In situ desulfurization of coke by novel activated sulfur sorbents during combustion

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Abstract

Silica-enhanced sulfur sorbents derived from pressure hydration of calcium hydroxide and coal fly-ash (F-Ash-CSH) were prepared at various pressure hydration reaction conditions and subsequently coagglomerated with Syncrude coke (produced as a by-product in the fluid coking of Athabasca oil sands bitumen by Syncrude Limited) and subjected to combustion and SO_2 analysis. The sulfur capture efficiency of the sorbents in the coke was found to depend on the calcium hydroxide:silica ($Ca(OH)_2/SiO_2$) molar ratio in the sorbent and to be independent of the hydration reaction time, pressure and temperature. Other combustion data, such as calorific value and ash content of the agglomerates, were affected in the same fashion. Morphological and chemical composition analysis of the sorbents and combustion ash products, using X-ray diffraction, atomic absorption spectroscopy and standard gravimetric analysis, revealed that the major constituent of the ash was calcium sulfate, which may be economically recoverable. In addition, other minor compounds, such as calcite, quartz, ilmenite and calcium–feldspar were also observed. These results further confirm that the sulfur capture activity of the sorbents in the coke depend mainly upon the Ca/S ratio, the combustion temperature and the type of sorbent used.

INTRODUCTION

The high sulfur and ash contents of Athabasca petroleum coke preclude its possible utilization as a solid fuel for industrial steam raising and process energy generation. Various processes for the control of sulfur dioxide emissions during petroleum coke combustion have been reported in the literature [1–6]. These desulphurization processes are not considered at present to be sufficiently attractive economically to allow the use of the coke as a fuel on a commercial scale.

In previous communications [7–9] we demonstrated the possibility of reducing SO_2 emissions during the combustion of Athabasca petroleum

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coke by coagglomerating the coke with conventional sulfur sorbents [$Ca(OH)_2$ and $NaHCO_3$] and silica-enhanced sorbents derived from pure silica (L-MT-CSH) and coal fly-ash (F-Ash-CSH) using a pressure hydration method [7,9]. It was observed that this approach required relatively higher calcium/sulfur (Ca/S) ratios, in the case of the conventional sorbents, to produce acceptable reductions in SO_2 emissions. The silica-enhanced sorbents were found to be highly active in the coke, at relatively lower Ca/S ratios, in terms of the SO_2 reduction during the combustion of the agglomerates. However, it was thought that varying the pressure hydration reaction conditions would affect the integrity and performance of the activated sorbents in the coke.

This paper describes results complementary to those obtained earlier [7–9], and is aimed essentially at the optimization of the desulfurization process of the sorbents in the coke during combustion. In this work, F-Ash-CSH sorbents were prepared under various pressure hydration reaction conditions and subsequently coagglomerated with Syncrude coke at a Ca/S ratio of 1.0, and the resulting agglomerate was subjected to combustion and SO_2 analysis. In addition, morphological and composition studies were carried out on these sorbents using energy dispersive scanning electron microscopy (SEM/EDX) and X-ray diffractometry (XRD). Chemical composition analysis of the combustion ash products of the agglomerates was also carried out by means of the above spectroscopic methods, in addition to atomic absorption spectroscopy (AAS) and standard gravimetric methods, with a view to obtaining qualitative and/or quantitative information on the combustion ash products. This information will provide a basis for the explanation of plausible mechanisms of the desulfurization reaction of the sorbents in the coke, as well as determining possible areas of applications of the by-product ash. The F-Ash-CSH sorbent was chosen for this investigation because of the availability and low cost of the coal fly-ash. The ultimate aim of this project is to determine the feasibility of the production of smokeless solid fuels, via coagglomeration of Athabasca petroleum coke with highly active sulfur sorbents, having high calorific value and low SO_2 emissions.

EXPERIMENTAL

Materials

Syncrude fluid coke samples were obtained from Syncrude Limited. Reagent grade $Ca(OH)_2$ and coal fly-ash (64 wt% SiO_2) obtained from TransAlta Utilities (Edmonton, Canada) were used. The coke and sorbent materials were used in the form of powder, with particle sizes in the range 180–212 μm. Cold lake bitumen was used as a binder.

