THE ALKALI SORPTION PROCESS BY SOLID SORBENTS
AT HIGH TEMPERATURE

by

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To my lovely wife, Angela Harder,
for her love, trust, patient and understanding.
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ABSTRACT

The aluminosilicate materials kaolinite, calcium montmorillonite and emathlite have been tested as solid sorbents for alkali vapour in controlled gaseous environments, in order to study their sorption characteristics.

The study used pan pelletised and extruded pellets in single pellet and fixed bed reactor systems under gaseous environmental conditions containing water vapour, hydrogen chloride and nitrogen at a temperature of 850°C. The means of producing the pellets and the composition of the gaseous environment were shown to determine the sorption performance of the sorbent pellets. The physical properties of the pellet (particle size, total pore volume, surface area, crush strength) significantly affect the sorption effectiveness, while the formation of reaction products is dependent upon the sorbents' chemical composition and on the sorption conditions. Reaction products identified under the various sorption conditions indicated possible pathways for alkali capture. Hydrogen chloride mixtures were shown to cause a reverse of the sorption process for some sorbents. A leaching method for extracting sodium from treated pellets enabled the type of bonding to be determined but not necessarily the prime sorption mechanism.

With the introduction of water vapour, some evidence was presented that the alkali sorption rate can change significantly. The previously reported effect of hydrogen chloride upon alkali capture by the sorbent material, calcium montmorillonite; shown by McLaughlin (1990) was confirmed and the effect was also investigated for emathlite and kaolinite. Reversibility depended upon the presence or absence of hydrogen chloride. Both water vapour and hydrogen chloride determine sorption activity and capacity. Likewise the structural characteristics of the pellet influences the sorption activity and capacity.

The sorption process is not due to aluminosilicate reaction alone but also due to replacement mechanisms. Conclusions are drawn regarding mechanism and theoretical model proposed.
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ABBREVIATIONS

AAS  Atomic Absorption Spectrophotometer
ABB  Asea Brown Boveri
ASME  American Society of Mechanical Engineers
ABGC  Air Blown Gasification Cycle
AFBC  Atmospheric Fluidised Bed Combustion
ACFBC  Atmospheric Circulating Fluidised-Bed Combustion system
BCURA  British Coal Utilisation Research Laboratory Association
BET  Brunauer-Emmett Teller
BJH  Barrett, Joyner and Hallender
BTU  British Thermal Unit
CPE  Chemical & Process Engineering
DIA  Digital Image Analysis
DOE  Department of Energy, USA
ECC  English China Clay, St. Austell, England
EDS  Energy Dispersive Analysis System
EPRI  Electric Power Research Institute
ESCA  Electron Spectrometry for Surface Analysis
ESP  Electrostatic Precipitator
FBC  Fluidised Bed Combustion
FBG  Fluidised Bed Gasification
FBR  Fixed Bed Reactor System
FGD  Flue Gas Desulphurisation
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>Hydrogen Chloride</td>
</tr>
<tr>
<td>HTHP</td>
<td>High Temperature and High Pressure</td>
</tr>
<tr>
<td>IEA</td>
<td>International Energy Agency</td>
</tr>
<tr>
<td>IGCC</td>
<td>Integrated Gasification Combined Cycle</td>
</tr>
<tr>
<td>MIP</td>
<td>Mercury Intrusion Porosimetry</td>
</tr>
<tr>
<td>PPCCCC</td>
<td>Pressurised Pulverised Coal Combustion Combined Cycle</td>
</tr>
<tr>
<td>PFBC</td>
<td>Pressurised Fluidised Bed Combustion</td>
</tr>
<tr>
<td>PFBG</td>
<td>Pressurised Fluidised Bed Gasifier</td>
</tr>
<tr>
<td>ppmv</td>
<td>parts per million (volume)</td>
</tr>
<tr>
<td>ppmw</td>
<td>parts per million (weight)</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluorethylene</td>
</tr>
<tr>
<td>RTI</td>
<td>Research Triangle Institute, USA</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SFG</td>
<td>Simulated Flue Gas</td>
</tr>
<tr>
<td>SPR</td>
<td>Single Pellet Reactor System</td>
</tr>
<tr>
<td>STA</td>
<td>Simultaneous Thermal Analysis</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
</tbody>
</table>
NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_s$</td>
<td>surface area of a grain [cm$^2$]</td>
</tr>
<tr>
<td>$A_{int}$</td>
<td>reaction interfacial area per unit volume of grains [cm$^2$/cm$^3$]</td>
</tr>
<tr>
<td>$A_p$</td>
<td>surface area of a pellet [cm$^2$]</td>
</tr>
<tr>
<td>$A_r$</td>
<td>cross-sectional area of the pipe [cm$^2$]</td>
</tr>
<tr>
<td>$b_{1,2}$</td>
<td>stoichiometric coefficients [-]</td>
</tr>
<tr>
<td>$C_{H_2O}$</td>
<td>concentration of water vapour at the surface of unreacted core in a grain [mole/cm$^3$]</td>
</tr>
<tr>
<td>$C_{H_2O_g}$</td>
<td>bulk gas concentration of water vapour [ppm]</td>
</tr>
<tr>
<td>$C_{HCl_g}$</td>
<td>bulk gas concentration of hydrogen chloride [ppm]</td>
</tr>
<tr>
<td>$C_{HCl_p}$</td>
<td>concentration of HCl in the pores of a pellet [mole/cm$^3$]</td>
</tr>
<tr>
<td>$C_{HCl,o}$</td>
<td>concentration of product, HCl, in the bed voidage [mole/cm$^3$]</td>
</tr>
<tr>
<td>$C_{NaCl}$</td>
<td>gas concentration of sodium chloride in a pellet [mole/cm$^3$]</td>
</tr>
<tr>
<td>$C_{NaCl_g}$</td>
<td>bulk gas concentration of sodium chloride [ppm]</td>
</tr>
<tr>
<td>$C_{NaCl_p}$</td>
<td>concentration of NaCl in the pores of a pellet [mole/cm$^3$]</td>
</tr>
<tr>
<td>$C_{NaCl,o}$</td>
<td>concentration of the reactant, NaCl, in the bed voidage [mole/cm$^3$]</td>
</tr>
<tr>
<td>$C_{sol,c}$</td>
<td>concentration of the solid reactant [mole/cm$^3$]</td>
</tr>
<tr>
<td>$C_{sol,p}$</td>
<td>concentration of the solid product [mole/cm$^3$]</td>
</tr>
<tr>
<td>$C_{uc,NaCl}$</td>
<td>reactant gas concentration at the surface of the unreacted core in a grain [mole/cm$^3$]</td>
</tr>
<tr>
<td>$C_{uc,HCl}$</td>
<td>product gas concentration at the surface of the unreacted core in a grain [mole/cm$^3$]</td>
</tr>
<tr>
<td>$d_p$</td>
<td>pellet diameter [mm, cm]</td>
</tr>
<tr>
<td>$D$</td>
<td>composite diffusivity accounting for Knudsen and bulk diffusion [cm$^2$/s]</td>
</tr>
<tr>
<td>$D_g$</td>
<td>diffusivity through the product layer in a grain (intr-grain diffusivity) [cm$^2$/s]</td>
</tr>
<tr>
<td>$D_m$</td>
<td>molecular diffusivity [cm$^2$/s]</td>
</tr>
<tr>
<td>$D_p$</td>
<td>intrapellet diffusivity; effective diffusivity in a porous pellet [cm$^2$/s]</td>
</tr>
<tr>
<td>$F_{g,p}$</td>
<td>Shape factor for the grain, pellet</td>
</tr>
<tr>
<td>$g_{ps}(X_p)$</td>
<td>conversion function deduced for chemical reaction control</td>
</tr>
<tr>
<td>$k$</td>
<td>Boltzmann constant [J/K] (1.38E-23J/K)</td>
</tr>
<tr>
<td>$k_s$</td>
<td>reaction rate constant group based on unit area of reaction interface [cm/s]</td>
</tr>
<tr>
<td>$k_s$</td>
<td>gas film mass transfer coefficient [cm/s]</td>
</tr>
<tr>
<td>$K_e$</td>
<td>equilibrium group based on concentrations [(mole/cm$^3$)$^{-1/2}$]</td>
</tr>
<tr>
<td>$K_e$</td>
<td>equilibrium group [dimensionless]</td>
</tr>
<tr>
<td>$K_s$</td>
<td>intrinsic forward reaction rate constant [(cm/s)(cm$^3$/mole)$^{-3/2}$]</td>
</tr>
</tbody>
</table>
\( K_s \) intrinsic backward reaction rate constant \([(\text{cm/s})(\text{cm}^2/\text{mole})]\)

\( L \) characteristic diameter [cm]

\( M_{\text{NaCl}} \) molecular weight of sodium chloride [58.44 g/mole]

\( M_{\text{N}_2} \) molecular weight of nitrogen [18 g/mole]

\( N_{\text{sh}^*} \) modified Sherwood number [-]

\( P \) pressure [atm]

\( P_0 \) atmospheric pressure [atm]

\( p_{\text{fg}}(X_g) \) conversion function deduced for intragrain diffusion control

\( p_{\text{fp}}(X_p) \) conversion function deduced for intrapellet diffusion control

\( q'(\xi) \) derivative with respect to \( \xi \) of \( q(\xi) \)

\( q(\xi) \) function that describes the progress of reaction of a grain under product layer diffusion influence

\( r_c \) radius of the unreacted core in a grain [cm]

\( r_g \) grain radius [cm]

\( r_p \) pellet radius [cm]

\( r_{\text{NaCl}} \) local rate of consumption of the gaseous reactant (NaCl) per unit volume of the pellet \([\text{mole}/(\text{cm}^3/\text{s})]\)

\( r_{\text{HCl}} \) local rate of generation of the gaseous product (HCl) per unit volume of the pellet \([\text{mole}/(\text{cm}^3/\text{s})]\)

\( R \) spatial coordinate measured from the center of the pellet [cm]

\( \text{Re} \) Reynolds number

\( \text{Sc} \) Schmidt number [-]

\( \text{Sh} \) Sherwood number [-]

\( t \) time [s]

\( t^* \) time [-]

\( t_b \) boiling point [K]

\( T \) temperature [K]

\( T^* \) temperature [-]

\( u \) superficial velocity [cm/s]

\( V_b \) liquid molar volume \([\text{cm}^3/\text{mole}]\)

\( V_g \) volume of the grains \([\text{cm}^3]\)

\( V_F \) volumetric flow rate \([\text{m}^3/\text{s}]\)
\( V_p \) volume of the pellets [cm³]

\( X_g \) solution from pellet-grain model by Newton-Raphson method and used to find the overall solids sodium content

**GREEK SYMBOLS**

\( \varepsilon \) porosity [-]

\( \varepsilon_p \) intrapellet porosity [-]

\( \varepsilon_i \) characteristic energy of the component [J]

\( \varepsilon_{NaCl-N2} \) characteristic energy NaCl-N2 [J]

\( \Psi \) concentration driving force

\( \nabla \) nabla operator

\( \eta \) position in the pellet

\( \nu \) dynamic viscosity [g/(cm²/s)]

\( \mu \) kinematic viscosity [cm²/s]

\( \xi \) local extent of reaction for the solid sorbent

\( \delta \) bulk gas density at the temperature and pressure of interest [g/cm³]

\( \delta_s \) sorbent density [mole/cm³]

\( \hat{\sigma}_g^2 \) dimensionsless group, which incorporates chemical reaction and diffusion through the product layer

\( \hat{\sigma} \) dimensionsless group, which incorporates kinetic and structural properties

\( \sigma_i \) characteristic length, [Ångstrom]

\( \sigma_{NaCl-N2} \) collision diameter (distance between molecules when the potential energy of interaction is zero) [K/mol]

\( \Omega_D \) diffusion collision integral [-]

\( \tau \) tortuosity factor [-]
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CHAPTER 1

INTRODUCTION

The search to meet energy demands with more efficient coal-based power generation plants is motivated by economic, environmental and political considerations. World coal consumption has increased from 84 quadrillion British thermal units (BTU) in 1985 to 93 quadrillion in 1996 despite declines in Western Europe, Eastern Europe, and the countries of the former Soviet Union. In 1996 coal accounted for 38 percent of the energy consumed worldwide for electricity generation. In the International Energy Outlook 99 forecast this share will fall slightly until 2020 (DOE, 1999a). This is because coal will face tough challenges, particularly in the environmental area. The environmental issues associated with coal use are dust, sulphur dioxide (SO$_2$), oxides of nitrogen (NO$_x$), and carbon dioxide (CO$_2$). Dust has been linked to respiratory problems in humans and SO$_2$ has been linked to acid rain. In the cases of CO$_2$ and methane (CH$_4$) a far more significant issue has sensitised scientific and public opinion about coal, which is the controversial 'green-house effect' and global climate change. These disadvantages of coal have led to national emission limits and international agreements in the case of the green-house gas carbon dioxide. Thus, realisation of more efficient coal-based power generation systems lead to considerable savings in coal consumption and thus reductions in emissions (ASME, 1998).

Currently the reserves of coal are significantly greater than those for oil and natural gas, which indicates that coal is likely to remain an important source of energy. The total recoverable reserves of coal around the world are estimated at 1,088 billions tons: enough to last another 200 years, but a technological challenge must be faced if these reserves are to be fully utilised. One approach has been to develop advanced coal-based power generation plants using clean-coal technology which is more efficient and more environmentally friendly than traditional combustion technology.
1.1 ADVANCED COAL-BASED POWER GENERATION PLANTS

Advanced coal-based power generation systems based on Fluidised Bed Combustion (FBC) or Fluidised Bed Gasification (FBG) offer the potential for higher efficiency, compliance with environmental standards and reduced plant installation costs. Some advanced coal based power generation systems offer the advantages of high temperature operation with a gas turbine and heat recovery with a steam cycle to gain greater efficiency.

During FBC, solids are fluidised and fuel particles are combusted to sustain a given process temperature. An Atmospheric Fluidised Bed Combustion system (AFBC) has low fluidising velocities that result in a bubbling bed. An Atmospheric Circulating Fluidised-Bed Combustion system (ACFBC) operates at gas velocities approximately seven to eight times those of AFBC. Pressurised Fluidised-Bed Combustion (PFBC) systems are similar to AFBC but operate under higher pressure.

With coal gasification, coal is converted to a combustible gas, fine particulates and ash or slag. The combustible gas is then burnt in the combustion chamber of a gas turbine. A high thermodynamic efficiency is achieved by using the full potential working temperatures of a gas turbine and utilising the waste heat in a steam turbine. The use of steam and gas turbines give this system the name of Integrated Gasification Combined Cycle (IGCC) process.

The application of fluidised bed technology offers advantages when compared with those of fixed bed or entrained flow. The advantages are: Under the fluidised bed operating condition, the likelihood of NO\textsubscript{x} production is greatly reduced in the temperature range of 800-1100\degree C. In addition the temperature range offers the advantage that tars are not formed. Tars are produced with the fixed bed in the lower temperature range. A further advantage of the fluidised bed technology is that ashes can be filtered from the gas stream in the lower temperature range. Slag melts do not occur as with the entrained phase gasifiers. Slag melts produce high alkali contents and sticky ash particles. With fluidised bed technology, 'in bed' desulphurisation can be achieved. The long residence times of the mixed gases allow desulphurisation with limestone with gas velocities of 3-6m/s and coal sizes of 0.1-0.3mm. In
general the limestone is added at the base of the fluidised bed. Using stationary fixed bed and entrained flow reactors, additional measures are needed for flue gas desulphurisation.

1.1.1 Combined Cycle Technology

In combined cycle technology, coal is either gasified or combusted under high pressure and temperature. After gas cleaning, gas at high pressure and temperature used to drive a gas turbine. Residual heat from the gas turbine exhaust and higher grade heat from the coal gasifier or combustor is used to raise steam to drive a steam turbine. The higher temperature of the gas turbine, permits higher power recoveries via the Brayton Cycle. Hence, the combined cycles are thermodynamically more efficient than the steam-based Rankine cycles (Thambimuthu, 1993).

Most combustion gas turbines use the Brayton Cycle to improved technical efficiency. This is especially achieved through a higher turbine inlet temperature (T_Inlet) in the gas turbine. The temperature leaving the gas turbine is limited to the ambient temperature (T_Out). The thermal efficiency (η) of the Brayton Cycle can be calculated by the Equation 1 represented below:

\[ \eta = \frac{\text{Work(Turbine)} - \text{Work(Compressor)}}{\text{Heat(In)}} = \frac{T_{\text{Inlet}} - T_{\text{Out}}}{T_{\text{Inlet}}} \quad [1] \]

Most combustion gas turbine cycles differ from conventional power cycles, such as the Rankine Cycle, in that gas turbine residuals cannot be returned to their initial conditions for reuse. In most conventional cycles water is converted to steam, than back to water, and then used again.

In conventional cycles the temperature of the working medium water is limited due to material problems (<600°C). On the other hand, there is the option to increase thermal efficiency e.g. by raising the gas turbine inlet temperature. According to the literature there are the combined cycle process types:
Pressurised Fluidised Bed Combustion (PFBC)

In a PFBC system, the hot pressurised combustion gases generated at around 850°C are cleaned of entrained particulates in a series of cyclones or in a single cyclone followed by a hot gas filter. Power is generated from the off gas from the combustor in a gas turbine and from steam in a steam turbine. The use of a fluidised bed limits the combustion temperature, basically to avoid softening and agglomeration of the ash, giving a gas temperature prior to the gas turbine of about 830°C. Figure 1 shows the general schematic of a supercharged PFBC combined cycle. The gas turbine compressor is used to provide the fluidising air for the bed and the excess power is used to drive an alternator. A waste heat boiler is installed after the gas turbine, in the supercharged PFBC design. The obtained steam together with steam production from an in-bed heat exchanger, drives the steam turbine. The turbocharged version of PFBC resulted from the desire to avoid turbine corrosion and the ease of cleaning of the particulates from the gas by installation of an above-fluidised bed heat exchanger. The heat exchanger leads to gas temperatures of 400 and 500°C. The gas turbine does not then produce electric power, the compressor simply provides the fluidising air.

The first ever pressurised fluidised bed combustor came into operation at the laboratories of the British Coal Utilisation Research Laboratory Association (BCURA) at Leatherhead in 1969. Since then further pilot scale rigs were built in the UK, USA, Germany, Finland and Sweden in order to examine the conditions for; bed fluidisation, tubebank materials and design, combustion efficiencies, sulphur retention, NOx, emissions, hot gas cleaning, gas turbine blade materials, coal feeding methods, instrumentation, turndown and control methods, ash disposal and utilisation. A technology cannot be said to have achieved its promise until a large plant has been operating for sufficient time to demonstrate reliable attainment of the target level of performance. Asea Brown Boveri (ABB) built bubbling PFBC plants and proved that the technology can be applied to conditions where the hot gas cleaning operates...
under moderate conditions. The ABB concept relies on the use of two high efficiency cyclones and a fabric filter for contaminant control. The use of the cyclones leads to a loss in efficiency due to the energy consumed by the cyclones. In addition, the design philosophy of ABB is based on the use of an industrial gas turbine with a low gas turbine inlet temperature of $830^\circ C$ which leads to a loss in efficiency (Thambimuthu, 1993).

![Schematic of a Supercharged Pressurised Fluidised Bed Combustion Combined Cycle](image)

**Figure 1:** Schematic of a Supercharged Pressurised Fluidised Bed Combustion Combined Cycle (Meadowcroft and Stringer, 1987).

**Pressurised Pulverised Coal Combustion Combined Cycle (PPCCCC)**

Among power plants based on coal combustion Pressurised Pulverised Coal Combustion Combined Cycles (PPCCCC) can achieve the highest electrical efficiencies. Figure 2 illustrates the basic concept extended by the inclusion of a ceramic heat exchanger. Pressurised pulverised coal combustion gases can directly enter the gas turbine to generate electricity. The cycle to date has not proven its acceptance because of problems associated with gas cleaning. By integrating a high temperature heat exchanger into the PPCCCC, a separation of solid ash particles can be achieved by using filter candles and an alkali removal unit. In Figure 2, the
precipitation of the remaining fly ash occurs below the ash fusion temperature. Therefore, the alkali removal unit is neglected (Ehlers and Leithner, 1997).

![Figure 2: PPCCCC Concept with Ceramic Heat Exchanger (Leithner et al 1999, Ehlers and Leithner, 1997).](image)

**Integrated Gasification Combined Cycle (IGCC)**

IGCC systems involve the complete gasification of the coal using stoichiometric quantities of air or oxygen \( (O_2) \), often with steam, to produce a flue-gas whose principal combustible components are carbon monoxide \( (CO) \) and hydrogen \( (H_2) \). Three main generic types of gasifier have been developed. They differ in their characteristics of the gas-solid contact zone, where the gasification reactions take place. These types are known as entrained flow, fixed and fluidised bed gasifiers. A representation of the basic type of coal gasifiers with their technical variations is shown in Figure 3. Fixed bed gasifiers operate with low temperature product gases and produce high levels of tars and oil. This complicates the heat recovery and gas cleaning process, and a separate sulphur removal process is necessary. Entrained gasifiers operate at high temperatures which lead to sticky ash and alkali contents. The gas must be cooled down to remove sulphur and alkali species.
The fluidised bed gasifier technique allows sufficient residence times to remove sulphur in-beds. Under the reducing hot gas conditions hydrogen sulphide ($H_2S$) reacts with CaO to give calcium sulphide (CaS) and water ($H_2O$):

$$CaO(s) + H_2S(g) \leftrightarrow CaS(s) + H_2O(g) \quad [2]$$

![Figure 3: Basic Type of Coal Gasifiers (Pintsch and Gudenau, 1991).](image)

The use of a sorbent such as CaO for desulphurisation depends on the chosen gasifier technique, the respective process condition and desulphurisation temperature. In order to meet emission limits for $NO_x$ modifications are necessary such as retrofitting of low $NO_x$ gas turbine burners. A comprehensive review of removal and/or reduction of nitrogen derived gases in hot gas coal gasification was described in an International Energy Agency (IEA) Coal research report by Thambimuthu (1993).

Table 1 indicates IGCC details of commercial demonstration plants of advanced coal gasifier technologies. Some of them are air blown, which reduces the need for a oxygen plant. Other IGCC plants show the need for gas cooling either after the cyclone stage due to unburned char and unused sorbent or after the gasifier due to the need for a lower desulphurisation temperature.
Table 1: Advanced Coal-based Gasification Demonstration Plants (DOE, 1995, 1999a,b,c,d).

<table>
<thead>
<tr>
<th>IGCC</th>
<th>Characteristic</th>
<th>Fixed Bed</th>
<th>Fluidised Bed</th>
<th>Entrained Flow</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Consortium</td>
<td>BG/GE and others</td>
<td>Wheeler/Kellog</td>
<td>Rheinbraun</td>
<td>Destic/PSI</td>
</tr>
<tr>
<td></td>
<td>Project</td>
<td>Westfield, UK</td>
<td>Pinon</td>
<td>HTW</td>
<td>Wabash</td>
</tr>
<tr>
<td></td>
<td>Gas-cooler</td>
<td>after gasifier</td>
<td>after first cyclone</td>
<td>after two cyclones</td>
<td>after gasifier</td>
</tr>
<tr>
<td></td>
<td>Temperature</td>
<td>593</td>
<td>600</td>
<td>540</td>
<td></td>
</tr>
<tr>
<td></td>
<td>after cooling [°C]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Oxygen/Air</td>
<td>Oxygen</td>
<td>Air</td>
<td>Oxygen</td>
<td>Air</td>
</tr>
<tr>
<td></td>
<td>Cyclone-number</td>
<td>Conventional</td>
<td>One</td>
<td>Two</td>
<td>One</td>
</tr>
<tr>
<td></td>
<td>BTU</td>
<td>Medium</td>
<td>Low</td>
<td>Low</td>
<td>Medium</td>
</tr>
<tr>
<td></td>
<td>Coal</td>
<td>High fines</td>
<td>Dried, Crushed</td>
<td>Brown</td>
<td>Dried</td>
</tr>
<tr>
<td></td>
<td>Efficiency [%]</td>
<td>43</td>
<td>44</td>
<td>47</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>[BTU/kWh]</td>
<td>8035</td>
<td>7800</td>
<td>&lt;9000</td>
<td>&lt;8000</td>
</tr>
<tr>
<td></td>
<td>Removal [lb/mBTU]</td>
<td>0.1 (99%)</td>
<td>0.045 (99%)</td>
<td>0.02</td>
<td>98%</td>
</tr>
<tr>
<td></td>
<td>Sulphur</td>
<td></td>
<td></td>
<td></td>
<td>90%</td>
</tr>
<tr>
<td></td>
<td>Nitrogen-oxides</td>
<td>0.15 (90%)</td>
<td>0.053</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sponsors</td>
<td>DOE (22%)</td>
<td>DOE (50%)</td>
<td>BMFT</td>
<td>DOE (48%)</td>
</tr>
<tr>
<td></td>
<td>Dry/Wet</td>
<td>Dry</td>
<td>Wet</td>
<td>Wet</td>
<td></td>
</tr>
</tbody>
</table>

BG, British Gas; GE, General Electric; DOE, Department of Energy; BMFT, Bundesministerium für Forschung und Technologie; BTU, British Thermal Unit; ABB, Asea Brown Boveri.

Table 1: Advanced Coal-based Gasification Demonstration Plants (DOE, 1995, 1999a,b,c,d).
Figure 4 shows an air blown IGCC plant recovering 99% of the sulphur from the coal gas in the elemental form. The sorbent is reused in this Research Triangle Institute (RTI) process. RTI included processes to remove two other contaminants: ammonia and hydrogen chloride (RTI, 1995).

![Flow Chart of IGCC Process Recovering Sulphur from Coal Gasification](image)

**Figure 4: Flow Chart of IGCC Process Recovering Sulphur from Coal Gasification (RTI, 1995).**

**Air Blown Gasification Combined Cycle (ABGC)**

Figure 5 shows the original design concept of the ABGC, known formerly as the British Coal Topping Cycle. The original concept involves partial gasification of coal to produce fuel-gas and separate combustion of residual char in a pressurised fuel Combustor. The fuel-gas of the air blown gasifier is cleaned by one cyclone before the fuel-gas is released into the gas turbine combustor. The gas turbine combustor is also fed by the combustion char of the PFBC. In the most recent ABGC process, Figure 6, the gas trap the between gasifier and gas turbine is held in a temperature range where the candle filter can be operated safely and fuel-gas contaminants can be removed during gas filtration. In addition, the unburned char is burnt in an atmospheric circulating fluidised bed combustor instead of a PFB Combustor. The predicted efficiency of the ABGC technique is around 46-47%. This is based on a General Electric gas turbine, Frame 9F, with an inlet temperature of 1260°C and a GEC Alsthom steam turbine, with an inlet temperature of 538°C (160bar of subcritical steam). Greater
Figure 5: Schematic of the Original Design Concept of the Air Blown Gasification Cycle (National Coal Board Report, 1985).

Figure 6: Schematic of the Air Blown Gasification Cycle (Coal Research Establishment, 1995).
efficiency with the ABGC is limited by developments in the gas and steam turbine technology and gas clean up. The gas-clean up of most advanced coal-based power generation systems involves cooling of the coal-derived gas, a lower efficiency is achieved.

1.1.2 Fuel-Gas Contaminants

In combined cycle operations, the fuel-gas produced contains solid particles as well as alkali species, which have to be removed before use in a turbine. Even minimum contamination can lead to serious damage due to corrosion-erosion-deposition interactions on gas turbine blades. Dust and vapourisation of alkali components reportedly are a major problem in combined cycle gas streams. Deposits are reported on turbine surfaces resulting from low melting alkali compounds acting as binding agents. To achieve the requirement for alkali control, a chemically reactive material is used to achieve both the removal of alkali vapour and small particles.

Both gasification and combustion of coal lead to a release of volatile alkali components which can be detrimental to turbomachinery and other equipment used in combined cycle processes. In the United Kingdom there was a major initiative to develop a hybrid gasification-combustion system known as the Air Blown Gasification Cycle (ABGC). The ABGC was originally developed by British Coal as the Topping Cycle. In the original design concept of the Topping Cycle, no alkali removal stage was planned, however the alkali removal stage was added due to concerns regarding alkali induced corrosion at the higher temperature. The intermediate stage in developing commercial ABGC technology is shown in Figure 7. This design concept was postponed because of problems associated with the candle filters at the higher temperatures. However, candle filter tests in British Coal's Grimethorpe facility, in the temperature range 780-850°C showed that although the collection efficiency of candle filters was very promising, internal inspection of the pressure vessel revealed many failures, such as high temperature effects of thermal expansion and material creep.
Recent Pressurised Pulverised Coal Combustion Combined Cycle research (PPCCCCC) in Germany showed that liquid ash separation with simultaneous alkali condensation is difficult at temperatures of 1300°C (Weber et al., 1993; Ehlers and Leithner, 1997). An alternative cycle at temperatures lower than 950°C was proposed, which included a ceramic heat exchanger and candle filters (Leithner et al., 1999). An alkali removal stage was considered for the high temperature operation. A flow sheet of a test facility is shown in Figure 8. The test rig uses natural gas and coal ash loads to simulate a secondary combustion air gas stream. The gas stream entering the ceramic heat exchanger flows through a gas cyclone and filter candles. Plans exist to incorporate a fixed bed reactor to allow alkali removal.

Other combustion research concentrated on multicontaminant control and the influence of pressure on alkali control. Jaanu and Orjala (1996) showed that the alkali capture on sorbent materials is enhanced under pressure. The alkali sorption rate was observed to be enhanced in sorbents under test. Nykaenen et al. (1996) showed theoretically that the gaseous environment
may significantly effect the overall emission values of the contaminates. It was shown that the addition of calcium carbonate (CaCO$_3$) plays an important role in the behaviour of alkali compounds in combustion. Calcium increases the amount of gaseous compounds by decreasing the amount of alkali sulphates (Na$_2$SO$_4$). The implication is that improvements in desulphurisation results in problems for alkali removal. This observation and implication was experimentally confirmed by Steffin (1999).

### 1.2 COAL-FIRED GAS TURBINES

Inherent in all coal-based advanced combined cycle power generation systems is the need for gas turbines fired on coal-derived fuel-gas. This provides an alternative route for improved efficiency using the Brayton Cycle.
However, impurities in the fuel-gas can damage turbine components by a combination of corrosion, erosion and deposition. The problems related to corrosion, erosion and deposition are dependent upon temperature (Meadowcraft and Stringer, 1987), particle size of ash (Hosegood, 1963; Meadowcraft and Stringer, 1987) and the compounds in the reducing and oxidising environment (Thambimuthu, 1993; Stringer and Banerjee, 1991). The implications of ‘corrosion, erosion and deposition’ are increased maintenance costs and/or losses in cycle efficiency. Therefore small improvements in this area of operation would lead to considerable savings in cost and improved technology applications for coal.

1.2.1 Corrosion

Major gas turbine tests showed that hot gases generated in PFBC pilot plants resulted in severe erosion phenomena rather than corrosion (Meadowcraft and Stringer, 1987). This may imply that erosion is more significant for the lifetime of a gas turbine than corrosion. However, cascade tests carried out by General Electric gave severe corrosion and erosion results for the alloy material IN 671 (50% Cr, 50% Ni), in PFBC off gas. Basically, corrosion of the heat-resisting material occurs when the original surface protection layer is damaged by chemical reaction through a second oxidant, usually sulphur. Sulphur diffuses through the protective oxide and reacts with the element in the alloy responsible for forming the oxide. Eventually, the dissolution (‘fluxing’) of the surface protection layer cannot be stopped, and a relatively rapid, non-protective oxidation follows. In a molten salt attack, a molten salt deposit forms on the surface of the alloy and dissolution of the protective layer occurs. The dissolution of the protective layer may be followed by a direct dissolution of the metal.

Stringer (1985, 1987) studied extensively the forms of corrosion and corrosion mechanism of the materials used in gas turbine hot components for the oxidising environment. Corrosion and corrosion mechanisms have been associated with the occurrence of alkali sulphates and other fuel impurities. Hancock (1987) and Meadowcraft and Stringer (1987) reported corrosion for sodium chloride and sulphate-chloride mixtures, respectively.
Corrosion By Alkali-Sulphates

Corrosion resulting from the presence of sodium sulphate ($\text{Na}_2\text{SO}_4$) has been extensively described by Stringer (1985). Generally neutral alkali sulphates do not lead to corrosion, but a difference from stoichiometry, on either the alkali-rich (basic salt) or sulphate rich (acidic salt) does. Two different forms of attack have been identified, a high temperature form (Types I, 850-950°C) and a low temperature form (Type II, 650-750°C).

Type I hot corrosion results from a fluxing process where modification of the sodium sulphate deposit chemistry permits ingress of sulphur into the underlying metal. This process leads to localised depletion of the protective elements and a progressive internal attack. The characteristics of this type of hot corrosion are: a porous oxide scale, an irregular metal interface and internal attack with metal sulphides.

With Type II corrosion the partial pressure of sulphur trioxide ($\text{SO}_3$) is as relevant as sodium sulphate in maintaining a low-melting deposit. This deposit readily fluxes the surface oxide. Type II hot corrosion is characterised by a pitting attack, with little or no internal sulphidation or alloy depletion. Thermodynamics favours the occurrence of sulphur trioxide within the temperature window 650-750°C.

In general, it appears that high chromium levels in the alloys are of benefit in combating corrosion. Cobalt-based coatings appear to be sensitive to Type II corrosion. Nickelbase-base alloys are favoured for rotating elements, whereas those of cobalt for static elements. Different coating compositions in the turbomachinery elements are used in order to maintain sufficient strength, toughness and corrosion behaviour at the elevated temperatures. These requirements also lead to different coating techniques such as diffusion, overlay and thermalbarrier coating (Radcliff, 1987).

Corrosion By Alkali Chlorides

Corrosion has been linked to the chlorine content in coal although some users of high chlorine coal do not report any corrosion (Stringer and Banerjee, 1991). Chlorine is the agent which leads to alkali chlorides ($\text{NaCl}$, $\text{KCl}$) during gasification and combustion. Stringer and
Banerjee (1991) observed accelerated corrosion rates on alloys when exposed to coals of different chlorine content. It was not clear whether the increased corrosivity resulted from either the chlorine content of the coal or other factors such as ash composition. Other tests by Sethi (1991) showed that this pattern does not show up in the absence of condensation on the probes. However, it is generally agreed that chlorine can significantly influence high temperature corrosion reactions (Hancock, 1987). When coal is burned or gasified, chlorine is released as HCl. The HCl then reacts with the sodium bound in the organic lattice to release alkali chlorides (Thambimuthu, 1993). Under the reducing conditions at temperatures higher than 600°C alkali species remain mainly in the vapor phase as chlorides. The much higher volatility of sodium in comparison to potassium reflects the higher sodium chloride contents in the gasifiers and combustors. However, the chlorides in turn can then produce a breakdown of the normally protective alloy.

**Corrosion By Sulphate-Chloride Mixtures**

Under reducing conditions the gaseous environment is richer in alkali (8.6ppmw NaCl) than under oxidising conditions (1.6ppmw NaCl). This reduced alkali concentration under combustion conditions is caused by reactions of volatile alkali chlorides with sulphur to give sulphates and hydrogen chloride (Ferguson, 1980):

\[
2\text{NaCl}_\text{(g)} + \text{SO}_3\text{(g)} + \text{H}_2\text{O}_\text{(g)} \leftrightarrow \text{Na}_2\text{SO}_4\text{(s)} + 2\text{HCl}_\text{(g)} \quad \text{and} \quad [3]
\]

\[
2\text{NaCl}_\text{(g)} + \text{H}_2\text{O}_\text{(g)} + \text{SO}_2\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)} \leftrightarrow \text{Na}_2\text{SO}_4\text{(s)} + 2\text{HCl}_\text{(g)}. \quad [4]
\]

If the equilibrium concentration of Na₂SO₄ in the combustion gas exceeds the saturation vapour pressure at the operating temperature (730-930°C) for the first stage stator and rotor blades, condensation and deposition of Na₂SO₄ can take place and, at the highest metal temperatures, the deposit will be molten (Cutler, 1987).

The corrosion potential then depends on the rate of deposition of alkali salt, and, of the alkali content of the deposits, that are not physically adsorbed or chemically ‘gettered’ by the ash particles. Corrosion of a nickel-base superalloy MA-6000 in presence of sodium...
sulphate/sodium chloride mixtures showed that the incorporation of sodium chloride remarkably accelerated the oxidation of the alloy (Sharma and Prakash, 1996). Many PFBC cascade and pilot plant experiments have been reported that the release of alkali is very dependent on combustion temperature, and that a reduction of alkali can mean the difference between catastrophic metal loss rates and acceptable corrosion on gas turbine blades. In cascade tests at the PFBC plant at Grimethorpe, bed temperatures up to 940°C led to significant corrosion, whereas with an 850°C maximum bed temperature corrosion was not detectable (uncooled cascade). Such a marked reduction with temperature is in accord with the predictions of Spacil and Luthra (1982) who calculated the alkali level in a combustion off-gas as a function of temperature and chlorine in coal. Other calculations showed that at 900°C alkali concentrations are in the range of 1-10ppmw (Scandrett and Clift, 1984b; Singh et al, 1986), this value is far above the recommended turbine target of 24ppbw.

In the case of a combustion temperature of less than 900°C, a significant fraction of the SO$_x$ can be present as SO$_3$ ($\geq$ 10%), the fraction increasing as the temperature is reduced and the pressure increases. Even with dolomite/limestone in the bed to absorb the sulphur emissions, SO$_3$ levels of 10-50ppm have been reported in a PFBC. This will allow the formation of low melting point sulphates and the occurrence of low temperature Type II corrosion. Indeed, as there will always be a temperature drop between combustor and turbine, Type II corrosion might be expected to be more prevalent than Type I hot corrosion (Meadowercoft and Stringer, 1987). Under gasification, the reducing conditions favour the formation of H$_2$S.

Corrosion By Other Species
In addition to chlorine (Cl$_2$); fluorine (F$_2$), bromine (Br$_2$) and iodine (I$_2$) can be found in coal. Fluorine occurs as the second most abundant halogen and may form hydrofluoric acid. The thermochemical and corrosive properties of alkali fluorides are as yet an un-studied phenomenon.

