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Kinetics of Mn-based Sorbents for Hot Coal Gas Desulfurization

Quarterly Report for the period of December 15, 1995 to March 15, 1996.
Task 2: Exploratory Experimental Studies: Single Pellet Tests; Rate Mechanism Analysis.

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1. INTRODUCTION

Currently, the Morgantown Energy Technology Center, Department of Energy (DOE/METC) is actively investigating alternative hot fuel gas desulfurization sorbents for application to the Integrated Gasification Combined Cycle (IGCC)[1]. Despite over 20 years of development[2-4], sorbent goals remain ambitious and no single sorbent is available commercially. Simply stated, a sorbent must be highly active towards sulfur at high temperatures and pressures, and under varying degrees of reducing atmospheres. Thus, high conversion of the metal oxide and low hydrogen sulfide exit partial pressures. 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. This cyclic process requires a holistic approach as any one criteria may eliminate a candidate sorbent from further consideration.

In response to stability difficulties of single and binary metal oxide sorbents, increasing effort is being directed towards incorporation of an inert component into sorbent formulation as witnessed by the various Zn-titanates[5-9]. Primarily, the inert component increases 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[9,10]. 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[9-11].

2. METHODS AND MATERIALS

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,
- and 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). This is represented in Figure 1. 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. All chemical compositions, vender information, and particle sizes have been reported previously[12-15].

Preparation

Preparation of the Mn-based sorbents is described in detail elsewhere[16]. Basically, feed powders were hand mixed and pelletized in a balling wheel forming "green" pellets. Green pellets were air dried for 1 day than dried to a constant weight at 100 °C. Dry pellets were calcined for four hours at 350°C. Immediately after calcination, pellets were placed in a high-temperature furnace (preheated to 500°C), 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). Initially, the indurated pellet size was set between 1-6 mm; however, it was later limited to the range of 1-3 mm.

Designations

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).

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 (TGA)[12] to determine reaction evolution and fractional conversion. The test conditions for reduction/sulfidation are reported in Table 1.

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Sample mass	200-800 mg
Reduction duration: $T > 550$ °C $T < 550$ °C	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.

Sample mass	200-800 mg
Regeneration Temperature	900 °C
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.

Each TGA test sample consisted of three pellets. The sulfided pellets were also regenerated in the TGA. Regeneration conditions are described in Table 2. 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 sulfur capacities' (based upon initial formulation and chemical analysis) are listed in Table 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

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.

Concentrations and breakthrough times will be measured. Also, regeneration SO_2 concentrations and breakthrough times will be measured. The reactor is of a new construction design (over that previously reported) and employs a 1" inner diameter tube and bed outlet thermocouple. It is shown in Figure 3. Characterization of fixed-bed pellets will include crush strength, sulfur analysis, porosimetry, and scanning electron microscopy.

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 2.

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 as exhibited in Figure 1. Sorbent formulations were than prepared as previously described.

A lower limit of 1100 °C was placed on sorbent induration temperature to preclude sintering during regeneration which is currently set at 900 °C. An induration upper limit of 1300 °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; alternatively, 1 lb / pellet for 1 mm pellets and 9 lb / pellet for 3 mm pellets. 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 is the kinetic screening of sulfidation and regeneration. The simple requirement was that the sorbent obtain a higher fractional conversion of Mn during a standardized TGA reduction/sulfidation test than C5-2 as described in Table 1. Sulfidation screening was primarily conducted at 500 °C. Sorbents showing sufficient sulfur absorption were regenerated according to the conditions in Table 2. Finally, the superior performing sorbents are to be tested in the fixed-bed reactor to determine their effectiveness when subject to recycle testing.

3. 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. The method of candidate sorbent screening is given in Figure 2. Subsequently described are the 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. Figure 4. describes the strength of the formulations using titania as substrate. The relatively large discrepancies in theoretical and actual sulfur capacities for the $MnCO_3$-TiO_2 formulations (see Table 3. formulations C6-2, C8-0, and C9-2) is an artifact of pelletization of titania mixtures as the titania preferential adheres to the balling tire leaving less titania in the "green" pellet. Thus, formulations with titania are actually higher in capacity than designed. As relatively few $MnCO_3$-TiO_2 formulations have been prepared it is difficult to draw definite conclusions regarding molar ratio of Mn to Ti. However, it is believed that the larger the Mn:Ti molar ratio (for a constant weight percent of bentonite), the higher the induration temperature required for necessary strength. Formulation C6-2 didn't require an induration temperature of 1100 °C to obtain the required strength, yet; an 1100 °C was used for due to the lower limit of 1100 °C for induration. In an effort to eliminate bentonite as a boding agent, a formulation (C8-0) with a low Mn:Ti molar ratio (2:1) was prepared. While C8-0 required a much higher induration temperature than the other titania formulations, it did achieve the requisite strength. Limited porosimetry analysis for unreacted pellets is given in Figure 7., and listed 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.

As can be seen from the TGA sulfidation tests in Figure 8., all Mn-Ti formulations react rapidly initially at 500 °C, with C6-2-1100 obtained 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 $MnCO_3$-TiO_2 absorption rates rapidly decrease 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 sulfidation cycle is believed to be negligible. Further testing of C6-2-1100 was conducted to determine the effect of pellet diameter on sulfidation kinetics (Figure 9.) which further suggests an intra-particle rate limitation. Also, the strong dependence of preparation temperature on strength and sulfidation fractional conversion is given in Figure 10. Formulation C9-2-1110 was eliminated from regeneration testing while C8-0-1230 was included. Both $MnCO_3$-TiO_2 sorbents are compared in Figure 11., and were completed regenerated as shown in Figures 12, and 13 for formulations C6-2-1100, and C8-0-1230, respectively.

$MnCO_3$-Al_2O_3 Formulations

The $MnCO_3$-Al_2O_3 group contains the majority of formulations investigated to date. Crush strength versus induration temperature is plotted in Figure 5. It can be seen that as the weight percentage of bentonite is increased, the required induration temperature for a given strength criteria is markedly decreased. This is isolated by comparing C5-5-1150 and C5-2-1250 which differ by only weight percent bentonite added, yet the difference in required induration temperature is approximately 100 °C. 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. Experimentation with porosity modifiers added to $MnCO_3$-Al_2O_3 formulations has been discontinued as the sensitivity of pore structure towards induration has not been fully explored.

MnO_2 ore-Al_2O_3 Formulations

The strength tests for the MnO_2 ore-Al_2O_3 formulations are summarized in Figure 6. 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. Therefore, bentonite may be an inadequate method of increasing strength as the cost of absorption capacity controls.

4. 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 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.

It is becoming increasingly clear that, current pellet formulations are limited by intra-particle transport resistances. As such, pore structure design and characterization are to be the direction of additional research through higher substrate fractions and no bentonite addition.

