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Project Title: **AN ATTRITION-RESISTANT ZINC TITANATE SORBENT FOR SULFUR** DE-FC22-92PC92521

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ABSTRACT

In the continuing search for good sorbent materials to remove sulfur for hot, coal-derived gases, zinc titanate sorbents have shown great promise. The objective of this project was to extend the work of prior investigators by developing improvements in the compressive strength and, therefore, the cycle life of these sorbents while maintaining good chemical reactivity. Fifteen formulations were prepared and evaluated. The best properties were obtained by blending relatively course (two micron) ZnO and TiO_2 powders to obtain a composition of 50%Zn_2TiO_4-50%TiO_2. When sintered at 1000°C, it had a compressive strength of 28 MPa or 147 N/mm, which is four times higher than values obtained by prior investigators. It also performed well in thermogravimetric analysis measurements of reactivity, both in screening tests and in simulated coal gas.

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EXECUTIVE SUMMARY

For hot-gas cleanup, zinc titanate sorbents for sulfur are now believed to hold great promise. They undergo fewer phase transformations during sulfidation-regeneration cycles than zinc ferrite and are less susceptible to zinc loss by evaporation. The objective of this project was to develop a zinc titanate sorbent that is stronger than previous formulations, without a large loss in chemical reactivity. The higher strength should provide more resistance to attritioning in fluidized bed reactors and more resistance to decrepitation in fixed bed reactors. The approach was to incorporate a zinc titanate compound in a structural matrix of TiO_2.

The project started with a study of phase transformations in the ZnO-TiO_2 system. A literature review revealed that an up-to-date phase diagram had not been published, so one was constructed to show the range of stability of three compounds: Zn_2TiO_4, Zn_2TiO_3, and $Zn_2Ti_3O_8$. Experiments conducted on phase stability showed that Zn_2TiO_4 was the dominant compound, and the others generally formed only as minor constituents when ZnO and TiO_2 were blended and sintered to form sorbent pellets.

A total of 15 sorbent formulations were prepared and evaluated. The variables in the preparations were composition, ZnO and TiO_2 particle size, and sintering temperature. The principal methods used for evaluation were crush strength and chemical reactivity through thermogravimetric analysis (TGA) measurements. These were supplemented with materials characterization studies, using optical microscopy, scanning electron microscopy, energy dispersive x-ray analysis, and surface area measurements.

Most of the TGA experiments consisted of carrying out two sulfidation-regeneration cycles at 650°C. A $1\%H_2S$ in H_2 was used for sulfidation. For regeneration, initially air was used, then a $5\%O_2$ in N_2 mixture was substituted to reduce the tendency toward sulfate formation. From these TGA measurements and crush strength measurements, the best combinations of properties were obtained for the following formulations:

(A) $50\%Zn_2TiO_4$-$50\%TiO_2$, made from 2 micron powders, sintered at 1000°C
(B) $50\%Zn_2TiO_4$-$50\%TiO_2$, made from 0.3 micron powders, sintered at 900°C
(C) $75\%Zn_2TiO_4$-$25\%TiO_2$, made from 0.3 micron powders, sintered at 700°C

These three formulations were then evaluated further by conducting three sulfidation-regeneration cycles in simulated product gas from a coal gasification process. The first two of the formulations listed above performed better than the third, so these two will be tested next year in fluidized bed and fixed bed reactors at the Research Triangle Institute.

The major objective of improving the crush strength of zinc titanate sorbents while maintaining good reactivity was met. Formulation A had a crush strength of 28 MPa or 147 N/mm, which is a factor of four higher than values reported by prior investigators.

It was expected that, for the same chemical composition and starting particle size of the sorbents, the chemical reactivity would increase continuously as the sintering temperature decreased. An exception to this expected behavior was obtained with many but not all of the sorbent formulations. For these sorbents, the poor reactivity resulting from low sintering temperatures is not understood and merits further study. Slight evidence was found that a structural change occurred, perhaps due to $ZnTiO_3$ and/or $Zn_2Ti_3O_8$ formation during sulfidation-regeneration cycles.

OBJECTIVES

The intent of this project was to improve the mechanical properties and durability of zinc titanate sorbents and make them more attractive for cleanup of hot gases produced by coal gasification. The specific objectives for this year were the following:

(a) Prepare materials with zinc titanate dispersed in a matrix of excess TiO_2
(b) Evaluate chemical reactivity and crush strength as functions of sintering temperature and chemical composition
(c) Characterize the sorbents using microscopy, surface area analysis, and x-ray diffraction
(d) Select the most promising formulation or formulations for future evaluation in fixed and fluidized bed reactors.

INTRODUCTION AND BACKGROUND

Modern methods of burning high-sulfur coal and converting high-sulfur coal to fuel gas all incorporate a provision for gas desulfurization. Integrated gasification combined cycle (IGCC) systems employing hot gas cleanup are very promising for electric power generation from coal. The thermal efficiency of such systems can approach 50%, compared to 30 to 35% for conventional coal-fired power plants. These IGCC systems, coupled with hot gas cleanup, have the potential to remove more than 90% of the sulfur and other pollutants from the coal. This subject has been a priority research area for the Illinois Clean Coal Institute (ICCI) and the Morgantown Energy Technology Center (METC) for several years under the category Gas Cleanup.

A two-part review and analysis of the literature on gas desulfurization at high temperatures was published recently by Swisher and Schwerdtfeger (1,2). They concluded that while research on sorbent materials has been extensive, continuing effort is important for three reasons. One is that commercial exploitation is just beginning, particularly in coal gasification, so there is still time to use results from research and development. A second reason is that systems requirements vary, so a single material may not serve all needs. The third is that all materials investigated have at least one shortcoming that should be remedied.

In recent years, the trend in research has shifted from relatively simple materials to mixed metal oxide compounds.

The compound that has received the most attention is zinc ferrite ($ZnFe_2O_4$). Pioneering work on $ZnFe_2O_4$ was done by Grindley and Steinfeld (3), who showed that it can reduce the H_2S concentration in hot gas streams to the low ppm range. After several years of follow-on research, it is now felt that certain limitations of $ZnFe_2O_4$ may be difficult to overcome. More specifically, it suffers from high Zn loss by vaporization at temperatures of 650°C and higher, and it is susceptible to decrepitation during sulfidation-regeneration cycles.

There is currently active research on a number of other mixed metal oxide compounds that offer promise. Zinc titanate compounds, for example, can be used at higher temperatures without excessive Zn loss and undergo fewer phase transformations than $ZnFe_2O_4$ during sulfidation-regeneration cycles (4-10). Some rather serious problems still remain, however, on attrition tendency and on sulfate formation during regeneration in fixed bed reactors. Partly because of these concerns, a workshop was held in January 1993, at METC, to discuss goals versus progress on zinc titanate and other sorbents under development (11).

In the project described here, the focus of the research was on improving durability. In the extension of the project next year, this effort will continue, and, in addition, research will be conducted on improving regeneration procedures to minimize sulfate formation.

EXPERIMENTAL PROCEDURES

For the preparation of sorbent materials, a procedure similar to that of Meng and Kay was used (12). For the first two batches of materials, reagent-grade ZnO and TiO_2 powders, -300 mesh size were used. The average particle size was 0.3μm. They were blended in a dilute solution of starch in water, then dried until the slurry had a consistency somewhat stiffer than toothpaste. Green pellets were made by extruding the paste through a 1.0 cm diameter metal tube and cutting to a length of 1.0 cm. With further drying, the starch in the material gave it sufficient green strength to withstand normal handling without deforming or breaking. For the third batch of material, it was desired to use larger ZnO and TiO_2 powders. There was no difficulty in purchasing TiO_2 powder with an average particle size of 2μm. However, ZnO of comparable size had to be prepared by purchasing ZnS and oxidizing it to ZnO. This process consisted to heating in air for 6 hours at 700°C. All three formulations were sintered by heating the cylindrical pellets in air and holding for 3 hours at temperatures ranging from 700 to 1100°C.

