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**SYNERGISTIC CAPTURE MECHANISMS FOR ALKALI
AND SULFUR SPECIES FROM COMBUSTION**

Final Report

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ABSTRACT

Experimental work was carried out on a 17 kW, 600 cm long, gas fired laboratory combustor, to investigate the post flame reactive capture of alkali species by kaolinite. Emphasis was on alkali/sorbent interactions occurring in flue gas at temperatures above the alkali dewpoint and on the formation of water insoluble reaction products. Time-temperature studies were carried out by injecting kaolinite at different axial points along the combustor. The effect of chlorine and sulfur on alkali capture was investigated by doping the flame with SO₂ and Cl₂ gases to simulate coal flame environments. Particle time and temperature history was kept as close as possible to that which would ordinarily be found in a practical boiler. Experiments designed to extract apparent initial reaction rates were carried using a narrow range, 1-2 μm modal size sorbent, while, a coarse, multi size sorbent was used to investigate the governing transport mechanisms.

The capture reaction has been proposed to be between alkali hydroxide and activated kaolinite, and remains so in the presence of sulfur and chlorine. The presence of sulfur reduces sodium capture by under 10% at 1300°C. Larger reductions at lower temperatures are attributed to the elevated dewpoint of sodium sulfate (~850°C) with subsequent reduction in sorbent residence time in the alkali gas phase domain. Chlorine reduces sodium capture by 30% across the temperature range covered by the present experiments. This result has been linked to thermodynamic equilibria between sodium hydroxide, sodium chloride and water.

An optimum temperature window between 900°C - 1100°C, in which the formation of water insoluble alkali alumino silicates is favored, has been reported. Above 1200°C the sorbent used here, melted. Sorbent melt at such low temperatures is probably due to the impurities (Ti, Fe, K) in kaolinite.

A simple first order kinetic model is proposed for sodium capture by metakaolinite and is best fitted by volume rate $k = 4.5 \pm 0.5 \times 10^7 \exp(-5300 \pm 150 \text{ kcal/RT}) \text{ cm}^3 \text{ gas/ cm}^3 \text{ porous solid.sec}$. Activation energies in the range of 6-10 kcal/mol gave model prediction results that compared very well with experimental data. Kinetics is the rate controlling mechanism for small particles under 3 μm, while intraphase pore diffusion was shown to be the controlling mechanism for particles larger than 3 μm. A maximum sorbent utilization of 50% was realized.

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1.0 INTRODUCTION

1.1 BACKGROUND

Fouling of heat transfer surfaces is a serious operational problem in conventional boilers burning lignite and sub bituminous coals. Such coals are rich in alkalis (sodium and potassium), and it is the presence of these alkalis that has been associated with the formation of hard bonded deposits on the convection and other heat transfer surfaces. Alkali induced, hard bonded deposits are difficult to control by on line cleaning alone. One possible solution is to inject suitable additives into the combustor that can react with the gas phase alkali species prior to the onset of condensation. In this work, we set to investigate in detail, the mechanisms governing alkali metal capture by clay additives (sorbents) when such additives are injected into a combustor environment that contains alkali species.

A suitable clay sorbent should reduce fouling in two ways: First, it should react fast with alkali gaseous species (NaCl , NaOH etc.) to produce "chemically benign" products (stable compounds that do not react further on contact with heat transfer surfaces). Such reaction products should be such that they are not associated with corrosion, fouling or slag formation. Second, deposits formed from a mixture of the ash and alkali-clay reaction products, should be of low bonding strengths on solid surfaces so that they can be removed easily by conventional soot blowing programs on heat transfer surfaces. To achieve the second goal, it is important that the capture products are not in a molten state that are likely to stick on heat transfer surfaces.

This work will attempt to focus on mechanisms that can be exploited in the pure gas-solid reaction regime between gaseous alkali species and particulate sorbent compounds. Mechanisms so identified in these studies are likely to be directly applicable in environmental engineering where control of toxic metal emissions from hazardous waste incineration plants is of critical importance. Linak and Wendt (1993), in a review paper on control of toxic metal emissions from incineration, addressed whether or not such metal vapor can be scavenged reactively by sorbents to form environmentally benign compounds. They argued that if the metal is to react with sorbent particles, the scavenging process must occur above the metal dew point, and since such a reaction may have a high activation energy, it can in fact, be enhanced by the high temperatures present in incinerators. Scotto (1992) investigated the capture of lead (as a typical toxic metal found in municipal and hazardous waste incineration system) by clay sorbents and showed that typically 99% capture of lead is possible when kaolin clay is injected into such an environment.

An added advantage to studying alkali metals is that since alkali metals are not toxic, they can be studied in more detail at combustor level where the risk of exposure is greater. The flue gas can be doped with varying concentrations without endangering the experimentalist, and if the combustor studies results can be matched (scaled) with the bench scale results, then this experience can be used to translate bench scale results of toxic metals such as mercury, chromium, etc. to practical combustor results without necessarily carrying out combustor studies on toxic metal vapors.

Sorbent injection is not the only method available for control of fouling in large scale boiler units. Other approaches to the control of fouling include; selective mining and blending of coals, prewashing of coals in slightly acidic solutions to remove the cations of Na^+ and K^+ , and to some extent, over design of boilers in terms of volume (surfaces) per unit power output (Sondreal, 1977). Each of these methods is carry prohibitively high costs, consequently, the use of cheap, relatively abundant, and technically understood clays, is a very attractive alternative.

Related research is currently underway focussed on the development of particulate control devices such as; (i) Electrostatic Precipitators (Research Cottrell), Granular Bed Filters (Combustion Power Company) and Ceramic Cross Flow Filters (Westinghouse). A review of these works can be found in literature (Saxena et al., 1985; Zakkay et al., 1989). High temperature particulate removal systems can be combined with successful sorbent injection programs for capture of alkali species from coal fired gas turbines where the allowable alkali level on turbine blades is usually more critical and typically requires 99% (and above) alkali removal efficiencies (Spiro et al.; 1990). Fast reaction rates, capture product stability and efficient sorbent utilization, therefore, become critical factors in the choice of sorbent to be used in such demanding environments.

1.1.1 Alkali Metals in Coal Mineral Matter

Coal mineral matter (non carbon inorganic matter) comprise mainly clay aluminosilicates, trace metal oxides, chlorine and sulfur. Depending on the coal, and its genealogical origin, the mineral matter content ranges from 9 to 20 wt. % in coal (Gluskoter, 1977). Aluminosilicates ($\text{Al}_2\text{O}_3 \cdot n\text{SiO}_2$) together with quartz (SiO_2) often account for 60 to 90 wt. % of the total mineral matter (Mitchell and Gluskoter, 1975; Gluskoter, 1977; Raask, 1977). The major mineral constituents of the aluminosilicates are kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$), Illite (potassium aluminosilicate) and quartz (SiO_2). Also present in the mineral matter are oxides of Ca, Fe, Mg, Na, K, together with chlorine and sulfur (Plogmann and Mackowsky, 1977). Alkali species (Na, K) exist in the mineral matter in trace amounts with the concentration of sodium typically in the range of 700 to 1000 ppm (wt) regardless of the coal rank (Neville and Sarofim, 1985; Raask, 1977). Sodium in lignites and sub bituminous coals is present as salts of organic matter, whereas in bituminous coal, it is partly associated with chlorine and partly with the silicates. Potassium, on the other hand, is present almost exclusively bound with the aluminosilicates (Raask, 1977; Wall et al., 1979). Much of the studies on ash fouling, has attempted to correlate fouling tendency of a coal with (1) its alkali content and (2) how the alkali metal is partitioned in the coal mineral matter. It is generally agreed that alkali species which exists as salts of organic matter (typically sodium) volatilizes fast during combustion at high temperatures and is released into the flue gas. At low temperatures, these fumes may condense either on the heat transfer surfaces or may be emitted as sub micron fumes with coal ash. Potassium bound with the aluminosilicates, typically remains in the aluminosilicate ash structure and is, to a much lesser extent, associated with fouling. In a recent study, Gallagher (1992) investigated the partitioning of alkali species in the coal matrix, their subsequent release during combustion and capture back into the ash matrix. He showed that under certain combustion conditions, sodium, may in fact displace potassium which would otherwise be immobile, bound in a stable mineral form as Illite.

The effect of the presence of chlorine on the release of alkali species into the flue gas during combustion has been studied and reported (Raask, 1977; Neville and Sarofim, 1985; Spiro, et al. 1985; Huffman et al., 1990; Gallagher, 1992). Sodium that occurs as chlorides is vaporized from the burning coal particle with little or no time for dissociation, or reaction say with silica that is present in coal (Wall et al., 1979). At higher temperatures, the release of sodium has been reported to decrease as increasing amounts react with silica to form molten silicates (Neville et al., 1985). In the same studies, carried in a bomb combustor, Neville et al. (1985) showed that up to 43% of sodium in coal was collected as fumes and hence provided a measure of the volatilization of sodium during combustion. The amount of sodium appearing in the fumes increased with Cl:Na ratio but decreased with respect to silica content in the parent coal.

The reactions of sodium, chlorine and silica were studied in a laboratory drop tube combustor by Wibberley and Wall (1982) in which they showed that alkali-silicate reactions can be predicted by thermodynamic considerations. In the same studies, formation of silicates was associated with significant melt.

The release of potassium from the aluminosilicate matrix has been linked to the presence of sodium chloride. Raask (1977) attributed its release to a substitution reaction between vaporized sodium chloride and the aluminosilicates as shown in Equation 1.1

Gallagher (1992), from experiments carried in a laboratory combustor, concluded that the release of potassium from the aluminosilicate did not take place in the presence of sodium alone or chlorine alone, but instead required the presence of both sodium and chlorine.

In a related study, Haynes, Neville and Quann (1981) investigated the fate of the volatile species that are released in the coal combustion environment. The hitherto held view was that once volatile trace species are released in the flue gas environment, such species condensed back onto the ash particle surfaces via diffusion controlled heterogeneous condensation. Using a laminar flow drop tube furnace, they showed that although most of the coal ash is found in the 5 to 10 μm range, over 90% of the condensed trace species was still found in the sub micron fume range (under 0.4 μm) and may exhibit a d^{-1} or d^{-2} dependence when diffusion controlled heterogeneous condensation should give exclusively $1/d^2$ dependence. This result was attributed to the high specific surface areas found in the sub micron ranges even when the super micron particles comprise the bulk of the mass. The mechanism for capture of volatile species was suggested to be that of surface reaction controlled deposition whereby trace species vapor react at the surface of sub micron mineral matter. It is an important result from sorbent injection point of view because it shows that in the absence of chemical reactive capture, injecting particles into a combustor may not result in significant physical capture of trace alkali species onto the sorbent particles, instead most of it will still be found as sub micron fumes that may not be easy to collect by conventional particulate collection devices. Gallagher (1992) reported that addition of silicates to coal reduced the fraction of alkalis found in the fume stages which can only be explained by a reaction phenomena rather than physical condensation. Sodium reaction with

silicates captured 70 to 95 % of total sodium for typical coals, thus concluding that silicate additive could be a viable technique for reducing the fraction of alkali in vapor during combustion.

1.1.2 Mechanism of Ash Fouling

The association of alkali species with fouling, like other results of coal combustion studies, has been in part evolutionary, in part based on statistical correlations, and in part based on fundamental characterization of the product ashes. A typical structure of ash deposits has been shown to consist of three distinct layers as shown schematically in Figure 1-1 (Benson, 1988). The three layers, formed sequentially as deposition progresses, lead to deductions of the possible mechanisms that underlie deposit formation. The first layer is a thin, millimeter size, whitish powdery layer of deposits all around the tube. This base layer contains a large amount of alkali sulfates, typically 57% (by wt.) Na_2SO_4 for a 10 ppm sodium in flue gas (Neville and Sarofim, 1983; Raask, 1985). It is postulated that the mechanism of formation of this layer involve transport of gas phase sodium by diffusion processes from the hot flue gas to the cooler heat transfer surfaces. This is followed by surface reactions between gas phase sodium chloride or hydroxide with O_2 , SO_2 , or SO_3 , forming alkali sulfates (Rosner, 1986; Benson, 1988; Steinberg, 1990).

The second layer is formed by inertial impaction of ash particles. The characteristic of this layer is that the particles look discrete, sintered and bonded together. The bonding strength and stickiness of this layer is thought to be due to the cementing properties of $\text{Na}_2\text{SO}_4(\text{c})$ and partly to the effect of molten sodium silicates ($\text{Na}_2\text{O} \cdot n\text{SiO}_2$) (Suzuki et al., 1988). The melting temperatures of sodium silicates can be as low as 650°C (Levin, 1964). This second layer of sintered deposits may build up to thick layers leading to a substantial reduction of heat transfer to the tubes, plugging of gas passages, or providing an environment which complex sulfates may form to cause metal corrosion (Reid, 1971). The final outer layer is generally comprised of loosely bound particulate matter. In many cases this layer is easier to remove by water jet soot blowing techniques.

The desirable characteristics of an in situ applicable sorbent includes three requirements. First, as stated earlier, the sorbent should react fast with gas phase sodium chloride and hydroxides to form inert products. The reaction time scale must be less than that set by the elevated dew points of sodium sulfates, and typically of the order of 1 to 2 seconds in a characteristic boiler. Second, the propensity to form significant amount of low-melt-temperature alkali silicates should be low. These molten silicates can also contribute to deposit bond strengths. Third, such a sorbent needs to be effective in minimal quantities that does not contribute to a significant coal ash dust loadings. Increased ash loadings may result in either blinding the flame or an overload of deposits.

1.1.3 Development and Characterization of Clay Sorbents.

Much of the progress in the development of effective alumino silicate additives to control the effect of alkali impurities was carried in the 1960's. This early work focussed on the control of corrosion that is induced by impurities found in liquid fuels. Extensive evaluation of silicates

Figure 1-1: Physical structure of a typical deposit on a boiler tube.

as additives was reported by Nelson and Lisle (1965). They showed that several high surface area silicates inhibited corrosion by adsorbing alkali sulfates. Kaolin ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$), Diatomaceous Earth (5% Al_2O_3 , 90% SiO_2) and Bentonite were found to be more effective in reacting with the complex alkali tri sulfates than non porous silica. Niles, as reported by Reid (1971), investigated kaolin and concluded that kaolin was a more effective additive where alkali sulfates were concerned.

A more extensive evaluation of clay sorbents for alkali control, under a combustion environment, was to be carried at Argonne National Laboratories by Lee and Johnson (1980) who reported results of screening studies in which Alundum (nearly pure alumina), Diatomaceous Earth, Silica gel, Kaolin and Activated Bauxite (80% Al_2O_3 , 10% SiO_2) were investigated by passing a simulated flue gas containing known amounts of alkali content through a fixed bed of clay sorbents. The results showed that Diatomaceous Earth and Activated Bauxite were the most promising sorbents. These results, unlike previous ones, did not report kaolin clay as the most effective sorbent, instead kaolin was found to have a tendency to become "fragile" in a fixed bed setup. Fragility led to fine particles being entrained into the flue gas. Capture rate was also reported to be independent of flue gas superficial velocity, a phenomena more specific to deep bed filtration at low temperatures, than to sorption-reaction mechanism.

Wibberley and Wall (1982) reported results of experiments carried in a drop tube furnace to investigate the formation of sodium silicates, in reactions between silica particles and synthetic flue gas containing sodium, chlorine, sulfur and water vapor. The silica particles were injected into a vertical tube furnace and allowed to fall through the hot zone under the influence of gravity and gas flow. The total residence time scales was between 1 to 3 seconds. They showed that sodium reacted with silica to form a thin layer of silicates on particle surface. This layer was in the range of 0.02 μm to 0.31 μm thick, and had an average composition between 9 and 36 wt% Na_2O . This work is of particular interest to our present work as it showed that alkali-silica reactions could take place in the time scales of 1 to 3 seconds.

More fundamental work on sorption-reaction was to be carried by Luthra and LeBlanc (1982), who proposed the possibility of using in situ sorbent injection as a means of alkali control. In bench scale, microbalance type set up, sorption-desorption kinetics experiments were carried on alumina and activated bauxite at 800°C - 900°C using a simulated flue gas containing NaCl and KCl. They showed that although adsorption was strong enough to reduce alkali concentrations in a flue gas, conventional approach of using packed bed of microporous sorbent particles may be uneconomic. This is because the mass transport of NaCl and KCl gas molecules to adsorption sites deep in the sorbent particle would be inordinately too slow. They suggested the problem could be circumvented by the injection of sub micron sorbent particles into a flue gas. The sub micron particles, while providing large surface areas for capture reactions, were not expected to cause damage to gas turbines, consequently they could be filtered only after the turbine for environmental reasons.

Scandrett and Clift (1984) examined the thermodynamic equilibrium of alkali-alumino silicate capture reactions. From calculations of dew points of alkali sulfates in a flue gas (probably the most damaging alkali species in flue gas), they showed that gas-solid capture need

to be exploited at temperatures above 850°C. Below this temperature, the formation of condensates may significantly inhibit extent of sorbent utilization.

Klinzing and Blanchere (1986) used a down fired, pulverized coal combustor to study the capture of sodium chloride from a flue gas by various adsorbents. They tested alumina (Al₂O₃), emathelite (15% Al₂O₃, 85% SiO₂) and porous silica glass (SiO₂) as possible adsorbents. A North Dakota, high sodium, lignite coal was mixed with adsorbents at a level of 5% (by weight) and the mixture fired into the furnace under self sustained flame conditions. The particle residence time scale was of the order of 1.5 to 3 seconds in a temperature range of 650°C - 900°C. Both fuel rich and fuel lean environments were considered. They reported that activated alumina was the most effective adsorbent and capture in this case was predominantly by physical adsorption. Some chemically fixed sodium on silica glass was also reported, although no functional relationships could be established between adsorption and temperature.

The work of Punjak and Shadman (1988) followed closely that of Luthra et al. (1982). Using bench scale microbalance set up, sorption-desorption experiments were carried out on alumina, silica, bauxite, emathelite and kaolinite. The product of capture was then subjected to water solubility tests to discriminate between reaction induced capture and physical adsorption. The water soluble alkali content was considered physisorbed while the water insoluble alkali content was considered chemisorbed. The results showed kaolinite as the most effective sorbent in forming water insoluble nephelite and kaliophilite as given by the capture reaction of Equation 1.2. The product of capture reaction was identified, using X-ray diffraction techniques, as nephelite, in case of sodium or kaliophilite, in the case of potassium.

Uberoi and Shadman (1990), using a similar apparatus as that of Punjak et al. (1988), studied the sorption desorption kinetics of sodium capture on kaolinite, bauxite and emathelite in the temperature range between 800 to 1100°C. They developed a diffusion reaction model to extract intrinsic reaction rate parameters from bench scale results. This model also accounted for both the effect of condensation on particle surface and in the pore condensation. The results showed that kaolinite and bauxite are more suited than emathelite for *in situ* removal of alkali vapor, while all the three are suitable for downstream removal. Kaolinite had the highest alkali capacity and the highest activation energy for alkali removal. The volume reaction rate coefficient, (k_v), was given as $2.1 \times 10^7 \exp(-31 \text{ kcal/RT}) \text{ cm}^3\text{gas/cm}^3 \text{ solid. sec.}$ Compared to reaction rates that had been reported previously by Wibberley et al. (1982), with time scales of seconds, the bench scale kinetics of Uberoi (1990) were slow with characteristic time scales of minutes. Gallagher (1992) later attributed the slow apparent reaction rates that were observed by Uberoi to the presence of chlorine and to low water content (~3%) of the simulated flue gas that was used in the bench scale studies. The effect of the presence of chlorine on the kinetics of alkali sorbent reactions has not been determined conclusively. There is, however, strong evidence that chlorine reduces significantly the extent of alkali capture by certain sorbents, particularly kaolinite (Wibberley et al., 1982; Gallagher, 1992).

Rizeq (1990) investigated the effect of alkali adsorption on the agglomeration of particles of bauxite, kaolinite, emathelite, lime and two types of coal ash. Using thermo gravimetric apparatus similar to that of Uberoi, together with detailed Scanning Auger Microscopic analysis of particulate samples, he showed that the agglomeration temperature of all substrates (sorbents) decreased as the captured alkali content increased. At low alkali loadings, alkali adsorption enhances particle agglomeration by forming new compounds of lower melting points, while at high concentrations, adhesion and agglomeration are caused by a layer of molten alkali which covers the exterior of the particles. In further studies performed on a 17 kW, 6 m long down fired combustor, Rizeq concluded that the bench scale kinetics of Uberoi could be used to predict alkali capture in a combustor. His model predictions that applied the same (Uberoi's) kinetics, however, showed that if indeed these kinetics were applicable, then capture should be dominated by physical condensation rather than reactive capture. Rizeq's experimental work did not attempt to discriminate, in its analysis, between physical capture and chemical reactive capture, and so, it is difficult to verify from Rizeq's work whether or not the bench scale kinetics of Uberoi can be applied in their present form, in a practical combustor. The results of Rizeq (1990) are by large inconsistent with the observations of other workers (Wibberley et al., 1982; Gallagher, 1992; Spiro et al., 1990 and lately Scotto, 1992). In all these other works, it has been noted that reactive capture (as opposed to physical capture) between kaolin and sodium (Lead in the case of Scotto) is the most likely dominant capture phenomena with a characteristic time scale of seconds, as opposed to Uberoi's bench scale kinetics that has characteristic time scale of the order of minutes. It is also to be noted that Rizeq's combustor studies used KCl as alkali source whereas Uberoi's kinetics were for NaCl as alkali source. Whether or not the kinetics of the two alkali species are the same has not been addressed.

Alkali capture is proposed to involve a reaction between gaseous alkali species and the $\text{Al}_2\text{O}_3\text{-SiO}_2$ bond structure, instead of separate reactions with alumina and silica alone. This probably explains why kaolinite with a near 50-50 alumina to silica composition, has consistently showed superior capture characteristics than alumina, silica, bauxite or emathelite. With bench scale studies pointing to kaolin clay as the most effective sorbent, more recent works have shifted attention to the interaction of kaolin within a combustor environment vis a vis their effect on fouling downstream. Specific issues such as deposit bond strengths, reaction time scales, and relative ratios of sorbent to ash content that would produce effective results need to be addressed.

Field experiments on the use of kaolin clay to control alkali species have been reported by several workers (Lindner et al., 1988; Spiro et al., 1990; Logan et al., 1990; Wall et al., 1990). Lindner, Kosminski and Williams (1988) reported results of the effect of additives on the behavior of South Australian brown coals. From experimental studies performed on 0.35 Mw furnace, deposits were examined after 8 hours of firing the brown coal with known amounts of additives. They showed that by injecting clay minerals into the combustion zone, superheater deposit strength could be reduced. The reduction was attributed to the formation of nephelite that reduced the amount of condensable sodium in flue gas. When calcium based sorbents were used to capture sulfur independently, no significant reduction of deposit bond strength was achieved as in the case of addition of kaolin. The addition of bauxite ultrafines, despite having higher alumina content and higher surface areas, did not show any superior effectiveness in terms of low deposit strengths. Both hydrated alumina and free silica were equally less superior than kaolin clay.

Spiro et al. (1990) carried experiments on deposit formation on turbine aerofoil blades with a focus on the ratio of sorbent additive to ash that would give the best results. Kaolin clay and coal were prepared to a fine, $0.6\ \mu\text{m}$ particle size, slurry mix. Sodium polyacrylate surfactant was added to the slurry giving the final "fuel slurry" composition of 0.8% (by weight of dry coal) kaolin, and 2.8 ppm sodium. The slurry was then burned in a turbine simulator with special measure taken to accommodate the presence of additives. On line measurements of deposition rates were measured on critical throat areas between aerofoils downstream. Other sorbents that were tested included alumina and boehmite. Kaolin clay was again the most effective sorbent in reducing deposition on aerofoils when compared to Boehmite (an hydrated $30\text{--}40\ \mu\text{m}$ alumina granule). Results showed that the reduction in critical throat area of their test turbine was negligible when kaolinite was added in an amount sufficient to match the coal ash.

Logan and Richards (1990) using electrically heated, drop tube laboratory combustor designed to operate at 1400°C , carried out deposition experiments at combustion zone temperatures of $1100\text{--}1300^\circ\text{C}$. Coal was mixed with mineral matter (clay) and then injected into the combustion zone. At the exit of the combustion zone the products of combustion were accelerated through a $3.2\ \text{mm}$ diameter nozzle, creating a jet which impinged on a flat $12.7\ \text{mm}$ diameter platinum disk. The resultant jet velocity of $300\ \text{m/sec}$ was within the range of a gas turbine. The rate of deposit build up was measured by weighing the amount of deposits after a specified time period. The sticking coefficient was calculated as the ratio of the weight gain to the total mass arriving at the target. The results of these experiments showed that up to 7.5% kaolin addition rate (percent by weight of coal) decreased significantly the stickability of downstream deposits.

The work of Wall and Lindner (1990) involved experimental studies in which a "synthetic" coal was mixed with sorbents in known quantities and burnt in a laboratory drop tube combustor. The synthetic coal was produced, first by leaching coal to remove ion exchangeable constituents comprised mostly of Na, K, Ca and Mg. After washing the leached coal, known amounts of inorganic constituents were added to it and the mixture made into a thixotropic slurry, which was then dried and ground to a known size classification. The added kaolin and silica had been separated into required size fractions. Their results showed that: (1) capture reactions proceeded within the coal combustion time scale and negligible capture reactions continued after combustion was complete. (2) influence of temperature on the amount of silicates formed was negligible. This was attributed to the increased parallel rate of coal combustion with increased temperature. (3) sodium, when supplied as sodium chloride, resulted in 3-5 times reduction of the amount of sodium capture products formed as compared to when sodium was added as sodium acetate. (4) sulfur depressed the amount of capture products but to a much lesser extent than chlorine. (5) kaolin, again, was the most effective sorbent as compared to either alumina or silica alone.

1.2 SCOPE OF THIS WORK

Recent studies on the fundamentals of alkali capture by adsorption and reaction have been carried using either thermal gravimetric apparatus (Luthra and Le Blanc, 1982; Punjak et al., 1988; Uberoi, 1990), or by using a differential reactor set up (Lee and Johnson, 1980; Lee and Swift, 1991). Combustor studies, on the other hand, have focussed on; (1) capture characteristics of various sorbents (Klinzing, 1986; Lindner et al., 1988;), (2) the effect of

additives on downstream fouling (Spiro et al., 1990; Logan et al., 1990; Wall et al., 1990), or 3) alkali induced agglomeration of sorbent particles (Rizeq, 1990).

However, one area that has not been addressed by combustor studies is that of extracting fundamental mechanisms that govern chemical reaction between gas phase alkali species and injected sorbent particles. In particular, there is need to differentiate between chemical reaction capture and physical capture such as condensation. This work will identify specific mechanisms that can be exploited to optimize capture by chemical reaction. It will address, in detail:

- Mechanisms: thermodynamics, mass transport, reaction kinetics and other theoretical aspects such as sintering, phase transformations etc. that govern optimum sorbent utilization.
- Reaction rate time scales and if possible derive the fundamental kinetic parameters.
- The effect of injection temperature and whether or not there exist a favorable temperature window for capture
- The effect of species present such as SO_2 , and Cl_2 .
- The effect of particle size and hence governing transport mechanisms.
- Sorbent morphology changes with temperature.

There is need to evaluate sorbents in an environment from which the results can be translated into practical use in an industrial scale boiler. The laboratory down flow combustor offers such an environment both in terms of residence time and temperature scales that can be realized. An appropriate experimental approach that can be used to extract time resolved data will be adopted. Romans et al. (1991), in a review on sorbents for capturing SO_2 in fluidized combustor, discussed several techniques for sorbent evaluation. The majority of data and results reported on sorbent evaluation have been obtained using either a thermo gravimetric analyzer (TGA) or a differential reactor. There are advantages and disadvantages to both systems. The thermal gravimetric approach of sorbent characterization, whereas having the advantage in terms of ability to use very small sample weights, accurate control of temperature-time history and gas composition, the simplicity in its design creates many disadvantages, notably: (1) use of unrepresentative samples (using milligrams to characterize tonnages), (2) Slow heating rates of sorbent compared to that of a practical combustor, (3) particles in the set up are stationary and is continuously exposed to fresh flue gas composition, therefore the flow and mixing characteristics of a combustor are unobtainable, (4) no particle-particle interaction and (5) limited temperature range. The differential reactor set up, in which sorbents are supported on a frame and a simulated flue gas passed through, is closer to deep bed filtration set up, and hence preferred over thermal gravimetric approach, for evaluating sorbents that can be used in a fluidized bed combustor. Its results are, however, limited in scope in their applicability on an *in situ* injection scheme. The down flow combustor, to be described in Section 3, offers an attractive and practical alternative that is closer to field studies. Extraction of fundamental mechanisms, reaction rates and uncoupling of partial effects, is however, difficult.

The sorbent of choice for this extensive study is kaolinite. A mathematical model that takes into account combustor temperature profile and flow characteristics, to predict alkali capture will be developed. It is the purpose of this work that parameters and models so developed will be practical, realistic and can be used in industrial scale design.

2.0 THEORY

Extensive research effort was expended in the 1980's, sponsored jointly by the U.S. Department of Energy, US Environmental Protection Agency, and industry, on sulfur dioxide control by limestone injection under the Limb project (Borgwardt et al., 1982). Details of these works can be found from several DOE reports on SO₂ control. In the absence of similar work on alkali metals, we have drawn a significant portion of our background theory from the literature on SO₂-Limestone experiments together with literature on Kaolinite clays and aluminosilicate structures, to postulate on probable interaction processes that may take place when kaolin clay is injected into a high temperature environment containing alkali species.

In a similar approach to that expounded by Kramlich (1983) on SO₂ control by limestone injection, *In-situ* reactive capture of gaseous alkali metals by kaolinite can be postulated to involve three main processes, namely:

- (1) The activation of kaolinite to metakaolinite as the particles are heated up to flue gas temperature immediately after injection.
- (2) Diffusion of the gas phase alkali species into the particle pore structure together with gas solid surface reactions, and
- (3) Deactivation of the sorbent through either the collapse of the pore structure with temperature and reaction extent, or through temperature induced solid phase transformations and melt (Wall et al., 1979; Wibberley et al., 1982).

In general, all the three processes are likely to take place simultaneously. They are closely linked to the local flue gas temperature, and the heating up rate that a sorbent particle is exposed to (Wall et al., 1979). This section discusses both the thermodynamic equilibria aspects and transport related processes that would affect sorbent reactivity and hence its effectiveness.

Thermodynamic equilibria is important because it sets somewhat an upper limit on capture that can be attained. In most instances, however, thermodynamic equilibria is unattainable depending on the time scale in which changes take place. In a review paper on thermal performance of large boilers, Wall et al., (1979) noted, for instance, that on rapid heating of kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$), the transformation reaction to metakaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), that would nominally take place at 400 to 600°C may not occur, instead, H₂O may be retained up to 1000° - 1200°C. Since it is metakaolinite that reacts with gaseous alkali species (Punjak, 1988), it is possible that rapid heating rates, that are a feature of combustion environments, can result in a significant reduction in kaolinite reactivity. Under such circumstances, thermodynamic equilibria studies are only useful as a guideline to the direction of progress of capture phenomena. Non thermodynamic equilibria issues such as adsorption and chemical reaction, sorbent sintering, particle heating rates, particle physical attributes and the flue gas environment are likely to be more important than equilibria.

2.1 THERMODYNAMIC EQUILIBRIA

Theoretical thermodynamic studies, to predict alkali capture by kaolinite, were carried out using the equilibrium computer program NASA-CET89 (Gordon & McBride, 1976). Similar source codes have been used previously by other workers (Raask, 1977; Durie et al., 1977; Gallagher, 1992) to predict the behavior of alkali/ash species in a coal flame environment. The equilibrium concentrations of alkali species and alumino silicates in the flue gas are calculated by free energy minimization methods. Luthra et al. (1982a) also used similar free energy minimizing codes to predict the equilibrium dew points of sodium sulfates and complex oxides of vanadium in gas turbines.

A disadvantage of using these codes, is that the predicted results are only as good as the number of species for which thermodynamic data are available, and are included in the program's data base. Such data bases are limited and have to be updated from time to time. Table A 2-1 and Table A 2-2 (Appendix) shows the alkali-alumina-silica species that were considered by the program in the present studies. The potassium system (Table A 2-1) is shown in the table to contain more potassium aluminosilicates than the sodium system. The latter (Table A 2-2), on the other hand, contains more sodium silicates. A decision was taken to use the potassium system as representative of the alkali-kaolinite reaction system. In doing so, weight was given to the presence of kaliophilite ($K_2 \cdot Al_2O_3 \cdot 2SiO_2$), a potassium analogue of nephelite ($Na_2O \cdot Al_2O_3 \cdot 2SiO_2$), in the potassium system. Nephelite has been identified positively as the product of reaction between metakaolinite and sodium hydroxide (Levin, 1964; Uberoi, 1990). The CET89 program was also used during experimentation to predict equilibrium flue gas compositions at various air and natural gas flowrates, the probable alkali dew points and the composition of stable alkali species.

2.1.1 Stable Alkali Species in Flue Gas.

Sodium, sodium with potassium, sodium with chlorine and sodium with sulfur, were each considered separately to study the dominant alkali species at an excess oxygen environment. Both sulfur and chlorine exist naturally in coal hence their effect on alkali capture is of interest. The results of these equilibrium simulations show that, in the absence of chlorine and sulfur, the dominant gas phase sodium species is the hydroxide, NaOH. Other species in lesser quantity include NaO, NaO₂ and atomic sodium (at high temperatures above 1500K).

The dominant condensate of sodium in a flue gas environment is the carbonate, Na₂CO₃(c). Gaseous Na₂CO₃(g), on the other hand, is not a significant species in the gas phase. Therefore, if equilibrium is followed, the condensation process is not from gaseous carbonate to condensed carbonate, but probably proceeds via a reaction mechanism of Equation 2.1

The significance of this argument is that the condensation mechanism may shed some light as to why certain volatile metals such as sodium are found to condense predominantly on the sub micron size range of the coal ash particles, whereas other metals such as lead are found in

significant concentrations on larger particles (ash particles greater than 10 μm in diameter) (Davidson et al. as reported by Linak et al., 1993). If, indeed, the alkali condensation is a $\text{NaOH} \rightarrow \text{Na}_2\text{CO}_3$ reaction process, then it requires a third body collision to effect. Large surface areas that are provided by the sub micron particles thus act as third body active sites for condensation to take place.

2.1.2 Effect of Chlorine

In the presence of Cl_2 , the dominant gas phase sodium species is NaCl(g) . Previous studies on sodium release in the presence of chlorine (Srivastachar, 1990; Gallagher, 1992), show that chlorine in the coal matrix volatilizes rapidly prior to sodium release. Once in the gas phase, it is converted to HCl(g) . The sodium hydroxide, formed from organically bound sodium then reacts with HCl to produce sodium chloride. Wibberley and Wall (1982) reported thermodynamic aspects of sodium, silica, chlorine and sulfur, and showed that in low chlorine atmospheres, where the molar ratio of Na:Cl is significantly greater than unity, sodium silicate is the main sodium compound. Conversely, as the chlorine concentration increases, more sodium chloride forms at the expense of both sodium silicate and sodium hydroxide. Gallagher (1992) proposed that sodium capture reactions with aluminosilicates probably proceeds as NaOH -metakaolinite reaction, and so as the fraction of chlorine increases in the flue gas, the more stable sodium compound is NaCl is formed and the fraction of NaOH available to react with aluminosilicates is reduced resulting in a reduction in the formation of sodium (alumino) silicates. One of the reaction mechanisms that has been proposed to account for sodium chloride formation (Gallagher, 1992) is:

The net effect of reactions 2.2 and 2.3 is that the presence of chlorine results in low NaOH concentrations in a flue gas. Experimental results of Wall et al. (1990), in which chlorine was shown to significantly reduce sodium capture by kaolinite, and the apparently slow reaction kinetics of Uberoi (1990), that were obtained with NaCl as alkali source in the presence of low H_2O concentrations, could now be reconciled by proposing that sodium capture proceeds through NaOH -metakaolinite reaction. As an extension of this argument, Gallagher calculated the equilibrium constant of Equation 2.3 as defined by Equation 2.4:

$$K_{eq} = \frac{[\text{H}_2\text{O}][\text{NaCl}]}{[\text{NaOH}][\text{HCl}]} \quad 2.4$$

Using the thermochemical data obtained from JANAF tables (Dow, 1971) to compute the equilibrium constant, the bench scale reaction rates of Uberoi and Shadman (1990), were then modified with respect to NaOH concentrations. A detailed derivation of the modified kinetics from the bench scale kinetics can be found in Section 6.3.4. The modified reaction rates were

three orders of magnitude higher than the initial bench scale kinetics, and were much closer to the experimentally observed phenomena. In the absence of independent experimental data, that are obtained from a practical combustor in the presence and absence of chlorine, it is difficult to reconcile the bench scale kinetics with Gallagher's arguments. This will be attempted in these studies.