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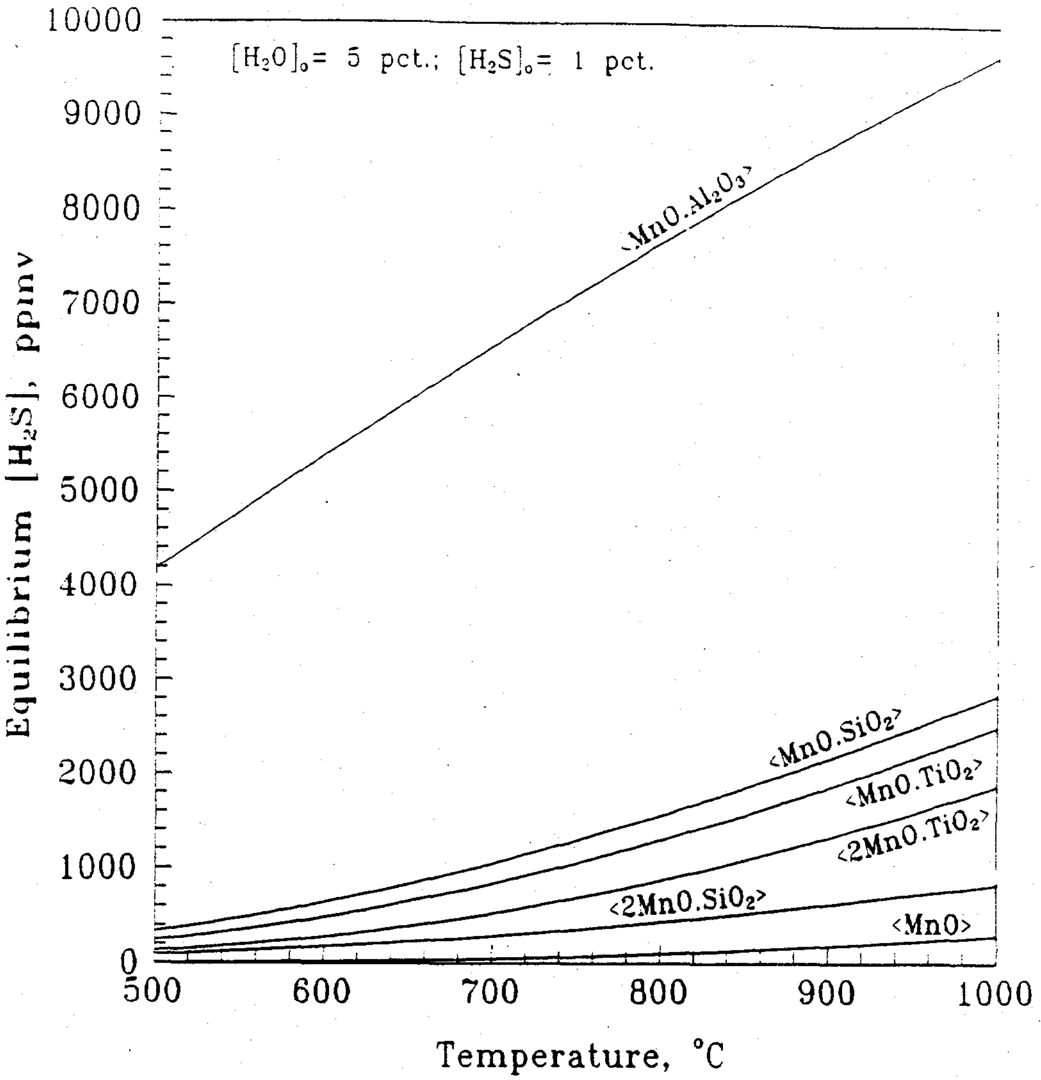

Figure 1. H_2S equilibrium concentrations for various MnO.Me_xO_y sorbents.

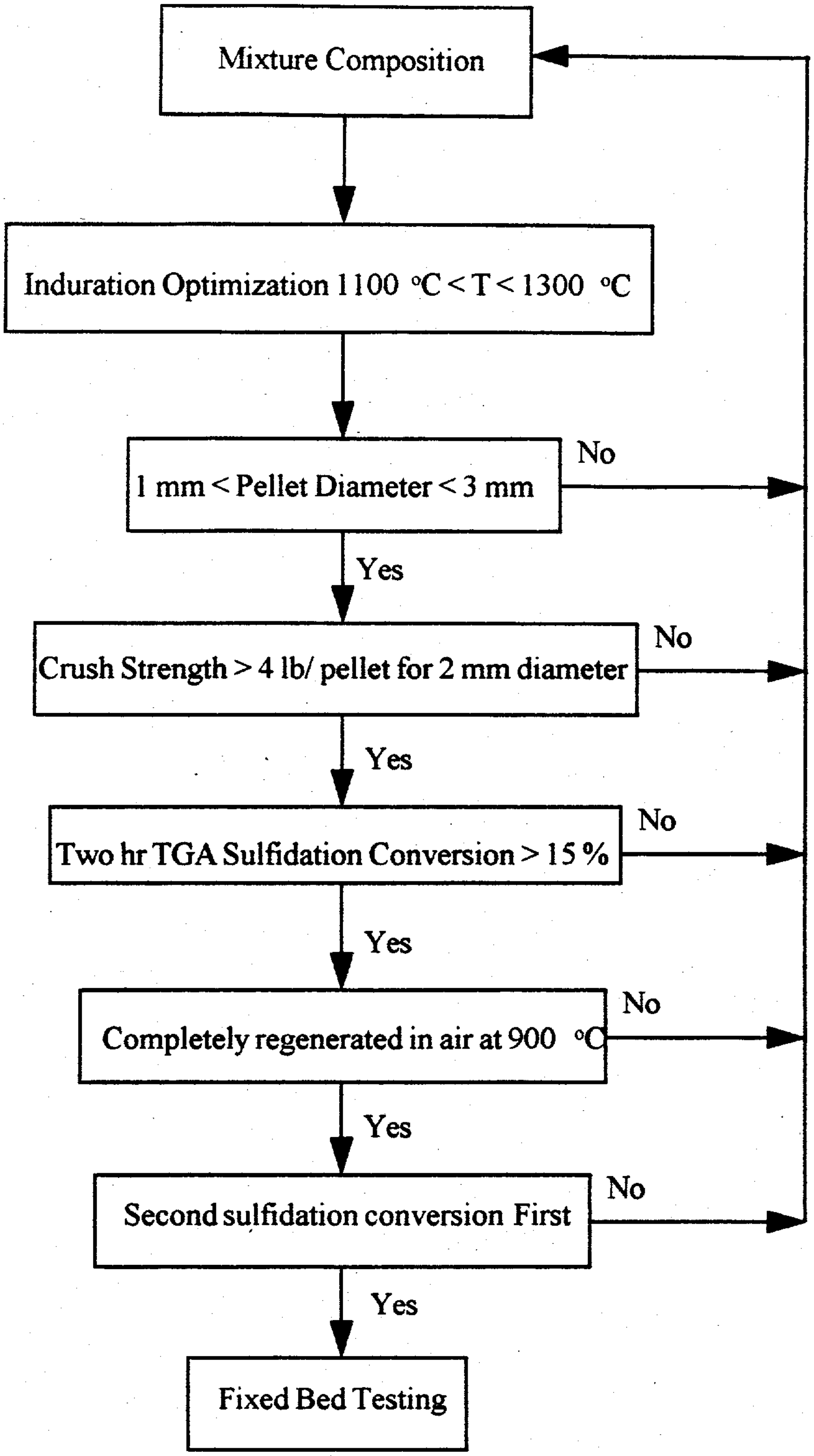

Figure 2. Screening Procedure for potential Mn-based desulfurization sorbents.

