

HIGH REACTIVITY AND ENHANCED CAPACITY CARBON DIOXIDE REMOVAL AGENTS WITH LOW SUSCEPTIBILITY TO DEACTIVATION

K. Mondal¹, D. Dasgupta¹, T. Wiltowski^{1,2}

¹Department of Mechanical Engineering and Energy Processes,
Southern Illinois University, Carbondale, IL 62901

²Coal Research Center,
Southern Illinois University, Carbondale, IL 62901

EXTENDED ABSTRACT

The first step of forming hydrogen from carbonaceous solid fuels is gasification, followed by water gas shift reaction and separation of the carbon dioxide and hydrogen. Capture of carbon dioxide in situ will result in increased production of hydrogen by the water gas shift reaction. Separation of H₂ from the coal gasification products supports existing H₂ markets (such as refineries and power production) and makes hydrogen economy a distinct possibility. The sequestration-ready aspect of hydrogen/carbon dioxide separation will be of consequence in power applications in the future. The capture of acid and greenhouse gases from process streams is a major concern. One of the most common methods is the absorption of the gases in liquid solvents.

The initial and the ultimate carbon dioxide capture by sorption/reaction in repeated calcinations-carbonation cycles is strongly influenced by its surface area, pore size, and volume characteristics of calcium oxide. The commercially mined-limestone/dolomite powders exhibit a very low initial surface area and porosity. In an effort to increase the purity of hydrogen in the product stream by separation of the product gases from gasification, a new process to produce Ca-based carbon dioxide sorbent with enhanced sorption capacities and life has been developed. The method allows customizing the particle sizes for use in both packed bed and fluidized bed reactors.

Experimental

Preparation: Morphologically altered high surface area CaO samples were synthesized. The exact preparation methods are not described due to proprietary reasons. Different surfactants were used to control the size of the particles as well as pore distribution. Cationic surfactants were used to increase the particle size while anionic surfactants were used to decrease the particle size.

Analysis: A Quantachrome Nova 2000 BET analyzer was used to obtain multipoint surface areas. Microtrac S3500 was used for particle size distribution determination. Thermogravimetric analysis was employed to obtain the weight change data during calcinations and carbonation cycles. TGA experiments were conducted isothermally in the temperature range 750 - 850 °C under nitrogen and CO₂ atmospheres for calcination and carbonation.

Results and Discussion

Figures 1 a, b and c are the plots of cumulative pore volume vs. pore radius for samples produced using different surfactants, different suspension densities of CaO and different concentration of anionic surfactant SDS at a constant suspension density of 2.56 g/L

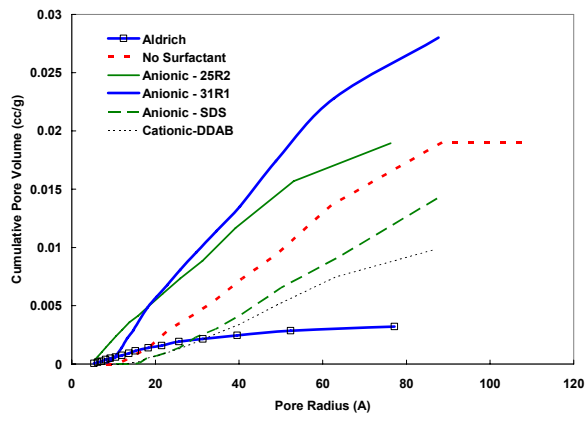
CaO, respectively. In addition, Figures 2 a-c presents histograms of the surface areas and mean pore radii of the different samples produced by varying surfactant type, suspension density and surfactant concentrations respectively. Figure 2a shows the effect of different surfactants. Figure 2b contains the data on surface area and mean pore size of solids obtained using different loadings of CaO and Figure 2c contains the data for solids obtained from different concentrations of SDS and 2.56 g/L of CaO in water. Figures 3 -6 contain the data of the cumulative size distribution of the calcium carbonates obtained after each treatment. The data in the figure show that the precipitation of CaCO₃ resulted in an 11 % increase in surface area. The addition of anionic surfactants yielded higher surface areas with the maximum increase (>25 %) obtained when SDS was employed. The particle size was significantly affected by the use of both surfactants 31 R1 and 25 R2 (not shown) with the mean size reducing to nearly half (of that obtained without the use of any surfactant) due to the use of the latter. The increase in SDS concentration during the preparation of the sorbent did not drastically change the particle size distribution. However, when the CaO loading was changed, the particle size distribution was observed to change drastically. The highest median diameter (> 100 μ m) was obtained for a CaO loading of 3.84 % corresponding to 24 times the saturation concentration. In general, increasing the CaO loading provided solids with better cycling properties. However, for use in a fluidized bed, larger diameter solids are preferred. As a result, the solids prepared from a 3.84 % CaO precursor solution was chosen for mass production. Increasing the 31R1TM surfactant decreased the particle size.

