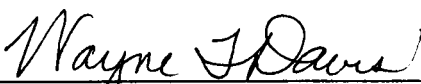
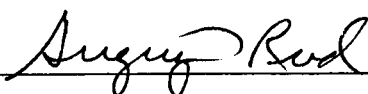


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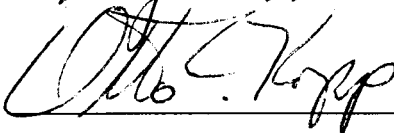
I am submitting herewith a dissertation written by Parham Mikell Cain entitled "Removal of Hydrogen Chloride from Flue Gas by Dry Sorbents Prepared from the Hydrothermal Reaction of Silica and Calcium Hydroxide". I have examined the final copy of this dissertation for form and content, and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Civil Engineering.


Wayne T. Davis, Major Professor

We have read this dissertation, and
recommend its acceptance:







Accepted for the Council:


Associate Vice Chancellor and Dean of the
Graduate School

REMOVAL OF HYDROGEN CHLORIDE FROM FLUE GAS BY
DRY SORBENTS PREPARED FROM THE HYDROTHERMAL
REACTION OF SILICA AND CALCIUM HYDROXIDE

A Dissertation
Presented for the
Doctor of Philosophy
Degree
The University of Tennessee

Parham Mikell Cain
December 1993

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To all my parents
and Jo

ACKNOWLEDGMENTS

It is with great appreciation that I would like to acknowledge my committee members, Drs. Wayne T. Davis, Terry L. Miller, Gregory D. Reed, and Otto C. Kopp. I have observed the demanding schedule of faculty members, and am genuinely grateful for the time they set aside to give me direction in my research. I am deeply appreciative for the support and encouragement offered by my major professor, Dr. Davis, for without his unqualified belief that I could pursue a doctoral degree in engineering, I would probably not have committed myself to the endeavor. The other key element in the process was the fellowship awarded to me for three consecutive years by the Waste Management Research and Education Institute, the first year of which was sponsored by Dixie Cement Company. I would like to thank the people who made that possible for both the tangible award itself and the intangible vote of confidence it carried.

Graduate work, by its nature, is a uniquely intense experience, and friendships forged with fellow students involved in the same pursuit take on particular significance. Perhaps the most important of these for me was the mutual friendship with Cindy McIlvaine and Rebecca Pullen, two women who were also returning to school after a professional life to pursue graduate work in engineering, a field that, likewise for them, had not been their undergraduate major. They were a saving grace, and will be lifelong friends. It just is not possible to describe the importance of their presence, but I know that they know. I wish to thank Arijit Pakrasi for allowing me to work with him in his doctoral research. It enabled me to determine my direction of research, and gave me the opportunity to work with one of the most exemplary students and finest individuals I have ever met.

I thank the Department of Geological Sciences for providing access to the x-ray diffractometer, and Dr. Otto Kopp and Dr. Ted Labotka for their advice and assistance in that arena. Drs. David and Carolyn Joy provided access to the scanning electron microscope, and enabled me to perform my own investigations for which I am appreciative.

I wish to thank my family for their love and their interest - both have been so important. My deepest appreciation is reserved for my husband who endured extremely limited access to his companion for five years, and probably complained only four times. He offered endless support in the form of encouragement, confidence, pride in my progress, and several years of the best dinners that I have ever had. I am happy to be able to return my companionship to him, although I believe I will leave the dinners in his hands.

ABSTRACT

Experimental work was performed to determine the cause(s) of reactivity enhancement exhibited by solids produced by hydrothermal reaction of silica and calcium hydroxide (CH) in tests in which the solids were reacted with flue gas containing hydrogen chloride (HCl). Three types of sorbents were prepared by reacting calcium hydroxide with amorphous silica, crystalline silica, and a low-calcium fly ash. In addition to reactivity tests, sorbents underwent powder x-ray diffraction analysis, surface area analysis, and scanning electron microscopy analysis.

Sorbents prepared using amorphous silica resulted in enhanced utilization over that of CH alone for all silica:CH mass ratios at all slurry times. The crystalline silica/CH sorbents resulted in no reactivity enhancement over that of CH, except in the case of high silica:CH ratio and long slurry time. Sorbents prepared from fly ash exhibited enhanced reactivity to an extent that was between that of the amorphous silica sorbents and the crystalline silica sorbents.

X-ray diffraction indicated that poorly crystallized calcium silicate hydrate formed from the amorphous silica/CH reactants, and that more calcium silicate hydrate formed with increasing silica:CH ratio and increasing slurry time. Little to no calcium silicate hydrate was seen in the x-ray patterns of the crystalline silica/CH sorbents. Scanning electron microscopy of the amorphous silica/CH sorbents pointed to the formation of the calcium silicate hydrate called C-S-H(I).

Within the limits of the experiments, utilization of the amorphous silica/CH sorbents was found to have a linear relationship with the molar SiO_2 :CaO ratio of the starting components as long as there was CH remaining in the solids (as

demonstrated by x-ray diffraction). Behavior of sorbents in which no CH remained differed from that of sorbents with a CH excess.

The degree of enhanced reactivity was related to the ability of the silica to dissolve in the high pH solutions. Greater availability of dissolved silica translated into proportionally more calcium silicate hydrate and less CH in the resulting sorbent. The cause of the reactivity enhancement was the increase in production of calcium silicate hydrate.

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1.0 INTRODUCTION

1.1 Municipal solid waste combustion

Municipal solid waste (MSW) incinerators may play an increasingly important part in the solid waste management problem. Dwindling landfill space and increasingly stringent environmental regulations have combined to encourage the use of incineration as a means of solid waste disposal (Seigies and Trichon, 1993). Presently, the great public opposition to incineration prevents it from making a significant contribution to the solution of the waste management problem.

1.1.1 Emissions from MSW incinerators

Emissions from MSW incinerators are related to the composition of the waste stream which varies by region and season. A typical waste stream comprises paper (40%), yard waste (17%), metals (8.5%), plastics (8%), food (7.5%), glass (7%) and "other" (12%) (Seigies and Trichon, 1993). Nitrogen oxides, sulfur dioxide (SO₂), carbon monoxide, particulate matter, and acid gases (HCl and HF) form the majority of pollutants emitted from incinerators. Small amounts of trace metals and trace organics which are emitted are referred to as toxic pollutants.

An emissions data base was compiled as part of a study prepared by DePaul and Crowder (1989). Uncontrolled emission factors were given for five different types of MSW incineration facilities. For each facility type the mean value and the standard deviation were given for a list of constituents. Table 1.1

Table 1.1 Emission Factors for Uncontrolled Incinerators ⁽¹⁾					
	Mean	Std. Dev.	High	Low	N
Particulate*	33.55	27.40	74.78	1.98	5
SO ₂ *	2.51	0.75	3.44	1.68	5
NO ₂ *	2.84	1.22	4.13	1.10	5
CO*	3.12	3.61	8.86	0.41	5
HCl*	6.79	1.76	8.94	5.17	5
HF*	0.27	0.26	0.07	0.005	5
As**	2,916	4,170	9,090	368	4
Be**	87.69	143.24	300	0.48	4
Cd**	11,328	14,756	37,300	700	5
Cr**	12,078	7,973	18,930	761	4
Pb**	137,313	90,764	262,000	17,000	5
Hg**	4,425	4,409	4,376	1,080	5
Ni**	8,785	6,025	10,166	2,190	3
PCDD ⁺	7,855	----	----	----	1
PCDF ⁺	9,475	----	----	----	1
PCB ⁺	14,129	19,946	28,233	25.8	2

*lb/ton

**10⁻⁶ lb/ton

+10⁻¹⁰ lb/ton

(1) Based on 5 incinerator types: mass burn waterwall, mass burn rotary waterwall, mass burn refractory, starved air, and refuse-derived fuel fired .

lists the average of the means for the different facility types in the study. No conclusion about any particular type of incinerator can be drawn from this data, but a range of values can be seen. The highest and lowest averages from the different facilities are listed without comment as to the type of facility. The last column, headed N, reports the number of facilities used in the average. However, values for PCDD and PCDF were determined from 1 facility, and are not actual averages.

1.1.2 Regulations and guidelines for MSW incinerators

In February, 1991, the United States Environmental Protection Agency (EPA) issued performance standards for new MSW incinerators and guidelines for existing facilities. Municipal waste incinerators with a capacity of greater than 250 tons per day (tpd) are regulated by New Source Performance Standards for new facilities and Emissions Guidelines for existing facilities. Emission limits are established for carbon monoxide, organics, metals, SO₂, HCl, and NO_x. The best demonstrated technology (BDT) designated by the Environmental Protection Agency (EPA) for new plants larger than 250 tpd includes good combustion practice, selective non-catalytic reduction (NO_x control), and a spray dryer followed by a fabric filter for control of organics, metals, and acid gases.

Standards for existing municipal solid waste incinerators are based on size. For existing plants with capacities between 250 and 1100 tpd, EPA has designated the BDT as good combustion practices, dry sorbent injection (DSI), and an electrostatic precipitator. For existing plants with greater than 1100 tpd capacity, the BDT is good combustion practices, a spray dryer, and an electrostatic

precipitator. Guidelines for facilities smaller than 250 tpd are currently being developed by EPA (Seigies and Trichon, 1993)

1.1.3 DSI process

In the DSI process, referred to as the BDT for existing plants with capacities between 250 and 1100 tpd, the acid gases, primarily HCl and SO₂, are controlled through gas-solid reactions with a dry sorbent, such as calcium hydroxide (CH). DSI technology involves injecting the dry sorbent into the flue gas ductwork downstream of the air preheater, in conjunction with humidifying the flue gas. The products from the gas-solid reactions, as well as the unreacted sorbent are collected for disposal in the existing particulate collector, such as an electrostatic precipitator or a baghouse.

Most of the work aimed at improving the DSI process has focused on improving the reactivity of the calcium-based sorbents. These investigations have looked at the use of high surface area hydrated limes, pressure hydrated dolomitic limes, and the use of hydrated limes with additives such as NaOH and NaCl (Peterson, 1990)

One type of improved sorbent, investigated primarily for its application to SO₂ removal, is produced from the reaction of fly ash with CH in aqueous solution. The dried solids have been found to be particularly reactive with SO₂. Little work has been done in the area of applying these fly ash/CH sorbents to HCl removal in the DSI process, largely because the emphasis has been on coal flue gas desulfurization.

1.2 Objectives

The objectives of this study were 1) to attempt to determine the mechanism(s) which cause dry sorbents, prepared hydrothermally from a silica-containing constituent and CH, to exhibit greater reactivity than CH alone when exposed to HCl in a gas stream and 2) to determine the optimum conditions for reactivity enhancement. In order to meet these objectives a series of sorbents were prepared in which certain conditions of preparation were varied in a controlled manner. These solids were then tested for their ability to react with gaseous HCl. After the performance of the prepared sorbents was ascertained, the sorbents were analyzed by a variety of methods in order to determine the mechanism(s) of enhanced reactivity.

If dry sorbents produced from CH and fly ash are to have practical application, it will be necessary to prepare the sorbents so that reactivity enhancement is consistently maximized. By understanding the mechanisms that control the enhancement, and determining the conditions under which the sorbent utilization is increased and decreased, it may be possible to determine the optimum conditions of preparation. This research should give insight into the aspects of the sorbents which are most important in enhancing reactivity. By using pure silica to react with CH in this study, instead of fly ash, the analyses were expected to be simpler than if fly ash had been used. It is hoped that the information gained in this study can be applied toward making fly ash a viable raw material in the production of dry sorbents for MSW incineration.

2.0 BACKGROUND

2.1 Bench scale tests of calcium hydroxide for HCl control

Calcium Hydroxide (hereafter referred to as CH) is typically used in DSI applications for HCl removal. This dissertation involves research which attempts to enhance the utilization of the CH in the gas-solid reaction by reacting it first in an aqueous solution with silica before applying it as a dry sorbent. Pakrasi (1991) gives a complete review of the DSI application of CH in HCl removal at the bench and pilot scales and for full scale MSW incinerators as well as of the reaction of HCl with CH. Results from Pakrasi's work form the foundation for the present study because in both studies the same reactor was used under identical process conditions. As sample preparation and analytical methods were also the same, the data from this study is directly comparable to analogous data from Pakrasi's study. Because of the relevance of Pakrasi's reactor tests, the results will be discussed in the following background sections.

2.1.1 Effect of moisture on CH utilization

Kinetic tests showed that, for dry gas containing 1000 ppmv HCl, increased reactor temperature had a positive effect on utilization, although final utilization was low compared to the tests employing humidified gas. Figure 2.1 shows the results of dry gas tests at temperatures ranging from 79 °C (175 °F) to 204 °C (400 °F). Maximum utilization, which occurred at 204 °C and

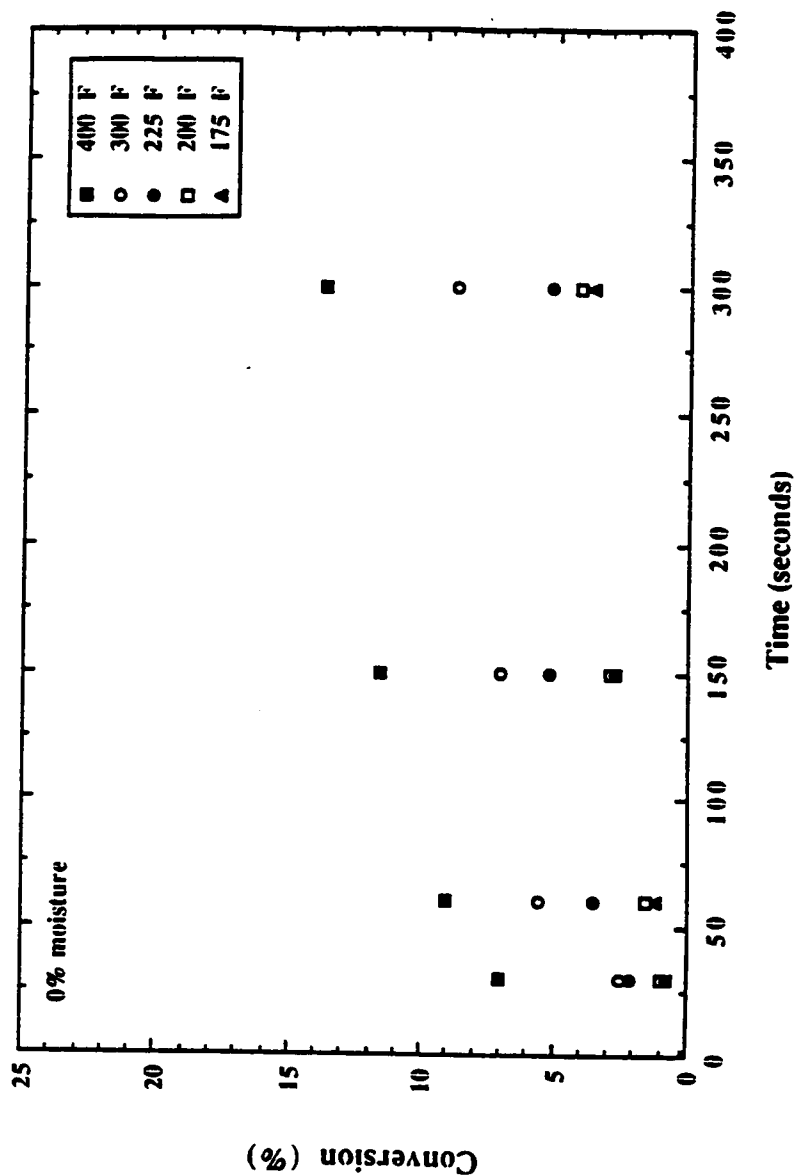


Figure 2.1. Sorbent conversion at 0% moisture and 1000 ppmv HCl.

Source: Pakrasi, A. 1992. Kinetic Studies on the Removal of Hydrogen Chloride from Flue Gas by Hydrated Lime Powders in a Bench Scale Fixed Bed Reactor. Doctoral Dissertation in Civil Engineering. University of Tennessee, Knoxville.

300 seconds of reaction time, was only 13.6%. Both the initial rate of conversion and the final conversion increased with temperature, indicating the possibility of a temperature activated reaction mechanism at these test conditions.

Tests were performed at moisture contents of 7%, 10%, and 20% (v/v). There was significant enhancement in the utilization of the CH with increasing moisture. Figure 2.2 shows the results for 10% moisture content over the same range of temperatures used in the dry tests. The final conversion with moisture was significantly higher than that seen in the dry tests. In contrast to the dry tests, the conversion increased as the temperature decreased when moisture was present in the gas stream. This was attributed to the increase in relative humidity.

2.1.2 Effect of BET surface area on CH utilization

In the study by Pakrasi, tests were performed to determine the effect of surface area on the CH utilization. Two sources of CH were used. One, from Tenn Luttrell, was 18 m²/g based on a BET surface area analysis. The other, obtained from "A/S Scansorb", had a BET surface area of 26 m²/g. It should be noted that the Tenn Luttrell CH used in Pakrasi's work and in the present work are from the same source, and had the same surface area. The tests were run with 10% volumetric moisture and 1000 ppmv HCl in the gas stream. Temperatures of the tests were 79 °C (175 °F), 107 °C (225 °F), and 204 °C (400 °F). The results are shown in Figure 2.3. With the exception of the highly reactive 175 °F tests, the higher surface area of the Scansorb CH resulted in approximately 15% higher utilization at both 107 °C and 204 °C. Based on Pakrasi's work, it is apparent that increased surface area of the CH and increased moisture

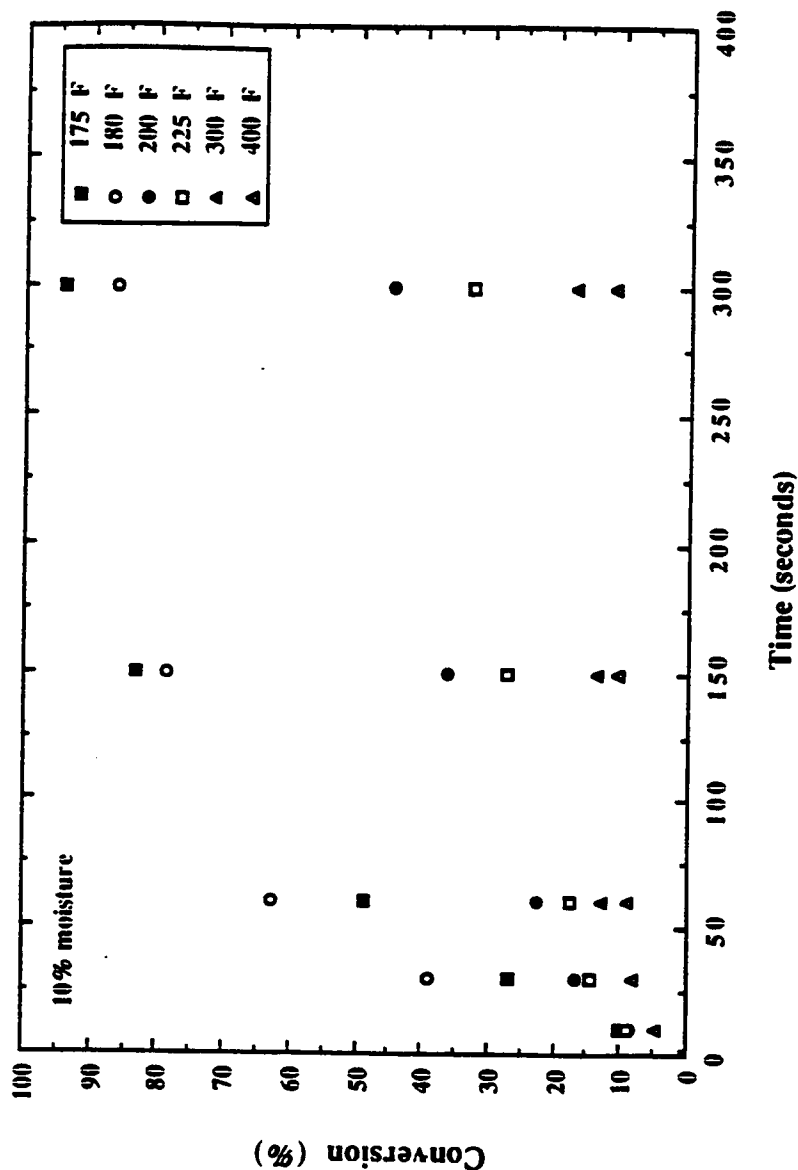


Figure 2.2. Sorbent conversion at 10% moisture, 1000 ppmv HCl and at temperatures from 70 °C (175 °F) to 204 °C (400 °F).

Source: Pakrasi, A. 1992. Kinetic Studies on the Removal of Hydrogen Chloride from Flue Gas by Hydrated Lime Powders in a Bench Scale Fixed Bed Reactor. Doctoral Dissertation in Civil Engineering. University of Tennessee, Knoxville.

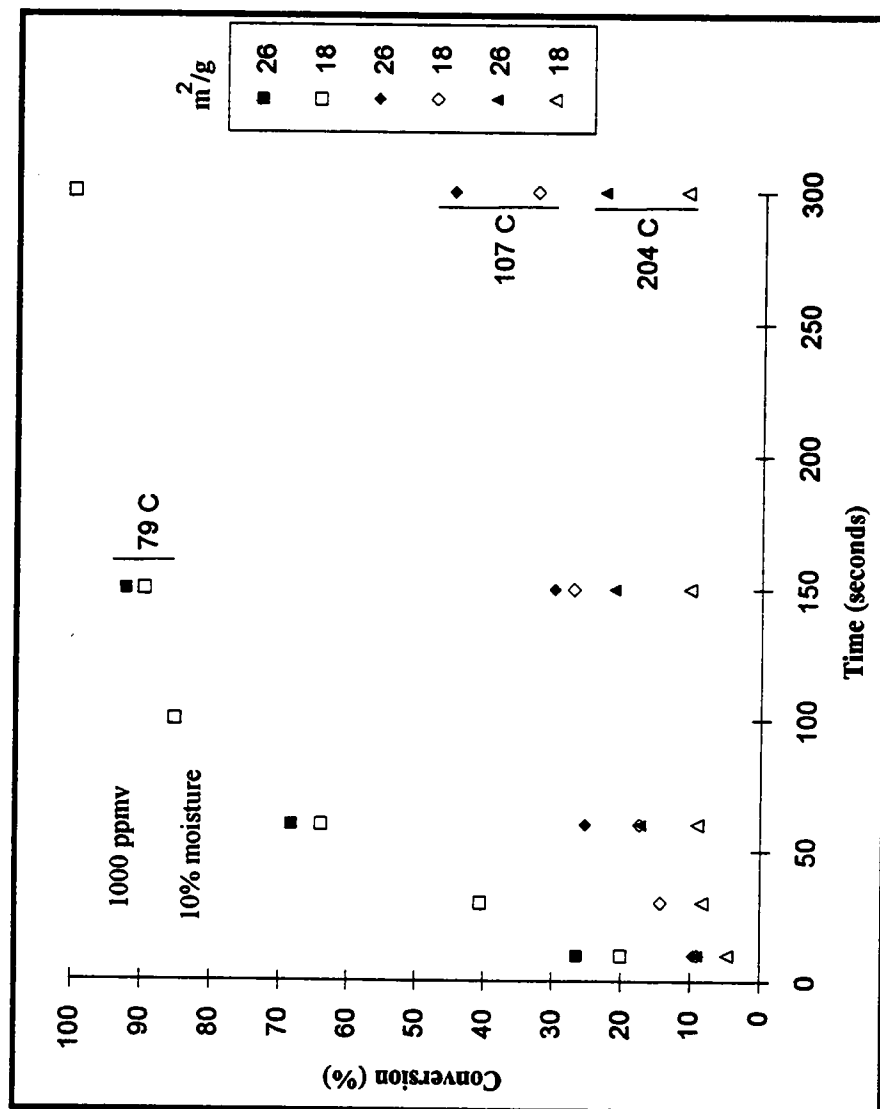


Figure 2.3. Effect of surface area on sorbent conversion at 1000 ppmv HCl and 10% moisture. Data from Pakrasi, 1992.

content of the simulated stack gas both enhance the overall reactivity of HCl with CH.

2.2 The use of fly ash/calcium hydroxide sorbents in dry sorbent injection for acid gas control

As mentioned in Chapter 1, a portion of this dissertation involves the bench-scale application of dry sorbents to remove HCl from MSWC flue gas, in particular by sorbents made by reacting fly ash with CH in an aqueous slurry in order to enhance reactivity. Previous studies utilizing such sorbents have been almost exclusively applied to flue gas desulfurization (e.g., Jozewicz and Rochelle, 1986; Jozewicz et al., 1986; Jozewicz et al. 1987b). The single such study which addressed the removal solely of hydrogen chloride alone utilized ground glass rather than fly ash as the silica source for the sorbent production (Jozewicz et al., 1991). One other study considered removal of HCl in combination with SO₂ by fly ash/CH sorbents (Jozewicz et al., 1990). This section summarizes the results from those studies in order to illustrate the enhanced reactivity of the hydrothermally prepared fly ash/CH (and glass/CH) sorbents with SO₂ and HCl. All studies were performed using sand-bed reactors which were similar to the reactor described in Chapter 4 of this dissertation.

2.2.1 SO₂ control

An excellent and comprehensive literature review of the use of fly ash/CH solids in both bench-scale and pilot-scale flue gas desulfurization studies was given

by Peterson (1990). The main points of the review of the bench-scale data are discussed in the following sections.

2.2.1.1 Effect of slurry temperature

Jozewicz and Rochelle (1986) investigated the effect of slurry temperature during sorbent preparation on the sorbent's reactivity with SO_2 in a sand-bed reactor. Figure 2.4 shows the results of the sorbents produced in slurries where the fly ash:CH weight ratio was 16:1. The results of this component ratio are typical of ratios from 1:1 to 20:1 in that the reactivity of the sorbents typically increased with increasing temperature and increasing fly ash:CH ratio (Jozewicz et al, 1988a). Jozewicz and Rochelle suggested that the limiting step of the fly ash/CH reaction was the dissolution rate of the silica from the glassy fly ash. They proposed that the dissolution rate was dependent on the temperature of the solution. The higher silica dissolution rate at increased temperatures in the slurries used to produce the sorbents resulted in higher reactivity of the sorbents when used in the sand-bed reactor.

In a later study Jozewicz et al. (1987b) prepared fly ash/CH sorbents at slurry temperatures exceeding 100°C (212°F). They found that of two fly ash/CH sorbents containing identical proportions of the two components, one slurried at 150°C (302°F) and the other at 230°C (446°F), the lower temperature sorbent exhibited greater reactivity with SO_2 . They suggested that the solids must have a large surface area and an amorphous structure to enhance reactivity, and cited Taylor (1964) in proposing that the sorbents had become more crystalline at the higher temperature, and were therefore less reactive with SO_2 .

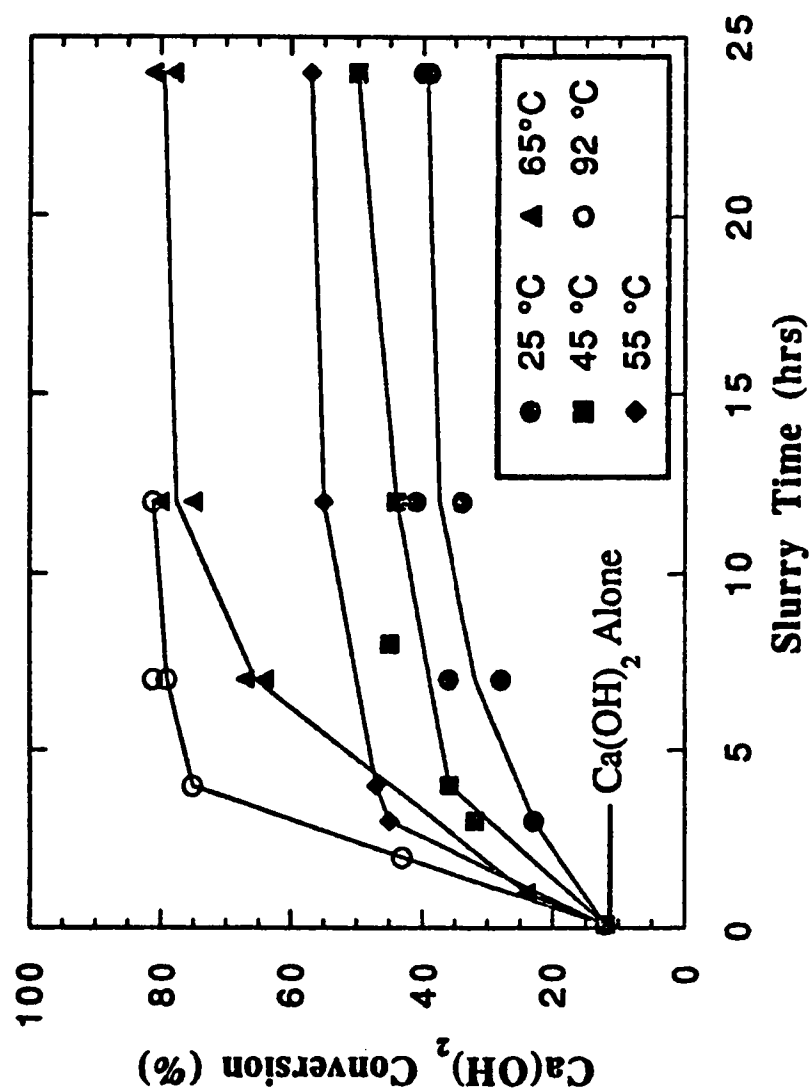


Figure 2.4. Effect of slurry temperature on reactivity of fly ash/CH solids with SO_2 .

Source: Jozewicz, W. and G.T. Rochelle. 1986. Fly Ash Recycle in Dry Scrubbing. *Env Prog.* 5(4):219-224.

2.2.1.2 Effect of fly ash:CH weight ratio

The weight ratio of fly ash to CH for the slurried materials was an important variable in the experiments performed by Jozewicz and Rochelle (1986). They demonstrated that increasing the fly ash:CH ratio from 0.5:1 to 20:1 on a weight basis increased CH utilization from 17 to 78%. These results are presented in Figure 2.5. They interpreted the increase in reactivity to be a result of increased reactive solids due to the greater amount of silica dissolved from the increased mass of fly ash.

2.2.1.3 Effect of fly ash type

Peterson (1990) compared the reactivity of fly ash/CH sorbents prepared from both high and low calcium fly ashes. Surprisingly, he found that low calcium fly ashes produced sorbents more reactive with SO_2 than did high calcium fly ashes. His fly ash dissolution experiments demonstrated that low calcium fly ashes had more total silica than high calcium fly ashes. Hence, the low calcium fly ashes resulted in the production of more calcium silicate hydrate which accounted for their increased reactivity. Peterson pointed out, however, that since some of the calcium present in the high-calcium fly ash was able to react with SO_2 , there was only a minor effect of fly ash type when the fly ash/CH sorbents were compared on a weight basis.

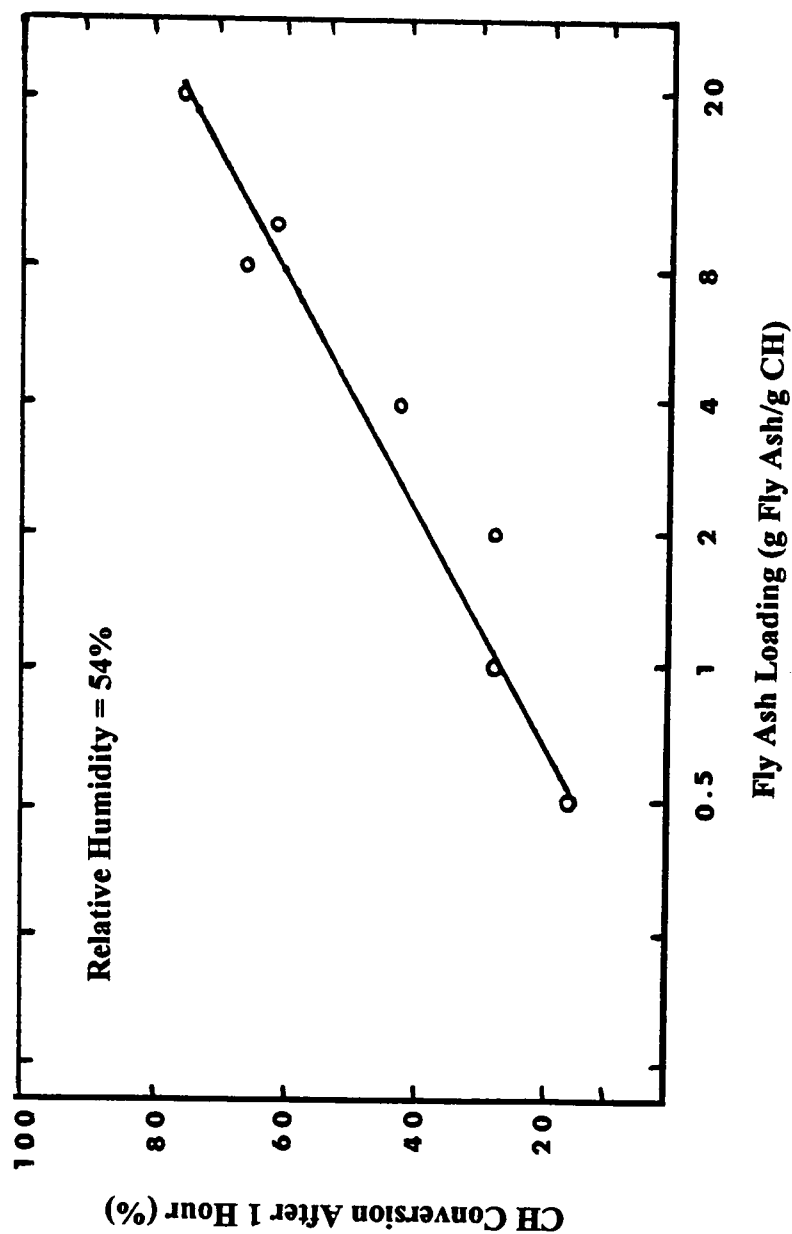


Figure 2.5. Effect of increasing fly ash:CH ratio on reactivity of fly ash/CH solids with SO₂ at relative humidity of 54%. After Jozewicz and Rochelle, 1986.

2.2.1.4 Effect of fly ash grinding

More recent studies have focused on methods of increasing the rate of formation of reactive calcium silicate hydrates from fly ash and Ca(OH)_2 . Grinding the fly ash to provide smaller particle size and increased surface area has shown some success, presumably by increasing the rate of silica dissolution. Hall et al (1991) found that the solids formed from fly ash and CH slurried at 90 °C (194 °F) showed significantly higher CH utilization for ground as compared to unground fly ash.

In a later study (Singer et al, 1991) in which fly ash suitability for sorbent preparation was investigated, it became evident that grinding fly ash does not invariably result in more reactive sorbents. In testing numerous fly ashes the investigators found that the reactivity actually decreased for some sorbents prepared with ground fly ash as compared to sorbents prepared with the same fly ash which had not been ground. This was the case in spite of the increased surface area of the sorbents prepared with ground fly ash. Table 2.1 presents the utilization and surface area results of four samples in the study which were prepared from both unground and ground fly ash to demonstrate this point. In all areas in Table 2.1, the utilization actually decreased as the surface area was increased by grinding. The authors offer the following explanation. In the grinding process a large fraction of soluble species, including alkalis, are probably washed from the fly ash and carried away in the wastewater. The reduced alkali content would have the effect of inhibiting pH development in the fly ash/CH slurry, which would result in a decreased rate of silica dissolution. Grinding may

Table 2.1. Fly ash/CH sorbent reactivity.

Sample	S1	S2	S3	S4
Utilization (%)	49	46	51	54
FASA ^a (m ² /g)	1.84	1.52	1.09	0.82
Ground Utilization (%)	42	36	36	41
Ground FASA (m ² /g)	3.02	4.41	5.40	2.62

^aFASA = Fly ash surface area

also change the solution chemistry by exposing inner surfaces, making chemicals accessible for reaction other than those accessible in unground fly ash. This too might cause a decrease in reactivity for SO_2 removal. The results also support the conclusions of Peterson (1990) that the fly ash must be finely ground (15 to 25 m^2/g) in order to significantly affect the silica dissolution rate. He found that moderate grinding (2-5 m^2/g) was not nearly so effective in enhancing the reactivity.

2.3 The $\text{CaO-SiO}_2\text{-H}_2\text{O}$ system

The reaction between fly ash and CH is referred to as pozzolanic. According to Webster's New Collegiate Dictionary a pozzolan "is a finely divided siliceous or siliceous and aluminous material that reacts chemically with slaked lime at ordinary temperatures and in the presence of moisture to form a strong slow-hardening cement". The fly ash contributes the silica to the pozzolanic reaction involving the CH. The products of this pozzolanic reaction, referred to as calcium silicate hydrates, are the focus of this dissertation. The literature reviewed in this section pertains to the formation of calcium silicate hydrates from pure silica and lime. It provides the background for discussing the experimental results of this dissertation involving sorbents produced by the pozzolanic reaction of silica and CH. Brief reviews of aspects of CH and silica pertaining to these reactions are given in the following two sections.

2.3.1 Calcium hydroxide

CH has a layered structure (Bernal and Megaw, 1935; Petch, 1961). The calcium atoms are octahedrally coordinated, and the oxygen atoms tetrahedrally coordinated. Its specific gravity is 2.30 (Lea, 1970). The solubility of CH in water decreases with rise in temperature. The solubility data are not all in close agreement, but some of the most reliable from Greenberg (1956), Bassett (1934), and Boynton (1980) are plotted in Figure 2.6. The solubility for CH is typically expressed as grams CaO per liter. Addition of CH to water in even very small amounts raises the pH very rapidly. Table 2.2 lists the pH values at 25 °C (77 °F) for increasing amounts of CH per liter.

2.3.2 Silica

2.3.2.1 Silica chemistry

Silica, according to Iler (1979), is a short convenient designation for "silicon dioxide" in all its crystalline, amorphous, and hydrated or hydroxylated forms. In analysis, the term "silica" indicates only that the silicon content is given in terms of weight of SiO₂, regardless of the form in which it is actually present. Crystalline silica has long-range three-dimensional internal order (i.e., an ordered atomic arrangement). Amorphous silica lacks the orderly atomic arrangement. Both occur in anhydrous and hydrous states.

At 25 °C crystalline silica has a solubility of 6 ppm. Amorphous silica has a solubility of 70 ppm as SiO₂. Iler (1979) says that this is the 'solubility' of

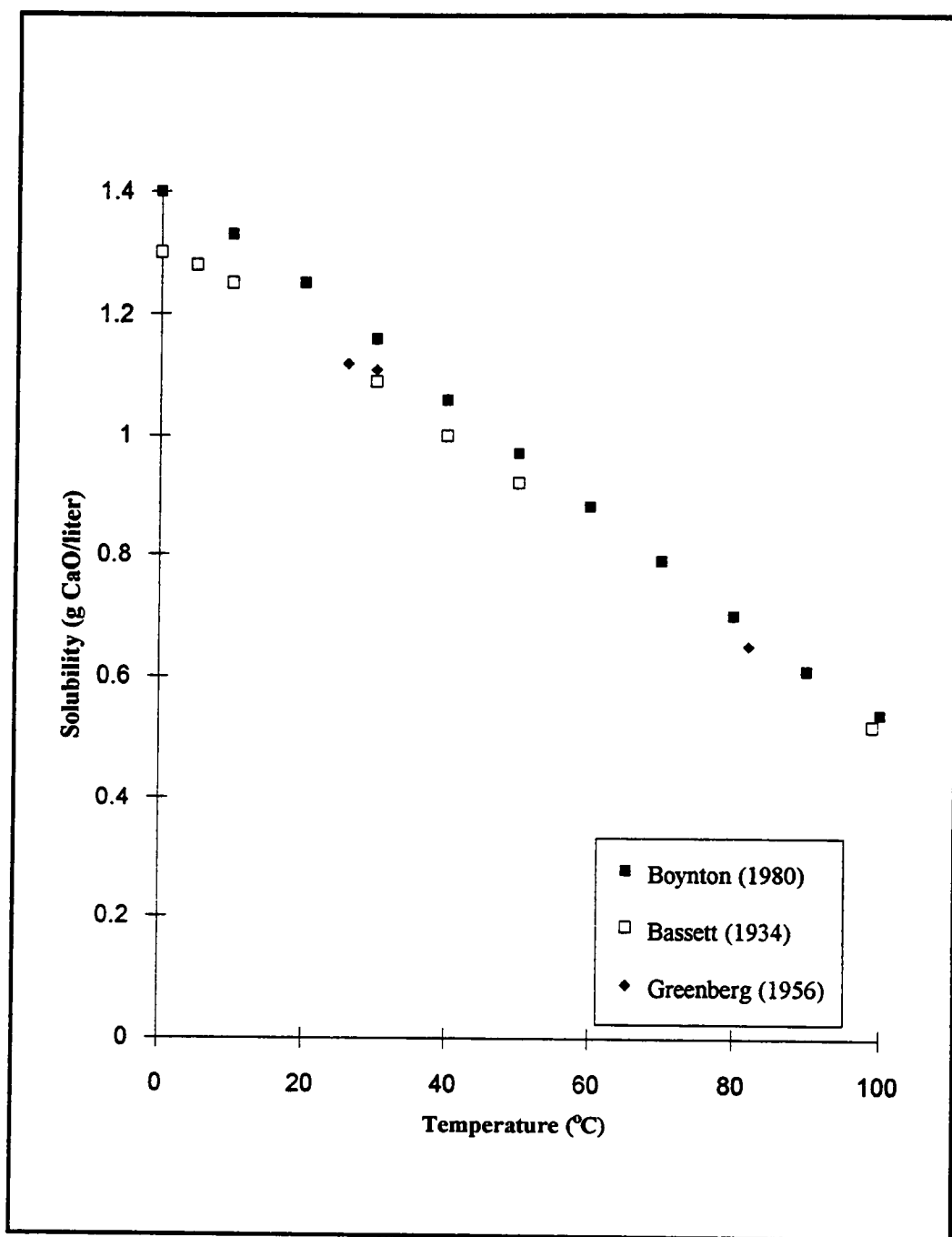


Figure 2.6. Solubility of CH expressed as CaO.

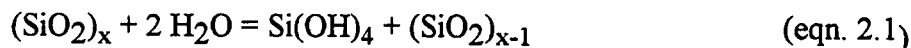
Table 2.2. pH of CH solutions at 25 °C.

CaO (g/l)	pH
0.064	11.27
0.065	11.28
0.122	11.54
0.164	11.66
0.271	11.89
0.462	12.10
0.680	12.29
0.710	12.31
0.975	12.44
1.027	12.47
1.160	12.53

anhydrous, nonporous, amorphous SiO_2 . However, except for fused SiO_2 glass, the common forms of amorphous silica consist of extremely small particles of amorphous silica, or porous aggregates, the surface of which is hydrated in the form of silanol (SiOH) groups attached to three siloxane (Si-O-Si) groups. These amorphous silicas exhibit a somewhat higher solubility so that most powders and gels have a solubility of 100-130 mg/l.

Iler explains that the soluble form of silica is monomeric, containing only one silicon atom and generally formulated as $\text{Si}(\text{OH})_4$. This form of silica is often called monosilicic acid or orthosilicic acid. Its state of hydration is not known, although at high pressure there is some indication that one water molecule is linked to each OH group, probably by hydrogen bonding. Of particular interest, in terms of the present study, is that soluble silica combines with metal ions to an increasing degree with increasing pH, thus reducing the concentration of free monosilicic acid (Iler, 1979).

Amorphous silica has rather complex solubility traits. There is an apparent increase in the solubility of amorphous silica from pH 9 to 10.7. This is due to the formation of the silicate ion ($\text{Si}[\text{OH}]_5^-$) which is in equilibrium with the silica monomer, $\text{Si}(\text{OH})_4$, as well as with the solid. The following equations give this relationship:



At pH higher than 10.7, as is the case of the solutions in the experimental section of this dissertation, equation 2.2 is driven to the right due to the conversion of Si(OH)_4 to ionic silicate species. Thus, no solid silica remains as it all becomes soluble. Goto (1955) measured the effect of pH on the solubility of silica at temperatures from 0-200 °C (32-392 °F). A graph of these results can be seen in Figure 2.7. Results of Alexander et al. (1954) for the solubility of very pure amorphous silica in water at different pH values are in agreement with those of Goto.

The dissolution of amorphous silica is dependent on its solubility, which in turn depends on the temperature and pH of the solution. Iler (1979) describes the dissolution process of silica in the following manner. In a neutral water solution the silica is dissolved by depolymerization through hydrolysis, and the solubility is the steady state concentration of Si(OH)_4 thus achieved. In alkaline solutions (e.g. ones which contains CH) the OH^- ion acts as a catalyst. Amorphous silica has a somewhat open arrangement due to its non-geometric nature, and some openings are large enough to accommodate the adsorption of the OH^- ion. This causes a silicon atom to go into solution. Up to a pH of approximately 11, silica hydrolyzes to soluble silica, Si(OH)_4 , and OH^- ions, so that the process continues in this manner. Above pH 11 the hydroxyl ions convert the Si(OH)_4 to Si(OH)_5^- so that the solution remains unsaturated with respect to Si(OH)_4 . In this way silica continues to dissolve. Figure 2.8 shows a conceptualization of the dependence of the silica dissolution process on the hydroxyl ion as represented by Taylor (1964).

Greenberg (1957a) demonstrated that the rate of dissolution of various types of silica in high pH solutions was related to the structure of the silica. Depolymerization is the mechanism of dissolution for silica. The activation energy

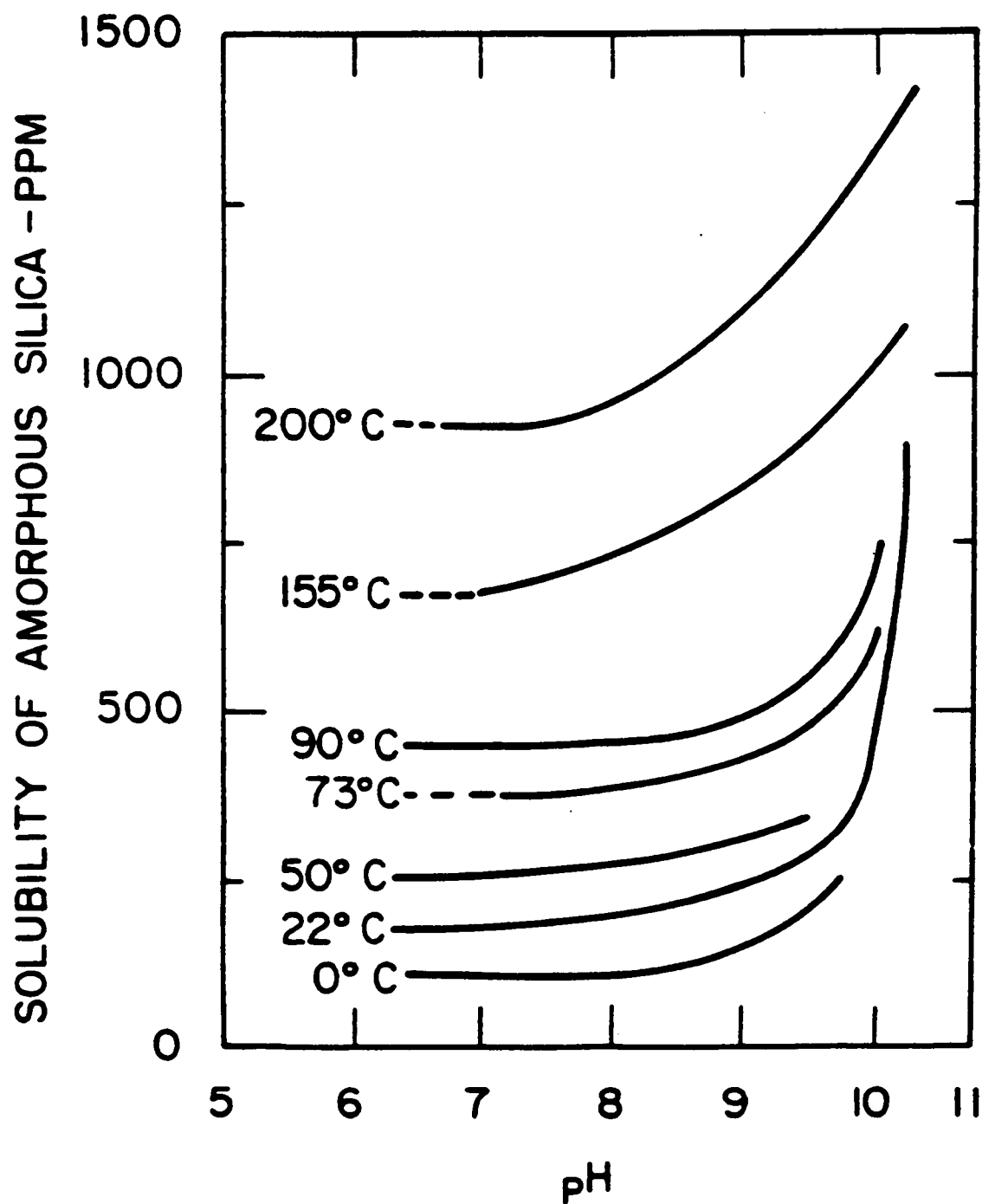


Figure 2.7. Solubility of amorphous silica versus pH at different temperatures.

Source: Iler, R.K. 1979. *The Chemistry of Silica*. John Wiley and Sons. New York. 866 pages.