Equilibrium simulations of the effect of chlorine on alkali capture by kaolinite were carried using potassium as alkali source. The results are summarized in Figure 2-1. Presented in the figures are simulations at a constant potassium concentration of 250 ppm. It is still not clear why it was only possible to simulate only up to a maximum of 20% chlorine (mole percent of potassium). Large concentrations of chlorine only resulted in the program terminating without convergence. Despite the fact that it was only possible to simulate a limited range of K/Cl ratios, the results are quite adequate for the discussion of trends therein.

Figure 2-1 A is the equilibria plot for potassium in the flue gas in the absence of chlorine or kaolinite. It shows the hydroxide and the condensate carbonate that starts to condense at 1200 K, as the dominant potassium species. Figure 2-1 B, with chlorine added, shows that $K_2CO_3(c)$ still begins to condense at 1200 K, while the chloride begins to condense at 1000 K. At high temperatures, however, all the chlorine is taken up as potassium chloride, with the remaining potassium existing as potassium hydroxide. Since the fraction of KCl remains constant at high temperatures, and since all the chlorine available is taken up in this fraction, we conclude that KCl is a much more stable, and preferred compound to KOH.

Figures 2-1 C & D shows the effect of adding kaolinite to the environments presented by Figures 2-1 A & B respectively. In both cases, alkali capture is dominated by the formation of kaliophilite ($K_2O \cdot Al_2O_3 \cdot 2SiO_2$). Some condensed phase potassium silicates is also shown to increasingly form at high temperatures above 1300 K. Of notable interest in Figure 2-1 D is the tendency, once again, of potassium chloride to remain in the gas phase at constant concentration at high temperatures. This may suggest that capture of alkalis, by kaolinite, may be limited by the alkali chlorides which are more stable thus maintaining some equilibrium concentration in the gas phase. This aspect of the effect of chlorine vis a vis equilibria limitations, will be investigated in detail in this work.

2.1.3 Effect of Sulfur

At high temperatures (above 1500 K), immediately in the post flame region, it has been shown that sodium-sulfur chemistry consist of Na, NaO_2 , NaOH, NaO, NaSH, $NaSO_2$, NaS and NaS_2 species (Durie, 1977; Steinberg, 1990). The dominant gas phase species, at both fuel lean and fuel rich stoichiometries, is still the hydroxide (NaOH) which accounts for over 70% of the total gaseous sodium (Durie, 1977). If solid sorbents are injected into this environment, alkali-sorbent reaction would still be expected to be dominated by the NaOH-Sorbent reaction.

Equilibrium dew point calculations show that the presence of sulfur also results in raised dew point of the alkalis as determined by the most significant condensate, $Na_2SO_4(c)$. Since the dew point of this condensate sulfate is relatively higher than that of the carbonate, typically 1250 K and above, the residence time available for gas phase capture reactions can be significantly

A: 250 ppm of potassium only.

B: 250 ppm K, and 50 ppm Cl

C: 250 ppm potassium and kaolinite.

D: Potassium, kaolinite and Cl₂.

Figure 2-1: Equilibrium distribution of major potassium species in an excess O₂ flue gas environment (SR=1.2), showing the effect of chlorine. Alkali capture is denoted by the presence of kaliophilite (K₂O·Al₂O₃·2SiO₂).

reduced. Condensate formation in the presence of sulfur is significantly different from that in the presence of chlorine. In the case of the Na-Cl system, both the gas phase and the condensate phase stable alkali species are the chloride (NaCl(g) , NaCl(c)). In the presence of sulfur, the dominant gas phase species is the hydroxide. No stable $\text{Na}_2\text{SO}_4\text{(g)}$ has been reported in any significant quantities. A bimolecular reaction path in which sodium gas phase species diffuses to solid surfaces, react with SO_2 or O_2 to form $\text{Na}_2\text{SO}_4\text{(g)}$ which then condenses as $\text{Na}_2\text{SO}_4\text{(c)}$ was proposed by Steinberg (1990) as follows:

It is then argued that although $\text{Na}_2\text{SO}_4\text{(g)}$ is a stable molecule, it probably requires a three body collision to form as opposed to sodium hydroxide and other sodium-sulfur species (NaSH , NaSO , NaS etc). This similarly leads to the conclusion that the formation of the sulfate condensate may only take place heterogeneously on solid surface contact.

Thermodynamic simulation of the interaction between potassium, SO_2 and kaolinite was carried using the CET89 computer program (Gordon et al., 1976). The results are shown in Figure 2-2 A, B, C, and D. Again, the codes were found to be sensitive to the sulfur content in the flue gas, possibly due to the formation of condensates with the attendant problem of instability and convergence. It was therefore not possible to exhaustively investigate a wide range of alkali/sulfur compositions. The simulations presented here were for a potassium concentration of 250 ppm and sulfur concentration of 80 ppm. The results of these simulations are described below.

In the absence of kaolinite (Figure 2-2 A & B), the dominant potassium species in flue gas is shown to be gaseous KOH , with condensates $\text{K}_2\text{CO}_3\text{(c)}$, and $\text{K}_2\text{SO}_4\text{(c)}$. Some trace gaseous potassium sulfate is also shown but only in a narrow temperature range between 1350 K and 1450 K (Figure 2-2 B). The dew point of the sulfate is shown to be 200 K higher than that of the carbonate.

When kaolinite is added to the flue gas environment (Figure (2-2 C & D), alkali capture is represented and dominated by the formation of water insoluble kaliophilite ($\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2\text{(s)}$). Liquid potassium silicate, $\text{K}_2\text{O} \cdot 4\text{SiO}_2\text{(l)}$, is also shown to form, but only, at temperatures above 1300 K. It is to be noted that, unlike the chlorine case, the fraction of potassium as kaliophilite shows an optimum peak in the temperature range between 1200 K and 1400 K. This optima is associated with the onset of condensation of potassium sulphate at temperatures below 1300 K, and the formation of potassium silicates at temperatures above 1300 K.

A: 250 ppm of potassium only

B: 250 ppm potassium, 80 ppm SO₂

C: Potassium and Kaolinite.

D: Potassium, Kaolinite, and SO₂.

Figure 2-2: Equilibrium distribution of major potassium species in an excess O₂ flue gas environment (SR=1.2) showing the effect of SO₂. Alkali capture is denoted by the presence of kaliophilite (K₂O·Al₂O₃·2SiO₂).

2.1.4 Equilibrium Dew point Calculations

Equilibrium dew point calculations for alkali species in an excess O₂ flue gas environment (SR=1.2) were carried out for sodium alone, sodium in excess chlorine environment, a binary equi-molar mixture of sodium and potassium, and sodium in excess sulfur environment. Sample results of these calculations are summarized in Figure 2-3. The sodium saturated vapor pressures were then fitted to Antoine's type relationship given as:

Sodium alone (in SR=1.2 flue gas)

$$\ln(P_{NaOH}^{sat}) = 16.99 - \frac{32030}{T} \quad 2.6$$

Sodium with excess chlorine,

$$\ln(P_{NaCl}^{sat}) = 15.86 - \frac{25610}{T} \quad 2.7$$

Sodium with excess sulfur in a flue gas environment,

$$\ln(P_{Na_2SO_4}^{sat}) = 6.18 - \frac{19020}{T} \quad 2.8$$

and for sodium and potassium in an equi-molar binary mixture;

$$\ln(P_{Na}^{sat}) = 18.02 - \frac{33024}{T} \quad 2.9$$

$$\ln(P_K^{sat}) = 18.13 - \frac{38126.8}{T}$$

2.1.5 Equilibrium Stability of Kaliophilite & Nephelite

Figure 2-4 shows fraction of potassium as kaliophilite when kaolinite is added to a flue gas that contains potassium at a level of 250 ppm in the absence and presence of SO₂. In the absence of sulfur, thermodynamic equilibrium shows that as high as 90% capture of potassium, in this case, could be achieved. This fraction remains constant at temperatures below 1200 K. At temperatures above 1200 K, the fraction of potassium as kaliophilite drops linearly with increase in temperature. This drop is probably due to the dissociation of kaolinite and the formation alkali silicates. Above 1500 K, no thermodynamically stable kaliophilite species is present.

Figure 2-3: Saturated vapor pressures for sodium and potassium in the presence and absence of sulfur.

Figure 2-4: Equilibrium fraction of potassium, captured by kaolinite as kaliophilite, in the absence and presence of sulfur.

It seems from these results that the presence of sulfur does not have any effect on the thermodynamic equilibrium of kaliophilite at temperatures above 1200 K. Below this temperature, possibly due to the formation potassium sulfate condensates, the fraction of kaliophilite reduces to about 50% (in this particular case) of the maximum kaliophilite in the system. The results, based on the equilibrium stability of kaliophilite, suggest that the temperature window of capture is in the region between 1100 - 1300 K.

2.1.6 Temperature Transformations of Kaolinite

Transformations of kaolinite with temperature were originally studied by Brindley & Nakahira (1959a,b). A more recent review of the data on kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) is presented by Bish et al. (1989) and Chakravorty (1991). There is general agreement that above 450°C, kaolinite progressively loses the hydroxyl bonds to become activated kaolin (metakaolinite). Surface area measurements by BET gas adsorption methods, show little change in the pore surface of metakaolin compared to kaolinite (Gastuche, 1963). This is so despite the fact that the release of water amounts to 20% of the space left behind. Consequently, this suggests that the transformation from kaolinite to metakaolinite, not only involve the loss of the hydroxyl bonds, but also some rearrangement of the Al-Si-O lattice structure with porosity unaffected.

Metakaolinite is stable only in the temperature regime between 450°C - 950°C. Above 950°C, it undergoes an exothermic transformation process and progressively transforms to more stable structures of Mullite as shown in Equation 2.10:

The time scale and kinetics of this transformation has been studied and reported by Tsuzuki and Nagasawa (1969). At heating rates of 5°C/min, complete transformation reaction occurred between 950 - 980°C in under 20 minutes. The reaction was also reported to be exothermic with activation energy of the order of 150 kcal/gmol. The transformation reaction of metakaolinite to stable 3:2 mullite via a 1:1 mullite is probably accompanied by the slow diffusion of the silicon atoms to form stable quartz (SiO_2) structures. Alternatively, at high temperatures, the released silicon can readily react with alkali species to form amorphous water soluble alkali silicates.

The presence of mullite phase, in place of metakaolinite, in coal ash at temperatures above 1000°C, has been reported by Mitchell and Gluskoter (1976), and by Suzuki (1988). Unlike metakaolinite, the mullite structure is a stable aluminosilicate (Chakravorty, 1991), which is unlikely to react with NaOH to form capture products.

Figure 2-5 shows a schematic diagram of the proposed high temperature transformations and capture processes between kaolinite and gaseous sodium hydroxide. Two parallel capture reactions are given as:

Figure 2-5: Temperature transformation reactions of kaolinite with sodium hydroxide.

2.11

with the products as nephelite and sodium silicates respectively. Studies on water solubility of silicates by Wilhelm et al. (1954) concluded that whereas nephelite and its potassium analogue, kaliophilite, are water insoluble, the silicates of sodium and potassium are water soluble at room temperatures (298 K). The capture products are therefore likely to consist of unreacted kaolinite and nephelite which are water soluble, together with condensates and alkali silicates which are water soluble. Alkali capture as nephelite or kaliophilite can be discriminated by simple room temperature water solubility tests. A complete capture reaction process can be proposed to consist of five interaction sub processes as shown in Figure 2-5 that may occur simultaneously. These are:

- (i) Activation of kaolinite at 450°C and above to metakaolinite.
- (ii) Diffusion of alkali species into the pore structure of kaolinite/metakaolinite.
- (iii) Capture reactions of Equation 2.11
- (iv) Deactivation reaction of Equation 2.10 at temperatures above 950°C.

2.1.7 Phase Equilibria of Nephelite, Kaliophilite and Sodium Silicates

Both nephelite and kaliophilite, products of alkali capture with kaolinite, exhibit liquid-solid phase equilibria at ordinary combustion temperature. In their pure form, the melting temperatures are typically 1500°C for nephelite and 1800°C for kaliophilite. The presence of other alkali silicates, however, results in lowering of the product melting points.

Figure 2-6 (Levin, 1964) shows a partial binary system between nephelite and sodium metasilicate. It can be seen that the presence of sodium metasilicate alone may lower the product melting temperature from 1500°C to around 900°C. Figure 2-7 (Levin, 1964) shows a binary mixture of nephelite and kaliophilite. The presence of potassium can be seen to result in raising the product melt temperature to a range between 1400°C - 1800°C. Given that as supplied kaolinite has a significant amount of trace potassium (under 1 % by weight), it is seen that the product of high temperature in-situ capture is more likely to be a complex solid-liquid solution of nephelite, kaliophilite and alkali silicates.

2.2 NON EQUILIBRIUM CONSIDERATIONS

Much of the discussion in the previous section has attempted to correlate alkali capture with thermodynamic, chemical and phase equilibria changes that would be expected to take place in a combustion environment. It is to be pointed that applicability of equilibria considerations will depend not only on the accuracy of the equilibrium calculation itself, but also on time scales and the ability of the system to approach equilibrium. Gas phase equilibria between species may

Courtesy Tilley, American Ceramic Society, 1964

Figure 2-6: Partial binary system of sodium metasilicate and nephelite(carnegite) (Levin, 1964)

Figure 2-7: Binary partial system of sodium metasilicate-nephelite (carnegite)(Levin, 1964)

be attainable but questions such as can the solid-solid transformations of metakaolinite to mullite take place in the time scale under consideration need to be addressed. If so, what are the effect of heating rates, on these transformations?

Considering that the residence time scale in an *in situ* injection scheme is under 2 seconds, other physical transport related phenomena are likely to be important in determining alkali capture. Included in this group of non equilibria issues are: physical changes upon injection, diffusion and reaction time scales, morphology changes with reaction, sorbent particle size and porosity, and sorbent sintering.

2.2.1 Physical Changes Upon Injection

Upon injection, sorbent particles undergo rapid acceleration to flue gas flow conditions. Simultaneously, the particles are heated up to flue gas temperature. It is expected that the characteristic acceleration and heating time scales are of the same order of magnitude, which strongly depend on particle size. Studies on the behavior of fine particles (less than 10 μm), when injected into a quiescent fluid at 1000 cm/s, show that the time scale for such particles to assume the fluid flow characteristics is of the order of 10^{-3} seconds (Hinds, 1977). In view of such short time scales as compared to the bench scale kinetics time scales, it is only reasonable to assume that particles do assume the flue gas time and temperature characteristics upon injection.

2.2.2 Diffusion and Reaction Time Scales

Diffusion and reaction has been studied at bench scale level by Luthra et al. (1982), Punjak (1988) and Uberoi et al. (1990). The kinetics that were reported by Uberoi (1990) suggest that complete sorbent utilization in the reaction controlled regime at 800°C would take place in time scales of minutes rather than seconds. However, these kinetics were derived using a compressed flake instead of fine particles and so it is possible that they may be significantly different from those that would prevail in the furnace. The modified kinetics of Gallagher (1992) suggest capture time scales, under similar conditions, of seconds. Experimental data in this work will attempt to reconcile these two extreme rate scenarios.

Three time scale regimes of interest in this work are (1) the pure reaction time scale, (2) product layer diffusion time scale and (3) pore (Knudsen) diffusion time scale. Depending on the controlling mechanism, the resultant sorbent utilization is expected to be a strong function of particle size.

2.2.3 Flue Gas Stoichiometry

Flue gas stoichiometry and the combustor flow characteristics is expected to be a strong factor in determining alkali capture. Particle flow patterns that may result in segregated regions of high and low particle number densities could result in significant deviations in the local alkali/sorbent loading ratios, which in turn would determine sorbent effectiveness. A plug flow reactor therefore offers an ideal environment for evaluating sorbents as it eliminates multi dimensional mixing problems. Flue gas stoichiometry would on the other hand be expected to

affect alkali capture through the fraction water content in the flue gas. In this work, capture will be evaluated in an excess O_2 environment of $SR=1.2$. This has been chosen as it is the most typical flue gas stoichiometry found in industrial practice.

2.2.4 Sorbent Sintering

As we continue to present various temperature related factors that would affect the performance of a porous sorbent, a brief mention is made here of the effect of sintering. Sintering as used in this work, refers to the loss of sorbent porosity with temperature and time. This definition follows closely that of Szekely et al. (1977), and Ranade (1979). Other definitions of sintering in related coal ash studies can be found in literature (Hupa et al., 1988; Kalmanovitch; 1988) and refers to the densification of ash deposits due to either solid state diffusion, or viscous flow of molten material between ash particles etc. This should be differentiated from the phenomena described here. In both cases, sintering in one form or another, will always cause a decrease in sorbent specific surface area.

Ranade (1979) reported that porous particle sintering parameter $\theta(t)$ (A dimensionless time function that describes the fraction of total accessible pore surface area of a sorbent still available for capture reactions due to sintering) at constant temperature can be correlated with specific pore surface area, and time according to Equation 2.12

$$\theta(t) = \frac{A(t) - A_e}{A_0 - A_e} = e^{-kt} \quad 2.12$$

where both an equilibrium specific surface area, A_e , and the sintering rate constant k , are functions of temperature and can only be determined experimentally. It is clear that this definition of sintering already raises more questions than answers especially given that pore surface area may be reduced simultaneously by sintering and by reaction. In the absence of reliable sinter models, much of the discussion of the effect of sorbent sintering is full of hand waving and empirical fits. Although not quantifiable, sorbent sintering still has an effect in reducing sorbent effectiveness.

2.2.5 Sorbent Characteristics

A fine, $1.0 \mu m$ mass-median size, narrow range, kaolin clay, supplied by Burgess Pigment Co. Ga., is to be used for the time temperature related experiments. These experiments are therefore ideal for the extraction of initial rate kinetics as a function of sorbent injection temperature. Effect of particle size will be investigated using a similar but coarse kaolin clay of size range $1 - 100 \mu m$. Porosity, pore size distribution and BET pore surface of the same sorbent had been measured and reported by Punjak (1988) and is shown on Table 2-1.

• **Table 2-1: Physical and chemical characteristics of Kaolinite.**

Sorbent	Median Size (μm)	Porosity (ϵ)	Mean pore size (cm)	Pore Volume (cm^3/gm)	Pore surface area (m^2/gm)
Kaolinite	1.00	0.58	180×10^{-8}	0.52	85
Composition of As-received Kaolinite (Weight %)					
Al_2O_3	SiO_2	Fe_2O_3	TiO_2	K_2O	Na_2O
52.1	44.9	0.8	1.4	0.8	—

2.3 CONCLUSIONS FROM THIS SECTION

- Needed research will focus on *chemical reaction* capture of sodium rather than physical capture such as condensation. Alkali capture to form reaction products such as nephelite and kaliophilite can be discriminated by simple room temperature water solubility tests.
- Thermodynamic equilibria, alkali dew points, temperature transformation of metakaolinite, sorbent sintering, reaction induced product melt, together with transport and reaction kinetics are all expected to simultaneously play part in determining sorbent effectiveness and their combined effects should be ascertained.
- Condensate $\text{Na}_2\text{SO}_4(\text{c})$ and low melt silicates, $\text{Na}_2\text{O} \cdot n\text{SiO}_2(\text{c})$ act as cementing agents that result in formation of hard bonded fouling deposits on heat transfer surfaces. High temperature sorbent injection is necessary to capture sodium before the onset of condensation. At the same time, a low temperature injection is necessary if the formation of the silicates are to be avoided. Optimum injection temperature should be investigated.
- *In situ* alkali capture is thermodynamically favored in the temperature window between 1100 - 1300 K
- Alkali dew points in the combustor may be significantly different from those predicted thermodynamically because of non equilibria effects. These include heterogeneous reactions to form carbonates and sulfates.
- Chlorine lowers and sulfur raises the alkali condensate thermodynamic dew point by 200 K respectively, and their presence may significantly shift the capture window and extent of sorbent utilization.
- Sulfur, based on thermodynamic equilibria, has negligible effect on alkali capture at high temperatures above 1200 K. Its presence probably affects alkali capture through the elevated dew points that reduces the gas phase residence time scales.

- Since the formation of alkali silicates results in lowering of the product melting temperatures, under ordinary combustion temperature, capture may be expected to significantly deviate from the classical gas-solid reaction models to gas-solid-liquid reactions.

3.0 EXPERIMENTAL WORK

This section describes the experimental work carried in support of the research objectives set in Section 1.3. Included here are descriptions of the experimental facilities that were used, the experimental design, procedures, sample preparations and sample chemical analysis. Results of parametric studies are presented in Section 4. Multivariable data reduction and statistical analysis is discussed in Section 5.

3.1 EXPERIMENTAL FACILITIES

The experimental facilities and particle sample analysis equipment at the University of Arizona, that were available for this research, are described in this section. The main part of the experimental facilities is the 17 kw, ϕ 0.15m x 6.00m plug flow combustor. A schematic of the combustor is shown in Figure 3-1. The supporting systems are the sorbent feed system, isokinetic sample extraction system, flue gas analysis trains and the ancillary trace additive feed systems. Other facilities that were used include: The Atomic Absorption spectrophotometer for bulk chemical analysis, Scanning Electron Microscope for detailed bulk and surface analysis, Scanning Auger Microprobe for thin layer surface analysis and X-ray Diffraction probe for crystalline structure analysis. Details of the combustor and the other related equipment are described below.

3.1.1 The Combustor

The design and construction of the 17 kW, downflow combustor is described in detail by Scotto (1992). It consists of 0.15 m inside bore fire tube, lined with high purity fibrous Alumina supplied by Zircar Corporation. The inner tube is wrapped with several layers of Kaowool (alumina/silica) ceramic fibre blanket. A total of 0.1 m thick insulation is used. The furnace is capable of burning both natural gas and coal. It has been used previously in work related to coal and coal ash alkali partitioning studies by Scotto and Wendt (1988), and by Gallagher (1992). Sorbent injection studies have been carried in the same furnace to study the capture of alkali species by injection of kaolinite (Rizeq, 1990), and to study the evolution and control of heavy metals (lead) from incineration plants (Scotto, 1992). For the purposes of our present work, some of the design features of the combustor that are of particular interest include:

- (1) Combustion environment temperature and time scales are representative of full scale boiler units (Figure 3-2). This is approximately 1-3 seconds space residence time in the temperature range of 1400°C - 700°C.
- (2) The furnace has been shown to be one dimensional with respect to temperature and gas phase concentrations (Glass, 1981). Under unidirectional flow conditions, particle time and temperature history after injection can be calculated, from which the rates of reaction can be inferred.
- (3) Access along the combustor axis is available for sorbent injection and extraction of particle samples.

Figure 3-1: Schematic of the $\phi 0.15 \text{ m} \times 6.00 \text{ m}$, 17kW laboratory combustor

Figure 3-2: Schematic of time and temperature profiles for a typical 500 MWe coal fired utility boiler and representative 0.15 m x 6.00 m laboratory combustor.

3.1.2 The Burner Plenum

Shown schematically in Figure 3-3, the burner plenum was designed and built by Scotto (1992). Besides supporting a stable flame at the top of the combustor, the burner plenum also acts as a mixing chamber for Cl_2 and SO_2 additives with combustion air. Natural gas is injected into the mixing annulus by four equi-spaced 6 mm diameter nozzles prior to exiting the plenum into the furnace cone. Alkali solution (0.1 - 0.2 moles/liter Sodium Acetate solution) is injected into the flame by an atomizer unit that runs through the plenum and protrudes by approximately 0.5 cm below the burner exit.

The burner zone has a cone angle of 18° to prevent back mixing and recirculation caused by flow expanding from the exit annulus. This design promotes uniform plug flow and produces an axisymmetric one dimensional flame. The ignition of the premixed fuel and air in the burner is prevented by both the water cooled inner atomizer unit and the correctly sized flow annulus that ensures mixture velocities are above the flame velocity for the range of rated burning conditions.

3.1.3 The Sample Ports

Along the length of the furnace are a total of fourteen ports that can be used for sorbent injection, particle sample extraction, sampling of furnace gases, and taking of temperature profiles. The sampling ports are separated by an approximate distance of 30 cm each giving a temperature resolution in the range between 50 to 100 K. Table 3-1 shows the port numbers and their corresponding axial position from the burner level.

3.1.4 Ignition and Safety Systems

The combustion flame is ignited by a gas pilot flame which is ignited by an electric spark. An ultra violet flame sensor monitors the continuity of both main and pilot flames and is connected to a safety interlock system. The pilot flame hole and the UV sensor are both located 10 centimeters below the burner cone, opposite each other, and in direct line of sight through the main flame. The UV sensor detects the hydroxyl radical emission of the natural gas. The port tubes are continuously flushed of obscuring smoke by a small air bleed, which also keeps the mullite tube cool and free of dripping slag which might otherwise plug these tubes. The pilot flame is premixed by an Eclipse venturi ratio control valve that entrains the natural gas into pilot air stream. The flow rate is above the flame velocity so that a flame stabilizes at the end of the pilot port tube to prevent flashback.

3.1.5 Furnace Instrumentation.

Exhaust flue gas is drawn from Port 14, cooled to around 2°C , then supplied to parallel gas analyzers where continuous analysis is done for CO_2 , CO, O_2 , and NO_x using: (1) Beckman Model 864 Analyzer for both CO_2 and CO, (2) Beckman Model 1040-F Paramagnetic Analyzer for Oxygen, and (3) Thermo-electron Analyzer model A10 with stainless steel converter for NO_x .

Figure 3-3: Schematic of the burner plenum assembly. Trace additives are premixed with air in the plenum. The alkali solution is injected directly into the flame.

Table 3-1: Ports and their distances along the vertical length of the furnace.

PORT	Distance (cm)
1	0.00
2	29.69
3	56.99
4	87.16
4b	114.46
4c	148.12
5	199.23
6	234.79
7	265.27
8	295.75
9	326.23
10	356.71
11	387.71
12	417.67
13	448.15
14	478.63

The furnace exhaust temperature is continuously monitored using a type K (Alumel/Chromel) thermocouple, mounted at the exhaust and connected to an Omega Model 604 digital thermometer. The furnace pressure and pressure drops are monitored by a set of manometers connected to a pressure tap at the exhaust port and along the combustor length. Flame presence is monitored by ultra violet detector described earlier. A type R (Rhodium/Platinum) high temperature thermocouple is connected to a portable probe for measuring temperature profiles.

3.1.6 Sorbent Feed System

Two problems associated with the feeding of ultra fine, clay based sorbents, are: (a) accurate metering of the particle feed rates and (b) feed line plugging from time to time during an experiment time period. The tendency of the sorbent to adsorb moisture from the compressed transport air can also result in the plugging of the feed screw tip and exit nozzle tip. Kaolinite also to bridge over feed screws which makes continuous feeding difficult.

Several types of sorbent feeders were considered for feeding of powdered materials (EEUA, 1977; Hamor and Smith, 1971; Woodcock and Mwabe, 1984; Burch et al., 1990). For these experiments, a conventional dilute phase, positive pressure, rotary screw fed, pneumatic conveyor was designed and constructed as shown in Figure 3-4. In this design, the rate of sorbent feed is regulated by preset conveying pressure (approximately 0.5 bar (gauge) at a volumetric flowrate of 28 liters/min (stp)), and by use of a variable speed screw. An auger bit screw of longer pitch (~10 mm) was found to ease the sorbent bridging problem better than a short pitch screw. A vibrator, mounted near the screw tip on the hopper wall, was intended to reduce particle agglomeration and sticking. There is however, strong evidence that the vibrator may not have been that useful.

Sorbent feed rate was regulated in the range of 0.5 gm/min to 4 gm/min, corresponding to a particle to flue gas mass loading of under 1%, and a particle number density under 10^6 particles/cm³. The conveying air required was set so as to give a continuous fluidized flow. The sorbent injection exit orifice was located at the furnace centerline so as to give a uniform particle feed into the assumed plug flow flue gas.

An approximate feed rate was estimated by weighing the hopper bin before and after experimentation. The Alkali to sorbent loading ratio which is used in the data analysis as an independent variable was, however, obtained *post-facto*, by bulk analysis of the isokinetically sampled particles and fumes. The assumption here is that the ratio of Na₂O to sorbent (Al₂O₃ + SiO₂) in the impactor sample is representative of the flow ratio in the combustor, in which the case the importance of isokinetic sampling cannot be underscored. Isokinetic sampling gives samples that are a true reflection of the furnace flow conditions. This is particularly true if there is no preferential tendency of any of the species to be lost to the furnace walls relative to the other species present.

3.1.7 Isokinetic Sampling System.

Particle samples were extracted from the furnace using an isokinetic particle sampling system as shown in Figure 3-5. The system consists of the sampling probe complete with the sample and diluent air flow lines, NO_x analysis trains and the cascade impactor.

3.1.8 Aspirated Isokinetic Sampling Probe

Particle sampling was carried using an aspirated isokinetic sampling probe (Figure 3-6). The probe can be used to extract samples from any of the fourteen ports along the furnace by locating it as near the flow axis as possible. Its principle of operation is an aspiration-dilution system, whereby the dilution air is injected into the inner return tube, creating a low pressure region that draws particle laden sample from the furnace into the probe. For a sampling rate of 30 liters/min, through a 1.00 cm diameter probe, at a temperature of 1000K, a cooling rate of the order of 10^6 K/sec was estimated using turbulent mixing length scales (Lumley, 1972). Under such a rapid cooling rate, it is reasonable to suppose that any reactions are frozen at point of sampling and the condensed species particle size distribution should reflect particle size distribution as exists in the furnace environment.

Figure 3-4: Positive pressure, screw fed sorbent delivery system.

Figure 3-5: Schematic of particle sampling system showing particle dilution lines, simultaneous NO_x monitoring, and the cascade impactor/pump layout.

Figure 3-6: Schematic of the isokinetic sampling probe showing sample dilution lines. A cooling rate of 10^6 K/S has been estimated.

The procedure for isokinetic sampling is as follows: Local flue gas velocity is calculated from known flue gas mass flowrate, burning conditions (SR), and local temperature using ideal gas relationships. A higher flue gas velocity assumes laminar flow profile while a lower velocity assumes a plug flow profile. In as much as practically possible, sampling velocity is regulated within this range. Volumetric sampling rate is calculated as product of sampling velocity and sampling probe cross section area. Dilution air flowrate is set to make up the total flow rate to 28 ambient cubic feet per minute, a sampling volume flowrate that is determined by the impactor specifications. For good control of the sampling rate, the furnace is doped with NO_x at a level of 500 to 700 ppm, by injecting pure Nitric oxide gas at Port 4b, just below the flame. Both furnace and sample stream NO_x are simultaneously monitored during sampling. In this manner, a dilution ratio between 15:1 and 20:1 can be maintained. It is noted here that a dilution ratio of 10:1 is the bare minimum for a natural gas flame system if condensation is not to take place on the sample lines at room temperatures.

3.1.9 Cascade Impactor

An Andersen 30 lpm aerodynamic cascade impactor was used for particle sampling. The impactor consists of a pre-separator cup, eight classified size stages, and an after filter. Aerodynamic size classification is achieved by a multiple exit orifice design as shown schematically in Figure 3-7. Stage particle size range is reported using the 50% cut off diameter (d_{50}) convention.

Table 3-2: Calibrated Andersen 30 lpm stage size classification.

Stage	Cup	1	2	3	4	5	6	7	8	AF
Lower 50% cut-off diameter (μm)	10.00	9.00	5.80	4.70	3.30	2.10	1.10	0.65	0.43	0.00
Upper 50% cut-off diameter (μm)	-	10.0	9.00	5.80	4.70	3.30	2.10	1.10	0.65	0.43

The particle diameter having a 50% collection efficiency, d_{50} , is a function of particle slip factor and stokes number (Hinds, 1982). Calibrated aerodynamic size classification is shown in Table 3-2 for particles of bulk density of 1.0 gm/cm^3 . For particles of different density, the d_{50} diameter is inversely proportional to particle density. Kaolinite used in this work has a bulk density of 1.11 gm/cm^3 (Burgess pigment Co., 1991), consequently, no corrections were necessary on the particle size distribution reported.

An impactor stage assembly is shown in Figure 3-7. Each stage consists of a multiple orifice top plate, and a stainless steel impingement bottom plate. Size classification is achieved aerodynamically as shown in the same figure (bottom). Stages 1 to 8 had two symmetrical half-circular substrates placed on the stainless steel impingement plate. The collection surfaces were

Figure 3-7: Impactor stage assembly (schematic) showing symmetrical distribution for both acid and water solubility tests.

assembled with a small amount of grease sprayed sparingly to reduce particle bounce and re-entrainment. Equal and symmetrical weights are deposited on the collection plates as shown on the same figure. One sample is then dissolved in 30 ml of acid and analyzed for elemental composition of Al, Si, Na and K. The other sample is dissolved in 30 ml of de-ionized water, at room temperature, for 24 hours and then analyzed for same elemental composition. The difference between the two results, after accounting for density differences between acid solution and water, is reported as water insoluble content of the sample. The after filter sample is not divided into two but instead is taken to consist of only water soluble fumes of sodium and potassium. The total filter sample was collected on a 0.2 μ m pore, nucleopore polycarbonate filters and contains fumes of particles with an aerodynamic diameter less than 0.43 μ m.

3.2 SAMPLE PREPARATIONS AND CHEMICAL ANALYSIS

Detailed chemical and physical analysis of the size segregated samples were carried out to ascertain governing mechanisms of capture. Three analytical techniques that were used include: (1) Atomic Absorption bulk analysis (AA), (2) Scanning Electron Microscopic analysis (SEM) and (3) Energy Dispersive X-ray analysis (EDX). Described below are detailed of each analysis technique and the sample preparation methods that were adopted in each case.

3.2.1 Atomic Absorption Analysis (AA)

A Perkin Elmer model 2380 atomic absorption spectrophotometer was used to determine the elemental chemical compositions of the size segregated samples from the combustor. The wavelength dispersion device used had a single pass monochromator that is equipped with a holographically ruled grating. The spectrophotometer can be used both in the absorption and emissions mode.

Two equal and symmetrical sample deposits were collected in each impactor stage except the cup and after filter. One sample was digested in acid while the other was dissolved in de ionized water at room temperature for 24 hours. Both samples were then analyzed using atomic absorption for elemental compositions of Na, K, Al and Si. The water insoluble capture was determined as the difference between the two results, after accounting for the density difference between the dissolving acid and water.

Samples for total elemental composition were digested in 30 ml of a 4:1:1 HF/HCL/HNO₃ acid solution. The reagent solution preparation procedure is included in Table B 3.1 (Appendix). Boric acid crystals was added to the dissolving acid to convert excess HF acid to flouoroborates. This is done to protect the glass lined AA nebulizer and burner. Cesium Nitrate is added to the dissolving acid solution to inhibit loss of metal by vaporization of ions in the high temperature flame. A typical ionization and vaporization reaction for sodium in a flame environment is shown in Equation 3.1:

The vaporized gaseous $\text{Na}^+(\text{g})$ can escape the flame region, thus contributing to the error in atomic absorption concentration readings. When present, cesium it loses its electron much more easily than sodium so that the number of free electrons increases shifting reaction 3.1 to the left and in effect inhibiting sodium vaporization.

The accuracy and precision of the atomic absorption/emission results depends, to a large extent, on the element analyzed. This is given as both the relative noise and the detection limits. Methods, accuracy and detection limits are presented in Appendix B.

Besides size distribution plots to show submicron enrichment by a particular species etc, the AA analysis results can be summarized by dividing the bulk analysis results into four broad categories, namely:

- (1) Proportion of alkali content that is water insoluble, and consequently considered as reacted alkali content.
- (2) Proportion of alkali content in the sorbent size range, that is water soluble. This fraction could be surface or capillary condensed alkali content, and water soluble alkali silicates.
- (3) Proportion of alkali content in the submicron, stage 8 and after filter. This fraction is expected to be dominated by the water soluble, condensed alkali species. Neville and Sarofim (1985) showed that whereas large particles ($> 0.65 \mu\text{m}$), may account for 99% of the total mass of ash particles, the bulk of condensed sodium is still found in the submicron range. The proportion of sodium in the submicron stages is therefore a measure of the fraction of sodium that had not been captured by the sorbent at the point of sampling.
- (4) Fraction of total silicon that is water soluble. This is an order of magnitude measure of the formation of water soluble alkali silicates. Due to low resolution for Si at low concentrations, no significance has been attached to this fraction.

3.2.2 Scanning Electron Microscopy Analysis (SEM)

SEM analysis results were used to characterize shape and morphology changes that accompany capture reactions. A JEOL, model JSM840A, scanning electron microscope was used for this purpose. Particle samples for SEM analysis were collected on hytrex membrane filters (Hytrex Filter Inc, MN). These are silver chloride coated, 47 mm diameter, $0.45 \mu\text{m}$ size filters. The filters were placed on stage 6 of the impactor (stage 6 is the mass modal-size plate for the sorbent particles used). The filter surface was painted with carbon graphite paint that resulted in good image contrast and also acted as a conductor between the sample and the microscope table, thereby reducing any charge build up during analysis as a result of the high energy electron beam. Prior to mounting on the microscope, the samples were further coated with a thin carbon layer.

3.2.3 Energy Dispersive X-ray Analysis (EDX)

The JSM840A scanning electron microscope has Energy Dispersive X-ray (EDX) capabilities. The EDX geometry consists of a fixed 40° take off angle with an inclined detector at a working distance of 39mm. It uses a Tracor Northern 5502, Series II microanalysis system. All x-ray micro analysis are carried under standardless quantitative analysis with ZAF correction factors (Goldstein, 1981).