Thermogravimetric analysis was conducted on the precipitated calcium carbonates, and the commercially available calcium carbonate from Aldrich, the CaO obtained from Fisher Scientific and commercially available dolomite. The carbonation cycles were 15 minute each and calcinations were carried out till no change was observed. The theoretical maximum uptake is 0.785 g CO₂/g of CaO. It was observed (Figure not shown) that the CaO precursor from Fisher scientific has the lowest CO₂ uptake while sample *SDS* has the highest uptake (100 %). The uptake by commercial CaO, also the precursor to the precipitated calcium carbonates, was less than 40 %, while that by the commercial calcium carbonate decreased monotonously from an initial value of 52 %. Similarly, the maximum uptake by dolomite was 40 %. Thus, the laboratory prepared calcium carbonates performed significantly better than the commercially available CaCO₃ and CaO for a single cycle as well as repeated cycles. The uptake by the sample to which no surfactant was added also showed nearly 100 % uptake of the theoretical maximum. However, the calcinations rate of the sample *SDS* was relatively faster as compared to the sample *no surfact.* Sample *31R1* also showed a promising carbonation response but the kinetics of calcinations was observed to be extremely slow. The calcium carbonate obtained from Aldrich showed very slow calcination kinetics and relatively poor carbonation characteristics. Figures 7-9 contains (CaO conversions by CO₂ at 750 °C for different synthesis routes) the response from the TGA for several calcination-carbonation cycles. The data is summarized in the % of maximum theoretical uptake vs. cycle # plot shown in the figures. In general, it was seen to decrease with the surfactant concentration. It was also observed that sorbent deactivation takes place with repeated cycles. The effect of temperature on the cycling properties was also studied. As expected, the conversion during carbonation was higher at lower temperatures. The use of the new precipitated CaCO₃ showed enhanced reactivity (more than twice) towards carbonation with better cycling characteristics. Nearly 100 % conversion is possible for the sample obtained from 3.84 % CaO suspension. As a result, the operational capacity of these materials for CO₂ capture is significantly higher than commercially available sorbents. Figures 10 -13 shows the TGA plots

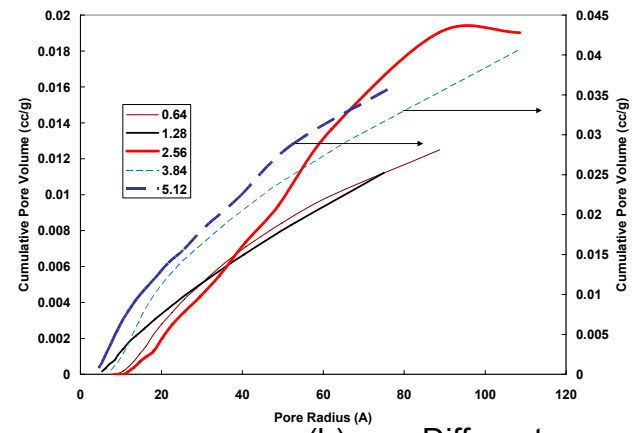
of selected samples at different temperatures (namely 750, 800 and 850 °C). Of particular interest are the plots on Figure 10 (TGA profiles for the commercially available sample from Sigma Aldrich) compared with the plots on Figures 11 -13. When analyzing these data, it was generalized that an increase in temperature resulted in a decrease in the extent and initial rate of carbonation. This decrease was, however, relatively small as compared to that effected by commercially available dolomite which showed only 40 % conversion in the first cycle, which further reduced to 20 % by the end of 4 cycles.

Conclusions

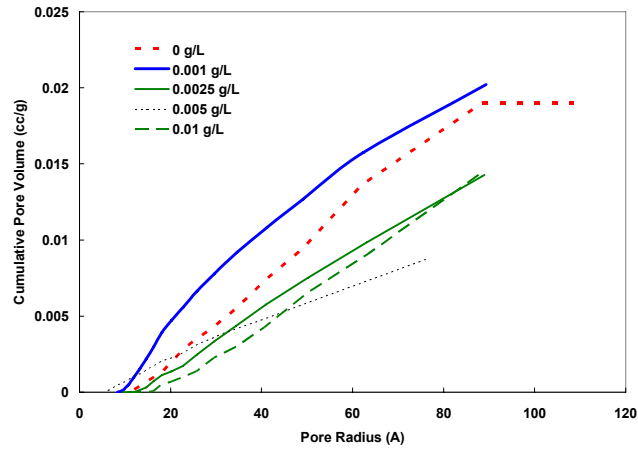
Samples with mean sizes ranging from 5 to 85 microns were produced. The fundamental carbon dioxide sorption on modified calcium oxide samples were studied using TGA reactor. Repetitive calcinations-carbonation reactions in pure nitrogen and carbon dioxide, respectively, were performed. Correlation of the removal efficiencies with BET surface area, pore size distribution, and particle size distribution are presented. The data from experiments with lab-synthesized removal agents is presented and compared with commercially available calcium carbonate and calcium oxide. The uptake by commercial CaO was less than 40 %, while that by the commercial calcium carbonate decreased monotonously from an initial value of 52 % to nearly 20 % after 11 cycles. On the other hand, the uptake by the laboratory synthesized samples showed nearly 100 % uptake of the theoretical maximum. Repeated cycling for over 11 cycles showed only a 5 % decrease in the capacity. The reactivities of the lab-synthesized removal agents were found to be greater than 10 times that of the commercially available Ca-based sorbents. Based on the data above data analysis we selected the applicable preparation conditions: a CaO suspension density of 3.84 g/L and an SDS concentration of 0.10 g/L.



