Hot coal gas desulfurization with manganese-based sorbents[1]

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Abstract

The objective of this project is to develop a pellet formulation which is capable of achieving low sulfur partial pressures and a high capacity for sulfur, loaded from a hot fuel gas and which is readily regenerable. Furthermore the pellet must be strong for potential use in a fluidized bed and regenerable over many cycles of loading and regeneration. Regeneration should be in air or oxygen-depleted air to produce a high-concentration sulfur dioxide.

Fixed-bed tests were conducted with several formulations of manganese sesquioxide and titania, and alumina. They were subject to a simplified fuel gas of the oxygen-blown Shell type spiked with a 30,000ppmv concentration of H_2S. Pellet crush strengths for 4 and 2mm diameter pellets was typically 12 lbs per pellet and 4 lbs per pellet, respectively.

For the most favorable of the formulations tested and under the criteria of break-through at less than 100ppmv H_2S and loading temperatures of 500$^{\text{o}}$C and an empty-bed space velocity of 4,000 per hour, breakthrough occurred an effective loading of sulfur of 27 to 29% over 5 loading and regeneration cycles. At 90% of this saturation condition, the observed level of H_2S was below 10ppmv.

For regeneration, a temperature of 900$^{\text{o}}$C is required to dissociate the sulfide into sulfur dioxide using air at atmospheric pressure. The mean sulfur dioxide concentration which is achieved during regeneration is 8% with empty-bed space velocities of 700/hr.

TGA tests on individual pellets indicate that bentonite is not desirable as a bonding material and that Mn/Ti ratios higher than 7:1 produce relatively non-porous pellets. Whereas the reactivity is rapid below 12% conversion, the kinetics of conversion decreases significantly above this level. This observation may be the result of plugging of the pellet pores with sulfided product creating inaccessible pore volumes or alternately an increase in diffusional resistance by formation of MnS.

Introduction

Department of Energy is actively investigating hot fuel gas desulfurization sorbents for application to the Integrated Gasification Combined Cycle Power Generation (IGCC). A sorbent must be highly active towards sulfur at high temperatures and pressures, under varying degrees of reducing atmospheres. High conversion of the metal oxide and low hydrogen sulfide exit partial pressures are required. Also, it must regenerate nearly ideally to maintain activity over numerous cycles. Furthermore, regeneration must yield a sulfur product which is economically recoverable directly or indirectly.

In response to stability difficulties to formulate single and binary metal oxide sorbents, effort is increasingly being directed towards incorporation of an inert component into sorbent formulation as witnessed by the various Zn-titanates. The role of the inert component is primarily to increase pore structure integrity while stabilizing the active metal oxide against reduction. The inert solid may also be used as a porous monolith for impregnated active metals. Mn-based sorbents are resistant to reduction to the metal in most coal gas atmospheres. However, their pore structure requires further investigation, as this may determine desulfurization kinetics due to intra-particle transport resistances.

Objective

The objective of this project is to develop a pellet formulation which is capable of achieving low sulfur partial pressures and a high capacity for sulfur, of being loaded from a hot fuel gas and which is readily regenerable. Furthermore the pellet must be strong for potential use in a fluidized bed and regenerable over many cycles of loading and regeneration. Regeneration should be in air or oxygen-depleted air to produce a high-concentration of sulfur dioxide.

Approach

Pellet Composition

Exploratory investigation of Mn-based sorbents began with the consideration of the following parameters of feed materials and preparation techniques. Composition variables were;
- Manganese source,
- Substrate composition,
- Mn to substrate molar ratio,
- Non-volatile binder wt %,
- Porosity enhancer composition,
- Porosity enhancement wt%.

The manganese sources were chosen from a commercially available $MnCO_3$ and a pyrolusite ore. Substrate were chosen based on thermodynamic equilibrium between the mixed metal oxide sorbent ($MnO.Me_xO_y$) and hydrogen sulfide (H_2S).
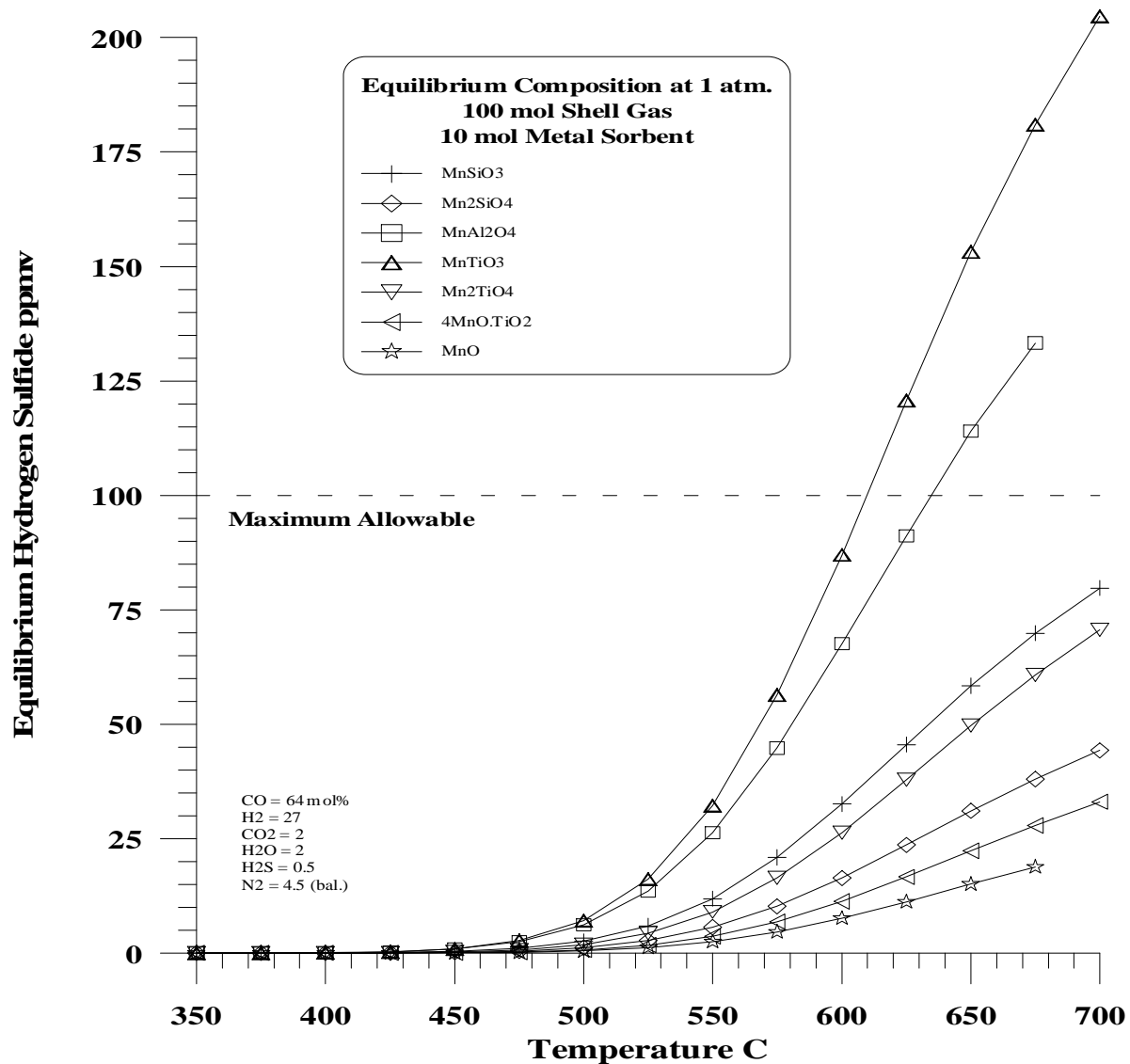
Figure 1. Equilibrium composition for Mn-based sorbents with various substrates in a simplified Shell type fuel gas.