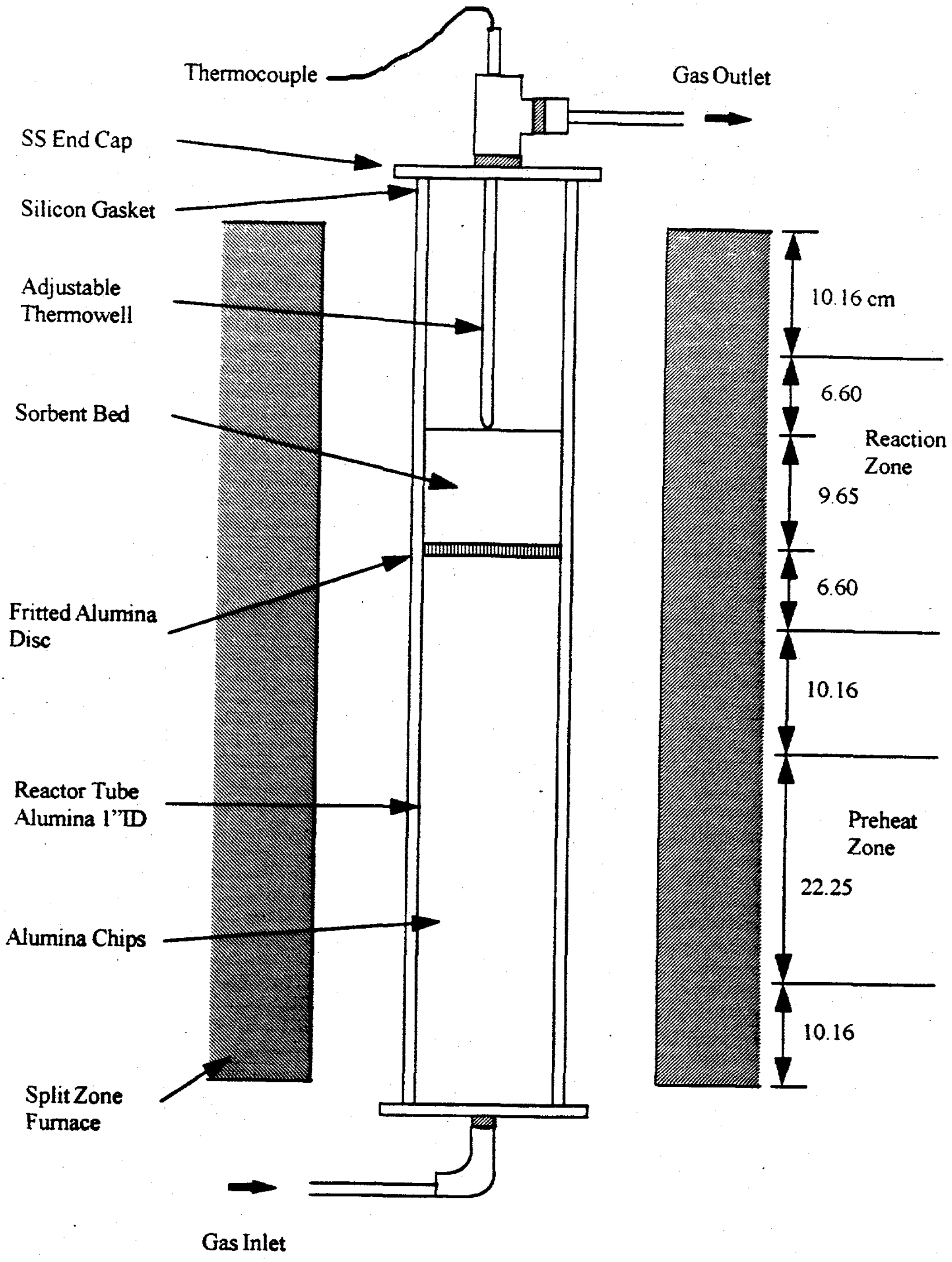

Figure 3. Detail of Desulfurization Reactor

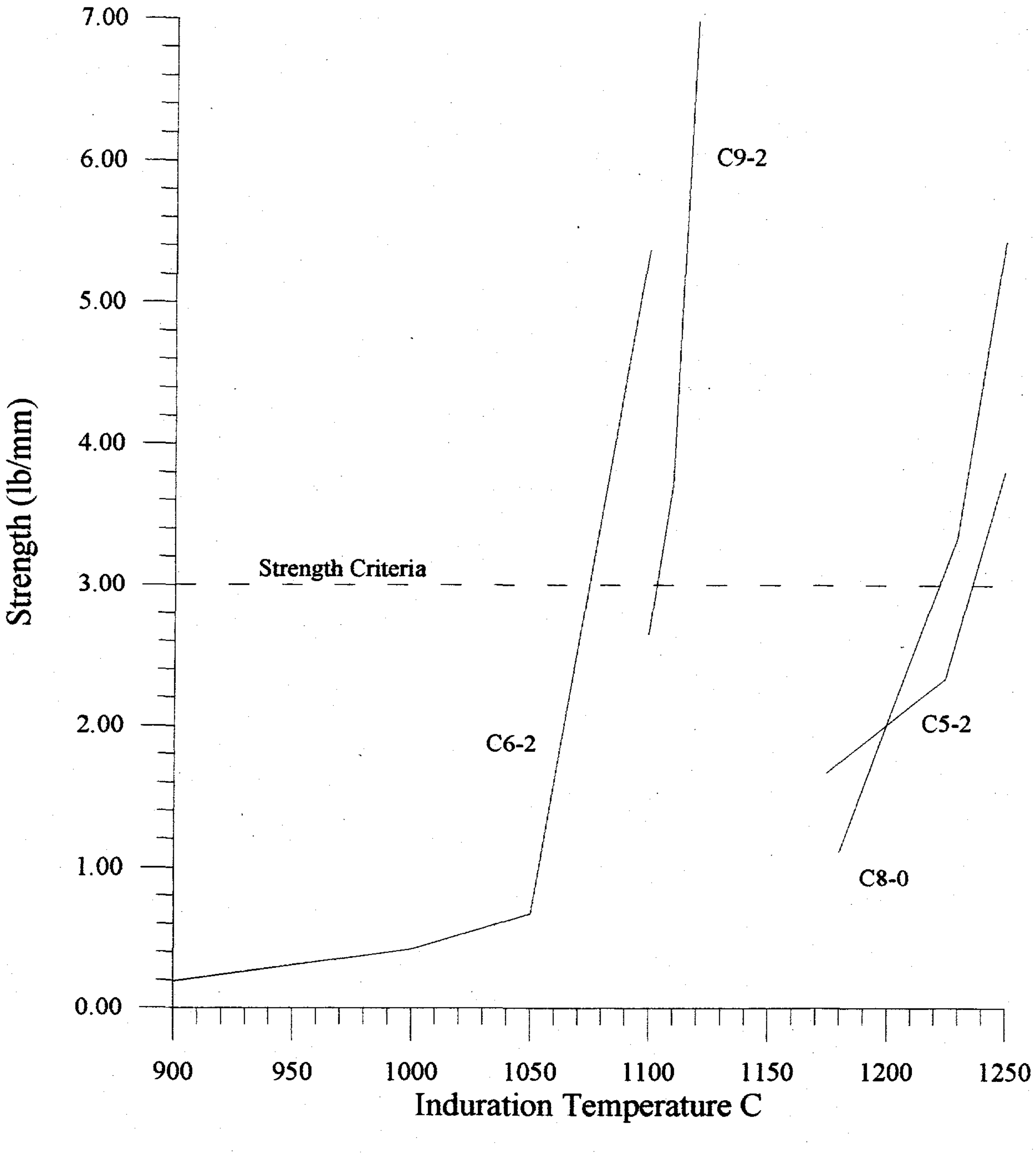

Figure 4. Crush strength results for $MnCO_3$-TiO_2 formulations.