(a) Different surfactants



(b) Different suspension densities



(c) SDS concentration

Figure 1 Cumulative pore volume vs. pore size

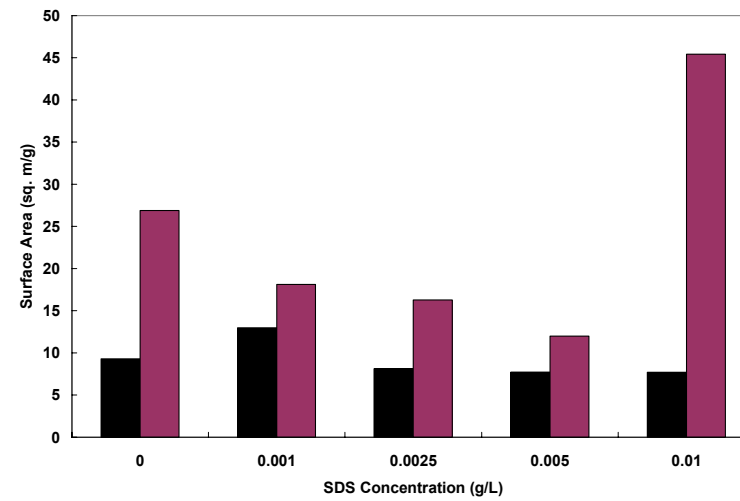
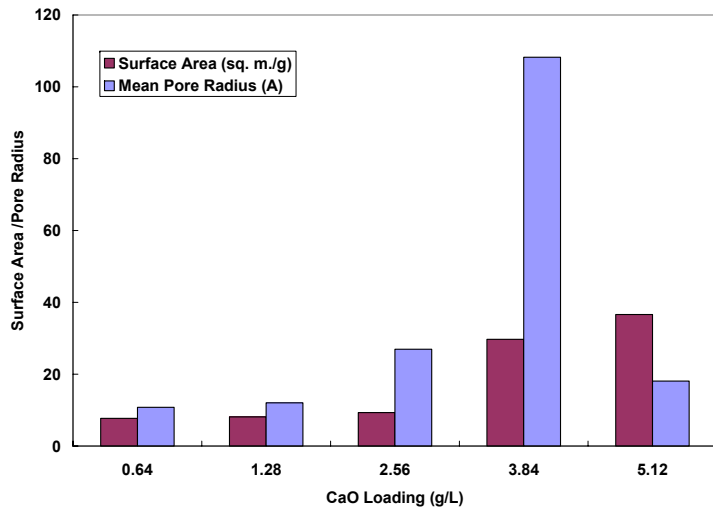
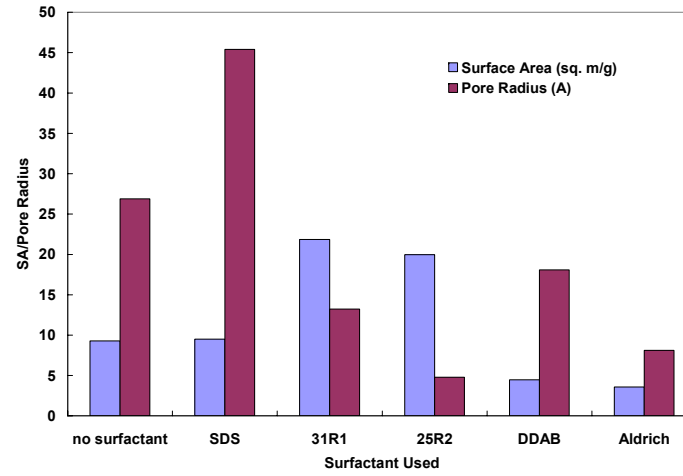


Figure 2: Comparison of pore size and surface area obtained for different treatments

