High Pressure TGA Studies on the Cyclic Use of Half-Calcined Dolomite to Remove Hydrogen Sulfide

George L. Kan, Arthur M. Squires, Robert A. Graff

The Clean Fuels Institute
Department of Chemical Engineering
The City College of New York
New York, N.Y. 10031

Candidate solids for absorption of hydrogen sulfide from a fuel gas at elevated pressure are the composite of iron oxide and fly ash developed by the U.S. Bureau of Mines (1), fully-calcined dolomite (2-4), and half-calcined dolomite (2,5).

Half-calcined dolomite absorbs hydrogen sulfide by the reaction:

$$[CaCO_3+MgO] + H_2S = [CaS+MgO] + H_2O + CO_2$$

For a given fuel gas at a given pressure, desulfurization by this reaction is best accomplished at a temperature just a bit below the temperature at which calcium carbonate would decompose at the partial pressure of carbon dioxide prevailing in the fuel gas.

Regeneration of the solid absorbent is by the reverse reaction, preferably conducted at the lowest possible temperature in order to obtain the highest possible concentration of hydrogen sulfide in the offgas, facilitating conversion of this species to elemental sulfur in a subsequent operation.

Absorption and regeneration cycles at atmospheric pressure and 750°C give the results seen in Figure 1. Although the absorption reaction is rapid, the regeneration reaction is slow, requiring more than 1 hour. There is a decline in capacity of the solid to about 23% of the total calcium after 6 cycles.

Cycling trials at elevated pressure have been carried out with a duPont thermogravimetric analyzer modified for operation at total pressures up to 30 atmospheres, with high partial pressures of steam, and with corrosive gases such as hydrogen sulfide. This equipment is described in reference 6.

In contrast to the results at one atmosphere, cycling at elevated pressure gives little change in capacity or reactivity beyond the first several cycles. Figure 2 gives results from 15 cycles carried out at 300 psig and 731°C. Absorption for 15 minutes was alternated with regeneration for 10 minutes. The capacity settles out at 40%. Figure 3 shows the course of the reactions in the first, 7th, and 15th cycles, and illustrates our finding that the reaction rates do not change much with cycling; only capacity changes. The regeneration reaction at 300 psig is extremely fast, running most of its course in the order of one minute.

Figure 4 shows 30 cycles with absorption for 19 minutes and regeneration for 5 minutes at 550°C. The 19 minutes absorption time

includes 13 minutes at 700°C and 6 minutes cooling time.

Figure 5 shows sulfur capacity versus cycle number for three runs, and illustrates the decline in capacity with decline in regeneration temperature.

Figure 6 illustrates the course of reactions in the last cycle of each of the three cycles plotted in Figure 5. It is fascinating that the observed reaction rates do not seem much to depend upon temperature. This suggests that the true rates are extremely fast, and that the observed rates are controlled by diffusion.

In the series of runs depicted in Figure 7, we varied the ratio of steam to carbon dioxide in the regeneration step to see if this is an important factor in the final capacity of the solid. It appears from Figure 7 that the capacity suffers at a low ratio of steam to carbon dioxide, such as 25/75. Above about 50/50, the ratio does not seem to have much effect. It may be noted that we have succeeded in a run of 15 cycles with a steam partial pressure in the vicinity of 19 atmospheres.

The effect of temperature in absorption and regeneration is shown in Figures 8 and 9. In both figures the duration of the absorption and regeneration steps are 21 and 4 minutes respectively, the time required for heating and cooling being included in the absorption time. Increasing absorption temperatures reduces capacity. The data in Figure 8 show a "deactivation energy" of 22 kcal/gmole. Capacity increases with regeneration temperature, but the temperature effect is not as strong as in absorption. From the data of Figure 9, the "activation" energy is 9 kcal/gmole.

Figure 10 shows the last cycle reaction rates for the four runs plotted in Figure 8. Figure 11 shows the capacity versus cycle number for the same runs.