TABLE 1

Pressure hydration reaction conditions for the silica-enhanced sorbents

Sample	$SiO_2/Ca(OH)_2$ [a]	Time (h)	Temperature (°C)	Pressure (psi) [b]
A-1	1:2	1	150	150
A-2	2:1	1	150	150
B-1	1:1	1	230	150
B-2	1:1	1	120	150
B-3	1:1	1	150	400
C-1	1:1	1	150	100
C-2 [c]	1:1	–	–	–

[a] Molar ratio.
[b] Cylinder pressure.
[c] Dry physical mixture of $Ca(OH)_2$ and SiO_2.

Pressure hydration reactions

The silica-enhanced sorbents (F-Ash-CSH) were prepared by batch pressure hydration of hydrated lime [$Ca(OH)_2$] and coal fly-ash, and were dried to constant weight in a vacuum oven maintained at 85°C as described previously [7,8]. In this work, an attempt was made to study the effects of varying pressure hydration conditions on the desulfurization action of the activated sorbents in the coke by preparing a range of silica-enhanced sorbents from coal fly-ash and $Ca(OH)_2$ at various pressure hydration conditions, as shown in Table 1. In this series of activated sorbents, the relative amount of $Ca(OH)_2$ to silica and the temperature and pressure of the hydration reaction were varied. Preliminary investigation of published work in this area [10–13] revealed that the pressure hydration reaction was independent of hydration time; therefore this was held constant at 1 h throughout this investigation.

A portion of the prepared sorbent was coagglomerated with Syncrude coke at a Ca/S ratio of 1.0 and later subjected to combustion and SO_2 analysis at 800°C to determine the effect of varying hydration conditions on the combustion data of the agglomerates. The other portion was used for morphological and chemical composition analysis, using SEM/EDX and XRD, with a view to ascertaining the effect of the various hydration conditions on the morphology and composition of the sorbents and hence their performance in the coke during combustion.

Preparation of agglomerates

The coke and a known amount of the sorbent were dry-mixed using a wrist shaker (Spex Mixer/mill) until a homogeneous mixture was obtained. A minimal amount of bitumen binder (< 5% based on the weight of coke)

was then added and the mixing was continued until satisfactory dry agglomerates with the required Ca/S mole ratios were obtained. Details of the preparation method are given elsewhere [7–9].

Combustion and SO₂ analysis

The ash content and the calorific values were determined according to ASTM D 3172-82 and ASTM D 3286-77 respectively [7–9]. Sulfur dioxide emission from the coke agglomerates was determined by burning about 0.2 g of the sample in a stream of oxygen at 800 °C using a modified ASTM D 3177-75 method as described previously [7–9]. The sulfur fixed in the ash after combustion was expressed as a percentage of the total sulfur in the original sample and reported as percent sulfur capture.

Chemical composition analysis

The ash products obtained on combustion of the above agglomerates were analysed using SEM/EDX, XRD, AAS, and standard gravimetric methods for determination of sulfates in carbonaceous materials [14]. In the last method, the SO_4^{2-} in the sample was determined by dissolution in a mixture of solvents (see below) and precipitated as $BaSO_4$. The total SO_4^{2-} present was estimated from the equation [14]

$$\%SO_4^{2-} = \frac{\text{wt. of BaSO}_4}{\text{wt. of sample}} \times 0.4115 \times 100$$

Solutions for AAS and gravimetric analysis were prepared by digesting the samples with a mixture of aqua regia (HCl/HNO₃), perchloric acid and hydrofluoric acid [14]. The results obtained were compared with corresponding results for the combustion ash products obtained from Syncrude coke coagglomerated with Ca(OH)₂ and pure silica (L-MT-CSH) as previously described [7–9].

RESULTS AND DISCUSSION

Effect of hydration conditions on sorbent morphology and composition

The surfaces and composition of the F-Ash-CSH sorbents prepared at varying conditions (see Table 1) were studied using a scanning electron microscope equipped with an energy dispersion system (SEM/EDX) and/or XRD. The results obtained are summarized in Table 2. For more detailed morphological data showing *d*-spacing and relative intensities of the peaks, see Table 3. Apart from sample B-1, the diffraction patterns of the samples were observed to be similar and to show Ca(OH)₂, SiO₂ and

TABLE 2

X-ray diffraction data of sorbents as a function of pressure hydration conditions