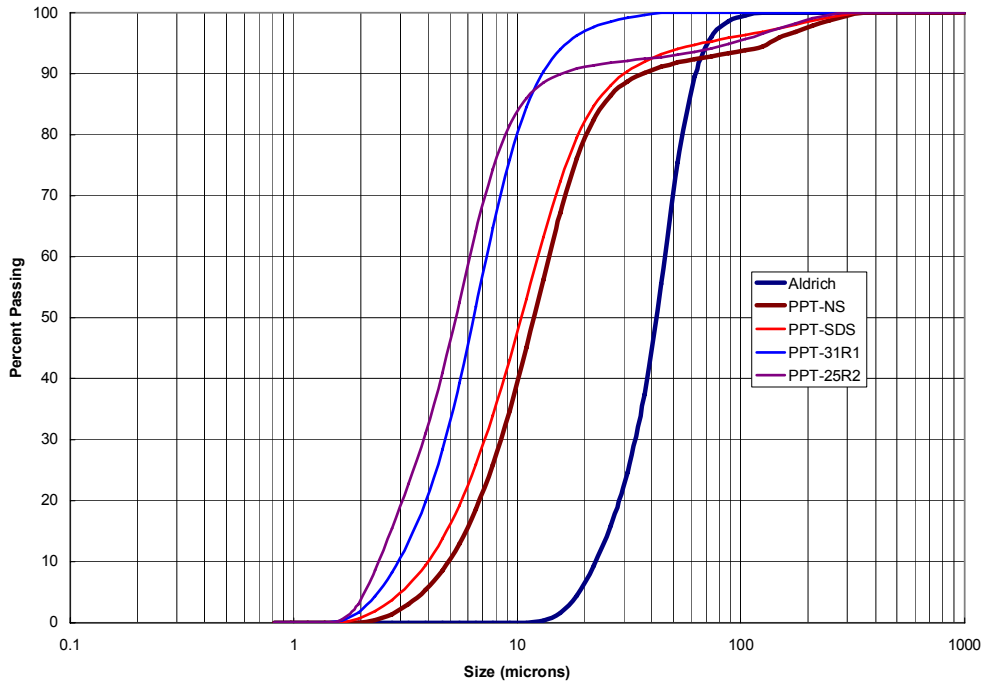


Figure 3. Particle size distribution for different surfactants

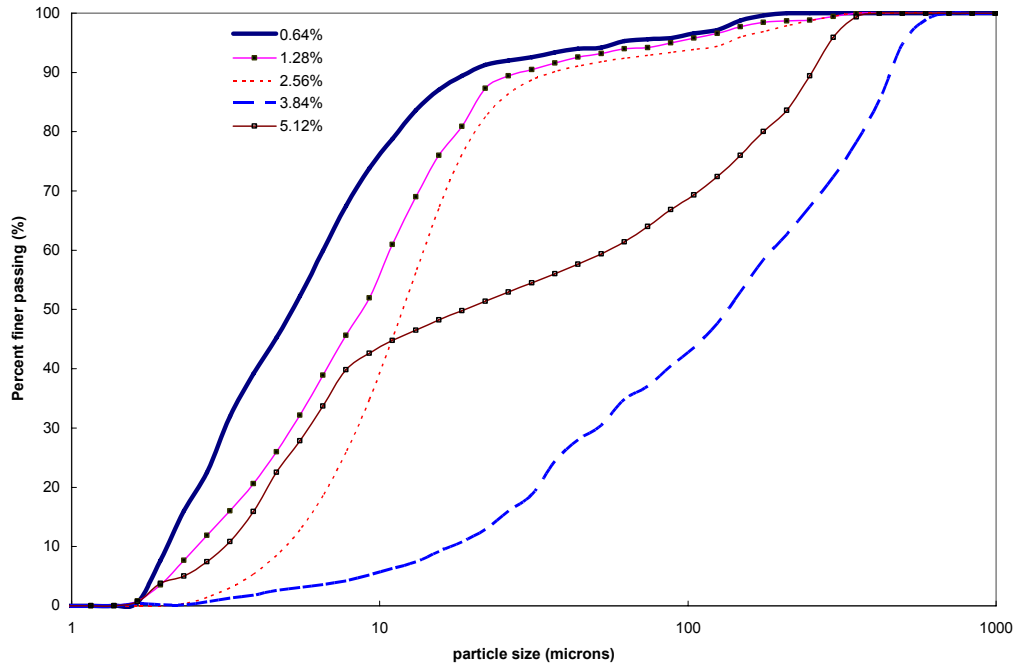


Figure 4. Particle size distribution for different suspension densities