EDX analysis was used as an independent analytical technique to verify selected results obtained from AA bulk analysis. In this way, an order of magnitude check on the water insoluble capture data obtained by subtracting water dissolved AA data from acid dissolved AA data, could be kept.

Selected samples that had been dissolved in water and analyzed using atomic absorption were prepared for EDX analysis by carefully decanting the water. The sediments were then dried and mounted on carbon painted hytrec filters. These were prepared for EDX analysis by coating them with a thin layer of carbon to increase conductivity to the sample holder table and thereby reduce charging. EDX results were then compared with the AA water insoluble data.

3.3 EXPERIMENTAL PROCEDURES

The furnace was heated up to steady temperature profile prior to the start of sorbent injection and sampling. Steady conditions were taken to be reached when the exhaust temperature did not change by 10°C within an hour. In the same period, an hourly log of fuel gas and total air flowrates was recorded. Exhaust temperature and exhaust flue gas composition was continuously monitored during the warm up period with water, instead of alkali solution, injected through the atomizer that runs directly into the flame to maintain constant mass flowrates. Included in Appendix B is a sample run sheet showing typical flow rates into the combustor, together with the temperature profile before sampling was started.

Final readings of gas, air and alkali solution flow rates were then adjusted to give a theoretical flue gas composition of $SR=1.2$, which was counter checked with the exhaust gas composition of O_2 , CO_2 for readings of 3.2% and 8.5% respectively. A significant deviation from these values was an indication of a system leak and had to be investigated and corrected before continuing with the experiments. The furnace temperature profile was then taken, starting from the bottom ports upwards. This ensured that a disturbance downstream, to insert a thermocouple probe, did not cause an appreciable change in temperatures upstream. Since the temperature profile is taken with the particle feed air in place, the injection port temperature was interpolated from an overall regressed temperature profile. The temperature value used as sorbent injection temperature is considered therefore to account for the effect of cooling of the flue gas by the particle transport air.

Sorbent feed port temperature was taken once again prior to the start of sorbent feed. The sampling pump was then started and sampling taken for a specific time period, usually between 30 to 40 minutes. At the end of sampling, each impactor stage sample was placed in tightly sealed plastic vials and labeled. A record was kept of the sampling conditions, any problems,

specific visual observations like sample color, visual size distribution etc. If at the end of a sampling period, there was evidence of over sampling, which is characterised by particles being re entrained from one stage to the next, the impactor samples were discarded and a new impactor prepared for repeat sampling. The impactor was routinely cleaned in an ultrasonic water bath that removed any submicron particles from a previous sample lot. A repeat sample was taken for every run condition. Details of sorbent feed techniques and that of isokinetic sampling techniques have been described in Section 3.1.6 and Section 3.1.7 respectively.

3.4 EXPERIMENTAL DESIGN

Two sets of experiments were planned and carried out in the combustor in attempt to uncouple highly correlated parameters. The first set of experiments were parametric studies in which experimental run conditions were kept constant and only single parameters changed. In as much as possible, only extreme conditions, such as the effect of excess chlorine as compared to no chlorine, was considered. This was done because of the difficulty in resolving small changes from global capture results in a large combustor. The results of these experiments are presented in Section 4. The second set of experiments were time and temperature experiments in which the focus was to obtain time resolved alkali capture data through variable injection point approach. The results of these experiments are analyzed in Section 5, in which multivariate statistical regression techniques have been employed to generate continuous capture functional relationships.

Screening experiments were used to select procedures and parameter levels that offered the best resolutions. Such parameters include: total mass flowrates, burn conditions, sampling and sorbent injection points, and alkali levels. The alkali levels used in the studies (typically 100 to 250 ppmV) are much higher than would be found in an ordinary coal combustion environment, but close to those used in bench scale experiments of Punjak (1988) and Uberoi (1990). This high concentration of alkali metal vapor was necessary so as to be able to achieve the kind of sensitivity necessary for the extraction of mechanisms, and also it could be used to compare combustor study results with the bench scale ones. To reduce the number of sensitivity experiments, the total mass flowrate and flue gas stoichiometry was kept constant throughout the experiment period.

3.4.1 Parametric Studies

In this group of experiments, "standard" experimental conditions (250 ppm Na, SR = 1.2, steady temperature profile) was maintained and a single change of variable introduced such as no chlorine and excess chlorine. Issues addressed included species recovery with and without sorbents, effect of chlorine, effect of sulfur, effect of particle size, effect of sorbent injection temperature on particle morphology in the absence of capture reactions, and the effect of sorbent injection temperature on particle morphology with capture reactions.

3.4.2 Time and Temperature Resolved Experiments

In designing time and temperature resolved experiments, an idealized alkali-sorbent interaction model in a one dimensional flow reactor is proposed. In this model, the injected sorbent particle takes the plug flow flue gas velocity and temperature immediately after injection. Capture reactions proceeds from this injection time and temperature, and continues until the particle crosses the dewpoint temperature line in the combustor. The total sodium captured by the sorbent particle is taken to be an integral function of local rate equation from injection point to the dew point. This idealized model is shown schematically in Figure 3-8.

A detailed discussion of the implicit assumptions in this idealized model is contained in Section 6. Presented below is a summary of some of the assumptions:

- (1) That alkali capture can be represented by a Lagrangian formulated integral function with the limits at point of injection, and at the dewpoint, as given in Equation 3.2:

$$g^* = \int_0^{\tau_{dew}} R'_s(p_1, \theta, x, n) dt \quad 3.2$$

where g^* is the water insoluble alkali capture in gm $\text{Na}_2\text{O}/\text{gm}$ sorbent. R'_s is some local capture rate function in gm $\text{Na}_2\text{O}/\text{gm}$ sorbent.sec. R'_s depends on the local alkali concentration p_1 , the local flue gas temperature θ , fraction of sorbent still left unreacted x and the particle number density in the flue gas, n . Integration is carried from injection to the dewpoint, τ_{dew} . In a one dimensional flow, under steady temperature profile, the time integral function can be transformed to a temperature integral by introducing some temperature transform function:

$$dt = \phi(\theta) d\theta \quad 3.3$$

so that Equation 3.2 becomes:

$$g^* = \int_T^{\tau_{dew}} R'_s(p_1, \theta, x, n) \phi(\theta) d\theta \quad 3.4$$

with T and T_{dew} being the injection temperature and dewpoint temperature respectively. The transform function $\phi(\theta)$ is derived in Section 6.

- (2) The time scale for particles to accelerate and heat up to local flue gas conditions is small compared to the reaction and residence time scales.
- (3) Eddies or particle hitting and bouncing on the furnace walls near the injection point can be ignored.

Figure 3-8: A schematic of alkali capture in a one-dimensional flow combustor, with the dew-point acting as a reaction cutoff point.

- (4) No further reactions take place below the dewpoint.
- (5) Single size particles.

It should be pointed out in passing that Equation 3.2 is only unique if the residence time τ_{dewpt} is much shorter than that which is required for complete reaction of the sorbent particle. In such a case, the dewpoint acts as a distinct reaction cut off point.

Since the upper limit of Equation 3.4 (dewpoint temperature) is at some specific, fixed but unknown point in the combustor, by varying the injection point, the sorbent residence time can be varied and g^* measured which can be correlated with injection position or temperature with residence time as an implicit parameter. Change in g^* with respect to change in residence time can then be derived, and used to estimate the initial reaction rates. The capture reaction to be investigated is proposed to be given by Equation 3.5 (Gallagher, 1992):

from which the corresponding sorbent mass gain, at complete reaction, is given as 0.27 gram Na_2O per unit gram of sorbent.

3.4.3 Response Surface Methodology (RSM)

An approach, adopted to derive results for alkali capture in an injection temperature and residence time space domain, at various alkali to sorbent loading ratios, is the response surface methodology (Hicks, 1982; Box, 1987; Mereb and Wendt, 1990). Response surface methodology comprises a group of statistical techniques for empirical model building and model exploitation. Lowell et al. (1982) used a similar response surface approach to successfully extract the kinetics of high velocity, high temperature sodium sulfate induced corrosion of a combustor test rig.

The response surface technique seeks to relate a response, or output variable to the levels of a number of predictors, or input variables, that affect it. If there is only one input variable, the output is a response curve. If there are two input variables, the response is a three dimensional surface. Once a response surface has been generated and the errors associated with it shown to be statistically random and normally distributed, it can be used to interpolate experimental results at conditions whereby a specific variable is kept constant. The advantage of this approach is that one is able to cover a wide range of experimental conditions without necessarily keeping any of the independent variables constant. The focus here is to cover an experimental domain as widely as possible. Its disadvantage is that, depending on the number of independent variables, it may require more experimental data so that not only the individual ranges of the independent variables are covered, but the joint combination of ranges are also covered. For the case of only two independent variables, a simple scatter diagram is all is needed during experimentation to assess regions of the domain that are not yet covered. Once the experimental domain is adequately covered, the response surface can be derived statistically

by least square linear or nonlinear regression. The steps used to derive a response surface in the present studies is as follows:

- (a) Define an experimentation domain, in terms of inputs and input levels.
- (b) Cover the experimentation domain with statistically "large" population of experimental data.
- (c) Propose a second order polynomial fit of the form:

$$y = a_0 + \sum_{i=1}^N a_i x_i + \sum_{i=1}^N \sum_{j=1}^N a_{ij} x_i x_j \quad 3.6$$

where N is the number of independent variables, a_{ij} 's are polynomial fit constants and $x_{i,s}$ are the independent variables. y is the measured output parameter. We can then use least squares methods to derive a response surface that adequately describes the capture response surface within the domain.

- (d) Carry out detailed selective replicate experiments.

It should be noted that the most important assumption, when using this approach, is that the errors associated with the experimental results are entirely random and can be accounted for statistically by regression. Implicit in our assumptions is that capture function is continuous and monotonic within the experimental domain.

3.4.4 Experimental Input Variables

A major difficulty in using the response surface experimentation technique described in the previous section lies in selecting a set of independent variables to constitute the experimental domain. A mechanistic approach is to carry out statistical "sensitivity" experiments (Hicks, 1982; Mereb and Wendt, 1990) to determine the degree of marginal contribution each independent parameter makes to the output variable and then decide as to what is important and what is not. In the case of our system, the simplifications due to steady, one dimensional flow conditions made this approach unnecessary, instead it can be shown that under special circumstances, the set of independent variables in our experimental set up collapses to the injection temperature T , the initial alkali to sorbent equivalence ratio ϕ and the species present.

The initial input variables are T , T_{dwp} , p_{i0} , n , v_p , θ , d_p , and SR. The special conditions referred above are: (i) narrow particle size distribution, in which d_p is constant, (ii) particle velocity follows closely the flue gas velocity, which at constant mass flowrate is only a function of local temperature θ via the ideal gas law, (iii) sorbent particle number density, n , in the flue gas and the initial alkali concentration p_{i0} which if kept constant, can be combined to one parameter of initial alkali/sorbent loading ratio, ϕ , (iv) T_{dwp} depends only on the species (SO_2 , Cl_2 etc.) present and is independent of capture reactions. These simplifications will be addressed

in detail in Section 6 under mechanistic modelling. The input variable set, therefore, reduces to the three variables T , ϕ and species present.

The experimental approach is to hold the species present in the flue gas, the total mass flowrate and the initial alkali concentration constant, and then build a multivariable capture response surface of g^* (gm $\text{Na}_2\text{O(i)}/\text{gm}$ sorbent) at different sorbent injection temperature T , and sorbent flowrate (indicated by ϕ). The results of these experiments are presented in Section 5 with the initial rate kinetics extracted from these data in Section 6. The conditions for the three response surfaces are given in Table 3-3 below with the combined experimental matrix of parametric studies, together with the time and temperature experiments given in Table 3-4.

Table 3-3: Conditions for base response surface for sodium only, sodium with excess chlorine and sodium with excess sulphur runs.

Condition	Level
Sorbent type	Kaolin clay, Burgess Pigment Co, Ga. 1-2 μm equivalent modal spherical size
Sorbent injection temperature range	850°C-1300°C
Sorbent sampling point	Port 11
Flue gas environment:	Excess O_2 (SR = 1.2); 450-480 gm/min
Alkali Solution	Sodium Acetate, 0.2 M, 20 cc/min ~250 ppm Na
Excess Cl_2/SO_2 flowrates:	250 cc/min ambient (21°C, 700 mmHg) ~500 - 700 ppmV

3.5 SUMMARY

- The combustor time and temperature history closely represent that of a practical boiler unit. Ideal plug flow reactor assumptions will be taken to hold.
- Isokinetic sampling system described uses a dilution-aspiration technique which serves two purposes. One, isokinetically obtained samples are representative of combustor flow conditions and can be used to calculate the total alkali to sorbent loading ratio. Two, the high cooling rates due to large dilution ratios (10:1 - 20:1) serves to "freeze" any further reactions at point of sampling.
- Particulate samples are deposited on symmetrical half circular substrates. One sample is dissolved in acid and the other in water, both are then analyzed using AA and the difference in results is reported as water insoluble alkali capture. EDX analysis is used to selectively verify the AA analysis results.

- The only independent variables for response surface experiments are (1) the sorbent injection temperature (T) and (2) the alkali to sorbent equivalence ratio (ϕ). This simplification is a consequence of the one dimensional plug flow assumptions, constant total mass flowrate and constant initial alkali partial pressure (p_{i0}).

Table 3-4: Multiple level experimental matrix for capture of sodium by in-situ injection of Kaolinite into a plug flow combustor.

Factor	Levels			Control & comments.
	Low	Medium	High	
Sorbent Injection Temperature T (°C)	800 - 1000	1000 - 1100	1100 - 1300	Good control once steady temperature profile is achieved. $\pm 10^\circ\text{C}$
Alkali level p_{NaOH} (ppm)	50 - 100	-	250 - 300	Depends on alkali recovery along the furnace.
Alkali/Sorbent Equivalence ratio ϕ (based on Nephelite)	0.1 - 0.25	0.25 - 0.45	0.45 - 3	Calculated from total bulk analysis (AA) of the Impactor samples. Control may be difficult in the extreme ranges.
SO ₂ :Na level (based on Na ₂ SO ₄) χ_{SO_2}	1:1	2:1	>5:1	Good control. Additive gases are metered independently before they are mixed with the combustion air in the plenum
Cl:Na level (based on NaCl) χ_{Cl}	1:1	2:1	>5:1	.
K:Na	-	-	1:1	Good control. Alkali Acetate solns used.
Particle size (μm)	1 - 2 (kinetics expts)	-	1 - 100	Particle size distribution known.

4.0 PARAMETRIC SCREENING STUDIES

The first set of experiments performed were parametric screening studies to investigate sodium capture and the influence of chlorine, sulfur, injection temperature, particle size etc on the same capture. Section 4.1 to Section 4.3, describes the experimental approach, temperature measurements and corrections, and methods of presentation and interpretation of the experimental results. Sections 4.4 to 4.11 discusses the uncoupled partial effects as could be discriminated by AA, EDX and SEM analysis techniques. Finally, from the information obtained in the previous sections, a mechanistic description of the interaction between the gaseous sodium species and the injected sorbent particle in a down flow combustor is proposed in Section 4.12.

Alkali capture, in this work, refers to all alkali oxides that is associated with the injected sorbent. Such capture may involve in-the-pore or external surface reaction between gaseous sodium species with the sorbent particles, capillary condensation in the pore structure, and surface condensation on the sorbent particles. Since this work focusses on reactive capture of alkali metals, the results presented, however, emphasize the formation of water insoluble alkali aluminosilicates.

4.1 EXPERIMENTAL CONDITIONS

The experimental procedure is already been described in Section 3. In the case of the parametric studies, the flue gas total flow rate was maintained at 400 - 420 standard liters/min or 450 - 480 gm/min as shown in Appendix B. Air and natural gas flowrates were adjusted to give a burn stoichiometric ratio of 1.2. The alkali solution was prepared from a reagent grade sodium acetate crystals dissolved in de ionized water to a 0.2 molar solution which was injected into the flame at 20 cc/min giving a total alkali concentration in the flue gas of 250 ppmV. Chlorine and SO₂ gases were added to the combustion air from 99% purity bottled gases at a flowrate of 250 cc/min ambient (21°C, 700 mmHg), giving a Cl molar concentration of 1000 - 1400 ppmV and an S concentration of 500 - 700 ppmV.

Fine and coarse kaolin clay, obtained from Burgess Pigment Co., Ga., was used in the experiments described in this section. The fine clay had a narrow size distribution between 0.5 - 3 μ m, with a modal size of 1.0 μ m. The coarse clay, used to investigate the effect of particle size on sorbent utilization, had a wide size distribution between 0.5 and 100 μ m with 60% of the total mass found in the +10 μ m range. Although the impactor could only size classify particles under 10 μ m diameter, the wide size distribution for this clay ensured a good distribution in all the eight impactor plates, consequently the effect of particle size on sodium capture by kaolinite could be extracted.

4.2 INTERPRETATION OF EXPERIMENTAL RESULTS

The capture reaction to be investigated was given in Equation 2.11 as that between NaOH and kaolinite to form nephelite ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$). The reaction stoichiometry gives a mass gain of 0.27 gm Na₂O per unit mass of kaolinite. Besides nephelite and unreacted kaolinite, other species present in the sampled particles include water soluble sodium silicates ($\text{Na}_2\text{O} \cdot n\text{SiO}_2$) which is formed from the reaction between NaOH and free silica, SiO₂, and the physisorbed or

condensed Na_2O . All the water soluble sodium is presented as $\text{Na}_2\text{O(s)}$. Nephelite and unreacted kaolinite are water insoluble, while the condensates and silicates are water soluble (Wilhelm et al., 1954) and can be discriminated by simple room temperature water solubility tests.

Impactor samples were analyzed, using atomic absorption techniques, for mass elemental compositions of Al, Si, Na, and K, which were then presumed to have existed as oxides of Al_2O_3 , SiO_2 , Na_2O , and K_2O . No attempt was made to identify the species although equilibria suggests that alkali condensates probably exists as carbonates and sulfates. Presentation of species composition as oxides is consistent with other studies on coal ash (Wendt et al., 1990). Besides AA analysis, selected samples were analyzed using energy dispersive x-ray (EDX) technique and the two results compared as an independent check on our AA data.

The impactor results are presented in the form of stacked bar graphs of plate mass loadings of Al_2O_3 , SiO_2 , $\text{Na}_2\text{O(i)}$, and $\text{Na}_2\text{O(s)}$. The latter two are water insoluble and water soluble sodium oxides respectively. Other plots derived from the impactor results include normalized fraction oxide plots and mass distribution plots of the water soluble sodium oxide. The impactor plate lower cut off diameter has been used in all cases as the representative particle size for each size cut. The derived results from the impactor samples are:

Total Sodium Capture:

Sodium oxide found in Plate 1 to Plate 7 (+ 0.65 μm particle range) is likely to have either reacted with kaolinite, chemisorbed, physisorbed or heterogeneously condensed on sorbent particles. This fraction of sodium oxide is considered as captured since it is bound with the sorbent particles. The submicron sodium oxide in the after filter (AF) and stage 8 (-0.65 μm) is considered as uncaptured fumes that may have homogeneously or heterogeneously condensed either in the furnace or in the sampling probe.

Sodium /Sorbent Equivalence Ratio:

In theory, the equivalence ratio could be calculated from the total feed flowrates of sorbents and sodium. However, due to the difficulties in closing a mass balance for the alkalis and the uncertainties in the measurements of the sorbent flowrate from the screw feeder, and knowing what fraction of the feed sorbent is actually entrained into the flue gas and not stuck on the furnace walls, the equivalence ratio was estimated from the bulk analysis of total species found in the impactor sample. If we assume that samples were obtained isokinetically, then the ratio of total sodium oxide sampled to kaolinite sampled reflects the entrained flow ratio of the two species. Unit mass equivalence ratio then is the ratio of Na_2O to sorbent ($\text{Al}_2\text{O}_3 + \text{SiO}_2$), normalized by 0.27 which is the mass stoichiometric ratio for nephelite.

Sorbent Injection Temperature:

The flue gas temperature was measured using a portable thermocouple as was described in Section 3. Figure 4-1 shows a typical temperature profile with the sorbent injection air in place at Port 3. Also shown in the same figure is the port peak temperature when the injection

Figure 4-1: Typical furnace temperature profile

Figure 4-2: Temperature profile at the beginning and end of an 8 hour experiment.

probe was withdrawn to allow for the insertion of the thermocouple probe. In most cases the difference between the peak port temperature without sorbent transport air and the regressed temperature was of the order of 10° to 20° C, which was accepted to be within the range of the experimental error. Figure 4-2 shows combustor temperature profile taken at the beginning and end of an 8 hour period. Steady running conditions are shown, consequently the sorbent injection temperature could be interpolated from the measured profiles before and after experimentation.

Temperature corrections to account for the difference between the thermocouple measured temperature and the flue gas temperature was attempted using the methods described by West et al. (1953). The corrected temperature, which depends on an estimated duct wall temperature, was of the order of 10°C higher than the thermocouple temperature reading, consequently the uncorrected thermocouple readings have been used in this work as the flue gas temperature.

4.3 ERROR ANALYSIS

The interpretation of our experimental results is subject to several errors from the measurement process. Of major interest are (i) errors from the flue gas sampling process, (ii) errors from temperature measurements and (iii) errors from the atomic absorption analysis.

Sampling errors were related to the combustor flow characteristics. The air and natural gas flowrates were metered using municipal gas meters. By continuously monitoring CO₂, CO and O₂ in the exhaust flue gas, a reasonable accuracy could be maintained on the total mass flowrate and burn stoichiometry. The flow Reynolds number in the combustor, based on a mean combustor diameter of 0.15 m, was calculated to be around Re=2000, which can be either a laminar or plug flow condition. Depending on whether we assume a laminar or a plug flow, the flue gas velocity at the centerline of the furnace would differ by a factor of 2. Since the isokinetic sampling flowrate depends on the assumed centerline velocity, there is a chance that a derived gas phase species concentration, calculated by closing a mass balance based on an estimated sampling flowrate, may contain errors as large as ±50%.

The sampling rate used in the present experiments was set to a mean velocity between laminar and plug conditions. To maintain this sampling rate, the flue gas was doped with 700 ppmV Nitric Oxide which was injected at Port 4b below the flame. NO_x analysis readings from the flue gas and the sample lines were simultaneously monitored to maintain a constant dilution ratio.

Errors in the injection temperature measurements has already been discussed in the previous section. It is estimated that the injection temperature readings presented contain an error margin of ±10°C.

Errors for the atomic absorption/emission analysis of the bulk samples are given in terms of detection limit and relative noise for each element and is shown in Appendix B. The relative error depends on the amount of each species sampled. During experimentation, sampling was carried over a long period of time (typically 30 to 40 minutes). This ensured that sample amounts were of sufficient quantity to reduce the relative errors. Long sampling periods also

served to average out any fluctuations in sampling flow conditions. For impactor plates with large sample amounts, the alumina to silica ratio was found to be constant and consistent with the as received compositional analysis of kaolinite. In the submicron plates, where the fraction of kaolinite was low when using the fine narrow size range sorbent, the Al/Si ratio was not always consistent with the as received kaolinite composition, suggesting that the error magnitudes were large.

The water soluble silicon readings were low and unreliable, consequently, they have been used only as an order of magnitude measure of the formation of water soluble silicates. The high sensitivity of the AA readings for Na and K, gave good, repeatable results for the alkali metals in the submicron and supermicron ranges.

4.4 FACILITY VALIDATION

Experiments were carried to validate the laboratory combustor through species mass balances and estimation of the dew point positions. An equimolar, 0.1 M, sodium acetate and potassium acetate solution was used as an alkali source, giving a sodium and potassium concentrations of 140 ppmv in the flue gas. The dew point was estimated to lie between 750°C - 850°C by Equilibrium analysis, using the CET89 Computer program (Gordon and McBride, 1976). No sorbents were injected into the combustor, instead only impactor samples of alkali metal rich flue gas was obtained from Port 6 and Port 12 which were at temperatures of 900°C and 720°C respectively. The two samples thus represented sampling below and above the dew point. The sampling rate was maintained at 1.57 SLPM in all the four samples presented.

Table 4-1 summarizes the results of these experiments. Species recovery, defined as the ratio of estimated gas concentrations assuming sampling is throughout isokinetic to the theoretical concentrations that are based on the feed flowrates into the combustor, is shown for each sample for sodium and potassium respectively. The table shows similar recoveries of 40% for both potassium and sodium with the ratio of the species consistent with the feed ratios. Further, the recoveries are shown to be independent of the sampling position, below or above the dew point.

The apparent low recoveries are not surprising. We had shown that the actual sampling flowrate may deviate from the combustor isokinetic conditions by a factor of $\pm 50\%$, consequently the calculated recoveries may be out by the same order of magnitude. What is interesting in these results, however, is the consistency of the recoveries in all the four samples considered, which suggest that the total alkali concentration in the flue gas was constant both below and above the dew point. A physical examination of the burner showed that alkali salts were deposited near the cooler exits of the burner. This suggests that most of the alkali losses took place near the burner exit and so explains the consistency in recovery along the combustor.

Table 4-1: Results of alkali sampling from Port 6 and Port 12.

Sample #	Sample Port #	Sampling time (mins)	Total alkali sampled (mass ppm in 30 ml)		% Alkali recovery (based on feed)		Mole ratio of K:Na
			K	Na	K	Na	
081	6	60	189.45	111.63	38.8	38.8	1.00
082	6	45	164.80	82.56	45.0	38.2	1.18
083	12	45	158.06	93.96	43.2	43.6	0.99
084	12	60	211.95	113.11	43.4	39.4	1.00

A plot of alkali mass fraction against particle size is shown in Figure 4-3 and Figure 4-4. The calibrated impactor size classification were corrected for the density of $\text{Na}_2\text{O(s)}$, which is 2.2 gm/cc (Perry, 1973). For the sample obtained at furnace temperatures above the thermodynamic dew point (Port 6), the bulk of the alkali species are found as submicron fumes under $0.29\mu\text{m}$ diameter which was collected mainly in the after filter (AF), while for the sample obtained at a furnace temperature below the dew point, the modal fume size is shown to have evolved from the after filter ($<0.29\mu\text{m}$) to stage 8 ($0.29 - 0.44\mu\text{m}$ size class). The shift from $<0.29\mu\text{m}$ fume to $<0.43\mu\text{m}$ particle is clear evidence that condensation had taken place in the combustor. This result is used later in this work to classify the alkali species in the two plates (AF and Stage 8) when sorbents are injected into the combustor, to represent the fraction of uncaptured alkali species that was in the flue gas at the point of sampling.

It is concluded from this section that:

- The uncaptured alkali condensates when sampled is to be found predominantly in the impactor stage 8 and after filter only.
- In the absence of sorbents, a marked shift of the modal aerosol size from the after filter to stage 8 of the impactor is an indication that the sample has been taken below the dew point.
- In spite of the above, a significant amount of sodium oxide is still found in the after filter even when samples are taken at furnace temperatures below the thermodynamic dew point.

4.5 SODIUM CAPTURE BY KAOLINITE

Sodium capture was investigated by injecting kaolinite at Port 3 at a furnace temperature of 1200°C . Sample number 244 was obtained from Port 11. The particle residence time in the combustor for this run was calculated to be 2.8 seconds. The bulk analysis of the sample gave an alkali to sorbent equivalence ratio of 0.33 or 0.09 gm Na_2O per gm sorbent, which is

Figure 4-3: Mass fraction distribution of sodium and potassium at 900°C.

Figure 4-4: Mass fraction distribution of sodium and potassium at 720°C.

representative of three times more sorbent over sodium. Other experimental conditions is already been given in Section 4.2.

A summary of this run shows that: 97% of total sodium sampled was captured by sorbent (i.e. found in the $+0.65\ \mu\text{m}$ size range and above). Reactively captured sodium to form water insoluble products accounted for 77.9% of the total sodium in the sample, giving a mean mass gain of 0.07 gm $\text{Na}_2\text{O}/\text{gm}$ sorbent. Compared with the total flow ratio of 0.09 gm $\text{Na}_2\text{O}/\text{gm}$ sorbent, the experimental mass gain represents a near 80% sorbent effectiveness. Similar experiments (same injection port) but at different sorbent flowrates, showed that in conditions of excess sodium over kaolinite, the capture capacity was limited to a mass gain between 0.11 - 0.13 gm $\text{Na}_2\text{O}/\text{gm}$ sorbent or 50% of the theoretical capture capacity of 0.27 gm $\text{Na}_2\text{O}/\text{gm}$ sorbent. Appendix E contains results of Energy dispersive X-ray (EDX) analysis of selected samples that had been dissolved in water, with the sediments dried before mounting on the microprobe for elemental analysis for comparison with the AA results. Wide area scans (approximately $3000\ \mu\text{m}^2$) and single particle scans were carried on each sample. The results of wide area scans were found to be in close agreement with the AA results. Individual particles had fluctuating readings between high and low alkali content. This, of course, is consistent with what would be expected as the fraction of alkali capture by an individual particle depends on the particle history. In all the cases presented, no higher than 20 wt% sodium in a particle was recorded, which corresponds to just under 50% sorbent utilization based on nephelite.

Three possibilities that may explain the apparently low maximum possible sorbent utilization in our system set up include: (1) probable short residence time compared to characteristic reaction time, (2) significant pore blockage with the progress of reaction, or (3) melt and sintering in the high temperature regime. Later in Section 6, we will address this through mechanistic modelling to show that the residence time may have been long enough for complete reaction, instead the apparently low maximum sorbent utilization may be explained by the latter two factors.

Figure 4-5 is a stacked bar graph of species mass loadings on each impactor plate showing the sampled sorbent to be found predominantly in a narrow size range between $0.65\ \mu\text{m}$ to $3.3\ \mu\text{m}$. Figure 4-6 presents the same impactor results as normalized mass fraction of the oxides in each plate. The water insoluble (reactively captured) sodium oxide does not show any clear dependence on particle size. There is some slight enrichment of the submicron plates by the water soluble (condensed or un captured) sodium oxide, although the result is not conclusive. While the narrow size distribution makes the extraction of the dependence of sodium capture on particle size difficult to determine from these experiments, it justifies our use of a single particle size to model sodium capture for this clay. The ratio of $\text{Al}_2\text{O}_3/\text{SiO}_2$ is shown to be near constant and is consistent with the as supplied sorbent. Water soluble and water insoluble sodium oxides, $\text{Na}_2\text{O}(\text{s})$ and $\text{Na}_2\text{O}(\text{i})$ respectively, are shown in the bar graph with sodium capture dominated by the formation of water insoluble product (nephelite).

Figure 4-7 shows the fraction mass distributions of the sorbent, the 78% water insoluble sodium $\text{Na}_2\text{O}(\text{i})$ and the 22% water soluble $\text{Na}_2\text{O}(\text{s})$. The two sodium distributions correlate with the kaolinite mass distribution. We conclude from the present experiments that kaolinite is an effective sorbent for scavenging sodium vapor in an in-situ application at characteristic residence

Figure 4-5: Sodium capture by kaolinite: Impactor mass loadings

Figure 4-6: Sodium capture by kaolinite: Species partitioning on each plate.

Figure 4-7: Sodium capture by kaolinite: Distributions of kaolinite, reacted $\text{Na}_2\text{O}(i)$ and water soluble $\text{Na}_2\text{O}(s)$.

times under 3 seconds. A near 99% scavenging is shown with capture dominated by chemical reaction to form water unleachable products. Only 50% of the theoretical sodium capture capacity of kaolinite was realized in our setup.

In order to speculate on the possible governing mechanism of capture, we will look at the distribution of the water soluble sodium oxide $\text{Na}_2\text{O(s)}$. This fraction of sodium has been proposed to be composed of either reacted sodium that formed water soluble silicates ($\text{Na}_2\text{O} \cdot n\text{SiO}_2$), physisorbed sodium oxide on the pore surfaces or heterogeneously condensed sodium oxide on external particle surface. The distribution of $\text{Na}_2\text{O(s)}$ is shown in Figure 4-7 to correlate very closely the sorbent mass distribution with very little fumes found in the submicron stages.

Haynes et al. (1981) reported that diffusion limited heterogeneous condensation is unlikely to be a significant capture mechanism, instead a more likely mechanism is that of surface reaction controlled deposition whereby the submicron particles ($\sim 0.4 \mu\text{m}$), which provide inordinately large surface areas, are enriched even though these submicron particles constitute only about 1% of the total particulate mass. Since no sub micron enrichment is shown in this case, external surface induced condensation is unlikely to account for this distribution. This suggests that the $\text{Na}_2\text{O(s)}$ was actually physisorbed (in the pore) or reactively captured in the pore structure to form soluble silicates. In both cases the dominant capture mechanism is likely to be in the reaction controlled regime in which the particle pore matrix "sees" the gaseous sodium prior to the particle coming down to the dewpoint line. This mechanism is consistent with the fact that significant reactively captured sodium has been achieved which is only possible if the pore volume and not the external particle surface had been utilized.

4.6 INFLUENCE OF CHLORINE ON SODIUM CAPTURE

We look at the effect of chlorine on sodium capture by kaolinite in a similar environment as was presented in Section 4.5. Several workers (Gibb and Angus, 1983; Raask et al., 1985; Gallagher, 1992) have shown that chlorine influences the mode of release of alkali metals from coal and their subsequent capture by the ash during combustion. In ordinary boilers, coal is the main source of chlorine while in high temperature incineration systems, most chlorine comes from surrogate wastes in the form of metal chlorides. Chlorine concentrations in the flue gas in coal units depends on the coal source with British coal reported to be generally rich in chlorine as sodium chloride (Gluskoter, 1977). In general, metal chlorides are more volatile than other metal species. Increased volatility results in lowered dew points which in a down-flow combustor means longer residence time for the injected sorbent in the alkali gas phase prior to the onset of condensation. For sodium, besides volatility, sodium chloride is a more stable and less reactive species than sodium hydroxide, so the applicable reaction rates should be significantly different in the presence of chlorine.

The effect of chlorine on sodium capture by kaolinite was investigated at a Cl:Na molar ratio of 5:1. The results are summarized in Figure 4-8. It is evident from the bottom figure that a significant proportion of the total water soluble sodium was found in the afterfilter which had existed in the combustor at the point of sampling as uncaptured fumes. Run number 303 presented here was similar to Run number 244 in the previous section, in terms of sorbent

Figure 4-8: Sodium capture by kaolinite in an excess chlorine environment. The bulk of the water soluble sodium is found in the submicron stages as uncaptured fumes.

flowrate as evidenced by an equivalence ratio of 0.37 and 0.33 respectively, sorbent injection temperature and sorbent residence time. The difference in the two results is interpreted as due to the influence of chlorine on sodium capture. A summary of the sample shows that 75% of the sodium sampled was captured by sorbents compared to 98% in the base case, 52% of the sodium in the sample was water soluble as compared to 22% in the base case and sorbent mass gain was 0.05 gm Na₂O/gm sorbent as compared to 0.07 gm Na₂O/gm sorbent in the base case. By all comparisons, sorbent effectiveness was reduced by 20 - 30 % due to the presence of chlorine.

The mass size distribution of the water soluble Na₂O best illustrates the effect of chlorine on sodium capture. Figure 4-9 compares the fraction mass distributions of the water soluble sodium between the base case and the excess chlorine case, and shows that a significant proportion of the water soluble sodium existed in the flue gas as uncaptured submicron fumes which were collected predominantly in the after filter and stage 8. These results are consistent with earlier works of Scotto (1992), and Gallagher (1992) where it has been shown that chlorine significantly reduces the metal capture capacity of kaolinite. This, has been postulated to be due to the NaOH-NaCl-H₂O equilibria that lowers NaOH concentration in the flue gas when chlorine is present.

4.7 INFLUENCE OF SULFUR ON SODIUM CAPTURE

This work was motivated in part by the need to develop bifunctional sorbents that can be used to simultaneously capture alkali species and sulfur dioxide. Sulfur capture by lime has been investigated and reported more extensively (Kramlich (1983, 1987), Borgwadt (1982), Hansen (1991 and others)) than sodium capture by kaolinite. In fact we have drawn from this body of literature to postulate possible capture scenarios in the absence of detailed bench scale studies on kaolinite. Although kaolinite is a promising sorbent for alkali capture, preliminary bench scale studies have shown that when mixed in slurry form with lime (CaO) and then dried so that the mix can simultaneously capture sodium and SO₂, it performed very poorly as a sorbent (Wu, 1993). Analysis of the resultant product by X-ray diffraction techniques showed that at high temperatures kaolinite probably reacts with lime (CaO) to form stable calcium aluminosilicate (CaO·Al₂O₃·2SiO₂). This reaction probably preempts any further reactions between gaseous sodium and kaolinite to form nephelinite.