The effect of steam and CO_2 level on regeneration rate was explored in the presence of partial pressures of H_2S. Figures 12 and 13 show five regeneration steps for the same stone in which only the regeneration atmosphere was changed from one cycle to the next. The sample reactivity was first stabilized by conducting 6 cycles in the same regeneration atmosphere (50% H_2O, 40% CO_2, 10% H_2). In all cases the a sorption conditions were unchanged. Lower initial rates result from the presence of H_2S as well as decreased H_2O and CO_2 partial pressures. With high CO_2 pressures (Figure 12), increasing the steam partial pressure increases the initial rate and the capacity. The effect is much more dramatic at low CO_2 pressures (Figure 13).

The complexities of the kinetic situation illustrated in Figures 12 and 13 are reminiscent of the "kinetic curiosities" reported eariler for the absorption reaction (5), and like them, the new complexities appear to reflect differences in the way in which crystallites of $CaCO_3$ or CaS grow within the solid microstructure. Examinations of microstructural properties of solids arising in this research will be reported elsewhere (7).

Acknowledgments

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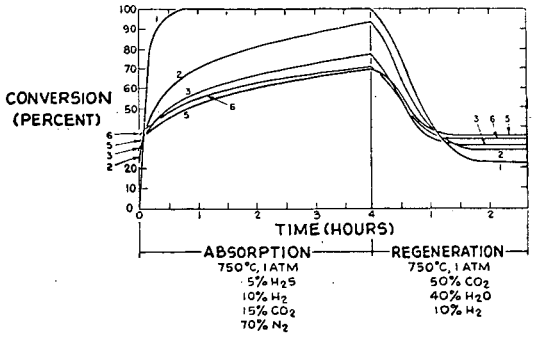

Figure 1. Sulfur absorption and regeneration cycles for half-calcined dolomite at 1 atm and 750°C.

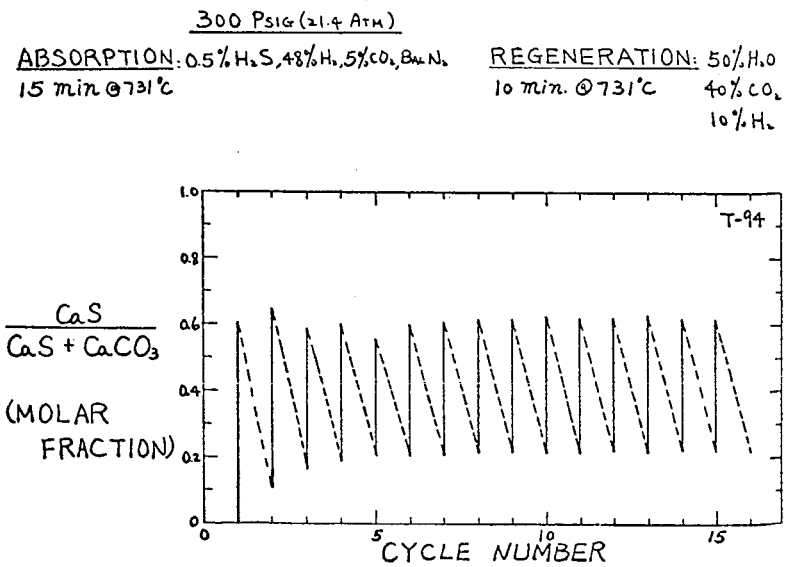

Figure 2. Molar fraction of calcium sulfide in half-calcined dolomite used in 15 cycles for absorption of hydrogen sulfide from simulated fuel gas.