Figure 1. is a thermodynamic analysis of the hydrogen sulfide levels which can theoretically be produced for a series of manganese oxide phases.

The molar ratio of Mn to substrate was varied in an attempt to optimize this parameter. Only bentonite was used as a non-volatile binder with 0,2, or 5% by weight added to various formulations. In an effort to increase the pore volume and surface area of the indurated pellet, volatile components were added to initial pellet mixtures. Finally, the amount of porosity enhancer was varied for a selected number of formulations.

Pellet Preparation

Feed powders were hand mixed and pelletized in a balling wheel forming "green" pellets. Green pellets were air dried for one day than dried to a constant weight at 100 °C. Dry pellets

were calcined for four hours at 350ºC. Immediately after calcination, pellets were placed in a high-temperature furnace (preheated to 500ºC), where the temperature was ramped up for two hours until final induration temperature was achieved. Due to the variety of pellet compositions, it was decided to restrict the induration length to two hours, at the designated temperature, for all formulations.

To date over 50 induration campaigns have been conducted for the fifteen present formulations (approximately four campaigns per formulation). The indurated pellet size was formulated in the range of 1-3 mm.

Characterization

Several methods of physical and chemical characterization were employed. Crush strength was the first parameter measured for all freshly indurated sorbent. Sorbent with requisite strength was then reduced and sulfided in a thermogravimetric analyzer to determine reaction evolution and fractional conversion. The test conditions for reduction/sulfidation are reported in Table 1.

Sample mass	200-800 mg
Reduction duration: $T > 550ºC$ $T < 550 ºC$	30 min 60 min
Sulfidation duration	120 min
Average pellet diameter	1-3 mm
Gas composition and flow rate	1 L/min H_2
H_2S concentration	30,000 ppmv
Pressure	1 atm

Table 1. Conditions of TGA reduction/sulfidation experiments for all formulations.

Each TGA test sample consisted of three pellets. The sulfided pellets were also regenerated in the TGA. Regeneration conditions are described in Table 2.

Sample mass	200-800 mg
Regeneration Temperature	900 ºC
Regeneration duration	60 min
Average pellet diameter	1-3 mm
Gas composition and flow rate	1 L/min Air
Pressure	1 atm

Table 2. Conditions of TGA regeneration experiments for all formulations.

A limited number of formulations were subjected to mercury porosimetry for pore structure characterization. This testing is currently limited to freshly indurated sorbent. Also, chemical analysis of unreacted and reacted sorbent was conducted to corroborate TGA data. Sorbent S capacities' (based upon initial formulation and chemical analysis) are listed in Table 3.

Formula	Sulfur Capacity Sg / 100g sorbent	Formula	Sulfur Capacity Sg / 100g sorbent
A1-0	28.8 (29.1)	C4-5	28.2 (27.9)
A1-2	28.1 (27.8)	C5-2	31.4 (33.4)
A2-2	29.8 (29.1)	C5-5	30.1 (30.7)
C4-2	29.3 (27.3)	C6-2	25.5 (31.7)
C4-2A	29.3 (27.5)	C7-2	23.0 (21.6)
C4-2D	29.3 (27.8)	C8-0	25.9 (28.3)
C4-2M	29.3 (*)	C9-2	32.6 (34.1)
C10-2	29.3 (27.6)		

Table 3. Formula designations and sulfur capacities based on; initial formulation and chemical analysis ( ).*Chemical analysis not available.

Formulation designations are described by listing sequentially; a letter, a number, a dash, a second number, a second dash, and finally a third number (ex. C6-2-1100). The first letter corresponds to the manganese source (C for $MnCO_3$, and A for MnO_2-ore). The first number refers to the molar ratio of Mn to substrate and the substrate composition (1,2,4,5,7 for alundum, 6,8, 9 for titania, and 10 for bauxite). The second number is the weight percent of bentonite binder. Note, some C4-2 formulations have letters following the weight percent bentonite. These letters refers to porosity promoters added, i.e., C4-2x (A for activated, D for dextrin, and M for MoO_3).

The most promising sorbents are to be further tested in an ambient pressure fixed-bed reactor. This will allow operational parameters of; space velocity, temperature, and gas composition, to be varied to determine sorbent performance during sulfidation and regeneration. Primarily, steady-state H_2S concentrations and breakthrough times are being measured. Also, regeneration SO_2 concentrations and breakthrough times are measured.

Characterization of fixed-bed pellets includes crush strength, sulfur analysis, porosimetry, and scanning electron microscopy.