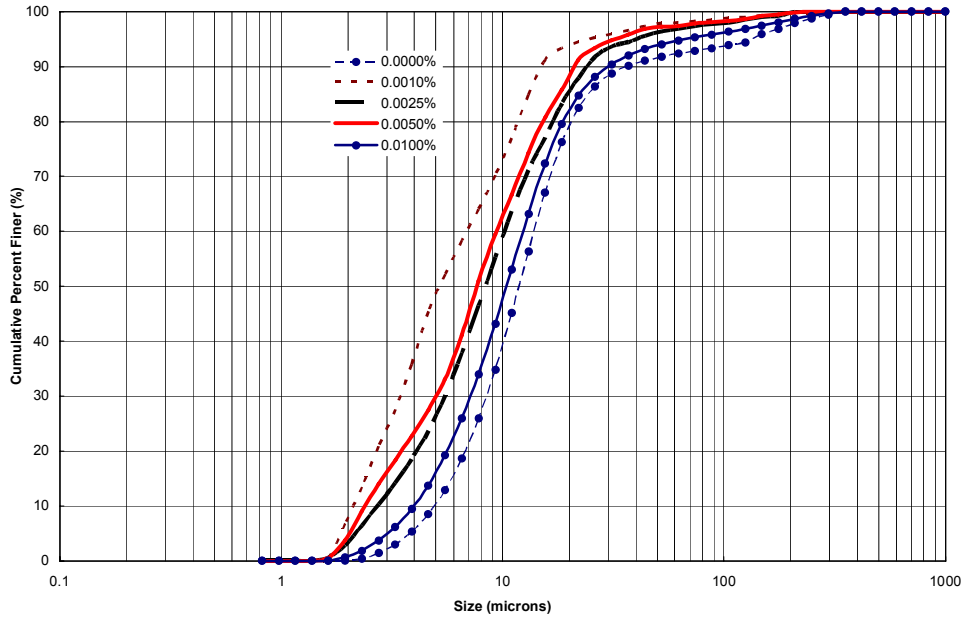


Figure 5. Particle size distribution for different concentrations of surfactant SDS

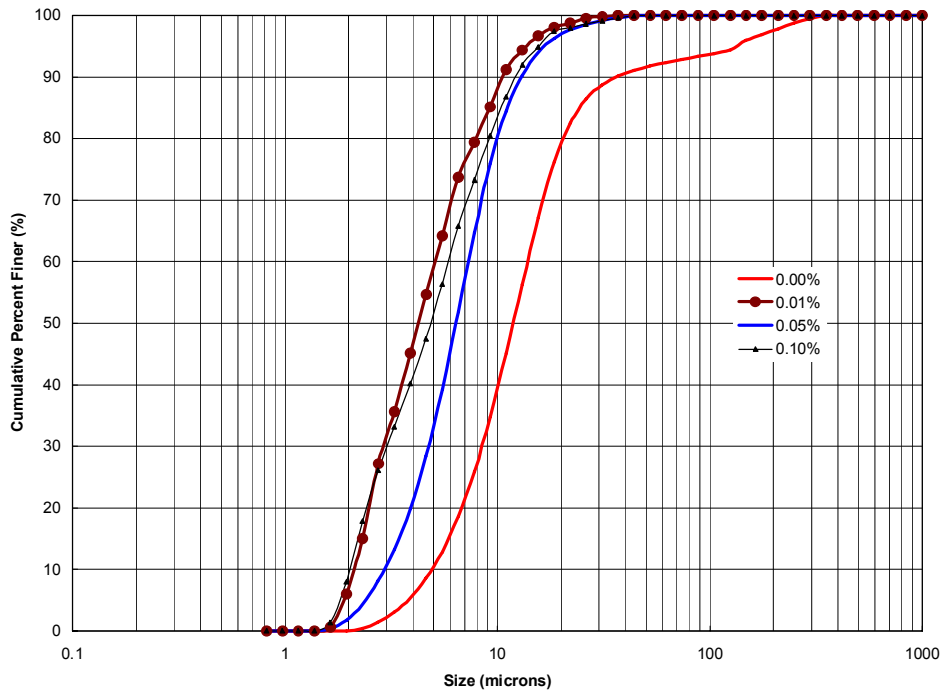


Figure 6. Particle size distribution for different concentrations of surfactant 31 R1