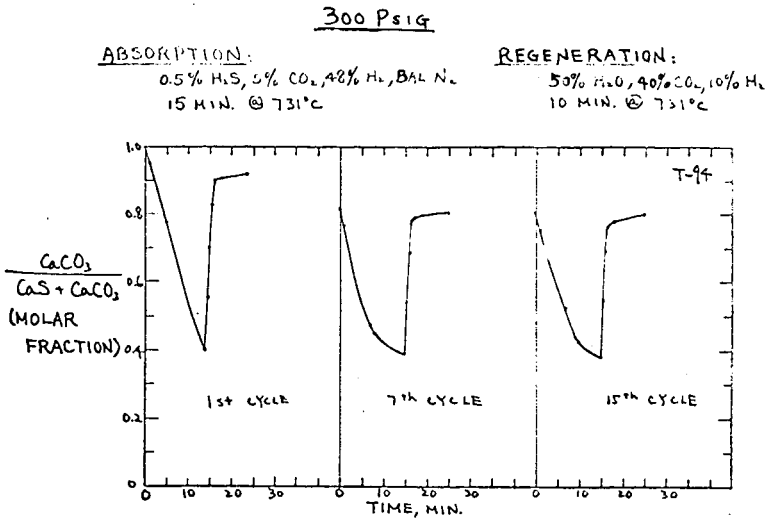

Figure 3. Course of reactions in first, 7th, and 15th cycles of Figure 2.

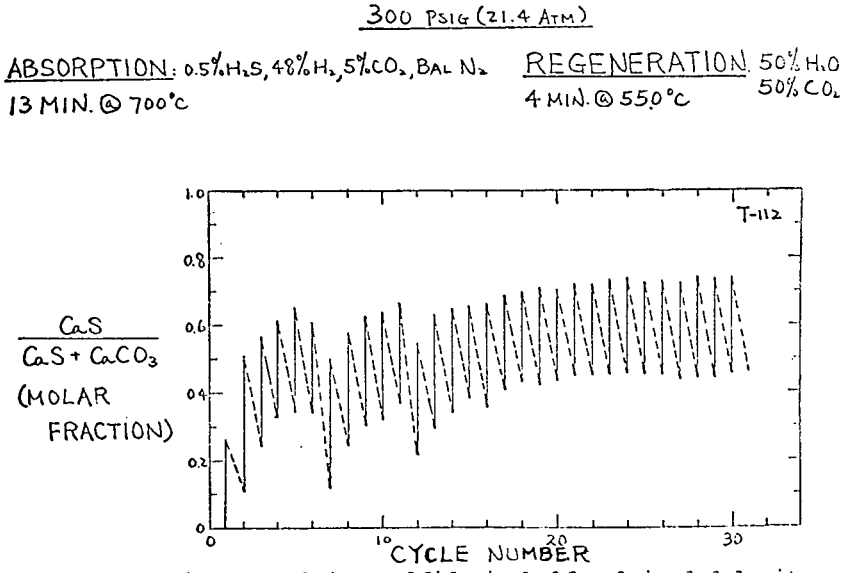

Figure 4. Molar fraction of calcium sulfide in half-calcined dolomite used in 30 cycles for absorption of hydrogen sulfide from simulated gas. Heating took about two minutes without H_2S present, cooling took about 6 minutes with H_2S mixture present.

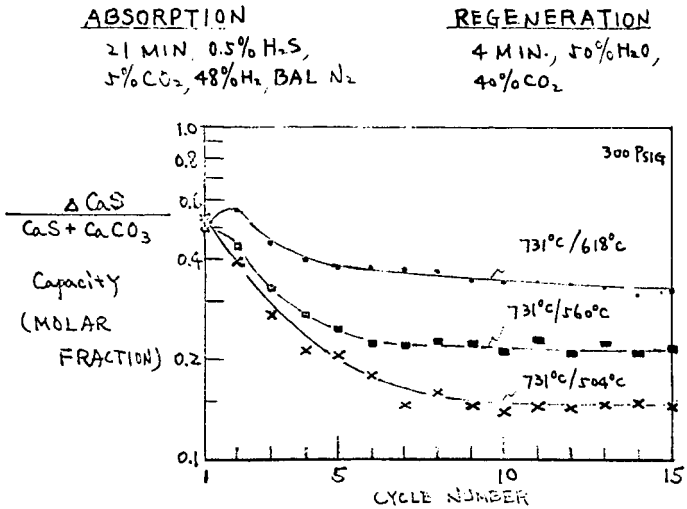

Figure 5. Capacity versus cycle number for three runs with absorptions at 731°C (the first temperature designated alongside each curve) and regenerations at 618°C, 560°C, and 504°C (the second temperature).