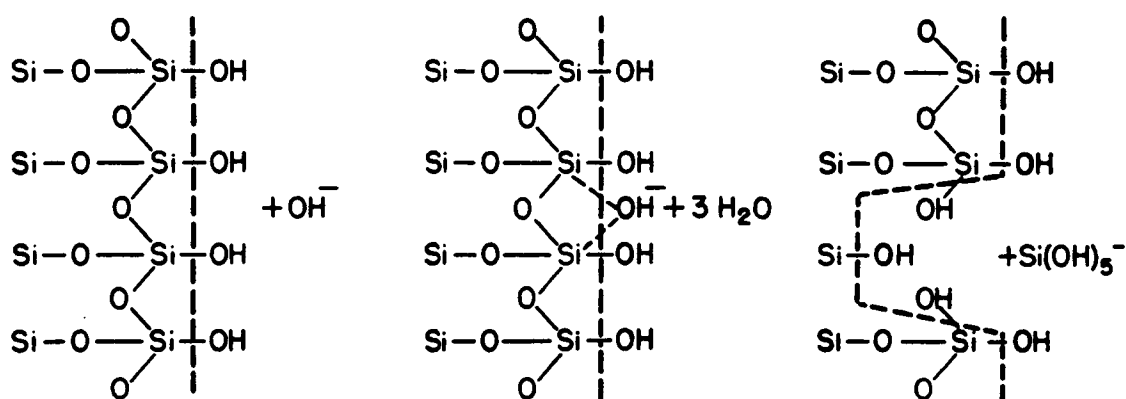


Figure 2.8. Proposed mechanism of dissolution of silica in water in the presence of hydroxyl ions. The dotted line represents the interface between silica on the left and water on the right.

Source: Iler, R.K. 1979. *The Chemistry of Silica*. John Wiley and Sons. New York. 866 pages

for depolymerization of silicas is greater for crystalline silica than for amorphous silica (21.5 kcal/mol for one type of amorphous silica and 26.19 kcal/mol for quartz), which accounts for the slower dissolution. The experiments demonstrated that amorphous silica was depolymerized in one hour at 40 °C (104 °F), but that quartz was essentially unchanged. After 72 hours at 75 °C (167 °F) quartz still showed very little depolymerization. Based on amorphous silica depolymerizing in one hour, and assuming that the two types of silica go through the same activated state in depolymerizing, Greenberg determined that quartz should depolymerize in 1900 hours.

2.3.2.2 Silica gels and precipitates

Iler (1979) states that microamorphous silicas includes sols, gels, and powders. He goes on to say that the difference between the formation of a silica gel and the formation of a silica precipitate is that in gel formation the concentration of silica particles in the three-dimensional network is the same as in the surrounding sol, but in the aggregates of a precipitate the concentration of silica particles is higher than in the surrounding liquid.

Degussa Corporation and W.R. Grace and Company were contacted for information regarding the manufacture of their silica products. Both companies produce silica for a variety of identical commercial uses including use as an adsorbent. Degussa refers to the products which it produces as "precipitated" silicas. W.R. Grace calls its products SYLOIDtm silica gels.

Literature provided by Degussa Corporation describes the precipitation process, which included filtering, washing, and drying as follows. Sodium silicate

and sulfuric acid solutions are added simultaneously with agitation to water. The acid must be rapidly mixed with the contents of the reaction tank to prevent formation of low pH areas where gelation might occur. The rate of formation of nuclei and the speed of particulate growth determine the course of the precipitation process. As the precipitation progresses, these small particles aggregate through siloxane (Si-O-Si) bridges to form three-dimensional networks that resist the high capillary pressure that develops during drying.

During the precipitation stage, product properties can be varied through changes in ratio and composition of reactants, reaction time, temperature, and concentration. Characteristics which can be varied by means of the precipitation process include chemical properties such as pH, silanol (SiOH) group density, and optical properties.

Filter cakes of high solids content are formed from the precipitate suspensions, and the salts formed during the precipitation process are washed out. The drying process at Degussa is carried out in spray dryers, which yield more spherical, softer silica agglomerates than other methods such as turbine or rotary drum dryers. The final product consists of 86-88% silicon dioxide, 10-12% water (half of which is chemically bound), salt residues formed during the reaction, and trace metal oxides.

Surface areas of Degussa's precipitated products range in BET surface area from 140 to 550 m²/g. The surface of precipitated silica has both internal and external surface area which allows for the easy absorption of liquids. The silicas contain both physically and chemically bound moisture. The physically bound moisture is removed by drying at 105 °C (221 °F) for two hours, and usually constitutes 5 % by weight. Chemically bound moisture, in the form of surface

silanol groups, is removed by igniting the dried silica for two hours at 1000 °C (1832 °F), and is also in the range of 5%.

2.3.3 Calcium silicate hydrates

2.3.3.1 General description

Numerous investigations have been made into the system $\text{CaO-SiO}_2\text{-H}_2\text{O}$ because of its bearing on the cement-forming processes. These studies are typically of two types. One involves the formation of calcium silicate hydrate phases in mixtures which contain the reactive components and water to solids ratios found in the production of cement. This means the slurries are actually thin pastes, not what we think of as aqueous slurries. The purpose of such studies is to explore the nature of the cement forming under various conditions. The binding and strength providing material of cements is composed of calcium silicate hydrates, and these studies often focus on the calcium silicate hydrate in situ as part of the hardened product. The temperatures of preparation are typically ambient, and the paste slurries are almost invariably maintained for days to years before sampling takes place. The other type of study is directed toward the chemical nature of the calcium silicate hydrates. This type of research involves forming calcium silicate hydrates in aqueous solutions containing CH (at or below saturation levels) and silica. The researchers in this type of study are concerned with what types of calcium silicate hydrates form, how they form and under what conditions of preparation. The temperature of formation is always an important factor, and many of the studies have involved relatively high temperature

(80-300 °C) preparations. In such studies the chemistry of the aqueous solution may be as important as the solids forming in it. The early chemistry studies, unfortunately, were not directed toward the reactive nature of the product solids as applied to gas-solid reactions.

Calcium silicate hydrate is a general term referring to the compounds formed in the $\text{CaO-SiO}_2\text{-H}_2\text{O}$ system. Some are naturally occurring and some are artificially produced. Table 2.3 contains a list of a number of the calcium silicate hydrates as well as their compositions, temperatures of formation, and characteristic x-ray diffraction spacings.

Only two of the listed calcium silicate hydrates are formed at temperatures below 100 °C (212 °F) (Kalousek and Prebus, 1958). (A third is in question.) They are referred to simply as C-S-H(I) and C-S-H(II)*. Results differ among studies with regard to whether C-S-H(II) forms below or only above 100 °C. Both hydrates encompass a range of CaO:SiO_2 molar ratios. They are poorly crystallized to amorphous compounds, and hence, are often referred to as gels. It is usually impossible to assign a simple chemical formula to these two compounds due to their physical and chemical complexities (Taylor, 1950). In the present study these are also the compounds of most interest as the sample preparation temperatures do not exceed 90 °C (194 °F).

* It is customary in cement chemistry to refer to CaO , SiO_2 , and H_2O as C, S, and H, respectively, with numerical designations for molar ratios. Due to the range of molar ratios represented by the calcium-silicate-hydrates referred to as (I) and (II), they are labeled by the initials C-S-H, where the hyphens are used to show that the composition $\text{CaO}\cdot\text{SiO}_2\cdot\text{H}_2\text{O}$ is not necessarily implied.

Table 2.3. Calcium Silicate Hydrates

Compound or Mineral ¹	Composition ²	Temperature of Formation (°C)	Characteristic X-Ray Diffraction Spacings (Å)			
Tricalcium silicate hydrate	C ₆ S ₂ H ₃	150-500	8.6	3.28	3.03	2.89
Calciochondrodite	C ₅ S ₂ H	250-800	5.42	3.79	3.31	3.02
C ₂ SH (A)	C ₂ SH	100-200	4.22	3.90	3.54	3.27
C ₂ SH (B) (hillebrandite)	C ₂ SH	140-300	4.74	3.51	3.32	3.00
C ₂ SH (C)	C ₂ SH ³	160-300	3.03	2.83	2.69	2.49
C ₂ SH (D) ⁴	C ₆ S ₃ H	350-800	3.06	2.89	2.86	2.82
Afwillite	C ₃ S ₂ H ₃	100-160	6.46	5.74	4.73	3.19
Foshagite	C ₄ S ₃ H	300-500	10	6.8	4.95	3.37
Xonotlite	C ₅ S ₅ H	150-400	3.65	3.23	3.07	2.04
CSH (A)	CSH ⁵	150-300	3.21	3.01	2.23	1.89
C ₂ SH ₂ ⁶ (or C-S-H II)	C _{1.5-2.0} S.aq	< 100	10.6- 9.8	3.07	2.85	2.80
CSH (B) ⁶ or (C-S-H I)	C _{0.8-1.5} S.aq	< 100	14-9	3.07	2.80	1.83
Crystalline Tobermorites	C ₅ S ₆ H ₉	60 (?)	14	5.53	3.25	3.07
	C ₅ S ₆ H ₅	110-140	11.3	3.07	2.97	2.80
	C ₅ S ₆ H	250-450	9.3	3.59	3.03	2.78
	C ₅ S ₆	450-650	9.7			
Gyrolite	C ₂ S ₃ H ₂	120-200	22	11	4.20	3.12
Truscottite	C ₆ S ₁₀ H ₃	200-300	19	9.4	4.13	3.14
Nekoite	C ₃ S ₆ H ₈	-----	9.3	3.36	2.82	2.47
Okenite	C ₃ S ₆ H ₆	-----	21	8.80	3.56	3.07
'Z-Phase'	CS ₂ H ₇	140-240	15.0	8.35	5.07	3.03

¹ See footnote page 21 for explanation of nomenclature.

² Approximate in some cases.

³ Probably a mixture of calciochondrodite (C₅S₂H) and a phase related to kolchoanite (C₃S₂).

⁴ Also known as Phase Y and occurs as the mineral dellaite.

⁵ Contains carbonate and is now known to correspond to scawtite 7CaO·6SiO₂·CO₂·2H₂O.

⁶ Similar to tobermorite, but poorly crystallized. Gels, or near amorphous samples, give weak x-ray patterns of one to three *hk* lines at about 3.05, 2.08, and 1.8 Å.

2.3.3.2 Chemical and structural description of C-S-H(I) and C-S-H(II)

Calcium silicate hydrates formed at temperatures below 100 °C (212 °F) are not compounds having uniform stoichiometric composition, but are a series of hydrates of continuously varying chemical composition. Their exact compositions depend on the conditions of hydration such as the original water to solids ratio and temperature of preparation. Calcium silicate hydrates are often discussed in terms of their CaO:SiO₂ ratio. Studies have shown that C-S-H(I), which has a calcium composition that can vary within the range given by the formula CaO_(0.8-1.5)SiO₂·nH₂O (SiO₂:CaO molar ratio ranging from 5:4 to 2:3), forms as a primary or intermediate product in a CaO-SiO₂-H₂O system in which the lime concentrations range from about 0.5 grams per liter up to concentrations close to saturation (Lea, 1970). Gard et al (1959) proposed that C-S-H (I) is inhomogeneous in its CaO:SiO₂ ratio on a small scale, and that the lime-rich regions form first. While C-S-H(I) may be the final product forming in solutions below 100 °C, it may be the intermediate product even at temperatures above 100 °C, giving way to the final product which is typically a well crystallized tobermorite or, less frequently, another crystalline calcium silicate hydrate phase (Taylor, 1964).

C-S-H(I) takes the character of thin, flexible sheets or crumpled foils, which may, on a very local scale, take on a layered structure, but is predominantly lacking in such order. The foils may be so thin and folded that the only observable features under the scanning electron microscope are the creases in the sheets. Figure 2.9 from Taylor (1964) is a photomicrograph of C-S-H(I).

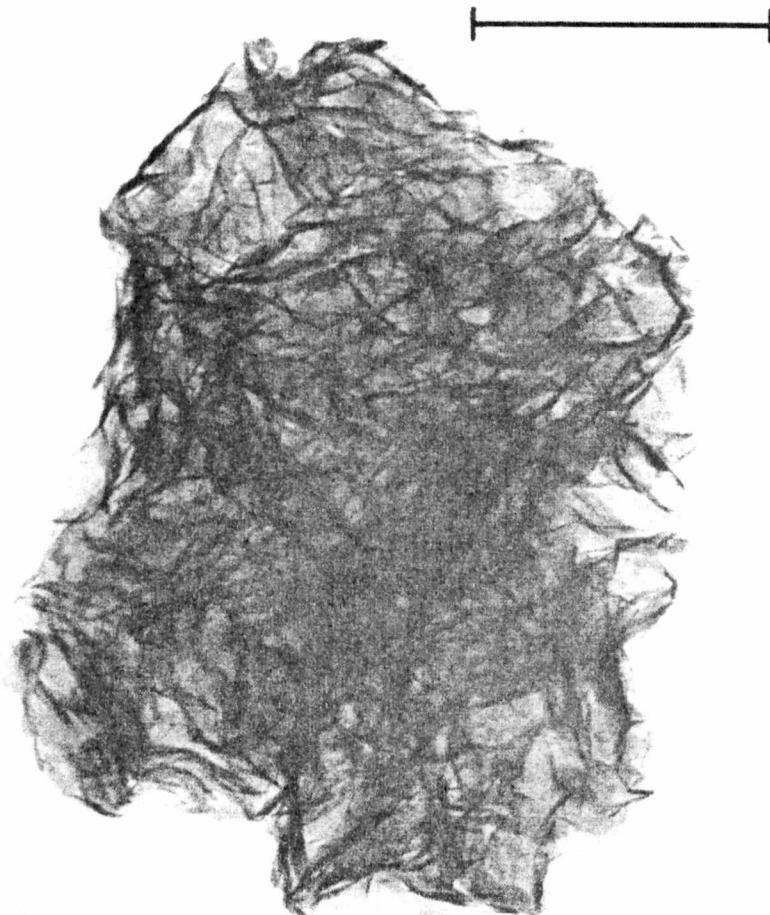


Figure 2.9. Crumpled foils of C-S-H (I). Bar scale = 1 μm .

Source: Taylor, H.F.W. 1964. *The Chemistry of Cements*. Vol.2, Academic Press, London.

Lea (1970) concluded that C-S-H(II), with a composition varying as $(\text{CaO})_{1.5-2}\text{SiO}_2 \cdot n\text{H}_2\text{O}$ ($\text{SiO}_2:\text{CaO}$ molar ratio ranging from 2:3 to 1:2), forms in aqueous solutions which are saturated with respect to lime. C-S-H(II) is distinguished from C-S-H(I) in appearance by its fibrous nature, or occasionally, its gel-like aggregates, when viewed under the scanning electron microscope.

Lea comments that C-S-H(I) and (II) are so closely related in their structure and properties that their distinction is difficult, and is almost impossible at $\text{CaO}:\text{SiO}_2$ ratios near 1.5:1. He goes on to say that these poorly crystallized hydrates do not form distinctly different phases, and in general, seem to be composed of a range of phases with varying $\text{CaO}:\text{SiO}_2$ content, water content, basal spacing, degree of crystallinity and other properties.

Figure 2.10 demonstrates the metastable equilibrium curve relating the $\text{CaO}:\text{SiO}_2$ ratios of calcium silicate hydrate preparations to the analytical concentration of CaO in the solution. This particular curve was selected by Taylor (1992) as typical from the results of many investigations. X-ray diffraction evidence shows that the central part of this curve and curve A in Figure 2.11 from Jennings (1986) represent the solubilities of C-S-H(I) preparations. Figure 2.11 includes metastable solubility curves for hydrous silica and CH. Taylor goes on to report the invariant points, based on combined data of Steinour (1954), Taylor (1950), and Jennings (1986). One point occurs for hydrous silica, C-S-H(I) with $\text{CaO}:\text{SiO}_2 \approx 0.8:1$, and solution with $\text{CaO} \approx 1 \text{ mmol/l}$ and $\text{SiO}_2 \approx 2 \text{ mmol/l}$. The other point occurs for CH, C-S-H(I) with $\text{CaO}:\text{SiO}_2 \approx 1.4:1$, and solution with $\text{CaO} \approx 22 \text{ mmol/l}$ and $\text{SiO}_2 \approx 1 \text{ } \mu\text{mol/l}$.

If the $\text{CaO}:\text{SiO}_2$ molar ratio of the solids is 1:1, the chemical formula is CaH_2SiO_4 (or $\text{CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$). It is not completely clear how the CH in excess

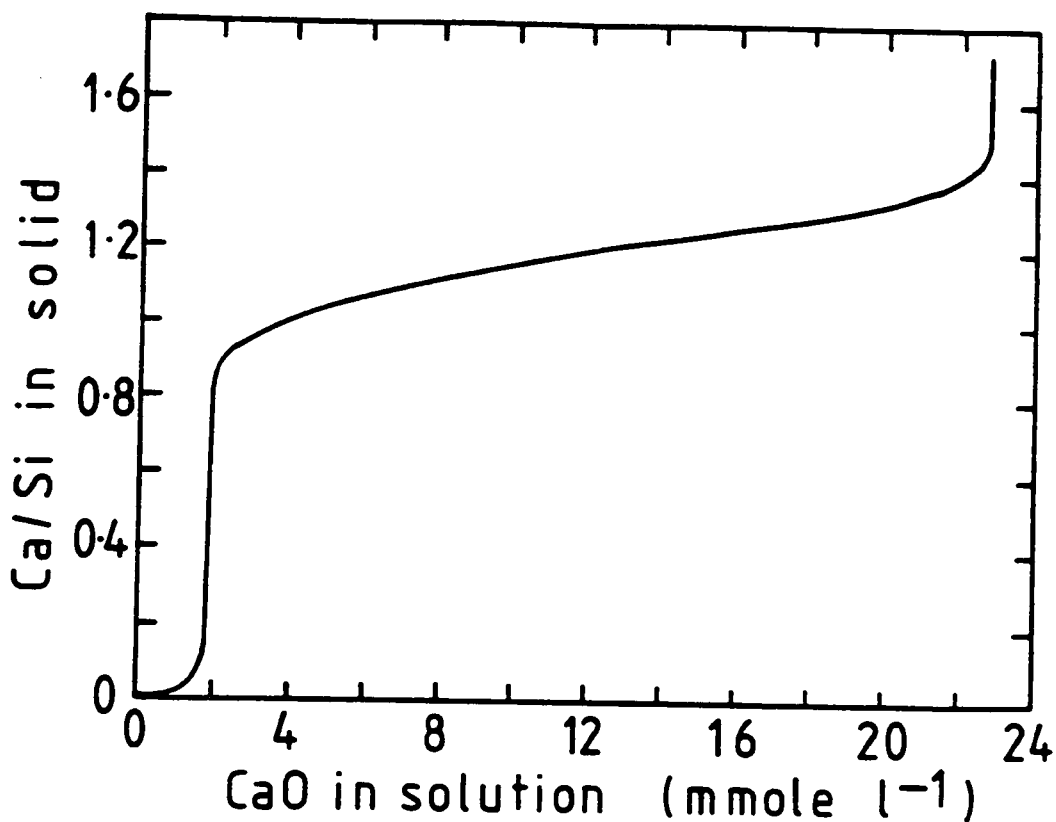


Figure 2.10. Metastable equilibrium curve relating the CaO:SiO₂ ratios of calcium silicate hydrate preparations to the analytical concentrations of CaO in solution, selected as typical from results of many investigations.

Source: Taylor, H.F.W. 1992. *Cement Chemistry*. Academic Press, New York. 475 pages.

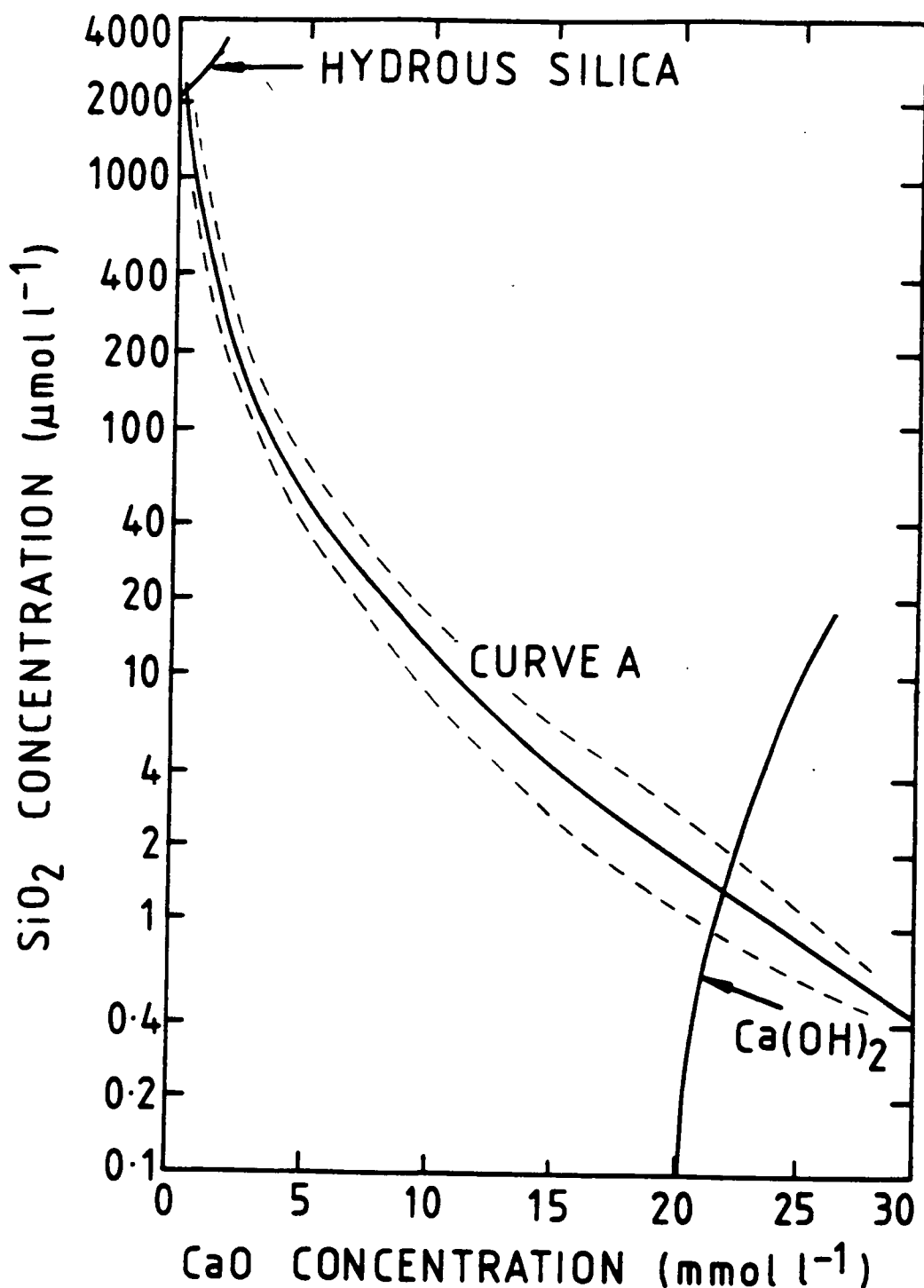


Figure 2.11. Concentration data for calcium silicate hydrate based on the results of many investigations. Dashed lines give an indication of the scatter of the data.

Source: Taylor, H.F.W. 1992. *Cement Chemistry*. Academic Press, New York. 475 pages.

of the 1:1 $\text{CaO}:\text{SiO}_2$ ratio is involved in the CaH_2SiO_4 solid. Pressler et al. (1956) concluded that the CH must enter into the calcium silicate hydrate as a solid solution. At $\text{CaO}:\text{SiO}_2$ ratios of 1 to 1.75 Greenberg and Chang (1965) regarded the calcium silicate hydrates as a solid solution of composition $\text{CaH}_2\text{SiO}_4 \cdot n\text{Ca}(\text{OH})_2$. Below the ratio of 1:1 $\text{CaO}:\text{SiO}_2$, they considered the solids to consist of mixtures of CaH_2SiO_4 (or $\text{CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$) and silica gel. Ciach et al (1971) concurred with this idea in concluding that the calcium silicate hydrates cannot be regarded as separate phases, but rather, as solid solutions of calcium silicate hydrate and CH. This is consistent with Grutzeck and Roy (1969) who showed that the $\text{CaO}:\text{SiO}_2$ ratio varies within the hydrated product.

X-ray diffraction studies of the poorly crystallized calcium silicate hydrates show just three characteristic interplaner spacings. The two-theta angle at which these spacings are detected correspond the position of the peaks on the strip chart pattern which is generated as the x-ray detector is rotated through an arc above the powder material. The heights of the peaks are directly proportional to the intensities of the diffraction effects. The first and strongest appears at 3.06 Å, followed by weaker spacings at 2.81 Å and 1.83 Å (Greenberg et al., 1960). A typical x-ray powder diffraction pattern is represented by Figure 2.12. Taylor et al. (1950) noted that the x-ray spacings appear to be independent of $\text{CaO}:\text{SiO}_2$ ratio between the limits of 1:1 and 1.5:1, which corresponds to the C-S-H (I) phase typically found in preparations below 100 °C. This indicates that C-S-H(I) can incorporate a substantial amount of calcium without changing its structure.

One of the more important calcium silicate hydrates from a cement perspective is tobermorite. It is a crystalline mineral, and is thought to be the final product of C-S-H(I) and (II) when these compounds form in high temperature

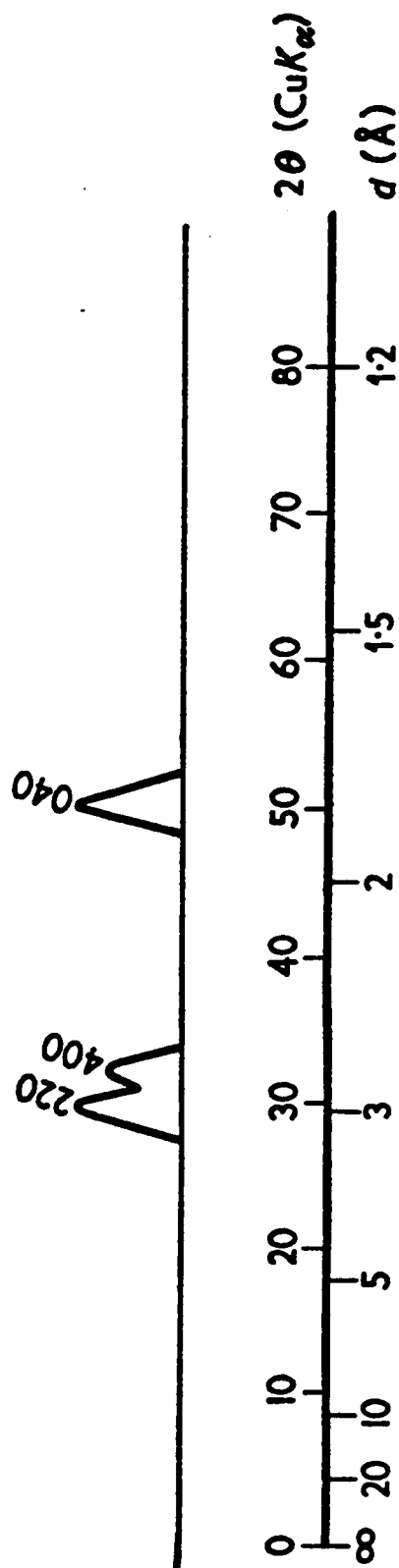


Figure 2.12. Representation of x-ray pattern for poorly crystallized calcium silicate hydrate. Peaks occur at 3.06, 2.81, and 1.83 Å.

Source: Taylor, H.F.W. 1964. *The Chemistry of Cements*. Volume 1. Academic Press, London.

solutions (above 100 °C). Megaw and Kelsey (1956) determined the structure of tobermorite by x-ray diffraction. It is similar to layer clay minerals in that it is composed of layers parallel to (001), which simply indicates that the layers are parallel to the a and b crystallographic axes and intersect the c axis. Whereas tobermorite has a set chemical formula of $\text{Ca}_4\text{Si}_6\text{O}_{18}$, the related, poorly crystallized C-S-H(I) and (II) have considerable variation in the $\text{CaO}:\text{SiO}_2$ ratio. This is better understood when considering the disordered structure of C-S-H(I) and (II). While the tobermorites have a crystalline layer structure of A-B-A-A-B-A (Figure 2.13) in which A is a layer containing SiO_3 chains and B a layer containing CH (Lea, 1970), an alternating structure of A-B-A-B is possible, thus allowing a higher $\text{CaO}:\text{SiO}_2$ ratio. The C-S-H(I) and (II) structures lack definite, repeatable structural sequences. Instead, they have a mixed layer structure with only local order of the tobermorite type.

In the 1950's and 1960's S. A. Greenberg, in association with numerous co-investigators, performed a substantial amount of research on the chemical nature of the $\text{CaO-SiO}_2\text{-H}_2\text{O}$ system. Greenberg and Chang (1965a) concluded that the constitution of C-S-H(I) and (II) depended in large part on the $\text{CaO}:\text{SiO}_2$ ratio. For ratios of 0.14:1 to 1.0:1, the solids consisted of mixtures of CaH_2SiO_4 and silica gel. For ratios of 1.0:1 to 1.75:1, the solid was regarded as a solid solution of $\text{CaH}_2\text{SiO}_4 \cdot n\text{Ca}(\text{OH})_2$. They derived a solubility product as well for CaH_2SiO_4 which applied for solids having $\text{CaO}:\text{SiO}_2$ ratios of 0.2:1 to 1.8:1. This solubility product was: $K_{\text{sp}} = a_{\text{Ca}} \cdot a_{\text{H}_2\text{SiO}_4} = 10^{-7.2}$.

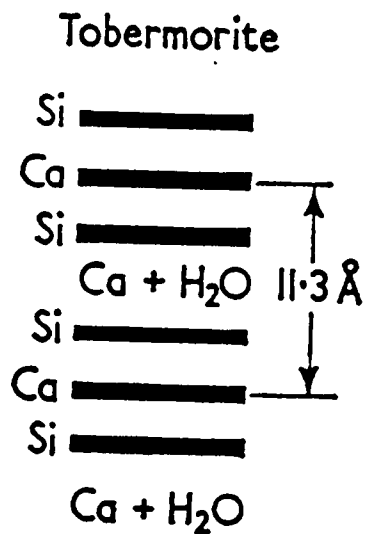


Figure 2.13. Diagrammatic representation of the sequence of layers in tobermorite.

Source: Gard, J.A., J.W. Howison, and H.F.W. Taylor. 1959. Synthetic Compounds Related to Tobermorite: an Electron-Microscope, X-ray, and Dehydration Study. *Mag. Concrete Res.* 11 (33):151-158.

2.3.3.3. Water content of calcium silicate hydrates

The water content of the calcium silicate hydrates is difficult to quantify. They have a large specific surface area which readily adsorbs water. This adsorbed water cannot be completely separated from the water of constitution (i.e., structurally bound) (Lea, 1970). Taylor (1953) determined that at ordinary temperatures, no hydrate with less than one molecule of water will be formed, and that in contact with an aqueous solution, the hydrate must contain at least 2 to 2.5 waters.

Greenberg (1954) used thermal dehydration weight loss curves to determine the total water contents (adsorbed and structurally bound) of several calcium silicate hydrates which had been prepared from the hydrothermal reaction of CH and "hydrated" silica at temperatures ranging from 93 to 186 °C (199 to 367 °F). The samples were dehydrated at a controlled heating rate of 8 °C/minute (46 °F/minute) up to 1000 °C (1832 °F). In all cases, except one, the samples had been vacuum dried in a dessicator over calcium chloride. Samples prepared at 148 and 170 °C (298 and 338 °F) contained decreasing amounts of water as the SiO₂:CaO molar ratio increased. The water content declined from 17.1 to 13.7% for the 148 °C samples, and from 14.8 to 10.9% for the 170 °C samples as the SiO₂:CaO ratios increased from 2:1 to 4:1. Greenberg prepared two calcium silicate hydrate samples at 93 °C from equimolar quantities of CH and silica. One was vacuum-dried and the other was not. He made two observations about these samples. One was that the vacuum-dried sample contained 20% water while the

one which had not been vacuum dried contained 29.3%. The other was that there was approximately 1% CH left unreacted in the vacuum-dried sample, while the other contained no remaining CH. No conclusions were stated for the second observation, but it indicates that the solids continued to undergo chemical reaction between the silica and the CH when vacuum drying was not performed, whereas the reaction ceased earlier when moisture was forcibly removed.

In summary, the calcium silicate hydrates which form in aqueous solutions below 100 °C are typically poorly crystallized gelatinous substances of variable $\text{CaO}:\text{SiO}_2$ and $\text{SiO}_2:\text{H}_2\text{O}$ ratios. CH appears to be incorporated into the structure of calcium silicate hydrate by means of solid solution. Although the $\text{CaO}:\text{SiO}_2$ ratio varies over defined ranges, the x-ray patterns do not vary accordingly, indicating that the basic calcium silicate hydrate structure remains the same, and that it is one without a great deal of order.

3.0 APPROACH

3.1 Experimental approach

The present study was directed toward the removal of HCl, which can reach significant concentrations in waste incineration flue gas due to the high proportion of plastics in the wastestream. As stated previously, the primary objectives of this study were to attempt to elucidate the mechanism(s) which cause sorbents, which have been prepared hydrothermally from a silica-containing constituent and CH, to exhibit greater reactivity than CH alone when exposed to HCl in a gas stream and to determine the optimum conditions for enhancement. Tests performed by Pakrasi (1991) on CH alone, as described in section 2.1, provided a baseline for the method of testing in the present study. Testing was performed at the outset of this study on sorbents prepared from fly ash and CH. The remainder, as well as the bulk, of this study focused on the use of pure forms of silica as the component added to CH in order to form dry sorbents which were tested for their reactivity with gaseous HCl. The purpose of using pure silica instead of fly ash as the source of silica was to eliminate the complexity associated with fly ash. Fly ash is predominantly silica, but it contains a host of other constituents as well. It is certainly possible that the interplay of these minor constituents with silica and CH affects the subsequent reactivity of the dry sorbent prepared from fly ash and CH. The goal of this study, however, was to scrutinize the interaction of silica and CH in the formation of hydrothermally prepared sorbents and the subsequent reactions with HCl. Using pure silica allowed a "cleaner" approach to the examination of the silica/CH reaction products, which

previous studies have indicated are the compounds responsible for the enhanced reactivity with HCl.

Fly ash, as a source of silica, has the potential to be a low cost, if not cost-free, additive which can be used in the preparation of sorbents for full scale field applications, while any pure form of silica is likely to be costly. At face value, the cost of pure silica might make its use in commercial production of sorbents prohibitive. However, unless the conditions of preparation are defined and the proportions of silica and CH known, it is not possible to make an actual determination of the viability of such a proposal. With this in mind, the goal of this study was to determine a set of conditions under which to develop the most reactive sorbent, and to make an examination of the individual hydrothermally prepared samples in order to discern the reasons for the enhancement.

Briefly, the course of study was the following. One fly ash was chosen to mix with the CH for baseline testing. For the subsequent and main sets of tests, two types of silica were chosen, one easily soluble at high pH (a condition always met when using CH in the proportions used in this study) and the other highly insoluble. With both silica varieties, and with the fly ash, a series of sorbents was prepared by reacting each with CH. Slurry time and component weight ratios were varied in the preparation process involving the pure silicas. A small aliquot (typically 50 mg) of each dry sorbent sample was then tested for reactivity with HCl in a specially designed reactor under process conditions which were held constant. Reactivity was determined by preparing filtrates from the reacted sorbents, and then analyzing them for calcium and chloride concentrations. In addition to the reactor tests, surface area analyses were conducted on the fly ash/CH sorbents and the silica/CH sorbents. Each sorbent prepared from the pure

silicas and CH also underwent powder x-ray diffraction analysis, and certain samples were analyzed by scanning electron microscopy. The purpose of these analyses was to characterize each sorbent sample in order to seek differences which might account for the degree of reactivity demonstrated by the corresponding sample.

3.2 Choice of silica sources

Previous studies have demonstrated that the hydrothermal reaction of CH with fly ash, which is approximately 50-60% silica, or with other purer forms of silica can result in materials which, when applied as dry sorbents in a gas stream, are more highly reactive with both HCl and SO₂ than CH alone. Most studies of similarly prepared sorbents have been directed toward flue gas desulfurization with fly ash/CH sorbents. Due to the limitations imposed by the dissolution rate of the silica from the fly ash, large amounts of fly ash have had to be mixed with a given amount of CH (Jozewicz and Rochelle, 1986). Logically, in a "real world" application, this would result in a greatly increased mass handling problem. Some of the previous experimental work also assessed other siliceous substances (e.g. bentonite, diatomaceous earth, and pumice). In such cases, if the silica was of a reactive nature, it was possible to dramatically decrease the necessary amount of the siliceous component to be mixed with a constant amount of CH in order to achieve a sorbent which was more reactive with SO₂ than CH alone (Jozewicz et al., 1988a). Only one study (Jozewicz et al., 1991) addressed the removal of HCl from flue gas by a sorbent prepared from a silica-bearing material other than fly ash. Instead of fly ash, ground bottle glass was employed, and again it was

possible to greatly lower the amount of material required to be added to CH in order to achieve sorbent reactivities equivalent to those of the sorbents prepared from fly ash and CH. The following sections discuss the three silica sources used in the course of this study.

3.2.1 Fly ash

The calcium content of fly ash (expressed as % CaO) can vary from 1% (Davis et al., 1982) to 30% (Peterson and Rochelle, 1988). Results from the Peterson and Rochelle (1988) study in which four samples of fly ash with calcium contents varying from 4 to 30% (as CaO) were slurried with CH for 12 hours at 85 °C (185 °F) and at a fly ash:CH ratio of 4:1 indicate that high calcium fly ashes prepared with CH tended to produce more reactive sorbents than low calcium fly ashes. In order to minimize the additive effect a high calcium fly ash might have upon hydrothermally prepared sorbents, a low calcium fly ash produced from a bituminous, low sulfur eastern coal (burned at Marshall Steam Plant) was chosen for the present study. The fly ash compositional analysis for this ash is given in Table 3.1. Table 3.2 gives the fly ash physical and chemical characteristics. These data are taken from the study by Davis et al. (1982). The chemical characteristics were from analyses conducted on a water-based slurry of 1.45 pounds of fly ash per gallon of water which had been mixed at 60 °C (140 °F). These conditions were chosen in order to simulate the condition to be tested at a spray dryer facility which was the focus of that particular study.

Table 3.1. Fly ash compositional analysis.

Component	%
Sulfur	0.41
CaO	5.75
Na ₂ O	12.47
MgO	1.44
K ₂ O	2.78

Table 3.2. Fly ash physical and chemical characteristics.

Mass mean diameter (μm)	14.0
Geometric standard deviation	2.1
Particle density (g/cm^3)	2.2
Surface area (m^2/g)	1.47
pH	4.8
Alkalinity (mg/l as CaCO_3)	0
Ca (mg/l)	321
Na (mg/l)	52
Total hardness (mg/l as Ca)	358

3.2.2 Amorphous silica

The experimental work involving amorphous silica makes up the dominant portion of this dissertation. Amorphous silica is a form of SiO_2 . The particular type used in the present research is sometimes referred to as silicic acid. This is somewhat of a misnomer as silicic acid is actually the silica monomer, $\text{Si}(\text{OH})_4$, and silicic acid, as such, has never been isolated from solution (Iler, 1979). However, by concentrating the monomer, condensation to a polymeric form occurs in which silanol (SiOH) groups occur only on the surface linked through three silica atoms in siloxane groups (i.e., Si-O-Si groups). The composition in the final state is $(\text{SiO}_2)_n$. It should be noted that at a neutral pH, silica, even amorphous silica, is relatively insoluble. At high pH (above 10.7), however, the amorphous silica rapidly goes into solution. (Refer to the discussion in Chapter 2). As mentioned earlier, the overall reaction rate between fly ash and CH_4 appeared to be limited by the dissolution rate of silica from the fly ash (Jozewicz and Rochelle, 1986). Because this study emphasized the nature of the products formed from the reaction between the silica in the fly ash and the CH_4 , rather than the rates of dissolution of the reactants or their rate of subsequent reaction to form CH_4 , it was desirable to utilize a type of silica which was highly soluble and would enable the products to form more readily and rapidly than would silica supplied by either fly ash or crystalline silica.

The amorphous silica used in this study came from a single batch manufactured by W.R. Grace and Company in Baltimore, Maryland. Its trade name is Syloid Silicatm: 244FP. Its chemical formula is $\text{SiO}_2 \cdot x \text{H}_2\text{O}$. The silica is synthetic, and should not be confused with crystalline silica such as quartz,

cristobalite, or tridymite or with diatomaceous earth or other naturally occurring forms of amorphous silica that frequently contain crystalline forms of silica.

Chemical and physical information for this silica is given in Table 3.3.

3.2.3 Crystalline silica

The crystalline silica was chosen for the purpose of offering a contrast to the performance of amorphous, soluble silica in the preparation of the silica/CH sorbents. Its source was a single batch of Min-U-Sil™, a very finely ground crystalline silica manufactured by U.S. Silica of Ottawa, IL. Physical and chemical characteristics are given in Table 3.4.

3.3 Choice of sorbent preparation conditions: slurry temperature, time, and component ratios

The slurry temperature of the aqueous solutions was 90 °C (194 °F) for all sorbent preparations. The water to solids ratio was 15:1 for all preparations. The preparation times and component ratios, however, varied depending on the silica source used. These are discussed separately below, according to silica type. The temperature choice was based upon the flue gas desulfurization studies of Jozewicz et al. (1988b and 1990) in which the optimum temperature for preparing sorbents at atmospheric pressure was found to be 90 °C. The greatest enhancement in reactivity with SO₂ occurred at this temperature. The water to solids ratio was based upon the (1988a) study of Jozewicz et al. in which the authors tested the reactivity of sorbents prepared from solutions initially containing

Table 3.3. Syloid™ silica physical and chemical characteristics.

Appearance	Dry White Powder
pH	7
Specific Gravity	2.6
Bulk Density (lb./gal, tapped)	6.9
Apparent Bulk Density (lb./ft. ³ , tapped)	51.8
Average Particle Size (μm)	4.0
Surface Area (m ² /g)	0.84
Silica as SiO ₂	99.7
Loss on Ignition at 1200 °F (649 °C) (%)	0.145

Table 3.4. Min-U-Sil™ silica physical and chemical characteristics.

Appearance	Dry White Powder
pH of 5% Slurry in H ₂ O	3-8
Specific Gravity	2.1
Particle Size (μm)	3
Surface Area (m ² /g)(1)	482
Mesh	-325
Silica as SiO ₂ (wt.% dried basis)	99.4
Loss on Ignition at 1750 °F (954 °C) (%)	8.5

(1) As measured in this study. Information not supplied by manufacturer.

4 to 85% solids. The optimum reactivity was found in the samples falling in the range of 5 to 10% solids content. The water to solids ratio of 15:1 used in this study falls nearly in the middle of this range at approximately 7%.

3.3.1 Fly ash

A single fly ash to CH ratio of 8:1 was chosen for this part of the study, and three slurry times of 4, 6, and 9 hours were used. Figure 2.4 in section 2.2 from Jozewicz and Rochelle (1986) demonstrates the typical effects of both slurry time and temperature. As discussed in that section, the reactivity of the sorbents with SO_2 continued to increase with increasing fly ash to CH ratio up to a ratio of 20; however, in order to work with a lower and more reasonable ratio, a fly ash to CH ratio of 8:1 was chosen for the present study. Because the final reactivity (albeit with SO_2 , not HCl) of the studies detailed in section 2.2 occurred between 8 and 10 hours of slurry time, the maximum slurry time for this study was taken as 9 hours.

3.3.2 Amorphous silica

Both length of slurry time and ratio of silica to CH were varied in preparing the sorbent samples in this group. Slurry intervals ranged from 15 minutes to 7 hours. Silica to CH ratios varied from 1:10 to 1:1. Choices for slurry times and component ratios were guided by previous studies on fly ash and CH mixtures.

Early studies on sorbents produced from fly ash and CH (e.g. Jozewicz and Rochelle, 1986; Jozewicz et al, 1988b), examined slurry times ranging from 0 to

24 hours. Later studies (e.g. Singer et al, 1991) confined the range of slurry times to 1-6 hours. For the present study, slurry times of 15 minutes, 1, 3, and 7 hours were chosen. Because the reaction between amorphous silica and CH was expected to proceed more rapidly than one between fly ash and CH due to solubility limitations, 15 minutes seemed a more appropriate minimum slurry time than 1 hour in order to provide information on activity occurring at early stages of reaction.

The component ratios used in early studies (e.g., Jozewicz and Rochelle 1986) for fly ash:CH ranged from 0.5:1 to 20:1. Later studies typically narrowed the ratio. For instance, Jozewicz et al (1988b) slurried fly ash with CH at weight ratios ranging from 3 to 5:1. For the current investigation the ratios of silica to CH chosen were 1:10, 1:5, 1:3, 1:2, and 1:1. These ratios were notably different than the ones referenced above for fly ash and CH. These lower amorphous silica:CH ratios were chosen because of the expected high silica availability in the slurry due to amorphous silica's increased solubility over that of fly ash. The resulting sample preparation matrix is represented in Table 3.5. The codes in the table give the sample designations for each time/ratio combination. For instance, 1:10-.25 indicates the sample with an amorphous silica:CH ratio of 1:10 which was slurried for 0.25 hours at 90 °C (194 °F)

Table 3.5. Sample preparation matrix for amorphous silica/CH sorbents.

Time	Amorphous silica:CH weight ratio				
	1:10	1:5	1:3	1:2	1:1
15 minutes	1:10-.25	1:5-.25	1:3-.25	1:2-.25	1:1-.25
1 hour	1:10-1	1:5-1	1:3-1	1:2-1	1:1-1
3 hours	1:10-3	1:5-3	1:3-3	1:2-3	1:1-3
7 hours	1:10-7	1:5-7	1:3-7	1:2-7	1:1-7

A silica dissolution study by Peterson (1990) lends some perspective to the silica choices of this study. Peterson slurried 1.25 grams of a low-calcium fly ash in one liter of water with 5 grams Na_2EDTA , and showed that 20% of the silica had dissolved from the fly ash at 30 minutes of slurrying and 50% by 4 hours. Based on that information, if 50% by weight of the present fly ash is SiO_2 glass, the total dissolved SiO_2 from the fly ash by 4 hours might be one quarter the weight of the fly ash. Thus the actual silica:CH weight ratio would be estimated as 2:1. If a ratio of silica:CH of 2:1 was expected at 4 hours for fly ash, the ratio most certainly would not be that high immediately as the silica in fly ash is not nearly so soluble as amorphous silica. Some lower ratio of silica:CH would be more representative of the actual conditions. This accounts for the choice of lower silica:CH ratios when utilizing amorphous silica in the sorbent preparations. The range of ratios in this study (silica:CH 1:10 through 1:1) correspond to a range of 5 to 50% of the amount of silica which might have been available from the fly ash at 4 hours.

3.3.3 Crystalline silica

The slurry times and component ratios for the crystalline silica/CH sorbents were dictated primarily by the earlier amorphous silica/CH tests. In order to be able to make direct comparisons, it was desirable to prepare the samples under the same sets of conditions. Thus, the slurry times were taken at 15 minutes, 1, 3, and 7 hours, and the silica to CH ratios at 1:5, 1:3, 1:2, and 1:1. The ratio of 1:10 was eliminated based on the expectation that the dissolution rate of the silica was going

to be so low that this ratio would demonstrate little, if any, enhancement. The sample preparation matrix is given in Table 3.6. "M" designates the sample as a Min-U-Sil™ silica sample.

Table 3.6. Sample preparation matrix for crystalline silica/CH sorbents.

Time	Crystalline Silica:CH weight ratio			
	1:5	1:3	1:2	1:1
15 minutes	M1:5-.25	M1:3-.25	M1:2-.25	M1:1-.25
1 hour	M1:5-1	M1:3-1	M1:2-1	M1:1-1
3 hours	M1:5-3	M1:3-3	M1:2-3	M1:1-3
7 hours	M1:5-7	M1:3-7	M1:2-7	M1:1-7

3.4 Choice of reactor test conditions

One set of reactor conditions was chosen for testing the reactivity of the hydrothermally prepared sorbents. These conditions were dictated by the earlier study of Pakrasi (1991) in which the author, using the same reactor which was used in the present study, tested the reactivity of CH over a variety of reactor conditions. For the present study it was necessary to choose a set conditions under which Pakrasi had demonstrated that CH alone did not achieve complete utilization. The idea behind this was to allow a substantial amount of room for demonstration of an increase in performance by the samples in the proposed matrix should they be more reactive than CH alone.

The test conditions in the sand-bed reactor were as follows. The concentration of the HCl in the gas was 1000 ppmv, the reactor temperature was 149 °C (300 °F), and the moisture content of the gas was 10-11% by volume. This is typical of waste incinerator conditions. The maximum utilization achieved

by the CH in Pakrasi's test under these reactor conditions was 17% as shown in Figure 2.2 of section 2.1.2.

4.0 EXPERIMENTAL APPARATUS AND PROCEDURE

The objective of this research was to prepare and characterize a series of sorbents, relating their character to their demonstrated ability to react with gaseous hydrogen chloride. In order to study the reactivity of the hydrothermally prepared sorbents with hydrogen chloride, tests were performed in a fixed bed reactor.

Specific surface area was measured for the prepared sorbents and micromorphology was determined by SEM analyses. X-ray diffraction provided evidence of the progression through time of the silica/CH reactants combining to form calcium silicate hydrate as products.

4.1 Sorbent preparation

The method of making the hydrothermally prepared sorbents for the initial reactor testing is presented in the first section below. It details how all sorbents in the matrices of Tables 3.5 and 3.6 in sections 3.3.2 and 3.3.3, as well as the fly ash/CH sorbents, were prepared. Results from the reactor tests of these sorbents, combined with x-ray diffraction analyses and surface area analyses, raised questions which were addressed by two tests involving modified sorbent preparation procedures. The method of preparing sorbents for these two tests are discussed in the following sections, 4.1.2 and 4.1.3.

4.1.1 General procedure of sorbent preparation

Sample slurring was carried out in 250 ml stoppered pressure vessels. The pre-weighed components (silica or fly ash and CH) were mixed as dry solids prior to adding them to water. The water to solids ratio was maintained at 15:1 grams/gram for all sample preparations by using 75 ml of deionized, distilled water and 5 grams of solids comprising the appropriate silica:CH ratios.

