CHLORIDE REMOVAL FROM A BIOMASS GASIFICATION PRODUCT STREAM BY A FIXED BED OF SELF-PREPARED SORBENT MATERIAL

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ABSTRACT

Biomass gasification is a carbon neutral technology for producing fuel gas or synthesis gas (syngas) from biomass materials. Contaminants must be removed from the product gas before it is delivered to downstream devices such as gas turbines, solid oxide fuel cells (SOFC) or catalysts for liquid chemical/fuel synthesis. Contaminants of concern, present in the product gas, include tar components, alkali metals, sulfur, trace elements and chlorine. Chlorine-containing molecules present in biomass fuels volatize under gasification conditions and cause serious corrosion and deposition damage in downstream process components. This hinders the feasibility of industrializing biomass gasification as a renewable energy production technology. An extensive literature review identified gas treatment using a solid sorbent material loaded in a fixed-bed reactor as a practical means of chloride removal from a gasification system at elevated temperature. Coal ash, a solid byproduct of coal power plants, has been found to perform well as a chloride sorbent due to its structure and chemical composition. No previous experimental studies have employed coal ash as a sorbent material in a biomass gasification process.

Coal ash was obtained from the Hawaiian Commercial & Sugar Company (HC&S) coal/biomass-fired boiler and from the AES Hawaii Power Plant and was used as the parent material in a variety of sorbent preparations. Preparation techniques, including various binder materials and hydration processes, were explored to manufacture the raw material into durable pellets or granules with a high affinity for chloride. The prepared materials were tested in a lab-scale experiment to identify sorbent preparations that provided the highest chloride adsorption capacity. A commercially available chloride

sorbent, BASF CL-760, was also tested to provide a basis for comparison. The two sorbents prepared by hydrating AES fly ash and bed material (limestone) provided the highest chloride adsorption capacity of the manufactured sorbents when subjected to a 400° C gas stream containing ~650 ppmw Cl⁻ and an average GHSV of about 1500 hr⁻¹. The AES fly ash and bed material sorbents provided an average adsorption capacity of 2.1% and 4.0% (g Cl⁻ per g used sorbent), respectively. The CL-760 was found to have an average chloride adsorption capacity of 2.4% when subjected to the same conditions.

The hydrated AES fly ash and bed material sorbents were subsequently tested in a benchscale fluidized-bed biomass gasifier. Each sorbent was loaded into a fix-bed operating at \sim 400°C. The gas flow through the bed was varied over the duration of the tests so that the chloride adsorption performance of the sorbents at increasing gas hourly space velocities (GHSV) could be evaluated. The hydrated AES fly ash sorbent was tested at GHSVs ranging from 8,909 hr⁻¹ to 52,111 hr⁻¹. The hydrated AES bed material sorbent was tested at GHSVs ranging from 3,237 hr⁻¹ to 13,266 hr⁻¹. Both sorbents were found to be most effective at removing chloride at the lowest GHSVs. At a GHSV of 8,909 hr⁻¹, the hydrated AES fly ash sorbent reduced the chloride concentration in the dry product gas from ~300 ppmv to ~50 ppmv, an 83% reduction. At a GHSV of 3,237 hr⁻¹, the hydrated AES bed material sorbent reduced the dry product gas chloride concentration from ~300 ppmv to ~10 ppmv, a reduction of about 97%. Pre- and post- sample analysis data were used to perform mass balance calculations that showed that between 85.8% and 99.2% of the chlorine input to the system could be accounted for in the test results. The analyses confirmed that the self-prepared sorbent materials are effective at the removal of chloride from a biomass gasification product gas stream.

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1.0 INTRODUCTION

Biomass, material of biogenic origin, provides an attractive source of domestically produced renewable energy that offers benefits for communities including decreased dependence on imported energy, increased domestic economic activity, and reduction of green-house gas emissions. Biomass offers a promising source of locally produced energy for Hawaii, the most oil dependent state, where 77% of the primary energy consumed is from imported fossil fuels (Abbas et al., 2009). Downturns in Hawaii's sugarcane and pineapple industries have already left acres of prime agricultural lands fallow and the future of large parcels of currently cultivated land is uncertain (Eagar, 2010; Loomis, 2010). Development of biomass energy ventures could serve to return lands to production and to develop other agriculturally suitable areas.

Biomass fuels include wood species such as eucalyptus, agricultural by-products such as sugarcane bagasse, and fast growing herbaceous crops such as switchgrass or banagrass. These fuels are renewable and potentially CO_2 neutral, depending on production processes. The fuel can be burned directly in a combustor to produce electricity or heat or it can be converted via gasification or pyrolysis to intermediate products that can be upgraded into chemical products such as biofuels. Biomass gasification is the partial oxidation of biomass using oxygen and/or steam at high temperatures (>750°C) with the general goal of maximizing the chemical enthalpy of the resulting gas. The substoichiometric oxidation of the biomass results in a combustible gas mixture called product gas that consists mainly of carbon monoxide (CO), hydrogen (H₂), carbon dioxide (CO₂) and methane (CH₄). Other constituents present in the product gas are

generally considered as contaminants. These contaminates include particulate matter, condensable hydrocarbons (tar) and other gas species containing sulfur, chlorine, alkali metals, nitrogen and other trace elements. Varying degrees of product gas cleaning are required to produce a suitable fuel for process heat or internal combustion engines. Additional contaminant removal and purification can make product gas a source of hydrogen or synthesis gas (H₂ and CO) for the production of fuels such as ethanol or diesel via the Fischer-Tropsch process.

The present study is concerned with the concentration of chlorine containing molecules in product gas. Chlorine is a naturally occurring inorganic constituent of biomass that can cause performance problems in thermochemical energy conversion facilities, such as biomass gasification units. Chlorine can react with alkali metals resulting in the formation of alkali chlorides in the product gas. Operational problems are caused by high concentrations of KCl and NaCl, which cause deposit formations, and hydrochloric acid (HCl), which is corrosive. These are serious issues for the industrialization of gasification units. Removing chloride from the gas stream can decrease maintenance costs and increase the viability of the energy conversion facility (Turn et al., 1997; Broström et al., 2007).

The purpose of this research is to identify an effective material for the adsorption of chloride from the biomass gasifier product stream at elevated temperature. Adsorption is the process of accumulating atoms or molecules on the surface of an adsorbent material to create a film of adsorbate (the molecules or atoms being accumulated). The process

differs from absorption, which is the diffusion of a substance into the volume of an absorbent material. The term sorption encompasses both processes, while desorption is the reverse process.

The effectiveness of the sorbent at elevated temperature is an important requirement in the overall goal of maximizing fuel enthalpy in the product gas stream. Tar and CH_4 are converted to CO and H_2 in the gas conditioning process over nickel or other precious metal catalysts at ~800°C and removing Cl⁻ from the gas phase prior to this step helps extend catalyst life. Tar condensation temperatures are typically 250 to 300°C, so removing Cl⁻ species at temperatures higher than this range is desirable.

An extensive literature review identified high temperature gas treatment by means of solid sorbent materials in fixed-bed reactor as a practical means of chloride removal from a gasification system. Adsorbents materials employed in fixed-bed reactors usually take the form of spherical pellets, rods, moldings, or monoliths with diameters between 0.5 and 10 mm. The material must have high thermal stability and abrasion resistance to maintain its structure in extreme industrial processes. In addition, the material should have small pore diameters and hence a higher exposed surface area to facilitate adsorption. The materials are designed to adsorb specific target molecules and hence have distinct pore structures to enable the fast transport of these species (Anon., 2011a).

Several studies have explored the ability of various materials to adsorb chloride from a stream of hot gas. The literature indicates that coal ash, a solid byproduct of coal power plants, is effective at removing HCl from high temperature gas streams (Hirabayashi et al., 1999). The literature also suggests that modification of the ash through hydration

techniques can improve its capacity to adsorb Cl⁻ (Hirabayashi et al., 2000; Hirabayashi et al., 2002).

A fixed bed of a coal ash based sorbent material may provide an effective means for removing chlorine from the biomass gasification system considering that the thermochemical equilibrium calculations (Section 0) indicate that HCl is the chlorine-containing species of greatest concentration in the product gas. Coal ash may also provide an effective means of removing other chlorine-containing species from the product gas such as KCl and NaCl. For coal ash to provide a practical means of removing chloride from an industrial biomass gasification system, the material must be processed into a sorbent material. If coal ash can be made into an effective chloride sorbent, the reuse of coal ash from local sources could provide environmental and economic benefits should a biomass gasification industry develop in Hawaii. No previous experimental studies have employed coal ash as a sorbent material in a biomass gasification process.

2.0 OBJECTIVES AND SCOPE

There is a lack of available information regarding the removal of chlorine-containing species from a biomass gasification product gas stream using solid sorbent materials. To obtain additional information, this study was undertaken with the following objectives:

- Determine the nature of the chlorine containing molecules present in the gasifier product gas;
- Identify and obtain parent materials for the formation of solid sorbents likely to provide chloride adsorption from the gasifier product gas stream;
- Test prepared sorbent materials in a lab-scale experimental apparatus that simulates the conditions of a fixed sorbent bed located downstream from a biomass gasifier;
- Identify the top performing materials and evaluate their performance as chloride sorbents in a bench-scale gasification unit.

To meet these objectives, the scope of this research includes the following:

- Conduct an extensive literature review related to chloride removal from biomass and other combustion systems;
- Calculate thermochemical equilibrium to determine the chemical composition of gasification product streams;
- Design and fabricate a lab-scale experimental apparatus to test sorbent materials in a simulated gasifier product gas stream;
- Compare the performance of commercially available and laboratory developed chloride sorbents under simulated and actual gasifier conditions.

3.0 BACKGROUND

The published literature was reviewed to gain a current understanding on chloride gas removal from hot gas streams. This section presents an overview of this background information as it pertains to the objectives of this study.

3.1 Methods for the Removal of Chloride from a Biomass Gasification System

There are numerous methods for the removal of chloride from a biomass energy production process. Chloride can be removed by pre-treatment methods before fuel conversion or by post-treatment methods downstream of the conversion process. The following sections contain a critical review of the current pre- and post-treatment techniques as described in the literature.

3.1.1 Pre-treatment Methods

Chlorine is a naturally occurring minor constituent in all biomass fuels. Chlorine is an essential micronutrient that serves as a catalyst in photosynthetic and enzymatic processes necessary for plant growth (Terry, 1977; Duong and Tillman, 2009). The chlorine content of a biomass fuel varies due to closeness of the ocean, fertilizer use and rainfall leaching of the soil (Bjoerkman and Stroemberg, 1997). In general, biomass fuels from field crops contain higher concentrations of chlorine than woody crops (Table 3-1).

Biomass Source	Cl Concentration (% in dry fuel)	Cl Concentration (mmol/100g dry fuel)
Switchgrass ^b	0.85	24.0
Rice straw ^a	0.58	16.4
Alfalfa stems ^a	0.50	14.1
Sugarcane ^b	0.44	12.5
Corn stover ^a	0.39	11.0
Lucerne ^b	0.28	8.0
Wheat straw ^a	0.23	6.5
Rape straw ^b	0.21	6.0
Rice hulls ^a	0.12	3.4
Switchgrass ^a	0.11	3.1
Urban wood waste ^a	0.06	1.7
Softwood sawdust ^a	0.05	1.5
Demolition wood ^a	0.05	1.4
Olive pits ^a	0.04	1.1
Bagasse ^a	0.03	0.8
Almond hulls ^a	0.02	0.6
Willow wood ^a	0.01	0.3
Almond shells ^a	0.01	0.3

Table 3-1: Summary of the chlorine concentrations in various biomass fuels.

a. (Duong and Tillman, 2009)

b. (Bjoerkman and Stroemberg, 1997)

Chlorine can be removed from a biomass system by pre-treatment methods that can be incorporated as part of the feedstock preparation process. These methods include fractionation and leaching. The fractionation process splits ground feedstock material into groups based on particle size because different particle sizes may act differently under combustion. The fractionation is usually performed using a mechanical shaker and screens of specific mesh size. Biomass materials that can be processed into quasi-spherical shaped particles (such as corn cobs) are easier to fractionate than biomass that produces cylindrical shaped particles (such as straw and grass) (Arvelakis and Koukios, 2002).

Leaching is a treatment process where raw biomass materials are washed to remove water-soluble inorganic elements such as K, Na, Ca, Cl, and S. Leaching can be performed by spraying, flushing or soaking biomass with water. Some fuels, such as sugarcane bagasse, are already leached during the raw sugar production process. Other fuels, such as straw and grass, can be naturally leached by leaving them in the fields through a rainy season. The most important factors affecting the performance of a leaching operation are particle size, retention time in water, and biomass-to-water ratio. After leaching, the material must be dried before thermochemical conversion and waste water must be disposed of in an environmentally sound manner (Turn et al., 1997; Dayton et al., 1999; Arvelakis and Koukios, 2002).

A study by Dayton et al. (1999) investigated the release of HCl(g), NaCl(g) and KCl(g) vapors along with $SO_2(g)$ from a variety of leached and un-leached fuels including wood, rice straw, wheat straw and switchgrass. Leaching biomass to reduce the amount of

chlorine and potassium in the fuel was shown to reduce the amount of chlorine and alkali metal vapors released during combustion. For fuels with high alkali metal and chlorine content, such as rice and wheat straw, the release of chlorine- and sodium-containing species in combustion decreased by >80% when leached. The study concluded that leaching is an effective means of reducing the alkali metal and chlorine vapors released from biomass fuel combustion (Dayton et al., 1999).

Turn et al. (1997) studied the efficiency of the leaching process for the removal of alkali species from banagrass fuel. The study employed the methods commonly used by the sugar industry. In the sugar production process, sucrose is extracted from cane by compression in a process called mechanical dewatering. The dewatering is usually followed by a rehydration step and another cycle of dewatering to extract remaining sugars. Turn et al. replicated the multistep process in the lab, splitting the harvested plant material into two batches and processing one batch into coarse particles and the other into fine particles, and analyzing the inorganic content of the fuels at each step in the dewatering process. The results showed that the multistep dewatering process reduced the chlorine content of the fuel in the fine fraction by as much as 98%. The coarse fractions also had substantial reductions, 10 - 20% (relative) less than the fine fraction (Turn et al., 1997).

A study by Arvelakis and Koukios (2002) on the effect of fractionation and leaching on the ash content and composition of biomass materials found that although these pretreatment techniques are able to remove chlorine, they are limited in their ability to remove it in large enough quantities to avoid operational problems during combustion. Olive residue samples responded better to the leaching treatment than corn cob and wheat straw samples, the difference being attributed to the complexity of the materials' microscopic structure. Fractionation significantly reduced (up to 50%) the ash content of each fuel but was found to actually produce a fuel with worse ash chemistry than the initial material. The best results were obtained when both fractionation and leaching techniques were combined in fuel pretreatment. The fuel was split into coarse (>1mm) and fine (<1mm) fractions and leached. Similar to Turn et al. (1997), the fine fraction showed a greater decrease in the chlorine content of the ash than the coarse fraction. Of the fuels tested, olive residue showed the largest chloride decrease at 96.5% when the fine fraction was leached. The study showed that the combined fractionation and leaching technique simultaneously reduces both the ash content of the fuel and improves the elemental composition of the remaining ash (Arvelakis and Koukios, 2002). Further study should be conducted in this area to determine what combination of fractionation and leaching is most effective for a wider variety of biomass fuels.

While the fractionation and leaching pre-treatment techniques have been shown effective at removing a portion of the chlorine content from biomass fuels prior to thermochemical conversion, pre-treatment is not able to remove all of the chlorine and the remaining amount still poses a problem. The effort and expense of pre-treatment may not be worth the gain especially if remaining chlorine atoms have to be removed by a post-conversion treatment process. The follow section describes post-treatment methods documented in the literature.

3.1.2 Post-Treatment Methods

There are a number of processes available for removing chloride vapors from a gas stream after thermochemical conversion. The amount and type of chloride containing compounds present in the product gas stream depends on the type of fuel and the process. The chloride concentrations in biomass fuels can vary between 100 and 7000 mg/kg and after combustion the gasification product gas can contain between 100 and 1000 ppm chloride (Bjoerkman and Stroemberg, 1997). Commonly employed methods for removing chloride vapors from energy production processes include quenching, spray drying and fixed beds of solid sorbent materials.

Quenching the gas stream in water is the simplest means of removing HCl vapor but will also condense "tar" species such as benzene and naphthalene. Disposing of the resulting aqueous solution in an environmentally benign way may be challenging and expensive. Moreover, converting the tar compounds to desirable permanent gas species (e.g. H_2 and CO) rather than scrubbing them improves system efficiency. In addition, quenching the gas stream drastically reduces the temperature, and reheating may be required downstream, depending on the system design and order of unit operations.

Spray dryers are commonly used to control emissions from incinerators. A spray dryer injects a mist of sorbent particles into a flowing hot gas stream. The fine dispersion of sorbent particles allows for a high degree of contact with chloride containing gases. A fabric filter can be integrated with a spray dryer to improve the efficiency of the chloride removal. As the sprayed sorbent deposits on the filter, it can react further with the flue gas (Liu et al., 2002). Similarly, a high-temperature sorbent can be sprayed into the

upper portion of the biomass conversion reactor. The partially reacted sorbent would then collect on a ceramic filter usually located just downstream. The sorbent would continue to react with the gas stream for a prolonged period of time until the filter is cleaned by back pulsing (Shemwell et al., 2000; Shemwell et al., 2002).

Another widely used method for controlling air emissions is to pass the gas stream through a fixed-bed reactor that traps the target pollutant in a sorbent material. This method has been praised as being the "most direct method of producing the highest quality fuel gas" (Dou et al., 2006) and allows for flexibility in system design because the fixed bed can be located at any point along the gas stream. Much of the past research on chloride removal from hot gas has focused on developing ideal fixed bed chloride sorbents. The ideal sorbent for the removal of chloride from a biomass product gas stream has a rapid rate of chloride adsorption, a high loading capacity, irreversible adsorption to prevent the release of adsorbed chloride during process fluctuations and compatibility with high temperatures (Turn et al., 1998a). Other factors of consideration include the cost to manufacture or purchase the sorbent product, the local availability of the material, and the environmental impact of its use and production. The remainder of this study focuses on pursuing ideal sorbents for chloride removal from a biomass gasification product stream using a fixed-bed reactor.

3.2 Mechanisms for Chloride Gas Removal by Solids

Solid sorbent materials remove molecules from a fluid stream by capturing them on their surfaces. The faster the sorbent is able to trap the target pollutant molecules, the more efficient the sorbent. According to Turn et al. (1998a), the rate at which a sorbent is able

to capture molecules is limited by the slower of two processes: molecular transport and adsorption. Molecular transport is simply the physical movement of the target molecules to the sorbent material. The factors that influence the rate of molecular transport include the flow rate of the gas stream, the concentration of the target molecules in the gas stream and the porosity of the sorbent material. Adsorption involves the attachment of the chloride containing molecules onto the crystal lattice structure of the sorbent material. The attachment is either the result of weak physical interactions among the gas and solid sorbent molecules, such as dipole-dipole or induced dipole attractions (physical adsorption), or it can be due to much stronger forces such as chemical bonding (chemisorption). Physical adsorption occurs very rapidly and can generally be reversed by reducing the vapor pressure of the adsorbate. Chemisorption, on the other hand, involves chemical reactions among gas and solid particles. In general chemisorption occurs more slowly than physical adsorption and can be more difficult to reverse without altering the sorbent surface (Turn et al., 1998a).

3.3 Experimental Methods for Chloride Sorbent Studies

The majority of the chloride sorption experimental studies reported in the literature have been carried out using fixed-bed reactors. The amount of captured chloride is usually determined by monitoring the chloride content of the gas exiting the packed sorbent bed and/or by analyzing the sorbent material after the test. A criterion often used to evaluate the chloride removal capability of a specific sorbent is the breakthrough time. Prior to breakthrough, chloride present in a gas stream passing through the fixed bed is adsorbed on the sorbent material. Breakthrough is reached when the chloride concentration of the gas exiting the reactor rises rapidly indicating that the sorbent has reached its loading capacity under the particular set of test conditions. The breakthrough characteristics of a sorbent are the dominant means of evaluating the efficacy of the sorbent operating under continuous flow conditions (Srivastava et al., 2008). The chloride capturing capacity of a sorbent is affected by parameters such as the sorbent particle size, porosity, total surface area, chloride concentration in the carrier gas, adsorption temperature, elapsed time of exposure, and gas residence time. Gas residence time is the amount of time a gas molecule spends in contact with the sorbent bed volume. Gas residence time can be calculated by dividing the volume of the fix-bed by the volumetric gas flow rate. The fixed-bed volume includes the volume of the sorbent particles (includes sorbent pore volume) and the volume between sorbent particles (intergranular volume). The inverse of gas residence time is gas hourly space velocity (GHSV). GHSV is defined as the volumetric gas flow rate divided by the volume of the sorbent bed and is frequently reported in units of inverse hours (h⁻¹). GHSV can be thought of as the number of gas volume changes the sorbent bed will experience per unit time.

3.4 Materials Tested as Chloride Sorbents

A variety of materials have been tested as solid sorbents for the removal of chorine from hot product gas streams. This section describes the characteristics of sorbent materials as determined through extensive testing over a wide range of operating conditions. Details of sorbent evaluations reported in the literature are summarized in Table 3-2. The summary includes information on sorbent characteristics, experimental methods, and evaluation results.