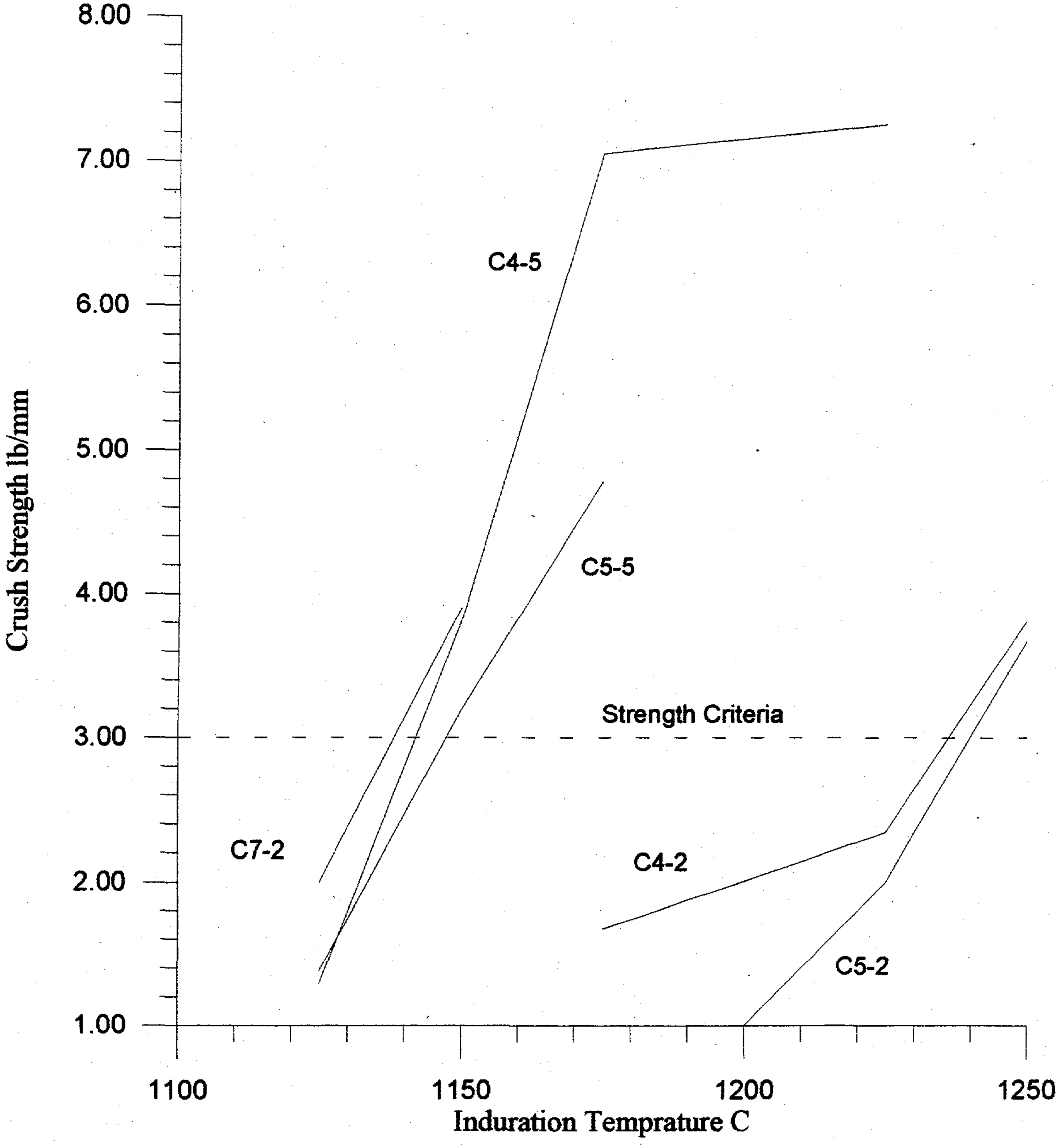

Figure 5. Crush Test results for $MnCO_3$ -Al_2O_3 formulations.

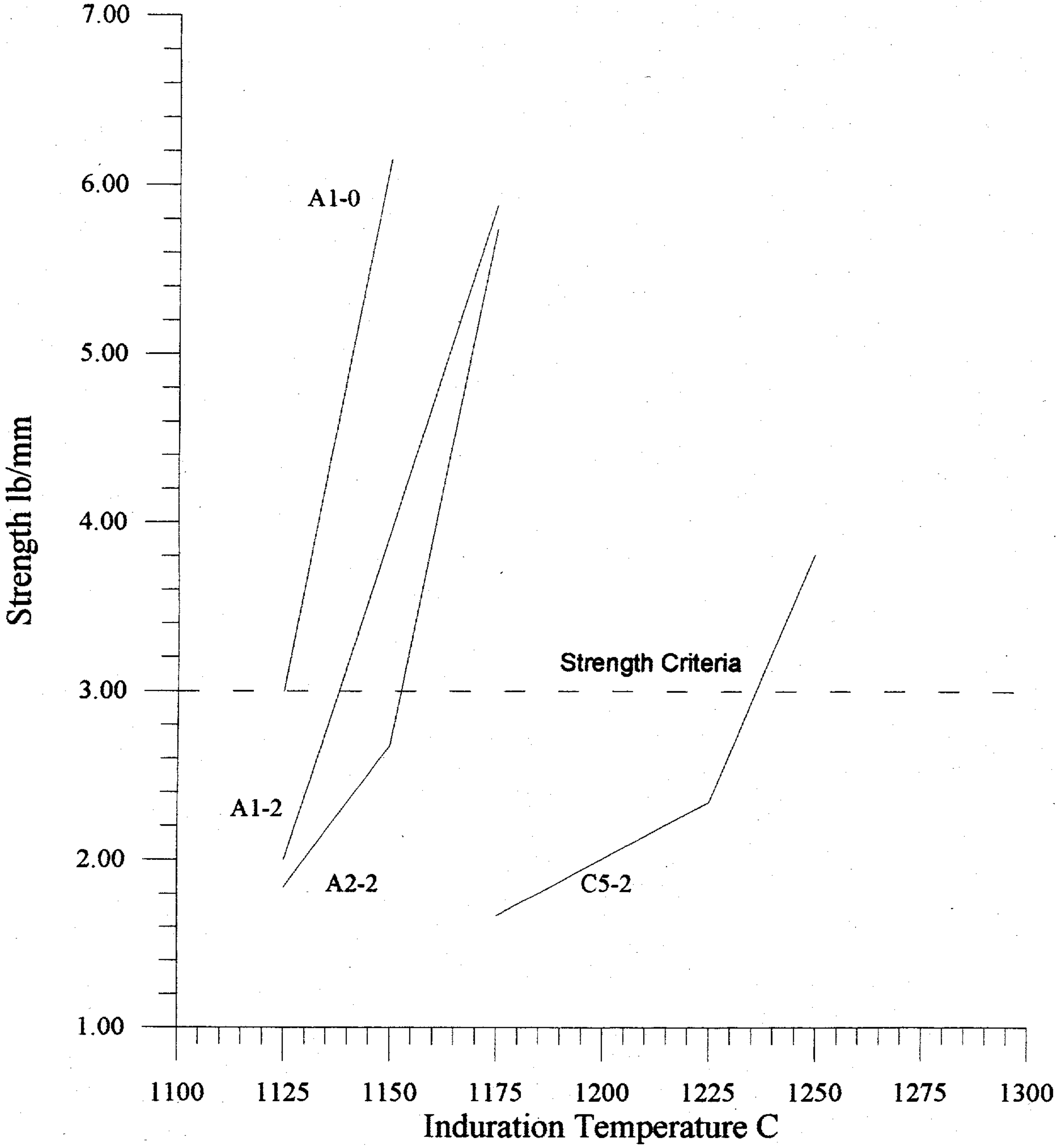

Figure 6. Crush Test results for MnO_2 Ore-Al_2O_3 formulations.

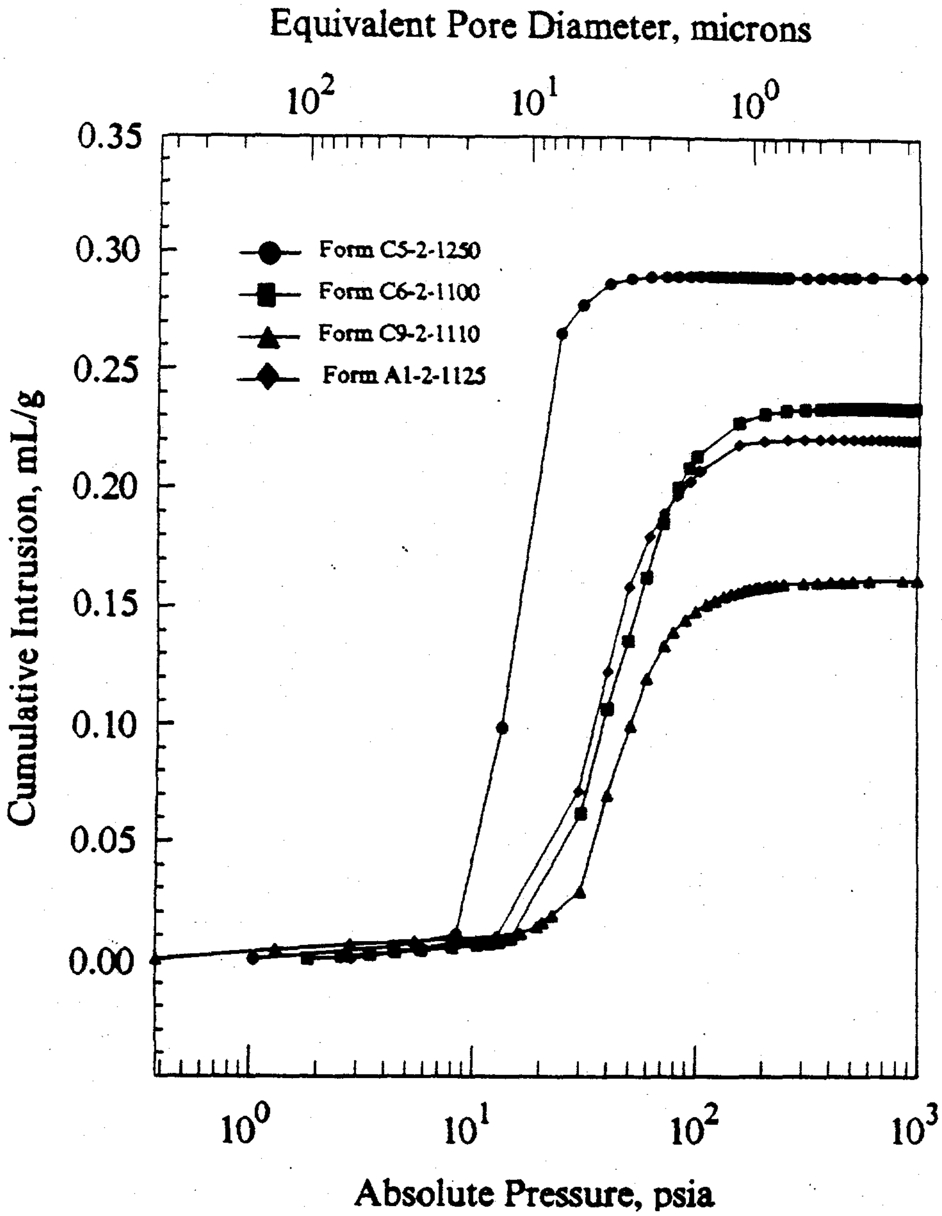

Figure 7. Mercury porsimetry results of selected unreacted pellet formulations.