Sorbent	$Ca(OH)_2$	SiO_2	$Ca_3Al_2(SiO_4)(OH)_8$	$CaO \cdot SiO_2 \cdot H_2O$
A-1	+	+	+	−
A-2	+	+	+	−
B-1	−	−	+	+
B-2	+	+	+	−
B-3	+	+	+	−
C-1	+	+	+	−
C-2	+	+	−	−

+, Observed; −, unobserved.

calcium aluminosilicate hydroxide $[Ca_3Al_2(SiO_4)(OH)_8]$ peaks. In the diffraction pattern of sample B-1, no separate $Ca(OH)_2$ and SiO_3 peaks were observed, indicating a complete reaction between the $Ca(OH)_2$ and SiO_2 owing to the higher hydration temperature. In addition, some peaks suspected to be due to hydrated calcium silicate $(CaO \cdot SiO_2 \cdot H_2O)$ were observed in the diffraction pattern of this sample. Visual inspection of the samples showed that sample B-1 was more porous than the other samples, as evidenced by the larger volume occupied by the sample after pressure hydration. The highly porous or amorphous nature of this sample was confirmed by the SEM micrograph shown in Fig. 1(b). Note the highly porous and/or spongy nature of sample B-1 relative to sample A-2, for instance (Fig. 1). The SEM micrograph of sample A-2 is shown here to represent the morphology of samples A-1, A-2, B-2, B-3 and C-1 because the micrographs of the latter samples were observed to be similar to that of sample A-2. Note that the diffraction patterns and SEM micrographs of samples C-1 and C-2 have been described previously [7,8], and are merely presented here for comparative purposes.

Effect of hydration conditions on sulfur capture activities

The effect of pressure hydration conditions on the sulfur capture activity of the F-Ash-CSH sorbents (prepared under the hydration conditions shown in Table 1) was studied by coagglomerating the various silica-enhanced sorbents with Syncrude coke at a Ca/S ratio of 1.0, and combustion at 800°C. The percent sulfur capture was estimated as before [7–9], and the results are shown in Table 4. Note that the sorbent sample identification codes correspond to those given in Table 1. The ash contents and calorific values for the agglomerates are also given in Table 4. It is evident from this table that the effect of hydration reaction temperature and pressure on percentage S capture is insignificant compared with the effect

TABLE 3

X-ray diffraction data for the silica-enhanced sorbents prepared at various pressure hydration conditions (Cu Kα radiation and Ni filter)

Sample [a]	d-spacing (Å)	Relative intensity (%)	Identified phase
A-1, A-2, B-2, B-3, C-1	5.02	44	$Ca_3Al_2(SiO_4)(OH)_8$
	3.26	23	
	2.76	100	
	2.50	19	
	2.41	26	
	2.24	56	
	1.99	64	
	4.90	74	$Ca(OH)_2$
	3.11	23	
	2.63	100	
	1.92	42	
	1.79	36	
	4.25	35	SiO_2
	3.35	100	
	2.26	06	
B-1	4.95	44	$Ca_3Al_2(SiO_4)(OH)_8$
	3.07	49	
	2.72	100	
	2.22	58	
	1.97	64	
	1.69	11	
	3.06	100	$CaO \cdot SiO_2 \cdot H_2O$
	2.81	80	
	2.50	19	
	1.84	80	
C-2 [b]	4.90	74	$Ca(OH)_2$
	3.10	23	
	2.62	100	
	1.92	42	
	26.6	100	SiO_2
	51.0	<1	

[a] See text for sample identification.
[b] Dry physical mixture of $Ca(OH)_2 /SiO_2$ at a molar ratio of 1.0.