The bulk densities of the sintered pellets were determined from their weights and volumes. Comparison of the bulk and theoretical densities was used to determine percent porosity. The crush strength of the pellets was determined with a plunger-type specimen holder designed and fabricated for the project. The load was applied and measured with an MTS Model S10 Mechanical Testing Apparatus. Five specimens were tested from each batch and averages calculated.

Pieces from the crushed pellets were used for sulfidation experiments in a Dupont Thermogravimetric Analysis (TGA) apparatus. All of the sulfidation and regeneration reactions were carried out at 650°C. Initially, a 1%H_2S in H_2 gas mixture was used for sulfidation, and air was used for regeneration. Later, a 5%O_2-95%N_2 mixture was used for regeneration to guard against sulfate formation. Screening tests of this nature could be done rather quickly, because the sulfidation reactions were complete in approximately 1 hour. This TGA database was used to select the best formulations for evaluation in a gas mixture similar to that produced in a Shell oxygen-blown entrained bed gasifier (13). Its composition is given in Table 1. The only difference between it and the TGA experimental gas composition is that N_2 was not used in the latter. The source of H_2S was a cylinder containing a prepared mixture of 1%H_2S in H_2. The desired gas compositions were obtained by controlling their flow rates with precision flowmeters.

TABLE 1. GAS COMPOSITION FROM SHELL OXYGEN-BLOWN ENTRAINED BED GASIFIER (13)

Species	Percentage	Percentage Without N_2
CO_2	2.0	2.1
CO	64.1	67.0
H_2S	0.2	0.2
N_2	4.4	----
CH_4	~0	----
H_2	27.3	28.6
H_2O	2.0	2.1
Total	100.0	100.0

Selected samples were characterized using x-ray diffraction, surface area analysis, and microscopy. The instrument used for x-ray diffraction was a Rigaku X-ray Diffractometer. Surface area measurements were carried out in a Quanta Sorb

BET instrument. The samples were outgassed in flowing helium at 200°C, followed by CO_2 adsorption at 195 K. For most of the microscopy work, a Hitachi S-570 Scanning Electron Microscope was used. One sample was characterized using transmission optical microscopy at the University of Missouri at Rolla.

RESULTS AND DISCUSSION

The first task in the project was to determine which titanate compound or compounds are in equilibrium with TiO_2 at the temperatures of interest for hot gas cleanup. A standard reference book on ceramic phase diagrams published in 1956 (14) showed the existence of only one compound, Zn_2TiO_4. In prior projects on zinc titanate sorbents (4,6), this compound, as well as Zn_2TiO_3 and $Zn_2Ti_3O_8$, were identified. There appeared to be uncertainties about the ranges of stability of these compounds, so a comprehensive review of published literature was conducted.

A thorough phase equilibrium study by Dulin and Rase (15) identified $ZnTiO_3$ as a stable compound up to a temperature of 945°C, where it decomposes to Zn_2TiO_4 and TiO_2. These authors also measured the melting temperature of Zn_2TiO_4 to be 1549°C, and corrected an error in the earlier phase diagram by showing there is no mutual solubility between Zn_2TiO_4 and TiO_2.

The third compound, $Zn_2Ti_3O_8$, was prepared and characterized by Bartram and Slepetys (16). They found that it began to decompose when the temperature was raised above 700°C. Yamaguchi, et al. (17) carried out differential thermal analysis measurements and found that $Zn_2Ti_3O_8$ transforms to $ZnTiO_3$ at 700°C, which then transforms to Zn_2TiO_4 at 965°C.

These and other articles found in the literature search still leave uncertainties in the temperatures and compositions over which the three titanates are stable. The main reason for difficulty in establishing phase boundaries is the sluggishness of the phase transformations. Our analysis of this literature resulted in construction of the phase diagram presented in Figure 1.

A number of experiments were conducted in which samples were held as long as two weeks at various temperatures. Then x-ray diffraction measurements were made to identify the phases present. The results were generally consistent with the diagram in Figure 1, but there were often mixtures of phases present when only one phase was expected. This

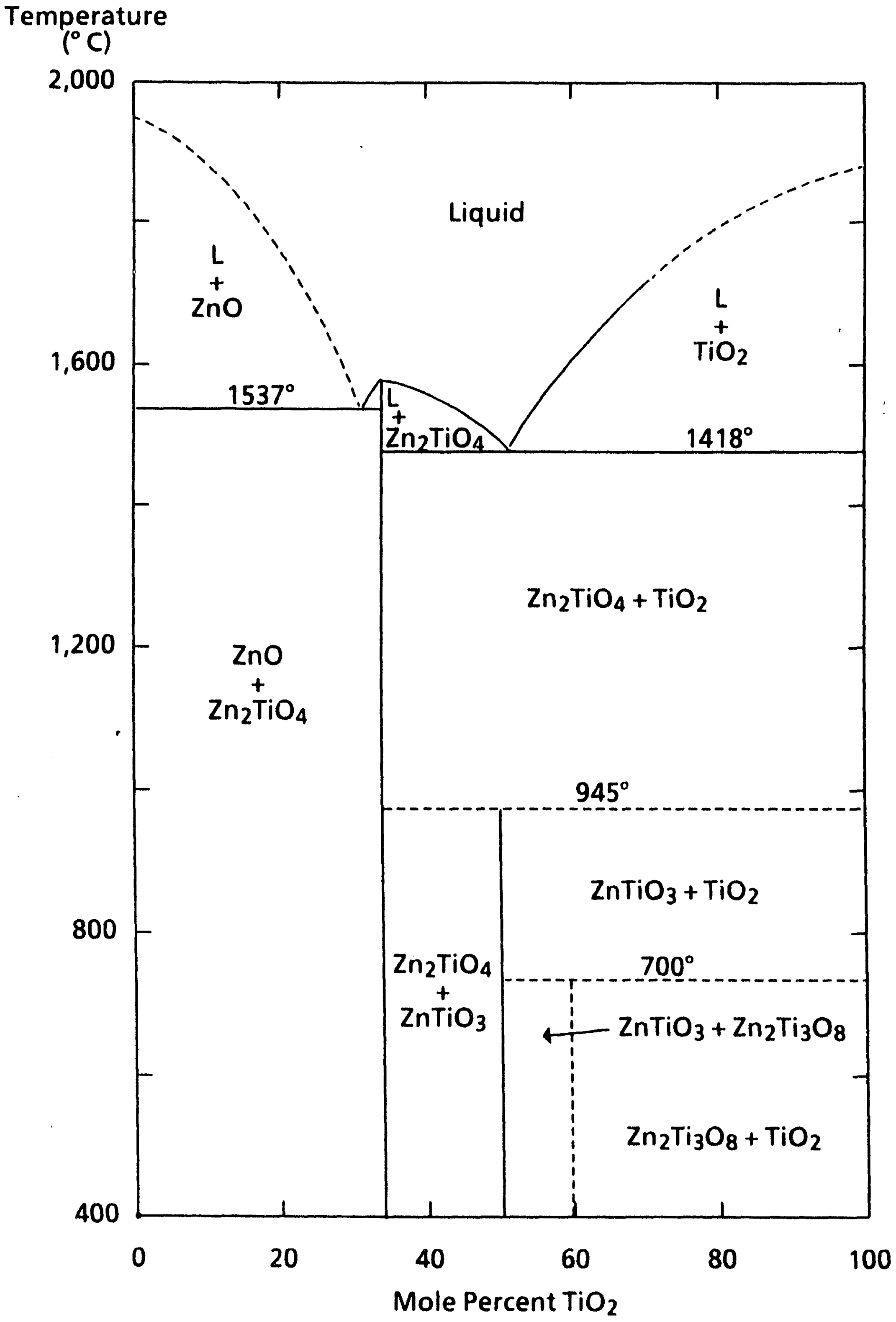

Figure 1. ZnO–TiO_2 Phase Diagram

observation is similar to the observations of prior investigators.

It is believed that Zn_2TiO_4 is the easiest compound to prepare, the most stable thermodynamically, and the dominant compound existing in sorbent materials prepared under a variety of conditions. Therefore, all of the formulations evaluated in this project are described with %Zn_2TiO_4 as a composition parameter, and the limited presence of the other two compounds is ignored.

