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Mercury and SO_3 Emissions in Oxy-Fuel Combustion

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Abstract

This paper presents results on experiments carried out at a 20 kW combustion rig simulating different extents of oxy-fuel recycle gas cleaning by impurities injection to the oxidant gas of the once-through combustion reactor. A comprehensive set of total (Hg^{tot}), elemental (Hg^0) and oxidized (Hg^{2+}) mercury as well as SO_3 concentrations was obtained before and after the combustion rig's baghouse filter for in total 14 air and oxy-fuel experiments with 3 Australian coals. Based on this data, an assessment in respect to Hg oxidation, SO_2/SO_3 conversion and Hg and SO_3 capture on the test rig's filter was performed. The air and the oxy-fuel experiments with different extents of recycle gas cleaning, revealed differences in the Hg and SO_3 formation and capture behavior: The Hg^{2+}/Hg^{tot} ratios in the flue gas are higher during oxy-fuel combustion compared to air-firing. This effect is even more pronounced at the filter outlet, after flue gas has passed through the filter ash. In some experiments, even a net oxidation of Hg^0 entering the filter to Hg^{2+} was observed. The Hg capture by ash in the baghouse filter has been found to reduce the Hg emissions considerably. However, the Hg capture was altered by the different oxy-fuel recycle configurations, leading to decreased Hg capture efficiencies on the filter for one of the coals. A coal-specific trend of increased SO_2/SO_3 conversion ratios with increased flue gas SO_2 levels was observed that could be related to the ash composition of the three different coals. This and the higher SO_2 concentrations in the flue gas lead to considerably higher SO_3 levels in oxy-fuel combustion with SO_2 recycling. During the experiments, also a considerable capture of SO_3 in the baghouse filter was observed (up to 80% under air- and up to 66% under oxy-fired conditions). A reduction of the SO_3 capture on the filter under oxy-fuel conditions may be related to the higher SO_3 levels in this process.

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Keywords: Oxy-fuel combustion; Hg; mercury emission; mercury oxidation; mercury speciation; mercury capture; SO_x; sulfur trioxide; SO_3; sulfuric acid; H_2SO_4

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1. Introduction and background

1.1. Oxy-fuel combustion

To reduce the impact of anthropogenic greenhouse gas emissions on the earth's climate, CO_2 capture and storage/utilization (CCS, CCU) technologies for coal-fired power generation were developed to concentrate the CO_2 for processing and sequestration/utilization. Oxy-fuel combustion is one of these CCS/CCU technologies. In oxy-fuel operation, coal is burned with a mixture of O_2 and recirculated flue gas, instead of air. The mixing of O_2 with recirculated flue gas is, among other issues, necessary to lower the temperature in the furnace which otherwise would exceed the limits of construction materials of the boiler [1]. Due to the lack of flue gas dilution by airborne N_2, the concentrations of flue gas components such as CO_2, SO_2 and H_2O under oxy-fuel-fired conditions generally increase considerably by a factor of around 4 [1–3]. Moreover, under oxy-fuel-fired combustion conditions higher Hg concentrations than in air-firing are expected. NO_x formation is also altered, being affected by O_2 injection conditions, burner configurations and airborne N_2 exclusion from the combustion [4]. SO_3 that is formed by an oxidation of SO_2, is known to be responsible for low temperature corrosion in cold parts of the flue gas train (e.g. air preheater, recycle lines), while the acid gases NO_x and SO_x together with condensed water form highly acidic and therefore corrosive liquids in the CO_2 compression system. The higher Hg concentrations in an oxy-fuel process have potential implications on environmental pollution as well as on corrosion of Al-alloys by Hg [5]. This Al corrosion can be particularly problematic in the CO_2 processing unit of an oxy-fuel plant, where Al-alloys are applied e.g. for heat exchangers.

Various oxy-fuel process configurations (wet/dry recycle, environmental control units) as well as process conditions (recycle rate, residence time and thermal profile) are possible and have a significant impact on the concentrations and reactions of impurities, such as SO_x and Hg [6, 7]. To minimize corrosive material attack and subsequent safety risks, these impurities must be controlled. However, the choice of control units will affect achievable reduction efficiencies and ultimately also plant costs and waste streams.

The performed experiments aim to show how different fuels and different oxy-fuel process configurations impact the SO_3, Hg^0 and Hg^{2+} concentrations in the flue gas and the SO_3 and Hg removal on a baghouse filter. Injection of impurities to the oxidant gas was used to simulate recycle concentrations of impurities without adversely affecting the reactor configuration. Using this method, it was possible to provide gas concentrations comparable to both fully cleaned "cold" recycle conditions and "hot recycle" impurity levels associated with limited/practical flue gas cleaning. A detailed description and assessment of the underlying experiments has been previously published in two articles by Spörl et al. [8, 9] (Reprinted in part with permission from [8, 9], Copyright 2014 American Chemical Society.). This paper aims to coherently summarize the main results of both those articles.

1.2. Hg^0 and Hg^{2+} generation and capture

Mercury occurs in coals mostly associated with sulfur compounds (e.g.: FeS_2) or organic fractions [10–13]. During combustion Hg is completely evaporated and converted to its elemental form Hg^0 [14], reaching Hg concentrations in a range of 1-20 $\mu g/m^3$ in air-fired systems [15]. During cooling of the flue gases and via the interactions with other flue gas compounds (most importantly Cl-containing species) Hg^0 becomes oxidized to Hg^{2+} (e.g. in form of $HgCl_2$) [11, 14–17]. The most important factors influencing the concentration levels, speciation and removal of Hg from flue gas are:

- Hg content of coal
- Cl (and Br) content of coal
- Combustion conditions
- SO_x concentrations and speciation
- Fly ash properties (UBC, Ca, catalytically active compounds)
- Temperature-residence time profile of the plant