of the relative molar amounts of $Ca(OH)_2$ and SiO_2 in the sorbent. For example, at a constant $SiO_2/Ca(OH)_2$ molar ratio of 1.0 in the sorbent, the S capture of the agglomerates was observed to be independent of hydration pressure and temperature within the limits of the conditions employed, and had an average value of about 60%. But holding the temperature and pressure constant and varying the molar ratio of $SiO_2/Ca(OH)_2$ in the sorbent had a significant effect on the S capture values obtained from the corresponding agglomerate (see Table 4). At a
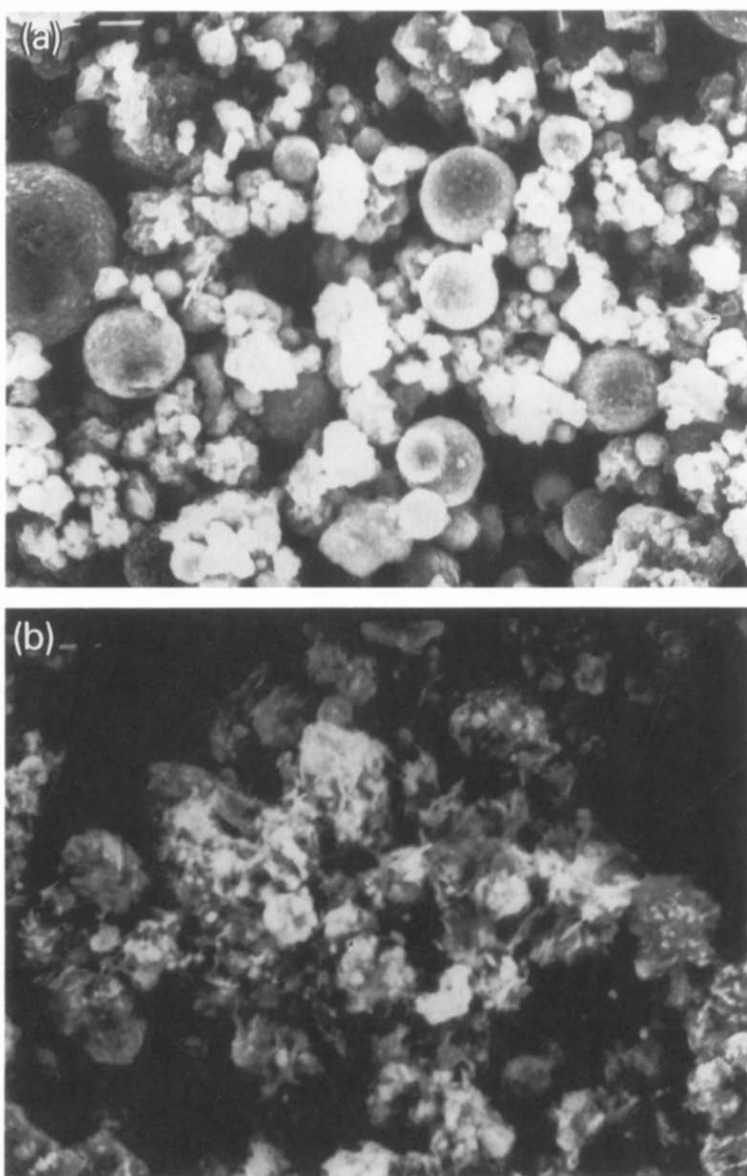
Fig. 1. Scanning electron micrographs of F-Ash-CSH sorbents prepared at varying pressure hydration conditions. (a) Sample A-2. Original magnification ×700. (b) Sample B-1. Original magnification ×1000. See text for sample identification.

$SiO_2/Ca(OH)_2$ ratio of 2.0, the agglomerate (coke + A-2) had a sulfur capture activity of about 71%, a value close to, but slightly lower than, that obtained from the corresponding agglomerate containing F-Ash-CSH (sample C-1) prepared at the initial conditions (see Table 1).

As expected, the agglomerate (coke + A-2) containing the sorbent with a $SiO_2/Ca(OH)_2$ ratio of 2.0 was observed to have the highest ash content

TABLE 4

Effect of pressure hydration conditions on combustion and SO_2 analysis of the agglomerates at a Ca/S ratio of 1.0

Agglomerate	S capture (%)	Ash content (wt%)	Calorific value (BTU/lb)
Coke + A-1	62.5	32.5	10855
Coke + A-2	70.7	45.0	8824
Coke + B-1	55.9	34.7	9990
Coke + B-2	61.2	37.8	10006
Coke + B-3	61.4	38.0	10092
Coke + C-1	76.6	38.8	9775

and the lowest calorific value (Table 4). The other samples had similar values regardless of the pressure hydration reaction conditions employed for the preparation of the sorbents. The above results suggest that our initial chosen conditions (i.e. temperature = 150 °C; pressure = 150 psi; $SiO_2/Ca(OH)_2 = 1.0$; time = 1 h) [7,8] may represent the conditions for the preparation of F-Ash-CSH sorbent with overall optimum performance in the coke during combustion.