Corrosion Control
Under oxidising condition, equilibrium between chlorides and sulphur dioxide is quickly established through a series of reactions summarised in Equation 4. At temperatures above
830°C, alkali corrosion properties increase, but a possible means of alkali corrosion control is through the reaction with aluminosilicates \((\text{Al}_2\text{O}_3 \cdot x\text{SiO}_2)\) represented by the Equation 5:

\[
2\text{NaCl}_\text{(s)} + H_2\text{O}_\text{(s)} + \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \leftrightarrow \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot 2\text{HCl}_\text{(g)} + 2\text{HCl}_\text{(g)}
\] [5]

Reaction products such as albite \((\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2)\) and HCl are formed.

1.2.2 Erosion and Deposition and Corrosion-Erosion-Deposition Interactions

In a gas turbine, erosion and deposition occur when particulates are transported to the stators and rotor. Inertial impaction is significant for erosive damage, while stickiness of ash and condensation of alkali vapours cause deposit damage.

**Erosion and Erosion Control**

The presence of particles in coal-based processes is a major cause of problems for gas turbines. Smaller particles will tend to follow the streamlines around a blade, but for larger particles, the damage per unit weight of particles increases rapidly with particle size up to about 20\(\mu\)m diameter. Wenglarz et al (1981) and Wenglarz and Tabakoff (1982) predicted expected lifetimes of gas turbines for the type of limiting distribution quoted in Table 2.

<table>
<thead>
<tr>
<th>Concentration [ppm]</th>
<th>Diameter [(\mu)m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;0.1</td>
<td>&gt;20</td>
</tr>
<tr>
<td>&lt;1</td>
<td>10-20</td>
</tr>
<tr>
<td>&lt;10</td>
<td>4-10</td>
</tr>
</tbody>
</table>

Table 2: Turbine Particle Size Limits Proposed by Electric Power Research Institute Predicted for Blade Lifetimes similar to that of the Gas Turbine (Meadowcroft and Stringer, 1987).

Details of unit operations for the recovery of particulates from gases at high temperature and pressure are reviewed in an IEA Coal Research report by Thambimuthu (1993). A relatively
large number of devices are available for use as primary, secondary and tertiary separators or filters in the high temperature process environment of gasification and combustion systems.

The use of high efficiency cyclones, as primary and secondary clean-up, can remove particles down to 5-10μm (Wheeldon et al, 1986). For advanced power generation cycles, further reduction, down to the limits proposed by the turbine manufactures, requires a tertiary stage. Rigid media (candle filters) and moving granular filters were considered promising as tertiary particulate filters, but during trials, the operating characteristics of candle filters raised doubts about their long-term mechanical performance (Stringer and Banerjee, 1991). Bossart et al (1990) showed that a combination of a single stage cyclone separator and a cross-flow barrier or moving bed filter, resulted in outlet particle loadings well below the more stringent particulate control levels specified for gas turbines. Westinghouse (Siemens-Westinghouse, since 1999) developed an integrated low emission clean-up system for direct coal-fired turbines up to 930°C (Newby et al, 1995). The concept of this filter is based on a ceramic filter vessel with the injection of sulphur sorbents, alkali sorbent, and selected deposit-modifying additives (iron) that produce a filter cake on the filter elements that is easily removed by pulsed cleaning. Granular bed filters, however, offer dust filtration with the separation of trace contaminants. This may lead to their increased use instead of rigid filters. In addition, the reducing atmosphere with more fines and alkali vapours favours this separation technique over rigid filters (Thambimuthu, 1993).

Deposition and Deposition Control
Deposition leads to fouling, and can also produce a local environment conducive to accelerated corrosion. For fouling to occur deposits have to be either sticky or certain components must act as a glue. Obviously, if the ash is initially partially or fully molten it will solidify on, and stick to, a cooler surface. However deposits can also be formed by condensation of vapours such as alkali sulphates. In PFBC gas with dolomite/limestone in the bed, calcium sulphate is the major deposit on the turbine blades. In practice, this also leads to deterioration in aerodynamic efficiency and hence loss of power from the turbine. As a consequence of deposition, washing or ‘nutshelling’ is necessary. This may have the effect of
increasing corrosion by allowing the corrosive species to be replenished (Meadowcraft and Stringer, 1987).

Corrosion-Erosion-Deposition Interactions

The interaction of corrosion with erosion can cause greatly increased corrosion. The synergistic effect of corrosion and erosion is shown in Figure 9 (Barkalow et al, 1980, Barkalow, 1984), which confirms the need to remove both particulates and vapour phase contaminants in order to significantly reduce damage to equipment.

![Diagram of corrosion-erosion interactions]

Figure 9: High Velocity Erosion-Corrosion Interactions (Meadowcraft and Stringer, 1987).

1.3 HOT GAS CLEANING AND MULTICONTAMINANT CONTROL

Hot gas cleaning for ‘contaminant removal for alkali salts, heavy metals and dust’ has been a subject of research for over twenty years and is still of concern. In the long term an integrated hot gas clean up concept with multicontaminant removal is required to achieve the goals of clean coal technology in the 21st century (DOE, 1999a).

Hot gas cleaning research is going on in areas in order to raise efficiencies by increased gas turbine inlet temperatures and minimising particulates and alkalis as the major contaminants.
Simultaneous removal of both solid particulate and gaseous contaminants has been reported by Turk et al (1996) and Rieger et al (1999). The removal of particulate contaminants has been shown an important requirement for the safe operation of turbomachinery by Seville et al (1996).

For environmental emissions, the major pollutants currently subjected to mandatory controls are gaseous contaminants, SO$_2$ and NO$_x$. Multicontaminant removal will be required exceeding the environmental emission standards for particulates, SO$_2$ and others. Sulphur removal research using regenerable metal oxide sorbents was shown to be effective but dependent upon attrition and reactivity of the sorbent (e.g. Research Triangle Institute).

1.4 SUMMARY

Advanced coal-based power generation technology offers the possibility to improve thermal efficiency, to generate electricity at minimum economic costs, and to comply with current and expected environmental standards.

In the coal gasification and combustion process coal is converted into a hot flue gas which contains particulates and gaseous compounds. In advanced combined cycle coal-based power generation plants this hot flue gas is used to fire a gas turbine which can be adversely affected by the dust and alkali loading to which it is exposed. High dust and alkali loads also limit the thermal efficiency achieved. Alkali compounds at high temperatures reportedly damage turbomachinery components by the combined effects of corrosion, erosion and deposition. This problem essentially restricts the use of gas turbines in the higher temperature range, unless an effective means of alkali removal is integrated into the hot gas cleaning system. The recommended turbine inlet level of gaseous alkali is currently 24ppbw. Most plants being developed at present operate at temperatures below 600°C where alkali vapour is not present. However, this leads to a decrease in the thermal efficiency of the plant. At higher temperatures a more comprehensive method of hot gas cleanup and contaminant control will be required.
CHAPTER 2

LITERATURE SURVEY

2.1 INTRODUCTION

Thermal efficiency in advanced coal based power generation plants can be increased by the integration of gas turbines with conventional steam turbines, but high levels of dust and vapour phase alkali, currently limit the application of this technology. At temperatures above 600°C alkali compounds in the vapour phase, damage turbomachinery components and hot-gas cleaning processes are required. Several research projects have been initiated to study the capture of alkali vapour from the hot gases; most concentrating on removal by solid sorbents in a fixed bed configuration (Table 3). In general, it has been reported that alkali removal at high temperature is best achieved by reaction with 'getters' and both experimental and theoretical work has been carried out to investigate these materials.

The initial release of alkali metals from coal has been the subject of considerable debate, but the general trend is that gaseous alkali content increases with increasing temperature, decreasing pressure, increasing chlorine content and decreasing sulphur content. Assumptions used to explain the initial release of sodium species are mainly connected with the presence of chlorine in coal. In the presence of chlorine the rapidly released HCl reacts with the sodium bound in the organic coal to release sodium chloride (NaCl). The release of NaCl by reaction or by direct evaporation also enhances the release of potassium (K), which is mainly present in the aluminosilicate clay minerals (Thambimuthu, 1993, Raask, 1985a). However, other studies suggest that the initial release of sodium (Na), in the absence of chlorine, is in the form of sodium hydroxide (NaOH) at high temperatures or as sodium oxide (Na₂O) at temperatures below 1037°C (Srinivasachar et al, 1990).

Under fluidised bed combustion flue gas conditions it was found that the alkali vapour concentration is a function of temperature and chlorine content. Lee et al (1984) summarised the data by a plot of the alkali (Na+K) vapour concentration in parts per million by weight as a
<table>
<thead>
<tr>
<th>Year</th>
<th>Sorbent/Temperature/Exposure time Short or Long</th>
<th>Inert/SFG</th>
<th>Gaseous Environment</th>
<th>Mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>1980 Lee &amp; Johnson</td>
<td>Kaolin/800-880°C/short</td>
<td>SFG¹</td>
<td>H₂O  0.018%</td>
<td>Chemical Reaction</td>
</tr>
<tr>
<td>1983 Mulik et al</td>
<td>Emathite/850°C/short</td>
<td>Ar</td>
<td>HCl [ppmv] 80</td>
<td>Physical Adsorption</td>
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<tr>
<td></td>
<td>SFG²  4.6%</td>
<td>N₂  80</td>
<td>NaCl [ppmv] 80</td>
<td></td>
</tr>
<tr>
<td>1984 Luthra &amp; LeBlanc</td>
<td>Activated Bauxite/800°C-900°C/long</td>
<td>Ar</td>
<td>HCl [ppmv] 0-312</td>
<td>Physical Condensation</td>
</tr>
<tr>
<td>1985 Lee and Myles</td>
<td>Activated Bauxite/800°C/long</td>
<td>SFG³  4.5%</td>
<td>HCl 4-12</td>
<td>Chemical Fixation</td>
</tr>
<tr>
<td>1986 Bachovechin et al</td>
<td>Emathite/775°C-900°C/long</td>
<td>N₂  2-6%</td>
<td>NaCl 6-12</td>
<td>Standard Reaction</td>
</tr>
<tr>
<td>1988b Punjak</td>
<td>Kaolin/800°C/long</td>
<td>N₂  2</td>
<td>HCl [ppmv] 100-260</td>
<td>Physical Condensation</td>
</tr>
<tr>
<td></td>
<td>Kaolin/800°C/long</td>
<td>SFG⁴  2</td>
<td>NaCl 100-260</td>
<td>Standard Reaction, Irreversible</td>
</tr>
<tr>
<td>1990b Uböri et al</td>
<td>Kaolin/800°C/long</td>
<td>SFG⁴  2</td>
<td>HCl 230</td>
<td>Adsorption &amp; Reaction</td>
</tr>
<tr>
<td></td>
<td>Emathite/800°C/long</td>
<td>N₂  2-6%</td>
<td>NaCl 150</td>
<td>Adsorption &amp; Reaction</td>
</tr>
<tr>
<td>1990 McLaughlin</td>
<td>Calcium Montmorillonite/827°C-927°C/long</td>
<td>N₂  5%</td>
<td>HCl [ppmv] 55-160</td>
<td>Strong Bonding</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N₂  5%</td>
<td>NaCl 40</td>
<td>Reaction, Reversible</td>
</tr>
<tr>
<td>1996 Chrysoholdou</td>
<td>Calcium Montmorillonite/Kaolin/650°C/200hours/600hours</td>
<td>N₂  6%</td>
<td>HCl 2.2</td>
<td>Physiosorption</td>
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<td></td>
<td>N₂  6%</td>
<td>NaCl 2.2</td>
<td>Standard Reaction, Reversible</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N₂  5%</td>
<td>NaCl 2.2</td>
<td>Standard Reactions, Reversible</td>
</tr>
<tr>
<td>1996a Turk et al</td>
<td>Kaolin/varied/short</td>
<td>SFG⁵  3%</td>
<td>HCl 132 +10% wt.</td>
<td>Mechanism and Effect of HCl</td>
</tr>
<tr>
<td></td>
<td>Emathite/varied/short</td>
<td>SFG⁶  3%</td>
<td>NaCl +10% wt.</td>
<td></td>
</tr>
<tr>
<td>1999 Steffin</td>
<td>Kaolin/varied/short</td>
<td>N₂  20%</td>
<td>HCl +20% wt.</td>
<td>Reactions producing HCl</td>
</tr>
<tr>
<td></td>
<td>Kaolin/varied/short</td>
<td>N₂  20%</td>
<td>NaCl +20% wt.</td>
<td>Reaction producing Chlorine</td>
</tr>
</tbody>
</table>

Table 3: Removal of Alkali Vapour by Solid Sorbents.
function of the gas temperature, see Figure 10. The measured alkali vapour concentration in PFBC flue gas is generally in the order 0.1 to 10ppmw. The basic findings, regarding the effects of chlorine content and temperature, are in agreement with the thermodynamic predications of Spacil and Luthra (1982). For the corresponding gasification environment Mojtabadi et al (1987) indicated that volatile species could persist as vapour through to the combustion stage of the gas turbine.

Studies by Mullik et al (1983), Scandrett and Clift (1984a, 1984b) and Singh et al (1986) appear to confirm the finding by Sinha et al (1987) that the alkali species remain mainly in the vapour phase as chlorides, although some also suggest oxides at the higher temperature. Thambimuthu (1993) concluded that the total vapour phase alkali concentration in the
gasification environment is at least one to three orders of magnitude higher than the proposed alkali contaminant control of 24ppbw by Bossart et al (1990) and Lee and Myles (1987).

Hodges and Richards (1989) studied the mode of occurrence of sodium, and other species, in the solid combustion products of UK coals by their water solubility. The coal was investigated under low temperature ashing. Water solubilities of the sodium compounds in the solid combustion products varied widely. This was thought to be indicative of the extent of reaction between coal sodium and the clay minerals, especially kaolinite.

Hosegood (1963) investigated the reactions of sodium compounds on UK ash surfaces of combusted pulverised coal. Two ashes were selected and classified into five particle size fractions. Each fraction was chemically analysed to determine water soluble, water insoluble (HCl soluble) and acid insoluble constituents. It was found that the ‘water soluble fraction of potassium, sodium, silicon (Si) and aluminium (Al) as oxides increased with smaller particle size fraction of two investigated ashes’.

Helble et al (1992) reported from ash analysis of low rank coal with kaolinite that ‘sodium undergoes a capture reaction, when silicon is present. Sodium is found primarily as nepheline (Na₂O · Al₂O₃ · 2SiO₂), in particles larger than 2μm. However, in particles smaller than 2μm sodium can exist as a thin external layer, caused by condensation from the vapour, while particles less than 0.43μm consist of a pure sodium (sulphate) fume’.

In a Technical Coal Research study (1992), coal ash analysis indicated that: there is a significant interaction between sodium and clay constituents which renders sodium water insoluble; that the addition of kaolinite to coal prior to ashing can significantly reduce the proportion of soluble sodium in the resultant high temperature ash; and that calcium and magnesium (Mg) containing mineralogical components will serve to decrease the portion of sodium which can react with kaolinite to form insoluble sodium aluminosilicates. The initiation of reaction could be due to particle size distribution and association of the mineralogical components. Kaolinite addition decreased the recovery of water soluble sodium in ash compared with the original coal. Therefore, kaolinite addition would be expected to have a beneficial effect by reducing fouling and corrosion. In contrast, calcite (CaCO₃) and magnesia
both served to increase the recovery of water soluble sodium which would increase hot corrosion.

Jackson and Ward (1956) postulated an exchange reaction to explain the frequent formation of potassium deposits when sodium chloride is present in the combustion chamber. The raw coal contains virtually all the potassium in a relatively non-volatile form as silicates. It was believed that the vapour pressures of the species were responsible for this exchange mechanism. The vapour pressures of potassium chloride and hydroxide are higher than those of the corresponding sodium compounds. Laboratory investigations by Jackson and Duffin (1963) showed sodium enrichment in a glazed surface layer of an aluminous porcelain furnace. A significant amount of KCl was collected on a cooled target. Substitution of the aluminous porcelain furnace eliminated the potassium deposit formation. Jackson (1963) related this finding to the general observation that the ‘roof’ material contains more potassium than the ‘floor’ and that on combustion, a greater portion of the alkali are retained by the ‘floor’ material.

Schulle et al (1999) showed that crushing the ash increases the capture ratio of sodium under PFBC conditions (800-850°C, 15bar). A vibration mill, a planetary mill and a ball mill were used. As a result the surface area of the mechanically activated ashes was increased. The smaller ash particles with different compositions showed an increased alkali sorption activity.

Evans and Williams (1999) showed that the existence of calcium oxide may significantly affect the formation of alkali oxides. Lower sodium and potassium oxide concentrations were found in flyash when lime was used for gas clean-up.

In summary, high temperature operation of advanced coal-based power generation plants is significantly dependent upon research & development for removal of alkali vapour from hot gases. Under the combustion and gasification condition, the alkali vapour concentration is a function of temperature and is significantly dependent upon the chlorine content in coal. During gasification volatile chlorides persist as vapour. The capture of alkali by fly ash particles can be related to the existence of minerals identified in coal, although particle size may also be important in the alkali capture mechanism. There are some indications that with
aluminosilicate materials, exchange mechanisms can take place, in which sodium displaces potassium from the structure.

2.2 ALKALI REMOVAL BY SOLID SORBENTS

Alkali removal as part of the hot-gas cleanup system used in combined cycle power generation plants operating at temperatures above 600°C, is essential to protect gas turbine components. Solid sorbents are an attractive option in this respect. Aluminosilicate materials (kaolinite, calcium montmorillonite and emathlite) have been found to chemically immobilise alkali salt vapours in contrast to activated bauxite, an alumina material, which appears to physically adsorb alkali. Solid sorbents capable of capturing and holding alkali compounds from hot gas streams are known as 'getters'.

Lee and Johnson (1980) tested six commercially available materials as granular sorbents for use in granular bed filters for the removal of alkali compounds. A laboratory fixed-bed combustor was used. The tests were carried out at 870-880°C under atmospheric pressure using either air, or simulated flue gas (SFG) containing 3% O₂, 16% CO₂, 180ppm SO₂ and 80ppm NaCl. Diatomaceous earth (see below) and activated bauxite were found to be most promising sorbents. They concluded that the effectiveness of these sorbents is related to their internal surface, which is primarily contributed by small pores. By performing water-leaching tests on the exposed sorbents it was found that the prime capture mechanism of NaCl by activated bauxite was physical adsorption. The sorbent could be regenerated to some extent by water washing. Diatomaceous earth was found to capture sodium through the formation of water insoluble complexes, suggested to be sodium aluminosilicates. Kaolinite was found to remove NaCl from the gas by chemical reaction to form water insoluble products thus the reaction products are either acid soluble or acid insoluble.

Johnson and Lee (1981) proposed the following reaction equation for sorbents with high alumina (Al₂O₃) contents:

\[ 2\text{NaCl} + \text{H}_2\text{O} + \text{Al}_2\text{O}_3 \rightleftharpoons \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 + 2\text{HCl} \]
On the basis of thermodynamical calculations, reactions for ‘getters’ with vapour phase alkali chlorides were proposed by Mulik et al (1983) and Scandrett and Clift (1984a, 1984b). A sorbent with a high silica (SiO$_2$) content reacts with water vapour and NaCl to give reaction products such as sodium disilicate (Na$_2$O·2SiO$_2$), sodium metasilicate (Na$_2$O·SiO$_2$), and sodium orthosilicate (2Na$_2$O·SiO$_2$). They suggested that the following reaction equations occur:

$$4\text{NaCl}_g + \text{SiO}_2(s) + 2\text{H}_2\text{O}_l \rightleftharpoons 2\text{Na}_2\text{O} \cdot \text{SiO}_2(s) + 4\text{HCl}_g \quad [7]$$

$$2\text{NaCl}_g + \text{SiO}_2(s) + \text{H}_2\text{O}_l \rightleftharpoons \text{Na}_2\text{O} \cdot \text{SiO}_2(s) + 2\text{HCl}_g \quad [8]$$

$$2\text{NaCl}_g + 2\text{SiO}_2(s) + \text{H}_2\text{O}_l \rightleftharpoons \text{Na}_2\text{O} \cdot 2\text{SiO}_2(s) + 2\text{HCl}_g \quad [9]$$

Under equimolar proportions of chloride and silicate, the formation of sodium metasilicate is favoured rather than sodium orthosilicate. Considering the equilibrium conversions, a pure silica is possibly not a useful ‘getter’.

In the following case, the equilibrium conversion was estimated to exceed 99% at 727°C and still be above 95% at 927°C. Free silica promotes the reaction scheme together with water vapour and NaCl:

$$2\text{NaCl}_g + \text{Al}_2\text{O}_3 \cdot \text{SiO}_2(s) + 5\text{SiO}_2(s) + \text{H}_2\text{O}_l \xrightarrow{\text{HCl}} \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2(s) + 2\text{HCl}_g \quad [10]$$

Mulik et al (1983) presented a series of reactions leading to the equation shown. However, these equations also involve hydrogen chloride to achieve a reaction which also produces Na$_2$O·Al$_2$O$_3$·6SiO$_2$ (Albite). Under acid conditions, Na$_2$O·Al$_2$O$_3$·2SiO$_2$ (nepheline) is not easily formed as a reaction product. The thermodynamics favour the formation of Na$_2$O·Al$_2$O$_3$·6SiO$_2$. 

28
Mulik et al (1983) identified the potential use of aluminosilicate materials to simultaneously remove volatile alkalis and particulate matter during pressurised combustion and gasification of coal. Atomic Absorption Spectrometry (AAS), Electron Spectrometry for Surface Analysis (ESCA) and x-ray diffraction (XRD) were used to identify the forms occurring in the reacted getter material. Initially 20 sorbents were exposed to 80ppmv NaCl in argon at 850°C at 11atm using a bench scale reactor. Sodium content was determined by AAS after extraction from the pellet by a three-stage treatment; water soluble, acid soluble and acid insoluble.

Determination of the content of solution bound sodium using a water-leach includes sodium adsorbing through either physical adsorption of the alkali chloride along the pellet surface, sodium adsorbing through the attraction of the alkali chloride or/and sodium sorbed species in the alumina or aluminosilicate lattice that results from polarisation of the attacking molecule. Typical water soluble alkali reactions can be written as

\[
\text{NaCl}_{(g)} + \text{Al}_2\text{Si}_2\text{O}_5\text{(OH)}_4_{(s)} \rightarrow \text{Na(Cl)} - \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 2\text{H}_2\text{O}_{(g)} \quad [11]
\]

\[
\text{NaCl}_{(g)} + \text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}_{(g)} \rightarrow \text{Na(Cl)} - \text{Al}_2\text{O}_3 + 2\text{H}_2\text{O}_{(g)} \quad [12]
\]

In contrast, acid (HCl) soluble sodium leachates are proposed to result from substitutions of sodium or potassium between the hexagonal network of the silicon-oxygen tetrahedral and/or the aluminium-oxygen/hydroxide octahedral where water had initially been positioned. Displacement reactions may occur similarly within this sodium soluble leach. For example, the sodium or potassium cation may replace hydrogen in exposed hydroxyl groups while simultaneously substituting the chloride anion at an adjacent hydroxyl site. Mulik et al (1983) assumes remained hydroxyl groups in the aluminosilicate network. These reactions can be written in the following manner:

\[
2\text{NaCl}_{(g)} + \text{Al}_2\text{Si}_2\text{O}_5\text{(OH)}_4_{(s)} \rightarrow \text{Al}_2\text{Si}_7\text{O}_{17}\text{(ONa}_2\text{)}_{(s)} + 2\text{HCl}_{(g)} + \text{H}_2\text{O}_{(g)} \quad [13]
\]
Similar reactions can also be written for potassium.

The hydrogen fluoride (HF) insoluble alkali content should specify aluminosilicate reaction complexes (Mulik et al., 1983). The reactions are proposed to result through the formation of a strong alumina or aluminosilicate bonds within the amorphous lattice or through a mechanism that collapses the lattice, entrapping the alkali into a non-releasable, cakelike structure. These reactions can be written as:

\[
\begin{align*}
\text{Na(Cl)}(s) + \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4(s) & \rightarrow \quad \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2(s) + 2\text{HCl}(g) + 2\text{Al}_2\text{O}_3(s) + 5\text{H}_2\text{O}(g) \quad [14] \\
4\text{NaCl}(s) + \text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}(s) & \rightarrow \quad 2\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3(\text{s}) + 4\text{HCl}(g) \quad [15] \\
2\text{NaCl}(g) + \text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}(s) & \rightarrow \quad \text{Al}_2\text{O}_3(\text{Na}_2\text{O},\text{H}_2\text{O})(\text{s}) + 2\text{HCl}(g) \quad [16]
\end{align*}
\]

It was concluded that for a material to be considered an effective getter, chemical reactions must occur to remove sodium from the vapour phase and sodium must be retained in either the acid soluble or insoluble form. Initially extraction of sodium from pellets (sorbent screening) was simplified by using a two stage leaching method. Subsequently, the leaching method was extended for some pellets under test. Extracted sodium from activated bauxite and emathlite indicated that the concentration of sodium in the water soluble, acid soluble and insoluble solution depends upon exposure time. Using a short-term exposure, solution bound sodium was found to be water-soluble and acid insoluble. In contrast, a long term exposure led to increased sodium contents in the acid leach (emathlite). Flue gases containing hydrogen chloride and hydrogen sulphide had an inhibitory effect on the sodium sorption process. In addition, it was found that sorption gettering in activated bauxite increases with a higher content of hematite (Fe$_2$O$_3$).
Following these tests a double balance thermogravimetric system was used to identify the most promising sorbent. In this apparatus a suspension system of two microbalances allowed weight changes to be measured of the salt remaining and the sorbent. Upwards flowing nitrogen as carrier gas was used.

Six getters were selected with a gettering capacity significantly better than that of activated bauxite, see Table 4. Emathlite and Ebony Novacite were identified as the most promising sorbents, however, Ebony Novacite with a small particle size was eliminated from further consideration (background potassium and residual carbon, costs). Additional tests showed that emathlite provides a high capacity but a low sorption rate. The tests were further extended to atmospheres containing water vapour. Sorption results were found to be affected by salt accumulation not linked to the sorption process. In some cases 50% discrepancies between expected and achieved sorption results were determined.

<table>
<thead>
<tr>
<th>Promising Sorbents</th>
<th>Composition of Getter Materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated Bauxite</td>
<td>7.0% SiO₂, 88.3% Al₂O₃, 1.2% Fe₂O₃, 3.0% TiO₂</td>
</tr>
<tr>
<td>Vansil</td>
<td>50.2% SiO₂, 0.21% Al₂O₃, 0.15% Fe₂O₃, 1.86% MgO</td>
</tr>
<tr>
<td>Novacite</td>
<td>99.12% SiO₂, 0.61% Al₂O₃, 0.04% Fe₂O₃, 0.15% TiO₂</td>
</tr>
<tr>
<td>Ebony Novacite</td>
<td>63.15% SiO₂, 19.16% Al₂O₃, 2.29% Fe₂O₃, 1.8% TiO₂, 0.15% MgO, 0.13% S, 3.24% C, 0.25% CaO</td>
</tr>
<tr>
<td>Zeolite</td>
<td>35% SiO₂, 55% Al₂O₃, 2.29% Fe₂O₃, 0.5% Na₂O</td>
</tr>
<tr>
<td>Diatomaceous Earth</td>
<td>92% SiO₂, 5% Al₂O₃</td>
</tr>
<tr>
<td>Emathlite</td>
<td>70.12% SiO₂, 13.29% Al₂O₃, 3.2% Fe₂O₃, 0.36% TiO₂, 2.47% MgO, 4.84% CaO, 0.1% Na₂O, 1.13% K₂O</td>
</tr>
</tbody>
</table>

Table 4: Promising Sorbent Material (Mulik et al, 1983).

In another study, Lee and Myles (1986) showed that the adsorption of alkali by activated bauxite was by physical adsorption and chemical fixation. Chemical fixation becomes dominant in the presence of sufficient water. In addition, activated bauxite captured sodium primarily as a condensed sodium sulphate, formed by the reaction of NaCl with SO₂. Sodium sulphate is water soluble and greater than 80% of the captured sodium was removed by water washing.
The residual sodium is believed to be present as an insoluble sodium aluminosilicate complex, formed through a gas-solid reaction of NaCl with clay impurities in the bauxite. The experiments were performed at 800°C under pressurised conditions (10 atm) and a gas composition of 3% O₂, 16% CO₂, 4.5% H₂O, 400 ppm SO₂, and up to 12 ppm NaCl.

Luthra and LeBlanc (1984) investigated the adsorption and desorption of alkali vapours by activated bauxite across a temperature range of 800-900°C. Sodium capture by adsorption and subsequently desorption was shown to be reversible in a dry argon atmosphere. The kinetics were found to be limited by transport through the pores in the adsorbent. The results showed that physical adsorption can be described by a Brunauer-Emmett-Teller (BET) isotherm. The overall rate of physical adsorption is very slow, limited by intraparticle diffusion. The adsorbates, NaCl and KCl, are compact diatomic molecules with large electric dipole moments (8.5 and 10.5 D for NaCl and KCl, respectively). Electrostatic interactions between these molecules are responsible for the large heats of vapourisation of the corresponding salts (185.9 and 179.3 kJ/mol at 800°C). In a similar way, their electrostatic, purely physical interactions with the surfaces of ionic solids such as Al₂O₃ can lead to unusually large adsorption energies and, thus, to physical adsorption on these solids at unusually high temperatures. They concluded, from their alkali adsorption studies in argon by activated bauxite and alumina at temperatures between 800°C and 900°C, that submicron smoke of alumina could be injected into a flue gas stream. The smoke would capture the particles and they would be small enough to not harm the turbomachinery. Luthra and LeBlanc used a Cahn microbalance for their adsorption experiments. The adsorbent specimen was suspended from the microbalance inside a quartz reaction tube. Argon served as carrier gas for alkali vapour, the salt was fixed in a bed at the lower end of the reaction tube.

Bachovchin et al. (1986) studied the alkali absorption of emathlite. It was suggested that the absorption reaction mechanism is due to ionisation and reaction. Potassium is simultaneously evolved from emathlite during sodium absorption. Potassium is not completely released prior to sodium absorption. Direct ionic exchange of potassium for sodium is not the mode of absorption in the initial stage of the reaction, rather it appears that transformations in the lattice are responsible for the formation of sodium silicate glass complexes. It was proposed that this arose through changes in the state of silicon in the aluminosilicate lattice. It was also
suggested that the number of vacancies in the lattice can increase with extended exposure time. Figure 11 shows the proposed reaction mechanism as a function of time. Water vapour may prime the lattice for sodium absorption. Water vapour in the gas, above a certain level, seemed to have no further effect on the alkali sorption kinetics. The alkali sorption kinetics on extruded emathlite pellets were found to depend on diffusion of sodium across the product glass layer.

Figure 11: Sorption Mechanism Proposed by Bachovchin et al (1986).

Punjak (1988a), Punjak and Shadman (1988b) and Punjak et al (1989) studied the kinetics and mechanism of adsorption of NaCl (50-230ppmv) by kaolinite, emathlite and bauxite under both nitrogen and simulated flue gas conditions (SFG, 15% CO₂, 2% H₂O, 3% O₂, 80% nitrogen) at a temperature of 800°C. The kinetics and mechanism of alkali sorption were found to depend on the gaseous atmosphere. The experiments performed showed that the maximum weight gain observed for kaolinite, was 5.2% under dry nitrogen and 26.6% under...
SFG conditions. The dependence of capacity on the gaseous environment, implied a difference between the mechanisms of adsorption under these two conditions.

It was believed that the mechanisms by which alkali is incorporated in kaolinite under nitrogen and SFG conditions can be different. In contrast to the SFG experiments, auger spectra revealed the presence of chlorine and sodium when treated in nitrogen. This was believed to indicate that, under a nitrogen environment, both sodium and chlorine can be retained. The system used in this work comprised a microbalance, a quartz reactor with inlets and outlets to maintain a controlled gas composition, a movable furnace and analysers for determining the composition of gaseous products. Sorbent flakcs were suspended from the microbalance directly above the alkali source which was placed in the bottom of the quartz reactor. The SFG was passed over the alkali source to vaporise and transport it to the sorbent.

Uberoi (1990a) and Uberoi et al (1990b) studied the effect of temperature on the kinetics and mechanism of the alkali sorption in kaolinite, emathlite and bauxite under simulated flue gas conditions using the same system at a temperature range of 800-1000°C. Under the SFG condition (15% CO$_2$, 2% H$_2$O, 3% O$_2$, 80% nitrogen), the aluminosilicate with the higher silicate content (emathlite) reacted to form albite at 800°C. At the higher temperature (1000°C), the reaction product albite was not found. XRD studies on saturated bauxite indicated the formation of nepheline and carnegieite$^1$ (polymorph of nepheline). Kaolinite and emathlite reacted irreversibly in the SFG atmosphere without HCl, however for bauxite 10% of the total weight was due to physisorption. It was concluded that the overall process of alkali sorption is rather a combination of physical and chemical processes, which depend upon the temperature and sorbent chemistry. Uberoi and Punjak used porous aluminosilicate disks (flake thickness 0.5mm) to demonstrate that reaction and condensation of sodium occurs simultaneously, and proposed a simultaneous reaction and condensation model for metakaolinite:

$$3\text{NaCl}_\text{(g)} + 2\text{H}_2\text{O}_\text{(g)} + \text{Metakaolinite}_\text{(s)} \rightarrow \text{Reaction Products}_\text{(g)} + \text{NaCl}_\text{(s)} + \text{2HCl}_\text{(s)}.$$  \hspace{1cm} [18]

$^1$In carnegieite the sodium is tetrahedrally coordinated whereas in nepheline the sodium cation is octahedrally coordinated, Falcone and Schubert (1986).
Under the simulated flue gas condition, the final reaction products formed during the alkali sorption process on kaolinite do not change. At 800°C and 1000°C, the reaction products were found to be nepheline and carnegieite. At the higher temperatures (1000°C), nepheline is the favoured reaction product.

McLaughlin (1990) initially used a Simultaneous Thermal Analyser (STA) to screen a range of materials as potential ‘getters’ (kaolin, emathlite, calcium montmorillonite, activated bauxite and sillimanite). Calcium montmorillonite and kaolin were selected for further investigation. Subsequent tests were conducted in a fixed bed reactor at atmospheric pressure at temperatures of 827°C and 927°C using 0.43-0.5 mm pan pelletised pellets as the sorption medium. The effect of an increasing HCl concentration on the sorption capacity of the pellets exposed to an inlet concentration of 40ppmv NaCl and 5% vol water vapour in a nitrogen stream, was determined. In the absence of HCl, the HF soluble sodium content increases as the water vapour concentration in the gas is increased from 0 to 5% vol. At the higher water vapour concentration, the saturation capacity of the solid increased to 12.6% wt. of sodium. With added HCl, there is a substantial reduction in saturation capacity. It was concluded that alkali breakthrough in the sorbent bed occurs sooner as the concentration of HCl in the gas phase increases. For the tests undertaken with a 160ppmv inlet HCl concentration, it was found that the saturation capacity of the sorbent pellets was reduced to 5.5% wt. of sodium. From these and other tests, it was found that increasing the HCl concentration had an inhibitory influence on the NaCl adsorption reaction. Sodium capture was found to be reversible (≈10,000ppmv, 0.02% water at 1,018°C). A two-reaction scheme was proposed based on the assumption that the rate of one reaction is sensitive to HCl concentration whereas the rate of the other was virtually independent of it.

Reaction 1 (non-acid) and 2 (high-acid):

\[ \text{NaCl}_{(s)} + \frac{1}{2} \text{H}_2\text{O}_{(s)} + b_{1\text{sor}bent} \leftrightarrow \text{Product}_{1,2} + \text{HCl}_{(s)} \]  \[19\]

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Calcium montmorillonite</th>
</tr>
</thead>
<tbody>
<tr>
<td>( b_{1,2} )</td>
<td>Stoichiometric coefficient of the sorbent [-]</td>
</tr>
<tr>
<td>Product 1,2</td>
<td>1, Nepheline ( \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2(s) ); 2, Albite ( \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2(s) )</td>
</tr>
</tbody>
</table>
On the basis of the two reaction scheme, McLaughlin developed an alkali sorption model for calcium montmorillonite, the ‘Two Reaction Model’, which links the convective mass balances of the gaseous reactants and products over the interparticle gas phase of a fixed bed section. McLaughlin (1990) estimated values for the Two Reaction Model parameters; reaction constant $k_a$, effective diffusivity $D_e$ and equilibrium group $K_e$, based upon fixed bed experimental results in the 827-927°C range. McLaughlin reported no major structural changes within calcium montmorillonite pellets at high temperatures (827°C and 927°C). However, when the sodium uptake progresses the sorbent attains a glassy phase. The formation of sodium di-silicate or a eutectic at 767°C was suggested.

Chrysohoidou (1996) tested alkali capture by calcium montmorillonite and kaolinite in gaseous environments of nitrogen, water vapour and hydrogen chloride at a temperature of 650°C and atmospheric pressure using McLaughlin’s fixed bed reactor. Chrysohoidou obtained different characteristic fixed bed profiles at 650°C to those obtained by McLaughlin in the temperature range 827-927°C for calcium montmorillonite. Tests comparing calcium montmorillonite and kaolin, showed kaolin to have a higher sorption capacity at this temperature. Fixed bed tests of 200 hours, 400 hours and 600 hours with sodium under HCl gas were performed with pan pelletised calcium montmorillonite pellets. The 650°C profiles did not show the characteristic knee shape of the the non-acid profiles at 827°C and 927°C which led to the development of the two reaction theory at 827°C and 927°C.

Turk et al (1996a) found that the alkali sorption process is significantly affected by the calcination process. The calcination of kaolin at 1,000°C results in an almost complete loss of its potential as an alkali sorbent. Thermogravimetric tests suggested a different reaction mechanism for alkali capture by emathlite and kaolin. It was shown that in a reducing atmosphere with steam, the presence of HCl inhibited the removal of alkali vapours for emathlite. HCl levels as high as 280ppmv had little effect on the alkali vapour removal of kaolin under these conditions. Mixtures of kaolin and emathlite were selected for further evaluation for industrial applications (DOE, 1994-1996).

