.2	-	-
4		13.6	71	-	-	-	12.86	7.2	26.2	2.3	-	-
6		21.8	76	-	-	-	12.96	9.6	34.9	2.4	-	-
8		28.2	81	-	-	-	12.96	10.5	39.5	0.2	-	<1
12		23.0	80	-	-	-	13.06	13.5	48.7	1.7	-	-
4/20/91	1/4/0/0											
5 min	0 point	5.1	23	-	-	-	11.30	1.5	-	13.8	-	-
4/30/91	1/2/0/0											
4	38% solids	25.0	54	-	-	-	12.42	9.0	29.0	2.6	-	-
7	add 20 ml water	29.8	61	-	-	-	12.56	10.7	41.0	2.9	-	-
8		27.7	60	-	-	-	12.57	10.9	45.4	2.4	-	-
10		29.8	60	-	-	-	12.61	11.0	47.7	1.9	-	-
12		29.1	59	-	-	-	12.62	12.5	50.0	2.1	-	-
6/24/91	1/2/0/0											
3	19% solids	15.6	78	-	-	-	11.71	3.0	11.4	7.6	-	-
6		26.5	77	-	-	-	12.07	6.1	24.4	2.4	-	-
8		26.2	77	-	-	-	12.09	5.6	28.5	3.7	-	-
12		31.7	66	-	-	-	12.24	6.1	33.3	1.9	-	-

Clinch River-Batch		area	% Ca	Si	Al	Fe	pH	Na+	K+	Ca++	SO4=	Al
7/23/91	1/2/0/0											
1	19% solids	7.0	27	-	-	-	11.61	1.0	1.4	12.8	-	-
2		10.7	33	-	-	-	11.63	1.6	4.2	8.6	-	-
3		16.5	45	-	-	-	11.84	3.2	8.2	4.2	-	-
4		22.3	48	-	-	-	12.11	4.5	15.4	6.3	-	-
5		25.2	46	-	-	-	12.20	6.3	21.5	2.6	-	-
8/1/91	1/2/0/0											
1	38% solids	7.2	24	-	-	-	11.58	2.5	3.6	14.8	-	-
2		9.8	32	-	-	-	11.69	3.7	10.8	12.3	-	-
3		17.5	56	-	-	-	12.05	8.9	32.1	6.1	-	-
4		19.1	48	-	-	-	12.18	11.1	41.8	1.6	-	-
5		23.2	50	-	-	-	12.34	12.0	50.8	1.1	-	-
8/2/91	1/4/0/0											
2	reagent Ca(OH)2	8.6	28	-	-	-	12.46	4.9	6.9	12.8	-	-
4	33% solids	20.4	55	-	-	-	12.54	8.0	29.0	1.3	-	-
6		22.6	67	-	-	-	12.63	10.8	42.3	1.1	-	-
8		20.5	73	-	-	-	12.67	12.5	48.2	0.9	-	-
10		21.6	75	-	-	-	12.64	11.6	41.8	1.5	-	-
8/15/91	1/4/0/0											
2	33% solids	7.6	34	-	-	-	12.31	2.3	5.5	13.6	-	-
4		20.4	64	21.7	5.9	-	12.52	8.1	27.9	3.8	-	-
6		22.4	70	33.4	7.8	4.1	12.59	12.2	42.8	1.5	-	-
8		23.6	76	37.7	8.9	-	12.66	11.5	49.2	1.3	-	-

Clinch River-Batch		area	% Ca	Si	Al	Fe	pH	Na+	K+	Ca++	SO4=	Al
	1/4/0/0											
0	22% solids	-	15.7	-	-	-	-	-	-	-	-	-
0.5	reactions at	-	17.8	-	-	-	-	-	-	-	-	-
1	100°C	-	22.5	-	-	-	-	-	-	-	-	-
2		-	31.1	-	-	-	-	-	-	-	-	-
	2/4/0/0											
0	22% solids	-	14.9	-	-	-	-	-	-	-	-	-
0.5	reactions at	-	16	-	-	-	-	-	-	-	-	-
1	100°C	-	19.3	-	-	-	-	-	-	-	-	-
2		-	25	-	-	-	-	-	-	-	-	-
8/21/92	1/4/0/0											
2	37% solids	8.4	21	-	-	-	12.43	3.1	5.1	11.2	-	-
4		22.4	55	-	-	-	12.59	9.8	29.2	4.6	-	-
6		27.3	72	-	-	-	12.65	13.6	41.0	0.8	-	-
8		28.1	79	-	-	-	12.71	15.2	48.5	0.8	-	-
8/31/92	1/2/0/0											
3.8	36% solids	23.5	48	-	-	-	12.64	12.2	-	1.2	-	-
6		25.2	62	-	-	-	12.71	15.0	53.6	-	-	-
8		27.7	64	-	-	-	12.69	14.3	49.7	-	-	-
10		28.6	69	-	-	-	12.78	18.1	-	-	-	-

Clinch River-Batch		area	% Ca	Si	Al	Fe	pH	Na+	K+	Ca++	SO4=	Al
12/14/93	1.5/4/0/0											
3	add Ca(OH)2	16.2	28	-	-	-	12.33	1.6	4.6	9.7	-	-
6	add Ca(OH)2	32.8	42	-	-	-	12.44	4.5	15.1	5.3	-	-
9	add Ca(OH)2	37.9	41	47.6	-	-	12.41	6.4	22.0	2.2	-	-
12	10% solids	37.3	40	52.6	-	7.1	12.60	7.9	25.9	4.8	-	-

Added calcium hydroxide at 3, 6, and 9 hours. % Ca based on calcium hydroxide added to that point.

Additives - Calcium Chloride

6/27/91	2/4/3/1											
3	0.1N CaCl2	7.8	77	-	-	-	11.57	9.9	9.7	104.3	8.9	-
5	20% solids	12.6	79	-	-	-	11.45	10.8	14.1	94.7	9.6	-
7		22.1	75	-	-	-	11.48	12.0	15.0	89.8	8.8	-
9.2		27.8	74	-	-	-	11.64	14.3	27.2	84.1	9.2	-
11		39.1	78	-	-	-	11.64	17.5	39.7	83.8	10.4	-
5/10/93	1/2/0/0											
2.7	0.2 N CaCl2	17.5	23	-	-	-	11.90	0.0	9.7	99.0	-	-
4	20% solids	28.4	31	-	-	-	11.80	0.0	14.9	85.5	-	-
6		61.6	49	-	-	-	11.90	0.0	30.5	68.8	-	-
8		88.4	66	-	-	-	11.90	0.0	36.2	53.0	-	-
12		120.	82	-	-	-	11.75	0.0	72.1	36.5	-	-

Clinch River-Batch		area	% Ca	Si	Al	Fe	pH	Na+	K+	Ca++	SO4=	Al
7/2/93	1/1/0/0											
2	0.6 CaCl2	24.4	-	-	-	-	11.91	11.7	20.6	-	-	-
4.5	20 % solids	49.2	-	-	-	-	11.87	16.6	34.6	-	-	-
6		74.6	-	-	-	-	11.92	17.0	33.1	-	-	-
8/6/93	1/1/0/0											
3	0.6 N CaCl2	26.2	26	-	-	-	-	-	-	-	-	-
5	16 % solids	45.7	40	-	-	-	-	-	-	-	-	-
7		67.5	54	-	-	-	-	-	-	-	-	-
9		88.9	61	-	-	-	-	-	-	-	-	-
12		119.	68	-	-	-	-	-	-	-	-	-

Additives - Gypsum & Calcium Sulfite

		area	% Ca	Si	Al	Fe	pH	Na+	K+	Ca++	SO4=	Al
1/28/91	1/4/3/1											
2	33% solids	3.5	62	-	-	-	12.76	37.0	2.6	12.4	17.6	-
4		7.1	62	-	-	-	12.78	38.1	6.5	12.1	21.7	-
6		13.2	71	-	-	-	13.04	40.7	14.4	11.1	22.6	-
8		18.1	90	-	-	-	12.98	42.5	22.6	10.9	27.2	<1
1/31/91	1/2/3/1											
2	33% solids	4.0	-	-	-	-	12.05	8.6	-	20.0	12.2	-
4		5.8	-	-	-	-	12.04	9.0	-	19.4	12.4	-
6		11.4	-	-	-	-	11.93	11.4	-	14.6	12.8	-
8		17.0	-	-	-	-	12.09	14.2	-	16.1	17.1	<1

Clinch River-Batch		area	% Ca	Si	Al	Fe	pH	Na+	K+	Ca++	SO4=	Al
2/17/91	1/3/0/0											
0	ran 13 hours	20.7	100	-	-	-	9.66	7.8	25.1	13.2	25.9	<1
1	added acid to	16.0	98	-	-	-	12.51	6.4	30.5	14.4	20.1	-
2	0.25/3/0/1.4	24.9	-	-	-	-	12.54	7.3	36.7	14.8	21.6	-
4	added Ca(OH)2	29.6	-	-	-	-	12.55	8.9	41.0	15.3	24.3	-
6	to 1/3/0/1.4	39.7	-	-	-	-	12.60	11.0	52.3	15.5	28.3	<1

Ran experiment to 13 hrs, sampled at 0 hrs and added H2SO4. Added Ca(OH)2 after 4 hr sample.

