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Characterization of ashes from a 100 kW_{th} pilot-scale circulating fluidized bed with oxy-fuel combustion

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ABSTRACT

Oxy-fuel combustion experiments have been carried out on an oxygen-fired 100 kW_{th} mini-circulating fluidized bed combustion (CFBC) facility. Coal and petroleum coke were used as fuel together with different limestones (and fixed Ca:S molar ratios) premixed with the fuel, for *in situ* SO_2 capture. The bed ash (BA) and fly ash (FA) samples produced from this unit were collected and characterized to obtain physical and chemical properties of the ash samples. The characterization methods used included X-ray fluorescence (XRF), X-ray diffraction (XRD), char carbon and free lime analysis, thermogravimetric analysis (TGA), and surface analysis. The main purpose of this work is to characterize the CFBC ashes from oxy-fuel firing to obtain a better understanding of the combustion process, and to identify any significant differences from the ash generated by a conventional air-fired CFBC. The primary difference in the sulfur capture mechanism between atmospheric air-fired and oxy-fuel FBC, at typical FBC temperatures (~850 °C), is that, in the air-fired case the limestone sorbents calcine, whereas the partial pressure of CO_2 in oxy-fuel FBC is high enough to prevent calcination, and hence the sulfation process should mimic that seen in pressurized FBC (PFBC). Here, the char carbon content in the fly ash was much higher than that in the bed ash, and was also high by comparison with ash obtained from conventional commercial air-firing CFBC units. In addition, measurements of the free lime content in the bed and fly ash showed that the unreacted Ca sorbent was present primarily as $CaCO_3$, indicating that sulfur capture in the oxy-fuel combustor occurred *via* direct sulfation. Limestone utilization for oxy-fuel combustion in this unit was generally lower than that in industrial-scale air-firing CFBCs, with better limestone performance found during combustion of petcoke running at relatively higher temperatures. The Brunauer–Emmett–Teller (BET) surface area and also the pore volume in the fly ash were much higher than in the bed ash and smaller size pores predominated in the fly ash samples.

1. Introduction

Carbon dioxide is one of the major greenhouse gases that contribute to anthropogenic global climate change [1] and oxy-fuel combustion is seen as one of the promising new technologies that can reduce such emissions to the atmosphere [2]. This process uses nearly pure oxygen (90%+) instead of air for combustion. To control the combustion temperature and make up the volume of missing N_2, most of the flue gas is recycled to the combustor. The CO_2 concentration is highly enriched (>90%) by recycling the flue gas and easy recovery can be achieved for further utilization or sequestration [3,4]. An additional advantage of this process is that the NO_x emissions are substantially reduced compared to the air-firing scenario since N_2 in the oxidant has been removed prior to combustion. For fluidized bed combustion (FBC) boilers, in addition to their excellent fuel flexibility, SO_2 emissions can also be controlled *in situ* by adding limestone sorbents with the fuel (for both air-fired and oxy-fuel combustion).

Most research and development (R&D) work on oxy-fuel combustion was focused on pulverized coal combustion previously, including the earlier work at CanmetENERGY (*e.g.*, [4,5]), and the origins can be traced to pioneering research carried out by Argonne National Laboratories in the 1980s [6]. Subsequently, in the 1990s, significant oxy-fuel R&D started elsewhere, with a number of small pilot plant programs, including CanmetENERGY (Canada), Air Liquide (US) and the International Flame Research Foundation (IFRF) R&D program in Ijmuiden (The Netherlands), looking initially at natural gas firing [3]. In addition to the early small-scale pilot plant work there were various economic evaluations of the technology *versus* back-end scrubbing, primarily for natural gas-fired systems and there are now two major reviews in the open literature available

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for interested readers, which describe such developments [3,7]. Extensive research has been carried out on emissions from oxy-fuel pulverized coal firing, such as NO_x, SO_x, as well as other micro-pollutants (e.g., [8,9]). There are also a few publications discussing ash formation under oxy-combustion of pulverized coals (e.g., [10–13]). There is already one large demonstration plant (30 MW_{th}) operating in Europe with more being planned in the future [14–16].

By contrast, to date oxy-combustion technology has received relatively little attention for oxy-fuel circulating fluidized bed combustion (CFBC), although the concept was examined over 30 years ago for bubbling FBC [17]. However, more recently oxy-fired FBC has become increasingly important as a potential technology, offering as it does fuel flexibility and the possibility of firing local or indigenous fuels, including biomass in a CO_2-neutral or even negative manner. One example of this is a paper on a 95 kW_{th} oxy-fuel combustion bubbling FBC reported by Romeo and co-workers [18], who studied the combustion characteristics, heat transfer and pollutants emissions under different O_2/CO_2 concentrations, achieved by mixing gases from cylinders.