Mönster (1996) studied the alkali sorption process on kaolin and emathlite at 870°C in McLaughlin’s fixed bed reactor. It was found that the alkali sorption content of extruded and
pan pelletised kaolin pellets were affected by the agglomeration process. The measured sodium sorption capacity for extruded pellets was diminished. In aluminosilicates, silicon replacement by aluminium leads to a negative charge in the tectosilicate network. This negative charge is balanced by cations such as sodium, potassium or calcium. Based on reaction products, a sorbent producing nepheline as reaction product has a sodium sorption capacity of 16.2% wt. and a sorbent producing albite is predicted to have a saturation capacity of 8.8% wt. When the reaction product is sodium disilicate, the sorption capacity of the sorbent is expected to be 25.3% wt. Furthermore, the gas-solid reaction between aluminosilicate sorbents and gaseous sodium chloride depends upon the temperature and on the silica:alumina ratio of the sorbent.

Steffin (1999) showed that calcined kaolin coated with NaCl and KCl (20-23% wt.) releases alkali in the gas phase through a desorption process (95%) or reacts the dotted aluminosilicate to nepheline and hydrogen chloride when treated under aluminosilicate reaction conditions. Using an oxygen gaseous environment, kaolin reacts with NaCl to produce chlorine. Under the aluminosilicate reaction conditions, kaolin profiles under the non-isothermal condition indicated knees. Steffin suggested two reactions to be relevant for the sodium sorption process. As reaction products were observed nepheline and hydrogen chloride. The sorbent effectiveness of the standard aluminosilicate reaction was found to be diminished by calcium. It was concluded that basic minerals lead to a comparably higher alkali emission in gas streams of advanced coal based power generation plants than those of an acidic mineral. Non-isothermal thermogravimetric analysis was employed with heat rates of 5°C/min in gaseous environments of nitrogen, oxygen/nitrogen, carbon monoxide/nitrogen and water vapour/nitrogen in the temperature range 200-1600°C.

Singh et al (1986) carried out a theoretical investigation of the effect of hydrogen chloride concentration on the gettering of volatile alkali for 20 candidate sorbent materials. Assuming that the alkali species were in equilibrium with the ‘getter’, for example kaolinite, through the reaction:

$$2NaCl(a) + H_2O(a) + Al_2O_3 \cdot 2SiO_2(s) \leftrightarrow Na_2O \cdot Al_2O_3 \cdot 2SiO_2(s) + 2HCl(a) \quad [20]$$

\[37\]
the equilibrium sodium chloride vapour concentration can be calculated from the knowledge of
the equilibrium constant \((K_p)\) based on partial pressure:

\[
K_p = \frac{p_{HCl}^2}{p_{NaCl}^2 p_{H_2O}} \quad [21]
\]

where \(p_x\) represents the partial pressure of the compound \(x\) (HCl, NaCl and H\(_2\)O). Using a
reducing gaseous atmosphere\(^2\), they calculated that for the materials under test the equilibrium
alkali concentration would be above the target value.

A reduction in the combustion reaction temperature to below 827°C would be required for the
gaseous alkali content to be reduced to the appropriate level. The getters most likely to be
effective are silica-alumina minerals such as kaolin. Getter efficiency would be improved by
removing HCl. In a gasifier, alkali levels can be reduced by gettering, and the most attractive
getters are the same as those identified for combustion.

In summary, the capture mechanisms of alkali by the sorbents is controversial (exchange
adsorption and standard aluminosilicate mechanisms). Leaching studies have been used to
identify possible variations in strength of bindings, which might indicate the reaction
mechanism. In water containing atmospheres, studies of the removal of volatile salts from hot
gases, using layered silicates such as kaolinite, calcium montmorillonite and emathlite have led
to the proposal of standard aluminosilicate reactions. Some of the proposed mechanisms are
based on the assumption that gaseous NaCl reacts at the surface of the hydrated silica lattice,
and consequently releases hydrogen chloride.

\(^2\) composition of 18% CO, 10% H\(_2\), 9% CO\(_2\), 3.8% vol H\(_2\)O, 300ppmv HCl, 200ppmv H\(_2\)S, 8.6ppmv NaCl,
1.7ppmv KCl
2.3 CHEMISTRY OF THE SORBENT AND REACTION PRODUCTS

Aluminosilicate materials have been shown to be effective sorbents for removing alkali vapours from gases. Layered aluminosilicates are composed of sheets of alumina octahedra and silica tetrahedra separated by hydroxyl groups. Linking one octahedral sheet with one tetrahedral sheet produces the double layer 1:1 lattice structure of kaolin. The uppermost plane of the octahedral sheet consists entirely of hydroxyl groups. A 2:1 clay lattice structure such as calcium montmorillonite and emathlite has two tetrahedral sheets sandwiching an octahedral sheet. The structures are schematically shown in Figure 12 and 13 (Mason and Berry, 1968).

Figure 12: Lattice Structure of Kaolinite (Mason and Berry, 1968).
As first emphasised by Marshall (1935) and Hendricks (1942), a wide variety of substitutions in octahedral and tetrahedral positions are possible within the structure, and they always leave it with a net negative charge which is satisfied externally by cations which are exchangeable. If the montmorillonite layers are not electrically neutral the charge is balanced by interlayer cations (e.g. Ca$^{2+}$) with water often associated with these cations. Földvari et al (1998)$^3$ reported that in the tetrahedral layer silicon ions are replaced by aluminium ions, and that in the octahedral layers aluminium ions may be replaced in general by iron (II), iron (III) or magnesium ions. Apart from the aforementioned substitutions any remaining hydroxyl groups may additionally produce substitution effects. The interlayer water is usually lost by about 450°C-700°C for Cheto type montmorillonite, but montmorillonite may retain hydroxyl groups up to 850°C-900°C with its structure preserved (Grim and Kulbicki, 1961). This has also been confirmed by thermal dehydroxylation studies by Xiang et al (1990).

$^3$ Furthermore it is reported that 80% of the exchangeable cations of montmorillonite are in the interlayer space. X-ray diffraction gives information on the cation exchange in the interlayer space only, and not on adsorption on the surface. Exchange ions are mainly hydrated, due to the electrostatic forces between the ion and electric dipole of the water molecule.
Kaolinite comprises of two types of structural hydroxyl group: internal, situated at the boundaries of the octahedral and tetrahedral lattices, and intrasurface, situated at the surface of the octahedral lattice of the kaolinite layer and interacting with the oxygen atoms of the tetrahedral lattice of the adjoining layer. Metakaolinite appears to have lost 75% of its hydroxyl groups by 570°C. Retained hydroxyls will be lost in the range 760°C and 955°C (Meinhold et al., 1992). For aqueous solutions Ma and Eggleton (1999) reported that the commonly believed cation exchange in kaolinite occurs due to the broken bonds around the crystal edges, the substitutions within the lattice, and the hydrogen of exposed surface hydroxyls. Particle size is more important than crystallinity in affecting kaolinite exchange capacity. Davis et al. (2000) showed that at high temperature kaolinite captures lead and sodium in preference to cadmium. It was concluded that competition for capture on sorbents between sodium and toxic metals is likely.

It appears that in the absence of water vapour residual hydroxyl groups in the structure of the clay minerals may be sufficient to lead to a reaction and possibly also to exchange or replacement reactions.

The addition of water vapour to the carrier gas may increases the alkali uptake, possibly by re-hydroxylation of the silica lattice

\[
\equiv \text{Si} - 0 - \text{Si}_{(s)} + \text{H}_2\text{O} \leftrightarrow 2 \equiv \text{Si} - \text{OH}_{(s)} \tag{22}
\]

Montmorillonite when heated above 500°C usually loses its interlayer water and will only re-hydrate very slow if at all. For example, Grim and Bradley (1948) found that calcium montmorillonite heated to 600°C for 1 hour picked up a small amount of interlayer water after 268 days. A slow re-hydration implies that standard aluminosilicate reaction in the initial sorption process is not fully understood.

Yadegarian and Schulz (1991) and Yadegarian et al. (1991) studied the hydroxylation of calcium montmorillonite by water at elevated temperatures. Water vapour added to a fluidised bed with pellets showed no increase in surface hydroxyl groups in calcium montmorillonite at 600°C. An increase in silica hydroxyl groups was noticed after extended exposure at 850°C,
but not for the alumina hydroxyl groups. The increase in surface hydroxyl groups was found to be insignificant, indicating little evidence for the hydroxylation of calcium montmorillonite by water vapour. In addition, there was no indication that a sodium for calcium ion exchange was taking place. It was concluded that the role of water in the standard aluminosilicate reaction is still unclear.

2.4 OBJECTIVES

This work aims to improve the understanding of the sorption of alkali vapours on sorbent pellets of kaolinite, calcium montmorillonite and emathlite to assess the alkali sorption mechanisms of the alkali sorption process of the sorbents.

Sorption must be studied on different pellets using pan pelletised and extruded pellets because pellet characteristics have been shown to influence the sodium content in pellets and chips, found in different ways.

Characterisation of the pellet is necessary. The pellet properties: pore volume, porosity, mean pore size, surface area, mean particle size, element distribution and compressive strength should be determined. The pellet characterisation can then be used to relate pellet characteristic to sorption performance.

Initial sorption activity tests are necessary to determine the effects of temperature, agglomeration and sodium chloride concentration on the sorption process. With the low turbine inlet value of 24ppb the effect of NaCl concentration on the alkali sorption must be assessed.

In order to improve the understanding of the sorption mechanisms of sorbent pellets of kaolinite and calcium montmorillonite of alkali vapours it is necessary to determine primarily gaseous environment effects. There is evidence to suggest that hydrogen chloride significantly influences the standard aluminosilicate reaction, possibly through a disturbance in equilibrium. Inhibitory effects of hydrogen chloride have been investigated in the past; however, the role of hydrogen chloride in the reversal of the alkali sorption process is unclear. The role of water
vapour in the alkali sorption process is not well understood, it is unclear whether water vapour or remaining hydroxyl groups lead to a standard aluminosilicate reaction in the initial alkali sorption process. It is suggested by using a single pellet reactor applying different gaseous environments, sorption and desorption profiles can be generated and used to give an insight into the alkali sorption characteristics and alkali sorption mechanisms of the target sorbents.

Further experiments can then be conducted to prove the experimental findings. Single layer treatment of sorbent material in a fixed bed reactor gives a reasonable amount of treated material which can be analysed.

Atomic absorption spectrometry and X-ray analysis will yield sodium content and reaction products formed. Solution bound sodium in leaches of water, HCl and HF will indicate whether sodium is bound in the water soluble, HCl soluble or HF insoluble form. The determination of the sodium content in solution bound leaches will be used to clarify the alkali sorption characteristics of the alkali sorption process. X-ray studies will be useful to identify reaction products and subsequently develop reaction schemes.

Table 5 presents the proposed alkali sorption programme to study the alkali sorption process. The chemical compositions of the target materials are listed in the Appendix (Table B.VII.1).
Table 5: Proposed Alkali Sorption Programme to Study the Alkali Sorption Mechanism.

<table>
<thead>
<tr>
<th>Agglomeration Method</th>
<th>Initial Sorbent Property</th>
<th>Desorption Sorption</th>
<th>Sorbent Agglomeration Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pan Pelletisation</td>
<td>Kaolinite</td>
<td>Influence of Water Vapour on Sorption</td>
<td>Calcium Montmorillonite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Influence of Temperature on Temperature Agglomeration</td>
<td>Kaolinite</td>
</tr>
<tr>
<td>Extrusion and Spheronisation</td>
<td>Analyse</td>
<td>Influence of NaCl concentration on Agglomeration</td>
<td>Emulsitite</td>
</tr>
</tbody>
</table>

Properties: Total Pore Volume, Porosity, Pore Diameter, Surface Area, Particle Size, Element Distribution.
The objectives of the project are:

a) Determine pellet properties (total pore volume/porosity/pore diameter, surface area, particle size, compressive strength, element distribution) and their relationship with raw material characteristics (pore diameter, surface area),

b) Investigate the initial sorbent activity including effects of temperature, agglomeration, alkali concentration,

c) Study the sorbent sorption characteristics (mechanism, role of water, role of hydrogen chloride, reversibility) of kaolinite, calcium montmorillonite and emathlite under different gaseous mixtures (sodium chloride, water vapour and hydrogen chloride specified in Table 5),

d) Determine the sodium content (with and without solution bound sodium) within pan pelletised kaolinite and calcium montmorillonite pellets when treated under different sorption and desorption conditions (specified in Table 5),

e) Identify the reaction products in treated kaolinite and calcium montmorillonite when treated under sorption and desorption conditions (specified in Table 5),

f) Review possible options for a revised alkali sorption model.
CHAPTER 3

EXPERIMENTAL METHODS

The literature suggested that key issues of the alkali sorption process still need to be investigated at high temperatures; to determine the differences in alkali sorption mechanisms of kaolinite, calcium montmorillonite and emathlite. An alkali sorption programme was proposed to investigate pellet properties (Section 3.1), initial sorption activities of extruded and pan pelletised pellets (Section 3.2) and sorbent sorption and desorption characteristics (Section 3.3) using a single pellet reactor system (Section 3.1). In addition it was proposed that analytical evidences from atomic absorption spectrophotometry and X-ray diffractometry could be used to identify the strength of sodium binding and to identify reaction pathways (Section 3.4).

3.1 SORBENT CHARACTERISATION AND ANALYSIS

The sorbent characterisation and analysis involve the physical and chemical properties of the sorbent/sorbent pellet. Physical properties comprise total pore volume/porosity/mean pore size, surface area, compressive strength and the mean particle size. Chemical properties are the element distribution of the sorbent.

Raw materials were selected (B.I-V) to produce pan pelletised pellets (Image E.VII.2). A summary of settings and modes of operation used is given at Appendix B.VIa. Pan pelletised kaolin and calcium montmorillonite pellets were heat treated by heating rapidly (flash calcination) and maintaining at temperature for sufficient time to allow equilibrium conditions to prevail (850°C, 24hours). A Carbolite furnace model, CSF 1200, was used. Extruded emathlite and kaolin pellets (Appendix B.VIb) were calcined in a muffle oven at 815°C for 4 hours. The chemical composition of the pellets is given in Table B.VII.1.
3.1.1 Total Pore Volume, Porosity and Mean Pore Diameter Measurements

Pore-structures were analysed by Mercury Intrusion Porosimetry (MIP). The total pore volume was calculated by the Washburn equation and the porosity was calculated by total intrusion volume and the entered volume of penetrometer. Using the obtained intrusion and total pore volume volume-based mean pore diameters were determined. The equipment used was a Micromeritics porosimeter, model 9220, capable of measuring porosity and distribution of pores in the pore diameter range of 0.001 to 360 μm. The contact angle was 130°C (Appendix C.I).

3.1.2 Surface Area Measurements

Raw material and pellet surface area measurements were performed on a 100CX Omnisorp instrument (Appendix D.I-II). Raw material and pellet surface areas were evaluated using the Brunauer-Emmett-Teller (BET) approach (Appendix D.VI).

3.1.3 Mean Particle Size Measurements

Particle size distributions of selected pellets and raw materials were analysed using a digital image analysis system Optimas 6.0 (Appendix E). The distribution patterns were processed by applying mathematical functions to digital images. Thresholds were used to identify the individual particles in the pellets (Appendix E.II-V).

3.1.4 Compressive Strength Measurements

Crush strength measurements were performed using an Instron 4500 device. Load displacement curves were used to determine the compressive strength of the pellets formed. Pellets were compressed at a constant compressing speed of 0.5mm/s. An example is presented in Appendix F.I to measure the first breakage point of a kaolinite pellet.
3.1.5 Element Distribution (Element Mapping)

Target pellets were examined microscopically using scanning electron microscopy (SEM; Hitachi S-3200N) to determine the morphological structure of the pellets. The sodium distribution within the pellets was obtained by applying scanning electron microscopy and the Energy Dispersive Analysis system (EDS; Hitachi). Chemical data acquisition of spectra was possible using the Oxford Link ISIS system 300 (Appendix G).

3.2 INITIAL ALKALI SORPTION ACTIVITY

Initial sorbent activity tests were used to give insight into phenomena connected with the effects of temperature, sorption performance of the used pellets and effects of alkali concentration. The initial sorbent activities were determined using a Single Pellet Reactor (SPR) developed by Schulz (Turk et al, 1996a).

3.2.1 SPR System

Using the SPR system, profiles were obtained which measured changes in weight over time, and which have been normalised, in terms of weight fraction based on original pellet weight.

A schematic of the experimental SPR system is shown in Figure 14. The SPR system consists of three basic sections; the gas-handling system (where nitrogen, water vapour and hydrogen chloride are mixed), the furnace/reactor unit with sodium vapour generator and the microbalance/sample unit. Image 1 shows the SPR system with its components (left: data collection system, furnace unit, microbalance/sample unit, right/middle: gas handling system with mass flow controllers, gas chromatograph for analytical purposes). The technical description can be found in Appendix A.I-III. The requirements of use of the SPR were: constant vapourisation rate of sodium chloride (Appendix A.III-IX) and homogeneous gas mixing (Appendix A.IX-X).
Figure 14: Schematic of Single Pellet Reactor System, Schulz (Turk et al., 1996a).
During the course of this work the gas handling system and the reactor unit was optimised. Gas mixing of nitrogen, water vapour and hydrogen chloride was found to be difficult. This is because hydrogen chloride tends to stay in the liquid phase at low concentrations (Schmidt, 1976). Controlled water vapour and hydrogen chloride environments were eventually created using an optimised gas-handling system (Figure 14). It was decided to run the hydrogen chloride line permanently and to change stainless steel valves and stainless pipes to polytetrafluoroethylene ones. The furnace-unit was configured in order to control the vapourisation rate of sodium chloride in the vapourisation zone and to react the appropriate getter materials in the reaction zone.

Image 1: Single Pellet Reactor System developed by Schulz.

Constant vapourisation rates of sodium chloride (see below) were obtained by placing a rectangular flat salt crystal (3.2x3.0x2.3mm, 40mg) in a platinum crucible and adjusting vapourisation temperatures. Temperature adjustment is necessary in order to compensate for loss in mass of the salt crystal over time. 'Getter' materials are mounted in a fine wire suspension in order to maintain an undisturbed gas flow around the pellet.
Mixing Studies

A series of mixing studies was performed in order to determine whether the gas mixtures entering the reactor unit were constant. The hydrogen chloride concentration was determined within mixed hydrogen chloride/water vapour/nitrogen gas. The observed concentration of hydrogen chloride was found to be in agreement with the calculated value (Figure A.X.1). Using the Dräger tube technique, hydrogen chloride gas was investigated through a change of coloration from blue to yellow using a pH reaction between bromophenolblue at room temperature (Appendix H). In order to investigate hydrogen chloride in gaseous mixtures containing water vapour, gas samples were dried using a permeation membrane. Sample gas passed the inner permeation membrane (Nafion tube, copolymer of tetrafluoroethylene, Perma Pure inc., New Jersey) while water vapour was absorbed into the membrane walls. The water absorbed was removed by a dry purge gas using a countercurrent gas stream (shell of the membrane). Hydrogen chloride remained in the nafion tubing. The water vapour content was determined using either gas chromatography or adsorption measurements on zeolite (Appendix I). Zeolite tests were performed to confirm the used water vapour content. Gas chromatography was used to measure the water vapour content on a comparable basis.

Controlled Vapourisation of Sodium Chloride (Calibration Runs)

A great deal of work was necessary to ensure a constant vapourisation rate of sodium chloride. Using adjusted vapour generator temperatures, a constant vapourisation rate of NaCl was obtained. Figure 15 shows that the required vapourisation rate of sodium chloride of 300 µg/hour was maintained over a time period of 50 hours.

Experimental Procedure

Nitrogen gas atmospheres with the same water vapour gas concentration but either with the presence or absence of hydrogen chloride (initial alkali sorption studies without HCl) were established by using nitrogen gas streams of 15ml/min and 50ml/min and passing these streams through liquid saturators at a temperature of 30.3°C (4.3% by volume) and 11.6°C (1.3% by volume), respectively. A 35ml/min hydrogen chloride in nitrogen gas stream was added to the low flow and high water vapour saturated gas stream. A gas trap, starting at 30.3°C (tempera-
Figure 15: Constant Vapourisation Rate of Sodium Chloride versus Time (Calibration Run).

temperature controlled water bath) and finishing at 50°C (oven with mixing coil), allowed production of a highly water saturated gas stream, which was then mixed with the 35ml/min gas stream. In the summer when the tap water did not allow a cooling of the fast flow and low water vapour saturated gas stream, the 35ml/min hydrogen chloride in nitrogen gas stream was changed to one with nitrogen only and water vapour in nitrogen runs were performed using this line. However, both 50ml/min gas with specified gas composition (1.3% volume water vapour, 80-150ppmv HCl) were used to study alkali sorption under different atmospheres.

The gas handling system, shown in Figure 14, shows the principles described and the options to switch between nitrogen only and hydrogen chloride in nitrogen mixtures.

To assemble the rig before a run, salt crystals (Hilger Analytical), cut to a standard size (3.2x3.0x2.3mm, 40mg), were placed into a platinum crucible. Fixation of the platinum crucible on a ceramic rod with an R-type thermocouple and wire system was possible by moving the ceramic rod with the R-Thermocouple to its high position. Image 2 shows the reactor unit with ceramic rod and the R-Thermocouple readout. The vapour generator can
also be seen. The dismounted reactor unit was centred into the furnace using a measuring instrument followed by adjustment of screws at the bottom furnace. Finally the furnace/reactor unit was fitted in the SPR block.

The electrical raising of the furnace/reactor unit to a suitable position allowed the user to change the sorbent pellet. In this position the top of the furnace was covered with a metal plate and the microbalance stabilised. After changing the sorbent pellet the microbalance was put in operation and the furnace/reactor unit raised with cooling seal to its top position. Prior to commencing a run the furnace temperature was increased up to 550°C (10°C/min) with nitrogen entering the furnace and finally to 862°C (Stanton Redcroft, 706 Temperature programmer). At 800°C the auxiliary heater was switch on (820°C). With this setting a sample temperature of 850°C was achieved. The temperature settings were held for an hour or longer in order to provide a stable base line. Before starting the run the West controller 6100 was switched on (650°C). The adjustable rod was moved upwards to a salt temperature of 688.2°C (Cropico thermocouple reader, DP6). The desired gas environment was entered into the reactor unit, the Quick Basic programme was started to allow temperature adjustment. During the run salt temperatures were recorded when appropriate (Figure A.IX.1). Room-, water bath- and sample temperature were recorded by data logger (Grant 1200). The total weight gain was recorded by chart-recorder and PC data acquisition. The microbalance signal was affected by zero drift resulting from variations in room temperature and this had to be eliminated by enclosing the balance head.
in a temperature controlled box. Weight trace variations due to buoyancy effects, were reduced by high gas inlet and purge gas flows (25μg). The auxiliary heater was protected through a 100ml/min gas stream entering the furnace reactor.

After every run the furnace/reactor unit was lowered to get it free from the hangdown of the microbalance system. Then the furnace unit was removed from the overall system. The dismounted reactor released also the adjustable rod with platinum crucible and remaining salt crystal. The replacement of the salt crystal involved the following procedure: removing the platinum crucible with tweezers, weighing the platinum crucible and finally cleaning the platinum crucible from salt (Table A.VIII.1).

3.2.2 Initial Sorbent Activity Experiments

Initial sorbent activity tests were performed using a treatment of standard aluminosilicate reaction condition, i.e. sodium chloride and water vapour was passed over the sorbent pellet (40ppmv NaCl was vapourised, the water vapour concentration was 1.3% by volume). In the following section this environment is defined as the standard-wet gaseous environment.

Temperature readouts to investigate the effect of temperature of the alkali sorption process for individual pellets were found to be necessary to ensure a comparatively steady environment.

To investigate the effect of agglomeration on individual pellets with the same raw material characteristics, pellets were produced using different modes of agglomeration. Mechanical strength tests identified whether the pellets produced were same.

When the effect of NaCl concentration was determined, the NaCl concentration was changed to a higher NaCl concentration by raising the vapourisation temperature. This led to a 56ppmv sodium chloride concentration.
3.3 SORPTION AND DESORPTION CHARACTERISTICS OF SORBENTS

Because the literature review indicated gaps and uncertainties of the role of water vapour and hydrogen chloride in the alkali sorption process, alkali sorption and desorption studies were proposed to compare the kinetics and mechanisms of the alkali sorption process for kaolinite, calcium montmorillonite and emathlite in different gaseous environments using a single pellet reactor (Section 3.2).

3.3.1 Defined Sorption and Desorption Atmospheres

Table 6 indicates the use of sorption and desorption environments containing sodium chloride, water vapour and hydrogen chloride used to investigate the influences of the gaseous environment on the alkali sorption process. In general, standard aluminosilicate reaction and NaCl dry conditions (standard-wet, NaCl-dry) were defined for the sorption environments. Nitrogen was used as carrier gas. Under the assumption that NaCl alone (NaCl-dry condition) could display a sorption profile, adsorption is assumed to be relevant to the alkali sorption process. With water vapour and sodium chloride present (standard-wet), the difference in uptake should indicate the contribution of chemical reaction to the sorption process. A standard aluminosilicate reaction can be proposed, see Equation 5. McLaughlin (1990) determined decreased uptakes with higher HCl concentration under standard aluminosilicate reaction conditions. Lower profile characteristics are proposed under the aluminosilicate reaction condition in the presence of hydrogen chloride.

Pre-treatment of pellets was achieved by sorption conditions using NaCl-dry and standard-wet. When pre-treated, a desorption mixture can lead to mass losses (possibly reversals in the standard aluminosilicate reaction process). The desorption gaseous environment consisted mainly of inert gas (nitrogen gas) and some mixtures. Desorption was assumed to occur under the following gaseous environmental conditions: nitrogen only and/or sodium chloride free (inert-dry), water vapour in nitrogen (inert-wet), HCl in nitrogen (inert-dry/HCl) and finally
<table>
<thead>
<tr>
<th>Agglomeration Method</th>
<th>Sorbent</th>
<th>Sorption Atmospheres</th>
<th>Desorption Atmospheres</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Single Pellet Reactor</td>
<td>Single Pellet Reactor</td>
</tr>
<tr>
<td>Pan Pelletisation</td>
<td>Kaolinite</td>
<td>NaCl-dry</td>
<td>Inert-dry/HCl</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Standard-wet</td>
<td>Inert-wet/HCl</td>
</tr>
<tr>
<td></td>
<td>Calcium Montmorillonite</td>
<td>NaCl-dry</td>
<td>Inert-dry/HCl</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Standard-wet</td>
<td>Inert-wet/HCl</td>
</tr>
<tr>
<td>Extrusion and Spheronisation</td>
<td>Kaolinite</td>
<td>NaCl-dry</td>
<td>Inert-dry/HCl</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Standard-wet</td>
<td>Inert-wet/HCl</td>
</tr>
<tr>
<td></td>
<td>Emathlite</td>
<td>NaCl-dry</td>
<td>Inert-dry/HCl</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Standard-wet</td>
<td>Inert-wet/HCl</td>
</tr>
</tbody>
</table>

**Gaseous Environment**

*a) Sorption*

<table>
<thead>
<tr>
<th>NaCl-dry</th>
<th>40ppmv NaCl, N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard-wet</td>
<td>40ppmv NaCl, 1.3%vol H₂O, N₂</td>
</tr>
<tr>
<td>Standard-wet/HCl</td>
<td>40ppmv NaCl, 1.3%vol H₂O, 100ppmv HCl, N₂</td>
</tr>
</tbody>
</table>

*b) Desorption*

<table>
<thead>
<tr>
<th>Inert-dry</th>
<th>N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inert-dry/HCl</td>
<td>100ppmv HCl, N₂</td>
</tr>
<tr>
<td>Inert-wet/HCl</td>
<td>1.3%vol H₂O, 100ppmv HCl, N₂</td>
</tr>
</tbody>
</table>
water vapour and hydrogen chloride in nitrogen (inert-wet/HCl). Should a pre-treated sorbent pellet (NaCl-dry) with subsequent exposure to inert-dry/HCl conditions display a desorption profile, the replacement mechanism may be relevant to the sorption process. It is also possible that NaCl alone would lead to a desorption profile; in this case physisorption will be relevant to the sorption process. No change in weight would indicate that chemical reaction led to a chemical fixation of the sodium. Reversibility of the standard aluminosilicate reaction is only plausible in the case where water vapour and hydrogen chloride alone (inert-wet/HCl) led to a loss in mass of reacted material.

Having defined the sorption and desorption environments, sorption and desorption profiles were determined using the SPR system, see Table 6.

### 3.4 SODIUM CONTENT AND REACTION PRODUCTS

Having determined the sorption and desorption profiles using the single pellet reactor technique (Section 3.3), atomic absorption spectrophotometry and X-ray studies were used to get further experimental evidence (Chapter 2). Single layer treatment of sorbent material gives reasonable amount of material which can be analysed (Section 3.4.1). Using different environmental conditions, single layer treatment was allowed for 100 hours (850°C). High density balls were placed at the top of the bed to help insure a uniform distribution of the gas throughout the single bed. Previously treated pellets (NaCl-dry, standard-wet) were exposed to inert-dry/HCl and inert-wet/HCl atmospheres, respectively. Desorption conditions were applied for 100 hours. Table 7 shows the sorption and desorption conditions used in the fixed bed reactor system (McLaughlin, 1990) and the experimental programme to analyse the pellets (Section 3.4.2). X-ray diffraction patterns were analysed by the X-ray diffractometer described in Section 3.4.3.

#### 3.4.1 Fixed Bed Reactor

A fixed bed reactor was used to treat sorbent material. The Fixed Bed rig (Appendix A.XI-XIII) used was originally developed by McLaughlin (1990).
<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Exposure Time</th>
<th>Sorption Atmospheres</th>
<th>Analysis</th>
<th>Desorption Atmosphere</th>
<th>Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[hours]</td>
<td>Fixed Bed Reactor</td>
<td>Sodium Content</td>
<td>X-ray</td>
<td>Fixed Bed Reactor</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>100</td>
<td>NaCl-dry</td>
<td>x&lt;sup&gt;1,2&lt;/sup&gt;</td>
<td>x</td>
<td>Inert-dry/HCl</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Standard-wet</td>
<td>x&lt;sup&gt;1,2&lt;/sup&gt;</td>
<td>x</td>
<td>Inert-wet/HCl (100hours)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Standard-wet/HCl</td>
<td>x&lt;sup&gt;1,2&lt;/sup&gt;</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>Calcium</td>
<td>100</td>
<td>NaCl-dry</td>
<td>x&lt;sup&gt;1,2&lt;/sup&gt;</td>
<td>x</td>
<td>Inert-dry/HCl</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>100</td>
<td>Standard-wet</td>
<td>x&lt;sup&gt;1,2&lt;/sup&gt;</td>
<td>x</td>
<td>Inert-wet/HCl (100hours)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Standard-wet/HCl</td>
<td>x&lt;sup&gt;1,2&lt;/sup&gt;</td>
<td>x</td>
<td></td>
</tr>
</tbody>
</table>

1 Determination of the solution bound sodium a) water soluble b) HCl soluble c) HF insoluble
2 Determination of the HF insoluble solution bound sodium

Gaseous Environment
a) Sorption
NaCl-dry 40ppmv NaCl, N<sub>2</sub>
Standard-wet 40ppmv NaCl, 1.3%vol H<sub>2</sub>O, N<sub>2</sub>
Standard-wet/HCl 40ppmv NaCl, 1.3%vol H<sub>2</sub>O, 100ppmv HCl, N<sub>2</sub>

b) Desorption
Inert-dry N<sub>2</sub>
Inert-dry/HCl 100ppmv HCl, N<sub>2</sub>
Inert-wet/HCl 1.3%vol H<sub>2</sub>O, 100ppmv HCl, N<sub>2</sub>
The requirements of use were: homogeneous and controlled gas mixing, constant vaporisation rate of sodium chloride and the production of equally treated pellets (top layer) for further chemical analysis.

**Experimental Procedure**

A homogeneous and controlled gas stream containing hydrogen chloride and water vapour in nitrogen was obtained by mixing a 100ml/min hydrogen chloride in a nitrogen gas stream (260ppmv) with a highly water vapour saturated gas stream (4.9% by volume, 32.7°C water bath, 70ml/min). A mixing trap and coil were electrically heated up to 35°C. The resulting gas stream containing 2% by volume water vapour and 150ppmv hydrogen chloride gas, was then passed to the gas inlet section of the fixed bed rig. The resultant gas mixtures were finally mixed with a salt vapour gas stream (1.6mg/hour) to produce gas mixtures containing 1.3% by volume water vapour, 40ppmv sodium chloride and 100ppmv hydrogen chloride.

Fixed bed preparation for a run was started by dismantling insulation of the fixed bed section and unhooking springs from the base plate of the fixed bed section. Once unhooked the fixed bed section was free and clamping in a stand was possible. Treated pellets within the fixed bed tube were removed using a vacuum probe assembly. The assembly with an adjustable suction probe pipe (3mm ID) was lowered and pellets were removed one at a time. The ceramic tube was then cleaned and filled with sorbent pellets. Nextel alumina wool filter pads were then placed in the condensation zone to adsorb the exit gas alkali. Placing of a single pellet layer (single layer) in the reactor tube was possible using a ceramic mesh. The filling procedure involved placing a 1mm kaolinite pellet layer on the bottom surface of the mesh. High density alumina balls of 2mm in diameter were used to provide further layering before the top layer with sorbent material was fitted. A further layer of alumina balls was put on top of the single sorbent layer (1.5-1.9mm) to ensure a uniform distribution of the downflow gas across the sorbent top layer.

Before refitting the fixed bed section, the salt vapour generation section was lowered so that a new salt crystal (210mg) could be placed onto a thermocouple and microbalance suspension arm. Springs and screws were undone to disconnect the salt vapour generation section and
microbalance unit. The movable vapour generation section was then lowered until the hangdown suspension with thermocouple and remaining salt crystal was free. The free hangdown was fixed in its current position by fitting a tool which held the upper rod tight. The salt crystal was changed. The fixed bed section was finally refitted, the hook and spring system was used to hold the fixed bed section with insulation and ceramic seal in its position. The fixed bed rig was raised 10°C/min after initial gas settings (170ml/min GIS, 100ml/min VGS). The temperature was raised to 550°C and then to a final set (Internal Coil 600°C, Gas Inlet 815°C, MS 820°C, Top Section 670°C, Lower Bed Section 810°C, Bed Section 820°C). The CRL455 controller was used to produce a constant sodium chloride vaporisation rate of 1.6mg/hour over 100 hours. The gas mixture was chosen and the initial salt crystal weight was 210mg. The CRL controller was switched on at internal coil temperature 650°C. The run started with this setting. The total weight loss recorded was affected by temperature zero drifts. As a consequence the balance head was enclosed in a temperature controlled box. The salt crystal weight after a run was 50mg+/−5mg. Treated pellets were chemically analysed for sodium content and reaction products.

3.4.2 Sodium Content

Sodium treated and untreated target pellets were analysed for their sodium content by flame atomic spectrophotometer (Perkin Elmer, A Analyst 100). The atomic spectrophotometer with sodium hollow-cathode lamp (589nm) and air-acetylene flame was used (Slit width 0.2mm, Oxidant flow 10l/min, Fuel flow 3l/min). Water soluble, HCl soluble and HF insoluble solution bound sodium and also HF insoluble solution bound sodium was determined (Appendix J.IV-X) in order to examine the extractable sodium in leachates and to compare the three stage method with the HF digestion method (Appendix J.I-III).

3.4.3 Reaction Products

X-ray patterns of uncalcined, calcined and treated pellets ground to powder (Fixed bed reactor) were collected on a Philips 1050 diffractometer. The scan was controlled by Hiltonbrookes software. Spectra were collected from 5-55° 2θ at a scan speed of 0.5deg/min.
in steps of 0.1°. Copper radiation at 40kV and 25mA was used and the system had a monochromator fitted. The spectra were analysed using ‘Traces’ software and a table of theta against inter atomic spacing was produced. The characteristic ‘fingerprints’ of the obtained patterns were compared to a standard to identify a mineral phase (Appendix K.I-VI).
CHAPTER 4

EXPERIMENTAL RESULTS

The literature review (Chapter 2) highlighted the fact that a great deal of work has been carried out on alkali removal. The studies indicated that the sorption mechanisms in kaolinite and calcium montmorillonite are not well understood. In addition, the literature review indicated gaps and differences regarding the alkali sorption process when exposed to certain environments and when using different pellets. Alkali sorption studies were proposed as a means of gaining a better insight into the reaction mechanism in kaolinite and calcium montmorillonite and the alkali sorption process (Chapter 1, 2). Sorbent characteristics have been analysed to relate the pellet properties to the alkali sorption process (Section 3.1). The single pellet and fixed bed reactor techniques were to use to investigate the proposed alkali sorption programme (Chapter 3). Work has been conducted with pan pelletised and extruded pellets. Pan pelletised pellets were used to get an insight into the alkali sorption mechanism whereas extruded pellets were used to see whether they would show similar characteristics. Extruded pellets were supplied by RTI. Pan pelletised pellets were manufactured using raw materials from ECC and LaPorte.

The experimental results cover sorbent characteristics and analysis (Section 4.1), initial sorbent activities (Section 4.2), sorption and desorption characteristics of sorbents (Section 4.3), and sodium content and reaction products (Section 4.4). The results of the experimental alkali sorption programme show that the sorbent characteristics of pan pelletised and extruded pellets are different in terms of pore volume, porosity, mean pore size, surface area, mean particle size, and compressive strength (Section 4.1). Initial sorbent activity results cover effects of pellet formation technique and temperature on the alkali sorption activity (Section 4.2). Finally sorption and desorption characteristics of sorbents show that the alkali sorption process is affected by the gaseous environment, reversibility, and water vapour content (Section 4.3). It is shown that the sodium content bound in kaolinite and calcium montmorillonite varies in water soluble ($H_2O$), HCl soluble and HF-insoluble leaching solutions and that the presence of certain hydrogen chloride mixtures leads to a change in
sodium content. Additional sodium sorption results can be used to generate a sodium sorption profile based on top layer treated pellets. Sodium phases are identified to show that the occurrence of reaction products depends upon the atmospheres used (Section 4.4).