The reactor consists of a 1" inner diameter tube and bed outlet thermocouple. Figure 2. is a schematic of the reactor system.
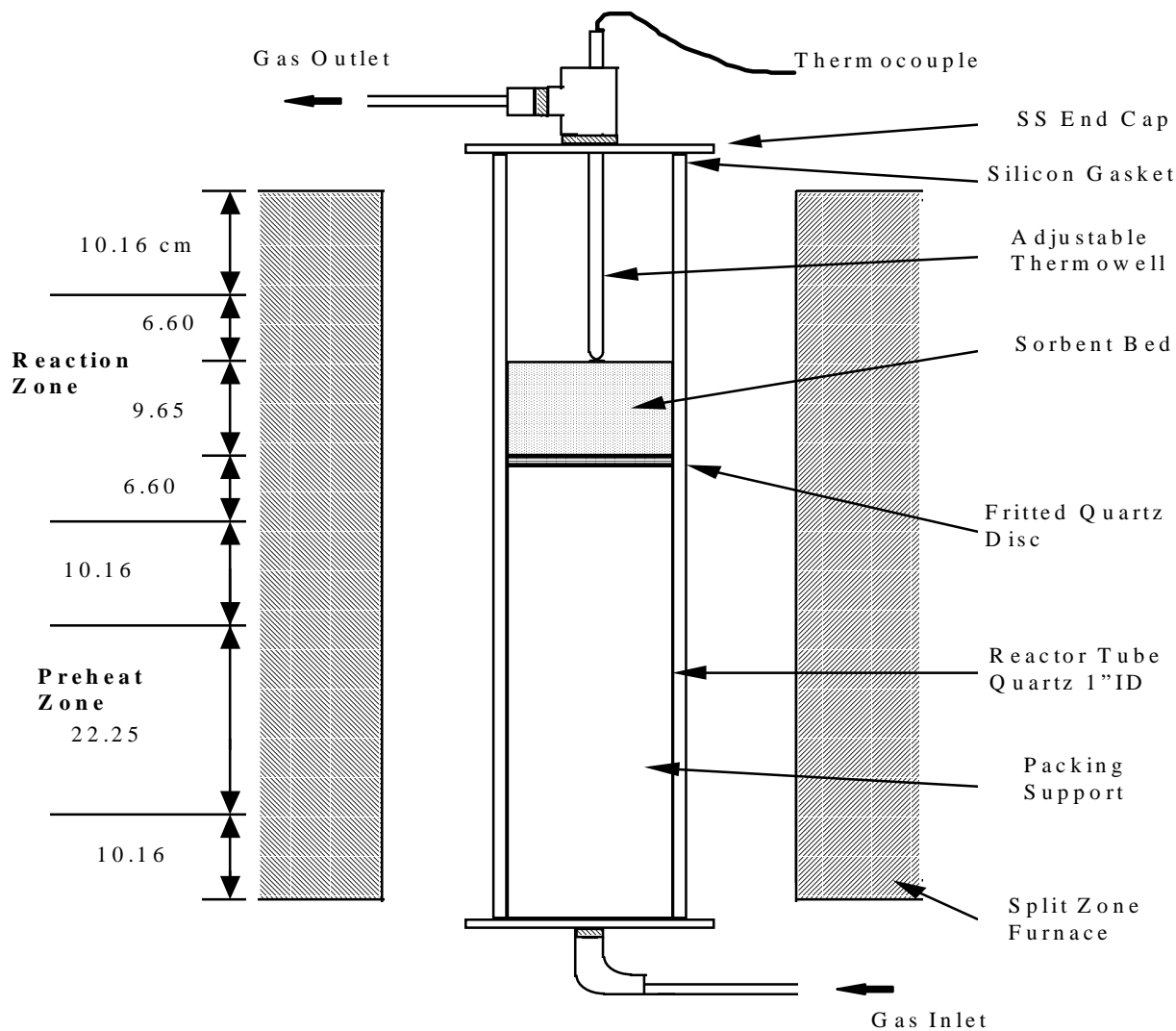
Figure 2. Desulfurization Reactor

Screening Protocol

The composition and preparation technique for sorbent formulation was based upon the fundamental requirement of desulfurization steady-state H_2S concentrations less than 50 ppmv. Further central requirements are; fully regenerable providing a sulfur product stream of at least 6 % SO_2, and activity retention for at least 50 cycles. The screening procedure is given in Figure 3.
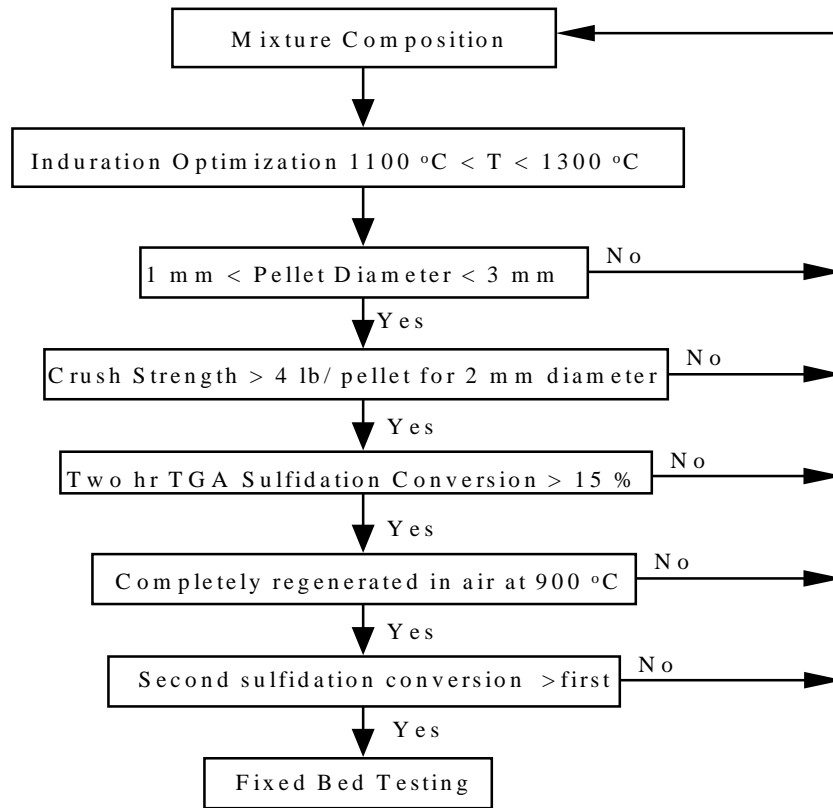
Figure 3. Strength and thermogravimetric screening protocol.