Equilibria studies using the computer program CET89 (Gordon et al., 1976) showed that when kaolinite was added to a flue gas containing potassium and SO₂, the fraction of captured potassium remained the same at high temperatures above 1300 K as would be found in the absence of sulfur. At low temperatures below 1200 K, potassium capture was reduced by as much as 50% in the presence of SO₂ and instead a significant proportion of potassium formed stable sulfate condensates. An explanation for these observation is that in the presence of SO₂, the dominant gas phase species still remained the KOH which at high temperatures reacted with kaolinite to form nephelinite. The difference is on low temperature condensates where K₂SO₄(c) was found to be dominant species over K₂CO₃(c), which exists in the absence of sulfur. K₂SO₄(c) is a more stable species than the carbonate and it condenses at high temperatures, hence its formation reduces significantly the proportion of alkali species in the gas phase to be captured by kaolinite. The dew point of the alkali sulfates have also been shown to be typically 200 - 300

Figure 4-9: Capture of sodium by kaolinite: Effect of chlorine.

K higher than the dew point of the carbonates hence the presence of SO_2 in a one dimensional flow combustor should result in a significant reduction in the reactor residence time available for gas-solid capture reactions.

Two similar samples were obtained at a sorbent injection temperature of 1000°C and used to show the effect of sulfur on sodium capture by kaolinite. As shown previously, the excess sulfur case was used with Na/S ratio greater than 5:1. A summary of the results show that total sodium capture was 89% in the base case compared to 77% in the presence of sulfur. 34% of the total sodium sampled was water soluble in the base case as compared to 45% in the presence of sulfur. Both results show a capture reduction of 10% due to the presence of SO_2 . Figure 4-10 shows the distribution of the water soluble sodium in two samples that had been injected at 1000°C at an alkali/sorbent flow equivalence ratio of 0.22. Again, uncaptured sodium is shown as a shift of the water soluble sodium towards the submicron plates of the after filter and Stage 8 when SO_2 is present. We conclude that although the presence of sulfur resulted in a reduction of sodium capture by around 10%, the reduction was less pronounced than was the case in the presence of chlorine. We attribute the observed reduction primarily to the reduced residence time as a result of the elevated dew point temperature of the sulfates.

4.8 INFLUENCE OF INJECTION TEMPERATURE

Comprehensive studies were carried out to investigate the effect of sorbent injection temperature on sodium capture by kaolinite in a down flow combustor. These studies were intended to reveal whether or not there exists a favorable temperature window at which sorbent utilization can be optimized. Also of interest was the possible structural changes a sorbent particle undergoes in a high temperature environment in the presence and absence of sodium species. To that end, high resolution scanning electron microscope images of sorbent particles that had been injected at different temperatures, were taken. Three areas addressed by the experiments in this section are: (1) Na_2O content of the sampled sorbent particles at different injection temperatures (AA analysis), (2) Sorbent melt at different temperatures in the absence of capture reactions (SEM analysis) and (3) reaction induced melt of the capture product (SEM analysis).

Drawing from the work of Kramlich (1983) on lime injection, it is postulated that upon injection, kaolinite particles undergo rapid heating from ordinary room temperature to flue gas temperature. Simultaneously in this time scale, the activation of kaolinite to metakaolinite together with probable sintering and melt may take place. Wall et al. (1979) reported that the activation reaction from kaolinite to metakaolinite depends on the heating rate so much so that although this reaction should take place at temperatures between $400 - 600^\circ\text{C}$, metakaolinite may not be formed up to temperatures of 1200°C if fast heating rates take place (Wall et al., 1979). Therefore, besides sorbent melt and sintering, fast heating rates (high injection temperatures) may also result in a reduction of the sodium capture capacity of kaolinite.

The results of two samples (Run number 245 and Run number 154) that were injected at Port 3 and Port 5 at 1200°C and 842°C respectively are discussed here. The sorbent flowrate in both samples was the same (i.e. the equivalence ratios of 0.32). The difference between the two samples was therefore the injection temperature (1200°C and 842°C) and the particle

Figure 4-10: Capture of sodium by kaolinite: Effect of sulfur.

residence time in the combustor (2.8 seconds and 1.8 seconds respectively). Sodium capture in the high temperature injection was 0.07 gm Na_2O /gm sorbent compared to 0.06 gm Na_2O /gm sorbent. The fraction water soluble sodium was 21% for high temperature injection against 30% for the low temperature injection. Figure 4-11 shows the distribution of the water soluble sodium oxide for both samples. Slight reduction in capture in the low temperature injection experiment compared to the high temperature one is shown as a slight enrichment of the submicron plates with water soluble Na_2O . It is evident that despite the large difference in injection temperature and residence time, there is only a marginal reduction in capture of under 10%. This suggests that capture reactions are fast so as to be near complete in the time scales covered by both experiments. The reduction in capture for the low temperature, short residence time experiment is probably due to the effect of the shorter residence time than injection temperature. Small reduction in capture for large temperature difference suggests that the reactions are probably of low activation energies.

Sorbent morphology changes with temperature in the absence of capture reactions was investigated by injecting sorbents at 1200°C, 1000°C and 800°C at Port 3, 4c and 5 respectively. Samples were collected from Port 11 and prepared for scanning electron microscopic analysis as was described in Section 3. Figure 4-12 shows two SEM images of particles that had been injected into the combustor at two extreme temperatures of 1200°C and 800°C. Significant structural deformation is shown in the sample that had been injected at high temperature by the existence of spherical particles which occupy nearly 30% to 40 % of the image area, compared to the low temperature injection image which does not show any spheres. An enlarged image of the as received sorbent was of the shape of a clay flake, so the existence of spherical particles in the two images is considered as evidence of sorbent melt. This result was surprising as kaolinite was not expected to melt at such low temperature, although it could explain the under 50% utilization of kaolinite already observed. A structural deformation with temperature can result in a reduction sodium capture capacity through pore closure and sintering.

What is the melting temperature of kaolinite? According to several authors on clays, kaolinite, as a clay, has no definite melting point. Newman et al., (1987) defined the melting point arbitrarily as the temperature at which the clay cone slumps such that the apex of its matrix structure touches the base. A pure clay slumps this way at about 1800°C. In reality, the impurities that exist in kaolinite, mainly Fe, K and Ti, probably reacts with silica to form low melt point metal silicates, which acts as source of partial sintering and melt at low temperatures. Depending on the extent of the temperature induced sorbent sintering (collapse of the pore structure), there is likelihood of a significant reduction of sorbent BET surface area and a consequent loss of sodium capture capacity.

Similar experiments as above but with sodium in the flue gas were carried and are presented in Figure 4-13, Figure 4-14 and Figure 4-15. These are SEM images of particulate samples that had been injected at 1200°C, 1000°C and 800°C respectively. The sodium concentration in the flue gas was 250 ppmV. All the three samples had near same sodium content as was estimated during SEM analysis using energy disperssive X-ray analysis (EDX) techniques with ZAF corrections (Goldstein, 1981).

Figure 4-11: Sodium capture by kaolinite: effect of injection temperature and residence time.

Figure 4-12. SEM image of sorbent particles that were injected into the combustor in the absence of sodium at 1200°C (Top) and 800°C (Bottom).

Figure 4-13. SEM image for samples in which sorbents were injected at 1200°C in the presence of 250 ppm sodium.

Figure 4-14. SEM image for samples in which sorbents were injected at 1000°C in the presence of 250 ppm sodium.

Figure 4-15. SEM image for samples in which sorbents were injected at 800°C in the presenced of 250 ppm sodium.

At 1200°C nearly all the particles had undergone extensive structural change as shown by the packed bed of spheres of uniform size estimated to be between 0.8 μm and 1.0 μm . At 1000°C, the particles were oval in shape suggesting a partial melt, while only isolated spheres are shown in the sample obtained from the 800°C injection temperature.

The results of these experiments are consistent with the partial phase diagram of $\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2\text{-Na}_2\text{O}\cdot\text{SiO}_2$ (Figure 2-6 Section 2) which showed that the capture product at high temperatures is likely to be solid-liquid solutions. The formation of liquid silicates may lead to pore plugging thereby reducing the sodium capture capacity of the sorbent. It is concluded that if severe structural deformation of the clay sorbent is to be avoided, sorbent injection should be kept at temperatures below 1000°C.

4.9 INFLUENCE OF PARTICLE SIZE

The influence of particle size on sorbent utilization is discussed in this section. The experimental conditions were similar to that presented in Section 4.1. We have already speculated that sodium capture in the 0.65 - 3.3 μm size range is probably limited by kinetics and not transport. This was based on the fact that the distribution of water soluble Na_2O followed closely the kaolinite mass distribution, suggesting that this fraction of sodium may have been physisorbed or condensed in the pore surfaces after near complete diffusion. The validity of this argument can now be tested by investigating the influence of particle size on sodium capture.

Coarse kaolin clay (Burgess Pigment Co. Ga) was injected at Port 3 at a temperature of 1200°C. Impactor samples were obtained from Port 11, at a temperature of 650°C. The total particle residence time in the combustor was estimated at 2.8 seconds. Figure 4-16 shows the as supplied particle size distribution of this kaolinite, while Figure 4-17 is the discrete size distribution that was obtained from the impactor. Although only 40% of the particles are in the under 10 μm size range, which can be classified by the impactor, a wider distribution in this region resulted in a better size segregation with large sample amounts on each stage. Large sample amounts on each stage leads to low relative errors from the AA analysis and hence a better resolution on size dependent sodium capture.

The mass fraction of Na_2O (gm Na_2O /gm Sorbent) is shown in Figure 4-18 plotted against particle diameter (d_{p0}). Total Na_2O fraction and the water insoluble fraction are shown in the same plot. Included in the plot are the $1/d_p$ and $1/d_p^2$ asymptotes. Sodium capture is shown to be dominated by *reactive* capture as demonstrated by the fraction of water insoluble Na_2O . Since all particles under 10 μm size had nearly the same velocity in flue gas, which in turn means the same residence time in the combustor, the difference in capture is interpreted to be due to the influence of particle size.

No clear size dependence is shown for particles under 3.00 μm . Between 3 - 9 μm the size dependence follows $1/d_p$, while at larger than 9.00 μm there appears as if the dependence approaches $1/d_p^2$. Particles under 3.00 μm are likely to be in the reaction controlled regime in which all pore BET surface "sees" the reactant sodium oxide gas. This result is therefore consistent with the observations made in Section 4.5 and we conclude that the extent of sorbent

Figure 4-16: Cumulative mass size distribution for course kaolinite. (Source: Burgess Pigment Co., Ga)

Figure 4-17: As sampled mass distribution for course kaolinite, showing the bulk of the sample in the cup (+10μm).

Figure 4-18: Plot of sodium mass fraction for a single run against particle size

Figure 4-19: Plot of water insoluble sodium oxide, expressed as percent sorbent utilization based on nephelite for two repeat runs, against particle size.

utilization for particles in this size range would only be limited by the sorbent capture capacity, the residence time, sintering and sorbent reactivity.

The $1/d_p$ dependence shown for particles larger than $3.00\ \mu\text{m}$, suggest that intraparticle diffusion is likely to be the controlling mechanism where transport resistances reduces the sorbent pore surface accessible to the reactant gas as the particle size increases. Figure 4-19 shows the results of repeat Run 352 and 353 in which the water insoluble sodium mass fraction is expressed as percent sorbent utilization based on complete reaction to form nephelite. This is calculated by dividing fraction water insoluble sodium oxide with the theoretical fraction if all the sorbent in the stage formed nephelite. Maximum sorbent utilization of 30% is shown in this case. In fact, depending on the sorbent flowrate, maximum utilization levels of 30% - 40% was found to be typical in all experiments.

It is not possible to match our experimental data with gas-solid reaction theory so as to extract fundamental parameters as kinetic rates and effective diffusion coefficients. Several workers (Szekelly et al., 1970; Villa et al., 1992) have proposed models that combine idealized "shrinking core model" for the reaction front and "structural models" for the pore structure. However, such models are difficult to apply as the kinetic parameters and the effect of particle-particle interaction or particles being "starved" of the reactant gas due to the presence of other particles is unknown. A further complication found in our system is that it is not isothermal and the net gas reactant species changes as capture proceeds. In Section 6, an asymptotic analysis will be used together with the estimated transport parameters to calculate an order of magnitude kinetic reaction rate for comparison with that to be derived from the response surface experimental results of Section 5. The $1/d_p^2$ dependence shown by the larger particles above $9.00\ \mu\text{m}$ suggests that the dominant controlling mechanism may be film diffusion. In this regime, only the outer surface of the particles is likely to be utilized. Overall utilization is consequently poor. It is unlikely that a sorbent injection scheme designed to operate in this regime can achieve the desired effect.

Finally, included in this section are results of several runs with the coarse kaolinite that show reproducibility in our data and can be used for future modelling of sodium capture in a down flow combustor set up. These results are only included for the sake of completeness.

Figure 4-20 shows size dependent profiles for four runs at different sorbent flowrates as shown by the calculated equivalence ratios. The profiles may appear quite different at first sight, however, when each curve is normalized by dividing sorbent utilization by the utilization of the smallest particle ($0.65\ \mu\text{m}$) for that run, the capture curves collapses to a single curve as shown in Figure 4-21.

A collapse onto a single curve in this form may suggest that the NaOH-metakaolinite reaction is probably a first order reaction with respect sodium concentration. We arrive at this conclusion in a round about manner as follows: as sodium capture progresses, the net sodium concentration in the flue gas also changes. The concentration profile that an individual particle sees depends on the sorbent flowrate. If the capture reactions are first order, then the particle size (i.e. the point of inflection) for which kinetics is the same order of magnitude as transport is independent of sodium concentration and in this case independent of the sorbent flowrate. If

Figure 4-20: Sodium capture at different sorbent flowrates

Figure 4-21: Sodium capture by kaolinite at different sorbent flowrates when normalized by the utilization of the $0.65 \mu\text{m}$ particle.

all the curves have the same point of inflection then when normalized, they collapse to a single curve. Conversely for higher order reactions, the point of inflection depends on the concentration the particles see which in turn depends on the sorbent flowrate. Therefore each flowrate will have a different point of inflection and it is unlikely that the capture results can collapse to one curve.

4.10 INFLUENCE OF PARTICLE RESIDENCE TIME

In a downflow combustor, at constant mass flow rate, the particle residence time in the gas phase depends on the sorbent injection port and the spatial position of the dew point. If the dew point is taken to be fixed in space, then the residence time depends on the injection port only. One complication of this set up is that changing the injection port also changes the injection temperature, and therefore it is not possible to isolate the effect of injection temperature from that of residence time.

It was shown in Section 2 through equilibrium considerations that the presence of SO₂ in the same environment as sodium does not significantly alter the concentration of the dominant gaseous NaOH, but instead raises the dew point which is determined by the dominant condensate Na₂SO₄(c). Raised dew point in a down flow combustor results in reduced residence time for any injection port. Therefore multiport injection experiments can be carried in the presence and absence of SO₂ to infer the effect of residence time. Another way of looking at the results of sodium capture in the presence of sulfur is to interpret them as the effect of residence time on sorbent utilization. Indeed this phenomena will be exploited in Section 6 to extract initial reaction rates from such experiments in an excess SO₂ environment.

4.11 INFLUENCE OF H₂O ON SODIUM CAPTURE

The effect of H₂O on capture reaction between NaOH, NaCl and Metakaolinite (Al₂O₃·2SiO₂) has not been investigated in detail. It is also not clear how the activation reaction of kaolinite to metakaolinite (Equation 4.1), which takes place through the loss of H₂O from the sorbent matrix, depends on the water content of the flue gas:

Borgwadt (1989) reported that water has a catalytic effect on sintering of lime (CaO) when used as a sorbent to capture SO₂. This phenomena has not been investigated in the case of metakaolinite and sodium. If the presence of water influences the rate and capacity of sodium capture by kaolinite, then it is to be expected that this is so either through the changed rates of sorbent sintering and activation, or through equilibria controlled NaOH concentrations in the flue gas especially when chlorine is present.

From the capture reaction (Equation 2.11), it may be argued that the presence of water should in fact inhibit capture by shifting equilibria to the left. However, following arguments that were put forward by Gallagher (1992), the presence of water in the same environment with other species such as chlorine, should in fact enhance sodium capture compared to when water

is absent. This is so because in the presence of chlorine, the dominant and stable but non reacting sodium species is NaCl(g). The fraction of NaOH, which is the reactant species increases with the increase in water content through the reaction mechanism of Equation 4.2 with the consequent increase in capture rates.

The present work, with 15 - 20% water content, recorded significantly high sodium capture in shorter time periods compared to the bench scale studies of Punjak (1988) and Uberoi (1990), who used a simulated flue gas that contained 3% H₂O. The high water content was due to the natural gas flame (15% H₂O at a stoichiometric ratio of 1.2) and also due to the dilute sodium acetate solution that was injected into the flame (5% H₂O in flue gas). It can not be ruled out whether or not the difference between the present results and the bench scale results are due to the water content or to elevated temperatures or both, and further research is necessary to reconcile this discrepancy. The water level was far in excess of the other reactants such that it is difficult to impute any evidence from experimental data on the influence of water on sodium capture.

It can be concluded that whereas it is possible to argue that the presence of water should enhance sodium capture in the presence of chlorine, no clear evidence has been presented in this work to qualitatively evaluate the effect of water. Further research may be necessary to determine, if any, the catalytic effect of water on sintering of metakaolinite.

4.12 MECHANISM OF ALKALI CAPTURE

A mechanistic description of sodium capture by kaolinite in a combustion environment was developed based on the information obtained from the studies discussed in the previous section. Figure 4-22 is a diagram of this description.

Alkali metal vapor diffuses into the sorbent flake pore matrix after injection. The gaseous species are then either physisorbed or chemisorbed to form nephelite and low melt temperature alkali silicates. Depending on the species formed, the residence time and the reaction temperature, some liquid phases of the reaction products may be formed as was shown in the nephelite-sodium silicate phase diagrams (Section 2). The liquid products may result in either partial melt or complete melt. Partial melt may lead to partial plugging of the pore structure which could result in reduced capture capacity of the sorbent. We have attributed the low sorbent utilization (under 50%) observed in this work to the reduction of the sorbent BET surface through reaction induced melts that accompany capture. Partially blocked pores due to melt may also increase the condensation tendencies of the gaseous sodium through capillary induced condensation in the pores. This may explain why the distribution of water soluble sodium followed closely the mass distribution of kaolinite instead of being shifted to the submicron stages as would be expected if condensation took place on external particle surfaces. One unknown is still the effect, if any, of continued reaction between gaseous sodium with the liquid phase silicates, on overall capture.

Figure 4-22: A conceptualized view of transport and structural changes that accompany capture reaction between alkali gas and a porous kaolinite flake. Oval like products and spheres have been identified by SEM analysis.

5.0 MULTI VARIABLE REGRESSION ANALYSIS

The purpose of this section is to interpolate, by regression, the experimental sodium capture data in a downflow combustor, so that continuous alkali capture curves can be derived. From these curves, the effect of injection temperature, residence time, sorbent flowrate, chlorine, and sulfur on sodium-kaolinite capture reactions can be determined. The regression approach is complimentary to the parametric work presented in Section 4, where the research objectives were addressed by comparative analysis of capture results from single impactor samples.

Although the parametric study approach gave qualitative results such as "the presence of chlorine causes a reduction of sodium capture by kaolinite", it is, however, limited in its ability to uncouple the cross effect of other variables that could not be held constant from one sample to the next. For example, changing the sorbent injection temperature by changing the sorbent injection port, simultaneously changes the sorbent residence time. Both the residence time and the injection temperature are coupled variables that can be uncoupled only through multivariable regression approach. Besides uncoupling closely related variables, there is need to predict sodium capture over a wider temperature domain. We need to answer, for instance, whether or not the effect of chlorine that has been observed at low sorbent injection temperature is the same or different at high temperature, and can we cross relate the presence of chlorine with injection temperature effect?

We will use a multi variable regression analysis, which is based on response surface experimentation technique (Hicks, 1982; Merib and Wendt, 1990; Neter, 1987), to (i) uncouple closely correlated variables, and (ii) show reproducibility in our experimental data. This approach looks at "large" impactor sample populations instead of "single" impactor samples and then applies least squares regression to generate capture "surfaces."

5.1 EXPERIMENTAL DATA

All the impactor samples, for statistical analysis, were taken from Port 13 downstream in the downflow combustor. The sample port temperature ranged between 600 and 650°C, and was estimated to be below the dewpoint of the most significant sodium condensates (NaCl, Na₂CO₃ and Na₂SO₄). Kaolinite was injected at Port 2 to Port 6 in the temperature range between 1300°C and 800°C respectively. The total sodium concentration was kept constant in the range between 250 - 300 ppmv. The *post facto* sodium to sorbent equivalence ratio, which depends on the sorbent flowrate, was in the range between 0.1 and 1.5. The three cases considered were: (1) sodium alone, (2) sodium in excess chlorine (Cl:Na > 10), and (3) sodium in excess SO₂ environments (S:Na > 5). A total of 30 impactor samples were taken for each of the three environments above and were then analyzed in terms of the mean water insoluble sodium capture $\bar{g}$, the standard error of the water insoluble sodium capture $s(\bar{g})$, and the modal water insoluble sodium capture g' . Both $\bar{g}$ and $s(\bar{g})$ were calculated by summing the water insoluble sodium capture in each impactor plate weighted by the mass fraction, f_i , of the total mass sampled in a plate.

$$f_i = \frac{\text{Mass sampled on plate } i}{\text{Total mass sampled by impactor}}$$

$$g^* = \sum_1^9 g_i f_i$$

5.1

$$s(g^*) = \left(\sum_1^9 (g_i - g^*)^2 f_i \right)^{\frac{1}{2}}$$

$$g' = g_i |_{\text{plate 6}}$$

The modal capture g' was obtained from plate 6 since this plate of the impactor had the largest sample amount, which consequently meant it had the lowest relative error from the atomic absorption analysis. The modal capture, the mean capture and the sample standard error serves as a guide to the error margin of our experimental data.

5.2 REGRESSION ANALYSIS

We have argued that alkali capture as an output parameter, is only a function of three independent parameters (inputs) of sorbent injection temperature (T) and Equivalence ratio (ϕ), and species present (Cl_2 , SO_2 etc.). This is a consequence of an experimental design in which the total flue gas mass flowrate and the total sodium concentration are held constant, while the sorbent injection temperature (point) and the sorbent flowrate are varied from one sample to the next. Since the flow is one dimensional, residence time is an implicit function of injection temperature. We are, therefore, interested in correlating the water insoluble sodium capture to the injection temperature and equivalence ratio.

5.2.1 The Experimental Domain

Figure 5-1 shows the experimental domain (T, ϕ) covered by the experimental data of Tables A 5-1 to A 5-9 (Appendix).

A total of 100 impactor samples were obtained (Table A 5-1 - Table A 5-9: Appendix) covering the three cases of "sodium only", sodium with chlorine and sodium with sulfur flue gas environments. A capture regression surface is to be developed for each case. A surface so developed can only be used to interpolate capture results in the region *jointly* covered by the experimental results and care must be taken not to extrapolate its use outside this domain.

5.2.2 Regression Formulation

Let the experimentally measured capture $g^*(T, \phi)$ be a discrete measurement of the true capture function value $g(T, \phi)$ such that:

Figure 5-1: The Experimental domain (T, ϕ).

$$g^*_i(T, \varphi) = g_i(T, \varphi) + e_i \quad 5.2$$

and e_i is the experimental error associated with the measurement of g^* . The dependency of g only on the input parameters of T and φ will be derived and discussed in detail in Section 6. At this point, it will be assumed that e_i is random and normally distributed about the true point of $g(T, \varphi)$ (Mulholland et al., 1968), and $g(T, \varphi)$ is a continuous and monotonic function.

We will digress here to point out that although we are treating T and φ as independent variables, they are experimentally measured variables which also have random errors, e_T and e_φ , respectively. Since, in classical regression analysis, independent variables would normally be considered to be devoid of any errors, the case in consideration is strictly referred to as "structural relation analysis" (Kendall and Stuart, 1979). The consequence of the subtle difference between classical regression analysis and structural analysis, in advanced theory of statistics, has been shown by Kendall et al. to pose difficulties in the interpretation of error margins of the first and higher order regression coefficients. This problem comes from the assumption that the error in the output parameter is normally distributed, and so if the input parameters have also random errors, then the fit coefficients will be a function of this error, and may not necessarily be normally distributed. A reader with keen interest in advanced statistics is referred to the book by the above author.

Apart from the above assumption of normally distributed errors, and that $g(T, \varphi)$ is continuous and monotonic, no other assumption is to be made on the exact nature of the function g , or on the rate of alkali adsorption/reaction function that it contains. The existence of thermodynamic dewpoints in the experimental domain may lead us to question the validity of the assertion that a continuous capture function exists. It is postulated that reactive capture takes place only above the alkali dewpoint (Linak and Wendt, 1993), and so if the domain covered by the experimental data is above the dewpoint, then it is inconceivable that any other discontinuities exists in this domain.

In this scenario of gas-solid interaction, reactive capture starts from the point of sorbent injection and stops at the dewpoint. The dewpoint, therefore, acts as a unique reaction cutoff point. This argument has been supported by our equilibrium studies of Section 2, and also by experimental results which did not show any significant alkali capture to take place when sorbents were injected below the dewpoint. Indeed, when sorbents were injected at Port 6 at a temperature of 800°C in an excess SO_2 environment (the dewpoint was estimated at 850°C), negligible capture was recorded, instead the bulk of the sodium was found to be water soluble.

The water insoluble capture $g(T, \varphi)$ will initially be approximated by all the terms of a multivariable second order curvilinear function as:

$$g_i = \beta_0 + \beta_1 x_{1,i}^2 + \beta_2 x_{1,i} + \beta_3 x_{1,i} x_{2,i} + \beta_4 x_{2,i}^2 + \beta_5 x_{2,i} + \beta_6 + e_i \quad 5.3$$

where $x_{1,i} = T_i(\text{K})/1273$, and $x_{2,i} = \varphi_i$. e_i is the experimental error, the deviation or the residual and may be positive negative or zero.

The choice of the curve to fit, to a large extent, depends on the experience and the prior knowledge of the problem by the experimentalist (Neter et al., 1974). In this case, we have opted to fit our data to a second order polynomial, for one, because we consider the second order term of the equivalence ratio, to be necessary instead of the first order term alone. Stated another way round, we expect some form of concave curvature that flattens out as the value of ϕ increases or as we approach excess sodium case. Two, the second order polynomial contains the cross terms of $T\phi$. It is expected that capture is strongly dependent on this cross term because g is an integral function of the product of alkali adsorption/reaction rate per particle, $R'_p(T)$, and the number of particles per unit volume of flue gas, $n(\phi)$.

In practice, other curves (surface functions) besides the curvilinear one, such as hyperbolas, exponential, geometric, etc exists (Spiegel, 1972) and may be attempted. However, in most practical experimental systems, second order polynomial fits have been found to be adequate (Neter, 1983) so long as such fits are strictly not used to extrapolate results beyond the experimental domain.

A measure of the "goodness of fit" of plane defined by the curvilinear function is provided by the sum of e_i^2 (Mulholland et al., 1968). This is the standard least square formulation. In more complicated formulations, however, it is possible to define the least square plane by considering normal distances from the data points to the plane instead of the vertical distance e_i . This is the principle of Orthogonal formulation (Kendall and Stuart, 1979). Orthogonal formulation in multivariable regression is particularly useful when the independent variables are correlated with one another, or are correlated with another variable not included in the regression model. In general, most computer packages today uses some form of orthogonal formulation in their algorithm (SPSS-X, 1986).

Equation 5.3 above is linear with respect to the fit coefficients $\beta_1, \beta_2, \dots$. If we transform the variables such that $X_1 = x_1^2$, $X_2 = x_1$, $X_3 = x_1 x_2$..etc, the fit polynomial becomes linear with respect to variables $X_1, X_2, X_3, \dots$ etc. such that:

$$y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_4 + \beta_5 X_5 \quad 5.4$$

The transformed variables $X_1, X_2, X_3, \dots$ can be considered now as a set of "independent" variables. It should be noted, however, that the new independent variables are very highly correlated with one another hence the significance tests on the fit coefficients β 's must take into consideration the effect of multicollinearity (Neter, 1983). We can solve for the least square regression plane of $X_1, X_2, \dots$ etc by determining the value of the coefficients β 's. This is done by solving simultaneously the normal equations that are obtained by formally multiplying Equation 5.4 by 1, $X_1, X_2, X_3, \dots$ successively and summing both sides (Spiegel, 1972):

$$\begin{aligned}
\sum_1^n y_i &= \beta_0 n + \beta_1 \sum X_{1,i} + \beta_2 \sum X_{2,i} \dots\dots \\
\sum_1^n X_{1,i} y_i &= \beta_0 \sum X_{1,i} + \beta_2 \sum X_{1,i} X_{2,i} \dots\dots \\
&\vdots \\
\sum_1^n X_{3,i} y_i &= \beta_0 \sum X_{3,i} + \beta_1 \sum X_{3,i} X_{1,i} \dots\dots
\end{aligned}
\tag{5.5}$$

5.2.3 Tests of Significance for Coefficients

Significance testing to accept or reject, wholly or in part, a fit model will first be discussed, and then we will show how some of the concepts of statistical tests of significance have been applied to drop "non significant" terms from the initial second order curvilinear fit model. This is done on the strength of "statistical hypothesis" (Neter et al., 1974).

Statistical hypotheses are statements about the probability distributions of "populations." In many instances, a statistical hypothesis is formulated for the sole purpose of rejecting or nullifying it. For instance, after calculating a coefficient for each polynomial term together with its standard error, we formulate an hypothesis that there is no difference between the coefficient's numerical value and zero (i.e. the observed difference between the coefficient and zero is merely due to random chance of sampling from a population whose mean is zero). This type of hypothesis is called the *null hypothesis* and is denoted H_0 (Mulholland et al., 1971). If on the supposition that $\beta_k = 0$ is true, we find that the observed results from our sample (which depends on how large the sample is and the sample standard error) differ markedly from those expected under the hypothesis, on the basis of pure chance using sampling theory, we conclude that the observed differences are *significant* and we would be inclined to reject the hypothesis (or not accept it on the basis of the evidence obtained). This is the basis of significance testing.

Two statistical tests of significance will be considered separately in this work. These are the partial t-test statistic for the significance of each coefficient β_k , and the overall F-test statistic or the analysis of variance (ANOVA) for the existence of an overall correlation between the experimental data and the regression predicted data (SPSS-X, 1986).

In the first test, the t-test statistic, it is hypothesized in turn that each coefficient $\beta_k = 0$ (H_0), and that the calculated value of β_k comes from a population which is normally distributed about zero. A student t-distribution is then used to accept or reject this hypothesis at a specified level of confidence, which for this work has been set at 95% confidence interval. The student t distribution, instead of the normal distribution is generally applicable to "small" sample populations (in sampling theory, the student t distribution approaches the normal distribution as the sample degree of freedom or the difference between the sample number and the number of fit coefficients, gets larger (Mulholland et al., 1971)).

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The partial t statistic tests whether or not each coefficient is uniquely not equal to zero as follows: From the regression estimate of β_k and its standard error $s(\beta_k)$, a parameter t^* (Box, 1987) can be defined as:

$$t^* = \frac{\beta_k}{s(\beta_k)} \quad 5.6$$

The value of t^* that is calculated can then be compared with the tabulated t-distribution value at any level of significance that is required. For example, if a sample of size n is fitted with p coefficients, then the degrees of freedom for this system is $n-p$, in which case if we choose a 95% confidence interval (two tailed test) as the significance level required for the estimate of the fit coefficient, then the range of β_k is given (Box, 1987) as:

$$\beta_k = \beta_k(\text{calc}) \pm t(0.975, n-p) \times s(\beta_k) \quad 5.7$$

where $t(0.975, n-p)$ can be read off from standard statistical tables. If the range above straddles zero, then we can say that within 95% confidence interval, the value of β_k that has been calculated is not significantly different from zero. Stated formally, at 95% confidence, the partial t test hypothesis (null hypothesis) is given as:

$$\begin{aligned} |t^*| < t(0.975, n-p) , \quad \beta_k &= 0 : H_0 \\ |t^*| > t(0.975, n-p) , \quad \beta_k &\neq 0 \end{aligned} \quad 5.8$$

To drop or maintain a term of a fit polynomial on the strength of a t-test for the next trial, one resorts to iteration. The approach adopted in this work is to start with a lower "reject" confidence interval, say 60% instead of 95%, and drop those terms that do not meet this criteria, then carry out another trial fit with the significant terms. After each successive run, the accept confidence interval should be raised until all the remaining terms in a fit model are significant to a preset confidence limit of 95%.

When a partial t test is used on a two variable quadratic model, there may exist two possibilities that suggests that a term is insignificant. These are (1) that all the coefficients related to one of the variables e.g Temperature, are insignificant, or (2) only one of the coefficients associated with the variable (say the quadratic or linear term) is insignificant (Box et al., 1987). The first case, all coefficients related to a variable are insignificant, does not necessarily mean the effect of the variable can be neglected from the model. There may still exist a strong correlation. The reason for this is that partial t tests only considers the marginal contribution of each term of the independent variable. Given that the other variables are included in the model, further tests have to be done before a conclusion is made. The second case, that is one of coefficients related to a variable is insignificant, points that the term may be dropped out from the model and a new fit attempted without it. The decision to drop or

maintain a term, however, will depend on the actual system under study, and is a subjective judgement of the experimentalist.

5.2.4 Analysis of Variance

The second test of significance is the analysis of variance test (ANOVA). This tests whether or not there exists an overall correlation between the experimental data and the regression predicted data. In comparing the two populations (experimental data and regression fit data), a test of goodness of fit can be taken by comparing their means and variances. A detailed interpretation of the ANOVA tests can be found in most of the literature referred to in this section. The principle of the ANOVA approach is to decompose the error term e_i into that due to "pure error" and that due to "regression." The two populations are then compared in terms of the coefficient of multiple regression R^2 (which should approach unity for a good fit), the sum of squares due to regression (SSR) and the sum of squares due to error (SSE). A test statistic F^* , is defined as:

$$F^* = \frac{MSSR}{MSSE} \quad 5.9$$

where MSSR and MSSE are the mean sum of squares due to "regression" and "error" respectively. The calculated F^* can be compared with the tabulated values of an F-distribution at a selected percentage level of significance, $F(\%, n-p, p-1)$, for various combination of degrees of freedom $n-p$ and $p-1$. The null hypothesis is then stated in a similar manner to the t test as:

$$\begin{aligned} \text{If } F^* < F(0.95, p-1, n-p), & \quad H_0 : \text{No Correlation} \\ \text{If } F^* > F(0.95, p-1, n-p), & \quad a \text{ Correlation} \end{aligned} \quad 5.10$$

The F-test also requires that if it is to be accepted that a correlation exists, the value of F^* should be much larger than $F(\%, n-p, p-1)$ and typically should be at least 10 times or more larger (Box et al., 1987). How good a fit has been achieved will then be measured by how close R^2 approaches unity and how large F^* is in comparison with tabulated F, and even then replicate experiments will still be required to test the fit.

5.2.5 Is a Response Surface Adequately Estimated?

As was stated earlier, the purpose of regression is to estimate a response surface that adequately fits the experimental data. The problem with such multi dimensional surfaces is that, it is conceivable that different response surfaces can share same planes within a confined region. It is with this in mind that care must be taken not to extrapolate such fitted response surfaces. Another source of misinterpretation is to make predictions outside the scope of the model by looking at the levels of the independent variables singly. In multiple regression, it is particularly easy to lose track of the region since levels of both independent variables *jointly* define the region. Thus, one cannot merely look at the ranges of each independent variable. In this regard we will use three dimensional plots to post our experimental results on the regression derived surfaces for visual guideline on the regions of applicability of fit.

The questions still to be addressed are "when is a fitted function sufficiently well estimated to permit useful interpretations?" "Should adequacy of fit be judged on the size of F and R^2 alone?" "If so how large an F is necessary?" First, the value of R^2 should approach unity. Second, according to Wetz (1973), as reported by Box et al., 1987, it is suggested that the calculated F should be at least larger than tabulated F by a factor of 10. The use of randomly obtained replicate data to test a regression model is another useful tool to adopt. We have used this in the case of the sodium in excess chlorine runs to show that replicate runs did also agree with the regression prediction.

5.2.6 Sodium Capture in "sodium only" Environment

The regression results for the first run using the second order curvilinear function is shown in Table 5-1. A total of 28 samples were used in this case. These results were obtained from the SPSS-X (1986) computer package. Included in the table are the partial t^* test statistic for each coefficient and the tabulated values of the student t distribution at 95%, 90% and 60% level of significance for a 23 degree of freedom.

Table 5-1: Second order regression results for sodium capture response surface in a "sodium only" environment.