Clinch River-Batch		area	% Ca	Si	Al	Fe	pH	Na+	K+	Ca++	SO4=	Al
3/7/91	1/2/3/1											
2	33% solids	6.9	-	-	-	-	12.11	7.1	1.1	23.5	11.3	-
4		9.2	-	-	-	-	12.05	7.3	-	22.5	11.8	-
6		11.9	-	-	-	-	12.15	8.0	-	24.4	12.1	-
8		15.5	-	-	-	-	12.10	10.2	-	17.9	12.4	<1
3/13/91	1/4/3/1											
2	33% solids	4.8	59	1.7	0.9	-	12.16	5.7	1.1	20.6	12.9	-
4		8.3	57	4.0	1.6	-	12.33	6.3	4.7	24.1	14.3	-
6		14.7	61	5.6	-	-	12.16	12.0	19.4	17.3	14.7	-
8		23.3	78	-	3.9	-	12.19	11.6	16.7	13.3	16.5	-
12		42.8	94	25.8	6.5	-	11.80	15.7	38.7	10.6	29.2	-
3/18/91	1/4/3/1											
22	33% solids	49.4	-	-	-	-	11.53	16.7	-	11.3	36.0	-
45		61.3	-	-	-	-	11.03	17.4	-	11.9	37.6	-
70		56.1	-	-	-	-	9.11	20.9	-	12.1	37.1	-
96		56.5	-	-	-	-	10.16	20.9	-	12.0	39.3	-

Clinch River-Batch		area	% Ca	Si	Al	Fe	pH	Na+	K+	Ca++	SO4=	Al
3/28/91	4.8/4/3/1											
12	30% solids	40.8	46	22.9	5.2	-	11.84	13.9	30.8	21.4	23.0	-
15		43.0	50	32.2	-	-	11.93	15.2	43.6	23.3	27.3	-
18		54.4	59	39.1	1.8	-	12.08	15.7	37.7	7.7	20.0	-
22		56.7	66	45.4	6.8	-	12.38	16.8	46.7	9.4	19.3	-
4/2/91	4/4/1/4											
11	25% solids	29.9	49	-	-	-	12.21	5.6	20.3	17.4	18.2	-
13		34.9	54	-	-	-	12.40	6.5	25.6	22.9	19.8	-
15		38.4	58	-	-	-	12.38	6.9	29.7	19.1	21.7	-
18		48.8	72	-	-	-	12.43	8.5	41.0	21.1	24.5	-
4/8/91	4/4/1/4											
3	25% solids	8.6	42	-	-	-	11.75	2.0	2.5	22.2	12.3	-
6		16.7	43	-	-	-	11.85	2.9	5.9	23.8	13.9	-
18.2		39.1	66	-	-	-	12.10	8.6	39.4	19.9	23.4	-
24		48.2	71	-	-	-	12.18	9.7	36.9	21.5	28.0	-
30		53.7	78	44.7	-	-	12.26	13.3	51.5	22.5	33.0	-
7/11/91	4/4/1/2											
24		48.7	75	46.5	9.5	-	12.10	15.8	-	12.7	37.3	-
33		58.2	84	56.5	12.1	-	12.20	18.0	-	18.4	45.9	-
36		53.2	88	56.5	10.9	-	12.00	19.2	-	13.7	50.0	-
48		47.4	94	86.1	-	-	11.90	21.0	-	13.0	60.5	-

Clinch River-Batch		area	% Ca	Si	Al	Fe	pH	Na+	K+	Ca++	SO4=	Al
9/23/91	1/4/0/0											
-0.5	3.5 hr from start	13.2	73	-	-	-	12.36	3.5	13.6	5.6	-	-
0	H2SO3 0/4/1.62/0	24.1	100	-	-	-	-	2.1	8.1	-	-	-
0.5	Ca(OH)2 .9/4/1.7/0	11.9	54	-	-	-	12.28	2.1	7.3	6.0	0.3	-
1		12.0	47	-	-	-	12.39	2.1	7.9	9.1	0.2	-
2		14.0	45	-	-	-	12.34	2.3	9.6	7.0	0.4	-
4		26.1	70	-	-	-	12.45	4.5	18.8	8.6	0.8	-
		area	%		area	%						
8/24/92	4/4/0/4	C	C		H	H						
12	solids dried hot at	17.5	90	-	33.9	53	12.26	5.8	18.6	15.0	18.5	-
17	200° F (H) or left	30.8	93	-	42.9	69	12.47	7.8	27.2	-	20.3	-
20	at room T then vac	31.2	92	-	46.2	74	12.30	8.4	30.8	13.9	21.6	-
22.5	dried (C)	41.3	-	-	48.0	77	12.32	9.2	34.6	13.6	23.1	-
25	18% solids	51.5	87	41.1	50.0	80	12.40	11.0	39.5	19.0	28.1	-
		area	%		area	%						
8/26/92	1/4/0/1	C	H		H	C						
1.5	dried as above	3.1	17	-	4.6	60	12.33	1.9	3.1	17.4	27.8	-
4	32% solids	11.1	43	-	16.9	-	12.36	4.4	12.4	8.6	19.8	-
6		25.5	66	-	27.6	-	12.39	7.6	22.1	6.1	17.7	-
8		38.7	81	-	42.9	87	12.18	11.3	35.4	4.8	27.7	-

Clinch River-Batch		area	% Ca	Si	Al	Fe	pH	Na+	K+	Ca++	SO4=	Al
10/4/92	4/4/1/4											
3	18% solids	11.0	11	4.8	-	-	12.49	3.2	3.4	24.3	13.6	-
6		19.9	23	9.1	-	-	12.50	5.7	8.6	24.8	14.7	-
18		49.7	59	25.2	-	-	12.51	13.6	33.8	17.3	24.3	-
24		57.6	69	34.5	-	-	12.46	15.7	43.6	12.8	28.6	-
30		63.7	75	36.9	-	-	12.49	18.9	53.2	14.7	33.3	-
Additives - Potassium Sulfate												
1/13/92	3/4/1/2											
9	0.045 M K2SO4	24.6	56	-	-	-	12.51	2.1	55.8	17.8	25.7	-
12	7.7% solids	34.0	69	-	-	-	12.54	2.7	62.7	18.3	27.6	-
15		42.4	78	-	-	-	12.46	3.0	65.2	14.9	29.8	-
18		49.3	85	-	-	-	12.51	3.9	65.5	17.9	31.8	-
21		55.0	89	-	-	-	12.40	4.5	-	13.7	35.9	-
Additives - Sodium Sulfate												
7/15/91	1/4/3/1											
3	0.07 N Na2SO4	5.6	58	-	-	-	12.12	64.1	3.7	11.0	33.9	-
5	33% solids	9.8	71	-	-	-	12.16	63.6	8.5	11.6	35.9	-
7		16.2	82	-	-	-	12.22	70.7	16.4	14.8	42.9	-
9		26.4	84	-	-	-	12.14	72.5	24.7	15.0	49.8	-

Ground Martwick - batch		area	% Ca	Si	Al	Fe	pH	Na+	K+	Ca++
Additives - Gypsum & Calcium Sulfite										
5/13/93	4/4/2/2									
3	20% solids	12.0	14	-	-	-	12.39	-	2.2	27.3
6		19.7	23	10.6	3.2	-	12.28	3.0	4.7	25.5
9		34.2	34	-	-	-	12.22	3.8	7.9	15.2
12		45.4	42	22.1	6.3	6.1	11.98	4.3	10.2	16.3
28		77.2	71	-	-	-	11.93	9.8	18.4	10.8
34		88.6	75	53.0	12.0	10.3	12.01	8.2	20.7	13.3
5/19/93	4/4/2/2									
15	20% solids	42.0	51	-	-	-	11.90	5.1	12.4	18.2
19		67.2	59	34.0	-	-	12.30	6.4	14.9	18.2
24		77.2	68	39.0	-	-	12.32	6.0	24.5	21.6
39		78.9	85	-	-	-	12.30	6.2	20.5	6.5
45		84.6	89	-	-	-	11.95	6.4	20.5	8.5
52		89.3	90	-	-	-	11.73	6.7	22.5	9.1

Martwick - batch

		area	% Ca	Si	Al	Fe	pH	Na+	K+	Ca++	SO4=	Si
5/19/92	1/2/0/0											
2	20% solids	10.0	22	-	-	-	12.44	1.0	1.1	14.5	-	-
4		12.7	25	7.1	-	-	12.45	1.6	2.5	11.7	-	-
6		19.3	34	21.0	-	-	12.56	2.3	7.3	11.2	-	-
8		24.1	42	29.0	-	-	12.61	3.8	12.2	8.9	-	-
12		31.2	59	48.0	-	9.3	12.63	5.7	21.6	4.1	-	-
7/20/92	1/2/0/0											
14	20% solids	37.3	65	-	-	-	12.50	7.7	23.3	2.6	-	<0.04
17	solids dried hot	40.5	72	43.0	-	-	12.52	8.3	23.7	1.7	-	-
20	(100°C) and	44.5	75	59.0	-	13.1	12.56	9.7	27.2	1.7	-	-
23.7	moderate (60°C)	43.3	77	-	-	-	12.54	9.3	27.4	0.6	-	-
26.5	conditions	40.5	78	67.0	-	-	12.58	10.1	30.0	1.5	-	<0.04