Substrate metal oxides were previously determined to quantitatively increase sorbent strength and porosity. Therefore, candidate substrates were evaluated according to their thermodynamic equilibrium between the Mn-substrate mixture and H_2S for typical operating desulfurization conditions. Sorbent formulations were then prepared as previously described.

A lower limit of 1100 ^{O}C was placed on sorbent induration temperature to preclude sintering during regeneration which is currently set at 900 ^{O}C. An induration upper temperature limit of 1300 ^{O}C was set due to furnace limitations. Therefore, all potential sorbents were required to be indurated in this temperature range for further consideration. Crush strength tests of freshly indurated sorbent was then conducted with the requirement of 1 lb / pellet / mm of diameter.

This was determined assuming the crush strength increased proportionally with the pellet cross-sectional area; thus, providing a basis for comparing different diameter pellets. Minimization of the induration temperature was conducted for all formulations. Following the preparation and strength screening the kinetic screening for sulfidation and regeneration was conducted.

Sulfidation screening was primarily conducted at 500 ^{O}C. Sorbents showing sufficient sulfur absorption were regenerated according to the previously described. Finally, the superior performing sorbents are to be tested in the fixed-bed reactor to determine their effectiveness when subject to recycle testing.

Results

Over fifty induration campaigns have been conducted among the fifteen Mn-based sorbent formulations. All indurated sorbents has been tested for crush strength and chemical analysis. Also, fifteen sorbent formulations have been tested in a TGA for at least one induration condition.

There are three main groups of formulations tested. They are the $MnCO_3$ supported with TiO_2 (with or without bentonite), $MnCO_3$ supported with Al_2O_3 (with or without porosity enhancers), and MnO_2 ore supported with alundum (with and without bentonite).

$MnCO_3$-TiO_2 Formulations

The results of the crush strength tests are given in Figures 4-6 for manganese carbonate/Titania; Manganese carbonate/Alumina; and Manganese ore/Alumina formulations, respectively.
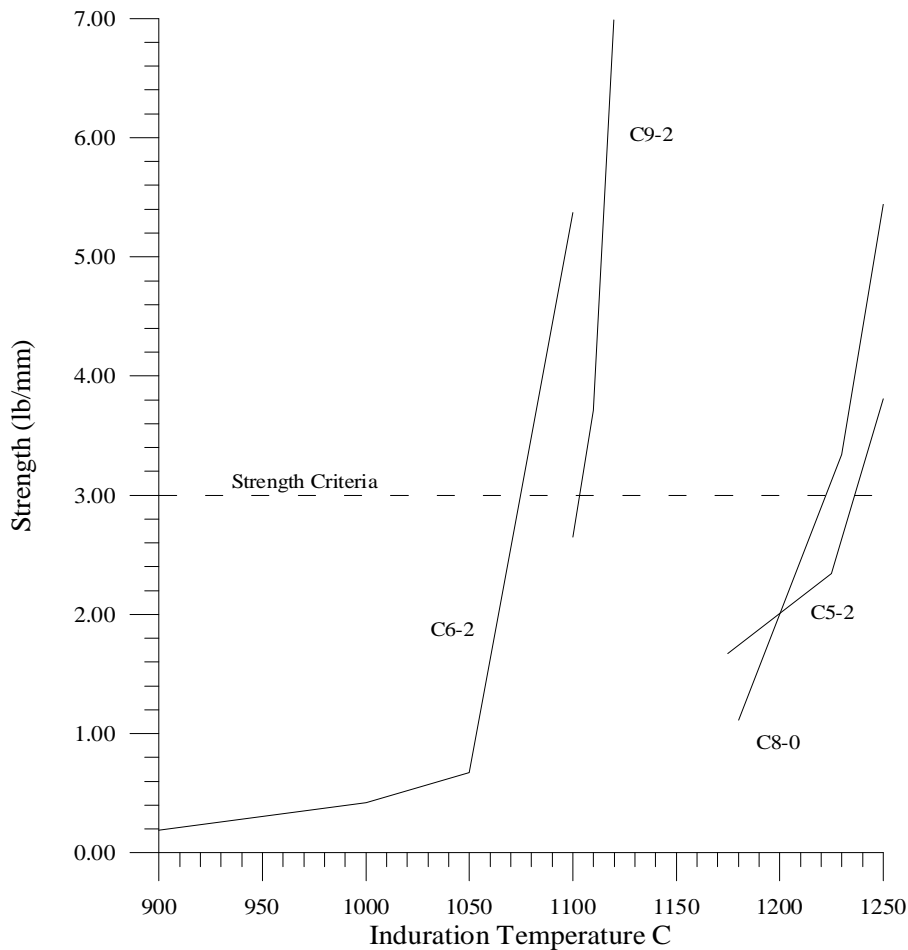

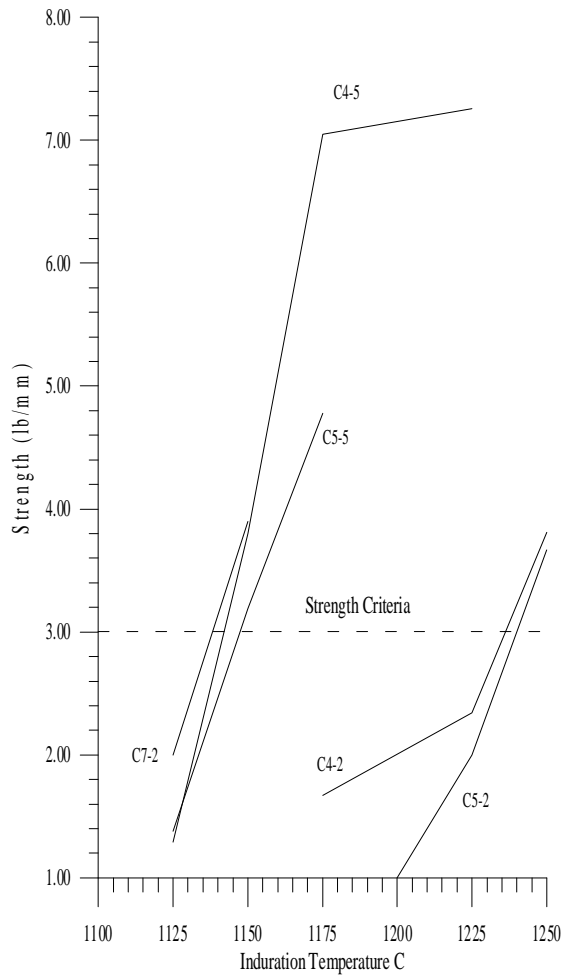**Figure 4.** Crush strength of Manganese carbonate/ Titania formulations.