A total of 15 formulations were prepared for property measurements, as described in Table 2. These properties will now be discussed, starting with Batch 1.

TABLE 2. DESCRIPTION OF SORBENT FORMULATIONS

	SINTERING TEMP. (°C)					
STARTING MATERIAL	700	800	850	900	1000	1100
BATCH 1 (75%Zn_2TiO_4, FROM FINE POWDERS)	X	X	X	X	X	X
BATCH 2 (50%Zn_2TiO_4 FROM FINE POWDERS)	X	X	X	X		
BATCH 3 (50%Zn_2TiO_4 FROM COARSE POWDERS)	X	X		X	X	X

Properties of 75%Zn_2TiO_4-25%TiO_2 sorbents made from fine powders: Table 3 gives a summary of the properties obtained by sintering pellets from this batch of material at temperatures ranging from 700 to 1100°C. As one would expect, the porosity decreases in a regular manner with increasing sintering temperature. Crush strength values are specified in two ways. Listed first are compressive stress values in MPa at which fracture occurred. The second set of values is expressed as force per unit height of the specimens in N/mm. The reason for including the latter is that most of the literature values are given in this form, and it has been found to be a good measure of the crush strength of catalyst materials. The results given are the averages obtained on five or six specimens. Note that the crush strength increases by more than a factor of ten as the sintering temperature increases from 700 to 1100°C. The same data are shown in graphical form in Figure 2.

The chemical reactivity results in Table 3 were obtained by carrying out two sulfidation-regeneration cycles at 650°C in

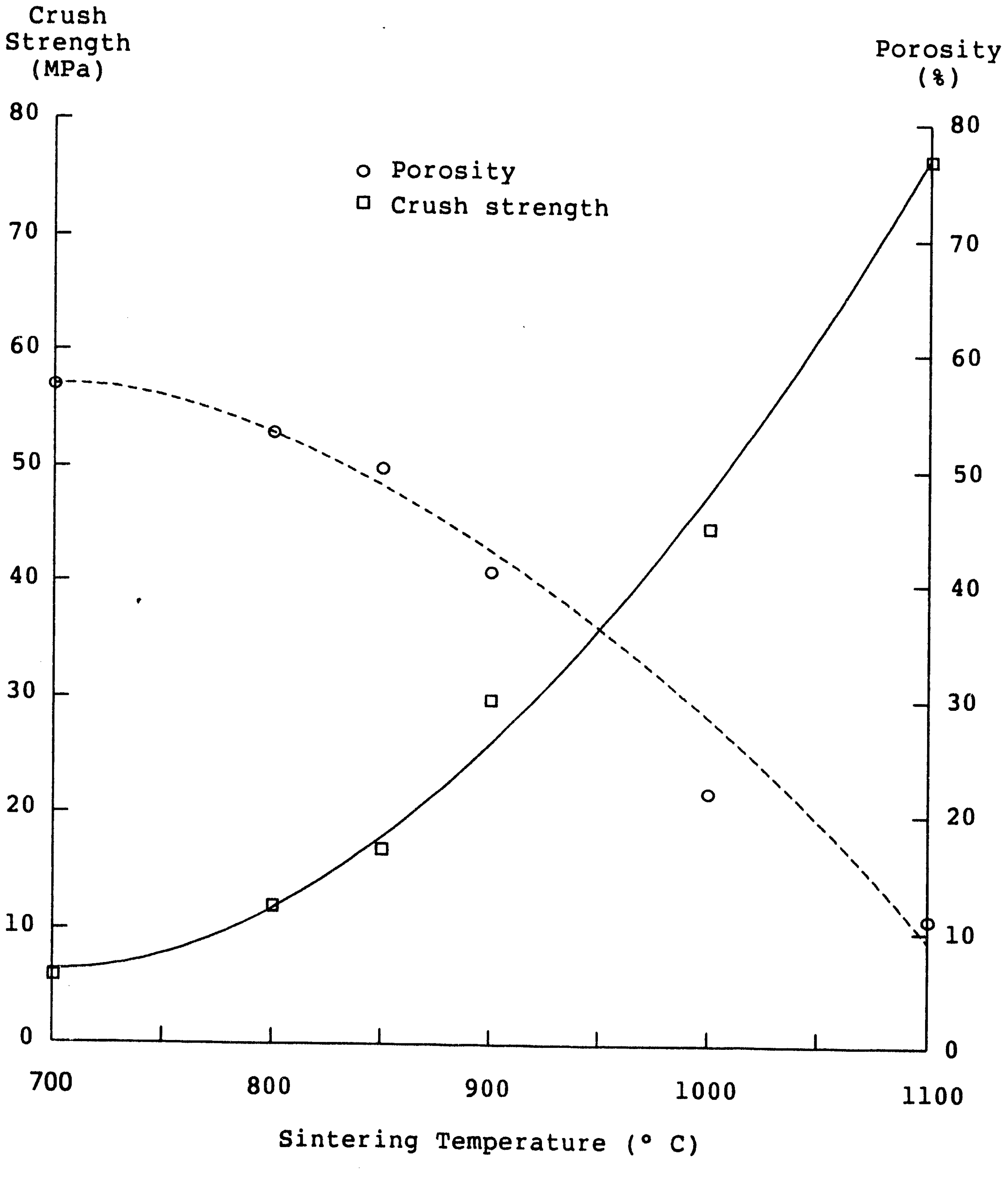

Figure 2. Effect of sintering temperature on crush strength and porosity of 75% Zn_2TiO_4-25% TiO_2 sorbents.

a thermogravimetric analyzer. A mixture of 1%H_2S in H_2 was used for sulfidation, and air was used for regeneration. Only the specimen sintered at 700°C was considered good. The TGA plot for this specimen is shown in Figure 3. The mass gain of 10% during sulfidation agrees with the theoretical mass gain for conversion of ZnO to ZnS in the material. The two cycles are nearly identical, and the reaction times are short.

TABLE 3. PROPERTIES OF 75%Zn_2TiO_4-25%TiO_2 SORBENTS MADE FROM 0.3 MICRON POWDERS

LOT NO.	SINTERING TEMP. (°C)	POROSITY (%)	CRUSH STRENGTH (MPa)	CRUSH STRENGTH (N/mm)	TGA REACTIVITY IN 1%H_2S
A-1	1100	11	77	410	---
A-2	1000	22	45	261	VERY POOR
A-3	900	41	30	176	POOR
A-7	850	50	17	143	2ND CYCLE POOR
A-4	800	53	12	100	2ND CYCLE POOR
A-5	700	57	6	40	GOOD

Figure 4 shows TGA data for a specimen sintered at 850°C. Regeneration during the first cycle was incomplete, and the second cycle did not reproduce the first. Thus the results given in Table 3 and Figures 3 and 4, illustrate the trade-off expected and confirmed between crush strength and reactivity. With higher sintering temperature, the strength increased but the porosity and reactivity both decreased.

Scanning electron microscopy did not prove to be very useful for characterizing this batch of material. Voids in the material could be seen, but no distinction could be made between the solid phases. A specimen sintered at 1100°C was examined by light transmission through a thin section. A photomicrograph obtained in this way appears in Figure 5. The large particle is TiO_2, and it probably formed from an agglomerate of fine particles in the starting material. The dark, continuous phase was shown by energy dispersive x-ray analysis (EDX) to be Zn_2TiO_4, and its amount appears to agree with the nominal composition of 75%Zn_2TiO_4.

Results on this batch of material will be discussed further after results are presented for the other formulations.