Tabulated percentiles of the t distribution at 95%, 90% and 60% confidence interval: $t(0.975,23)=2.07$; $t(0.95,23)=1.71$; $t(0.80,23)=0.858$				Is β_k significant?
Coefficient	Value	std. err	t^*	
$\beta_0 T^2$	-0.144 ± 0.408	0.204	0.704	No
$\beta_1 T$	0.265 ± 0.786	0.393	0.673	No
$\beta_2 T\phi$	0.163 ± 0.203	0.102	1.595	Yes
$\beta_3 \phi^2$	-0.163 ± 0.006	0.004	45.158	Yes
$\beta_4 \phi$	0.090 ± 0.170	0.085	1.053	Likely
β_5	-0.124 ± 0.380	0.191	0.648	No

By comparing the values of t^* and the tabulated t distribution values, we conclude that the coefficients with respect to T^2 and T terms are unlikely to be significant, while strong significance is shown for the $T\phi$ term, and some significance, although rather weak for the ϕ^2 and ϕ terms. The quadratic and the linear terms of injection temperature (T^2 , T terms) were then dropped, and a new fit model proposed using all the ϕ terms and the cross term, $T\phi$ such that:

$$g(T, \phi) = \beta_1 T\phi + \beta_2 \phi^2 + \beta_3 \phi \quad 5.11$$

The results for the fit of Equation 5.11 are shown in Table 5-2. This time all the coefficients were found to be non zero at 95% confidence limit. It was then taken that a regression fit had been achieved, and an analysis of variance could be attempted to show that a correlation exists between experimental data and predicted capture by Equation 5.11.

Table 5-2: The final regression fit for sodium capture response surface in a "sodium only" environment.

Tabulated percentiles of the t distribution at 95% confidence interval: $t(0.975,25)=2.06$				Is β_k significant at 95% confidence?
Coefficient	Value	std. err	t*	
$\beta_1 T^\circ \varphi$	0.0881 ± 0.064	0.0329	2.68	Yes
$\beta_2 \varphi^2$	-0.1451 ± 0.054	0.0274	5.29	Yes
$\beta_3 \varphi$	-0.1681 ± 0.088	0.0440	3.83	Yes

The final fit function for "sodium only" environment is therefore given as:

$$g^* = (-0.145 \pm 0.054)\varphi^2 + (0.088 \pm 0.064)T\varphi + (0.168 \pm 0.088)\varphi \quad 5.12$$

It is concluded from this fit that, in sodium only environment, sodium capture by kaolinite is a weak function of higher order terms of injection temperature, instead it is a strong function of alkali to sorbent loading ratio and the cross terms of injection temperature and equivalence ratio.

Table 5-3 shows an analysis of variance results obtained by comparing the experimental capture data and sodium capture results that is predicted by the final regression fit of Equation 5.12. An R^2 value of 0.95, which approaches unity was calculated. Also shown is a F^2 value of 218. This is much larger than the tabulated F distribution value at 95% significance level, $F(0.95,2,25)=3.39$. Both results suggest a very strong correlation has been established between the experimental data and the regression fit data.

A plot of the distribution of residuals against the independent variables of T and φ is shown in Figure 5-2. The residual plot shows that there is no bias, or systematic trends, in the departures of the residuals from zero with respect to any of the independent variables. It is concluded that the residuals are normally distributed about nought, a pre-requisite for the use of the least square method that required that all errors associated with experimental results are random.

As evidence of goodness of fit, Figure 5-3 shows a three dimensional response surface generated by Equation 5.12. Experimental data has been posted on the same figure to show that they lie on the same surface. Finally, Figure 5-4 shows a two dimensional plot of experimental sodium capture against the regression predicted capture. The error bars have been calculated as unit standard errors from the impactor sample analysis. The above results shows that the fit

Figure 5-2: A residual plot against independent parameters T and ϕ , showing 'normal' distribution about zero.

Figure 5-3: Response surface of sodium capture by kaolinite in a 'sodium only' environment as generated by regression. Experimental results are posted on the surface.

Figure 5-4: Experimental sodium capture plotted against the regression fit capture. The values of R^2 and F^* suggest that a strong correlation has been established by the fit equation.

equation adequately predicts sodium capture within the region that is covered by our experimental data. It can thus be used as an interpolation function.

Table 5-3: Analysis of Variance results for least square fit of Equation 5.12.

Analysis of Variance for Na only system					
Source of Variation	Sum of squares	degree of freedom	Mean sum of squares	F*	R ²
Regression	0.0286	(p-1)=2	0.0143	218.9	0.945
Error	0.0016	(n-p)=25	0.00007		
Total	0.0303	n-1=27			
# points:	28	Std err:	0.0083	Reject level F(0.95,p-1,n-p)=3.39	

5.2.7 Sodium Capture in Excess Chlorine Environment

Sodium capture results for runs in which sodium level was kept at 250 ppm and Cl₂ was at ~700 ppm (1400 ppm Cl) are summarized in Table A 5-3 to Table A 5-5 (Appendix). A total of 35 impactor samples were considered for this analysis. The results for the first regression run with all the terms of the second order curvilinear fit are shown in Table 5-4. The quadratic and linear terms of injection temperature are shown to be less significant.

Table 5-4: Second order regression results for sodium capture response surface in a "sodium in excess chlorine" environment.

Tabulated percentiles of the t distribution at 95%, 90% and 60% confidence interval: t(0.975,30)=2.04; t(0.95,30)=1.70; t(0.80,30)=0.854				Is β_k significant?
Coefficient	Value	std. err	t*	
$\beta_0 T^2$	0.055 $\pm$ 0.290	0.149	0.369	No
$\beta_1 T$	0.148 $\pm$ 0.620	0.314	0.472	No
$\beta_2 T^{\circ}\varphi$	0.145 $\pm$ 0.071	0.036	4.037	Yes
$\beta_3 \varphi^2$	-0.067 $\pm$ 0.037	0.018	3.612	Yes
$\beta_4 \varphi$	-0.029 $\pm$ 0.079	0.040	0.740	Likely
β_5	0.109 $\pm$ 0.320	0.164	0.662	Likely

The quadratic and linear terms of injection temperature were dropped from the model and a new run attempted. After the second attempt, the linear term of alkali to sorbent equivalence ratio was found to be insignificant and a final fit achieved with the $T\phi$, ϕ^2 and constant terms only. This gave the best fit for sodium capture in the presence of chlorine as:

$$g^* = (0.107 \pm 0.026)T\phi - (0.055 \pm 0.028)\phi^2 + (0.016 \pm 0.006) \quad 5.13$$

Table 5-5 shows the results of the final fit for sodium capture in excess chlorine environment. All the terms of the fit were found to be significant at 99% confidence interval and above.

Table 5-5: Final regression fit for sodium capture in an excess chlorine environment.

Tabulated percentiles of the t distribution at 99% confidence interval: $t(0.975, 25) = 2.48$				Is β_k significant at 99% confidence?
Coefficient	Value	std. err	t^*	
$\beta_1 T\phi$	0.1066 ± 0.026	0.0134	7.90	Yes
$\beta_2 \phi^2$	-0.0548 ± 0.028	0.0142	3.86	Yes
β_3	0.0161 ± 0.006	0.0031	5.21	Yes

The results of an analysis of variance on this fit is contained in Figure 5-5, with Figure 5-6 showing the three dimensional regression plot that is generated by Equation 5.13. As in the previous case, the experimental results have been posted on the surface of this plot.

Both the three dimensional plot and the two dimensional plots show that a good fit has been achieved for which $R^2 = 0.87$ and $F^* = 99.5$. Six replicate runs which were not used in regression analysis are plotted in Figure 5-5 to further show repeatability of our data. It is concluded that a fit function has been derived that can be used to interpolate sodium capture in an excess chlorine environment.

5.2.8 Sodium Capture in Excess Sulfur Environment

In similar experiments to that of chlorine, the furnace combustion air was doped with approximately 700 ppmv of sulfur dioxide gas, while sodium concentration was kept at 250 -300 ppmv. Kaolinite was injected at Port 2 to Port 5 in the temperature range between 1300°C and 850°C. A total of 29 impactor samples were taken and analyzed for sodium capture in gm Na_2O per unit gm sorbent. A summary of the results is contained in Table A 5-4 to Table A 5-9 (Appendix).

Table 5-6 shows a summary of the first run with all the terms of the second order curvilinear equation. The results shows that unlike the previous two cases of "sodium alone" and sodium with excess chlorine runs where the T^2 and T terms were dropped after the first trial, the sulfur environment exhibits strong injection temperature dependence consequently the T^2 and

Figure 5-5: Plot of regression fit against experimental water insoluble sodium capture in an excess chlorine environment.

Figure 5-6: Response surface of water insoluble sodium capture in excess chlorine environment, plotted against sorbent injection temperature and alkali/sorbent equivalence ratio.

T terms could be dropped. All the terms of the second order curvilinear function were found to be significant at 95 % confidence interval, consequently no further fit iteration was attempted. The sodium with sulfur case shows a strong dependence on injection temperature. This phenomena, which is probably due to the raised dewpoints of the sodium sulfate condensate resulting in reduced gas phase domain residence time for the sorbent particles, will be exploited in Section 6 to extract the initial reaction rates of adsorption/reaction.

Table 5-6: Second order regression results for sodium capture response surface in a "sodium in excess sulfur" environment.

Tabulated percentiles of the t distribution at 95 %, 90 % and 60 % confidence interval: $t(0.975,23)=2.07$; $t(0.95,23)=1.71$; $t(0.80,23)=0.858$				Is β_k significant?
Coefficient	Value	std. err	t^*	
$\beta_0 T^{*2}$	-0.360 ± 0.263	0.132	2.73	Yes
$\beta_1 T^*$	0.754 ± 0.577	0.289	2.60	Yes
$\beta_2 T^* \varphi$	0.372 ± 0.094	0.047	7.91	Yes
$\beta_3 \varphi^2$	-0.061 ± 0.055	0.028	2.18	Yes
$\beta_4 \varphi$	-0.274 ± 0.122	0.061	4.49	Yes
β_5	0.383 ± 0.318	0.159	2.40	Yes

An analysis of variance between the experimental data and the regression fit data gave an F^* of 99.5 and an R^2 value of 0.87, both of which suggest that a strong correlation had been established. The results of sodium capture in an excess SO_2 environment is finally summarized in Figure 5-7, which is a response surface plot of sodium capture against sorbent injection temperature and equivalence ratio. The response surface plot predicts the dewpoint to be in the region of 850°C. Experimental data are posted in this plot to show the region of applicability of the fit equation:

$$g^* = -0.360T^{*2} + 0.754T^* + 0.372T^*\varphi - 0.061\varphi^2 - 0.274\varphi + 0.383$$

$$T^* = \frac{T(K)}{1273} \quad 5.14$$

Figure 5-8 shows a two dimensional plot of the of experimental capture against regression fit capture. A good correlation is shown between the fit and the experimental data, hence the fit equation can be used to interpolate sodium capture.

Figure 5-7: Response surface of sodium capture by kaolinite in an 'excess SO_2 ' environment as generated by least square regression. Experimental data are posted on the surface.

Figure 5-8: Experimental sodium capture against regression fit. The values of R^2 and F^* suggests that a strong correlation has been established by the fit equation.

5.2.9 Discussion of Results

Regression has been used to interpolate discrete sodium capture data to generate continuous capture curves. The effect of chlorine and sulfur on sodium capture at different sorbent injection temperatures and different sorbent flowrates can now be compared.

The first comparison is based on the shape and form of the response surfaces that have been generated. Both the sodium alone and sodium with excess chlorine environments show very similar shapes in which the dewpoint is outside the experimental domain, and the injection temperature effect is only through the cross term $T\phi$. The similarity in their shapes supports the hypothesis we had put forward that in both environments, sodium capture probably proceeds via the same mechanism of NaOH-Metakaolinite reaction, and the presence of chlorine reduces the total concentration of NaOH via the NaOH-NaCl-H₂O equilibria. The effect of injection temperature, in both environments, is weak because of the lower dewpoints and hence the long residence times for near completion of capture reactions to take place. The chlorine and sodium alone response surfaces also indicate that all our experiments were carried above the dewpoint. The dewpoint can be estimated by extrapolating the capture curves to be somewhere around 700°C.

The presence of SO₂ results in a significant elevation of the dewpoint to around 850°C. In a one dimensional flow reactor, the elevated dewpoints also results in a reduction of the sorbent residence time in the alkali gas phase domain. Significant reduction of sodium capture in the presence of sulfur can be attributed to the significant reduction in the gas phase residence time. This is best illustrated by the shape of the response surface which clearly shows insignificant sodium capture at temperatures below 850°C for all the sorbent flow rates.

In summary, this section has established that a response surface experimentation technique which is based on variable sorbent injection points instead of variable sampling points, together with statistical regression can be combined to successfully generate continuous alkali capture interpolation functions. The use of a response surface to extract rate kinetics of sodium induced corrosion on a combustor test rig was previously reported by Lowell et al. (1982). This scheme is exploited in Section 6.

Figure 5-9 shows the effect of chlorine and sulfur at different sorbent injection temperatures at a constant equivalence ratio of 0.45. An Equivalence ratio of $\phi=0.45$ has been selected for this comparative analysis because it is a flowrate that was covered by experimental data in all the three cases considered. Taking the sodium alone as base case, the effect of chlorine is seen to reduce sodium capture by as much as 30% at all the injection temperatures that were covered by our experiments. We have already attributed this reduction in sodium capture in the presence of chlorine to NaOH-NaCl-H₂O equilibria. The effect of sorbent residence time in the gas phase domain is shown by comparing the base case sodium capture with sodium capture in presence of SO₂, which results in reduced residence time through elevated dewpoints.

Figure 5-9: Comparative effect of Cl and S on sodium capture at different sorbent injection temperatures for $\phi=0.45$

6.0 MECHANISTIC MODEL

This section presents mathematical models that can be used to reproduce the experimental results of Section 4 and Section 5. In doing so, more insight is shed into the experimentally observed phenomena. One part of mechanistic modelling attempts to extract apparent reaction rate parameters from the experimental data, the other part presents a general capture model which accepts reaction rates as adjustable parameters to predict alkali capture in a combustor.

Two independent approaches have been adopted to derive the apparent initial reaction rates from experimental data. In the first approach, Section 6.1, the apparent initial rates are calculated by combining the response surface sodium capture data from Na-SO₂ system (Section 5) with an assumed one dimensional particle time and temperature history in a plug flow reactor. Differentiation of the capture integral function with respect to limit parameter of injection temperature is then used to estimate the initial reaction rate. Detailed discussion of the assumptions and simplifications that are made is presented. A computer package for parameter estimation is finally used to fit the temperature dependent rates to an Arrhenius type equation. The second approach, Section 6.2, uses the experimental results of the effect of particle size to estimate the apparent reaction rates. The results of Section 6.1 and Section 6.2 are compared and are shown to be in close agreement. Mechanisms governing alkali capture by kaolinite are identified.

Section 6.3 presents a model for alkali capture in a plug flow reactor. Prediction of sodium capture using the NaOH-kaolinite kinetics from this work (Section 6.1 and 6.2) are compared with those of Uberoi (1990) and Gallagher (1992). The effect of chlorine is addressed. The present kinetics are shown to be superior in predicting sodium capture by kaolinite in a combustor.

6.1 ESTIMATION OF THE INITIAL RATES OF REACTION

The initial reaction rates are to be extracted from the response surface experimental data of Na-SO₂ system by applying Liebnitz theorem (Greenberg, 1978) of differentiation of an integral with respect to limit parameter. It is only the initial rates that can be extracted this way because the experimental data and the experimental design were such that alkali capture (an integral function) is resolved with respect to injection temperature (a limit parameter). In terms of combustion variables, it is at the limiting point of sorbent injection, that the local gas phase alkali concentration is known, the local temperature was measured and known, and the sorbent particle structure is still intact so that the fraction of sorbent that is available for capture reactions can be taken as unity. Once reactions start, the local rate of reaction will depend, among other things, on local alkali concentration (C_i), particle number density in flue gas (n), the fraction of sorbent particle that is still left unreacted (χ), local temperature (θ), particle sintering, etc. These are highly correlated parameters which are difficult to uncouple from the input-output type data found in this work. Despite this, initial reaction rates are still useful as they can be used to predict an upper bound capture attainable in a practical sorbent injection system.

A Lagrangian formulation of reactively captured sodium oxide, g^* (gm Na₂O/gm sorbent), in a one dimensional plug flow reactor is given by the integral Equation 6.1:

$$g'' = \int_0^{\tau_{dewp}} n_1 R'_p(p_1, \theta, \chi, n) dt \quad 6.1$$

where n_1 is the number of particles per unit mass of sorbent and depends only on the particle mean size d_p , $R'_p(p_1, \theta, \chi, n)$ is the local reaction rate in gm Na_2O /particle/sec, which depends on the local alkali partial pressure p_1 , local temperature θ , extent of reaction of particle $1-\chi$, and the number of particles per unit volume of flue gas n ($\#/ \text{cm}^3$ gas). τ_{dewp} is the residence time between the injection point and the dewpoint. Before we continue to develop Equation 6.1, we will consider some of the implicit assumptions that are contained therein. Most of these assumptions are based on a simple, constant cross section, plug flow reactor model.

6.1.1 Assumptions

- (i) Plug flow reactor, hence a one dimensional flow of flue gas and particles.
- (ii) Low particle to fluid mass loading ($m_p/m_g \ll 1$).
- (iii) Steady logarithmic temperature profile that is independent of capture reactions.
- (iv) Particle temperature follows closely the uncorrected flue gas temperature profile, and also particle velocity follows the flue gas velocity.
- (v) Reaction is linear and first order with respect to local concentrations.
- (vi) The dewpoint is a unique point in the combustor between sorbent injection and sampling points, below which no further reactions take place.

Assumption (i), plug flow reactor, is necessary to enable the calculation of particle time and temperature history from the measured flue gas temperature profile. This assumption may not hold near the injection point where eddies, particles bouncing off the walls and re-entrainment is expected to take place. Studies on the behavior of small particles (less than $10 \mu\text{m}$), when injected into a quiescent fluid at 1000 cm/sec , show that the time scale for such particles to assume the characteristics of the fluid field is of the order of 10^{-3} seconds (Hinds, 1977). With such short time scales, it is likely that the assumption is justified.

Assumption (ii), low particle to fluid loading, is justified. The maximum sorbent flowrate was estimated at 5 gm/min for a flue gas mass flowrate of 450 gm/min , corresponding to a solid/fluid mass loading ratio of the order of 1 %.

Assumption (iii), steady logarithmic temperature profile independent of capture reactions, is a consequence of the post flame assumption that axial convection is dominant over conduction, no heat sources except the upstream flame, and the dominant heat loss is only through the furnace walls. This assumption is much closer to experimental results than a linear temperature profile assumption. It is also not conceivable that any capture reactions can affect the temperature profile.

Assumption (iv), particle velocity and temperature follows that of the flue gas, has been shown to be true (Glass, 1981). In his calculations, Glass showed that the average deviation between particle velocity and that of the flue gas, for particles under 10 μm diameter, is less than 2%.

Assumption (v), linear first order reactions, has been shown in Section 4 and Section 5 to be true. Linear assumptions are necessary if "shooting" methods is to be applied to back up initial reaction rates.

Assumption (vi), that reactions are frozen at a unique point as indicated by the dewpoint, is an idealization of the capture phenomena and need to be considered in detail. This assumption requires that the thermodynamic dewpoint lie between the sorbent injection point and the sampling point. The dewpoint then acts as a distinct cut off point below which no further reactions take place. It is an idealization but one which is realistic.

We will attempt to make use of the elevated dewpoints of the Na-SO₂ system to extract initial reaction rates by recognizing that if the dewpoint remains fixed in space, changing the sorbent injection point changes the effective "reactor" residence time. Rates can be extracted from experimental data this way only if the dewpoint lie relatively closer to the sorbent injection point(s) than to the sampling point. In such a case, changing the injection point, gives a larger marginal change in the time scale available for gas-solid reactions. It was shown in Section 5.2 that this is the case for the Na-SO₂ system. Where the dewpoint is nearer the sampling point down stream, and if the time scale this represent is longer than that necessary for complete reaction, changing a sorbent injection point may not result in a significant difference in capture as there is still enough time available for complete capture to take place. This is apparently the case with the sodium in excess chlorine and "sodium only" runs. The latter two results reflect more of the marginal effect of sorbent sintering with temperature, than the effect of injection temperature on reaction rates. For these reasons, the experimental data for sodium with excess sulfur are the only ones to be used for deriving the initial reaction rates.

6.1.2 Capture Reaction Formulation

We start from Equation 6.1, in which the water insoluble sodium, that has been captured by a measurable mass of sorbent, is given by g^* (gm Na₂O/gm Sorbent) as:

$$g^* = \int_0^{t_{\text{exp}}} n_1 R'_p(p, \theta, x, n) dt \quad 6.2$$

with the number of particles per unit mass of sorbent for assumed uniform spheres:

$$n_1 = \frac{6}{\rho_p \pi d_p^3 (1 - \epsilon)} \quad 6.3$$

Hence Equation 6.1 can be rewritten as:

$$g^* = \int_0^{\tau_{\text{damp}}} \frac{6}{\rho_p \pi d_p^3 (1-\epsilon)} R'_p(p, \theta, x, n) dt \quad 6.4$$

ρ_p is the particle skeletal density in gm/cm³ and ϵ is the particle porosity. To convert from a time integral to a temperature integral, we introduce chain rule for temperature time rate of change:

$$\frac{d\theta}{dt} = \frac{d\theta}{dx} \cdot \frac{dx}{dt} = \frac{d\theta}{dx} \cdot v_p \quad 6.5$$

where x is the axial distance along the reactor, t is real time after sorbent injection, v_p is the flue gas (particle) velocity and $d\theta/dx$ is the steady temperature gradient along the axial length of the combustor. The local flue gas velocity, at constant mass flow rate and constant reactor cross section area, is only a function of the local temperature θ (Ideal gas law). Hence,

$$v_p = c \theta \quad 6.6$$

which for a mass flowrate of 450 gm/min and a reactor diameter of 0.152 cm is given as $v_p = 0.12 \theta$ (cm/sec). The combustor temperature gradient can be obtained from the experimental temperature profile in the form of Equation 6.7:

$$\frac{d\theta}{dx} = -a\theta + b \quad 6.7$$

This fit is shown in Appendix F and is adequately estimated by the mean values of constants a and b given as; 0.00285 cm⁻¹ and 1.83 K/cm respectively.

Equation 6.5 can be written as:

$$dt = \frac{d\theta}{v_p(\theta) \cdot \frac{d\theta}{dx}(\theta)} \quad 6.8$$

then Equation 6.8 is in effect the time to temperature transform function:

$$dt = \phi(\theta) d\theta \quad 6.9$$

which from the constants a , b , c above (at our experimental conditions) gives;

$$\phi(\theta) = \frac{1}{-3.42 \times 10^{-4} \theta^2 + 0.22 \theta} \quad 6.10$$

Substituting Equation 6.9 into Equation 6.4, the integral capture g^* can be formulated with respect to local temperature as:

$$g^*(T, p_{10}, n) = \int_T^{T_{dewp}} \frac{6}{\rho_p \pi d_p^3 (1-\epsilon)} \cdot R'_p(p_1, \theta, x, n) \phi(\theta) d\theta \quad 6.11$$

Equation 6.11 cannot be integrated explicitly to determine g^* because the reaction rate term $R'_p(p_1, \theta, x, n)$ is not known. However, it is noted that provided that all experiments are carried at same initial alkali concentration (p_{10}) at the point of sorbent injection, and provided that the reactions are not complete before the dewpoint, it can be taken for granted that g^* will depend only on the starting conditions of T , p_{10} and n . Partial differentiation of Equation 6.11 with respect to the limit parameter, T using liebnitz theorem gives:

$$\frac{\partial g^*}{\partial T} \Big|_{p_{10}, n} = \frac{6}{\rho_p \pi d_p^3 (1-\epsilon)} \left(\int_T^{T_{dewp}} \frac{\partial}{\partial T} (R'_p(\theta) \phi(\theta)) d\theta - R'_p(T) \phi(T) + R'_p(T_{dewp}) \phi(T_{dewp}) \right) \quad 6.12$$

The integral term in Equation 6.12 goes to zero because $R'_p(\theta) \phi(\theta)$ is not a function of T . Reaction rate at the dewpoint, $R'_p(T_{dewp}) = 0$; from the definition that reactions stop at the dewpoint hence Equation 6.12 reduces to:

$$\frac{\partial g^*}{\partial T} \Big|_{p_{10}, n} = \frac{-6}{\rho_p \pi d_p^3 (1-\epsilon)} \cdot R'_p(p_{10}, T, x=1, n) \phi(T) \quad 6.13$$

Therefore, if we substitute for $\phi(T)$ from Equation 6.10, the initial rate of reaction (R'_p) in gm $\text{Na}_2\text{O}/\text{particle}/\text{sec}$ is given as:

$$R'_p(p_{10}, T, x=1, n) = (-3.42 \times 10^{-4} T^2 + 0.22 T) \frac{\rho_p \pi d_p^3 (1-\epsilon)}{6} \cdot \frac{\partial g^*}{\partial T} \Big|_{p_{10}, n} \quad 6.14$$

or the initial rate (R_p) in gm $\text{Na}_2\text{O}/\text{gm sorbent}/\text{sec}$ is given by as:

$$R_p(p_{10}, T, x=1, n) = (-3.42 \times 10^{-4} T^2 + 0.22 T) \cdot \frac{\partial g^*}{\partial T} \Big|_{p_{10}, n} \quad 6.15$$

The particle number density n depends only on the sorbent flowrate which at constant initial alkali concentration (at point of injection) p_{i0} , can be combined to a single parameter by introducing the total alkali/sorbent equivalence ratio (φ), as follows:

Let the total sodium oxide mass flowrate ($\dot{M}_{Na_2O}$) be related to the flue gas mass flowrate ($\dot{M}_g$), total alkali partial pressure (p_{i0}) and flue gas Molecular weight (M_w) as:

$$\dot{M}_{Na_2O} = \frac{31 p_{i0} \dot{M}_g}{M_w} \quad 6.16$$

where 31 is the equivalent gm Na_2O per gram mole of sodium. If the alkali/sorbent equivalence ratio is defined as:

$$\varphi = \frac{\dot{M}_{Na_2O}}{0.27 \times \dot{M}_p} \quad 6.17$$

where $\dot{M}_p$ is the sorbent mass flowrate. 0.27 is the stoichiometric ratio of Na_2O to kaolinite for the nephelite ($Na_2O \cdot Al_2O_3 \cdot 2SiO_2$) formation reaction. The particle number density in the flue gas, n , is given by the ratio particle number flowrate to flue gas volume flowrate:

$$n = \left(\frac{\#particles}{cm^3} \right) = \left(\frac{6\dot{M}_p}{\rho_p \pi d_p^3 (1-s)} \right) \cdot \left(\frac{M_w}{\dot{M}_g R \theta} \right) \quad 6.18$$

where R is the gas constant. Combining Equation 6.16, Equation 6.17 and Equation 6.18 gives the initial alkali/sorbent equivalence ratio as:

$$\varphi = \left(\frac{1}{0.27n} \right) \cdot \left(\frac{186}{\rho_p \pi d_p^3 (1-s)} \right) \left(\frac{p_{i0}}{R\theta} \right) \quad 6.19$$

From which the independent variables of (p_{i0} , T , n) collapses to (T , φ) so that $R'_p(p_{i0}, T, n) \rightarrow R'_p(T, \varphi)$, and $g^*(p_{i0}, T, n) \rightarrow g^*(T, \varphi)$. It is now possible to determine the initial rate of reaction from the experimental results of $g^*(T, \varphi)$ which is given by Equation 6.20 below:

$$R_g(T, \varphi, x=1) = (-3.42 \times 10^{-4} T^2 + 0.22 T) \cdot \frac{\partial g^*}{\partial T} \Big|_{\varphi} \quad 6.20$$

Experimental results in Section 5 gave $g^*(T, \varphi)$ for the $Na-SO_2$ system as:

$$g^*(T, \varphi) = -0.360T^{-2} + 0.754T^{-1} + 0.372T^{-1}\varphi - 0.061\varphi^2 - 0.274\varphi - 0.383$$

6.21

$$T^* = \frac{T(K)}{1273}$$

hence

$$\left. \frac{\partial g^*}{\partial T} \right|_{\varphi} = -4.44 \times 10^{-7}T + 2.92 \times 10^{-4}\varphi + 5.92 \times 10^{-4}$$

6.22

Which for a particle of mean size $d_p = 2 \times 10^{-4}$ cm (Aerodynamic impactor measurements), porosity $\epsilon = 0.58$, and skeletal density $\rho_p = 2.64$ gm/cm³ (Suzuki, 1988), the initial rate in gm Na₂O/particle/sec at $\varphi = 1$ is given as,

$$-R'_p(T, \varphi) = \sum_{k=1}^{k=3} a_k T^k$$

$$a_1 = 8.92 \times 10^{-16}$$

6.23

$$a_2 = -1.86 \times 10^{-18}$$

$$a_3 = 7.06 \times 10^{-22}$$

Alternatively, the initial rate in gm Na₂O/gm sorbent/sec is given as

$$-R'_s = \sum_{k=1}^{k=3} a_k T^k$$

$$a_1 = 1.92 \times 10^{-4}$$

6.24

$$a_2 = -4.00 \times 10^{-7}$$

$$a_3 = 1.52 \times 10^{-10}$$

Equation 6.24 gives the initial global rates, at $\varphi = 1$, in the region between 0.08 to 0.10 gm Na₂O/gm sorbent/sec for a temperature range between 850°C - 1300°C.

6.1.3 Apparent Intrinsic Reaction Rates

Figure 6-1 is a plot of sodium capture against alkali/sorbent equivalence ratio at different running conditions of injection temperature and species present. The figure shows that alkali

Figure 6-1: Sodium capture plotted against alkali/sorbent equivalence ratio(ϕ) at different running conditions of injection temperatures and species present. Linearity is shown upto $\phi=0.5$.

capture is linear with respect to the equivalence ratio upto $\varphi=0.5$ to 0.6. Above this range, capture is less dependent on alkali/sorbent equivalence ratio as shown by the scatter in the plot.

This suggests that excess alkali concentrations are approached at alkali/sorbent equivalence ratio above 0.6 in which case capture is dependent on other factors such as injection temperature and species present. It has also been shown by both the AA bulk analysis and SEM analysis of individual reacted particles that 50% sorbent utilization, based on nephelite stoichiometry reaction, is the maximum that could be obtained in our system. These observations lead us to conclude that capture results above $\varphi=0.5$ approaches conditions that can be described as an excess alkali environment. The reaction rate parameters derived at $\varphi=1$ should, therefore, approach intrinsic parameters in which the effect of particle-particle interaction or the effect of particles being "starved" of the reactant gaseous alkali species is negligible.

Equation 6.23 is the correlation for the rate of reaction per particle per second. To derive the rate coefficient (k_v) in the units of $\text{cm}^3 \text{ gas} / \text{cm}^3 \text{ pore volume of particle/sec}$ for an assumed first order reaction in reaction controlled regime with all the pore volume accessible to the gaseous sodium, the terms of the reaction rate per particle can be partitioned as:

$$\left(\frac{\text{gm Na}_2\text{O}}{\text{particle .sec}} \right) = \left(\frac{\text{cm}^3 \text{ gas}}{\text{cm}^3 \text{ porevol. sec}} \right) \left(\frac{\text{gmol Na}}{\text{cm}^3 \text{ gas}} \right) \left(\frac{\text{cm}^3 \text{ porevol}}{\text{particle}} \right) \left(\frac{\text{gm Na}_2\text{O}}{\text{gmol Na}} \right) \quad 6.25$$

or

$$R'_p = (k_v) \cdot \left(\frac{p_{\text{Na}}}{RT} \right) \cdot \left(\frac{\pi d_p^3}{6} \right) \cdot (31) \quad 6.26$$

Combining Equation 6.14, Equation 6.22 and Equation 6.26, the kinetic reaction rate k_v at $\varphi=1$, is then given as:

$$k_v = \frac{\rho_p \cdot RT}{31 p_{\text{Na}} \phi(T)} \frac{(1-\epsilon)}{\epsilon} \cdot \frac{\partial g^*}{\partial T} \Big|_{\varphi=1} \quad 6.27$$

and using the values for $\rho_p=2.64 \text{ gm/cm}^3$, $\epsilon=0.58$ (Tsuzuki, 1969; Uberoi, 1990), and $p_{\text{Na}}=100 \text{ ppm}$ (corresponding to an alkali recovery of 40% as was shown in Section 4.2.2), together with the partial derivative of g^* with respect to T , the rate parameter, k_v , is given as:

$$k_v(T) = \sum_{k=1}^{k=3} a_k T^{k+1}$$

$$a_1 = -9.83 \quad 6.28$$

$$a_2 = 2.02 \times 10^{-2}$$

$$a_3 = -7.68 \times 10^{-6}$$

A plot of Equation 6.28 is shown in Figure 6-2 with the initial rate term found to be in the range of 4 to 10×10^6 ($\text{cm}^3 \text{gas}/\text{cm}^3 \text{porous solid} \cdot \text{sec}$). The form of Figure 6-2 suggest that the intrinsic volume rate can be fitted to an Arrhenius type equation of $k_v = k_0 \exp (-E / RT)$. Using a computer software for parameter estimation through non linear regression (White, 1976), the best fit of k_v was found to be given by:

$$k_v = 4.5 \pm 0.5 \times 10^7 \exp (-5300 \pm 150 (\text{cal/gmol}) / RT) \text{ cm}^3 \text{gas}/\text{cm}^3 \text{pore vol} \cdot \text{sec}$$

Other activation energies were attempted and plotted for comparison with experimental data. Figure 6-2 shows the best fits of k_v that were achieved with activation energies of 6, 10 and 20 kcal/gmol (values given in the figure). It is apparent from the plot that activation energies between 6 to 10 kcal/gmol are realistic. However, activation energy of 20 and above do not give good fits. It is therefore concluded that, based on experimental data, the initial rate adsorption/reaction of sodium with kaolinite in units of gm $\text{Na}_2\text{O}/\text{gm}$ sorbent/sec is best given as:

$$\frac{d[\text{Na}_2\text{O}]}{dt} = 31 k_v \cdot V_p \cdot C_{\text{Na}} \quad 6.29$$

where $[\text{Na}_2\text{O}]$ is in gm Na_2O per gram mass made up of porous particles, $k_v = 4.5 \pm 0.5 \times 10^7 \exp (-5300 \pm 150 (\text{cal/mol}) / RT) \text{ cm}^3 \text{gas}/\text{cm}^3 \text{pore volume} \cdot \text{sec}$, V_p = Sorbent pore volume in cm^3/gm sorbent, and C_{Na} = Sodium concentration in $\text{gmol Na}/\text{cm}^3 \text{gas}$. The interpretation of this model is that reaction is kinetically controlled with the all the pore volume accessible to the reactant gaseous sodium species. It is to be noted that this model applies to the initial rate only under kinetically controlled reactions in which all the sorbent pore is available. No assumption is made on how the reaction rate changes once reactions start.

6.2 MECHANISMS GOVERNING ALKALI METAL CAPTURE

Let us consider the solid material forming the porous sorbent to react with gaseous NaOH irreversibly according to the scheme:

Figure 6-2: Initial reaction rate kinetics derived from experimental data. Activation energies under 10 kcal/gmol is shown to adequately fit the data, with the best fit achieved at $E = 5.3$ kcal/gmol

The starting point for the gas-solid reaction formulation is the pseudo steady state gaseous species balance equation for an n th order reaction:

$$D_e \nabla^2 C_1 - k C_1^n = 0 \quad 6.31$$

In which, depending on the governing mechanisms, the boundary conditions may take any of the following forms:

$r=0$	$\nabla C_1 = 0$	Symmetry
$r=r^*$	$\rho_m dr^*/dt = bk C_1^n$	In case of applicability of the shrinking core model.
$r=d_p/2$	$-D_e \nabla C_1 = k_m (C_1^\infty - C_1)$	Film transport condition.
	$C_1 = C_1^\infty$	Film resistance negligible.

where	ρ_m	is the molar density of solid
D_e		is the effective diffusivity in a porous particle
d_p		is the spherical particle diameter
r		is the distance coordinate perpendicular to the moving reaction front.
b		is the stoichiometric factor
k		is the reaction constant, and
n		is the reaction order.

For a continuous flow system, an auxiliary equation to match the number of particles in the flow stream and the extent of reaction of individual particles with the net bulk phase gaseous species concentration, C_1^∞ , has to be included. In general, the governing equations have to be solved numerically. For most practical purposes, however, the results sought are not the time and spatial dependencies of C_1 and r^* , but rather the extent to which the particles have reacted for a given residence time and injection temperature.

Some solutions to the equations of the type above (Szekely et al., 1970, 1975; Sohn et al., 1972; Villa et al., 1992) have incorporated what is generally termed as "structural models," in which the porous particle is idealized to consist of either non porous micro particles (grains), or an ordered honeycomb pore structure. It is, however, still difficult to find simple models that are immediately accessible for the interpretation of experimental data or for the prediction of the behavior of a given system. The difficulty arises from determining the "grain sizes" in these structural models (Szekely et al., 1975) and from the limitations that these models are based on. For example, two assumptions that are pertinent in most structural models and which deviate significantly from our present system are: (1) that the system is isothermal, and (2) that the solid structure is macroscopically uniform and is unaffected by the reaction. We have seen from our Scanning Electron Microscope analysis that significant structural deformation did take place with capture.

To overcome these difficulties, we shall examine our experimental data in terms of asymptotic behavior. This approach, borrows heavily from the results of gas-solid catalysis and uses the analogues of the Thiele modulus and Dahmkholer numbers to estimate possible reaction rate parameters (Romans, et al., 1990). The first task therefore is to estimate relevant transport parameters.