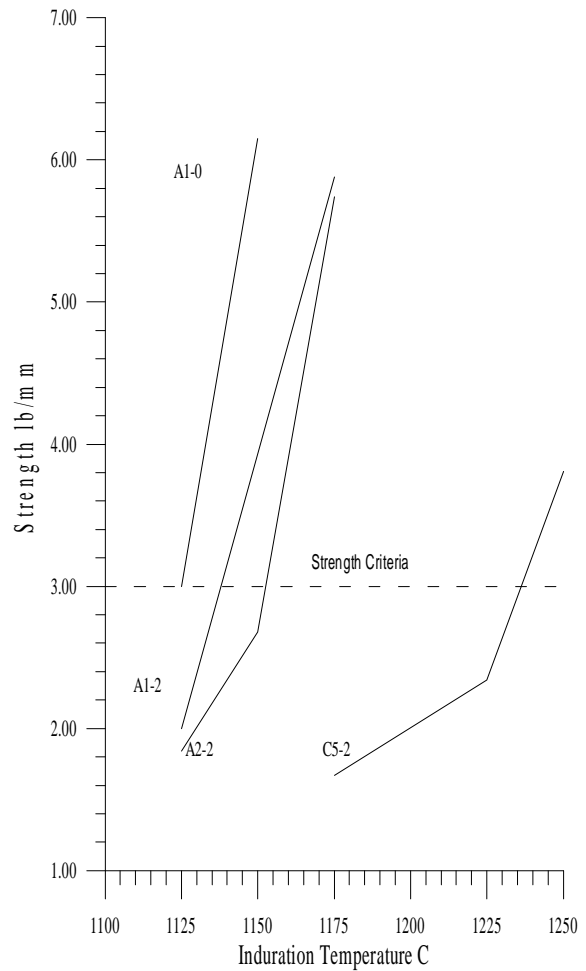**Figure 5.** Crush strength of Manganese carbonate/ Alumina formulations.

Figure 6. Crush strength of Manganese ore/ Alumina formulations.

Limited porosimetry analysis is summarized in Table 4. Comparing C6-2-1100 and C9-2-1110, the former has a larger intrusion volume while having a similar mean pore diameter. This points to more surface area in C6-2-1100 pellets than in C9-2-1110. Further porosimetry data is required, especially of C8-0-1230.

Pellet Properties	A1-2-1125	C6-2-1100	C9-2-1110	C5-2-1250
Total Intrusion Volume, Ml/g	0.2220	0.2328	0.1618	0.2901
Total Pore Area, m^2/g	0.490	---	0.199	0.103
Median Pore Diameter (volume), mm	4.7579	4.1741	4.1157	10.9701
Median Pore Diameter (area), mm	0.0142	---	2.9058	10.0270
Average Pore Diameter (4V/A), mm	1.8116	---	3.2474	11.3167
Bulk Density, g/ml	---	2.1073	2.4126	1.8807
Apparent Density (skeletal), g/ml	---	4.1357	3.9580	4.1390
Porosity, %	---	49.05	39.05	54.56

Table 4. Results of Mercury porosimetry of freshly indurated pellets.

TGA results on sulfidation tests are shown in Figure 7. and Figure 8. for $MnCO_3$/TiO_2 and other selected formulations.
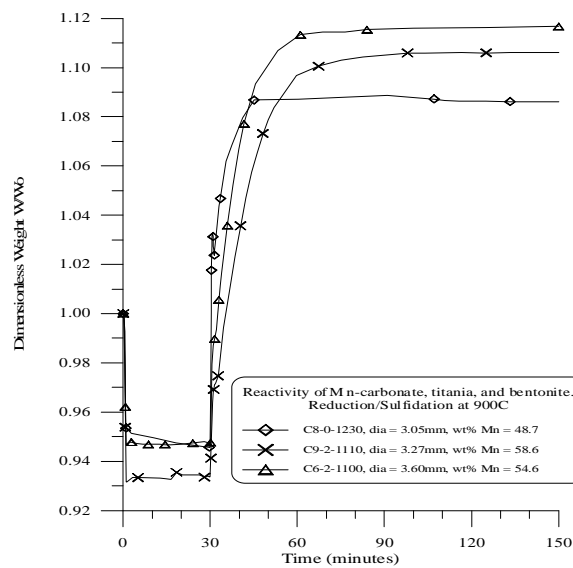

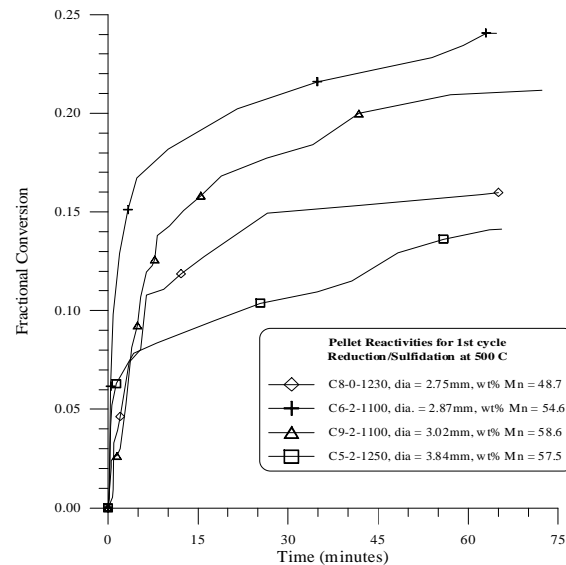**Figure 7.** $MnCO_3$/TiO_2 reactivity evolution.