Additives - Gypsum & Calcium Sulfite

		area	% Ca	Si	Al	Fe	pH	Na+	K+	Ca++	SO4=	Si
1.5	7/13/92	7.5	36	-	-	-	12.31	3.0	0.9	20.9	12.5	-
4	2/4/1/1	9.1	38	-	-	-	12.34	3.9	1.5	26.0	13.9	-
6	20%solids	11.5	44	-	-	-	12.33	3.5	2.3	25.8	13.5	-
8		15.5	48	8.3	-	-	12.28	3.7	3.4	22.4	13.8	-
12		22.7	57	-	-	-	-	4.3	6.9	21.7	14.4	-

Martwick - batch		area	% Ca	Si	Al	Fe	pH	Na±	K±	Ca±±	SO4=	Si
10/2/92	3/4/1/2											
14.3	20% solids	28.0	36	-	-	-	12.44	3.9	6.0	28.5	14.3	-
17		33.5	41	24.0	5.9	-	12.48	4.7	7.7	20.2	14.3	-
21.1		42.1	49	-	-	-	12.49	5.5	9.9	25.8	14.9	-
24		47.6	55	-	-	-	12.46	6.0	11.0	21.7	22.4	-
28		58.8	59	43.0	7.2	7.7	12.47	7.9	13.5	20.3	16.1	-
11/6/92	4/4/1/2											
27	20% solids	55.9	79	44.0	6.7	-	12.33	5.7	13.8	22.9	16.0	-
30		55.7	61	-	-	-	12.27	5.8	12.5	17.3	14.9	-
34		56.4	67	43.0	8.3	-	12.34	6.5	14.7	19.8	17.1	-
49.5		70.9	57	-	-	-	12.30	8.6	19.2	18.0	26.7	-
4/22/93	4/4/1/2											
49	20% solids	73.3	71	50.1	-	-	12.14	-	20.0	31.3	-	-
53		76.4	71	-	-	-	12.06	-	18.1	15.0	-	-
56.5		77.8	77	-	-	-	12.08	-	20.3	13.7	-	-
61		91.6	78	53.1	9.1	14.3	12.04	-	26.3	13.7	-	-

Shawnee-Batch		area	% Ca	Si	Al	Fe	pH	Na+	K+	Ca++	SO4=	Cl-	Si	Al
8/9/91	1/4/0/0													
2	28% solids	14.8	21	-	-	-	12.16	4.6	4.5	20.1	-	-	-	-
4		16.1	25	-	-	-	12.27	5.2	1[illegible]	22.2	-	-	-	-
6		22.4	41	-	-	-	12.27	10.4	8.1	16.4	-	-	-	-
8		36.5	74	-	-	-	12.43	10.1	22.9	2.5	-	-	-	-
12		81.3	94	-	-	-	11.97	16.3	44.9	1.7	-	-	-	1.9
8/29/91	1/4/0/0													
2	17% solids	12.0	41	-	-	-	12.34	4.1	4.1	26.8	-	-	-	-
4		15.6	40	-	-	-	12.24	4.6	3.7	22.7	-	-	-	-
6		17.6	48	-	-	-	12.26	6.1	6.6	14.5	-	-	-	-
8		34.2	72	-	-	-	12.47	8.8	20.5	6.9	-	-	-	-
10/2/91	1/2/0/0													
8	17% solids	29.8	64	-	-	-	12.49	7.4	15.5	3.4	-	-	-	-
12		53.1	92	-	-	-	12.73	13.4	58.7	0.3	-	-	-	-
15		60.1	95	-	-	-	12.74	12.6	44.6	0.5	-	-	-	-
18		76.4	96	-	-	-	12.63	13.6	39.5	0.1	-	-	-	1.3
21		72.0	96	-	-	-	12.58	11.7	41.8	0.3	-	-	-	1.4

Shawnee-Batch		area	% Ca	Si	Al	Fe	pH	Na+	K+	Ca++	SO4=	Cl-	Si	Al
10/7/91	1/2/0/0													
1	ground ash	15.0	31	-	-	-	12.42	2.7	5.3	31.0	-	-	-	-
3	17% solids	14.8	41	-	-	-	12.45	2.7	5.8	25.5	-	-	-	-
5		22.7	39	-	-	-	12.31	3.7	9.0	9.2	-	-	-	-
7		39.7	73	23.0	15.0	-	12.61	8.3	37.4	3.8	-	-	-	-
9		50.9	83	-	-	-	12.73	13.6	45.9	1.6	-	-	-	0.3
Additives - Calcium Chloride														
4/16/92	1/1/0/0													
13	0.6 N CaCl2	94.1	82	63.0	15.0	-	11.79	23.8	45.1	162	-	-	-	-
16	17% solids	102	83	-	-	-	11.84	21.7	44.4	125	-	257	-	-
18		109	85	72.0	14.0	-	11.80	22.3	47.4	116	-	244	-	-
21		116	88	-	-	-	11.83	24.6	52.1	116	-	272	-	-
25.4		133	88	73.0	19.0	13.7	11.79	26.5	55.9	110	-	288	-	-
4/22/92	1/2/0/0													
2	0.6 N CaCl2	12.8	38	4.3	-	-	11.89	12.0	14.3	225	-	546	-	-
4	17% solids	19.2	60	14.0	11.0	-	11.90	15.3	15.4	204	-	411	-	-
6		37.6	73	23.0	-	-	11.79	20.1	21.9	173	-	442	-	-
9		67.7	88	41.0	12.0	-	11.80	27.5	45.1	196	-	434	-	-
12		98.2	90	61.0	-	-	11.23	31.0	47.8	186	-	468	-	-

Shawnee-Batch		area	% Ca	Si	Al	Fe	pH	Na+	K+	Ca++	SO4=	Cl-	Si	Al
5/14/92	1/1/0/0													
33.5	0.3 N CaCl2	110	92	67.0	-	-	12.06	17.1	39.5	51.5	-	203	-	-
37.5	17% solids	117	92	74.0	21.0	-	12.04	17.2	39.7	50.3	-	136	-	-
42.5		122	92	76.0	-	11.6	12.05	18.2	48.7	54.0	-	162	-	-
48		129	91	80.0	24.0	-	12.12	19.0	45.6	58.0	-	144	-	-
		area	%								area		%	
9/9/92	1/2/0/0	atm	vac								vac		atm	
2	0.2 N CaCl2	10.5	16	4.1	-	-	11.97	7.7	6.2	108	11.1	185	17	-
4	dried at 200°F	14.5	20	5.4	-	-	12.00	7.4	7.7	98.8	13.4	200	23	-
6	vacuum and	19.5	29	9.9	-	-	12.09	8.4	9.4	105	20.6	172	37	-
8	atmospheric	33.6	42	17.0	-	-	12.03	11.0	14.9	74.8	35.2	160	51	-
12	17% solids	74.7	76	48.0	-	-	12.08	18.0	37.0	52.0	77.4	146	82	-
9/22/92	1/1/0/0													
14	0.2 CaCl2	88.9	64	52.0	17.0	-	12.27	22.8	41.8	46.3	-	120	-	-
18.1	17% solids	105	71	63.0	20.0	-	12.34	20.3	42.8	42.0	-	113	-	-
23.5		116	76	65.0	22.0	-	12.31	23.0	46.9	38.5	-	144	-	-
26		122	77	-	-	-	12.33	21.2	48.7	35.0	-	118	-	-
28		129	79	-	-	-	12.30	22.1	51.8	37.5	-	111	-	-

Shawnee-Batch		area	% Ca	Si	Al	Fe	pH	Na+	K+	Ca++	SO4=	Cl-	Si	Al
Additives - Gypsum and Calcium Sulfite														
7/24/91	2/4/3/1													
1	28% solids	11.0	40	2.8	1.2	-	11.40	6.4	2.3	24.0	12.2	-	-	-
2		11.5	6	-	-	-	11.40	7.0	2.4	24.8	12.7	-	-	-
3		11.0	36	-	-	-	11.40	7.9	2.7	23.1	13.2	-	-	-
5		12.4	34	-	-	-	11.40	8.2	4.9	25.4	12.9	-	-	-
7		19.8	29	6.7	2.5	-	11.50	9.1	-	22.1	13.8	-	-	-
8/10/91	1/4/3/0													
2	28% solids	11.6	26	-	-	-	12.25	8.8	3.2	24.1	12.0	-	-	-
4		11.5	35	-	-	-	12.26	8.9	3.6	23.1	11.8	-	-	-
6		13.1	43	-	-	-	12.26	9.9	4.7	20.4	11.1	-	-	-
8		20.9	60	-	-	-	12.25	11.1	9.4	12.5	6.3	-	-	-
12		46.5	93	-	-	-	11.51	20.3	44.9	4.1	17.4	-	-	-
2/26/92	2/4/3/1													
18.5	17% solids	58.4	90	32.0	9.0	7.5	11.85	12.0	17.9	14.5	23.5	-	-	-
21.5		70.8	92	-	-	-	10.82	13.2	18.6	12.3	27.8	-	-	-
24.7		71.1	93	-	-	-	10.98	14.0	19.4	12.6	29.5	-	-	-
27		83.9	95	-	-	-	11.26	17.1	23.7	11.3	26.9	-	-	-