6.2.1 Estimation of Transport Coefficients

The Chapman-Enskog equation (Bird, Stewart & Lightfoot, 1960) for the molecular diffusivity of two gas pairs is given as:

$$D_{AB} = 1.8583 \times 10^{-3} T^{\frac{3}{2}} \frac{\left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{\frac{1}{2}}}{p \sigma_{AB}^2 \Omega_{D,AB}} \quad 6.32$$

With D_{AB} in cm^2/s , T in K, p in atm, σ_{AB} in Angstrom units and $\Omega_{D,AB}$ is a dimensionless function of the temperature and the intermolecular potential field for a molecule of A and B. M_A and M_B are molecular weights of species A and B. In the absence of data for NaOH gas, CO_2 - N_2 parameters (Reid et al., 1977) are used:

$$\Omega_{D,AB} = \left(\frac{\epsilon_A}{k} \cdot \frac{\epsilon_B}{k} \right), \quad \sigma_{AB} = \frac{1}{2}(\sigma_A + \sigma_B) \quad 6.33$$

	M_i	$\sigma_i(\text{\AA})/k$
CO_2	44	3.941195.2
N_2	28	3.79871.4
Air	28.9	3.71178.6

Sample calculations for D_{AB} at 1500 K is shown in Equation 6.34,

$$D_{\text{CO}_2-\text{N}_2} = \frac{1.858 \times 10^{-3} 1500^{\frac{3}{2}} \left(\frac{44+28}{44 \times 28} \right)^{\frac{1}{2}}}{(3.8695)^2 (0.842)} \quad 6.34$$

giving D_{AB} as $2.0 \text{ cm}^2/\text{s}$. Knudsen diffusivity, for NaOH in metakaolinite, is determined by,

$$D_k = 9.70 \times 10^3 \frac{d}{2} \left(\frac{T}{M_A} \right)^{\frac{1}{2}} \quad 6.35$$

where d_p is the average pore diameter in centimeters, and T is the temperature in Kelvin. Punjak (1988) measured the average pore size of metakaolinite as $d_p = 180 \times 10^{-8}$ cm, and a porosity of 0.58. Substituting into Equation 6.35, the Knudsen diffusivity at 1500 K is $D_k = 0.054$ cm²/s. This compares with 0.036 cm²/s calculated by Punjak at 800°C. At such small pore size, Knudsen diffusivity would be expected to dominate. The effective diffusivity is calculated by Equation 6.36,

$$D_e = \left(\frac{D_{AB} D_k}{D_{AB} + D_k} \right) \quad 6.36$$

giving

$$D_e = 0.052 \text{ cm}^2/\text{s}$$

Film diffusion coefficient, k_m , can be calculated from Nusselt number correlation for a spherical particle in a fluid flow field by Equation 6.37 (Levenspiel, 1976):

$$Nu = \frac{k_m d_p}{D_{AB}} = 2 + 0.6 Sc^{\frac{1}{3}} Re^{\frac{1}{2}} \quad 6.37$$

Where Re is particle Reynolds number based on particle slip velocity and Sc is the fluid Schmidt number. For gases, Sc is of the order of unity. The velocity of particles of size less than 10 μm diameter, has been shown to approximate that of the flue gas velocity (Glass, 1981), making the particle Reynolds number to approach zero. A Nusselt number of 2 is therefore justified. The film diffusion coefficient becomes:

$$k_m = \frac{2 D_{AB}}{d_p} \quad 6.38$$

Substituting Nu , and D_{AB} into Equation 6.37, the interface transport coefficient k_m for a 2.0 μm particle at 1500 K, is: $k_m = 2 \times 10^4$ cm/s.

In conclusion, the transport parameters to be used at 1500 K are estimated to be:

$$\begin{aligned} D_{AB} &= 2.0 \text{ cm}^2/\text{sec} \\ D_e &= 0.052 \text{ cm}^2/\text{sec} \\ k_m &= 2.0 \times 10^4 \text{ cm/sec} \end{aligned}$$

6.2.2 Estimation of The Gas Phase Alkali Concentration

In Section 4.2.1, it was shown that flue gas alkali concentration backed from impactor samples is much lower than alkali concentrations that are calculated from feed flowrates to the furnace. Alkali concentrations, backed up from impactor results, is to be used in evaluating reaction kinetics. Table 6-1 show AA results for impactor 352 and 353. The sampling probe diameter is 0.336" and the furnace diameter is 6". Under isokinetic sampling conditions, the gas phase alkali concentration is calculated to be in the range of 65-70 ppm, which corresponds to an alkali recovery of 25%. A concentration of 70 ppm is consistent with the 100 ppm used previously in Section 6.1.

Table 6-1: AA data used to estimate gas phase alkali concentration

Impactor #	Sampling time (mins)	AA reading of total mass of Na sampled. (ppm in 30ml dissolving acid)	Equivalent flue gas concentration (ppm)
352	30	85.40	70.1
353	30	78.10	64.2

6.2.3 Asymptotic Analysis of Experimental Data

Coarse kaolinite (1 - 100 μm size) was used to evaluate effect of particle size on sorbent utilization, a phenomena that could not be discriminated from the narrow size-range particle experiments. The normalized results of sample 352, 353, 362, and 363 given in Section 4, show that two regimes of alkali/ sorbent interactions exist. These are: (1) Small particle size range (below 3 μm), for which no size dependent capture is exhibited and (2) Large particle size range, for which a clear size dependence is shown. To estimate the kinetic parameters, we draw asymptotes in the two regions above and then interpolate, the particle size for which both transport and kinetic rates are in same order of magnitude. This is referred to as the point of inflection. If we assume that the gas solid reaction is first order with respect to gas phase concentration of sodium, then the point of inflection is independent of concentration or extent of reaction (Romans et al., 1990; Sohn and Szekey, 1972), but instead, depends only on the non dimensional ratios of reaction and transport rates.

Figure 6-3 show fraction sorbent utilization plotted against impactor lower cut off diameter for sample 352 and 353. The figure is derived by normalizing sorbent utilization with the utilization of the smallest particle size, in this case the 0.65 μm particle. Two asymptotes extrapolating regions of transport dependence and regions of kinetic dependence show that the particle size corresponding to the point of inflection is 2.0 μm . At the point of inflection, the characteristic dimensionless ratio of transport rates to kinetic rates (either Damkholer number or Thiele modulus) are of the order of unity. With the transport coefficients known, an order of magnitude calculations for kinetic reaction rates can be calculated for comparison with results in section 6.1. The possible governing mechanism can then be discriminated.

and capture g^* is given as:

$$g^* = 0.27 \phi \left(\frac{p_{i0} - p_i}{p_{i0}} \right) \quad 6.51$$

Other model parameters are given as $\rho_p = 2.64$ gm/cc, $\epsilon = 0.58$, $R = 82.05$ cm³atm.g-mol⁻¹K⁻¹, 1.987 cal/gmol K, $p_{i0} = 100 \times 10^{-6}$ atm, k_0 and E are adjustable.

Equations 6.48 and Equation 6.49 are two simultaneous linear first order ODEs which can be solved numerically by the implicit trapezoidal computation scheme. The trapezoidal rule combines the inherent stability of the implicit schemes with the added advantage of a second order accuracy (Ferziger, 1981). The computation scheme is implemented in FORTRAN program MODEL.FOR and is included in Appendix C. Step by step computation is carried with the stop conditions set by the alkali dewpoint, the sampling point, complete alkali capture or maximum sorbent utilization.

6.3.2 Reproduction of Experimental Results

The first step is to use the model and the model parameters that were derived from the Na-SO₂ system to predict sodium capture in the same system. The purpose of this is to show that this model can be used to reproduce experimental results by adjusting the parameters k_0 , E and T_{dewpt} only. Close agreement is expected. It is also expected that some over prediction should be observed as we are using the initial kinetics that are linearly scaled with respect to alkali concentration, without taking into account the effect of the extent of sodium capture on local reaction rates. An improvement in this model would require the inclusion of some structural parameter term that changes with the extent of particle conversion. Parametric studies can, however, be carried for this system to investigate marginal effect of choice of such parameters as the activation energy, and the probable alkali dewpoint.

The simulation results for sodium capture profiles in an excess SO₂ environment using the already derived kinetic parameters is shown in Figures 6-5 and 6-6. Also shown in the same figures is the simulated temperature profile. In the simulation presented, sorbent particles are injected at Port 3 at a temperature of 1600 K. It is shown that 99% capture in under 1 second can be achieved by a kaolinite flowrate that is equal to an alkali to sorbent equivalence ratio of 0.1 to 0.25.

Figure 6-7 shows a comparative plot between the experimental results of capture response surface for sodium in excess SO₂ and the model predicted results. These plots show that what has been observed experimentally can be described mathematically, which was the purpose of our first task in modelling. Different capture characteristics can then be predicted in the same manner by adjusting the kinetic and dewpoint parameters.

Finally, Figure 6-8 shows model prediction results plotted against experimental results for sodium in excess SO₂ environment. Over prediction is shown which is consistent with what

Model parameters: $k_0 = 5.97 \times 10^7 \text{ cm}^3 \text{ gas/cm}^3 \text{ part.sec}$
 $E = 6 \text{ kcal/gmol}$
 Dewpoint = 1073 K
 Injection point, port 3, (30 cm)

Figure 6-5: Model prediction of percent alkali capture at various alkali/sorbent equivalence ratio plotted against furnace axial distance.

Figure 6-4: Flowfield (control volume) between section 1 and 2.

Combining Equation 6.44 and Equation 6.45 into Equation 6.43, the volumetric reaction rate in $\text{gmol Na/cm}^3 \text{gas} \cdot \text{sec}$, at any alkali concentration, p_i and any alkali/sorbent equivalence ratio is then given as:

$$R_v(\varphi, \theta) = \left(\frac{1}{0.27\varphi} \right) \left(\frac{p_{i0}}{R\theta} \right) \left(\frac{\varepsilon}{1-\varepsilon} \right) \left(\frac{31}{\rho_p} \right) \left(k_o e^{-\frac{E}{R\theta}} \right) \frac{p_i}{R\theta} \quad 6.46$$

It is noted that all terms in Equation 6.46 are known with the only adjustable parameters being the kinetic terms of k_o and E . Returning to the gas phase capture balance Equation 6.42 and with the dispersion term already dropped, the gas phase equation can be written as:

$$\frac{d}{dx}(UC) = - \left(\frac{1}{0.27\varphi} \right) \left(\frac{p_{i0}}{R\theta} \right) \left(\frac{\varepsilon}{1-\varepsilon} \right) \left(\frac{31}{\rho_p} \right) \left(k_o e^{-\frac{E}{R\theta}} \right) \frac{p_i}{R\theta} \quad 6.47$$

The auxiliary equations describing the local flue gas temperature, gas phase alkali concentration and velocity are:

$$\frac{d\theta}{dx} = -2.85 \times 10^{-3} \theta + 1.83 \text{ K/cm}$$

$$C_i = \frac{p_i}{R\theta} \quad 6.48$$

$$U = 0.12 \theta$$

Equation 6.47 and equation 6.48 combines to a single ODE of the form:

$$\frac{dp_i}{dx} = -\beta(p_{i0}, \varphi, k_o, E, \theta) p_i \quad 6.49$$

$$\beta = - \left(\frac{31}{0.12} \right) \left(\frac{1}{0.27\varphi} \right) \left(\frac{p_{i0}}{R\theta^2} \right) \left(\frac{\varepsilon}{1-\varepsilon} \right) \left(\frac{1}{\rho_p} \right) k_o e^{-\frac{E}{R\theta}}$$

The initial conditions at the point of injection x_o , are:

$$\begin{aligned} \theta(x_o) &= T \\ p_i(x_o) &= p_{i0} \end{aligned} \quad 6.50$$

The latter value of k_{int} is two orders of magnitude larger than that estimated from response surface experimental results. Consequently, film diffusion as a rate limiting step, is rejected. The same conclusion had been arrived at from the $1/d_p$ dependence of the experimental sorbent utilization results.

The conclusions from this Section are:

- The initial rate kinetics derived by response surface analysis are in close agreement with those estimated from coarse kaolinite experiments. These are two independent approaches that give the same result.
- The rate controlling step, for kaolinite particles of size range greater than $3.00\mu\text{m}$, is likely to be the intraphase diffusion. Kinetics is controlling for sizes under $3\mu\text{m}$.
- The apparent activation energy calculated is much lower than that of the bench scale studies of Punjak (1988). How realistic our present kinetics are will be investigated using the independent experimental data from the sodium only system. It is however evident that activation energies in the range of 5 to 20 kcal/gmol should give acceptable model results.
- Kinetic rates are correlated by a first order reaction with respect to sodium concentration in which $k_r = 4.5 \pm 0.5 \times 10^7 \exp(-5300 \pm 150 \text{ cal/RT}) \text{ cm}^3\text{gas/cm}^3 \text{ porous solid/sec}$.

6.3 MODEL FOR ALKALI CAPTURE IN A PLUG FLOW REACTOR

A general model for alkali metal capture in a plug flow reactor is to be developed. In the absence of any other kinetics, we will use the initial rate kinetics, scaled linearly with respect local alkali concentration. Since we are using initial rates to integrate throughout without taking into account that the actual rates would be lower as the remaining unreacted sorbent decreases, the model predicted alkali capture should naturally be expected to be higher than the experimental values. The model presented here would thus give an upper bound capture prediction for any given set of reaction kinetics. Apart from model development, this section addresses itself to three major areas:

First, the initial kinetics derived from the Na-SO₂ system are to be used in the present model to predict the *same* results. This is done to show that the experimentally observed phenomena can be predicted mathematically by simple choice of rate constant k_0 , activation energy E and the dewpoint T_{dwp} . Second, the model developed is to be used to predict the results of the Na-only system. This can be seen as testing the model and the kinetics from this work on independent set of data. The kinetics derived in the previous sections and the bench scale kinetics of Uberoi (1990) are compared in the same model to show that the former are superior. Finally, the effect of chlorine on sodium-metakaolinite reactions is addressed. Results of this work, that of Uberoi (1990) and that of Gallagher (1992) are compared to show that the active reactant is likely to be NaOH and not NaCl.

6.3.1 Development of Model Equations

In order to develop appropriate mathematical relationships amongst the system variables, consider a small flow field bounded by the wall of the reactor and cross sections 1 and 2 at a distance Δx apart (Figure 6-4). An Eulerian formulation of capture within this control volume will be considered.

The gas phase conservation of species can be written as:

$$UC|_x - D_p \frac{dC}{dx} \Big|_x = UC|_{x+\Delta x} - D_p \frac{dC}{dx} \Big|_{x+\Delta x} - R_v \Delta x \quad 6.42$$

$$\frac{d(UC)}{dx} - D_p \frac{d^2 C}{dx^2} - R_v = 0$$

U is the fluid velocity in cm/sec, D_p is the reactor dispersion term, which for a plug flow reactor, approaches zero. R_v is the reactor volumetric capture rate in gmol Na/ cm³ gas. sec. R_v can be formulated to account for the effect of particle loading in the control volume in consideration. For first order reactions, we can scale the initial reaction rates linearly with respect to the net alkali concentration after injection. Consequently, the simplified formulation of the volumetric rate is a product of rate per particle multiplied by the particle number density in the flowfield.

$$R_v = R'_p \left(\frac{\text{gmNa}_2\text{O}}{\text{particle} \cdot \text{sec}} \right) \cdot n \left(\frac{\# \text{ of particles}}{\text{cm}^3 \text{ gas}} \right) \quad 6.43$$

Reaction rate per particle at a local alkali concentration p_1 , and local flue gas temperature θ , was given earlier as:

$$R'_p = (k_0 \exp(-E/RT)) \cdot \left(\frac{\pi d_p^3 \epsilon}{6} \right) \cdot \left(\frac{p_1}{R\theta} \right) \quad 6.44$$

with k_0 , and E already been determined in Section 6.2. Any other values of k_0 and E that are similarly defined can be used. The number of particles per unit volume of flue gas was given as:

$$n \left(\frac{\# \text{ Particles}}{\text{cm}^3} \right) = \left(\frac{1}{0.27\phi} \right) \cdot \left(\frac{186}{\rho_p \pi d_p^3 (1-\epsilon)} \right) \cdot \left(\frac{p_{10}}{R\theta} \right) \quad 6.45$$

Figure 6-3: Normalized sorbent utilization for run 352 and 353, showing the point of inflection at 2.00 μm particle.

6.2.4 Kinetic Reaction Rate Parameters

The particle size for which both transport and kinetics are the same order of magnitude has been determined as 2.0 μ m. Runs 352 and 353 had sorbents injected at port 3, at a temperature of 1200°C (1500 K). The impactor derived gas phase sodium concentration was 70 ppm.

First, let us assume that the dominant transport controlling mechanism, for large particle size, is intraphase diffusion. The characteristic ratio of kinetics reaction rate and intraphase diffusion rate is the Thiele modulus. Thiele modulus, for a spherical reacting particle, assuming first order kinetics, is given as:

$$\phi = \frac{d_p}{6} \sqrt{\left(\frac{k_{int}(1-\epsilon)}{D_e} \right)} \quad 6.39$$

where k_{int} is the volume intrinsic reaction rate in cm³gas/cm³ solid.sec, ϵ is particle porosity and d_p is particle diameter in cm. The value of Thiele modulus for which both intrinsic rates and diffusion rates are same order of magnitude is suggested by Smith (1981) as 0.3. Substituting this in Equation 6.39, for a particle size of a 2.0 μ m, and an effective diffusivity of 0.052 cm²/s, the intrinsic reaction rate parameter is calculated as:

$$k_{int} = \left(\frac{0.09 \times 36 \times 0.052}{0.42 \times 4.0 \times 10^{-4}} \right) = 10.0 \times 10^6 \frac{\text{cm}^3 \text{gas}}{\text{cm}^3 \text{solid.sec}} \quad 6.40$$

which compares very well with the apparent volume rates (k_v) that were calculated from the response surface analysis shown in Figure 6-1 which at 1500 K is, $k_v = 8.00 \times 10^6$ cm³gas/cm³solid.sec.

Now, let us assume that the controlling transport mechanism for the large particle size is the interface film diffusion. The characteristic dimensionless ratio of film diffusion rate and kinetic rate is the Damkholer number given as:

$$Da = \frac{k_{int}(1-\epsilon)d_p}{6k_m} \quad 6.41$$

At point of inflection (2.00 μ m particle), the suggested Damkholer number at which transport rate is same order of magnitude as kinetic reaction rate is 0.1 (Smith, 1981). Substituting, with k_m from Equation 6.38, the intrinsic reaction rate parameter is:

$$k_{int} = 143.00 \times 10^6 \text{ cm}^3 \text{gas/cm}^3 \text{solid.sec}$$

Model parameters: $k_0 = 5.97 \times 10^7 \text{ cm}^3 \text{ gas/cm}^3 \text{ part.sec}$
 $E = 6 \text{ kcal/gmol}$
 Dewpoint = 1073 K
 Injection point, port 3, (30 cm)

Figure 6-6: Model prediction of un captured alkali concentration along the furnace for various alkali/sorbent equivalence ratio.

A: Experimental sodium capture by kaolinite in a flue gas containing SO₂

B: Model prediction with $k_0 = 5.97 \times 10^7 \text{ sec}^{-1}$, $E = 6.00 \text{ kcal/mol}$

Figure 6-7: Plots of experimental and model generated capture surfaces.

Model prediction using best fit kinetic parameters that have been derived from the same data.

$$k_p = 5.97 \times 10^7 \text{ cm}^3 \text{ gas/cm}^3 \text{ solid.sec}$$

$$E = 6 \text{ kcal/mol}$$

$$T_{dwp} = 1100 \text{ K}$$

Sodium (100 ppm), SO₂ (500 ppm)

Figure 6-8: Model prediction of water insoluble sodium capture plotted against experimental results. The kinetic parameters used in the model were derived from the same experimental data.

was expected. A dewpoint of 1100 K has been shown to give good model prediction results. This is in agreement with the experimentally estimated dewpoint for the Na-SO₂ system which was at 1123 K.

In conclusion, a model whose predictive results are consistent with experimentally observed phenomena has been developed. The next step is to test this model on independent experimental data from the Na-only system.

6.3.3 Model Prediction in Sodium Only Environment

We now investigate the use of the same model parameters on an independent environment. In our earlier arguments, the effect of SO₂ on sodium capture was attributed, to a large extent, on the changed dewpoint with the gaseous reactants remaining unchanged. Therefore, the model parameters can be applied to the sodium alone system by using the dewpoint temperature applicable to the sodium only environment (estimated at 973 K by extrapolating the continuous capture results of Section 5.2)

Figure 6-9 shows model prediction of sodium capture in sodium alone environments, using the kinetics from this work, plotted against experimental results. Also plotted in the same Figure is the model prediction results when the bench scale kinetics of Uberoi (1990) are used in the same model. In predictions, a dewpoint of 973 K was used in the calculations.

Good agreement between experimental results and model prediction is shown for our kinetics. No correlation, however, can be seen between experimental results and model prediction results that uses the bench scale kinetics. The results of this section confirm two things:

- (1) That the hypothesis that in both sodium alone and sodium with SO₂, capture reactions proceed as a gas solid reaction between sodium hydroxide and metakaolinite is plausible.
- (2) Bench scale kinetics of Uberoi (1990), in their present form, are unlikely to be useful in predicting alkali metal capture in a combustor.

6.3.4 Effect of Chlorine

We now address ourselves to the effect of chlorine on sodium-kaolinite reactions. Parametric studies in the previous section had shown that the presence of chlorine resulted in a reduction of sodium capture by as much as 30%. The purpose of this section is to reconcile our results with the bench scale results. The bench scale kinetics of Uberoi (1990) were obtained from an environment in which the alkali source was sodium chloride and we have shown that a discrepancy exist when the same bench kinetics are used in our model to predict experimentally observed results. Gallagher (1992) attempted to use the same kinetics to predict capture of sodium by kaolinite that is bound in coal ash and concluded that, in their present form, the bench scale kinetics were too slow to predict what was experimentally observed phenomena.

Kinetics from this work:

$$k_p = 5.97 \times 10^7 \text{ cm}^3 \text{ gas/cm}^3 \text{ porous solid.sec.}$$

$$E = 6 \text{ kcal/mol}$$

Bench Scale kinetics: uberoi (1990)

$$k_p = 1.92 \times 10^{10} \text{ cm}^3 \text{ gas/cm}^3 \text{ porous solid.sec}$$

$$E = 32 \text{ kcal/mol}$$

Figure 6-9: Model prediction of sodium capture in sodium only environment plotted against experimental results. Present kinetics is compared with the bench scale kinetics of Uberoi (1990).

The bench scale capture studies of Uberoi (1990) analyzed sodium capture results by proposing that sodium chloride reacts with metakaolinite to form nephelite as given in Equation 6.52

The simulated flue gas in the bench scale experiments was 80% N₂, 15% CO₂, 3% O₂, 2% H₂O, and between 50 and 500 ppm Na, at a temperature of 800°C. The kinetics of this reaction was then given as $k_p = 1.92 \times 10^{10} \text{ cm}^3 \text{ gas} / \text{cm}^3 \text{ solid} \cdot \text{sec}$ and $E = 32 \text{ kcal/mol}$. If indeed the above reaction proceeds through the hydroxide-metakaolinite reaction, then complete reaction mechanism can be written as:

Gallagher (1990) suggested that the rates that were calculated using Equation 6.52 could have been underestimated especially if the effect of water in the system was not accounted for. To account for NaCl-NaOH-H₂O equilibria, it was then proposed that the species of interest can be related by stoichiometry as follows.

$$[NaCl] = [Na] - [NaOH] \quad 6.55$$

$$[HCl] = [NaOH] \quad 6.56$$

$$[H_2O] = [H_2O]_0 - [NaOH] \approx [H_2O]_0 \quad 6.57$$

where $[Na]$ is total sodium concentration and $[H_2O]_0$ is the total water concentration which is much higher than other reactants' concentrations. These relationships can be used in an equation for the equilibrium coefficient K_{eq} .

$$K_{eq} = \frac{[NaOH][HCl]}{[NaCl][H_2O]} = \frac{[NaOH]^2}{([Na] - [NaOH]) \cdot [H_2O]_0} \quad 6.58$$

The concentration of NaOH can then be found explicitly.

$$[NaOH] = \frac{1}{2} \left(-K_{eq}[H_2O]_0 + \sqrt{(K_{eq}[H_2O]_0)^2 + 4K_{eq}[H_2O]_0[Na]} \right) \quad 6.59$$

The initial reaction rate given by Uberoi (1990) was calculated with respect to total sodium concentration [Na] and can now be transformed to a reaction rate with respect to NaOH concentration such that

$$\begin{aligned} \text{Rate} &= k[\text{Na}] = k'[\text{NaOH}] \\ k' &= \frac{k[\text{Na}] \text{ Bench scale}}{[\text{NaOH}]} \end{aligned} \quad 6.60$$

The transformed rates can be written as

$$k' = \frac{k [\text{Na}]}{\frac{1}{2}(-K_{eq}[\text{H}_2\text{O}]_o + \sqrt{(K_{eq}^2[\text{H}_2\text{O}]_o^2 + 4K_{eq}[\text{H}_2\text{O}]_o[\text{Na}]})} \quad 6.61$$

where k is the bench scale kinetics of Uberoi (1990). Since the NaOH concentration is much lower in the presence of chlorine, it can be seen that the transformed rates should be much higher than what was calculated in bench scale. Using the results of Equation 6.61, Gallagher calculated new modified intrinsic rates from the bench scale kinetics as given in Table 6-2.

Table 6-2 Sodium reaction rate calculations

Temp (K)	1023	1073	1148
ΔG°_f (kJ/gmol)	127.24	127.29	127.35
$\ln(K_{eq})$	-14.96	-14.27	-13.34
[Na] (ppmv)	55	127	482
[NaOH] (ppmv)	0.6	1.3	3.9
$\ln k$ (Bench scale)	16.13	16.86	17.84
$\ln k'$ (Transformed)	20.66	21.47	22.65

The bench scale kinetics of Uberoi (1990) were $k_o = 1.92 \times 10^{10} \text{ cm}^3\text{gas}/\text{cm}^3 \text{ solid}.\text{sec}$, $E=32 \text{ kcal/mol}$ and the transformed kinetics are $k_o = 2.43 \times 10^{13} \text{ cm}^3\text{gas}/\text{cm}^3 \text{ porous solid}.\text{sec}$, $E=37.5 \text{ kcal/mol}$.

Figure 6-10 shows results of model predicted sodium capture using the bench scale kinetics of Uberoi (1990) and the transformed kinetic data as suggested by Gallagher (1992), plotted against our experimental capture results that were obtained in a sodium alone environment. Good correlation is shown between experimental results and model predictions using the modified kinetics that have taken into account the effect of NaOH-NaCl-H₂O equilibria.

□ Uberoi (1990): Assumes NaCl as reactant

$$k_s = 1.92 \times 10^{10} \text{ cm}^3 \text{ gas/cm}^3 \text{ solid.sec}$$

$$E = 32 \text{ kcal/mol}$$

● Gallagher (1992): Assumes NaOH as reactant
(in equilibrium with NaCl)

$$k_s = 2.43 \times 10^{13} \text{ cm}^3 \text{ gas/cm}^3 \text{ solid.sec}$$

$$E = 37.5 \text{ kcal/mol}$$

Figure 6-10: Model prediction of sodium capture in a sodium only environment plotted against experimental results. Kinetic parameters from Uberoi (1990) and Gallagher (1992) are compared.

As already had been observed, no correlation is shown between experimental data and model prediction that uses the bench scale kinetics.

We conclude that sodium capture proceeds via the NaOH-metakaolinite reaction. The presence of chlorine results in a significant reduction of sodium that exists as sodium hydroxide hence reducing the concentration of the reactant species.

6.3.5 This Work in Perspective

The capture reaction model presented in this section can be used to reproduce experimentally observed phenomena. It has been applied successfully as a predictive model to carry out parametric studies on the effect of k_0 , E and the dewpoint on overall capture. It has also been used to address whether it is NaOH or NaCl that participates in sodium metakaolinite capture reaction. The bench scale kinetics of Uberoi (1990) which appear extremely slow, give model prediction results that correlate well with experimental data, but only after they have been transformed to account for the NaCl-NaOH-H₂O equilibria. This work has shown conclusively that in all the three cases considered, sodium alone, sodium with chlorine and sodium with SO₂, it is the gas phase sodium hydroxide that probably reacts with metakaolinite to form nephelite.

The fast reaction rates and intrinsic kinetic parameters that have been extracted in this work need to be considered in perspective with those of previous workers. First, there is no doubt that significant alkali capture was recorded. EDX analysis results (Appendix E) independently confirmed the results of the AA analysis and hence the order of magnitude of water insoluble sodium content. The sorbent residence time scales were of the order of 1-2 seconds and so the reaction rates calculated are reasonable. Second, the kinetic parameters that were extracted from sodium with excess SO₂ runs were applied in our model to predict the results of sodium capture in sodium alone runs with very good results achieved. It is thus clear that both the reaction rates and the kinetic parameters extracted are realistic. The apparent activation energy that fits our experimental results, however are much lower than previously reported. By varying both the pre-exponential factor, k_0 and the apparent activation energy, E , we have shown that good agreement between model prediction and experimental data can still be achieved upto $E=10$ kcal/mol. Activation energy of 20 kcal/mol however, does give poor prediction of alkali capture. The transformed bench scale kinetic parameters with an activation energy of 37 kcal/mol show good prediction results but only in a narrow temperature range between 1000°C - 1100°C. Figure 6-11 shows that the transformed kinetics tend to over predict at high temperatures and under predicts at low temperatures. Our kinetics predict experimental data with the same consistency across the temperature range. Given that bench scale kinetics were obtained from single temperature experiments, while our present kinetics have been obtained from a wide temperature range, we believe that the kinetics derived in this work best describes mechanisms that govern alkali capture in a combustor.

Model prediction using:

Left : Kinetics of Uberoi (1990) as modified by Gallagher (1992)

Right: Kinetics from this work

Figure 6-11: Percent deviation between model predicted capture and experimental capture, plotted against sorbent injection temperature. Kinetic parameters from this work gives better prediction at all temperatures.

7.0 CONCLUSIONS

An experimental method was developed for studying gas-solid reactions in a laboratory downflow combustor in the time and temperature regimes similar to that ordinarily found in industrial scale boilers. The method utilized variable sorbent injection points together with response surface experimentation techniques and least square regression to derive continuous sodium capture functional relationships. Unique to this work is the simplifications and approach that exploit the one dimensionality of our system to extract realistic initial rate kinetics for comparison with the bench scale kinetics.

Alkali capture by chemical reaction between gas phase alkali species and kaolinite prior to the onset of condensation, has been investigated and reported. Parametric studies, theoretical equilibria calculations, time-temperature experimentation together with statistical regression techniques have been combined to extract the governing mechanisms of capture.

Kaolinite is effective in capturing alkali species in an in-situ application through chemical reaction between alkali hydroxide and metakaolinite. The capture reaction is given as:

Reaction 7.1 was found to correlate best as a first order reaction with respect to sodium concentration. The kinetics of this reaction was further investigated in an environment that approaches excess sodium over kaolinite. It is only under such an environment that the effect of particle-particle interactions can be eliminated and the apparent intrinsic rates inferred. Rate of sodium capture in gm Na₂O/gm sorbent.sec is best given by;

$$\frac{d[\text{Na}_2\text{O}]}{dt} = 31 k_v \cdot V_p \cdot C_{\text{Na}} \quad 7.2$$

where

[Na₂O] is in gm Na₂O per gm sorbent

$k_v = 4.5 \pm 0.5 \times 10^7 \exp(-5300 \pm 150(\text{cal/mol})/RT) \text{ cm}^3\text{gas}/\text{cm}^3\text{solid}.\text{sec}$

V_p = Sorbent pore volume in cm³/gm sorbent.

C_{Na} = Sodium concentration in gmol Na/ cm³ gas.

Implicit in equation 7.2 is that all the pore volume is accessible to the reactant gaseous sodium species.

The optimum sorbent injection window was found to be in the range of 900°C - 1100°C. We link this optima to the onset of condensation on one hand, and to the transformations of metakaolinite at high temperatures to form stable mullite structures with the subsequent release of silicon species, on the other hand. The latter, free silica, reacts with sodium hydroxide to form amorphous, water soluble, low melt temperature sodium silicates which result in significant melt of the capture products. These silicates can also contribute significantly to the formation of

hard bonded deposits on heat transfer surfaces. We have reported in this work what appeared as significant sorbent melt at temperatures above 1200°C.

Besides the kinetics, species present and water content in flue gas, the alkali dewpoint has been shown to be the most important parameter to be considered in an *in situ* sorbent application.

Sulfur reduces sorbent effectiveness through the raised dewpoint of the sulfate condensate with the consequent reduction in the gas phase residence time scale available for gas solid reactions.

Chlorine, depending on flue gas water content, reduces sorbent effectiveness by 30%. This result was found to be consistent throughout the injection temperature range considered in this work. Modeling results have shown that this phenomena can be accounted for exclusively by thermodynamic equilibria considerations.

The capture phenomena is kinetically controlled when using kaolinite under 3.00 μm particle diameter. Intraphase diffusion has been shown to be the rate controlling mechanism for particles larger than 3 μm . Therefore, sorbent utilization scales as $1/d_p$ for larger particles above 3.00 μm . A sorbent utilization of 50%, based on the formation of nephelite, was the maximum recorded. It is, however, recommended that 30% to 40% utilization should be considered typical and realistic for design purposes.

A sodium to sorbent equivalence ratio of 0.1-0.25 has been found to be effective in scavenging 99% and above of the sodium in the flue gas in under 1 second. The reported sodium to sorbent ratio corresponds to a sorbent flowrate in the range of 35 gm to 14 gm of sorbent per unit gram of Na_2O . In high sodium coal, where typically Na_2O is 10% by weight of the coal ash, a sorbent feed rate that matches the ash content would suffice.

7.1 FUTURE WORK

The low apparent activation energies recorded in this work may require that more fundamental bench scale studies on the sorption-desorption kinetics of capture at a wide temperature range be carried so as to reconcile present results with bench scale studies. The effect of water concentration in the overall capture reaction need to be investigated further. Model predictions show that flue gas water content is important. This was not investigated in this work, instead all our runs had a water concentration between 15 to 20 % vol. High concentration of water may have accounted for our fast reaction rates. The effect of flue gas stoichiometry was not investigated in this work. It is recommended that future work should look into this. The results of coarse particle experiments can be modelled further to extract, in detail, the fundamental governing mechanisms.

REFERENCES

- Benson, S. A., E. N. Steadman, M. L. Jones and D. P. Kalmanovitch, "In Situ Determination of Temperature Distributions in Ash Deposits in a Pilot Scale Furnace". Engineering Foundation Conference on Mineral Matter and Ash Deposition from Coal, Santa Barbara, California February 22-28, p423-434., 1988.
- Bird, R. B., W. E. Stewart and E. N. Lightfoot, Transport Phenomena. NY, John Wiley & Sons. (1960)
- Bish, D. L. and R. B. Von Dreele., "Structure of Kaolinite; Rietveld Refinement of Non-Hydrogen Atomic Positions in Kaolinite", *Clays & Clay Minerals.*, 37(4): 289-296, (1989)
- Borgwart, R. H., G. R. Gillis and N. F. Roache, "IERL-RTP Research on Sulphur Capture in LIMB", Paper presented at The Joint EPA/EPRI Symposium on Stationary Combustion NOx Control, Dallas, November 3, 1982.
- Borgwart, R.H., "Sintering of Nascent Calcium Oxide", *Chemical Engineering Science*, 44 (1), pp 53-60 (1989)
- Box, G. E. P., Empirical Model Building and Response Surfaces. N.Y., J. Wiley (1987)
- Brindley, G. W. and M. Nakahira, "The Kaolinite-Mullite Reaction Series: II, Metakaolin", *J. American Ceramic Soc.* 42(7): 314-318 (1959a)
- Brindley, G. W. and M. Nakahira, "The Kaolinite-Mullite Reaction series: III, The High Temperature phases", *J. American Ceramic Soc.* 42(7): 319-324 (1959b)
- Bulens, M., A. Leonard and B. Delmon, "Spectroscopic Investigation of Kaolinite-Mullite Reaction Sequence", *J. American Ceramic Soc.* 61(1-2): 81-90 (1978).
- Burch, T. E.; R. B. Conway and W. Y. Chen, "A Practical Pulverized Coal Feeder for Bench Scale Combustion Requiring Low Feed Rates", *Rev. Sci. Instrum.* . 62(2): 480-483 (1990).
- Burgess Pigment Company, Ga. "Burgess kaolin clay-technical specifications", Ga. (1991).
- Chakravorty, A. K., "Interpretation On the Changes of Co-ordination Number of Al in Thermal Changes of Kaolinite", *Clay Sci.* 8: 45-57 (1991)
- Dow Chemical Company. (1971). IANAF Tables of Thermochemical Data.
- Durie, R. A., J. W. Milne and M. Y. Smith, "The Deposition of Salts from Hydrocarbon Flames Containing Sodium and Sulfur Species", *Combust. Flame* 30(3): 221-230 (1977)

EEUA. (1963). Pneumatic Handling of Powdered Materials. EEUA Handbook No. 15. London., Constable and Co.

