will be established better after the full-scale tests of limestone addition are completed by TVA.

Reaction Rates

Attempts to predict the rate at which these reactions will proceed have been unsuccessful. One of the problems here is the complication involved in surface reactions of a gas on a solid where adsorption on the surface, the chemical activity of the surface molecules, and diffusion within the solid all can affect the overall rate of reaction. Another problem is that of mass transfer of the SO$_2$ to the particles of CaO which can be treated theoretically using something akin to a heat-transfer analogy. But for the present, at least, no good model is available whereby reaction kinetics in this heterogeneous system can be predicted.

A few obvious conditions can be identified that should increase reaction rate: pulverize the limestone or dolomite as finely as possible to increase surface area per unit volume, since these are surface reactions; inject the pulverized stone at the highest possible temperature not leading to dead burning or to excessive reaction with coal-ash slag; mix the pulverized stone rapidly and completely with the flue gas, that every molecule of SO$_2$ reaches one of CaO; and provide the longest possible residence time below 2000 F for CaO or 1300 F for MgO to insure maximum capture of SO$_2$.

The answer to the problem of reaction kinetics lies in laboratory measurements. Experimental measurements of the rate of the reaction of lime and magnesia with SO$_2$ in flue gas are now being made in several laboratories, largely with the support and encouragement of the Public Health Service.

Relative Reactivity of SO$_2$ and SO$_3$

The system sulfur-oxygen favors the formation of SO$_3$ at high temperatures and of SO$_2$ at low temperatures. Equilibrium at 2000 F, for example, in an atmosphere containing 5 percent O$_2$ is for 2 percent SO$_3$ and 98 percent SO$_2$ in terms of sulfur oxides.

At 1500 F, the distribution is about 15 percent SO$_3$ and 85 percent SO$_2$. While at 1000 F, it is 50 percent SO$_2$ and 5 percent SO$_3$. Below about 900 F, essentially all the sulfur oxide at equilibrium will be SO$_2$.

The reactivity of SO$_3$ is much greater than that of SO$_2$ at normal flow gas levels. Studies of external corrosion in boiler furnaces [4] using radioactive S$^{35}$ have shown experimentally that 30 ppm of SO$_3$ is 2400 times more reactive toward a surface of Fe$_2$O$_3$-Na$_2$SO$_4$ at 1200 F than is 2300 ppm of SO$_2$. Under such conditions, SO$_3$ is literally many thousands of times more active than SO$_2$ on a mol-for-mol basis. Whether this same ratio holds for reaction with CaO and MgO is unknown.

In an earlier part of this same corrosion studies [5], it was shown that about half of an MgO coating on a simulated boiler tube was converted to MgSO$_4$ in a 3-hr exposure to a furnace atmosphere containing 30 to 40 ppm SO$_2$. This is not a rapid conversion, but at a temperature of 1100 to 1200 F and with relatively thick coatings of MgO on an iron surface, it is an indication that the rate of reaction is at least measurable at these temperatures.

The implication here is that SO$_2$ may be captured by lime and magnesia much more rapidly than SO$_3$. If that is indeed the case, then deliberate conversion of SO$_3$ to SO$_2$ in flue gas would increase the effectiveness of added lime and magnesia. It would also increase the problems with external corrosion and deposits in boiler furnaces. For the present, then, no firm conclusions can be reached, and air-pollution specialists must fall back on laboratory experimentation and full-scale plant tests to provide practical data on which future developments can be based.

Conclusions

1. Thermochemical calculations indicate that CaO is capable of removing essentially all SO$_2$ from flue gas below about 1800 F if enough time is available.

2. Magnesia is equally effective, but the temperature cannot exceed about 1200 F for MgO to leave only 1 ppm SO$_2$ in the flue gas at equilibrium.

3. The upper temperature limit for CaO to remove any SO$_2$ from flue gas is about 2250 F, and for MgO about 1550 F.

4. Uncalcined limestone is theoretically capable of desulfurizing flue gas below 1400 F, but equilibrium probably will be attained quite slowly.

5. Slugging reactions between added limestone and coal ash may remove part of the added lime which otherwise might react with SO$_3$. The resulting calcium silicates will be less effective than CaO in capturing SO$_2$.

6. There have been no indications so far in field tests that added lime or magnesia will cause increased slagging or fouling with coal-fired boiler furnaces, but that possibility should not be ignored entirely.

7. The rate at which lime and magnesia will capture SO$_2$ in flue gas cannot be predicted, and experimental measurements of reaction rates is necessary to know how rapidly equilibrium will be reached in these systems.