<u>Properties of 50%Zn_2TiO_4-50%TiO_2 sorbents made from fine powders</u>: By increasing the excess TiO_2 content from 25 to

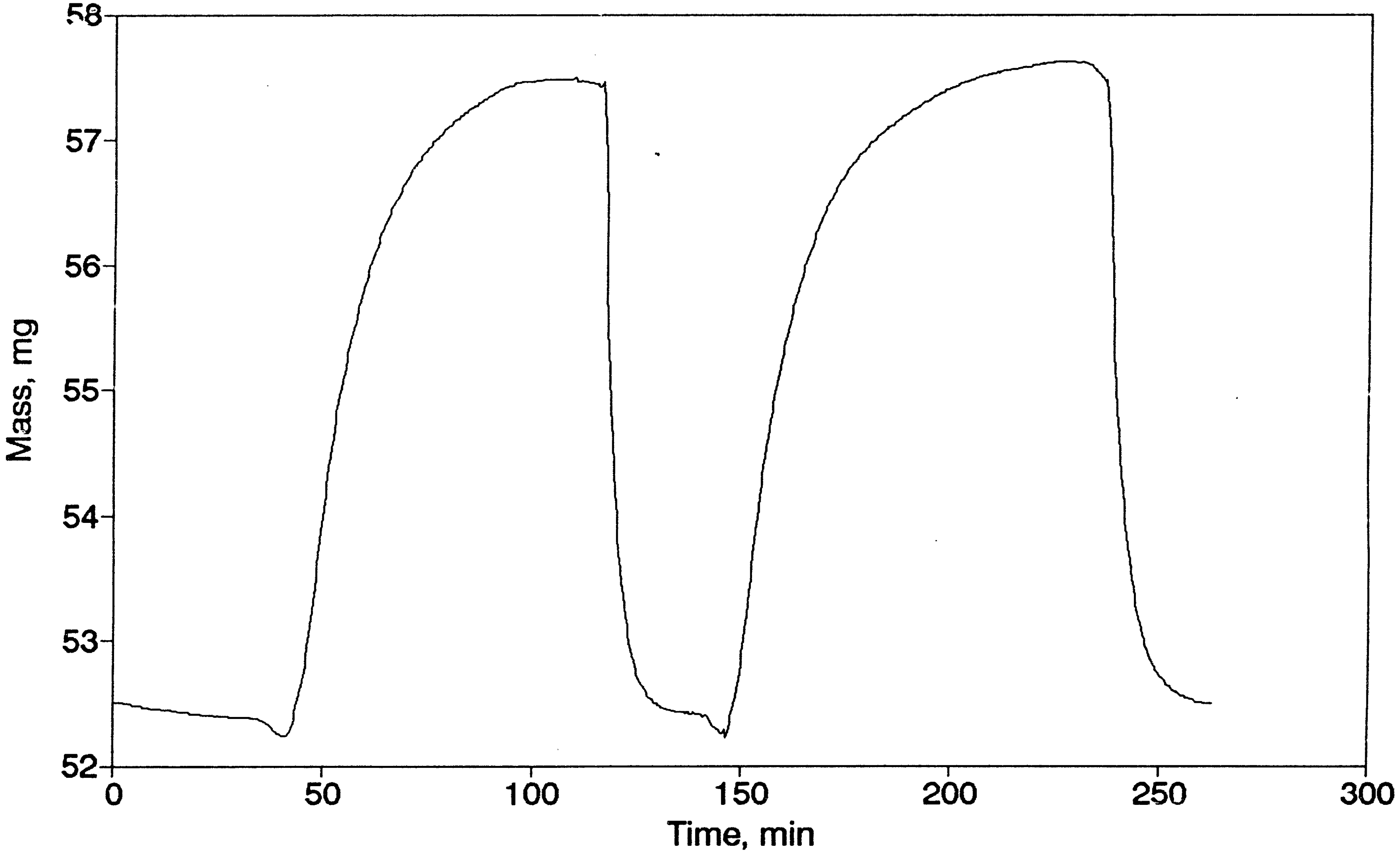

Fig. 3 Sulfidation in H_2 + 1% H_2S, followed by regeneration in air of 75% Zn_2TiO_4 - 25% TiO_2 specimen made from fine powders, sintered at 700°C, and tested at 650°C.

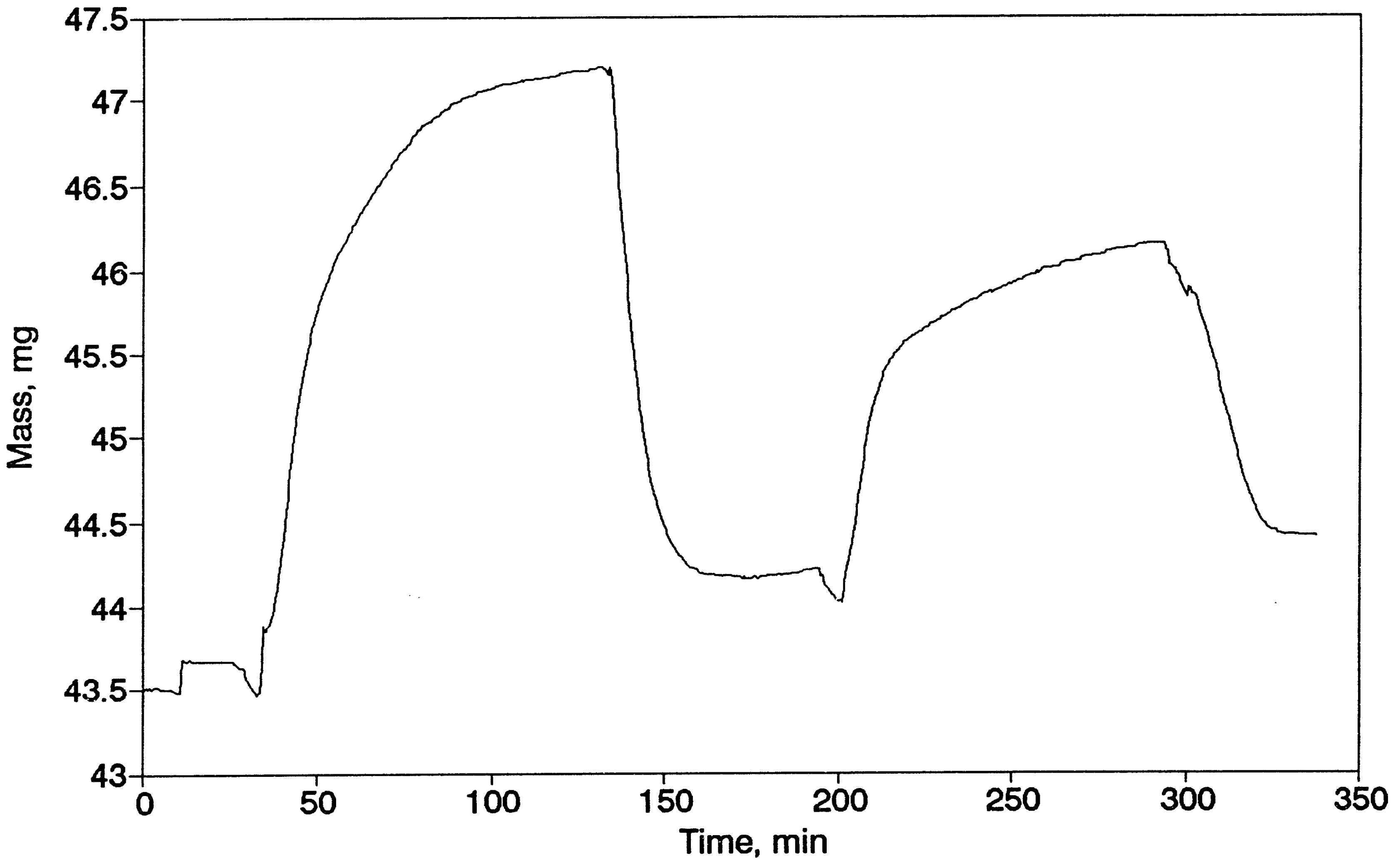

Fig. 4 Sulfidation in H_2 + 1% H_2S, followed by regeneration in air of 75% Zn_2TiO_4 - 25% TiO_2 specimen made from fine powders, sintered at 850°C, and tested at 650°C.