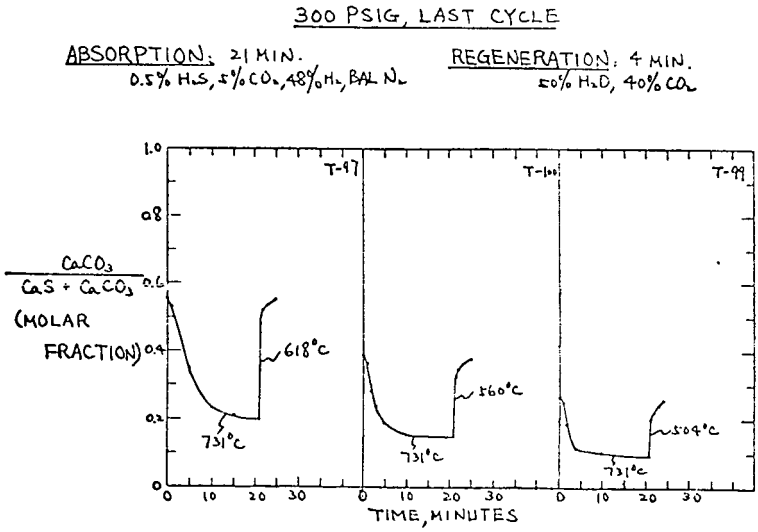

Figure 6. Cycle of absorption and regeneration for each of the three runs of Figure 5.

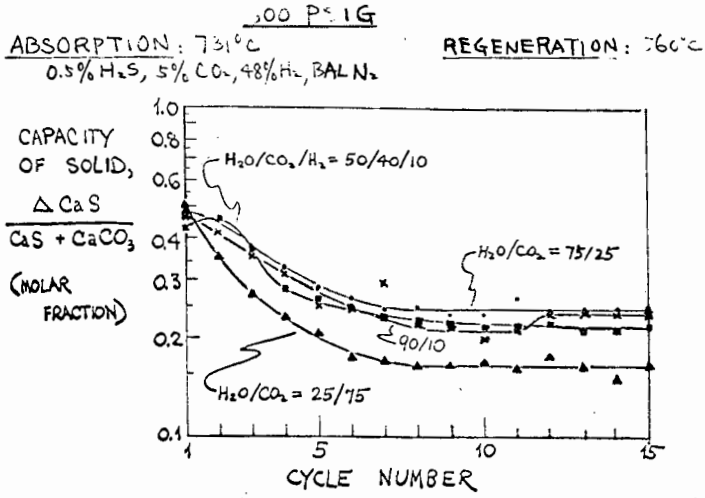

Figure 7. Capacity versus cycle number for four runs with steam/carbon dioxide/hydrogen ratios in regeneration gas as shown alongside the curves.

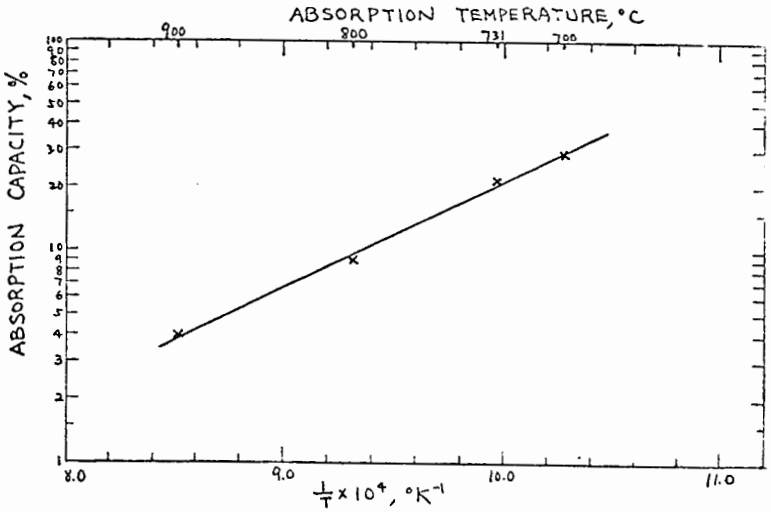

Figure 8. Variation in solid capacity with absorption temperature, for regeneration at 560°C. Absorption = 21 minutes (including heating and cooling); regeneration = 4 minutes.