Acknowledgments

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References


DISCUSSION

David T. Clay2

As Mr. Reid pointed out in his paper, the dry limestone injection system potentially has both advantages and disadvantages. Since NAPCA has committed a great deal of manpower and funds (3.3 million dollars) to this project, I would like to state the potential advantages NAPCA feels this process has. In addition to those pointed out earlier in the session by Mr. Falkenberry and Mr. Zawadzki, the dry limestone system has the greatest potential of any system for application to 200-MW or smaller boilers and its flexibility allows it to swing with the boiler's load demand. Under normal atmospheric conditions the process would enable a utility company to burn a higher sulfur coal without increasing its SO$_2$ emissions. Under adverse atmospheric conditions, e.g., during inversions, the process could be used to keep SO$_2$ emissions below maximum allowable limits. Although this process is not the final answer, to date it appears to be the only process practical for application to small, older utility boilers. More efficient systems could be employed on the larger boiler units without resulting in the eco-

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onomic problems that would plague the smaller units.

Mr. Reid's work has accomplished the fundamental thermodynamic description of the dry limestone injection process. Since the completion of this study, NAPCA has initiated a broad program to supplement the large-scale tests mentioned throughout the session and to aid in the future application of the optimized process. Studies of kinetic and process variables have been done under contracts with Battelle Memorial Institute, Babcock and Wilcox Company, and Peabody Coal Company, and by NAPCA in-house. Some of these studies have been mentioned earlier in this session. To aid in the future application of the dry limestone process, NAPCA has studies under way to:

1. Develop a recovery system for limestone. Encouraging results have been achieved to date. It is anticipated that future optimization of a recovery process will result in a test facility at the dry limestone injection test site.

2. Determine the effects of limestone injection on electrostatic precipitator performance.

3. Measure limestone distribution patterns by use of holographic photography.

4. Develop an empirical equation based on standard dimensionless numbers for quantifying the effects of variables on limestone distribution.

5. Correlate limestone-SO₂ reactivity with outstanding petrographic and mineralogic characteristics of various limestones.

6. Relate far infrared absorption characteristics to deadburning of the limestone.

7. Develop a modeling equation to describe the initial transient particle conditions between injection and simultaneous calcination and sulfation.

Based on results from some of these studies, I would like to mention a few items concerning Mr. Reid's conclusions.

Unfortunately, none of the workers to date has been able to achieve the thermodynamic efficiency Mr. Reid reports possible. It appears from prior work that the unoptimized process may be able to remove only about 65 percent of the SO₂ released during combustion.

As was pointed out, MgO could theoretically remove SO₂. On a pound-per-pound basis, however, the limestones have been shown to be more effective than dolomites. Further, since higher reaction rates can be achieved at higher temperatures and since CaO absorbs better than MgO under these conditions, it is felt that dolomite addition has no advantage over limestone addition.

In support of Mr. Reid's third conclusion, I would like to mention that the West Virginia University Coal Research Bureau reports that under oxidizing conditions CaSO₄ breaks down between 1800 deg F and 2500 deg F. This temperature limit should not be confused with the injection temperature where one is striving for fast calcination with relatively little deadburning. The best estimated injection temperature range is around 2600 deg F.

One point of interest in relation to the slagging problems comes from Combustion Engineering's work at Detroit Edison. They reported that roughly 90 percent of the limestone was conveyed out of the furnace with the flyash. Consequently, it is anticipated that most of our slagging problems will occur in the superheater region. TVA will be studying the slagging problem at Shawnee.

The kinetics of the process are currently being studied by both Battelle and NAPCA. Models have been developed to describe the reaction of calcined material with SO₂. Under study at present are heat transfer relations to describe particle conditions before calcination and sulfation.

Finally, Mr. Reid's paper points out many problem areas. It was these problems that motivated initiation of the studies I have briefly described. It is time now though to try out the initial designs on a large-scale unit. Through process optimization TVA will seek to determine the optimum capabilities of the dry limestone injection system.

Authors' Closure

Mr. Clay has made important points about the usefulness of thermochemical calculations in predicting the behavior of limestone particles injected into boiler-furnace atmospheres. It should be stressed again, perhaps, that such calculations simply define whether or not a chemical reaction is likely, and they express only the equilibrium concentration of the reactants at any specified temperature. Calculations like these are useless even in estimating how long it will take to approach this equilibrium, and hence the experimental work described by Mr. Clay at TVA and in the laboratory is necessary to establish probable reaction rates under practical conditions.

The final decision on the usefulness of injected limestone or dolomite in capturing SO₂ in flue gas will depend on solving many engineering problems, such as those mentioned by Mr. Clay. These thermochemical calculations simply set the boundary conditions to establish maximum attainable performance.