The 75 ml of water (without the solids) was placed in stoppered pressure vessels, which in turn were placed in a preheated 90 °C (194 °F) oil shaker bath. All preparations were carried out at 90 °C, a temperature which bench scale studies had suggested as an optimum for slurring fly ash and CH (Singer et al, 1991). The water in the pressure bottles was allowed to reach 90 °C (approximately 1 hour). The solids were then delivered into the vessels by means of a funnel, and the vessels were continuously shaken in the oil bath for the designated slurry times. It should be noted that each pressure vessel contained a discrete sample batch representing just one length-of-preparation time. This is in contrast to a possible setup in which portions of sample might be removed in series from a single container at the specified sample periods (e.g., 15 minute, 1 hour, 3 hours, etc.). The use of oil in the shaker bath prevented any significant evaporation of the heat conveying medium, thus eliminating the need to replace fluids in the shaker bath as would likely have been necessary over a period of 7 hours if water had been used in the shaker bath.

At the end of the slurry time the solids were vacuum filtered, then dried in a microwave oven for 10 minutes on medium low*. The solids were dry to the

* Microwave drying as a method to prevent further reaction of the components was initially employed by Jozewicz et al (1987a) who used BET surface area development to demonstrate that

touch at this point. A subjective test of touching the solids immediately upon their finishing the 10 minute drying cycle made it evident that they were not being subjected to temperatures as high as 90 °C, which would have caused a sense of discomfort at that temperature. The importance of this information is to confirm that the sample did not exceed the slurry temperature of 90 °C as demonstrated by the fact that the materials could be touched without causing discomfort from the heat. Following microwave drying the solids were placed in an oven, and maintained at 75 °C (167 °F) for 48 hours. The objective of this was to develop a consistent level of dryness in all samples, a condition not necessarily assured by just filtering and microwave drying. All samples were placed in glass containers, and stored in a desiccator over Drierite™ (CaSO₄). Sample containers were removed from the dessicator only to weigh out the necessary portions for reactor tests.

4.1.2 Procedure for addition of calcium chloride or non-reacted calcium hydroxide

This set of samples was prepared in order to determine if the addition of calcium chloride, which is deliquescent, or CH after the sorbent had been slurried, filtered, and dried might have a beneficial effect on reactivity. Details of the rationale for this experiment are given in section 5.3.1.3 in which the results of the reactor tests for these samples are also given. In each case 10 or 20 mg of the calcium chloride or CH was mixed with a 50 mg aliquot of the sorbent which was prepared at a silica:CH ratio of 1:1 and had been slurried for 3 hours (1:1-3).

microwave drying, for the purpose of rapidly stopping hydration reactions, resulted in the same degree of enhancement of the product as oven drying

The formula for the particular calcium chloride employed in the tests is $\text{CaCl}_2 \cdot \text{H}_2\text{O}$. One of its characteristics is that it attracts moisture. Because of this, precautions were taken to keep it as dry as possible prior to adding it to the sorbent sample. The calcium chloride was stored in a dessicator, and removed in order to weigh out the 10 mg. The 10 mg aliquot was immediately put back into the dessicator. It was later added to the 1:1-3 sample prior to placing the sample in the reactor. Following the addition of the 10 mg of calcium chloride and further mixing in the mortar to insure even distribution, the sample was emptied onto the sample bed for testing, immediately placed in the reactor, and subjected to the reactivity test.

Adding dry CH to the 1:1-3 sorbent entailed simply adding 10 mg of CH to the 50 mg of 1:1-3 after it had been mixed with sand in the mortar, and then further mixing the material to evenly distribute the CH. As above, the sample was emptied onto the sample bed for testing, immediately placed in the reactor, and subjected to the reactivity test

4.1.3 Procedure for controlled rate addition of individual components

This set of samples was prepared in a manner designed to determine if the method of mixing the samples in solution might have an effect on the surface area and reactivity of the resulting sorbent. As with the addition of calcium chloride, the details of the rationale for this experiment are given in section 5.3.2.3 in which the results of the surface area analyses for these samples are also given.

For each sample preparation there was a baseline solution of 2.5 gram of either CH or amorphous silica slurried in 5 ml water. A solution containing 2.5

grams of the other component slurried in 70 ml. of water was added at a controlled rate. The original water to solids ratio of 15 to 1 thus remained the same when the two solutions were completely mixed. There were two types of sample for each hot and cold of addition:

1. Cold slurry added to cold baseline slurry
2. Hot slurry added to hot baseline slurry

Cold addition slurry to cold baseline slurry

Initially 2.5 grams of baseline component (either silica or CH) were mixed with 5 ml cold deionized, distilled water (of ambient temperature: approximately 25 °C) in a beaker. Then 2.5 grams of the other component were mixed in 70 ml of cold deionized, distilled water in a separate beaker. As this amount of material far exceeded its saturation limit in this amount of water, the 70 ml mixture was mechanically mixed with a magnetic stirrer so that the solids remained evenly suspended in the water for the duration of its addition to the baseline slurry. The addition slurry was fed by a pump through tubing at a constant rate of 14 ml/minute. to the baseline slurry. It took 5 minutes to accomplish complete addition of 70 ml. The mixture was then stirred for an additional 10 minutes for a total slurry time of 15 minutes from the time of starting addition. The mixtures were then filtered and dried according to the general sorbent preparation method detailed in section 4.1.1.

Hot addition slurry to hot baseline slurry

The heated mixtures were prepared in the same proportions as the cold mixtures. Both the baseline slurry and the addition slurry were heated separately to 90 °C in the hot oil bath. The outlet end of the tubing from the pump was placed in the vessel containing the baseline slurry, and the intake end of the tubing in the addition slurry vessel. The addition slurry was metered in by the pump while the two containers remained in the hot oil bath. After the 5 minutes mixing/addition period, the mixture was shaken in the hot oil bath for another 10 minutes before filtering.

Samples and Sample Designations

- Addition of amorphous silica to CH (i.e., amorphous silica in 70 ml, CH in 5 ml)
 1. cold to cold
 2. hot to hot:

- Addition of CH to amorphous silica (i.e., CH in 70 ml, amorphous silica in 5 ml)
 1. cold to cold
 2. hot to hot

4.2 Sorbent reactivity tests

The reactivity of each sorbent sample was determined in a two step procedure. First a small amount of sample was placed in the sample chamber of the reactor. The reactor was run at a specified set of conditions (i.e., HCl concentration, pressure, temperature, and humidity), and the sample was allowed to come in contact with a specified concentration of carrier gas containing HCl. These conditions, discussed in Chapter 3 under "Choice of reactor test conditions" are 1000 ppmv HCl in the gas stream, 149 °C (300 °F) in the reaction chamber, and 10 -11% moisture in the gas stream. Following the reactor test, the extent of sorbent utilization was determined analytically. Comparison of sorbent utilization results determined the relative reactivity of the sorbents. The following sections detail the equipment used in the experimental work, the method of preparing and testing the sorbents, and the method of determining the extent of sorbent utilization (i.e., the sorbent reactivity).

4.2.1 Equipment and procedure

The first of the two following sections describes the reactor apparatus, its design, and how reactor tests were performed. The second section describes the procedure for preparing the 50 mg aliquot of each sorbent batch for a reactor test. It should be noted that a single batch of sorbent was roughly 5 g total. Only a small portion was removed for a reactor test; the remainder of the batch was unaltered and still available for other analyses such as x-ray diffraction or scanning electron microscopy (SEM).

4.2.1.1 The reactor

The reactivity tests for removal of hydrogen chloride by the hydrothermally prepared sorbents were carried out in a bench-scale fixed-bed reactor. The schematic of the experimental set up is shown in Figure 4.1. The test gas was a mixture of hydrogen chloride and water vapor in an inert carrier gas of nitrogen. In actual incinerators the flue gas would also contain appreciable quantities of carbon dioxide and oxygen. However, Karlsson et al. (1981) have shown that 10% carbon dioxide in the gas stream has an insignificant effect on the removal of hydrogen chloride by CH at the reactor temperature of this study. As the hydrothermally prepared sorbent was expected to be at least as reactive with HCl as CH (and possibly more so), it was expected that carbon dioxide would have even less of an effect in this study. In light of these expectations, all the tests were carried out with hydrogen chloride and nitrogen only.

The nitrogen gas from the gas cylinder was first metered through a calibrated flowmeter, and the gas pressure and temperature immediately downstream were measured to enable the calculation of the molar flow rate. The gas was then heated to the desired temperature by electric strip heaters which were wound around the copper tubing through which the gas flowed. The heaters were connected to a controller which allowed regulation of the gas temperature by controlling the heat rate input.

Following heating of the gas, water vapor was added to it at a controlled rate. A Harvard brand calibrated constant flowrate syringe pump injected water through 1/8 inch stainless steel tubing, at a preset rate, to a thermally controlled

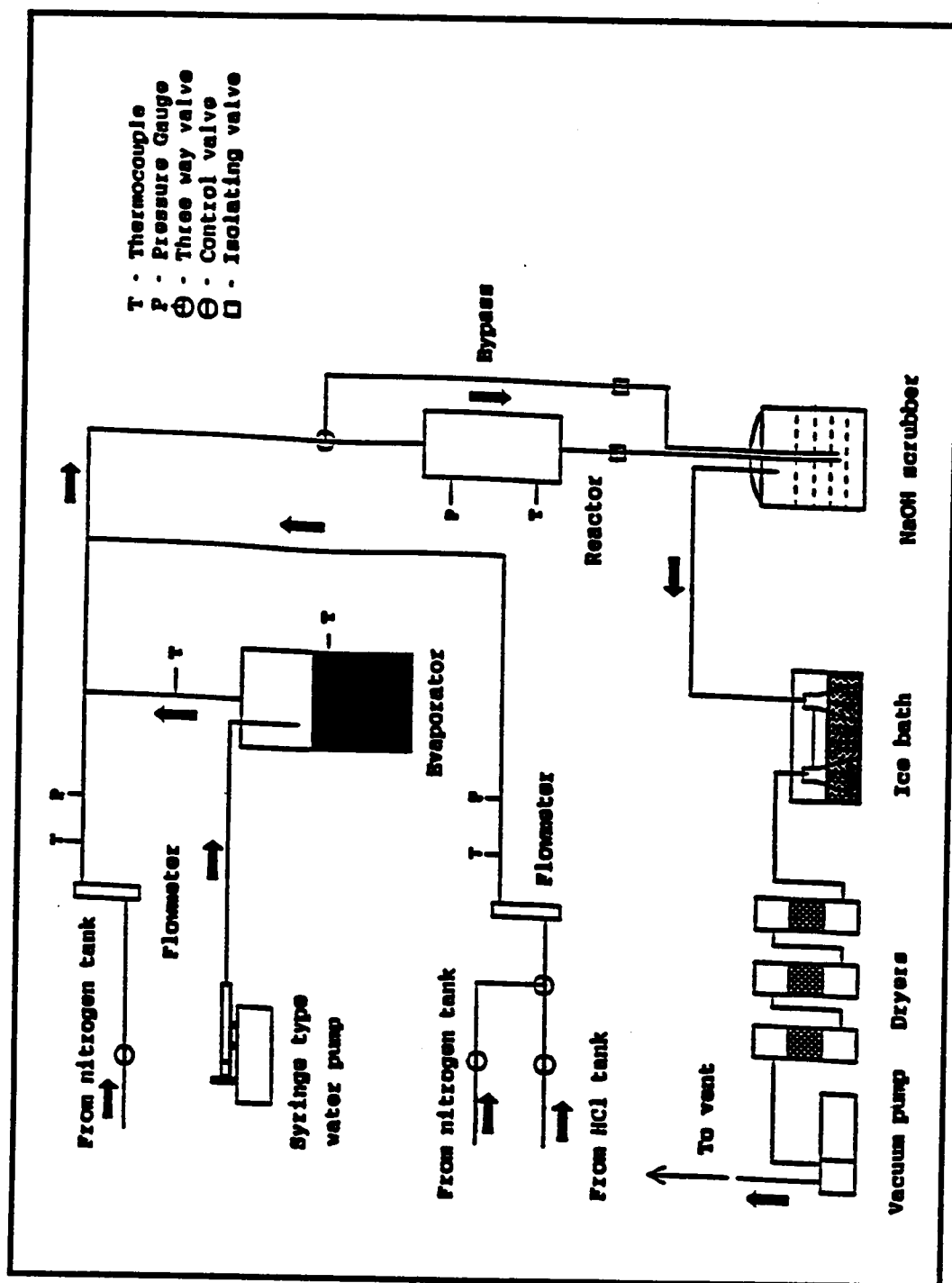


Figure 4.1. Experimental reactor setup for the sorbent utilization tests. After Pakrasi, 1992.

evaporator. The evaporator consisted of a steel cylinder with a 4 inch diameter and an 8 inch length. The cylinder was closed at the bottom, and had inlet and outlet connections at the top. A cross sectional view of the evaporator is shown in Figure 4.2. The evaporator was partially filled with quartz sand and was heated by electric strip heaters wound around the outside surface of the cylinder. Prior to initiating water injection, the evaporator was heated to between 177 and 204 °C (350 and 400 °F). As the water contacted the hot sand bed it evaporated immediately. The sand bed acted as a heat reservoir, ensuring steady evaporation of the injected water. A thermocouple was placed 1 cm beneath the surface of the sand in order to monitor the temperature immediately below the contact area of the injected water. Temperatures below 100 °C (212 °F) at this location were considered to indicate water build up due to insufficiently rapid evaporation. The heat input rate to the evaporator was controlled in order to maintain the temperature at this point at well above 100 °C, the typical maintenance temperature being in the range of 232 °C (450 °F). This ensured complete and steady evaporation of the injected water.

A second thermocouple was located at the exit of the evaporator in order to monitor the temperature of the steam generated. By varying the heat input rate to the evaporator, the temperature of the steam was kept high enough (usually 232 °C or higher) to avoid condensation of the water vapor upon its contacting with the nitrogen gas. Similar evaporator designs have been used by other researchers for fixed bed kinetic studies (Jozewicz et al., 1990; Karlsson et al., 1981). Checkout test performed prior to starting up reactor tests demonstrated that steady and complete evaporation was being achieved at test conditions. The

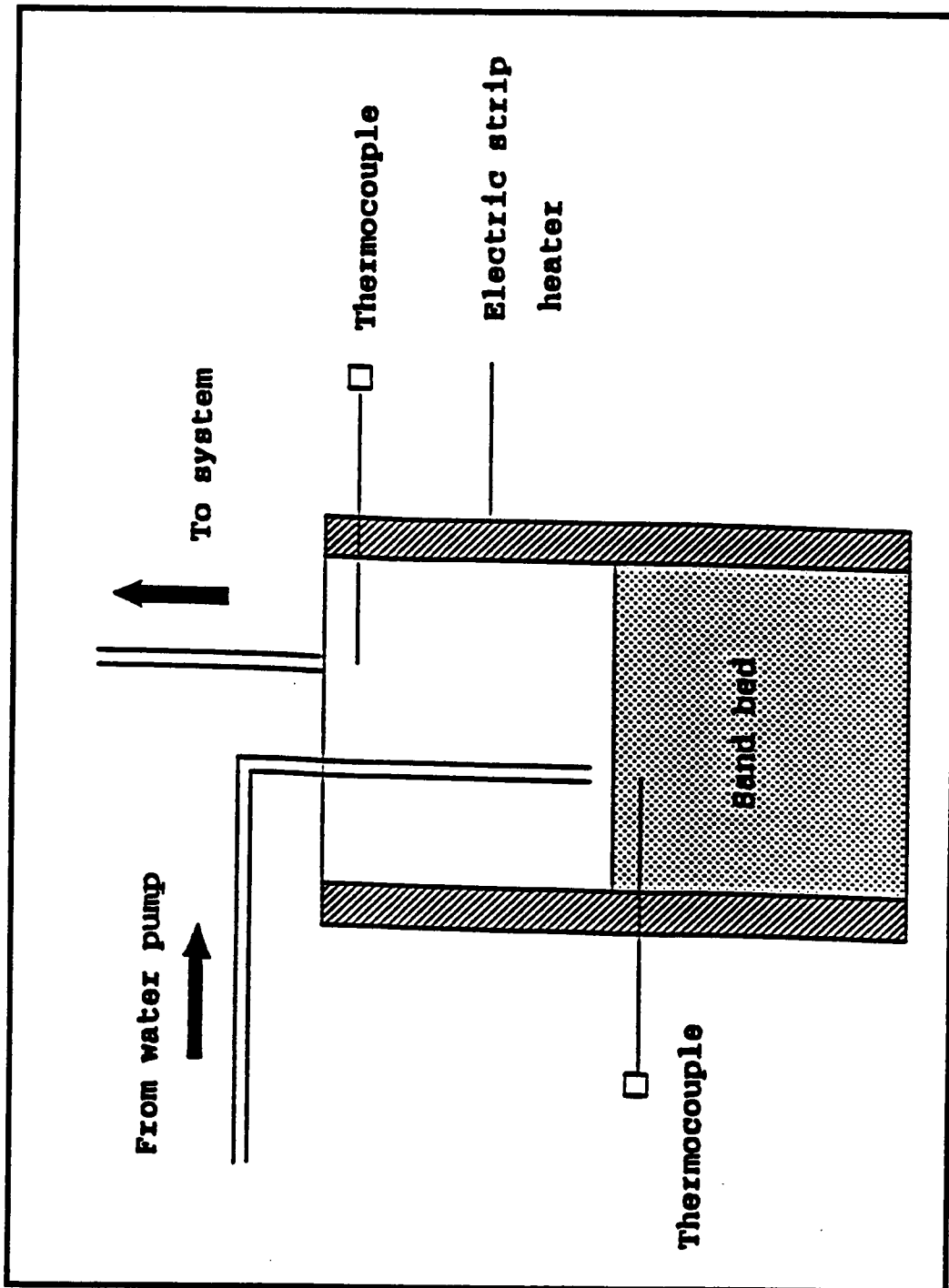


Figure 4.2. A sectional view of the evaporator. After Pakrasi, 1992.

evaporated water was injected directly into the hot nitrogen gas stream as shown in Figure 4.1.

Downstream of the evaporator hydrogen chloride gas was injected, at the designated concentration, into the hot and humidified gas stream. Locating the hydrogen chloride injection point after the water injection point minimized the possibility of corrosion from condensed water. The hydrogen chloride injection line was connected to the hydrogen chloride cylinder as well as a pure nitrogen gas cylinder by way of a three way valve as shown in Figure 4.1. The nitrogen could then be used to purge the injection line after each test in order to eliminate any residual hydrogen chloride.

In order to avoid handling problems and risks associated with pure hydrogen chloride, a mixture with pure nitrogen was used in these tests. The hydrogen chloride gas mixture was first metered by a calibrated flowmeter before being injected into the heated carrier gas stream. The pressure and temperature of the dry hydrogen chloride gas was measured immediately after the flowmeter to enable calculation of the molar flow rates. Unidirectional flow valves were installed both in the heated carrier gas line and the hydrogen chloride gas line ahead of the injection point as shown in Figure 4.1. These valves prevented the accidental back flow of hydrogen chloride gas into the evaporator.

The simulated flue gas, at the desired temperature and concentration, then passed through the tubular reactor shell containing the sorbent, which was supported on a glass fiber filter. A three-way valve upstream of the reactor allowed the reactor to be bypassed whenever required, for instance, during withdrawal of the sorbent after reaction. The test gas was heated in the tubes and

in the reactor shell by electric strip heaters. The entire system was insulated on the outside to reduce heat loss as well as for operational safety.

The reactor assembly consisted of a cylindrical reactor shell, a matching flange with a wire mesh support, and a sorbent holder. A sectional view of the assembled reactor is shown in Figure 4.3. The reactor shell was a stainless steel tube (316L SS) approximately 20 cm long and 4.75 cm inside diameter. The reactor was maintained at the test temperature by electric strip heaters. The heat input rate was controlled by a variac, which was operated automatically in an ON/OFF mode by a temperature controller connected to a thermocouple located in the reactor shell at approximately 5 cm above the sorbent bed. A pressure tap in the reactor was connected to a pressure gauge to monitor the gas pressure during testing. The reactor was always maintained under a slight vacuum in order to prevent accidental leakage of hydrogen chloride to the ambient air, and also to minimize the corrosive effects of the gas.

The matching flange was also made of 316L SS, and was outfitted with wire mesh to support the sample holder. A silicone rubber gasket was placed between the upper flange of the reactor shell and the lower matching flange in order to ensure leak-free operation. The outlet from the lower flange was connected to flexible Teflon tubing, which was in turn connected to the gas scrubbing system as shown in Figure 4.1. A gate valve at this point was used to completely isolate the reactor when the reactor was being bypassed, as at such times as the sorbent sample was being removed or replaced in the reactor.

The sorbent sample was spread over a glass microfiber filter, which was supported on a 316 SS wire mesh screen in a sample holder. The sample holder was a short cylindrical tube approximately 4 cm in height and 4.75 cm inside

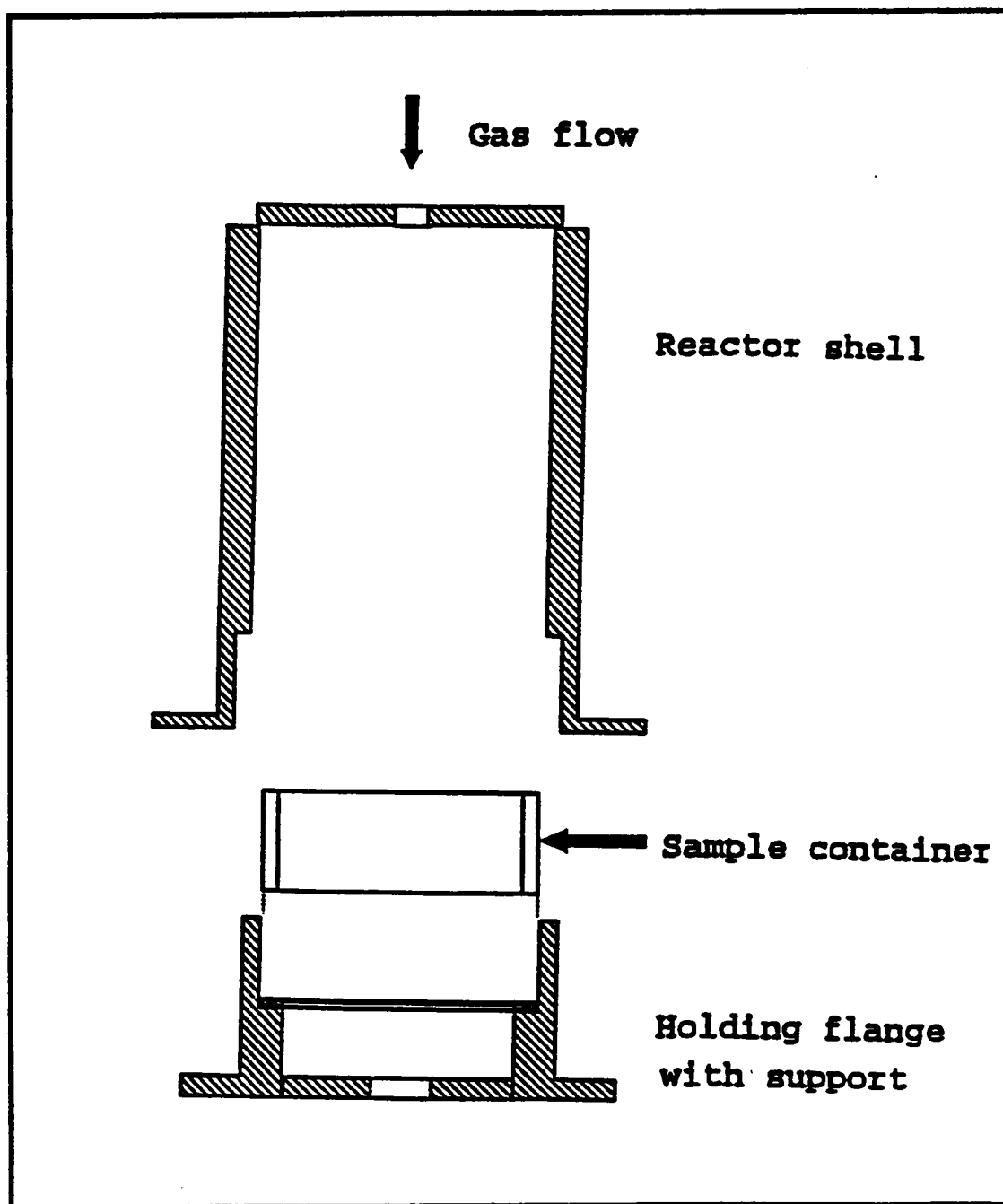


Figure 4.3. A sectional view of the reactor assembly. After Pakrasi, 1992.

diameter as shown in Figure 4.3. During each test, the sorbent was spread on the filter inside the sample holder. After each test, the lower flange of the reactor was disconnected from the reactor shell by opening the bolts, and the sample holder was replaced by another sample holder containing a new sorbent sample to be used in the next test. During this exchange the reactor was bypassed by operating the three way valve and closing the outlet valve on the lower flange. The entire reactor assembly was insulated to prevent loss of heat and for operator protection.

Both the test gas line from the reactor outlet and the reactor bypass line were connected to a final scrubber. The scrubber was a 20 liter glass bottle approximately half filled with 5N sodium hydroxide solution (or just water which was changed frequently to avoid saturation). The gas was directed through a glass tube, exiting at the baseline of the glass container where it entered the solution by means of a glass dispersing frit. The hydrogen chloride from the gas was completely removed in this scrubber. The still moist air passed out of the container through another tube and through two ice-cooled condensers to remove most of the water, then through a silica gel drying tube to remove any remaining moisture. These precautions were taken to prevent moisture from entering the downstream pump. The 3/4 hp Gast suction pump provided the suction necessary to create the slight vacuum in the reactor. The outlet of the pump was vented to an exhaust hood.

Several precautions were taken to avoid corrosion resulting from the hydrogen chloride. The entire hydrogen chloride injection system was made of Teflon tubes and equipped with a Teflon flowmeter, nickel cadmium thermocouples, and Viton™ or Teflon™ fittings. For at least 5 days following any reactor testing, pure nitrogen flow was maintained through the system to create a

positive pressure and avoid infiltration of ambient moisture. A slight vacuum was always maintained in the reactor during the tests or whenever hydrogen chloride was used. After each test, the hydrogen chloride line was thoroughly flushed with dry nitrogen. Leak checks in the system were conducted before each day of testing to ensure that no ambient air could infiltrate. In addition, hydrogen chloride flow was initiated only after the system had been at the proper temperature for at least 30 minutes to avoid absorption of the acid gas by any condensed moisture inside the system.

4.2.1.2 Reactor sample preparation

In order to prevent possible agglomeration of the sorbent powder, as well as to ensure adequate gas-solid contact and prevent channeling, the sorbent used for testing was dispersed in quartz sand in preparation for testing. Following the work of previous researchers (Jozewicz et al., 1988b, on fly ash and CH; Karlsson et al., 1981, on CH alone), it was decided to mix the sorbent with sand in a 50 to 1 sand/sorbent ratio. It had been observed that approximately 1 gram of sand was required to cover the sample bed of this reactor. As 50 mg of sorbent was used for each test, 2.5 grams of sand was used as the dispersant, providing ample coverage without unduly increasing the pressure drop. The sand selected for this purpose was grade F-75 manufactured by US Silica. Physical and chemical properties of this sand are given in Appendix A.

The amount of sorbent to be used in a test was determined by trial and error. The choice was directed by the need to optimize between maintaining differential conditions in the reactor and avoiding analytical limitations. It was

determined that 25 to 50 mg of sorbent could meet these conditions. For all routine reactor tests 50 mg of material was used. Repeat tests and reproducibility of results demonstrated that these choices were appropriate.

Sorbent and sand were weighed out separately in an analytical balance, and were then mixed in a nonporous mortar and pestle made of agate. The two solids were mixed thoroughly for approximately 2 minutes before transferring to the glass microfiber filter which rested on the screen support of the sample holder. Shaking the sample holder slightly created an even distribution of sand and sorbent over the entire bed.

4.2.2 Determination of sorbent utilization

A two-step procedure was followed for determining the utilization of the sorbent. First a liquid filtrate was prepared from the reacted solids, and then analyses were run on the liquid to determine chloride and calcium concentrations. The following two paragraphs describe the procedures.

Immediately after a sorbent sample had been subjected to a reactor test, the contents of the sample holder, i.e., the mixture of reaction product, any non-reacted sorbent, the sand, and the glass fiber filter were placed in a 500 ml beaker. One hundred ml of deionized, distilled water was measured out, and 30 ml of this initially added to the beaker with the sample. Five drops of concentrated sulfuric acid were added to dissolve the calcium silicate hydrate in the sorbents prepared from fly ash and CH. Five drops of concentrated nitric acid were added to dissolve the calcium silicate hydrate in the sorbents prepared from pure silica and CH. The mixture was stirred and heated at 60 °C (140 °F) for 5 minutes, and the

remaining 70 ml of water added for another 5 minutes of stirring. The solution was vacuum filtered, and calcium and chloride concentrations were measured in this filtrate to determine the sorbent utilization.

Calcium concentration analyses were performed using an atomic absorption spectrometer, and chloride concentrations were determined by one of two methods. The sorbents prepared from fly ash and CH were tested early in the study when an ion chromatograph was available for chloride analyses. Chloride analyses for all sorbents prepared from silica and CH were performed with an Orion chloride ion electrode. The moles of Ca^{2+} and Cl^- were calculated from the results of the calcium and chloride analyses. The utilization of the sorbent was determined from the molar ratio of calcium and chloride in the filtrate. The following equation, based on the stoichiometry of the reaction was used in the utilization calculation.

$$\text{Fractional utilization} = [(\text{moles Cl}/2)/\text{moles Ca}]$$

4.3 Other procedures

Other procedures carried out on the sorbent samples are widely accepted routine analyses. The following sections briefly detail the particular instruments and methods applied in this study for powder x-ray diffraction, scanning electron microscopy, and BET surface area analyses.

4.3.1 X-ray diffraction

In order to determine the which crystalline phases were present in the hydrothermally prepared sorbents, powder x-ray diffraction analyses were performed on a Siemens D500 X-ray Diffractometer in the Department of Geological Sciences at the University of Tennessee. The x-ray diffractometer interfaced with a computer, enabling the operator to control the analyses by means of commands in the software package designed specifically for that purpose. All analyses were done at 40 kV and 30 mA. The software contained files of the two-theta values and relative intensities of peaks for minerals listed in the Powder Diffraction Files (JCPDS, 1983). The JCPDS files contain x-ray diffraction data prepared by the Joint Committee on Powder Diffraction Standards. The JCPDS file two-theta values for peaks associated with particular mineral phases were compared to the peaks generated by the sorbents in order to identify the compounds present in the sorbents.

The powder-like sorbent was mounted in a sample holder with a small depression in the center into which the sample was hand-packed. Care was taken to avoid loose packing in order to eliminate transparency effects, as the diffraction occurs from a volume, not just the surface. The surface of the sample was made flat by pressing a glass microscope slide firmly down on the top of the material so that the top of the sample was made flush with the top of the sample holder. This eliminated roughness or curvature in the sample surface which would have the potential to produce systematic deviations in the positions and breadths of observed reflections. Consistent sample height in the sample holder helped to

avoid sample-height displacement errors, which manifest as peak displacements in the patterns.

4.3.2 Scanning electron microscopy

The micromorphology of the sorbent samples was observed using a Hitachi S-800 scanning electron microscope. All samples were in a dry, powdered form, and had only to be blown onto sticky carbon tape on the stainless steel stub in order to be mounted. The sample material is one of low conductivity, so in order to counter the effects of negative charging, the samples were Au-Pd coated. The beam energy was maintained at 10 kV for all samples. Some charging was still observed at the higher magnifications.

4.3.3 BET surface area analyses

The BET surface area analyses were conducted using a Micromeritics ASAP 2000 Automated Surface Area Analyzer. A small amount of dry sample (typically 0.5 to 1.0 gram) was degassed at 250 °C (482 °F) and an absolute pressure of 15-19 mm Hg for at least 12 hours. Following the degassing procedure, nitrogen gas at 77 K was introduced into the sample tube incrementally. The amount of gas adsorbed by the sample at various partial pressures was automatically recorded by the analyzer. After adsorption phase readings were completed, the desorption readings were obtained by decreasing the partial pressure of nitrogen in the sample tube in small decrements, and recording the quantity of nitrogen desorbed. The adsorption and desorption isotherms

generated in this manner provided the necessary information for calculating the surface area of the sorbent samples.

5.0 RESULTS AND DISCUSSION

5.1 Verification of methods

Several preliminary tests were required prior to performing the tests described in Chapter 4. Verification that the experiments would provide the information they were designed to give was necessary. The questions addressed were the following. Would the method of filtrate preparation dissolve the solids so that all the calcium tied up in calcium silicate hydrate would go into solution for analysis? How much sample was lost between weighing out the required amount and preparing the filtrate for analysis, and was the loss consistent from one test to another? Were there background levels of calcium and chloride to be factored into the analytical results? Did the sand or glass fiber filters used in the reactor react with any chloride during testing? The discussions in this section address these questions.

5.1.1 Efficiency of dissolution

It was well established by Pakrasi (1991) that CH is effectively dissolved and analytically accounted for in the filtrate when using the present method of filtrate preparation. It was necessary to establish in the present study that calcium silicate hydrate would also completely dissolve, in order to demonstrate that all the calcium and chloride would be accounted for when performing sorbent utilization tests. Dr. Wojciech Jozewicz and Mr. Carl Singer, both of Acurex Corporation in

Research Triangle Park, NC, said in telephone conversation that they achieved dissolution of calcium silicate hydrate by adding 4 drops of 25% sulfuric acid to 20-30 ml of solution which contained 50 mg of solids. The complex stoichiometry of calcium silicate hydrate makes absolute confirmation of a mass balance accounting difficult, but they noted that when adding more sulfuric acid, there was no additional calcium in the filtrate indicating that all calcium was removed from the calcium silicate hydrate.

Because sulfate ions presented an interference with the electrode method of chloride analysis used in this study, nitric acid was used for dissolution of all silica/CH sorbents instead of sulfuric acid*. To establish the efficacy of this method of dissolution, side-by-side tests using sulfuric and nitric acid were performed on the sorbent batch prepared from a 1:1 component ratio with a 1 hour slurry time. Two tests were run for each acid type. In the first test 5 drops of concentrated acid were added to the solution containing 50 mg of calcium silicate hydrate-containing sorbent. In the second test 12 drops were added. The solids remaining after sorbent dissolution from each test (presumably disaggregated glass fiber filter and quartz sand only) were then subjected to two additional dissolutions to determine if there was additional calcium in the subsequent dissolutions. Results in Table 5.1 demonstrate that all methods accounted for approximately the same amount of calcium. These calcium analyses were performed on an inductively coupled plasma (ICP) furnace due to its linearity and ability to be accurate at very low concentrations.

* Sulfuric acid was used in the fly ash/CH utilization determinations as these were carried out by ion chromatography in which sulfate ions were not an interference.

Table 5.1. Triple dissolution results for calcium recovery from calcium silicate hydrate-containing sorbent.

Acid	Number of Drops	Dissolution Number	Expected Ca (mg/l)	Actual Ca (mg/l)
HNO ₃	5	1	130	133
		2	0	1.4
		3	0	<1.0
HNO ₃	12	1	130	130
		2	0	1.3
		3	0	1.2
H ₂ SO ₄	5	1	130	135
		2	0	2.5
		3	0	0.8
H ₂ SO ₄	12	1	130	122
		2	0	4.5
		3	0	9
H ₂ SO ₄ *	12	1	130	126
		2	0	3

*Repeat test for sulfuric acid with 12 drop. Only first two dissolutions performed.

As mentioned in Chapter 2, there is no set stoichiometric formula for calcium silicate hydrate. When just silica is utilized in the reaction with CH, it should be possible to determine a maximum theoretical calcium content of the sorbent if all calcium used in the aqueous reaction is assumed to be contained in the subsequent solids. Table 5.1 reflects expected values of calcium as well as analytically determined values. The close match between expected and actual values not only supports the use of nitric acid in the method of dissolution, but provides evidence as well that all the calcium in the reactants is accounted for in the hydrothermally prepared sorbents. Addition of 12 drops of acid in either case was not more effective than the addition of 5 drops. For this reason 5 drops of nitric acid were utilized in all tests performed on the silica/CH sorbents.

5.1.2 Recovery of sample mass

From the time the sorbent samples were weighed to the time they were placed in the 500 ml flask for filtrate preparation, operations such as transfer from the weighing pan to the mortar, mixing with the sand, transfer from the mortar to the sample holder bed, and transfer once more to the flask could have resulted in some loss of sample. Five samples of CH (50 mg each) taken through the entire process of reactor testing resulted in filtrate analyses representing mass recoveries ranging from 70 to 79% with an average of 75.4%. In the same manner, seventeen sorbent samples prepared from amorphous silica and CH resulted in mass recoveries ranging from 65 to 81%, with an average of 76.1%. It was assumed that any material lost was identical to that which was recovered such that the ratio of calcium to chloride in the recovered material was not altered by material lost.

This meant that any sample losses did not affect the accuracy of the utilization calculation because the same filtrate was used for both calcium and chloride analyses, and the utilization was based on the ratio of these components. The ratio would remain the same regardless of the actual amount of material used. The utilization calculations were thus also insensitive to any slight error in dilution volume during filtrate preparation.

5.1.3 Background levels of calcium and chloride

Since only 50 mg of sorbent were used in each reactor test, it was necessary to determine if the results were significantly affected by background levels of calcium or chloride in the other materials used in the tests. Analytical detection levels for calcium and chloride were 3 ppm and 0.1 ppm, respectively. The distilled, deionized water and the filtrates prepared from the quartz sand and the glass fiber filters showed virtually no calcium and chloride as they exhibited levels below the detection limits for the instruments. The silicas, the fly ash, and the CH also exhibited no chloride above the detection levels.

5.1.4 Chloride uptake of the sand and glass fiber filter in the reactor

In the course of a reactor test, both the sand and the glass filter were exposed to the hydrogen chloride gas along with the sorbent sample. Although both of these materials have been found to be inert to acid gases in other studies (Jozewicz et al., 1990; 1991), it was necessary to check for chloride uptake in the reactor of the present study. The chloride uptakes of the sand and filter were

checked during the course of Pakrasi's (1992) work during a kinetic test in the fixed-bed differential reactor. The reactor conditions were 79 °C (175 °F) and 25% relative humidity at 1000 ppmv hydrogen chloride concentration. The test was carried out exactly like an actual test except that there was no CH in the sample bed. The results of this test are shown in Figure 5.1, and for comparison this figure also includes the chloride uptake of 25 mg CH at the same test conditions. The figure clearly shows that the chloride uptakes of the sand and the filter are insignificant compared to the CH. Based on these observations, no corrections were made in the utilization calculations due to the presence of either the sand or the filter in the sample bed.

5.2 Fly ash/CH sorbents

5.2.1 Sorbent reactivity tests

Fly ash/CH sorbent preparation and testing was performed in a preliminary phase of study. At that time comparisons were being made with Pakrasi's (1992) kinetic tests utilizing CH. Because of this, the fly ash/CH sorbent samples were tested in the reactor for times ranging from 100 seconds to 600 seconds. Specifically, the samples slurried for 4, 6, and 9 hours were each tested in the reactor for 100, 300, and 600 seconds.

Figure 5.2 shows the effect of the increasing reaction time for the 4, 6, and 9 hour samples (as well as Pakrasi's baseline results for CH). In each case utilization increases with length of reaction time, and appears to be approaching a maximum by 600 seconds. While each sorbent demonstrated increasing utilization

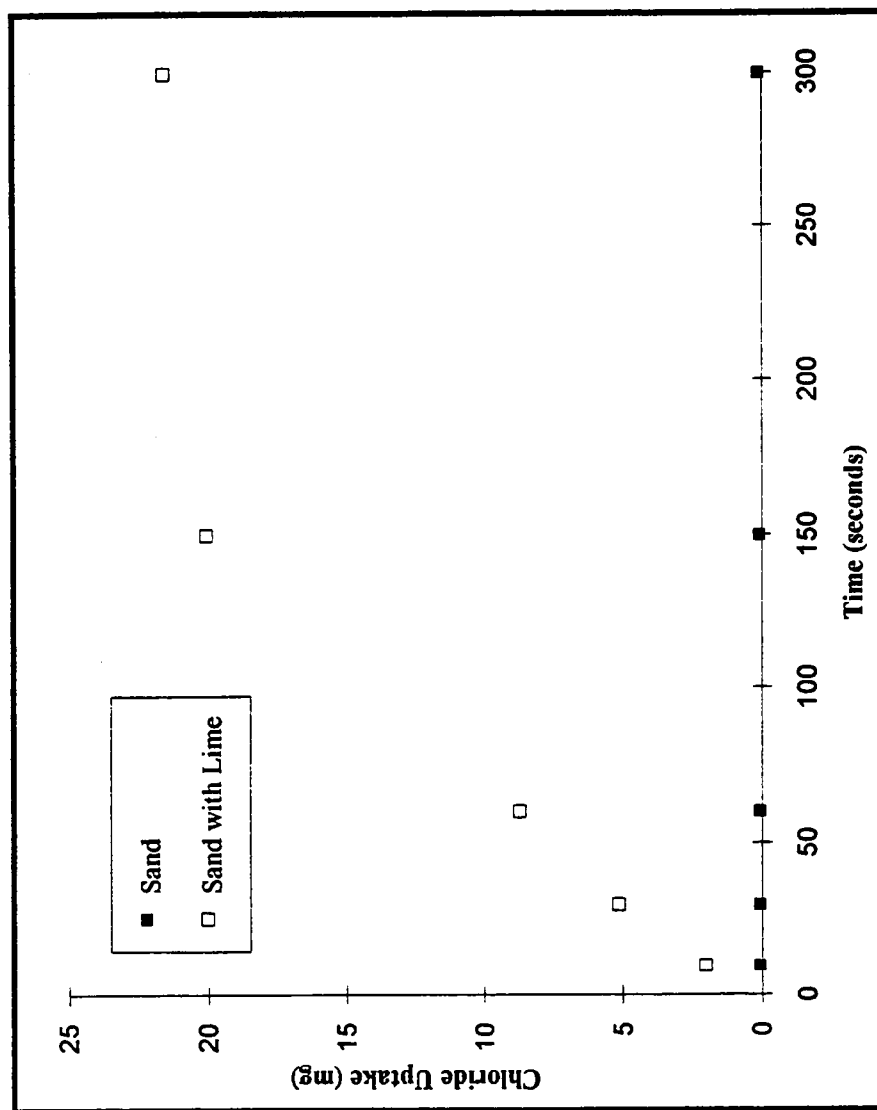


Figure 5.1. Chloride uptake by the sample bed in a blank test and a lime test at 1000 ppmv HCl. Data from Pakrasi, 1992.

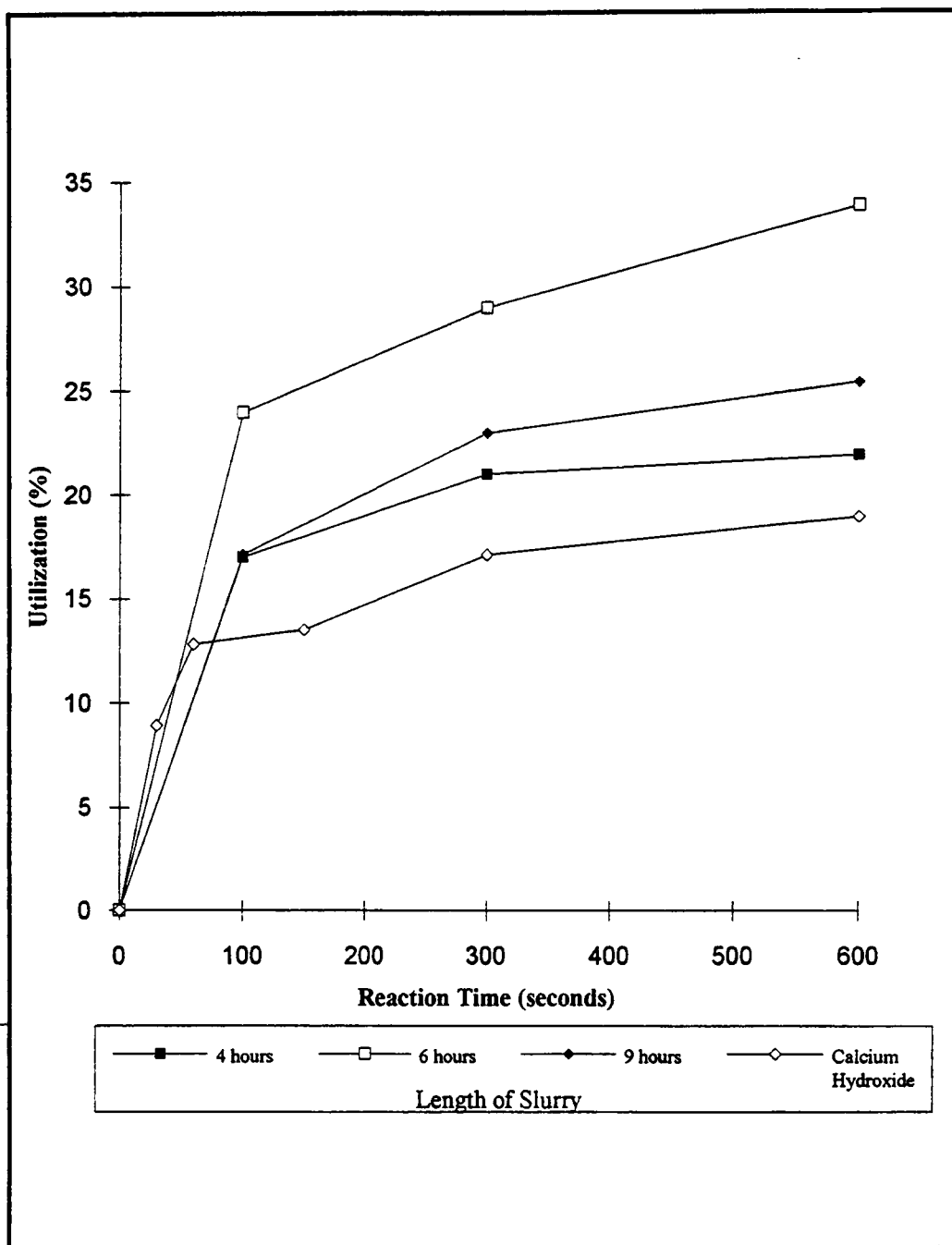


Figure 5.2. Effect of reaction time on fly ash/CH sorbent for increasing slurry time.

with increasing reactor test time, it can be seen that the sample slurried for 6 hours had the greatest maximum utilization at 34%, and offered the greatest enhancement as compared to plain CH.

The interesting development with these sorbents was that the 9 hour sample, rather than continuing to increase in utilization over the 6 hour sample, actually decreased in utilization with results nearer to those of the 4 hour samples than the 6 hour samples. Similar decreases were noted in earlier studies with SO₂ (Jozewicz et al., 1987b) and HCl (Jozewicz et al., 1991).

5.2.2 Surface area analysis

BET surface area was determined for the three sorbents. These results are plotted against slurry time in Figure 5.3. The maximum utilization for each of the slurry times is also shown. Maximum observed utilization for each of the three sorbent preparations occurred at 600 seconds. The vertical axis is for both surface area and utilization. Surface area increased steadily from 8 m²/g for the 4 hour slurry to 13 m²/g at 6 hours, to 18 m²/g at 9 hours slurry time. The figure demonstrates that utilization, however, did not exhibit a concomitant increase between 6 and 9 hours of slurry.

The fly ash by itself had a surface area of 3.1 m²/g, and the CH alone had a surface area of 17 m²/g. With the 8:1 fly ash to CH ratio used, the dry mixed, pre-slurry surface area of the combined components should have been approximately 4.6 m²/g. Measured BET surface area for the dry mix was 5.1 m²/g, which is in close agreement with the calculated value.

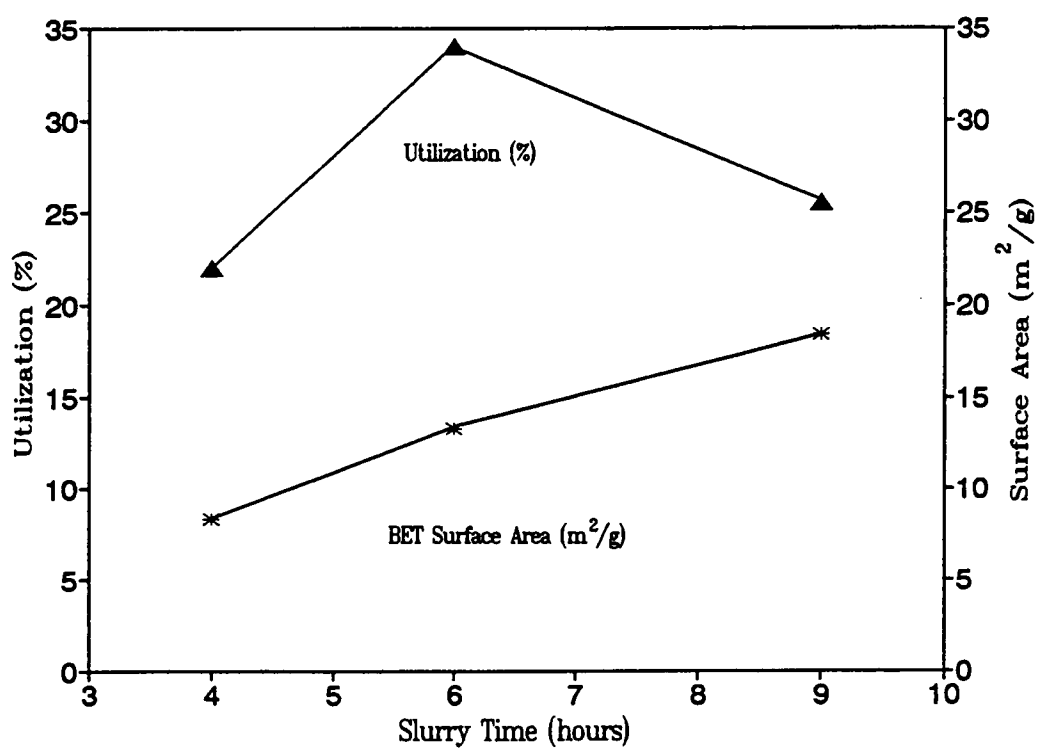


Figure 5.3. Effect of slurry time on surface area and maximum utilization of fly ash/CH sorbent.