4.1 SORBENT CHARACTERISATION AND ANALYSIS

Extruded and pan pelletised pellets (Formulation B.VIa/b and Images E.VI-VII) have been characterised by pore volume, surface area, mean particle size, crush strength and element composition. Video scans were used in order to determine the sodium distribution within treated pellets.

4.1.1 Total Pore Volume, Porosity and Mean Pore Diameter Results

Table 8 shows the results of mercury intrusion measurements, leading to pore volume, porosity and mean pore diameter. The pore volume and porosity of pan pelletised pellets were higher as those of pellets formed by extrusion. The mean pore diameter of kaolinite (RTI) was higher than those of pellets formed by extrusion. The mean pore diameter of kaolinite (RTI) LaPorte) appear to have a larger mean pore diameter and total pore volume than the equivalent extruded pellets (Table C.I.1).

<table>
<thead>
<tr>
<th>Agglomeration/ Sorbent</th>
<th>Pore Volume [ml/g]</th>
<th>Microporosity [%]</th>
<th>Mean Pore Diameter based on volume [μm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extrusion/</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kaolinite (RTI)</td>
<td>0.222</td>
<td>34</td>
<td>0.072</td>
</tr>
<tr>
<td>Emathlitite (RTI)</td>
<td>0.186</td>
<td>30</td>
<td>0.077</td>
</tr>
<tr>
<td>Pan pelletisation/</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kaolinite (ECC)</td>
<td>0.340</td>
<td>35</td>
<td>0.642</td>
</tr>
<tr>
<td>Ca.Mont. (LaPorte')</td>
<td>0.360</td>
<td>49</td>
<td>&gt;10</td>
</tr>
</tbody>
</table>

*RTI (Research Triangle Institute), USA, 'Supreme kaolin (ECC, English China Clay, UK), 'Ca Mont.=calcium montmorillonite (LaPorte, UK)

Table 8: Pore Volume, Microporosity, and Mean Pore Diameter of Pellets under Tests.
4.1.2 Surface Area Results

The surface areas of the calcined pellets, measured using nitrogen BET adsorption (Figure D.IV.2), are given in Table 9. In general, the calcination temperature significantly reduced the surface area of the air-calcined material (Table D.III.1, Figure D.IV.I/II). Calcined calcium montmorillonite pellets (LaPorte) showed a similar decrease in surface area with increases in temperature as the unagglomerated material; 750°C (30m²/g), 800°C (16m²/g) and 850°C (3m²/g). The pelletisation process does not significantly reduce the available surface area. The

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Raw Material</th>
<th>Air-treatment [°C]</th>
<th>Calcined Material</th>
<th>Calcined Pellet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emathlite (RTI⁹)</td>
<td>&gt;80</td>
<td>815</td>
<td>-</td>
<td>7</td>
</tr>
<tr>
<td>Cal.Mont. (LaPorte⁷)</td>
<td>87</td>
<td>750</td>
<td>32</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td></td>
<td>800</td>
<td>16</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>850</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>Kaolin (RTI⁹)</td>
<td>14</td>
<td>815</td>
<td>-</td>
<td>14</td>
</tr>
<tr>
<td>Kaolin (ECC⁶)</td>
<td>14</td>
<td>850</td>
<td>-</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td></td>
<td>900</td>
<td>-</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td></td>
<td>950</td>
<td>-</td>
<td>11</td>
</tr>
<tr>
<td>Kaolin (ECC⁶)</td>
<td>10</td>
<td>850</td>
<td>9</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>900</td>
<td>8</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>950</td>
<td>1</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 9: Surface Area of Raw Material, Calcined Material and Pellets.

The surface area of kaolinite (ECC) remains stable up to 900°C (14m²/g), above which it is affected by the calcination temperature (11m²/g). The manufacturer’s values for raw materials are listed in Table 9 for comparison (see also Appendix B.III-IV).

Fullsorb isotherms of extruded emathlite and kaolinite both RTI indicated a fullsorb isotherm of type IV (BET-BJH, Figure D.VI.1). Kaolinite (ECC) and calcium montmorillonite (LaPorte) fullsorb isotherms in a more open structure (Figure D.VI.I/II) showed the occurrence of fullsorb isotherms with a low pressure hysterizes (Appendix D.V). Mesopores
(0.002-0.05\mu m) were found in extruded emathlite pellets, whilst macro (>0.05\mu m) and mesopores were found in pan pelletised kaolin pellets.

### 4.1.3 Mean Particle Size Results/Microstructure

The mean major particle length within kaolinite (supreme, ECC) pellets was measured at 0.4\mu m. Emathlite (RTI) and calcium montmorillonite (LaPorte) particle lengths are in the range of 2-44\mu m; Rieger (1998); Rieger et al, 1999, McLaughlin (1990), Chrysohoidou (1996). The particle size distribution data were obtained from images (SEM) and by applying mathematical functions to them via an image processing programme (Processed images E.II.2 and E.III.2, Data E.IV and E.V).

Kaolinite showed needle and grain forms (Appendix E.II.2 and E.III.2). Emathlite and calcium montmorillonite (LaPorte) showed a microstructure of grains with non uniform size and composition as well an irregular shape (Image G.II.b.1 and Image E.VI.1).

Extruded kaolinite pellets supplied by RTI showed a homogeneous micro-structure. The kaolin pellets (Image E.VI.2, RTI) were found to be less dense in comparison to emathlite (Image E.VI.1, RTI). Emathlite showed a grain formation. Within the emathlite grains further particles exist, which were found to be of varying colour and composition (Appendix E.VII.1). Pan pelletised pellets of calcium montmorillonite (LaPorte) showed a porous structure (Image E.VII.2).

### 4.1.4 Compressive Strength Results

Load tests showed the following compressive strength hierarchy: extruded emathlite pellets (80N/pellet, RTI) > extruded kaolinite (19N/pellet, RTI) > pan pelletised calcium montmorillonite (0.4/N/pellet, LaPorte) > pan pelletised kaolinite (0.1N/pellet, ECC). The compressive strength of kaolinite pellets was less than that of emathlite and calcium montmorillonite for both pan pelletised and extruded pellets.

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The mean major particle length within kaolin (grade D) was measured to be 1.1\mu m.
4.1.5 Element Distribution (Element Mapping)

Digital x-ray element maps for kaolinite (ECC) exhibited sodium, chlorine, and aluminium whereas those of emathlite (RTI) and calcium montmorillonite (LaPorte) exhibited sodium, chlorine, silicon, and calcium.

In pan pelletised pellets, captured sodium was found throughout the pellet (Image 4), whereas the extrusion and rolling technique produced a sodium distribution on the surface of the pellet only (Image 3). The white colour indicates sodium. Appendix G.V indicates similar characteristics for pan pelletised and extruded pellets.

Chlorine signals were investigated in order to see whether chlorine was retained. In a 'reacted' zone of kaolinite, the ratio of Na:Cl was higher than 20:1. Using a treatment under standard conditions with HCl, chlorine signals were found to be beyond the background level. The Na:Cl ratio was found to be 1:1. Investigated counts from the EDS/SEM system are summarised, at Appendix G.II.

The Si:Al ratio was investigated in kaolinite and emathlite (both RTI) in order to determine discrepancies from the normal ratio. The Si:Al ratios were found to vary, see Appendix G.II. Using a treatment under standard-wet condition, the ratio in extruded kaolinite was found to be lower than 1:1. The silicon content effect on sodium distribution was investigated. The homogeneous distribution of sodium within the pan pelletised pellet (calcium montmorillonite) appears to be inversely related to the presence of silicon in the pellet. Areas with a high silica content showed a lower sodium concentration whereas areas with a lower silica content showed a higher sodium concentration (Element Distribution G.III.1).

Calcium seems to have a negative influence on sodium sorption for calcium montmorillonite. The sodium distribution is reduced in calcium montmorillonite under a diminished oxygen level and high calcium content. This result was obtained by performing line scans of areas of interest, see Linescan G.IV.1.
Image 3: Sodium Video Map in Treated Extruded Kaolin (RTI) Pellet (white indicates sodium).

Image 4: Sodium Video Map in Treated Pan Pelletised Calcium Montmorillonite (LaPorte) Pellet (white indicates sodium).
4.2 INITIAL SORBENT ACTIVITY

To determine the influence of temperature and pellet formation on alkali sorption, these factors were varied and the effect on the initial sorbent activity of the sorbent under standard-wet conditions was investigated. Sorption was studied with pan pelletised and extruded pellet sorbents consisting of kaolinite and calcium montmorillonite. Activity was defined as the gain in weight associated with sodium chloride per time under the standard-wet environmental condition. Reproducibility profiles are given for calcium montmorillonite when treated under NaCl-dry conditions. The determined profiles appeared similar (Appendix L.I).

4.2.1 Effect of Temperature

The effect of temperature on the uptake of alkali vapour by kaolinite (ECC) and calcium montmorillonite (LaPorte) was determined by measuring alkali sorption rates of pellets for the alkali sorption process. Four temperatures were used (800°C, 825°C, 850°C, 875°C) under standard-wet conditions to investigate the initial activity of pan pelletised calcium montmorillonite and kaolin. Both materials showed increased initial activity as temperature increased, see Figures 16 and 17. The figures show Arrhenius plots. With the use of initial activities instead of rate constants, initial activities were plotted against 1/T. The temperature range was chosen in order to avoid complications with temperature gradients. A narrow strict control of the temperature was maintained.

Higher temperatures led to a substantial increase in initial activity for calcium montmorillonite and kaolinite. At the lowest temperature used (800°C, 1.25E-3°C⁻¹) kaolinite produced high initial activity of 0.4x10⁻³mg/min, however calcium montmorillonite produced a tiny initial activity. From Figure 17, the weight increase per time associated with alkali sorption in calcium montmorillonite was 0.8x10⁻³mg/min at 825°C (1.21E-3C⁻¹) and 1.7x10⁻³mg/min at 850°C (1.18E-3°C⁻¹). The weight increase per time associated with alkali sorption in kaolinite was 0.4x10⁻³mg/min at 800°C, 0.8x10⁻³mg/min at 825°C, 1.1x10⁻³mg/min at 850°C and 1.3x10⁻³mg/min at 875°C (1.14E-3°C⁻¹). The weight gain difference in a one hour time interval was used to calculate the rate.
Figure 16: Effect of Temperature on Sorption (standard-wet) on Pan Pelletised Kaolinite (ECC).

Figure 17: Effect of Temperature on Sorption (standard-wet) on Pan Pelletised Calcium Montmorillonite (LaPorte).
### 4.2.2 Effect of Agglomeration

To see whether the means of producing pellets affected the initial alkali sorption activity and alkali sorption profile pan pelletised and extruded pellets were treated under standard-wet conditions.

Table 10 compares the initial alkali sorption activities of aluminosilicate pellets in a gaseous environment with water vapour according to the pellet formation process. The initial reactivity of pan pelletised kaolin (ECC) and calcium montmorillonite (LaPorte) was higher than that of kaolin and emathlite (both RTI) pellets produced by the extrusion method. The sodium concentration is assumed to be slightly higher than 40ppmv, because this value was obtained as the average sodium chloride concentration across the experimental time range.

<table>
<thead>
<tr>
<th>Agglomeration Method</th>
<th>Sorbent</th>
<th>Initial Activity (850°C) [ mg/min x 10⁻³ ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extrusion and Spheronisation</td>
<td>Kaolin (RTI)</td>
<td>1.46</td>
</tr>
<tr>
<td></td>
<td>Emathlite (RTI)</td>
<td>0.77</td>
</tr>
<tr>
<td>Pan Pelletisation</td>
<td>Kaolinite (ECC)</td>
<td>2.00</td>
</tr>
<tr>
<td></td>
<td>Ca. Mon. (LaPorte)</td>
<td>1.58</td>
</tr>
</tbody>
</table>

Table 10: Initial Activity of Aluminosilicate Materials at 850°C.

Figure 18 shows that the means of producing pellets affected the shape of the sorption profiles. Pan pelletised pellets of grade D kaolin (ECC) and calcium montmorillonite (LaPorte) showed significantly higher profile characteristics than pellets produced by manual methods. Dotted lines indicate the use of calcium montmorillonite, whereas the straight lines indicate the use of grade D kaolin. The pellets were exposed to 45 +/- 5ppmv NaCl (average) and 1.3% by volume water vapour. The profiles were affected by a fall in salt concentration, the determined concentration is the average concentration.
Figure 18: Effect of Agglomeration on Alkali Sorption Profile.

4.2.3 Effect of NaCl Concentration

For a first-order reaction, weight gain should depend upon the duration of exposure to NaCl.

Figure 19: NaCl Sorption on Kaolinite (RTI) Pellets exposed to Different NaCl Concentration.
at a given concentration. The product of the partial pressure of NaCl and time, therefore, is a useful index of the accumulated exposure of a pellet. Figure 19 compares the sorption results of tests on this basis. The sorption results (standard-wet) of the extruded kaolinite pellets (RTI) are shown, sorption rates increased with a rising NaCl concentration.

### 4.3 SORPTION AND DESORPTION CHARACTERISTICS OF SORBENTS

Sorption and desorption profiles for kaolinite, emathlite and calcium montmorillonite were determined in order to investigate sorbent sorption characteristics (role of water, effect of hydrogen chloride). Under a treatment with NaCl-dry, standard-wet and standard-wet/HCl, sodium sorption profiles were generated. It is suggested that gaseous environment and pellet properties are a major factor in the alkali sorption mechanism/process.

The alkali sorption experimental programme which was carried out showed that the alkali sorption process is influenced by the composition of the gas. Desorption tests carried out to investigate the effect of hydrogen chloride on the sorption process showed that hydrogen chloride is a significant factor in producing different alkali sorption results (Section 4.3.2). Experiments were conducted to investigate the role of water vapour in the alkali sorption mechanism/process. Water vapour was found to be a significant factor in the alkali sorption mechanism/process.

#### 4.3.1 Effect of Gaseous Environment

In general, gaseous environmental effects for the sorbents under test were found to exist for all emathlite and calcium montmorillonite pellets and pan pelletised kaolinite pellets when exposed to the environmental conditions of NaCl-dry, standard-wet and standard-wet/HCl. Independent of the gaseous environment effect it was observed that the alkali sorption profiles of pan pelletised pellets were much higher than those of extruded pellets.
The alkali sorption profiles of individual extruded kaolinite pellets (RTI) from treatment with a NaCl-dry, standard-wet and standard-wet/HCl condition are shown (Figure 20). Initially the sorption rates of the profiles appear to be different, but at the end of exposure the profiles became similar. It cannot be said whether the shape of the sorption profiles were affected by the gaseous environment. Figure L.I.1 indicated that pellets of the same formulation technique produced ‘identical’ sorption profiles in the same gaseous environment. The weight increase per time associated with alkali sorption was $0.27 \pm 0.03 \times 10^3 \text{mg/min}$ with an exposure time of 39 hours. The initial sorption rate was found to be five times higher than the rate after 39 hours.

The sorption profiles for pan pelletised kaolinite (ECC) are in Figure 21. The profiles appear to be similar, but the individual pellets show same differences in initial rates. At the end of exposure, the gas mixture with a treatment standard-wet showed the highest rate. The weight increase per time associated with alkali sorption was $0.4 \times 10^3 \text{mg/min}$ for the treatment under NaCl-dry and standard-wet/HCl condition and $0.7 \times 10^3 \text{mg/min}$ for treatment under standard-wet conditions.

Figure 20: Sorption Profile for Extruded Kaolinite (RTI) at 850°C.

$^2$ The weight gain of a time interval was used to calculate the rate for the time interval for the time range 38-40 hours.
Figure 21: Sorption Profiles for Pan Pelletised Kaolinite (Supreme, ECC) at 850°C.

The sorption profiles for emathlite (RTI) and calcium montmorillonite (LaPorte) showed a significant variation according to gaseous environment. The profiles for calcium montmorillonite and emathlite are seen in Figure 22 and 23. In general, the exposure times for these profiles were shorter than those of kaolinite. The exposure time for the calcium montmorillonite profiles were twice as long as those of the emathlite profiles.

Under standard-wet conditions, the profiles of calcium montmorillonite (LaPorte) and emathlite (RTI) appear to be same and remain steep whereas the profiles for standard-wet/HCl and NaCl-dry show saturation kinetics. The weight increase per time associated with alkali sorption for emathlite in standard-wet conditions was $0.2 \times 10^{-5} \text{mg/min}$ over 15 hours, and $0.1 \times 10^{-5} \text{mg/min}$ at 39 hours$^3$ (Mönter, 1996). The derived rate term (39 hours) exposure was based on sorption experiments with falling salt concentration. Under standard-wet conditions, calcium montmorillonite gave a rate of $0.1 - 0.2 \times 10^{-3} \text{mg/min}$.

---

$^3$ extrapolated from a sorption run 40ppmv NaCl and 2.1%vol H$_2$O
Saturation kinetics for calcium montmorillonite (LaPorte) and emathlite (RTI) profiles were observed during the initial stage of the alkali sorption process; the results are seen in Figure 22 and 23. The exposure time for the calcium montmorillonite profiles was twice as long as those of emathlite.

Under the treatment NaCl-dry, it can be seen that the sorption level for calcium montmorillonite was ten times that of observed of emathlite; 0.06 and <0.006 in terms of weight fraction, respectively. The exposure time reflects that saturation under the condition of NaCl-dry occurs faster in emathlite than it does for calcium montmorillonite.

Using standard-wet conditions, the profiles for calcium montmorillonite (LaPorte) remain steep whereas the sorption profiles treated under the standard-wet/HCl condition do not, see Figure 23. With added HCl, a gaseous environment effect occurs.

Figure 22: Sorption Profiles for Extruded Emathlite (RTI) at 850°C.
Figure 23: Sodium Sorption Profiles for Pan pelletised Calcium Montmorillonite (LaPorte) at 850°C.

Using NaCl-dry and standard-wet/HCl conditions saturation kinetics were observed for both calcium montmorillonite (LaPorte) and emathlite (RTI). The profiles do not show a gaseous environment effect for calcium montmorillonite but show a small environmental effect for emathlite. The increased profile characteristic for emathlite when treated under standard-wet/HCl conditions can be seen in Figure 22. The result shows that the standard-wet/HCl condition can shift the profile to a higher plateau.

4.3.2 Desorption Profiles

To see whether pre-treated kaolinite (NaCl-dry, ECC) would be affected by an inert-dry atmosphere with hydrogen chloride, pre-treated kaolinite (NaCl-dry) was exposed to hydrogen chloride, see Figure 24. The kaolinite used to remove alkali from the inert/HCl atmosphere displayed an almost complete reverse. Sorption was allowed for >40 hours then on changing to an inert-dry environment the sorption stopped. Weight loss was not observed. Finally, with the introduction of inert-dry/HCl conditions desorption occurred.
Figure 24: Desorption Profile in the case of Pre-treated Kaolinite (NaCl-dry, ECC) when Exposed to HCl (inert-dry/HCl).

To see whether water vapour alone would lead to a desorption profile for pre-treated kaolinite (RTI), pre-treated kaolinite (NaCl-dry) was exposed to water vapour alone (Figure 25). With water vapour added, the sorption profile (weight fraction, 0.048; exposure time 54.7 hours) maintained its level. Desorption was not observed.

Figure 25: Pre-treated Kaolinite (NaCl-dry, RTI) Exposed to Water Vapour alone (Inert-wet).
Pre-treated pan pelletised kaolinite (standard-wet, ECC) exposed to a desorbing mixture (inert-dry and inert-wet/HCl) led to insignificant desorption, see Figure 26. With the change of atmosphere to an inert-dry condition (68 hours), the sorption stopped and remained on the same level for one hour. Finally the ‘desorbing’ mixture inert-wet/HCl was added, desorption was found to be insignificant. The sorption profile up to 68 hours was affected by a fall in salt concentration. The average salt concentration was determined.

Pan pelletised calcium montmorillonite exposed to NaCl (LaPorte) displayed desorption characteristics when NaCl was removed and HCl was added to the gas mixture (Figure 27). Using the treatment under the NaCl-dry condition, sorption was permitted for 35 hours. With HCl added and sodium chloride removed, desorption occurred within 13 hours. The desorption process was stopped by changing to an inert-dry atmosphere (time period 48-58 hours). A nitrogen environment was used to confirm that no other effects were involved. To gain desorption, HCl was added. Desorption was permitted for 10 hours. This conclusively proves that desorption will take place with an environment containing hydrogen chloride in nitrogen.

![Graph showing weight fraction over time](image)

Figure 26: Pre-treated Pan Pelletised Kaolinite (ECC) Exposed to a ‘Desorbing’ Atmosphere (Inert-dry and Inert-wet/HCl).
To see whether water vapour alone would lead to a desorption profile within NaCl-treated calcium montmorillonite (LaPorte); NaCl treated calcium montmorillonite was exposed to water vapour alone. Desorption condition with water vapour alone was initiated after 30 hours. Desorption was not observed, see Figure 28.

Figure 27: Desorption Profile in the Case of Pre-treated Calcium Montmorillonite (NaCl-dry, LaPorte) when Exposed to Hydrogen Chloride.

Figure 28: Pre-treated Calcium Montmorillonite (NaCl-dry, LaPorte) exposed to Water Vapour alone.
Pre-treated pan pelletised calcium montmorillonite (standard-wet, LaPorte) exposed to a reversing mixture (inert-wet/HCl) produced a significant desorption profile. The desorption profile for calcium montmorillonite is shown in Figure 29. Sorption was initiated under standard-wet conditions. Sorption treatment was maintained for nearly 60 hours. Sorption was stopped by an inert-dry gaseous atmosphere. Using the inert-dry atmosphere, desorption was not observed. Finally, the desorbing mixture (inert-wet/HCl) was added. A significant desorption was observed. It was not obvious whether the desorption profile resulted from the combination of hydrogen chloride and water vapour.

![Figure 29: Desorption Profile when Pre-treated Calcium Montmorillonite (standard-wet, LaPorte) was exposed to Hydrogen Chloride and Water Vapour.](image)

To see whether the desorption profile resulted from either the combination of hydrogen chloride and water vapour or water vapour alone (inert-wet), pre-treated calcium montmorillonite (standard-wet) was exposed to an inert-wet atmosphere (Figure 30). With the change of the atmosphere, the sorption stopped (45.2 hours, weight fraction 0.057) and no weight loss occurred.

80
Figure 30: Pre-treated Calcium Montmorillonite (standard-wet, LaPorte) exposed to Water Vapour alone.

It was not clear whether the combination of temperature increase and a salt-free atmosphere (inert-dry) lead to desorption. Figure 31 shows a profile of calcium montmorillonite (LaPorte) initially treated with NaCl-dry and inert-dry condition for a short time. Using a salt-free atmosphere (inert-dry), a temperature increase was initiated. The temperature rate from 850°C to 950°C was 10°C/min. The temperature change led to a change of weight fraction. The new level was maintained for one hour, a change in level was not observed. To see whether a temperature decrease to the 850°C level would affect the weight fraction, the temperature was decreased to 850°C. A change in level occurred again due to the temperature change, the level at 850°C was same before the temperature variations. The procedure was again proceeding and it was observed that the weight fraction was in agreement with that of the two procedures.

Emathlite pellets (RTI) used to remove alkali from a water and nitrogen atmosphere displayed a partial reverse in the sodium sorption process, attaining a new, lower, equilibrium level, when subsequently exposed to a hydrogen chloride and nitrogen atmosphere without sodium chloride present, shown in Figure 32. It was interesting that the partial reverse was in the
height of sorption under the NaCl condition, see Figure 32 and 22. Treatment under an inert condition did not lead to desorption.

![Graph showing sorption under different conditions](image)

**Figure 31**: Pre-treated Calcium Montmorillonite (NaCl-dry, LaPorte) exposed to Salt-free and Temperature Increased Atmosphere.

![Graph showing reverse in sodium sorption](image)

**Figure 32**: Reverse in Sodium Sorption Process in Emathlite Pellets (RTI) with the Introduction of Hydrogen Chloride.
4.3.3 Effect of Water Vapour

To investigate whether sorption profiles are affected by water vapour content, water vapour was added to the mixture after initial exposure. Figure 33 shows a sorption profile for calcium montmorillonite (LaPorte) initially pre-treated with NaCl-dry and subsequently exposed to standard-wet conditions. Sorption occurred for 28 hours (Weight fraction 0.042). Once the inert-dry conditions were changed to standard-wet, a step change was observed. The step change started with a steep slope. The rate decreased to a constant level. In the case of emathlite, the rate did also change when the treatment under standard-wet/HCl conditions was changed to a standard-wet (Appendix L.II.1).

![Graph showing effect of water vapour on alkali sorption process after initial NaCl saturation.](image)

Figure 33: Effect of Water Vapour on Alkali Sorption Process after Initial NaCl Saturation.

To see whether pre-treated kaolinite (NaCl-dry, ECC) also exhibits a step change in the alkali sorption process; pre-treated kaolinite (NaCl-dry) was exposed to a standard-wet/HCl condition (47 hours). A step change occurred, which persisted for over one hour. The steep step (47 hours) reduced to a constant rate. The new rate was found to be higher than that of before the test. With HCl removed, the sorption profile remains steep. In contrast to the other Figures, Figure 34 shows straight lines. This result is due to the time interval shown.
4.4 SODIUM CONTENT AND REACTION PRODUCTS

Single layer fixed bed tests (top layer) were carried out to measure the sodium content bound in kaolinite (ECC) and calcium montmorillonite (LaPorte) when treated with NaCl-dry, standard-wet and standard-wet/HCl. The sodium content was analysed from various fractions to determine the reaction mechanism (Section 4.4.1). Additionally, pre-treated kaolinite and calcium montmorillonite (standard-wet, NaCl-dry) were exposed to proposed ‘desorbing’ mixtures (inert-wet/HCl; inert-dry/HCl), respectively. This enabled the sorbent sorption property - desorption of sodium - to be investigated (Section 4.4.2). Calcium montmorillonite pellets were also short term treated with NaCl, to investigate sodium sorption in the early stage (Section 4.4.3).

Single layer fixed bed tests were also carried out to identify possible reaction products formed from kaolinite and calcium montmorillonite when treated as above. The formed phases, identified by X-ray diffraction analysis, were analysed to derive possible reaction equations (Section 4.4.4).
4.4.1 Sodium Content in Various Fractions of Calcium Montmorillonite and Kaolinite

Sodium contents were analysed to determine whether calcium montmorillonite and kaolinite sorbed sodium in a water soluble, HCl soluble and/or HF insoluble form (Table J.VII-VIII). The extractable contents of calcium montmorillonite and kaolinite differed with water leaching, HCl leaching and HF leaching solutions. In both cases, the sodium content leached by water was found to be negligible, see Table 11.

<table>
<thead>
<tr>
<th>Condition (100 hours)</th>
<th>Water leached Sodium [gNa/g solid]</th>
<th>HCl leached Sodium [gNa/g solid]</th>
<th>HF leached Sodium [gNa/g solid]</th>
<th>Total Sodium [gNa/g solid]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Kaolinite</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaCl-dry</td>
<td>0.001</td>
<td>0.046</td>
<td>0.016</td>
<td>0.063</td>
</tr>
<tr>
<td>Standard-wet/HCl</td>
<td>0.001</td>
<td>0.037</td>
<td>0.026</td>
<td>0.064</td>
</tr>
<tr>
<td>Standard-wet</td>
<td>0.001</td>
<td>0.071</td>
<td>0.006</td>
<td>0.078</td>
</tr>
<tr>
<td><strong>Calcium Montmorillonite</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaCl-dry</td>
<td>0.000</td>
<td>0.001</td>
<td>0.045</td>
<td>0.046</td>
</tr>
<tr>
<td>Standard-wet/HCl</td>
<td>0.000</td>
<td>0.001</td>
<td>0.046</td>
<td>0.047</td>
</tr>
<tr>
<td>Standard-wet</td>
<td>0.000</td>
<td>0.011</td>
<td>0.058</td>
<td>0.069</td>
</tr>
</tbody>
</table>

Table 11: Sodium Content in Various Extracts (leaches) of Calcium Montmorillonite (LaPorte) and Kaolinite (ECC).

The leachable sodium content of pan pelletised kaolinite was found to be higher when leached using the HCl solution. In calcium montmorillonite it was found to be higher if HF leach is used. Using a treatment with NaCl-dry and standard-wet/HCl, the total sodium content in both leaching solutions was lower than with a treatment under standard-wet conditions.

4.4.2 Sodium Content in Treated Pellets Exposed to HCl Mixtures

Using a treatment under the standard-wet conditions, desorption of sodium in calcium montmorillonite (LaPorte) was observed when exposed to an atmosphere of standard-wet/HCl condition. The sodium content was found to be diminished by 31% (see Figure 35). Kaolinite did not show any desorption under same procedure (Table J.IX.1).
Figure 35: Desorption of Sodium when Pre-treated Sorbent (standard-wet) was Exposed to an Inert-wet/HCl Atmosphere.

Figure 36: Desorption of Sodium when Pre-treated Sorbent (NaCl-dry) was Exposed to an Inert-dry/HCl Atmosphere.
Pre-treated calcium montmorillonite (NaCl-dry, LaPorte) and kaolinite (ECC) exposed to an inert-dry/HCl atmosphere showed desorption of sodium (Figure 36). The sodium content of calcium montmorillonite was diminished by 49%, whereas the sodium content of kaolinite was diminished by 56%. The sodium content was determined by AAS.

4.4.3 Sodium Sorption Profile

Using a treatment with NaCl-dry condition, a sodium sorption profile was generated for calcium montmorillonite (LaPorte) based on three atomic absorption spectrometry results (0 hours, 24 hours and 100 hours, J.X.1). Figure 37 shows that calcium montmorillonite sorbed sodium according to saturation kinetics. The dotted sodium profile of calcium montmorillonite (standard-wet) is shown for comparison. The sodium content of 7.1% wt. after 100 hours was measured and used to compare it to the sodium content at 24 and 100 hours (NaCl-dry). It appears that the sodium sorption in pan pelletised calcium montmorillonite occurs in steps.

To see whether ‘Single Pellet Reactor’ results would agree with ‘Fixed Bed Reactor’ results, weight fraction results of calcium montmorillonite (LaPorte) treated with NaCl were compared. Figure 38 shows that the weight fraction of the ‘single’ layer agrees with single pellet reactor treated calcium montmorillonite across in a very narrow range.

4.4.4 Reaction Products

Table 12 identifies possible reaction products for calcium montmorillonite (LaPorte) and kaolinite (ECC) in certain gaseous environments when either pre-treated or pre-treated and further exposed to other mixtures. Albite (Powder Diffraction file (PDF), 9-466), Nepheline (PDF, 9-458), Carnegieite (PDF, 11-220), and Silicon oxide (PDF, 33-1161) were identified. The X-ray diffraction patterns of calcium montmorillonite, kaolinite, albite and nepheline were produced on the Philips 1050 diffractometer. Tables KII-VI.1 gives a breakdown of all major peaks in the sorbent and their reaction products.
Figure 37: Sodium Sorption Profile for Pan Pelletised Calcium Montmorillonite (NaCl-dry, LaPorte) based on AAS Results.

Figure 38: Sodium Sorption and SPR profile for Pan Pelletised Calcium Montmorillonite (LaPorte).
Table 12: Reaction Products Formed by Aluminosilicate Materials when Exposed to Sorption and Desorption Gaseous Environment.

<table>
<thead>
<tr>
<th>Reaction Products</th>
<th>Calcium Montmorillonite</th>
<th>Kaolinite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Albite&lt;sup&gt;1&lt;/sup&gt;</td>
<td>Nepheline&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>Gaseous Atmosphere&lt;sup&gt;5&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial Treatment with NaCl</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>NaCl-dry</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>NaCl-dry Inert-dry/HCl</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Standard-wet</td>
<td>Yes, but&lt;sup&gt;6&lt;/sup&gt;</td>
<td>Yes</td>
</tr>
<tr>
<td>Standard-wet Inert-wet/HCl</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Standard-wet/HCl</td>
<td>Yes, but&lt;sup&gt;6&lt;/sup&gt;</td>
<td>No</td>
</tr>
</tbody>
</table>

<sup>1</sup> Diffraction Powder file (9-466), Albite - Sodium aluminium silicate, low temperature form, NaAlSiO<sub>4</sub>, Smith (1956)
<sup>2</sup> Diffraction Powder file (9-458), Nepheline - Sodium aluminium silicate, Na<sub>2</sub>KAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>, Barrer and White (1952)
<sup>3</sup> Diffraction Powder file (23-1161), Sodium oxide, low quartz
<sup>4</sup> Diffraction Powder file (11-220), Carnegieite
<sup>5</sup> Based on 100 hour runs with 40 ppmv NaCl, 1.3% by volume H<sub>2</sub>O, 100 ppmv HCl, N<sub>2</sub> balance, 850°C
<sup>6</sup> Based on compared pattern (Appendix K): Some peaks with low intensity
<sup>7</sup> Based on compared pattern (Appendix K): Some peaks with low intensity, run with shutdown
<sup>8</sup> ND - Not Determined
CHAPTER 5

DISCUSSION OF EXPERIMENTAL RESULTS

In this Chapter, experimental results of Chapter 4 will be discussed to evaluate and review the alkali sorption process/mechanism of kaolinite and calcium montmorillonite: Sorbent characteristics and analysis (Section 5.1); initial sorbent activity (Section 5.2); sorption and desorption characteristics of sorbents (Section 5.3); sodium content and reaction products (Section 5.4). The effects of sorbent sorption characteristics (e.g. reversibility, reaction mechanism) on the alkali sorption process are discussed.

5.1 SORBENT CHARACTERISATION AND ANALYSIS

The results showed that by changing the mode of pellet production, the internal structure of a pellet is significantly affected. The void content of pan pelletised pellets is so high that it leads to fragile pellets. Heat-treatment results in a higher strength; however, pellets are still fragile. In contrast, pellets produced by extrusion have an enhanced mechanical strength but less internal voidage.

5.1.1 Total Pore Volume, Porosity and Mean Pore Diameter Results

With the mercury intrusion analyses it was shown that the total pore volume and porosity in pan pelletised pellets was higher than that of extruded pellets. The total pore volume of pan pelletised pellets was determined to be of the order of 0.35 cm$^3$/g whereas the total pore volume of extruded pellets was less than 0.22 cm$^3$/g. The porosity values of pan pelletised pellets (35-49%) differ from the extruded pellets (30-34%).

The pore volume and porosity data indicated (Table 8) that the pan pelletisation technique produces pellets with a more open structure (calcium montmorillonite (LaPorte), Image E.VII.2.) than the extrusion technique (emathlite, E.VII.1). It is anticipated that the more open
structure increases the number of possible sorption sites. The result means that the sorbent sorption characteristics, alkali activity and capacity are affected.

A smaller mean pore diameter was found in kaolinite than was found in emathlite and calcium montmorillonite for both pan pelletised and extruded pellets. It is possible that the smaller pore sizes in kaolinite increases the possibility of alkali sorbent interactions. It was noticed by Lee and Johnson (1980) that the effectiveness of a sorbent for NaCl vapour is generally related to its internal surface area. High internal surface area is primarily contributed to by small pores.

It was shown that the calcination procedure reduced the availability of small pores (macro- and meso-pores). It appears that the loss of structural water resulted in pores of greater size. A loss of structural water is in agreement with the predictions of the thermochemistry of the sorbents. Thermochemistry predicts the loss of structural water and furthermore the dehydration of the sorbents (Brindley and Nakahira, 1959). When kaolinite is dehydrated according to the reaction

\[ 2Al_2Si_2O_5(OH)_4 \rightarrow 2Al_2Si_2O_7 + 4H_2O \]

the theoretical weight loss is 14%. In this work agglomerated kaolinite pellets loose no more than 13% weight when heat-treated at 850°C for 24hours (Rieger, 1997). The loss of 13% in weight should increase the availability of larger pores. This could mean that residual hydroxyl groups are present.

5.1.2 Surface Area Results

Surface area measurements\(^1\) were performed in order to evaluate the effect of air-calcination on the surface area of the sorbent and sorbent pellets. In general, calcination significantly reduced the surface area of both the sorbent and the sorbent pellets (Table 9). The pelletisation procedure had only a minor effect on the surface area. The result indicates that calcination of the sorbent affects the surface area much more than the means of producing the pellet.

\(^1\) BET nitrogen adsorption at minus 196°C.
It is believed that the determined surface area stability of the calcined sorbents can be related to the high-temperature sorbent chemistry. The high-temperature sorbent chemistry predicts the loss of hydroxyl groups in kaolinite and montmorillonite (Brindley and Nakahira, 1959; Grim and Kulbicki, 1961; Meinhold et al, 1992). The upper temperature limit for retaining hydroxyl groups in kaolinite was reported to be about 950°C. The upper limit in montmorillonite was found to be in the range 850-900°C. With the hydroxyl groups removed, the sorbent layer structure collapses. Once collapsed, it is possible that the surface area is diminished. It was found that the surface areas of the sorbents were affected in the temperature ranges where the layer structures of kaolinite and montmorillonite collapsed. The relationship is interesting. It also appears that the high temperatures affect the pore sizes and therefore the porosity.

At a temperature of 850°C, the surface area of kaolinite was found to be eight times that of calcium montmorillonite. It is very likely that the higher surface area of kaolinite will lead to a higher sorbent activity and capacity in kaolinite.

5.1.3 Mean Particle Size Results/Microstructure

The median particle length of kaolinite was found to be 0.4μm whereas those of calcium montmorillonite and emathlilite were found to be in the range of 2-44μm\(^2\). The particle length of the major axis was measured in calibrated units and averaged to give the mean particle length of the sorbent particles.

It is likely that the smaller particle sizes of kaolinite increase the occurrence of smaller pores. With smaller pores, the effectiveness of the sorption process increases. It is also possible that the smaller particle sizes in kaolinite increases the availability of hydroxyl groups. With smaller particles the chemical interaction of components in the gas stream with the sorbent increases.