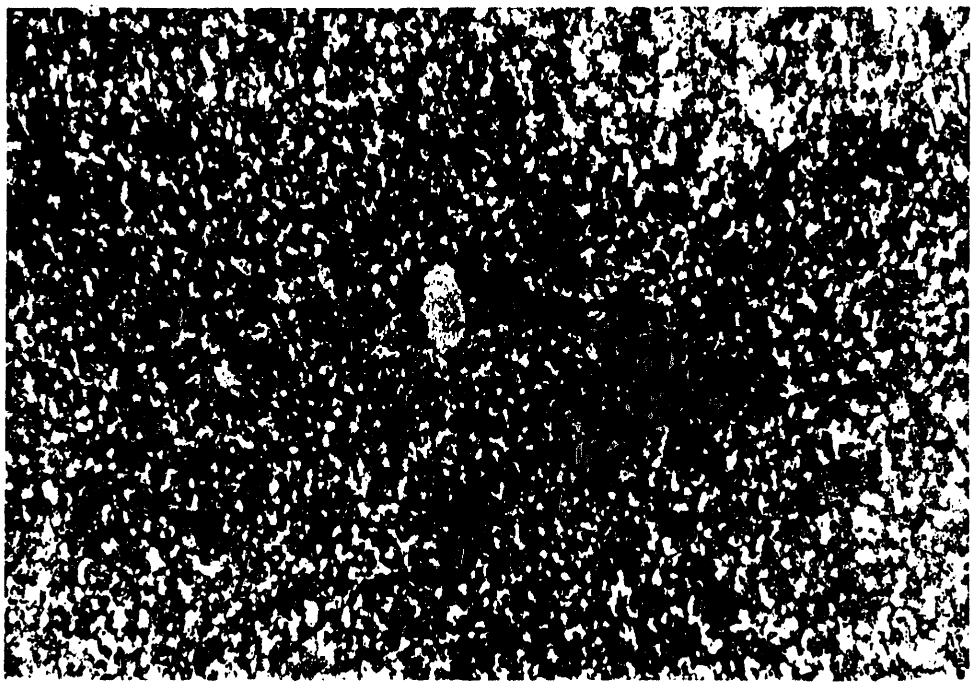

Fig. 5 Optical transmission micrograph of 75% Zn_2TiO_4 - 25% TiO_2 after sintering at 1100°C.

50% could, in principle, result in good chemical reactivity at a higher strength level. By reducing the amount of ZnO in the material, however, the sulfur capacity should decrease. Data obtained to investigate these effects are given in Table 4. A smaller range of sintering temperatures was used, so the variations in properties are corresponding smaller than in Table 3. Note in Table 4 that good reactivity was obtained for a sintering temperature of 900°C, with a crush strength of 10 MPa or 56 N/mm. These strength values are higher than the values of 6 MPa or 50 N/mm for the only formulation with good reactivity in Table 3. TGA data for the specimen from Table 4 sintered at 900°C are shown in Figure 6(a) and (b). The first and second cycles are almost identical, but as expected, the sulfidation mass gain is 7%, compared to 10% in Figure 3. The times for complete sulfidation are in the range of 60 to 80 minutes in both Figure 3 and Figure 6.

TABLE 4. PROPERTIES OF 50%Zn_2TiO_4-50%TiO_2 SORBENTS MADE FROM 0.3 MICRON POWDERS

LOT NO.	SINTERING TEMP. (°C)	POROSITY (%)	CRUSH STRENGTH (MPa)	CRUSH STRENGTH (N/mm)	TGA REACTIVITY IN 1%H_2S
B-1	900	47	10	56	GOOD
B-2	850	52	8	49	GOOD
B-3	800	52	7	44	2ND CYCLE POOR
B-4	700	50	5	31	2ND CYCLE POOR

It should be mentioned that the gas used for regeneration for this group of specimens was changed from air to a mixture of 5%O_2 in N_2. The change was made to guard against sulfate formation, which has a tendency to occur when the exothermic heat of reaction causes an increase in the specimen temperature. However, no evidence was found for a difference in behavior, presumably because the single, small particles used in the TGA experiments were cooled adequately by the flowing gas.

Properties of 50%Zn_2TiO_4-50%TiO_2 sorbents made from coarse powders: In preparing the third and last batch of sorbents, the particle size of the ZnO and TiO_2 starting materials was increased from 0.3 to 2 microns. The idea behind this series of experiments was that the pore sizes in the sintered pellets should increase with the particle size and perhaps improve the reactivity. The results are summarized in Table 5. A good combination of properties was obtained for the specimen sintered at 1000°C. It is not surprising

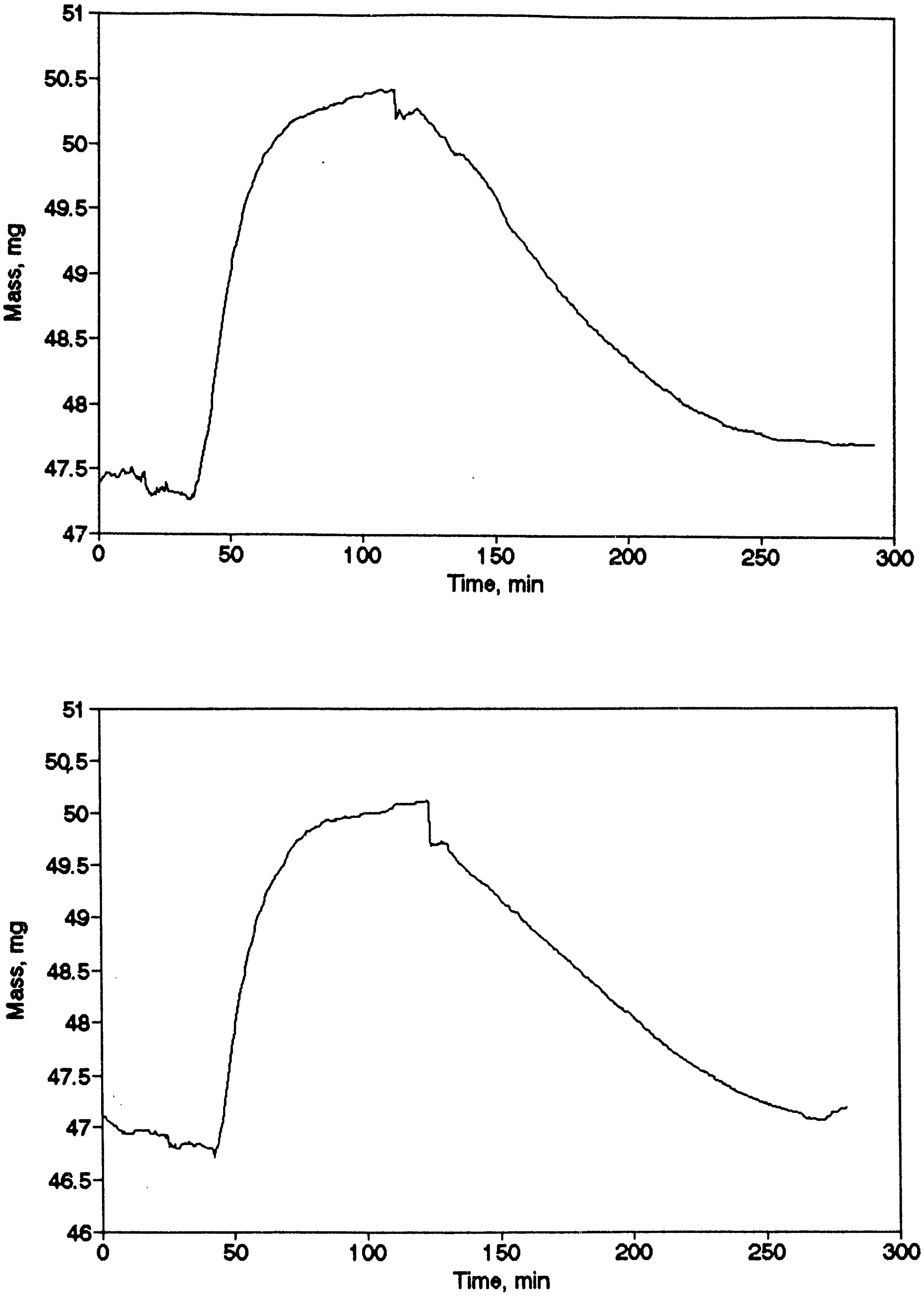

Fig. 6 Sulfidation in H_2 + 1% H_2S, followed by regeneration in 5% O_2 +95% N_2 of 50% Zn_2TiO_4 - 50% TiO_2 specimen made from fine powders, sintered at 900°C, and tested at 650°C. (a) first cycle, (b) second cycle

that a higher sintering temperature was needed to obtain good properties with this batch of sorbents because of the larger particle sizes of the ZnO and TiO_2 powders used in the preparation. The crush strength of the specimens sintered at 1000°C was 28 MPa or 147 N/m, which is significantly higher than for the best sorbents from the first two batches. TGA data for the 1000°C material are reproduced in Figure 7. The sulfidation and regeneration times are nearly the same as the best material from the second batch, which was tested under the same conditions.

