Sulfur Release during Alternative fuels Combustion in Cement Rotary Kilns

Cement production is an energy-intensive process, which has traditionally been dependent on fossil fuels. However, the usage of selected waste, biomass, and by-products with recoverable calorific value, defined as alternative fuels, is increasing and their combustion is more challenging compared to fossil fuels, due to the lack of experience in handling the different and varying combustion characteristics caused by different chemical and physical properties, e.g. higher moisture content and larger particle sizes. When full combustion of alternative fuels in the calciner and/or main burner is not achieved, partially or unburned solid fuels may drop into the material bed in direct contact with the bed material of the rotary kiln. The combustion of alternative fuels in direct contact with the bed material of the rotary kiln causes local reducing conditions and may alter the input and the behavior of minor elements into the kiln system. The minor elements of concern are sulfur, chlorine, so dium, and potassium, which are known to be circulating or volatile elements in the kiln system. Compounds containing these elements evaporate, when exposed to high temperatures, and may subsequently condense in cooler parts of the plant. High internal circulation seriously affects the process stability and operation of the cement kiln system, such as material build-ups in the cyclones and/or in the rotary kiln as rings, and on a longer time-scale by shell corrosion. This thesis provides a detailed analysis of the circulating ion of the volatile elements and the transformation of different species containing these elements at different locations in the cement plant. This is complemented by thermodynamic calculations for a better understanding of the inorganic chemistry in the rotary kiln. The main focus is given to SO2 release due to decomposition of calcium sulfate in the kiln inlet and the modification of the sulfur circulation during alternative fuel combustion, because sulfur is the most affected element by reducing combustion conditions. Sulfur release from cement raw materials during alternative fuel combustion is experimentally investigated using pine wood and tire rubber particles in a pilot scale set-up, which is able to simulate the process conditions in the material inlet end of an industrial rotary kiln. The SO2 release increases with decreasing fuel particle size, oxygen content in the freeboard gas, and increasing sulfur content in the bed material. Experiments with wood with different degree of volatiles show that the sulfur release mainly takes place during devolatilization. This is supported by the finding of the industrial investigation on sulfur released, where no clear relationship is observed between the carbon from the fuel, mainly expected to be in the form of char, entering in the rotary kiln and the sulfur recirculation. The effect of different concentrations and binary mixtures of the main reducing agents released from fuels on sulfur release are investigated experimentally in order to separate the influence of the simultaneous phenomena occurring in the experimental set-up, such as mixing the fuel with the bed material, heating up of a particle. 5 iii Abstract Cement production is an energy-intensive process, which has traditionally been dependent on fossil fuels. However, the usage of selected waste, biomass, and by-products with recoverable calorific value, defined as alternative fuels, is increasing and their combustion is more challenging compared to fossil fuels, due to the lack of experience in handling the different and varying combustion characteristics caused by different chemical and physical properties, e.g. higher moisture content and larger particle sizes. When full combustion of alternative fuels in the calciner and/or main burner is not achieved, partially or unburned solid fuels may drop into the material bed in direct contact with the bed material of the rotary kiln. The combustion of alternative fuels in direct contact with the bed material of the rotary kiln causes local reducing conditions and may alter the input and the behavior of minor elements into the kiln system. The minor elements of concern are sulfur, chlorine, so dium, and potassium, which are known to be circulating or volatile elements in the kiln system. Compounds containing these elements evaporate, when exposed to high temperatures, and may subsequently condense in cooler parts of the plant. High internal circulation seriously affects the process stability and operation of the cement kiln system, such as material build-ups in the cyclones and/or in the rotary kiln as rings, and on a longer time-scale by shell corrosion. This thesis provides a detailed analysis of the circulating ion of the volatile elements and the transformation of different species containing these elements at different locations in the cement plant. This is complemented by thermodynamic calculations for a better understanding of the inorganic chemistry in the rotary kiln. The main focus is given to SO2 release due to decomposition of calcium sulfate in the kiln inlet and the modification of the sulfur circulation during alternative fuel combustion, because sulfur is the most affected element by reducing combustion conditions. 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The effect of different concentrations and binary mixtures of the main reducing agents released from fuels on sulfur release are investigated experimentally in order to separate the influence of the simultaneous phenomena occurring in the experimental set-up, such as mixing the fuel with the bed material, heating up of a particle.
Further development regarding particle motion according to the rotational speed may be needed. Furthermore, a model for predicting the tendency of build-ups for a kiln system is developed based on the prediction of SO$_3$ and Cl concentrations in the hot meal. The predictions can be performed for a kiln system operating only with fuel in the calciner and kiln burner, and the influence of bypass operation can be added as well as alternative fuels substitution in the kiln inlet. The sulfur release in the inlet of the rotary kiln can be minimized if the fuel combustion takes place at temperatures lower than 800 °C and can be avoided when the volatile gases from fuels are not released in contact with the bed material. The reducing agents are CO, CH$_4$ and H$_2$, which are introduced under the bed material in the high temperature rotary drum to characterize the SO$_2$ release under variation of temperature, oxygen content in the gas, and time of exposure. A threshold concentration for each reducing gas, below which no SO$_2$ release occurs, is found. The reducing concentration and the time of exposure are of high importance for SO$_2$ release because it is shown that introducing the same total amount of gas, the highest reducing agent concentration for a short period released a higher total SO$_2$ amount compared to the lowest concentration during a long period. A mathematical reaction based model for predicting sulfur release caused by volatiles from wood particles fired in the material kiln inlet is developed and evaluated against pilot scale data, which shows that the model follows the experimental data tendency. The model can predict SO$_2$ release varying particle size, fill degree, and firing degree but the effect of sulfur content in the bed cannot be predicted. Further development regarding particle motion according to the rotational speed may be needed. Furthermore, a model for predicting the tendency of build-ups for a kiln system is developed based on the prediction of SO$_3$ and Cl concentrations in the hot meal. The predictions can be performed for a kiln system operating only with fuel in the calciner and kiln burner, and the influence of bypass operation can be added as well as alternative fuels substitution in the kiln inlet. The sulfur release in the inlet of the rotary kiln can be minimized if the fuel combustion takes place at temperatures lower than 800 °C and can be avoided when the volatile gases from fuels are not released in contact with the bed material.

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