Figure 8. Mn-based formulation reactivity at 500°C.

All Mn-Ti formulations react rapidly initially at 500$^{\text{O}}$C, with C6-2-1100 obtaining the highest fractional conversion. Formulation C9-2, which has a higher Mn:Ti molar ratio than C6-2-1100, did not produce greater sulfidation kinetics or sulfur capacity.

With bentonite as a bonding agent, it is believed that higher Mn:Ti ratios greater than 7:1 produced less reactive pellets. This may be explained by porosimetry data which suggest C6-2-1100 has higher surface area than C9-2-1110. All rates on the $MnCO_3$-TiO_2 formulations decrease rapidly between 12-20% conversion. This kinetic deceleration may be due to plugging of the pellet pores with sulfur creating inaccessible pore volume or a large increase in diffusional resistance from MnO to MnS.

Sintering during the first reduction and sulfidation cycle is believed to be negligible. Further testing of C6-2-1100 was conducted to determine the strong dependence of preparation temperature on strength and sulfidation fractional conversion, given in Figure 9.The effect of pellet diameter on sulfidation kinetics as is shown in Figure 10. suggests intra-particle rate limitation. The effect of temperature is given in Figure 11. for C6-2-1100.
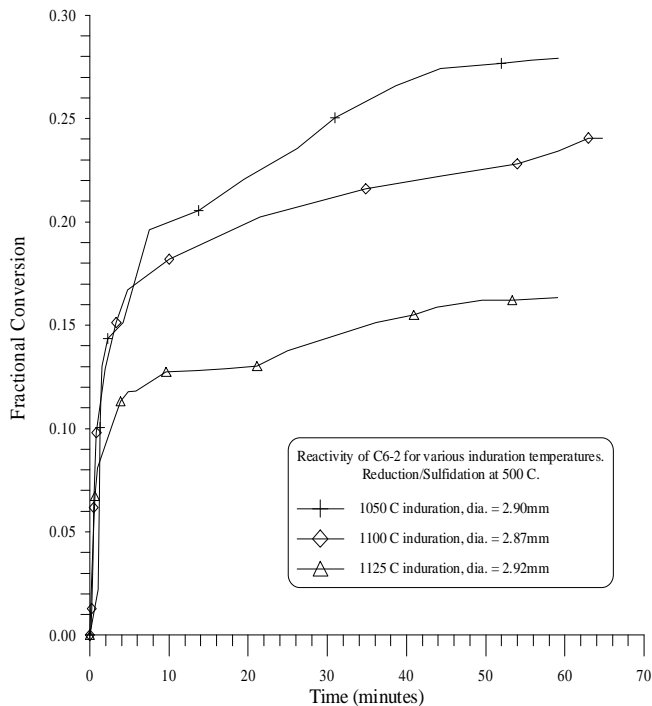

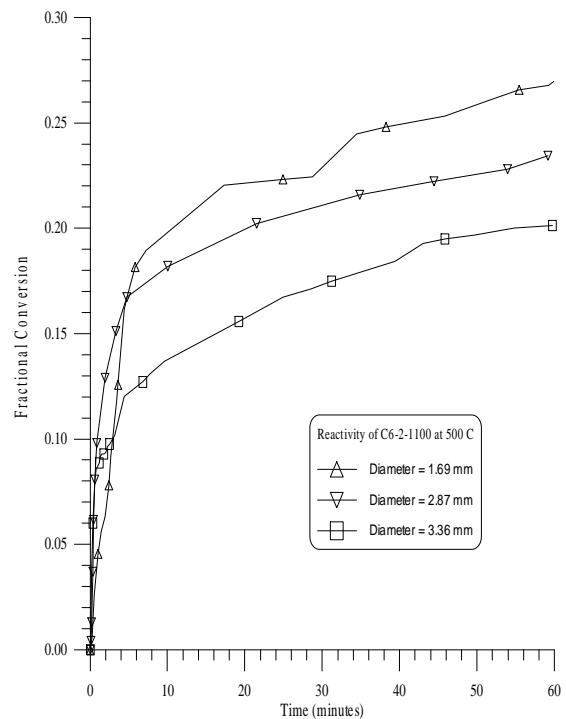**Figure 9.** Effect of preparation temperature on reactivity for C6-2-1100.