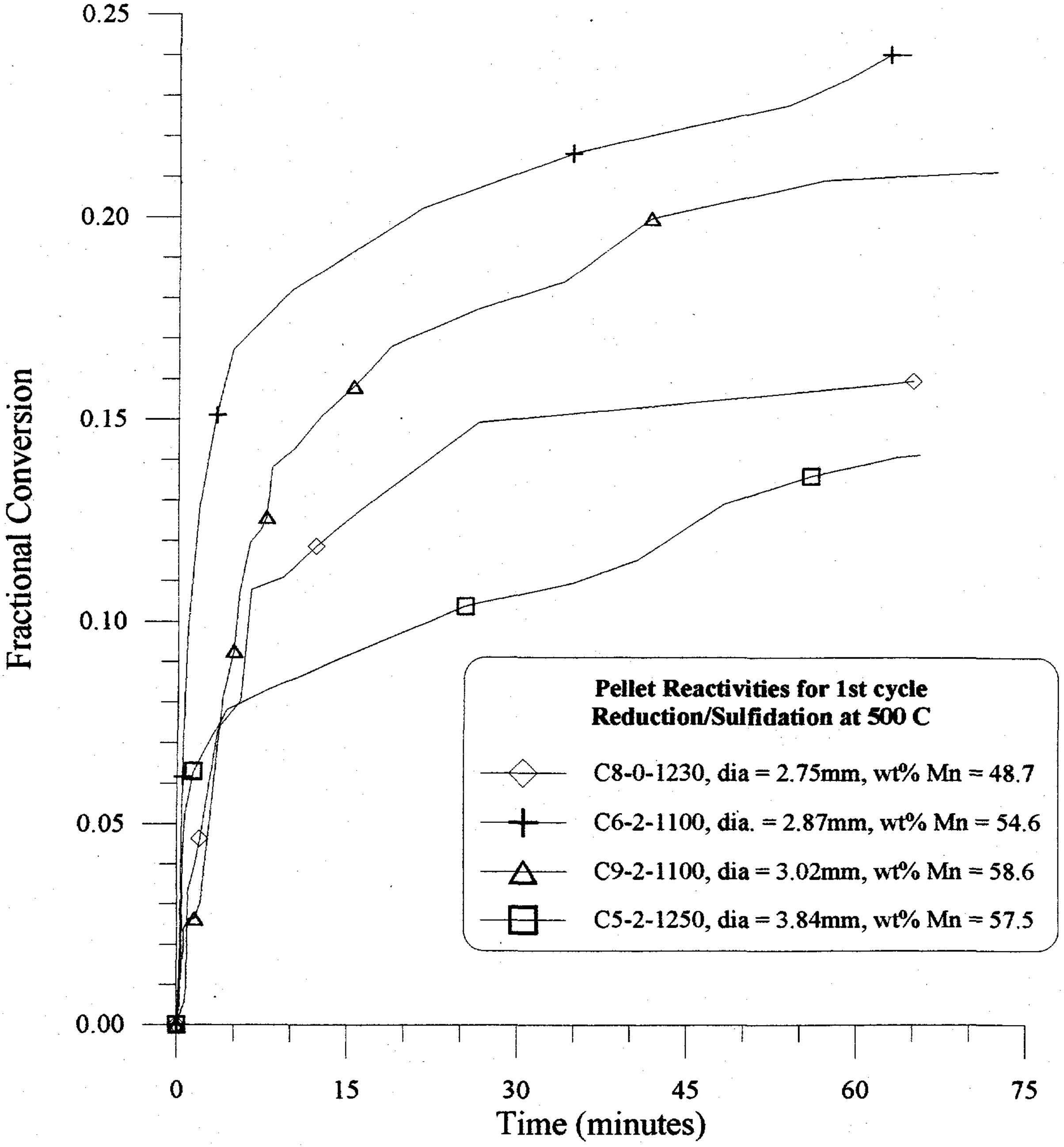

Figure 8. First cycle sulfidation conversions for $MnCO_3$ -TiO_2 pellets at 500 ^oC.

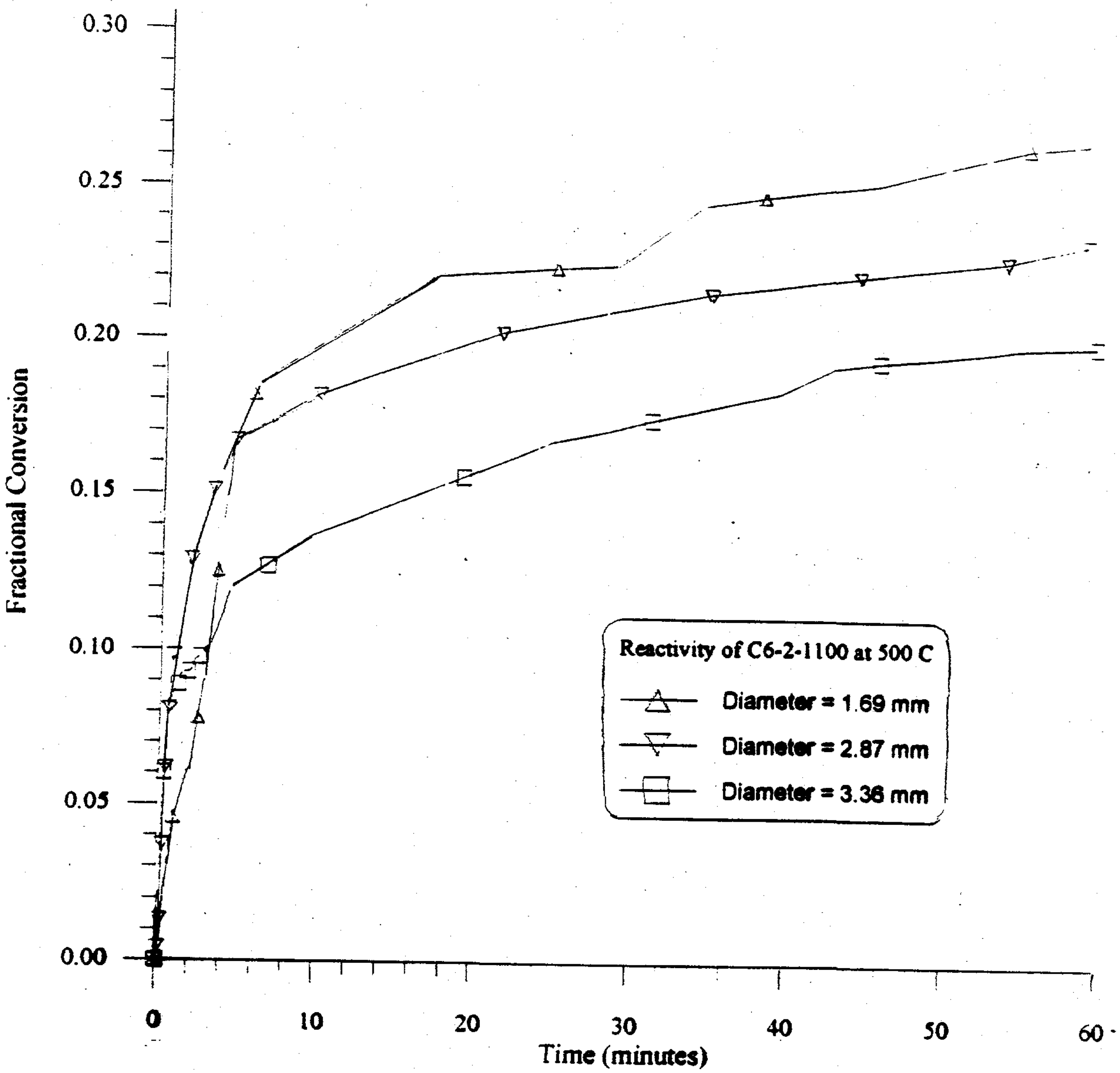

Figure 9. First cycle sulfidation reactivities of C6-2-1100 at 500 °C for various pellet diameters.