Gibb, W.H., Angus, J.G., "The Release of Potassium from Coal During Bomb Combustion", J. Inst. of Energy, 36 (428), 149-157 (1983)

Ferziger, J. H., Numerical Methods for Engineering Application. NY, J. Wiley & Sons (1981).

Gallagher, N. B., Alkali Metal Partitioning in a Pulverized Coal Combustion Environment., PhD Dissertation, University of Arizona, Tucson, 1992.

Greenberg, M. D., Fundamentals of Applied Mathematics. Prentice-Hall, N.J. (1978)

Glass, J. W., Fuel Nitrogen Conversion During Fuel Rich Combustion of Pulverized Coal and Char., PhD Dissertation, University of Arizona, Tucson, 1981.

Gluskoter, H.J., "An Introduction to The Occurrence of Mineral Matter in Coal", Ash Deposits and Corrosion Due To Impurities in Combustion Gases., Proceedings of the International Conference on Ash Deposits and Corrosion From Impurities in Combustion Gases, Henniker, NH, June 26 - July, 1. Eds Bryers R.W., (1977)

Goldstein, J. I. and D. E. Newbury., Scanning Electron Microscopy and X-Ray Micro Analysis. N.Y, Plenum Press (1981).

Gordon, S. and B. J. McBride., Computer Program for the Calculation of Complex Chemical Equilibrium Compositions. Rocket Performance. Incident and Reflected Shocks. and Chapman-Jouguet Detonations., NASA SP-273, NASA Scientific and Technical Office, Washington, D.C., 1976.

Hamor, R. J. and I. W. Smith., "Fluidizing Feeders for Providing Fine Particles at Low Stable Flows", Fuel. 50: 394 (1971).

Hansen, P.F.B, Sulfur Capture in Fluidized Bed Combustors, PhD dissertation, department of Chemical engineering, Technical University of Denmark, Lyngby, 1991.

Haynes, B.S., M. Neville, R.J. Quann, A.F. Sarofim., "Factors Governing the Surface Enrichment of Fly Ash in Volatile Trace Species", Journal of Colloid and Interface Science, 87(1) 266-278 (1982)

Hicks, R. C., Fundamental Concepts in the Design of Experiments. NY, Holt, Rinehart and Winston, 1982.

Huffman, G. P., F. E. Huggins, N. Shah and A. Shah, "Behaviour of Basic Elements During Coal Combustion", Prog. Energy Combust. Sci. 16: 243-251 (1990)

Hupa, M., B. J. Skrivars and A. Moilanen. "Measuring the Ash Sintering Tendency by a Laboratory Method", Paper presented at Engineering Foundation Conference on Mineral Matter and Deposition From Coal, Santa Barbara, p103-115, August 1988.

Kalmanovitch, D. P. and F. Melvin, "An Effective Model of Viscosity for Ash Deposition Phenomena", Paper presented at Engineering Foundation Conference on Mineral Matter and Ash Deposition From Coal, Santa Barbara, California, 89-101, 1988.

Kramlich, J. C., J. A. Cole and W. R. Seeker, "The High Temperature Calcination and Sulphation of Sorbents for Sulfur Dioxide Control", SPO Peer Review, EER Corporation, March 1983.

Lee, S. H. D. and R. F. Henry, "Alkali Metal Vapor Removal From Pressurised Fluidised Bed Combustor Flue Gas", Argonne National Laboratory Report No: ANL/FE-84-18, 1985.

Lee, S. H. D. and W. M. Swift, "A Fixed Granular-Bed Sorber for Measurement and Control of Alkali Vapors in PFBC", ASME J., Fossil Fuel Combustion, p 1095-1103 (1991).

Levenspiel, O., Chemical Reaction Engineering, NY, John Wiley & Sons (1972)

Levin, E. M., C. R. Robbins and H. F. McMurdie., Phase Diagrams for Ceramists, American Ceramic Society, 1964.

Linak, W.P.; J.O.L. Wendt, "Toxic Metal Emissions From Incineration: Mechanisms and Control", Progress in Energy and Combustion Science, In
Lindner, B.; "Comparison of Structural Models for Gas-Solid Reactions in Porous Solids Undergoing Structural Changes", Chemical Engineering Science, 36(9): 1519-1527 (1981)

Lindner, E. R., A. Kosminski and R. G. Williams, "Effects of Additives on Fouling Behavior Characteristics of South Australian Brown Coals", Paper presented at Engineering Foundation Conference on Mineral Matter and Ash Deposition From Coal., Santa Barbara, California, p331-345, August 1988.

Logan, R. G. and G. R. Richards, "A Study of Techniques for Reducing Ash Deposition in Coal-Fired Gas Turbines", Prog. Energy Combust. Sci. 16: 221-233 (1990).

Lowell, E. C. and D. L. Deadmore., "The Kinetics of High Velocity High Temperature Corrosion of U-700", Paper presented at The Electrochemical Society Conference on Corrosion in Fossil Fuel Systems, Detroit, MI, p 365-394, 1982.

Lumley, J. L. and H. Tennekes., A First Course in Turbulence. Cambridge, MA, The MIT Press., 1972.

Luthra, K. L. and H. S. Spacil., "Impurity Deposits in Gas Turbines from Fuels Containing Sodium and Vanadium", J. Electrochem. Soc. 129(March): 649-656 (1982a)

Luthra, L. K. and H. O. LeBlanc, "Reducing High Alkali Vapor Activities in Coal-Fired Combined-Cycle Systems by Adsorption", Paper presented at The Electrochemical Society Conference on Corrosion in Fossil Fuel Systems, Detroit, MI, p 101-110, 1982.

Mereb, J.B. and Wendt, J.O.L., "Reburning Mechanisms in a Pulverized Coal Combustor", Paper presented at The Twenty-Third Symposium (International) on Coal Combustion-The Combustion Institute, Orleans, France, July 1990.

Mitchell, S.M., H.J. Gluskoter., "Minerology of Ash of Some American Coals: Variations with Temperature and Source", *Fuel.*, 55 (1976)

Nelson, W. and E. S. Lisle., *J. Inst. Fuel.* 38: 179 (1965)

Neter, J., Applied Linear Regression Models., R.D. Irwin, 1983.

Neter, J. and W. Wasserman., Applied Linear Statistical Models., London., R.D. Irwin, 1974.

Neville, M., A.F. Sarofim., "The Fate of Sodium During Pulverized Coal Combustion", *Fuel*, 64 384-390 (1985).

Newman, A.C.D., Chemistry of Clays and Clay Minerals., Min. Soc. Mon. No: 6, J. Wiley, NY, (1987).

Perry, J.H., Chemical Engineer's Handbook., Mc Graw-Hill Book Company, 5 th edition, NY, 1973.

Plogmann, H., M. T. Mackowsky, " Analysis of Mineral Matter in Coals of Ruhr Under Gasification Conditions", Ash deposits and Corrosion Due To Impurities in Combustion Gases., Proceedings of the International conference on Ash Deposits and Corrosion From Impurities in Combustion Gases, Henniker, NH, June 26 - July, 1 Eds Bryers R.W., 1977.

Punjak, W.A., High Temperature Interactions of Alkali Vapours with Solids During Coal Combustion and Gasification., Ph.D Dissertation, University of Arizona, Tucson, 1988.

Raask, E., Mineral Impurities in Coal Combustion: Behavior, Problems, and Remedial Measures. N.Y, Hemisphere Publishing Corporation, 1985.

Raask, E., "The Mode of Occurrence and Concentration of Trace Elements in Coal", *Prog. Energy Combust. Sci.*, 11, 97-118 (1985b)

Ranade, P. V. and D. P. Harrison, "The Grain Model Applied to Porous Solids with Varying Structural Properties", *Chemical Engineering Science*, 34(3-5): 427-432 (1979).

Reid, T. W., External Corrosion and Deposits. Fuel and Energy Science Series. N.Y, Elsevier (1971)

Rizeq, G.R., Alkali Induced Agglomeration of Aluminosilicate Particles During Coal Combustion and gassification, Ph.D Dissertation, University of Arizona, Tucson, 1990.

Romans, D. E., A. W. Scaroni and B. G. Miller., "Evaluation of Sorbents for Capturing SO₂ in Fluidised Bed Combustion Systems", ASME J., Fossil Fuel Combustion, 33: 93-100 (1991)

Rosner, D. E. and B. Liang., "Laboratory Studies of the Deposition of Alkali Sulphate Vapors from Combustion Gases Using Flash Evaporation Technique", Chemical Engineering Communications 42: 171-196 (1986)

Rosner, D. E. and R. Nagarajan., "Transport-Induced Shifts in Condensate Dew-Point and Composition in Multicomponent Systems with Chemical Reaction", CES 40(2): 177-186 (1985)

Saxena, S.C., R.F. Henry, W.F. Podolski., "Particulate Removal from High Temperature, High Pressure Combustion Gases", Prog. Energy Combust. Sci. 11,193-251 (1985)

Scandrett, L. A. and R. Clift., "The Thermodynamics of Alkali Removal from Coal Derived Gases", J. Inst. Energy 57(433): 391-397 (1984).

Scotto, M. V., Mechanisms Governing the Abatement of Metal Emissions from Waste Incineration, Ph.D Dissertation, University of Arizona, Tucson, 1992.

Smith, J. M., Chemical Engineering Kinetics. Chemical Engineering Series. N.Y., McGraw Hill, 1981.

Sondreal, E. A., G. H. Gronhovd, P. H. Tuft and W. Beckering., "Ash Fouling Studies of Low Rank Western U.S. Coals", Paper presented at The Conference on Ash Deposits and Corrosion from Impurities in Coal Combustion, Henniker, NH. Hemisphere Publishing Co, Ed Bryers, R.W., 1977.

Spiro, C.L., J. Wong, F.W. Lytle, R.B. Greigor, D.H. Maylotte, S.H. Lamson., "Forms of Potassium and Its Combustion Products", Fuel., 65 327-336, 1986.

Spiro, C. L., C. C. Chen, G. S. Kimura, R. G. Lavigne and P. W. Schields, "Deposit Remediation in Coal-Fired Gas Turbines Through the Use of Additives", Prog. Energy Combust. Sci. 16: 213-220 (1990).

SPSS-X, 2nd ed., Mc Graw Hill, New York, NY, (1986)

Srinivasachar, J., J. Helble, D. O. Ham and G. Domazetis, "A Kinetic Description of Vapor Phase Alkali Transformations in Combustion Systems", Prog. Energy Combust. Sci. 16: 303-309 (1990).

Steinberg, M. and K. Schofield., "The Chemistry of Sodium With Sulfur in Flames", Prog. Energy Combust. Sci. 16: 311-317 (1990).

Szekely, J. and J. W. Evans., "A Structural Model for Gas-Solid Reactions With Moving Boundary", *Chemical Engineering Science* 25: 1091-1107 (1970).

Szekely, J. and M. Propster., "A Structural Model for Gas Solid Reactions With a Moving Boundary-VI ; The Effect of Grain Size Distribution on the Conversion of Porous Solids", *Chemical Engineering Science* 30: 1049-1055 (1975).

Toole-O'Neal, B., "Furnace Sorbent Injection", *J. Air Waste Man. Assoc.* 40(12): 1716-1718 (1990)

Tsuzuki, Y. and K. Nagasawa., "A Transitional Stage to The 980° C Exotherm of Kaolin Minerals", *Clay Science.* 3(5): 87-102 (1969)

Uberoi, M., W. A. Punjak and F. Shadman., "The Kinetics and Mechanisms of Alkali Removal from Flue Gases by Solid Sorbents", *Prog. Energy Combust. Sci.* 16: 205-211 (1990)

Uberoi, M. and F. Shadman., "Simultaneous Condensation and Reaction of Metal Compound Vapors in Porous Solids", *Ind. Eng. Chem. Res.* 30(No.4): 624-631 (1991).

Villa, L. T., O. D. Quiroga and G. V. Morales., "The Shrinking Core Model for Non-Catalytic Gas-Solid Reactions With Arbitrary Order With Respect to The Gaseous Reactant and General Boundary Conditions", *Trans IChemE.* 70(Part A): 276-281 (1992)

Wall, T.F., A. Lowe, L.J. Wibberley, I.M. Stewart., "Mineral Matter in Coal and The Thermal Performance of Large Boilers", *Prog. Energy Combust. Sci.*, 5, 1-29, 1979.

Wall, T. F. and R. L. Lindner., "Sodium Ash Reactions During Combustion of Pulverised Coal", Paper presented at The Twenty-Third Symposium (International) on Coal Combustion-The Combustion Institute, Orleans, France, July 1990, p1313-1321.

Weintraub, M., S. Goldberg and A. A. Orning., "A Study of Sulfur Reactions in Furnace Deposits", *Trans. ASME.* (October, 1961): 444-450 (1961).

Wendt, J. O. L., T. W. Peterson, E. A. Basham and M. V. Scotto., "Quench-Induced Nucleation of Ash Constituents During Combustion of Pulverized Coal in a Laboratory Furnace", Paper presented at The Twenty-Second Symposium (International) on Coal Combustion-The Combustion Institute. p239-247 (1988)

West, W. E. and J. W. Westwater., "Radiation-Conduction Correction for Temperature Measurements in Hot Gases", *Ind. Eng. Chem.* 45, 1953.

White, J. W., Parameter Estimation Through Nonlinear Regression., Software manual, Department of Chemical Engineering, University of Arizona, 1976.

Wibberley, L. J. and T. F. Wall., "Alkali-Ash Reactions and Deposit Formation in Pulverised-Coal-Fired Boilers: The Thermodynamic Aspects Involving Silica, Sodium, Sulphur and Chlorine", *Fuel*. 61: 87-92 (1982)

Wilhelm, E., The Physical Chemistry of Silicates. Chicago, University of Chicago Press, 1954.

Woodcock, C.R.; P.O. Mwabe., "An Approach to The Computer-Aided Design of Dilute Phase pneumatic Conveying Systems", *Proc. Pneumatech 2 Conf.*, Canterbury, UK, September, 1984.

Wu, B., Private Communication, Department of Chemical Engineering, University of Arizona, Tucson, 1993.

Zakkay, V., E.A.M. Gbordzoe, R. Radhakrishnan, K.M. Sellakumar, J. Patel, R. Kasinathan., "Particulate and Alkali Capture from PFBC Flue Gas Utilizing Granular Bed Filter (GBF)", *Combust. Sci. and Tech.* 68,113-130 (1989)

APPENDIX

A: DATA FOR PLOTS USED IN TEXT

TABLE A 2-1: Sample input data for CET89 simulation of potassium, kaolinite and chlorine in flue gas environment.

REACTANTS

H	2.0000	O	1.0000		.0000	.0000	.0000	.003100	M	L	700.000	F
C	1.0000	H	4.0000		.0000	.0000	.0000	.895000	M	G	700.000	F
C	2.0000	H	6.0000		.0000	.0000	.0000	.081100	M	G	700.000	F
C	3.0000	H	8.0000		.0000	.0000	.0000	.033900	M	G	700.000	F
N	1.5618	O	0.4196	C	.0030	.0000	.0000	1.000000	M	G	700.000	O
CL	2.0000		0.0000		.0000	.0000	.0000	.000020	M	G	700.000	O
AL	2.0000	O	3.0000		.0000	.0000	.0000	.001000	M	S	700.000	F
SI	1.0000	O	2.0000		.0000	.0000	.0000	.002000	M	S	700.000	F
K	1.0000		0.0000		.0000	.0000	.0000	.000200	M	S	700.000	O

