

MINERALOGICAL ASPECTS OF FLUE GAS DESULFURIZATION

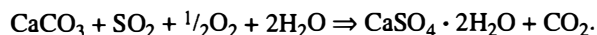
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In the late seventies and early eighties of the twentieth century SO₂ emissions reached a maximum with about 90000 tons of SO₂ in Austria in the year 1980 [1]. The prime emittants being oil and coal fired power plants. Since then the SO₂ emissions have been successively reduced at constant or increasing productivity of the power plants. The annual SO₂ emissions in Austria have now levelled out at about 5000 tons [1]. The reduction of SO₂ emissions by more than 90 % was achieved by the installation of desulfurization systems which is now mandatory in caloric power plants. The most efficient means of removing sulphur dioxide is the so called "wet" process in which an aqueous slurry of finely grained limestone is contacted with the flue gas. The slurry is dispersed into the exhaust gas stream of a power plant as fine droplets through a series of nozzles. SO₂ is adsorbed onto the droplets of the spray and via a number of elemental reactions this leads to the conversion of calcite to gypsum. The bulk reaction may be written as [2]:



Provided that conversion is complete, that is the fraction of residual carbonate in the solid reaction product is less than 5 % per volume, the gypsum produced may be used as construction material and has an economic value. Process engineers therefore try to tune the desulfurization plants so that they can meet the two basic requirements: (1) a desulfurization grade of > 95 % and (2) residual carbonate content in the produced gypsum of < 5 %.

In many desulfurization plants the quality goals can be reached, but some plants are problematic with respect to the purity of the produced gypsum even after thorough process optimisation. Unsatisfactory product quality despite of optimised plant and process design may be due to low quality of the limestone that is used for preparation of the limestone slurry. Manufacturers of desulfurization plants usually have rather crude quality criteria. Regarding the limestone slurry 90 % of the limestone powder must have a particle size of less than 44 µm. It must contain more than 90 % CaCO₃ and less than 3 % MgCO₃. So far no further specifications of quality standards for the limestone raw material were considered. This motivated mineralogical and petrographical studies on limestones used, on intermediate solid-liquid and liquid-liquid reaction products and on the product gypsum in order to identify potential additional quality criteria that would allow to better select appropriate raw materials.

Experiments were done on a producing power plant in Vojany (eastern Slovakia). The most important process parameters, pH and density (i.e. solid particle content) of the intermediate product in the spray reactor, were varied systematically. In addition the natural variation of the sulphur content of the coal and the exhaust gas was monitored and two sorts of limestones were used for the slurry. It was found that the standard process parameters of pH = 5.6 at a density of 1090 g/l slurry resulted in the lowest possible residual carbonate content of the produced gypsum. This indicates that the standard parameters indeed guarantee an optimised process. A change from a limestone with a MgCO₃ content of about 3 wt.% to a limestone with a MgCO₃ content of 6 wt.% caused an increase in the residual carbonate fraction in the product gypsum from about 1.5 to 3 vol.%. This may be due to the fact that the kinetics of dolomite dissolution in acidic environments is slow compared to the kinetics of calcite dissolution. This allows dolomite particles to be carried through the process without significant reaction. An additional effect is that high MgCO₃ contents of the limestone entail high magnesium concentrations in the liquid of the reactor. Magnesium concentrations in the liquid phase of the slurry in the spray reactor may get as high as 3000 ppm. This may lead to partial or complete conversion of calcite to dolomite in the reactor. Above a pH-value of 5.8 of the liquid phase of the slurry the precipitation of dolomite is possible. This secondary dolomite formation may withdraw a significant fraction of the originally available CaCO₃ from the desulfurization process and lead to an elevated residual carbonate content in the form of dolomite in product gypsum.

Another effect may be due to physical interactions among solid particles. A large fraction (up to 80 % per volume) of the residual carbonate in product gypsum is represented by agglomerates, which are comprised of small (< 10 µm) particles of calcite and sheet silicates such as muscovite. In the range of 4 < pH < 8, calcite has a positive surface charge and muscovite has a negative surface charge. The pH conditions in a desulfurization reactor is such that carbonates and sheet silicates have opposite surface charges and thus tend to form aggregates. In such agglomerates calcite appears to be sheltered from the acid attack and it may be carried through the process without reaction.

The mineralogical and chemical composition of the limestone to be used as raw material for limestone slurry in desulfurization systems has a measurable effect on the quality of the product gypsum. On the one hand, the MgCO₃ content of the raw material should be as low as possible to minimize introduction of primary and secondary dolomite particles, which may be carried through the desulfurization process without reaction. On the other hand chemically nominal inert particles such as sheet silicates may lead to elevated residual carbonate contents in the product gypsum by physical particle-particle interactions. We recommend further specification of the quality criteria for limestone raw materials. In particular we propose reduction of the maximum allowed MgCO₃ content and addition of a mineralogical criterion that specifies a maximum tolerable sheet silicate content of the raw material.

References

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- [2] BROGREN & KARLSSON (1997): A Model for Prediction of Limestone Dissolution in Wet Flue Gas Desulfurization Applications. - Ind. Eng. Chem. Res. 1997, 36, 3889-3897.