Moving Granular-Bed Filter for Multi-Contaminant Control

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ABSTRACT

In addition to the control of ash particulates, a moving granular-bed filter can control other contaminants found in high-temperature, high-pressure coal gas streams through the use of chemically-reactive filter media. Under sponsorship of the U. S. Department of Energy, a laboratory test program is underway to evaluate the following three types of chemically-reactive filter media: a clay-based filter medium for the control of alkali and heavy metals in either reducing or oxidizing environments, a sodium-based filter medium for the control of halogens and metaloids in reducing-gas environments, and a nickel catalyst for the destruction of ammonia and hydrogen cyanide in a reducing-gas environments. The test program calls for the evaluation of techniques for forming reactive clay filter media and the evaluation of the structural and chemical properties of clay media, nahcolite (NaHCO₃) media, and media composed of nickel catalysts. Initial results of the development of a clay-based filter medium are presented.

INTRODUCTION

Combustion Power Company’s granular-bed filter (GBF) has demonstrated the ability to remove particulates from high-pressure and high-temperature coal gas streams. This is accomplished by the impaction and capture of ash particle on the filter medium. The filter media used in the demonstration tests were 2 millimeters (mm) and 3 mm mullite spheres, which are believed to be chemically inert with respect to the constituents in coal gases. In scale-up studies of the GBF, the size of the filter medium changed to a nominal ¼ inch diameter to increase the capacity of the filter. The new filter medium is a dense ceramic material which is probably inert with respect to the coal gas constituents. For the control of particulates and other contaminants, the inert filter medium will be replaced with a filter medium which is either chemically or catalytically reactive with
respect to selected constituents in the gas stream. A chemically reactive filter medium will have a finite life and will need to be replaced on a periodic basis, most likely during a scheduled plant outage. Alternatively, the filter medium could be replaced on line by the introduction of fresh filter medium in place of spent filter medium should the life of the chemically-reactive filter medium not be compatible with a normal outage sequence. The objective of the test program is to develop and evaluate filter media which are both chemically reactive and have the structural properties required of a GBF filter medium.

The test program will develop and evaluate potential filter materials which have been demonstrated to be reactive to contaminants in coal gas streams in either gasification or combustion environments. Contaminants which may be controlled with a GBF using specialized filter media include alkali, halogens, ammonia, hydrogen cyanide, and trace metals. Four types of sorbents which could be developed are: (1) A clay-based filter medium for the control of alkali and some heavy metals in either reducing- or oxidizing-gas environments, (2) a sodium-based filter medium for the control of halogens and some heavy metals in reducing-gas environments, (3) a nickel catalyst for the destruction of NH₃ and HCN in a reducing-gas environment, or (4) a silica-based sorbent for the control of cesium and lead.

EVALUATION OF POTENTIAL SORBENTS

Clay for the Control of Alkali

The presence of alkali species in pressurized fluidized-bed combustion (PFBC) or integrated gasification combined-cycle (IGCC) gas streams is of concern because of the potential corrosion which alkali species can cause in a gas turbine. Also, alkali species are associated with low-melting compounds which can provide the "glue" for forming deposits on turbine and heat exchanger surfaces. For these reasons, turbine manufacturers have placed restrictions on the amount of alkali (sodium and potassium) that can enter a gas turbine.

Several investigators have reported successful alkali removal from high-temperature gas streams with sorbents of activated bauxite, attapulgus clay, calcium montmorillonite clay, diatomaceous earth, kaolin clay, and emathlite clay. Emathlite, a type of fullers earth, was found to be a leading getter of alkali [1]. The clay had a high capacity for sodium and binds the sodium irreversibly. At extreme conversions, the clay was found to become sticky. This could be a problem for GBF operation, but is unlikely to occur as these extreme conversions are not realistically obtained. Kaolin, bauxite, and emathlite were all found to be capable of removing alkali from coal conversion streams [2]. Kaolin and emathlite adsorption of alkali was an irreversible process. The maximum sorption capacity of the kaolin was about 25 percent, while that of bauxite and emathlite was about 15 percent. Screening of alkali sorbents [3] found the following alkali getters: activated bauxite, calcium montmorillonite clay, attapulgus clay, zeolite ZSM-5, emathlite clay, kaolin clay, and diatomaceous earth. Kaolin, emathlite, and calcium montmorillonite clays all performed equally well. Calcium montmorillonite was chosen for further investigation because of it produced the strongest pellets.
Sodium Compounds for the Control of Halogens

Emissions of chlorine from a coal-fired power plant can range from 50 parts per million, volume (ppmv) to several thousand ppmv, depending on the chlorine content of the coal and the coal processing technique [4]. The presence of chlorine in a coal gas stream can cause acidic corrosion of downstream equipment such as turbine blades and heat exchangers. It can act as a poison of molten carbonate fuel cells electrodes. Besides having an adverse effect on equipment, the emission of HCl into the atmosphere can have deleterious effects.