NAMELISTS

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&INPT2 KASE=1, TP=T, T=800,900,1000,1100,1200,1300,1400,1500,
TRACE=1.0E-08,PSIA=F, ERATIO=T, MIX=0.8333, HP=F, TRNSPT =F,
/&END
```

APPENDIX A --continued

Table A 2-2: Species considered in the equilibrium simulation for potassium

SPECIES BEING CONSIDERED IN THE POTASSIUM SYSTEM									
J 6/62 K	J 3/66 KCN	J 3/63 KH	J12/67 KO	J12/70 KOH	J12/79 ALN(S)	J12/79 AL2O3(A)	J12/79 AL2O3(L)	J 9/67 AL2SiO5(AN)	BAR 73 AL2Si2O7 (S)
J12/61 K2	K11/77 K2CO3	J 3/66 K2C2N2	K11/77 K2O	J12/70 K2O2H2	J 9/67 AL6Si2O13(S)	J12/61 K(S)J12/61	K(L)		
J 6/77 OH	J 3/77 O2	J 6/61 O3	J 3/67 SI	J 3/67 SIC	BAR 73 KALSi3O8(S)	J 3/66 KCN(S)	J 3/66 KCN(L)	J12/70 KOH(A)	J12/70 KOH(B)
J 3/67 SIC2	J12/60 SIC4H12	J12/76 SIH	RUS 79 SIH2	RUS 79 SIH3	J12/70 KOH(L)	J 6/71 KO2(S)	BAR 77 K2AL2Si2O 8(S)	J 3/66 K2CO3(S)	J 3/66 K2CO3(L)
J 6/76 SIH4	J 3/67 SIN	J 9/67 SIO	J 9/67 SIO2	J 3/67 SI2	J 6/63 K2O(S)	J 9/63 K2O2(S)	BAR 77 K2SiO3(S)	BAR 77 K2SiO3(L)	BAR 77 K2Si4O9(1)
J 3/67 SI2C	J 3/67 SI2N	J 3/67 SI3	J 6/79 AL(S)	J 6/79 AL(L)	BAR 77 K2Si4O9(2)	BAR 77 K2Si4O9(L)	J 3/67 SI(S)	J 3/67 SI(L)	J 3/67 SIC(B)
J 6/67 SIO2(LQZ)	J 6/67 SIO2(H QZ)	J 6/67 SIO2(CR)	J 6/67 SIO2(L)	L 1/84 SI2N2O(S)	J 3/67 SI3N4(A)				

APPENDIX A --continued

Table A 2-3 : Species considered in the equilibrium simulation for sodium

SPECIES BEING CONSIDERED IN THE SODIUM SYSTEM									
J3/66 NACN	J 3/63 NAH	J12/67 NAO	J12/70 NAOH	J 6/62 NA2	J 3/63 NAALO2(B)	J 3/66 NACN(S)	J 3/66 NACN(L)	J12/70 NAOH(A)	J12/70 NAOH(L)
J3/66 NA2C2N2	K10/74 NA2O	J12/70 NA2O2H2	J 3/77 O	J 6/77 OH	J 6/63 NAO2(S)	BAR 77 NA2AL2S I4O12(S)	BAR 77 NA2AL2S I6O16(1)	BAR 77 NA2AL2S I6O16(2)	J 3/66 NA2CO3(1)
J 3/77 O2	J 6/61 O3	J 3/67 SI	J 3/67 SIC	J 3/67 SIC2	J 3/66 NA2CO3(2)	J 3/66 NA2CO3(L)	J 6/68 NA2O(C)	J 6/68 NA2O(A)	J 6/68 NA2O(L)
J12/60 SIC4H12	J12/76 SIH	RUS 79 SIH2	RUS 79 SIH3	J 6/76 SIH4	J 6/68 NA2O2(A)	J 6/68 NA2O2(B)	BAR 73 NA2SIO3(S)	BAR 73 NA2SIO3(L)	BAR77 NA2SIO5(1)
J 3/67 SIN	J 9/67 SIO	J 9/67 SIO2	J 3/67 SI2	J 3/67 SI2C	BAR77 NA2SIO2 5(2)	BAR77 NA2SIO2 5(3)	BAR77 NA2SIO2 5(L)	BAR 77 NA4SIO4(S)	BAR 77 NA4SIO4(L)
J 3/67 SI2N	J 3/67 SI3	J 6/79 AL(S)	J 6/79 AL(L)	J12/79 ALN(S)	BAR 73 NA6SIO2 7(S)	J 3/67 SI(S)	J 3/67 SI(L)	J 3/67 SIC(B)	J 6/67 SIO2(LQZ)
J12/79 AL2O3(A)	J12/79 AL2O3(L)	J 9/67 AL2SIO5(AN)	BAR 73 AL2SIO7(S)	J 9/67 AL6SIO2O13(S)	J 6/67 SIO2(HQZ)	J 6/67 SIO2(HC R)	J 6/67 SIO2(L)	L 1/84 SI2N2O(S)	J 3/67 SI3N4(A)
L 3/81 H2O(S)	J 3/79 H2O(L)	J 6/62 NA(S)	J 6/62 NA(L)	J 3/63 NAALO2(A)					

APPENDIX A -continued

TABLE A 2-4 Percent equilibrium distribution of potassium in an excess O₂ flue gas(SR=1.2) containing potassium, kaolinite and chlorine. (CET89)

T, DEG K	K	KCL	KOH	KCL(S)	K ₂ OAL ₂ SI ₂ O ₅ (S) (Kaliophilite)	K ₂ CO ₃ (S)	K ₂ SI ₄ O ₉ (c)
800	0.00	0.12	0.00	19.83	76.58	3.47	0.00
900	0.00	4.37	0.11	13.55	78.48	3.50	0.00
1000	0.00	17.25	3.40	0.00	79.12	0.22	0.00
1100	0.00	19.28	3.72	0.00	76.99	0.00	0.00
1200	0.00	19.15	4.22	0.00	76.63	0.00	0.00
1300	0.00	18.25	5.19	0.00	76.56	0.00	0.00
1400	0.02	19.22	30.43	0.00	24.13	0.00	26.21
1500	0.09	19.04	55.35	0.00	0.00	0.00	25.52

APPENDIX A —continued

Table A 2-5: Percent equilibrium distribution of potassium in an excess O₂ flue gas (SR=1.2) containing potassium, kaolinite and SO₂. (CET89)

T(K)	KOH	K ₂ SO ₄	K ₂ Al ₂ Si ₂ O ₈ (S) (Kaliophilite)	K ₂ SO ₄ (A/B)	K ₂ O4SiO ₂ (c)
1500	56.75	1.69	0	0	41.42
1400	20.83	5.46	61.48	0	12.2
1300	2.99	4.28	85.88	6.48	0
1200	0.19	0.44	55.65	43.71	0
1100	0.02	0.03	39.98	59.96	0
1000	0	0	39.05	60.94	0
900	0	0	39.02	60.97	0
800	0	0	39.02	60.97	0

Table A 2-6 Saturated vapor pressure of alkali condensates

	Temperature (C)			
Sat vap(ppm)	Na ₂ CO ₃	K ₂ CO ₃	Na ₂ SO ₄	K ₂ SO ₄
50	881	775	1105	1046
100	911	800	1133	1077
200	944	827	1162	1107
300	964	844	1178	1126
400	979	856	1187	1135
500	990	866	1193	1141

APPENDIX A —continued

Table A 4-1: Temperature profile for run 26 before and after experimentation

Port	Position (cm)	T(C) before experiments	T(C) after 8 hours.
1	0		
2	29.69	1298	1298
3	56.99	1183	1264
4	87.16	1143	1176
4b	114.46	1060	1086
4c	148.12	990	944
5	199.23	963	990
6	234.79	933	955
7	265.27	893	931
8	293.75	853	901
9	326.23		
10	356.71		
11	387.71	740	780
12	417.67		
13	448.15	652	674
14	478.63		

#083	Stage #	Lower cut off d ₅₀ (microns)	Upper cut off d ₅₀ (microns)	Acid dissolved samples (mass ppm in 30 ml fluid)	
				K	Na
9	AF	0.29	0.29	34.58	16.96
8		0.29	0.44	106.85	66.40
7		0.44	0.74	11.55	7.37
6		0.74	1.42	1.66	0.85
5		1.42	2.22	1.01	0.60
4		2.22	3.17	0.55	0.43
3		3.17	3.91	0.48	0.42
2		3.91	6.07	0.45	0.39
1		>6.07	50.00	0.93	0.55

Table A 4-3: AA raw data for sample 083

Stage #	Lower cut off d ₅₀ (microns)	Upper cut off d ₅₀ (microns)	Acid dissolved samples (mass ppm in 30 ml fluid)	
			K	Na
9	AF	0.29	145.85	72.10
8		0.44	8.88	4.88
7		0.74	1.76	0.90
6		1.42	2.85	1.43
5		2.22	1.61	0.85
4		3.17	1.05	0.64
3		3.91	0.94	0.58
2		6.07	0.89	0.60
1		>6.07	50.00	0.59

Table A 4-2: AA raw data for sample 082

APPENDIX A--continued

APPENDIX A --continued

Table A 4-4: AA raw results for sample no 244 (sodium only case)

Sample #244	Lower Cut off d_m (microns)	Upper Cut off d_m (microns)	Acid dissolve samples (mass ppm in 30 ml fluid)			Water dissolved samples (mass ppm in 30 ml fluid)		
			Al	Si	Na	Al	Si	Na
9	AF	0.43	0.30	0.80	0.27	0.10	0.00	0.25
8	0.43	0.65	1.40	2.30	0.64	0.10	0.50	0.39
7	0.65	1.10	8.20	11.90	4.20	0.00	0.35	1.20
6	1.10	2.10	21.10	26.20	9.22	0.10	0.50	1.85
5	2.10	3.30	21.00	26.30	5.44	0.10	0.40	1.11
4	3.30	4.70	6.40	8.50	1.05	0.00	0.00	0.34
3	4.70	5.80	6.00	7.70	0.83	0.10	0.15	0.29
2	5.80	9.00	7.00	10.80	1.19	0.10	0.30	0.25
1	>9.00	50.00	18.40	23.00	5.19	0.00	0.20	0.61

APPENDIX A --continued

Table A 4-5: AA raw results for sample no 303 (sodium with excess chlorine case)

Sample # 303	Lower Cut off d_{50} (microns)	Upper Cut off d_{50} (microns)	Acid dissolved samples (mass ppm in 30 ml fluid)			Water dissolved samples (mass ppm in 30 ml fluid)		
			Al	Si	Na	Al	Si	Na
9	AF	0.43	0.30	0.50	11.06	0.00	0.00	11.06
8	0.43	0.65	1.15	2.90	1.57	0.10	0.30	1.50
7	0.65	1.10	8.90	12.00	2.80	0.40	0.82	1.11
6	1.10	2.10	30.15	27.00	5.30	0.60	0.62	1.34
5	2.10	3.30	8.80	12.55	1.75	0.40	0.63	0.66
4	3.30	4.70	2.60	4.70	0.76	0.10	0.18	0.38
3	4.70	5.80	1.00	2.00	0.39	0.10	0.06	0.30
2	5.80	9.00	3.65	4.80	1.04	0.40	0.38	0.54
1	>9	50.00	30.90	40.00	9.36	3.40	2.80	3.34

APPENDIX A --continued

Table A 4-6: AA raw data for sample no: 174 (sodium with excess sulfur case)

Sample # 174	Lower Cut off d_{50} (microns)	Upper Cut off d_{50} (microns)	Acid dissolved samples (mass ppm in 30 ml fluid)			Water dissolved samples (mass ppm in 30 ml fluid)		
			Al	Si	Na	Al	Si	Na
9	AF	0.43	0.90	1.20	7.38	0.00	0.00	7.38
8	0.43	0.65	6.00	7.80	4.24	0.30	1.00	3.22
7	0.65	1.10	22.20	26.60	4.74	0.60	3.50	1.79
6	1.10	2.10	35.40	42.70	6.23	0.40	1.20	2.13
5	2.10	3.30	22.40	27.80	3.15	0.40	0.90	0.99
4	3.30	4.70	17.00	21.50	2.31	0.00	0.60	0.82
3	4.70	5.80	9.80	12.30	1.30	0.00	0.10	0.55
2	5.80	9.00	14.00	17.60	1.63	0.10	0.30	0.54
1	>9	50.00	41.00	53.00	7.64	0.20	1.20	2.12

APPENDIX A -continued

Table A 4-7: AA raw data for sample no: 154 (sodium alone, low temperature injection)

Sample #154	Lower Cut off d_m (microns)	Upper Cut off d_m (microns)	Acid dissolved samples (mass ppm in 30 ml fluid)			Water dissolved samples (mass ppm in 30 ml fluid)		
			Al	Si	Na	Al	Si	Na
9	AF	0.43	0.40	0.90	2.07	0.00	0.00	2.07
8	0.43	0.65	7.10	9.00	2.59	0.40	0.80	0.79
7	0.65	1.10	20.60	26.20	5.25	0.20	1.20	1.98
6	1.10	2.10	25.70	31.40	7.10	0.10	2.30	1.80
5	2.10	3.30	12.90	16.70	3.81	0.00	1.00	0.97
4	3.30	4.70	5.00	6.60	2.42	1.00	1.50	1.19
3	4.70	5.80	2.00	3.30	1.76	0.15	1.00	0.45
2	5.80	9.00	2.80	5.20	1.96	0.30	0.50	0.65
1	>9	50.00	22.80	41.70	7.56	0.10	0.45	0.89

APPENDIX A—continued

Table A 4-8: Effect of potassium on sodium capture

Sample #	Log. Temp(°C)	K/Na mean	K/Na modal(ss)
091	1160	1.695	1.88
092	1160	1.762	1.49
093	1160	2.2087	2.11
094	1160	2.4105	4.12
096	1160	1.667	1.304
131	850	0.5	0.717
132	850	1.05	0.9
133	980	1.55	1.201
134	980	1.19	1.409

APPENDIX A --continued

Table A 4-9: AA Raw data for sample no: 351

Sample #351	Lower Cut off d ₅₀ (microns)	Upper Cut off d ₅₀ (microns)	Acid dissolved samples (mass ppm in 30 ml fluid)			Water dissolved samples (mass ppm in 30 ml fluid)		
			Al	Si	Na	Al	Si	Na
9	AF	0.43	0.20	0.40	0.06	0.00	0.00	0.06
8	0.43	0.65	2.70	3.40	0.71	0.20	0.00	0.25
7	0.65	1.10	25.20	32.10	5.11	0.00	0.80	0.68
6	1.10	2.10	79.80	98.90	15.50	0.00	2.70	2.98
5	2.10	3.30	67.20	86.60	10.38	0.30	0.40	1.61
4	3.30	4.70	49.30	63.40	6.05	0.00	0.80	1.11
3	4.70	5.80	39.40	51.22	4.39	0.40	0.60	0.81
2	5.80	9.00	54.80	69.50	4.98	0.10	0.60	0.98
1	9.00	10.00	109.60	138.10	5.99	0.10	0.30	1.10
Cup	> 10	100	611.5	831.50	37.34	0.00	0.20	1.10

APPENDIX A --continued

Table A 4-10: Summary results of sample no: 351

Sample #351	Ratio of Insoluble alkali to Kaolinite		Ratio of soluble alkali to Kaolinite			Stage by stage mass partition (Fraction of total mass in each stage)		
	Na2O(i)	Total mass fraction	Na2O(s)	Total mass fraction	Al ₂ O ₃ /SiO ₂	Al2O3	SiO2	Na2O(t)
dp								
10	0.0166	0.0164	0.0005	0.0005	0.6483	0.3867	0.5965	0.0168
9.00	0.0131	0.0129	0.0029	0.0029	0.6996	0.4051	0.5791	0.0158
5.80	0.0214	0.0208	0.0052	0.0051	0.6950	0.3994	0.5747	0.0259
4.70	0.0262	0.0254	0.0059	0.0057	0.6781	0.3915	0.5774	0.0311
3.30	0.0291	0.0281	0.0065	0.0063	0.6854	0.3927	0.5729	0.0344
2.10	0.0378	0.0362	0.0069	0.0066	0.6840	0.3888	0.5684	0.0429
1.10	0.0465	0.0440	0.0111	0.0105	0.7112	0.3930	0.5525	0.0545
0.65	0.0513	0.0484	0.0079	0.0074	0.6920	0.3861	0.5580	0.0559
0.43	0.0501	0.0465	0.0272	0.0253	0.7000	0.3822	0.5460	0.0717
0.00	0.0000	0.0000	0.0655	0.0615	0.4407	0.2871	0.6514	0.0615

APPENDIX A --continued

Table A 4-11: AA raw data for sample no: 352

Sample #352	Lower Cut off d_{50} (microns)	Upper Cut off d_{50} (microns)	Samples dissolved in Acid (mass ppm in 30 ml fluid)			Samples dissolved in water (mass ppm in 30 ml fluid)		
			Al	Si	Na	Al	Si	Na
9	AF	0.43	0.20	0.20	0.09	0.00	0.00	0.09
8	0.43	0.65	0.20	0.20	0.16	0.00	0.70	0.10
7	0.65	1.10	6.30	7.80	2.26	0.00	1.10	0.29
6	1.10	2.10	31.90	39.70	10.08	0.00	1.30	1.07
5	2.10	3.30	30.10	37.30	6.77	0.00	1.20	0.61
4	3.30	4.70	24.00	29.60	4.17	0.00	0.20	0.72
3	4.70	5.80	15.60	19.20	1.95	0.00	0.30	0.33
2	5.80	9.00	29.30	36.40	2.70	0.00	0.45	0.36
1	9.00	10.00	80.60	99.50	3.77	0.10	0.20	0.38
Cup	> 10	100	190.9	228.30	10.75	0.00	0.36	0.38

APPENDIX --continued

Table A 4-12: Summary results for sample no: 352

Sample # 352	Ratio of Insoluble alkali to Kaolinite		Ratio of soluble alkali to Kaolinite			Stage by stage mass partition		
dp	Na2O(i)	Total mass fraction	Na2O(s)	Total mass fraction	Al2O3/SiO2	Al2O3	SiO2	Na2O(total)
10	0.0164	0.0162	0.0006	0.0006	0.7371	0.4172	0.5660	0.0168
9.00	0.0125	0.0123	0.0014	0.0014	0.7140	0.4109	0.5754	0.0137
5.80	0.0237	0.0230	0.0036	0.0035	0.7095	0.4040	0.5694	0.0266
4.70	0.0309	0.0298	0.0063	0.0061	0.7162	0.4023	0.5618	0.0359
3.30	0.0428	0.0407	0.0089	0.0085	0.7147	0.3963	0.5545	0.0491
2.10	0.0607	0.0569	0.0060	0.0056	0.7113	0.3897	0.5478	0.0625
1.10	0.0836	0.0764	0.0099	0.0091	0.7083	0.3792	0.5353	0.0855
0.65	0.0928	0.0839	0.0137	0.0123	0.7120	0.3759	0.5279	0.0962

APPENDIX A --continued

Table A 4-13: AA raw data for sample no: 353

Sample #353	Lower Cut off d ₅₀ (microns)	Upper Cut off d ₅₀ (microns)	Acid dissolved samples (mass ppm in 30 ml fluid)			Water dissolved samples (mass ppm in 30 ml fluid)		
			Al	Si	Na	Al	Si	Na
9	AF	0.43	0.10	0.20	0.30	0.00	0.00	0.30
8	0.43	0.65	0.10	0.70	0.95	0.01	0.00	0.92
7	0.65	1.10	3.90	4.80	1.90	0.00	0.00	0.57
6	1.10	2.10	15.40	18.60	5.99	0.00	0.50	1.00
5	2.10	3.30	24.00	28.70	6.99	0.01	1.10	0.96
4	3.30	4.70	18.70	23.70	3.95	0.00	0.00	0.58
3	4.70	5.80	10.60	13.80	1.47	0.00	0.00	0.43
2	5.80	9.00	20.50	27.00	2.11	0.00	0.00	0.34
1	9.00	10.00	60.80	80.00	3.20	0.10	0.50	0.43
Cup	> 10	100	168.2	192.70	12.19	0.00	0.50	0.50

APPENDIX A --continued

Table A 4-14: Summary results for sample no: 353

Sample # 353	Ratio of Insoluble alkali to Kaolinite		Ratio of soluble alkali to Kaolinite			Stage by stage mass partition		
	Na2O(i)	Total mass fraction	Na2O(s)	Mass fraction	Al2O3/SiO2	Al2O3	SiO2	Na2O(t)
10	0.0216	0.0211	0.0009	0.0009	0.7694	0.4253	0.5527	0.0220
9.00	0.0130	0.0128	0.0020	0.0020	0.6699	0.3952	0.5899	0.0148
5.80	0.0247	0.0240	0.0047	0.0046	0.6693	0.3895	0.5819	0.0286
4.70	0.0283	0.0272	0.0117	0.0112	0.6771	0.3882	0.5734	0.0384
3.30	0.0527	0.0497	0.0091	0.0085	0.6955	0.3863	0.5554	0.0582
2.10	0.0761	0.0699	0.0121	0.0111	0.7371	0.3899	0.5290	0.0810
1.10	0.0975	0.0873	0.0195	0.0175	0.7298	0.3777	0.5175	0.1048
0.65	0.1016	0.0887	0.0435	0.0380	0.7162	0.3644	0.5089	0.1267

APPENDIX A --continued

Table A 4-15: AA raw data for sample no: 362

#362	Lower Cut off d_{50} (microns)	Upper Cut off d_{50} (microns)	Acid dissolved samples (mass ppm in 30 ml fluid)			Water dissolved samples (mass ppm in 30 ml fluid)		
			Al	Si	Na	Al	Si	Na
9	AF	0.43	0.50	1.50	0.56	0.00	0.00	0.54
8	0.43	0.65	4.10	6.30	1.38	0.00	0.00	0.72
7	0.65	1.10	28.00	38.00	6.08	0.00	0.00	1.45
6	1.10	2.10	34.00	45.00	6.74	0.00	0.00	1.50
5	2.10	3.30	29.20	38.60	4.99	0.00	0.00	1.27
4	3.30	4.70	16.90	24.50	2.68	0.00	0.00	0.66
3	4.70	5.80	7.40	11.40	0.94	0.00	0.00	0.37
2	5.80	9.00	12.20	19.30	1.24	0.00	0.00	0.43
1	9.00	10.00	35.80	51.70	1.40	0.10	0.20	0.37
Cup	> 10	100	76.8	94.10	2.39	0.00	0.20	0.80

APPENDIX A --continued

Table A 4-16: AA raw results for sample no:363

#363	Lower Cut off d ₅₀ (microns)	Upper Cut off d ₅₀ (microns)	Sampled dissolved in Acid (mass ppm in 30 ml fluid)			Samples dissolved in Water (mass ppm in 30 ml fluid)		
			Al	Si	Na	Al	Si	Na
9	AF	0.43	2.80	3.90	0.76	0.00	0.00	0.76
8	0.43	0.65	10.40	13.60	1.52	0.00	0.00	0.57
7	0.65	1.10	34.00	43.90	4.44	0.00	0.00	1.08
6	1.10	2.10	53.70	70.20	6.82	0.00	0.00	1.53
5	2.10	3.30	36.20	46.70	3.69	0.00	0.00	1.13
4	3.30	4.70	24.60	32.60	2.24	0.00	0.00	0.74
3	4.70	5.80	15.80	22.20	1.10	0.00	0.00	0.41
2	5.80	9.00	40.00	52.80	1.60	0.00	0.00	0.45
1	9.00	10.00	215.00	275.00	5.17	0.10	0.20	0.52
Cup	> 10	100	307.7	372.90	8.68	0.00	0.20	0.80

APPENDIX A --continued

Table A 5-1: Response surface results for sodium alone

Sodium capture by Kaolinite: Na Acetate only runs										
Run No	Injection Temp(C)	Sample Temp(C)	ER(φ)	Sample Qty(mg)	Flow Rate (gm/min)	Total alkali capture.		Water insoluble capture		
						%Na st1-7	%Na (ins)	Impactor Av (gm/gm)	St 6 modal (gm/gm)	Regr. (gm/gm)
111	1284	639	1.978	8.3	371	31.9	13.0	0.072	0.11	0.1095
112	1284	682	0.8943	19.9	371	83.6	44.7	0.1117	0.11	0.1151
113	1284	803	0.5675	34.8	371	85.8	61.1	0.0969	0.14	0.0998
114	1284	803	0.5024	47.0	371	86.6	76.8	0.0812	0.12	0.0909
116	1284	916	0.4448	21.7	371	84.8	62.7	0.0779	0.10	0.0814
121	1043	639	0.2151	58.0	448	89.0	62.9	0.0378	0.03	0.0464
122	1043	682	0.1634	69.3	448	90.2	65.1	0.0297	0.03	0.0342
123	835	639	0.3114	42.7	448	77.6	52.1	0.0453	0.04	0.0496
124	835	639	0.1626	50.5	448	72.2	33.4	0.0173	0.01	0.0253
151	988	695	0.2033	42.1	480	91.7	65.9	0.0374	0.06	0.0433
152	1125	695	0.6377	14.4	480	89.1	60.8	0.1082	0.12	0.1064
153	895	695	0.3892	21.0	480	84.8	70.2	0.0763	0.07	0.0667
154	842	695	0.3230	31.9	480	89.0	70.2	0.0633	0.06	0.0521

APPENDIX A --continued

Table A 5-2: Response surface results for sodium alone

Sodium capture by Kaolinite: Na Acetate runs										
Run No	Injection Temp(C)	Sample Temp(C)	ER	Sample Qty(mg)	Flow Rt (gm/min)	Total alkali capt.		Water insoluble capt		
						%Na at 1-7	%Na(inc)	Impactor (gm/gm)	St 6 modal (gm/gm)	Regr. (gm/gm)
241	991	728	0.0868	41.6	474	79.3	53.0	0.0128	0.01	0.0149
242	1112	728	0.1086	62.3	474	93.2	64.4	0.0195	0.03	0.0163
243	1112	728	0.1441	63.5	474	94.7	76.6	0.0303	0.04	0.0263
244	1244	728	0.3320	26.6	474	97.2	77.9	0.0722	0.10	0.0625
245	1244	728	0.3170	20.9	474	97.1	79.2	0.0701	0.09	0.0592
271	1236	728	0.5576	23.5	474	94.6	69.5	0.1082	0.16	0.0984
272	1236	728	0.5070	27.9	474	98.5	50.0	0.0707	0.09	0.0922
341	1023	600	0.1484	20.0	474	99.6	82.7	0.0343	0.04	0.0307
342	1023	600	0.1444	18.9	474	99.0	87.9	0.0354	0.04	0.0297
343	878	600	0.0922	25.0	474	95.5	84.3	0.0217	0.02	0.0148
344	878	600	0.0965	66.9	474	97.9	89.0	0.0240	0.02	0.0157
345	825	600	0.0931	31.8	474	92.6	86.1	0.0220	0.02	0.0115
346	825	728	0.0904	25.7	474	90.6	82.9	0.0209	0.02	0.0110

APPENDIX A --continued

Table A 5-3: Response surface results for sodium with excess chlorine

Sodium capture by Kaolinite in the presence of excess chlorine: Na ~250 ppm, Cl ₂ ~700 ppm.										
Run No	Injection Temp(C)	Sample Temp(C)	ER(φ)	Sample Qty(mg)	Flow Rt (gm/min)	Total alkali capt.		Water insoluble capt		
						%Na at1-7	%Na(inc) at1-7	Impactor (gm/gm)	St 6 modal (gm/gm)	Regr. (gm/gm)
201	980	728	0.1918	39.1	474	90.3	74.6	0.0400	0.05	0.0345
202	980	728	0.0760	137.1	474	89.2	71.2	0.0151	0.02	0.0227
203	1123	728	0.1143	56.1	474	91.9	70.6	0.0226	0.03	0.0257
204	1123	728	0.2674	25.7	474	85.9	54.0	0.0403	0.06	0.0425
205	1202	728	0.2469	21.3	474	91.8	65.5	0.0451	0.06	0.0394
206	1202	728	0.2210	28.8	474	92.7	68.3	0.0422	0.04	0.0365
207	1278	728	0.1955	24.3	474	82.0	55.5	0.0303	0.04	0.0314
208	1278	728	0.4454	14.3	474	65.2	42.9	0.0533	0.11	0.0588
231	933	728	0.1471	94.5	474	90.9	76.2	0.0313	0.03	0.0296
232	1148	720	0.0841	150.6	474	93.0	70.1	0.0218	0.03	0.0215
233	1211	720	0.1559	68.9	474	93.4	70.4	0.0307	0.04	0.0287
234	1012	720	0.1075	99.2	474	89.4	78.2	0.0235	0.03	0.0261
221	1211	720	0.3897	29.6	474	71.1	46.3	0.0504	0.06	0.0540

APPENDIX A --continued

Table A 5-4: Response surface results for sodium with excess chlorine

Sodium capture by Kaolinite in the presence of excess chlorine: Na ~250 ppm, Cl ₂ ~700 ppm.										
Run No	Injection Temp(C)	Sample Temp(C)	ER(φ)	Sample Qty(mg)	Flow Rt (gm/min)	Total alkali capt.		Water insoluble capt		
						%Na st1-7	%Na(inc) st1-7	Inspector (gm/gm)	St 6 model (gm/gm)	Regr. (gm/gm)
301	1349	679	3.1740	9.1	474	27.9	11.8	0.1044	0.12	0.0968
302	1349	679	1.5150	10.7	474	40.0	21.3	0.0900	0.11	0.0968
303	1196	679	0.3682	24.7	474	75.1	48.4	0.0498	0.06	0.0521
304	1196	679	0.2914	34.0	474	60.1	31.0	0.0489	0.08	0.0443
305	947	679	0.2302	18.3	474	89.0	62.9	0.0405	0.05	0.0376
306	947	679	0.2014	22.5	474	84.9	60.5	0.0340	0.04	0.0350
291	1236	724	0.3753	35.5	474	93.2	78.5	0.0522	0.09	0.0524
292	1236	724	0.4137	33.8	474	94.6	74.5	0.0561	0.12	0.0562
321	1000	690	0.2185	24.9	474	70.1	56.0	0.0342	0.04	0.0373
322	1000	690	0.2355	25.3	474	84.3	79.2	0.0521	0.06	0.03893
323	1000	690	0.1789	61.9	474	86.0	76.0	0.0380	0.04	0.0310
324	1230	690	0.5006	6.8	474	67.6	57.3	0.0801	0.09	0.0640
325	1230	690	0.4595	7.9	474	69.7	61.6	0.0670	0.09	0.0604

APPENDIX A --continued

Table A 5-5: Response surface results for sodium with excess chlorine

Sodium capture by Kaolinite in the presence of excess chlorine: Na ~250 ppm, Cl ₂ ~700 ppm.										
Run No	Injection Temp(C)	Sample Temp(C)	ER(φ)	Sample Qty(mg)	Flow Rt (gm/min)	Total alkali capt.		Water insoluble capt		
						%Na at 1-7	%Na(ins) at 1-7	Impactor (gm/gm)	St 6 modal (gm/gm)	Regr. (gm/gm)
326	910	690	0.3145	8.0	474	65.8	56.1	0.0493	0.05	0.0436
327	910	690	0.2465	16.5	474	73.4	67.7	0.0466	0.04	0.0382
331	850	690	0.3144	158.0	474	63.3	57.5	0.0505	0.05	0.0419
332	850	690	0.3952	7.0	474	63.5	42.9	0.0474	0.06	0.0462
333	940	690	0.5764	4.6	474	50.9	26.6	0.0428	0.07	0.0591
334	940	690	0.7146	3.6	474	48.9	24.0	0.0479	0.07	0.0628
335	1130	690	0.2608	649.7	474	90.9	64.9	0.0472	0.04	0.0434
336	1130	690	0.7456	3.6	474	48.2	37.3	0.0776	0.06	0.0766

APPENDIX A –continued

Table A 5-6: Response surface results for sodium with excess SO₂

Sodium capture by Kaolinite in the presence of excess SO ₂ : Na ~250 ppm, SO ₂ ~700 ppm; SR=1.2										
Run No	Injection Temp(C)	Sample Temp(C)	ER(φ)	Sample Qty(mg)	Flow Rt (gm/min)	Total alkali capt.		Water insoluble capt		
						%Na at 1-7	%Na(ina)	Impactor Av. (gm/gm)	St 6 modal (gm/gm)	Regr. (gm/gm)
161	865	689	0.6157	18.9	475	32.4	10.4	0.018	0.0091	0.0149
162	921	689	0.1472	62.5	475	43.4	19.8	0.0082	0.0031	0.0171
163	1016	689	0.1240	21.6	475	63.8	36.0	0.0125	0.0130	0.0229
164	1152	689	0.2059	25.1	475	79.6	51.0	0.0293	0.0480	0.0364
165	1228	689	0.2149	31.9	475	84.0	56.6	0.034	0.0484	0.0377
166	1301	689	0.2285	48.5	475	89.8	65.1	0.0415	0.0686	0.0377
171	1281	747	0.2636	54.9	475	81.9	52.5	0.0386	0.1100	0.0438

APPENDIX A --continued

Table A 5-7: Response surface results for sodium with excess SO₂

Sodium capture by Kaolinite in the presence of excess SO ₂ : Na ~250 ppm, SO ₂ ~700 ppm; SR = 1.2										
Run No	Injection Temp(C)	Sample Temp(C)	ER(φ)	Sample Qty(mg)	Flow Rt (gm/min)	Total alkali capt.		Water insoluble capt		
						%Na at 1-7	%Na(ina)	Impactor Av. (gm/gm)	St 6 modal (gm/gm)	Regr. (gm/gm)
172	1228	747	0.2424	44.8	475	82.6	53.6	0.0363	0.0677	0.0416
173	1174	747	0.2116	52.4	475	81.1	63.2	0.0374	0.0382	0.0374
174	1014	747	0.2196	48.9	475	77.3	54.6	0.0335	0.0349	0.0307
175	910	747	0.1490	98.1	475	78.5	54.9	0.0229	0.0146	0.016
251	1187	670	0.6314	31.7	475	92.8	49.4	0.0871	0.1297	0.0802
252	1187	670	0.6088	8.7	475	84.3	37.3	0.0634	0.0764	0.0785
253	1187	670	0.1838	36.8	475	91.5	59.5	0.0305	0.0419	0.0338
254	1187	670	0.1601	43.1	475	95.7	74.7	0.0334	0.0403	0.0306

APPENDIX A --continued

Table A 5-8: Response surface results for sodium with excess SO₂

Sodium capture by Kaolinite in the presence of excess SO ₂ : Na ~250 ppm, SO ₂ ~700 ppm; SR=1.2										
Run No	Injection Temp(C)	Sample Temp(C)	ER(φ)	Sample Qty (mg)	Flow Rt (gm/min)	Total alkali capt.		Water insoluble capt		
						%Na at 1-7	%Na(ins)	Impactor Av. (gm/gm)	St 6 modal (gm/gm)	Regr. (gm/gm)
255	1187	689	0.3478	17.6	475	95.0	57.8	0.0562	0.0594	0.0539
256	1187	689	0.1496	70.1	475	98.7	73.3	0.0306	0.0395	0.0292
261	1298	740	0.3038	18.2	475	94.1	51.5	0.0437	0.0595	0.0496
262	1298	740	0.3658	18.1	475	98.0	57.8	0.0591	0.0797	0.0587
263	1298	740	0.1750	59.1	475	99.1	69.2	0.0338	0.0544	0.029
264	1073	740	0.2126	26.6	475	95.8	75.4	0.0448	0.0374	0.0342
265	1073	740	0.1005	67.9	475	96.1	81.0	0.0227	0.0275	0.0228
266	1167	740	0.1133	52.3	475	93.8	68.5	0.0217	0.0384	0.0245
267	1167	740	0.1235	67.4	475	95.3	74.3	0.0256	0.0233	0.0262
315	1061	694	0.1513	23.8	475	84.7	79.8	0.0337	0.0374	0.0277
316	1216	694	0.2054	17.9	475	88.8	85.7	0.0491	0.0578	0.0365

APPENDIX A --continued

Table A 5-9: Response surface results for sodium with excess SO₂

Sodium capture by Kaolinite in the presence of excess SO ₂ : Na ~250 ppm, SO ₂ ~700 ppm; SR = 1.2										
Run No	Injection Temp(C)	Sample Temp(C)	ER(φ)	Sample Qty(mg)	Flow Rt (gm/min)	Total alkali capt.		Water insoluble capt		
						%Na st1-7	%Na(ina)	Impactor Av. (gm/gm)	St 6 modal (gm/gm)	Regr. (gm/gm)
311	1165	689	0.2907	12.4	475	74.9	41.5	0.0337	0.0341	0.0330
312	1165	689	0.3762	7.8	475	88.5	68.5	0.0719	0.0798	0.0768
313	1165	689	0.2940	11.0	475	86.5	51.8	0.0425	0.0441	0.0465
314	1061	689	0.1255	25.7	475	81.3	57.8	0.0203	0.0221	0.0210
317	1216	689	0.2048	18.1	475	88.1	77.6	0.0444	0.0544	0.0466
318	1216	689	0.1841	41.4	475	92.1	79.7	0.0410	0.0481	0.0405
281	1236	725	0.8633	19.2	475	94.1	50.8	0.1066	0.1200	0.1034
282	1236	725	0.5550	21.1	475	96.3	68.8	0.0815	0.1000	0.0786
283	910	725	0.9010	6.8	475	27.9	20.1	0.0197	0.0200	0.0218

APPENDIX A —continued

Table A 6-1: Experimental and best fit Intrinsic rates

Temp(K)	kintr(expt)	k _o for E=6,10,20	Best fit of intrinsic rates at different activation energies.		
			E=6 kcal	E=10 kcal	E=20 kcal
850	4063400	59718000	4010200	3167800	1281100
875	4338600	2.80e+08	4253100	3492600	1557200
900	4612600	1.00e+10	4499500	3834700	1877200
925	4884200		4193900	2245300	2139000
950	5151700		4569900	2666000	2539700
975	5413700		4962600	3143800	2994900
1000	5668300		5371700	3683300	3508900
1025	5914000		5796700	4289200	4086100
1050	6148900		6237400	4966100	4730900
1075	6371100		6693300	5718600	5447800
1100	6578600		7164200	6551400	6241200
1125	6769600		7649500	7469100	7115400
1150	6941700		8149000	8476100	8074800
1175	7093000		8662100	9577100	9123600
1200	7221100		9188500	10776000	10266000

APPENDIX A —continued

Table A 6-2: Experimental and model prediction results for sodium with excess SO₂ case

Temp (T/1273)	ER (φ)	Experimental (gm/gm)	Model prediction at a dewpoint of 1123 K (gm/gm)	Model prediction at a dewpoint of 1073 K (gm/gm)
0.8934	0.616	0.018	0.0063	0.0242
0.9378	0.147	0.0082	0.0196	0.0275
1.0126	0.124	0.0125	0.0276	0.0302
1.1175	0.206	0.0293	0.0458	0.0487
1.1759	0.215	0.034	0.05	0.0523
1.2358	0.229	0.0415	0.0546	0.0566
1.2193	0.264	0.0386	0.0594	0.0622
1.1759	0.242	0.0363	0.0542	0.0571
1.1352	0.212	0.0374	0.0476	0.0504
1.0097	0.22	0.0335	0.0367	0.0431
0.928	0.149	0.0229	0.0173	0.0262
1.1461	0.631	0.0871	0.0788	0.0888
1.1175	0.609	0.0634	0.0729	0.0833
1.1461	0.184	0.0305	0.0437	0.0457
1.1461	0.15	0.0306	0.0374	0.0386
1.1461	0.16	0.0334	0.0395	0.0409
1.1461	0.348	0.0562	0.0634	0.0692
1.1683	0.205	0.0491	0.0482	0.0504

APPENDIX A —continued

Table A 6-3: Comparative results of model predictions of water insoluble capture, using present kinetics, kinetics of Uberoi (1990) and equilibrium modified kinetics.

Injection Temp (C)	ϕ	Experimental	This work E=6000	Uberoi (1990)	Gallagher(1992)	% dev Gallagher	%dev This work
1279	1	0.112	0.1301	0.0028	0.1346	20.179	16.161
1279	0.894	0.1117	0.1298	0.0028	0.1355	21.307	16.204
1279	0.568	0.0969	0.1078	0.0028	0.1306	34.778	11.249
1279	0.502	0.081	0.1013	0.0028	0.1301	60.617	25.062
1279	0.448	0.0779	0.095	0.0028	0.1196	53.53	21.951
1042	0.215	0.0378	0.0513	0.0006	0.0439	16.138	35.714
1042	0.163	0.0297	0.0415	0.0006	0.0372	25.253	39.731
834	0.311	0.0453	0.0393	0.0001	0.0066	-85.43	-13.245
834	0.163	0.0173	0.0308	0.0001	0.0064	-63.006	78.035
987	0.203	0.0374	0.0472	0.0004	0.0317	-15.241	26.203
1123	0.638	0.1082	0.0991	0.0011	0.1076	-0.55453	-8.4104
893	0.389	0.0763	0.0538	0.0001	0.0148	-80.603	-29.489
840	0.323	0.0633	0.0408	0.0001	0.0072	-88.626	-35.545
991	0.087	0.0128	0.0232	0.0004	0.0205	60.156	81.25

APPENDIX A -continued

Table A 6-4: Comparative results of model predictions of water insoluble capture, using present kinetics, kinetics of Uberoi (1990) and equilibrium modified kinetics.

Injection Temp (C)	φ	Experimental	This work E=6000	Uberoi (1990)	Gallagher (1992)	% dev Gallagher	% dev This work
1111	0.109	0.0195	0.0291	0.001	0.0292	49.744	49.231
1111	0.144	0.0303	0.038	0.001	0.0381	25.743	25.413
1244	0.332	0.0722	0.0773	0.0023	0.0889	23.13	7.0637
1234	0.558	0.1082	0.1037	0.0022	0.1302	20.333	-4.159
1234	0.507	0.0707	0.0989	0.0022	0.1293	82.885	39.887
1244	0.317	0.0701	0.0749	0.0023	0.085	21.255	6.8474
1023	0.148	0.0343	0.038	0.0005	0.0328	-4.3732	10.787
1073	0.144	0.0354	0.0371	0.0005	0.0322	-9.0395	4.8023
870	0.092	0.0217	0.0232	0.0001	0.0093	-57.143	6.9124
870	0.097	0.024	0.024	0.0001	0.0094	-60.833	0
821	0.093	0.0224	0.0214	0.0001	0.005	-77.679	-4.4643
821	0.09	0.0209	0.021	0.0001	0.005	-76.077	0.47847
998	0.9	0.094	0.0891	0.0004	0.0475	-49.468	-5.2128
973	0.85	0.09	0.083	0.0003	0.0374	-58.444	-7.7778

APPENDIX B: SAMPLE RUN SHEET, AA ANALYSIS PROCEDURES, ACCURACY AND ERROR ANALYSIS

SAMPLE RUN SHEET

PARTICLE SAMPLING CONDITIONS

RUN NO: 15 **DATE:** 28-4-92 **ADDITIVES:** Na Acetate, 0.2 M soln, 20 cc/min.

Purpose: Inject sorbents at ports 4, 4c, 5 and 6. Sample at port 11

	Gauge setting	Actual (CFM)	Density (gm/ltr)	Standard. lt/min	mass flowrate gm/min
Nat. gas	50	1.25	0.728	32.6	23.73
Primary Air	16psi/1.8	11.5	1.184	300.0	355.20
Kaol. Air	6psi/0.35	1.34	"	35.0	41.40
Pilot Air	50 psi, 70/120	0.68	"	17.8	21.10
UV Air	55 psi/13	0.59	"	15.5	18.35
Soln. Water	60 psi/20	20 cc/min	1gm/cc	————	20
Total flow rate (M)					479.8 gm/min

Diluent MIN flow rate = $(26.32 - 0.00549M) = 23.68$ l/min; Set point = 46.2 Dil ratio = 10:1

Diluent MAX flow rate = $(26.32 - 0.00274M) = 25.02$ l/min; Set point = 49.2 Dil ratio = 20:1

Total Sampling rate = 26.32l/min

Main rotameter set point = 97

DATA: 1 cu ft = 28.32lts; STP = 298,760; Density = 1.184 g/l (air), 0.728 g/l (gas) Mw (air) = 28.97; Mw (gas) = 17.80 ; Mw (flue gas at SR=1.2) = 27.952; Isokinetic sampling rate = $0.00274 \cdot \text{mass flowrate (gm/min) slpm (plug flow)}$, Alkali soln = $0.2 \cdot \text{Mw (gm/litr)}$ = 111808/(mass flowrate) PPM

Temperature Profile

Port #	2	3	4	4B	5	6	7	8	11	13
T (C)	1230	1169	1049	945	863	837	805	776	661	573

Table B 2-1: Composition of Reagent solutions for AA analysis.

Solution	Reagent Quantity
Dissolving acid	30% vol HF, 10% vol HCl, 10% vol HNO ₃ , and 50% vol deionized water
Boric acid	26 gm H ₂ BO ₃ crystals in 1.00 liter water.
Cesium nitrate	1.435 gm CsNO ₃ crystals in 500 ml water.

Table B 2-2: Atomic Absorption/Emission methods and detection limits for Al, Si, K & Na.

##	Flame/mode	Detection limit	Noise (%)	Wavelength (nm)	Slit width	Linear range (ppm)
Na	C ₂ H ₂ /Air (em)	0.012	2.0	589.0	0.4	1.0
K	C ₂ H ₂ /Air (em)	0.043	2.0	766.5	1.4	2.0
Al	C ₂ H ₂ /N ₂ O (abs)	1.100	2.5	396.2	0.7	150.0
Si	C ₂ H ₂ /N ₂ O (abs)	2.100	3.0	251.6	0.2	150.0

Table B 2.3: Average Concentrations and Relative Errors for AA analysis.

Element	Concentration(ppm)		Relative error (%)	
	Range	"Typical value"	Range	"Typical value"
Na	0.10-5.00	0.2	14-2.25	8
K	0.05-1.00	0.2	88-6.30	24
Al	1.00-4.00	2.0	93-30.0	58
Si	0.50-7.00	2.5	423-36.0	86

APPENDIX C: THE SHRINKING CORE MODEL

Shrinking core model for a constant size spherical particle, constant gas phase concentration, constant temperature and constant reaction time for all the particles. Conditions clearly not met by our present system but used as a guide. Sorbent flowrate was in excess hence fraction total sodium to sorbent is nearly the same as fraction water insoluble sodium (see table).

- X_s Dimensionless solid conversion.
 τ Dimensionless time for complete conversion.
 d_p Particle radius size
 v Reaction stoichiometry
 C_{Ag} Gas phase concentration
 k_0 Intrinsic reaction rate constant.
 ρ_b Solid bulk density
Defining extent of particle utilization X_s as:

$$X_s = 1 - \left(\frac{d_p}{d_p}\right)^{\frac{1}{3}} \quad (100)$$

Then for:

1. Film diffusion controls

$$\tau = \frac{\rho_b d_p}{6k_0 v C_{Ag}} \quad (101)$$
$$X_s = \frac{1}{d_p}$$

2. Ash diffusion controls

$$\tau = \frac{\rho_b d_p^2}{24vD_s C_{Ag}} \quad (102)$$
$$1 - 3(1 - X_s)^{\frac{2}{3}} + 2(1 - X_s) = \frac{1}{d_p^2}$$

3. Reaction controls

$$\tau = \frac{\rho_p d_p}{4\nu k_0 C_{A_0}} \quad (4)$$

$$1 - (1 - X_p)^{\frac{1}{3}} = \frac{1}{d_p}$$

The model equation was fitted to one single point (9 μm size particle), evaluating a proportionality constant at this point, and using this constant to extrapolate results for other sizes.

The results shown in Figure C-1 shows that any of the three reaction mechanisms are likely to be important in our studies consequently further analysis is necessary to discriminate the unlikely mechanisms.

Figure C-1: Experimental normalised fraction sorbent utilisation showing the effect of particle size on alkali capture for Runs 352 & 353. A shrinking core model, with constant reaction temperature and constant gas phase concentration, is shown.

APPENDIX D: LISTING OF COMPUTER PROGRAM MODEL FOR

```

      IMPLICIT REAL *8 (A-H,O-Z)
      REAL *8 K0
      CHARACTER *20 OUTPUT,INPT2,LOOP
      COMMON /PARA/K0,E,PHI,A,B,C,PA0,RHOP,POR

      LOOP='TRUE'
C     THIS PROGRAM PREDICTS ALKALI CAPTURE IN THE KINETICALLY
      CONTROLLED REACTION
C     REGIME
C     The program stops iteration when either temperature is below the dewpoint
C     or the sampling point is reached
C     or all the alkali is captured, PA=0
C T   Temperature in K
C Pa0 Gas phase initial concentration ppm
C PA  Gas phase concentration of NaOH in ppm
C PHI   Alkali to sorbent equivalence ratio
C Theta BET surface function, theta = 1 at injection
C G  Capture by reaction in gm Na2O/gm sorbent
C X  Furnace axial position in cm
C A,B   Temperature profile constants  $dT/dX = aT + b$ 
C C  Particle velocity profile  $dX/dt = cT$ 
C Alpha Empirical constant for particle sinter
C R  Gas constant 1.987 cal/gmmol
C
      POR=0.58

      OPEN(UNIT=7,FILE='INPUT.TXT',STATUS='OLD')
      READ(7,10) OUTPUT
      READ(7,10) INPT2
10    FORMAT(A12)
      READ(7,*) K0,E,RHOP,A,B,C
      READ(7,*) PHI,PA0,X,T,TDWPT,DX
      CLOSE(7)
      OPEN(UNIT=8,FILE=OUTPUT,STATUS='UNKNOWN')
      WRITE(8,*) 'CAPTURE MODEL FOR ',OUTPUT,'E=',E
      WRITE(8,20)'T','ER','g' exp't','g' model'
20    FORMAT(A12,2X,A12,2X,A12,2X,A12)
      PA0=PA0*1E-6
C     Start computation
      OPEN(UNIT=9,FILE=INPT2,STATUS='OLD')
      DO WHILE('TRUE')
      READ(9,*,END=70)TEMP,PHI,GEXPT
        TEMP=TEMP*1273

```

Input file for MODEL.FOR

SOEXPT.TXT

SO2EXPT.DAT

5.97E7,6000,2.64,0.002847,1.83,0.12

1.0,100,30,1600,1123,2

LINE 1 : OUTPUT FILE NAME

LINE 2 : FILE CONTAINING EXPERIMENTAL RESULTS TO BE COMPARED

LINE 3 : k_p , E, Particle density (g/cc), Temperature gradient coefficients

A,B: $dT/dX = AT + B$ and flue gas velocity coefficient C, $dX/dt = CX$

**LINE 4 : ϕ , Initial sodium concentration (ppm), Initial conditions for temperature profile;
X, T(K)**

TDWPT (dewpoint temperature) and DX.

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3 of 3

APPENDIX E AA/EDX COMPARATIVE ANALYSIS RESULTS

Table E 4-1: EDX/AA Analysis for sample 1166

Comparison between AA water insoluble composition & EDX composition (Data in Mass %)										
Sample # 1166	Atomic Absorption		Energy Dispersive X-Ray Analysis						ApproxP art. Size (μm)	Apprx Scan area (μm^2)
Element	Impactor Average	Stage Average	Area Averages			Particle Analysis				
			#1	#2	#3	#1	#2	#3		
Al	39.1	38.6	39.5			40.1	32.9		0.8	1000
Si	50.3	48.4	53.7			57.8	47.4			
K										
Na	10.6	13.1	6.8			2.1	19.7			

```

DO WHILE(T.GT.TEMP)
  A1=1-A*DX/2
  A2=1+A*DX/2
  A3=B*DX
  T=T*A1/A2+A3/A2
  X=X+DX
ENDDO
T2=T
PA=PA0
CAPT=0
DXP=10
GS=0
DO WHILE(X.LE.388)
  CALL RV(T,ALPHA,BETA)
  A1=(1-ALPHA*DX/2)
  A2=(1+ALPHA*DX/2)
  A3=BETA*DX
  PA=PA*(A1/A2)+A3/A2
  X=X+DX
  CAPT=100*(PA0-PA)/PA0
  GS=0.27*PHI*(PA0-PA)/PA0
  A1=1-A*DX/2
  A2=1+A*DX/2
  A3=B*DX
  T=T*A1/A2+A3/A2
  IF(T.LE.TDWPT) GOTO 50
  IF(GS.GE.(0.13))GOTO 50
ENDDO
50  WRITE(8,60)T2/1273,PHI,GEXPT,GS
60  FORMAT(F8.4,8X,F6.3,8X,F7.4,8X,F7.4)
  T=1600
  X=30
ENDDO
70  STOP
END

C  Volumetric rate calculations
SUBROUTINE RV(T,ALPHA,BETA)
IMPLICIT REAL *8(A-H,O-Z)
REAL *8 K0
COMMON /PARA/K0,E,PHI,A,B,C,PA0,RHOP,POR
R=1.987
R2=82.05
RT=EXP(-E/R/T)
RT=k0*RT*PA0*31*POR/(((1-POR)*R2*T*T*0.27*PHI*RHOP)
RT=RT/C

```

BETA=0
ALPHA=RT
RETURN
END

APPENDIX E --continued

Table E 4-2: AA/EDX analysis sample 956

Comparison between AA water insoluble composition & EDX composition (Data in Mass %)										
Sample #956	Atomic Absorption		Energy Dispersive X-Ray Analysis						ApproxP art. Size (μm)	Apprx Scan area (μm^2)
Element	Impactor Average	Stage Average	Area Averages							
			#1	#2	#3	#4	#5	#6		
Al	39.3	36.7	35.1	35.2	35.1	36.7	35.8	35.2	1.0-1.5	3000
Si	50.7	48.1	47.8	47.2	47.6	50.0	48.6	46.4		
K	7.30	12.5	13.9	14.3	14.3	9.57	11.9	14.6		
Na	2.71	2.72	3.16	3.33	3.02	3.71	3.73	3.81		

APPENDIX E --continued

Table E 4-3: AA/EDX analysis for sample 921

Comparison between AA water insoluble composition & EDX composition (Data in Mass %)										
Sample # 921	Atomic Absorption		Energy Dispersive X-Ray Analysis						ApproxP art. Size (μm)	Apprx Scan area (μm^2)
Element	Impactor Average	Stage Average	Area Averages							
			#1	#2	#3	#4	#5	#6		
Al	36.5	36.9	41.2	31.8	26.5	34.1	24.6	38.6	1.0	1000
Si	53.5	55.7	55.7	42.5	47.3	46.1	44.4	52.9		
K	6.6	5.1	2.63	21.8	24.8	16.6	29.9	6.95		
Na	3.5	2.3	0.53	3.96	1.39	3.2	1.4	1.49		

APPENDIX E --continued

Table E 4-4: AA/EDX analysis for sample 1341

Comparison between AA water insoluble composition & EDX composition (Data in Mass %)										
Sample # 1341	Atomic Absorption		Energy Dispersive X-Ray Analysis						ApproxP art. Size (μm)	Apprx Scan area (μm^2)
Element	Impactor Average	Stage Average	Area Averages							
			#1	#2	#3	#4	#5	#6		
Al	38.1	37.7	41.8	34.9	42.4	41.4	41.4	41.9	10.0	1000
Si	54.4	50.0	54.9	53.9	52.9	54.6	53.7	53.7		
K	4.27	6.58	2.30	10.5	3.03	2.27	3.52	1.67		
Na	3.21	5.78	0.98	0.74	1.67	1.77	1.38	2.73		

APPENDIX E --continued

Table E 4-5: AA/EDX analysis for sample 1316

Comparison between AA water insoluble composition & EDX composition (Data in Mass %)										
Sample # 1316	Atomic Absorption		Energy Dispersive X-Ray Analysis						ApproxP art. Size (μm)	Apprx Scan area (μm^2)
Element	Impactor Average	Stage Average	Area Averages							
			#1	#2	#3	#4	#5	#6		
Al	40.9	39.6	41.8	41.6	41.5	41.9	40.8	41.2	1.0	1000
Si	54.4	53.5	55.4	56.3	57.1	56.2	56.7	55.8		
K	1.7	3.0	2.08	0.66	0.71	0.60	1.83	1.42		
Na	3.5	3.8	0.77	1.38	0.66	1.37	0.61	1.12		

APPENDIX F:

OTHER EXPERIMENTAL RESULTS

Figure F-1: Combined temperature gradients for five furnace runs at a mass flowrate of 450–480 gm/min, from which mean temperature gradient was calculated.

NOMENCLATURE:

D_{AB}	Molecular diffusion coefficient, cm^2/s
D_e	Effective diffusion coefficient, cm^2/s
D_k	Knudsen diffusivity coefficient, cm^2/sec
d_p	Particle diameter, cm
E	Activation energy, kcal/gmol
g	Water insoluble capture, $\text{gm Na}_2\text{O/gm sorbent}$.
k_0	Arrhenius pre exponential rate constant, $\text{cm}^3 \text{ gas/ cm}^3 \text{ porous solid. sec}$
k_v	Apparent volumetric reaction rate, $\text{cm}^3 \text{ gas/cm}^3 \text{ solid. sec}$
k_{int}	Intrinsic rate constant, $\text{cm}^3 \text{ gas/ cm}^3 \text{ solid. sec}$
k_m	Mass transfer coefficient, cm/s
m_{tg}	Flue gas mass flowrate, gm/sec
m_{wtg}	Flue gas molecular weight
m_p	Particle mass flowrate, gm/sec
p_i	Partial pressure of species sodium, atm .
p_{i0}	Initial partial pressure of sodium at injection
R	Gas law constant, $\text{cm}^3 \text{ atm g-mol}^{-1} \text{ K}^{-1}$
R_g	Global reaction rate, $\text{gm Na}_2\text{O/gm sorbent. sec}$
R_p	Reaction rate per particle, $\text{gm Na}_2\text{O/particle. sec}$
T	Sorbent injection temperature, K
T_{ex}	Sorbent sampling temperature, K
t	Time
v_f	Flue gas velocity, cm/s
$X_{0.65}$	Utilization of a $0.65 \mu\text{m}$ particle
x	Axial position in the combustor after injection, cm

Greek symbols

β	Regression fit coefficients
ϵ	Dimensionless sorbent porosity
η	Effectiveness factor
θ	Local flue gas temperature, K
ρ_p	Sorbent particle skeletal density, gm/cm^3
τ	Sorbent residence time, sec
$\phi(\theta)$	Time-temperature transformation function.
x_i	Species i as a parameter in flue gas
φ	Sodium to sorbent mass equivalence ratio.

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