Fuel 89 (2010) 894–903

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

High-temperature sorbents for Hg, Cd, Pb, and other trace metals: Mechanisms and applications

Jost O.L. Wendt *, Sung Jun Lee

University of Utah, Chemical Engineering, Room 3290 MEB, Salt Lake City, UT 84112, USA

ARTICLE INFO

Article history:
Received 16 October 2008
Accepted 23 January 2009
Available online 14 February 2009

Keywords:
Trace metals
Mercury
Sorbents
Sequestration

ABSTRACT

This paper is concerned with the sequestration of mercury, cadmium, lead, sodium and potentially other volatile and semi-volatile metals by high-temperature mineral, non-carbon based dispersed sorbents. The focus here is on kaolinite and lime powders (for Pb, Cd, and Na), and on intimate kaolinite/calcite/lime mixtures (for Hg), both of which undergo morphological and chemical changes when exposed to high temperatures. These changes play critical roles in the metal capture mechanisms, initially enhancing metal capture, either through a eutectic melt on the surface, or through some other transformation, but ultimately causing sorbent de-activation through a catastrophic melt that causes pore closure.

Results and interpretation from two types of experiments are presented. The first employed a 20 kW downflow combustor, a low-pressure impactor and application of the aerosol fractionation method to quantitatively determine the fraction of metal sequestered by the sorbent at the sampling point. The second employed an externally heated quartz reactor and simulated flue gases containing mercury and injected sorbent. Quantitative, rate models have been extracted from the data to describe the global reactions of dispersed kaolinite with lead, sodium, and cadmium metal vapors. They have also been derived for the global reaction of cadmium with dispersed hydrated lime, which was ineffective for Na and Pb but very effective for Cd. Qualitative results showing the effective scavenging of Pb and Cd by the intimate kaolinite/calcite/lime mixture are also presented.

The intimate kaolinite/calcite/lime mixture was also shown to capture metallic mercury through two mechanisms, namely, an in-flight mechanism and one involving interactions between Hg, the sorbent and the quartz reactor walls. The in-flight mechanism had similarities to those observed previously between kaolinite, lead, cadmium and sodium, in that mineral transformations played a key role in both sorbent activation and sorbent de-activation. At a constant residence time, the in-flight mechanism exhibited a maximum effectiveness at 900 °C, followed by apparent de-activation. Spent in-flight sorbent showed the presence of calcium silicates and calcium aluminosilicates. The wall deposit mechanism increased in efficacy with temperature and did not show a maximum, and showed the presence of substantial amounts of captured mercury. Adding to the complexity of this process is that Hg capture by this mixture required the presence of O_2 in the flue gas, albeit at low levels of 4000 ppm.

1. Introduction

The emission of trace metals such as lead, cadmium and mercury from coal combustors and incinerators, is a matter of concern. The emission of sodium can be a problem in gasifiers and combined cycle processes. Sodium, lead and cadmium are considered to be semi-volatile metals, in that they are vaporized at high flame temperatures, but nucleate and condense to form particles at lower temperatures. Mercury is vapor at all temperatures in a combustion process, unless adsorbed or scavenged on substrates. It can cause serious corrosion on aluminum components at cryogenic temperatures.

Activated carbon can absorb metal vapors by physi-sorption, often augmented by chemical reaction between adsorbed species on the carbon surface. Physi-sorption is effective at lower temperatures, say, around 380 K. Among the toxic metals, Pb, Cd and Hg, only Hg is vapor at physi-sorption temperatures, and so, although activated carbon may be effective for Hg, it fails to work for Pb, Cd, or Na, the other metals under consideration here. What is needed is a *high-temperature* sorbent which can effectively scavenge a wide range of metals, including mercury, at temperatures where both semi-volatile metals and volatile metals are in the vapor form. This paper will review of mechanisms of interaction at high

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* Corresponding author. Tel.: +1 801 585 1025; fax: +1 801 585 9291.
E-mail address: jost.wendt@utah.edu (J.O.L. Wendt).

0016-2361/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.fuel.2009.01.028

temperatures between various mineral based sorbents and both semi-volatile metals, such as Na, Pb, and Cd, and also a volatile metal, mercury. Sorbents considered are kaolinite, hydrated lime, and a special intimate mixture of kaolinite/calcite/lime, hereafter referred to as *MinPlus*, which is the name under which it is marketed.

As far as mercury is concerned, there are a number of technologies currently being pursued for its mitigation from coal fired power plans [1,2]. Many of these involve injection of activated carbon [3–7] or chemically modified forms of activated carbon, which are thought to adsorb and/or oxidize mercury vapors at temperatures lower than 200 °C. Problems with carbon based sorbents are that they can diminish the properties of the fly ash for cement utilization, they can catch fire in bag houses and/or hoppers downstream, and they cannot be used upstream of hot side electrostatic precipitators where the carbon may ignite. In this paper the focus for the mercury sorption portion is on non-carbonaceous sorbent, *MinPlus*. Such a mercury scavenging sorbent is desirable because it can be used upstream of hot side electrostatic precipitators, and because it enhances rather than diminishes fly ash utilization properties. Previous work on calcium based sorbents has been described in Ref. [8], and on sorption using fly ash and inorganic particles in Refs. [3] and [9–11].