Sodium minerals containing sodium bicarbonate or sodium carbonate react with HCl, forming NaCl, CO₂ and H₂O. Researchers at Physical Science, Inc., evaluated shortite (NaCO₃·2CaCO₃) and trona (NaCO₃·NaHCO₃) as sorbents for the removal of HCl vapors [5]. Shortite had a higher reactivity than trona. Laboratory and bench-scale experiments at SRI International evaluated nahcolite (NaHCO₃), shortite, and dawsonite (NaAl(OH)₂CO₃) for the removal of HCl from simulated coal gas [6]. All the tested sorbents reduced HCl concentration from 300 ppmv to 1 ppmv. Nahcolite had a superior sorption capacity with the spent sorbent containing as much as 54 wt% chloride and was chosen for further investigation.

Nickel Catalyst for the Dehydrogenation of Ammonia

Coal is typically composed of 1-2 percent organic nitrogen which is converted into ammonia, hydrogen cyanide, and nitrogen during the carbonization or gasification of coal. The extent of ammonia formation depends on coal properties and the processing conditions. High-temperature gasification such as a Texaco oxygen-blown gasifier produces about 2000 ppmv of ammonia, while lower temperature gasification such as an air-blown Lurgi or General Electric gasifier produces concentrations of about 5000 ppmv [7]. If unabated, the ammonia can be converted into high levels of oxides of nitrogen in the turbine combustor.

Researchers at Research Triangle Institute began investigating the use of ammonia decomposition catalyst in conjunction with the H₂S sorbent zinc titanate [8]. At temperatures below 800 degrees Celsius (°C), none of the catalyst investigated were effective in a high-H₂S environment. The direction of the program has changed to determining the life of ammonia decomposition catalyst operating at temperatures above 800°C in a high-H₂S environment. It is expected that this work will provide a foundation for the proposed tests to develop ammonia catalyst for use in a GBF.

Clay or Sodium Sorbents for Control of Selected Trace Metals

The fate of trace elements from advance power cycles is currently being investigated in several Department of Energy (DOE) programs. Measurements were conducted at American Electric Power's PPBC Tidd plant to determine the emissions of hazardous air pollutants [9]. Similar measurements are being conducted at Destec's Louisiana Gasification Technology, Inc., IGCC plant [10]. The results of these programs will help determine the need for control of trace elements from advance coal-fired power systems.
Researchers proposed a method for determining the likely reactivity between trace metals and potential sorbents [11]. If the potential sorbent and the trace metal form solutions or mixtures according to phase diagrams, then it is likely that the potential sorbent will be reactive with respect to the trace metal. By consulting the phase diagrams published by the American Ceramic Society, researchers determined that alumina silicates are likely sorbents for barium, beryllium, chrome, lead, cobalt, strontium, and uranium. Silica was also a likely sorbent for all of the above elements as well as cesium and strontium.

CLAY SORBENTS SCREENING TESTS

The current scope of work is focusing on developing a clay-based media for alkali control. The clay sorbent screening tests were the first tests conducted. The purpose of the clay screening tests was to evaluate the relative reactivity of candidate clays for the sorption of selected metal compounds, specifically alkali. The clays were evaluated in gasification and PFBC gas environments. Five candidate clays have been identified as having potential for removing alkali and other metals from high-temperature coal gas streams. These clays are:

- Emathlite [4],
- Kaolin [5],
- Bauxitic kaolin,
- Attapulgite [6], and
- Calcium montmorillonite [6].

The chemical composition of each clay was determined. A loss on ignition analysis was performed on each clay as part of the chemical analysis. Table 1. shows the mineral analysis along with the loss of ignition (LOI) values for these clay samples.