Tuble 5 2: Summary of the parameters and mange of previous studies on the femoval of emotion not gas streams	Table	3-2:	Summary	of the	parameters a	and findin	gs of	previous	studies of	n the remo	oval of	f chloride	from hot g	as streams.
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	1			1	1									1		1	1			
			Surface Area	Pore Volume	Pore Diameter	Inlet Gas Removal		Source/ Composition of host			Concentration of	Reaction	Space	Breakthrough	Chlorine	Removal				
	Sorbent Name	Sorbent Description	(sq m/q)	(mL/a)	(A)	Species	Reactor type	gas	Sorbent Delivery	Sampling Method	Inlet Gas (ppm)	Temp (C)	velocity	Time (h)	Content (%)	Efficiency (%)	Conclusions			
		Potassium combined with						J.				1.07			17		Did not effectively adsorb the HCI gas. Within 3 hours inlet			
	K-C	carbon material	1030.0	0.46									9074	1	17		and outlet concentrations the same.			
		Iron combined with carbon										350					Did not effectively adsorb the HCl gas. Adsorbed HCl at a			
	Fe-C	Fe-C material	naterial	naterial	material	83.0	0.44									11108	0	23		steady rate of 45% of inlet concentration from hour 3 onward.
											1820			7	48	-	Completely captured HCI for 7 hours			
										Outlet gas trapped in ion exchange		100		0	40		Enterna laward blab lawards and an and for solution			
1					p/2		Fixed-Bed	HCI and Nitrogon	Fixed bed microreactor. Pyrex glass	water trap and analyzed with Ion obcomptograph (DIONEX: DX 120)		200	1	0			Extreme low and high temperatures are not favorable for HCI adcoption. The optimum temperature for HCI adcorption is			
					IVa	nci	Microreactor	HCI and Nitrogen	(diameter = 8mm; length= 470 mm)	Ion exchange trap changed in 1 hour		270	12390	4			adsoprion. The optimum temperature for HCI adsorption is 350C.			
		Calcium combined with								intervals.		400		5						
	Ca-C	carbon material	40.0	0.11							1090			11	53	_				
										-	3900	-	5760	3	50	-				
												350	20769	3	51	-				
											1820		40000	11	58		smaller particle size increases sorbent performance			
													12390	2	21					
	Na2CO3					Syngas from	Bench scale		Reagents mixed fuel in stoichiometric	Outlet gas passed through sodium						99.9	Na2CO3 is efficient in eliminating Clivanor, Calcium			
2	CaO	Commercial sorbents				PVC and RDF	two-stage	Steam and oxygen	ratios	hydroxide trap, dried with a calcium		600				81.1	compounds do not show satisfactory chlorine removal			
	Ca(OH)2					blended with	gasification unit			chloride trap, and analyzed by a gas-						//.4	. ,			
3	ChlorOut	Commercial sorbents				KCI			Injection into a full scale circulating	In-situ alkali chloride monitor (IACM).	15	800					KCI concentration was reduced from more than 15 ppm to			
3	Onioroda	Commercial Sorberns				1001			fluidized bed boiler	Berner type low pressure impactor	10	000					approx. 2 ppm			
		Prepared from alkali and																		
	EC 11	alkaline earth metal	3.2	0.02	247.8									63	13		The EC11 sorbent is the best sorbent for HCI removal, having			
	2011	substances (Na2CO3,	5.2	0.02	247.0					Dissolving HCl vapor in a solution of				0.5			the highest breakthrough chloride capacity and the highest			
4	5040	MgO, Ca(OH)2, CaO)	407.0	0.45	47.0	HCI			Fixed-bed Bench-scale	NaOH	1000	550	3000	4.0		-	saturation chloride capacity. The high adsorptive capacity			
	EC12 EC12	Inductrial Catalucta	127.9	0.15	47.3	-								4.0	32	-	may be due to a combination or necessary amount or reactive			
	EC13	industrial Galatysis	6.4	0.06	340.2	-								2.0	16	-	component and favourable structure.			
		Prepared from alkali- and	-											-						
		alkali-earth-metal																		
	EC1	compounds (NaHCO3,								Adsorption in NaOH solution and				5			EC1 is the best sorbent for HCI removal. It displays a better			
		CaCO3, Ca(OH)2,				HCI				analyzed chemically for CI- by	1000	550	3000				adsorption capacity likely due to its large amount of reactive			
5	EC12	Mg(OH)2, et al.)							Fixed had Bapah saala	Titration (GB3558,1983)				4	-		component and its favorable structure.			
3	EC12 EC13	alkali- and alkali-earth-					The bearbearbearbearbearb					2	1							
	EC14	metal compound (~8-17								1.8		1								
		Ni-3 is a Commercial	-3 is a Commercial HCL NH3					800 ppm HCl, 500 Bange 300-				1		EC1 sorbent and Ni-3 catalyst almost remove 100% HC1 and 1-						
	EC1 and Ni-3 Catalyst	Catalyst				CS2, 1-MN					ppm NH3, 350 ppm Range	550	1000				MN and deactivations are not observed from 300 to 550 C.			
		B 1 14 B004									CS2, 550 ppm 1-MN									
		Prepared with 70% Montmorillopito (MMT)																		
	E1	(Mainly SiO2 and Al2O3)	136.2	0.20	89.8	HCI		70% N2 and 30% O2						7.2	48					
		and 30% MgO								Dissolving HCI vapor in a solution of							E1 is the best sorbent for HCI removal, indicating that better			
	E2	Commercial Catalyst	127.9	0.15	47.3	HCI				NaOH and measured by AgNO3	1000	550	3000	4.0	32		necessary amount of reactive component and favorable			
	E3	Prepared with 50% MMT;	12.1	0.05	300.8	HCI				Titration				2.1	20		structure			
		50% MgO																		
	E4	Prepared with 30% MiNT;	16.4	0.07	289.2	HCI								2.0	19					
	Activated Al2O3	Commercial	258.3	0.20	45.0											98				
	Kaoline	Drepoted from Notural	16.6	0.11	257.9	Alkali metal						840	1000			80	The activated Al2O3 has the highest sodium content among the			
6	Bauxite	Minerale	10.2	0.09	188.3	vapor (NaCl)			Fixed-bed Bench-scale			640	1000			90	four sorbents tested.			
	Acidic White Clay	Win Icrais	8.7	0.04	356.9									-		82				
1								70% N2 and 30% O2									Compared to the single removal of alkali metal vapor, HCl in			
																	inlet gas affects the chemical adsorption equilibrium of			
	E1 after Al2O3															89.4	sorbents in the process of removing alkali metal vapor and			
	21 0101 / 1200					Alkali and HCI					800 to 1000 ppm NaCl		0000				decresase the removal efficiency of NaCl vapor. E1 sorbent			
						Vapor					and HCI and small		3000				sui removes almost 100% HCI. The combined removal of HCI and alkali metal vanor by different solid sorbents is feasible.			
											amount moistule						and and motal vapor by unterent solid sorberits is leasible.			
	E1 after Kaoline															80				
	E1 after Bauxite															70.1				
1		1		1	1	1		1	1	1	1	1	1	1	1	03.2				

Table 3-2: Summary of the parameters and findings of previous studies on the removal of chloride from hot gas streams (continued).

						Inlet Gas		Source/					Hourly		Saturation				
	Sorbort Namo	Sorbort Description	Surface Area	Pore Volume	Pore Diameter	Removal	Postor type	Composition of host	Sarbant Dolivory	Sampling Mothod	Concentration of	Reaction	Space	Breakthrough	Chlorine	Removal	Conclusions		
	SUBERT Name	Ca3Al2(SiO4)0.8(OH)8.8	(sq mg)	(mb/g)	(^)	opecies	Reactor type	yas	Sorbent Delivery		inier Gas (ppin)	700	Velocity	Time (II)	Content (%)	Linciency (78)	COndusions		
7	Hydrogarnet	rogarnet synthesized by hydrothermal reaction	ized by 43.0 ermal reaction		43.0		4	HCI			Vertical tube reactor. Fluidized Bed Combuster	Automatic HCl analyzer Kyoto Electrons Manufacturing	1000	800					
	Ca(OH)2		15.0	1									1						
	Ca(OH)2 with high surface area	e Commercial	45.0			-													
	FBC Coal Ash 1	Raw ash [SiO2(47.2), Al2O3(21.6), Fe2O3(1.30), CaO(9.99), MgO(2.03), Na2O(0.09), K2O(0.83)] Ash water hvdrated		-												3			
8	FBC Coal Ash 2	Raw ash [SiO2(30.8), Al2O3(13.1), Fe2O3(5.19), CaO(22.6), MgO(0.93), Na2O(0.11), K2O(0.83)] Ash water hvdrated		-		HCI	Fixed bed reactor	N2		Fourier Transfom Infrared Spectrophotometer	1000	200				3			
	FBC Coal Ash 3	Raw ash [SiO2(24.3), Al2O3(13.7), Fe2O3(6.98), CaO(45.5), MgO(0.65), Na2O(0.05), K2O(0.61)] Ash water bydrated	4.1		10.0											11	-		
		Ash PG 5% aq. Hydrated Ash ethanol 50% aq.	21.1	ł	100.0											40			
		Hydrated Commercial NaHCO3	21.7					Simulated coal gas											
	Nahcolite (NaHCO3) Pelle	powder with bentonite or ts sodium silicate binders made into pellets by extrusion						representative of Texaco oxygen-blown gasifier	Fiver-had Bench-scale		1750 ppm HCl; 3000		3000		Maximum ~55 wt%		Pellets with sodium silicate binders 10% higher maximum chloride canacity than bantonite binder cellets. Sodium silicate		
	Nahcolite Granules	Commercial NaHCO3 powder with kaolinite and bentonite binders made into granules with spray dryer						Simulated coal gas			H2O	550	3000		As high as 50 wt%		Palets aggiouty that borrows bright than 500 C. No problem with bentonite. Spray drying preparation causes superior reactivity and chloride capacity than the raw nacolite powder. Comparable attittion resistance as commercial FCC catalyst. Dependent of LIOS did and fields the LIOL teams to colite powder.		
9	Nahcolite Pellets made from Trona Ore VS Nahcolite	m			HCI	HCI		Simulated coal gas	Fixed-bed Bench-scale at Elevated Pressure (150 psig)		HCI: 1750 ppm; H2S: 3180 ppm; Steam: 25%	500	3500	> 20			chloride capacity of the sorbent.		
	Pellets made from Trona Ore VS Nahcolite			-							1750 ppm HCI	500	3000	~2 for Trona; ~12 for					
	Commercial Sorbent VS Nahcolite	Commercial sorbent from United Catalyst, Inc.							Fluidized-bed		HCI: 360 ppm; H2S: 4200 ppm; Steam: 15%	480	4180	~3 for UCI; ~13 for Nahcolite			UCI soment is made for guard bed applications rather than for bulk removal of HCI vapor		
	Grade #2 Sodium bicarbonate powder for initial 110 h. 100 lbs. spra dried nahcolite granules fo last 5 h.	Spray-dried nahcolite y- granules from Research r Triangle Institute						Hot coal gas stream	Circulating fluidized-bed facility located at the GE Pilot-scale Fixed-bed Gasifier facility		580				Spray-dried sorbent: 38 wt% (utilization of 71%)	97% with both sorbents			

Table 3-2: Summary of the parameters and findings of previous studies on the removal of chloride from hot gas streams (continued).



Table 3-2: Summary of the parameters and findings of previous studies on the removal of chloride from hot gas streams (continued).

						Inlet Gas		Source/					Hourly		Saturation		
	Sorbent Name	Sorbent Description	(sq m/g)	Pore Volume (mL/g)	Pore Diameter (A)	Species	Reactor type	gas	Sorbent Delivery	Sampling Method	Inlet Gas (ppm)	Temp (C)	velocity	Breakthrough Time (h)	Chlorine Content (%)	Removal Efficiency (%)	Conclusions
13	Bagasse fly ash (BFA)	BFA from flue gas duct of sugarcane-bagasse-fired boilers: Ash [30.98% (SiO2 (51.05%), AI2O3 (10.75%), CaO (6.04%), Fe2O3 (3.45%), MgO (1.10%))], Fixed Carbon (43.03%)	168.8	0.05	24.0	Phenol			Continuous packed column of BFA			30					The sorptive capacity of BFA for phenol was found to be 9.93 mg/g. This is higher than the sorption capacities of other sorbents reported in literature.
	Activated carbon-supported copper catalyst	CuO on 10 % wt coconut shell-derived activated carbon	897.0	0.19	21.6	Simultaneous		Synthetic flue gas stream generated by the combustion of								~92	HCI does not cause a decrease in SO2 activity over WAC catalysts. HCI and SO2 can be removed simultaneously. The
14	Activated carbon-supported iron catalyst	Fe2O3 on 10 % wt coconut shell-derived activated carbon	850.0	0.16	21.2	SO2/HCI catalytic oxidation and		simulated feed waste composed of sawdust, low-denstiy	 Pilot-Plant fluidized bed incinerator system dry scrubber I 	R.O.C. National Institute of Environmental Analysis (NIEA) method A412.70A	SO2: 1500-2000 ppm; NOx: 150 - 250 ppm; HCI: 425 - 530 ppm	Between 516 and 200	o			~95	AC-supported catalysts exhibit a higher activity than α-Al2O3 for removing SO2, HCl and NO simulraneously, especially over CuO/AC and V2O5/AC catalysts. For all WAC catalysts tested,
	Activated carbon-supported vanadium oxide catalyst	V2O5 on 10 % wt coconut shell-derived activated carbon	708.0	0.16	21.8	NO reduction		polyethylene (LDPE), sulfure (S), polyvinyl chloride (PVC).									individual removal efficiencies for SO2, HCl, and NO are found to be above 70, 90, and 55% repectively.
15	Hydrated Lime	Ca(OH)2				HCI		Nitrogen and oxygen	Membrane reactor		2094						

Sources:

- 1. (Bhaskar et al., 2002)
- 2. (Borgianni et al., 2002)
- 3. (Broström et al., 2007)
- 4. (Dou et al., 2001)
- 5. (Dou et al., 2002)
- 6. (Dou et al., 2007)
- 7. (Fujita et al., 2004)
- 8. (Hirabayashi et al., 2002)
- 9. (Krishnan et al., 1996)
- 10. (Li et al., 2004)
- 11. (Lee et al., 2003)
- 12. (Liu et al., 2002)
- 13. (Srivastava et al., 2008)
- 14. (Tseng et al., 2003)
- 15. (Yan et al., 2003)

3.4.1 Ca-Based Sorbents

Calcium-containing materials such as slaked or hydrated lime (Ca(OH)₂) and limestone (CaCO₃) have been traditionally used to remove HCl from hot fuel gases using dry scrubbing processes. Solid calcium oxide (CaO) and calcium hydroxide (Ca(OH)₂) are currently used to control HCl emissions from municipal waste combustion and hazardous waste incineration. This method often involves the injection of the dry Ca-based sorbent into the post-flame region of the reactor. When Ca(OH)₂ is injected into flue gas at temperatures greater than 400°C, CaO is formed:

$$Ca(OH)_2 \leftrightarrow CaO + H_2O$$

Injection of calcium carbonate (CaCO₃) at temperatures greater than 650°C also forms CaO:

$$CaCO_3 \leftrightarrow CaO + CO_2$$

CaO is more desirable as an HCl sorbent than $Ca(OH)_2$ and $CaCO_3$ because it is more porous and has a higher surface area. CaO reacts with HCl to form calcium chloride (CaCl₂):

$$CaO + 2HCl \leftrightarrow CaCl_2 + H_2O$$

The reaction is favorable at high temperatures and largely irreversible since HCl reaches equilibrium with CaCl₂ at concentrations less than 0.1 ppm (at 350°C) (Gullett et al., 1992). The melting point of CaCl₂, 772°C, imposes a physical limit on the reaction. A study on the direct reaction of Ca(OH)₂ and HCl at temperatures between 60 and 1000°C found that maximum sorption occurs in the 500-600°C range. A large HCl-binding

capacity was also observed at temperatures below 150°C in the presence of moisture. The particle size did not affect the capacity of the sorbent and initial surface area only had minor effects (Weinell et al., 1992).

Chisholm and Rochelle (1999) studied the ability of $Ca(OH)_2$ to simultaneously adsorb HCl and SO₂ in simulated humidified flue gas. The study demonstrated that the adsorption of HCl by $Ca(OH)_2$ is sensitive to relative humidity. At 120°C, the removal efficiency of the sorbent was found to increase with increasing relative humidity (from 0% to 19%) due to the reactivity of the acid gas increasing with increased humidity. The HCl sorption capacity of $Ca(OH)_2$ was also found to be unaffected when HCl concentrations fluctuated at levels below 1000 ppm. Increasing the HCl concentrations to 2,000 and 3,500 ppm, however, was shown to decreases the HCl-binding capacity of $Ca(OH)_2$ (Chisholm and Rochelle, 1999).

Liu et al. (2002) investigated the reaction characteristics of Ca(OH)₂, HCl and SO₂ in flue gas emitted by a laboratory incinerator using a spray dryer integrated with a fabric filter. HCl concentrations, SO₂ concentrations and relative humidity (between 40 – 80 %) were varied in the study. The results showed that while increasing HCl concentrations between 500 to 2000 ppm did not affect the HCl removal efficiency, increasing SO₂ concentrations from 500 to 2000 ppm improved the SO₂ removal capability of the spray dryer. An HCl removal efficiency of more than 98% was achieved at a relative humidity of $45\pm5\%$ (Liu et al., 2002).

Both Chisholm and Rochelle (1999) and Liu et al. (2002) have shown that hydrated lime has a high HCl removal efficiency in high temperature and high relative humidity environments. In addition, the calcium-based scrubber process is relatively simple and easily operable, and therefore, relatively inexpensive as a means of controlling HCl emissions (Fujita et al., 2004). These properties make Ca-based sorbents attractive candidates for HCl removal in a biomass gasification system. Researchers have pointed out, however, that materials other than CaO should be developed for HCl emission control because the removal efficiency is not high enough at high temperatures and operational problems can result when $CaCl_2$ scales are deposited on reactor walls (Fujita et al., 2004; Dou et al., 2007).

3.4.2 Na-Based and K-Based Sorbents

According to equilibrium thermodynamic calculations performed by Krishnan, Canizales et al. (1996), at temperatures as high as 527° C, only sodium and potassium compounds are capable of reducing HCl vapor concentrations to levels less than 1 ppm. Potassium compounds are superior at producing the lowest HCl vapor levels, but the vapor pressure of KCl (g) is higher than that of NaCl (g), and therefore, the use of potassium compounds over sodium compounds would cause the release of more alkali vapor in the hot gas. In addition, the use of sodium compounds is more environmentally sustainable because sodium is more plentiful in nature. Krishnan states that nahcolite (NaHCO₃) is the most suitable of all the major sodium minerals in the U.S for the removal of HCl. 17.5 billion tons of economically recoverable nahcolite are available in northwestern Colorado area alone (Krishnan et al., 1996).

A previous study by Krishnan, Tong et al. (1986) showed that the nahcolite mineral is highly reactive with HCl and has a high chloride capture capacity. According to Krishnan, Canizales et al. (1996), when nahcolite (NaHCO₃) is heated to temperatures above 150°C, it is converted to soda ash:

$$2NaHCO_3 = Na_2CO_3 + H_2O(g) + CO_2(g)$$

By releasing CO_2 , a porous and reactive sorbent is formed. When the sorbent is exposed to HCl, it reacts readily to form NaCl:

$$Na_2CO_3 + 2HCl (g) = 2NaCl + H_2O (g) + CO_2 (g)$$

Krishnan, Canizales et al. (1996) performed fixed-bed and fluidized-bed reactor studies with self-prepared nahcolite sorbents produced using bentonite, kaolinite or sodium silicate binders. For comparison, sorption experiments were also performed using pellets made from trona ore (Na2CO₃·NaHCO₃) and a commercial chloride guard product produced by United Catalyst, Inc. The study found that both the trona ore and the commercial chloride guard have significantly less chloride capacity than nahcolite pellets. The study concluded that the nahcolite pellets used in the fixed-bed studies have a maximum chloride content of about 55% weight and that the nature of the binder does not affect the HCl reactivity, although the maximum chloride capacity of pellets made with sodium silicate binder was 10% higher than pellets made with bentonite binder. The nahcolite granules used in fluidized-bed studies were also shown to have a high reactivity for HCl and a high chloride capture capacity with spent sorbent containing as high as 50wt% chloride (Krishnan et al., 1996).

A study by Gupta and O'Brien (2000) used a zinc titanate sorbent for the desulfurization of hot syngas which contained HCl vapors. The study showed that a portion of the incoming HCl was removed from the gas stream and permanently retained by the sorbent. The zinc titanate sorbent was prepared using sodium-containing bentonite as the binder and it was concluded that the sorbent was retaining chloride due to the reaction between the sodium oxide present in the binder and HCl:

$$Na_2O + 2HCl \leftrightarrow 2NaCl (s) + H_2O$$

The thermodynamics of this reaction are very favorable, so the reaction gets close to completion and is practically irreversible. The study concluded that sodium-oxide containing materials have the potential to remove HCl down to low levels and thus may be advantageous as sorbents (Gupta and O'Brien, 2000).