4. Materials and methods

4.1. Sorbents

The composition of the three sorbents investigated are shown in Table. 1. As noted above, the kaolinite/calcite/lime sorbent mixture is, for brevity, denoted here as *MinPlus*. It is manufactured from a thermal process for which the feedstock is a solid by-product from paper recycling processes. It is essentially a mixture of kaolinite and lime/limestone sorbents.

Kaolinite is a common mineral with many industrial and commercial uses and its properties of have been well studied. Kaolinite is usually found to be composed of a series of stacked platelets. Fig. 1 shows the typical structure of well-ordered kaolinite on the left, compared to the less structured morphology of *MinPlus* (at a lower magnification) on the right. Of particular interest to this work is the process of calcination, which is a process whereby chemistry and crystalline structure of the mineral is modified by exposure to increased temperatures [12]. There exist two different calcination mechanisms: (1) ramp and soak calcination (typical of Thermo Gravimetric Analyses), in which phase changes occur slowly, ultimately forming mullite, which is inert; and (2) flash calcination (typical of disperse injection into hot flue gas), in which heating is rapid, reaction times are short, and mullite formation is hindered.

Table 1
Summary of sorbent compositions (wt%).

Sorbent	Kaolinite [$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$]	Calcium hydroxide [$Ca(OH)_2$]	Calcium carbonate [$CaCO_3$]	Major impurities
Kaolinite	97%			1–2% TiO_2
Hydrated lime		99%		0.2 FeO 0.3 Al_2O_3
MinPlus	45%	1% (22% CaO)	33%	0.1 TiO_2

Fig. 2 shows results of differential thermal analysis of *MinPlus* (under ramp and soak conditions). These showed that this sorbent was reactive and responded to temperature changes. The trace with the various peaks shows heat taken in (endothermic) and given out (exothermic) from reactions that occur as a function of temperature. After initial fluctuations the first peak is denoted as caused by $Ca(OH)_2$ conversion to CaO at approximately 400 °C, while the second peak describes $CaCO_3$ calcination to CaO and CO_2, which is expelled at approximately 700 °C. Significantly, there are two mass neutral conversions to (possibly) gehlenite and mullite occurred sequentially between 880 °C and 1000 °C. The most important conclusion to be drawn from Fig. 2 is that *MinPlus* sorbent is reactive over a wide temperature range, over which it undergoes important transformations. Some of these reactions are internal solid reactions/transformations, which are often slow compared to gas/solid reactions, and may not occur under flash calcination conditions. These transformations are similar, but not necessarily identical, to those reported between kaolinite and calcite mix by Refs. [13] and [14]. Fixed bed experiments reported elsewhere [15] suggest that one of these transformations results in shrinkage of sorbent particles. Clearly, like its sister sorbent, kaolinite, *MinPlus* transforms chemically under the influence of heat and high temperatures.

4.2. Experimental procedure for Na, Pb and Cd sorption experiments

For Na, Pb and Cd sorption studies a 6 m tall, 0.15 m ID, vertical combustor, was operated at 18 kW load [16–18], and possessed a temperature profile shown in Fig. 3, which was unchanged between test conditions. The quartz and upper wall of the furnace were constructed with SiC-lined refractory, to prevent metal uptake by the furnace wall. The lower wall was constructed of vacuum formed yttria stabilized zirconia ($ZrO_2 \cdot Y_2O_3$) cylinders [17], specifically because cadmium was less reactive with the zirconia than with alumina. In addition to furnace wall inertness with re-

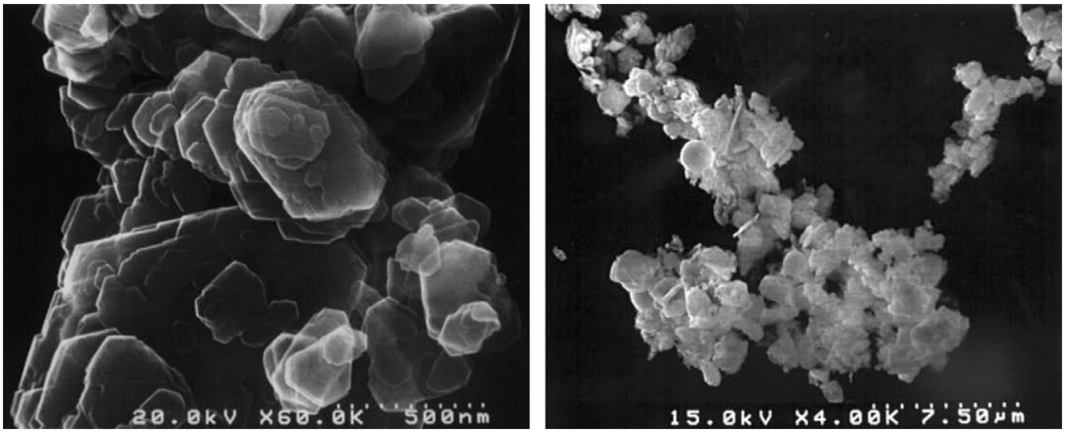

Fig. 1. Field SEM images of Kaolinite (left) and of *MinPlus* (right).