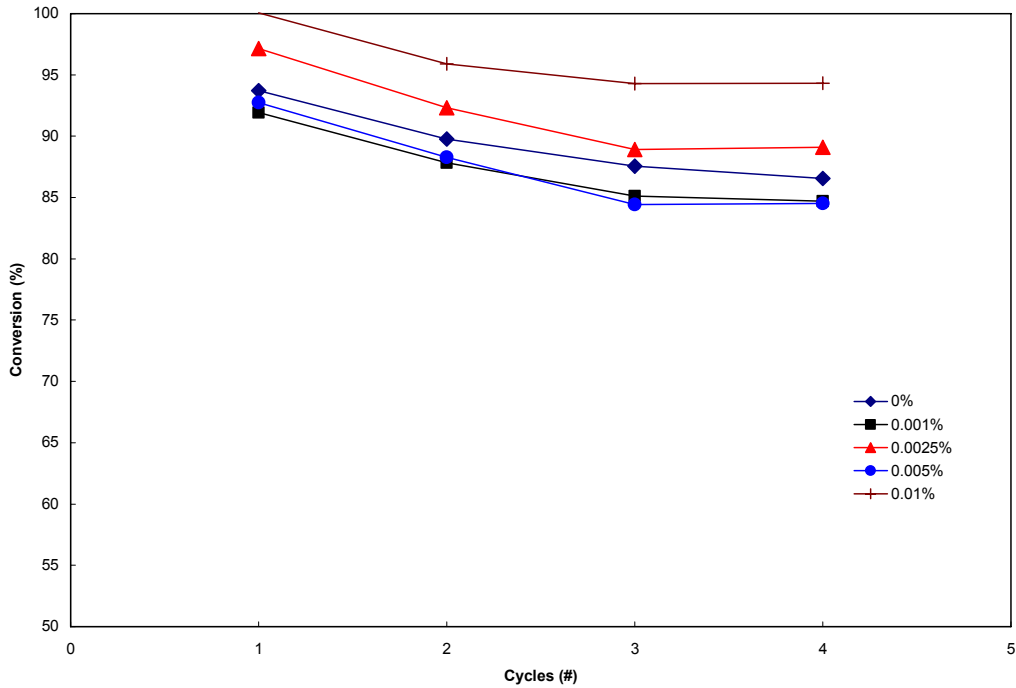


Figure 7 Effect of SDS Concentration on Extent of Carbonation due to repeated Calcination and Carbonation (CaO = 2.56 % during the preparation, 800 °C during TGA, 15 minute carbonation cycle)

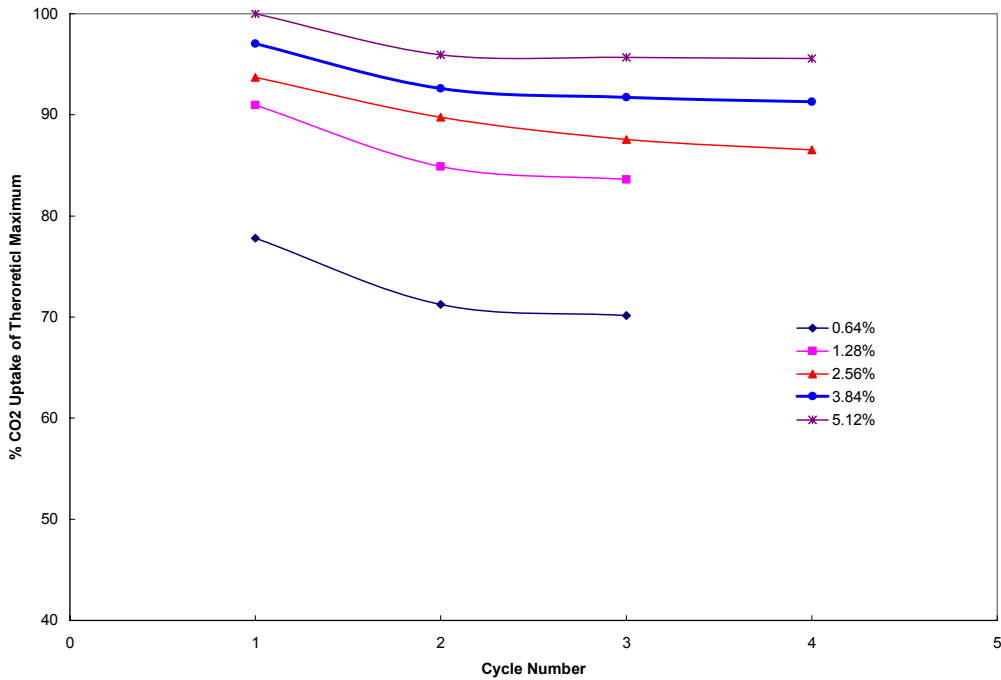


Figure 8 Effect of CaO Suspension Density on Extent of Carbonation due to repeated Calcination and Carbonation (800 °C during TGA, 15 minute carbonation cycle)

