Identification of $CaSO_4$ Formed by Reaction of CaO and SO_2

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The injection of calcium-based sorbents into coal-fired boilers for reaction with, and reduction in the levels of, sulfur dioxide (SO_2) in the flue gas has undergone considerable research and development. Significant effort has also been made in developing models for the overall reaction

$$CaO + SO_2 + 1/2\ O_2 \leftrightarrow CaSO_4$$

in order to better predict the effects of system and sorbent variables upon performance. Development of internal surface area (Borgwardt and Bruce, 1986) and pore structure (Hartman and Coughlin, 1974) is necessary for measurable reaction to occur. Further, since the calcium sulfate ($CaSO_4$) product has a larger molar volume than the reactant, calcium oxide (CaO), the extent of pore volume development may control the levels of reaction. The molar volume of $CaSO_4$ is related to its density. One of the earlier references (Hartman and Coughlin, 1974) to the $CaSO_4$ product density uses the molar volume value of 52.2 cm^3/mol or 2.6 g/cm^3. This leads to a product/reactant expansion ratio,

$$Z = \nu_{CaSO_4}/\nu_{CaO},$$

of 52.2/16.9, or 3.09. Use of this particular handbook value (Weast, 1968) of density (or its associated Z value) has continued in subsequent papers (Hartman and Coughlin, 1976; Ramachandran and Smith, 1977; Hartman et al., 1978; Bhatia and Perlmutter, 1981; Sotirchos and Yu, 1985; Reyes and Jensen, 1987; Borgwardt et al., 1987; Kocaefe et al., 1987; Simons and Garman, 1986; Yu and Sotirchos, 1987). One instance (Hartman and Trnka, 1980) is noted where the value of 2.97 g/cm^3 (45.8 cm^3/mol) has been used, cited from an unidentified handbook. This last case results in a Z value of 2.71. Apparently the earliest documented reference questioning the commonly-accepted molar volume value is by Dam-Johansen (1987). This work determined a molar volume of 48.06 cm^3/mol from a model comparison with experimental porosity/conversion data. Deviation from the inferred 46.0 cm^3/mol (2.96 g/cm^3) value was attributed to experimental errors and an insufficient model.

The value of Z is significant particularly for modeling the sulfation reaction. Since the larger volume product fills or blocks sorbent pore volume, slowing or stopping the reaction, the ability of models to appropriately simulate laboratory reaction results is contingent upon proper determination of the physical parameters involved. To this end, analyses to identify the form of the $CaSO_4$ product and determine its density (molar volume) were performed.

Experimental Method

Samples of calcium hydroxide [$Ca(OH)_2$] and calcium carbonate ($CaCO_3$) were reacted at 800°C for 5 min supported on quartz wool in a fixed-bed reactor. Preheated reactor gas [0.3% SO_2, 5% oxygen (O_2), balance nitrogen (N_2)] at 23 L/min and standard temperature and pressure (STP) passed through the sample bed, converting the sample to the reactive CaO form and then partially reacting it to form $CaSO_4$. (Further details of similar experimental procedures are available in Borgwardt and Bruce, 1986.) The samples were analyzed by x-ray diffraction (XRD), helium pycnometry, atomic absorption spectroscopy (AA), ion chromatography (IC), and thermogravimetric analysis (TGA).

XRD analyses for compound identification were performed on a diffractometer with a copper Kα target source running at 50 kV and 40 mA. The entrance aperture was 1.0 degree and the

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detector slit was 0.05 degree. Spectra were identified by computer comparison with the Joint Committee for Powder Diffraction Spectra (JCPDS) spectral files. Density measurements were performed on a helium pycnometer which measures solid sample volume. Calibration with manufacturer-supplied standards ensured instrument accuracy and precision. TGA measurements determined the weight percent of trace $Ca(OH)_2$ and $CaCO_3$ in the sample product, while AA and IC measurements determined the weight percent of $SO_4^=$ and Ca^{++}, respectively.

Results and Discussion

Figure 1 shows the XRD spectrum of the sample product formed from the reaction of $Ca(OH)_2$ with SO_2. This spectrum is overlaid with the spectrum for CaO to account for incomplete conversion to product $CaSO_4$. The XRD spectrum from the $CaCO_3$ sample product was nearly identical to that from the $Ca(OH)_2$ sample product, except for slightly higher CaO peaks. The higher CaO peaks are due to the longer time for calcination of the $CaCO_3$ than dehydration of the $Ca(OH)_2$. For both calcium-based precursors, the analysis identified the sample product to be calcium sulfate anhydrite, JCPDS registry No. 37-1496. This is an orthorhombic crystal structure with a density of 2.995 g/cm^3 (45.46 cm^3/mol). Figure 1 shows that the CaO and $CaSO_4$ spectra account for all major and minor peaks present in the sample spectrum, affirming the identity of the $CaSO_4$ product.