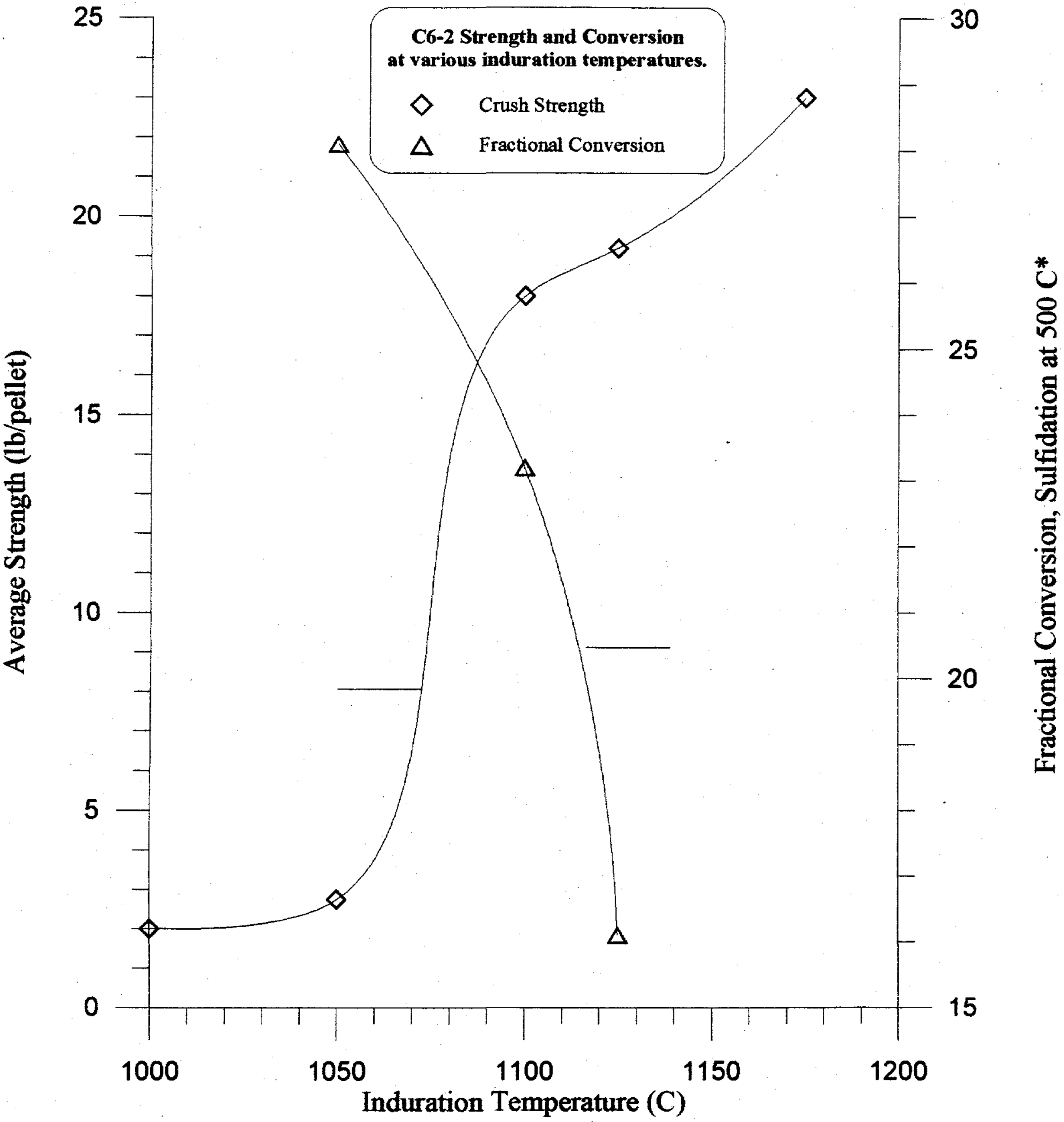

Figure 10. Strength and first cycle conversion for C6-2 as a function of preparation temperature. *TGA standard test given in Table 1. at 500 ^{o}C

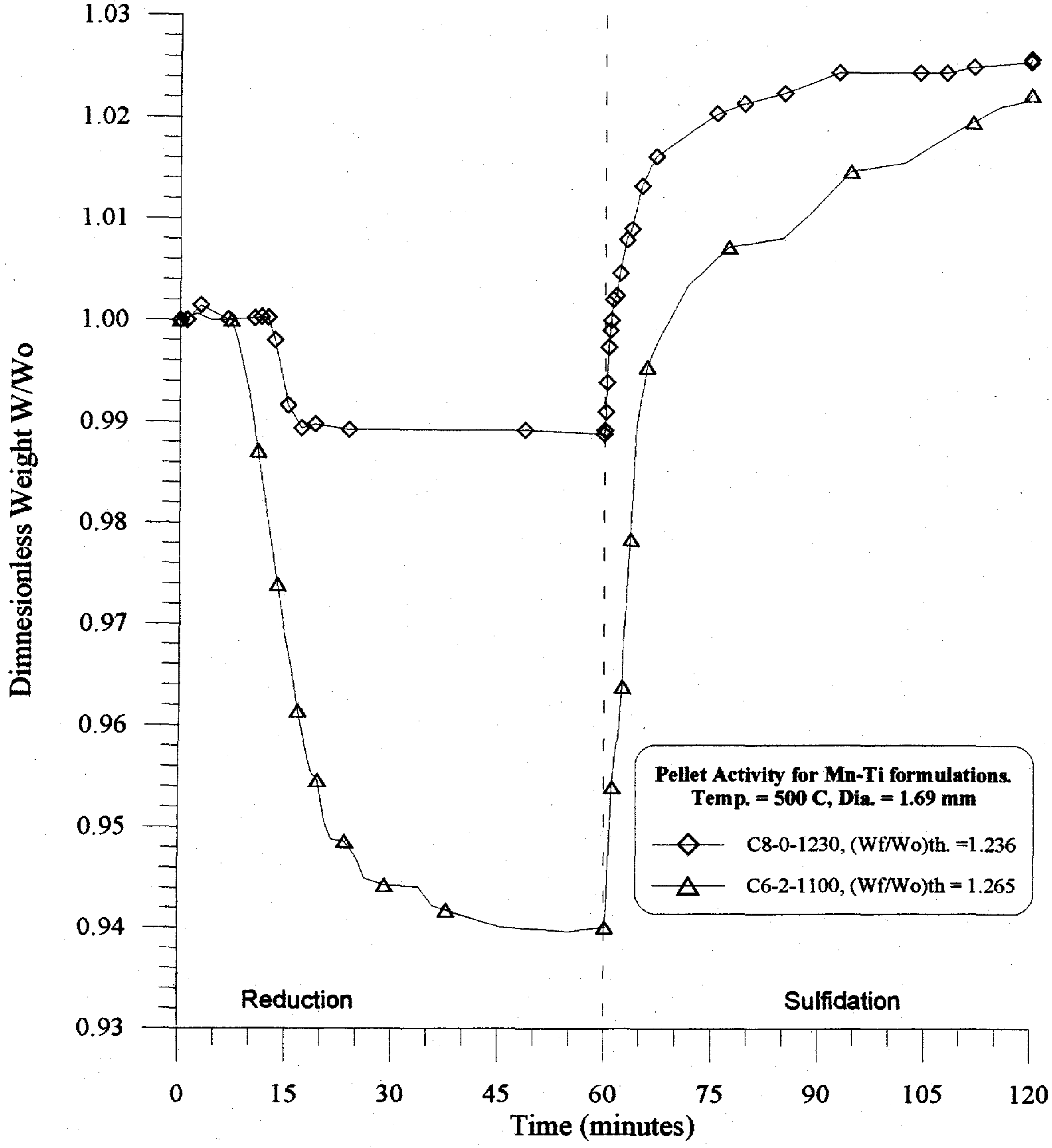

Figure 11. Comparison of C6-2-1100 and C8-0-1230 reduction/sulfidation for 1.69 mm pellets.

