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MINERALOGICAL ASPECTS OF FLUE GAS DESULFURIZATION SYSTEMS

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Abstract

During the wet desulfurization process of flue gas gypsum is produced through reaction between sulfur dioxide of the flue gas and limestone slurry. In some power plants gypsum with carbonate contents of 5 to 15% is produced despite of process optimization. We present mineralogical and petrographical studies aimed at the identification of the parameters that control the purity of the gypsum. Our observations suggest that two material properties of the limestone raw material used have a profound influence on the limestone/gypsum conversion: (1) High Mg contents of the limestone raw material may cause high levels of carbonate impurities due to the comparatively sluggish reaction kinetics of dolomite, (2) nominally inert silicate impurities with active surfaces such as sheet silicates may armor carbonate particles because of electrostatic effects and this way reduce the carbonate reactivity. Both effects could be largely avoided if entry criteria for the limestone raw material were extended.

Introduction

The reduction of SO_2 emissions by more than 90% since the late seventies and eighties of the twentieth century was achieved through the installation of desulfurization systems, which is now mandatory in caloric power plants. The most efficient means of removing sulfur dioxide from flue gas is the so called “wet” process, in which aqueous slurry of fine grained limestone is dispersed into the exhaust gas stream as fine droplets through a series of nozzles. SO_2 is absorbed onto the droplets and, via a number of elemental reactions, this leads to the conversion of calcite to gypsum. The bulk reaction may be written as (Brogren & Karlsson 1997):

$CaCO_3 + SO_2 + 1/2\ O_2 + H_2O \rightarrow CaSO_4{*}2H_2O + CO_2$

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 these specifications are routinely met, but some plants are problematic with respect to the purity of the produced gypsum due to the low quality of the limestone that is used for preparation the limestone slurry. Manufacturers of desulfurization plants usually have rather crude quality criteria regarding the limestone slurry. Therefore 90% of the limestone powder must have a particle size less than 44 µm, it must contain more than 90 wt. % $CaCO_3$ and less than 3 wt. % $MgCO_3$.

So far no further specifications for the quality of the limestone raw material were considered. This motivated mineralogical and petrographical studies on the limestone used, on intermediate solid-liquid and liquid-liquid reaction products and on the produced gypsum in order to identify potential additional quality criteria that would allow to better select appropriate raw materials.

Results

Characterization of solid phases

Thermogravimetry-Differentialthermoanalyses (TG-DTA)

For a given limestone raw material, the level of carbonate impurities is primarily influenced by pH and slurry density. At low density of the absorber slurry and simultaneously high pH the highest content of residual carbonate was measured. Under standard conditions there are the lowest carbonate contents. In general the values of the absorber slurry are higher than those of the product gypsum, which testifies to the efficiency of the lamella separator.

A change of a limestone with a $MgCO_3$ content of about 3 wt.% (Margecany limestone) to a limestone with a $MgCO_3$ content of 6 wt.% (limestone used in Nováky) caused an increase in the residual carbonate fraction in the produced gypsum from about 1.5 to 3 wt.%. This may be due to the fact that the kinetics of dolomite dissolution in acidic environment is slow compared to the kinetics of calcite dissolution.

Scanning electron microscopy (SEM)

The produced gypsum crystals (“belt filter gypsum”) are idiomorphic with a length of about 80-120µm. Their length to width ratio is about 3:1 which corresponds to optimal crystal growth.

There are three types of carbonate particles in the produced gypsum. The simplest forms are isolated carbonate particles with a size up to 150 µm. These carbonates are relicts of the limestone and they usually have a rough surface with etch pits. Other carbonate types are calcite particles which are partially replaced by dolomite. Replacement of calcite by dolomite probably occurred during the desulfurization process in a Mg- rich absorber slurry.

The third type of carbonate impurity is represented by agglomerates. Three types of agglomerates may be distinguished: (1) Agglomerates comprised of carbonate (mainly calcite) and sheet silicates (e.g. muscovite, biotite). (2) Agglomerates that primarily consist of carbonate particles e.g. calcite-calcite, calcite-dolomite. (3) Agglomerates, which consist of fly ash and other particles, e.g. small gypsum crystals, carbonate crystallites, silicate melt particles.

X-Ray-Diffraction (XRD)

The main residues from acid treatment of the limestones with 10 wt.% HCl phases are dolomite ($CaMg(CO_3)_2$), quartz (SiO_2) and muscovite ($KAl_2(AlSi_3O_{10})(OH)_2$).

Characterization of the liquid phase

Cations

The liquid phase of the absorber slurry has Ca^{2+} concentrations between 260 and 515 mg/l. During the second part of the monitoring there are big fluctuations of the concentrations.

There are constant potassium and sodium concentrations between 40 and 120 mg/l. There is no iron in the samples and hardly any manganese (up to 120 mg/l).

The measured magnesium concentrations are in general above 1000 mg/l (with a maximum at 3100 mg/l). There are two interesting observations: (1) the high Mg-concentrations of the Nováky samples and (2) the huge Mg-variations in the Nováky samples up to a factor of 3.

Anions

The most important anion in the liquid phase of the absorber slurry is the SO_4^{2-}. The maximum concentrations are above 30 g/l and they are elevated in the Margecany samples. The NO_3^- concentrations increase in the Nováky samples, however the Br^- concentrations decrease by half.

Discussion

Agglomerates

A large fraction of the residual carbonate in the product gypsum is represented by agglomerates, which are comprised of small (< 50 µm) particles of calcite and sheet silicates such as muscovite.

The pH conditions in a desulfurization reactor ($5 < pH < 6$) are such that carbonates and sheet silicates have opposite surface charges and thus tend to form aggregates. In such agglomerates calcites appears to be sheltered from the acid attack through armouring by sheet silicates, and they may be carried through the process without reaction.

Secondary dolomites

Dolomite may be of primary or secondary nature. Secondary dolomites usually form along cracks in calcites. In contrast, primary dolomites occur as isolated particles or they form replacement structures in calcites, which are not associated with fractures. Due to the fact that the dissolution of dolomites in acidic environment is comparatively slow, formation of secondary dolomite in the slurry tank may withdraw a significant fraction of originally available $CaCO_3$ from the desulfurization process. This may contribute to elevated residual carbonate content in the form of dolomite in the product gypsum.

Effects of the Mg-contents in the absorber slurry

High Mg contents of the limestone entail high Mg concentrations in the liquid of the reactor. This may lead to partial or complete conversion of calcite to dolomite in the reactor.

At magnesium concentrations of 2300 mg/l of the liquid phase of the slurry the saturation index of dolomite is positive above a pH value of 5.8 and thus a precipitation of dolomite is possible. An elevated p_{CO2} causes a decreasing saturation pH for dolomite.

A plot of the total residual carbonate content and the dolomite content of the residual carbonate fraction shows a big difference between the two limestone types but the same negative correlation. This means that high Mg contents produce less residual carbonate, because the dolomite content has a strong influence on the solubility product of calcite.

Conclusions

It was found that mineralogical and chemical composition of the limestone used as raw material for the limestone slurry in desulfurization systems has a measurable effect on the quality of the product gypsum.

We recommend further specifications of the quality criteria for limestone raw materials. In particular we propose reduction of the maximum allowed $MgCO_3$ to minimize introduction of primary and secondary dolomite particles. In addition a mineralogical criterion that specifies a maximum tolerable sheet silicate content of the limestone is necessary to reduce the residual carbonate content in the produced gypsum that is due to the formation of mixed calcite-sheet silicate agglomerates.

References

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