TABLE 5. PROPERTIES OF $50\%Zn_2TiO_4-50\%TiO_2$ SORBENTS MADE FROM 2 MICRON POWDERS

LOT NO.	SINTERING TEMP. (°C)	POROSITY (%)	CRUSH STRENGTH (MPa)	CRUSH STRENGTH (N/mm)	TGA REACTIVITY IN $1\%H_2S$
C-1	1100	--	--	---	2ND CYCLE POOR
C-2	1000	42	28	147	GOOD
C-3	900	44	28	153	2ND CYCLE POOR
C-4	800	43	22	115	FAIR
C-5	700	43	6	33	POOR

Because of the coarser structure in this series of specimens, it was thought that scanning electron microscopy might be more fruitful than with the finer structured specimens. Accordingly, specimens that had been sintered at 900°C were examined in three conditions. The structure of an as-sintered specimen is shown in Figure 8(a). The pore channels appear black and are easy to resolve. No visual distinction can be made between the titanate and TiO_2 phases. Energy Dispersive X-ray Analysis (EDX) was conducted on ten particles at the surface. In five of them, the metal content was found to be 93 to 99%Ti (weight basis), so the particles were undoubtedly TiO_2. In the other five particles, the metal content ranged from 28 to 65%Ti. The theoretical value for Zn_2TiO_4 is 27. A major uncertainty in the data was the amount of Ti detected from particles beside and beneath the particle being analyzed. Therefore, it was not possible to determine whether the titanate was all Zn_2TiO_4 or whether other titanate compounds were present as well.

Figure 8(b) shows a similar specimen after sulfidation, which should contain a mixture of ZnS and TiO_2. Pores appear to constitute a smaller fraction of the surface. Constriction of pores is to be expected, because ZnS has a lower density than ZnO (4.0 vs. 5.6 g/cm^3). Referring now

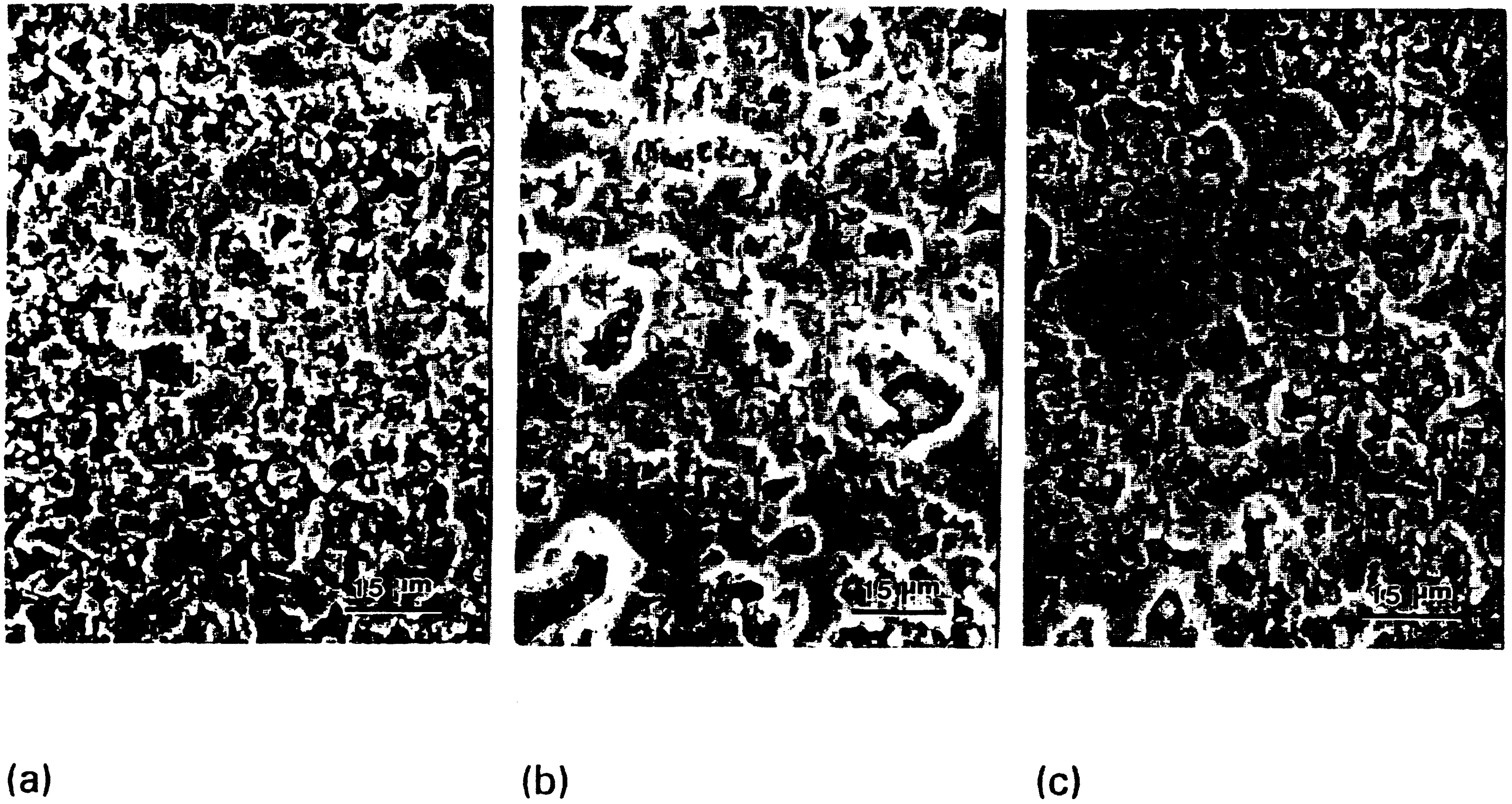

Fig. 8 Scanning electron micrographs of 50% Zn_2TiO_4 - 50% TiO_2 specimens made from coarse powders. (a) after sintering at 900°C, (b) after second sulfidation in H_2 + 1% H_2S at 650°C, (c) after second regeneration in 5% O_2 + 95% N_2 at 650°C.