Shawnee-Batch		**area**	**% Ca**	**Si**	**Al**	**Fe**	**pH**	**Na+**	**K+**	**Ca++**	**SO4=**	**Cl-**	**Si**	**Al**
5/5/92	4/4/3/1													
24.5	17% solids	52.3	65	43.0	-	-	12.54	7.4	19.6	9.3	9.4	-	-	-
28		76.0	61	-	-	-	12.51	7.3	22.9	5.6	9.4	-	-	-
30		74.6	60	55.0	11.0	9.2	12.60	11.4	21.9	8.7	9.6	-	-	-
33		99.5	64	52.0	-	-	12.58	7.3	18.7	9.9	9.9	-	-	-
38		87.0	65	56.0	-	-	12.58	8.2	19.1	8.0	10.3	-	-	-
8/12/92	1/4/3/1													
1	17% solids	11.6	33	-	-	-	12.23	3.9	1.6	21.0	13.0	-	-	-
3		9.8	40	1.8	-	-	12.29	4.0	1.7	21.3	12.6	-	-	-
5		12.8	43	-	-	-	12.26	4.1	2.1	22.0	12.2	-	-	-
7		14.2	-	4.2	-	-	12.27	4.7	3.5	15.7	12.9	-	-	-
9/14/92	4/4/3/1	area cold	% cold			area hot						% hot		
12	17% solids	39.3	56	5.3	6.9	38.7	12.26	7.7	12.9	17.4	22.5	50	-	-
14.8	all vacuum	44.7	66	33.0	8.3	48.5	12.42	8.7	17.7	18.7	17.0	57	-	-
18	dried hot -	-	76	25.0	8.2	57.5	12.41	10.3	16.2	18.1	14.0	65	-	-
21.4	200° F or	64.1	76	40.0	9.3	65.6	12.50	11.7	24.2	16.0	13.0	71	-	-
25	cold - 130°	74.3	75	45.0	10.6	76.2	12.47	13.3	26.9	12.2	12.9	66	-	-
9/28/92	4/4/0/2													
12	17% solids	47.4	47	23.0	8.2	-	-	-	-	-	-	-	-	-
14.8		62.3	55	21.0	7.1	-	12.50	9.3	17.4	18.8	17.3	-	-	-
19		76.3	68	34.0	11.0	-	12.47	12.2	25.5	14.4	21.3	-	-	-
23.5		90.8	68	53.0	16.0	-	12.46	13.0	27.4	17.8	22.5	-	-	-

Shawnee-Batch		area	% Ca	Si	Al	Fe	pH	Na+	K+	Ca++	SO4=	Cl-	Si	Al
7/16/93	4/4/0/2													
20	ground ash	95.0	-	-	-	-	-	-	-	-	-	-	-	-
20.6	added ash at	93.6	-	-	-	-	-	-	-	-	-	-	-	-
22	20.7, 21 and	97.4	-	-	-	-	-	-	-	-	-	-	-	-
23	21.5 hr	99.6	-	-	-	-	-	-	-	-	-	-	-	-
25	10% of total	105	-	-	-	-	-	-	-	-	-	-	-	-
Additives - Potassium Hydroxide														
7/3/92	1/4/0/0													
1	0.1 N KOH	15.4	20	-	-	-	12.75	1.2	83.8	0.7	-	-	0.1	-
2	5% solids	19.5	43	-	-	-	12.76	1.4	84.0	0.6	-	-	0.2	-
3		24.3	62	-	-	-	12.74	1.8	87.2	0.2	-	-	0.4	-
5		37.3	76	-	-	-	12.73	2.3	86.4	-	-	-	1.3	-
7		43.2	79	-	-	-	12.73	2.7	86.5	-	-	-	1.2	-
Additives - Sodium Hydroxide														
9/25/91	1/4/0/0													
1	0.03 M NaOH	14.7	46	2.5	-	-	12.32	26.0	4.3	19.7	-	-	-	-
2	23% solids	15.3	-	-	-	-	12.37	26.1	3.7	20.3	-	-	-	-
3		14.8	46	-	-	-	12.36	26.7	4.3	19.4	-	-	-	-
5		17.6	47	-	-	-	12.36	28.1	6.5	12.5	-	-	-	-
7		36.8	74	-	-	-	12.47	32.4	39.9	1.7	-	-	-	-

Shawnee-Batch		area	% Ca	Si	Al	Fe	pH	Na+	K+	Ca++	SO4=	Cl-	Si	Al
10/15/91	1/4/0/0													
1	0.05 N NaOH	14.0	43	-	-	-	12.54	50.4	0.9	8.6	-	-	-	-
2	5% solids	16.5	40	-	-	-	12.55	51.7	1.3	10.4	-	-	-	-
3		19.6	58	10.0	-	-	12.55	51.7	1.6	3.6	-	-	-	-
5		32.7	77	26.5	-	-	12.53	53.0	4.0	1.0	-	-	-	-
7		39.3	89	44.0	-	11.1	12.57	54.3	11.9	0.7	-	-	-	2.1
10/18/91	1/4/0/0													
1	0.1 N NaOH	14.2	39	5.6	-	-	13.08	99.1	1.1	1.1	-	-	-	0.6
2	5% solids	18.7	63	13.0	-	-	13.08	101	2.3	0.3	-	-	-	1.6
3		28.8	74	24.4	-	-	13.04	96.5	3.8	0.03	-	-	-	3.7
5		41.0	77	49.0	8.2	-	13.03	95.7	4.8	0.02	-	-	-	2.2
7		46.2	90	42.0	11.0	-	-	-	-	-	-	-	-	-
10/30/91	1/1/0/0													
1	0.1N NaOH	15.2	30	-	-	-	12.76	88.1	1.8	1.3	-	-	-	0.1
2	5% eq ash	21.7	34	-	-	-	12.72	94.9	8.6	0.6	-	-	-	0.7
3		27.8	44	-	-	-	12.80	98.7	13.6	0.7	-	-	-	1.3
5		31.4	51	42.0	-	8.1	12.83	102	10.6	0.3	-	-	-	1.3
7		33.3	59	54.0	14.0	-	12.86	92.4	13.8	0.9	-	-	-	1.1

Shawnee-Batch		area	% Ca	Si	Al	Fe	pH	Na+	K+	Ca++	SO4=	Cl-	Si	Al
11/5/91	1/4/0/0													
5	started with	39.0	62	-	-	-	12.69	102	4.6	0.04	-	-	-	4.5
6	0.1 N NaOH	48.1	68	-	-	-	11.54	83.5	4.4	8.3	-	-	-	0.7
7	added HCl to	46.7	78	-	-	-	11.73	93.0	1.8	7.8	-	-	-	0.7
8	neutralize it	49.2	80	-	-	-	11.86	94.8	3.6	7.3	-	-	-	0.4
9	at 5 hr	43.8	65	-	-	-	11.91	96.7	4.0	7.6	-	-	-	-
	5% solids													
11/6/91	1/4/0/0													
1	0.5N NaOH	14.2	40	-	-	-	13.27	-	3.3	-	-	-	-	9.3
2	5% solids	15.5	50	-	-	-	13.27	-	4.7	-	-	-	-	10.5
3		17.8	42	-	-	-	13.27	-	5.1	-	-	-	-	10.6
5		20.6	50	-	-	-	13.28	-	4.9	-	-	-	-	10.4
7		22.1	25	36.0	6.1	-	13.28	-	6.1	-	-	-	20.7	10.0
11/12/91	1/4/0/0													
7	0.05N NaOH	43.9	82	-	-	-	12.51	59.6	4.7	0.2	-	-	-	-
8	4.2% solids	49.6	90	-	-	-	12.50	46.9	4.9	0.3	-	-	-	-
10		55.9	87	-	-	-	12.49	46.5	5.4	0.1	-	-	-	-
12		64.0	81	-	-	-	12.49	46.5	5.5	0.1	-	-	-	-