Borgianni et al. (2002) studied the gasification of polyvinyl chloride (PVC), which creates similar chloride related pollution problems as biomass gasification due to the high chlorine content of the plastic. In this study, PVC was blended with refuse-derived fuel (RDF) and chemicals intended to react with chloride to form inert compounds. The chloride-reacting substances included sodium carbonate (Na₂CO₃) and two calcium compounds (CaO and Ca(OH)₂). These reagents were mixed with PVC in stoichiometric ratios. The fuel blends were gasified under a variety of operating conditions and the chloride content of the product gas and ash was compared to the content of the fuel. The results showed that under certain operating conditions, Na₂CO₃ in PVC/reagent ratios as low as 1.2 times stoichiometric caused almost all (99.9%) of the chlorine contained in the fuel blend to remain in the ash while little enters the product gas. The study concluded that Na₂CO₃ is efficient at satisfactorily removing chloride evolving from blends containing RDF and up to 20% PVC, while calcium compounds were not adequate for chloride removal under any of the ratios and operating conditions tested (Borgianni et al., 2002). This study suggests that gasifying fuels mixed with sodium compounds could provide an effective means for controlling chloride emissions by prohibiting the release of chloride vapors.

These studies indicate that sodium based sorbents are efficient at removing chloride from a hot gas stream. Even if a sodium compound isn't used as the main active component in the sorbent, sodium bentonite could be used as a binder in HCl sorbent preparations. In addition to sodium, potassium compounds are also highly reactive with HCl vapor and present another option for chloride sorbents. While these studies indicate that sodium may be superior to calcium for chloride removal, the effects of humidity on the reaction haven't been investigated. Since H_2O is a product in many of the reactions described above, a humid gasification environment may affect the efficiency of the sodium sorbent. In comparison, calcium based sorbents have been shown to be efficient HCl removers over a wide range of operating conditions including high levels of humidity (Weinell et al., 1992; Chisholm and Rochelle, 1999; Liu et al., 2002), thus calcium may prove to be a more versatile sorbent material than sodium or potassium.

3.4.3 Mg-Based Sorbents

Li et al. (2004) performed a study to develop a highly efficient sorbent for the high temperature removal of HCl using a natural, inexpensive mineral called meerschaum, the active component of which is the magnesium compound $H_4Mg_2Si_3O_{10}$. Four sorbents were prepared from meerschaum and alkali metal and alkaline-earth compounds. The sorbents were tested in a fixed-bed reactor under conditions of 650°C, 2500 h⁻¹ space velocity and 1800 ppm HCl input concentration. Two commercial HCl sorbents were also tested for comparison. The study concluded that the sorbent made of 45%
meerschaum (H₄Mg₂Si₃O₁₀), 30% Ca(OH)₂, 10% Na₂CO₃ and 7% NaHCO₃ had a breakthrough chlorine content of 37.2% (at 650°C), which is higher than that of the two industrial sorbents. Li et al. discovered that the optimal temperature for HCl removal by the meerschaum sorbent is 550°C. As the temperature is increased toward 550°C, the breakthrough chlorine content of the sorbent increases due to the release of volatile impurities from the sorbent, which creates micropores that increase the reactivity. At temperatures above 550°C, the sorbent removes less chloride because the pore-making substances in the sorbent breach at these temperatures and cause the surface area to decrease. Another reason for the reduced reactivity at high temperatures is attributed to Ca(OH)₂ partially decomposing to CaO according to the reaction:

$$Ca(OH)_2 \leftrightarrow H_2O + CaO$$

At temperatures above 550°C, therefore, changes in the sorbent constituents are the cause of the reduced adsorption of chloride (Li et al., 2004).

Like Krishnan's (1986 and 1996) investigations with the nahcolite mineral, Li's (2004) work with meerschaum shows that certain natural mineral compounds have promising HCl sorption properties. The next section describes several studies that explore the HCl capturing capabilities of minerals containing aluminum.

3.4.4 Al-Based Sorbents

Fujita et al. (2004) used hydrogarnet $[Ca_3Al_2(SiO_4)0.8(OH)_{8.8}]$, a component of cement minerals, as a sorbent for HCl gas at high temperatures. The study found that hydrogarnet can capture HCl gas at high temperatures (>700°C) and fix it as chlorinate mayenite $[Ca_{12}Al_{10}Si_4O_{32}Cl_6]$ and $CaCl_2$. Under such extreme conditions, traditional

sorbents such as CaO and Ca(OH)₂ cannot be used. Theoretically, hydrogarnet can capture 22.1% (wt) chlorine. Hydrogarnet was also found capable of decreasing the formation of hazardous by-products such as dioxins (Fujita et al., 2004).

A study by Dou et al. (2007) looked into the single and combined removal of HCl and alkali metal vapor from high-temperature coal-derived gas. Thermodynamic calculations show that NaCl and KCl are the major alkali metal vapor species in the gas. Three HCl sorbents designated E1, E3 and E4 were prepared by pelletizing different mixtures of montmorillonite (MMt) and Mg(OH)₂ (70%/30%, 50%/50%, and 30%/70% respectively). MMt, the main constituent of bentonite, is a natural mineral that contains mainly SiO₂ and Al₂O₃. 10% glycol and amine were added as texturing agents. A commercial HCl sorbent was also obtained for the test. The commercial sorbent, designated E2, was prepared by wet impregnation of alkali or alkaline-earth compounds on Al₂O₃. When tested in a fixed-bed reactor, sorbent E1 showed the best HCl adsorption capacity, which indicates that this specific combination of MMT and Mg(OH)₂ produced a sorbent with the necessary amount of reactive component and a favorable structure (Dou et al., 2007).

Dou et al. (2007) also tested the natural minerals bauxite (aluminum ore), kaoline $(Al_2Si_2O_5(OH)_4)$ and acidic white clay and activated Al_2O_3 as sorbents for NaCl removal. They removed 90%, 80%, 82%, and 98% of the NaCl vapor, respectively. Tests showed that the removal of the alkali metal vapor by activated Al_2O_3 is a chemical adsorption process in the presence of moisture and results in HCl emissions. Since the adsorption of alkali metal vapor produces HCl emissions, it is feasible to remove chloride vapor with a series of sorbents. Dou found that when activated Al_2O_3 and sorbent E1 were placed in the reactor, 89.4% of NaCl vapor and 100% of the HCl was removed. The experiment showed that the although the efficiency of NaCl vapor removal decreased, the combined removal of HCl and alkali metal vapor is feasible in a reactor by different solid sorbents (Dou et al., 2007).

These studies illustrated the HCl binding properties of mineral compounds containing aluminum including hydrogarnet, montmorillonite/bentonite, bauxite, kaoline, and acidic white clay. These and other compounds containing aluminum seem promising as potential HCl sorbents and are worthy of future study.

3.4.5 Composite sorbents

Studies have prepared HCl sorbents using a mixture of several components. Dou et al. (2001 and 2002) tested the removal of HCl vapor from high-temperature coal-derived gas using a self-prepared sorbent along with three commercially available sorbents. The self-prepared sorbent was made by pelletizing powders of alkali- and alkali-earth-metal compounds (NaHCO₃, CaCO₃, Ca(OH)₂, Mg(OH)₂, etc.) with 5% bentonite as the binder and 8% glycol as the texturing agent. The commercially available sorbents contained ~8-17 wt % alkali- and alkali-earth-metal compounds supported on activated aluminum oxide (α -Al₂O₃). The results of the analysis showed that the self-prepared sorbent had the highest capacity for chloride removal with a saturated chloride content of 43.02% (Dou et al., 2001; Dou et al., 2002).

A study by Bhaskar et al. (2002) evaluated the HCl capturing potential of calcium, iron, and potassium sorbents as well as the optimum reaction conditions under which the sorbent capacity would be maximally utilized. Each sorbent was prepared by mechanically kneading 90 wt % reactive component (CaCO₃; Fe₃O₄; K₂CO₃) with 10 wt % phenol resin. 10% water was added and the mixture was molded into pellets and calcined in a nitrogen atmosphere. The calcinations converted the phenol resin into carbon and changed the hygroscopic nature of the material. The sorbents were then reacted with HCl in a fixed-bed reactor under various experimental conditions. The study found that calcium based carbon composite sorbent outperformed all others. The calcium sorbent was shown capable of capturing 46 wt% HCl for 11 hours before breakthrough. The potassium based sorbent adsorbed only 4 wt% HCl when breakthrough was reached after one hour. The iron sorbent was not capable of adsorbing HCl gas fast enough to avoid an immediate breakthrough. The iron sorbent steadily reduced the HCl concentration by 45%, however, indicating that it was capable of reacting with HCl, just not as rapidly as the calcium based carbon composite.

Bhaskar's study (2002) indicates that calcium based carbon composites have potential uses for the removal of HCl from high temperature gasification flue gas. While such activated carbon composites are promising as chloride sorbents, Srivastava et al. (2008) points out that their use as sorbents in developing countries is limited due to high costs and losses of up to 15% during regeneration (Srivastava, 2008). It is important to consider economic and environmental factors in the development of an HCl sorbent for future biomass gasification applications. The next section explores the potential of ash, a common waste material, to capture HCl.

3.4.6 Ash-Based Sorbents

Using recycled materials as chloride sorbents is of interest because these materials could provide low-cost, locally available and environmentally sustainable sorbents. Several studies by Hirabayashi et al. (1999, 2000 and 2002) have investigated the HCl sorption properties of coal ash. Coal ash is generated from coal combustors and ash reuse is an important waste management issue. Current uses for coal ash include adding it to cement or asphalt mixtures and as a component in fill-material for land reclamation projects. Coal ash could potentially be used in the development of chloride sorbents since it contains 5-40% CaO (Hirabayashi et al., 2000).

Hirabayashi et al. (1999) investigated the HCl sorption characteristics of ash from various coals that were collected from different discharge points on a fluidized bed combustor (FBC). The tests were conducted using dry gas under high temperature conditions (500 – 600° C). The HCl adsorption capacity of the bottom ash was found to be similar to that of CaO derived from CaCO₃. The activation energy for the chlorination of the ashes was also found to be similar to that of CaO at 12 kJ/mol. The HCl capacity of bottom ash was shown to be higher than the capacity of fly ash. This difference was attributed to the structural differences between the ashes and potentially the nature of the Ca compound in each of the ashes (Hirabayashi et al., 1999).

Hirabayashi et al. (2000) report that coal ash contains the following Ca components originating from the coal mineral or from sulfur sorbents injected into the combustor: $CaCO_3$, CaO, $Ca(OH)_2$, C_2S and crystallized $CaSO_4$. The following reactions are involved in an HCl removal process with coal ash:

$$CaO(s) + 2HCl(g) \leftrightarrow CaCl_2(s) + H_2O(g)$$
$$CaCO_3(s) + 2HCl(g) \leftrightarrow CaCl_2(s) + H_2O(g) + CO_2(g)$$
$$Ca(OH)_2(s) + 2HCl(g) \leftrightarrow CaCl_2(s) + 2H_2O(g)$$

A study by Hirabayashi et al. (2000) aimed to optimize the reaction between HCl and coal ash at low temperature (200°C) by improving the reactivity of the ash through several hydration processes. Ash from a fluidized bed coal combustor was first slaked with water to enhance the formation of crystallized Ca(OH)₂ and to increase the pore surface area (slaking is the term for the traditional process of exposing lime to H₂O). The result was a sorbent with a high capacity for HCl removal at low temperatures. Alcohol hydration was also applied to enhance the HCl sorption capacity of the ash. Water hydrated, propylene glycol (PG) hydrated, and ethanol (Et-OH) hydrated coal ash samples were tested in a fixed-bed reactor. Alcohol hydration was shown to enhance the HCl sorption capacity (46% HCl removal for Et-OH hydrate samples compared to 40% for PG hydrate samples). This was explained by the larger surface areas of the large pores (>100 nm) in the Et-OH hydrate samples compared to the PG hydrate samples (Hirabayashi et al., 2000).

Hirabayashi et al. (2002) conducted further study on the hydration of coal ash to enhance the HCl sorption characteristics of the material. The paper, published in Japanese, describes how three kinds of coal burn ash discharged from fluidized bed coal combustion were hydrated with deionized water and with solutions of alcohols including methanol, ethanol, diethylene glycol, propylene glycol and also glycerin. The temperature of these hydration solutions was varied from 0 to 80°C. The hydrated sorbent materials were then tested under conditions that simulated the flue gas capture for a municipal waste incinerator including a HCl concentration of 1,000 ppmv and a temperature of 200°C. The study concluded that the HCl sorption of the hydrated coal ash sorbent material increased with higher concentrations of CaO in the material. Also, the HCl sorption capacity of the ash material increase with the temperature of the hydration solution. The hydration process was found to cause an increase in the surface area of the coal ash pores for pore radiuses between 0.001 µm and 0.01 µm. The hydration process was also shown to generate Ca(OH)₂ with a higher crystallinity in the ash. The coal ash hydrated with glycerin was found to have the best ability to remove HCl, removing over 70% of the HCl (Hirabayashi et al., 2002).

Srivastava et al. (2008) investigated the ability of a packed bed of bagasse fly ash to remove phenol (C_6H_5OH) from an aqueous solution. The bagasse fly ash was found capable of removing more than 99.5% of phenol during tests, and the adsorptive capacity of the ash for phenol was found to be 9.93 mg/g (Srivastava et al., 2008). While this study does not relate directly to HCl removal, it shows that ash can be potentially used as a sorbent for the other chemicals and may be able to simultaneously remove several pollutants.

These studies demonstrate that scientific and technical knowledge about the use of coal ash as a chloride sorbent has been previously gained, but mostly under dry homogeneous gas conditions. Very little attention has been devoted to developing a coal ash based sorbent for the removal of chloride from a biomass gasification product stream. While these studies seem to indicate that coal ash may provide a sensible means of efficiently capturing HCl, it should be noted that the effect of humidity on the sorbent performance was not explored in any of Hirabayashi's studies. Since H₂O is the product of the reactions of HCl with the Ca compounds contained in the ash, the presence of water in biomass gasification product gas may hinder the HCl capturing capabilities of an ash-based sorbent. Further study should be focused on determining if coal ash is able to efficiently remove chloride containing compounds from a humid biomass gasification product stream. Along with exploring the hydration methods to improve the sorbent characteristics of coal ash, the sorptive qualities of coal ash from various types of combustors could be investigated.

3.5 Breakthrough Theory

When designing a fix-bed sorption column, the most important criterion is the column breakthrough. Breakthrough occurs as the sorption capacity of the sorbent reaches its maximum. To quantify and compare the breakthroughs of sorbents, 50% breakthrough time can be determined. 50% breakthrough occurs when the inlet gas concentration is twice the outlet gas concentration. The breakthrough characteristics of a sorbent determine the bed length (z) and the operating lifespan and regeneration time of the bed. Breakthrough is affected by factors including the operating variables of the reactor (temperature, pressure, reactor length, etc.) and the characteristics of the sorbent and sorbate (Srivastava et al., 2008). Models used for the prediction of the breakthrough characteristics are discussed in the following sections.

3.5.1 Bed Depth Service Time (BDST) Model

The BDST model assumes that the sorption rate is determined by the surface reaction occurring between the sorbent and sorbate. The initial part of the breakthrough curve is described by the Bohart-Adams model:

$$ln\left(\frac{c_o}{c}-1\right) = ln\left[exp\left(kN_o\frac{z}{u}\right)-1\right] - kc_ot \tag{1}$$

Where C_o is the initial concentration of the sorbate (mg/L), C is the target concentration of the sorbate at time t (mg/L), k is the sorption rate constant of the column [L/ (min mg)], Z is the length of the bed (cm), N_o is the sorptive capacity of the sorbent bed (mg/L), and U is the linear flow velocity of the gas through the bed (cm/min).

N_o can be evaluated from the slope of the linear version of eq 1:

$$t = \frac{N_o}{C_o U_o} Z - \frac{1}{kC_o} \ln \left(\frac{C_o}{C} - 1\right)$$
⁽²⁾

And the rate constant, k, is equal to the intercept, I, where:

$$I = -\frac{1}{kC_o} ln\left(\frac{C_o}{c} - 1\right) \tag{3}$$

When $C_0/C = 0.5$, 50% breakthrough has occurred and t equals the half-time, $t_{0.5}$, which can be determined by (Srivastava, 2008):

$$t_{0.5} = \frac{N_o}{C_o U} Z \tag{4}$$

3.5.2 Yoon and Nelson Model

The 50% breakthrough time can also be determined using the Yoon and Nelson Model. This model is based on the assumption that the rate of decrease in the probability of a molecule being adsorbed by the sorbent is proportional to the probability of adsorption and breakthrough:

$$\ln\left(\frac{c_o}{c} - 1\right) = k_{YN}t - t_{0.5}k_{YN}$$
(5)

where k_{YN} is the Yoon-Nelson rate constant (min⁻¹). The slope and intercept of the linear plot of $\ln\left(\frac{C_0}{c}-1\right)$ versus *t*, yields the values of k_{YN} and $t_{0.5}$, respectively (Srivastava, 2008).

3.5.3 Estimation of Breakthrough Curve

The models described above can be used to predict the breakthrough behavior of a sorbent. The fit between predicted values and experimental data can be quantified with linear regression coefficients (\mathbb{R}^2). The error between experimental and theoretical values of C/C_o can be calculated using the equation for Marquardt's percent standard deviation (MPSD):

$$MPSD = 100 \sqrt{\frac{1}{N-P} \sum_{i=1}^{n} \left[\frac{\binom{(C_{C_o})_{exp} - \binom{(C_{C_o})_{theo}}}{\binom{(C_{C_o})_{exp}}} \right]^2}$$
(6)

Where *N* is the number of data points and *P* is the number of parameters (or degrees of freedom). The percent deviation (ϵ) between the experimental and theoretical values for 50% breakthrough times can also be calculated (Srivastava, 2008):

$$\epsilon = 100 \left(\frac{t_{0.5exp} - t_{0.5cal}}{t_{0.5exp}} \right) \tag{7}$$

4.0 EXPERIMENTAL METHODS

The methods and apparatuses used to collect the experimental data for this study are described in the following sections.

4.1 Biomass Feedstock

Leucaena leucocephala, a fast growing, nitrogen-fixing tree, was used as the biomass fuel in all the gasification tests for this research (Figure 4-1). *Leucaena* was harvested from plots on the University of Hawaii Experiment Station at Waimanalo on Oahu. The trees were delimbed, and the bolt wood was chipped. The chips were dried in a forced ambient air drying bed to the equilibrium moisture content of ~10% dry mass basis and then hammer milled to pass a 3 mm mesh screen. The chips were sampled and subjected to ultimate (C, H, O, N, S and Cl), proximate (volatile, fixed carbon and ash), heating value and elemental ash analyses (Si, Al, Ti, Fe, Ca, Mg, Na, K, P, S, Cl, and CO₂) by Hazen Research, Inc., Golden, CO. Hazen also determined the energy content of the fuel in terms of the higher heating value (HHV).



Figure 4-1: Processed *Leucaena leucocephala* biomass fuel used as feedstock in the gasifier tests.

4.2 Bench-Scale Fluidized-Bed Biomass Gasifier

The Hawaii Natural Energy Institute (HNEI) bench-scale fluidized-bed gasification unit located at the University of Hawaii at Manoa (UHM) was available for this study (Figure 4-2). Detailed descriptions of the gasification system can be found in the literature (Turn et al., 1998b; Turn et al., 1998c; Turn et al., 2001; Cui et al., 2010; Cui et al., 2011), but a brief description is provided here.

The gasifier reactor is constructed of 310 stainless steel pipe, with a bed diameter of 89 mm and a freeboard diameter of 152 mm. The reactor is externally heated by four, 4 kW heaters. Pressure taps, thermocouples and probe access ports are located along the height of the reactor. The biomass fuel is fed to the gasifier reactor from a sealed fuel hopper by a variable speed metering screw.



Figure 4-2: The Hawaii Natural Energy Institute's bench-scale fluidized-bed gasification experimental apparatus located at the University of Hawaii at Manoa.

Besides biomass fuel, nitrogen and steam are also input to the reactor. Nitrogen is added to the windbox below the distributor by a mass flow controller. Steam is directed to the windbox from a steam generator that receives deionized water from a calibrated, precision metering pump. Nitrogen is used as an inert trace gas to permit calculation of gas yields and to control the fluidization of the bed material. The bed material consists of alumina beads with diameters in the range of $210-420 \mu m$.

The flow exits the reactor and then passes through a heated silicon carbide (ceramic) filter element with a pore size of 3 μ m (Pall Process Filtration Corporation, Cortland, NY). The filter element is 60 mm in diameter and 490 mm in length and is typically operated at temperatures ranging from 600 to 850°C. The ceramic filter enclosure is

equipped with a high-pressure, back-pulse system that delivers a burst of nitrogen to purge accumulated particles from the face of the filter element.

At the exit of the filter, the product gas can be directed to downstream reactor vessels for contaminant removal. The bulk of the gas stream, however, is directed through the "bypass" line. A sampling point is also located at the exit of the filter vessel to provide a slip stream of the product gas for characterization. Samples collected from this port are referred to as "bypass samples" in this discussion. The bypass line includes a heat exchanger to cool the gas and remove condensate, a coalescing filter to remove entrained aerosol and a gas meter that indicates the gas flow rate and provides a record of the total gas volume over the duration of the test. The bypass gas is then directed to a flare for disposal.

Gas that is not sent to the bypass can pass through reactor vessels including a sulfur compound removal vessel, a chloride removal vessel, a tar-cracking unit and a water-gas shift (WGS) reactor. The treated gas stream then passes through a separate heat exchanger, coalescing filter and gas meter to record the gas flow rate and total gas volume of the treated stream. The treated gas can then be directed to the flare for disposal or to a compressor for gas storage. Stored gas can be used for hydrogen purification studies using pressure swing adsorption (PSA) or other appropriate technologies using product gas from biomass gasification, such as Fischer-Tropsch synthesis or other liquid fuel or chemical production. These units are available but were not used for this research, so they will not be described further.