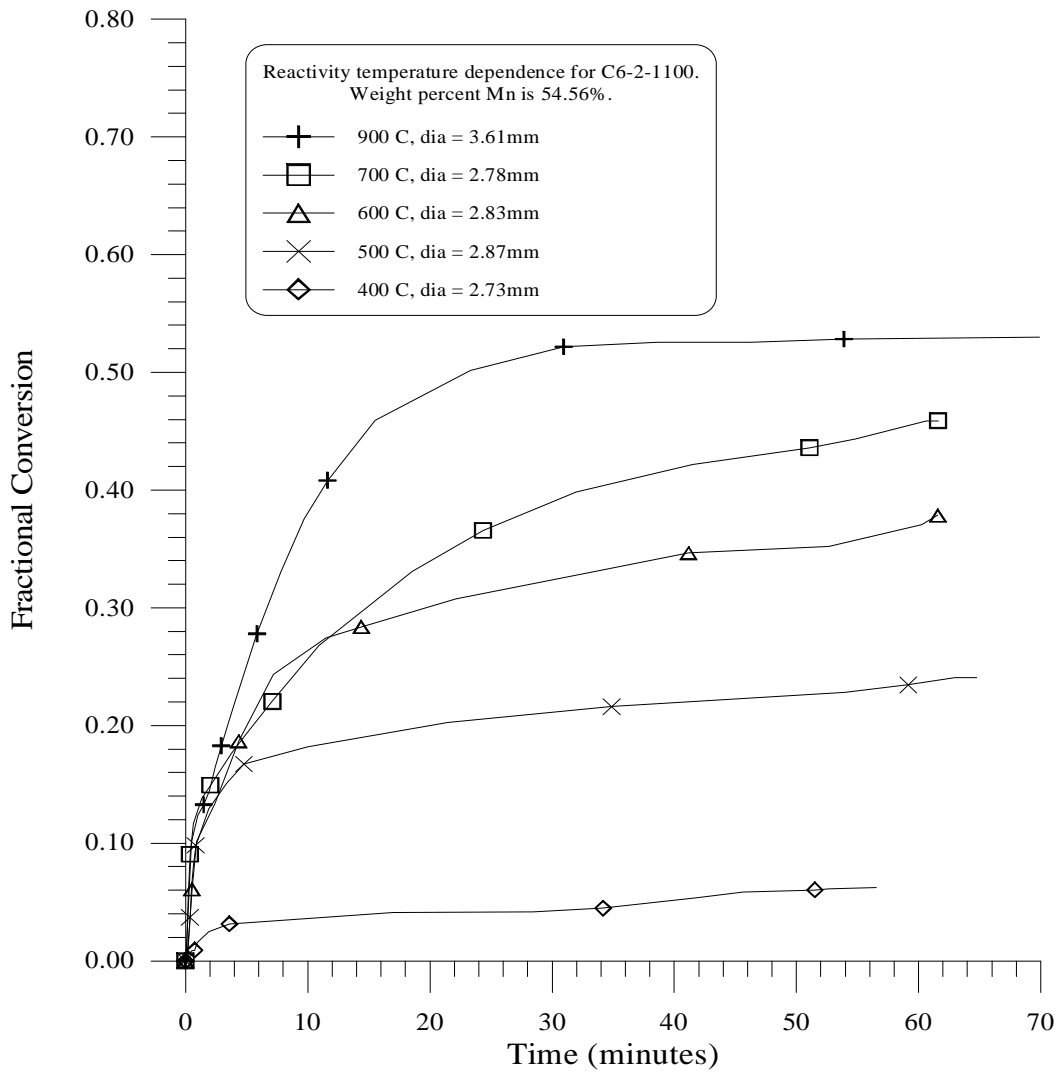**Figure 10.** Effect of pellet diameter on reactivity for C6-2-1100.

Figure 11. Effect of sulfidation temperature on reactivity for C6-2-1100.

Formulation C9-2-1110 was eliminated from regeneration testing while C8-0-1230 was included. Both $MnCO_3$-TiO_2 sorbents are completed regenerated as shown in Figures 12, and 13 for formulations C6-2-1100, and C8-0-1230, respectively.

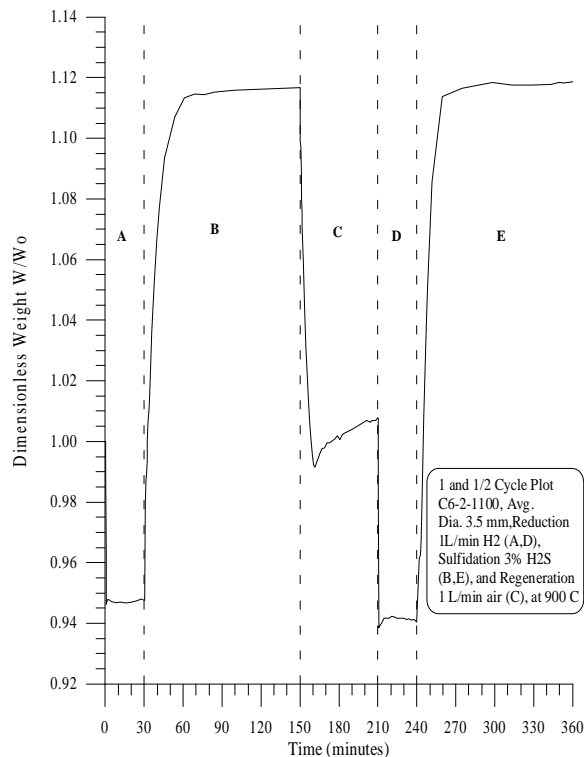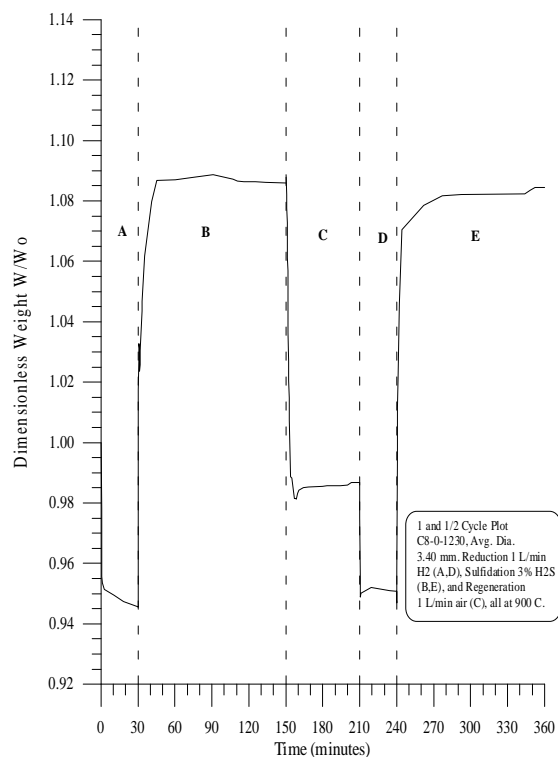**Figure 12.** 1 and 1/2 cycle plot for C6-2-1100.
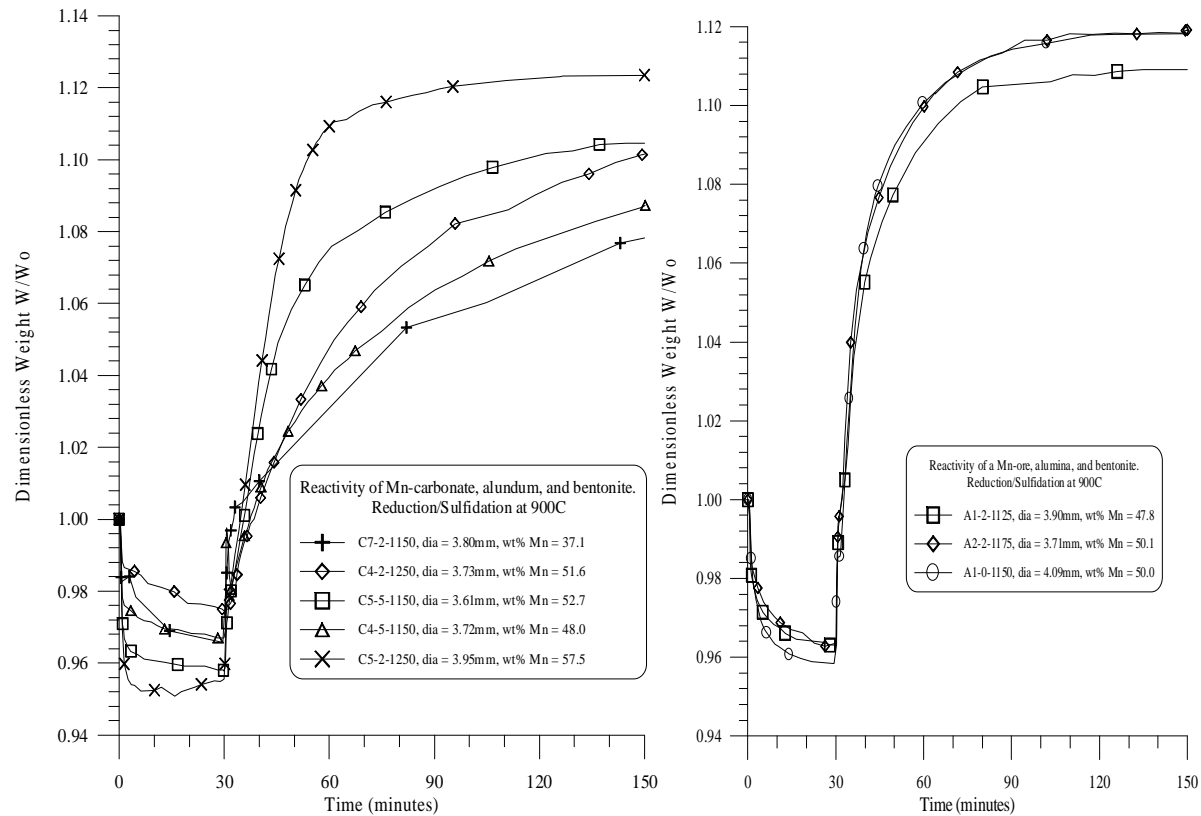
Figure 13. 1 and 1/2 cycle plot for C8-0-1230.