Currently the R&D work on oxy-fired CFBC technology is being undertaken in numerous countries, including Canada, Finland, Poland, China and the United States among others. Alstom and Foster Wheeler have explored the oxy-fuel CFBC concept using pilot-scale tests [19,20]. Alstom's work included tests in a unit of up to 3 MW_{th} in size, but did not involve recycle of flue gas [21]. Foster Wheeler's work [19] also involved pilot-scale testing, using a small (30–100 kW) CFBC owned and operated by VTT (Technical Research Centre of Finland) and this work along with CanmetENERGY's work with its own 100 kW CFB combustor [22–24] appears to be the first in which units were operated with oxy-fuel combustion FBC using flue gas recycle. CanmetENERGY has two pilot plants which are capable of being operated in the oxy-fuel mode, with full flue gas recycle: a nominally 75 kW unit and a larger 0.8 MW_{th} unit. Foster Wheeler has recently completed 8 months of trials at CanmetENERGY using the larger 0.8 MW_{th} unit [25], as a prelude to building a 30 MW_{th} oxy-fuel CFBC demonstration plant in Spain [26]. Foster Wheeler is also the first company to commercialize supercritical CFBC technology (Łagisza Power Plant, Poland) and with this technology as the basis, it is now working with the power company ENDESA (Spain) on the technology development of a 300 MW_e supercritical Flexi-burn™ CFBC, which would allow a CFBC boiler to operate either in air- or oxy-firing conditions. The predicted CO_2 capture for the Flexi-burn CFBC technology is 90% of emissions and it is anticipated that it could be available by 2020 [27].

Other recent work has been reported by Czakiert and co-workers [28], who studied fuel conversion (i.e., sulfur, nitrogen and carbon) in a 100 kW_{th} oxygen-enriched air combustion CFB (oxygen concentration up to 28%) with no flue gas recycle. They concluded that combustion efficiency improved with elevated oxygen partial pressure and conversion ratio of fuel-N_2 to NO_x increased under oxy-firing conditions. Krzywanski et al. [29] have developed a mathematical model for oxy-fuel CFBC which considered hydrodynamics of bed material, fuel combustion, flue gas desulfurization, and heat and mass transfer. Again, the major research interest has been focused on emissions of SO_x, NO_x and CO produced from oxy-fuel FBC combustion. Although there are a few publications regarding oxy-fuel pulverized coal combustion ash, no open literature can be found so far discussing the properties of oxy-fuel FBC ash. It should be noted that Wang et al. [30] discussed the influence of the water content in flue gas on carbonation of fly ash under oxy-fuel CFB conditions. They suggested the carbonation effects are likely to be enhanced by water over a wide range of temperatures. However, it should also be noted that the fly ash used was produced from an air-fired CFB boiler and the focus of their study was to investigate the potential for back-end fouling due to calcined limestone carbonation, for situations where indirect sulfation occurs in the bed under oxy-fuel combustion conditions. Namely, they were concerned with the combustion of unreactive fuels, which would require high temperatures of 900 °C and above, as a result of which indirect sulfation would occur in the bed, after which fouling due to carbonation of the CaO in the spent sorbent might arise at temperatures of 800 °C or less, in flue gases with a high CO_2 partial pressures as is the case with an oxy-fuel CFBC.

In the current work, a series of ash samples produced from CanmetENERGY's 100 kW mini-CFBC reactor during oxy-fuel combustion of different feedstocks was collected and analyzed. Various chemical and physical analysis methods, including X-ray fluorescence (XRF), X-ray diffraction (XRD), char carbon and free lime analysis, thermogravimetric analysis (TGA), and surface analysis, were utilized to characterize these ashes. The aim of this work was to provide the first published information on ashes produced from oxy-fuel combustion in CFBC. This will allow a better understanding of both the process and ash disposal issues, as well as allowing a comparison of oxy-fuel combustion ash with conventional air-firing CFBC ash. In the configuration of oxy-fuel FBC with flue gas recirculation, the partial pressure of CO_2 is high enough to prevent calcination of limestone particles. The sulfur capture mechanism under this condition, which should be similar to that occurring in the pressurized FBC (PFBC), is also discussed. It should be noted that since there are significant differences existing between oxy-fuel pulverized coal and FBC combustion, in terms of the operating temperature range, particle size range, and addition of limestone for SO_2 capture in FBC, the comparison of ashes produced from these two different systems is not investigated in this paper.

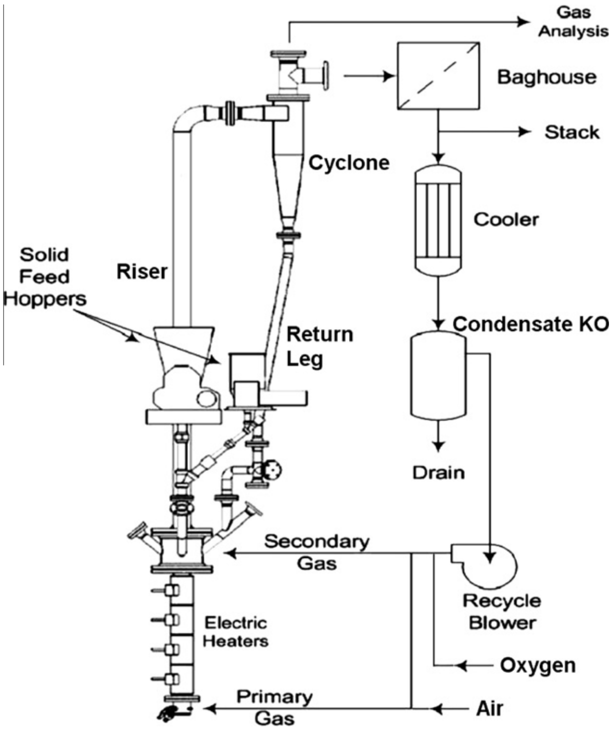

Fig. 1. Schematic of the mini-CFBC at CanmetENERGY.