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Electronic signals from thermocouples, pressure transducers, on-line gas analyzers, and gas meters are processed using two, 32 channel multiplexer amplifiers (Model SCXI-1100, National Instruments, Austin, TX) and a 12 bit, analog to digital converter board (National Instruments, Austin, TX) controlled by a personal computer.

4.2.1 Biomass Gasifier Apparatus for Chloride Removal Investigations

For this research, the gasifier was configured such that the product gas stream exiting the ceramic filter unit could be directed to a chloride removal vessel (Figure 4-3). The reactor is an 89 mm inner diameter stainless steel vessel that can be loaded with a bed of solid sorbent material. The vessel is equipped with heating elements that allow for control of the bed temperature up to 800°C. A practical lower temperature limit of 300°C is mandated by the condensation point of tar compounds.

At the exit of the reactor vessel a provision is made to direct a slip stream of the gas to a sampling system for characterization. Samples collected from this port are referred to as "treated samples" in this discussion. The dry gas that exits the sampling system passes through a coalescing filter, a vacuum pump and then a gas meter that indicates the gas flow rate and provides a record of the total gas volume drawn through the impinger during the sampling period. The gas is then disposed in the flare.



Figure 4-3: Schematic of the bench-scale fluidized-bed gasifier detailing the components of the system that were utilized for this study.

4.2.2 Biomass Gasifier Test Procedure and Conditions

In preparation for each test, the bed material and biomass fuel were weighed and placed in the reactor and fuel hopper, respectively. The fuel feed rate was calibrated over a range of screw speeds prior to the test. The gasifier bed was preheated to the desired temperature using the external heaters, with air flowing through the reactor until a stable temperature profile was attained. The gas flow was then switched from air to the desired mixture of steam and nitrogen. After the reactor stabilized again, the fuel feeder was turned on and the test officially began. Flow was directed through the bypass line to the flare during the initial period of feeding until the gasifier attained a steady operating condition. It normally required about two hours before this steady state was reached. When steady conditions were attained, the product gas flow was directed to the downstream fixed-bed reactor vessel containing the sorbent to be tested. Quantitative sampling, as described in Section 4.2.3, was performed when the system attained a steady temperature and product gas distribution. At the conclusion of the test, fuel, fluidizing gases, and system heaters were shutdown simultaneously. After the system cooled, the remaining fuel was removed from the feed hopper, the collected char was recovered from the ceramic filter, the bed material was removed from the reactor and the sorbent material was removed from the fixed-bed reactor. Each of these items were weighed and sampled.

A summary of typical gasifier operating conditions is provided in Table 4-1. The gasifier was operated at 800°C with a fuel feeding rate of ~1 kg per hour and steam feeding rate of ~2 kg per hour. Alumina-silicate beads (~10 kg) were used as the bed material in the gasifier for each test. Nitrogen flowed to the reactor at a rate of 10 L min-1 to aid in fluidization. The temperature of the filter was maintained at 650°C. The chloride sorption bed vessel was operated to maintain a temperature of 400°C with the control point measured at the center of the fixed bed.

Average reactor temperature (°C)	800
Fuel feed rate (kg/hr)	1.0
Steam feed rate (kg/hr)	2.0
Steam/dry biomass ratio (-)	2.0
Nitrogen feed rate (L/min)	10
Ceramic filter temperature (°C)	650
Chloride sorbent bed temperature (°C)	400

Table 4-1: Typical gasifier operating conditions and primary process parameters.

4.2.3 Biomass Gasifier Product Gas Sampling and Analytical Methods

The product gas stream was quantitatively sampled for the analysis of permanent gas species, sulfur and nitrogen species, tar species, water content and ammonia and chloride concentrations. Samples were taken at the exit of the high temperature ceramic filter or downstream of the fixed-bed reactor vessel. Samples from two locations can be collected in unison if desired. The sampling program for a particular test depends upon the test objective. For the chloride sorbent tests, the gas stream was sampled for the quantification of chloride concentrations in the pre- and post-sorbent treated gas stream ("bypass gas" and "treated gas" respectively). Analysis of the samples was used to characterize sorbent performance. Other samples were collected to quantify the operational conditions of the gasifier during the tests.

4.2.3.1 Chloride Samples

The chloride samples were collected by passing a sample gas stream through a single stainless steel impinger that contained 150 ml of dilute sulfuric acid (0.2 N) as trapping solution (Norton and Brown, 2005). The impinger was placed in an ice bath. The sample

flow through the impinger was maintained at ~ 2 L/min using a vacuum pump, and a total of 40 L of dry gas were extracted for each sample. Two impingers in series were used in the initial gasification testing described in Section 4.3.1, and the results showed that the first impinger captured >99% of the total Cl⁻. Thereafter, only a single impinger was used for the gasification tests described in Section 4.6.

As the product gas passes through the impinger, the chloride is extracted from the gas stream and is held in the trapping solution. The final solution was recovered after each test and chloride concentrations were measured with a combination chloride ion-selective electrode (Model 9617B, Orion Research, Inc.). A primary calibration standard was prepared by dissolving reagent-grade NaCl in a 0.2 N H_2SO_4 solution. Lower concentration calibration standards were produced by serially diluting the primary standard. The dry gas volume drawn through the impinger was related to the chloride concentration of the post-sample solution to calculate the chloride concentration of the product gas.

4.2.3.2 Water Sampling

The water content of the gasifier product gas was sampled using a series of two impingers that contain 100 ml of 2-propanol (IPA) as a trapping solution. The impingers were placed in an ice bath. The sample flow through the impinger set was maintained at ~ 4 L/min using a vacuum pump, and a total of 80 L of dry gas was extracted for each sample. The trapping solution was recovered from each of the impinger sets and refrigerated until analyzed. The water content was analyzed using the *ASTM E203-08 Standard Test Method for Water Using Volumetric Karl Fischer Titration* using a Karl Fischer titrator (Model DL31, Mettler-Toledo, Inc., Columbus, OH). The water content

of the impinger trapping solution was related to the gas volume drawn through the impingers to calculate the partial pressure of water in the product gas.

4.2.3.3 Permanent Gas Sampling

A sample from the bypass or treated gas was directed to an online gas chromatograph (AutoSystem, Perkin-Elmer, Norwalk, CT), equipped with a 1.5 m \times 3 mm packed column (Carboxen 1000, Supelco, Bellefonte, PA) and a thermal conductivity detector (TCD). A sample was injected by an automatic sampling valve every 20 min and the gas species H₂, N₂, CO, CH₄, CO₂, C₂H₄, and C₂H₆ in the gas sample are quantified.

The bypass gas stream is also directed to a three-channel, online, nondispersive infrared (NDIR) gas analyzer (model URAS 10E, Applied Automation/Hartmann and Braun, Bartlesville, OK), equipped to analyze CO, CO₂, and CH₄, and a continuous-flow, thermal conductivity detector (model CALDOS 5G, Applied Automation/Hartmann and Braun, Bartlesville, OK), which measures the product gas H₂ concentration. An additional gas stream is directed to a chemiluminescent analyzer for the detection of oxides of nitrogen as NO (model 10-AR, Thermo Environmental Instruments, Franklin, MA). The online analyzers are calibrated prior to each test using certified zero and span gases. During the test, the online analyzers are continuously monitored to gage the system performance and to determine when the system has reached a steady state.

4.2.3.4 Solid Samples

The fuel and stream inputs are simultaneously stopped at the conclusion of a test and the system is purged with bottled N_2 . Solid samples remaining in the gasifier bed and filter chamber are collected after each test. For the final gasification tests described in Section

4.6, the filter char was subjected to ultimate (C, H, O, N, S and Cl), proximate (volatile, fixed carbon and ash) and elemental ash analyses (Si, Al, Ti, Fe, Ca, Mg, Na, K, P, S, Cl, and CO₂) by Hazen Research, Inc., Golden, CO.

4.3 Preliminary Investigations of Chloride in the Biomass Gasifier

To develop an initial understanding of the nature of chloride in a biomass gasification system, initial investigations were performed with the bench-scale gasifier system, and a thermo-chemical equilibrium model was used to predict the chemical composition of the bypass gas entering the chloride removal reactor vessel. The results of this preliminary investigation defined the methods used for the remainder of the research, including the design of the lab-scale experimental apparatus for the testing of lab-manufactured chloride sorbent materials.

4.3.1 Initial Bench-Scale Gasification Investigations

Ten tests were performed where five different materials were loaded in the fix-bed chloride removal reactor vessel. The materials included inert ceramic balls, two nickel catalysts (Sud-chemie G91 and Sud-chemie C11-NK), zinc oxide (Sud-chemie G-72E) and a commercially available chloride sorbent (BASF CL-750). The tests, identified with the TYYYYMMDD nomenclature, were conducted as follows: T20080318 (Zinc Oxide G-72E); T20080403 (Nickel Catalyst G91); T20080408 (Ceramic Balls); T20080411, T20080417 and T20080425 (Nickel Catalyst C11-NK); T20080930, T20081125, T20081211 and T20081219 (BASF CL-750). The wet gas GHSV in the fixed-bed reactor during the four CL-750 tests averaged at about 1,500 hr⁻¹, 2,000 hr⁻¹, 4,300 hr⁻¹ and 3,500 hr⁻¹ for the 20080930, 20081125, 20081211 and 20081219 tests, respectively.

The bypass and treated gas streams were sampled over the course of each test. The results from the analysis of these samples provided data on the typical levels of chloride present in the gasifier product stream as well as the ability of the tested materials to remove chloride under system operating conditions. Importantly, these initial tests verified that the methods used to evaluate sorbent materials in the gasifier are capable of producing statistically valid results.

4.3.2 Thermochemical Equilibrium Calculations

To develop a sorbent capable of sufficiently removing chloride from the biomass gasifier syngas, the molecular form of the chlorine present in the gasifier should be well understood. A thermochemical equilibrium model was developed to predict the chemical composition of the biomass gasification product stream. Although a kinetic model would provide a more detailed view of the chemical formations occurring over time within the system, it was necessary to use an equilibrium model because not enough is currently known on the reaction rate parameters required for kinetic modeling (Turn, 2007).

The equilibrium calculations were performed using the software package, FactSage© 5.4.1. A brief description of the software and its capabilities provided by FactSage is reproduced below:

"FactSage©, one of the largest fully integrated database computing systems in chemical thermodynamics in the world, was introduced in 2001 and is the fusion of the FACT-Win/F*A*C*T and ChemSage/SOLGASMIX thermochemical packages. FactSage is the result of over 20 years of collaborative efforts between Thermfact/CRCT (Montreal, Canada) www.crct.polymtl.ca and GTT-Technologies (Aachen, Germany) www.gtt-technologies.de.

The FactSage package runs on a PC operating under Microsoft Windows® and consists of a series of information, database, calculation and manipulation modules that access various pure substances and solution databases. FactSage has several hundred industrial, governmental and academic users in materials science, pyrometallurgy, hydrometallurgy, electrometallurgy, corrosion, glass technology, combustion, ceramics, geology, etc. It is used internationally in graduate and undergraduate teaching and research.

Users have access to databases of thermodynamic data for thousands of compounds as well as to evaluated and optimized databases for hundreds of solutions of metals, liquid and solid oxide solutions, mattes, molten and solid salt solutions, aqueous solutions, etc. The FactSage software automatically accesses these databases. The evaluated databases for oxides, slags, mattes, etc. have been developed by optimization of literature data using advanced modeling techniques, several of which have been developed at the CRCT. FactSage can also access the databases for steels, light metal alloys and other alloy systems developed by The Spencer Group, GTT-Technologies and the CRCT.

With FactSage you can calculate the conditions for multiphase, multicomponent equilibria, with a wide variety of tabular and graphical output modes, under a large range of constraints. For example, general N-component phase diagram sections can be easily generated with a wide choice of axis variables; matte/metal/slag/gas/solid equilibria can be accurately calculated, tabulated and plotted for industrial systems; multicomponent predominance and EpH diagrams can be readily produced; the course of equilibrium or non-equilibrium solidification can be followed; complex heat balances can be computed; and so on" (Anon., 2010).

The FactSage model was applied to perform two sequential equilibrium calculations. The first calculation predicted the composition of the product gas at the outlet of the fluidizedbed. The calculation used the results of the Hazen elemental analysis of the biomass fuel¹, the chemical composition of the bed material, and the steam and nitrogen feed rates into the system as inputs and was performed at the gasifier temperature (~800°C). The second calculation predicted the composition of the product gas at the outlet of the filter and used the results of the first calculation as input. The second calculation was performed at a range of potential filter operating temperatures ($400 - 700^{\circ}$ C) to investigate how the filter temperature affects the concentration of chloride-containing molecules in the product gas. All calculations were performed at a pressure of 101.3 kPa to represent the normal operating pressure of the gasifier unit.

The inputs to the first calculation were based on the assumption of an average fuel feed rate of 1 kg/hr, a 2.0 kg/hr steam-feeding rate (steam-to-fuel feed ratio of 2.0), a nitrogen feed rate of 12 L/min and 10.0 kg of bed material loaded in the reactor. The bed material was included in the equilibrium calculations because previous research by Turn (2007)

¹ Leucaena leucocephala sample analyzed by Hazen Research, Inc., Golden, CO for Turn, Scott, Hawaii Natural Energy Institute April 4, 2007

found that the outer lay of the bed material can act a sink to impact the gas phase release of inorganic fuel elements. The study concluded that 1.08% of the actual bed material mass (equal to a 1- μ m-thick outer layer of the bed particles) should be included in the chemical equilibrium calculations so that the predicted potassium, sodium and chlorine concentrations in the biomass gasification product gas best match the concentrations suggested by the experimental data (Turn, 2007). To be consistent with these findings, 108 g of bed material were input into the equilibrium equations. The chemical inputs described above were normalized to the total moles of carbon input into the reactor and were input into the FactSage program (Table 4-2).

Biomass Fuel (Leucaena) Composition:	Moles relative to one mole of carbon
С	1.000000
Н	1.375980
Ν	0.005007
S	0.000353
0	0.557581
Cl	0.000836
Si	0.000096
Al	0.000019
Ti	0.000002
Fe	0.000018
Ca	0.001113
Mg	0.000537
Na	0.000173
Κ	0.000861
Р	0.000200
Bed Material Composition:	
Al ₂ O ₃	0.001039
$Al_6Si_2O_{13}$	0.010442
SiO ₂	0.000312
TiO ₂	0.000390
Fe ₂ O ₃	0.000208
Other Gasification Inputs:	
H ₂ O (Steam)	2.511893
Nitrogen	0.666269

Table 4-2: Summary of inputs to the FactSage thermo-chemical equilibrium calculations.

4.4 Sorbent Preparations

This research focused on quantifying the HCl sorbent capacity of lab-prepared sorbents made using locally available materials including coal ash from two power plants and limestone from a quarry on the island of Oahu. The sorption characteristics of the materials were investigated with and without modification by hydration techniques (calcination and slaking). The sorption performance of the prepared sorbent materials were compared to those of BASF CL-760, a commercially available high temperature HCl sorbent manufactured by the BASF Corporation. The results of this work were used to prepare a sorbent that provides chloride adsorption in the biomass gasifier product stream.

4.4.1 Raw Material Collection from HC&S and AES

Two coal ash samples were collected from Hawaiian Commercial & Sugar's coal/biomass-fired boiler located in Puunene, Maui, HI. The samples were obtained on July 2, 2010. During this period, the HC&S boiler was burning only coal and was not burning biomass. The first ash sample was collected directly from the boiler (Figure 4-4). The hot sample was placed into a galvanized steel can and allowed to cool overnight before being stored in a sealed five gallon plastic bucket. This sample is referred to as the "Unquenched HC&S Coal Ash" (Figure 4-5). The second sample was of ash that had been quenched in water after it had left the boiler. A conveyor removed the ash from the water and deposited it in the bed of a dump truck for disposal. The sample was extracted from the truck bed (Figure 4-6) and labeled "Quenched HC&S Coal Ash" (Figure 4-7). A sample of the coal was also collected from the conveyor belt that delivers the coal from its storage location to the boiler. This sample is referred to as "HC&S Virgin Coal."



Figure 4-4: Picture of the unquenched coal ash being collected from the HC&S boiler.



Figure 4-5: Picture of the as-received HC&S unquenched ash sample.



Figure 4-6: Picture of the quenched coal ash being collected at HC&S.



Figure 4-7: Picture of the as-received HC&S quenched ash sample.

Raw material samples were also collected from the Applied Energy Services (AES) Hawaii, Inc. medium-size, 180 MW, coal-fired electrical power station located within the Campbell Industrial Park in Kapolei, Oahu, HI. Samples of the fly ash and bottom ash produced from the coal combustion process at the facility were provided by AES. These samples were labeled "AES Fly Ash" and "AES Bottom ash" (Figure 4-9), respectively. A sample of the coal feedstock was also collected (Figure 4-10). Powdered limestone (200 mesh size) is input into the AES coal combustion process as a fluidized-bed material to capture sulfur. A sample of the limestone was collected from the holding area outside of the AES plant. The sample, labeled "AES Bed Material" (Figure 4-11), is representative of the gravel-sized limestone material that is delivered to AES by Pacific Aggregate (Sphere, LLC). Pacific Aggregate markets this product as "coral chip" and produces it from its quarry in Waianae, Oahu.



Figure 4-8: Picture of the as-received AES fly ash sample.



Figure 4-9: Picture of the as-received AES bottom Ash sample.



Figure 4-10: Picture of the as-received AES coal sample.



Figure 4-11: Picture of the as-received AES bed material sample.

4.4.2 Sorbent Preparation Methods

The techniques used to prepare the sorbent materials for this study are described in the following sections.

4.4.2.1 Pellet Preparation

The HC&S quenched ash and unquenched ash samples and the AES fly ash, bottom ash and bed material samples were used as the parent material in a variety of sorbent preparations. The materials were crushed into powder, mixed with various binder materials and formed into pellets using a manual pellet press (Part 2800, Reflex Analytical Corp., Ridgewood, NJ) with a 3.18 mm (1/8 inch) pellet die (Part No. 2804 Reflex Analytical Corp., Ridgewood, NJ). The ratio of parent material to binder material and the type of binder material was varied until pellets of sufficient strength to undergo testing were formed (Figure 4-12 and Figure 4-13). The investigated binder materials included kaolin powder (Code 1814, Baker & Adamson, General Chemical Division, Allied Chemical & Dye Corp., New York, NY), cement (Hawaiian Cement Ultramortar, Knife River Corp., Aiea, HI), potato starch (Code 8180, Mallinckrodt Inc., Hazelwood, MO) and corn starch (ARGO®, ACH Food Companies, Inc., Memphis, TN). In addition, the literature review indicates that calcium oxide (CaO) can be successfully used to form chloride adsorbents (Section 3.4.1), so CaO powder (C117-500, Fisher Scientific Company, Fair Lawn, NJ) was mixed into some of the sorbent preparations. Dependent on the binder material used, the sorbent preparations were either air dried or were heated to 315°C in an oxidizing environment to remove volatile materials before undergoing testing. All the sorbent recipes that included starch, for instance, were heated before undergoing testing in the fixed-bed reactor.



Figure 4-12: The pellets formed with the hydrated AES fly ash were durable.



Figure 4-13: Once dried, the pellets that were formed with hydrated AES bottom ash were fragile and crumbled easily.

4.4.2.2 Hydration Process

A previous study concluded that the maximum HCl sorption capacity of coal ash is obtained after the material is calcined and then hydrated in a solution of 7% glycerin (Hirabayashi et al., 2002). Based on this research, the sorbent materials were prepared using a similar process (Figure 4-14). The material was placed in a programmable muffle furnace (Model 58, Fisher Scientific, Hanover Park, IL) that was purged with a constant flow of bottled nitrogen. The heating routine programmed into the furnace (Figure 4-15) first involved drying the raw material at 150°C for three hours. The material was then calcined at 850°C for six hours to expel volatile materials including CO₂. The calcined material (Figure 4-16) was brought down to 105°C and was then hydrated in a solution containing 7% glycerin (G33-4, Fisher Scientific, Fair Lawn, NJ) and 20% corn starch

(ARGO®, ACH Food Companies, Inc., Memphis, TN) by weight in deionized water. The material was slaked in the hydration solution for about one hour while being stirred by a magnetic rod. The calcination and slaking process dissolved the 10 mm (0.375 inch) AES bed material into a slurry without any mechanical means of size reduction. The hydrated solution was then placed back into the furnace to dry at 105°C for six hours. The dried material was crushed by hand and sifted through two U.S.A. Standard Test Sieves meeting the ASTM E-11 specification. 100% of the crushed material was made to pass through a US Std. No. 7 mesh (Cat. No. 04-881E, Fisher Scientific, Hanover Park, IL). The material was then sifted through a US Std. No. 16 mesh (Cat. No. 57334-108, VWR International, LLC). The granules that were retained by the No. 16 mesh were collected as the sorbent material. These granules have diameters of between 2.8 mm (0.11 in) and 1.18 mm (0.0469 in). The sorbent granules were then cooked at 450°C for six hours to burn off volatile materials (including starch). The final material was weighed and later tested as a chloride sorbent (Figure 4-17).