It would in theory be interesting to take the slurry length back to time zero. However, there is no such thing as a "zero" slurry time as the components must be wetted in order to have been slurried at all, and this places the time at greater than zero. In an attempt to ascertain what the starting surface area was for material once it had been placed in the aqueous solution, but not allowed to slurry for appreciable time, the fly ash and CH were mixed for 1 minute in water. After immediate vacuum filtration and drying the measured BET surface area was 2.9 m²/g. This is less even than the fly ash alone, leading to the possible conclusion that the CH was in solution and lost in the filtrate. However, a check on the solubility of CH indicates that only 25% of the lime should have been in solution at 90 °C. Hence, if none of the CH had reacted to form another phase, only 25% should have been lost in the filtrate. A possible explanation for the low surface area following this procedure is that there was a pore-clogging effect as a result of slurrying that reduced the surface area. The same slurry procedure on the fly ash alone resulted in a BET surface area of 2.45 m²/g, slightly lower than that of the mixed components.

5.2.3 Discussion

It is evident that surface area does increase with increased slurrying time. As Jozewicz et al. (1991) reported in their glass/CH sorbent study, increased utilization did not always correlate with increased surface area. They postulated that the samples which had increased surface area, yet decreased utilization, might have achieved a greater degree of crystallization which somehow had a detrimental

effect on reactivity due, perhaps, to the calcium becoming so securely locked into the solid that it could not enter easily into reaction.

In the present test, reactivity increased for 4 to 6 hours of slurring, but decreased somewhere between 6 and 9 hours. Surface area and slurry time correlation with reactivity are apparent up to a point in the present experiments. These results indicate that something is occurring during the slurry phase of sorbent preparation which results in samples which have lower reactivity with HCl in the fixed bed reactor, although their surface area is greater.

5.3 Amorphous silica/calcium hydroxide sorbents

As mentioned in the Chapter 3, the primary focus of this study was on the character of the product formed by the reaction of silica and CH. Because the material apparently responsible for the enhanced reactivity of fly ash/CH sorbents in earlier studies was calcium silicate hydrate, formed from CH and the silica dissolved from fly ash, the following sets of tests utilized amorphous silica, rather than fly ash to form calcium silicate hydrate which would be free of the myriad of compounds in fly ash not relevant to the present research. At the outset it was assumed, based on a review of the literature, that calcium silicate hydrate would form in these experiments. Experimental evidence, provided primarily by x-ray diffraction and scanning electron microscopy during the course of this work, later supported this. Those results are discussed within the appropriate sections.

5.3.1 Sorbent reactivity tests

The reactor conditions under which the amorphous silica/CH sorbents were tested for reactivity were identical to those of the fly ash/CH tests. Temperature in the reaction chamber was 149 °C (300 °F), gas moisture was 10% by volume and HCl concentration was 1000 ppmv. All reactor tests were performed for 600 seconds, providing data comparable to the maximum utilization values of the fly ash/CH results. Samples were prepared according to the matrix shown in Table 3.5.

5.3.1.1 Effect of slurry time

Initially, only the 15 minute, 1 hour and 3 hour slurry times were employed in the preparation of the sorbents comprising the five sorbent ratios. Results of utilization as it relates to slurry time for these samples are shown in Figure 5.4. Initial utilization values for non-slurried samples of silica:CH ratios of 1:5 and 1:1 were 20 and 21%, respectively. These two values probably reflected the CH in its original form, and have not been plotted because they were not representative of slurried sorbents. In addition, two points are shown for CH at 0 and 3 hours. The zero hour CH is merely the CH in its original form. The three hour sample was prepared by slurrying CH, alone in water, for three hours. This was done to ascertain whether simply slurrying the CH could account for any of the enhancement demonstrated in the reactivity tests. In actual fact, the results indicate that some slight enhancement may have been accorded by heating and slurrying the CH. The 15 minute and 3 hour samples tests were performed three

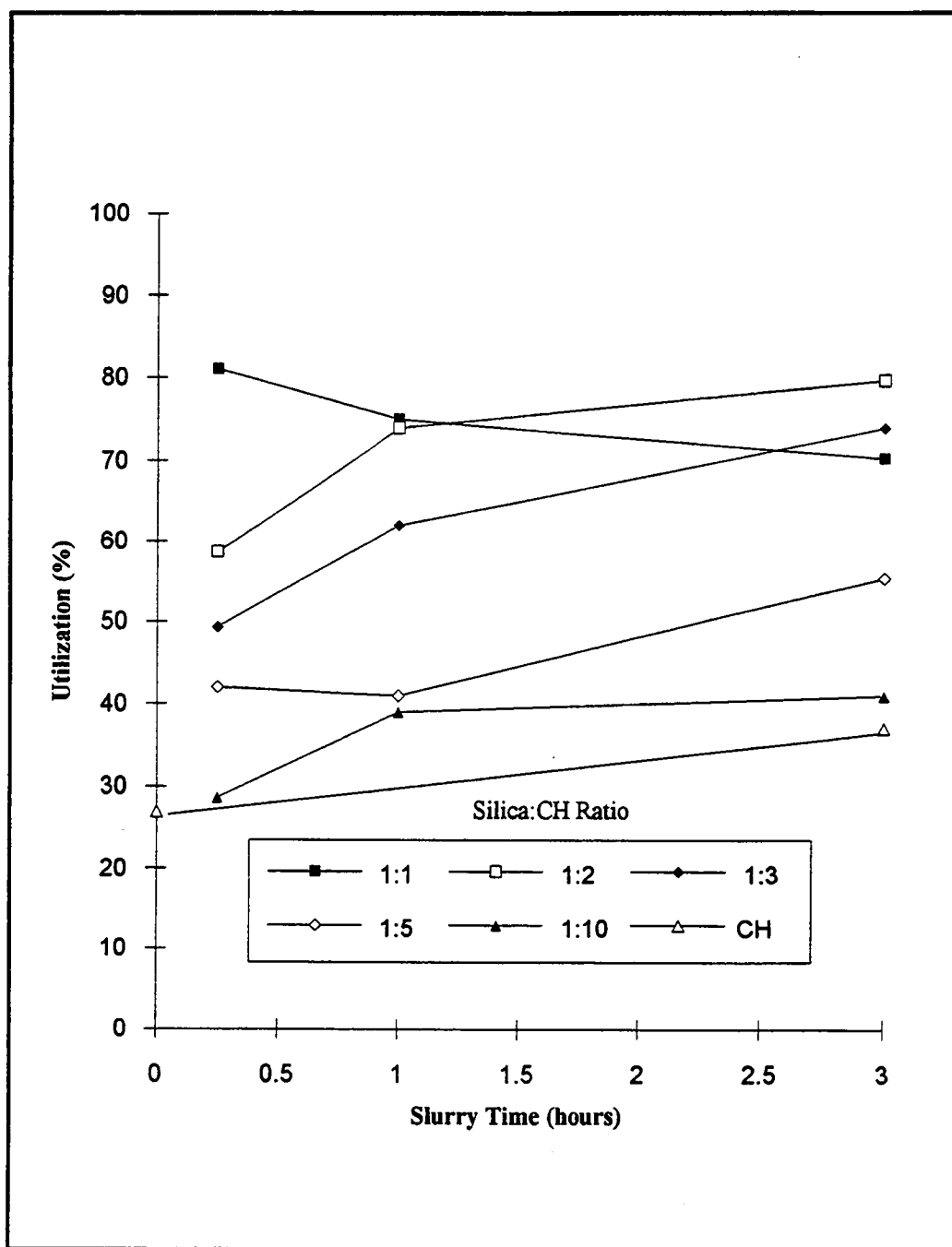


Figure 5.4. Effect of slurry time on utilization for amorphous silica/CH sorbents.

times each. The data points plotted in Figure 5.4 are the average values for the three tests. Plotting the upper and lower ranges for each of the test sets would have made the graph confusing. Instead, the percentage differences of the high and low values from the mean utilization value are given in Table 5.2. The majority of the high and low utilization values fell within 10% of the value of the mean utilization. High and low percentage differences for the 1:10-.25 sample were unusually large due to the fact that one test result was anomalously low. The three utilization values for this sample were 14%, 35%, and 37%.

Except for the 1:1 ratio of silica:CH, increasing the slurry time caused an increase in reactivity. The 1:1 ratio, however, had a reverse trend. This raised the question of whether this was an anomaly due to error or an actual trend, and whether, if slurried for longer times other preparations might also experience a decline in reactivity. To answer these questions a batch of each sorbent ratio was prepared by slurrying the preparation for 7 hours. By virtue of the new slurry time being greater than twice as long as the previous longest slurry time, this was determined to be an appropriate choice.

Figure 5.5 includes the results from the reactor tests on the 7 hour samples in addition to the results shown in Figure 5.4. It can be seen that the amorphous silica:CH ratios of 1:10, 1:5, and 1:3 each demonstrated continued increase in utilization toward a plateau with increasing slurry time. The silica:CH ratio of 1:2, in addition to the 1:1 ratio, however, demonstrated an initial increase in utilization followed by a decrease at longer slurry times. The 1:2 preparation decreased after 3 hours slurry, while the 1:1 began its descent after only 15 minutes. The 1:1 preparation exhibited its greatest reactivity at the earliest slurry time, never achieving a comparable performance for any longer slurry time.

Table 5.2. Mean utilization, high and low values, and percentage difference from the mean of the high and low values for three tests on the 15 minute and 3 hour amorphous silica/CH samples. CH alone is included.

Sample	Mean Utilization (%)	High Value	High Value Difference * (%)	Low Value	Low Value Difference (%)
1:1-.25	81	87	7	78	4
1:2-.25	59	62	5	56	5
1:3-.25	49	53	8	45	8
1:5-.25	42	47	12	36	14
1:10-.25	29	37	28	14	52
1:1-3	70	73	4	68	3
1:2-3	80	84	5	77	4
1:3-3	74	78	5	71	4
1:5-3	55	59	7	53	4
1:10-3	41	46	12	36	12
CH-0 hours	27	28	4	25	7
CH-3 hours	37.5 (avg. of 2 samples)	38	1	37	1

*Differences are as compared to mean utilization.

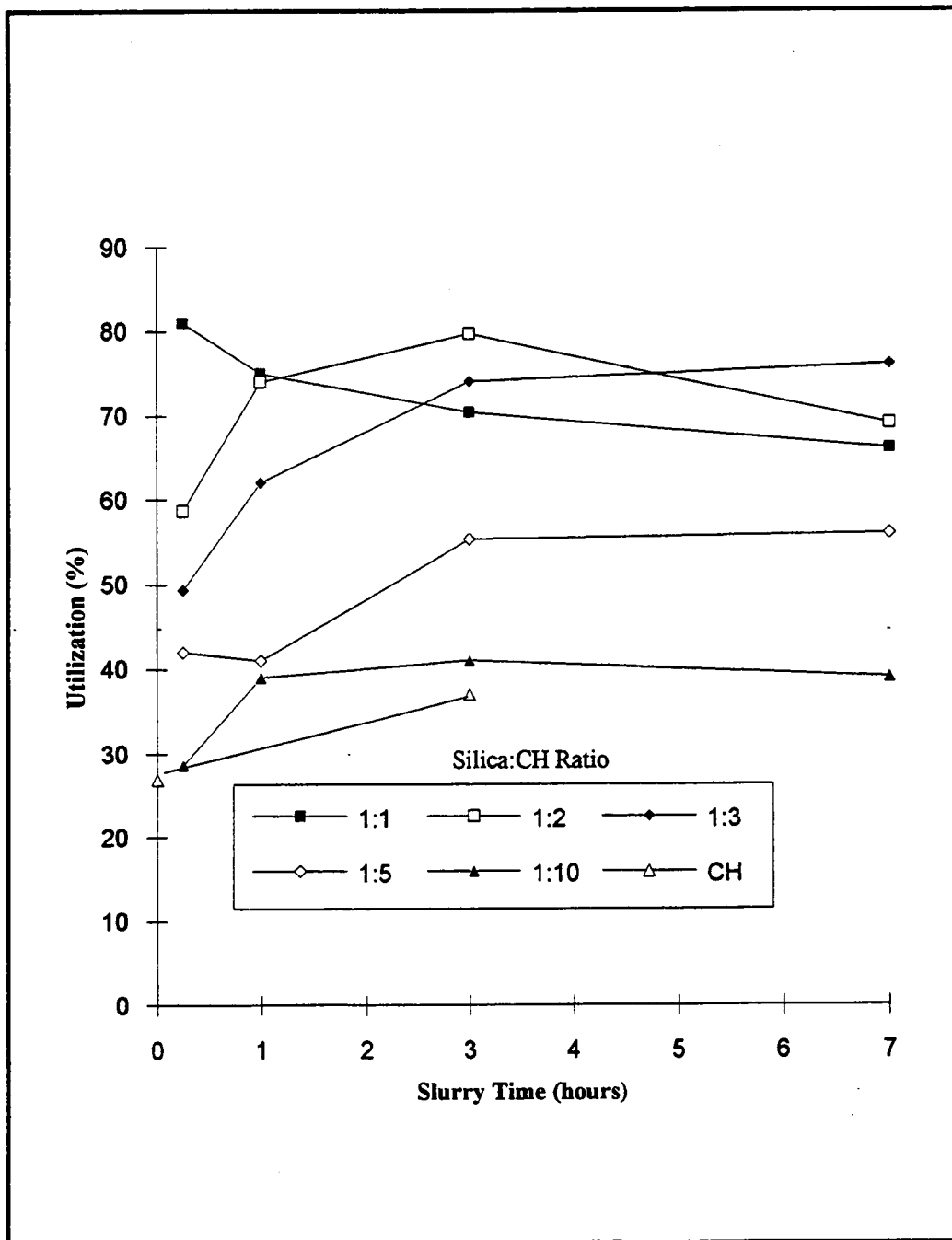


Figure 5.5. Effect of slurry time on utilization for amorphous silica/CH sorbents with 7-hour samples included.

Interestingly, the decrease in utilization of the 1:1 and 1:2 ratio samples is such that at 7 hours both had fallen below the performance for the 1:3 sample for the same slurry time.

It is possible that two trends are at work in these results. The first is that the reactivity, as demonstrated by the utilization results, increases with increasing silica:CH ratio. This appears to be true in a general sense, despite the decreases noted above. The second trend is the decrease in reactivity, experienced after an initial increase, for preparations containing higher proportions of amorphous silica. In fact, results imply that the higher the silica content, the earlier that the reversal occurs. Other researchers' work, performed specifically on calcium silicate hydrate (not for sorbent study), suggest that, above a certain molar ratio of silica to CH, the structural nature of the calcium silicate hydrate changes. The possible connection of this phenomenon to the present utilization results is discussed in section 5.3.7.

A further set of experiments was performed to determine the reactivity of the 1:1 ratio sorbent preparation in which the slurry times were shorter than 15 minutes. This pursuit was suggested by the early and very high utilization of the 1:1 ratio sample, which only decreased as slurry time increased. Graphically (Figure 5.5) it appeared that the utilization for silica:CH 1:1 samples might continue to increase as the time was shortened. Six additional sorbent batches were prepared by slurrying the silica and CH in 1:1 weight proportions. The slurry times, in ascending order, were 10 seconds, 30 seconds, 72 seconds, 3 minutes, 6 minutes, and 9 minutes. These samples were tested for reactivity under identical reactor conditions as the previous samples. The results, presented on a log time scale, are seen in Figure 5.6. The baseline CH value from the earlier tests is given

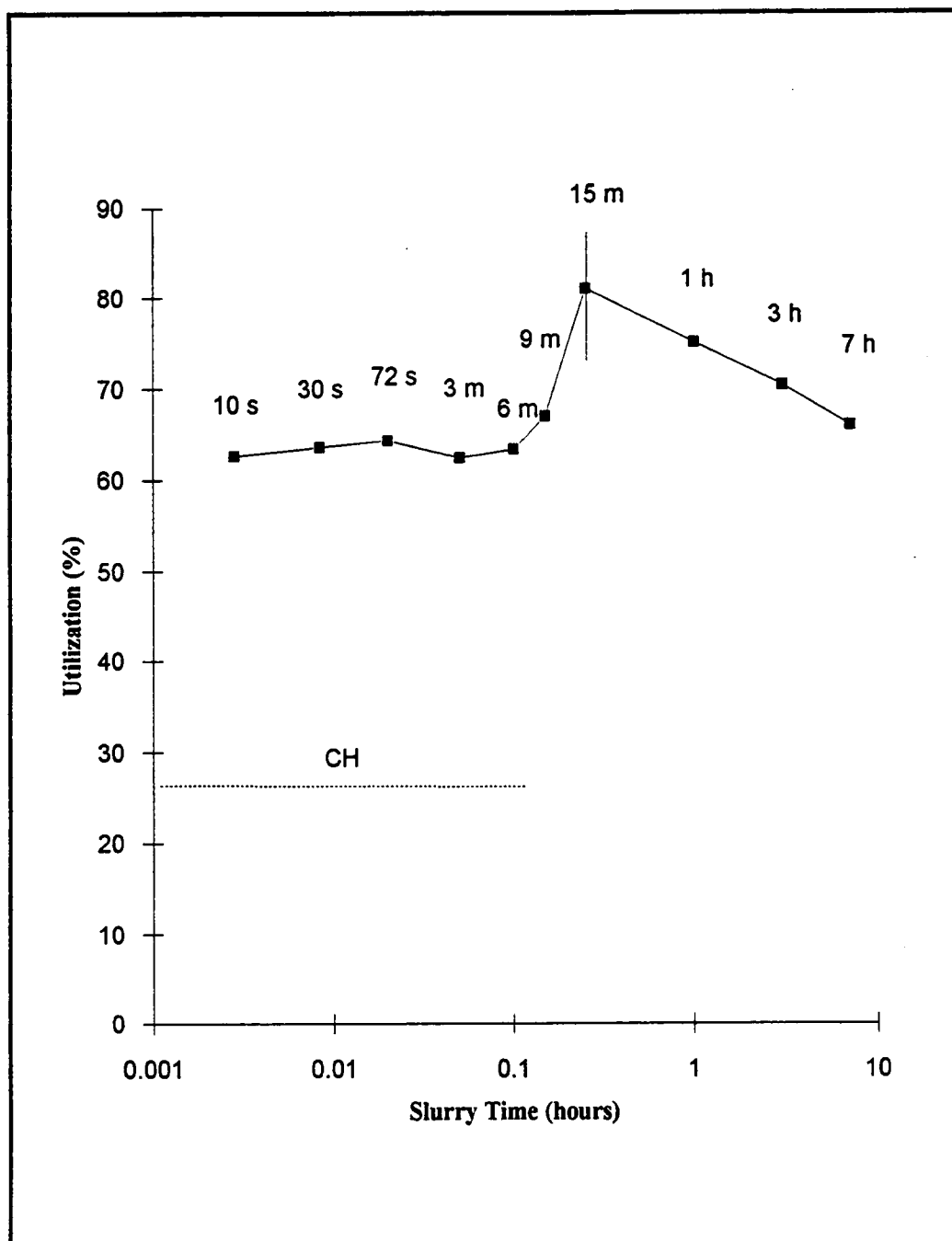


Figure 5.6. Effect of slurry times on 1:1 amorphous silica/CH sorbent shown on log scale.

for reference. It can be seen that no sample exceeded the reactivity of the 15 minute sample from the earlier results. Replotting the data on a normal arithmetic scale, as in Figure 5.7 aids in a conceptual evaluation. Evidently, even the shortest feasible slurry time (10 seconds) results in significant enhancement of the material over CH alone. However, there is little, if any actual, change before approximately 9 minutes, after which point the utilization increases by more than 10% at 15 minutes, thereafter decreasing steadily out to 7 hours of slurry time. The 1:1-.25 point on the graph represents the average of four repeat tests. The values ranges from 73 to 87%. Had only the lowest value been plotted, the dramatic and short-lived increase would not be as evident; yet the entire curve would still show an early maximum in reactivity. It is this one point alone which might give the impression that the 1:1 ratio preparation is the most reactive sorbent. Without it the curve beyond 15 minutes (see Figure 5.5) falls below the performance of the silica:CH ratio of 1:2 and, for longer slurry times, below that of the 1:3 ratio.

The observation that the utilization so quickly (i.e., in 10 seconds of slurry time) increased to greater than 60 %, and showed little change until 15 minutes slurry time indicates that the actual time over which reaction occurred between the silica and CH may not be as short as the slurry times imply. Although the sorbent preparations were vacuum filtered immediately upon completion of slurring, the formation of calcium silicate hydrate may have continued during the 10 minute period of microwave drying, or perhaps for some smaller part of that time until the solids were sufficiently dry that reaction ceased. This would suggest that reaction time for this method of preparation can never be less than approximately 10 minutes. The graph supports such an assertion in that the 9-minute slurry was the first to exhibit a possible increase in utilization, and the first

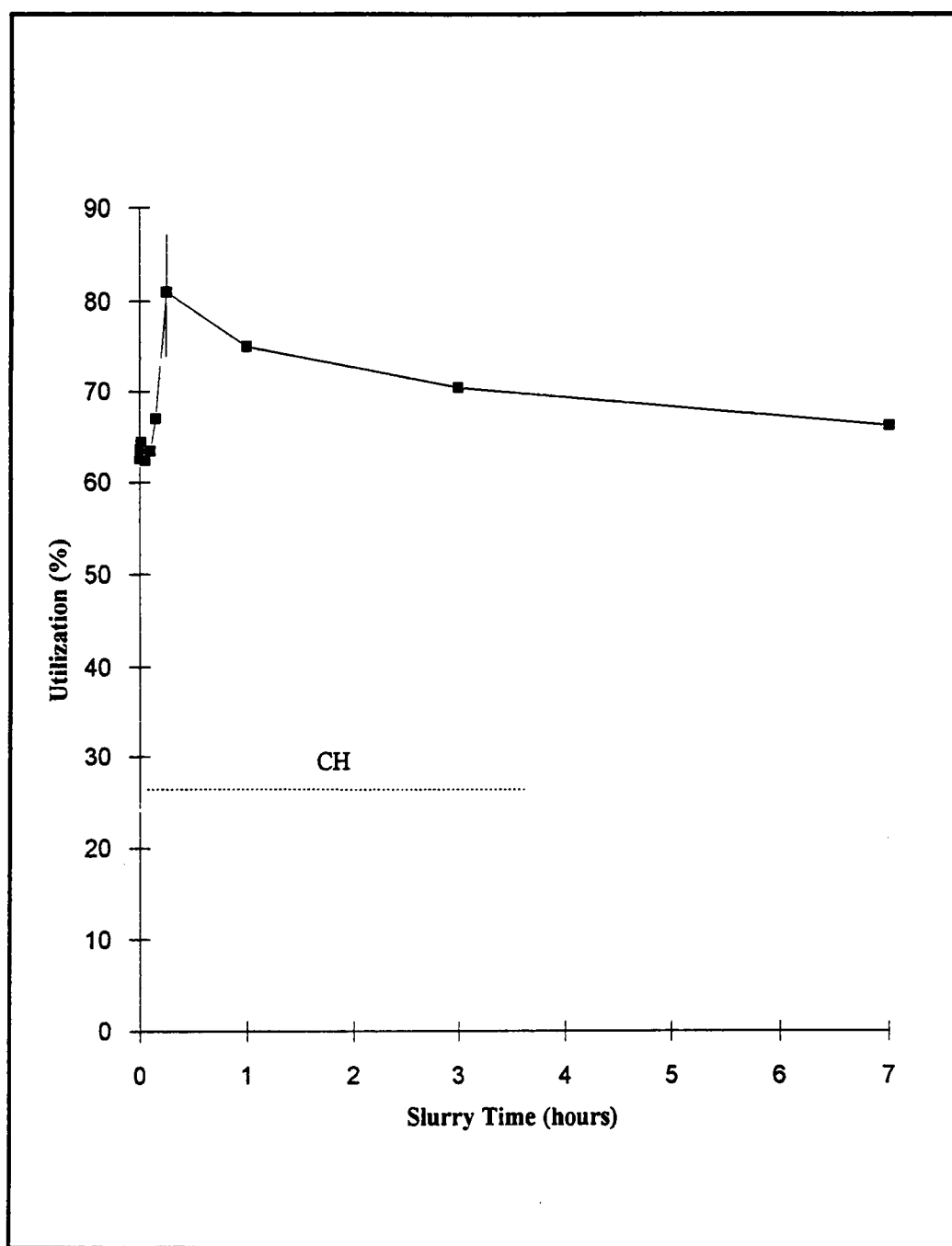


Figure 5.7. Effect of slurry times on 1:1 amorphous silica/CH sorbent shown on arithmetic scale.

clear increase occurred sometime between 9 and 15 minutes. The method of sorbent drying, which was the method used by Jozewicz and his co-workers for the sorbent research described in chapter 2, may have precluded instantaneous quenching of the reaction. If reaction does, in general, continue beyond the point at which the solids are removed from the aqueous slurry, it is probably impossible to prevent such activity using the current preparation procedures. Freeze-drying the solids immediately should quench the reaction, but this has not been investigated as a possible sorbent preparation procedure to this point.

5.3.1.2 Effect of silica fraction

Another perspective on the reactivity tests is given by plotting utilization as a function of the component ratios. The component ratios can be quantitatively expressed as the overall silica fraction of the two mixed components. In Figure 5.8 the silica:CH ratio of 1:10 corresponds to the silica fraction of 0.1, and the silica:CH ratio of 1:1 corresponds to the silica fraction of 0.5, as it is one half silica. This plot clearly illustrates that by increasing the amount of silica in the sample preparation, a significant enhancement in utilization is effected. It is evident as well that equivalent slurry times at each silica fraction do not result in proportional increases in reactivity. This is particularly well demonstrated by the silica:CH ratios of 1:3 and 1:1. At a ratio of 1:3 (silica fraction of 0.25) the 7 hour slurry has the greatest utilization, and the 15 minute slurry the least. At the increased silica fraction (0.5) of the 1:1 ratio, all four slurry times are completely reversed so that the 15 minute slurry has the greatest utilization and the 7 hour the least.

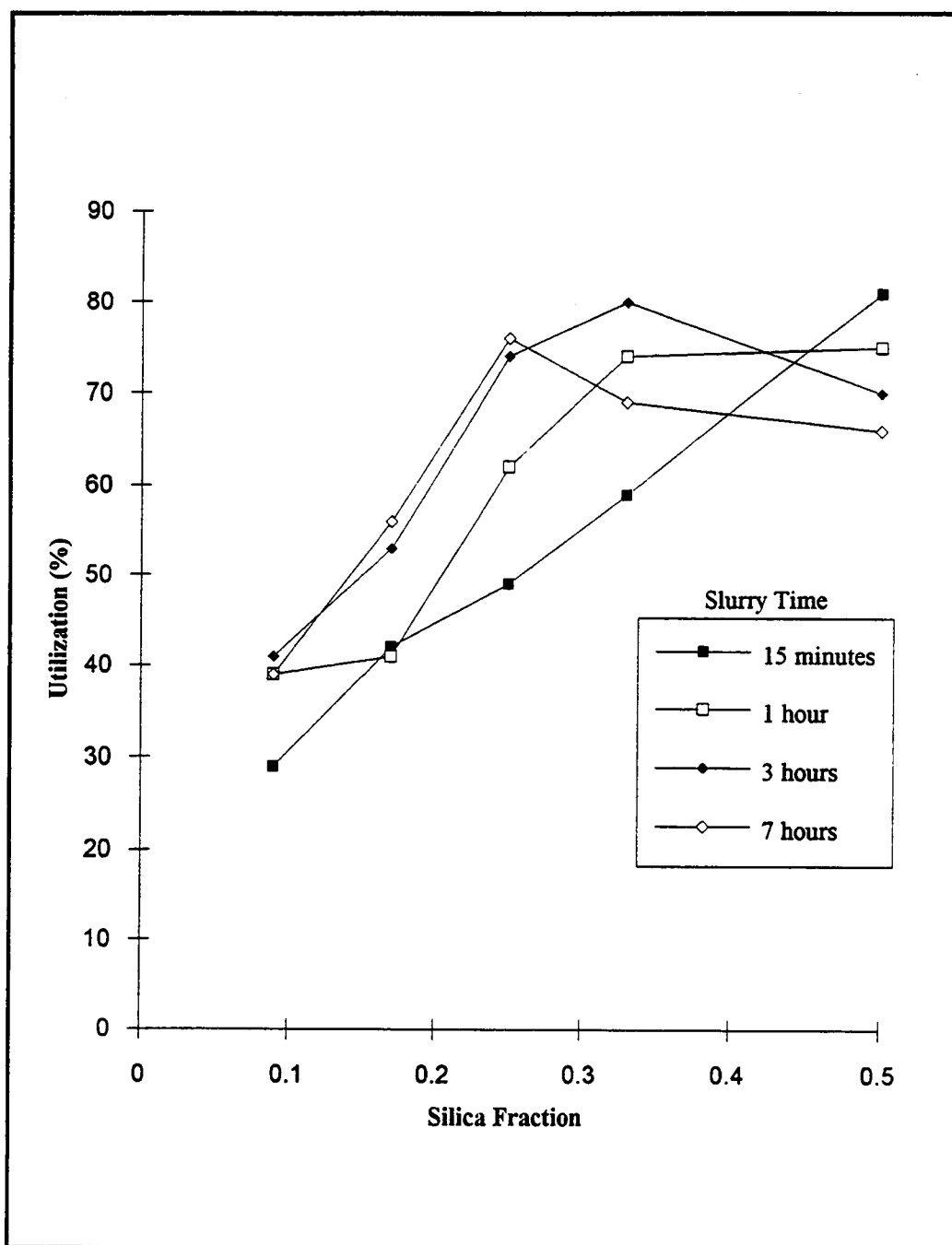


Figure 5.8. Effect of component ratio on utilization for amorphous silica/CH sorbents.

The reactivity results, presented here in terms of silica fraction, and earlier in terms of slurry time, indicate that the performance of the hydrothermally prepared sorbents is a complex interaction of both the amount of silica added and the length of time the material is slurried. An increase in the slurry time does not always lead to increased utilization. In addition, while increasing the silica fraction generally increases the utilization, just the opposite was found at the highest silica fractions.

5.3.1.3 Addition of calcium chloride and calcium hydroxide

A set of tests was performed in which either CaCl_2 or CH was added in dry form to 50 mg. aliquots of the silica:CH 1:1 ratio sorbent batch which had been slurried for 3 hours during sorbent preparation. (Refer to section 4.1.2 for preparation details.) Due to the organization of this dissertation the results of this test are discussed in this section. However, the motivation for performing the test was a result of the x-ray diffraction analyses, which are discussed in detail in a later section. It was observed by way of x-ray diffraction that samples for all the silica:CH ratios, except 1:1, regardless of the length of time they were slurried, still contained CH in addition to newly formed calcium silicate hydrate. The 1:1 ratio sorbent still contained small amounts of CH at 15 minutes and 1 hour of slurry time, but none at 3 and 7 hours. As discussed previously in section 5.3.1.1, the utilization of sorbent samples of this silica:CH ratio decreased after 15 minutes of slurry time. The question was then raised as to the importance of the presence of CH in the sample in initiating the reaction of the solids with the HCl in the reactor

gas stream possibly due to its hygroscopic nature. It was believed already that the calcium silicate hydrate in the sorbents were responsible for the increased reactivity, but was it possible that CH needed to be present as well for the enhancement to be effective?

Greenberg and Chang (1965a) noted that the products of the reaction of calcium oxide, silica, and water mixtures (i.e., calcium silicate hydrate) began to dissolve completely in hydrochloric acid at a $\text{CaO}:\text{SiO}_2$ molar ratio of 1:1. Pakrasi (1992) noted that one of the reaction products of CH and HCl was calcium chloride (CaCl_2). CaCl_2 is known to be hygroscopic. If it were able to attract some moisture from the humidified gas stream, perhaps hydrochloric acid would form from the combination of water and HCl. Then, as Greenberg and Chang suggested, the calcium silicate hydrate in the hydrothermally prepared sorbents might begin to dissolve. It was theorized in the present study that such dissolution might activate the reactive sites in the calcium silicate hydrate, leading to enhanced reactivity with the HCl in the gas stream. If such were the case, then the enhanced reactivity would not be initiated if the CH were not present in sufficient quantity, and the declining performance of the sorbent of silica:CH ratio of 1:1 might thus be explained. In addition, if moisture was the necessary component, then another hygroscopic compound such as calcium chloride might perform the same function. With these ideas as the basis for formulation, an experiment was designed to determine if the addition of CH or CaCl_2 to a sorbent lacking CH would boost its reactivity.

Reactor tests were run on samples of silica:CH ratio of 1:1 which had been slurried for 3 hours (1:1-3) and to which 20 and 40% by weight of CaCl_2 or CH had been added prior to placing the sample in the reactor. The details of the

sample preparation were given in section 4.1.2. In addition, control samples of 1:1-3 without additives were tested in the reactor. In spite of having replicate data points for the 1:1-3 sorbent preparation, it seemed logical to run a side by side control with the samples which contained the additives. The 1:1-3 sample was chosen as the one to which CaCl_2 and CH were added since the 1:1 silica:CH series demonstrated the highest reactivity, the 3 hour batch had exhibited decreased utilization as compared to the 15 minute and 1 hour sample, and x-ray diffraction demonstrated that no CH was remaining in the sample slurried for 3 hours.

Ultimately, the test results did not help prove or disprove the theory that it was necessary to attract moisture in order to provide hydrochloric acid in which to dissolve the calcium silicate hydrate so that they might become reactive. Indeed, it was not proven that the addition of CaCl_2 or CH caused adsorption of moisture at all. Figure 5.9 gives the results in bar graph form. The sample which contained no additive, and was thus the baseline value, exhibited a utilization of 67%. This was insignificantly lower than the value of 70% for the sample which contained 20% CaCl_2 . The sample containing 40% CaCl_2 demonstrated even lower utilization with a value of 62%. The lower utilization exhibited by the sample containing 40% CaCl_2 may possibly be explained by the observation that the addition caused the sample to become lumpy due to agglomeration of the particles resulting from the moisture attracted to the sample as it was mixed in the mortar. This lumpiness may have caused the material to behave in a less than ideal manner when submitted for the reactor test. These results indicate that the samples with addition of CH performed approximately the same as the sample

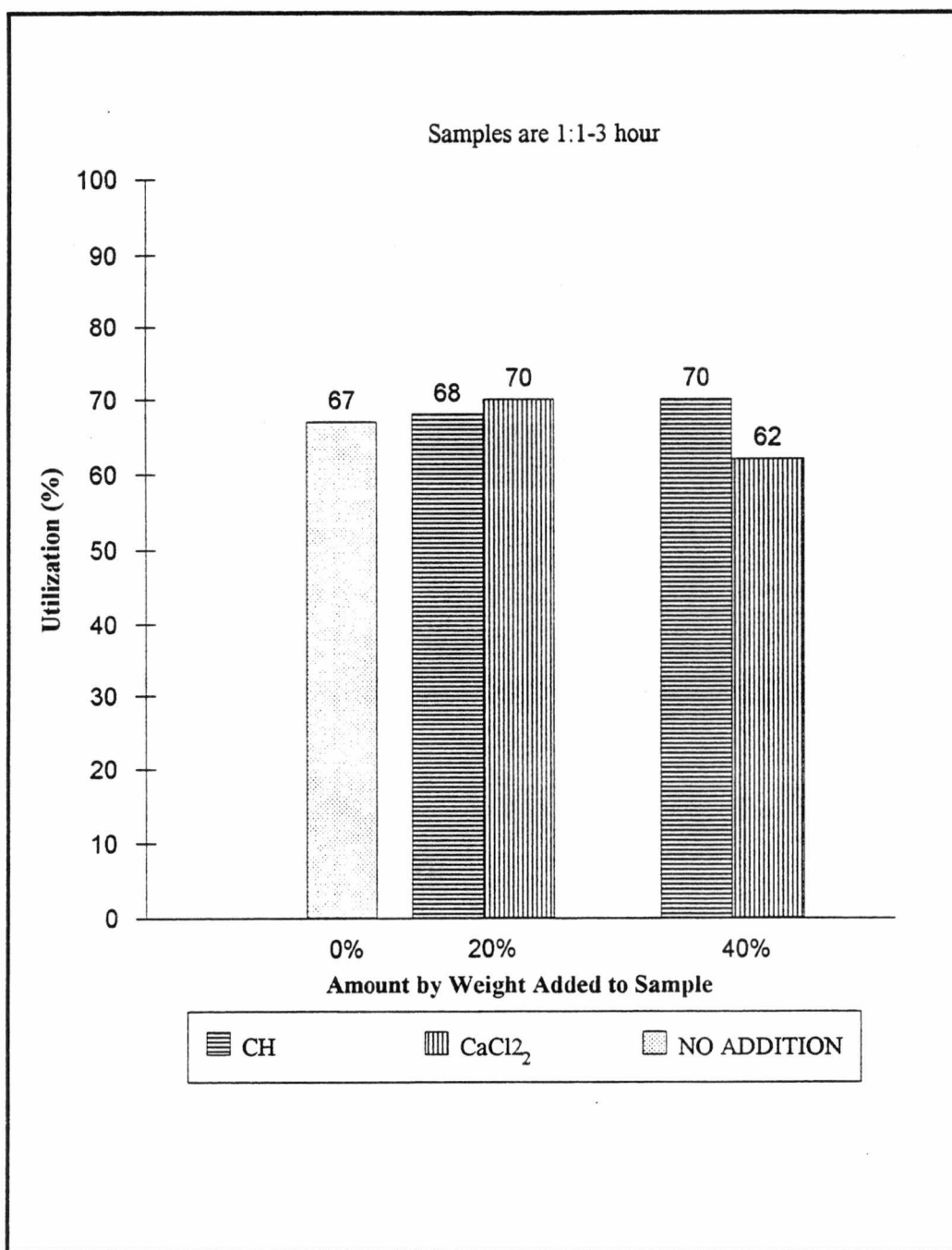


Figure 5.9. Effect of CH and calcium chloride addition on utilization for amorphous silica/CH sorbents.

containing no additives. There was no evidence to suggest that the enhanced reactivity of the silica:CH ratio of 1:1 was due to the presence of CH.

Because adding CH and CaCl_2 to the samples changed the proportions of the analytes in the filtrates which were analyzed, it was necessary to correct for the molar amounts added to the samples. Correcting for added mass required subtracting out the appropriate molar amounts from the results of calcium and chloride analyses. In section 5.1.2 on sample mass recovery, it was pointed out that some loss of sample did not affect the results because the utilization is calculated as a ratio of the calcium and chloride in the filtrate. However, subtracting molar amounts of these analytes, based on the mass of CaCl_2 or CH added to the sample, makes any mass lost important. In order to account for mass lost, the average percentage of material lost, as determined in section 5.1.2, was also subtracted from the calcium and chloride analysis results. This amount was 25%. The results presented in Figure 5.9 reflect those corrections. The calcium and chloride added to the 1:1-3 samples was subtracted out before the utilization was calculated. It was assumed that the calcium in the CaCl_2 added to samples would not react with HCl in the gas stream because it was already combined with 2 chlorine atoms. Thus, the calcium and chloride could be directly subtracted. Earlier tests determined that CH alone had a utilization of 27%. So, in order to correct for the chloride in the filtrates of samples with added CH, it was assumed that the additional CH had a utilization of 27%, and the corresponding chloride was subtracted from the sample.

5.3.1.4 Controlled rate addition of individual components

The method of preparing the samples for this experiment was given in section 4.1.3. Because the motivation for performing this set of tests was based on the relationship between surface area of the sorbent and its reactivity, the details of the rationale have been left for discussion in section 5.3.2.2 in which surface area analysis results are presented. Briefly, however, the purpose of this experiment was to determine if surface area and reactivity could be increased by modifying the method of slurrying the silica and CH. The reactivity results are presented here.

Five samples were tested in the reactor under conditions which were applied to all samples in this study (with the exception of a single test in which the gas was not humidified). Again, these conditions were: reaction chamber temperature of 149 °C (300 °F), 10% volumetric moisture in the gas stream, HCl gas stream concentration of 1000 ppmv, and 600 seconds exposure time for reaction. Figure 5.10 demonstrates the utilization values obtained for samples. A sample of the silica:CH 1:1 ratio slurried for 15 minutes was run side by side to provide a within-test baseline. The other four sample preparations were also slurried for a total of 15 minutes, so their utilization results are comparable to the 1:1-.25 minute sample. This sample exhibited 79% utilization which is in close agreement with the earlier average of 81% for this sample batch. The hot addition preparations demonstrated higher utilization than the cold additions. In both cases the metered addition of silica to a base of CH was more reactive than the reverse situation of adding CH to a base of silica. The heated samples, however, are so close in value that the differences are easily attributable to experimental error. No

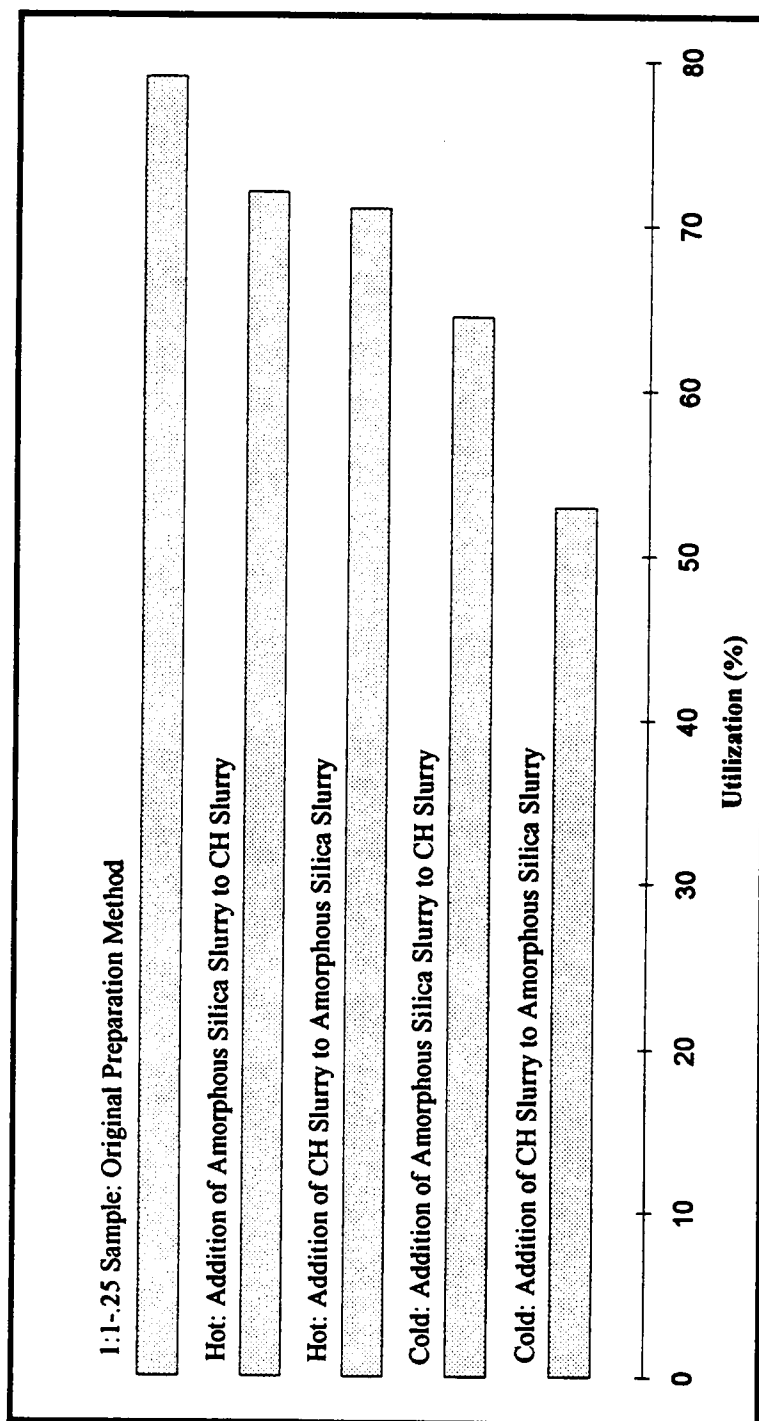


Figure 5.10. Effect of controlled rate addition of components on sorbent utilization.

sample prepared by the controlled rate addition demonstrated higher reactivity than the sample prepared in the routine manner.

5.3.1.5 Test Without gas humidification

All reactor tests, exclusive of this one, were run under identical conditions so as to eliminate process variables as factors when comparing utilization results. The set of tests reported in this section was the only one in which any reactor condition was changed. Rather than humidifying the gas stream to the constant 10% by volume, no water was injected. Thus the gas stream was completely dry. The purpose of this was to determine how much effect the gas humidification had upon the ability of the sorbents to be reactive.

Samples of all silica:CH ratios, which had been slurried for either 15 minutes or 3 hours, were tested under dry reactor conditions. The results are plotted in Figure 5.11. Analogous data points from the earlier tests in which the gas was humidified are included for comparison. Dry test results are connected with solid lines, and the humidified test results are shown with dashed lines. With one exception all dry test results are considerably lower than the comparable humidified test values. Of particular interest is the exception, which is the 1:1-.25 minute sample. This is the sample which was seen in Figure 5.5 to exhibit the highest utilization in humidified tests and which, when placed in context with the short slurry time test values (refer to Figures 5.6 and 5.7) seemed anomalously high. It is this same sorbent batch which again appears anomalously high in context with the other dry test results. This may indicate that the 1:1-.25 minute sample batch contained more moisture than the batches slurried for shorter and

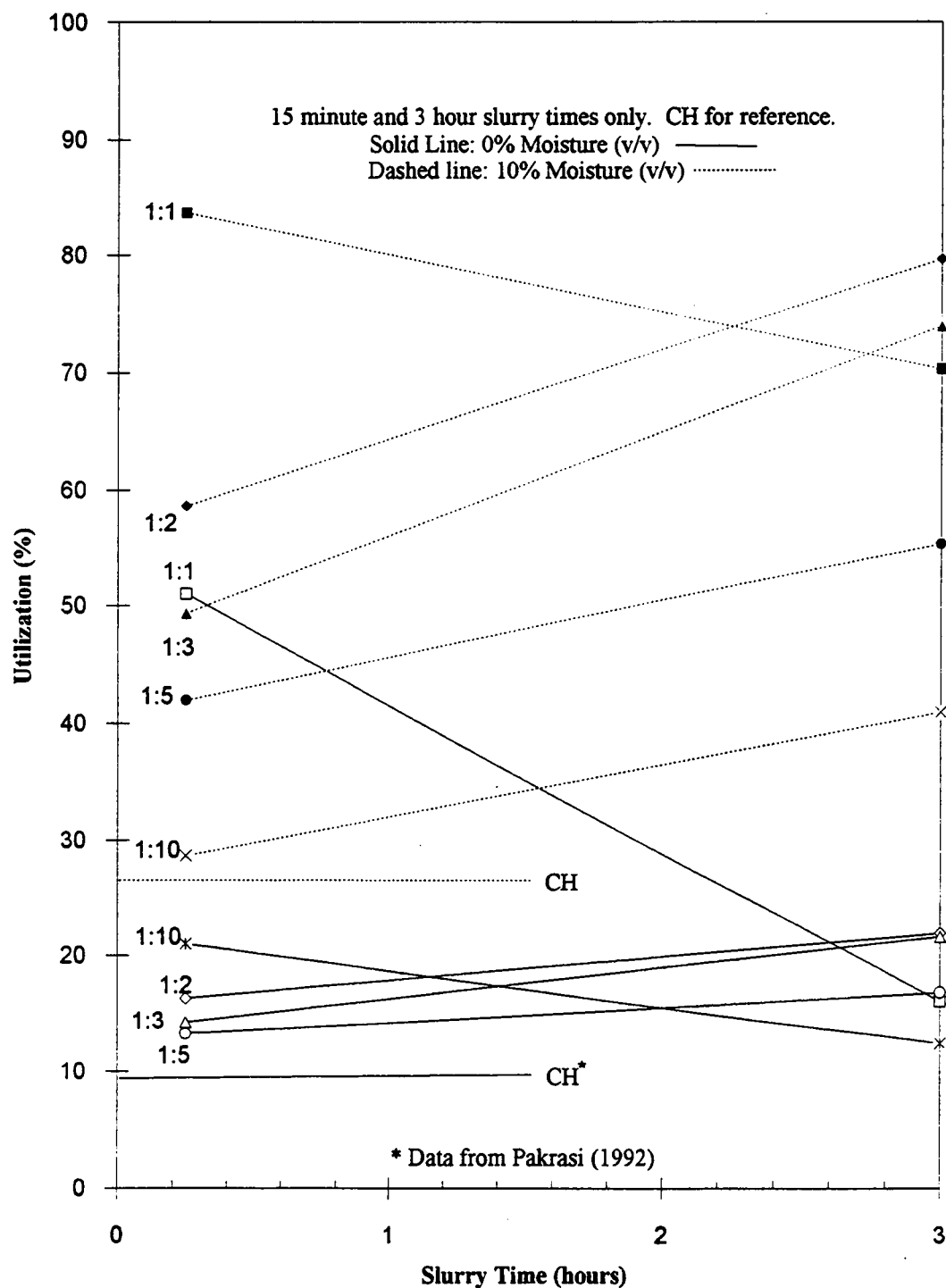


Figure 5.11. Effect of 0% and 10% (v/v) moisture on amorphous silica/CH sorbents.

longer times. Inherent moisture could account for this particular sorbent's high reactivity in both humidified and dry reactor tests, based on the fact that moisture, at least in the gas stream, increases sorbent utilization.