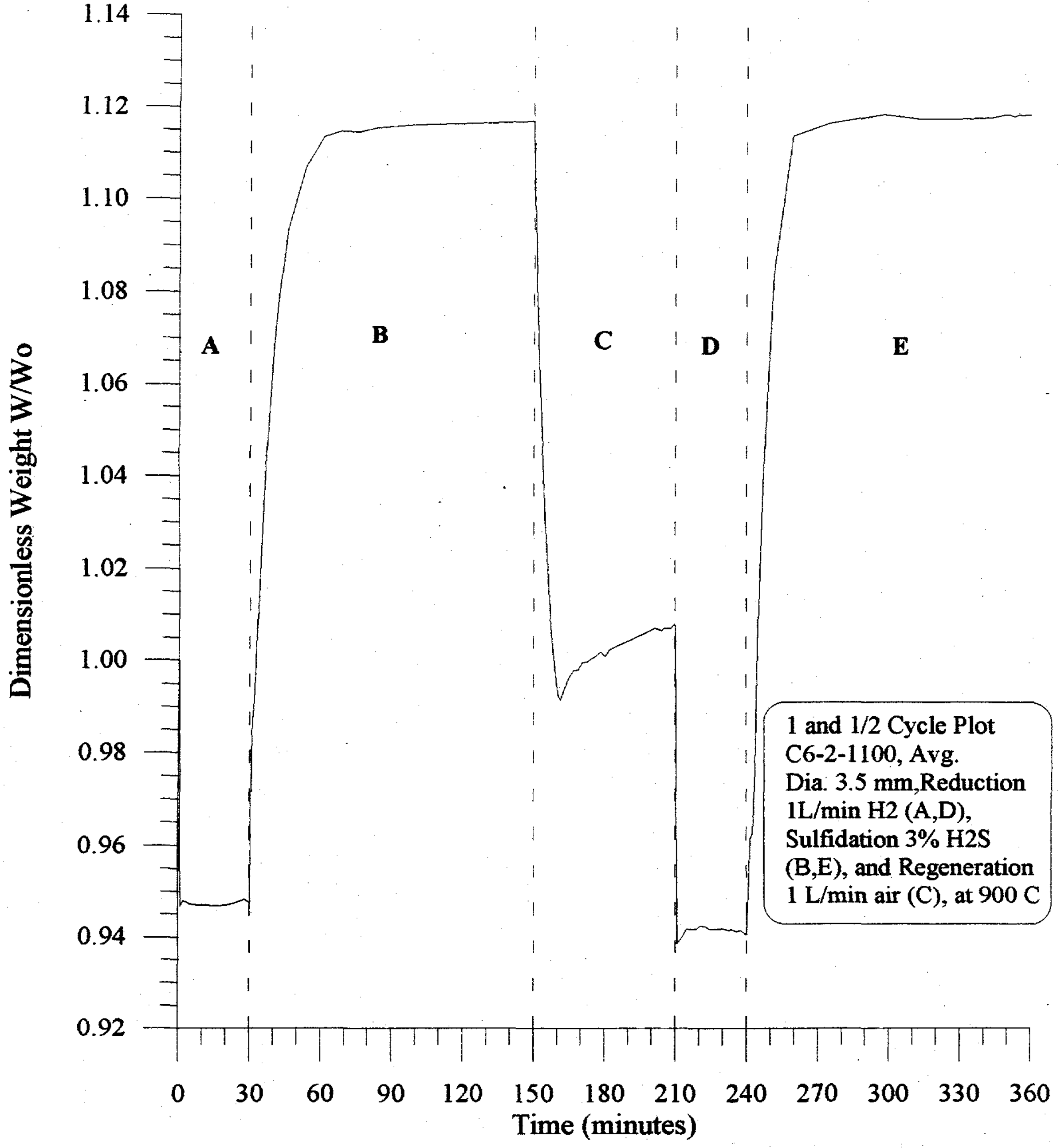

Figure 12. 1 and 1/2 cycle plot for C6-2-1100 at 900 °C.

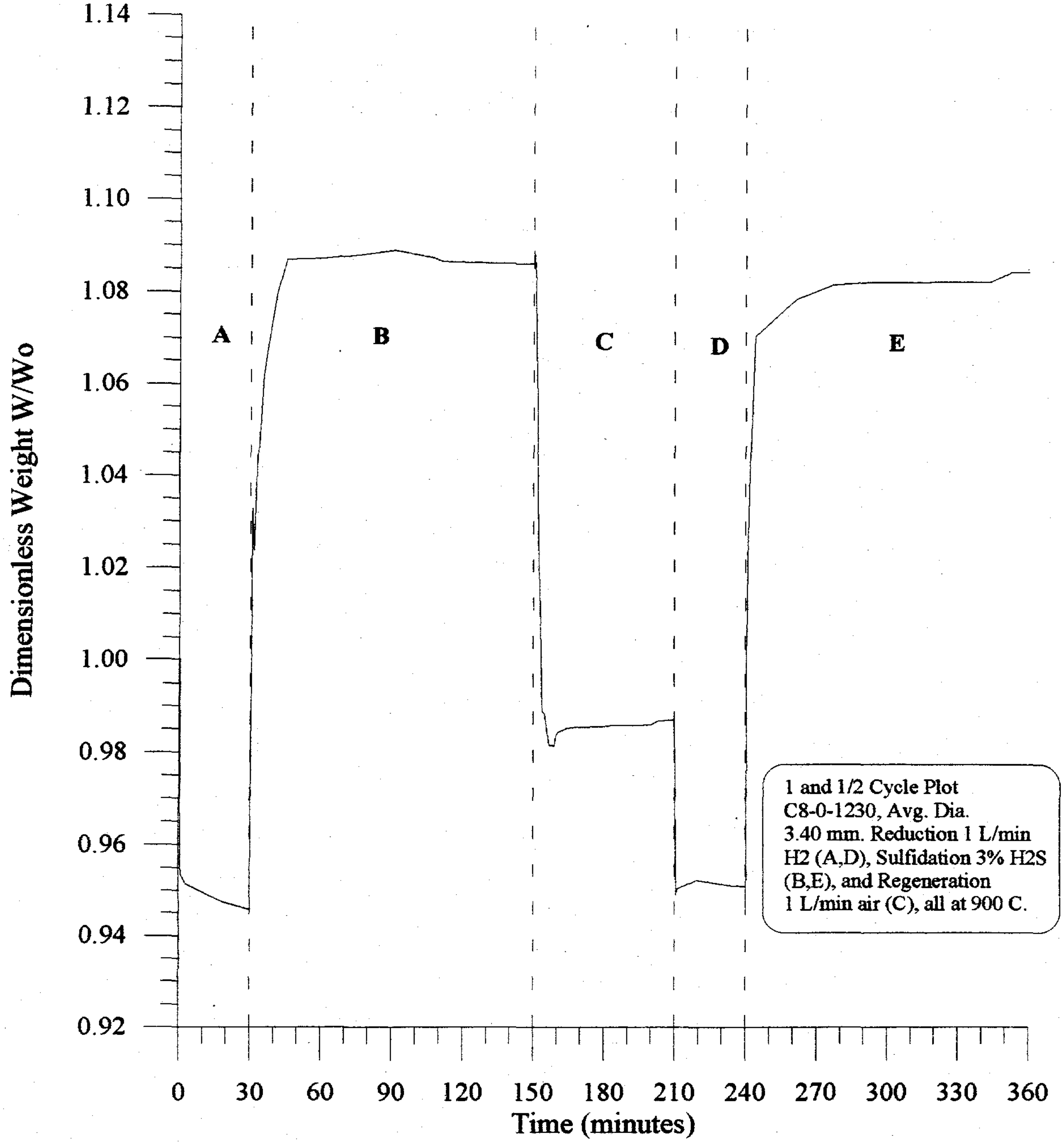

Figure 13. 1 and 1/2 cycle plot for C8-0-1230 at 900 ^{o}C.