Raw Parent Material



Calcined Material



Hydrated Material



Prepared Sorbent

- Raw parent material dried at 150°C for 3 hours
- Temperature increased to 850°C at rate of 5°C/min
- Material calcined at 850°C for 6 hours in a nitrogen environment
- Temperature decreased to 105°C at rate of -2°C/min
- Hot material (105°C) added to room temperature hydration solution containing 7% glycerin and 20% starch by weight in deionized water
- Material slaked in hydration solution for 1 hour while being stirred
- Solution placed in oven at 105°C for 6 hours to dry
- Material crushed and granules with diameters between 2.8 mm and 1.18 mm separated as the sorbent material
- Sorbent granules cooked at 450°C for 6 hours to burn off volatile species




Figure 4-15: The heating routine for the calcination step of the hydration process.



Figure 4-16: A sample of AES bed material after being calcined at 850°C for 6 hours.



Figure 4-17: The finished sorbent material prepared with hydrated AES bed material and reduced to granules between 2.8 mm and 1.18 mm in diameter.

4.4.3 Other Materials Obtained for Chloride Adsorption Testing

In addition to the sorbents prepared with HC&S unquenched ash and quenched ash samples and the AES fly ash, bottom ash, and limestone bed material samples, commercially available materials were obtained for chloride adsorption testing. These materials include a commercial chloride sorbent (CL-760, BASF, Iselin, NJ), a coconut shell activated carbon (OLC Plus 12X30, Calgon Carbon Corporation, Pittsburgh, PA) and a lime fertilizer product (Garden Lime, Organic Traditions[™], The Espoma Co., Millville, NJ).

BASF CL-760 is a spherical surface modified "promoted chloride adsorbent" that "offers the benefits of the leading chloride adsorbent CL-750 with even greater HCl pickup... It is custom formulated to provide optimum adsorption of HCl from vapor and liquid phase

process streams." BASF CL-760 is applicable for use in vapor phase chloride traps in catalytic reforming processes, HCl removal from liquid naphtha reformate streams at both ambient and elevated temperature, and "removal of HCl and free chloride ions from a variety of vapor and liquid phase streams in numerous petrochemical production processes" (Anon., 2009).

4.5 Lab-Scale Sorbent Testing

The following sections describe the laboratory scale apparatus and methods used in evaluating candidate sorbents.

4.5.1 Experimental Apparatus

A lab-scale experimental apparatus was designed and built to test the chloride sorption capacity of individual sorbent materials under conditions that simulate a fixed-bed reactor located downstream of a biomass gasifier. Simulating the biomass gasifier product stream requires hot gas that contains permanent gas species, water, and chloride in the appropriate representative concentrations. Other species measured in the biomass product gas, sulfur and nitrogen containing molecules, tar species, ammonia, and trace elements, were not included in the gas stream supplied to the experimental apparatus.

All of the wetted components of the experimental apparatus including the reactor column and the gas and liquid delivery lines and fittings are made of HCl resistant materials such as quartz or polytetrafluoroethylene (PTFE). Special consideration was given to the material selection not only to enhance the durability of the apparatus, but also to prevent the adsorption of chloride compounds on the working surfaces of the system. By avoiding HCl reactive materials such as stainless steel, the adsorption of chloride could only be attributed to the sorbent material undergoing testing. Shake-down testing was performed to ensure that the system components were not interfering with the transport of HCl through the system.

A vertically oriented quartz tube 121.9 cm (4.0 feet) in length and 1.6 cm in inner diameter was used as the reactor column (Item 16X19, Technical Glass Products, Inc., Painesville Twp., OH). For each test, ~4 g of sorbent material was placed at the approximate midpoint of the column and is held in place by a ~1 g plug of quartz wool (Item 338-222-50, Fisher Scientific, Hanover Park, IL). The depth of the sorbent bed was dependent on the bulk density of the sorbent material, but ranged from 1.6 to 5.7 cm for these tests. Because the sorbent fixed bed was placed in the middle of the relatively long reactor column, it was assumed that gas flow was distributed evenly across the bed cross-section.

The reactor column was heated by a tube furnace (Thermolyne 21100, Barnstead/Thermolyne Corp., Dubuque, IA) to an operational temperature of ~400°C at the middle of the sorbent bed. The set point for the tube furnace chamber temperature was calibrated prior to the test. For these tests, the calibration results indicated that the furnace should be set to 375° C to maintain the sorbent bed temperature at 400° C.

A compressed gas cylinder containing a gas mixture designed to replicate concentrations of the permanent gas species in the biomass gasification product stream (Table 4-3) was ordered from Airgas Gaspro, Honolulu, HI. The bottled gas was supplied to the apparatus through a stainless steel combustible gas regulator (Model 3810-CGA350, Matheson Tri Gas, Newark, CA) and was metered into the reactor column at a flow rate of ~40 cc/min at room temperature by a mass flow controller (Brooks Instrument Model 5850 E C4BD3SD2A, Process Controls Inc., Aiea, HI). A cylinder of compressed nitrogen gas was also supplied to the system through a brass nitrogen regulator (3122-CGA580, Matheson Tri Gas, Newark, CA) and was also metered into the apparatus by the Brooks 5850 mass flow controller. The nitrogen was initially used for the shake-down testing of the apparatus and was also used to purge the system before and after each test. The mass flow controller was calibrated to deliver the mixed gas at the appropriate rate using a mini-BUCK Calibrator M-1 electronic bubble flow meter (APB-801000, A. P. Buck Inc., Orlando, FL).

	Composition of the mixed gas cylinder	Composition of carrier gas in the sorbent column at reactor temperature
Mixed Gas:		
Nitrogen (%)	37.0	18.5
Hydrogen (%)	33.0	16.5
Carbon Dioxide (%)	15.0	7.5
Carbon Monoxide (%)	10.0	5.0
Methane (%)	5.0	2.5
Water (%)	0.0	50.0
Chloride (ppmw)	0	600 - 700

Table 4-3: Typical composition of the gas stream in the experimental apparatus.

A dilute hydrochloric acid solution with a chloride (Cl⁻) concentration of ~2,500 ppmw was metered into the carrier gas stream at a rate of ~0.03 ml/min by a peristaltic pump consisting of a 100 rpm Masterflex® L/S® Digital Drive (EW-07523-90, Cole-Parmer Instrument Co., Vernon Hills, IL), a low-pulsation synchronous flow multichannel pump head (HV-07534-04, Cole-Parmer Instrument Co.) and 0.19 mm ID Microbore PVC

tubing (HV-06416-10, Cole-Parmer Instrument Co.). The speed of the peristaltic pump drive was calibrated to deliver the appropriate flow prior to the test. The hydrochloric acid solution joined the carrier gas stream at the entrance to the reactor column. The temperature of the column caused the HCl solution to vaporize and mix with the carrier gas to form a gas stream that was representative of the gasification product gas (Table 4-3). The gas stream had a Cl⁻ concentration of ~650 ppmw and a gas hourly space velocity (GHSV) of ~1,000 h⁻¹ as it passed through the sorbent bed.

The gas stream exiting the sorbent column was quenched in a glass receiving flask that contains deionized water as a chloride trapping solution. The trapping solution was cooled by room temperature water circulated through the jacket surrounding the flask by a pump. A type K thermocouple (Omega Engineering, Inc., Stamford, Ct) monitors the temperature of the flask over the duration of the test. A chloride ion selective electrode (9617BNWP, Thermo Scientific Orion, Waltham, MA) measured the concentration of the chloride contained in the trapping solution. The electrode reading (in mV) was continuously monitored and recorded by a data acquisition system (CR23X Micrologger, Campbell Scientific, Inc., Logan, UT). The electrode was calibrated with serial dilutions of a 10,000 ppmw Cl⁻ primary calibration standard prepared by dissolving reagent-grade HCl in deionized water. The calibration curve was applied to the electrode reading to determine the concentration of the chloride in the trapping solution.

The CR23X Micrologger also recorded the readings from the thermocouple in the flask and a second type K thermocouple located in the middle of the tube furnace chamber. The furnace chamber temperature data was used to determine when the fixed bed temperature had reached a steady state, and thus, when chloride sorption testing could begin. The alarm signal wires from a general purpose hazardous gas detector (HIC-822, Industrial Test Equipment Co., Port Washington, NY) was also wired to the CR23X Micrologger. If the hazardous gas monitor detected a gas leak, the Micrologger was programmed to stop the test by actuating a relay to shut off power to the tube furnace, peristaltic pump, and mass flow controller. The components of the lab-scale experimental setup are shown in Figure 4-18, Figure 4-19 Figure 4-20 and Figure 4-21.



Figure 4-18: Schematic of the lab-scale experimental apparatus for testing chloride sorbent materials.



Figure 4-19: The lab-scale experimental apparatus for testing the chloride sorbents.



Figure 4-20: The experimental apparatus includes the: (1) data acquisition system, (2) tube furnace controller, (3) tube furnace, (4) reactor column, (5) mass flow controller, (6) hazardous gas alarm, (7) mixed gas cylinder, (8) nitrogen cylinder and (9) gas flow calibrator.



Figure 4-21: The lower half of the experimental apparatus includes the: (10) peristaltic pump, (11) trapping solution flask, (12) reactor column entering the flask, (13) chloride ion selective electrode in the flask, and (14) thermocouple in the flask.

Over the course of a test, the liquid level in the receiving flask increased due to the water vapor present in the gas stream. As discussed previously, water was metered into the apparatus by the peristaltic pump at a rate of ~0.03 ml/min. To insure that the trapping solution maintained a stable concentration throughout the duration of the test, a separate line pumped fresh solution into the flask at a rate of ~0.03 ml/min. To keep the flask from overflowing, a separate, larger diameter line operated by the peristaltic pump evacuated solution from the flask at a constant rate of approximately 0.06 ml/min. This insured that the Cl⁻ concentration within the flask only increases dramatically due to the breakthrough of the sorbent material. When there was no sorbent loaded in the reactor

column, or when a sorbent material was ineffective at adsorbing Cl⁻, the increase in the Cl⁻ concentration in the trapping solution was predicted over the course of the test by

$$\begin{bmatrix} \text{Cl}^{-} \end{bmatrix}_{\substack{Flask \\ @ t}} = \begin{bmatrix} \text{Cl}^{-} \end{bmatrix}_{\substack{Flask \\ @ t - \Delta t}} + \frac{\Delta t}{M_{Soln}} \left(\begin{bmatrix} \text{Cl}^{-} \end{bmatrix}_{IN} - \begin{bmatrix} \text{Cl}^{-} \end{bmatrix}_{OUT} \right)$$
(8)

Where,

$$[Cl^{-}]_{Flask}$$
 is the concentration of chloride in the flask (g Cl⁻/g soln) at time t;

- $\begin{bmatrix} Cl^{-} \end{bmatrix}_{Flask}_{@t-\Delta t}$ is the concentration of chloride in the flask (g Cl⁻/g soln) at the previous time step $(t-\Delta t)$;
- Δt is the time step of data acquisition routine (0.08333 minutes for these tests);
- M_{Soln} is the mass (g) of the trapping solution in the flask at the onset of the test (~300 g minutes for these tests);
- $[C\dot{l}^{-}]_{IN}$ is the rate (g Cl⁻/min) that chloride is added to the flask from the gas (assuming no adsorption);
- $[C\dot{l}^{-}]_{OUT}$ is the removal rate (g soln/min) that chloride is removed from the flask with the trapping solution that is pumped out of the flask.

4.5.2 Initial Testing of the Experimental Apparatus

The initial testing of the experimental apparatus was conducted to determine its ability to produce scientifically valid results. The tests were performed with the same conditions as a typical sorbent performance test except that no sorbent material was loaded in the reactor column. With the column containing only the quartz wool plug that normally supports the sorbent bed, it was expected that all of the Cl⁻ injected into the column

would be collected in the trapping solution. The increase in the Cl⁻ concentration in the trapping solution was determined from the chloride electrode data and was compared to the theoretical increase in Cl⁻ concentration as determined by Equation 8.

The initial testing was used to determine if changes to the design were necessary. Of concern was the composition of the trapping solution. The apparatus was designed to use pure deionized water as the trapping solution. Of concern was whether sulfuric acid should be added to the trapping solution since a 0.2 N sulfuric acid solution was used to collect the chloride and ammonia samples during the gasification tests. In addition, whether Chloride Ionic Strength Adjuster (CISA) should be added to the trapping solution for the lab-scale experimental tests. According to the chloride ion selective electrode user's manual, when analyzing samples with the electrode, CISA should be added to the samples and standards to create a uniform background ionic strength that provides more reproducible measurements. The addition of CISA to the trapping solution and standards used for this experimental investigation may not be necessary, however, because it is expected that ions other than Cl- will only exist in low concentrations.

4.5.3 Evaluation of Sorbent Performance

The methods used to evaluate the sorbent performance are described in the following sections.

4.5.3.1 Breakthrough Testing

The chloride sorption capacity of the candidate sorbents was determined by breakthrough testing in the experimental apparatus under conditions that were representative of a biomass gasifier environment (typically [CI⁻]: 650 ppmw, GHSV: 1000 hr⁻¹, bed temperature: 400°C). Approximately 4 g of sorbent material was loaded into the reactor column. When the temperature of the sorbent bed reached a steady-state, the test was started by turning on the peristaltic pump and initiating the injection of HCl into the system. The chloride concentration of the trapping solution within the flask was continuously monitored by the ion selective electrode and the data acquisition system. The sorbent breakthrough was defined as the time where the chloride concentration in the trapping solution first attained a 5.0 ppmw increase from the initial concentration. The breakthrough curves for all the tested sorbent materials were compared to determine the top performing chloride sorbent materials.

4.5.3.2 Determination of the Maximum Gas Hourly Space Velocity

The two self-prepared sorbent materials with the greatest chloride sorption capacity were selected for further testing to determine when increasing the gas hourly space velocity (GHSV) impaired the ability of the materials to adsorb chloride from the gas stream. The experimental apparatus test conditions were selected to reproduce the conditions typical of the fixed-bed sorbent reactor in the HNEI biomass gasifier facility (Bed Temperature: 400° C, [CI⁻]: ~12 ppmw, [H₂O]: ~50%). Each sorbent material was loaded into the reactor column such that bed length to bed diameter (L/D) ratio was equal to 1.0. Over the course of each test, the peristaltic pump and the mass flow controller delivery rates were periodically adjusted to increase the GHSV of the gas flow through the sorbent bed from 1,000 hr⁻¹ to as much as 54,000 hr⁻¹. The rate increases were systematically adjusted to insure that the gas composition remained constant at each set point. The

chloride concentration in the trapping solution was monitored at each GHSV set point to observe the point where the increased GHSV led to unsatisfactory sorbent performance.

4.6 Bench-Scale Gasifier Evaluation of Self-Prepared Sorbent Materials

The two self-prepared sorbent materials that were found to have the greatest chloride sorption capacity in the lab-scale experimental tests were tested as chloride sorbents in the HNEI bench-scale biomass gasification unit. The performance of each sorbent material was evaluated during a single gasification test over a range of gas hourly space velocities (GHSVs) to further test the effect of gas residence time on the chloride adsorption capacity of the materials. The general test procedures for the gasifier tests were described in detail in Section 4.2, and therefore, will not be reproduced here. The specific details of these tests are described as follows.

4.6.1 Bench-Scale Gasifier Testing Method

For each test, the self-prepared sorbent material was loaded into a 50.8 mm (2.0 in) internal diameter reactor column to a height of ~50.8 mm, creating a fixed bed with an L/D ratio of 1.0. Over the course of each test, the flow through the sorbent reactor was incrementally increased to provide a range of GHSV's. For the sorbent evaluation Test ID # T20110518, the GHSV was varied from 8,789 hr⁻¹ to 51,412 hr⁻¹ over the course of the test. For Test ID # T20110525, the GHSV was varied from 3,121 hr⁻¹ to 12,788 hr⁻¹. Each test routine involved four GHSV set points. For each GHSV set point, the outlet gas stream from the sorbent reactor was sampled three times. During each test, three samples were also collected from the chloride reactor inlet gas stream. Each sample was collected by passing the gas stream through a single stainless steel impinger cooled by an ice bath. Each impinger contained 150 ml of dilute sulfuric acid (0.2 N) as the trapping

solution. The sample flow rate through the impinger was maintained at ~ 2 L/min using a vacuum pump, and a total of 40 L of dry gas were extracted for each sample. The post-sample solutions were recovered after each test and the chloride concentrations were measured with a chloride ion selective electrode (9617BNWP, Thermo Scientific Orion, Waltham, MA). The electrode was previously calibrated with serial dilutions of a 10,000 ppmw Cl⁻ primary calibration standard prepared by dissolving reagent-grade HCl in deionized water. The dry gas volume drawn through the impinger was related to the chloride concentration of the impinged solution to calculate the chloride concentration of the product gas.

4.6.2 Elemental and XRD Analyses of the Sorbent Materials

The sorbent parent materials, the hydrated sorbent preparations pre- and post- chloride breakthrough testing in the lab-scale apparatus, and the hydrated sorbent preparations pre- and post- bench-scale biomass gasification testing were subjected to elemental analyses (Si, Al, Ti, Fe, Ca, Mg, Na, K, P, S, Cl, and CO₂) performed by Hazen Research, Inc., Golden, CO and to x-ray diffraction (XRD) analyses performed by The Mineral Lab, Inc., Golden, CO. The filter char samples collected after each biomass gasification test were also subjected to elemental ash analyses. The Mineral Lab XRD analyses were performed as follows:

"A representative portion of each sample was ground to approximately -400 mesh in a steel swing mill, packed into a well-type plastic holder and then scanned with the diffractometer over the range, 3-61 °28 using Cu-Ka radiation. The results of the scans are summarized as approximate mineral weight percent concentrations on the enclosed table. Estimates of mineral (crystalline phases) concentrations were made using our XRF-determined elemental compositions and the relative peak areas on the XRD scans. Some of these samples appear to contain "amorphous" (noncrystalline) material. Amorphous material appears only as a broad elevation in the background of the XRD scan so its composition cannot be determined and the estimate of its concentration must be considered an educated guess based on the difference between the total mineral concentration and 100%. The detection limit for an average mineral in these samples is -1-3% and the analytical reproducibility is approximately equal to the square root of the amount. "Unidentified" accounts for that portion of the XRD scan which could not be resolved and a "?" indicates doubt in both mineral identification and amount" (Dalheim, 2010).

4.6.3 Mass-Balance of Bench-Scale Biomass Gasification Tests

Two mass balances were calculated for each bench-scale biomass gasification test. The first calculation balanced the chloride for the gasifier system over the entire duration of the test. The total Cl input was determined by multiplying the amount of *Leucaena* fuel input to the reactor by the Cl content of the fuel. The total Cl output was estimated as the sum of the Cl content of the product gas and the Cl content of the filter char. The Cl output in the product gas was estimated by multiplying the mean chloride concentration in the untreated product gas by the total volume of product gas produced during the test. The Hazen Research elemental ash analysis results for the Cl content of the filter char sample was multiplied by the amount of filter char collected at the end of test to determine the Cl output in the char.

Water and N_2 were excluded from the input streams in the mass balance calculation under the assumption of negligible Cl contribution from pure water (grade II, deionized water) and compressed N_2 that were used in the tests. A significant amount (~ 9.5 kg) of bed material was used in the fluidized bed during each gasifier test. Chlorine elements may have potentially been retained on the surface of bed material (Turn et al. 1998c). Also, unreacted char remained embedded with the bed material that was difficult to separate. Compared with the weight of char collected from the filter, the amount of bed char was commonly 16-19%. The bed material and the bed char were not analyzed for chlorine concentration and were not included in the mass balance calculation.

The second mass-balance calculation compared the Cl inputs and outputs to the fixed-bed sorbent reactor over the duration of the gas treatment period. The inputs included the freshly prepared sorbent materials and the untreated product gas. The outputs included the post-test sorbent materials and the treated product gas. The Cl contents of the preand post- gasification test sorbents were determined by multiplying the Hazen Research results for the elemental ash Cl content of the materials by the amount of material loaded into and collected from the reactor, respectively. The Cl input to the reactor by the untreated product gas was estimated by multiplying the mean chloride concentration in the untreated product gas by the total volume of syngas passed through the reactor. The Cl output from the reactor due to the treated product gas was estimated by taking the sum of the mean chloride concentration in the treated product gas by the total volume of treated product gas passed through the impinger for each of the four GHSV set points.

5.0 RESULTS AND DISCUSSION

The experimental results for the investigations into the biomass fuel properties, the initial bench-scale gasifier and thermochemical equilibrium chloride concentrations, and the lab-scale and bench-scale biomass gasifier tests of the self-prepared sorbent materials are presented and discussed in the following sections.

5.1 Fuel Properties

The results of the Hazen analyses of the biomass fuels used in this study are presented in Table 5-1. The "20070404 *Leucaena*" sample was collected from the *Leucaena* fuel used in the initial biomass gasification investigations described in Section 4.3.1 and in the thermochemical equilibrium calculations described in Section 4.3.2. The "T20110518 & T20110525 *Leucaena*" sample is of the biomass fuel used in the gasifier evaluation of the self-prepared sorbent materials described in Section 4.6. Both *Leucaena* fuel samples are from the University of Hawaii Experiment Station at Waimanalo, Oahu. The results of the proximate analysis show that the mean chlorine concentration of the dry *Leucaena* fuel is 0.121%, which is comparable to that of switchgrass fuel (Duong and Tillman, 2009). The results of the ultimate analysis of the fuel ash after being calcined at 600°C indicate that the ash contains an average of 4.54% Cl. On average, 38.2% of the chlorine in the *Leucaena* fuel is retained in the ash.