5.3.2 BET surface area analysis

5.3.2.1 Effect of slurry time and silica fraction

BET surface area analyses were performed on all the amorphous silica/CH sorbents. The results in m^2/g are plotted against the length of slurry time in Figure 5.12. The surface area increased with slurry time for all silica:CH ratios except for 1:1, whose surface area was $44 \text{ m}^2/\text{g}$ at 15 minutes slurry time, fell slightly at 1 and 3 hours, and returned to $44 \text{ m}^2/\text{g}$ for the 7 hour slurry. This particular ratio exhibited either a decrease or no change. It is the same silica:CH ratio which had the greatest utilization for the shortest slurry time, contrary to the dominating trend of increasing utilization with increasing slurry time (refer to Figure 5.5). Except for the 1:1 ratio, the surface areas ranged from 23 to $28 \text{ m}^2/\text{g}$ for the 15 minute slurry samples to between 48 and $90 \text{ m}^2/\text{g}$ for the 7 hour slurry samples. Evidently, the lower silica:CH ratios (1:10, 1:5, 1:3, and 1:2) developed increased surface area in response to the increased slurry time. It appears that somewhere between the silica:CH ratios of 1:2 and the 1:1, the character of the calcium silicate hydrate changes, and the material can no longer develop surface area matching or exceeding those values of lower silica:CH ratios. This reversal of trend is evident in Figure 5.13 in which the surface area is plotted against the weight fraction of silica in the sorbent (i.e., the component ratio in relative terms).

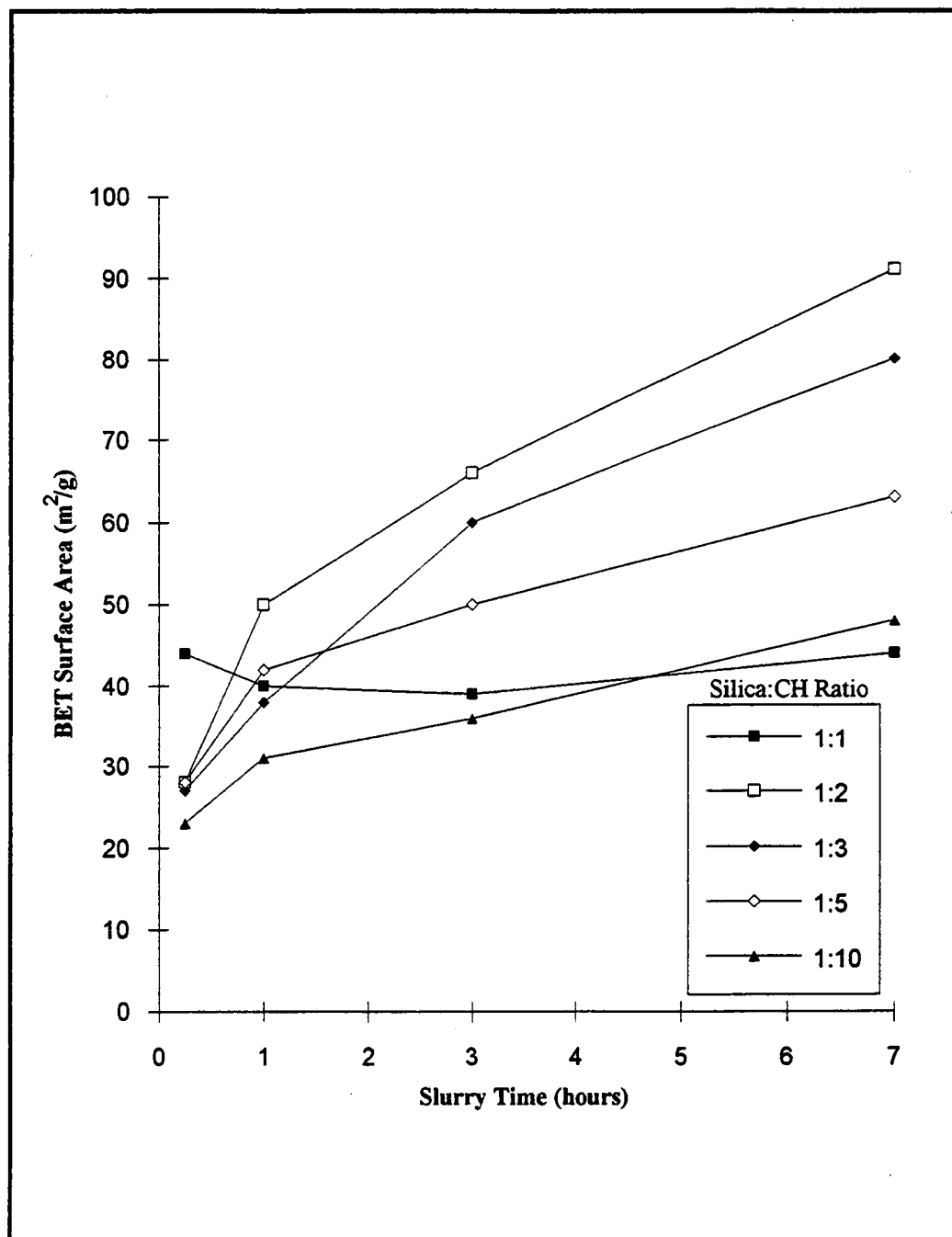


Figure 5.12. Effect of slurry time on the development of surface area in amorphous silica/CH sorbents.

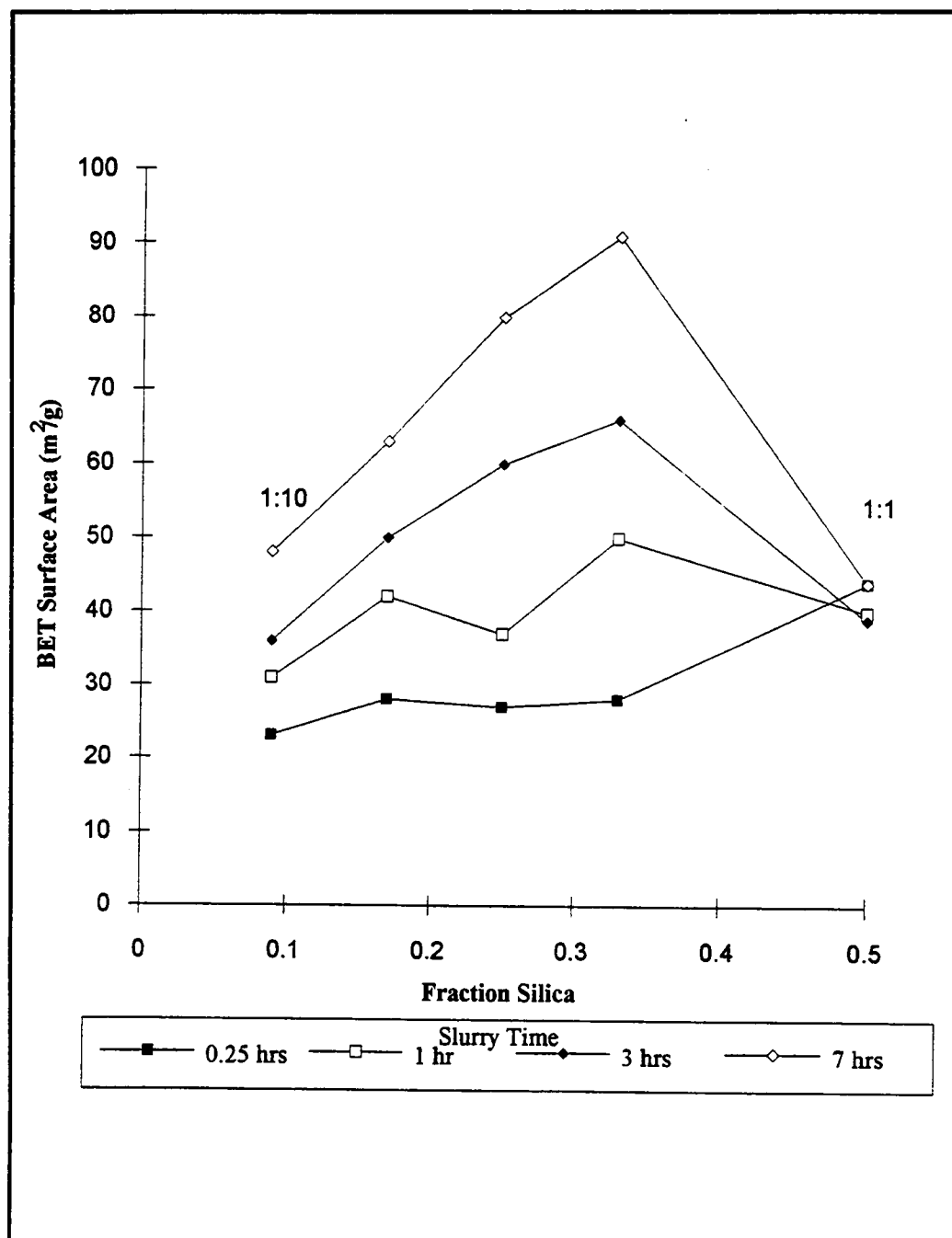


Figure 5.13. Effect of component ratio on BET surface area for amorphous silica/CH sorbents.

Each of the lower ratios exhibited increasing surface area with increasing silica fraction. Each solid line connects data for a single slurry time. At the silica fraction of 0.5, which is the silica:CH ratio of 1:1, this trend reversed itself for slurry times greater than 15 minutes.

Surface area was also determined for the 1:1 silica:CH ratio sorbents which had been prepared by slurrying the components for short lengths of time. The graph of these results is given in Figure 5.14. The utilization results for the same samples have been plotted on the figure, as well. As with the utilization the surface area at 10 seconds was not considerably different than that at 15 minutes or 7 hours. At 10 seconds and 9 minutes the sorbent had a surface area of 36 and 37 m²/g, respectively. This increased to only 44 m²/g at 15 minutes. While the trend of both parameters was very much the same, and utilization appears to be related to surface area, no particular insight was gained except to note that the final surface area was very much the same as the initial surface area and enhanced reactivity occurred early.

5.3.2.2 Effect of controlled rate addition

This experiment was undertaken to investigate the possibility of retaining the amorphous silica's high surface area during the sorbent preparation process in order to increase the overall surface area of the resulting solids. The surface area of the amorphous silica was determined to be 482 m²/g. Yet, after 10 seconds of slurry time with an equivalent amount of CH, the surface area of which was 18 m²/g, the surface area of the hydrothermally prepared material was 36 m²/g. Based on weight proportions alone, the pre-slurry surface area of the silica and CH

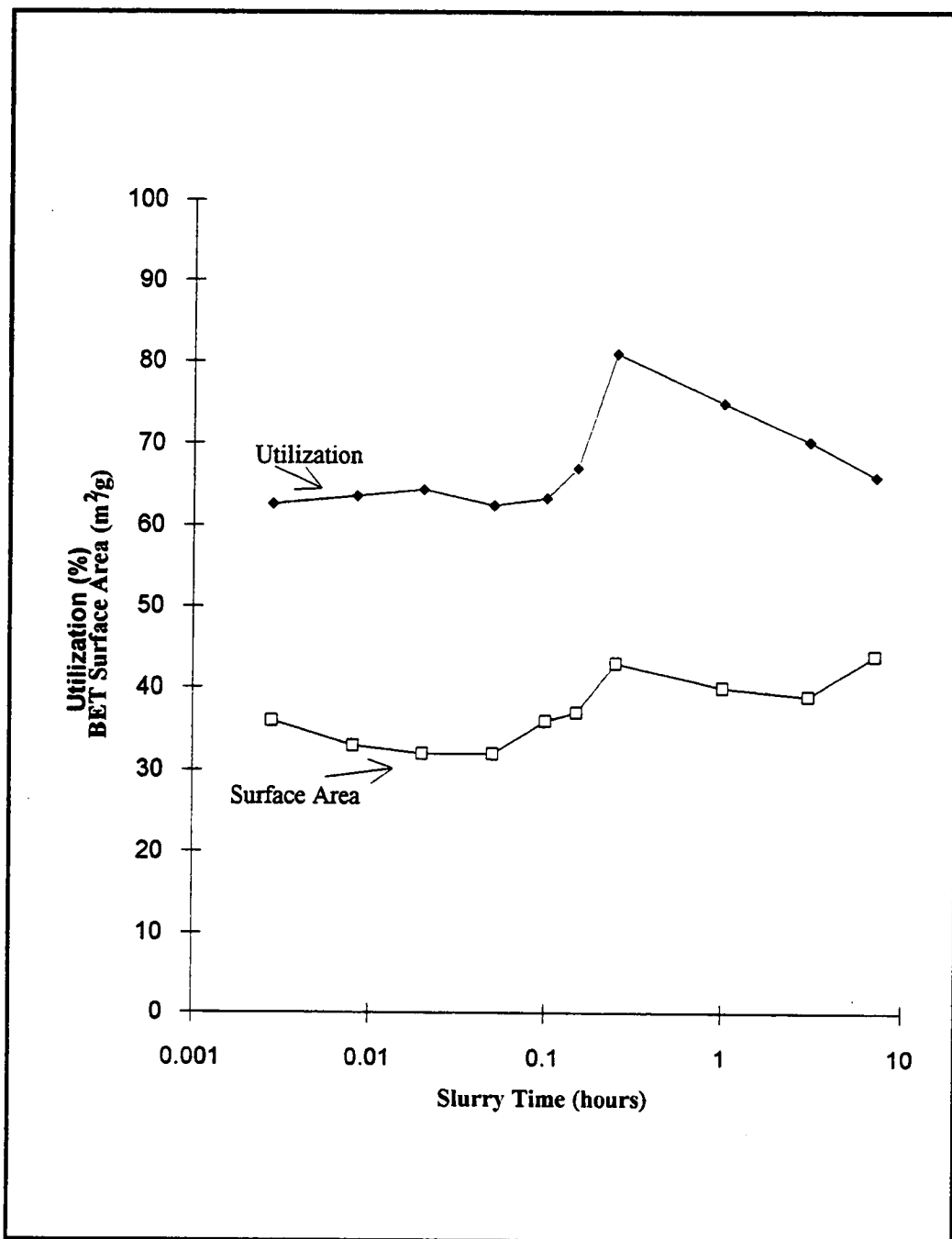


Figure 5.14. Utilization and surface area development in silica:CH 1:1 samples.

mixed would have been 250 m²/g. The dramatic loss of surface area, when comparing 250 to 36 m²/g, seems to be due to the rapid solubility of the silica under the high pH conditions created by the CH. This is further supported by the fact that the silica, slurried for three hours without the addition of CH, exhibited a surface area of 386 m²/g. This demonstrates that loss of surface area experienced when the two components are slurried together is not merely a result of silica's response to water. The slight drop in surface area of the amorphous silica when slurried with no CH addition may be due to the fact that it is slightly soluble in water, thus causing some slight alteration of the surface structure.

Greenberg (1957) proposed that the reaction between CH and a similarly soluble form of silica in aqueous solutions of 82 °C (151 °F) occurred not in solution, but in situ on the solid surfaces. Greenberg et al. (1960) theorized that the reaction is initiated on the silica surface with CH, and that, as the CH content increases, the CH becomes diffused throughout the polymeric silica structure. If indeed the reaction were initiated on the surface of the amorphous silica in the present study, then preventing immediate dissolution of the silica and thus retaining the silica in solid form should increase the surface area of the products. It was known that pH controls the solubility of silica and that the routine method of sorbent preparation caused an immediate rise in pH and subsequent dissolution of the silica. The goal of this portion of the present study was to determine if the method and rate of adding CH to silica in solution, or vice versa, might affect the dynamics of dissolution and reaction, and thus affect the resulting surface area. The method of preparation was described in section 4.1.3 of the chapter on experimental procedures. Four samples resulted from adding CH to silica or silica

to CH in hot or cold solutions. The proportions of components were 1:1, and the slurry time was 15 minutes.

Figure 5.15 demonstrates the surface area results. They follow the same trend as did the utilization results in section 5.3.1.4. The addition of silica to CH in solution resulted in higher surface area than adding CH to silica, and the hot addition preparations demonstrated higher surface area than did the cold additions. The original sorbent preparation, in which both components were slurried together from the start, was still the best performer. Additional information gained from this experiment is that the amorphous silica appeared to enter solution rapidly in cold solutions as well as hot solutions as evidenced by the surface area of the cold additions. The sample in which CH was added to silica had a surface area of 21 m²/g, and the reverse addition had a surface area of 25 m²/g, both little more than the surface area of CH alone, and dramatically less than that of the silica. The probable cause of the lower surface area for the cold-processed samples as compared to the hot-processed samples is that the calcium silicate hydrate was able to form more rapidly aided by heat than without heat.

5.3.2.3 Relationship between sorbent utilization and BET surface area

Figure 5.16 demonstrates graphically the relationship between BET surface area and sorbent utilization for all the amorphous silica/CH sorbents. In general, there is a positive relationship between the two parameters. The equation for the best fit line is $Y = 35.33 + 0.56X$, and the regression coefficient, R^2 , is 0.31. While the 1:1 silica:CH ratio had the sample with the highest utilization, the 1:2 ratio had a sample with nearly the same utilization, and it was the 1:2 and 1:3

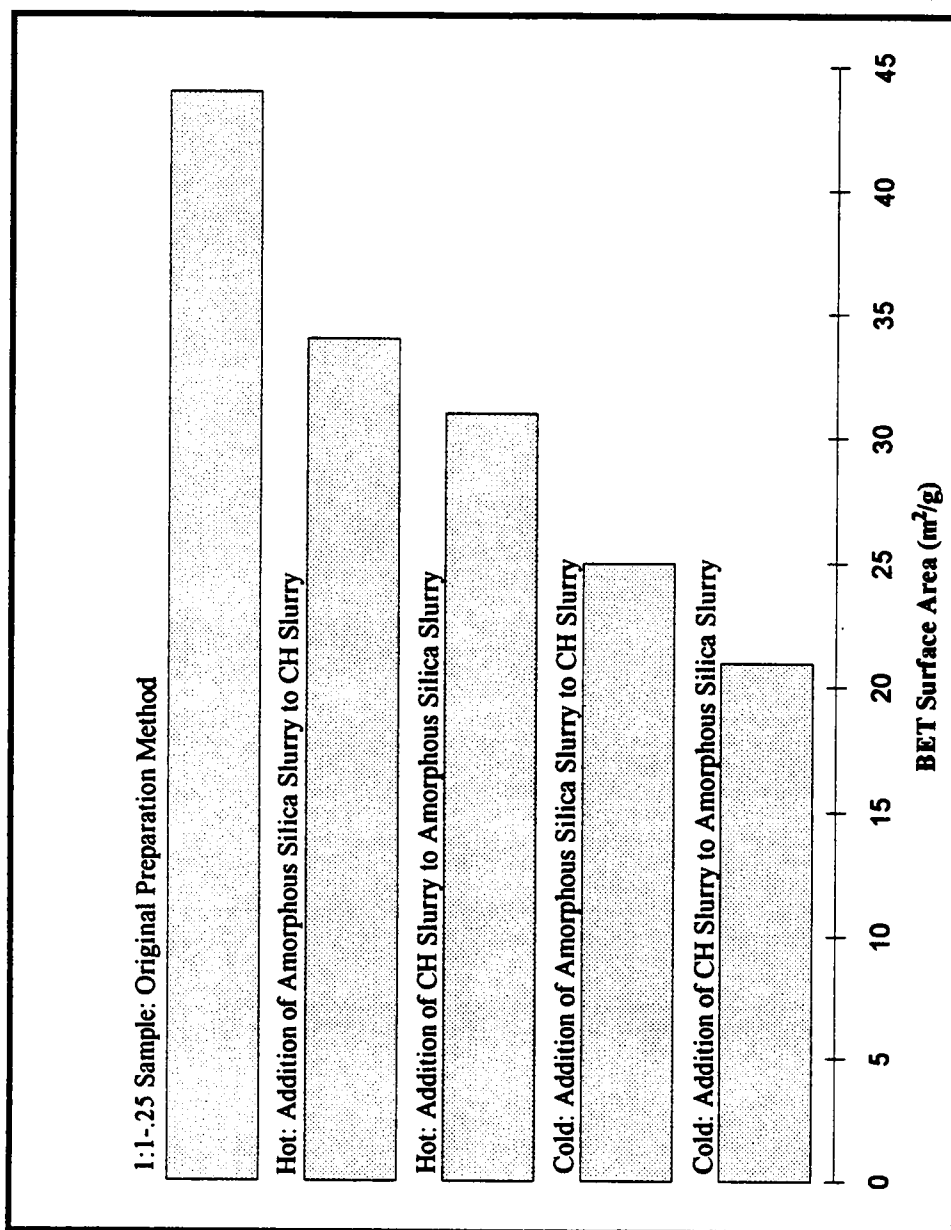


Figure 5.15. Effect of controlled rate addition of components on BET surface area.

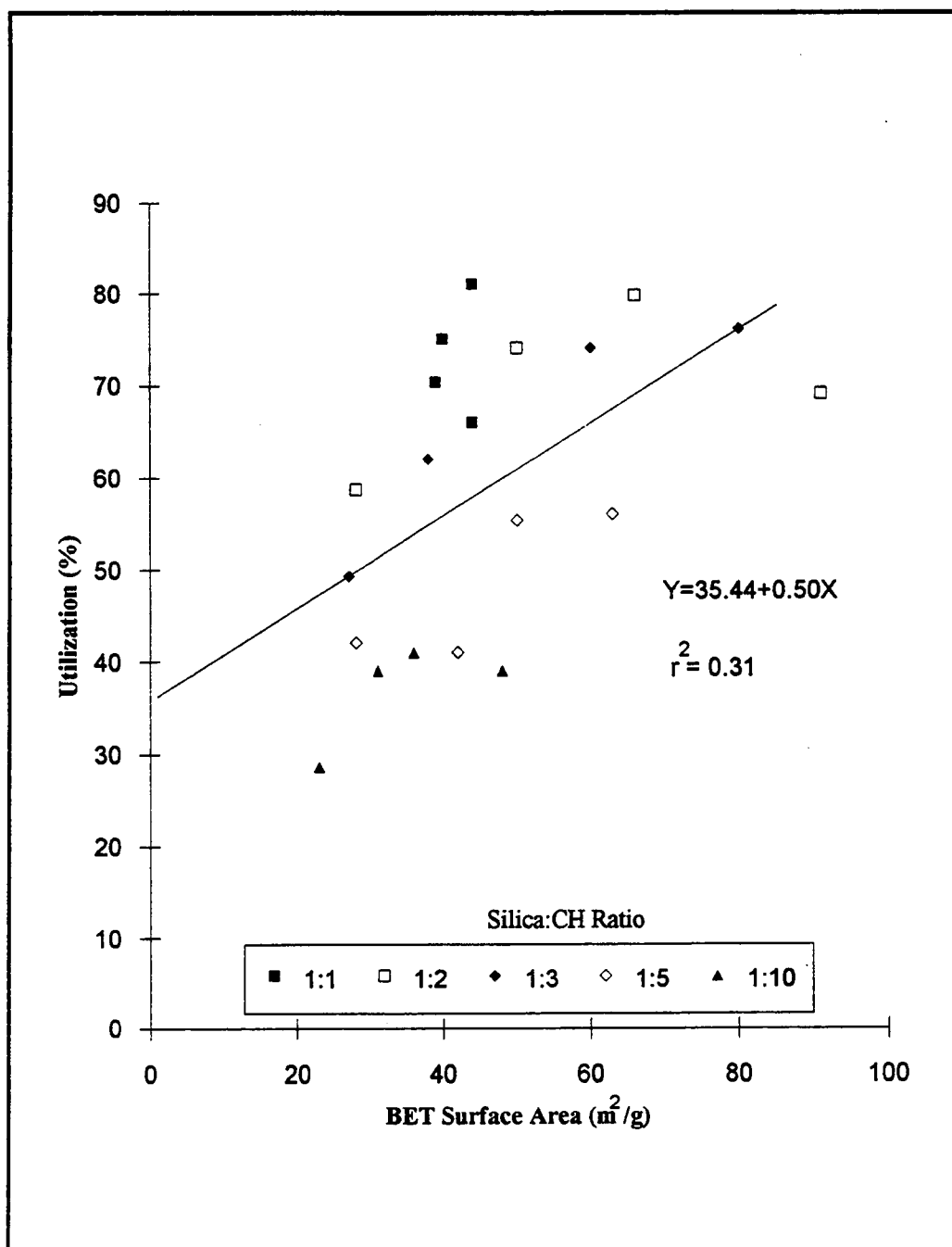


Figure 5.16. BET surface area versus utilization for amorphous silica/CH sorbents.

ratios which had the samples with the highest BET surface area. The R^2 value indicates that only 31% of the variation in utilization can be accounted for by the change in surface area.

5.3.4 X-ray diffraction analysis

Powder diffraction analysis was performed on many of the sorbents in order to assess the phase progressions as a result of slurry time length and component ratio. By comparing the peaks on the x-ray patterns, it was possible to observe the decrease in CH with ongoing reaction of the CH and silica over increasing slurry time. At the same time it was possible to see that the calcium silicate hydrate phase was increasing. Alternately, for any constant slurry time, it was evident from the patterns that the amount of calcium silicate hydrate phase formed was greater for samples containing proportionally more silica. Figure 5.17 demonstrates how to read the legend on the x-ray patterns.

The blue vertical lines in Figure 5.18 demonstrate the location of the peaks for the calcium silicate hydrate referred to in the JCPDS files simply as calcium silicate hydrate (file #33-306), which refers to the least crystalline calcium silicate hydrate. (The calcium silicate hydrates with greater structural integrity are given actual mineral names.) These are the JCPDS two-theta values for the peaks associated with this phase. Refer to Chapter 2 for a discussion of the calcium silicate hydrate which would be expected under the preparation conditions of this study. There are three peaks associated with this phase, and their locations are well illustrated by the vertical lines. This phase is known to be fairly amorphous. Its lack of a well-defined structure explains why there are only three peaks. The

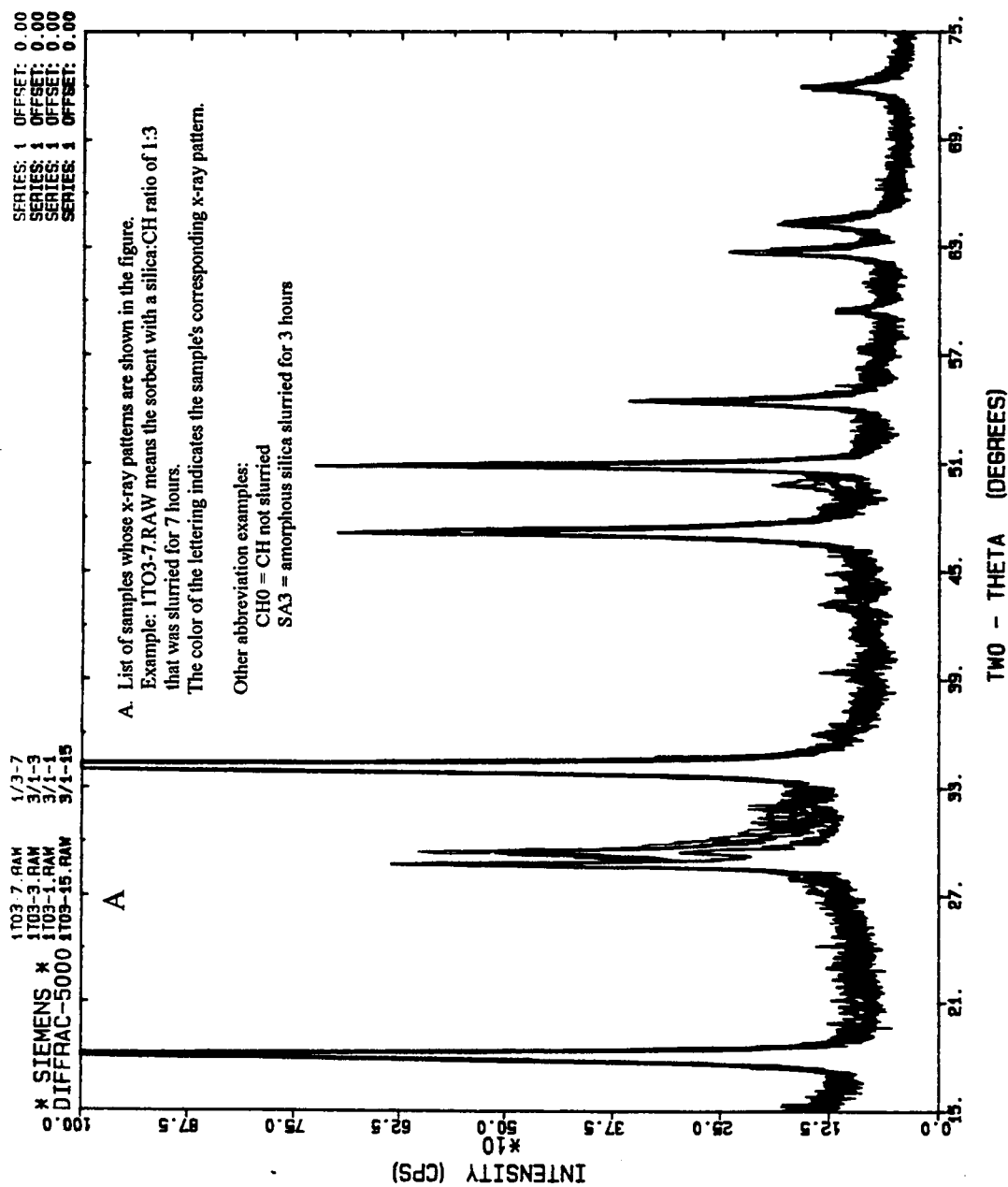
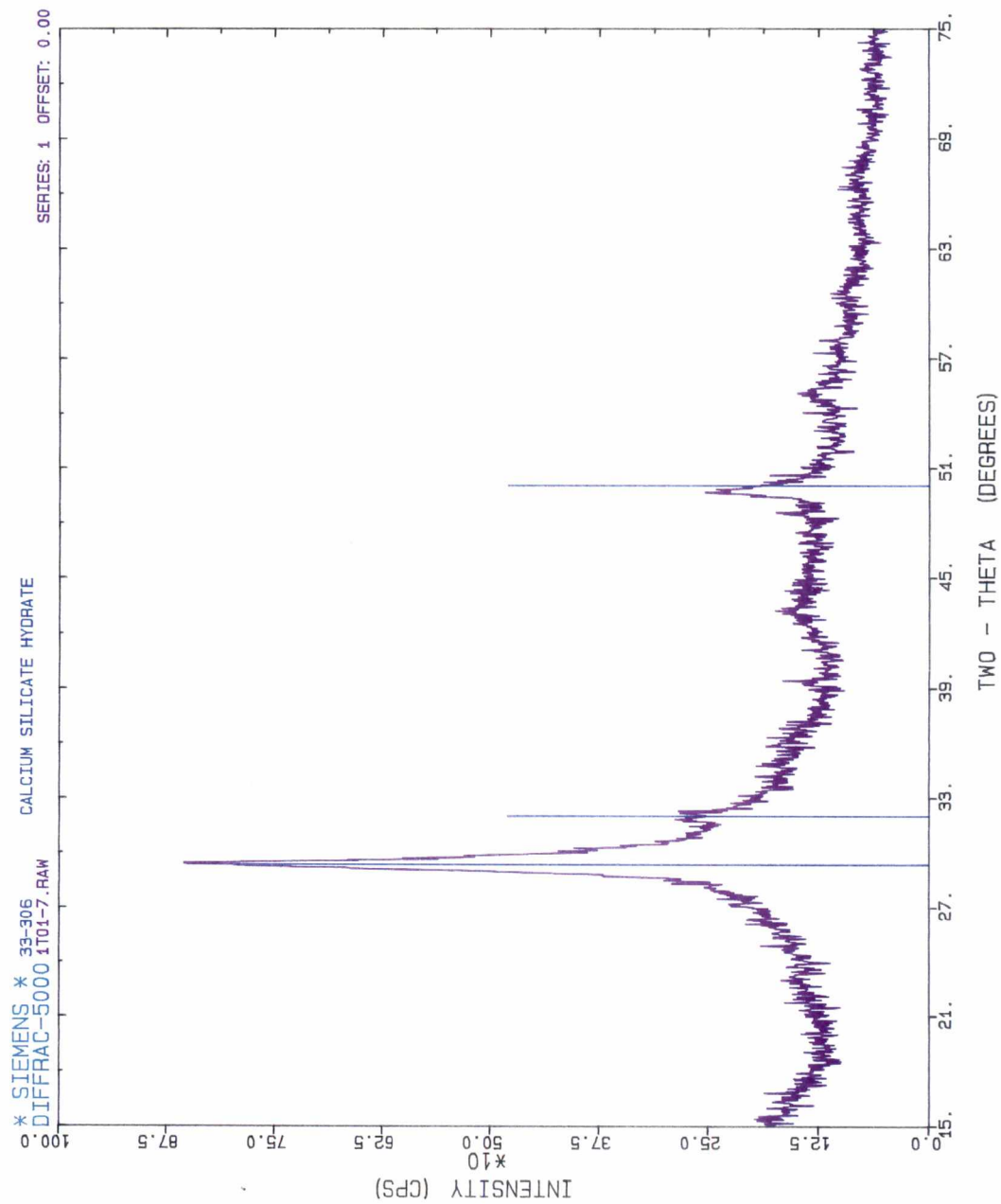


Figure 5.17. Explanation of legend for x-ray diffraction patterns.

Figure 5.18. X-ray diffraction pattern of sorbent prepared from amorphous silica:CH ratio of 1:1, slurried for 7 hours.

Note: Vertical lines demonstrate the three calcium silicate hydrate peaks at 29.5, 32, and 50° two-theta.



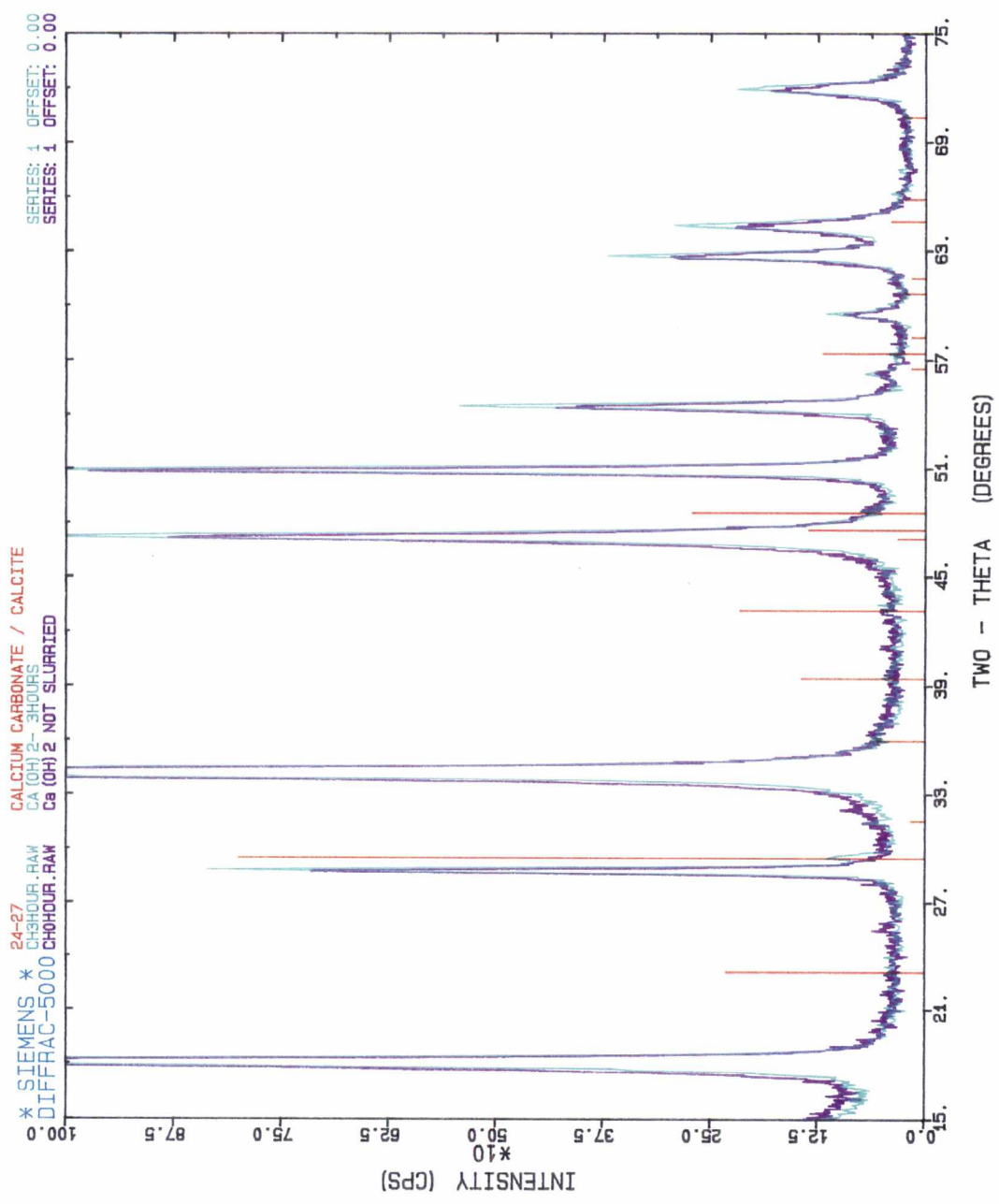
x-ray pattern presented in Figure 5.18 was from the 1:1 silica:CH ratio sorbent batch which had been slurried for 7 hours. The CH was absent and the silica, if present, was amorphous. Thus the remaining peaks were the result of the calcium silicate hydrate. In all the sorbent x-ray diffraction patterns that demonstrated calcium silicate hydrate peaks, the far left peak of the three calcium silicate hydrate peaks (i.e., the one at the lowest two-theta angle) consistently exhibited the greatest intensity. For that reason, it has been referred to in this text as the primary peak, denoting nothing more than its prominence.

There is a small apparent misalignment in Figure 5.18 between the published location of the far right peak (i.e., the vertical line) and the location of the corresponding actual peak produced by this sample. Historically, this peak has been reported at both 1.82 Å (Taylor, 1986) and 1.83 Å (Brunauer, 1962). The vertical line from the JCPDS data is placed, in this case, at 1.82 Å (two-theta = 50.05°). The actual peak produced by the sample occurs at 1.83 Å (two-theta = 49.81°). Both locations are consistent with the literature.

Figure 5.19 demonstrates the peaks obtained from the samples designated as CH. Both the peaks for CH in its original form and for CH after it had been slurried for three hours, then vacuum filtered and dried, are shown. The vertical lines demonstrate the expected locations of the calcium carbonate peaks. The purpose of showing where the calcium carbonate peaks would be expected is to illustrate the amount of this compound which developed in three hours of slurrying CH. Calcium carbonate occurs as a result of the reaction of the calcium in the CH with atmospheric carbon dioxide. The calcium carbonate peak of greatest intensity occurs very close to the primary calcium silicate hydrate peak. It

Figure 5.19. X-ray diffraction patterns of CH.

Note: One sample was slurried for 3 hours in the absence of silica. The other was not slurried. Vertical lines indicate the two-theta values at which calcium carbonate occur. The small peak at 29.5° two-theta demonstrates that a minor amount of calcium carbonate formed during three hours of slurrying the CH.



was necessary to determine if the calcium silicate hydrate peak might actually be a calcium carbonate peak. This was done by slurrying the CH without silica in order that no calcium silicate hydrate would form. This allowed the peak occurring at this position to be identified as calcium carbonate without confusion. Clearly, only a minimal amount of calcium carbonate was formed during a lengthy slurry. The pronounced peaks in this position in the diffraction patterns of the silica/CH sorbents in the following sections, therefore, are attributable to calcium silicate hydrate.

Figure 5.20 is a diffraction pattern of the amorphous silica in both its original form and after it had been slurried for three hours. As this type of silica is amorphous, it exhibits no true peaks, but it does produce a characteristic "amorphous" hump centered at two theta equals 22° . As with the CH, the three hour slurry caused no discernible displacement in the diffraction pattern. It will be later noted that in the patterns produced by the sorbents little or no evidence of this hump remains, indicating the removal of silica as SiO_2 .

5.3.4.1 Effect of slurry time and component ratio

Diffraction patterns for silica:CH ratios of 1:10, 1:5, 1:3, 1:2, and 1:1 shown in Figure 5.21 (a), (b), (c), (d) and (e), respectively, demonstrate the effect of increasing slurry time for a given silica:CH ratio. The patterns for the 15 minute, 1 hour, 3 hour, and 7 hour slurry times are illustrated, superimposed on one another in order to facilitate comparison from one slurry time to the next. Vertical lines indicate the three peaks which represent calcium silicate hydrate. All other peaks represent CH. The x-ray patterns, viewed progressively from

Figure 5.20. X-ray diffraction patterns of amorphous silica.

Note: One sample was slurried for 3 hours in the absence of CH. The other was not slurried. The location of the "hump" in the pattern is characteristic for amorphous silica.

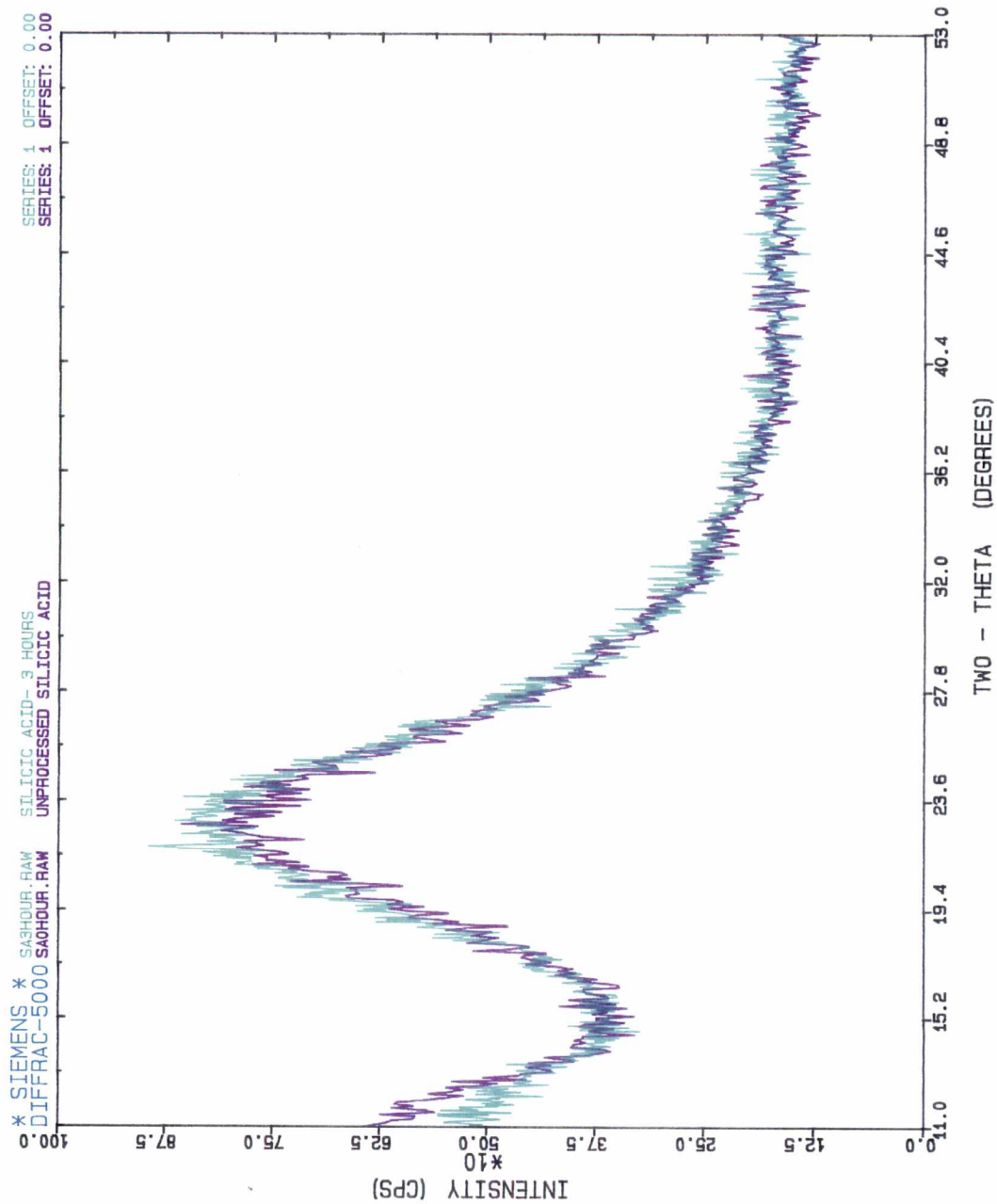
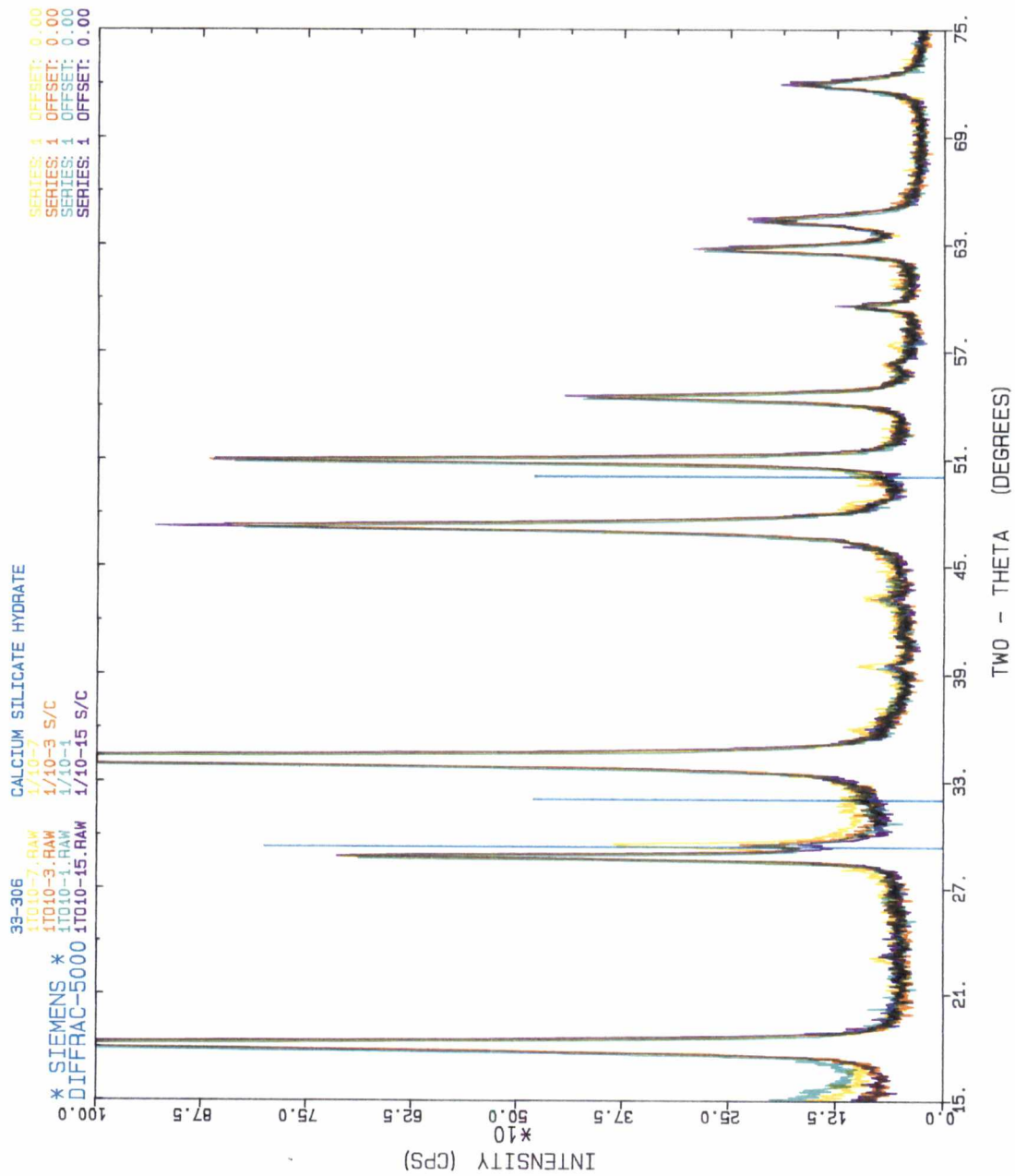
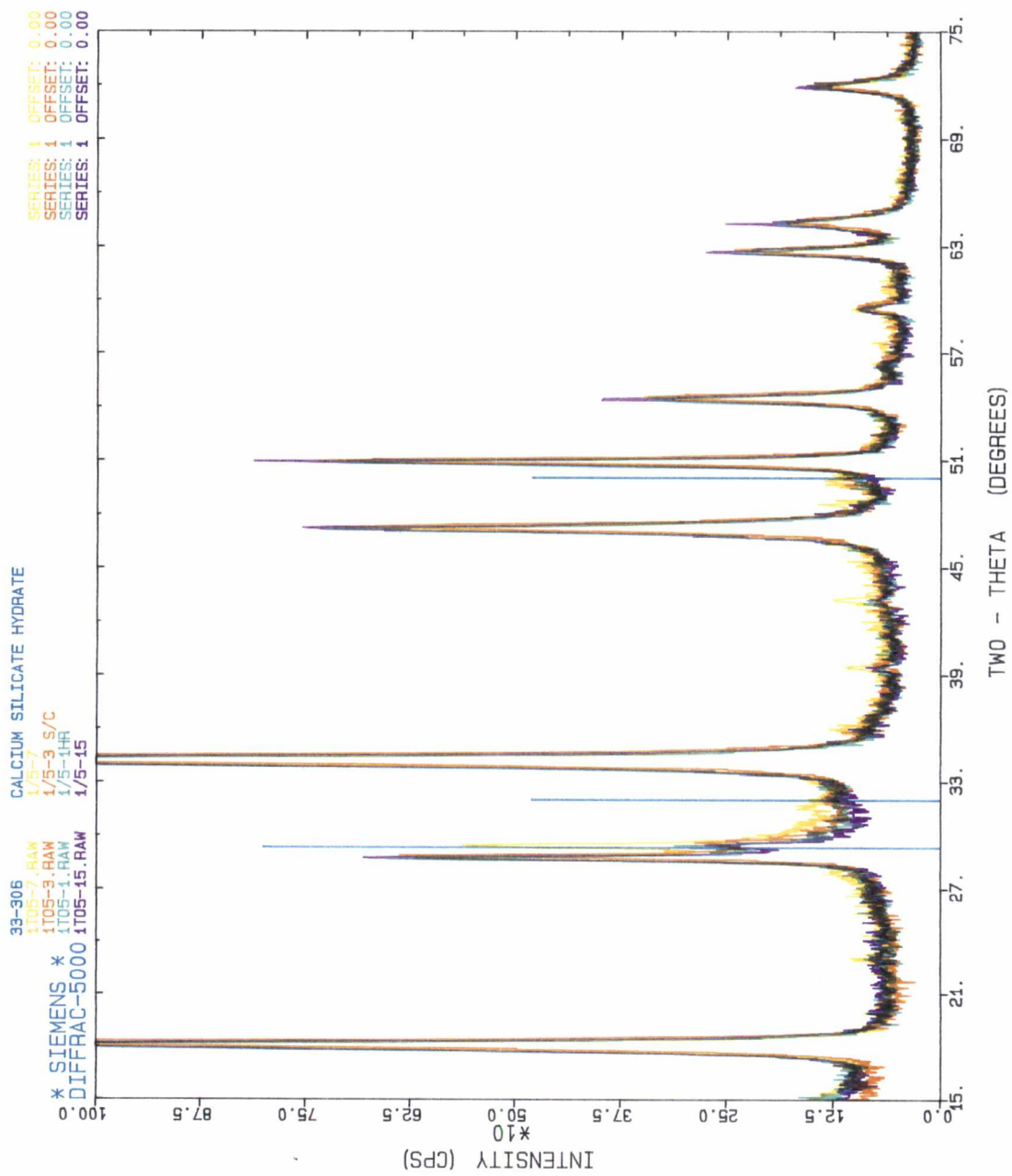
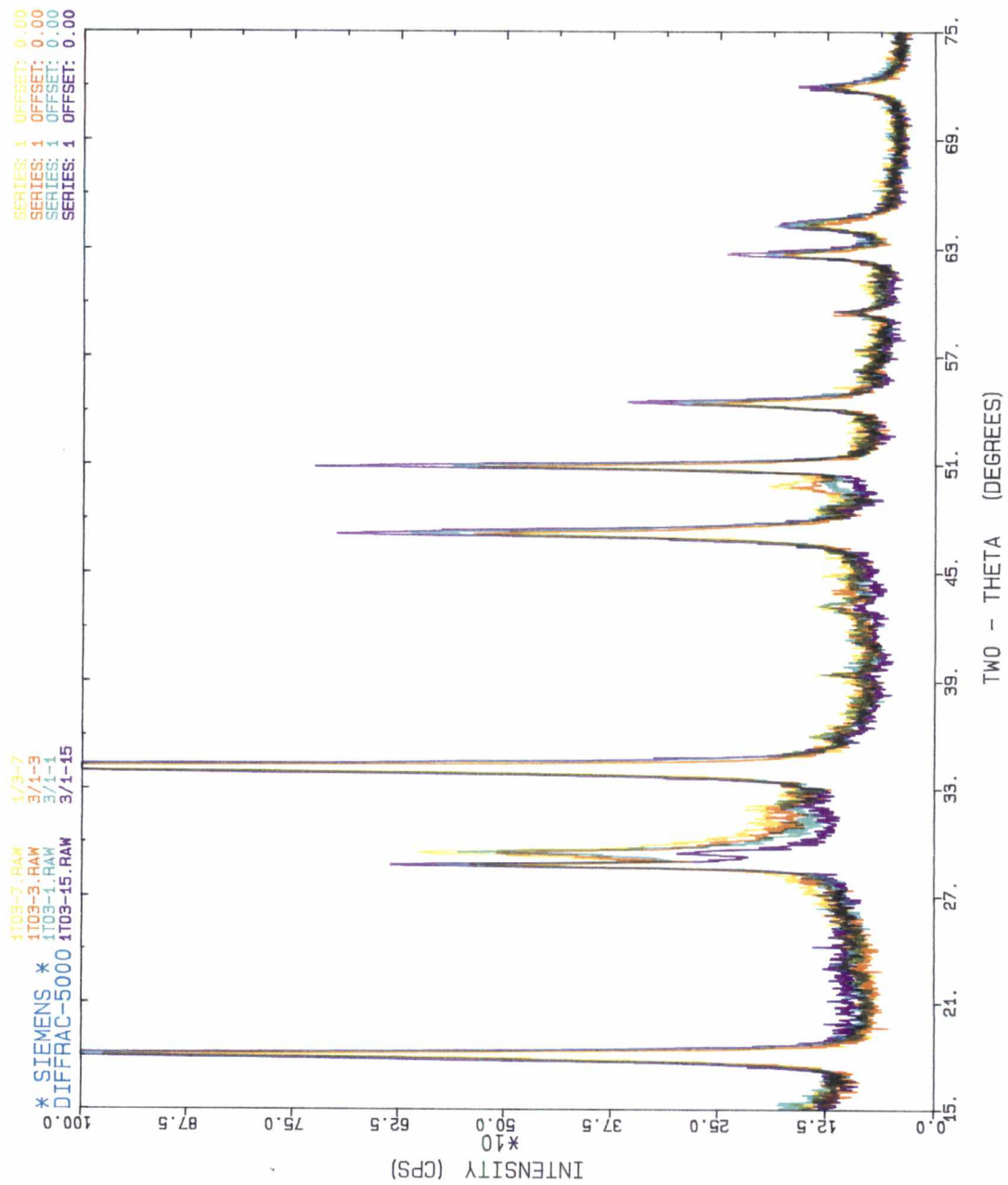


