Low SO2 Emission Preheaters for Cement Production

The most common way of producing cement today is effected through what is known as the dry process. If the raw materials used in this process contain sulphide, the plant layout can lead to emissions of SO2 from the preheater tower. SO2 emissions are most often caused by the oxidation of pyritic sulphide, which occurs between 300 and 600 °C. Of the formed SO2, around 50% is often said to be emitted from the preheater. However, large variations in this number have been observed, with the circulation of CaO from the calciner given as the main reason for this phenomenon. One of the experimental goals in this thesis has been to produce CaO with a large surface area in order to increase the absorption of SO2. For this purpose flash calcination of CaCO3, calcination under vacuum, calcination in a fixed bed and a fluid bed has been tested between 650 °C and 850 °C. The results showed that flash calcination at low temperatures resulted in the largest surface area, about 140 m2/g CaO. The material produced from all of the methods was a mixture of CaO and CaCO3, meaning that the material was only partly calcined, but with the particle surface area being comprised by CaO.

One focus in this thesis was to investigate the reaction between CaO and SO2 in the temperature interval where SO2 is formed within the preheater tower, in order to understand the role of CaO in connection with SO2 emission. The experiments were conducted using CO2 concentrations up to 25 %. The reaction times in all cases were less than 1 second, which was possible using an entrained flow reactor. Furthermore, the experimental results were found to be limited by both external and internal diffusion. The reaction product was identified as a mixture of CaSO3 and CaSO4. For temperatures below 600 °C no effect from O2 was observed. At low CO2 concentrations the CaO conversion with respect to SO2 increased with both temperature and surface area. At high CO2 concentrations no effect or even a negative effect of temperature was seen. In general, CO2 was found to inhibit the CaO/SO2 reaction. Based on the CaO experiments under carbonating conditions it was concluded that CaO recirculation within the preheater tower does not influence the SO2 emission to any significant extent. This conclusion is opposite to what previously has been stated. Modelling of experimental results concentrates on the results obtained for CaO in non-CO2-enriched atmospheres. Due to external and internal diffusion limitations and very short reaction times, a time-dependent grain model with chemical reaction between SO2 and CaO at the shrinking core interface in the non-porous grains was used and found to describe data very well. The outcome of the modelling was that the chemical reaction between SO2 and CaO is so fast that the observed rates exclusively are determined by solid state diffusion in the product layer of the non-porous CaO grains. An activation energy of 115 kJ/mole was found to fit all CaO sources very well, even though data fitting by the least sum of squares method showed that this figure could be between 90 kJ/mole and 140 kJ/mole, with a corresponding change of preexponential factors. The ability to predict emissions is very important in the design of cement plants. In this thesis the zone model concept has been applied to the modelling of the cyclone stages in a preheater tower. The idea is to account for the complex flow pattern in a cyclone stage by dividing it into zones, each zone having special features. In this manner the model can account for gas/solid heat exchange, gas/solid separation, different gas and solid residence times, etc. The model was evaluated against SO2 data from five full-scale plants, showing satisfactory results in two cases. An investigation of the parameters showed that it was possible to obtain satisfactory results in four out of five cases by allowing the CaCO3 surface area available for SO2 absorption to be about 4 m2/g instead of the measured surface areas, which was up to around 10 m2/g.