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The potential oxidation characteristics of $CaCr_2O_4$ during coal combustion with solid waste in a fluidized bed boiler: A thermogravimetric analysis

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HIGHLIGHTS

- Cr oxidation was determined by the formation, oxidation and sulfation of $CaCr_2O_4$.
- Nucleation and growth model was fitted to the formation and oxidation of $CaCr_2O_4$.
- $CaCr_2O_4$ sulfation could be described by shrinking core model.
- Available calcium content affected not only oxidation rate but also product species.
- $CaCr_2O_4$ sulfation was easier to occur than $CaCr_2O_4$ oxidation.

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ABSTRACT

$CaCr_2O_4$ (Cr (III)), mainly generated through the decomposition of $CaCrO_4$ (Cr (VI)), is a significant intermediate for toxic Cr (VI) formation during solid fuel combustion. In this study, the formation, oxidation and sulfation kinetics of $CaCr_2O_4$ were analyzed to forecast the potential of $CaCr_2O_4$ oxidation during co-firing of coal and solid waste in a circulating fluidized bed boiler. The results indicated that the formation and oxidation of $CaCr_2O_4$ were fitted to a single step nucleation and growth model while $CaCr_2O_4$ sulfation was fitted to a shrinking core model. $CaCr_2O_4$ formation through $CaCrO_4$ decomposition was favored in oxygen-lean atmosphere and considerably suppressed in the presence of oxygen. In contrast, $CaCr_2O_4$ oxidation was mainly determined by the contacts between $CaCr_2O_4$ and $CaSO_4$/CaO, which influenced not only oxidation rates but also the product species. Moreover, the oxidation reactivity of $CaCr_2O_4$ was higher in the presence of CaO than that of $CaSO_4$. On the other hand, $CaCr_2O_4$ sulfation can occur more easily than $CaCr_2O_4$ oxidation, the reaction rate of which was deeply affected by sulfate product layer. Findings in this study suggested that spraying calcium in furnace for desulphurization may increase the risk of $CaCr_2O_4$ oxidation. Measures including the adjustment of Ca/S ratio in blended fuel (with added limestone) and operating conditions (such as temperature and local atmosphere) in co-firing system could be taken to control $CaCr_2O_4$ formation and oxidation.

1. Introduction

In China, large amounts of organic solid wastes (such as municipal sludge, paper sludge, waste clothes) need urgent treatment (N.B.S. China, 2019). Co-firing solid waste with coal in a circulating fluidized boiler (CFB) is an efficient and cost-effective method for energy recovery from these wastes (Fu et al., 2019). During combustion, air pollution control devices equipped in coal-fired power plants have good performance on controlling pollutant emissions (e.g. heavy metals, SO_2, NO_x) (Xue et al., 2020; Wen et al., 2015). Different from arsenic (As), lead (Pb) and other semi-volatile traced elements, chromium (Cr) is less volatilized and distributed more in bottom ash (Chen et al., 2019; Zhao et al., 2018). More

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