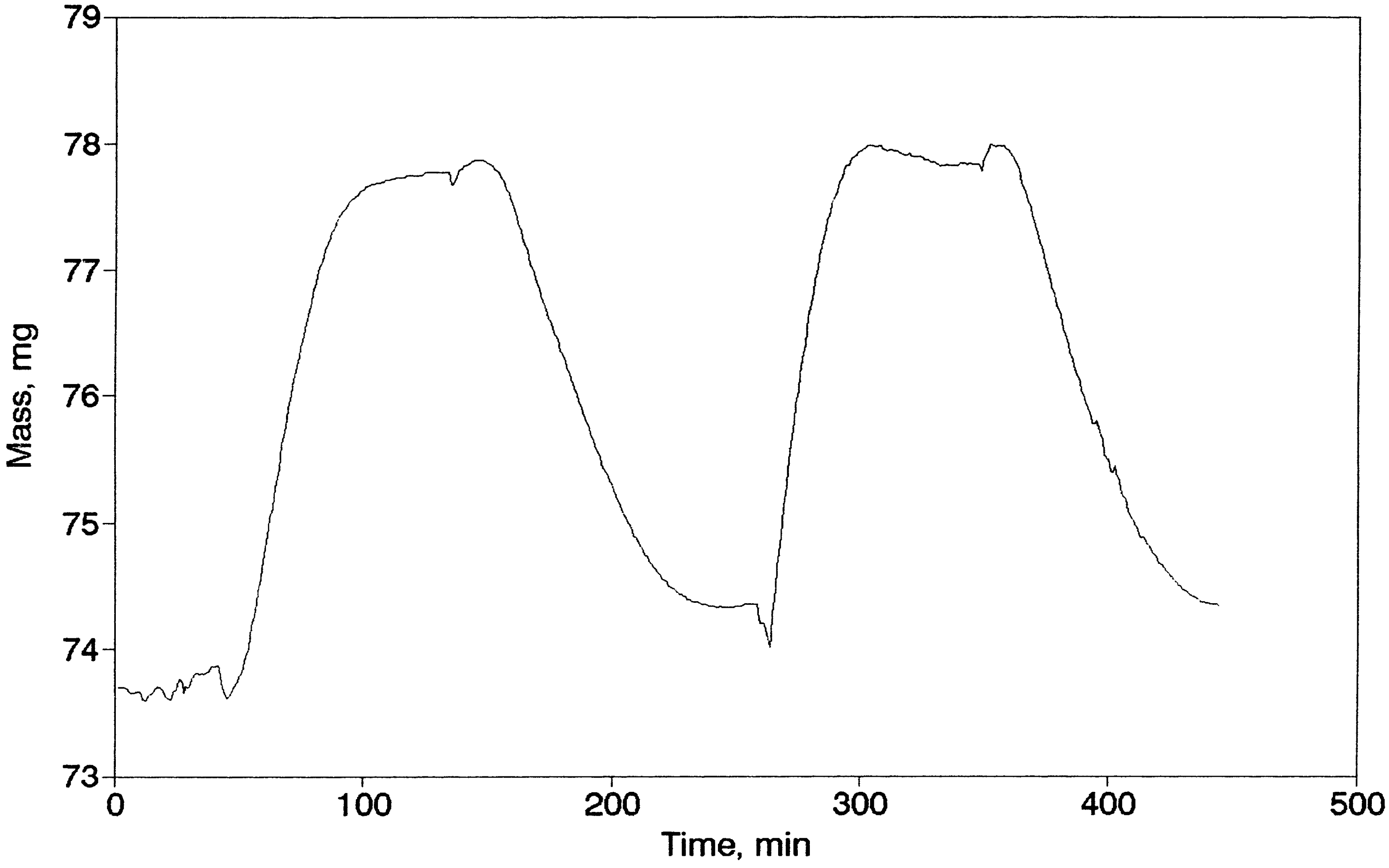

Fig. 7 Sulfidation in H_2 + 1% H_2S, followed by regeneration in 5% O_2 + 95% N_2 of 50% Zn_2TiO_4 - 50% TiO_2 specimen made from coarse powders, sintered at 1000°C, and tested at 650°C.

to Figure 8(c) for a specimen after regeneration, it appears that there has not been a full recovery of the pore fraction observed for the as-sintered material in (a). This result implies that mass transport has occurred and caused some pore closure. The same formulation had exhibited some degradation in TGA reactivity between the first and second cycles (see Table 5). Thus, the microscopy and TGA results are consistent.

In general, one might expect the porosity and the chemical reactivity to increase progressively as the sintering temperature of the sorbents decreases. This behavior was obtained from the first batch of sorbents (see Table 3), but not for the second and third batches (see Tables 4 and 5). For the latter two, there was essentially no variation in porosity and almost no shrinkage of the pellets during sintering. The explanation is believed to lie in the refractory nature of TiO_2, which was present in a higher concentration (50 vs. 25%) in these materials. It is not understood why the TGA reactivity is worse for sintering temperatures of 700 and 800°C. A possibility is that $ZnTiO_3$ and/or $Zn_2Ti_3O_8$ form during sulfidation-regeneration cycles and causes an adverse structural change in the sorbents. From the phase diagram in Figure 1, it can be shown that these compounds could form at temperatures below 945°C. The minor changes in appearance of the specimen shown in Figure 8 could be due to this effect.

Surface Area Measurements: For the first two batches of sorbents, BET measurements were made for the as-sintered condition. The results are plotted in Figure 9. For both batches, the surface area decreased continuously with increasing sintering temperature. For the composition $50\%Zn_2TiO_4-50\%TiO_2$, there was no change in % porosity with sintering temperature, meaning that there were fewer, larger pores obtained at high temperature. The sintering behavior of the $75\%Zn_2TiO_4-25\%TiO_2$ material was different in that the % porosity and BET surface area decreased along similar curves with increasing sintering temperature.

Sulfidation-Regeneration Tests in Simulated Coal Gas: In the last task in the project, the best sorbent formulation from each of the three batches of material were selected. These were (a) $75\%Zn_2TiO_4-25\%TiO_2$ from fine powders sintered at 700°C, (b) $50\%Zn_2TiO_4-50\%TiO_2$ from fine powders sintered at 900°C, (c) $50\%Zn_2TiO_4-50\%TiO_2$ from coarse powders sintered at 1000°C. Three sulfidation-regeneration cycles were carried out on each of these in simulated coal gas of the composition listed in Table 1. Because there was only 0.2% H_2S in the gas, the times for complete sulfidation were