Shawnee-Batch		area	% Ca	Si	Al	Fe	pH	Na+	K+	Ca++	SO4=	Cl-	Si	Al
11/13/91	1/4/0/0													
5	0.03N NaOH	30.3	81	26.0	7.3	-	12.44	30.0	1.9	0.1	-	-	-	-
7.7	2.5% solids	46.2	90	46.0	12.0	10.1	12.33	29.9	3.0	-	-	-	-	-
9		47.3	92	-	-	-	12.31	30.3	3.8	-	-	-	-	-
12		55.8	91	-	-	-	12.30	32.2	4.3	0.03	-	-	-	-
11/18/91	1/4/0/0													
7.1	0.01N NaOH	51.8	97	50.0	14.0	11.7	12.23	11.0	3.1	0.9	-	-	-	-
9	2.5% solids	46.0	93	-	-	-	12.10	10.6	3.8	1.0	-	-	-	-
11		63.4	97	-	-	-	11.96	10.8	4.4	0.1	-	-	-	-
13		65.9	98	-	-	-	11.96	10.7	5.0	0.8	-	-	-	-
11/21/91	1/4/0/0													
13	0.03N NaOH	74.6	97	69.0	15.0	-	12.31	30.0	4.8	0.2	-	-	-	-
16	2.5% solids	83.2	97	71.0	16.0	-	12.27	27.3	4.6	0.1	-	-	-	-
19		84.1	98	-	-	-	12.28	28.4	4.7	0.1	-	-	-	-
22		87.1	88	-	-	-	12.29	30.8	5.0	0.1	-	-	-	-
1/16/92	1/4/0/0													
7	0.1 N NaOH	46.0	68	45.0	-	-	12.73	123.2	3.6	0.03	-	-	3.8	-
10	3.3% solids	60.5	67	43.0	8.7	-	12.71	112.3	4.1	-	-	-	3.6	-
13		70.4	82	53.0	-	-	12.71	113.0	5.1	-	-	-	3.4	-
15		69.2	78	58.0	13.0	-	12.72	120.7	5.0	-	-	-	3.3	-

Shawnee-Batch		area	% Ca	Si	Al	Fe	pH	Na+	K+	Ca++	SO4=	Cl-	Si	Al
2/4/92	1/4/0/0													
2	0.2 N NaOH	20.5	45	-	-	-	13.02	-	2.5	-	-	-	-	8.0
4	4.2% solids	24.5	51	-	-	-	13.02	-	3.4	-	-	-	-	9.0
6		31.0	63	28.0	5.2	8.1	13.02	-	4.0	-	-	-	-	9.3
9		38.1	55	-	-	-	13.03	-	5.3	-	-	-	-	9.9
12		44.1	68	-	-	-	13.03	-	6.2	-	-	-	9.7	9.9
3/18/92	1/2/0/0													
3	0.05 N NaOH	26.9	41	-	-	-	12.69	59.1	2.5	2.2	-	-	-	-
4	4% solids	34.1	50	28.0	7.5	-	12.68	59.6	4.0	1.7	-	-	-	-
5		35.5	64	37.0	9.0	-	12.70	58.3	4.9	1.4	-	-	-	-
6		39.3	71	47.0	12.0	-	12.73	60.4	6.2	1.3	-	-	-	-
7		37.7	72	48.0	-	-	12.74	63.5	6.2	1.4	-	-	-	-
4/17/92	1/4/0/0													
2	0.5N NaOH	15.6	8	-	-	-	13.26	-	4.6	-	-	-	-	-
4	10% solids	17.5	49	-	-	-	13.26	-	6.0	-	-	-	-	-
6		12.7	51	-	-	-	13.26	-	7.4	-	-	-	-	-

Silica Fume - batch		area	% Ca	Si	pH	Na+	Ca++	K+	Si
8/18/92	1/1/0/0								
0.5	10% solids	45.8	36	-	12.30	0.8	18.8	1.2	0.06
1		84.8	61	-	12.33	0.8	1.1	1.2	-
2		122.0	86	-	12.22	0.7	9.1	1.1	-
4		129.0	90	119	11.93	0.8	4.4	1.2	0.11
10/29/92	1/1/0/0								
0.5	CaO	56.8	41	-	12.46	-	8.1	1.3	-
1	10% solids	114.0	68	-	12.53	-	10.8	1.2	-
2		141.0	84	-	12.33	-	7.5	-	-
4.2		134.0	90	-	12.20	-	0.4	1.2	-
11/17/93	2/1/0/0								
3	10% solids	99.7	-	-	-	-	10.4	-	-
6		107.0	-	92	-	-	11.3	-	-
9		111.0	-	96	-	-	13.7	-	-
Additive - NaOH									
8/11/92	1/1/0/0								
0.5	0.01 N NaOH	44.9	43	-	12.30	11.0	6.7	1.2	0.08
1	10% solids	78.0	66	-	12.34	8.8	9.9	1.3	-
2		107.0	85	-	12.25	7.0	6.5	1.3	-
4		116.0	88	-	12.13	7.1	4.7	1.3	0.09

Silica Fume - batch		area	% Ca	Si	pH	Na+	Ca++	K+	Si
9/3/92	1/1/0/0								
0.5	0.1 NaOH	46.8	63	-	12.60	70.1	0.1	1.0	1.19
1	10% solids	57.3	73	-	12.57	62.0	0.6	0.8	-
2		69.4	75	-	12.55	58.2	1.6	0.7	-
3.7		86.9	77	92.4	12.54	53.3	2.4	0.7	0.08
11/17/92	1/1/0/0								
0.5	0.1 N NaOH	63.3	60	-	12.94	-	0.9	1.1	-
1	CaO	75.8	66	-	12.87	-	1.3	0.9	-
2	10% solids	96.1	74	-	12.85	-	2.4	0.7	-
4		133.2	78	-	12.85	-	2.5	0.7	-
12/16/92	1/1/0/0								
0.5	CaO pebble	59.4	71	-	12.50	54.3	1.4	1.1	0.24
1	0.1 N NaOH	69.7	76	-	12.54	43.9	1.9	0.9	-
2	10% solids	79.0	80	-	12.52	39.4	2.9	0.7	-
4	no preslake	101.0	83	-	12.51	37.2	4.3	0.7	-
12/18/92	1/1/0/0								
0.5	CaO pebble	52.3	72	-	12.64	53.5	1.8	1.1	0.28
1	0.1 N NaOH	67.4	74	-	12.59	42.7	2.1	0.8	-
2	10% solids	78.4	79	-	12.54	39.7	2.8	0.7	-
4		100.3	82	-	12.34	38.9	2.6	0.7	0.06

ADVACATE - CSTR		area	% Ca	Si	Al	Fe	pH	Na+	K+	Ca++	SO4=	Si	Al
12/15/92	1/2/0/0												
19	6.1 hr	18.0	22	-	-	-	12.49	1.2	4.0	19.1	1.51	-	-
21	17 % solids	19.8	21	-	-	-	12.50	1.1	4.3	18.9	1.66	-	-
23		19.8	21	15.0	3.4	3.5	12.48	1.1	3.9	18.9	1.54	-	-
24		18.4	22	-	-	-	12.38	1.1	3.9	14.1	1.42	-	-
2/4/93	1/2/0/0												
24	9.6 hr	31.0	23	-	-	-	12.56	-	9.9	17.0	-	-	-
32	21% solids	31.3	27	-	-	-	12.57	-	9.9	17.8	-	-	-
34		33.9	27	18.1	9.4	-	12.58	-	9.7	18.6	-	-	-
35		32.6	28	-	-	-	12.44	2.7	10.5	9.5	-	<0.2	<0.2
2/24/93	1/2/0/0												
48	16 hr	34.4	38	-	-	-	12.56	-	16.2	16.6	-	-	-
50	23% solids	35.0	37	-	-	-	12.56	-	14.2	15.6	-	-	-
52		34.9	37	-	-	-	12.55	-	14.1	15.1	-	-	-
53		35.6	37	23.5	-	-	12.48	3.7	14.5	11.1	-	-	-
3/18/93	1/2/0/0												
34	24 hr	39.9	40	-	-	-	12.60	-	15.6	14.7	-	-	-
50	21% solids	41.6	45	23.0	12.6	2.3	-	-	-	-	-	-	-
72		35.9	47	32.0	-	-	12.57	-	20.3	13.1	-	-	-
75		38.5	-	33.0	12.6	-	12.55	-	19.5	12.5	-	-	-
78		37.4	48	33.0	11.1	-	12.57	-	-	13.3	-	-	-
79		38.2	48	-	-	-	12.48	-	19.7	9.1	-	<0.2	<0.2

Clinch River-CSTR		area	% Ca	Si	Al	Fe	pH	Na+	K+	Ca++	SO4=
4/5/91	1/4/0/0										
19	6 hr	19.7	65	-	-	-	12.46	9.0	24.7	2.3	-
20	33% solids	23.4	71	-	-	-	12.52	11.7	37.9	2.4	-
8/13/91	1/4/0/0										
23	9.8 hr	19.0	91	-	-	-	12.54	3.9	14.2	9.3	-
32	19% solids	21.4	88	-	-	-	12.57	5.2	16.2	8.2	-
34		22.2	84	-	-	-	12.58	5.0	24.9	8.1	-
36		22.3	83	-	-	-	12.51	5.8	19.4	4.2	-
Additives - Calcium Chloride											
3/4/92	2.5/4/0/0										
d2	0.25 N CaCl2	61.2	86	-	-	-	12.25	20.2	53.4	76.8	-
50	16.9 hr	70.8	89	-	-	-	12.26	22.0	53.4	75.4	-
53	24% solids	71.7	85	-	-	-	12.25	21.4	60.7	70.2	-
56		77.8	88	72.6	12.9	-	12.16	21.0	58.1	69.0	-
57		75.0	89	63.5	17.1	8.1	11.98	20.3	66.4	78.5	-
Additives - Gypsum & Calcium Sulfite											
5/8/91	1/4/0.5/0.5										
19	5 hr	25.6	89	-	-	-	11.91	3.6	12.1	23.5	16.8
23	20% solids	27.1	76	25.7	4.9	-	11.95	4.1	12.8	25.9	16.3
26.5		17.3	95	-	-	-	11.89	4.9	17.0	21.3	16.7