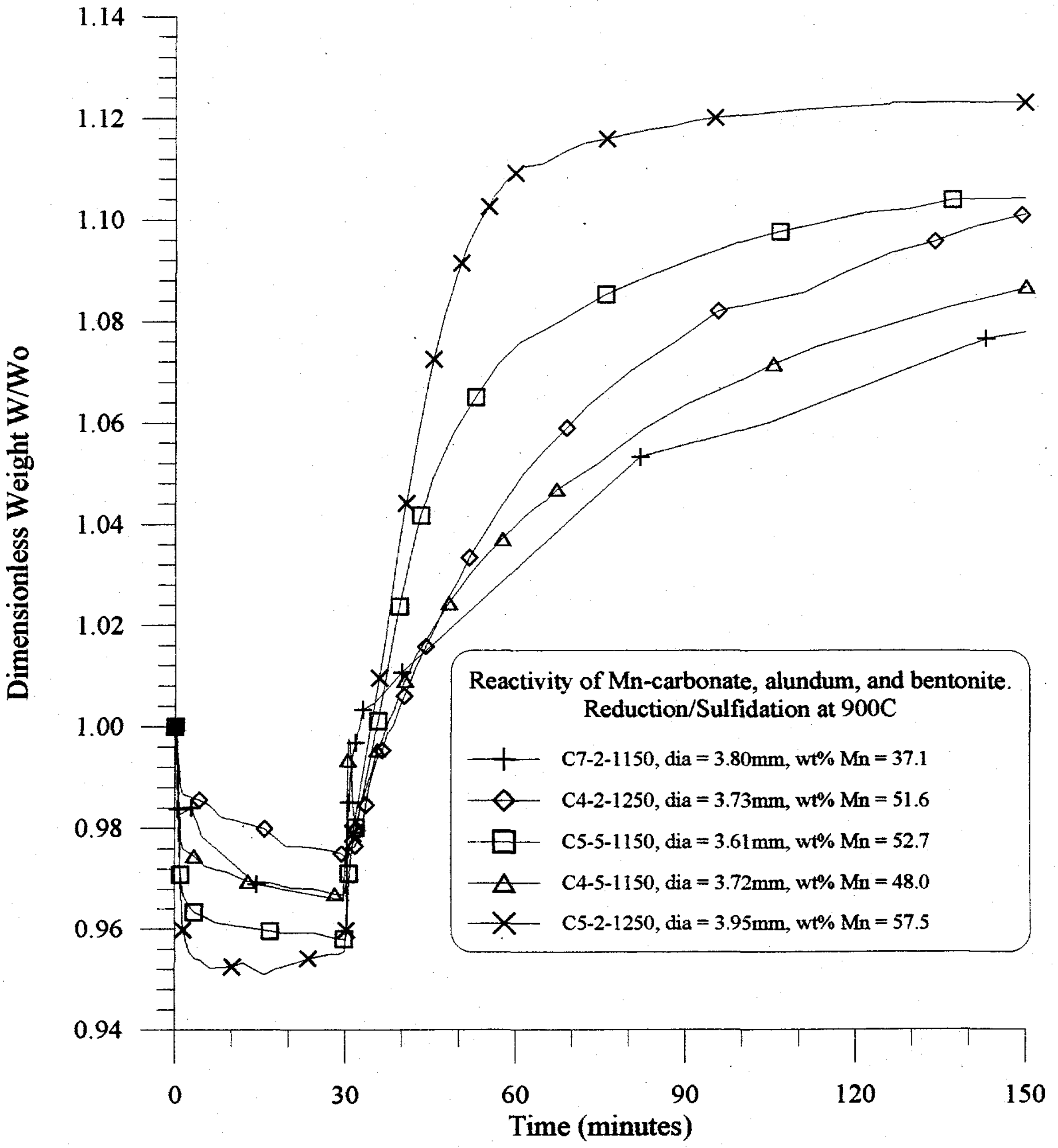

Figure 14. Comparison of first reduction/sulfidation of $MnCO_3$-Al_2O_3 formulations at 900 °C.

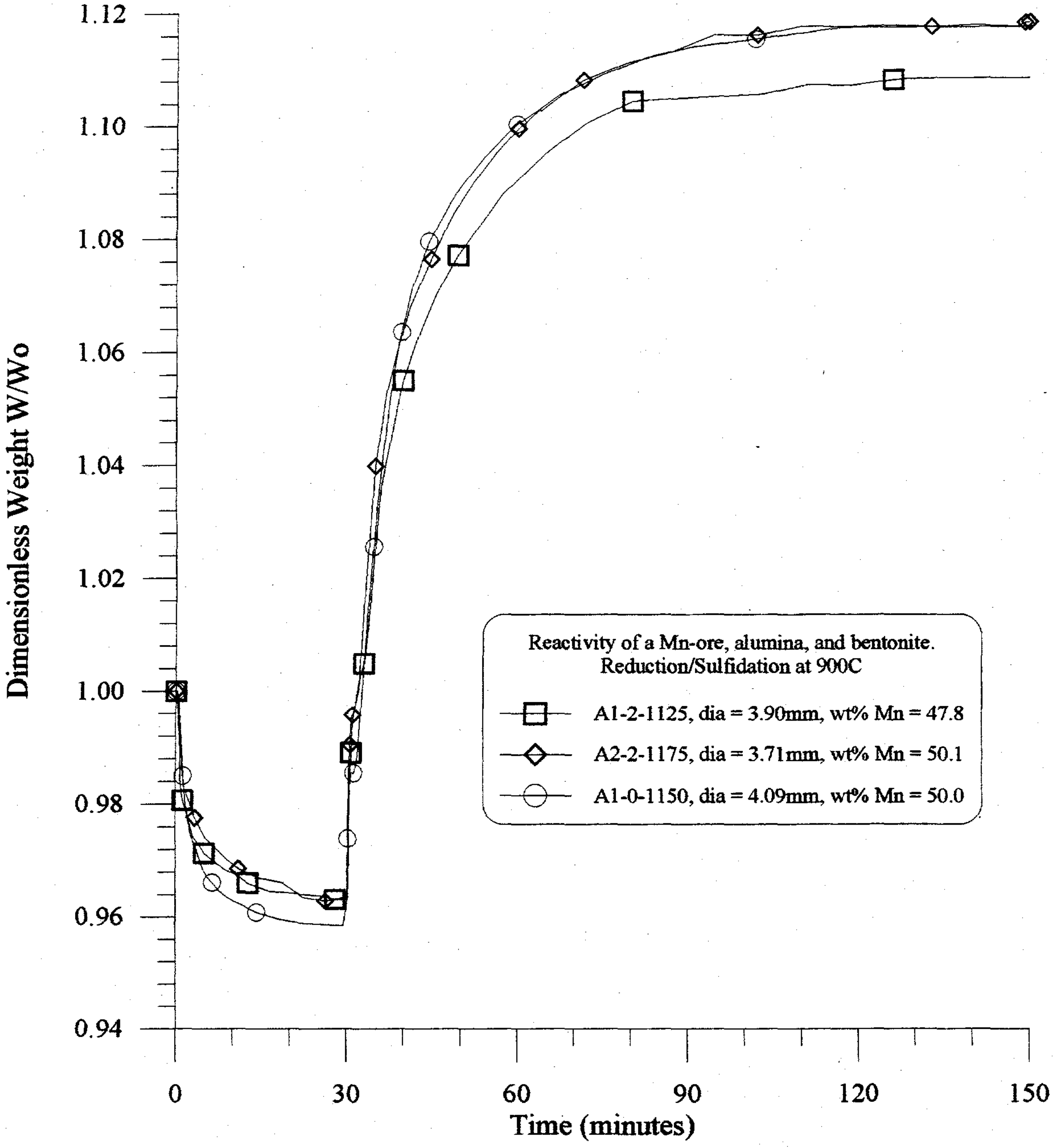

Figure 15. Comparison of first reduction/sulfidation of MnO_2 Ore-Al_2O_3 formulations at 900 °C.