There is little to find in the literature about the influence of particle size on the alkali sorption process. Helble et al (1992) reported that particles larger than 2μm would form alkali silicates

\(^2\) derived from literature
whereas smaller particles would provide other forms. Considering Helbles et al. observations and the above ones it would appear that particle size is a factor within the alkali sorption process, see Chapter 4. Chrysohoioudou (1996) showed that particle size significantly affected curve fitting.

Scanning electron microscopy and digital image processing techniques were found highly efficient in getting a 'good' digital image with a mean particle length value. The digital picture must provide sufficient resolution of the particles. Particles agglomerated in dense pellets cannot be resolved sufficiently, pan pelletised pellets can. Spreading of calcined material on a sticky film provides information on particle sizes without the interference of agglomeration factors. With agglomeration of the particles into a pellet, the mean major grain size increases. Although not observed, it is believed that the mean major particle length of calcium montmorillonite was affected. Grain sizes of the calcium montmorillonite raw material (2.8 μm) were compared with mean grain sizes determined by Chrysohoioudou, 1996 (30 μm and 44 μm depending on the produced pellet diameter).

5.1.4 Compressive Strength Results

Pan pelletised and extruded pellets were load tested to test their characteristic breakage point. In general, it was observed that the friability of a pellet produced by the pan pelletisation technique is higher than that of pellets produced by extrusion. The mechanical strength of a pan agglomerated pellet cannot be significantly improved by adding more water. This implies that pan pelletisation will not produce pellets able to meet the demands of mechanical strength required to survive the stress in moving and fixed bed processes.

It was found that the friability of pan pelletiser kaolinite pellet was higher than that of a pan pelletiser calcium montmorillonite pellet. In general, the strength of the forces between the particles decreases quickly with increasing distance. Therefore, seeds ('green pellets') are used to agglomerate pellets. Different particle size distributions are used to increase the number of contacts between the particles. In this work pan agglomeration was characterised by the growth of particles after the addition of liquid binders. Agglomeration was influenced mainly by interfacial forces and capillary pressure at freely movable liquid surfaces. Particle size
distribution is less relevant to the binding mechanism. Adding water was found to be more important than changing the particle size distributions.

Manually formulated pellets (10N/pellet) were produced with similar characteristics to extruded pellets. By equating a manually formulated pellet to a pellet made by extrusion, it was possible to study the influence of agglomeration on alkali sorption profiles with same raw material characteristics.

The mechanical strength values of the extruded pellets were tested by RTI\(^3\) and found to concur with this work. Because of the similarity in relative mechanical strength values, further evaluation studies were considered unnecessary.

**5.1.5 Element Distribution (Element Mapping)**

The sodium distribution in extruded pellets exhibited shrinking core behaviour within the treated pellet, whereas that within pan pelletised pellets indicated a homogeneous distribution, see images 3 and 4. This implies that pellets formed by extrusion will have a lower sodium sorption capacity than those formed by pan pelletisation. Therefore, it seems that sorbent sorption capacity of a pellet must be defined in relation to its pellet formation technique. Sodium was not found in pellets which were untreated.

In a ‘reacted’ zone of kaolinite, the ratio of Na:Cl was higher than 20:1, which in turn means chlorine was not retained in kaolinite (Appendix G.II). Cross sections of methanol washed pellets set in epoxy for investigation did not yield valid results because of chlorine content of the epoxy hardener material. In addition, the treatment time of 15 hours was found to be insufficient to investigate the chlorine signal within pellets produced by extrusion technique, because it did not provide a signal beyond the background level (basis 10 counts). However, the results indicate that chlorine was not retained by kaolinite and emathlite when the pellets were treated under the standard aluminosilicate reaction conditions.

\(^3\) ASTM D 4179—Standard Test Method for Single Pellet Crush Strength of Formed Catalyst Shapes, Chattation Model No. DFIS 100 digital force gauge (0-450N/pellet). 20 pellets were crushed to obtain an average crush strength and standard deviation.
It was reported by Mönter (1996) that the 'homogenous sodium distribution within pellets is influenced by the chemical composition of a grain. The finding was confirmed in this study. It was found that grains with a very high silicon content negatively influenced the alkali sorption process in the grains (Appendix G.III.1). In the case of a high calcium oxide content, a similar negative influence was observed. The results imply that the chemical composition of a pellet affects the alkali sorption process.

Using treatments under different environmental conditions, silica:alumina ratio varied (Appendix G.IIa). A ratio change indicates a change of composition or rearrangement of atoms either locally or in general. It has been shown by Bachovchin et al (1986) that solubilisation of silicon occurs from the HF bound form into the HCl soluble form when treated according to a standard aluminosilicate reaction condition. This suggests a replacement mechanism. In addition, the melting point of silica drops significantly in the presence of water vapour. It was shown by Mason and Berry (1968) that silica melts at 1700°C under dry conditions whereas in the presence of water vapour at approximately 1100°C. This indicates that the stickiness of a sorbent at elevated temperatures depend upon the silica:alumina ratio and the gaseous environment.

5.2 INITIAL SORBENT ACTIVITY

In order to gauge the alkali sorption rates of target pellets for the alkali sorption process initial sorbent activities were determined. The influence of temperature and pellet formation on the alkali sorption process was determined using a standard-wet conditions. Sorption was studied on pan pelletised and extruded pellets types consisting of kaolinite and calcium montmorillonite.

5.2.1 Effect of Temperature

For many reactions the temperature dependency of a reaction can be represented by rate expressions (reaction rate constant by Arrhenius’ law). In this work a simple rate expression is used to show that an increase in temperature leads to an increase in rate. An increased initial
alkali sorption activity was observed in kaolinite and calcium montmorillonite with an increasing temperature (temperature range 800°-875°C; Figure 16 and 17).

The initial sorption rates in calcium montmorillonite increased more dramatically than those observed with kaolinite. The low activity of calcium montmorillonite at a temperature of 800°C was surprising when compared to kaolinite. It seems that calcium montmorillonite is less reactive than kaolinite. This seems unlikely due to the silica:alumina ratio of the sorbents. Ternary Phase diagrams (Na₂O · Al₂O₃ · SiO₂, Levin et al, 1964, Appendix N.I) favour the formation of reaction products for calcium montmorillonite rather than for kaolinite. However, it could also be inferred that particle size produces the increased sorption rate of kaolinite. The particle size of kaolinite was found to be significantly smaller than that of calcium montmorillonite. At higher temperatures, the initial sorption rates of calcium montmorillonite approach those of kaolinite. This means that temperature variation affected the performance of the sorbent as an alkali getter. It is likely that the difference in particle size distribution affects the rate of reaction.

The increase of initial alkali sorption activity with temperature agrees with the findings of Uberoi et al (1990). Uberoi et al (1990) showed that alkali sorption activity increases with temperature for kaolinite, when single pellets were exposed to gaseous environments from 800-1000°C (150ppmv). Uberoi’s initial alkali sorption activity results showed that the weight increase per time associated with alkali sorption in kaolinite was 4x10⁻³ mg/min at 800°C and 7x10⁻³ mg/min at 900°C. A direct comparison of the rates determined by Uberoi with the rates determined here would be misleading because the alkali concentration and pellet properties used were different. Pressed flakes were found to result in a similar initial rate as extruded pellets (850°C, 40hours rate, Uberoi et al, 5.5x10⁻³ mg/min, here 4.5x10⁻³ mg/min).

5.2.2 Effect of Agglomeration

Experimental results have shown that the alkali sorption process is affected by the mode of pellet formation, see Table 10. Pellets produced by the pan pelletiser technique exhibit a higher initial sorption activity than those produced by the extrusion technique. The effect of pellet
formation on the alkali sorption process was investigated for sodium sorption profiles from different production modes using the same materials (Figure 18). The results imply that the means by which pellets are produced affects the uptake. It is likely that intrapellet diffusivity is a rate controlling step for the extruded pellets because reactants cannot diffuse to available sorption sites.

The effect of agglomeration on alkali sorption agrees with the findings of Mönter (1996), Bachovchin et al (1986) and other researchers. Bachovchin et al (1986) found that commercially extruded pellets were less reactive than laboratory pressed pellets. A thirty percent reduction in sodium absorption rate was observed for the extruded pellets. However, it was concluded that extrusion pellets are suitable for industrial use. Mönter (1996) showed that the sodium content of extruded kaolin pellets was diminished of the order of three times when compared with pellets of the pan pelletiser technique. The results indicate that initial sorption activity is affected by the mode of pellet formation to a lesser extent than the sorbent sorption capacity. It appears that the formulation of a suitable pellet with a high alkali loading capacity is difficult.

The result that the production method of pellets can significantly affect the initial sorption activity and sorption capacity indicates that alkali sorption results may be unique for a pellet type. With the element mapping technique it was shown, that the sodium distribution in a pellet was affected. It seems worthwhile to relate sorption results to the various analytical techniques used to explain diffusional limitations within a pellet. Common limitations (such as the formation of a product layer) could be better explained.

5.2.3 Effect of NaCl Concentration

It has been shown that sorption rates were significantly affected by the NaCl concentration. Reasonable sorption rates cannot be achieved at low NaCl concentration which indicates that research and development on gas turbine machinery components is also vital to achieving higher thermal efficiency of coal-based power generation plant. In addition, the sorption profiles indicate first order sorption kinetics with respect to NaCl.
5.3 SORPTION AND DESORPTION CHARACTERISTICS OF SORBENTS

Experiments have been carried out to investigate primarily the effect of gaseous environment on the kinetics and mechanisms of the alkali sorption process for primarily kaolinite, calcium montmorillonite and emathlite (Section 4.3). Gaseous environment experiments led to sodium sorption profiles under 'NaCl-dry', 'standard-wet' and 'standard-wet/HCl' conditions. In addition, desorption profiles resulted from experiments of pre-treated sorbent when further exposed to 'desorbing' mixtures (Section 4.3.2). Water vapour was shown to play a major role in the alkali sorption process (Section 4.3.3).

5.3.1 Effect of Gaseous Environment

Fundamental studies were carried out to investigate alkali sorbent interactions (NaCl-dry, standard-wet, standard-wet/HCl) on pan pelletised and extruded target sorbents. Kaolinite and calcium montmorillonite sorbent were used as they have a different mean particle size and composition. The change of the gaseous environment (role of water and hydrogen chloride) was shown to be successful in generating sorbent sorption profiles for sodium capture of either a same/similar or a different shape depending on the exposure time and gaseous environment.

The sorption profiles for emathlite and calcium montmorillonite indicated that the alkali sodium interactions influenced the profile characteristics of calcium montmorillonite and emathlite. The profiles of calcium montmorillonite and emathlite are seen in Figure 22 and 23. In general, using a treatment under the standard-wet condition, steep profiles in calcium montmorillonite and emathlite were determined. Steep profiles are not seen in the cases of NaCl-dry and standard-wet/HCl. The result with apparently enhanced uptakes may indicate that the alkali sorption process was promoted by a standard aluminosilicate reaction following reaction Equation 5. In the presence of water, standard aluminosilicate reaction would be expected to dominate. Certainly a higher uptake under the standard aluminosilicate reaction conditions (Equation 5) was observed. The saturation kinetics in calcium montmorillonite and emathlite when treated with NaCl-dry and standard-wet/HCl may imply that adsorption or reaction contributes to the alkali sorption process. The alkali sorption profiles in a NaCl-dry
environment would appear to indicate the existence of adsorption, since assuming there are no -OH groups present. In the case of residual -OH groups, reaction is relevant to the alkali sorption process.

In the case of a standard-wet and standard-wet/HCl treatment for calcium montmorillonite, a gaseous environment effect was observed. The profile for standard-wet, remained steep whereas that for standard-wet/HCl did not, see Figure 23. Apparently enhanced profiles were determined in the presence of water vapour. With HCl added, the standard aluminosilicate reaction was inhibited. The inhibiting effect of hydrogen chloride was observed to be higher in calcium montmorillonite than that observed in emathlite.

Using a treatment NaCl-dry and standard-wet/HCl, saturation kinetics were determined for calcium montmorillonite (Figure 23). The similarity of the saturation profiles for both treatments imply that the standard-wet/HCl condition did not cause an environmental gaseous effect. The water vapour content in the gaseous environment standard-wet/HCl did not lead to a higher level. This can imply that a standard aluminosilicate reaction with HCl was disturbed and that the profiles under the used environments may have resulted from the same sorption mechanism.

In contrast to calcium montmorillonite, emathlite showed a lower level when treated under the standard-wet condition with HCl (Figure 22 and 23). The result implies that a treatment under standard-wet/HCl condition in calcium montmorillonite shifted the profile to a higher level. This is due to the different chemical composition.

Using a treatment NaCl-dry, adsorption appeared to be relevant to the alkali sorption process for calcium montmorillonite and emathlite. But it is possible that remaining hydroxyl groups in calcium montmorillonite led to reaction.

Calcium montmorillonite profiles implied that once the initial sorption process of the NaCl conditions slows down a standard aluminosilicate reaction promotes the alkali sorption process. But, it is also possible that condensation of water vapour in the pellet raised the level of sorption of water vapour. It has been re-established here that sorption under the standard-
wet condition occurred long enough to show that a step change was due to an aluminosilicate reaction not due to water vapour condensation in pores (see also sodium content results for the condition standard-wet and NaCl-dry, Section 4.4).

Emathlite did not show the trend ‘initial sorption’ followed by a standard aluminosilicate reaction. A greater gaseous environmental effect occurred within emathlite compared to that of calcium montmorillonite. Using a treatment under the standard-wet condition (Appendix L.III.1), the profile was found to be higher than the profile when treated with standard-wet/HCl. It appears that a standard aluminosilicate reaction dominated the overall sorption process.

The finding that emathlite generates a higher profile when treated standard-wet is in agreement with sorption profiles determined by Mulik et al (1983) and Bachovchin et al (1986).

The alkali sorption profiles of extruded kaolinite are in Figure 20. Under the NaCl-dry, standard-wet and standard-wet/HCl sorption condition; the sorption profiles appear to be similar. However, they became different with the water vapour present. The sorption profiles for pan pelletised kaolinite are in Figure 21. The sorption profiles again appear to be similar, indicating only small differences when treated under standard aluminosilicate reaction conditions. Figure 21 shows that the alkali sorption profile treated with a standard-wet condition started with the lowest rate, compared to the other mixtures. In the end, the rate was found to be highest. It is likely that water vapour has a beneficial effect on the alkali sorption process of kaolinite.

The similarity of the profiles for extruded kaolinite in the three gaseous environments would appear to indicate that in this case the alkali sorption process is initially dominated by either adsorption or reaction, and is independent of the applied gas environment.

It has been shown by Punjak and Shadman (1988b) that levelling off characteristics for kaolinite occur in nitrogen (260ppmv) and that higher profiles are observed using a treatment under simulated flue gas environment conditions containing 2% by volume water vapour. It was assumed that at the higher alkali concentration, the metal vapour concentration in the
sorbent pores becomes higher than the saturation concentration for condensation, the metal vapour physically condenses in the sorbent pores and may subsequently react with the solid. But in the case studied here, the alkali concentration is low (40ppmv). It appears that NaCl either ‘adsorb’ or ‘react’ with kaolinite depending on the existence of remaining -OH groups.

Furthermore, sorption characteristics appear to be governed by particle size, internal structure and sodium chloride concentration. Smaller particles give rise to smaller pores under the same agglomeration method and therefore a greater internal structure. Particles in kaolinite pellets are of the order of 20 times smaller than those of calcium montmorillonite. This would also explain why the alkali sorption level for kaolinite has not been reached within the time scales of the experiments performed. The assumption that the remaining hydroxyl groups in kaolinite would lead to the aluminosilicate reaction seems invalid because the aluminosilicate reaction under the water vapour containing atmosphere is apparently not enhanced, unlike emathlite and calcium montmorillonite. Furthermore, sorption profiles of emathlite indicate that standard aluminosilicate reaction rather than sorption under NaCl-dry condition seems dominating the alkali sorption process. The profiles of calcium montmorillonite indicated that sorption under NaCl-dry occurs first, followed by standard aluminosilicate reaction.

5.3.2 Desorption Profiles

Desorption profiles were observed in desorption experiments for pre-treated kaolinite, emathlite and calcium montmorillonite when exposed to ‘desorbing’ mixtures containing hydrogen chloride. It seems likely that reaction equilibrium was affected.

Pre-treated calcium montmorillonite (standard-wet) exposed to an inert-wet atmosphere with hydrogen chloride showed a desorption profile, see Figure 29. The standard aluminosilicate reaction following reaction Equation 5 has the solid sorbent, NaCl, and water vapour on the left and hydrogen chloride and reaction products on the right. With the added ‘reversing’ mixture, it seems possible that the equilibrium (in the case of a reversible standard aluminosilicate reaction) was affected.
It is also possible that water vapour alone can lead to desorption when pre-treated calcium montmorillonite (standard-wet) is further exposed to an inert-wet atmosphere. It was determined that desorption under an inert-wet atmosphere does not occur. This result is in agreement with findings by Bachovchin et al. 1996. With the water vapour environment, sorption levels did not change.

Pre-treated pan pelletised kaolinite (standard-wet) exposed to an inert-wet atmosphere with HCl led to little desorption, see Figure 26. It seems that desorption was limited. The lack of desorption may imply that HCl did not affect the NaCl equilibrium at this stage of the alkali sorption process.

Desorption profiles were determined when pre-treated kaolinite and calcium montmorillonite (NaCl-dry) were exposed to an inert-dry atmosphere with hydrogen chloride (Figure 24 and 27). Assuming the existence of -OH groups, it appears that pre-treatment led to reaction (e.g. replacement reaction). In the case of a replacement reaction, the sorbent and NaCl appear on the left and hydrogen chloride and the ‘reacted’ sorbent on the right. With hydrogen chloride added from the right (in terms of a replacement reaction), the equilibrium would move to the left and NaCl would be released. It seems possible that desorption of mass resulted from sodium. The desorbed sodium could indicate that the reaction equilibrium was affected. But it could be also that the inert-dry environment led to desorption.

In order to see whether a salt free atmosphere may lead to desorption, pre-treated calcium montmorillonite was exposed to nitrogen alone (Figure 27). Desorption did not occur, sodium is possibly strongly bound. In addition, the combination of a salt free environment and increase in temperature (100°C) did not lead to desorption (Figure 31). It has been stated by McLaughlin (1990) that alkali vapour is retained either through reaction or is strongly adsorbed. McLaughlin showed that alkali vapour was retained up to 1000°C by getter materials. Unbounded alkali was released in a simple screening method, whereas the bonded alkali remained. Similar results with remained bonded alkali were also determined by Turk et al. (1996a). Desorption experiments in a salt free environment have been also performed by Mulik et al. (1983) and Luthra and LeBlanc (1981, 1984). Mulik et al. (1983) investigated ‘desorption’ on activated bauxite by changing the sodium chloride concentration from about...
10ppmv to about 0.002ppmv after a 40 hours period of adsorption. ‘Desorption’ was limited to the range 10-25%. Mulik concluded that this would be evidence of an irreversible step in the ‘adsorption process’. The lack of reversibility implied that fast intrinsic kinetics, such as for physical adsorption, may be incorrect. It has been reported by Datz et al (1961) that the high temperature environment favours gaseous sodium chloride rather than a dissociation of sodium chloride. In the case that sodium chloride bonding occurred strongly, sodium chloride release in the gas would be expected when the gas was made up salt free.

Desorption of sodium possibly occurred for calcium montmorillonite under a treatment inert-wet/HCl (Figure 29). But it is possible that instead of sodium other elements were desorbed. Similar aspects are valid under a treatment inert-dry/HCl, when pre-treated (standard-wet). It appears that confirming results are necessary to show that sodium is desorbed (see Section 4.4 and 5.4).

An inert-dry/HCl atmosphere, led to a desorption profile when emathlite was pre-treated under a standard-wet condition (Figure 32). It cannot be said whether the final level was achieved in emathlite. It is not known, whether a higher hydrogen chloride concentration could affect the desorption gap.

5.3.3 Effect of Water Vapour

Pre-treated calcium montmorillonite (NaCl-dry and standard-wet/HCl) exposed to gaseous atmospheres (standard-wet) showed increases in sorption rates (Figure 33, Appendix L.II/III). With water vapour added to the treatment condition NaCl-dry, the increased sorption rate occurred for several hours leading to a ‘step change’. It is most likely that the aluminosilicate reaction following reaction Equation 5 can progress. However it is possible that condensation of water took place which could also explain this outcome. Chrysohoidou (1996) reported that the HCl concentration increased when pre-treated calcium montmorillonite (NaCl-dry) is exposed to standard-wet condition. It appeared that the higher HCl production may resulted from the standard aluminosilicate reaction.
Pre-treated kaolinite (extended exposure, NaCl-dry) exposed to gaseous atmospheres (standard-wet/HCl) showed a S-shape sorption profile (step change). A possible explanation for the S-shape form is that either water condensation or rehydration of silica and/or alumino groups took place. It may be possible that the aluminosilicate reaction led to the S-shape form. However, it cannot be said with confidence that the S-shape form resulted from aluminosilicate reaction according reaction Equation 5. With HCl removed, the slope remained steep. It appears that with HCl removed, the kinetic was unaffected. The slope of the sorption profile was steeper with the changes of the environment. The higher reaction rates with the change of the environments tell us that alkali sorption was probably enhanced through an aluminosilicate reaction.

5.4 SODIUM CONTENT AND REACTION PRODUCTS

5.4.1 Sodium Content in Various Fractions of Calcium Montmorillonite and Kaolinite

Sodium content was determined by AAS after sodium extraction from the pellet (leaching method, Section 3.4.2 and Appendix J.I-III). A solution method giving water soluble, HCl soluble and HF insoluble bound sodium. The leaching results tell us about the strengths of the sodium binding only. With the exposure time and process condition, it may be possible that the extraction forms (water soluble, HCl soluble and HF insoluble) change.

In previous work it has been claimed by Mulik et al. (1983) that a leaching result can be used to identify possible 'gettering reactions'. In addition, it was assumed that water soluble sodium content identifies adsorption, whereas the HCl soluble sodium content specifies replacement/exchange mechanism. The HF insoluble sodium content tells us about sorption complexes. Here, it is believed that this concept may be valid when changes in the extraction form are unlikely (sufficient exposure time).

It has been shown in sodium content studies that kaolinite bound sodium is mainly in the HCl soluble form, whereas it was bound in calcium montmorillonite in the HF insoluble form, see Table 11. Assuming that the definitions by Mulik et al. (1983) could be used to identify possible gettering reactions/mechanisms, a replacement mechanism could be the preferred
reaction mechanism in kaolinite, whereas reaction was the preferred mechanism in calcium montmorillonite. The finding that calcium montmorillonite bound sodium mainly in the HF insoluble form could confirm McLaughlin’s Two Reaction Theory in part, that reactions are expected. Standard aluminosilicate reactions were proposed under treatments with standard-wet and standard-wet/HCl condition. In the case of long term exposure, emathlite was reported to bind sodium mainly in the HF insoluble form. Emathlite has the same layer structure as calcium montmorillonite. It seems likely that both sorbents bind sodium with the same alkali sorption mechanism. In the case of kaolinite Lee and Johnson (1980) reported that sodium was bound in the water insoluble form. The result has been confirmed here. In addition it was shown that kaolinite sorbs sodium mainly in the HCl soluble form. The result could indicate a differing reaction mechanism in kaolinite to that of calcium montmorillonite.

The sodium content in kaolinite and calcium montmorillonite when treated NaCl-dry and standard-wet with HCl was found to be lower than that of a treatment under standard-wet conditions for both sorbents, respectively. It is very likely that the additional bound sodium resulted from a standard aluminosilicate reaction.

For both sorbents, physical adsorption was excluded as the prime sorption mechanism. It was found that kaolinite and calcium montmorillonite sorbs sodium strongly and not in a water soluble form.

It has been determined that the sodium content under a treatment NaCl-dry for kaolinite (crush strength > 0.4N/pellet) was higher than that determined for calcium montmorillonite (Table 11). This was the case, although the kaolinite pellets were found to be stronger than those of calcium montmorillonite. It is possible that the sorbent characteristic particle size influenced the alkali sorption capacity of the pellets under test.

Treatment under the standard-wet/HCl and NaCl-dry condition resulted in a similar sodium content for both calcium montmorillonite (4.7wt.%, 4.6wt.%) and kaolinite (6.4wt.%, 6.3wt.%), respectively. The treatment under standard-wet condition led to a higher sodium content for calcium montmorillonite (6.9wt.%) and kaolinite (7.8wt.%). The results imply that the addition of HCl reduces the alkali uptake. The same result has been reported for calcium
montmorillonite by McLaughlin (1990) and Chrysohoidou (1996). McLaughlin's experiments with 0, 55, 110, 160ppmv HCl, 40ppmv NaCl and 5% vol. H2O reduced the uptake to 11.8wt.%, 6.5wt.%, 5.3wt.% and 5wt.%, respectively at 827°C. At the lower temperature, 650°C, Chrysohoidou (1996) showed that the uptake was reduced to 3.5wt.% instead of 5wt.% (200 hours, 0-160ppmv HCl, 5% vol. H2O, 2.2ppmv NaCl). Chrysohoidou (1990) also found that kaolinite performs well when exposed to differing gaseous environment. Adding HCl, the sodium content was not affected. As shown earlier on, alkali sorbent interactions in kaolinite have not been seen with a batch of pellets used in the single pellet reactor, see Figure 20 and 21.

It was found that the difference in sodium content of standard-wet and NaCl-dry treated pellets was bound in the HCl soluble form (Table 11). This disagrees with findings by Bachovchin et al (1986). Bachovchin et al (1986) showed that the sodium content within the HCl soluble and HF insoluble phases increased linearly with exposure time in emathlite.

The water soluble, acid soluble and acid insoluble sodium contents in NaCl treated pellets were found to be surprising. They indicated a) that calcium montmorillonite 'reacts' with NaCl and b) that replacement reactions occur in kaolinite. It appears that the leaching method tells us only about the strength of the sodium binding. It is not clear whether it would provide directly the prime sorption mechanism. However, assuming that the chemical composition of the sorbent does not influence the leaching result, it appears that calcium montmorillonite bound sodium stronger than the sorbent kaolinite. Using NaCl-dry in argon, Mulik et al (1983) showed that 13 of 19 sorbents bound the alkali content in the water insoluble form. Assuming that the screened sorbents bound sodium similarly, it appears that sodium sorption under a treatment NaCl-dry condition occurs by reaction (according to the definition by Mulik et al, 1983).

Sodium uptake under dry conditions has been reported by a number of other researchers, e.g. Uberoi et al (1990) and McLaughlin (1990). The NaCl results have not been explained, yet. Chrysohoidou (1996) summarised: 'If water is absent, then the mechanism would require hydroxyl groups to be retained in the calcined sorbent pellets. Total loss of hydroxyl groups and the collapse of the sorbent structure does not occur until 900°C. Residual -OH groups
may still exist in the sorbent's structure. Under the assumption that residual OH groups are available, it is expected that the remained -OH groups may lead to reaction, possibly under production of reaction products. It seems important whether reaction products could be identified when a pellet is subject to a treatment under the NaCl-dry or standard-wet condition with HCl. In addition, it is of relevance whether hydroxyl groups could be regenerated in the aluminosilicate lattice. Yadegarian (1992) did not confirm an increase of =SiOH and =AlOH groups with a number of experiments on water treatment of calcium montmorillonite at 600°C. However, an increase in =SiOH groups was noticed after 96 and 117 hours of treatment at 850°C.

5.4.2 Sodium Content in Treated Pellets Exposed to HCl Mixtures

To investigate the 'sodium desorption', pre-treated calcium montmorillonite and kaolinite (NaCl-dry and standard-wet) were exposed to proposed 'desorption' mixtures. In either case desorption occurred with one exception.

Desorption of sodium was observed for pre-treated calcium montmorillonite (standard-wet) when exposed to an inert-wet atmosphere with HCl (Figure 35). Assuming a reversible standard aluminosilicate reaction following reaction Equation 5, it seems possible that a back reaction could occur. The standard aluminosilicate reaction has the sorbent, NaCl and water vapour on the left and HCl and reaction products on the right. With HCl added and NaCl removed from the left, the equilibrium could move to the right. But, it is not obvious whether the desorbed sodium resulted from a breakdown of reaction products (Section 5.4.4) or salt-free atmosphere (Section 5.3.2) or hydrogen chloride alone.

Kaolinite did not show any desorption when pre-treated kaolinite (standard-wet) was exposed to an inert-wet atmosphere with HCl (Figure 35). The result differs from that determined here for calcium montmorillonite. There is nothing in the literature as to whether pre-treated kaolinite (standard-wet) could desorb sodium under a different environmental condition. Chrysohoidou (1996) treated pellets under standard-wet condition with HCl from the beginning. The sodium content was not diminished. Turk et al (1996a) reported that kaolinite is not affected by a gaseous environment containing HCl (Section 2). But it is also possible that sorption sites
were not saturated in the first place. In this case the standard aluminosilicate reaction cannot progress according to reaction Equation 5 during the initial sorption process. Desorption would the most unlikely result. Sodium could be strongly sorbed to the surface of the aluminosilicate material.

Sodium was desorbed when NaCl treated calcium montmorillonite and kaolinite was exposed to an inert-dry atmosphere with HCl (Figure 36). In the case that a sodium chloride free atmosphere did not lead to desorption (Section 5.3.2), it is possible that either a replacement reaction or a reverse reaction occurred. Adsorption has been shown to be irrelevant. With an assumed replacement mechanism, the sorbent material and NaCl are on the left and transformed sorbent and HCl on the right. With HCl added from the right, the equilibrium of the replacement reaction is disturbed. NaCl could be released.

Pre-treated calcium montmorillonite and kaolinite exposed to an inert-dry/HCl atmosphere lost 50% in sodium content. A dramatic loss in sodium content could imply that hydrogen chloride plays an important role in the aluminosilicate sorption process.

5.4.3 Sodium Sorption Profile

A sodium sorption profile was generated under NaCl-dry condition for calcium montmorillonite based on three atomic absorption spectrophotometer results (0hours, 24hours and 100hours). Figure 37 shows that calcium montmorillonite sorbed sodium according to saturation kinetics. The profile characteristic of first and zero order kinetics tells us that the sorption under NaCl-dry condition was limited. The compared sodium content results, NaCl-dry and standard-wet, tells us that a simultaneous alkali sorption sorption process is unlikely.

The sorption results in the single pellet and fixed bed reactor system could be the same (Figure 38). To establish the same conditions in the reactors, the superficial velocities in the reactors were made up identical (3.5cm/s). The pellet properties of the used pellets were specified to be the same because they came from the same batch. With pellets of the same production method but different pellet diameter (3 and 1.7mm), exposure was allowed under the same treatment (NaCl-dry). Instead of 4.5wt.% sodium uptake with the single pellet reactor, a sodium uptake
of 4.1wt.% was determined for the fixed bed treated pellets (Figure 37). The smaller sodium uptake for the single layer treated pellets can be explained by the differing fluid flow regimes around the fixed bed and single pellets.

5.4.4 Reaction Products

The reaction products formed (albite and nepheline) through standard aluminosilicate reaction conditions lost their reacted state when further exposed to a reversing gaseous mixture (inert-wet/HCl), see Table 12. In the case of a standard aluminosilicate reaction (calcium montmorillonite), the reaction equation has NaCl, the sorbent and water vapour on the left and HCl and reaction products on the right. With HCl added and NaCl removed, it is possible that the equilibrium moves to the left (in case of a reversible standard reaction). However, it is not obvious, whether this loss in reacted state resulted in a lower sodium content (Section 5.4.2). There is nothing in the literature whether the reacted states of albite and nepheline can be removed with a change of gaseous environment.

Using a treatment standard-wet, kaolinite reacted to nepheline and carnegieite. With HCl added and NaCl removed, reaction products remained in kaolinite (Table 12). It appears that kaolinite is unaffected when exposed to a gaseous environment containing water vapour and hydrogen chloride. It is important that kaolinite and calcium montmorillonite were treated in the same batch. Differences in HCl content are therefore not thought to be of relevance for the differing results. The breakdown of the d-spacing pattern imply some variations. But finally they were considered to be useful to identify nepheline and carnegieite. The layer structure of kaolinite is different to that of calcium montmorillonite. It is possible that the different layer structure has led to the different result than that obtained with calcium montmorillonite. It is also possible that the reaction products formed in kaolinite are more stable than those of calcium montmorillonite. It is known, that the 1:1 meta-kaolinite structure is not stable.

Only albite was formed from calcium montmorillonite when reacted under standard-wet condition with HCl (Table 12). The standard aluminosilicate reaction equation has the sorbents, NaCl and water vapour on the left and HCl and reaction products on the right. With hydrogen chloride added from the beginning, the formation of reaction products could be
disturbed. The d-spacing pattern of albite was found to be weak. The result implies that with added HCl, the identification of reaction products was difficult. It seems possible that the standard aluminosilicate reaction under the standard-wet/HCl condition was diminished. It must be questioned whether difficult identification of reaction products could justify a standard aluminosilicate reaction scheme under the treatment standard-wet/HCl. This could have significant implication for the Two Reaction Model proposed by McLaughlin (1990). Quartz was found when the sorbent was standard-treated, whereas it was not when treated under a standard-wet condition with HCl. It seems that hydrogen chloride inhibits the formation of silicon oxide and the reaction cannot proceed.

Calcium montmorillonite reacted with NaCl/water vapour to form nepheline and also albite. Previously, there was evidence (McLaughlin (1990)) that calcium montmorillonite reacted with NaCl/water vapour to produce only nepheline. The implication is that the previously accepted Two Reaction Theory proposed by McLaughlin (1990) is more complex. But it also appears that reaction equilibrium resulted in either one or two reaction products depending on the experimental conditions. With the occurrence of albite and nepheline in the absence of HCl, the aluminosilicate reactions following reaction Equation 19 is as valid as reaction Equation 5. Nepheline has two silicon atoms in its formulae, whereas albite has six. It appears that silicon changes its state with extended exposure. Bachovchin et al (1986) showed that the extractable HF insoluble silicon form of emathlite (treatment NaCl/water vapour) transforms into the HCl soluble form. This may confirm that silicon changes its state within emathlite.

In the case that kaolinite has been treated under a standard-wet condition with HCl, reaction products were not observed. The absence of reaction products under these conditions implies the absence of a standard aluminosilicate reaction for kaolinite.

It has been determined that kaolinite and calcium montmorillonite reacted with NaCl. Albite and nepheline were not formed. The result for kaolinite is in agreement with findings by Steffin (1999). The absence of reaction products implies that ‘remaining’ OH-groups in kaolinite do not lead to a standard aluminosilicate reaction under the treatment NaCl-dry. The result means also that either reaction (e.g. replacement reaction) or strong bonding could be relevant to the alkali sorption process.
5.5 REQUIREMENTS FOR FURTHER MODELLING

The modelling of alkali uptake must ideally take into account reaction mechanism, process conditions, diffusion and mass transfer limitations. In this work the reaction mechanism of alkali sorption was studied. It was shown that the mechanisms of uptake of calcium montmorillonite depends on the level of water vapour present and the absence of water vapour. Hydrogen chloride also affects the level of uptake. The mechanisms can differ from these previously reported (McLaughlin, 1990; Chrysohoidou, 1996).

The mechanism of the alkali sorption described in this work is based on a Replacement/Aluminosilicate Reaction. The aluminosilicate reaction of calcium montmorillonite is most likely reversible as shown experimentally in this work.

\[
2\text{NaCl}(s) + H_2O(l) + Al_2O_3 \cdot xSiO_2(l) \leftrightarrow \text{Na}_2O \cdot Al_2O_3 \cdot xSiO_2(l) + 2HCl(l) \quad [5]
\]

Depending on the environmental conditions (presence or absence of hydrogen chloride and water vapour) and exposure time, the mechanism leads to either one or two reaction products (nepheline with \(x=2\) or albite with \(x=6\)). This mechanism was previously employed by McLaughlin (1990) and Chrysohoidou (1996) who assumed either nepheline or albite would be formed. This study has demonstrated that both nepheline and albite can be formed simultaneously when water vapour is present.

The sodium sorption and desorption experiments with NaCl and HCl respectively suggest that under the dry environment a replacement mechanism can be defined. The reaction equation for the replacement mechanism is given below.

\[
4\text{NaCl}(s) + Al_2Si_2O_5(OH)_{4(s)} \leftrightarrow Al_2Si_2O_5(ONa)_{4(s)} + 4HCl(s) \quad [23]
\]

This mechanism suggests that the hydrogen in the hydroxyl groups left after calcination is replaced by sodium (thereby balancing the charge). Modelling of the alkali sorption process
must be modified to take account of the new mechanisms suggested by the experimental investigations reported in this study.

It has been claimed by McLaughlin (1990) that the alkali sorption process is better described by the Two Reaction mechanism. Two reactions were assumed depending upon the presence or absence of hydrogen chloride. In this study, it was shown that the formation of reaction products is significantly affected by the presence of water vapour, exposure time and process conditions. In particular, under the water vapour containing sorption conditions without hydrogen chloride, reaction (5) gave two separate reaction products simultaneously. Furthermore, it was shown conclusively that the reaction products disappear when exposed to a hydrogen chloride or hydrogen chloride/water vapour environment. In other words, the reaction mechanism is reversible and this must be accounted for in the modelling.

The formation of the reaction products significantly depends upon the presence of water vapour, exposure time and process conditions. Consequently, the maximum capacity of the sorbent for alkali species must be theoretically calculated and accounted for. Furthermore, the formation of reaction products depends upon the silica/alumina ratio, silica content in the sorbent and the presence of HCl. It was observed that kaolinite did not form reaction products under aluminosilicate reaction conditions with HCl (water vapour content <1.5% by volume) up to an exposure of 100 hours. It is likely, however, that reaction products would eventually be formed. This could mean that the sorbent capacity could be influenced. McLaughlin (1990) showed that for sorbents with a high silica/alumina ratio in the presence of water vapour there could be a difference of 7% in capacity depending on the presence or absence of HCl.