Clinch River-CSTR		**area**	**% Ca**	**Si**	**Al**	**Fe**	**pH**	**Na+**	**K+**	**Ca++**	**SO4=**
5/13/91	1/4/0.5/0.5										
12	8.6 hr	34.4	89	-	-	-	11.84	4.6	12.7	17.0	19.5
15	19% solids	37.1	93	-	-	-	11.90	5.2	14.1	17.0	19.8
28		32.8	93	33.4	6.2	-	11.88	5.1	13.9	13.3	20.1
29.5		52.5	93	42.2	7.8	4.8	11.62	5.4	16.0	16.0	21.5
5/29/91	1/4/0.6/0.4										
26	12.6 hr	33.5	95	-	-	-	11.72	5.2	21.2	20.2	19.6
36	21% solids	40.4	-	-	-	-	11.32	4.9	22.9	13.1	21.4
47		43.3	-	-	-	-	11.29	3.7	15.1	12.9	19.8
49		40.7	97	-	-	-	11.28	3.6	14.3	11.1	19.7
6/20/91	1.8/4/0.5/0.5										
14	12.3 hrs	42.8	94	-	-	-	11.86	4.4	19.7	16.4	13.2
25	19% solids	29.9	93	-	-	-	11.87	5.3	24.4	11.0	15.8
30	feed varied	40.8	92	-	-	-	11.92	5.6	25.6	9.0	16.1
37		46.1	88	46.6	7.7	-	11.93	5.5	27.2	10.3	15.1
7/2/91	3/4/0.7/0.7										
25	17.5 hr	39.2	87	-	-	-	12.00	6.0	18.7	24.5	12.1
49	18% solids	16.7	88	-	-	-	11.98	7.3	23.2	21.8	19.5
61		26.6	83	51.4	-	-	11.94	9.3	32.4	21.9	15.3
62.5		28.0	84	-	-	-	11.92	10.1	36.2	16.8	14.1

Clinch River-CSTR		area	% Ca	Si	Al	Fe	pH	Na+	K+	Ca++	SO4=
7/18/91	1/8/1/1										
11	5.1 hr	11.8	64	-	-	-	11.41	4.0	6.4	24.2	13.2
15	21% solids	13.2	78	-	-	-	11.24	3.9	7.1	24.0	12.5
15.5		12.7	79	-	-	-	11.21	4.0	7.9	18.5	14.8
8/20/91	3/4/0.7/0.7										
23	17.5 hr	20.6	63	-	-	-	12.42	44.8	42.6	5.5	26.1
53	18% solids	26.4	81	-	-	-	12.53	31.4	33.8	5.7	15.5
55		27.4	80	-	-	-	12.51	29.9	34.9	5.8	15.7
57		27.0	82	53.1	-	-	12.45	18.6	36.7	6.0	14.9
11/28/92	2.8/4/0.7/1.2										
38	16.8 hr	19.1	78	-	-	-	12.41	6.6	19.6	23.2	16.3
50	20% solids	19.2	80	45.4	7.2	-	12.42	6.9	21.5	24.2	15.9
52		20.2	81	-	-	-	12.43	8.6	26.7	24.2	18.1
53		19.5	79	-	-	-	12.31	8.6	31.8	17.7	18.8
4/28/92	1.8/4/0.5/0.9										
d2	11.2 hr	29.0	71	-	-	-	12.58	5.4	14.1	23.5	17.6
39	18% solids	33.0	80	-	-	-	12.86	>500	28.7	14.3	109
42	possible sodium	37.1	80	-	-	-	12.79	-	22.3	11.0	83.3
44	contamination	38.3	76	-	-	-	12.75	-	21.0	13.3	74.7
45		34.1	76	-	-	-	12.63	-	21.9	10.6	104

Ground Martwick - CSTR		**area**	**% Ca**	**Si**	**Al**	**Fe**	**pH**	**Na+**	**K+**	**Ca++**
Additves - Gypsum & Calcium Sulfite										
6/4/93	4/4/2/2									
23	8.1 hr	32.2	32	-	-	-	12.52	-	5.3	29.3
26	19% solids	30.9	30	-	-	-	12.52	-	5.5	32.5
29		31.2	33	16.5	6.9	5.4	12.53	-	4.9	29.0
30		31.7	33	-	-	-	12.42	2.35	6.6	24.3
6/8/93	4/4/2/2									
25	12.6 hr	34.0	43	-	-	-	12.54	-	7.3	30.0
38	21% solids	31.7	46	-	-	-	12.52	-	7.9	29.3
40		31.0	47	25.0	8.3	8.2	12.50	-	7.6	26.8
41		35.4	45	-	-	-	12.53	2.91	7.9	27.0
6/10/93	4/4/2/2									
46	16.3 hr	43.4	58	-	-	-	12.24	-	7.7	27.0
52	16% solids	39.0	58	-	-	-	12.19	-	7.0	25.0
54		41.9	56	32.0	5.4	-	11.41	-	6.8	29.3
57		39.1	60	-	-	-	12.06	2.30	7.0	26.8

Martwick - CSTR		area	% Ca	Si	Al	Fe	pH	Na+	K+	Ca++	SO4=
11/2/92	1/2/0/0										
10	4.1 hr	22.7	22	-	-	-	12.78	1.8	3.9	19.4	-
12	18% solids	24.2	23	-	-	-	12.74	2.0	4.3	16.4	-
13		25.9	24	13.0	3.1	4.9	12.75	2.0	4.3	15.6	-
14		26.9	22	-	-	-	12.78	1.9	4.6	16.0	-
15		25.3	29	-	-	-	12.61	2.0	5.5	11.5	-
Additives - Gypsum & Calcium Sulfite											
11/12/92	2/4/1/1										
16	5.8 hr	15.8	17	-	-	-	12.73	2.9	2.3	30.3	12.2
19	15% solids	17.0	22	-	-	-	12.73	2.3	2.4	29.3	12.1
21		18.0	23	-	-	-	12.74	2.3	2.5	30.0	12.2
23		19.1	24	-	-	-	12.75	2.3	2.5	31.0	12.1
24		16.2	26	-	-	-	12.60	2.3	2.8	25.0	12.3
12/8/92	3/4/1/1										
25	11.4 hr	22.1	24	-	-	-	12.44	3.0	5.9	29.0	12.7
38	20% solids	26.9	33	-	-	-	12.40	2.9	7.3	24.8	13.4
42		28.3	35	-	-	-	12.48	2.7	7.2	29.0	13.6
48		29.8	38	-	-	-	12.47	2.6	7.1	28.8	13.1
50		28.9	41	20.0	4.2	-	12.30	2.7	6.9	27.0	13.3

Martwick - CSTR		area	% Ca	Si	Al	Fe	pH	Na+	K+	Ca++	SO4=
1/29/93	4/4/1.2/1.5										
36	15.9 hr	30.4	35	-	-	-	12.42	2.2	5.6	29.0	-
49	18% solids	32.0	35	-	-	-	12.40	2.7	5.8	27.5	-
51		30.3	36	-	-	-	12.42	2.6	6.1	29.5	-
53		33.1	43	13.0	3.8	4.7	12.44	2.3	5.8	29.8	-
53.5		30.9	42	14.2	-	-	12.24	2.6	6.0	23.6	-

Shawnee-CSTR		area	% Ca	Si	Al	Fe	pH	Na+	K+	Ca++	SO4=	Cl-
12/9/91	1/4/0/0											
9	3 hr	16.1	31	-	-	-	12.49	2.5	2.5	25.0	-	-
10	19% solids	16.8	39	3.5	-	-	12.49	2.6	2.3	25.6	-	-
11		15.7	33	-	-	-	12.48	2.8	2.5	24.9	-	-
12/10/91	1/4/0/0											
d2	6.4 hr	49.5	84	-	-	-	12.58	7.0	16.1	8.3	-	-
18	24% solids	38.1	77	-	-	-	12.46	7.2	10.5	9.7	-	-
19		38.8	82	25.0	-	7.3	12.53	5.3	10.4	13.9	-	-
20		38.1	79	-	-	-	12.53	5.2	10.5	13.0	-	-
12/11/91	1/4/0/0											
d3	9.2hr	40.7	88	-	-	-	12.49	5.8	12.4	9.1	-	-
27	21% solids	38.2	94	34.0	-	7.1	12.43	5.3	12.4	7.4	-	-
29		36.5	92	-	-	-	12.43	5.3	11.0	8.7	-	-
30		32.0	93	-	-	-	12.32	7.5	11.9	5.7	-	-
1/20/92	1/2/0/0											
19	5.9 hr	44.6	61	-	-	-	12.57	6.9	13.5	11.6	-	-
20	20% solids	49.2	60	-	-	-	12.55	6.4	12.7	11.9	-	-
21		50.0	60	35.0	-	-	12.57	6.1	13.0	11.8	-	-