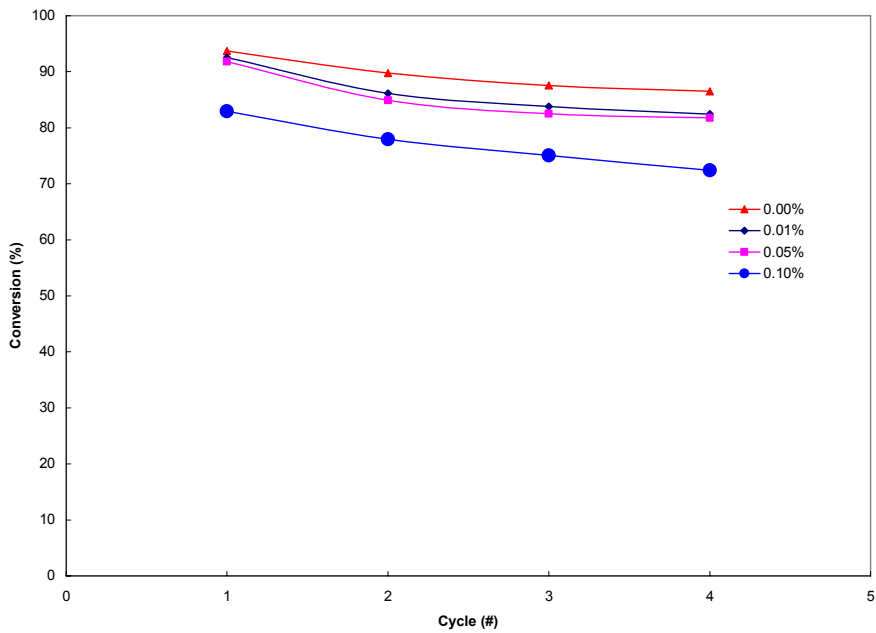


Figure 9 Effect of 31R1TM Concentration on Extent of Carbonation due to repeated Calcination and Carbonation (CaO = 2.56 % during the preparation, 800 °C during TGA, 15 minute carbonation cycle)

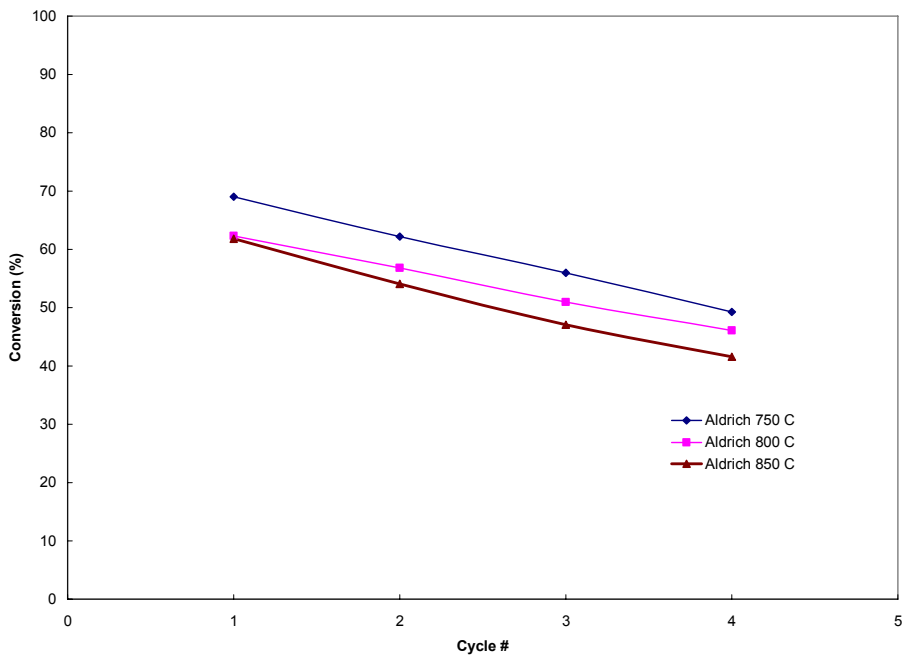


Figure 10 Effect of Temperature on Extent of Carbonation due to repeated Calcination and Carbonation (Aldrich CaCO₃, 15 minute carbonation cycle)

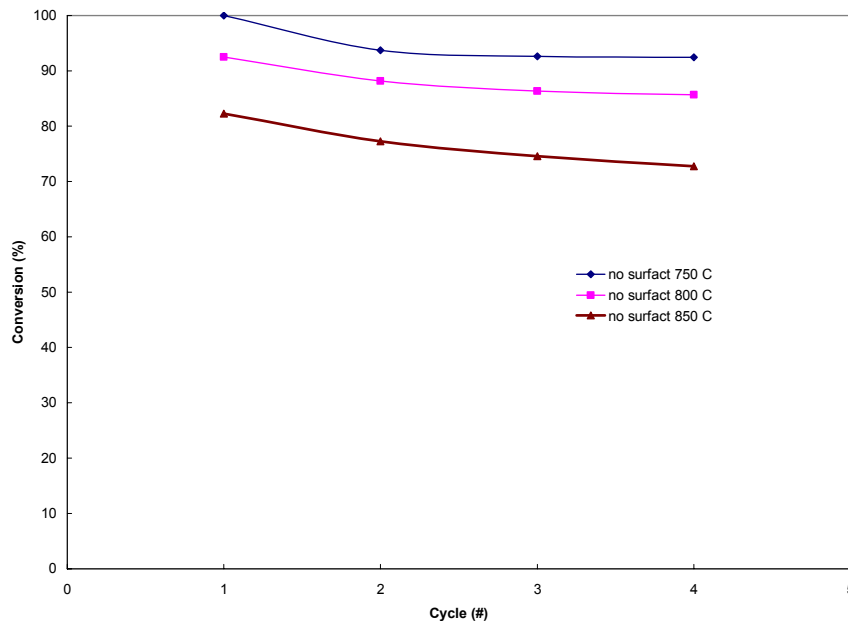


Figure 11 Effect of Temperature on Extent of Carbonation due to repeated Calcination and Carbonation (CaO = 2.56 % during preparation, no surfactant, 15 minute carbonation cycle)