Meinhold et al (1992) suggested that 25% of the hydroxyl groups are left after calcination up to 950°C. In this work it is proposed that hydrogen left can be exchanged with sodium. This would correspond to an approximate uptake of 11% by weight. Calcination experiments conducted in this study showed that hydroxyl groups left after calcination may account for an uptake of 3% by weight. Single pellet reactor experiments using extruded kaolin pellets show an uptake of 7%. In contrast pan pelletised kaolinite pellets show an uptake of higher than 11% by weight. This difference in uptake is caused by the sodium distribution within the pellet. The sodium distribution in extruded pellets was shown to display shrinking core
behaviour within the treated pellet, whereas those of pan pelletised pellets indicated a
distribution of sodium throughout the pellet. Furthermore with greater particle sizes, regions
of chemical control must be considered. In particular, grain sizes greater than 5 micrometer
may lead to chemical reaction control. Simulations on retained hydroxyl groups should
concentrate on the effects of particle size distribution. With a small particle size (<5μm)
simulations should account for a maximum of 25% of left hydroxyl groups in the
aluminosilicate material.
CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS

The aim of this dissertation was primarily to extend present knowledge in the alkali sorption mechanisms of kaolinite, calcium montmorillonite and emathlite. The investigation of the alkali sorption mechanisms of these target sorbents is important for the development of more efficient coal based power generation plants. Recent alkali sorption studies were carried out by Chrysohoidou (1996) into the removal of alkali vapours at a temperature of 650°C for British Coal's development of the Topping Cycle, today described as the Air Blown Gasification Cycle. A packed bed with sorbents of kaolinite and calcium montmorillonite was considered to be a viable means of removing alkali at the high temperature. Dust separation in combustion gases at higher temperatures above 1200°C was attempted but found to be impractical, as an alternative removal of alkali vapours by packed beds within the temperature range 650°C-950°C was therefore considered to warrant further study. A shortcoming that still hinders the commercial implementation of alkali removal by short-term is the lack of knowledge of the exact sorption mechanisms of kaolinite, calcium montmorillonite and emathlite.

A programme of study was proposed to investigate the alkali sorption mechanisms of kaolinite, calcium montmorillonite and emathlite. This was achieved using sorbent pellets formed by extrusion and pan pelletisation. Pellet properties were characterised. Experiments were then conducted using an optimised single pellet reactor to study the initial sorbent activity of the formed pellets and to investigate the sorbent sorption and desorption characteristics. Experiments were initially carried out to determine the influence of the gaseous environment on the alkali sorption process, but were later extended to determine the reversibility characteristics of the alkali sorbent sorption process. These results were then used to specify final experiments to investigate solution bound sodium and reaction products.
Pellet Properties

Pellets produced using the extrusion technique were found to be suitable for industrial purposes, e.g. moving or fixed bed, whereas pan pelletised pellets were found so fragile as to be suitable only for laboratory use. Pore volume and porosity data for the pellets under test indicated that the pan pelletisation technique produces pellets with a more open structure, than pellets produced by extrusion. The higher the pore volume and porosity the greater the anticipated sodium sorption effectiveness of the sorbent. Pore size distribution was found to be affected by the calcination procedure with the smaller pore sizes disappearing. For the kaolinite material (Supreme and grade D) studied, the surface area remained stable up to 900°C, possibly up to 940°C. At 850°C, the surface area of the calcined kaolinite was eight times that of calcium montmorillonite. The higher surface area of kaolinite was confirmed through a smaller median particle size. A smaller median particle raises the number of smaller pores in kaolinite. This means that the opportunity for alkali sorbent interaction is increased. The calcination temperature affected the surface area stability of the sorbent under test, for both sorbent and sorbent pellet. The implication is that a higher calcination temperature adversely affects the pore structures of the sorbent and sorbent pellets. This result is interesting because it may relate collapses of the inner structure of the sorbents/surface area stability to calcination temperature. But it is very likely that the porosity and pore sizes were also affected.

Initial Sorbent Activity

The rate of initial sorption increases with temperature. At lower temperatures, sorption for calcium montmorillonite is limited. This has not been shown to be true for kaolinite. This means that both particle size and sorbent chemistry affect the performance of the sorbent at lower temperatures.

The means of producing pellets significantly affected initial sorption activity and sorption uptake. The implication is that the determined sorption rates are unique for the pellet types under test, pellet properties must be determined. This also means that the initial sorption activity can be largely influenced by diffusion.

The initial sorption rate increases with higher alkali concentrations. This implies that alkali sorption is difficult at low concentrations such as the 24ppb alkali gas turbine inlet value.
Sorption Characteristics of Sorbents

Changes in the composition of the gaseous environment was shown to significantly affect the sodium sorption process. This is independent of the sorbent used. The gaseous environmental effects can be affected by a disturbance in the gaseous composition. It is likely that gaseous compounds such as CO₂, CO₃, and H₂S can affect the sorption process. The implication is that the scaling up of a process without an understanding of gaseous environmental effects should be avoided.

Under standard aluminosilicate reaction conditions weight changes over time were found to display different characteristics (gaseous environmental effects) in the presence or absence of hydrogen chloride. Reduced uptakes under the reaction condition with HCl confirmed that previously observed inhibitory effects of HCl for calcium montmorillonite was also present for kaolinite and emathlite. In the cases of calcium montmorillonite and emathlite the inhibitory effects with hydrogen chloride were greater than for kaolinite. The effect has been shown to be related to the particle size of the sorbent.

Gaseous environmental effects for NaCl sorption and standard aluminosilicate reaction sorption conditions with HCl were found to be small or non-existent. A gaseous environmental effect with water vapour present (positive) occurred but not in kaolinite or calcium montmorillonite under the experimental condition. Previously environmental effects were reported under experimental conditions with a higher water concentration. From these experiments it was concluded that alkali sorption is likely due to be dominated by a single sorption mechanism, and moderated by a subsequent mechanism.

It has been shown that the exposure to hydrogen chloride in the case of pre-treated kaolinite and calcium montmorillonite (NaCl) causes a dramatic loss in mass. The result means that the loss in mass could have resulted from the loss in sodium weight. It has been re-established here that a sodium chloride free atmosphere did not lead to a release of initially bound mass, and that a replacement mechanism could be possible.

To see whether the standard aluminosilicate reaction is reversible, reacted pan pelletised calcium montmorillonite was further exposed to hydrogen chloride and water vapour and a
significant loss in mass was observed. It was re-established here, that reductions in mass are not expected in water vapour or sodium chloride free atmospheres. In the case of hydrogen chloride alone, a loss in mass was noted. This means that either hydrogen chloride alone or hydrogen chloride/water vapour led to loss in mass. It was concluded that further experiments were needed to determine whether reversibility was possible in calcium montmorillonite under standard aluminosilicate reaction conditions, see below. Desorption experiments are sparse in the literature with the exception of a sodium chloride free atmosphere.

The desorption experiments have shown that a previously reported non-reverse in NaCl sorption was upheld. This implies that sodium or sodium chloride is strongly bound. It has been re-established here that calcium montmorillonite sorbed sodium remains strongly bound when the temperature is increased in a salt free environment. This is also frequently reported in the literature. A non reversal of NaCl sorption was concluded. The result means that chemisorption rather than physisorption appears to apply to the alkali sorption process.

It has been shown that the addition of water vapour to pre-saturated calcium montmorillonite (NaCl) results in a step change. This is not covered in detail in the literature elsewhere but can be evaluated from various aspects. The step change means that adding water vapour to a treatment NaCl, is a necessary condition to allow a further sorption process under standard aluminosilicate reaction conditions. From the results it can be concluded that water vapour in the system increases the sorbent capacity.

Under a treatment leading to the standard aluminosilicate reaction, the sorption rate is slow, this means the standard aluminosilicate reaction is reaction controlled. This is in agreement with the reviewed literature.

**Sodium Content and Reaction Products**

From the water soluble, HCl soluble and HF insoluble sodium solution measurements it has been possible to conclude that replacement mechanism is the preferred reaction mechanism in kaolinite, whereas it is chemical reaction in calcium montmorillonite. However, from the leaching results it can be also concluded that chemical reaction under the sodium chloride condition is unlikely for calcium montmorillonite unless water vapour is present. It must be therefore concluded that the leaching results with water soluble, HCl soluble and HF insoluble
sodium content does not necessarily provide direct information of the prime sorption mechanism, although it will give an indication of how strongly sodium is bound. With the deferring chemical composition of the sorbents it can be also concluded that the water soluble, HCl soluble and HF insoluble contents in a leachate was possibly affected by the chemical composition of the sorbent. Because sodium was not readily leached out with water (NaCl sorption condition), physisorption appeared to be discountable as the prime sorption mechanism.

Essentially HF insoluble sodium data confirmed that the loss in mass resulted from loss in sodium content. This means that the sodium measurements confirm the inhibitory effects of hydrogen chloride on sorption in calcium montmorillonite and kaolinite.

It has been re-established with the HF insoluble sodium content that the resulting diminished mass is due to loss of sodium. The result means that hydrogen chloride has a significant role in the reverse of the alkali sorption process. From the experiments it can be concluded that the replacement mechanism is relevant to the sorption process. This means that the reversing effects of hydrogen chloride must be considered for fixed bed and moving bed operations. Absence of hydrogen chloride is probably required to achieve a higher efficiency for coal based power generation plants. In addition, calcium montmorillonite and kaolinite are major mineral constituents in some coals. With hydrogen chloride present in the flue gas, alkali components bound on these clay minerals are released depending on the gaseous conditions and their binding. It must be concluded that the occurrence of hydrogen chloride is a key issue for alkali removal, efficiency increase for advanced coal based power generation plants and for combustion and gasification in general.

Water vapour was added to the pre-saturated sorbent to produce a step change in the sorbent profile. The implication is that water vapour leads to a higher sorbent sorption capacity. The result also means that a simultaneous sorption process seems unlikely. This is sparsely reported in the literature.

From the single pellet and fixed bed reactor results it can be concluded that in the case of similar pellet characteristics and the same process conditions, comparable results will be observed.
It has been concluded from the loss of reacted states of formed reaction products (nepheline and albite), that the standard aluminosilicate reaction of calcium montmorillonite is reversible, the reaction Equation 5 is shown below

\[
2\text{NaCl}_2 + \text{H}_2\text{O}_2 + \text{Al}_2\text{O}_3 \cdot \text{xSiO}_2 \Rightarrow \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{xSiO}_2 + 2\text{HCl}_6 \quad [5].
\]

Having established the performance of the aluminosilicate reaction to be reversible, the performance of an alkali retention unit should consider the reaction reversal. This means that an alkali sorption model is needed to calculate reaction reversal.

From the occurrence of two reaction products under standard aluminosilicate reaction conditions, it has been shown that the temporarily accepted Two Reaction scheme was due to one reaction. This means that the standard aluminosilicate reaction is either in parallel or series. It remains unresolved which one is valid.

From the weak d-spacing peaks of the reaction product albite under a standard aluminosilicate reaction condition with HCl (calcium montmorillonite) and compared HF insoluble solution sodium data it has been concluded that the aluminosilicate reaction contributes very little to the total uptake, this disagrees with the standard aluminosilicate reaction proposed by McLaughlin (1990). In addition, reaction products were not formed by kaolinite under standard aluminosilicate reaction conditions with HCl or the NaCl condition (confirming results in the literature). From the results it can be concluded that a further sorption mechanism is relevant to the sorption process. A replacement mechanism is proposed (replacement mechanism not producing reaction products), the reaction equation for which is given below

\[
4\text{NaCl}_2(aq) + \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4(aq) \leftrightarrow \text{Al}_2\text{Si}_2\text{O}_5(\text{ONa})_4(aq) + 4\text{HCl}_6.
\]

However, because sodium or sodium chloride was found to be strongly sorbed, it must be considered, that besides an replacement mechanism, chemisorption could be also relevant. 'No reaction products were found under a NaCl dry condition'.

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From the programme of study it can be concluded that new alkali sorption mechanisms were proposed based on a replacement and standard aluminosilicate reaction mechanism. In terms of the proposed replacement mechanism, the requirements for further modeling work were described. The standard aluminosilicate reaction was shown to be reversible. A model approach need to consider reaction reversal. Sodium video maps of treated pellets of kaolinite, emathlite and calcium montmorillonite showed that the distribution of captured sodium depended upon the pellet production method. From the sodium distribution in pellets it was concluded that pellets formed by the extrusion technique sorbed sodium according to a shrinking core behaviour within the pellet whereas pan pelletised pellets sorbed sodium according to a homogenous distribution/grain theory. The pellet grain model is of significance for calcium montmorillonite and emathlite due to their grain sizes and different chemical composition whereas the homogeneous model is of significance for kaolinite with its small mean particle size.

6.2 RECOMMENDATIONS

It has been shown that the alkali sorption process is a combination of physical and chemical processes, which are dependent on sorbent chemistry (chemical properties), agglomeration (physical properties), and the applied atmosphere (temperature, pressure, gas mixture). Although this work has been able to answer some key questions on the use of the most suitable sorbent, many aspects still need to be investigated.

1) Uncalcined and calcined pellets should be investigated to determine the change of pore structures during the calcination process.

2) The surface area should be measured from pellets before and after treatment in order to confirm that there is no loss of surface area during sorption. This is especially important for gaseous environments to allow standard aluminosilicate reaction. To ensure there are no structural changes, pellets need to be exposed for long periods of time. In these long time exposure experiments the gaseous environment should be changed as well as the sorbent material to determine structural changes (e.g. glass formation).
3) The role of particle size on the alkali sorption process under NaCl condition should be investigated in order to determine the sodium uptakes under this environment.

4) The chemical properties of the sorbent pellet under tests (chemical composition) has been shown to be a factor in the alkali sorption process. A factor was found to be that calcium has a possible negative influence on the performance of the alkali sorption process. This has significant implications not only for the coal-derived gases (e.g. sulphur dioxide removal) and also the alkali sorption process. Further investigations are necessary to determine the sorbent sorption effectiveness when the chemical composition of the pellets changes.

5) Further experiments, at different temperatures and gaseous environment are required to determine further essential data, e.g. initial sorption activity and capacity for gaseous environments not investigated here.

6) Alkali sorbent interactions were found to be dependent upon the gaseous environment. As a consequence, further work is recommended to investigate the effects of the constituents of gaseous atmospheres. Under reducing conditions, the effects of H₂S, CO, and CO₂ need to be investigated. The effect of carbon deposition may significantly affect the performance of the sorbent as a promising sorbent.

7) Although reversibility issues have been resolved during the course of this work, it is not clear whether an increased hydrogen chloride concentration would lead to greater desorption under the standard aluminosilicate reaction condition with HCl.

8) The effect of water vapour on alkali sorption has been investigated at low concentration. It is not clear to what extent the water vapour concentration increases the uptake under controlled gaseous conditions.

9) Step changes should be investigated to investigate the role of water vapour. To investigate the step changes, pre-treated calcium montmorillonite pellets (NaCl-dry) should be exposed to water vapour and sodium chloride.
10) To clarify the sorption mechanism under the treatment NaCl dry, chlorine, HCl, and sodium concentrations must be investigated to gain a further insight in the alkali sorption mechanism. Although exit gas analysis has shown the evidence for hydrogen chloride under a treatment NaCl dry, further measurements are required to show that the proposed mechanism occurs.

11) The alkali sorption process was found to be reversible depending on the gaseous environment and process conditions. The pellet grain model with the Szekely approximation cannot be simply applied.

12) Modelling is still needed when the exact alkali sorption process has been determined.
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APPENDIX A

DESCRIPTION OF SINGLE PELLET REACTOR (SPR) AND FIXED BED REACTOR (FBR) SYSTEM

A.I Technical Description of the SPR System

The single pellet reactor was developed from a Stanton Redcroft Simultaneous Thermal Analyser (STA 780). The apparatus was progressively upgraded by Schulz (Turk, 1996a) in the course of this study. Figure 14 showed a schematic of the system used in its final application. The single pellet reactor system consists of three basic components; the gas-handling system (where nitrogen, water vapour and hydrogen chloride are mixed), the furnace/reactor unit and sodium vapour generator and the microbalance/sample unit. The gas handling system provided a controlled gaseous environment of nitrogen or mixtures of water vapour and/or hydrogen chloride in nitrogen to the furnace/reactor unit. The use of a gas handling system with mass flow controllers, heated PTFE tubing (ID 1.6mm, Omnifit), tube end fittings, flow change over valves (1.5mm bore, Omnifit), 3 way valve (1.5mm bore, Omnifit), temperature controlled liquid saturators (hart scientific, isotherm 3002, 30.3°C+/−0.1°C) and heated mixing coil (50°C/min) for hydrogen chloride has many advantages. Mass flow controllers, heated PTFE tubing, tube end fittings and flow change over valves provide much more controlled stable gas streams whereas the temperature-controlled liquid saturators provide introduction of 1.3% by volume water vapour to the gas streams when required. This means that gas mixing can take place without disturbance. As the result, the gas handling system is simple to use and robust. A particular advantage of the gas handling system is the hot-gas trap to mix water vapour and hydrogen chloride without condensation. Visible tube endings allowed checking of the gas stream entering the reactor unit.

Other work done improved the reactor/furnace unit with a vapour generator. The reactor/furnace unit and sodium vapour generator was reconstructed in order to control the vaporisation rate of sodium chloride in the vaporisation zone, to prevent condensation of sodium vapour on the microbalance system and to allow long term runs. The electrical furnace
was operated isothermally or with linear temperature programs up to 20°C/min from 20°C to 1000°C. A temperature controlled heating coil wound around the cooling circuit caused shutdown of the equipment if an interruption to the water supply occurred. This allowed the equipment to be run over night. An auxiliary heater (820°C) was installed at the top of the furnace section to prevent condensation of sodium vapour on the microbalance suspension. The microbalance was purged with a gas flow of 50ml/min, 25ml/min entered the bottom arm with counterweight the other 25ml/min the hangdown suspension. The purge gas flow was adjusted to be equal to the flow entering the base of the reactor unit. The reactor/vapour generator insert consisted of a 1cm diameter pure alumina reactor tube (120mm) with a concentric 4 bore (1.5mm ID) ceramic rod fitted with an R-type thermocouple and a 4mm platinum crucible. Sodium chloride vapour was generated by passing the gas stream around a ‘flat’ salt crystal in the platinum crucible. The salt crystal temperature was controlled by a computer programmed vapour generator wound on the reactor tube heater (West controller 6100, input range 6726, 9600baud, Address 1, integral time 0.22, derivative time 0.05, Conversion of half duplex signal, RS485, in full-duplex signal, RS485/232 through converter, Quick basic 4.5 programme, Microsoft MS-DOS, 007-095-054). During a run the crucible was held at a given height by adjusting the ceramic support rod. In order to generate a constant sodium chloride vapourisation rate three calibration (Appendix A.III-VII) runs were performed by suspending the crucible from the sample holder and measuring the temperature profile required to generate a constant rate (300µg/hour, +/-10µg, 40ppmv NaCl). Temperature adjustment by temperature profile is necessary in order to compensate for loss in mass of the salt crystal of same size and weight over time. The temperature profile was then used to control the crystal temperature during the run, with the crucible at the same height but mounted on the ceramic support rod. A vapour generator in the vaporisation zone was installed to smooth the temperature variation along the platinum crucible. Flat salt crystals instead of upright crystals were used to avoid radiation and diffusion effects at the top of the crucible. Weight measurements of a platinum crucible before and after the run allowed checking of the average constant salt concentration. Appendix A.VIII presents salt consumption data and achieved salt vapour concentration. The temperature profiles versus exposure time are given. The maximum variation in salt concentration was 3ppmv NaCl. The salt concentration data are given for the performed gaseous environment runs.
The microbalance/sample unit enabled sorbent pellets to be held in the reaction zone at the top of the furnace/reactor unit, by a Pt/Rh fine wire mounting system. The use of the fine wire sample holder lead to the advantage to have undisturbed flow around the pellet. The fine wire system has also the advantage that glass formation does not damage the pellet mounting system which was connected to the hangdown of an C.I. electronic microbalance in order to allow weight changes in the sorbent to be monitored by chart recorder and PC data logging (Digital Volt Meter 197, IEEE Card, IO Tech, 80386 PC, Quick basic 4.5 programme). The hangdown/sample holder assembly included a thermocouple to allow the sample temperature to be monitored.

A.III  Constant Vapourisation Rates over Time

Constant vapourisation rate (Calibration run)

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<td>293</td>
<td>35.63</td>
<td>295</td>
<td>48.98</td>
<td>300</td>
</tr>
<tr>
<td>18.63</td>
<td>294</td>
<td>25.42</td>
<td>297</td>
<td>36.77</td>
<td>299</td>
<td>50.12</td>
<td>312</td>
</tr>
<tr>
<td>18.63</td>
<td>298</td>
<td>26.70</td>
<td>312</td>
<td>37.62</td>
<td>293</td>
<td>50.43</td>
<td>306</td>
</tr>
<tr>
<td>18.63</td>
<td>298</td>
<td>27.02</td>
<td>296</td>
<td>38.97</td>
<td>302</td>
<td>50.72</td>
<td>302</td>
</tr>
<tr>
<td>19.48</td>
<td>298</td>
<td>27.77</td>
<td>286</td>
<td>39.53</td>
<td>304</td>
<td>51.48</td>
<td>313</td>
</tr>
<tr>
<td>19.78</td>
<td>298</td>
<td>29.30</td>
<td>286</td>
<td>40.64</td>
<td>304</td>
<td>51.87</td>
<td>302</td>
</tr>
</tbody>
</table>

Average: 300μg/hour +/- 8μg
A.IV  SPR Data Acquisition and Salt Vapour Control Programme

***************
'Data logging and control programme for SPR
***************
'Written by Michael Rieger
'02/99 spr99_7
'Compiled and run with quick basic 45
'Communications with Digital Volt Meter (DYM 197) through IEEE Card (IO-Tech)
'and with West-Controller 6100 through converting the RS-485 signal
'Half-Duplex) of the controller in a Full-Duplex signal
'Serial RS-485/RS-232 converter 9600 baud)
'Initial ramp through Stanton-Redcroft 706 temp. controller (warm up)
'Vaporisation run conditions with 40 mg salt crystal in platinum crucible
'temperature 651°C, setting for DP6 688°C(marked position; 13.4cm top seal),temperature increase 1°C in 5.33 hrs

***************
'Open data file
***************
CLS
INPUT "Enter data filename (Default - DUMMY.dat): "; filename$
    IF (filename$ = "") THEN
        filename$ = "a:\dummy.dat"
    END IF
OPEN filename$ FOR OUTPUT AS #8 'this file keeps a record of data file name
PRINT #8, filename$, DATES$, TIMES$
PRINT #8, ""
PRINT #8, "TIME      DVM"
PRINT #8, "------------------"
CLOSE #8
'Establish communications with personal DVM 197 and personal ieee488 card
'open ieee488 communications to Digital volt meter

OPEN "\dev\ieeeout" FOR OUTPUT AS #1
'Reset personal488
IOCTL #1, "Break"
PRINT #1, "Reset"
'Open file to read responses from personal488
OPEN "\dev\ieeein" FOR INPUT AS #2

Establish communications to temperature controller

OPEN "com1:9600,e,7,1" FOR RANDOM AS #3
COM(1) ON

'Surface of program (screen)/Panic bottom

CLS
ON KEY(1) GOSUB 1000
ON KEY(2) GOSUB 3000
ON KEY(3) GOSUB 3000
ON KEY(9) GOSUB 3000
KEY(1) ON
KEY(9) ON
CLS
WHILE 1 = 1
LOCATE 1, 1: PRINT "F1=Alkali sorption"
LOCATE 1, 20: PRINT "F2=Set-point Temperature"
LOCATE 1, 45: PRINT "F3=Salt vaporisation"
LOCATE 1, 67: PRINT "F9=Quit"

A.V
WEND
RETURN

1000 ' Temperature controller programme
LOCATE 4, 31: PRINT "**************************************************************************"
LOCATE 5, 31: PRINT "*"
LOCATE 5, 33: PRINT "Alkali sorption"
LOCATE 5, 49: PRINT "*"
LOCATE 6, 31: PRINT "**************************************************************************"
LOCATE 10, 1: PRINT "Temperature"
LOCATE 12, 1: PRINT "-Time"
LOCATE 13, 1: PRINT "-Controller-protocol"
LOCATE 15, 1: PRINT "DVM/Weight"
LOCATE 17, 1: PRINT "DVM"
LOCATE 18, 1: PRINT "Weight"
LOCATE 19, 1: PRINT "Time"
LOCATE 20, 1: PRINT "Wait-loop"

'Establish communications with temperature controller 6100
FOR Z = 1 TO 167
IF Z = 1 THEN
   LOCATE 12, 30: PRINT TIMES
   ON COM(1) GOSUB gotchar
   a$ = "L1S*"
   PRINT
   PRINT #3, a$gotchar:
   FOR i = 1 TO 9
      NEXT i
   LOCATE 13, 30:
   WHILE NOT EOF(3)
      c$ = INPUT$(1, #3)
      PRINT c$;
   WEND
   A.VI
ELSE

    FOR k = 1 TO 47270
        h = k
        h = (47270 - h) / 1000
        LOCATE 20, 30: PRINT USING "##": h
    NEXT k

'Enable 195 SRQ on Illegal Command
PRINT #1, "OUTPUT 20;M2X"

'Set 195 to Autorange, DC Volts
PRINT #1, "OUTPUT 20;F0R0X"

Dvm1 = 0

FOR 1 = 1 TO 3
    PRINT #1, "ENTER 20"
    INPUT #2, R$
    Dvm1 = Dvm1 + VAL(MID$(R$, 5))

NEXT 1

Dvm1 = (Dvm1 / 3) * 1000
D$ = TIMES$

LOCATE 17, 30: PRINT USING "##.#####": Dvm1;
LOCATE 17, 37: PRINT "mv"
LOCATE 18, 30: PRINT "##.#####"
LOCATE 18, 37: PRINT "mg"
LOCATE 19, 30: PRINT TIMES$
OPEN filenames FOR APPEND AS #8
PRINT #8, TIMES$, Dvm1
CLOSE #8

END IF

NEXT Z
GOTO 1000

3000'
END
A.VIII Salt Weight Measurements and Temperature Profile

Weight measurements of a platinum crucible before and after the run allowed checking of the average constant salt concentration.

<table>
<thead>
<tr>
<th>Run</th>
<th>Salt before [mg]</th>
<th>Salt afterwards [mg]</th>
<th>Run time [hours]</th>
<th>Concentration [µg/hour]</th>
<th>Concentration [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>011</td>
<td>39.68</td>
<td>28.66</td>
<td>38.64</td>
<td>286</td>
<td>39</td>
</tr>
<tr>
<td>019</td>
<td>40.08</td>
<td>25.55</td>
<td>52.07</td>
<td>280</td>
<td>38</td>
</tr>
<tr>
<td>023</td>
<td>39.29</td>
<td>25.84</td>
<td>49.28</td>
<td>273</td>
<td>38</td>
</tr>
</tbody>
</table>

Calculation of concentration based on ideal gas law and velocity of 50ml/min in single pellet reactor, Molar Mass (NaCl)=58.44g/mol, Temperature used was 292.15K

Table A.VIII.1: Weighing of Platinum Crucible.

The salt crystal temperature was controlled by a computer programmed vapour generator wound on the reactor tube heater; the platinum crucible temperature was measured in order to investigate whether the increase in temperature was achieved.

<table>
<thead>
<tr>
<th>Run 011</th>
<th>Run 019</th>
<th>Run 023</th>
</tr>
</thead>
<tbody>
<tr>
<td>00.0</td>
<td>688.1</td>
<td>00.0</td>
</tr>
<tr>
<td>11.3</td>
<td>691.6</td>
<td>06.5</td>
</tr>
<tr>
<td>14.6</td>
<td>692.9</td>
<td>20.2</td>
</tr>
<tr>
<td>17.0</td>
<td>693.4</td>
<td>28.4</td>
</tr>
<tr>
<td>24.3</td>
<td>694.6</td>
<td>42.2</td>
</tr>
<tr>
<td>38.64</td>
<td>698.3</td>
<td></td>
</tr>
</tbody>
</table>

Table A.VIII.2: Achieved Temperatures by Salt Vapour Temperature Control Programme.
Figure A.IX.1: Salt Temperature versus Run Time.

A.IX Mixing Studies

Techniques and HCl source

In order to investigate water vapour and hydrogen chloride mixes, containing 100ppmv hydrogen chloride, gas samples were dried using a permeation membrane. A nafion (copolymer of tetrafluoroethylene) permeation tubing (62.5cm length, I.D. of 1.25mm), manufactured by perma pure inc., New Jersey, was used. Water vapour and hydrogen chloride was measured according to Appendix I.I and H.I. A gas cylinder with hydrogen chloride in nitrogen content of 300ppmv was used to produce the defined gas stream. A series of investigations were performed in order to evaluate the performance of this system. It was found that changes in cylinder flow rate affected the measured hydrogen chloride content. At high flow rates the hydrogen chloride concentration was found to be slightly below that stated by the supplier, however at flow rates of 10ml/min a constant concentration of 180ppmv was obtained. This is because at low flow rates loss of hydrogen chloride content occurs between the gas cylinder and the gas-handling system. As a result of these variations in concentration mixing experiments were performed using an intermediate flow of 100ml/min. Investigation of the hydrogen chloride content of a new gas cylinder stated by the supplier to contain 300ppm
hydrogen chloride gave a lower concentration than specified (200ppmv). This problem has not be resolved but the value is stable.

A series of mixing studies were performed in order to determine whether the gas mixtures entering the reactor unit are controlled. The hydrogen chloride concentration has been determined within mixed hydrogen chloride/water vapour/nitrogen gas. The observed concentration of hydrogen chloride agreed with the calculated value, which implies that controlled conditions were obtained. Calculated and observed concentrations of hydrogen chloride (100ml/min) are shown in Figure A.X.1. It can be seen that the gas mixing measurements were successful in different gaseous environments.

![Figure A.X.1: Calculated and Observed Concentration of Hydrogen Chloride.](image)
DESCRIPTION OF FIXED BED REACTOR (FBR) SYSTEM

A.XI Technical Description of the FBR System

The FBR System have been described in detail by McLaughlin (1990) and Chrysohoidou (1996). In the course of this work; the gas handling system was changed. The completely assembled system with the improved gas handling system, gas inlet section (GIS), mixing section (MS, alumina tube, 17.5cm length), vapour generation section (VGS, ultra pure alumina tube, 17cm length, 1.2cm ID) and fixed bed section (FBS, 20cm length, 2.5cm ID) is shown in Appendix A.XIII.1. The gas handling system of this rig was rearranged to allow different gas mixtures to be used. The use of temperature controlled mass flow controllers (Negretti, M2545, 32°C), heated PTFE (ID 1.6&3.2mm) tubing and gas mixing section provided a homogeneous gas stream. A constant sodium chloride concentration from 40ppmv was produced in the VGS by sublimation of a sodium chloride crystal in a nitrogen carrier gas by an on-line method for measuring sodium chloride vapour concentration at elevated temperatures. A salt crystal was suspended directly on an R-type thermocouple (Platinum-Rhodium) attached to the microbalance. A handling system was designed to facilitate its installation. The sodium chloride gas stream was jet mixed through a 0.23mm nozzle (length 5cm) into the mixing section of the fixed bed reactor. There it was mixed with the gas inlet stream of the gas-handling system. The mixed gas stream through the fixed bed expressed as superficial velocity (3.5cm/s) was adapted to be the same as in the SPR reactor. The contact between gas mixtures and sorbent was achieved by passing the salt- and water laden gas downwards through the fixed bed. Thus the lifting of the pellets from the support ceramic plate was avoided.

The power supply to the heater coils is via two adjustable B-20 Variac transformers, set at 110V and 40V, and a Stanton Redcroft ZUSM 207B transformer supplying 75V, 20V and 18V. A RS Variac supplies 17V to the trace heater on the gas inlet and HCl injection point. Heating was performed by Thermocoax insulated heater wire, sheathed with Inconel. External heating coils of 2.5mm Thermocoax wire, were used to heat to the required temperature. A secondary coil of 1.5mm wire was added to the bottom of the bed section to reduce the
gradient across the sorbent bed. All the heaters were connected to programmable PID controllers (West3400 & 3750) and via them their temperature is monitored and controlled by the computer. The weight loss rate was calculated by Personal Computer, which was finally connected to the CRL455 controller (proportional band 0.5, integral term 0.7, derivative term 10, R-thermocouple: range and type 16, 300 baud, CRL mode) though an RS-232 connection. A proportional-integral control algorithm determined the appropriate temperature of the vapour generator to keep the weight loss rate as constant as possible. The experimental procedure comprised preparation of the fixed bed rig, run conditions, and gas supply settings.

A.XII/XIII Image and Schematic of the Fixed Bed Reactor system

Figure A.XIII.1: Schematic of McLaughlin’s (1990) FBR System.
APPENDIX B

DESCRIPTION OF THE SORBENTS, AGGLOMERATION AND CHEMICAL COMPOSITION OF THE SORBENTS

B.I Material Description - Kaolinite

Kaolin material originated from English China Clay, UK and Albion Kaolin Co, USA. Technical data sheets of the materials are enclosed below. Kaolin is a material approximating the mineral kaolinite in composition. The approximate chemical composition is $\text{Al}_2\text{O}_3.2\text{SiO}_2.5\text{H}_2\text{O}$. Linking one octahedral sheet with one tetrahedral sheet produces the double layer 1:1 lattice structure of kaolin. The uppermost plane of the octahedral sheet consists entirely of hydroxyl groups (Alexander, 1989). During heating kaolin undergoes a series of dehydration reactions and lattice rearrangements. These include: shrinkage and loss of pore water from the lattice, volatilisation of residual organic material inclusions, volatilisation of pyretic sulphur, and loss of hydroxyl water at 500 to 950°C. After the free moisture has been removed the kaolinite crystal is continuously dehydrated from so-called structural water. During this process the structural water arises by proton exchange reactions between two OH-groups within the clay mineral structure. The OH-groups are converted to oxidic oxygen bridging bonds (Freund, 1965). The octahedral lattice is destroyed and aluminium remains in a more or less tetrahedral co-ordination with $\text{O}^{2-}$ ligands. The highly disordered metastable structure obtained from the kaolinite structure by removal of OH-groups above 550°C is called meta-kaolin. Meta-kaolin shows an exothermic reaction at 950°C, which corresponds to a recrystallisation reaction in the dehydrated kaolinite. At 1050-1200°C a second exothermic reaction occurs and the structure transforms to a mullite phase with a further release of cristobalite (Brindley and Nakahira, 1959, 1962).
B.II Material Description - Emathlite and Calcium Montmorillonite

Emathlite (Type 600) was supplied by RTI, USA. Emathlite consists mainly of quartz and cristobalite and to a lower content of clay minerals (calcium montmorillonite), and feldspars. The structure of quartz consists of a silicon oxygen tetrahedra with each oxygen linked to a silicon atom in a neighbouring tetrahedron. When heated, emathlite predominately forms SiO$_2$ (Quartz). Transition of secondary species depends on the pre-treatment (Bachovchin, 1986).

Calcium montmorillonite (Fullers' Earth) originated from LaPorte, Redhill, UK. The technical data sheet is enclosed. Calcium montmorillonite consists of two tetrahedral sheets sandwiching an octahedral sheet (2:1 layer structure). Some Mg$^{2+}$ are substituted for some Al$^{3+}$ in the octahedral sheet. The resulting layer charge is balanced by interlayer cations (mainly Ca$^{2+}$ with small amounts of K$^+$ and Na$^+$). The general formula for a montmorillonite structure is $(M^+y.nH_2O)(Al_{2-y}Mg_y)(Si_4O_{10})(OH)_2$, where $M^+$ is the interlayer cation ($y$ varies with the source of the material). All montmorillonites lose the majority of their interlayer water in the range 100-200°C giving a partially collapsed structure. All interlayer water appears to be lost by 450°C, and after heating to temperatures greater than 450°C, most montmorillonites will not re-hydrate (Alexander, 1989). This is taken to indicate that the counter ions are able to move into hexagonal cavities in the tetrahedral silica sheets. Continued heating beyond 450°C leads eventually to the loss of hydroxyl groups. The loss of OH groups takes place in two stages (Alexander, 1989). A first loss at around 700°C, with the original structure being essentially retained, followed by a second loss a 800-900°C associated with the collapse of the lattice. Calcium montmorillonite has a high cation exchange capacity and adsorptive capacity (Worral, 1986).
**SURREY FINEST**

**TYPICAL CHARACTERISTICS**

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>High Purity Natural Calcium Montmorillonite Clay</td>
</tr>
<tr>
<td>Free Moisture</td>
<td>7%</td>
</tr>
<tr>
<td>pH - 10% w/w suspension</td>
<td>8.2</td>
</tr>
<tr>
<td>Surface Area (B.E.T.)</td>
<td>79 m²/g</td>
</tr>
<tr>
<td>Cation Exchange Capacity</td>
<td>78 meq/100g dry wt</td>
</tr>
<tr>
<td>True Density</td>
<td>2.930 kg/m³</td>
</tr>
<tr>
<td>Apparent Bulk Density</td>
<td>800 kg/m³</td>
</tr>
</tbody>
</table>

**SIEVE ANALYSIS (B.S.S.)**

| Cumulative finer than 100 (150 microns) | 99.0% |
| Cumulative finer than 200 (75 microns) | 99.0% |
| Cumulative finer than 300 (45 microns) | 94.0% |

**CHEMICAL ANALYSIS**

<table>
<thead>
<tr>
<th>Oxide</th>
<th>% Dry wt basis</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>55.2%</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>13.7%</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>8.1%</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.7%</td>
</tr>
<tr>
<td>MgO</td>
<td>3.3%</td>
</tr>
<tr>
<td>CaO</td>
<td>6.3%</td>
</tr>
<tr>
<td>Na₂O</td>
<td>Trace</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.6%</td>
</tr>
<tr>
<td>Loss on Ignition</td>
<td>9.9%</td>
</tr>
</tbody>
</table>

B.III
B.IV Technical Data Sheet - Kaolinite (Supreme)

Data clays
Supreme and Speswhite are highly refined clays of ultrafine particle size and high brightness.