Shawnee-CSTR		area	% Ca	Si	Al	Fe	pH	Na+	K+	Ca++	SO4=	Cl-
1/21/92	1/2/0/0											
d2	8.8 hr	47.0	67	-	-	-	12.57	7.7	16.3	9.1	-	-
28	21% solids	48.7	75	-	-	-	12.68	14.3	36.0	6.6	-	-
30		49.1	70	-	-	-	12.63	11.3	32.1	8.8	-	-
32		45.7	66	33.0	-	-	12.60	9.3	28.7	10.0	-	-
33		43.4	67	-	-	-	12.56	10.0	25.1	7.5	-	-
1/28/92	1/2/0/0											
13	ground ash	21.6	32	-	-	-	12.54	2.5	4.3	21.8	-	-
14	3.8 hr	21.1	34	-	-	-	12.53	2.3	4.2	19.6	-	-
15	19% solids	22.9	33	9.3	-	4.7	12.54	2.3	4.4	20.1	-	-
1/29/92	1/2/0/0											
21	ground ash	48.6	66	-	-	-	12.57	4.7	13.8	12.8	-	-
23	6.5 hr	53.5	65	-	-	-	12.57	5.0	14.4	11.6	-	-
24	17% solids	52.3	67	41.0	-	12.2	12.56	5.1	15.4	11.5	-	-
25		51.4	69	-	-	-	12.50	6.8	18.1	6.3	-	-
3/1/92	1/4/0/0											
7	2.1 hr	15.0	22	-	-	-	12.54	4.6	2.7	35.4	-	-
8	37% solids	14.5	22	3.3	-	-	12.53	4.3	3.0	36.0	-	-
9		16.6	3	-	-	-	12.42	4.6	3.6	27.0	-	-

Shawnee-CSTR		area	% Ca	Si	Al	Fe	pH	Na+	K+	Ca++	SO4=	Cl-
3/10/92	1/1/0/0											
20	5.4 hr	49.0	40	-	-	-	12.70	8.9	19.5	11.3	-	-
21	24% solids	49.4	42	27.0	-	-	12.69	8.5	19.8	11.3	-	-
22		41.3	42	-	-	-	12.68	8.7	23.4	11.8	-	-
3/17/92	1/1/0/0											
d2	10 hr	54.8	46	-	-	-	12.74	13.1	26.6	9.0	-	-
29	24% solids	57.1	49	-	-	-	12.71	11.2	21.2	10.2	-	-
31		52.7	50	-	-	-	12.77	11.3	28.0	10.2	-	-
32		55.2	48	-	-	-	12.73	11.3	27.1	9.6	-	-
33		55.5	43	38.0	-	-	12.68	11.4	26.6	5.9	-	-
Additives - Calcium Chloride												
3/25/92	1/2/0/0											
13	0.21N CaCl2	23.7	33	-	-	-	12.13	6.2	6.9	115.3	-	193
14	3.9 hr	23.4	33	11.0	-	4.1	12.16	5.9	7.4	110.3	-	206
15	16% solids	25.5	34	-	-	-	12.14	5.8	8.1	103.3	-	159
3/26/92	1/2/0/0											
26	0.22N CaCl2	48.8	80	-	-	-	12.21	12.6	17.0	75.8	-	205
28	8.8 hr	55.3	79	21.0	-	-	12.22	12.3	17.3	70.0	-	182
30	21% solids	62.7	79	35.0	-	-	12.21	12.8	18.1	71.7	-	163
31		71.1	80	37.0	-	-	12.05	13.3	20.1	62.9	-	195

Shawnee-CSTR		area	% Ca	Si	Al	Fe	pH	Na+	K+	Ca++	SO4=	Cl-
5/8/92	1/1/0/0											
25	0.3 N CaCl2	48.9	51	-	-	-	12.29	8.7	12.7	84.5	-	177
29	8.7 hr	53.2	53	33.0	-	-	12.26	10.7	15.1	99.3	-	249
32	20% solids	52.0	54	29.0	-	-	12.28	10.6	14.2	85.5	-	224
33		57.1	55	32.0	-	-	12.17	10.6	19.1	78.3	-	188
5/18/92	1/4/0/0											
18	0.2 N CaCl2	23.4	68	-	-	-	12.24	8.0	11.5	106.5	-	185
20	5.9 hr	26.7	64	-	-	-	12.26	7.5	10.1	95.8	-	159
22	19% solids	30.6	66	-	-	-	12.25	7.2	10.5	95.3	-	161
23		35.1	66	17.0	-	-	12.13	7.6	11.4	89.5	-	172
6/5/92	1/2/0/0											
16	0.2 N CaCl2	22.4	51	-	-	-	12.18	8.7	13.1	104.3	-	201
20	5.7 hr	30.8	54	-	-	-	12.18	9.5	16.2	105.8	-	185
22	21% solids	33.9	59	-	-	-	12.18	9.6	17.1	101.8	-	180
22.5		35.2	56	20.0	-	-	12.06	9.7	18.7	93.3	-	187
7/2/92	1/2/0/0											
24	0.2 N CaCl2	39.7	58	-	-	-	12.30	10.8	21.8	101.3	-	183
27	5.9 hr	37.7	60	-	-	-	12.31	9.8	19.2	96.5	-	173
30	19% solids	37.4	64	-	-	-	12.29	11.8	18.8	97.8	-	197
35		37.6	65	-	-	-	12.30	10.3	20.1	105.0	-	196
36		39.2	59	24.0	-	-	12.17	10.4	21.4	102.3	-	196

Shawnee-CSTR		area	% Ca	Si	Al	Fe	pH	Na+	K+	Ca++	SO4=	Cl-
3/10/93	1/1/0/0											
32	0.28 N CaCl2	61.5	57	-	-	-	12.21	-	31.5	84.0	-	-
45	15.9 hr	75.1	61	-	-	-	12.20	-	35.1	75.8	-	-
48	20 % solids	79.3	60	-	-	-	12.25	-	38.5	77.0	-	-
50		76.5	62	45.0	-	-	12.26	-	39.2	78.5	-	-
51		77.2	62	-	-	-	12.11	-	36.9	74.8	-	-
Additives - Gypsum												
7/8/92	2/4/0/1.5											
24	5.6 hr	26.3	62	-	-	-	12.41	4.8	8.3	25.8	14.0	-
27	19% solids	33.9	60	-	-	-	12.42	4.2	7.4	22.7	14.3	-
30		30.5	64	-	-	-	12.43	4.9	9.0	24.9	14.1	-
31		31.3	61	-	-	-	-	-	-	-	-	-
32		34.1	52	18.0	-	-	12.30	5.0	9.0	21.0	14.9	-
7/16/92	3/4/0/1.2											
26	9 hr	30.3	64	-	-	-	12.46	3.4	8.0	25.8	14.4	-
29	21% solids	31.0	62	-	-	-	12.43	3.6	8.0	25.0	13.9	-
34		30.5	59	25.0	-	-	-	4.0	10.2	26.5	15.4	-
35		31.8	57	-	-	-	12.44	4.0	9.6	25.3	14.7	-
36		36.0	52	21.0	-	-	12.29	4.3	10.8	18.8	15.2	-

Shawnee-CSTR		area	% Ca	Si	Al	Fe	pH	Na+	K+	Ca++	SO4=	Cl-
3/3/93	4/4/0/1											
35	12.9 hr	53.4	53	-	-	-	12.49	-	10.6	27.0	-	-
47	16 % solids	55.3	61	-	-	-	12.53	-	15.3	22.8	-	-
51		58.7	62	-	-	-	12.52	-	15.5	21.9	-	-
52		58.7	60	35.0	-	5.9	12.41	-	18.5	17.0	-	-
3/26/93	3/4/0/1											
24	8.7 hr	56.8	51	-	-	-	12.50	-	8.2	27.5	-	-
28	17% solids	58.6	55	-	-	-	12.49	-	11.4	26.0	-	-
30		54.5	52	-	-	-	12.49	-	8.3	27.0	-	-
31		63.6	44	-	-	-	12.38	-	8.3	21.8	-	-
7/21/93	4/4/0/1											
27.5	15 hr	71.3	61	-	-	-	12.44	-	-	-	-	-
51.5	19% solids	47.8	62	-	-	-	12.47	-	-	-	-	-
56		51.2	59	-	-	-	12.48	-	-	-	-	-
60		56.7	61	-	-	-	12.46	-	-	-	-	-
62		57.4	64	-	-	-	12.45	-	-	-	-	-
63		63.5	61	-	-	-	12.36	-	-	-	-	-

Shawnee-CSTR		area	% Ca	Si	Al	Fe	pH	Na+	K+	Ca++	SO4=	Cl-
8/12/93	4/4/0/1											
24	18.4 hr	69.2	62	-	-	-	12.28	-	-	-	-	-
48	19% solids	60.5	76	-	-	-	12.29	-	-	-	-	-
53		55.8	70	-	-	-	12.24	-	-	-	-	-
58		60.5	71	-	-	-	12.50	-	-	-	-	-
61		57.4	74	-	-	-	12.09	-	-	-	-	-
62		55.5	72	-	-	-	12.00	-	-	-	-	-

Appendix C

X-ray Diffraction Data

The following tables provide a summary of the X-ray diffraction data obtained at the University of Texas. The ten highest intensity peaks are presented for each material examined. The experiment is described in the column headings. The last line of the heading provides the date of the experiment and reactant weight ratio (hydrated lime/silica source/calcium sulfite hemihydrate/gypsum). The letters next to the peak intensities indicate the material causing the peak.