Chemical composition analysis of combustion ash products

It has been reported earlier that agglomerates similar to the ones used in this study, when burnt at around 800 °C, generate ash products which contain mainly hydrated metal silicates and calcium sulfate [13]. These materials may be useful in the manufacture of cement and/or gypsum board [15]. In an attempt to quantify the relative amounts of these materials in the combustion ash from the present agglomerates, and to clarify further the desulfurization reactions of the sorbents in the coke, the combustion ash products from Syncrude coke coagglomerated with $Ca(OH)_2$ and F-Ash-CSH at Ca/S ratios of 1.0 and 2.0 were analysed by means of AAS and XRD. The XRD data obtained are summarized in Table 5. The *d*-spacings and relative intensities of the observed peaks are shown in Table 6. It can be seen from these tables that the major component in the ash obtained from the coke/$Ca(OH)_2$ agglomerates in anhydrite ($CaSO_4$). Other minor compounds observed include calcite ($CaCO_3$), lime (CaO) and oldhamite (CaS). The $CaCO_3$ is most probably formed from the reaction between the CO_2 combustion product and CaO in the sorbent. Additionally, the presence of minor quantities of oldhamite (CaS) in the ash product is an indication of a reaction between lime (CaO) and H_2S formed during combustion. Since H_2S gas was not detected in the exit gas stream, we believe that the small amounts of H_2S produced in the non-oxidizing void
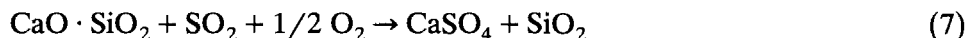
TABLE 5

X-ray diffraction data of the combustion ash products obtained from Syncrude coke coagglomerated with $Ca(OH)_2$ and F-Ash-CSH at the Ca/S ratios shown

Sample	Ca/S ratio	Major components observed	Minor components observed
Coke + $Ca(OH)_2$	1.0	Anhydrite	Calcite, oldhamite
	2.0	Anhydrite	Calcite, lime, quartz, oldhamite
Coke + F-Ash-CSH	1.0	Anhydrite, quartz	Calcite, ilmenite ($FeTiO_3$), oldhamite, Ca-feldspar, unidentified minor compounds

zones within the reacting mass are rapidly oxidized to SO_2 once they diffuse into the gas phase. On the other hand, if the H_2S formed comes in contact with CaO in the agglomerate matrix, oldhamite is formed as an intermediate product, which could subsequently be oxidized to $CaSO_4$. From these results, it is reasonable to assume that the following desulfurization reactions occur to a greater or lesser extent during combustion.

$$2CaO + 2SO_2 + O_2 \rightarrow 2CaSO_4 \tag{1}$$

$$CaO + CO_2 \rightarrow CaCO_3 \tag{2}$$

$$CaO + H_2S \rightarrow CaS + H_2O \tag{3}$$

$$CaS + 2O_2 \rightarrow CaSO_4 \tag{4}$$

$$H_2S + 1.5\ O_2 \rightarrow SO_2 + H_2O \tag{5}$$

The data obtained from the coke/F-Ash-CSH are more complex in nature in that quartz (SiO_2) and several minor compounds including ilmenite ($FeTiO_3$), calcium-feldspar ($CaAl_2Si_2O_8$) and other unidentified minor compounds were observed in this diffraction pattern in addition to the above compounds. This may be due to the composite nature of the coal fly-ash already referred to earlier. However, in both cases $CaSO_4$ appears to be the major constituent of the ash product, indicating that the following overall desulfurization reactions may be valid for $Ca(OH)_2$ and silica-enhanced sorbents in the coke, respectively.

$$CaO + SO_2 + 1/2\ O_2 \rightarrow CaSO_4 \tag{6}$$

$$CaO \cdot SiO_2 + SO_2 + 1/2\ O_2 \rightarrow CaSO_4 + SiO_2 \tag{7}$$

Further kinetic investigation would need to be carried out in order to establish the rate determining step of the desulfurization process, thereby ensuring proper control of the reaction.