**SPECIFICATION**

<table>
<thead>
<tr>
<th></th>
<th>Supreme</th>
<th>Speswhite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brightness (ISO)</td>
<td>87.5 ± 1.0</td>
<td>84.5 ± 0.7</td>
</tr>
<tr>
<td>+ 60 mesh (% max.)</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>+ 16 microns (% max.)</td>
<td>0.3</td>
<td>0.5</td>
</tr>
<tr>
<td>= 2 microns (%)</td>
<td>80 ± 0.3</td>
<td>80 ± 0.3</td>
</tr>
<tr>
<td>= 1 microns (% min.)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Moisture (% max.)</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>pH</td>
<td>5.0 ± 0.3</td>
<td>5.0 ± 0.1</td>
</tr>
</tbody>
</table>

**TYPICAL PROPERTIES**

<table>
<thead>
<tr>
<th></th>
<th>Supreme</th>
<th>Speswhite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yellowness</td>
<td>4.2</td>
<td>4.7</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>2.6</td>
<td>2.6</td>
</tr>
<tr>
<td>Surface area (BET1 m²/g)</td>
<td>16</td>
<td>14</td>
</tr>
<tr>
<td>Oil adsorption (g/100g)</td>
<td>43</td>
<td>63</td>
</tr>
<tr>
<td>Water soluble salt content (%)</td>
<td>0.20</td>
<td>0.20</td>
</tr>
<tr>
<td>Chemical analysis by X-ray fluorescence</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂ (%)</td>
<td>47</td>
<td>47</td>
</tr>
<tr>
<td>Al₂O₃ (%)</td>
<td>38</td>
<td>34</td>
</tr>
</tbody>
</table>

Particle Size Distribution Graph overleaf

CAS No. 1332-58-7  1332-58-7

**Typical Particle Size Distribution(s)**

Equivalent spherical diameter [μm]
B.V  Technical Data Sheet - Kaolin (grade D)

<table>
<thead>
<tr>
<th>SPECIFICATION</th>
<th>Grade B</th>
<th>Grade C</th>
<th>Grade D</th>
<th>Grade E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brightness (ISO)</td>
<td>82.5 ± 0.7</td>
<td>81.0 ± 0.7</td>
<td>79.2 ± 1.7</td>
<td>77.2 ± 1.0</td>
</tr>
<tr>
<td>+ 200 mesh (% max.)</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td># 100 mesh (% max.)</td>
<td>13</td>
<td>13</td>
<td>13</td>
<td>13</td>
</tr>
<tr>
<td># 200 mesh (% max.)</td>
<td>45</td>
<td>45</td>
<td>45</td>
<td>45</td>
</tr>
<tr>
<td>Moisture (% max.)</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>pH</td>
<td>5.0 ± 0.5</td>
<td>5.0 ± 0.5</td>
<td>5.0 ± 0.5</td>
<td>5.0 ± 0.5</td>
</tr>
</tbody>
</table>

Typical Values:

- Yellowness: 5.2 5.7 5.7 5.7
- Specific gravity: 2.6 2.6 2.6 2.6
- Surface area (BET m²/g): 10 10 10 10
- Oil absorption (g/100g): 38 38 38 38
- Water soluble salt content (%): 0.13 0.13 0.13 0.13

Chemical analysis by X-ray fluorescence:

- SiO₂ (%) 47 47 47 50
- Al₂O₃ (%) 57 57 57 53

CAS No.: 1332-58-7 1332-56-7 1332-58-7 1332-58-7

Particle Size Distribution

Graph: Typical Particle Size Distribution(s)
B.VIa Agglomeration - Pan Pelletisation

Pan pelletisation procedures were performed according to Pietsch, 1991. Porous pan pelletised pellets were formed from powdered materials using an Erweka balling disc (Heusenstamm, FRG), distilled and dimineralised water was used as binder. The drum (0.4m ID) was rotated at speeds varying from 5-32rpm depending on the material used. As the pan rotated, its slope varied 5-65°. 200g samples were used to produce calcium montmorillonite and kaolin pellets of different size (Eulalio, 1999).

Figure B.VI.: Pan pelletiser (ID. 0.4m; Angle: 50°C; Drum speed: 40% of critical speed (20rpm for the shallow dish).

B.VIb Agglomeration - Extrusion and Spheronisation

In the extrusion and spheronisation process, a paste composed of clay and water was extruded from a 3-mm die forming cylindrical rodes or extrudates. These cylindrical extrudates were converted into 3-mm spheres in a spheroniser (Turk et al, 1996).
B.VII  Chemical Composition of Kaolinite, Calcium Montmorillonite and Emathlite

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Kaolinite</th>
<th>Emathlite 600</th>
<th>Calcium Montmorillonite&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RTI</td>
<td>ECC&lt;sup&gt;a&lt;/sup&gt;</td>
<td>RTI&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>51.15</td>
<td>47.60</td>
<td>68.79</td>
</tr>
<tr>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>44.17</td>
<td>37.30</td>
<td>7.75</td>
</tr>
<tr>
<td>Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.62</td>
<td>0.60</td>
<td>2.98</td>
</tr>
<tr>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1.73</td>
<td>0.03</td>
<td>0.39</td>
</tr>
<tr>
<td>CaO</td>
<td>0.10</td>
<td>0.05</td>
<td>5.83</td>
</tr>
<tr>
<td>MgO</td>
<td>0.10</td>
<td>0.25</td>
<td>2.73</td>
</tr>
<tr>
<td>K&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>0.15</td>
<td>1.09</td>
<td>1.04</td>
</tr>
<tr>
<td>Na&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>0.10</td>
<td>0.40</td>
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<sup>a</sup>Supreme with 96% of kaolinite and 4% of mica, English China Clay (ECC), UK
<sup>b</sup>Research Triangle Institute (RTI), USA
<sup>c</sup>LaPorte, Redhill, UK
<sup>d</sup>Trade name (Fullers' Earth)
<sup>e</sup>Chemical composition based on loss of ignition

Table B.VII.1: Chemical Composition of Kaolinite, Calcium Montmorillonite and Emathlite.
APPENDIX C

PORE SIZE MEASUREMENTS

Background
Mercury porosimetry is based on the capillary law governing liquid penetration into small pores. This law, in the case of a non-wetting liquid like mercury and cylindrical pores was expressed by the Washburn equation (Micromeritics operators manual, 10/1993). The powder 3ccm powder penetrometer (Partnumber 920-61714-00) was used with a total steam volume of 3cc, a maximum head pressure of 0.412psia/MPa and a penetrometer constant of 10.79μl/pF, to allow mercury intrusion in low and high pressure port of a Micromeritic porosimeter, 9220. As reference sample was used Micromeritics silica alumina (Partnumber 004-16822-00).

C.I Mean Pore Diameters of Extruded and Pan Pelletised Kaolinite, Calcium Montmorillonite and Emathlite

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<th>Kaolinite, pan pelletised</th>
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<td>Cumulative volume [ml/g]</td>
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<td>Cumulative volume [ml/g]</td>
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Table C.I.1: Pore Size Distribution of Pan Pelletised and Extruded Pellets.
C.II Pore Diameter of Uncalcined and Calcined Kaolin Pellets

Figure C.II.1: Pore Diameters of Uncalcined and Calcined Kaolin Pellets.
APPENDIX D

SURFACE AREA MEASUREMENTS

D.I Background

A mass flow controller of the Coulter device was used to perform experiments with continuous flow method (Coulter Technical Instructions). Nitrogen was applied as adsorbate for the surface area measurement. Excess volume was filled with helium. Helium is used because it is a non-adsorbing gas at a temperature of -196°C. Continuous and static methods were used to perform experiments after estimating an appropriate weight of sample and short-outgassing procedure (Coulter Omnisorp instructions PN4237006, 08/91, Operation Instructions, Rieger 1999). The cleanliness of the sample was obtained by flushing the adsorbent with nitrogen and helium. A reference sample calcined kaolin was chosen (8570, US Department of Commerce, National Institute of Standards and Technology, Gathersburg) to check the Coulter equipment measurements.

D.II Data Acquisition and Detailed Procedure

Analysing an appropriate sample weight/Reference Material:
A chart supplied by the manufacturer was used to estimate an appropriate weight of sample suitable for N₂. One gram of calcined kaolin was heated up to 300°C and was then outgassed for one hour.

Static and Continuous Flow Method of the Omnisorb Equipment
Omnisorp and static flow method - the mass flow controller was used for manifold dosing
Using the static flow method the mass flow controller was used to dose the calibrated manifold with adsorbate (dose pressure). Once the target manifold pressure was reached the mass flow controller was turned off. The pressure was equilibrated within the manifold and a dosing volume and pressure was applied to the sample and the pressure was again equilibrated (equilibrated pressure). The volume of gas adsorbed was calculated from the difference between the dosing pressure and the equilibrated pressure. The volume of the sample bulb

D.I
provide the volume of gas adsorbed. The dead space determination was performed with helium (helium calibration) which is a non-adsorbing gas at the temperature used for the measurement.

Omnisorp and Continuous Flow Technique - Manifold was dosed and equilibrated before the sample valve was opened.

The continuous flow method was used to flow the adsorbate continuously to the mass flow controller (0.3ml/min), and directly to the sample. The volume adsorbed by the sample was calculated by integrating the flow rate over time and subtracting the dead volume (volume of the manifold, holder, and the sample), from the volume of gas dosed to the sample. This volume was calculated from the helium calibration measurement which was performed automatically before the adsorption commences.

To confirm that the results were not affected by a change in flow it was checked that a agreement was available with representative isotherms determined by a static method. A one hour outgassing time was used. The outgassing temperature was set up either to 20°C or 70°C. An outgassing temperature of 70°C was used when the calcination occurred more than 24 hours previously. The cleanliness of the sample - removing of all physisorbed species - was obtained by flushing the adsorbent with N₂/He adsorption/desorption cycles at least twice. No measurements were performed when the ultimate vacuum pressure fell below 10⁻⁴ torr. The adsorbent was evacuated after every adsorption/desorption cycle.
D.III Surface Area Stability of Aluminosilicate Materials

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Surface area stability of kaolin grade D (English China Clay, England) and of calcium montmorillonite (Redhill, La Porte)

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Table D.III.1: Surface Area of calcined Grade D and Calcium Montmorillonite.
D.IV Nitrogen Adsorption on Kaolin Grade D/CaClum Montmorillonite

Figure D.IV.1: Nitrogen Adsorption on Kaolin Grade D.

Figure D.IV.2: Nitrogen Adsorption on Calcium Montmorillonite.
D. V. Fullsorb-Isotherms and BET Plots

Figure D.V.1: Fullsorb-isotherm of Kaolin, Pan Pelletised, 800°C, 24hours Air Calcined.

Figure D.V.2: Fullsorb-isotherm of Calcium Montmorillonite, Pan Pelletised, 800°C, 24hours Air Calcined.
D.VI Fullsorb-Isotherms and BET Plots

Figure D.VI.1: FullsorbIsotherms - Extruded Kaolinite and Emathlite, Air Calcined 815°C.

Figure D.VI.2: BET Plot of Calcined Calcium Montmorillonite.
APPENDIX E:

PARTICLE SIZE MEASUREMENTS

Background
Digital images were obtained by scanning electron microscopy (see below). The digital images were image processed via an image analysis system package (Optimas 7.0). The system uses mathematical functions (filter, distribution functions) to identify objects. The system was used to obtain the median major particle length in sorbent pellets.

Digital image and processed image are shown on same page to allow comparison.
E.II Image and Processed Image of Kaolinite (Supreme)

Image E.II.1: Inner Structure of a Kaolinite Pellet (Equated to be a Pellet of Extrusion Technique).

Image E.II.2: Processed Image: Median Filter (3x3), Erode and Dilate, Watershed Separate and Threshold 127.
E.III Image and Processed Image of Kaolin (Grade D)

Image E.III.1: Inner Structure of Kaolin Pellet (Equated to be a Pellet of Extrusion Technique).

Image E.III.2: Processed Image: Average Filter (3x3), Erode and Ticken 2 and Treshold 198.
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Table E.IV.1: Calculation of MAL of Kaolinite.
### Table E.V.1: Calculation of MAL of Kaolinite

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E.VI Extruded and Spheronised Pellet, Calcined 815°C (4hours)

Image E.VI.1: Extruded and Spheronised Emathlite Pellet, Calcined 815°C (4hours).

Image E.VI.2: Extruded and Spheronised Kaolinite Pellet, Calcined 815°C (4hours).
E.VII Pellets of the Extrusion and Pan Pelletiser Technique

Image E.VII.1: Extruded and Spheronised Emathlite Pellet, Grain structure composed of Smaller Particles, Calcined 815°C (4hours).

Image E.VII.2: Porous Pan Pelletised Calcium Montmorillonite Pellet, Calcined 850°C (24hours).
APPENDIX F

CRUSH STRENGTH MEASUREMENTS

Background
Load on a particle leads to breakage. The breakage characteristics of load-displacement curve can be used to analyse the breakage point (fracture points). Different load cells were used to determine the breakage points of agglomerated pellets. Ten pellets were load tested to determine the first break point.

F.I Crush Strength Characteristics of Pan Pelletised Kaolinite

Figure F.I.1 shows a typical load displacement curve for pan pelletised kaolinite. At a displacement of 0.1; the first break point of kaolinite was found to be at about 0.3 N for this pellet. The standard deviation for kaolinite pellets were found to be +/-10 percent. Extruded pellets were found to be less affected in the standard deviation.

Figure F.I.1: Load-Displacement Curve of Pan Pelletised Kaolinite.
APPENDIX G

ELEMENT DISTRIBUTION (ELEMENT MAPPING)

Background
An electron beam was generated within an electron gun by heating up a tungsten hairpin filament to approximately 2300°C. The electron beam was accelerated by a high voltage, in general 0.3-40kV, and focused on the surface of the epoxy mounted, ground and polished, carbon treated specimen by means of an electron-optical system. Interactions between this primary electron beam and the sample interaction volume cause generation of secondary electrons, this secondary electron signal was used to generate an image.

The preparation of the pellets of the SEM analysis was done by vacuum mounting in a mixture of epofix resin and expofix hardener. Fifteen parts by volume of expofix resin (Bisphenol-A-Diglycidether) was mixed with two parts of epofix hardener. The components were mixed thoroughly. Mounted pellets were obtained by placing mould and pellets in an epovac vacuum apparatus to remove air and to suck mounting medium into the mould. When the resin block was solid the specimen was ground on a wheel in order to find the desired cross-section of the pellet. An appropriate smoothness of the cross-section of the pellet was obtained using grinding papers 500, 1200[1 minute], 2400[1 minute], and 4000[1 minute] and polishing papers 6μm Dur (3 minutes, 150 rpm), and 1μm Dur (3 minutes, 150 rpm). The polishing cloths were impregnated with diamond PP sprix spray (1 mm). After every step the specimen was washed with methanol and the cross-section was examined by the optical microscope. In addition a carbon film was placed on top of the specimen to avoid charging under the microscope. Two carbon fibres were heated to 2,000°C in a vacuum apparatus to prepare the specimen for the SEM apparatus.

EDS: X-rays were produced by energy dispersion method when primary and electron beam and surface atoms occurring in the specimen. The signals produced were collected by detector and speed map software. The acquisition times varied depending on the count rates. 70 frames per map were used to produce a map with sodium. However, long term acquisition, allowed
element mapping (70 frames) of sodium, chlorine, silicon, aluminium, oxygen, calcium and potassium.

G.IIa Na/Cl and Si/Al-ratio

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Table G.IIa Na/Cl and Si/Al-ratio

G.IIb Calcium Montmorillonite Pellet for Element Mapping

Image G.IIb.1: Calcium Montmorillonite Pellet for Element Mapping.
G.III Element Mapping of Calcium Montmorillonite

Image G.III.1: Digital X-ray Element Map of Sodium, Aluminium, Silicon, Chlorine, and Calcium in a Treated Calcium Montmorillonite Pellet.
Image G.IV.1: Linescan Across the Calcium Montmorillonite Pellet Representing the Sodium, Aluminium, Silicon, Calcium, Titanium and Iron Distribution.
G.V Element Distribution within Extruded Pellet

Image G.V.1: Digital X-ray Element Map of Sodium, Silicon, Chlorine, Calcium and Iron in Extruded Emathlite Pellet.

Image G.V.2: Digital X-ray Element Map of Sodium, Silicon, Chlorine, Potassium and Iron in Extruded Pellet.
G.VI Element Distribution within Extruded and Pan Pelletised Pellet


APPENDIX H

HCL MEASUREMENTS

Background
Hydrogen chloride were investigated through a change of coloration from blue to yellow using a pH reaction between hydrogen chloride and bromophenolblue at room temperature. The change in coloration was obtained through suction of a gas sample through a Draeger tube. The discoloration over a length of the Draeger tube is a measure of the concentration of Hydrogen chloride. The principle of the reaction shows the following reaction scheme:

\[ HCl + Bromophenolblue \rightarrow yellow \text{ reaction product} \]

H.I Dräger Tubes and HCl Content

HCl Measurements with Dräger tubes were performed under NaCl-dry/HCl (NaCl/HCl/N₂), standard-wet/HCl (NaCl/HCl/H₂O/N₂) and standard-wet (HCl/H₂O/N₂) conditions. However, Dräger tubes were found to be sensitive to water vapour (manufacturer information, max. 20,000ppm). Water vapour was therefore adsorbed selectively into a nafion permeation tubing (62.5cm length, ID. of 1.25mm), New Jersey, when a high water vapour concentration was used. In principle the water vapour was selectively absorbed into the membrane and removed by dry purge gas. Mass balances indicated that both, water vapour and hydrogen chloride could be measured without any loss in content when sufficient equilibrated. However, a water vapour concentration higher than 13,000ppm (1.3% by volume) was avoided in the course of this work.

HCl measurement led to differences of up to 25% in the hydrogen chloride content. This deviation in HCl complies with the maximum error stated by the supplier.
APPENDIX I

WATER VAPOUR MEASUREMENTS

Background
The detection of water vapour gas by gas chromatography uses thermal conductivity between the pure carrier gas and the mixture produced when water vapour is present in the carrier gas. By using the dual-channel detector normally four tungsten-rhenium filaments are connected as a bridge circuit, two filaments being located in each channel. The presence of a water component in the carrier gas flowing through the sample channel changes the resistance of the filaments in the channel, unbalancing the bridge and producing a signal related to the sample from which the chromatogram is plotted. HCl water vapour mixtures can corrode the filaments. As a consequence a mixture containing HCl cannot be analysed by gas chromatography, although some applications are reported in the literature.

To measure the water vapour content, waterphilic sorbents can be used to measure weight changes over time.

1.1 Analysis of the Water Content using Zeolite

Water vapour gas exposed to zeolite tubes were finally used to proof that the condition of 1.3% by volume was achieved. The change in weight of the zeolite was determined to recalculate the water content after exposure to a water vapour containing gas stream. It was found that the theoretical saturation value at a certain temperature (Handbook of Chemistry and Physics, 1974) agreed with that investigated by weight change, flow and appropriate gas law constant. Zeolite was dried in a desiccator and transferred into an aluminium tube with inlets and outlets. The tube was then exposed to the gas stream for sufficient time.

Water vapour contents were also determined on a 2m x 0.32cm x 2mm column off 80-100 mesh Poropak Q (Port B) in conjunction with a 2m x 0.32cm column off 60-80mesh Poropak QS (Port A) in a Perkin Elmer Model 8310 gas chromatograph with a hot-wire detector and a Perkin Elmer recorder. The conditions for these measurements were; column temperatures,
120°C; detector temperature, 150°C; column B - pressure controlled, 190kPa; column A - flow control, 120kPa; negretti gas sampling valve; carrier gas, Helium. Finally, this technique was used for quick analysis using the area underneath the peak as a mass for the water vapour concentration. Internal standards were initially used but did not lead to a desired value. This was because of the gas valve used.
APPENDIX J

SODIUM CONTENT

Background
The sodium content was determined by Atomic spectroscopy. Analytical atomic spectroscopy utilising the emission, absorption, or fluorescence of light at discrete wavelength by atoms in a vaporised sample for the determination of the elemental composition of the sample. The sample (e.g. sodium), usually an aqueous solution, is introduced into a high temperature device, where it is dissociated into its component atoms. The atomic spectrophotometer consisted of a light source (emitting the spectrum of sodium), a sample atomiser (an air-acetylene flame), a monochromator to isolate the sodium source emission line, and a detector/readout system to allow measurement of the change in source line intensity by sample atom absorption.

J.I-III.0 Sodium Standard Solutions and Extractable Sodium from Pellets

Calibration was made with sodium standard. 0.1ml of 10038ppmv Na standard solution (BDH 456052Q, A8015073-088, sodium nitrate in 2% nitric acid, expiration date, 02.2000, Inductively coupled plasma mass spectrometry [ICP-MS] standard) was added to distilled and deionised water (0.5 μMHO/cm) and 8ml 12.5% wt. HNO₃ in a 100ml polymethylpentene (PMP) volumetric flask to produce a 10ppmv sodium solution. Before the solution was finally made up to 100ml, 1ml of an ionisation inhibitor solution (20g/l) was added (Caesium chloride, Fluka 31807, CAS 7647-17-8). From this solution a series of 20ml sodium standards (0.05,0.1,0.5,1,1.5,2,5,10ppm) were prepared in universal tubes. To allow use of solutions for AAS and ICP-MS 1ml 46ppmv Cobalt solution was added to the universal tube (spiking reagent for ICP-MS). 100ml standard blanks contained destilled and deionised water with and without caesium chloride and also 8ml of 12.5% wt. HNO₃ to identify any matrix effects. The calibration graph was established by plotting absorbency against concentration (slope 0.83 +/- 0.05, correlation coefficient 1.0). Previous methods to chemically analyse the sodium content considered the acid insoluble fraction of sodium within ground treated pellets (McLaughlin, 1990; Chrysohoidou, 1996; Mönter, 1999). The new method involves water soluble, HCl.
soluble and HF insoluble fractions. 40mg (Chrysohoidou (1996), 20mg for acid insoluble fraction) powder samples ground from top layer treated pellets were transferred into PTFE lined bombs. Grinding below 100mesh was be avoided because of the chemical changes that may take place (Langmyhr and Sveen, 1965).

5ml of deionised water was added to the bomb, which was then closed using a PTFE lined bomb cap and heated in a Carbolite furnace for 1 hour at 100°C (Lee and Johnson, 1980; Bachovchin et al, 1986). The bomb was cooled naturally and the contents transferred to a plastic tube (Universal) which was then centrifuged at 2800rpm (rounds per minute) for 10 minutes (Omiigrue 2.0 RS, 23cm OD.). Before centrifugation the PTFE lined bomb was cleaned with 1ml destilled and deionised water to obtain 8ml end volume in the universal tube. The universals were tarred against each other. Lower centrifugation rounds per minutes should be avoided. The water leach was the water soluble fraction whereas the solid residue contains the acid soluble fraction. The water leach was transferred into a 100ml polymethleneaproplylene (PMP) flask and made up to 100ml with destilled and deionised water. The solution was transferred into a 150ml PMP bottle. 1ml of the solution was refrigerated (Eppendorf) whereas 1ml CsCl was added into the 150ml bottle. The solution was refrigerated (4°C).

To obtain the HCl soluble residue the sample was diluted on a 1:1 volumetric basis (2ml+2ml, twice) with 12.5% wt. HCl. The solution was transferred back to the PTFE lined bomb (HCl leaching, Bachovchin et al, 1986), closed and heated in a Carbolite furnace for 1 hour at 100°C. After the cooling procedure, the solution with residue was transferred into a universal tube in a fume cupboard. The solution was centrifuged and the supernatant was diluted according expected sodium concentration (8ml acid soluble leach made up to 100ml solution, destilled and deionised water PMP flask). The solution was prepared for refrigeration as above.

The literature suggests that a sample can be best decomposed with just HF not a mixture of acids (Langmyhr and Sveen, 1965). Chrysohoidou (1996) found that an acid proportion of first 4ml HNO₃ and then 2ml HF was appropriate in digesting a sample. HNO₃ is used because of problems reported with hydrofluoric, perchloric, nitric acid mixtures (Maqueda, 1986). As the result the solid residue was HF treated as follows: The solid residue was transferred into an open HF beaker (PTFE) for HF digestion. The PTFE beaker stands in a drilled position of a
21 beaker heating block. 2ml HNO₃ proportions were used to transfer the residue. The heating block was improved through external temperature adjustment. However, new safety restrictions were to comply (Safety Policy: SP/06/98). A scrubber system was installed to neutralise the vaporised agents during the digestion process. The risks, fan failure, air failure, power shutdown, were considered and as a consequence the fume cupboard with scrubber facility including hot plate was connected to the building management security system. A risk reduction of contact with HF was achieved through equipment and facilities (fume cupboard with scrubber facility, running water all the time, special stands), personal protective equipment (safety spectacles, a full face visor, rubber and microtouch gloves with the external being HF resistant, full length plastic apron, laboratory coat with press stud fastening, personal HF kit for lab and home), spillage kit and spill procedure (neutralising agent calcium carbonate for spills, neutralising solution for gloves potassium carbonate), second person around and procedures for safety and incidents.

The acid insoluble digestion procedure was performed as follows.

a) Samples with 4ml HNO₃ (12.5%, Analytical Reagent, Fisons, N2300/PB17) were heated to bring them to dryness.

b) 2ml of hydrogen fluoride was added and fully evaporated. A mirror with PTFE tube allowed observation of when dryness of the sample was achieved.

c) The digestion steps a+b were repeated as many times as required.

d) At the end of the digestions, 8ml HNO₃ was added.

e) After 10 minutes the heating block was switched off. The period of time needs shortening because not all beakers were found in solution.

e) The samples were made up to 100ml solutions with deionised water and refrigerated according to above procedure.

The sample solutions and standard solutions obtained were finally diluted according to . Universals were used only, an end volume of 21ml were obtained with 1ml cobalt solution. The samples were finally analysed at Rooney laboratories by atomic absorption spectrometry (Report No. 49429). The instrument was used in the concentration range 0.1-5ppm Na as with the prepared sample and standard solutions.

J.III
J.III.1 Sample AAS Readings (Rooney Report No. 49429,1)

The average of the AAS readings for each standard, standard blank and sample solution was found. The equation of the calibration curve was specified. The linearity of the calibration curve was ideal (Regression coefficient 1). The readings were:

ROONEY LABORATORIES LTD.
Analytical and Consultant Chemists

7 Lennox Mall,
Lister Road,
Basingstoke,
Hampshire.
RG22 4DF
Tel: 01256 469941
Fax: 01256 470669
email: rooney@rooney-labs.demon.co.uk
VAT Reg No. 199 6474 91

Your Ref: Order No. W170277
Our Ref: LR. 49429A

Mr M Rieger
Department of Chemical and Process Engineering
School of Engineering in the Environment
University of Surrey
Guildford
Surrey
GU2 5XH

Laboratory Report No. 49429A
10 December 1999

Samples: Aqueous extracts

Date of sample receipt: 07 December 1999
Date of completion of testing: 10 December 1999
Test method used: Direct AES

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J.V
### J.11.3 Sample AAS Readings (Rooney Report No. 49429.3)

10/12 '90 16:29 FAX 01256 470659

**Rooney Laboratories Ltd.**

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#### HF leach

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#### HF only

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**Reason for re-issue of report:**
The previous report had 4 typographical errors on page 2 listing dilution factors as 1:10 rather than 1:40, and one sample weight incorrect. Repeat analysis of these extracts has been performed and is reported above.

Managing Director
## Table J.VII.1:

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<th>SUM [g]</th>
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<th>SUM [g]</th>
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Table J.VIII.1:
HF extractable sodium from pre-treated pan pelletised pellets (NaCl-dry and standard-wet) when exposed to HCl mixtures

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<th>ppm</th>
<th>Std.</th>
<th>Di.</th>
<th>ID</th>
<th>We.</th>
<th>SUM</th>
<th>SUM_g</th>
<th>g_sample</th>
<th>STD</th>
<th>SUM</th>
<th>SUM_g</th>
<th>g_sample</th>
<th>+/-Sample</th>
<th>SUM_STD</th>
<th>Total ug</th>
<th>Std. ug</th>
<th>ug/ml 100ml ug/ml 100ml</th>
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Table J.IX.1:
Calcium Montmorillonite treated under NaCl-dry conditions.

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<th>SUM g/g sam</th>
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<th>Std. ug</th>
<th>ug/ml</th>
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<tr>
<td>010 NaCl-dry</td>
<td>0.429</td>
<td>0.002</td>
<td>20</td>
<td>151</td>
<td>0.02386</td>
<td>0.00086</td>
<td>0.0360</td>
<td>0.0000040</td>
<td>0.00168</td>
<td>0.0070</td>
<td>8.6</td>
<td>858</td>
<td>0.04</td>
<td>4</td>
</tr>
</tbody>
</table>

*2nd layer powder and undigested powder near the top beaker led to smaller sodium content

Table J.X.1:
APPENDIX K

REACTION PRODUCTS

Background
A monochromatic x-ray beam was used to strike the powdered sample that, ideally has crystals randomly arranged in every possible orientation. In the produced powders, the various lattice planes are present in different possible orientation. For each set of planes, at least some crystals are oriented at the Bragg angle, $\theta$, to the incident beam and thus, diffraction occurs for these crystals and planes. The target pellets were ground to a fine powder with an agate motor and pestle and irradiated. Diffracted beams were finally analysed via Hiltonbrookes software. The plotted d-spacing and intensity lines were opposed to the Powder Diffraction file standard (International Centre for Diffraction Data formerly the Joint Committee on Powder Diffraction Standards).

The Bragg approach to diffraction is to regard as built up in layers or planes such that each acts as a semi-transparent mirror. Some of the X-rays are reflected off a plane with the angle of reflection equal to the angle of incidence, but the rest are transmitted from adjacent planes within the crystal. When two X-ray beams are reflected from the adjacent planes within the crystal, the perpendicular distance between the planes, the d-spacing, $d$, and the angle of incidence, or Bragg angle, $\theta$, are related by Bragg’s law ($n\lambda=2d \sin \theta$).

K.I Results on the d-Spacing Measurements

D-spacings were obtained from X-ray diffraction studies on raw calcium montmorillonite and kaolinite powder, on calcined material, on treated kaolinite and calcium montmorillonite (standard-wet, standard-wet/HCl, NaCl-dry) and pre-treated kaolinite and calcium montmorillonite when further exposed to inert-dry/HCl and inert-wet/HCl condition. The following Tables identify possibly reaction products for calcium montmorillonite and kaolinite in the applied gaseous environment.
K.II Calcium Montmorillonite Exposed to Certain Gaseous Environment to Form Albite

Powder Diffraction file - Albite: Sodium Aluminium Silicate (9-466)

<table>
<thead>
<tr>
<th>Intensity</th>
<th>100</th>
<th>25</th>
<th>20</th>
<th>15</th>
<th>15</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>d-spacing</td>
<td>3.2</td>
<td>3.78</td>
<td>6.39</td>
<td>4.03</td>
<td>3.66</td>
<td>2.93</td>
</tr>
</tbody>
</table>

Air-Calcined calcium montmorillonite

<table>
<thead>
<tr>
<th>Intensity</th>
<th>25</th>
<th>29</th>
<th>26</th>
<th>24</th>
<th>NO</th>
</tr>
</thead>
<tbody>
<tr>
<td>d-spacing</td>
<td>3.18</td>
<td>4.06</td>
<td>3.46</td>
<td>3.00</td>
<td></td>
</tr>
</tbody>
</table>

NaCl-dry (100hrs)

<table>
<thead>
<tr>
<th>Intensity</th>
<th>65</th>
<th>100</th>
<th>57</th>
<th>55</th>
<th>NO</th>
</tr>
</thead>
<tbody>
<tr>
<td>d-spacing</td>
<td>3.18</td>
<td>6.37</td>
<td>4.02</td>
<td>2.97</td>
<td></td>
</tr>
</tbody>
</table>

NaCl-dry pellets exposed to inert-dry/HCl (100hrs)

<table>
<thead>
<tr>
<th>Intensity</th>
<th>38</th>
<th>100</th>
<th>33</th>
<th>NO</th>
</tr>
</thead>
<tbody>
<tr>
<td>d-spacing</td>
<td>3.18</td>
<td>6.32</td>
<td>2.99</td>
<td></td>
</tr>
</tbody>
</table>

Standard-wet/HCl $\left(N_2/H_2O/HCl\right)$ (100hrs)

<table>
<thead>
<tr>
<th>Intensity</th>
<th>53</th>
<th>34</th>
<th>67</th>
<th>39</th>
<th>34</th>
<th>45</th>
<th>100</th>
<th>YES, but low intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>d-spacing</td>
<td>3.17</td>
<td>3.69</td>
<td>6.32</td>
<td>3.98</td>
<td>3.69</td>
<td>2.97</td>
<td>3.3</td>
<td></td>
</tr>
</tbody>
</table>

*Slit changed 6.32 peak to 6.6, slit was changed to get more precision for the other peaks

Standard-wet $\left(N_2/H_2O\right)$ (100hrs)

<table>
<thead>
<tr>
<th>Intensity</th>
<th>44</th>
<th>23</th>
<th>100</th>
<th>27</th>
<th>23</th>
<th>35</th>
<th>YES, but low intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>d-spacings</td>
<td>3.18</td>
<td>3.72</td>
<td>6.3*</td>
<td>4.00</td>
<td>3.72</td>
<td>2.97</td>
<td></td>
</tr>
</tbody>
</table>

*slit change changed 6.3 peak to 6.8, examplified by N2/HCl/H2O

Standard-wet $\left(N_2/H_2O\right)$ pellets exposed to inert-wet/HCl (100hrs)

<table>
<thead>
<tr>
<th>Intensity</th>
<th>55</th>
<th>44</th>
<th>36</th>
<th>NO</th>
</tr>
</thead>
<tbody>
<tr>
<td>d-spacing</td>
<td>3.18</td>
<td>4.00</td>
<td>2.91</td>
<td></td>
</tr>
</tbody>
</table>

Table K.II.1: Albite Formation as the Reaction Product from Calcium Montmorillonite.
### Albite Formation as the Reaction Product from Kaolinite

#### Powder Diffraction file - Albite: Sodium Aluminium Silicate (9-466)

<table>
<thead>
<tr>
<th>Intensity</th>
<th>100</th>
<th>25</th>
<th>20</th>
<th>15</th>
<th>15</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>d-spacing</td>
<td>3.2</td>
<td>3.78</td>
<td>6.39</td>
<td>4.03</td>
<td>3.66</td>
<td>2.93</td>
</tr>
</tbody>
</table>

#### Air-Calcined kaolinite

<table>
<thead>
<tr>
<th>Intensity</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>d-spacing</td>
<td></td>
</tr>
</tbody>
</table>

#### NaCl-dry (100hrs)

<table>
<thead>
<tr>
<th>Intensity</th>
<th>100</th>
<th>96</th>
</tr>
</thead>
<tbody>
<tr>
<td>d-spacing</td>
<td>6.37</td>
<td>4.13</td>
</tr>
</tbody>
</table>

#### NaCl-dry pellets exposed to inert-dry/HCl (100hrs)

<table>
<thead>
<tr>
<th>Intensity</th>
<th>68</th>
<th>77</th>
<th>100</th>
<th>81</th>
</tr>
</thead>
<tbody>
<tr>
<td>d-spacing</td>
<td>3.25</td>
<td>3.82</td>
<td>6.37</td>
<td>2.99</td>
</tr>
</tbody>
</table>

#### Standard-wet/HCl (100hrs)

<table>
<thead>
<tr>
<th>Intensity</th>
<th>47</th>
<th>100</th>
<th>95</th>
</tr>
</thead>
<tbody>
<tr>
<td>d-spacing</td>
<td>3.23</td>
<td>6.41</td>
<td>4.15</td>
</tr>
</tbody>
</table>

#### Standard-wet (100hrs)

<table>
<thead>
<tr>
<th>Intensity</th>
<th>19</th>
<th>22</th>
<th>100</th>
<th>17</th>
</tr>
</thead>
<tbody>
<tr>
<td>d-spacing</td>
<td>3.23</td>
<td>3.80</td>
<td>4.12</td>
<td>3.60</td>
</tr>
</tbody>
</table>

#### Pre-treated pellets (standard-wet) exposed to standard-wet/HCl (100hrs)

<table>
<thead>
<tr>
<th>Intensity</th>
<th>52</th>
</tr>
</thead>
<tbody>
<tr>
<td>d-spacing</td>
<td>3.21</td>
</tr>
</tbody>
</table>

Table K.III.1: Albite Formation as the Reaction Product from Kaolinite.
K.IV Calcium Montmorillonite Exposed to Certain Gaseous Environment to Form Nepheline

<table>
<thead>
<tr>
<th>Powder Diffraction file - Nepheline: Sodium Aluminium Silicate (9-458)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intensity</td>
</tr>
<tr>
<td>d-spacing</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Air-Calcined calcium montmorillonite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intensity</td>
</tr>
<tr>
<td>d-spacing</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>NaCl-dry (100hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intensity</td>
</tr>
<tr>
<td>d-spacing</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Standard-wet/HCl (100hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intensity</td>
</tr>
<tr>
<td>d-spacing</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Standard-wet (100hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intensity</td>
</tr>
<tr>
<td>d-spacing</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>NaCl-dry pellets and then exposed to inert-dry/HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intensity</td>
</tr>
<tr>
<td>d-spacing</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pre-treated calcium montmorillonite (standard-wet) further exposed to standard-wet/HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intensity</td>
</tr>
<tr>
<td>d-spacing</td>
</tr>
</tbody>
</table>

Table K.IV.1: Nepheline Formation as the Reaction Product from Calcium Montmorillonite.
# K.V Kaolinite Exposed to Certain Gaseous Environment to Form Nepheline

<table>
<thead>
<tr>
<th>Powder Diffraction file - Nepheline: Sodium Aluminium Silicate (12-198)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Intensity</strong></td>
</tr>
<tr>
<td><strong>d-spacing</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Powder Diffraction file - Nepheline: Sodium Aluminium Silicate (9-458)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Intensity</strong></td>
</tr>
<tr>
<td><strong>d-spacing</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Air-Calcined kaolinite</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Intensity</strong></td>
</tr>
<tr>
<td><strong>d-spacing</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>NaCl-dry (100hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Intensity</strong></td>
</tr>
<tr>
<td><strong>d-spacing</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pre-treated pellets (NaCl-dry) exposed to inert-dry/HCl (100hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Intensity</strong></td>
</tr>
<tr>
<td><strong>d-spacing</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>standard-wet/HCl (100hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Intensity</strong></td>
</tr>
<tr>
<td><strong>d-spacing</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>standard-wet (100hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Intensity</strong></td>
</tr>
<tr>
<td><strong>d-spacing</strong></td>
</tr>
<tr>
<td>d-spacing peak 7 und 6.7 disappeared under the water vapour condition</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>pre-treated kaolinite (standard-wet) pellets exposed to inert-wet/HCl(100hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Intensity</strong></td>
</tr>
<tr>
<td><strong>d-spacing</strong></td>
</tr>
</tbody>
</table>

Table K.V.1: Nepheline Formation as the Reaction Product from Kaolinite.
K.VI Kaolinite and Calcium Montmorillonite Exposed to Certain Gaseous Environment to Form Carnegieite

a) Kaolinite and Carnegieite.