ADVACATE CSTR 24 hr residence time + 50 hr batch 5/2/93 50 1/2/0/0		**ADVACATE CSTR 24 hr residence time + 26.5 hr batch 5/8/93 26.5 1/2/0/0**		**Shawnee batch reaction 16 hr 0.6 N $CaCl_2$ 4/16/92 1/1/0/0**	
d (Å)	Intensity ($100*I/I_0$)	d (Å)	Intensity ($100*I/I_0$)	d (Å)	Intensity ($100*I/I_0$)
3.3317	54 A	3.3297	53 A	7.7235	86 Cl
3.1344	71	3.1315	73	3.8851	46
3.0749	67	3.0254	100 C	3.7780	47
3.0243	100 C	2.8037	51	3.3315	59 A
2.7544	70	2.7583	59	3.0227	55 C
2.6135	54 O	2.6169	67 O	2.8661	100
2.5189	56	2.5167	44	2.5132	44
1.9990	60	1.9093	51 C	2.3092	79 Cl
1.7100	57	1.8424	54	2.1163	48
1.6495	67	1.6485	45	1.6569	45

ADVACATE material		**Clinch River CSTR 12.3 hr residence time 6/20/91 1.8/4/0.5/0.5**		**Clinch River CSTR 17.5 hr residence time 7/2/91 3/4/0.7/0.7**	
d (Å)	Intensity (100*I/I_0)	d (Å)	Intensity (100*I/I_0)	d (Å)	Intensity (100*I/I_0)
5.4977	44 CS	8.9018	100 S	8.8333	82 S
3.3419	76 A	8.0971	14	8.0763	26
3.1314	100 CS	4.4533	63 S	4.4384	100 S
3.0249	95 C	4.2400	17 A	4.0501	32
2.6130	82 O	4.0563	22	3.3271	28 A
2.5134	57 CS	3.9913	9	3.1449	13
1.9424	57	3.3863	19	3.0228	19 C
1.9217	45	3.3343	54 A	2.8710	15
1.8416	67 CS	3.0274	28 C	2.2293	17
1.7933	51	2.2829	10	2.1859	15

Clinch River batch 22 hr reaction 3/28/91 4.8/4/3/1		**Shawnee batch 12 hr 0.2 N NaOH 2/4/92 1/4/0/0**		**ADVACATE CSTR 24 hr residence time 5/2/93 1/2/0/0**	
d (Å)	Intensity (100*I/I_0)	d (Å)	Intensity (100*I/I_0)	d (Å)	Intensity (100*I/I_0)
8.9067	100 S	4.2484	59 A	5.5379	38
5.5240	13	3.9060	51	4.9188	71 O
4.8946	16 O	3.8423	49	3.1375	60
4.4564	58 S	3.5854	50	3.0986	44
3.9970	14	3.3356	100 A	3.0344	68 C
3.3356	13 A	3.0231	58 C	2.6166	100 O
3.1428	27	2.6897	51 N	1.9231	30 O
3.0279	13 C	2.6217	53	1.9143	24
2.8726	10	2.6027	49	1.7945	32
2.6204	36 O/S	2.5126	54	1.7895	27

Clinch River CSTR
5 hr residence time
5/8/91 1/4/0.5/0.5

d (Å)	Intensity (100*I/I_0)
8.8905	100 S
7.5532	32 G
4.4543	75 S
4.2607	15 G
3.9897	11
3.7875	11
3.3795	15
3.3403	25 A
3.1444	12
3.0534	24 G

The peaks identified by letters are attributed to the species below:

A - silicon oxide, quartz

C - calcium carbonate

O - calcium hydroxide

Cl - β-$Ca_4Al_2O_6Cl_2 \cdot 10H_2O$

N - $Na_4Ca_8Si_5O_{20}$

G - gypsum, $CaSO_4 \cdot 2H_2O$

S - $Ca_4Al_2SO_{10} \cdot 12H_2O$

CS - calcium sulfite hydrate

Appendix D

Drying Solids

It became apparent during this study that variations in the solids analyses were greater than for the solution analyses. The causes for this are examined in this appendix.

D.1 BACKGROUND

In past research, drying temperatures varied from 70 to 120° C with vacuum drying of material containing gypsum performed at a temperature between the two extremes. The early drying for this work was done at 80 to 90° C with no vacuum for materials containing no gypsum or at 55 to 60° C with a vacuum if gypsum was present. The standard deviation from experiment to experiment was discussed in Appendix A and it was noted that the solids analyses had a significantly greater unexplained standard deviation.

D.2 INVESTIGATION

This deviation in results prompted an examination of the impact of the drying method on the solids analyses. The optimum drying technique would limit exposure of the sample to carbon dioxide (vacuum) and dry the sample as fast as possible without additional reaction or loss of any waters of hydration (from gypsum or the product material). Ideally, the drying method would be the same for all samples taken so they may be compared directly with no concern of the drying technique biasing the results. Several drying techniques were compared to identify the optimum method and determine the deviation between the past methods and the ideal method. The ideal or optimum method should result in lower calcium utilization, indicating less reaction during the drying period.

Drying methods are compared in Figure D.1. Calcium utilization and surface area are plotted against the difference between the two measures for each drying method. Solids samples were divided into two parts and dried at the conditions indicated. The deviation shown is plotted against the measure from the better drying method (that resulting in a lower calcium utilization). The better method was always the higher temperature, lower vacuum technique. The extreme comparison is shown by the triangles and illustrates the effect of prolonged exposure to air without drying, as the sample was left at room temperature for a day prior to vacuum drying. This has an extreme impact on calcium utilization, causing it to be biased extremely high. The surface area is biased low with wide variability in the deviation between the drying methods.

The other two comparisons are between the methods used previously in this research and the best method (vacuum drying at 200° F). Both the previous methods show a positive bias in the calcium utilization and a smaller negative deviation in the surface area. The reaction that occurs during drying apparently reduces the surface area while consuming calcium hydroxide. The two current methods compare well with each other, so that comparisons between materials dried with each of the two past methods should be valid.

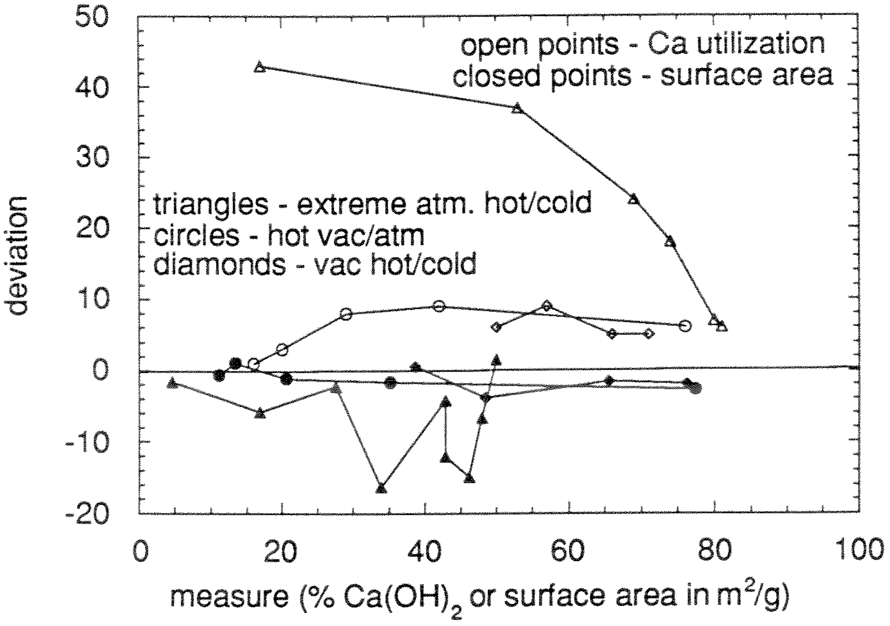

Figure D.1 Comparison of drying techniques

Samples compared included a Clinch River ash batch experiment with gypsum present, a Shawnee ash batch experiment with calcium chloride present, and a Shawnee ash batch experiment with gypsum present. Each set of solids samples were dried at the conditions shown and the deviation between the results of two drying methods is plotted against the more accurate measure (least calcium hydroxide reaction).

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Vita

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