	,	Т20110518 &	
	20070404	T20110525	
Samples	Leucaena	Leucaena	Average
Proximate Analysis (%, Dry)			U
Ash	0.87	0.87	0.87
Volatile matter	83.10	82.80	82.95
Fixed carbon	16.03	16.04	16.04
Sulfur	0.05	0.034	0.042
Energy Content (MJ/kg)			
HHV	19.52	19.17	19.34
MMF	19.70	19.41	19.56
MAF	19.69	19.39	19.54
Ultimate (Dry, ash free, %)			
[C]: Carbon	53.08	53.86	53.47
[H]: Hydrogen	6.13	6.24	6.19
[N]: Nitrogen	0.31	0.39	0.35
[S]: Sulfur	0.05	0.03	0.04
[O]: Oxygen (by difference)	39.56	38.32	38.94
[Cl]: Chlorine	0.131	0.110	0.121
Ash	0.87	1.16	1.02
Elemental analysis of ash (%, 600°C ash)			
SiO ₂	2.92	1.80	2.36
Al_2O_3	0.48	0.64	0.56
TiO ₂	0.09	0.05	0.07
Fe ₂ O ₃	0.73	0.80	0.77
CaO	31.70	23.10	27.40
MgO	11.00	5.27	8.14
Na ₂ O	2.72	1.92	2.32
K ₂ O	20.60	25.10	22.85
P_2O_5	7.20	6.38	6.79
SO ₃	1.69	2.43	2.06
Cl	4.05	5.02	4.54
CO_2	17.16	18.71	17.94
Total	100.34	91.22	95.78
Ash Fusion Temperatures (°C)			
Oxidizing Atmosphere			
Initial	1369	>1482	1426
Softening	1371		
Hemispherical	1372		
Fluid	1378		
Reducing Atmosphere			
Initial	1424	>1482	1453
Softening	1438		
Hemispherical	1443		
Fluid	1452		

Table 3-1. Lenguena fuel properties as determined by fiazen research analysi	Table 5-1:	Leucaena fuel	properties a	s determined	by Hazen	Research analys	sis.
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5.2 Initial Bench-Scale Gasification Investigations

A comparison of the average chloride concentrations in the gas stream exiting the fix-bed sorbent reactor over the course of the initial gasification investigations is provided in Figure 5-1. The results show that the chloride concentrations of the gas samples collected from the inlet of sorbent bed are comparable to the samples that passed through the ceramic balls, the two nickel catalysts and the zinc oxide, indicating that these compounds have little to no chloride adsorption capacity under the test conditions. The chloride concentrations in the product gas that passed through the bed of BASF CL-750 sorbent material during four separate gasifier tests, however, were considerably lower than the chloride concentrations in the inlet gas stream (Figure 5-2). These results indicate that the CL-750 sorbent is capable of significantly reducing HCl levels in the gasification product gas under typical operating conditions.

Error bars were applied to the data to illustrate the variability in the results of replicate experiments. The span of each error bar represents one standard deviation from the calculated mean. The mean and standard deviation reported for each sorbent material in Figure 5-1 were calculated from replicate data collected during a single or replicate gasifier test. The ceramic balls, G91, and ZnO materials each underwent one gasifier test, during which three or four replicate chloride samples were collected. The chloride concentration results for the Cll-MK and CL-760 sorbent materials as well as the "inlet" were calculated from larger sample sizes, totaling 12, 12 and 23 data points collected over three, four and ten gasifier tests, respectively. The error bars do not represent the experimental uncertainty due the resolution of the instruments used in the analysis and do not take into account the sample size (by calculating the standard error for instance).



Figure 5-1: Results from the initial tests of five materials in fixed-bed reactors.



Figure 5-2: Summary of differences between the average chloride concentrations in gasifier product gas at the inlet and outlet of the fixed-bed reactor during four experiments in which the BASF CL-750 was tested.

5.3 Thermochemical Equilibrium Calculations

The FactSage[®] thermochemical equilibrium calculation results are presented in Figure 5-3 through Figure 5-7. The results indicate that the composition of the biomass gasifier product gas varied with the temperature of the ceramic filter element and that chlorine-containing species of highest concentration in the product gas stream is hydrogen chloride (HCl). Other chlorine-containing species present in product gas in significant concentrations include KCl, NaCl, (KCl)₂, (NaCl)₂. Many other chloride-containing species exist, but in significantly smaller concentrations. These results are consistent with the results of previous studies that have used equilibrium calculations to conclude that high temperature gasification processes release chlorine primarily in the form of hydrogen chloride (Bjoerkman and Stroemberg, 1997; Li et al., 2004).

The results showed that when the temperature of the filter element was varied in the FactSage model from 300°C to 800°C, the HCl concentration peaks at about 300 ppmv (dry gas) at 400°C. At higher filter temperatures, the equilibrium concentration of HCl decreases to about 200 ppmv (Figure 5-3). The equilibrium concentrations of the four other significant chlorine-containing gas species increased at temperatures higher than 400°C (Figure 5-4 through Figure 5-7). The equilibrium concentrations of the (NaCl)₂ and (KCl)₂ gas peaked at a temperature of 700°C at 4.0 and 1.8 ppmw, respectively, and subsequently decrease when the gas composition was calculated at 800°C. The combined concentrations of the two prevalent solid chlorine species in the gasification product gas, KCl (sylvite) and NaCl (halite), were shown to exist at detectable concentrations at lower filter temperatures (Figure 5-8). This result is consistent with the condensation temperatures of these species at approximately 500°C (Turn et al., 2001).



Figure 5-3: FactSage results for the equilibrium concentrations of HCl in the *Leucaena* gasification product gas as a function of filter temperature.



Figure 5-4: FactSage results for the KCl equilibrium concentrations in the *Leucaena* gasification product gas as a function of filter temperature.



Figure 5-5: FactSage results for the NaCl equilibrium concentrations in the *Leucaena* gasification product gas as a function of filter temperature.



Figure 5-6: FactSage results for the $(KCl)_2$ equilibrium concentrations in the *Leucaena* gasification product gas as a function of filter temperature.



Figure 5-7: FactSage results for the $(NaCl)_2$ equilibrium concentrations in the *Leucaena* gasification product gas as a function of filter temperature.



Figure 5-8: FactSage results for the combined concentrations of the solid chlorinecontaining species in the *Leucaena* gasification product gas, KCl (sylvite) and NaCl (halite), as a function of filter temperature.

5.4 Lab-Scale Tests of Self-Prepared Sorbents

The results of the lab-scale investigations of the chloride sorbents are described in the following sections.

5.4.1 Initial Testing of the Experimental Apparatus

The results of the initial testing of the experimental apparatus confirmed that the increase in the chloride concentrations in the deionized water trapping solution as measured by the chloride ion selective electrode sufficiently match the theoretical values predicted by Equation 8 (Figure 5-9). The correlation between the experimental and theoretical values confirms that the experimental apparatus produces scientifically valid results. The results also confirm that deionized water is sufficient as a CI⁻ trapping solution and that using a 0.2 N sulfuric acid trapping solution is not necessary. Further testing on the addition of CISA to the trapping solution and calibration standards showed that the addition of the CISA to the trapping solution did not have a measurable effect on the ability of the electrode to detect chloride concentrations. The addition of CISA to the calibration standards did, however, make it slightly more difficult to fit a regression curve to the calibration data. Due to these results, neither sulfuric acid nor CISA were added to the trapping solution in the experimental apparatus. Pure deionized water was used as the trapping solution for all subsequent lab-scale chloride sorbent evaluations.



Figure 5-9: Comparison of the chloride concentrations measured in the trapping solution during the initial lab-scale testing conducted on March 19, 2010, with theoretically predicted values.

5.4.2 Evaluation of Sorbent Performance

The following sections describe the results of the chloride sorbent tests in the lab-scale experimental apparatus.

5.4.2.1 Breakthrough Testing

A summary of the results of the chloride sorption breakthrough tests for the materials analyzed in this study are summarized in Table 5-2. Several of the sorbent preparations were found to have a low capacity for chloride adsorption (Figure 5-10). The top performing self-prepared chloride sorbent materials produced breakthrough curves that were comparable with those produced by commercial BASF CL-760 (Figure 5-11).

In general, the highest performing chloride sorbents included hydrated AES bed material granules, hydrated AES fly ash granules, BASF Cl-760 and reagent grade, CaO-based sorbent preparations. These materials were shown to have Cl⁻ adsorptive capacities greater than 1.0% (g Cl⁻ per g sorbent). The materials that showed a medium chloride sorption ability included AES fly ash pellets (hydrated and non-hydrated), AES bottom ash (hydrated and non-hydrated; pellets and granules), Garden Lime and cement-based sorbent preparations. These sorbents have Cl⁻ adsorptive capacities ranging from 1.0% to 0.34%. Lower Cl⁻ adsorptive capacities were observed with sorbents prepared with non-hydrated AES bed material, HC&S ash (quenched and unquenched) and Calgon AC.

Based on the results of the lab-scale breakthrough tests, the hydrated AES fly ash granules and the hydrated AES bed material granules were selected as the top performing self-prepared sorbent preparations and were advanced to further testing in the HNEI bench-scale biomass gasifier. The hydrated AES fly ash and hydrated AES bed material sorbents provided an average chloride adsorption capacity in the lab-scale tests of 2.1% and 4.0% (g Cl⁻ per g sorbent), respectively.

The sorbent preparation techniques were observed to have a significant impact on the chloride capacity of the various materials. In general, the hydration technique was found to improve sorbent performance. Granulation rather than pelletization was also observed to generally improve the chloride capacity of the material. Pelletization may have reduced performance because the manual pellet press used to form the pellets could have reduced the pore structure of the materials. Although the addition of the potato starch to the hydration solution was found to enhance the durability of the hydrated AES fly ash sorbents, the preparations were still brittle when compared to other sorbents. The AES

bed material granules were more durable than the fly ash sorbents and the addition of potato starch to the hydrated solution did not have an appreciable impact on the strength of the material. Adding starch to the hydrated AES bed material sorbent formulation was observed to lower the sorbent capacity of the material.

Sorbent Preparation						ed-Bed Co	<u>Results</u>				
				Bed	Sorb.					B.T.	
	Sorb.	Sorb. Dia.	Sorb.	Dep.	Dens.	H2O	Temp.	[Cl ⁻]	GHSV	time	Cl capacity
Sorb. Ingreds.	Shape	(mm)	Bed (g)	(cm)	(g/cc)	Cont.	(°C)	(ppmw)	(1/hr)	(min)	g Cl/g sorb.
CL-760	Sph.	3.18	4.0486	2.5	0.81	50.7%	400	1244	2209	674	2.53%
CL-760	Sph.	3.18	4.0236	2.5	0.80	51.9%	400	1273	2264	594	2.35%
CL-760	Sph.	3.18	4.0063	2.5	0.80	52.3%	400	1285	2286	644	2.61%
CL-760	Sph.	3.18	4.0591	2.5	0.81	52.7%	400	1294	2303	593	2.41%
Calgon Activ. Carb.	Gran.	n/a	4.0367	4.5	0.45	53.0%	400	1301	1289	77	0.32%
CL-760	Sph.	3.18	4.0177	2.5	0.80	51.7%	400	618	2256	1084	2.08%
CL-760	Sph.	3.18	4.0073	2.5	0.80	52.7%	400	629	2301	1524	3.04%
CL-760	Sph.	3.18	4.0006	2.5	0.80	55.0%	400	657	2420	964	2.11%
CL-760	Sph.	3.18	4.0006	2.5	0.80	55.4%	300	662	2394	1465	3.77%
CL-760	Sph.	3.18	4.0000	2.5	0.80	56.1%	300	671	2430	1628	4.32%
CL-760	Sph.	3.18	4.0040	2.5	0.80	56.1%	300	670	2430	1043	2.75%
CL-760	Sph.	3.18	4.0062	2.5	0.80	14.4%	300	737	2387	498	1.42%
CL-760	Sph.	3.18	4.0017	2.5	0.80	14.2%	300	731	2384	594	1.68%
CL-760	Sph.	3.18	4.0129	2.5	0.80	17.0%	300	873	2463	845	2.94%
80% HC&S Ash	Pell.	3.18	4.0002	3.0	0.66	14.3%	300	734	1988	238	0.68%
20% Cement											
100% Cement	Pell.	3.18	4.0167	2.5	0.80	53.9%	400	644	2317	181	0.37%
90% HC&S UQ Ash	Pell.	3.18	4.0209	3.7	0.54	53.6%	400	641	1557	30	0.06%
10% Pat. Starch											
40% HC&S UQ Ash	Pell.	3.18	4.0209	3.4	0.59	53.7%	400	641	1559	791	1.61%
40% CaO											
20% Pat.Starch											
	Sorbent P Sorb. Ingreds. CL-760 S0% HC&S Ash 20% Cement 100% Cement 90% HC&S UQ Ash 10% Pat. Starch 40% CaO 20% Pat.Starch	Sorbent Perset Sorb. Ingreds. Sorb. CL-760 Sph. S0% HC&S Ash Pell. 30% HC&S UQ Ash Pell. 90% HC&S UQ Ash Pell. 10% HC&S UQ Ash Pell. <tr td=""> 40% HC&GO</tr>	Sorbent Pursuition Sorb. Ingreds. Sorb. Sorb. Ingreds. Sorb. CL-760 Sph. Clagon Activ. Carb. Gran. CL-760 Sph. CL-760 Sph. CL-760 Sph. CL-760 Sph. CL-760 Sph. CL-760 Sph. Strate J.18 Strate J.18 <tr< td=""><td>Sorbent Preparation Sorb. Ingreds. Sorb. Sorb. Dia. Sorb. Sorb. Ingreds. Sorb. 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 Table 5-2: Summary of chloride sorption testing results.

Sorbent Preparation						Fixed-Bed Conditions						<u>Results</u>	
		Sorh	Sorh Dia	Sorh	Bed Den	Sorb. Dens	Н2О	Temn	[C]]	GHSV	B.T. time	Cl canacity	
Test ID	Sorb. Ingreds.	Shape	(mm)	Bed (g)	(cm)	(g/cc)	Cont.	(°C)	(ppmw)	(1/hr)	(min)	g Cl/g sorb.	
100804	80% CaO 20% Pat.Starch	Gran.	n/a	4.0033	6.3	0.32	52.2%	400	643	888	2144	4.26%	
100806	72% HC&S Ash 28% CaO	Pell.	3.18	4.0200	2.5	0.80	53.2%	400	655	2285	2256	4.64%	
100809	HC&S Ash 7% wt. Glycerin	Pow.	n/a	4.0020	3.0	0.66	53.5%	400	659	1916	24	0.05%	
100810	Garden Lime	Gran.	n/a	4.0033	1.6	1.24	53.4%	400	657	3584	276	0.57%	
100816	AES Fly Ash	Pell.	3.18	4.0174	2.2	0.91	54.1%	400	666	2646	462	0.98%	
100817	AES Fly Ash	Pell.	3.18	4.0187	2.5	0.80	55.7%	850	686	4022	10	0.02%	
100819	AES Bottom Ash	Pell.	3.18	4.0153	2.0	1.00	53.8%	400	662	2889	215	0.45%	
100823	AES Bottom Ash	Gran.	2.8-1.18	4.0017	2.0	1.00	58.3%	400	718	3203	201	0.51%	
100824	AES Bed Matterial	Gran.	2.8-2.0	4.0119	1.8	1.11	54.0%	400	665	3228	63	0.13%	
100824	AES Fly Ash	Pell.	3.18	4.0009	3.0	0.66	54.3%	400	668	1947	172	0.37%	
100826	AES Fly Ash 7% wt. Glycerin	Pell.	3.18	4.0185	2.5	0.80	54.3%	400	668	2337	468	1.00%	
100830	AES Bed Matterial	Pell.	3.18	4.0092	2.0	1.00	53.4%	400	657	2865	101	0.21%	
100901	AES Fly Ash	Pell.	3.18	4.0183	2.7	0.74	53.9%	400	663	2145	175	0.37%	
100907	AES Fly Ash 7% wt. Glycerin	Pell.	3.18	4.0078	2.5	0.80	53.2%	400	655	2285	280.5	0.58%	
100908	AES Fly Ash 7% wt. Glycerin	Pell.	3.18	4.0143	2.5	0.80	53.2%	400	655	2285	281.1	0.58%	
100908	AES Bottom Ash 7% wt. Glycerin	Pell.	3.18	4.8986	2.0	1.22	53.0%	400	653	2843	165	0.34%	

Sorbent Preparation						Fixed-Bed Conditions						<u>Results</u>	
		Sorb.	Sorb. Dia.	Sorb.	Bed Dep.	Sorb. Dens.	H2O	Temp.	[Cl ⁻]	GHSV	B.T. time	Cl capacity	
Test ID	Sorb. Ingreds.	Shape	(mm)	Bed (g)	(cm)	(g/cc)	Cont.	(°C)	(ppmw)	(1/hr)	(min)	g Cl/g sorb.	
100910	AES Bed Material 7% wt. Glycerin 20% wt. Pat. Starch	Gran.	2.0-1.18	4.0006	5.3	0.38	52.8%	400	650	1068	2083	4.23%	
100915	AES Bottom Ash 7% wt. Glycerin 20% wt. Pat. Starch	Pell.	3.18	4.0810	2.0	1.01	53.0%	400	653	2844	188	0.38%	
100916	AES Bed Material 7% wt. Glycerin 20% wt. Pat. Starch	Gran.	2.8-1.18	4.0057	5.3	0.38	53.3%	400	656	1080	2166	4.49%	
100917	AES Bed Material 7% wt. Glycerin 20% wt. Pat. Starch	Gran.	2.8-1.18	4.0046	5.0	0.40	53.1%	400	654	1140	1696	3.49%	
100920	AES Bed Material 7% wt. Glycerin 20% wt. Pat. Starch	Gran.	2.8-1.18	4.0005	5.0	0.40	52.7%	400	649	1130	1792	3.63%	
100930	AES Bottom Ash	Gran.	2.8-1.18	4.0043	2.0	1.00	51.4%	400	637	2748	291	0.56%	
101002	Garden Lime	Gran.	n/a	4.0037	1.8	1.11	51.9%	400	643	3086	508	1.00%	
101007	AES Fly Ash 7% wt. Glycerin 20% wt. Pat. Starch	Pell.	3.18	3.9996	2.5	0.80	52.3%	400	649	2242	459	0.92%	
101008	AES Fly Ash 7% wt. Glycerin 20% wt. Pat. Starch	Pell.	3.18	4.0034	2.7	0.74	52.8%	400	655	2099	541	1.11%	

Sorbent Preparation						Fixed-Bed Conditions						<u>Results</u>	
		Sorb.	Sorb. Dia.	Sorb.	Bed Dep.	Sorb. Dens.	H2O	Temp.	[Cl ⁻]	GHSV	B.T. time	Cl capacity	
Test ID	Sorb. Ingreds.	Shape	(mm)	Bed (g)	(cm)	(g/cc)	Cont.	(°C)	(ppmw)	(1/hr)	(min)	g Cl/g sorb.	
101012	AES Fly Ash 7% wt. Glycerin 20% wt. Pat. Starch	Gran.	2.8-1.18	4.0074	5.7	0.35	52.2%	400	647	980	1278	2.55%	
101014	AES Fly Ash 7% wt. Glycerin 20% wt. Pat. Starch	Gran.	2.8-1.18	4.0015	5.5	0.36	55.9%	400	693	1102	1430	3.32%	
110209	AES Bed Material 7% wt. Glycerin 10% wt. Pat. Starch	Gran.	2.8-1.18	4.0044	5	0.40	51.7%	400	642	1108	971	1.90%	
110214	AES Fly Ash 7% wt. Glycerin 10% wt. Pat. Starch	Gran.	2.8-1.18	4.0004	5.5	0.36	50.9%	400	631	990	1299	2.47%	
110215	AES Bottom Ash 7% wt. Glycerin 10% wt. Pat. Starch	Gran.	2.8-1.18	4.0084	3.0	0.66	51.4%	400	637	1833	511	0.99%	
110216	AES Bed Material 7% wt. Glycerin 10% wt. Pat. Starch	Gran.	2.8-1.18	4.0015	5.0	0.40	51.3%	400	637	1098	1102	2.13%	
110217	AES Fly Ash 7% wt. Glycerin 10% wt. Pat. Starch	Gran.	2.8-1.18	4.0030	5.3	0.38	51.2%	400	635	1034	1240	2.38%	



Figure 5-10: The chloride breakthrough results for the materials with low chloride adsorption capacities when a fixed-bed of ~ 4 g of sorbent material was subjected to a 400°C gas stream containing ~650 ppmw Cl⁻ at a GHSV of ~ 1500 hr⁻¹.



Figure 5-11: The chloride breakthrough curves for the materials that showed high chloride adsorption capacities when a fixed-bed of ~ 4 g of sorbent material was subjected to a 400°C gas stream containing ~650 ppmw Cl⁻ at a GHSV of ~ 1500 hr⁻¹.