<table>
<thead>
<tr>
<th>Carnegieite (11-220)</th>
<th>Intensity</th>
<th>100</th>
<th>95</th>
<th>85</th>
<th>50</th>
<th>50</th>
<th>45</th>
<th>30</th>
<th>25</th>
<th>25</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>d-spacing</td>
<td>4.17</td>
<td>2.56</td>
<td>4.18</td>
<td>2.9</td>
<td>2.54</td>
<td>2.55</td>
<td>2.26</td>
<td>3.76</td>
<td>3.3</td>
<td>2.08</td>
<td></td>
</tr>
<tr>
<td>standard-wet treated (100hrs)</td>
<td>Intensity</td>
<td>100</td>
<td>39</td>
<td>19</td>
<td>15</td>
<td>11</td>
<td>11</td>
<td>10</td>
<td>22</td>
<td>19</td>
<td>11</td>
</tr>
<tr>
<td>d-spacing</td>
<td>4.12</td>
<td>2.56</td>
<td>4.27</td>
<td>2.90</td>
<td>2.50</td>
<td>2.54</td>
<td>2.29</td>
<td>3.80</td>
<td>3.23</td>
<td>2.08</td>
<td></td>
</tr>
<tr>
<td>pre-treated kaolinite (standard-wet) and then exposed to inert-wet/HCl (100hrs)</td>
<td>Intensity</td>
<td>81</td>
<td>38</td>
<td>61</td>
<td>51</td>
<td>NA</td>
<td>38</td>
<td>34</td>
<td>77</td>
<td>68</td>
<td>30</td>
</tr>
<tr>
<td>d-spacing</td>
<td>4.15</td>
<td>2.56</td>
<td>4.29</td>
<td>2.86</td>
<td>NA</td>
<td>2.56</td>
<td>2.30</td>
<td>3.82</td>
<td>3.25</td>
<td>2.08</td>
<td></td>
</tr>
<tr>
<td>NA- Peak physically there but not analysed</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

b) Calcium Montmorillonite and Carnegieite

<table>
<thead>
<tr>
<th>Carnegieite (11-220)</th>
<th>Intensity</th>
<th>100</th>
<th>95</th>
<th>85</th>
<th>50</th>
<th>50</th>
<th>45</th>
<th>30</th>
<th>25</th>
<th>25</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>d-spacing</td>
<td>4.17</td>
<td>2.56</td>
<td>4.18</td>
<td>2.9</td>
<td>2.54</td>
<td>2.55</td>
<td>2.26</td>
<td>3.76</td>
<td>3.3</td>
<td>2.08</td>
<td></td>
</tr>
<tr>
<td>standard-wet treated (100hrs)</td>
<td>Intensity</td>
<td>25</td>
<td>25</td>
<td>25</td>
<td>24</td>
<td>25</td>
<td>14</td>
<td>25</td>
<td>30</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>d-spacing</td>
<td>4.13</td>
<td>2.50</td>
<td>4.29</td>
<td>2.87</td>
<td>2.50</td>
<td>2.27</td>
<td>3.82</td>
<td>3.32</td>
<td>2.11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pre-treated calcium montmorillonite (standard-wet) and then exposed to inert-wet/HCl (100hrs)</td>
<td>Intensity</td>
<td>31</td>
<td>31</td>
<td>31</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>d-spacing</td>
<td>2.51</td>
<td>2.51</td>
<td>2.51</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table K.VI.1: Carnegieite Formation as the Reaction Product from Kaolinite and Calcium Montmorillonite.
APPENDIX L

SORPTION PROFILES

L.I Validation of Experimental Results: Similar Sorption Profiles under Same Exposure Conditions

Figure L.I.1: Reproduced Sorption Profiles under Same Conditions (Pan Pelletised Calcium Montmorillonite, LaPorte).
L.II Step Change in Profile Characteristic (Calcium Montmorillonite, pan pelletised, LaPorte) in the Case of Removed HCl

Figure L.II.1: Pre-treated Calcium Montmorillonite (standard-wet/HCl, LaPorte) Exposed to Standard-wet Conditions.
L.III Step Change in Profile Characteristic (Emathlite, extruded, RTI) Profile in the Case of Removed HCl

Figure L.III.1: Pre-treated Emathlite (standard-wet/HCl, RTI) Exposed to Standard-wet Conditions.
APPENDIX M

PELLET GRAIN MODEL

M.I Pellet Grain Model for a Single Pellet

The pellet-grain model is described in detail by Szekely and Evans (1970, 1971), Szekely and Probster (1975), Szekely et al (1976), and Sohn and Szekely (1972, 1973a, 1973b). Szekely and co-workers made several simplifying assumptions in developing their solution to this model of a gas-solid reaction. These must be assessed for the SPR system used in this work. The main factors are:

1. *The pellet is isothermal.* The pellet is supported on a fine wire sample holder (microbalance hangdown) in constant temperature environment controlled to +/-1°C. Therefore the individual pellet can be considered isothermal.

2. *The resistance due to external mass transfer is negligible.* This is considered valid for laboratory scale units, practical systems involving packed beds of solid particle may be fully or partially rate controlling. In alkali sorption studies a sufficiently high superficial velocity has been used (4cm/s) and therefore this assumption could be valid. The external gas film mass transfer coefficient, $k_{mf}$, was calculated to be 47.3cm/s for pellet diameters of 3mm ($T=850°C$, $V=50ml/min$, Pipe diameter=1.1cm, $ε=0.3$, tortuosity=4).

3. *The viscous flow contribution to mass transfer within the pellet is negligible.* The pressure drop within the single pellet suspended from the SPR should be negligible.

4. *The pseudo-steady state approximation is valid.* This implies that the rate at which the reaction interface moves within a grain/pellet is low in comparison to the rate of transport of the reactant gas to that interface.

5. *Diffusion of the gaseous reactants through the product layer of the individual grains is not rate-limiting.* This assumption may be valid if grains are used which are small in size (kaolin grades). However, if grains are used which limit the diffusion within the grain than this assumption may not valid. Chrysohoidou (1996) showed that the diffusion of the gaseous reactants and products through the product layer of calcium montmorillonite grains is of relevance. But the individual grains of calcium montmorillonite have got a different
chemical composition (silica/alumina ratio). This implies that a grain reacts may better than another. However, the main result remains a calcium montmorillonite grain of certain size limits the diffusion of the gaseous reactants and products through the product layer of the grain.

6. The solid structure is macroscopically uniform and unchanged by reaction. Glass formation has been observed for emathlite and calcium montmorillonite. As a result this assumption is not valid when the reaction progresses.

7. The diffusion within the pellet is either equimolar counterdiffusion or is at low concentration of the diffusing species. This assumption should be valid as long as the reaction conditions are not changed dramatically (change of the environment).

8. The reaction is first order with respect to the reactant gas and zero order with respect to the solid. This assumption can be investigated using different NaCl concentrations in the SPR.

Chrysohoidou (1996) concluded that the effect of diffusional resistance of the product layer around the individual grains has to be considered. This is shown below.

Within the framework of the above assumptions, the reversible sodium chloride reaction scheme:

\[ \text{NaCl}_\text{(g)} + \frac{1}{2}\text{H}_2\text{O}_\text{(g)} + b_{1,2}\text{rect.} \leftrightarrow \text{product}_\text{(s)} + \text{HCl}_\text{(g)} \]

\(b_{1,2} = \text{stoichiometric coefficient}\)

was combined with the conservation of gaseous reactants and products in the pores of the pellet (Szekely et al 1976)

\[ \frac{1}{R^2} D_p \frac{\partial}{\partial R} (R^2 \frac{\partial C_{\text{NaCl}_\text{p}}}{\partial R}) - r_{\text{NaCl}} = 0 \]

\[ \frac{1}{R^2} D_p \frac{\partial}{\partial R} (R^2 \frac{\partial C_{\text{HCl}_\text{p}}}{\partial R}) - r_{\text{HCl}} = 0 \]
where

\[ R = \text{spatial co-ordinate measured from the centre of the pellet [cm]} \]

\[ r_{i,NaCl} = \text{local rate of consumption of the gaseous reactant (NaCl) per unit volume of the pellet [mole/(cm}^3\text{s)} \]

\[ r_{i,HCl} = \text{local rate of generation of the gaseous product (HCl) per unit volume of the pellet [mole/(cm}^3\text{s)} \]

\[ C_{NaCl,p} \& C_{HCl,p} = \text{gas concentrations of NaCl and HCl in the pores of a pellet [mole/cm}^3\text{]} \]

\[ D_p = \text{intrapellet diffusivity; effective diffusivity in a porous pellet [cm}^2\text{s]} \]

The local, position-dependent rate of consumption of gaseous reactant in a finite volume of a pellet is given for first order kinetics

\[
r_{i,NaCl} = A_{acti}[K_s C_{uc,NaCl} C_{sol,r} C_{H_2O}^{1/2} - K_{s^{-}} C_{uc,HCl} C_{sol,p}]
\]

Spherical grains were assumed and

\[
r_{i,NaCl} = 3(1 - \varepsilon_p) \frac{r_p^2}{6} k_s \left( \frac{C_{uc,NaCl}}{K_s} - \frac{C_{uc,HCl}}{K_s} \right)
\]

where

\[ r_{i,NaCl} = \text{local rate of consumption of the gaseous reactant (NaCl) per unit volume of the pellet [mole/(cm}^3\text{s)} \]

\[ R = \text{spatial co-ordinate measured from the centre of the pellet [cm]} \]

\[ k_s = \text{reaction rate constant, based on unit area of reaction interface} = K_s C_{cell} C_{H_2O}^{1/2} [\text{cm/s}] \]

\[ K_s = \text{intrinsic forward reaction rate constant} = [\text{cm/s}(\text{cm}^3/\text{mole})^{3/2}] \]

\[ K_s^- = \text{intrinsic backward reaction rate constant} = [\text{cm/s}(\text{cm}^3/\text{mole})] \]

\[ K_e^0 = \text{equilibrium constant based on concentrations} = (K_s C_{sol,r})/(K_s C_{sol,p}) [(\text{mole/cm}^3)^{1/2}] \]

\[ C_{sol,r} = \text{concentration of the solid reactant [mole/cm}^3\text{]} \]

\[ C_{sol,p} = \text{concentration of the solid product [mole/cm}^3\text{]} \]

\[ K_s^0 = \text{equilibrium group} = K_s [H_2O]^{1/2} [-] \]

\[ C_{uc,NaCl} = \text{reactant gas concentration at the surface of the unreacted core in a grain [mole/cm}^3\text{]} \]
C_{HCl} = \text{product gas concentration at the surface of the unreacted core in a grain [mole/cm}^3]\]
C_{H_2O} = \text{concentration of water vapour at the surface of the unreacted core in a grain [mole/cm}^3]\]
A_{inf} = \text{reaction interfacial area per unit volume of grains} = 3(1-\varepsilon_p)\frac{r_c^2}{r_g^3} [cm^2/cm}^3]\]
\varepsilon_p = \text{intrapellet porosity [dimensionless]}\]
r_c = \text{radius of the unreacted core in a grain [cm]}\]
r_g = \text{grain radius}\]

The mathematical representation led to a set of simultaneous differential equations which had to be solved numerically. In complicated systems it is quite often desirable to work with dimensionless numbers because such treatment provides both an overview of the interaction of the various parameters and a convenient framework for the interpretation of the dimensionless values.

Consequently, Szekely and Evans (1971) and Szekely and Probster (1975) in order to recast the pellet grain model in a dimensionless form, defined initially a dimensionless concentration driving force, \( \Psi \), a local extent of reaction for the solid sorbent, \( \xi \), and a position in the pellet, \( \eta \), as follows when spherical geometry is assumed:

\[
\Psi = \frac{C_{NaCl,p} - C_{HCl,p}}{K_a}
\]
\[
\xi = \frac{A_g r_c}{(3 \varepsilon_p V_g)}
\]
\[
\eta = \frac{A_p R}{3 V_p}
\]

\( C_{NaCl,o} \) and \( C_{HCl,o} \) = concentration of the gaseous reactant and product in the bed voidage [mol/cm}^3]\]
\( C_{NaCl,p} \) and \( C_{HCl,p} \) = concentration of NaCl and HCl in the pores of a pellet [mole/cm}^3]\]
\( A_g \) and \( A_p \) = surface area of a grain and a pellet respectively [cm}^2]\]
\( V_g \) and \( V_p \) = volume of a grain and pellet respectively [cm}^3]\]

In this case the rate of regression of the reaction interface within a grain may be written, for a first-order reaction, as follows:

M.IV
In this case the rate of regression of the reaction interface within a grain may be written, for a first-order reaction, as follows:

\[
\frac{\partial \xi}{\partial t^*} = -\psi \left[1 - \bar{\sigma}_g^2 q'(\xi)\right]^{-1}
\]

where:
- \(q'(\xi)\) = derivative with respect to \(\xi\) of \(q(\xi)\)
- \(q(\xi)\) = function that describes the progress of reaction of a grain under product layer diffusion influence
- \(\bar{\sigma}_g\) = group, which incorporates chemical reaction and diffusion through the product layer
- \(t^*\) = time [-]
- \(t\) = time [s]
- \(b_{1,2}\) = stoichiometric coefficients [-]
- \(s_0\) = sorbent density [mole/cm\(^3\)]

and where \(\bar{\sigma}_g^2\) has been defined by

\[
t^* = \frac{b_{1,2} k_s}{\delta_s} \left(\frac{A_g}{F_g V_g}\left(c_{NSI} - \frac{C_{HCl,0}}{K_o}\right)\right) t
\]

and \(q'_{p0}(\xi)\) is the derivative with respect to \(\xi\) of \(q_{p0}(\xi)\) which is defined as

\[
q_{p0} = 1 - 3\xi^2 + 2\xi^3
\]

for spherical grains (\(F_s\) & \(F_p\)=shape factors for the pellet and the grain). The function \(q_{p0}\) has the same significance as that deduced for the intrapellet diffusion control (\(p_{p0}\)), see below, that is, it describes the progress of the reaction of a grain under diffusional influence. However, when intragranular diffusion is taken into account the conservation of the gaseous reactant within the pellet gives
\[ \nabla^2 \psi - 2 F_p F_g \hat{\sigma}^2 \left( \frac{g_{r_g}^{k-1}}{[1 - \hat{\sigma}^2 q_{r} (\xi)]} \right) \psi = 0 \]

\( \nabla = \text{nabla operator} \)

\( \hat{\sigma} = \text{dimensionsless group, which incorporates kinetic and structural properties} \)

To avoid the computational burden of solving the differential equations numerically, Chrysohoidou (1996) applied the approximate solution developed by Evans and Ranade (1980) which was based on the idea of the law of additive reaction times. This law is based on the idea that the time required to attain a certain conversion is additive for all the resistance's which act in series. To solve the approximate solution, Chrysohoidou (1996) used the following term with a Newton-Raphson iterative procedure to calculate the pellet fractional conversion (\( X_p \) is the solution form pellet-grain model by Newton-Raphson method and used to find the overall solids sodium content).

\[
t^* = g_{r_g} (X_g) + \hat{\sigma}^2 p_{r_g} (X_g) + \hat{\sigma}^2 p_{r_{pp}} (X_g) + \hat{\sigma}^2 p_{r_{pp}} (2X_g / N_{sh *}) + (0.21X_g - 0.31X_g^2) \cdot (1 + \hat{\sigma}^2) \cdot \exp\{-0.9(\ln(\hat{\sigma} / 1.08))^2\}
\]

where

\[
g_{r_g} (X_g) = \left( 1 - (1 - X_g) \right)^{1/F_g}
\]

\[
p_{r_g} (X_g) = 1 - 3(1 - X_g)^{2/3} + 2(1 - X_g) \; \text{; spherical pellets}
\]

\[
\hat{\sigma}^2 = \frac{k_s r_g}{6D_g} \left( 1 + \frac{1}{K_e} \right)
\]

\[
\hat{\sigma}^2 = \frac{\sigma^2}{2F_p F_g} = \frac{r_g^2 (1 - \varepsilon_g) k_s}{6D_p r_g} \left( 1 + \frac{1}{K_e} \right) \; \text{; spherical grains},
\]

\[
\sigma = \frac{V_p}{A_p} \left[ \frac{(1 - \varepsilon_p) k_p}{2D_p} \left( \frac{A_g}{F_g V_g} \right) (1 - \frac{1}{K_e}) \right]^{1/2}
\]

\[
t^* = \frac{bk_{r_g}}{\delta_s} \left( \frac{A_g}{F_g V_g} \right) (c_{NaCl} - \frac{C_{HCl,0}}{K_e}) t
\]

\[
N_{sh *} = \frac{k_{r_p}}{d_p}
\]

M.VI
dp = pellet diameter [mm, cm]

\( D_g \) = diffusivity through the product layer in a grain (intragrain diffusivity) \([\text{cm}^2/\text{s}]\)

\( g_g(X_g) \) = conversion function deduced for chemical reaction control

\( k \) = Boltzmann constant \([\text{J/K}]\) (1.38E-23J/K)

\( k_s \) = reaction rate constant group based on unit area of reaction interface \([\text{cm/s}]\)

\( k_g \) = gas film mass transfer coefficient \([\text{cm/s}]\)

\( N_{sh}^* \) = modified Sherwood number [-]

\( r_g \) = grain radius \([\text{cm}]\)

\( r_p \) = pellet radius \([\text{cm}]\)

\( p_{pp}(X_g) \) = conversion function deduced for intrapellet diffusion control

\( X_g \) is the solution form pellet-grain model by Newton-Raphson method and used to find the overall solids sodium content

\( \varepsilon_p \) = intrapellet porosity [-]

\( \hat{\sigma} \) = dimensionsless group, which incorporates kinetic and structural properties

In general \( \hat{\sigma}^2 \) represent a dimensionsless number, which incorporates chemical reaction and diffusion through the product layer whereas \( \hat{\sigma} \) incorporates kinetic and structural properties. When the \( \hat{\sigma}^2 \) value is bigger than 10, the reaction of an individual grain is expected to be controlled by the intragrain diffusion. As \( \hat{\sigma} \) approaches zero, the process is reaction controlled and as it approaches infinity, the process is diffusion controlled Szekely et al (1976).

The terms on the right are the asymptotic expressions which can be related to the control of the reaction:

**chemical reaction controls:**

\[
t^* = g_{g_g}(X_g) = 1 - (1 - X_g)
\]
intragrain diffusion controls:

\[ t^* = \hat{\sigma} g^2 \tau_{p_g}(X_g) = \hat{\sigma} g^2 [1 - 3(1 - X_g)^{2/3} + 2(1 - X_g)] \]

intrapellet diffusion controls:

\[ t^* = \hat{\sigma}^2 \tau_{p_g}(X_g) = \hat{\sigma}^2 [1 - 3(1 - X_g)^{2/3} + 2(1 - X_g)] \]

external mass transport controls:

\[ t^* = \hat{\sigma}^2 \tau_{p_g}(2X_g / N_g^* ) \]

\( g_{p_g}(X_g), p_{p_g}(X_g), p_{p_g}(X_g) = \) conversion functions deduced for varying controls

The approximations have been improved by addition of these further terms

\[ (0.21X_0 - 0.31X_0^2) \cdot (1 + \hat{\sigma}^2) \cdot \exp\{-0.9(ln(\hat{\sigma} / 1.08))^2\} \]

These solutions are often referred as “exact solutions”.

Parameter

Parameter used in the program are molecular gas diffusivity of sodium chloride, effective diffusivity in a porous pellet, gas film mass transfer coefficient, Reynold number, Schmidt number, and derived from literature.

The molecular gas diffusivity of sodium chloride in nitrogen was calculated in the following way (Reid et al, 1977):

\[ D_{NaCl-N_2} = 1.858 \times 10^{-3} T^{3/2} \frac{\left[ (M_{NaCl} + M_{N_2}) / M_{NaCl} M_{N_2} \right]^{1/2}}{p \sigma_{NaCl-N_2}^2 \Omega_D} \]
where \( D_{NaCl-N2} \) = diffusion coefficient of the binary gas system sodium chloride and nitrogen, [cm\(^2\)/s]

\[ T = \text{temperature, [K]} \]

\[ t_b = \text{boiling point [K]} \]

\[ M_{NaCl} = \text{molecular weight of sodium chloride [58.44 g/mole]} \]

\[ M_{N2} = \text{molecular weight of nitrogen [18 g/mole]} \]

\[ P = \text{pressure, [atm]} \]

\[ \sigma_{NaCl-N2} = (\sigma_{NaCl}+\sigma_{N2})/2 \text{ [K/mole], collision diameter (distance between molecules when the potential energy of interaction is zero), where } \sigma_i = 1.18 V_b^{1/3} \]

\[ \sigma_i = \text{characteristic length, [Angstrom]} \]

\[ V_b = \text{molar volume [V_{NaCl}=27.098 cm^3/g-mole, V_{N2}=27.098 cm^3/g-mole]} \]

\[ \Omega_D = \text{diffusion collision integral [-]} \]

\[ f(T^*), T^* = kT/\varepsilon_{NaCl-N2} \]

\[ \varepsilon_{NaCl-N2} = (\varepsilon_{NaCl}\varepsilon_{N2})^{1/2}, \varepsilon_i = 1.15 t_b \cdot k \]

\[ \varepsilon_i = \text{characteristic energy parameter of NaCl and N2 [J]} \]

\[ T^* = \text{Temperature [-]} \]

\[ k = \text{Boltzmann constant [J/K] (1.38E-23 J/K)} \]

As molecular diffusivities were calculated: 900°C (0.87 cm\(^2\)/s), 850°C (0.8 cm\(^2\)/s), 800°C (0.71 cm\(^2\)/s), 750°C (0.64 cm\(^2\)/s), and 650°C (0.5 cm\(^2\)/s).

The effective diffusivity in a porous pellet, \( D_p \), has been calculated according to Ramachandran and Smith (1977). The effective diffusivity for a monodisperse unsintered porous pellet containing only macropores is given by

\[ D_p = \frac{D \varepsilon}{\tau} = D \cdot \varepsilon^2 \]

\( D = \text{composite diffusivity accounting for Knudsen and bulk diffusion [cm}^2\text{/s]} \)

\( D_p = \text{Intrapellet diffusivity; effective diffusivity in a porous pellet [cm}^2\text{/s]} \)

\( \tau = \text{tortuosity factor [-]} \)

\( \varepsilon = \text{porosity [-]} \)

M.IX
since

\[ \tau = \frac{1}{\varepsilon} \]

and D is a composite diffusivity accounting for Knudsen and bulk diffusion. Knudsen diffusion can be considered negligible due to relatively large pores (Mclaughlin, 1990). The use of non-porous pellets may alter this neglition. As a result, the intrapellet effective diffusivity of sodium chloride at 650°C was calculated as 0.02 cm²/s. A porosity of 0.2 was assumed. Chrysohoidou (1990) calculated an effective diffusivity of 0.25 cm²/s.

The gas film mass transfer coefficient, \( k_g \), was calculated according the equation

\[ k_g = \frac{Sh \cdot D_m}{L} = \frac{Sh \cdot D_m}{2 \cdot r_p} \]

where

- \( L \) = characteristic diameter (* pipe diameter) [m]
- \( r_p \) = pellet radius [m]
- \( D_m \) = molecular diffusivity [cm²/s]
- \( Sh \) = Sherwood number, \( Sh = f(Sc, Re) \)
- \( Sc \) = Schmidt number [-]
- \( Re \) = Reynolds number [-]

Ranz and Mashall (1952) used the following mass transfer equation for a single pellet:

\[ Sh = 2 + 0.6 \cdot Sc^{1/3} \cdot Re^{1/2} \]

As Reynolds (Re) and Schmidt (Sc) numbers were defined

\[ Re = \frac{d_p u}{\mu} = \frac{2r_p u \delta}{\nu}; \quad Sc = \frac{\mu}{D_m} = \frac{\nu}{\delta \cdot D_m} \]

M.X
where \( d_p = \) pellet diameter [cm]  
\( r_p = \) pellet radius [cm]  
\( D_m = \) molecular diffusivity [cm\(^2\)/s]  
\( u = \) superficial velocity = \( V_F/A_r \) [cm/s]  
\( V_F = \) volumetric flowrate [m\(^3\)/s]  
\( A_r = \) cross-sectional area of the pipe [cm\(^2\)]  
\( \mu = \) kinematic viscosity [cm\(^2\)/s]  
\( \nu = \) dynamic viscosity [g/(cm\(^2\)/s)]  
\( \delta = \) bulk gas density at the temperature and pressure of interest [g/cm\(^3\)]

is. Wakao and Funazkri (1978) applied a mass transfer correlation on a fixed bed.

\[
Sh = 2 + 1.1 \cdot Sc^{1/3} \cdot Re^{1/2}.
\]

Chrysohoilidou (1996) calculated two gas film mass transfer coefficients for the temperature 650°C. As gas film mass transfer coefficient for the pellet diameter 0.425-0.5 mm was found 58.1 cm/s and as that of 0.5-0.6 mm 50.26 cm/s. Calculations by the author have given a ten times higher value. This was because within the intrapellet diffusivity term porosity was considered.

This gas film mass transfer coefficient has been compared with those calculated for the single pellet reactor for a temperature of 850°C. As gas film mass transfer coefficient for the pellet diameter 3 mm was calculated 47.3 cm/s.
McLaughlin developed an alkali sorption model for calcium montmorillonite, the Two Reaction Model. The model is based on alkali capture as a combination of two separate, simultaneously, reversible first order reactions. The rate of one reaction is assumed to be sensitive to the HCl concentration in the gas phase (Reaction 1), whereas the rate of the other is virtually independent of it (Reaction 2), the sum of the sodium uptake due to each reaction leads to the overall uptake. This model in conjunction with Sohn and Szekely's grain model permits the convective mass balances to be resolved by considering the bulk fluid hydrodynamics of the fixed bed.

McLaughlin defined values for the two reaction model parameters; reaction constant, $k$, effective diffusivity, $D_e$ and equilibrium group, $K_e$ based upon fixed bed experimental result in the 827-927°C range. Chrysohoidou adjusted McLaughlin’s recovered parameters based on values obtained at 0-160ppmv HCl, 40ppmv NaCl and 5% by volume of vapour at 923°C with run duration's of 73 and 98 hours. The predicted values generated using the model concur with measured fixed bed profiles, however, the principle disadvantage of the model is that the sodium uptake along a layer of the fixed bed is affected by the previous layer. In this study it was shown that the former Two Reaction model faces problems, particularly accurate prediction of the reaction constant. Single pellet reactor indicated differences in the mechanism. In extracting parameters allowance must be made for the occurrence of initial sorption (e.g. replacement mechanism) before/with aluminosilicate reaction. Consequently parameters for the reaction must be extracted after adjusting for 'chemisorption'/reaction which is achieved by discounting the initial exposure time. Bearing in mind that the Two Reaction model is sensitive to the parameter reaction constant and insensitive to that of effective diffusivity and equilibrium group, only the reaction constant under aluminosilicate reaction condition was determined (Appendix: M.XIII).

It was found that the newly generated parameter was 0.03 cm/s for the aluminosilicate reaction. McLaughlin's model gives a reaction constant of 0.0187 cm/s which is similar to SPR modelling, 0.03 cm/s, indicating a higher level in confidence under non-acid condition.
M.XIII Pellet Grain Model Programme for a Single Pellet with One Standard Aluminosilicate Reaction

M.XIII PROGRAMME

Pellet grain model: for a single pellet and aluminosilicate reaction

C pellet grain model for a single pellet and aluminosilicate reaction taking place
C program c:\ftn\53.for
C ks1=0.2cm/s, ke1=5000, Dg1=0.001cm/s
C The numerical evaluation is estimated from the Newton-Raphson solution, whereas the analytical value is estimated from the Szekely approximation
C
C program test53
C state of agreement - time loop, newton/raphson loop
C
..... double precision xlast1
real delti,time,ti
real*8 MNA,Mna1,F1,FTOT, XF, XF1
integer tint,j,jmax
C
C time progression parameter - time loop
C
..... ti=2160000 /* real time [s]
tint=6 /* divisor of ti/loop steps
time=0 /* initial time
C
C time step
C
..... delti=ti/tint /* time step
C
C iteration progression parameter - newton/raphson loop
C
..... jmax=3 /* maximum number of iterations
C
C output data
C - da53_8.out (time parameter/data)
C - da53_9.out (iteration parameter/data)
C - da53_10.out (raphson,grain/pellet data)
C - da53_11.out (grain, numerical evaluation of dxg1)
C
..... open (unit=8, file='a:\da53_8.out')
open (unit=9,file='a:\da53_9.out')  /* time loop
open (unit=10,file='a:\da53_10.out')  /* raphson1
open (unit=11,file='a:\da53_11.out')  /* grain1

c Pellet conversion related to experimental

c measured weight gain (g Na/g initial solid)

MNA=0.0D0  /* total pellet Na uptake [g Na/g solid]
MNA1=0.0D0  /* total pellet Na uptake grain 1 [g Na/g solid]
F1=9.9D0/100.0D0 /* Na uptake due to reaction 1

MNA=(F1*xlast1)
MNA1=(F1*xlast1)

print *, 'total pellet sodium uptake [g Na/g solid] = ', MNA
Xf=MNA/flot
Xfl=MNA1/flot

print *, 'overall pellet conversion = ', Xf
print *, 'pellet conversion grain 1 = ', Xfl

write (15, ('xf=', E13.6, ' ', 'xfl=', E13.6)) Xf, Xfl

13 continue

end

c subroutine raphson1

subroutine raphson1 (jjmax,time,delti,xlast1)
double precision xguess,fim,dfim,xlast1

c initial system parameter - xlast1

c
xlast1=0.0d0  /* initial value for conversation
xguess=xlast1  /* start value of solution of time step

do 100 j=1,jmax  /* start value of solution of time step

time=time

call grain1 (time,xguess,fun,dfun,dx)

condition for the pellet that has been saturated the end

of experiment time

c
If (xguess.ge.1.0d0) then
xguess=1.0
print *, 'xguess is set to 1', xguess
endif

c newton-raphson method using derivate
c -Numerical Recipes (The Art of Scientific Computing)
c -Press, William H.; Cambridge University Press, 1989
c -S. 254, Chapter 9.4
c x_i+1 = x_i - f(x_i)/f'(x_i)
xguess=xguess-fun/dfun
dx=fun/dfun
xguess=xguess-dx

c output loop parameter, xguess and dx
write (9,'("j=",i2," jmax-*,i2," xguess-1 dl3.6,",","dx-'",dl3.6)' ) jjmax,xguess,dx
end of loop
100 continue
dxg1=(xguess-xlast1)/delti /* numerical evaluation of dxg1
xlast1=xguess /* end value of solution of time step
writing dxg and xlast data in a file
write (10,'("dxg1=",d13.6," ","xlast1=",d13.6," "') dxg1,xlast1
end

subroutine grainl
*******************************************************************************
subroutine grainl (time,xguess,fun,dfun,dx)
*******************************************************************************
double precision sig1,sig,sherw,cin2,tstar,tstar1,tstar
  ,eqn1,eqn2,eqn3,d_eqn1,d_eqn2,d_eqn3,dxg_dt1
real*8 rp,etap,ks1,dgas,rg,ke1,de1,kg,cnacl,cna,n_cna
integer bl
xg=xguess /* xg is a solution of xguess at time t and j

condition for the pellet that has been saturated the end
of experiment time
If (xguess.ge.1.0d0) then
  xguess=1.0
  print *, 'xguess of grainl is set to 1', xguess
  goto 10
endif

M.XV
constants

\[ \rho = 4.12 \times 10^{-3} \text{ moles sorbent/cm}^3 \text{ for Fullers Earth, Kaolin} \]
\[ r_p = 0.0275 \text{ cm} \]
\[ \epsilon_p = 0.2 \]
\[ d_{gas} = 0.25 \times 10^{-3} \text{ cm}^2/\text{s} \]
\[ r_g = 2 \times 10^{-4} \text{ cm} \]
\[ k_g = 5.26 \times 10^{-3} \text{ cm}^2/\text{s} \]

parameter to optimize

\[ k_e = 5 \times 10^3 \text{ cm}^2/\text{s} \]
\[ k_s = 0.2 \]
\[ D_e = 1 \times 10^{-3} \text{ cm}^2/\text{s} \]
\[ b = 1 \]

concentration terms

- NaCl here 5.6 ppmv
- HCl here 0.001 ppmv

\[ c_{NaCl} = 5.6 \times 10^3 \times 1.303 \times 10^{-11} \text{ moles/cm}^3 \]
\[ c_{Na} = c_{NaCl} \]
\[ n_{Na} = 1 \times 10^{-3} \]

\[ c_{HCl} = 1.0 \times 10^{-3} \times 1.303 \times 10^{-11} \text{ moles/cm}^3 \]
\[ c_{HCl} = c_{HCl} \]
\[ n_{HCl} = 1 \times 10^{-3} \]

intrinsic reaction rate, 1st order

\[ c_{NaCl} = c_{Na} - c_{HCl}/k_e \]
\[ c_{Na} = c_{Na} - c_{HCl}/k_e \]
\[ c_{Na} = n_{Na} 	imes c_{NaCl} - n_{HCl} 	imes c_{HCl}/k_e \]

sigma, sigma for szekely approximation

\[ \sigma_1 = r_p^{2.5} \frac{\epsilon_p}{6d_{gas}r_g} \frac{1}{k_e} \]
\[ \sigma = k_s \frac{r_g}{6.0D0 \times D_e} \frac{1}{k_e} \]
\[ \sigma = k_g \frac{r_p}{d_{gas}} \]

time calculation based on the rate of movement of the reaction interface within a grain

\[ \text{condition if } t_{star} = \text{time for complete conversion is a criterion whether } x_g \text{ should stop proceeding to bigger} \]
c values than 1, if tstar-tstar less than 0.005 then
c xguess = 1 go further to 10
c ........................................
tstar1=1.0d0+sig1*(1.0d0+2.0d0/sherw)+(0.21d0-0.31d0)*
1  (1.0d0+sig1)*exp(-0.9d0*(((1.0d0/2.0d0))/
2  1.08d0)**2)
tstar=b1*ksl*cin2*time/(rho*rg)
if ((tstar1-tstar).lt.0.005d0) then
   xguess=1.0
   print *, 'xguess=',xguess
   goto 10
endif

c eqnl=g(xg) ; equation 4.22, term of chemical reaction control
c eqn2=p(xg) ; equation 4.24, term intragrain diffusion control
c eqn3 ; equation 4.26, expression of additive terms

c ....................................................
eqnl=1.0D0-(1.0D0-xg)**(1.0d0/3.0d0)
eqn2=1.0d0-3.0d0*(1.0d0-xg)**(2.0d0/3.0d0)+2.0d0*(1.0d0-xg)
eqn3=(0.21d0*sig1)*exp(-0.9d0*(log((sig1**(1.0d0/2.0d0))/1.08d0)**2))
1  *exp(-0.9d0*(((1.0d0/2.0d0))/1.08d0)**2)

c fun = Value of function at xguess

c ....................................................
fun=eqnl+eqn2*sig11*(eqn2+2.0d0*xg/sherw)+eqn3-tstar

c Calculation of derivate of function xg
c d_eqnl=g(xg) ; eqn 4.22, derivate, chemical reac. cont.
c d_eqn2=p(xg) ; eqn 4.24, derivate intragrain diffiision con.
c d_eqn3 ; eqn 4.26, derivate expression of additive terms

c ....................................................
d_eqnl=(1.0d0-xg)**(-2.0d0/3.0d0)/3.0d0
d_eqn2=2.0D0*(1-xg)**(-1.0d0/3.0d0)-2.0d0
d_eqn3=(0.21d0-0.62d0*xg)*(1.0d0+sig1)
1  *exp(-0.9d0*(((1.0d0/2.0d0))/1.08d0)**2)

c D_fun is value of derivate at xguess

c ....................................................
dfun=d_eqnl+sig1*(d_eqn2+2.0d0*xg/sherw)+sig*d_eqn2+d_eqn3

c calculation of quotient fun/dfun (Newton raphson)
c ....................................................
dx=fun/dfun

c analytical calculation of dxg/dt
c ....................................................
dxg_dt1=((b1*ksl*cin2)/(rho*rg))/dfun

data output
c
write (11,("cin2=",d13.6,"","sig1=",
1 "d13.6","","sig=",d13.6,"","sherw=",d13.6,";
2 "tstar1=",d13.6,"","tstar=",d13.6,"","xguess=";
3 d13.6,"","eqn1=",d13.6,"","eqn2=",d13.6,";
4 "eqn3=",d13.6,"","fun=",d13.6,"","d_eqn1=",d13.6,
5 "","d_eqn2=",d13.6,"","d_eqn3=",d13.6,";
6 "dfun=",d13.6,"","dx=",d13.6,"","dxg_dt1=",d13.6,
7 "") cin2,sig1,sig,sherw,tstar1,tstar,xguess,eqn1,eqn2,
8 eqn3,fun,d_eqn1,d_eqn2,d_eqn3,dfun,dx,dxg_dt1
10 return
end
c
APPENDIX N

TERNARY PHASE DIAGRAM

N.1 Predictions with Phase Equilibrium Diagrams

Figure N.1.1: Na$_2$O-Al$_2$O$_3$-SiO$_2$ Phase Diagram (Levin et al, 1964).