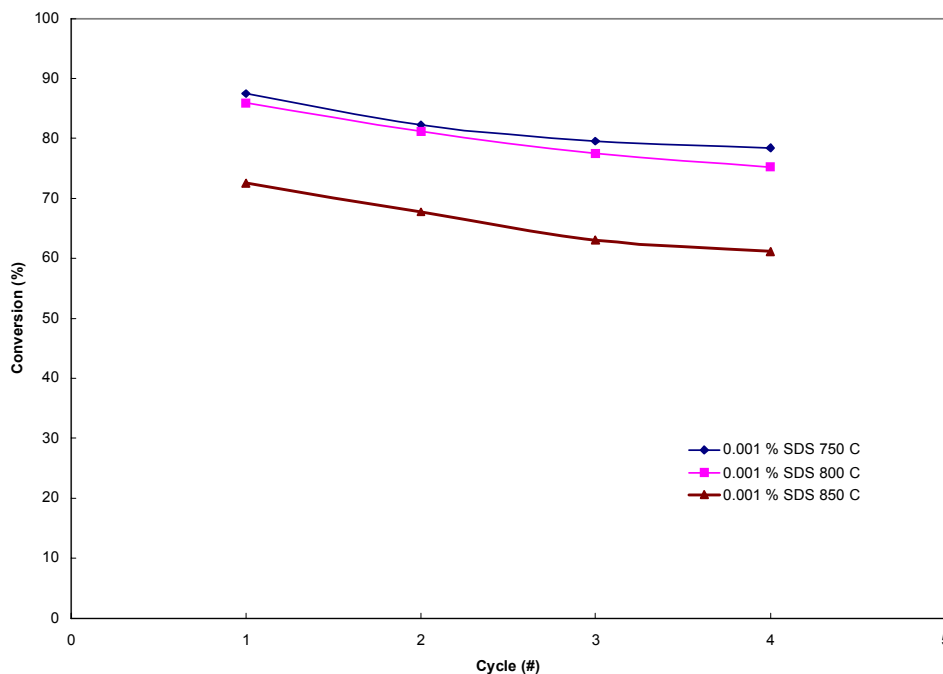


Figure 12 Effect of Temperature on Extent of Carbonation due to repeated Calcination and Carbonation (CaO = 2.56 % during preparation, SDS = 0.001 %, 15 minute carbonation cycle)

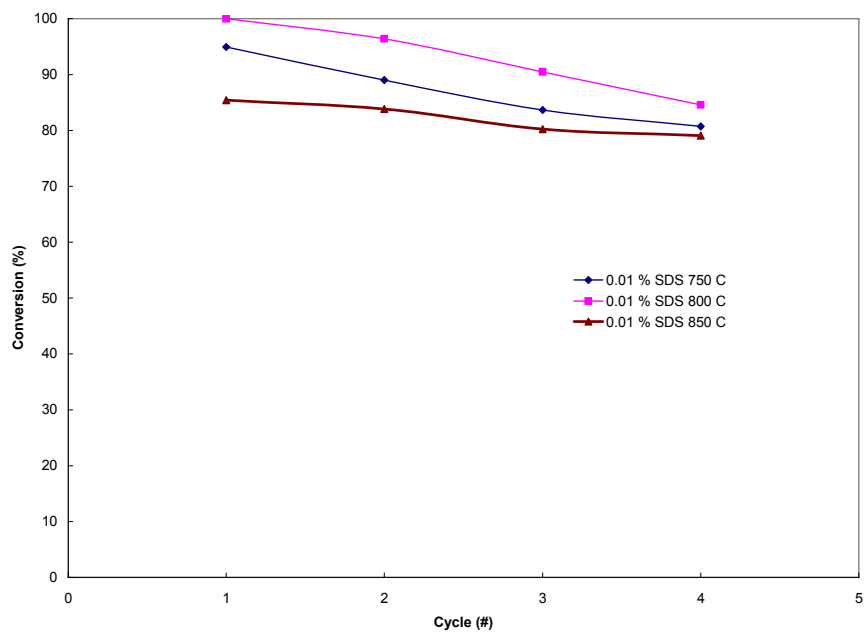


Figure 13 Effect of Temperature on Extent of Carbonation due to repeated Calcination and Carbonation (CaO = 2.56 % during preparation, SDS = 0.01 %, 15 minute carbonation cycle)