5.4.2.2 Determination of the Maximum Gas Hourly Space Velocity

The results of the gas hourly space velocity (GHSV) tests of the self-prepared hydrated AES fly ash and hydrated AES bed material sorbents showed that each sorbent material continued to adsorb chloride at exceedingly high GHSV's. Chloride breakthrough of the hydrated fly ash and hydrated bed material sorbents were not observed until the GHSV through the fixed bed was increased to approximately 54,000 hr⁻¹ and 20,000 hr⁻¹, respectively. The results of these analyses could have been affected by the limitation of the lab-scale apparatus to effectively transport chloride through the experiment at extreme GHSV's. In addition, the chloride concentrations in the gas stream for the GHSV tests (~12 ppmw) were significantly lower than the typical chloride concentrations in the gas stream for the breakthrough tests (~650 ppmw). Further investigation of the lab scale apparatus to adequately predict the maximum GHSV of suitable for prepared sorbent materials may be warranted in future research.

5.5 Bench-Scale Gasifier Evaluation of Self-Prepared Sorbent Materials

The results of the chloride adsorption analyses of the self-prepared hydrated AES fly ash and hydrated AES bed material sorbents in the HNEI bench-scale biomass gasification system are presented in Figure 5-12 and Figure 5-13. The error bars in the figures show one standard deviation of the three [CI⁻] measurements at each set point from the mean. The results indicate that the hydrated AES fly ash sorbent is capable of reducing the chloride concentrations in product gas at lower GHSVs (<23,155 hr⁻¹), but at higher GHSVs the sorbent was unable to significantly adsorb chloride. At a GHSV of 8,909 hr⁻¹, the sorbent reduced the chloride concentration in the dry product gas from ~300 ppmv to ~50 ppmv, a reduction of about 83%. The hydrated AES bed material sorbent was capable of reducing the chloride concentrations in dry product gas over the range of GHSVs tested, but at higher GHSVs the sorbent adsorbed less chloride. At a GHSV of $3,237 \text{ hr}^{-1}$, the sorbent reduced the dry product gas chloride concentration from ~300 ppmv to ~10 ppmv, a reduction of about 97%. At 13,266 hr⁻¹, the highest GHSV tested, the hydrated AES bed material sorbent reduced the chloride concentration in the dry product gas by 63% to 110 ppmv.

The material formulations were observed to maintain their structural integrity after testing in the gasifier (Figure 5-14 through Figure 5-17). The only significant change in the appearance of the hydrated AES fly ash sorbent material was a darkening in color, which may be due to the adsorption of tar species. No significant changes were observed in the appearance of the pre- and post-test hydrated AES bed material sorbent. Data on the typical concentrations of the permanent gas species during the gasifier tests is provided in Figure 5-18. The oscillation in the concentrations of the gas species is due to the filter back-pulses using nitrogen gas.

The results of the biomass gasifier analyses indicate that both sorbent preparations were capable of reducing the chloride concentrations in the biomass gasification product stream when the GHSV through the bed is ~9,000 hr⁻¹ or less. Additional testing should be performed to determine appropriate GHSV's to attain desired Cl⁻ outlet concentrations suitable for targeted uses of the product gas, e.g. syngas production. A GHSV of 1,000 hr⁻¹ was recommended by the manufacturer (BASF Corp.) of the CL-760 sorbent. The trend in the results suggests that the chloride sorption performance of the self-prepared sorbents is likely to be improved at GHSVs on the order of 1,000 hr⁻¹.


Figure 5-12: The experimental results of the T20110518 bench-scale biomass gasification analysis of the hydrated AES fly ash sorbent.



Figure 5-13: The experimental results of the T20110525 bench-scale gasification analysis of the hydrated AES bed material.



Figure 5-14: Hydrated AES fly ash sorbent granules prior to being evaluated in the T20110518 bench-scale biomass gasification test.



Figure 5-15: Hydrated AES fly ash sorbent material that were unloaded from the fixedbed reactor after the T20110518 bench-scale biomass gasification test.



Figure 5-16: Hydrated AES bed material sorbent granules prior to being evaluated in the T20110525 bench-scale biomass gasification test.



Figure 5-17: Hydrated AES bed material sorbent granules that were unloaded from the fixed-bed reactor after the T20110525 gasification test.



Figure 5-18: The concentrations of the permanent gas species during the T20110518 gasifier test as measured by the continuous gas analyzers and GC. The gas concentrations are not corrected to an N₂-free basis.

5.6 Elemental Ash and XRD analyses of the Prepared and Tested Sorbents

The results of the Hazen analyses of the coal and ash samples collected from HC&S facility on Maui on July 2, 2010 are presented in Table 5-3. These results show that the quenched and unquenched coal ash samples are roughly identical in chemical composition, with only an appreciable difference in the concentration of C (0.15% and 0.03% for the quenched and unquenched coal ash samples, respectively). The data also show that compared to the fuel analysis, the coal ash is enriched in Si, Al, Ti and Na and depleted in Fe, Ca, Mg, K, P and S after the combustion process. The Cl concentration of the ash was not changed pre- and post- combustion. The initial (deformation) ash fusion temperature of the HC&S coal sample was found to be 1311°C in an oxidizing atmosphere and 1056°C in a reducing atmosphere. The combustion process increased the ash fusion temperatures of the material to beyond the upper limit for the test (1482°C).

The Hazen results of the analyses of the coal and ash samples collected from the AES Hawaii Power Facility on August 11, 2010 and bed material sample collected from AES on August 24, 2010 are presented in

Table 5-4. The data shows that the coal ash and the bed material combine in the two output streams as evidenced by the differences in concentrations of elements. For instance, the high Ca content of the bed material is reflected in the Ca concentrations of the bottom and fly ash. Whereas Ca was depleted in the coal ash by the HC&S combustion process from 4.63% to about 1.2%, the Ca content in the AES coal ash increased from 4.47% to 37.40% and 25.80% for the AES fly and bottom ash,

respectively. Of the elements identified as potentially capable of adsorbing chloride (Ca, Na, Mg and Al), Ca is of greatest concentration in the AES output stream, while Al is of significant concentration in the HC&S output (~25%). Since sulfur, like chlorine, is undesirable in the gasification product gas, the partitioning of sulfur in the output streams was also of interest. The sulfur content of the AES coal ash (5.50%) was also observed to be more highly enriched in the bottom ash (32.50%) than in the fly ash (14.70%). Finally, the Hazen results show that the HC&S coal sample contains about twice as much ash as the AES coal sample (14.79 % and 7.88% respectively) and that the higher heating values (HHV) of the two fuels were both on the order of 28 MJ/kg.

The results of the elemental ash analyses and the x-ray diffraction (XRD) analyses of the hydrated AES fly ash sorbent preparations pre- and post- chloride breakthrough testing in the lab-scale apparatus and pre- and post- bench-scale biomass gasification testing are presented in Table 5-5. The XRD results show that the CaO detected in the raw fly ash may have been converted to Ca₂Al₂SiO₇ due to the hydration process. The results of the elemental ash analyses and the XRD analyses of the hydrated AES bed material sorbent preparations (Table 5-6) indicate that the hydration process enriches Ca and Ca(OH)₂ and depletes C and CaCO₃. Subjecting the hydrated material to the chloride sorption tests does the reverse by depleting Ca and Ca(OH)₂ and enriching C and CaCO₃. For both the hydrated AES fly ash and the hydrated AES bed material sorbents, the results also show that a significant amount of Cl is gained by each material after undergoing chloride sorption testing. These results indicate that the self-prepared sorbents are successful at adsorbing chloride from the hot gas streams.

1	-		
		HC&S	HC&S
	HC&S	Quenched	Unquenched
	Coal	Coal Ash	Coal Ash
Proximate Analysis (%, Dry)			
Ash	14.79		
Volatile matter	43.92		
Fixed carbon	41.29		
Sulfur	0.507		
Energy Content (MJ/kg)			
HHV	28.54		
<u>Ultimate (Dry, ash free, %)</u>			
[C]: Carbon	70.28		
[H]: Hydrogen	5.29		
[N]: Nitrogen	1.10		
[S]: Sulfur	0.51		
[O]: Oxygen (by difference)	8.03		
[Cl]: Chlorine	0.011		
Ash	14.79		
Elemental analysis of ash (%, 600°C ash)			
SiO ₂	36.56	59.28	59.53
Al ₂ O ₃	16.44	25.39	24.56
TiO ₂	0.49	1.21	1.23
Fe_2O_3	34.60	1.93	2.16
CaO	4.63	1.20	1.21
MgO	2.93	0.74	0.82
Na ₂ O	0.31	0.59	0.59
K ₂ O	1.35	0.41	0.45
P_2O_5	0.59	0.41	0.52
SO ₃	0.82	0.04	0.06
Cl	0.03	0.03	0.03
CO ₂	0.06	0.15	0.03
Total	98.81	91.38	91.19
Ash Fusion Temperatures (°C)			
Oxidizing Atmosphere			
Initial	1311	>1482	>1482
Softening	1321		
Hemispherical	1330		
Fluid	1351		
Reducing Atmosphere			
Initial	1056	>1482	>1482
Softening	1082		· - · • •
Hemispherical	1088		
Fluid	1094		

 Table 5-3: Properties of the HC&S coal and ash samples.

-		-		
	AES	Bottom	AES Fly	AES Bed
	Coal	Coal Ash	Coal Ash	Material
Proximate Analysis (%, Dry)				
Ash	7.88			
Volatile matter	46.37			
Fixed carbon	45.75			
Sulfur	1.009			
Energy Content (MJ/kg)				
HHV	28.18			
Ultimate (Dry, ash free, %)				
[C]: Carbon	72.20			
[H]: Hydrogen	5.00			
[N]: Nitrogen	1.43			
[S]: Sulfur	1.01			
[O]: Oxygen (by difference)	12.48			
[Cl]: Chlorine	0.006			
Ash	7.88			
Elemental analysis of ash (%, 600°C ash)				
SiO ₂	33.06	16.66	30.42	1.31
Al_2O_3	14.59	6.18	13.18	0.77
TiO ₂	0.54	0.34	0.52	0.11
Fe ₂ O ₃	32.67	4.55	7.97	0.49
CaO	4.47	37.40	25.80	39.00
MgO	1.74	0.65	0.74	0.29
Na ₂ O	0.32	0.10	0.26	0.04
K ₂ O	1.30	0.50	1.05	0.06
P_2O_5	0.57	0.26	0.46	0.10
SO ₃	5.50	32.50	14.70	0.01
Cl	0.02	0.09	0.03	0.07
CO_2	0.31	0.64	1.39	42.68
Total	95.09	99.87	96.52	84.93
Ash Fusion Temperatures (°C)				
Oxidizing Atmosphere				
Initial	1121	1452	1203	>1482
Softening	1247	1455	1207	
Hemispherical	1254	1463	1210	
Fluid	1273	1468	1216	
Reducing Atmosphere				
Initial	1084	1461	1169	>1482
Softening	1087	1466	1203	
Hemispherical	1088	1471	1207	
Fluid	1091	1480	1216	

 Table 5-4: Properties of the AES coal, ash and bed material samples.

1 2	-		U U		
	100811	101007	110301 Breakthrough	110418	110518 Gasifier
	AES	Hydrated AES	Tested 110131	Hydrated AES	Tested 110418
	Coal Fly	Fly Ash	Hydrated AES Fly	Fly Ash	Hydrated AES
	Ash	Granules	Ash Granules	Granules	Fly Ash Granules
Elemental analysis of ash (%, 600°C)					
SiO ₂	30.42	28.62	31.39	31.27	29.18
Al_2O_3	13.18	12.38	14.14	14.63	13.57
TiO ₂	0.52	0.53	0.51	0.64	0.57
Fe_2O_3	7.97	7.50	7.80	7.84	7.51
CaO	25.8	23.70	23.3	24.80	25.6
MgO	0.74	1.12	1.15	0.75	0.72
Na ₂ O	0.26	0.19	0.21	0.16	0.17
K ₂ O	1.05	0.99	1.10	1.06	0.99
P_2O_5	0.46	0.43	0.30	0.33	0.37
SO ₃	14.7	13.5	11.71	15.06	15.1
Cl	0.03	0.04	1.76	< 0.01	1.49
CO_2	1.39	3.73	4.12	3.12	3.06
Total	96.52	92.73	97.49	99.66	98.33
XRD Results (Approx. Wt%)					
CaCO ₃	<3		5		
Ca(OH) ₂	<5				
$CaSO_4$	26	24	22	25	25
$Ca_2Al_2SiO_7$		10		15	15
SiO ₂	8	7	7	6	6
Ca_2SiO_4		<5?			
(Na, Ca)Al(Si,Al) ₃ O ₈		<3			
Fe ₂ O ₃	<3	7	<3	8	7
"Amorphous"	>35	<45	>45	40	>40
"Unidentified"	<5	<5	<5	<5	<5
		105			

Table 5-5: Properties of the hydrated AES Fly Ash sorbents pre- and post- testing.

105

	100811	101007	110301 Breakthrough	110418	110518 Gasifier
	AES	Hydrated AES	Tested 110131	Hydrated AES	Tested 110418
	Coal Fly	Fly Ash	Hydrated AES Fly	Fly Ash	Hydrated AES
	Ash	Granules	Ash Granules	Granules	Fly Ash Granules
CaO	11				
(Fe,Mg,Zn,Cu,Ni)(Fe,Al,Cr) ₂ O ₄			5		
$CaAl_2SiO_6$	<3				
$CaCl_2*2H_2O$					
CaAl ₂ O ₄			<5		
Ca ₅ ((P,S,Si)O4) ₃ (Cl,OH,F,CO ₃)					<5?
$Ca_5(SiO4)_2CO_3$					

	100824	100914 Hydrated	110228 Tested		
	AES	AES Bed	110131 Hydrated	110509 Hydrated	110525 Gasifier Tested
	Bed	Material	AES Bed Material	AES Bed Material	110509 Hydrated AES
	Material	Granules	Granules	Granules	Bed Material Granules
Elemental analysis of ash (%, 600°C ash)					
SiO ₂	1.31	1.79	1.73	1.73	0.95
Al ₂ O ₃	0.77	0.94	0.90	1.70	1.32
TiO ₂	0.11	0.11	0.07	0.10	0.07
Fe ₂ O ₃	0.49	0.54	0.43	0.57	0.50
CaO	39.00	61.00	53.6	55.70	44.60
MgO	0.29	0.58	0.45	0.32	0.28
Na ₂ O	0.04	0.05	0.03	0.04	0.03
K ₂ O	0.06	0.05	0.02	0.23	0.07
P_2O_5	0.10	0.20	0.09	0.14	0.12
SO ₃	0.01	0.09	0.04	0.03	0.18
Cl	0.07	0.06	1.70	0.01	0.85
CO_2	42.68	23.32	39.68	25.94	40.18
Total	84.93	88.73	98.68	86.50	89.15
XRD Results (Approx. Wt%)					
CaCO ₃ (Calcite)	>95	54	95	66	93
Ca(OH) ₂ (Portlandite)		44		30	
(Na, Ca)Al(Si,Al) ₃ O ₈			<1?		
"Unidentified"	<5	<5	<5	<5	<5
$Al_6Si_2O_{13}$ (Mullite)					
CaCl ₂ *2H ₂ O (Sinjarite)			<1?		
Ca ₅ (SiO4) ₂ CO ₃ (Spurrite)					<5

Table 5-6: Properties of the hydrated AES bed material sorbents pre- and post-testing.

5.6.1 Mass-Balance of Bench-Scale Biomass Gasification Tests

The data collected for each of the bench-scale gasifier evaluations of the self-prepared sorbent materials (T20110518 and T20110525) were used to calculate a chloride mass-balance over the entire gasifier system and over the fixed-bed sorbent reactor. The calculations took into account the average temperatures of the product gas stream recorded at the center of the fixed-bed reactor (371.8°C and 394.9°C) and at the gas flow meters (24.5°C and 28.0°C) for the T20110518 and T20110525 tests, respectively.

The chloride mass-balance calculation over the gasifier system included the Cl input due to the *Leucaena* fuel and the Cl outputs represented by the Cl contents of the filter char (Table 5-7) and the gasifier product gas stream. The calculated Cl output accounted for 85.8% and 94.8% of the calculated overall Cl input to the gasifier for the T20110518 and T20110525 tests, respectively (Table 5-8).

The chloride mass-balance calculation over the fixed-bed sorbent reactor included the Cl content of the pre-test sorbent material and the untreated product gas stream (Table 5-9). The Cl outputs from the reactor included the post-test sorbent material and the treated product gas stream. The results of the mass-balance over the fixed-bed reactor show that the calculated Cl output accounted for 92.4% and 99.2% of the calculated Cl input to the reactor for the T20110518 and T20110525 gasifier tests, respectively (Table 5-10).

For each mass-balance calculation, the chloride output results were slightly lower than chloride input results. These results are consistent with the fact that potential chloride sinks were not accounted for in the calculations. These sinks include the fluidized bed bed-material and the bed char. Had these materials been analyzed for chloride content and included in the mass-balance calculations, the output/input Cl ratio may have been greater. In any case, the close agreement between the input and output chloride mass-balance results validates the methods used for the bench-scale gasifier evaluations of the self-prepared sorbents.

1 1	T20110518	T20110525
	Filter Char	Filter Char
Provimate Analysis (% Dry)	Ther Char	Thief Char
Ash	9.29	7 84
Volatile matter	3 77	3.9/
Fixed carbon	86.94	88.22
Sulfur	0 029	0.013
Energy Content (MI/kg)	0.027	0.015
HHV	30.67	31.09
Illtimate (Dry. ash free. %)	50.07	51.07
[C]: Carbon	90.57	92.20
[H]: Hydrogen	0.35	0.43
[N]: Nitrogen	0.05	0.43
[S]: Sulfur	0.03	0.02
[O]: Ovygen (by difference)	-0.03	<0.01
[C]]: Chlorine	0.245	0.335
Δsh	9 29	0.333 7 84
Flemental analysis of ash (% 600°C ash)).2)	7.04
SiO2	24.40	6.03
	1 92	1 29
TiO	0.20	0.12
Fe ₂ O ₂	1.56	2 20
$C_{2}O_{3}$	27.40	2.20
ΜαΟ	613	6.93
Na ₂ O	1.03	0.48
K ₂ O	8 73	13.10
$P_2 O_5$	7.15	8.16
SO ₂	0.78	1 44
Cl	2.73	4 67
CO_2	4.56	15.04
Total	86.59	88.96
Ash Fusion Temperatures (°C)		00000
Oxidizing Atmosphere		
Initial	1272	>1482
Softening	1274	
Hemispherical	1275	
Fluid	1279	
Reducing Atmosphere		
Initial	1260	>1482
Softening	1279	· 1.02
Hemispherical	1348	
Fluid	1357	

 Table 5-7: Properties of the filter char samples.

INPUTS	T20110518	T20110525
Feedstock: Leucaena		
Feedstock in, wet kg	14.85	14.55
Feedstock out, wet kg	3.73	2.95
Feedstock fed, wet kg	11.12	11.60
Total run time, hr	8.17	8.90
Feedrate, wet kg/hr	1.36	1.30
Moisture content, % wet basis	7.65	7.65
Feedrate, dry kg/hr	1.26	1.20
Dry fuel fed, kg	10.3	10.7
Fuel chlorine, % dry	0.11	0.11
Cl- Input, g	11.3	11.8
OUTPUTS		
Filter Char		
Filter char collected, g	1,016.3	1,045
Char chlorine, % dry	0.245	0.335
Cl- output in char, g	2.49	3.50
Product gas		
Total measured dry gas flow, liters	16,967	17,863
Total dry gas volume @ STP, liters	15,572	16,199
Mean [Cl-] in dry inlet gas at STP, ppmv	292.2	299.0
Total Cl- in inlet gas at STP, liters	4.550	4.843
Total Cl- output in gas, g	7.20	7.67
Cl- output, g	9.69	11.17
Output Cl-/Input Cl-, %	85.8	94.8

 Table 5-8: Chloride mass-balance over the entire gasifier system.

INPUTS	T20110518	T20110525
<u>Sorbent</u>		
Sorbent bed, g	43.0	233.3
Elemental analysis, chlorine, %	0.01	0.01
Cl- input from sorbent, g	0.004	0.023
Product Gas Inlet		
Total measured dry gas through reactor, liters	5,260.50	6,920.10
Average gas measurement temperature, C	24.5	28.0
Average gas measurement pressure, atm	1	1
Total dry gas volume @ STP, liters	4,828	6,275
Mean [Cl-] in dry inlet gas at STP, ppmv	292.2	299.0
Total Cl- in inlet gas at STP, liters	1.41	1.88
Total Cl- in inlet gas at STP, g	2.23	2.97
Total Cl- input, g	2.24	2.99

 Table 5-9: Chloride mass-balance inputs over the fixed-bed sorbent reactor.