Table 7 shows quantitative data from the chemical composition analysis of the combustion ash products, as determined by AAS and standard

TABLE 6

X-ray diffraction data of the combustion ash from the agglomerates at the Ca/S mole ratio shown (Cu K_a radiation and Ni filter)

Sample	Ca/S ratio	d-spacing (Å)	Intensity	Identified phase
Coke/Ca(OH)₂	1.0	3.52	vs	$CaSO_4$
		2.86	s	
		3.86	m	
		2.49	m	
		2.85	m	CaS
		2.03	w	
		3.06	vs	$CaCO_3$
		3.85	m	
		2.49	m	
		2.29	m	
Coke/Ca(OH)₂	2.0	3.49	vs	$CaSO_4$
		2.86	s	
		2.09	m	
		1.88	m	
		3.86	w	
		2.85	m	CaS
		2.02	w	
		2.40	w	CaO
		1.70	vw	
		3.05	vs	$CaCO_3$
		3.85	m	
		3.28	m	
Coke/F-Ash-CSH	1.0	3.49	vs	$CaSO_4$
		2.85	s	
		2.20	w	
		2.32	w	
		3.34	m	SiO_2
		4.25	vw	
		2.45	vw	
		2.84	m	CaS
		2.01	w	
		3.85	w	$CaCO_3$
		2.08	w	
		2.27	vw	
		4.07	2	Ca-feldspar
		3.23	w	
		3.78	w	Unidentified minor compounds
		3.59	w	
		2.75	w	

TABLE 7

Chemical composition analysis data (wt%) of combustion ash products of Syncrude coke coagglomerated with the sorbents at the Ca/S ratio shown

Element/anion	Sample 1 [a]	Sample 2 [b]	Sample 3 [c]
Ca	46.8	52.1	41.1
Si	16.6	10.6	18.1
Al	13.1	8.1	12.1
Fe	3.6	4.5	4.7
V	0.7	0.6	0.8
Ti	0.8	0.8	0.9
Ni	0.1	0.07	< 0.05
Pb	1.8	0.4	0.6
Cr	< 0.1	< 0.1	< 0.1
SO_4^{2-}	15.09	20.01	9.93
$CaSO_4$	21.3 [d]	28.3 [d]	14.1 [d]

[a,b] Coke/Ca(OH)$_2$, Ca/S = 1.0 and 2.0 respectively.
[c] Coke/F-Ash-CSH, Ca/S = 1.0.
[d] Values obtained from stoichiometric analysis.

gravimetric methods. It is clearly evident from this table that calcium, which may be present as $CaSO_4$, CaS, $CaAl_2Si_2O_8$, etc., is the major component of the ash products. This observation is supported by the above XRD data (or vice versa). The total sulfur present in the ash was determined gravimetrically by precipitation as barium sulphate, and the value obtained was converted to percent sulphate (% SO_4^{2-}) as described in the experimental section. The values obtained, which represent the total sulfur fixed as sulfates in the ash, are also shown in Table 7. It can be seen from this table that % SO_4^{2-} present in the ash was in the order sample 2 > sample 1 > sample 3 (see Table 7 for sample identification). As expected sample 2 (coke/Ca(OH)$_2$; Ca/S = 2.0) had the highest % SO_4^{2-} of 20. The reason for the much lower % SO_4^{2-} present in the coke/F-Ash-CSH (Ca/S = 1.0) is not clear at the present time. It is important to note that quantitative XRD analysis of the ash products will be highly informative in that it will reveal the exact amount of the $CaSO_4$ relative to the other minor compounds present in the ash. However, we can fairly accurately estimate the total amount of $CaSO_4$ from Table 7. If we assume that all the SO_4^{2-} are derived from $CaSO_4$, then the % $CaSO_4$ in the ash can be calculated stoichiometrically (see Table 7).

CONCLUSIONS

1. Desulfurization action of the sorbents in the coke appears to be independent of the pressure hydration reaction time, temperature and pressure but dependent on the Ca(OH)$_2$/SiO$_2$ molar ratio in the sorbent.

The results suggest that the following pressure hydration conditions: temperature = 150 °C, time = 1 h, pressure = 150 psi (including the vapor pressure of water at 150 °C), $Ca(OH)_2/SiO_2$ molar ratio = 1.0, represent optimum preparation conditions for the silica-enhanced sorbents in terms of percent sulfur capture, calorific value and ash content of their coke agglomerates after combustion.

2. The combustion ash products from the agglomerates contain mainly $CaSO_4$ and silicates, which may find some applications in the manufacture of gypsum board and the cement industry.

3. The results obtained from this work and from previous work [7–9] demonstrates the feasibility of the combustion of the present system to generate process energy with environmentally acceptable SO_2 emissions. However, detailed process cost analysis, desulfurization reaction kinetics, combustibility and carbonization studies need to be carried out on the agglomerates to determine whether they can be used commercially as fuel.

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