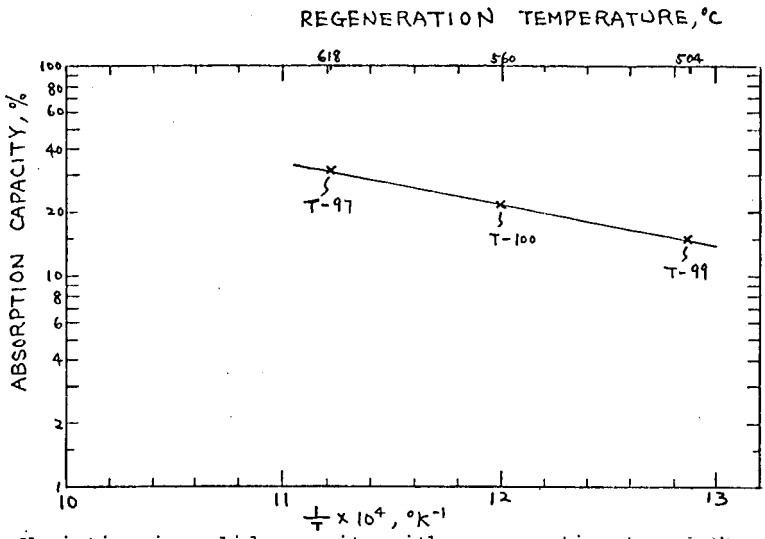

Figure 9. Variation in solid capacity with regeneration temperature, for absorption at 731°C. Times are same as in Figure 8.

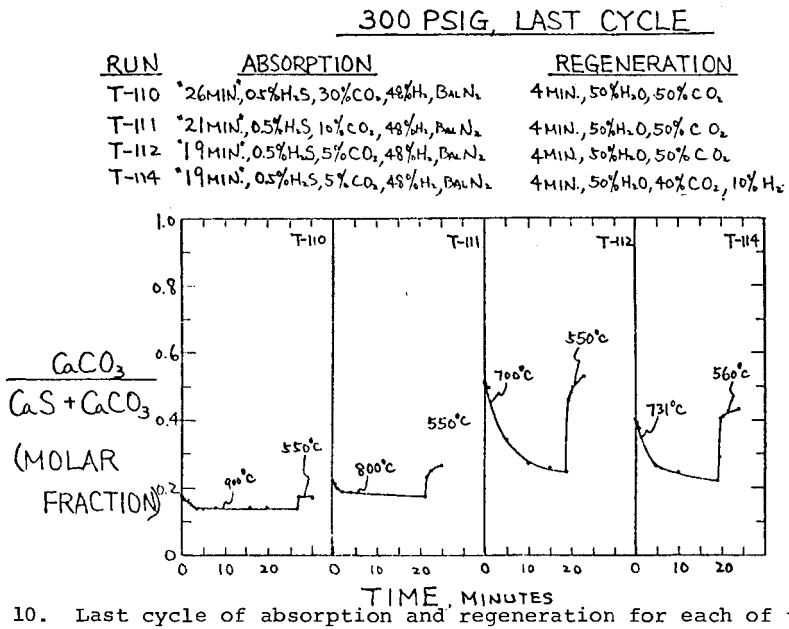

Figure 10. Last cycle of absorption and regeneration for each of the four runs of Figure 8.