OUTPUTS	T20110518	T20110525
Sorbent		
Gasifier tested sorbent, g	73.0	261.0
Elemental analysis of ash, chlorine, %	1.49	0.85
Cl- output from sorbent, g	1.09	2.22
Product Gas, Reactor Outlet		
Bed volume, liters	0.1	0.6
Setpoint 1		
Mean reactor GHSV at reactor temp, wet gas, hr ⁻¹	8,909	3,237
Mean flow rate of wet gas at reactor temp, LPM	15.29	28.77
Dry gas volume through reactor @ STP, liters	356	1,004
Mean [Cl-] in dry outlet gas at STP, ppmv	52.3	11.4
Cl- in outlet gas at STP, liters	0.0186	0.0115
Setpoint 2		
Mean reactor GHSV at reactor temp, wet gas, hr ⁻¹	23,155	5,882
Mean flow rate of wet gas at reactor temp, LPM	41.45	54.09
Dry gas volume through reactor @ STP, liters	904	1460
Mean [Cl-] in dry outlet gas at STP, ppmv	63.8	29.0
Cl- in outlet gas at STP, liters	0.577	0.0423
Setpoint 3		
Mean reactor GHSV at reactor temp, wet gas, hr ⁻¹	45,739	9,081
Mean flow rate of wet gas at reactor temp, LPM	89.42	83.51
Dry gas volume through reactor @ STP, liters	2,045	1,707
Mean [Cl-] in dry outlet gas at STP, ppmv	187	76.5
Cl- in outlet gas at STP, liters	0.289	0.131
Setpoint 4		
Mean reactor GHSV at reactor temp, wet gas, hr ⁻¹	52,111	13,266
Mean flow rate of wet gas at reactor temp, LPM	89.42	122.00
Dry gas volume through reactor @ STP, liters	2,045	2619
Mean [Cl-] in dry outlet gas at STP, ppmv	124	110
Cl- in outlet gas at STP, liters	0.253	0.289
Total Cl- in outlet gas at STP, liters	0.619	0.474
Total Cl- output in outlet gas at STP, g	0.98	0.75
Total Cl- output, g	2.07	2.97
Output Cl-/Input Cl-, %	92.4	99.2

 Table 5-10: Chloride mass-balance outputs over the fixed-bed sorbent reactor.

5.7 Discussion and Recommendations

The results of the lab-scale and bench-scale tests of the hydrated AES fly ash and hydrated AES bed material sorbents (referred to as the self-prepared sorbents from here out) indicate that the materials are capable of adsorbing chloride from the biomass gasification product stream. The elemental analysis results indicate that adsorption of chloride containing molecules is likely due to the high Ca content of the sorbents (Table 5-5 and Table 5-6). The comparatively low Ca content of the ash sourced from HC&S (Table 5-3) explains why sorbents prepared using the HC&S material were not effective at adsorbing chloride.

The hydration process improves the reactivity of the AES sourced self-prepared sorbent materials by enhancing the formation of crystallized hydrated lime (Ca(OH)₂) and by increasing the surface area of the pores in the material (Hirabayashi et al., 2000; Hirabayashi et al., 2002). When the sorbent is reacted in the fixed-bed at temperatures below 400°C, Ca(OH)₂ can remove HCl from the product gas by forming calcium chloride (CaCl₂) on the surface of the sorbent material:

$$Ca(OH)_2(s) + 2HCl(g) \leftrightarrow CaCl_2(s) + 2H_2O(g)$$

At temperatures greater than 400°C, Ca(OH)₂ is converted to lime (CaO):

$$Ca(OH)_2$$
 (s) \leftrightarrow CaO (s) + H₂O (g)

The CaO also reacts with the HCl in the product gas to produce CaCl₂:

$$CaO(s) + 2HCl(g) \leftrightarrow CaCl_2(s) + H_2O(g)$$

Both reactions are likely to occur when the fixed-bed is operated at 400°C.

The HCl capturing ability of hydrated lime is commonly employed in the pollution control systems of municipal and hazardous waste incinerators. In addition to removing HCl, lime is also used to remove sulfur and carbon dioxide from various industrial processes. The remainder of this section describes the potential implications of using the self-prepared sorbent materials for the adsorption of chloride from an industrial scale gasification process in Hawaii. The reactivity of lime-based sorbents with other gas species is discussed as well as an initial qualification of the potential economic and environmental implications of using the self-prepared sorbent materials. The discussion also provides recommendations for future research to further the understanding of the topic.

5.7.1 Sorbent Reactivity with Other Product Gas Species

Various forms of lime are also know to react with other common contaminates of hot gas streams including SO₂, H₂S, NO_x, CO₂, H₂O and tar components (Chisholm and Rochelle, 1999; Liu et al., 2002; Shemwell et al., 2002; Stein et al., 2002; Chin et al., 2005; Zeman, 2008). The ability of lime to react with product gas species other than HCl is of concern because this characteristic could potentially diminish the chloride removal efficiency of the self-prepared sorbent materials. A decrease in the HCl removal efficiency can be expected because interactions between the sorbent particles and gas species other than HCl can lead to pore-clogging as well as the formation of product layers on the sorbent surface that would block further reactions with HCl. In addition, HCl would be competing with other gas species for a limited number of active physical adsorption sites on the sorbent surface.

The interaction of the self-prepared sorbents with carbon dioxide is of particular concern because the gasifier product gas stream contains high concentrations of CO_2 (~17% during the T20110518 gasifier test). Carbon dioxide (CO_2), is known to be reactive with both CaO and Ca(OH)₂ to form CaCO₃ (Zeman, 2008). CaO exposed to CO₂ at 1 bar, 600°C yields:

$$CaO(s) + CO_2(g) \rightarrow CaCO_3(s)$$

Similarly, Ca $(OH)_2$ exposed to CO₂ at 1 bar, 300°C, yields:

$$Ca(OH)_2(s) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(g)$$

In addition to CO₂, the sulfur containing molecules present in the gasifier product gas may also affect the HCl removal capacity of the sorbent. The sulfur species present in the HNEI bench-scale gasifier product gas stream include hydrogen sulfide (H₂S), carbonyl sulfide (COS) and thiophene (C₄H₄S) in concentrations of ~100 ppmv, ~2 ppmv and ~2 ppmv, respectively, on a N₂ free basis (Cui et al., 2010). Previous studies on the simultaneous sorption of HCl with flue gas species including SO₂, CO₂, O₂ and moisture using hydrated lime have found that the presence of HCl increases the ability of Ca(OH)₂ to remove SO₂ and CO₂ (Chisholm and Rochelle, 1999; Liu et al., 2002; Shemwell et al., 2002; Stein, et al. 2002; Chin et al., 2005). This phenomenon is explained by the ability of HCl to prevent the formation of product layers (CaCO₃ and CaSO₃·½H₂O) on the sorbent surface that would have otherwise caused the sorbent to prematurely stop reacting with the product gas (Chin et al., 2005). At higher HCl concentrations (above ~800 ppm), however, the removal of SO₂ by hydrated lime is reduced. The reduction in the sorption of SO_2 can be "attributed to the fact that HCl [sorption] and dissociation is thermodynamically favored" (Stein et al., 2002).

The findings of previous studies suggest that the CO₂ and S containing compounds present in the gasifier product gas will not significantly affect the HCl adsorption performance of the self-prepared sorbent materials. To gain further insight on the chemical interactions occurring between the sorbent bed and the species in the product gas, thermochemical equilibrium calculations were carried out using the FactSage© model described in Section 4.3.2. The thermochemical equilibrium calculation result for the composition of the product gas exiting the ceramic filter at 650°C (as discussed in Section 0) was used to define the composition of the gas entering the fixed-bed reactor. The thermochemical equilibrium of the gas stream in the fixed-bed reactor was calculated at 400°C and 1 atm. with and without the presence of the self-prepared sorbent material. The Hazen elemental analysis results for the hydrated AES bed material was used to define the additional elements available for reaction in the fixed-bed reactor with the sorbent present.

The FactSage[®] thermochemical equilibrium results for the gas composition exiting the fixed-bed show that the addition of the self-prepared sorbent material significantly reduces the concentration of the chloride in the gas stream from 327 ppm to 0.05 ppm. The results for all of the other gas species present in the dry product gas in relatively significant concentrations (H₂, N₂, CO, CO₂, CH₄, NH₃, H₂S and COS) show that the sorbent does not have a significant positive or negative effect on the concentration of these other gas species. Further study to quantify the effect that the multiple species in

the product gas have on the chloride sorption characteristics of the self-prepared sorbents is recommended. Such information will aid in the design of a contaminate removal system that is optimized for the removal of target molecules.

5.7.2 Sorbent Regeneration

Once the sorbent material reaches its capacity for chloride adsorption, the regeneration of the sorbent material to regain reactivity is desirable so that material costs can be kept to a minimum. *In situ* regeneration of the sorbent bed is desired because it avoids physical disturbances to the gasification system. Zeman (2008) discusses a method for the regeneration of hydrated lime that has been used as sorbent for CO_2 removal from a hot gas stream at 600°C. The regeneration process occurs *in situ* and requires that the spent sorbent material is heated to 900°C and exposed to a stream of CO_2 . The material is then cooled to 300°C and exposed to steam in an atmosphere of CO_2 . Finally, the hydrated material is reused to adsorb CO_2 from a flue gas stream at 600°C (Zeman, 2008).

A process similar to the one described by Zeman (2008) may potentially regenerate the spent self-prepared sorbent materials *in situ*. A regeneration process could significantly reduce the costs in an industrialized biomass gasification application because regeneration could be repeated multiple times. Zeman (2008) repeated the sorption/regeneration cycle of hydrated lime ten times. After the ten cycles, the CO_2 adsorption capacity of the hydrated lime material had decreased by less than 40%. The decay in the adsorption performance of the material is attributed to sintering on the surface of the lime, which seals the pore spaces. The rate of the decay in sorbent performance can be attributed to the regeneration techniques used (temperatures, gas

atmosphere, pressures) and the properties of the original material (Zeman, 2008). It is recommended that future research be conducted to determine if a similar *in situ* hydration process can be developed to regenerate the self-prepared sorbent materials after they have reached their chloride adsorption capacities.

5.7.3 Economic Considerations of the Self-Prepared Sorbent Materials

Fly ash and bed material collected from the AES Hawaii Power Plant were parent materials used to prepare the top performing chloride sorbents in this study. The economic implications of utilizing these materials to produce chloride sorbents for an industrial biomass gasification facility in Hawaii were estimated. The economic estimations were based on the requirements for an assumed biomass to electricity power production facility with an electrical output of 20 MW. Assuming a biomass to electricity conversion efficiency of 20% and the energy content of Leucaena fuel (~19 MJ/kg), the power facility demand for dry biomass fuel is slightly over 450,000 kg per day. The average chlorine content of *Leucaena* fuel is 0.12% on a dry weight basis (Table 5-1), meaning the facility will produce 550 kg of chlorine each day. Based on the biomass gasification system mass balances derived for this study (Table 5-8), about 65% of this chlorine mass (358 kg/day) will be contained in the product gas. The lab-scale chloride breakthrough tests showed that the chloride adsorption capacities of the hydrated AES fly ash and hydrated AES bed material sorbents are 2.1% and 4.0% (g Cl⁻ per g used sorbent), respectively. To adsorb 358 kg of chloride from the biomass gasification product gas stream, about 9,000 kg of AES bed material sorbent and 17,000 kg of AES fly ash sorbent will be required each day assuming that the sorbent is not regenerated. If a regeneration process is utilized, it can be assumed that the amount of required sorbent material can be reduced by a factor of five (Zeman, 2008).

The costs of manufacturing the amount of hydrated AES fly ash and hydrated AES bed material sorbents for a 20 MW biomass to electricity power production facility were estimated and compared to the approximate cost of purchasing commercial chloride sorbents. The costs of the self-prepared sorbents were estimated based on the costs of the materials used in the sorbent recipes. Additional costs such as shipping charges, sales tax, energy, capital stocks and labor were not accounted for in this analysis.

It was assumed that AES Hawaii Inc. would supply its fly ash material free of charge since the alternative (disposing of this waste stream in a landfill facility) will likely result in a cost for the company. The material used as bed material by the AES Hawaii Power Plant can be purchased directly from Pacific Aggregate (Sphere, LLC) by the truck-load. Pacific Aggregate sells the "coral chip" product for \$0.03 USD per kg (\$27.58 per US ton). The material comes as gravel in 1.5875 cm (5/8 inch) minus size (Anon., 2011b). The whole-sale price of the bed material was applied to these calculations since the analysis assumed that the sorbent would be manufactured on the industrial scale.

The hydrated AES fly ash and hydrated AES bed material sorbents prepared for this study were made using food grade starch, reagent grade glycerin and deionized water. This economic analysis assumes that food grade starch and reagent grade glycerin would be used for the production of the sorbents on the industrial scale, although lesser quality ingredients may potentially be used to produce effective sorbents at much lower costs. Food-grade corn starch can be purchased in bulk from HFM Foodservice Corporation's Oahu Distribution Center in Honolulu. HFM sells a 22.7 kg (50 lb.) bag of National Starch brand "mellow gel" corn starch for \$25.32 USD (Anon., 2011c). According to their website, reagent grade glycerin can be purchased in bulk from Fisher Scientific, Inc. for \$6,055.63 per 200 L drum. The costs of the corn starch and the glycerin at \$1.12 USD per kg and \$24.01 USD per kg, respectively, were used to estimate the costs of manufacturing the self-prepared sorbents. The economic calculations also assumed that industrial quality water would be used for the production of the sorbents rather than deionized water. Future work exploring the effects that low cost and locally produced alternatives have on the performance of the self-prepared sorbent materials may be warranted.

The preparation of the sorbents for the experimental investigations of this study involved forming the materials into granules with diameters between 2.8 mm and 1.18 mm. This process resulted in a significant amount of sorbent material being discarded. The preparation technique resulted in sorbent yields of 19.6% and 45.5% by weight of the parent material for the hydrated AES fly ash and hydrated AES bed material sorbents, respectively. An industrial sorbent production process is likely to reduce the amount of waste significantly by recycling the waste material back into the sorbent preparation processes. Regardless, the economic calculations accounted for the waste factor by applying the experimentally derived values.

With these assumptions, the cost of manufacturing the hydrated AES fly ash and hydrated AES bed material sorbents were estimated to \$3.85 USD per L and \$1.92 USD per L, respectively (Table 5-11). The bulk densities of the hydrated AES fly ash and hydrated

AES bed material sorbents are 0.35 kg/L and 0.40 kg/L, respectively, so the costs of each sorbent could also be expressed as \$10.99 USD per kg and \$4.79 USD per kg. These costs were compared to that of purchasing a commercial chloride sorbent. A quote provided by Süd-Chemie Inc. for their ActiSorb® Cl 2 and ActiSorb® Cl 3 products, which are adsorbents for the gas phase removal of HCl, ammonium chlorides and organic chloride adsorbent products is on the order of \$4.66 USD per L (Brunson, 2008). The results of this brief economic analysis indicate that the costs of manufacturing the self-prepared sorbent materials are on the order of the costs of purchasing commercial sorbent materials. Future study may be warranted to provide a more detailed analysis on the costs associated with local production of industrial chloride sorbent materials.

As previously stated, either 9,000 kg of AES bed material sorbent or 17,000 kg of AES fly ash sorbent will be required each day to adsorb the chloride produced by a 20 MW biomass to electricity power production facility. Based on this economic evaluation, it will cost \$42,842 and \$187,289 per day to produce this much AES bed material and AES fly ash sorbent, respectively. Assuming that the sorbents are capable of undergoing five regeneration cycles, these costs are reduced to \$8,568 and \$37,458, respectively. It should be noted that a 20 MW_e scale was selected for the biomass conversion facility for estimating sorbent requirements and that electricity production would not warrant this type of cleanup or cost.

Input Material Costs Assumptions	
AES Fly Ash (US \$/kg)	0.00
AES Bed Material (US \$/kg)	0.03
Deionized Water (US \$/kg)	0.00
Corn Starch (US \$/kg)	0.47
Glycerin (US \$/kg)	1.68
Calculated Costs for Prepared Sorbents	
Hydrated AES Fly Ash (US \$/L)	0.79
Hydrated AES Bed Material (US \$/L)	1.06
Hydrated AES Fly Ash Granules (US \$/L)	3.85
Hydrated AES Bed Material Granules (US \$/L)	1.92
Commercial Sorbent Purchase Costs	
Süd-Chemie ActiSorb® Cl 2 (US \$/L)	4.66
Süd-Chemie ActiSorb® Cl 3 (US \$/L)	4.66

Table 5-11: Approximate material costs for manufacturing the hydrated AES fly ash and hydrated AES bed material sorbents.

5.7.4 Environmental Considerations of the Self-Prepared Sorbent Materials

In addition to economics, the environmental implications of utilizing ash from the AES Hawaii power plant and bed material from the Pacific Aggregate quarry to produce chloride sorbents for an industrial biomass gasification facility in Hawaii should be considered. A detailed environmental analysis that includes estimation of the internal and external environmental costs and benefits is beyond the scope of this study, but information gathered on the current use of the materials provides some useful insight.

Either 9,000 kg of AES bed material or 17,000 kg of AES fly ash material would be utilized daily to manufacture the chloride sorbent required by a 20 MW_e -scale biomass

conversion facility. Typically, the AES facility produces about 200,000 kg of ash per day (Hignite, 2007). To dispose of this waste stream, a portion of the fly ash is used as an admixture in Hawaiian Cement Company concrete and the remaining ash is disposed in a landfill. Both means of handling the waste stream pose environmental risks because of the potential that harmful substances may escape from the ash.

The Air Pollution Control Permit issued by the Hawaii Department of Health (HDOH) for the AES facility indicates that the ash contains several pollutants including lead, arsenic, cadmium, chromium, mercury, nickel and selenium (Hignite, 2007). Due to the risks posed by these substances, the HDOH regulates the disposal of the AES ash. The solid waste management permit issued by the HDOH allows AES fly ash to be used as an admixture in concrete products so long as the concentrations of total and leachable metals do not exceed defined limits. In 2005, the permit limitation for leachable mercury (0.00025 mg/L) was exceeded in several composite ash samples. In response, a study by AES Hawaii, Inc and the URS Corporation showed that leachate from final concrete products containing fly ash (up to 90 percent cement replacement) do not contain detectable mercury concentrations. Following the study, the HDOH agreed to consider raising the leachable mercury limit by over 20 times to 0.0055 mg/L (McCann et al., 2007).

The risks posed by the disposal of coal ash have raised public concerns in the past. In 2006, Maili residents questioned the disposal of AES ash in the Pacific Aggregate quarry, because the ash contains trace levels of arsenic. Shortly after these concerns were raised,

the HDOH informed the operator of Pacific Aggregate that the quarry would not be allowed to continue receiving the ash as fill material (Leone, 2006).

A Best Management Plan (BMP) will help to mitigate the risks of using the AES ash in the industrial production of a chloride sorbent. The used sorbent can likely be disposed of in the same way as the AES coal ash. Currently, the AES ash is disposed of at the PVT Integrated Solid Waste Management Facility in Nanakuli. According to the HDOH solid waste management permit issued to the PVT Land Company Ltd., the operator of the Nanakuli facility, the AES Hawaii ash can only be accepted for beneficial use and may not be disposed of in the landfill. The ash is beneficially used as a protective layer on the synthetic liner of the landfill, to fill void space for fire prevention and as a fire barrier between landfill cells (Yamada, 2011).

As an alternative to AES ash, bed material could be used to manufacture the sorbent. The AES bed material is mined from the Pacific Aggregate quarry in Waianae, Oahu (Figure 5-19). The limestone mining operation poses a potential risk to environmental quality and public health due to its close proximity to residential properties, a public school, conservation areas and the coastal ecosystem. This risk must be carefully evaluated and weighed against the risks associated with employing the AES ash. Assuming that the HDOH assigns and enforces stringent BMPs on the mining operation, the risks to the air, surface water and ground water quality can be properly managed. In addition, BMP's that are designed to reduce the visual impact of quarry operation, such as planting a visual barrier of fast growing trees supplied with permanent irrigation, can be imposed to protect the aesthetics of the area (Ramos and Panagopoulos, 2006).

Additional work is warranted to compare the environmental risks and benefits of importing a ready-made chloride sorbent with one manufactured locally.



Figure 5-19: This aerial image of the Pacific Aggregate Quarry in Maili, Hawaii, shows the close proximity of the operation to the residential community and the marine environment and also illustrates the effect it has on the aesthetics of the area (Google Maps).

6.0 CONCLUSION

Self-prepared sorbent materials were developed for the removal of chloride from a biomass gasification product stream. Of the parent materials used in the sorbent formations, fly ash and bed material from the AES Hawaii power plant were found to produce sorbents with the greatest chloride removal capacity. The calcination and slaking of these materials in a hydration solution containing 7% wt. glycerin was critical to enhancing the sorption capacity of the sorbents. The hydrated materials performed best as chloride sorbents when they were formed into granules. The lab-scale chloride breakthrough investigations showed that when subjected to a 400°C gas stream containing ~650 ppmw CI⁻ and an average GHSV of about 1500 hr⁻¹, the hydrated AES fly ash and hydrated AES bed material sorbent preparations provided chloride adsorption capacities of 2.1% and 4.0% (g CI⁻ per g used sorbent), respectively. These adsorption capacities are comparable to that of the BASF CL-760 commercial sorbent, which was found to have an average chloride capacity of 2.4% when subjected to the same conditions.

The self-prepared hydrated AES fly ash and hydrated AES bed material sorbent materials were tested in the HNEI bench-scale biomass gasifier. The test results indicate that both sorbent preparations are capable of reducing the chloride concentrations in the biomass gasification product stream at GHSVs of ~9,000 hr⁻¹ or less. Considering that a fixed sorbent bed is usually designed to have a GHSV of about 1,000 hr⁻¹, the self-prepared materials show promise as chloride adsorbents for a biomass gasification system. Mass-balance calculations on the chlorine input and output streams for the biomass gasifier

tests were able to account for between 85.8% and 99.2% of the chlorine in the results. The analyses confirmed that the self-prepared sorbent materials are effective at removing chloride from the biomass gasification product gas stream. The environmental and economic implications of preparing chloride sorbents using AES fly ash and AES bed material as parent materials were considered. If biomass gasification becomes a valuable part of Hawaii's future renewable energy profile, this investigation into the development of chloride adsorbents from locally available parent materials may provide relevant information on the balance of the overall economic and environmental costs and benefits of biomass energy production.

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