The identification of this $CaSO_4$ form, having a higher density than previously ascribed to the $CaSO_4$ product, led to further efforts to verify the density. Since the XRD spectra identified the same $CaSO_4$ for both $CaCO_3$ and $Ca(OH)_2$ sorbents, helium pycnometer analyses were done only on the reaction product of $Ca(OH)_2$. TGA, AA and IC results (accounting for 99.5% of the sample product mass) determined the $Ca(OH)_2$, CaO, $CaCO_3$ and $CaSO_4$ composition of the reacted product. These results, when combined with the helium pycnometry analyses, determined the sample density. The results from five trials indicate a compound with a mean density of 2.98 g/cm^3 (standard deviation of 0.08).

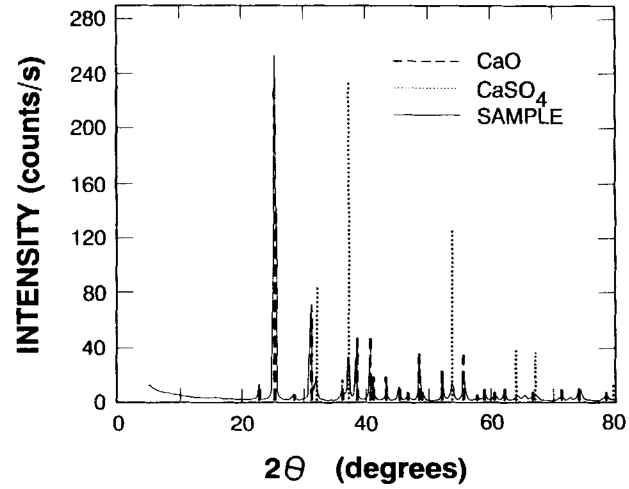

Figure 1. XRD spectra of $Ca(OH)_2$ sulfation sample with CaO spectra (JCPDS No. 37-1497) and $CaSO_4$ anhydrite spectra (JCPDS No. 37-1496).

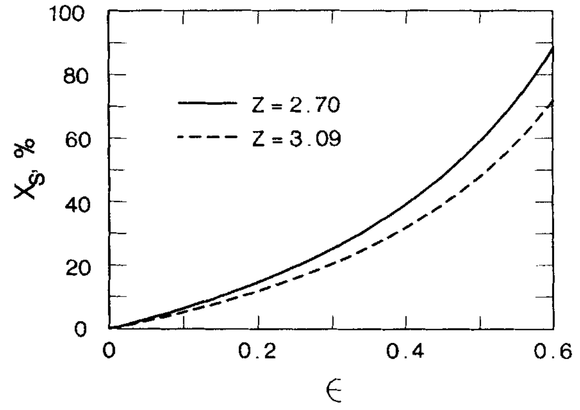

Figure 2. Maximum conversion based on complete filling of initial porosity with Z = 3.09 and 2.70.

Figure 2 shows the impact of this density determination upon pore-volume-limited sulfation of the CaO and compares it with the more commonly-used density value. The molar volume ratio Z, 2.70, calculated from the density determined in this work, suggests that considerably more reaction can occur within the porous matrix than with the commonly-cited value of 3.09. For $Ca(OH)_2$ that develops its theoretical porosity during dehydration to CaO, its theoretical porosity, ϵ, is

$$1 - \nu_{CaO}/\nu_{Ca(OH)_2} = 1 - 16.9\ cm^3/mol/33.1\ cm^3/mol = 0.489.$$

Likewise, for calcination of $CaCO_3$, ϵ is

$$1 - \nu_{CaO}/\nu_{CaCO_3} = 1 - 16.9\ cm^3/mol/36.9\ cm^3/mol = 0.542.$$

These molar volume values are derived from Weast (1968). The maximum conversion based upon complete pore filling of the porosity by the larger volume product can be calculated from

$$X_s = \epsilon/(Z - 1)(1 - \epsilon)$$

Thus, the maximum expected conversion for $Ca(OH)_2$ is 56.3% and for $CaCO_3$ is 69.6%.

While this Z value helps to account for some of the excesses of the X_s values noted experimentally (Kocaefe et al., 1987; Gullett et al., 1988), it does not fully account for reaction levels (up to 90% conversion) observed by Borgwardt and Bruce (1986). Nonetheless, the magnitude of the density change will have a significant effect upon sulfation models that incorporate reaction limitations based upon pore filling or blocking.

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Notation

ϵ = original porosity
ν_{CaO} = molar volume of CaO, cm^3/mol
ν_{CaSO_4} = molar volume of $CaSO_4$, cm^3/mol

X_s = conversion to product based on complete pore volume filling, %
Z = molar volume ratio of $CaSO_4/CaO$
2Θ = angle of detector to x-ray beam, deg

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