<table>
<thead>
<tr>
<th></th>
<th>Albion Kaolin</th>
<th>Emathlite 3000</th>
<th>Emathlite 600</th>
<th>Attapulgite</th>
<th>Ca Montmorillonite</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{P}_2\text{O}_5 )</td>
<td>&lt; 0.046</td>
<td>3.57</td>
<td>3.59</td>
<td>0.84</td>
<td>&lt; 0.034</td>
</tr>
<tr>
<td>( \text{SiO}_2 )</td>
<td>41.13</td>
<td>60.39</td>
<td>60.95</td>
<td>46.93</td>
<td>42.5</td>
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<tr>
<td>( \text{Na}_2\text{O} )</td>
<td>&lt; 0.027</td>
<td>0.29</td>
<td>0.3</td>
<td>&lt; 0.027</td>
<td>1.02</td>
</tr>
<tr>
<td>( \text{K}_2\text{O} )</td>
<td>0.16</td>
<td>0.86</td>
<td>0.91</td>
<td>0.55</td>
<td>0.44</td>
</tr>
<tr>
<td>( \text{SO}_3 )</td>
<td>&lt; 0.12</td>
<td>0.14</td>
<td>0.18</td>
<td>0.30</td>
<td>1.45</td>
</tr>
<tr>
<td>MgO</td>
<td>0.043</td>
<td>2.49</td>
<td>2.49</td>
<td>7.16</td>
<td>4.01</td>
</tr>
<tr>
<td>CaO</td>
<td>0.057</td>
<td>5.02</td>
<td>5.33</td>
<td>3.56</td>
<td>9.78</td>
</tr>
<tr>
<td>( \text{Al}_2\text{O}_3 )</td>
<td>36.27</td>
<td>7.46</td>
<td>6.86</td>
<td>7.80</td>
<td>14.25</td>
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<tr>
<td>( \text{TiO}_2 )</td>
<td>1.51</td>
<td>0.35</td>
<td>0.32</td>
<td>0.32</td>
<td>0.073</td>
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<tr>
<td>( \text{Fe}_2\text{O}_3 )</td>
<td>0.50</td>
<td>2.87</td>
<td>2.78</td>
<td>2.75</td>
<td>1.12</td>
</tr>
<tr>
<td>Loss on ignition</td>
<td>13.78</td>
<td>9.81</td>
<td>8.87</td>
<td>21.61</td>
<td>20.87</td>
</tr>
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Thermogravimetric Analyzer (TGA) Reactivity of Clay Samples

The reactivity of the above clay samples for alkali absorption was determined using a TGA. A mixture of calcined clay and 10 wt.% was prepared by calcining the clay at 850 °C for 12-24 hours in a muffle furnace, then cooling the calcined sample in a desiccator and grinding the sample using a mortar and pestle. The ground sample was then sieved through an ATM Sonic Sifter to obtain particles less than 325 mesh. Similarly, NaCl powder was ground and sieved to obtain particles less than 325 mesh. The calcined clay sample and NaCl powder were then mixed to obtain a sample containing 10 wt.% NaCl.

The prepared samples were tested in the TGA. The TGA test procedure involved heating the sample in nitrogen at a rate of 15 °C/min to 1000 °C, followed by an isothermal treatment at 1000 °C until the rate of weight change became nearly zero. Figure 1 shows the TGA reactivity profiles of the these clay samples plotted in terms of weight fraction versus temperature. Based on the procedure developed by McLaughlin [3], the sample that lost the least amount of weight should have the highest sodium capture capacity. Also, included in this figure is the TGA reactivity of a non-getter, which in this case was an α-alumina sample and was prepared using the same procedure that was used for preparing the other clay samples. From these TGA results, it appears that attapulgite and emathlite may be good candidates for sorbing the alkali vapors. More TGA tests are underway to further confirm these results.

![TGA Screening of Various Clays](image)

**SUMMARY**

It is a technically advantageous concept to be able to capture gas stream contaminants as well as particulate in a single vessel. Not only would the gas stream cleanup process in power systems be simpler with a single vessel, but capital and operating costs would be lower. A GBF is the perfect candidate for multi-contaminant control. This test program to develop multi-contaminant
control media to control gas stream contaminants as well as particulate in a GBF has just been initiated and initial results show that attapulgite and emathlite may be good candidates for sorbing alkali vapors in a high-temperature, high-pressure gas stream.

References