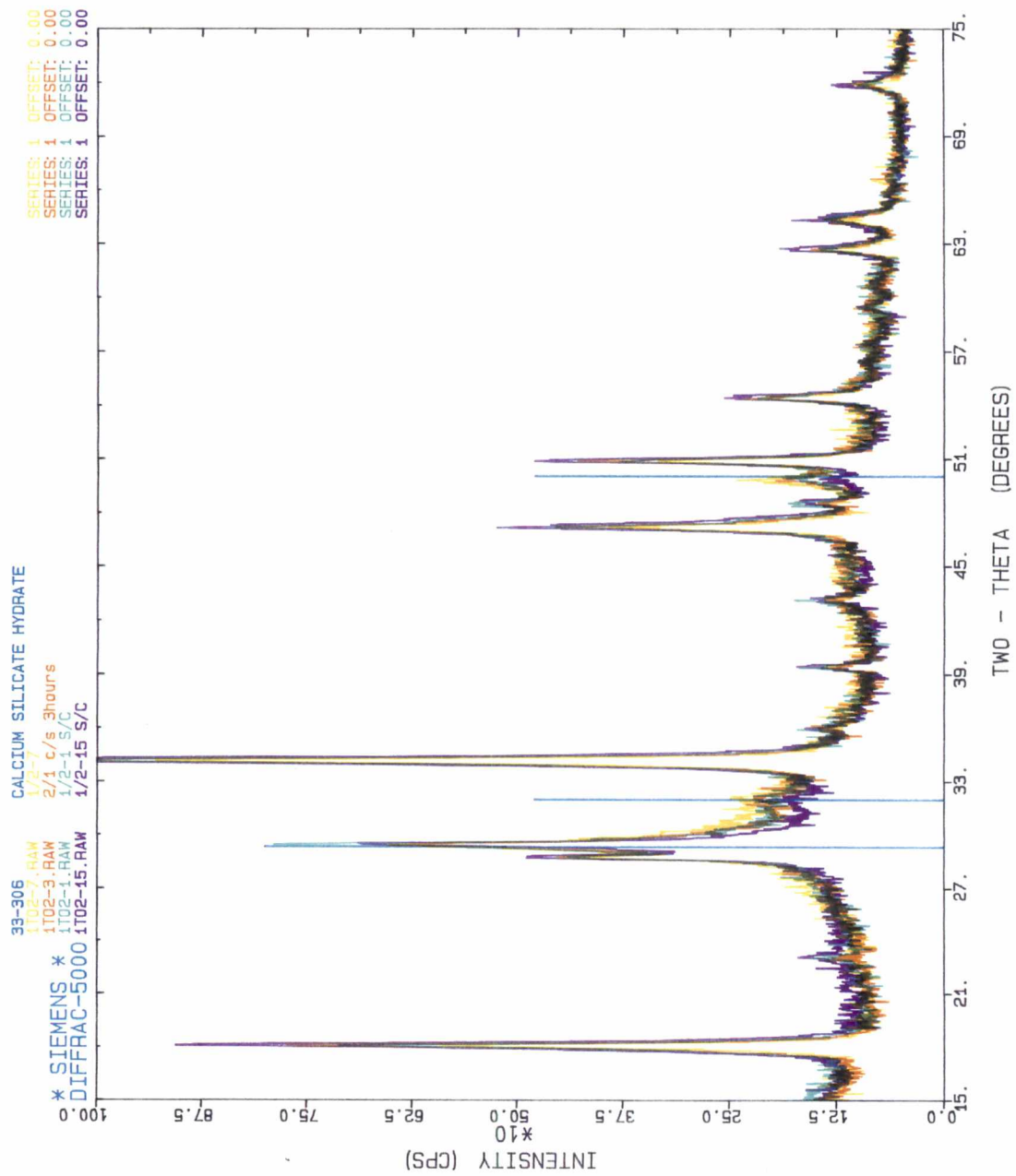
Figure 5.21. X-ray diffraction patterns demonstrating the effect of increasing slurry time on the development of calcium silicate hydrate peaks. (a) amorphous silica:CH ratio of 1:10, (b) amorphous silica:CH ratio of 1:5, (c) amorphous silica:CH ratio of 1:3, (d) amorphous silica:CH ratio of 1:2, (e) amorphous silica:CH ratio of 1:1.

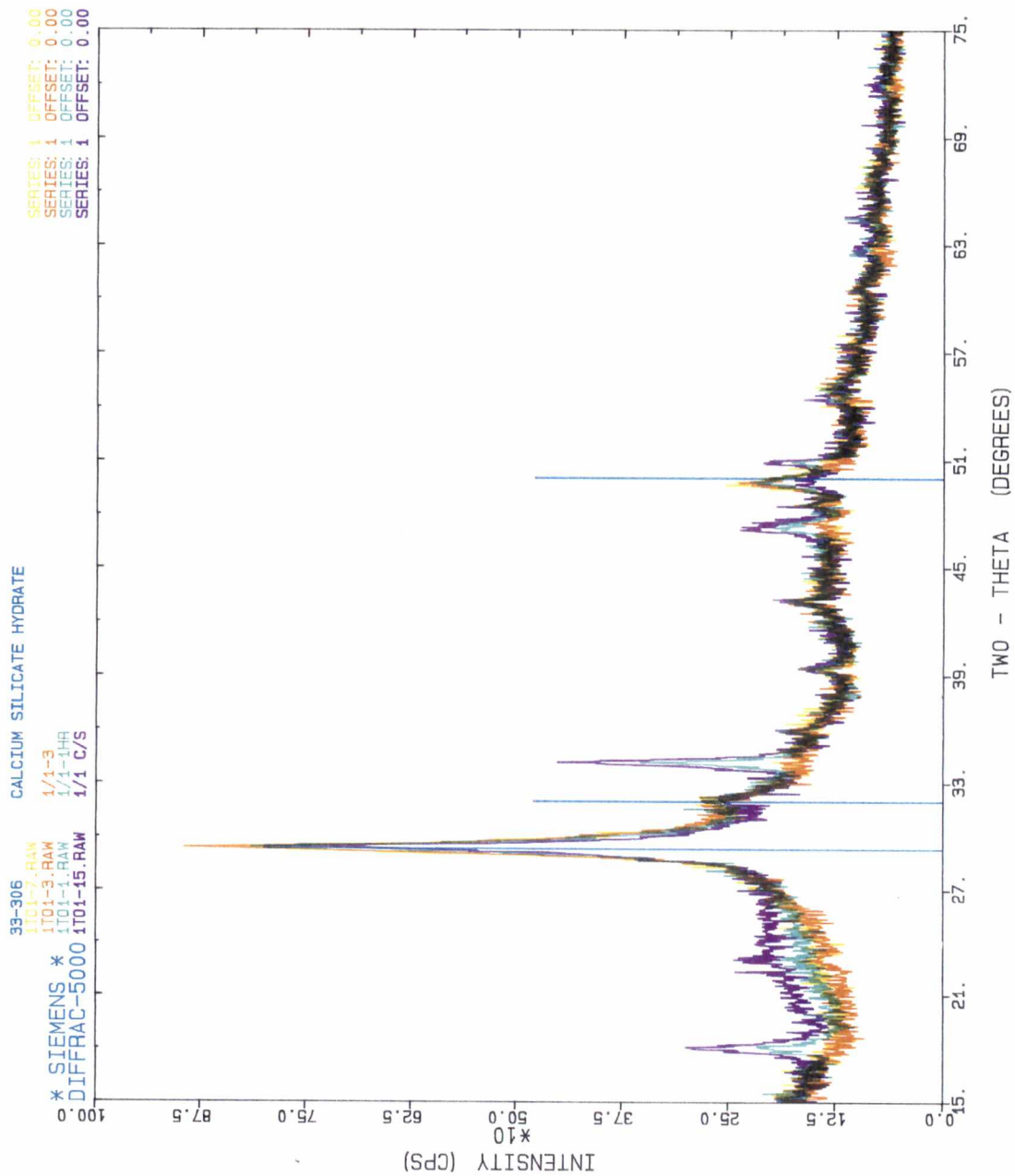
Note: The vertical lines demonstrate the three calcium silicate hydrate peaks at 29.5, 32, and 50° two-theta. All other peaks are due to CH. The absence of CH peaks for the 3 and 7 hour slurry times in (e) demonstrate that all the CH has been utilized in reaction with silica to produce calcium silicate hydrate. The 15 minute slurry time exhibits a slight hump in the pattern between 21 and 27°, indicating that there was unreacted silica at that time. By 7 hours there is no evidence of an excess of silica or CH. (a) through (d) demonstrate that there was excess CH at all slurry times for these ratios.











Figures 5.21 (a) through (e), demonstrate that more calcium silicate hydrate was able to form as the silica:CH ratio was increased, and, correspondingly, that there was less CH remaining at each higher silica:CH ratio. In each figure the progressive decrease in intensity of the CH peaks between 15 minutes and 7 hours reflects the loss of CH by reaction with silica which caused an increase in the intensity of the calcium silicate hydrate peaks as more of that compound was formed.

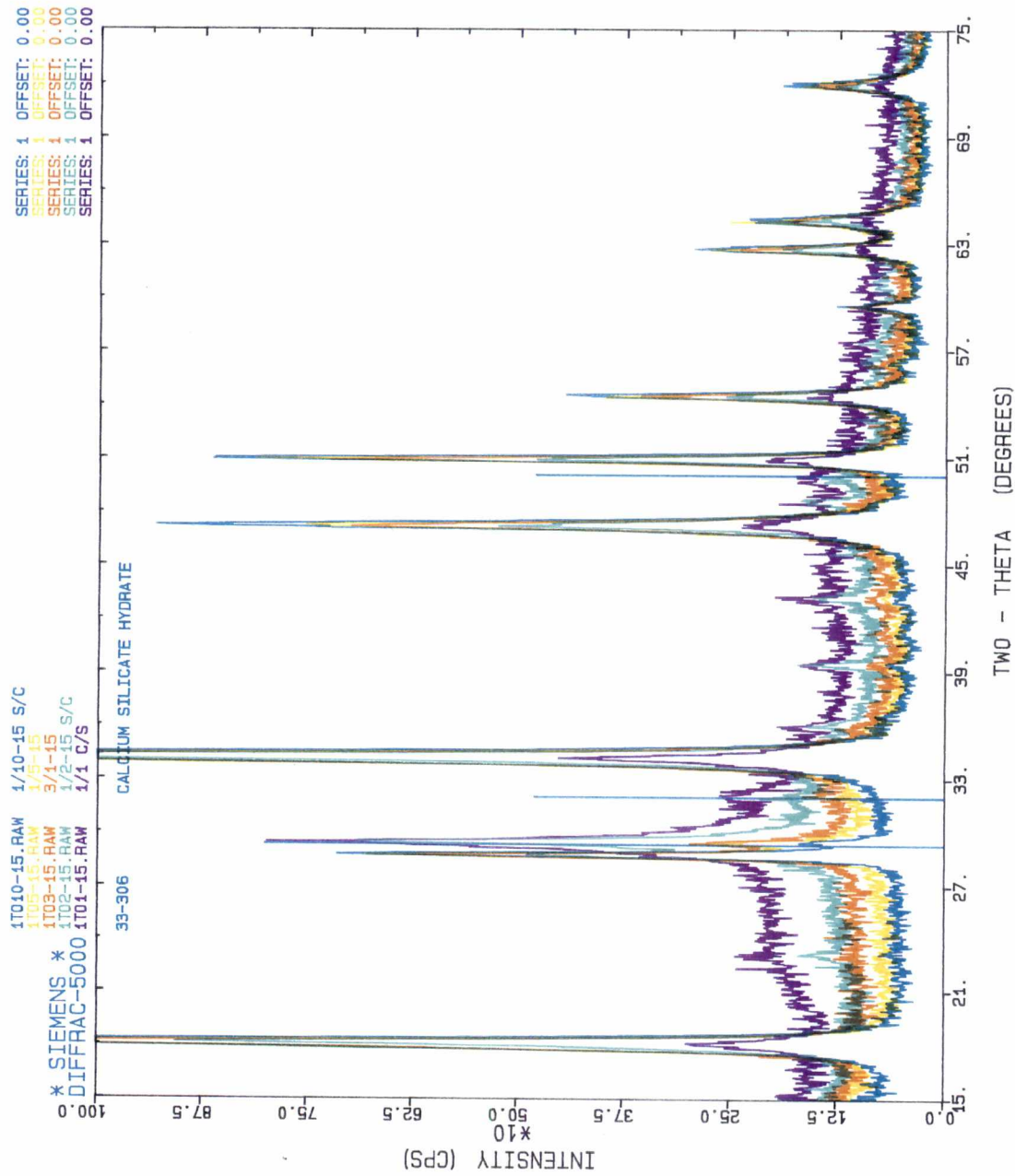
Figure 5.21 (e) is the only x-ray pattern to demonstrate an absence of CH at any slurry time. The samples which were slurried for 3 and 7 hours have no peaks in the CH two-theta locations, as evidenced by the way in which the plotter trace is drawn across the base of the CH peaks which were made by the 15 minute and 1 hour samples. Apparently, the 1:1 ratio contained enough silica to cause complete reaction of the CH. Another element seen in this figure and not occurring in patterns of the silica:CH ratios containing less silica is the remnant of the silica hump between 22 and 27° two-theta in the sample slurried for 15 minutes. It, too, is gone by 7 hours of slurry.

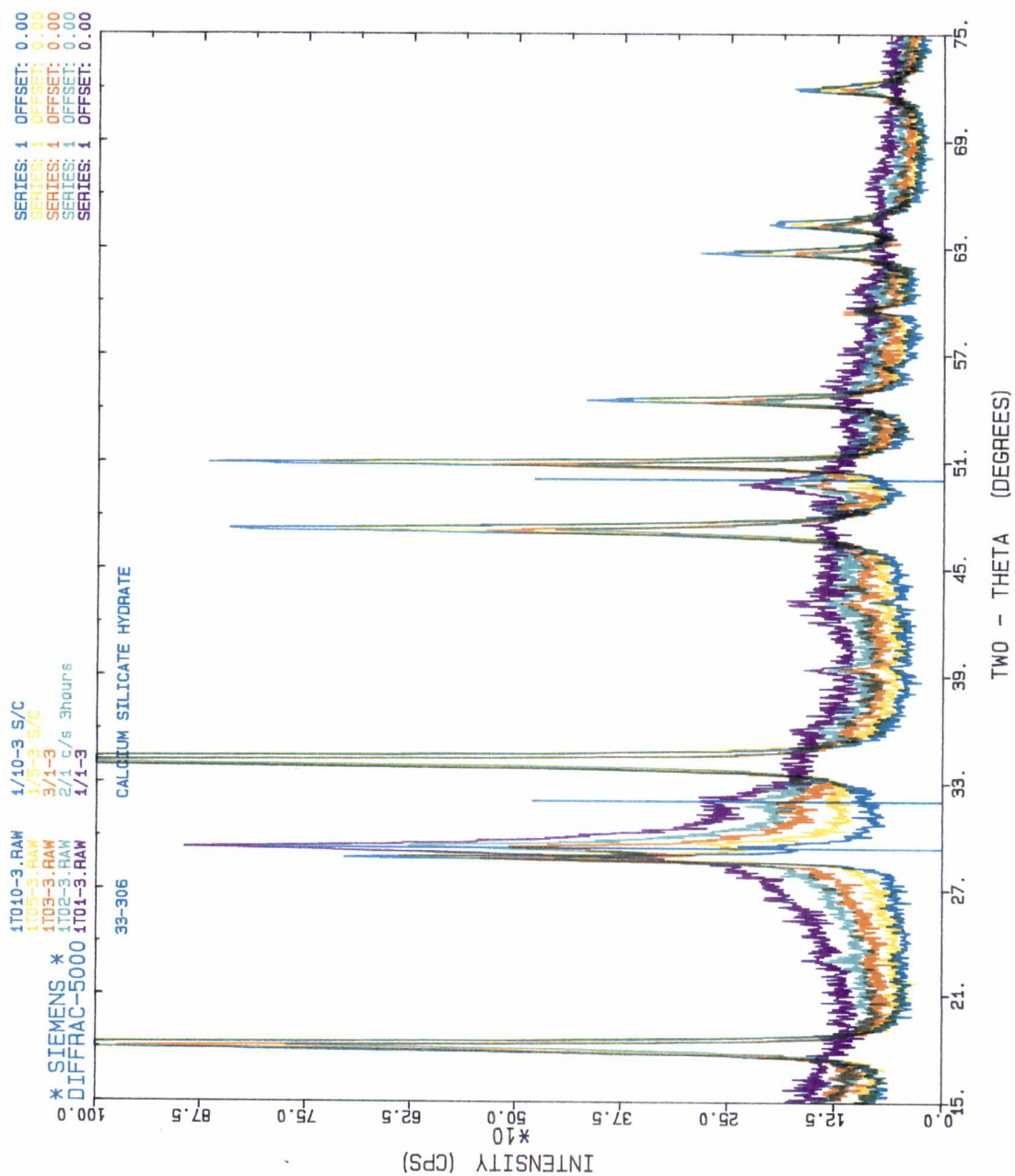
At the silica:CH ratios of 1:10, 1:5, and 1:3, the intensity of the primary peak (the first on the left) increases at each longer slurry time (Figure 5.21 (a), (b), and (c), respectively). Conversely, the primary peak appears to reach a maximum in intensity, followed by a decrease in intensity, after 1 hour at the 1:2 ratio and after 3 hours at the 1:1 ratio, (Figure 5.21 (d) and (e), respectively).

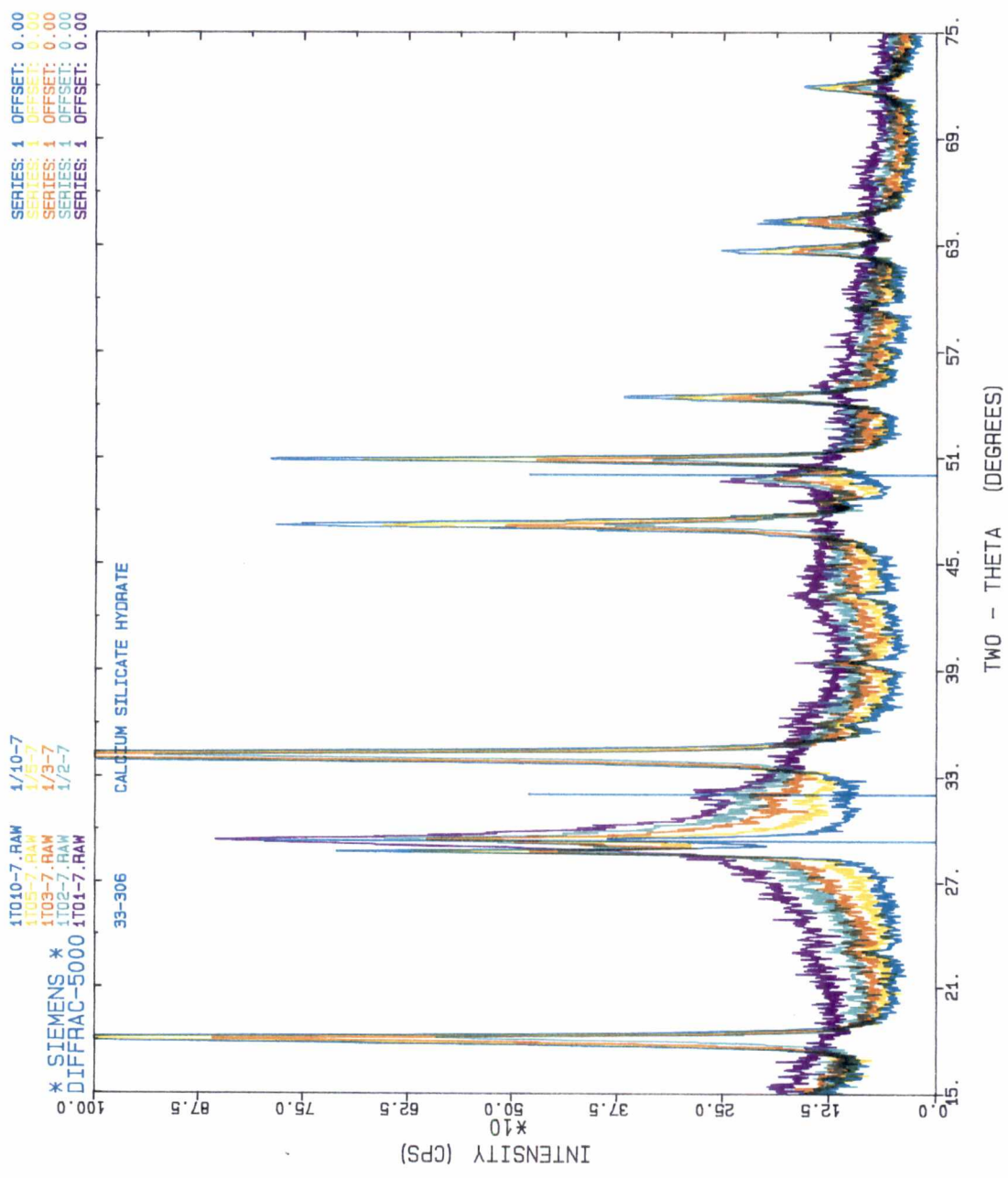
Figures 5.22 (a), (b), and (c) shows the effect of increasing the silica:CH ratio at a single slurry time on the development of calcium silicate hydrate as reflected by the increasing intensity of the peaks for this phase. Each figure is

Figure 5.22. X-ray diffraction pattern demonstrating the effect of increasing amorphous silica:CH ratio on the development of calcium silicate hydrate peaks for 3 slurry times. (a) 15 minute slurry, (b) 3 hour slurry, (c) 7 hour slurry.

Note: The vertical lines demonstrate the three calcium silicate hydrate peaks at 29.5, 32, and 50° two-theta. All other peaks are due to CH.







composed of five patterns, one for each silica:CH ratio, superimposed on one another. All five samples represented in a single figure were slurried for the same length of time. As a result, slurry time is a constant in the figures, and the change in peak heights of the calcium silicate hydrates are the response solely to the change in silica:CH ratio. These figures make apparent the amorphous hump associated with the calcium silicate hydrate. The hump occurs approximately between 23 and 38° two theta, and is most apparent between 26 and 31°. Figure 5.22 (a) demonstrates it most clearly where the vertical gaps occur between colored traces in this two-theta range. While each sorbent with successively more silica has a higher base line than the preceding one, the hump representing amorphous material is still higher. Both the first and middle calcium silicate hydrate peaks are located on top of this hump in the x-ray diffraction pattern. The two primary observations from this set of patterns are that at any one slurry time the intensities of the three calcium silicate hydrate peaks are greater for the sorbents prepared with the higher proportions of silica and that the CH remaining in association with these is less. The implication of these observations is that more calcium silicate hydrate has been formed due to the availability of silica. At the same time, the CH remaining is accordingly less because it has been reacted with silica.

An attempt was made to measure the area under the primary calcium silicate hydrate peak in order to achieve a semi-quantitative representation of the amount of calcium silicate hydrate forming. The purpose of this exercise was to determine if utilization and area under the peak exhibited similar trends which would indicate a relationship between the amount of calcium silicate hydrate produced and the extent of utilization. The analytical reproducibility of hand

packed samples is questionable, and such measurements may not be reliable. The results of the area measurements were inconclusive, possibly for the reason referenced.

In summary, the x-ray diffraction analyses provided the first conclusive evidence that, in spite of the differences in sorbent utilization demonstrated in the reactor tests, the solids forming by reaction during slurring were not passing through a sequence of distinctly different phases. Indeed, it appeared that only the calcium silicate hydrate known as C-S-H(I) was forming. This particular hydrate, which was discussed in detail in section 2.2.3, is one of only two which form at slurry temperatures below 100 °C (212 °F), and is a rather amorphous material, which exhibits very few peaks in x-ray powder diffraction. X-ray diffraction studies of these poorly crystallized calcium silicate hydrate show just three characteristic spacings. The first and strongest appears at 3.06 Å, followed by weaker spacings at 2.81 Å and 1.83 Å (Greenberg et al., 1960). These spacings are demonstrated by peaks on the two-theta scale at 29.5, 32, and 50°, respectively.

5.3.5 Scanning electron microscopy analysis

The following sections describe the SEM observations of sorbents produced in this study. The morphology of the calcium silicate hydrate which form in solutions at temperatures less than 100 °C were described in section 2.2.3 on calcium silicate hydrate. C-S-H(I) was said to occur as thin, flexible sheets or crumpled foils. C-S-H(II) was described as fibrous in nature. It will be noted that none of the sorbents in the SEM photomicrographs of the present study presented

a fibrous or acicular morphology supposedly associated with C-S-H(II). The samples viewed by SEM in the course of this work tended to demonstrate the crumpled foil appearance in varying degrees of development (similar to Figure 2.9), although some samples tended to have an amorphous appearance, probably relating to the degree of crystalline development. Figure 5.23 is an SEM microphotograph of CH and amorphous silica in the dry mixed (non-reacted) state. The starting morphological appearance can be seen in the figure. CH occurs in the right half of the photomicrograph, as noted by the angular and somewhat stacked appearance of the grains. The amorphous silica occupies the left half of the photomicrograph.

5.3.5.1 Effect of slurry time

Figures 5.24, 5.25, and 5.26 are photomicrographs of the silica:CH 1:1 ratio sorbents as the slurry time progresses from 10 seconds to 15 minutes to 7 hours, respectively. Each figure shows images at 6,000 and 12,000 times magnification. At only 10 seconds of slurry time the solid has an amorphous appearance. Figure 5.24 (a) has a CH appearance with amorphous coating. Figure 5.24 (b) looks more like the original (non-reacted) silica, but with slightly more surface character. Doubling its magnification, (Figure 5.24 c) demonstrates that there may be some incipient foil morphology in the background of the photo. The 15 minute slurry sorbent displays a dramatic development of the crumpled foil morphology (Figure 5.25 (a)). In error, the magnification was 6,900 rather than 6,000. As a result, the bar scale shown in the figure represents 4.3 μm , rather than 5 μm . Figure 5.25 (b) is 12,000 times magnification of the same area as

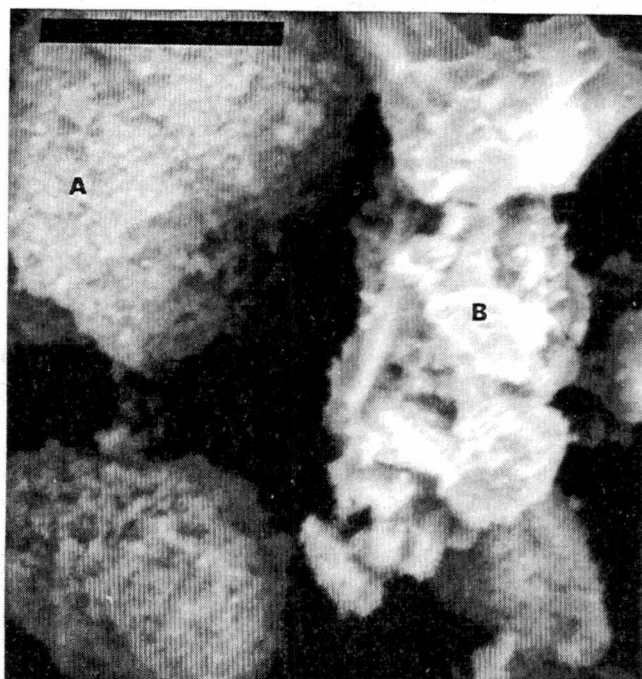
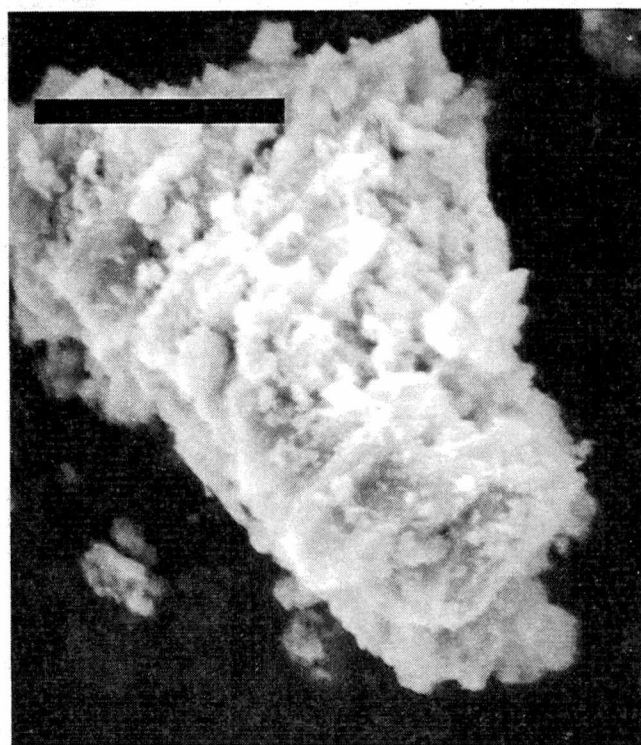


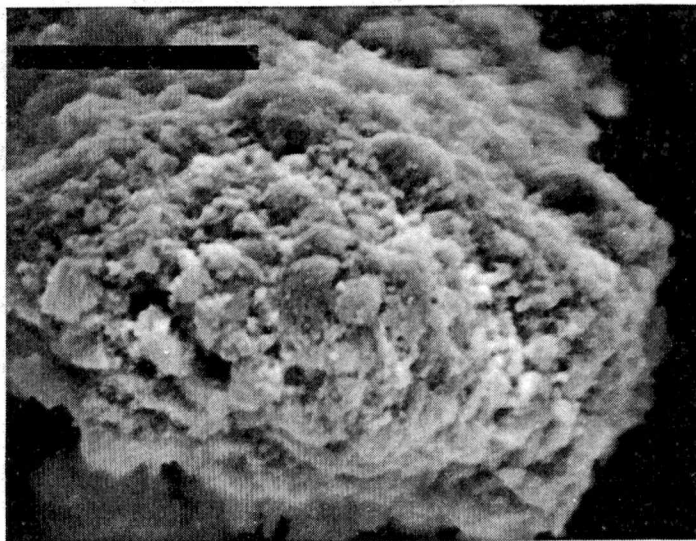
Figure 5.23. Electron photomicrograph of CH and amorphous silica, dry mixed. A = amorphous silica. B = CH. Bar = 5 μ m.



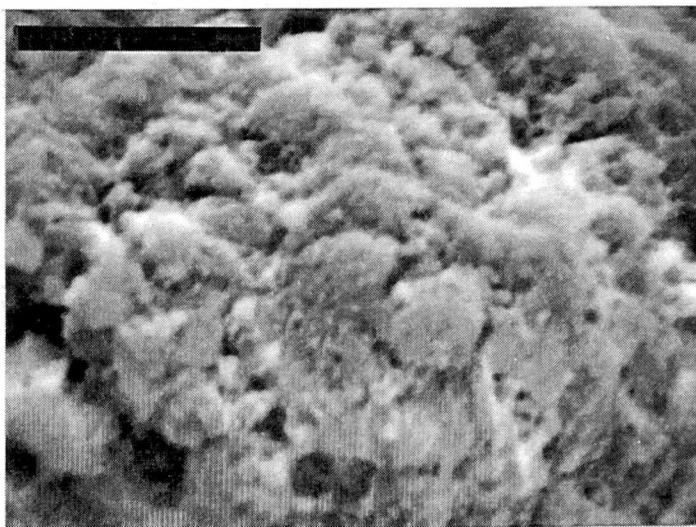
(a)

Figure 5.24. Electron photomicrographs of amorphous silica:CH 1:1 ratio sorbent. Sorbent slurried for 10 seconds.

(a) Particle retains CH appearance. Bar scale = $5\mu\text{m}$.



(b)

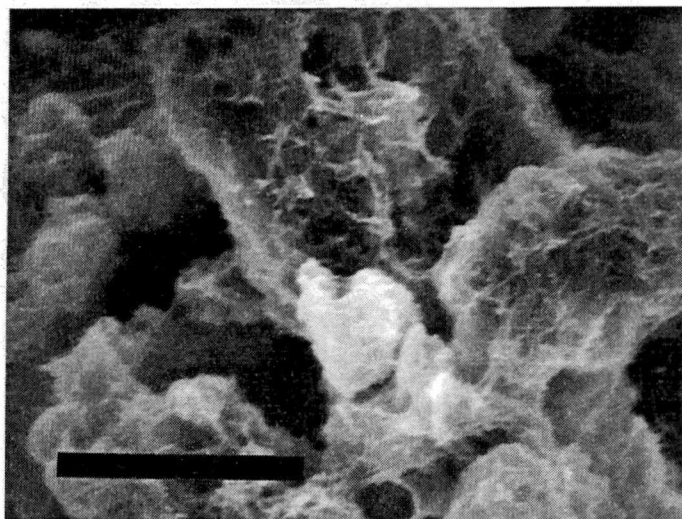


(c)

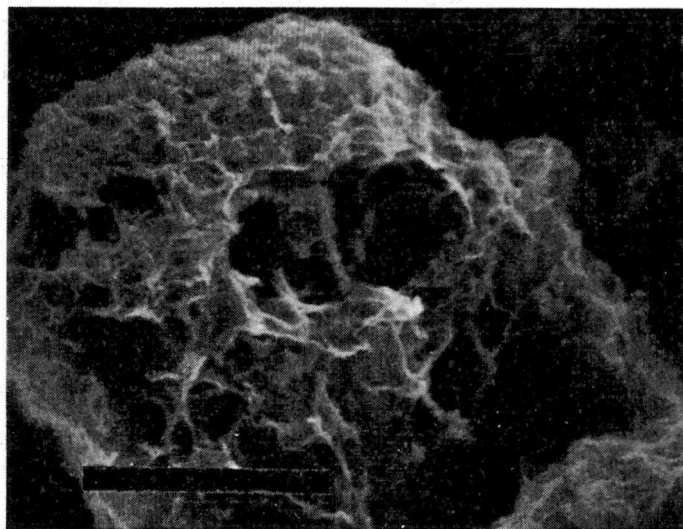
Figure 5.24. (continued)

(b) Particle retains amorphous silica appearance.
Bar scale = $5\mu\text{m}$.

(c) Magnification of (b). Bar scale = $2.5\mu\text{m}$.



(a)

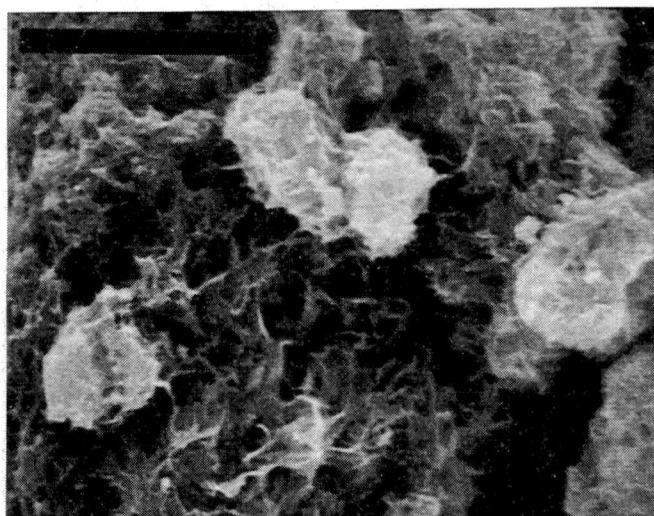


(b)

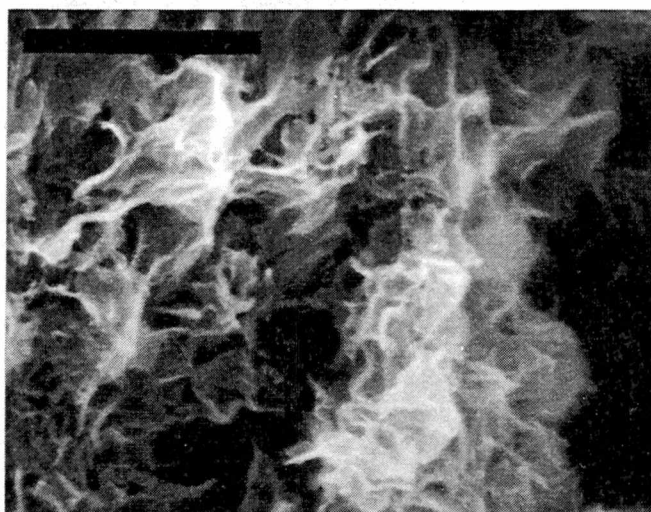
Figure 5.25. Electron photomicrographs of amorphous silica:CH 1:1 ratio sorbent. Sorbent slurried for 15 minutes.

(a) Bar scale = $4.3\mu\text{m}$.

(b) Magnification of (a). Bar scale = $2.5\mu\text{m}$.



(a)



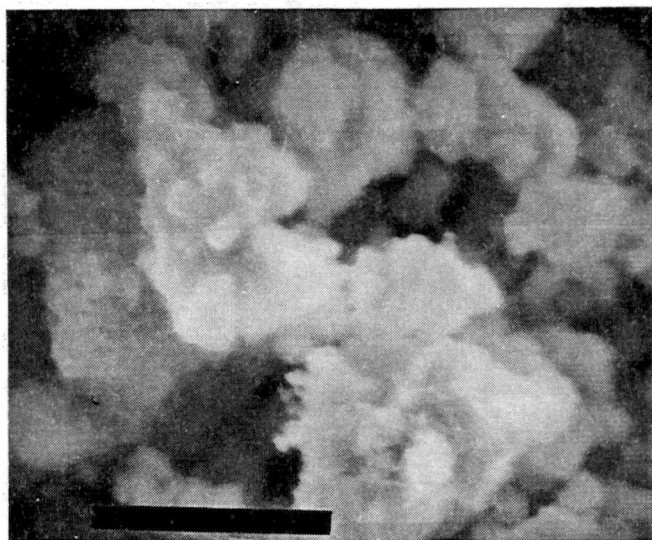
(b)

Figure 5.26. Electron photomicrographs of amorphous silica:CH 1:1 ratio sorbent. Sorbent slurried for 7 hours.
(a) Bar scale = 5 μm .
(b) Magnification of (a). Bar scale = 2.5 μm .

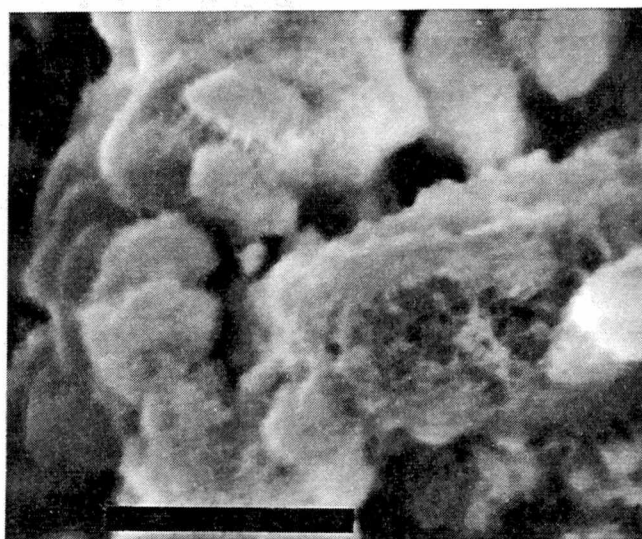
photograph (a). The solids' appearance is much more open than that of the 10 second slurry. The 7 hour slurry sorbent exhibited in Figure 5.26 (a) and (b) do not appear greatly different from the 15 minute samples. The fact that the 6,000 times magnification of the 7 hour sorbent looks to be the same magnification as the 12,000 times magnification of the 15 minute sorbent, and the 12,000 magnification of the 7 hour sorbent appears to be even more greatly magnified probably reflects a greater development of the surface at 7 hours than at 15 minutes.

5.3.5.2 Effect of component ratio

Sorbents in Figure 5.27 (a), (b), and (c) are 3 hour slurries of silica:CH ratios of 1:5, 1:3, and 1:2 respectively. Angular CH grains are apparent in photograph (a) which has the lowest silica:CH ratio. This is probably because the CH is in such high proportion that large quantities of non-reacted CH remained in the solids after slurrying. The material has an otherwise amorphous appearance, although some possible crumpled foil formation can be seen in the upper right part of the photograph. Some remnants of angular grains can be seen in photograph (b) of the silica:CH 1:3 ratio sorbent, and may be residual CH. Some visible surfaces are covered with a clearly emerging morphology, possibly the crumpled foils. The development of the surface is most apparent in photograph (c) of the sorbent of silica:CH 1:2 ratio. No definable CH outlines can be found. While it is known from x-ray diffraction that CH is present in this sorbent, it is no longer apparent in the photomicrograph at this component ratio and length of slurry. This phenomenon of increasing surface definition with increasing proportions of silica in



(a)

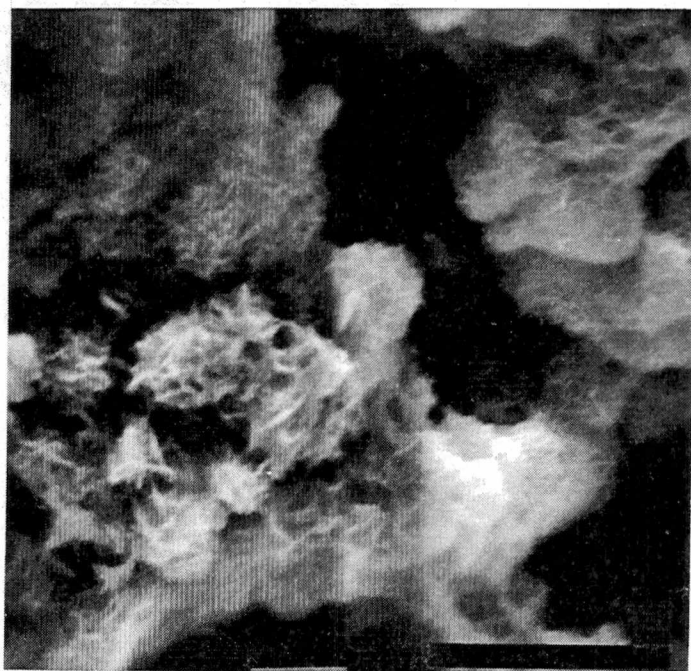


(b)

Figure 5.27. Electron photomicrographs of sorbents slurried for 3 hours. Bar scale = 5 μm .

(a) Amorphous silica:CH ratio 1:5.

(b) Amorphous silica:CH ratio 1:3.



(c)

Figure 5.27. (continued)

(c) Amorphous silica:CH ratio 1:2

the component ratio was noted by Taylor (1992). He ascribes the increasing degree of crystallinity to the increasing silica:CH ratio.

5.3.6 Determination of optimum silica addition

Up to this point the determination of sorbent performance has been made on a calcium basis. The utilization results were determined by comparing the amount of chloride removed by the calcium in the sorbent to the amount of chloride which would have been removed if the calcium had reacted at 100% efficiency. There are two additional ways to evaluate the sorbent's performance. One is by determining the mass of HCl removed per mass of silica added to the sorbent. This would demonstrate the optimum amount of silica to be added to the CH. The other method of evaluation, relevant from a mass-handling perspective, is the determination of the mass of HCl removed on a total sorbent mass basis (i.e., CH plus silica, not just on the basis of calcium content). While it is academically interesting to determine just how high the utilization of the calcium in the sorbents can be pushed, it is of little use in the real world if it requires so much silica that the overall mass of sorbent required to remove the HCl could not be handled realistically.