$MnCO_3$-Al_2O_3 Formulations

The $MnCO_3$-Al_2O_3 group contains the majority of formulations investigated to date. As the weight percentage of bentonite is increased, the required induration temperature for a given strength criteria is markedly decreased. To reduce the induration temperature, formulations high in Al_2O_3 and bentonite were produced. This proved unsuccessful as presumably the bentonite reduces capacity and $MnO.Al_2O_3$ equilibrium with H_2S in unfavorable. Reduction/sulfidation tests for $MnCO_3$-Al_2O_3 formulations is presented in Figure 14.

MnO_2 ore-Al_2O_3 Formulations

The required induration temperature for these formulations is generally much less than for $MnCO_3$-Al_2O_3 formulations as the gangue constituents (primarily silicates) have a relatively low sintering temperature. The reactivities for all ore-based pellets is given in Figure 15.

Formulations A2-2-1175 and A1-0-1150 have identical weight fractions of Mn; yet, A2-2-1175 has 2% bentonite and relatively less alundum then A1-0-1150. Interestingly, their reduction and sulfidation curves look qualitatively identical at 900°C. The exception is that A1-0-1150 reduces more completely as expected from lack of bentonite. Use of bentonite is probably a poor method of increasing strength since it diminishes absorption capacity and rate.

Left chart

Y-axis: Dimensionless Weight W/W_o
Y-axis values: 1.14, 1.12, 1.10, 1.08, 1.06, 1.04, 1.02, 1.00, 0.98, 0.96, 0.94
X-axis: Time (minutes): 0, 30, 60, 90, 120, 150

Reactivity of Mn-carbonate, alundum, and bentonite.
Reduction/Sulfidation at 900C

+ C7-2-1150, dia = 3.80mm, wt% Mn = 37.1
◇ C4-2-1250, dia = 3.73mm, wt% Mn = 51.6
□ C5-5-1150, dia = 3.61mm, wt% Mn = 52.7
△ C4-5-1150, dia = 3.72mm, wt% Mn = 48.0
✕ C5-2-1250, dia = 3.95mm, wt% Mn = 57.5

Right chart

Y-axis: Dimensionless Weight W/W_o
Y-axis values: 1.12, 1.10, 1.08, 1.06, 1.04, 1.02, 1.00, 0.98, 0.96, 0.94
X-axis: Time (minutes): 0, 30, 60, 90, 120, 150

Reactivity of a Mn-ore, alumina, and bentonite.
Reduction/Sulfidation at 900C

□ A1-2-1125, dia = 3.90mm, wt% Mn = 47.8
◇ A2-2-1175, dia = 3.71mm, wt% Mn = 50.1
○ A1-0-1150, dia = 4.09mm, wt% Mn = 50.0

Conclusions

• Pellet strength is primarily determined by induration temperature. All formulations made to date have met the crush strength required. The sensitivity of this parameter requires further optimization.

• Preliminary work appears to indicate titania is a superior substrate than alumina probably because the manganese/titania bond is chemically weaker than the manganese/alumina bond. This means the manganese which is tied up in forming a spinel has a higher activity in the titania form than the alumina form and is more effective in reacting with sulfur.
• Bentonite addition increases the strength of the pellet, however; it reduces the pellet absorption capacity for a given induration condition. Furthermore, it seems as bentonite addition can be avoided by increasing the substrate fraction.

• Current pellet formulations are limited by intra-particle transport resistances. Pore structure design and characterization are to be the direction of additional research through higher substrate fractions and with no bentonite addition.

Future Activities

The last year of this three year program will be devoted to optimizing the most favorable formulations which have been developed with respect to increasing the rate of loading and reducing the loading and the regeneration temperatures.

Acknowledgement