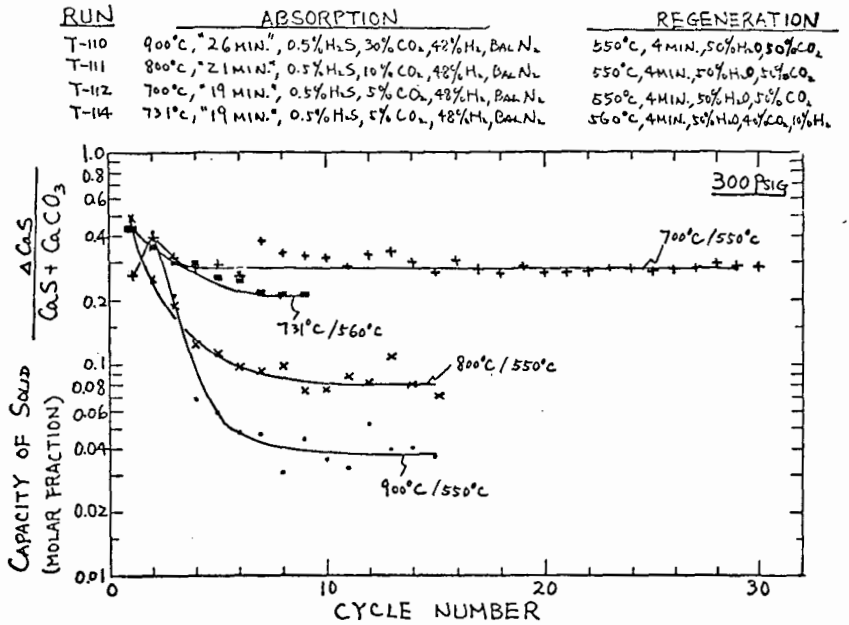

Figure 11. Capacity versus cycle number for the four runs of Figure 8.

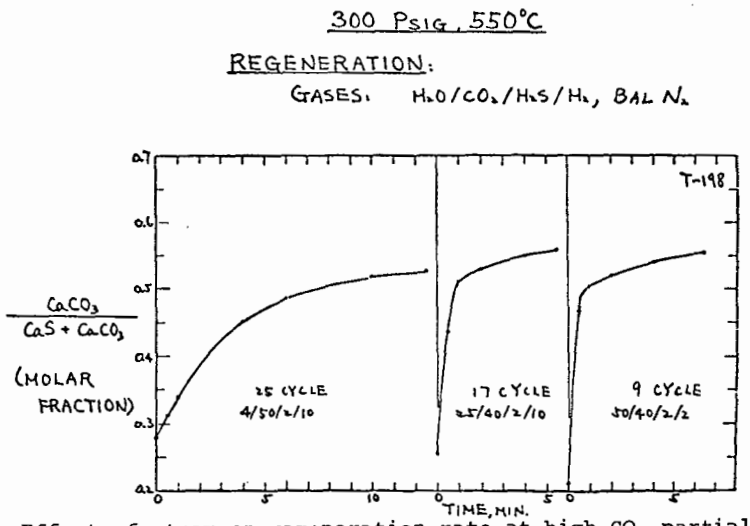

Figure 12. Effect of steam on regeneration rate at high CO_2 partial pressure in presence of H_2S. Three cycles of the same sample. Absorption at 700°C, 0.5% H_2S, 5% CO_2, 48% H_2, balance N_2.

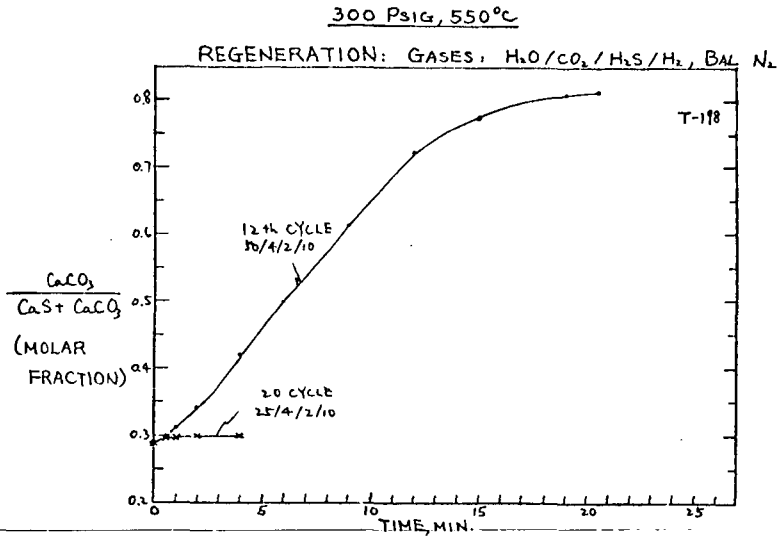

Figure 13. Effect of steam on regeneration rate at low CO_2 partial pressure in presence of H_2S. Same sample and absorption conditions as in Figure 12.