Determination of the mass of HCl removed per gram of SiO_2 added was made for each silica:CH ratio. The value of the maximum utilization for each ratio was employed for the calculation. CH alone exhibited 27% utilization on a calcium basis. Thus anything above 27% was attributed to the addition of silica. Figure 5.28 shows the graph of these calculations. Again the component ratio has been converted to silica fraction for quantitative plotting. CH alone cannot be

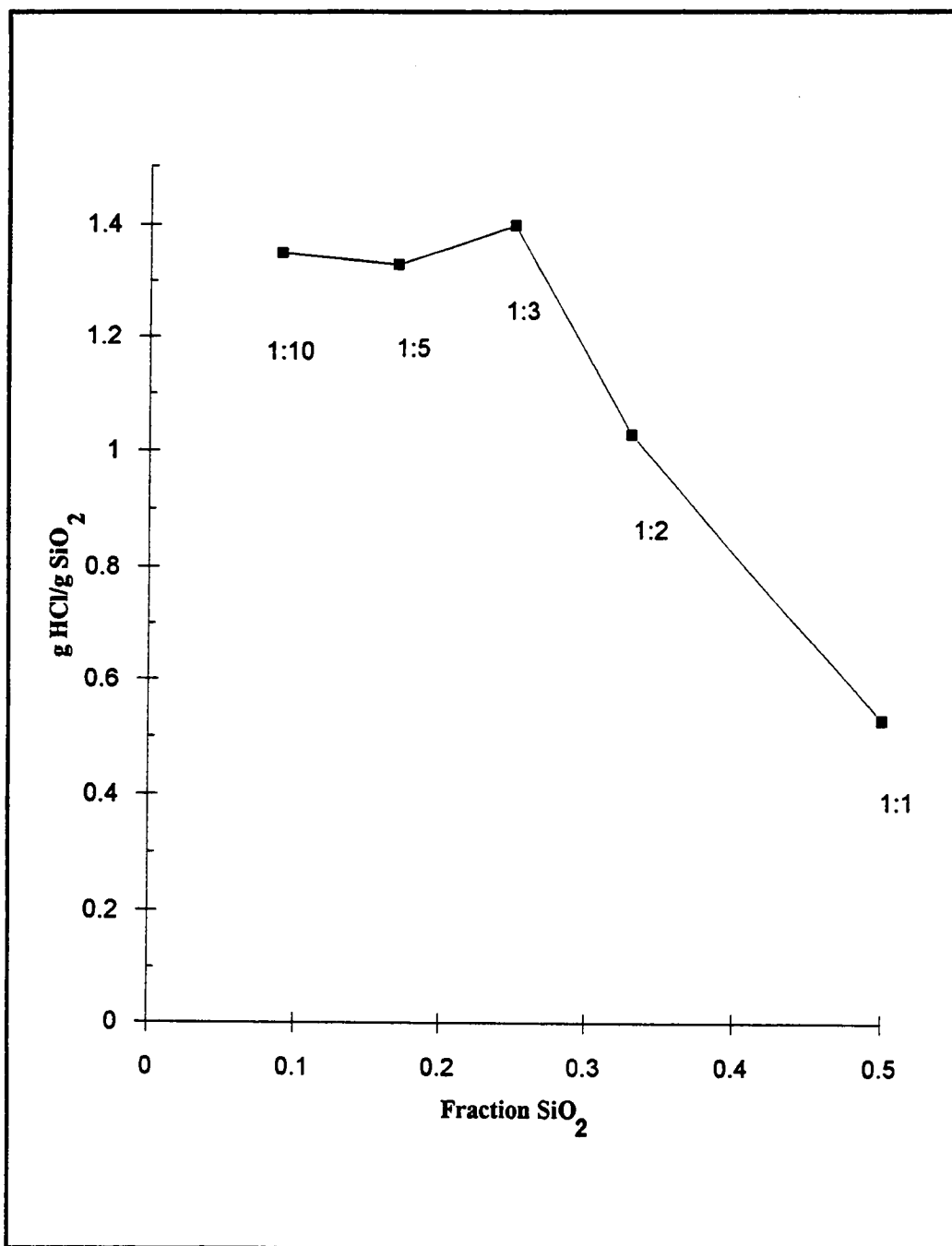


Figure 5.28. Removal of HCl based on amorphous silica addition.

plotted as it has no silica. The lower three silica:CH ratios were essentially the same as far as grams HCl removed per gram silica (g HCl/g SiO_2), ranging between 1.33 and 1.40 g HCl/g SiO_2 . After that point the removal dropped sharply with the silica:CH 1:2 ratio removing 1.03 g HCl/g SiO_2 and the 1:1 ratio removing only 0.53 g HCl/g SiO_2 . Although the 1:1 ratio sorbent had the highest utilization, it has the poorest HCl removal to SiO_2 addition ratio.

Determination of the mass of HCl removed per total mass of sorbent was also made for the highest utilization value for each silica:CH ratio. The calculations were made by dividing the grams of HCl removed per mass of sorbent for the given silica:CH ratio. Since this determination can be made regardless of whether or not silica is present, CH was able to be included. Figure 5.29 shows the results. CH alone had the lowest mass removal to total mass ratio at 27%. The mass utilization increased to a maximum of 56% at the silica:CH ratio of 1:3, and thereafter declined to 40% for the 1:1 ratio. Again, the silica:CH 1:3 ratio was the best performer. This shows that increasing silica in the sorbent preparation resulted in better mass utilization only up to the silica:CH 1:3 ratio. Thereafter, even though the total HCl removal could be increased by adding silica, the tradeoff was a decline in mass efficiency.

5.3.7 Relationship between sorbent character and sorbent utilization

As stated in the objective, a major goal of this research was to discover how the individual sorbents differed from one another in order that such characteristic differences could be correlated with the sorbent's reactivity. The differences, as it turned out, were not so distinct as to readily account for why

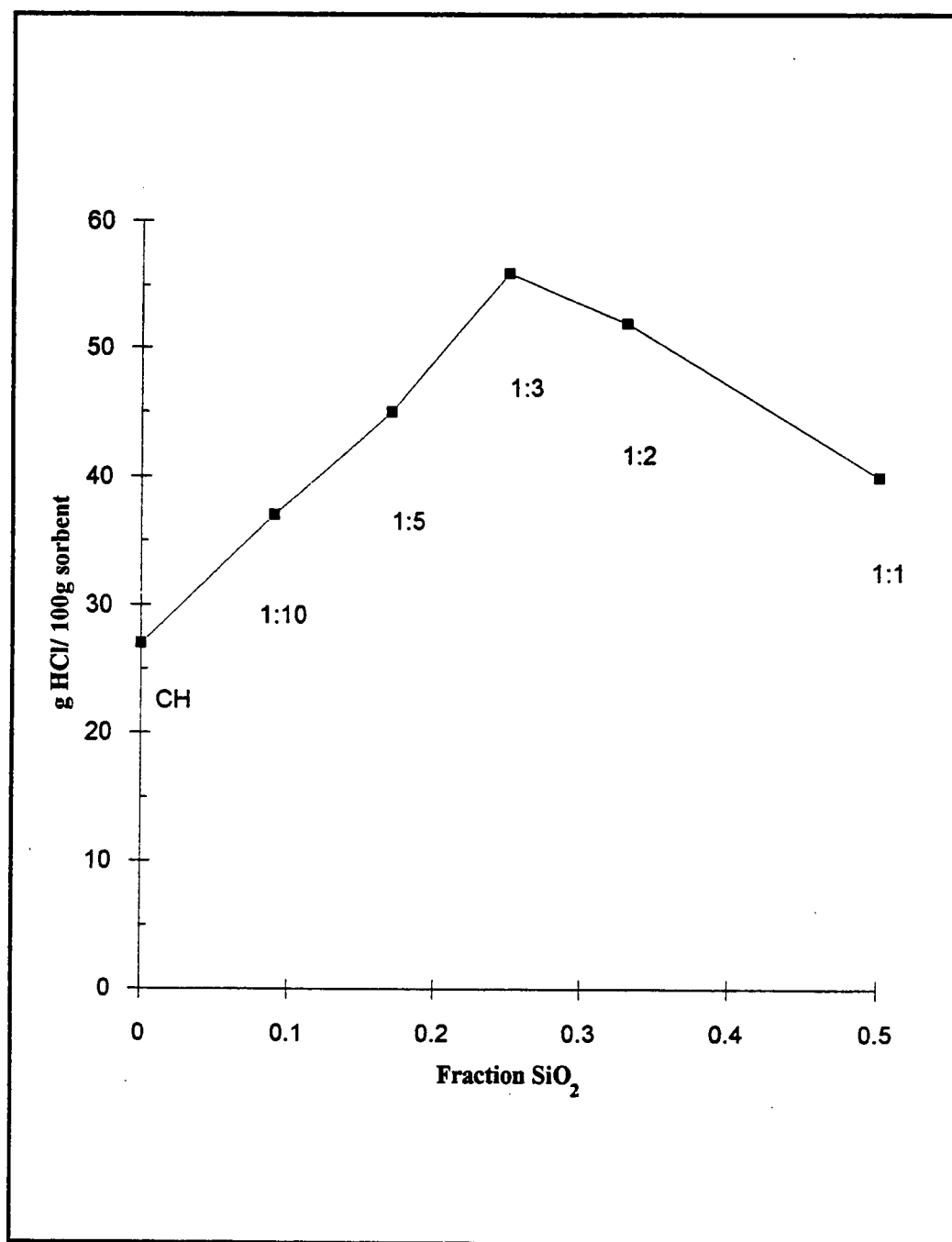


Figure 5.29. Total sorbent mass utilization.

some sorbents were more reactive than others. Clearly, the addition of silica was responsible for the enhancement of reactivity with HCl which was demonstrated by the sorbents in this study. Section 5.3.7.1 describes the development of an empirical model relating the increased utilization to both the amount of silica in the slurry materials and the length of slurry time. Section 5.3.7.2 considers other factors possibly related to the mechanism(s) which caused enhanced reactivity.

5.3.7.1 Conceptual model

The previous discussions showed that neither correlation with surface area (Figure 5.16) nor the development of different calcium silicate hydrate phases could account for the increase in utilization of CH demonstrated by the amorphous silica/CH sorbents. X-ray diffraction demonstrated that only one calcium silicate hydrate phase formed from the reaction of silica and CH. However, x-ray diffraction also demonstrated that the quantity of calcium silicate hydrate increased with both increasing slurry time (Figure 5.21) and increasing silica:CH ratio (Figure 5.22). This suggested that the reason for the utilization increase was simply the increase in the proportion of the calcium silicate hydrate relative to the unreacted CH remaining in the sorbent. If this were true, there should be a relationship between utilization and $\text{SiO}_2\text{:CaO}$ ratio which depended on slurry time as well. Therefore, an empirical model was developed based on the experimental data of this study. The model related the increased utilization to both silica:CH ratio and slurry time, demonstrating that the increase in utilization was linearly related to the molar $\text{SiO}_2\text{:CaO}$ ratios of the sorbents, and logarithmically related to slurry time. The data points from the utilization results of the silica:CH ratios of

1:10 to 1:2 were used in the model development. X-ray diffraction analyses had earlier demonstrated that at each of these ratios there was an excess of CH. The silica:CH 1:1 results were omitted from this exercise because the utilization and the surface area results of these samples had demonstrated a departure from the behavior seen for the other four silica:CH ratios. Unlike the other four silica:CH ratios, the x-ray diffraction analyses of the 1:1 ratio indicated that CH had been entirely consumed in reaction with silica for slurry times greater than 1 hour.

The weight ratios of the 1:10 through 1:2 series were converted to molar ratios in terms of SiO_2 and CaO. The conversion values are listed in Table 5.3. At each slurry time, increased utilization beyond that of CH alone was plotted against the corresponding SiO_2 :CaO ratios of the four samples. CH alone has a utilization of 27%; thus, anything greater than 27% can be attributed to the addition of the silica, and constitutes increased utilization. As discussed in section 5.3.1.1, it was not possible to experimentally determine values for utilization at extremely short slurry times, but theoretically, the utilization must extend back to that of CH alone as no enhancement of the CH would have occurred before the silica reacted with CH for at least a small time. At time zero, the utilization was represented by the value for CH alone. Thus, the increased utilization for CH was plotted at zero on each graph. Four graphs were generated in this fashion, one for each slurry time. The regression line was forced through zero. The graphs for 15 minutes, 1 hour, 3 hours, and 7 hours can be seen in Figures 5.30 through 5.33, respectively. The best fit equation and R^2 values are given in each figure. The high degree of correlation demonstrated that at any given slurry time, t , utilization had a linear relationship with SiO_2 :CaO molar ratio. Thus an equation of the form

Table 5.3. Conversion table for weight ratios to molar ratios.

Silica:CH Component Weight Ratios	SiO ₂ :CaO Molar Ratios
1:1	1.23
1:2	0.62
1:3	0.41
1:5	0.25
1:10	0.12

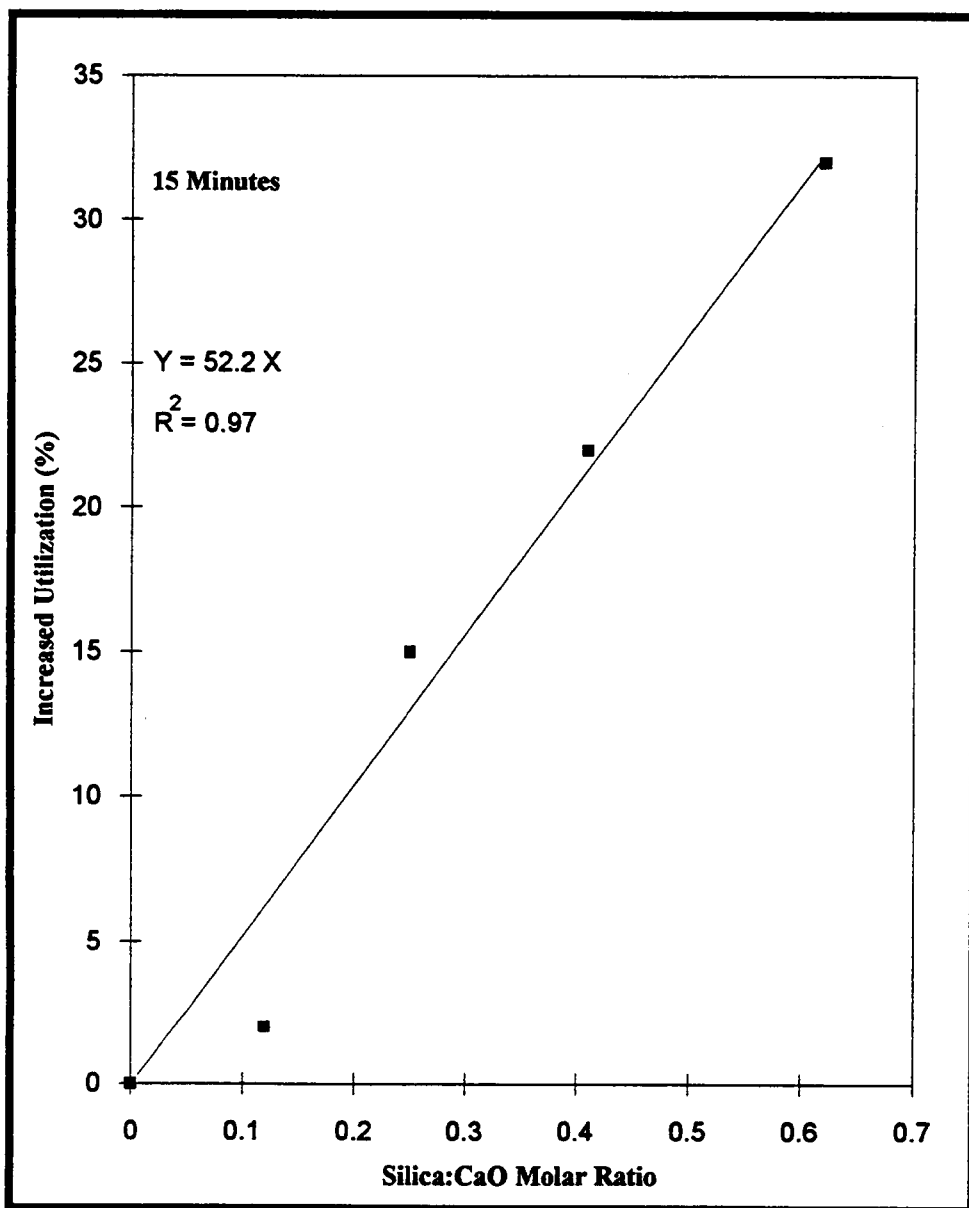


Figure 5.30. Increased utilization versus SiO_2 :CaO molar ratio at 15 minutes of slurry time.

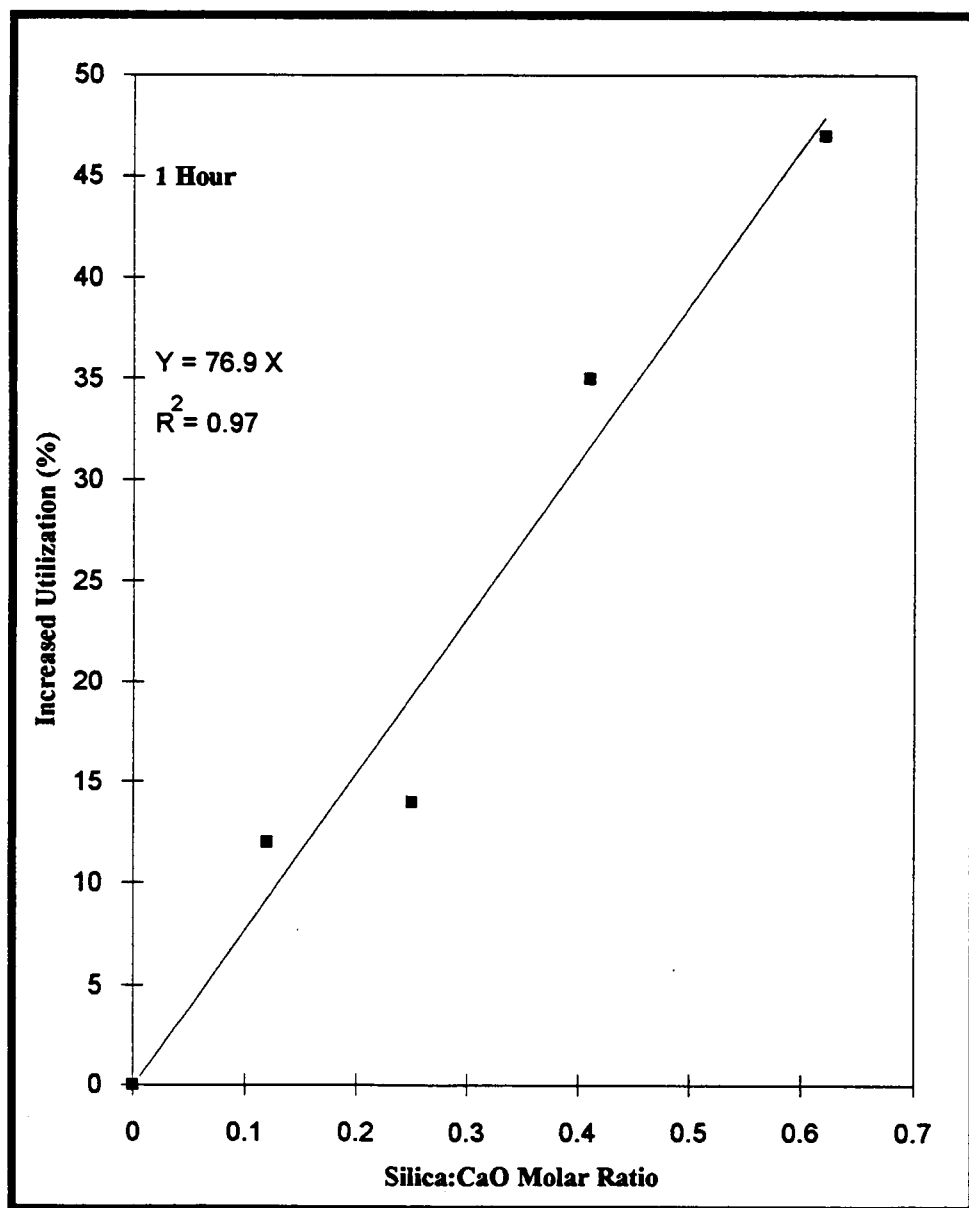


Figure 5.31. Increased utilization versus SiO_2 :CaO molar ratio at 1 hour of slurry time.

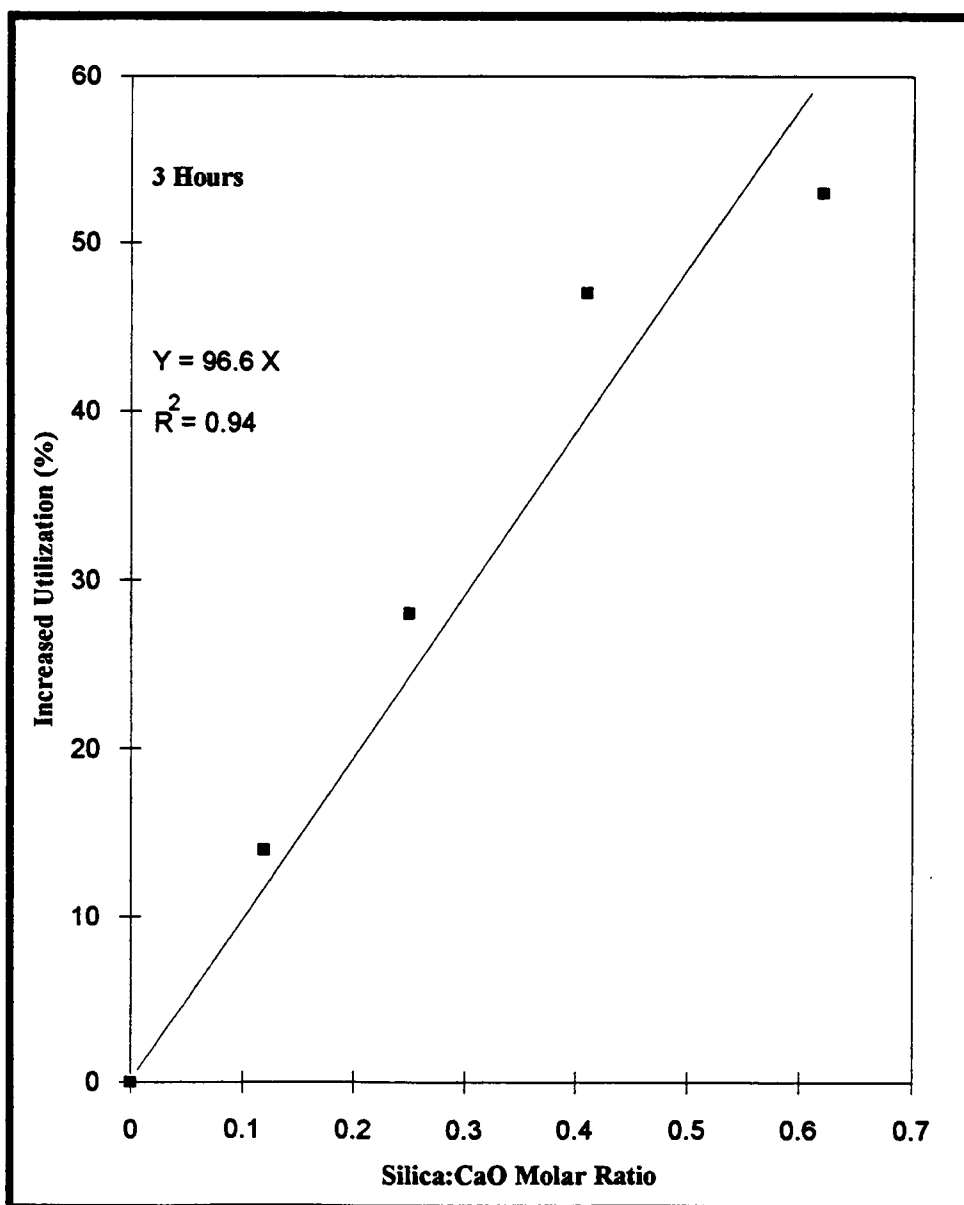


Figure 5.32. Increased utilization versus SiO_2 :CaO molar ratio at 3 hours of slurry time.

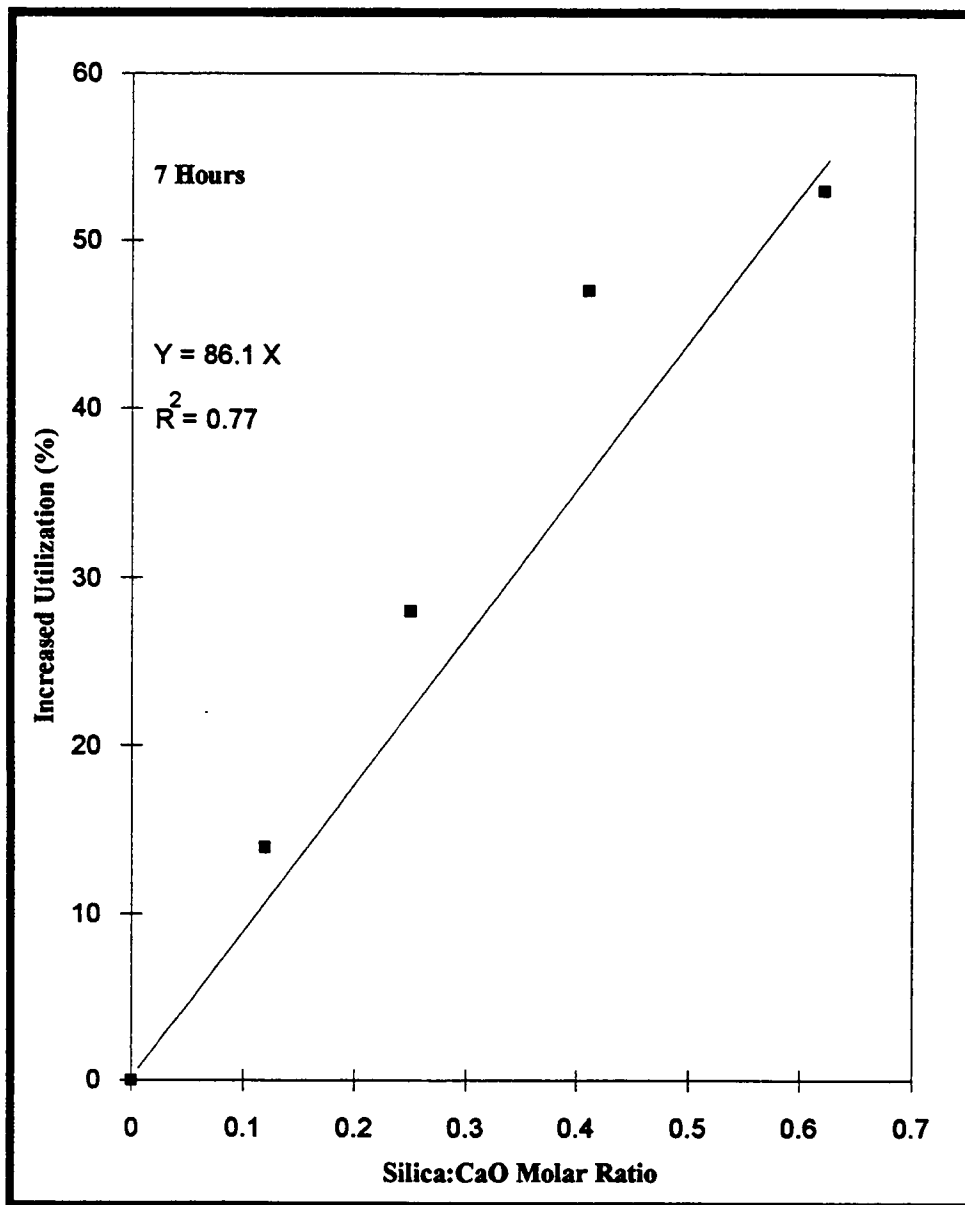


Figure 5.33. Increased utilization versus SiO_2 :CaO molar ratio at 7 hours of slurry time.

$$\text{utilization (\%)} = m \frac{\text{SiO}_2}{\text{CaO}} + b \quad (\text{eqn. 5.2})$$

described the relationship between increased utilization and SiO₂:CaO ratio for all slurry times between zero and 7 hours. The Y-intercept, b, in equation 5.2 was zero as the regression lines had been forced through zero. The value for slope, m, in equation 5.2 was derived by determining the relationship between the individual slopes of the four graphs in Figures 5.30 through 5.33 and slurry time. The values for slopes and time were plotted on a graph (Figure 5.34). The individual slopes were plotted on a logarithmic scale versus the inverse of time. The equation of the best fit line is

$$m = \exp \left(4.53 - \frac{0.146}{t} \right). \quad (\text{eqn. 5.3})$$

The R² value of 0.95 demonstrates that 95% of the variation in slope of the best fit lines relating increase in utilization to the SiO₂:CaO ratios (Figures 5.30-5.33) can be accounted for by the slurry time.

Equation 5.3 predicts that as time approaches zero, the slope of utilization vs. SiO₂:CaO ratio will also go to zero. This prediction is consistent with the facts since, at zero slurry time, the utilization is 27% (i.e., for CH alone), regardless of the SiO₂:CaO ratio. As time becomes infinite, equation 5.3 says that the slope approaches 93. The actual slope at three hours slurry time (Figure 5.32) was 96.6. This slope and the maximum predicted slope are in close agreement, indicating that the maximum utilization does not increase beyond that seen at approximately three hours of slurry time.

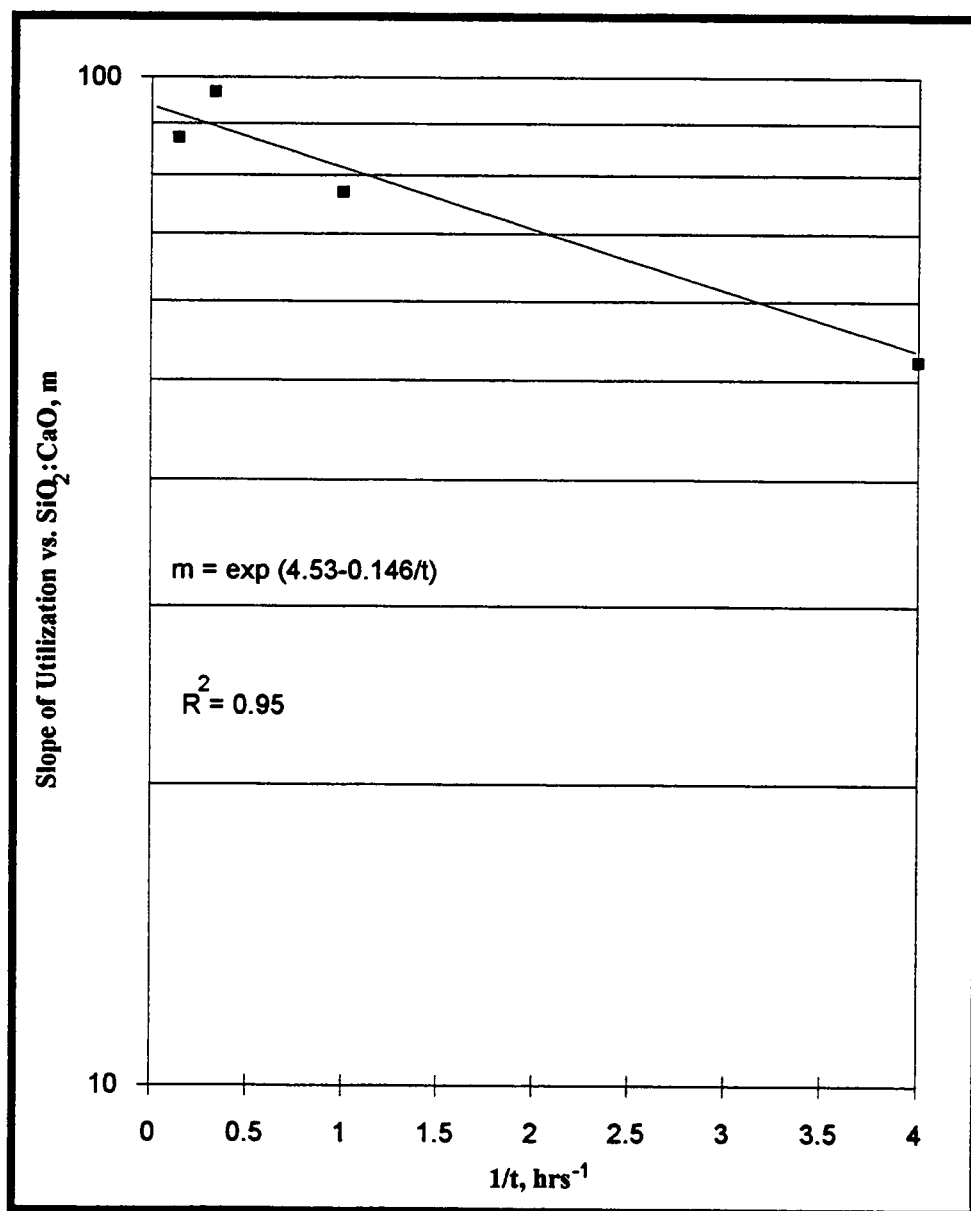


Figure 5.34. Slope versus time.

The high degree of correlation in the equations describing the relationship of increased utilization with both the molar ratios of the starting components in the sorbents and slurry time demonstrates conclusively that enhanced utilization was the result of both increasing silica and increasing slurry time. Increasing those two variables translates into an increase in the relative proportion of calcium silicate hydrate produced in the slurry. Anytime there was a greater proportion of calcium silicate hydrate in the resulting sorbent, there was correspondingly less CH remaining. Equations 5.2 and 5.3 reflect the fact that it was simply the relative proportions of calcium silicate hydrate and CH, which constituted the overall sorbent at any SiO₂:CaO ratio or any slurry time, that controlled the degree of enhancement.

If further utilization tests were performed, equation 5.2, in which equation 5.3 was substituted for "m", should predict new utilization values within the time and SiO₂:CaO ratio limits of the experimental data used to develop the equation. For predicting actual utilization, instead of just increased utilization, the Y-intercept of equation 5.3 would become 27, in adding back the 27% removed for the CH baseline value. The equation would then be

$$\text{utilization (\%)} = \left[\exp \left(4.53 - \frac{0.146}{t} \right) \right] \left(\frac{\text{SiO}_2}{\text{CaO}} \right) + 27. \text{ (eqn. 5.5)}$$

The utilization equation should not be used to predict conditions under which 100% utilization would occur. As stated earlier, the equation applies only for the silica:CH ratios and slurry times of the data used to derive it. In such cases

excess CH remained in the sorbent after slurring. Although it is not valid, it is possible to calculate a value for the $\text{SiO}_2\text{:CaO}$ ratio in equation 5.5 which would make the value of utilization equal to 100%. For a 7-hour slurry time, t , $\text{SiO}_2\text{:CaO}$ would have to be 0.8:1. This molar ratio falls between the molar ratios for the silica:CH 1:2 and 1:1 sorbents (Table 5.3). As demonstrated earlier, the slurries become calcium deficient in that interval, and the sorbent behavior was demonstrated to change, no longer adhering to the empirical model.

The facts that equation 5.4 cannot validly be used to predict 100% utilization and the observed data never achieved 100% utilization should not be viewed as a problem, but rather as a limitation which is typical of gas-solid reactions. Gas-solid reactions are generally limited to less than 100% utilization, for instance, by buildup of product layer on the surface of particles or by pore plugging. Such is the case for the CH in these tests in which 27% was the maximum utilization observed. In dry sorbent tests, under reactor operating conditions identical to those of the present study, Pakrasi (1992) concluded that high resistance to gas diffusion in the solid product layer, which was produced by the reaction of CH and HCl, prevented the utilization of CH from reaching 100%. Davis and Keener (1982) had similar results in flue gas desulfurization tests using soda ash as the dry sorbent. They concluded that buildup of an impervious ash later prevented interparticle gaseous diffusion. So, it is not surprising that the enhancements observed in this study resulting from the formation of calcium silicate hydrate did not achieve 100% utilization, but rather seem to be limited to approximately 75-80% as shown in Figure 5.5.

5.3.7.2 Other considerations

5.3.7.2.1 The role of pore size in sorbent utilization

Although surface area was not well correlated with utilization, it is possible that the size of the pore openings was important, as well, in determining the extent to which the sorbents were utilized. If a large proportion of the surface area occurred in small diameter pores, reaction at the entrance to the pores might tend to plug the pores preventing further access to the reaction sites inside the pore spaces. The surface area analyses would then over estimate the available reaction site surface area. The degree to which the pores were interconnected might also have influenced the availability of reaction sites. Pore plugging by reaction products tends to more greatly limit access to the reaction sites in dead-end pores than in pores which are interconnected, thus providing access to the HCl by more than one entrance.

According to Skalny and Odler (1972), there is evidence for the presence of micropores in calcium silicate hydrate which are not only very small, but inaccessible to N_2 molecules during surface area measurements. They found that amorphous calcium silicate hydrate (the type formed at temperatures less than 100 °C (212 °F), e.g., those in the present study) contains micropores which can be entered by water molecules but not by N_2 . In this case, the surface area analyses performed by means of nitrogen adsorption in this study would have underestimated the surface area which might have been available for reaction with HCl. It seems unlikely, however, that these water vapor-accessible pores would facilitate reaction with HCl in utilization tests since the adsorption of water in

surface area analyses was performed at 22 °C (72 °F), and the temperature in the reaction chamber is 149 °C (300 °F), and would tend to evaporate the water.

5.3.7.2.2 The roles of silica and moisture in sorbent utilization

The roles of moisture contained in the sorbent with regard to the sorbent's utilization are speculative. Based on the fact that moisture in the gas stream had the effect of increasing utilization (Figure 5.11), it is reasonable to suppose that moisture in the calcium silicate hydrate also contributed to enhancement. The following are discussions of how this might occur.

One of the industrial uses of amorphous silica is as a moisture adsorbent. The question can be asked as to whether the mechanism of enhanced utilization in the present sorbents is adsorption of moisture from the gas stream in the manner of silica, which in turn absorbs HCl, having little to do with the CH component. The calcium silicates formed in the process of reacting this amorphous silica with CH are hydrates which contain water in amounts which vary depending on the conditions of preparation. Whether or not the tendency of calcium silicate hydrate to adsorb water is directly related to its formation from silica is unclear. The fact that calcium silicate hydrates prepared with increasing ratios of silica contain decreasing amounts of total water (adsorbed and structurally bound; refer to section 2.3.3.2) argues against the same relationship for moisture adsorption in both silica and calcium silicate hydrate. It also seems unlikely that moisture from the gas stream would be adsorbed by the sorbent at the reaction temperature of 149 °C (300 °F) and gas stream moisture content of 10% by volume, which gives a relative humidity of 2.2%, . It is also possible that the water retained in the

sorbent during sorbent preparation may have facilitated the reaction. This, too, is difficult to support as the sorbent samples were conditioned in the gas stream for 15 minutes prior to the addition of HCl. This conditioning at 149 °C (300 °F) should have allowed the sorbent to achieve equilibrium moisture conditions prior to contact with the HCl. Any adsorbed moisture should have desorbed in the conditioning process. Structurally bound water, on the other hand, could still remain in the solids. Skalny and Odler (1972) suggest that water is adsorbed in micropores. If this water is held tightly enough in the micropores that it does not desorb during sample conditioning in the reactor, or if it is structurally bound, it might then be available to serve as an enhancement to reactivity.

One way in which tightly held moisture might be released involves the dissolution of the calcium silicate hydrate in the sorbent, which in turn would free both moisture and calcium for reaction with HCl. This line of thought is based on Greenberg and Chang's (1965a) statement that calcium silicate hydrates of a molar $\text{SiO}_2:\text{CaO}$ ratio of 1:1 began to dissolve completely in hydrochloric acid. No other details were given. If the equilibrium moisture content of the solids were such that hydrochloric acid could form by means of absorption of HCl by the moisture, the calcium silicate hydrate might then begin to dissolve, releasing structural water and making calcium available. This water might then become involved briefly in facilitating the reaction between gas and solid before the water was vaporized by the hot gas stream. Further research is needed to determine the extent, if any, to which adsorbed and/or structurally bound moisture plays a role in enhancement of the sorbent's reactivity with HCl.

5.3.7.2.3 The role of sorbent and reaction product molar volume in sorbent utilization

Molar volumes may play an important role in developing enhanced reactivity in the calcium silicate hydrate sorbents. Pakrasi (1992) pointed out that the molar volume of CaCl_2 , which is the solid reaction product of solid CH and gaseous HCl, has a molar volume that is 52% higher than that of CH, and that the increased volume might act to block pores or create a reaction product surface layer which effectively decreased the rate of diffusion to the extent of stopping the reaction. Unlike CH, calcium silicate hydrate have a higher molar volume than CaCl_2 . Excluding any structural water, a calcium silicate hydrate with a $\text{SiO}_2\text{:CaO}$ molar ratio of 1.25:1 would have a molar volume only 6% less than the reaction product CaCl_2 . A calcium silicate hydrate with a $\text{SiO}_2\text{:CaO}$ molar ratio of 1:1 would have a molar volume 4.2% greater than CaCl_2 , and one with a $\text{SiO}_2\text{:CaO}$ molar ratio of 0.67:1 would have a 23% greater molar volume than CaCl_2 . None of these has the disadvantage, with regard to molar volume, that CH has in which the reaction product has such an increase in molar volume (52%) over the initial solid. The sorbents in the present work are more likely to experience an increase in pore space or a lower rate of reaction product buildup and pore plugging than would CH in the same circumstances. This may account for some of the reactivity enhancement.

5.3.8 Discussion

The materials formed when amorphous silica and CH are reacted in heated aqueous slurries can be best characterized by referring to the literature on the formation of calcium silicate hydrate from solution. The experiments in the present study involving amorphous silica and CH resulted in materials which were identified as the calcium silicate hydrate called C-S-H(I) by x-ray diffraction and SEM analyses. By their very nature these solids are difficult to characterize as they tend to be amorphous and have the ability to incorporate increasing amounts of calcium without producing a change in the x-ray pattern. They can vary in water content without changing anything from an analytical standpoint except basal spacing, which is typically absent in the poorly crystallized calcium silicate hydrates (Lea, 1970).

X-ray diffraction analyses indicated that only one calcium silicate phase developed, regardless of sorbent ratio and length of slurry time. As discussed in section 2.3.3.1, there are only two calcium silicate hydrates which form at temperatures less than 100 °C. They are C-S-H(I) and C-S-H(II), and there is a lack of agreement on the existence of C-S-H(II) at such temperatures. SEM work demonstrated that the sorbents in this study (silica:CH mass ratios of 1:1, 1:2, 1:3, and 1:5) had the crumpled foil morphology which is characteristic of the C-S-H(I) phase. It is reasonable to expect that the silica:CH 1:10 sample would have had the same morphology, although it was not examined. This indicates that all the calcium silicate hydrate formed in all the sorbent samples was of the C-S-H(I) type. As noted in section 2.3.3.1, the chemical formula varies for this phase, but ranges from $\text{CaO}_{(0.8)}\text{SiO}_2 \cdot n\text{H}_2\text{O}$ to $\text{CaO}_{(1.5)}\text{SiO}_2 \cdot n\text{H}_2\text{O}$ depending on the

conditions of preparation. The probable $\text{SiO}_2\text{:CaO}$ molar ratio in the calcium silicate hydrates formed in the sorbents with silica:CH mass ratios between 1:10 and 1:2 was 0.66:1. This corresponds to C-S-H(I) with the maximum molar CaO in the formula, $\text{CaO}_{(1.5)}\text{SiO}_2 \cdot n\text{H}_2\text{O}$. This deduction is based on the fact that calcium silicate hydrate forming in the presence of excess CH should contain the maximum possible CaO (as CH is available), which for C-S-H(I) is 1.5 moles CaO per mole SiO_2 (or 0.66 moles of SiO_2 per mole of CaO). The silica:CH 1:1 sorbents would not have had this formula since there was not enough CH. The $\text{SiO}_2\text{:CaO}$ molar ratio of the starting components for the silica:CH 1:1 mass ratio was 1.23:1, which converts to a calcium silicate hydrate formula of $\text{CaO}_{(0.81)}\text{SiO}_2 \cdot n\text{H}_2\text{O}$. The hydrated calcium silicates in the foregoing discussion should not be confused with crystalline forms of calcium silicate hydrate which can form at higher temperatures, and which have set stoichiometric formulas (refer to Table 2.3).

5.4 Crystalline silica/calcium hydroxide sorbents

The experiments in the previous section demonstrated that amorphous silica dissolves extremely rapidly at the high pH values generated in the sorbent preparation slurries. The data reported in this section reflect the much lower dissolution rate of crystalline silica, which resulted in a slower rate of calcium silicate hydrate production. The utilization, surface area, and x-ray diffraction results in this section offer a marked contrast to those of the previous one.

5.4.1 Sorbent reactivity tests

The reactor conditions under which the crystalline silica/CH sorbents were tested for reactivity were identical to those of the fly ash/CH and amorphous silica/CH tests. Temperature in the reaction chamber was 149 °C (300 °F), gas humidity was 10% by volume, and HCl concentration was 1000 ppmv. All reactor tests were performed for 600 seconds, providing data comparable to the results from the amorphous silica tests as well as the maximum utilization data points of the fly ash/CH results.

5.4.1.1 Effect of slurry time

The lower depolymerization rate of crystalline silica as compared with amorphous silica was discussed in section 2.2.2, and is demonstrated clearly in the following results from the present work. The utilization results, as they relate to length of slurry time, are plotted in Figure 5.35. Several things are immediately apparent. One is that, except for a single point, none of the samples performed better than the 3 hour CH, and only three exhibited higher utilization than the original CH. The highest utilization at 39% was observed for the silica:CH 1:1-7 hour sample. These results are in sharp contrast to those of the amorphous silica/CH sorbents of which no sample demonstrated lower utilization than the original CH, and, in spite of the increase in utilization of the CH at 3 hours of slurry, all other samples slurried for a comparable amount of time had higher utilization.

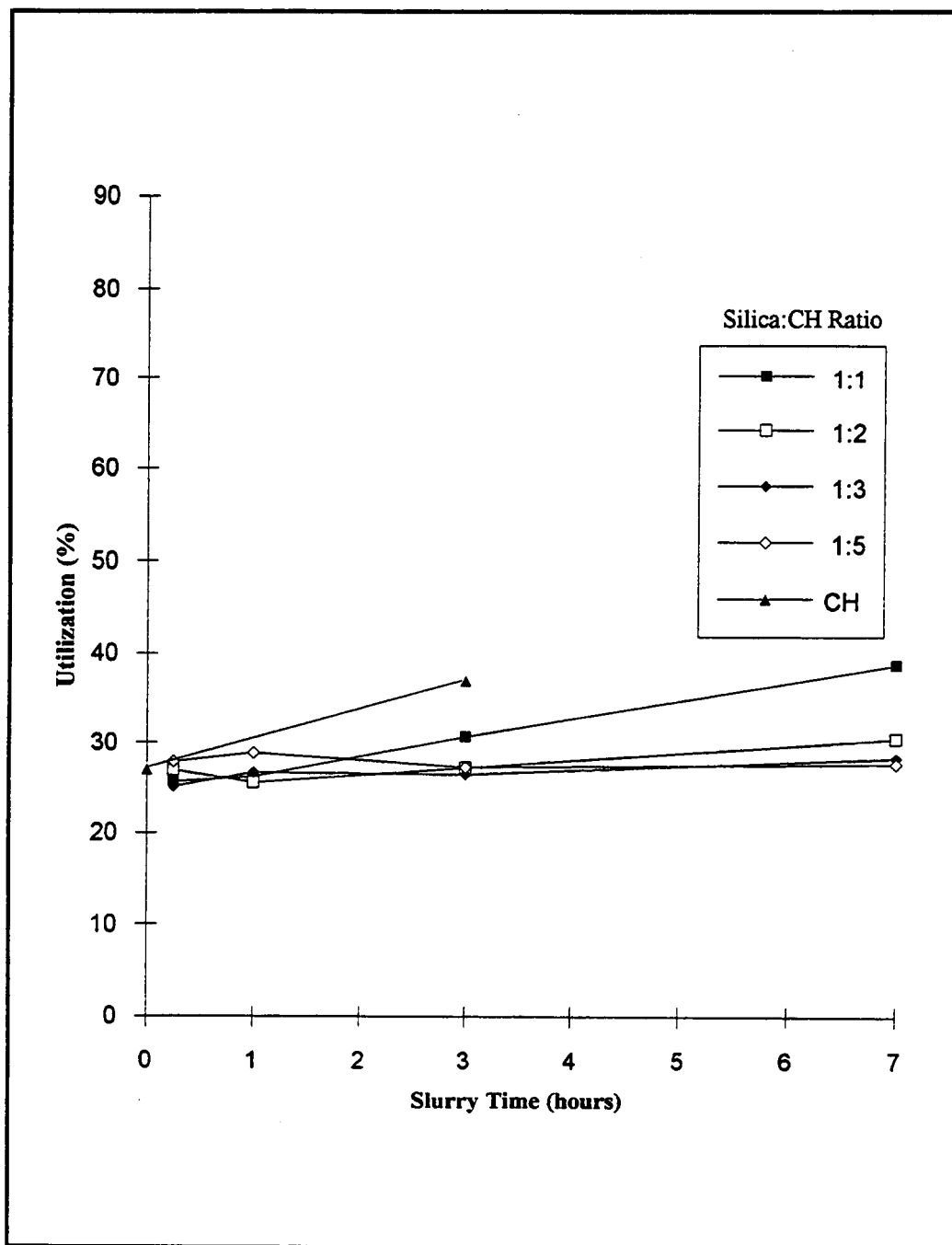


Figure 5.35. Effect of slurry time on utilization for crystalline silica/CH sorbents.

Apart from the solitary sample with 39% utilization seen in Figure 5.35, the sorbents all appear to react at approximately the same utilization as the CH alone. Although experimental error was not determined for this series of sorbents, if the experimental error of the amorphous silica/CH sorbents were applied (Table 5.2), the sorbent utilization values of the crystalline silica/CH sorbents would be indistinguishable from that of CH. The likely reason for this, as demonstrated by x-ray diffraction, is that the sorbents have developed such a meager amount of calcium silicate hydrate that the reactivity is not enhanced. The reasonable explanation for the heightened performance of the crystalline silica:CH 1:1 sample which was slurried for 7 hours is that it had the time and the silica resource to dissolve a greater amount of silica than the other samples, and thus to form enough calcium silicate hydrate to enhance reactivity.

5.4.1.2 Effect of silica fraction

Figure 5.36 presents the utilization results in a manner which demonstrates the effect of component ratio. As in section 5.3.1.2, the component ratio is scaled in terms of silica weight fraction. The silica:CH 1:1 samples are seen on the far right at 0.5 fraction silica, and the silica:CH 1:5 samples are between 0.1 and 0.2 fraction silica. The utilization of the original CH is shown in dashed line on the left side of the plot for reference. It is apparent from the graph that increasing the silica proportion to 0.5 has the greatest effect on increasing utilization. The seven-hour line also demonstrates that a long slurry time is

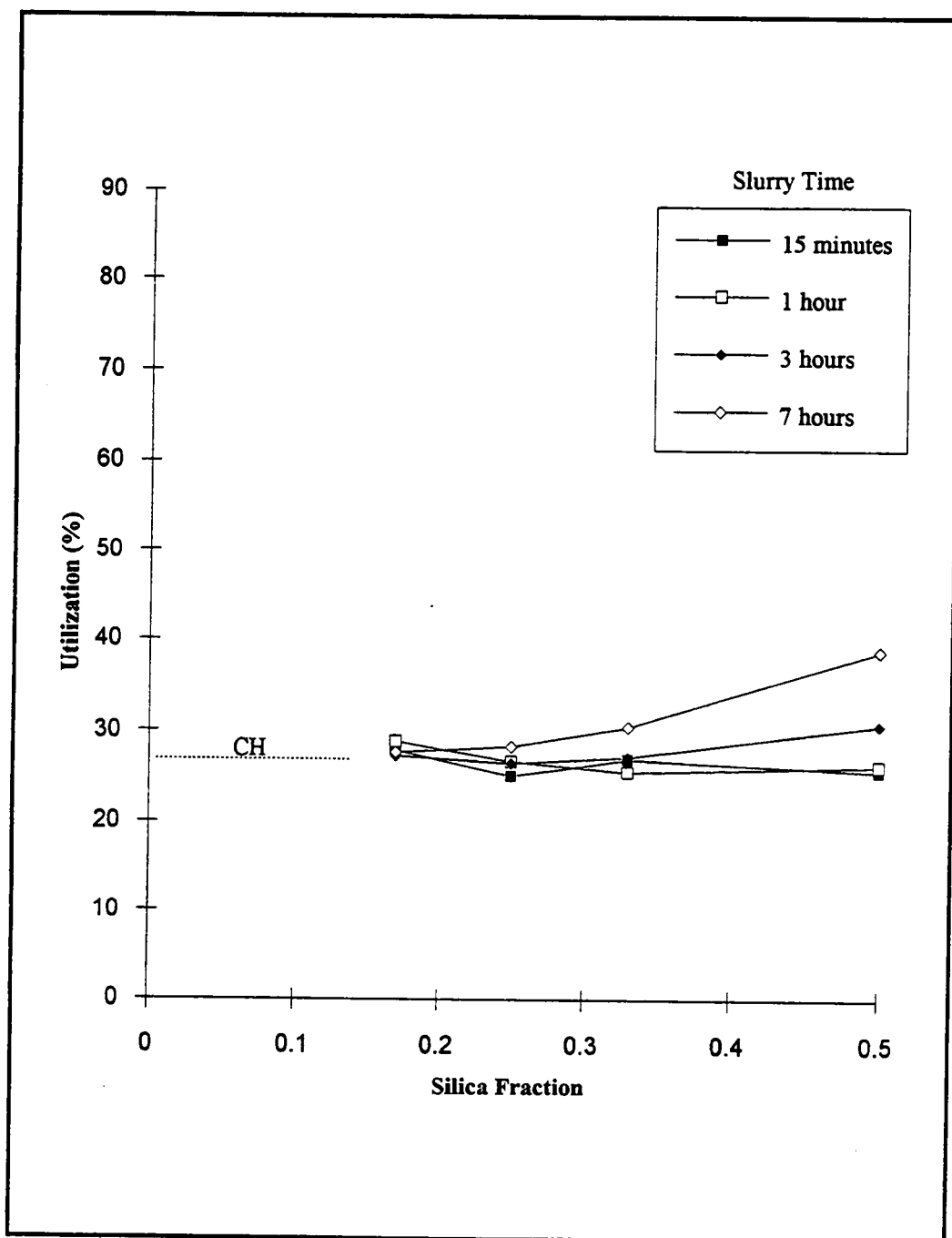


Figure 5.36. Effect of component ratio on utilization for crystalline silica/CH sorbents.

required to develop samples whose utilization increases above the remainder of the samples, most of which demonstrate no reactivity enhancement.

5.4.2 BET surface area analysis

5.4.2.1 Effect of slurry time and silica fraction

A plot of BET surface area versus slurry time is shown in Figure 5.37. The same axis scales used in Figure 5.12 were used here to facilitate comparison between the development of surface area in amorphous silica/CH sorbents and crystalline silica/CH sorbents. The production of calcium silicate hydrate is reflected in small increases in surface area for all but the lowest silica component ratios. The data indicate that the preparation with the most silica (silica:CH 1:1) ultimately developed the greatest surface area, while the one with the least silica (silica:CH 1:5) demonstrated no increase in surface area, presumably because there was not enough silica in solution during slurring to produce much calcium silicate hydrate. The surface area never increased beyond a maximum of $31 \text{ m}^2/\text{g}$. When compared to surface area values near $90 \text{ m}^2/\text{g}$ for amorphous silica/CH sorbents, it is clear that production of calcium silicate hydrate was limited by the dissolution rate of the silica.

The degree of utilization in the sorbent series appears to have a close relationship with the development of surface area. The effect of component ratio (silica fraction) on surface area is presented in Figure 5.38. A comparison of Figure 5.36 with Figure 5.38 demonstrates that utilization and surface area tend to mimic one another in their respective increase and development. Again, the higher

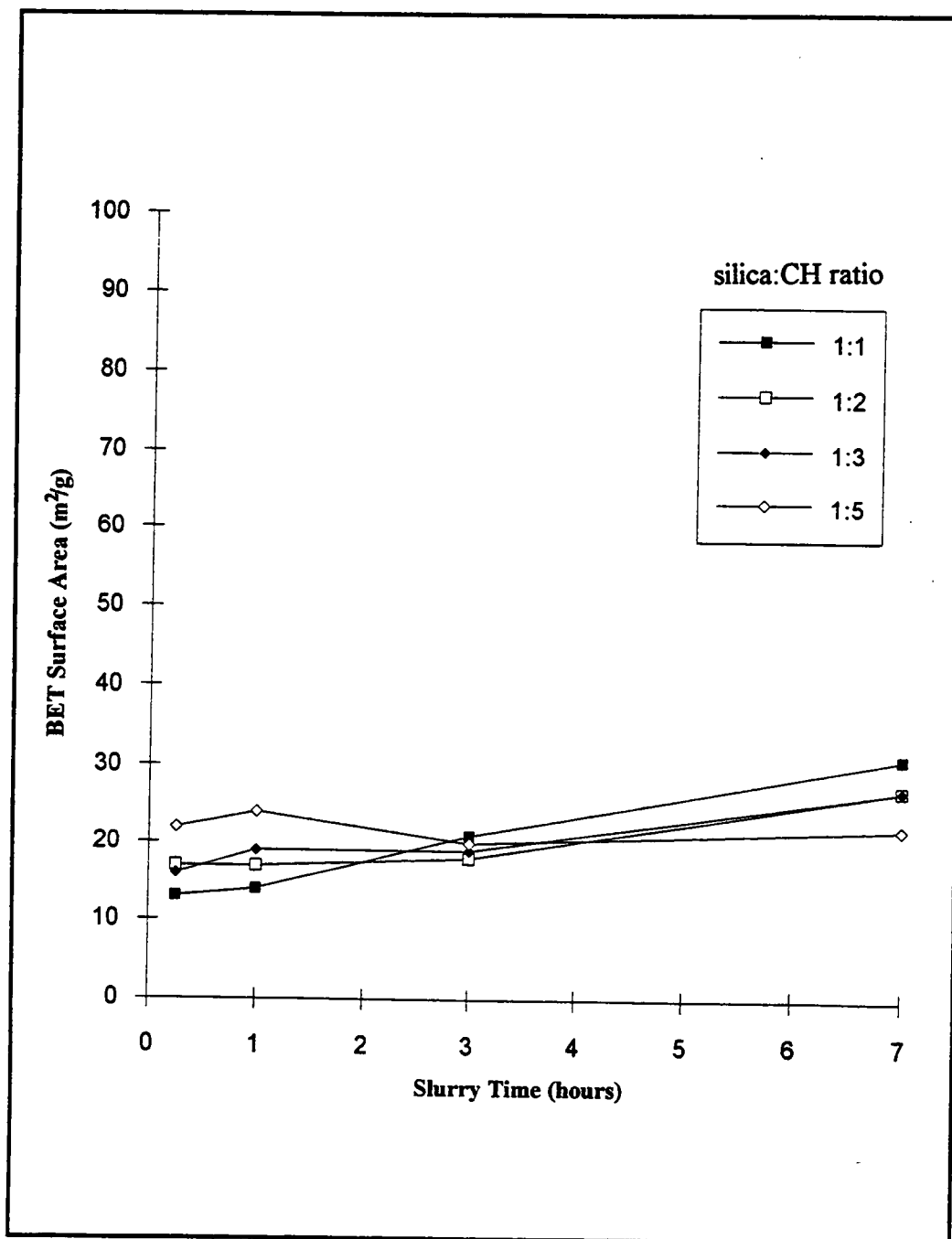


Figure 5.37. Effect of slurry time on development of surface area in crystalline silica/CH sorbents.

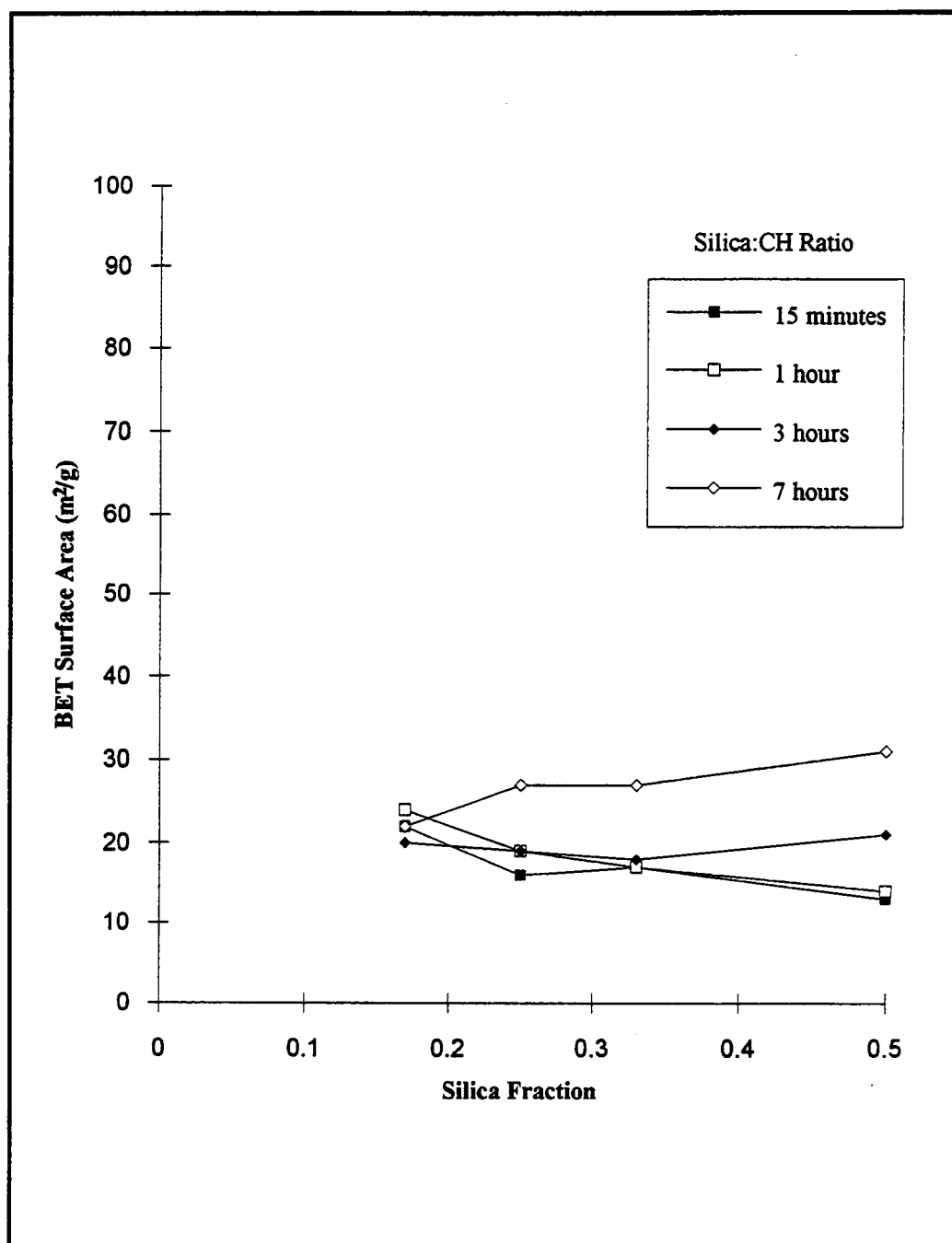


Figure 5.38. Effect of component ratio on development of surface area in crystalline silica/CH sorbents.

silica fraction had the highest utilization, but it required 7 hours slurry time for any of the samples to demonstrate a noticeable increase. Figure 5.39 is a correlation plot of utilization and surface area for the crystalline silica/CH sorbents. The equation of the best fit line for least squares regression was $Y = 17.48 + 0.52X$ ($R^2 = 0.63$). The relationship exhibits less scatter than the comparable plot for amorphous silica/CH sorbents (Figure 5.16). In spite of references to increased sorbent utilization when using the crystalline silica/CH samples, the increases in utilization were just a minor amount above that of CH alone, and most samples exhibited lower utilization than CH.

5.4.3 X-ray diffraction

X-ray diffraction analysis was performed on the 15 minute and 7 hour samples for each component ratio of the crystalline silica/CH sorbents. Due to the fact that crystalline silica has a crystallographic structure which results in numerous SiO_2 peaks, the x-ray patterns have a more cluttered appearance than those of the amorphous silica/CH sorbents. Figure 5.40 is an x-ray diffraction pattern of the silica:CH 1:3-15 minute crystalline silica/CH sorbent. The SiO_2 and CH peaks are well represented in this pattern. The vertical lines indicate the locations and relative intensities expected for peaks of those compounds.

Figures 5.41 (a), (b), (c), and (d) are arranged in order of increasing silica proportion, and show the overlain patterns of the 15 minute and 7 hour sorbents for the silica:CH 1:5, 1:3, 1:2, and 1:1 samples, respectively. In contrast to the patterns for the amorphous silica/CH sorbents, it is evident that there is not a great deal of reaction occurring between silica and CH. This is demonstrated by the

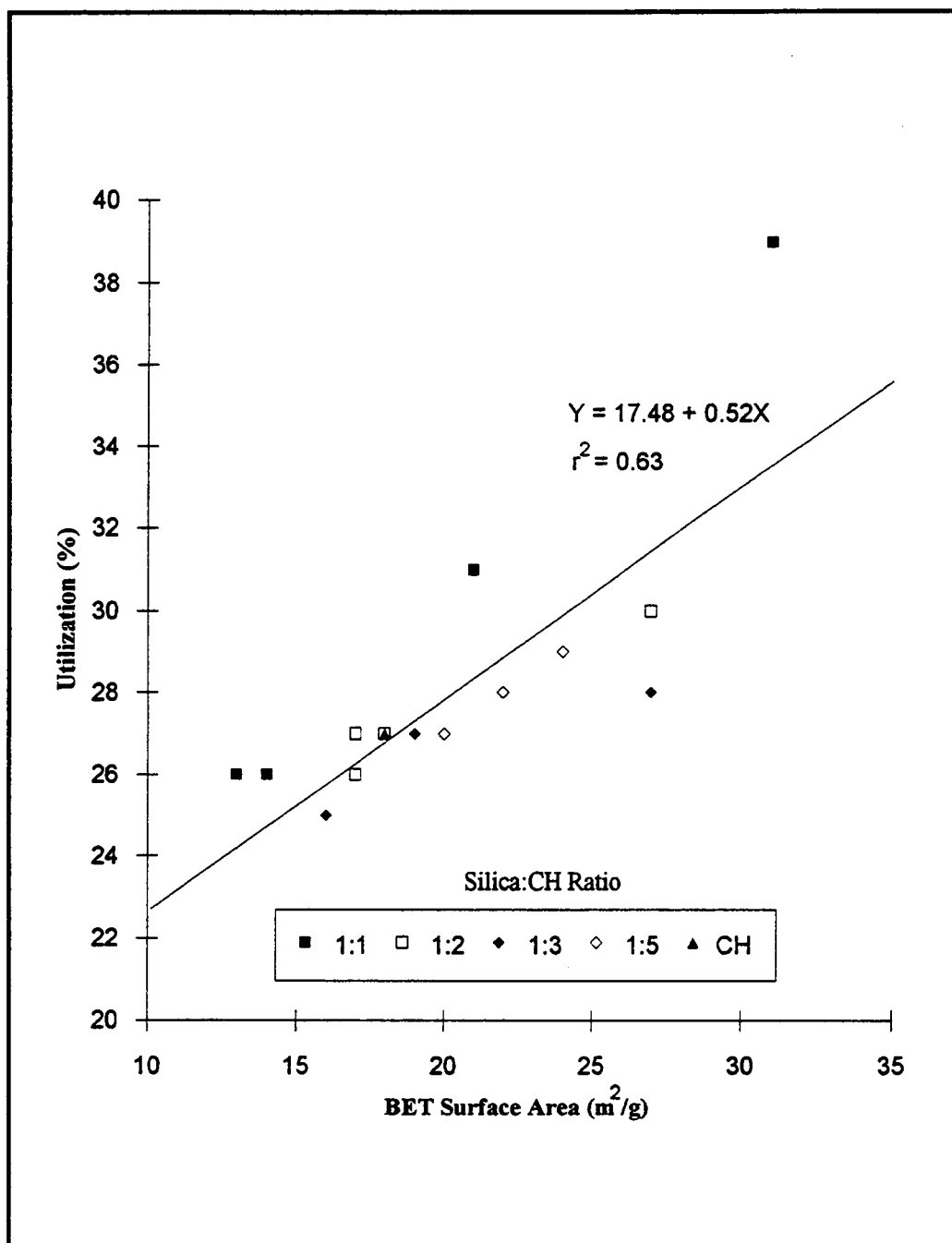


Figure 5.39. BET surface area versus utilization for crystalline silica/CH sorbents.

Figure 5.40. X-ray diffraction pattern of sorbent prepared from crystalline silica:CH ratio of 1:3, slurried for 15 minutes.

Note: Red vertical lines demonstrate two-theta locations for CH peaks. Green vertical lines demonstrate two-theta locations for crystalline silica peaks. The letter "M" in the legend refers to Min-U-Sil™ silica. Ex.: M1TO5-15.RAW is the sample prepared from a crystalline silica:CH ratio of 1:5 which was slurried for 15 minute.

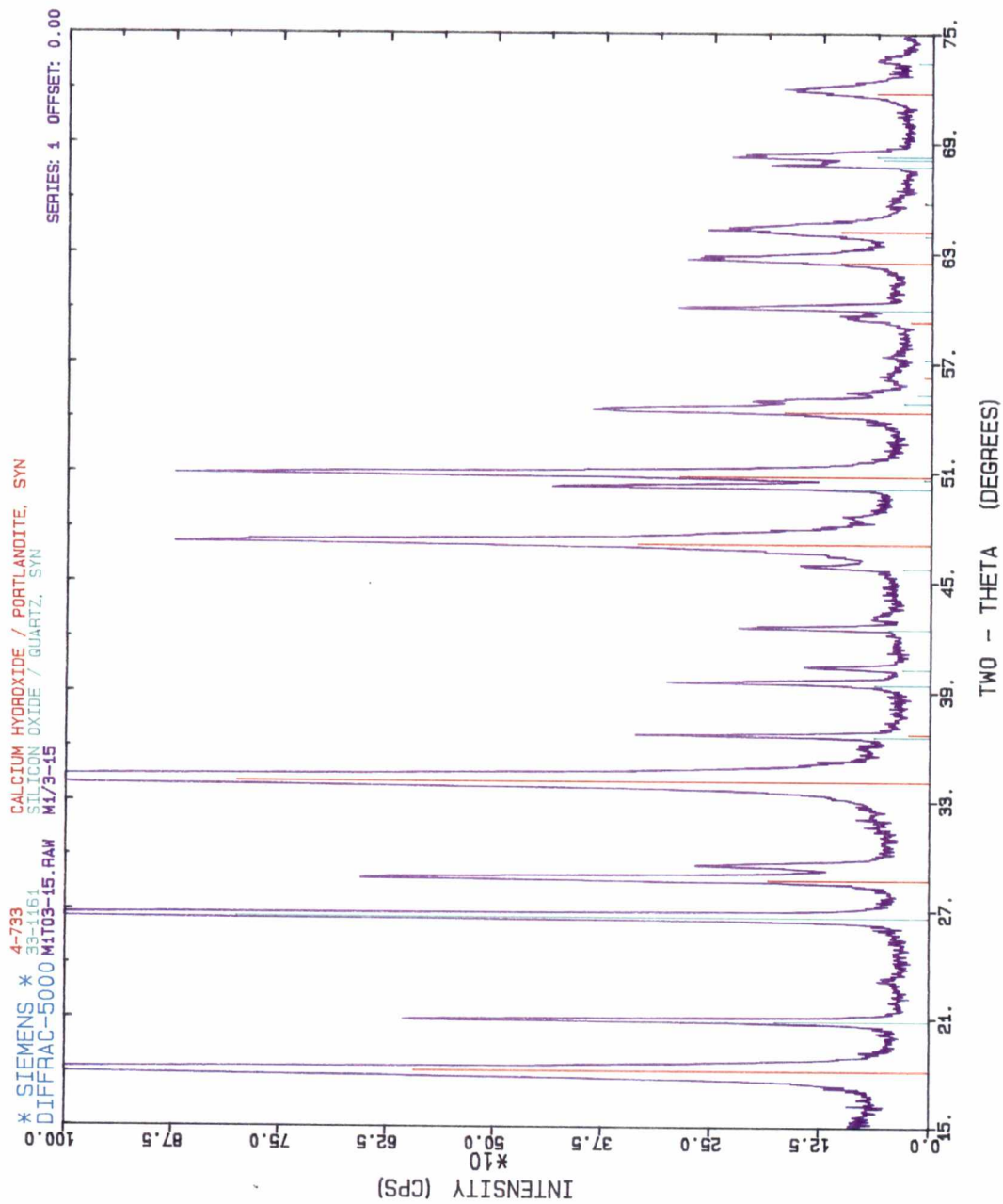
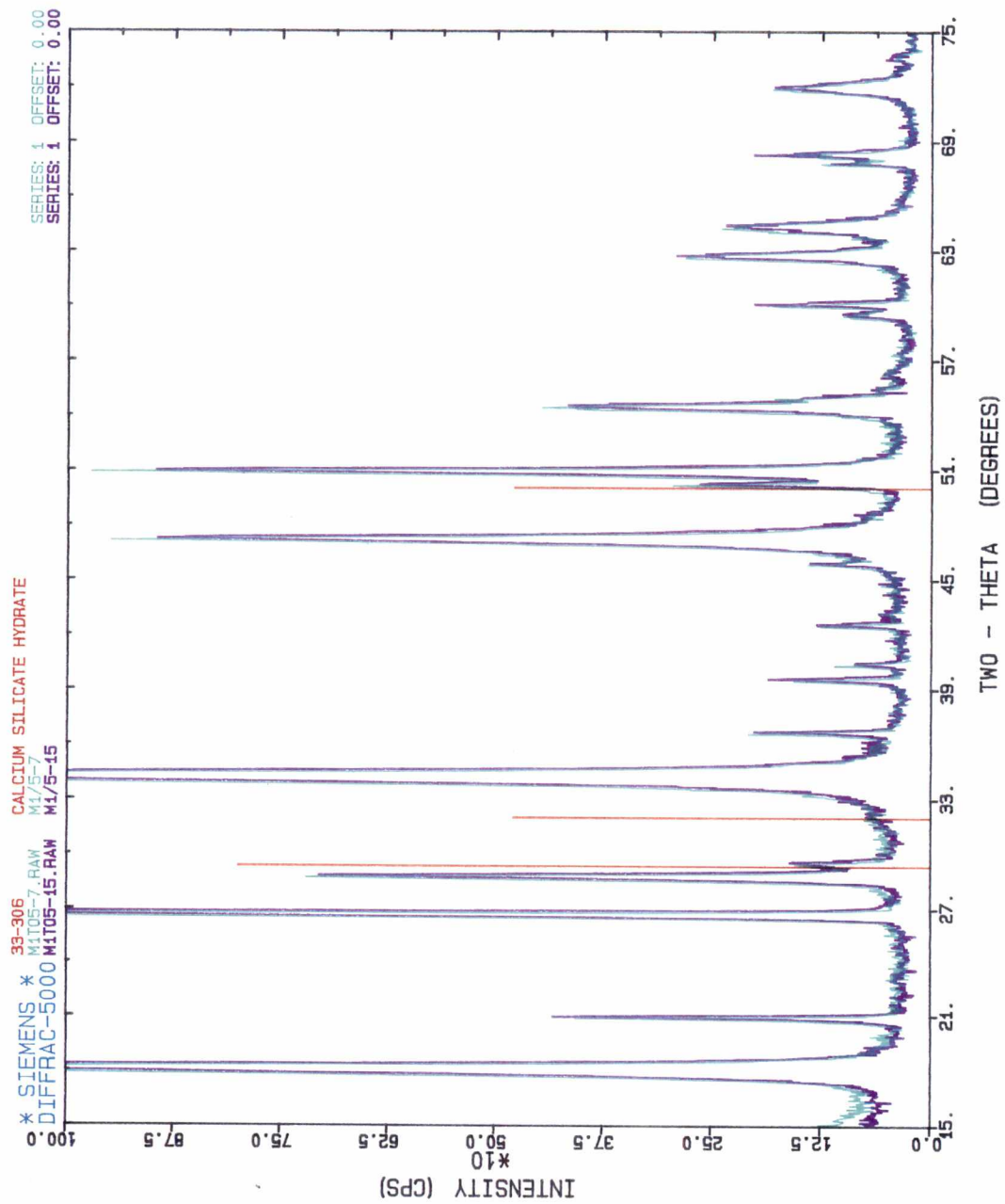
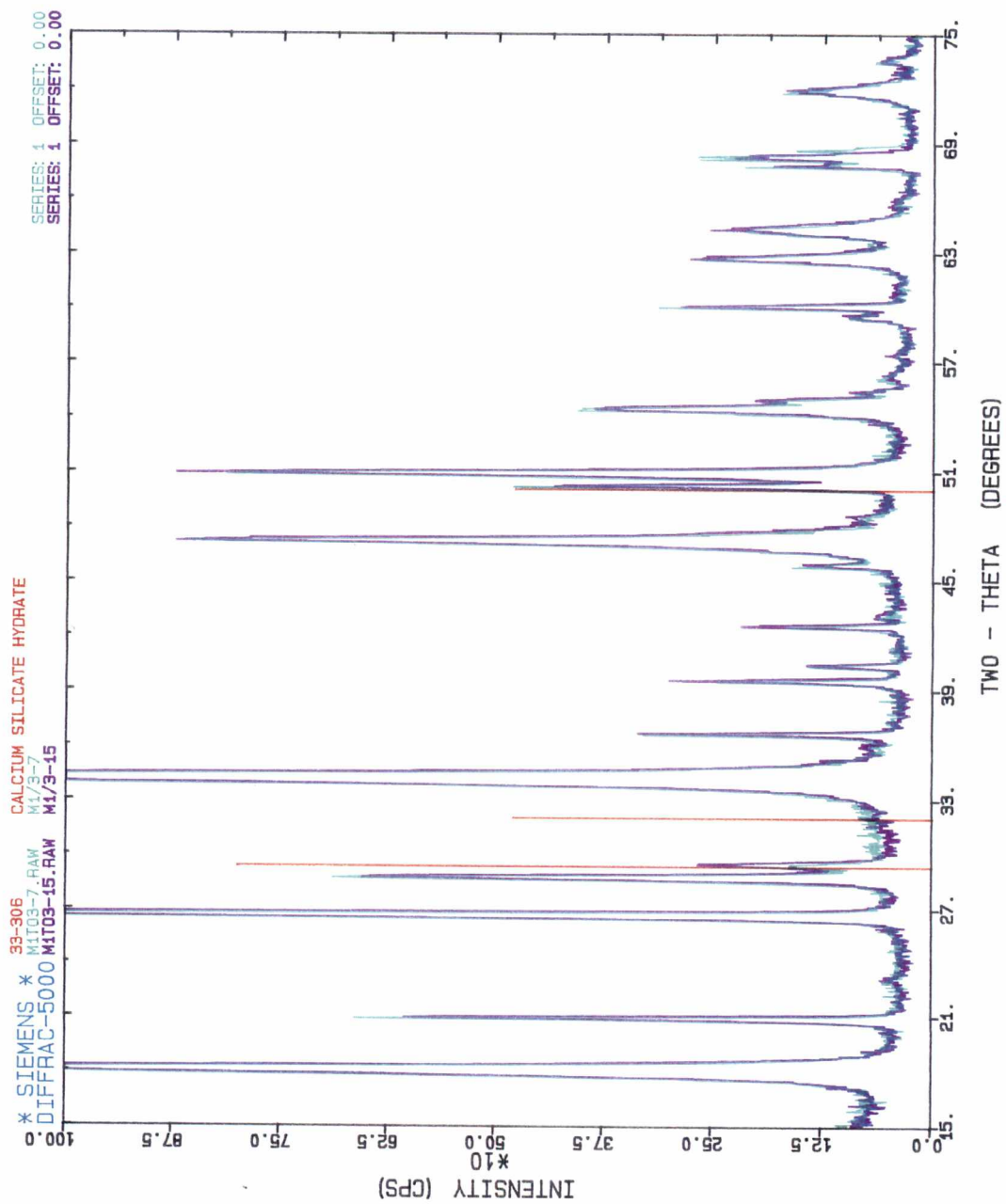
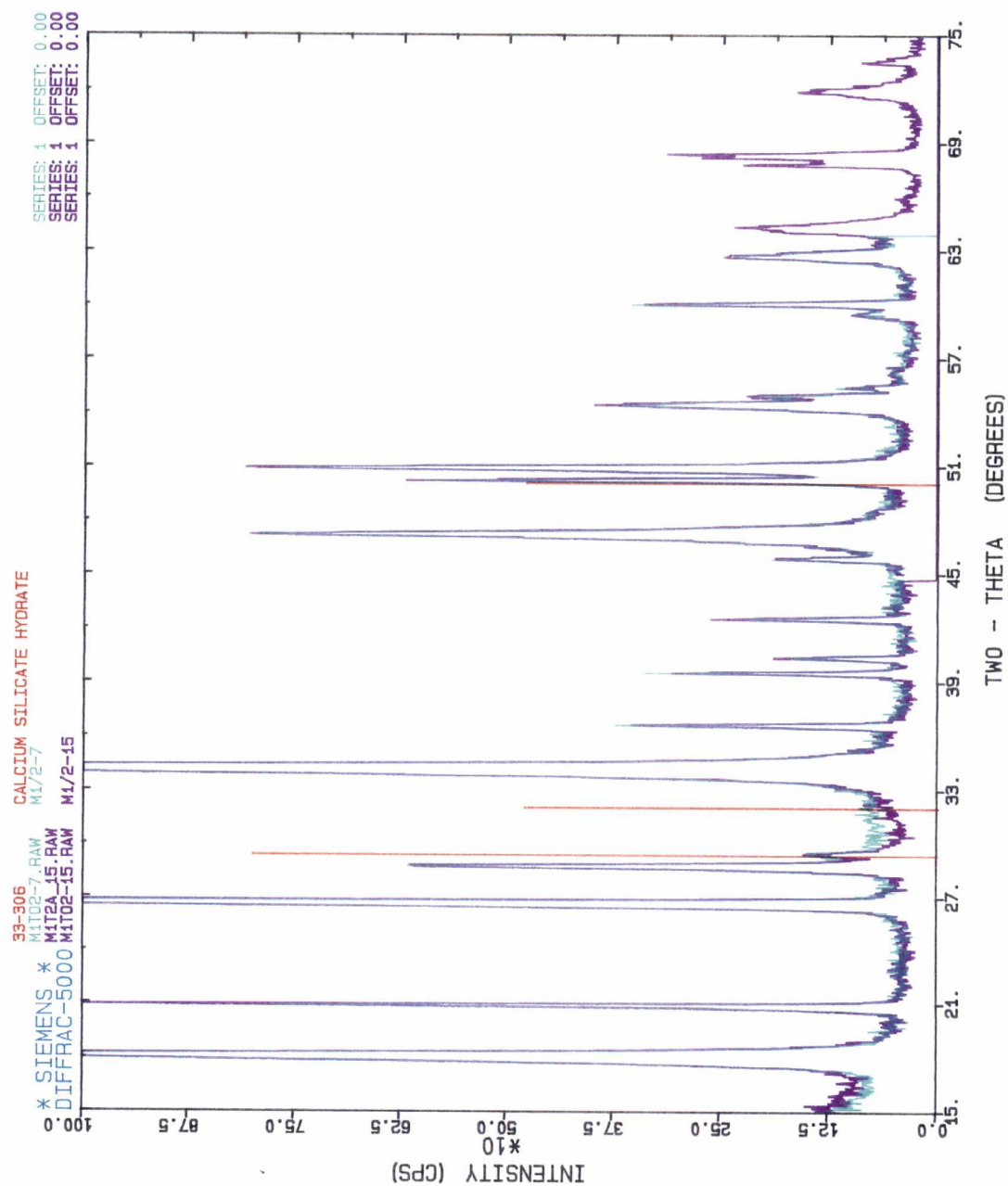


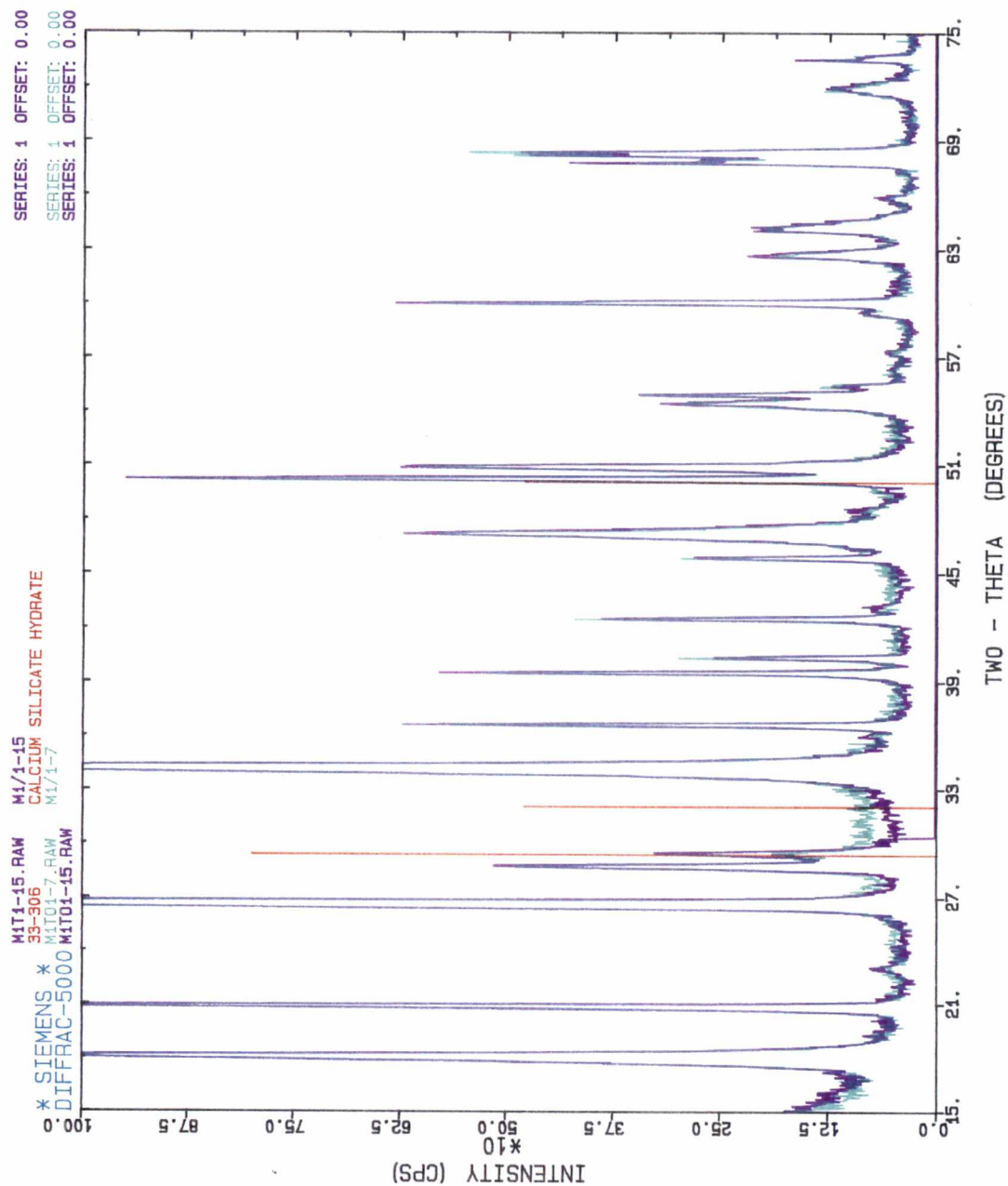
Figure 5.41. X-ray diffraction patterns demonstrating the effect of increasing slurry time on the development of calcium silicate hydrate peaks. (a) crystalline silica:CH ratio of 1:5, (b) crystalline silica:CH ratio of 1:3, (c) crystalline silica:CH ratio of 1:2, (d) crystalline silica:CH ratio of 1:1.

Note: Vertical lines demonstrate two-theta locations for calcium silicate hydrate peaks. Peak at 29° is only peak evident in a calcium silicate hydrate location. This peak may indicate the presence of a minor amount of calcium carbonate. Due to technical problems, the 15 minute samples in (c) and (d) had to be analyzed in two stages. Both purple legend designations refer to the one purple x-ray pattern in the figure.









persistence of the silica and CH for the entire duration of the 15 minute to 7 hour slurry time. More importantly, there is only minor evidence for the formation of calcium silicate hydrate, and it is demonstrated only by the development of the primary peak occurring at a two-theta value of 29.5° . The vertical lines have been included to point out where the peaks of calcium silicate hydrate would occur if they were present. In the absence of the other two peaks associated with calcium silicate hydrate, it is suspected that this peak, which has been referred to as the primary calcium silicate hydrate peak, may actually represent calcium carbonate instead, as the location of the most intense calcium carbonate peak is the same as that of the primary peak for calcium silicate hydrate.

The amorphous hump associated with the production of calcium silicate hydrate seems to be a more accurate marker of the increasing amount of calcium silicate hydrate which is expected with the increasing proportions of silica. Figures 5.41 (a-d) demonstrate an increase in the intensity of the hump after 7 hours of slurry. The hump is best seen between 30 and 33° two-theta, and its intensity is best noted by observing the increasing vertical gap between the 15 minute and 7 hour trace in each pattern. This gap is progressively greater with increasing silica proportions in the sorbent preparations, reflecting the relatively greater amounts of calcium silicate hydrate forming as a result of the greater amounts of dissolved silica. The primary calcium silicate hydrate peak in each pattern, on the other hand, displays inconsistent behavior. The expectation is that the primary peak for each silica:CH ratio would increase with increasing silica proportion relative to the next lower silica:CH ratio. Instead the silica:CH 1:1 and 1:3 ratios have 15 minute peaks of approximately the same intensity, and in both instances the 7 hour peak is unexpectedly lower than the 15 minute peak. The silica:CH 1:2 and 1:5 ratios

exhibit a lower peak than either of the other two, and neither demonstrates an increase in the peak intensity at 7 hours as compared to 15 minutes. If, as mentioned above, the small peak at 20.5° two-theta is calcium carbonate, the amorphous hump is the only evidence of the calcium silicate hydrate which formed in the slurry, and the manner in which the intensity of the hump increased with time and with increasing silica is consistent with the behavior displayed by the amorphous silica/CH sorbents in x-ray diffraction analysis.

5.4.4 Discussion

Figures 5.35 and 5.36 reflect the fact that the way to produce more calcium silicate hydrate is either to increase the slurry time in order that there is time enough for an adequate amount of silica to dissolve or to increase the amount of solid silica in the slurry so that at any given time there is a greater total amount of silica surface exposed to the solution making dissolved silica available for reaction with CH. Although the use of crystalline silica did not cause notable reactivity enhancement, the exercise proved instructive because it was possible to examine the behavior of the calcium silicate hydrate formation in "slow motion" relative to the tests involving amorphous silica. The production of calcium silicate hydrate from crystalline silica was slower than from either amorphous silica or fly ash. The work with crystalline silica, however, offered the advantage of employing pure silica which meant that the analytical results could be compared directly to those of the amorphous silica/CH sorbents.

6.0 CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The primary goal of this study was to characterize the compounds which form in the reaction between the silica from fly ash and CH, but to create them from pure silica, rather than fly ash, in order that they might be more easily analyzed. The objective was to relate the character of the sorbents to their reactivity, and then to determine the mechanism(s) which accounted for the enhanced reactivity with HCl. The three sorbent series, amorphous silica/CH, fly ash/CH, and crystalline silica/CH, formed a continuum based on the availability (by means of dissolution) of the silica from the silica sources and the subsequent rate of reaction in the formation of calcium silicate hydrate. Table 6.1 illustrates this concept. The amorphous silica was highly soluble in high pH solutions, and reacted with the CH rapidly, producing the most reactive sorbents due to the relatively large quantities of calcium silicate hydrate. The glassy silica in the fly ash

Table 6.1. The three silica sources in order of solubility.

Silica Source	Degree of Solubility	Rate of Production of Calcium Silicate Hydrate
Amorphous silica	Highly soluble	Rapid
Fly ash	Intermediate solubility	Intermediate
Crystalline silica	Minimally soluble	Slow

was less soluble than amorphous silica because it consists of aluminosilicate chains (Mehta, 1989) which have a higher degree of polymerization, and, hence, dissolve less readily, than pure silica. The production of calcium silicate hydrate from fly ash was slower as a consequence, but not as slow as the production from crystalline silica, which, as a result of its well-defined structure, dissolved extremely slowly even at high pH. The surface areas of the fly ash and the crystalline silica in this study (1.47 and 0.84 m²/g) respectively, were considerably lower than the surface area of the amorphous silica (486 m²/g). This was another significant reason that the amorphous silica dissolved more rapidly than the other two forms of silica.

The results of this research confirmed previous observations regarding the enhancement of reactivity of CH with HCl when the CH is reacted in aqueous solution with a silica-containing component to form a dry, powdered sorbent. Although the results apply only to the sorbents prepared from the specific silica sources cited in this work, the potential to enhance the reactivity of CH has implications for possible application to dry sorbent injection processes. The following statements summarize the conclusions of this study.

1. The addition of silica in the form of amorphous silica or fly ash into a heated aqueous slurry with CH resulted in enhanced reactivity over that of CH alone. Utilization tests demonstrated that all silica/CH sorbents employing non-crystalline silica resulted in improved utilization of CH. The crystalline silica/CH sorbents demonstrated no increase in utilization over that of CH in most cases because calcium silicate hydrate formation was limited by the

relative insolubility of the crystalline silica. The availability of silica in solution seemed to have been the key factor in producing the reactive sorbents from all silica types. Both amorphous silica and fly ash were able to provide dissolved silica more readily than crystalline silica.

2. The cause of utilization enhancement was the production of calcium silicate hydrate. The addition of silica without slurring resulted in no enhancement of utilization. After slurring the silica and CH, increased utilization was noted, and the only reaction product that was indicated by x-ray diffraction was calcium silicate hydrate. The lack of evidence for any other phases and the fact that slurring CH by itself did not appreciably enhance utilization demonstrated that it was the calcium silicate hydrate which caused the enhanced reactivity of CH in reactor tests with HCl.
3. The proportion of the sorbent which is composed of calcium silicate hydrate (as opposed to CH) controls the extent of increased utilization. For the amorphous silica/CH sorbents there is a linear relationship between the ratio of silica:CH in the starting components and utilization. Utilization has a logarithmic relationship with time. These relationships hold as long as there was excess CH in the slurry.
4. Only one type of calcium silicate hydrate formed in the slurries prepared from amorphous silica and CH. It was identified as C-S-H(I). This particular type of calcium silicate hydrate is one of only two which form at temperatures lower

than 100 °C. Its stoichiometric formula ranges from $\text{CaO}_{0.8} \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$ to $\text{CaO}_{1.5} \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$.

5. Surface area of the calcium silicate hydrate was not a good predictor of utilization. However, the development of surface area associated with the formation of calcium silicate hydrate may have been involved in reactivity enhancement. The amorphous silica:CH ratios of 1:10, 1:5, 1:3, and 1:2 (with the exception of the 7 hour 1:2 sample) consistently demonstrated increasing utilization and surface area, both with time and with increasing silica proportion. Both trends probably reflect the production of more calcium silicate hydrate. More calcium silicate hydrate results in higher surface area because more of the material is calcium silicate hydrate and less is CH, which has a lower surface area.

6.2. Recommendations for further study

Reactor test conditions, including gas moisture content, were held constant in the experiments of this study so that the effect of varying the parameters of sorbent preparation could be determined. The effects of varying slurry time and silica:CH ratio related primarily to the quantity of calcium silicate hydrate which could be produced. It would be appropriate to determine next the effect moisture has on the utilization of the sorbents. There are at least two aspects of this approach. One is to determine the impact of changing the gas stream moisture on reactivity. This can be done by either changing the reactor temperature or changing the volume of moisture in the gas stream, thus changing the relative

humidity. Pakrasi (1992) demonstrated that relative humidity was important in both the reaction rate and the final utilization of CH with HCl. The single test in this study in which sorbents were reacted in a dry gas stream demonstrated that reactivity was dramatically lower without 10% moisture in the gas, and indicate that gas stream moisture content has an important influence on reactivity. The other aspect regarding the role of moisture in sorbent utilization is the moisture content of the prepared solids. Determining the amount of water in the prepared solids, both adsorbed and structurally bound, might provide insight into the mechanism of reactivity enhancement. The practical application of how the moisture content of the products relates to reactivity would be in determining the sorbent preparation conditions which result in particular moisture contents for the solids.

The amorphous silica that was used in this study resulted in sorbents with greatly improved reactivity. Cost of the silica was not a consideration in this study because the purpose of its use was to aid in the investigation of the reactive solids produced when fly ash is employed as the silica source. It is unlikely that amorphous silica would be an economically viable raw product in the production of commercial sorbents. However, if it were possible to cost-effectively recycle the silica, the use of such a raw material might be possible. Investigating this possibility would involve determining the compound(s) produced from the reaction of calcium silicate hydrate and HCl. If, as is the case with CH and HCl, the reaction product is simply CaCl_2 , this very water soluble salt might be separated from the silica portion of the sorbent, thereby allowing reuse of the silica in further sorbent preparation. The structure and ability of this remaining silica would need to be evaluated to determine if it could be used as a source of silica to form

additional calcium silicate hydrate. Although the use of pure silica in this study was for the purpose of modeling the reaction product of fly ash and CH, the high reactivity sorbent produced when amorphous silica was used suggests further study of amorphous silica as the silica source rather than fly ash.

In order to understand the mechanism of reactivity enhancement, the silica component in the amorphous silica/CH sorbents should be increased to cover ratios of silica:CH beyond the ratio of 1:2. Naturally, more information on the effect of temperature of preparation would be desirable; however, this greatly expands the matrix of trials required. It was evident from the utilization tests and surface area analyses that the nature of the calcium silicate hydrate changed between the silica:CH ratios of 1:2 and 1:1. This occurrence may be related to the lack of CH as the silica content increases to the point where there is excess silica rather than excess CH. Although it is unlikely that sorbents consisting of high quantities of silica are going to be useful in commercial applications due to the low concentrations of calcium in the materials, the behavior of the materials might provide insight into the mechanism(s) responsible for making the CH used in producing calcium silicate hydrate more reactive with HCl than CH alone.

Finally, in an attempt to understand the aspects of calcium silicate hydrate that influence utilization, the roles of pore sizes, pore distributions, and molar volumes of reactants and products should be investigated to determine the role each plays in enhanced reactivity.

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APPENDIX



PRODUCT DATA

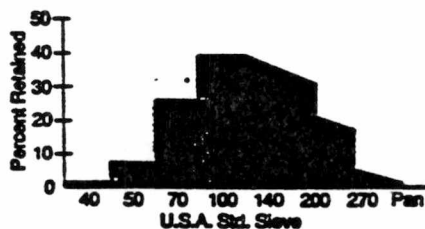
F-75

Mine: Ottawa, Illinois

Form Number: 5022

Date: June, 1967

TYPICAL SIZE ANALYSIS:



U.S.A. Std. Sieve	Millimeter Designation	% Retained On Sieve		% Retained Cumulative		% Passing
		Mean	Range	Mean	Mean	
40	.425	0.3	0-1	0.3	99.7	
50	.300	6.0	3-9	6.3	93.7	
70	.212	25.4	20-30	31.7	68.3	
100	.150	39.9	35-45	71.6	28.4	
140	.106	22.0	17-27	93.6	6.4	
200	.075	5.8	3-9	99.2	0.8	
270	.053	0.8	0-2	100.0	0	
Pan		T	0-0.5	T		

TYPICAL PHYSICAL PROPERTIES:

Mineral	Quartz	Melting Point	3100°F
Color	White	Theoretical Surface Area (cm ² /gm)	138
Grain Shape	Rounded	Actual Surface Area (cm ² /gm)	162
Sphericity (Krumbein)	.8/7	Coefficient of Area	1.17
Roundness (Krumbein)	.8/7	Base Permeability	71
Hardness (Moh)	7.0	Moisture Content Dry (Max.)	<1
Specific Gravity	2.65	Acid Demand (pH-7)	<1
Bulk Density - Compacted (lbs/ft ³)	104	AFS Grain Fineness (Range)	71-79
Uncompacted (lbs/ft ³)	92	pH	Neutral

VITA

Parham Mikell Cain was born in Charleston, South Carolina on November 24, 1958. She attended Ashley Hall High School from 1973 to 1976 and the College of Charleston from 1976 to 1980. In 1981 she moved to Knoxville, Tennessee to attend graduate school at the University of Tennessee. Upon graduating with a Master of Science degree in geology, she acquired a teacher's certificate, and taught high school for a year. Realizing that it was easier to work year round than teach school, she left teaching and went to work for IT Corporation in New Jersey. She transferred back to the Knoxville office of IT, and worked there until she returned to the University of Tennessee to pursue studies in engineering. She worked full time for Dr. Wayne Davis in the Department of Environmental Engineering while completing the necessary undergraduate engineering courses prior to beginning the doctoral program in Civil and Environmental Engineering in 1990. The full three years were funded by a fellowship from the Waste Management Research and Education Institute.