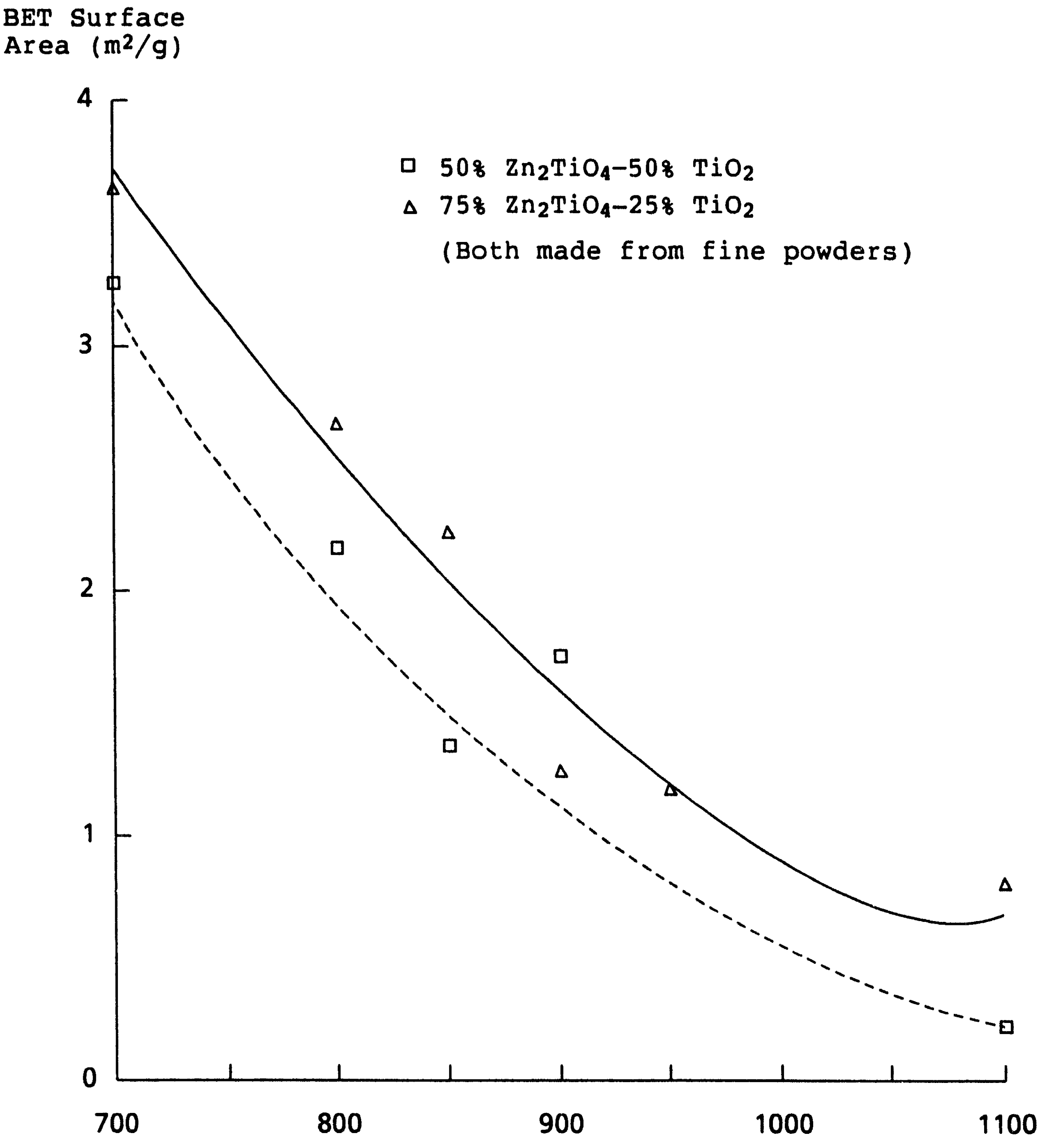

Figure 9. Variations of BET surface area with sintering temperature for two sorbent compositions.

7 to 8 hours. During these lengthy tests, difficulty was encountered with drift in the TGA instrumentation. After each cycle, the specimen mass was checked with a platform balance, but there was still more uncertainty in the data than with the TGA experiments described earlier. The results of the most successful test are shown in Figure 10. The differences between the second and third cycles are clearly within the experimental uncertainty, and perhaps all three are within the uncertainty. Thus, there was either no degradation or a modest degradation after the first cycle.

For the 50%Zn_2TiO_4-50%TiO_2 material made from coarse powders and sintered at 1000°C, the test results were also promising. There was an apparent increase in the sulfidation rate between the first, second and third cycles. Otherwise, the data were similar to those shown in Figure 10.

For the 75%Zn_2TiO_4-25%TiO_2 material sintered at 700°C, there was an apparent small but steady degradation from the first to the third cycle. Since this formulation also had the lowest crush strength of the three, it is judged to be inferior to the others, even though its sulfur capacity is higher because of a higher ZnO content.

Crush Strength Comparisons: Since a major objective of this project, was to improve the strength of zinc titanate sorbents, it is important to show how the data obtained here compare to data from other investigations. Such a comparison is given in Table 6. The crush strength is specified in N/mm, since only force per height units are given in other publications. The crush strength values listed for this project can be seen to be higher than those reported by other investigators for both zinc titanate and zinc ferrite formulations. The data obtained here for the 50%Zn_2TiO_4-50%TiO_2 material made for coarse powders of 147 N/mm is particularly noteworthy, and may represent a major advance in zinc titanate technology. The last entry in the table is for a sorbent in which fine Ni and Ni-Cu alloy particles were dispersed in an Al_2O_3 matrix. Al_2O_3 has better structural properties than TiO_2, so it was possible to obtain higher crush strengths than for the zinc titanate formulations studied in this project.

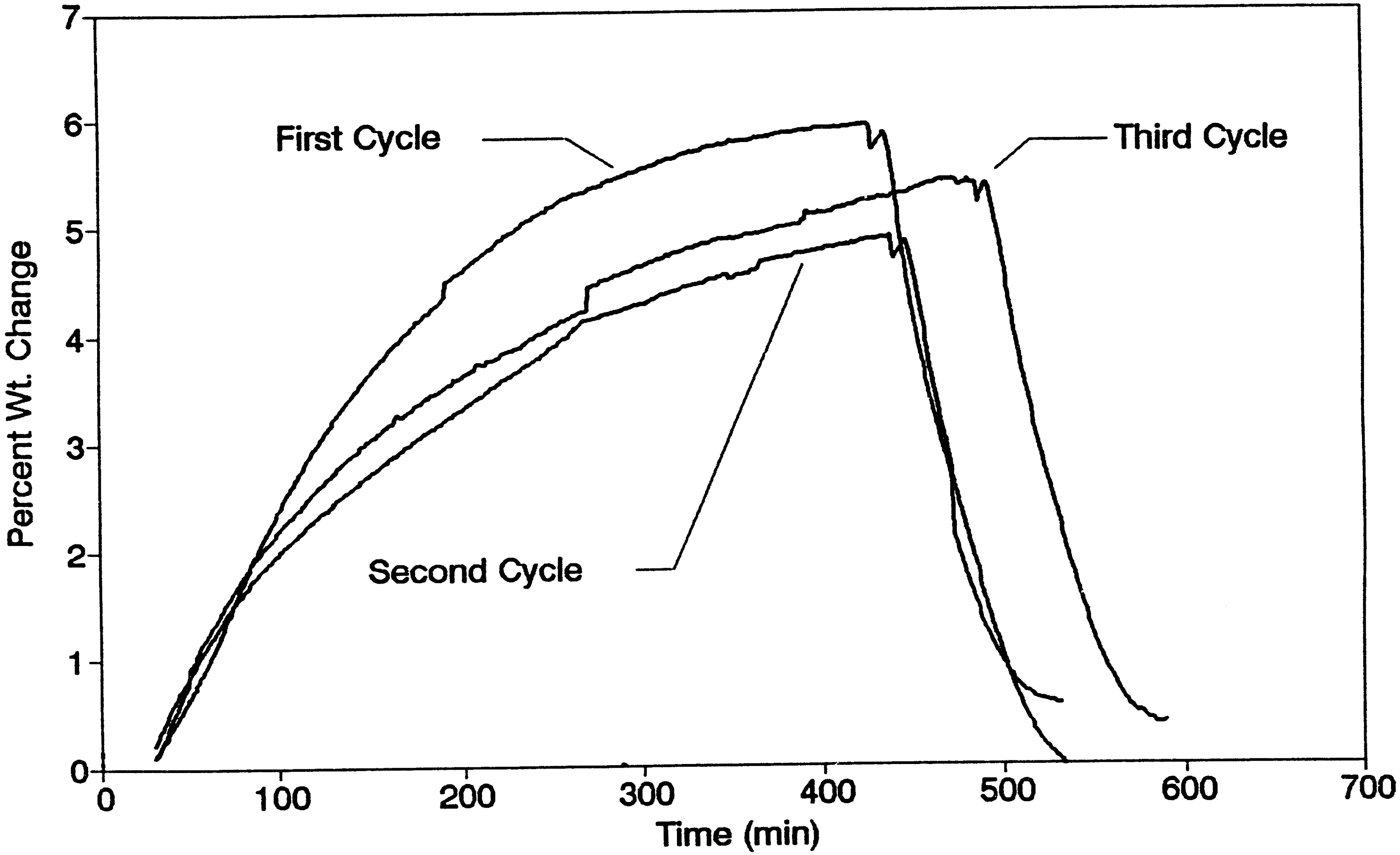

Fig. 10 Three sulfidation-regeneration cycles in simulated coal gasification product gas for 50% Zn_2TiO_4 - 50% TiO_2 specimen made from fine powders, sintered at 900°C, and tested at 650°C.

TABLE 6. CRUSH STRENGTH COMPARISON

SORBENT	CRUSH STRENGTH (N/mm)	INVESTIGATORS
ZINC TITANATE (a) $75\%Zn_2TiO_4$, FINE POWDERS, 700°C SINTER	40	THIS PROJECT
(b) $50\%Zn_2TiO_4$, FINE POWDERS, 900°C SINTER	56	THIS PROJECT
(c) $50\%Zn_2TiO_4$, COARSE POWDERS, 1000°C SINTER	147	THIS PROJECT
ZINC TITANATE	16	GASPER-GALVIN AND AMITAY (7)
ZINC TITANATE	36	GRINDLEY (18)
ZINC TITANATE	29	GANGWAL, ET. AL (6)
ZINC FERRITE	18-28	AYALA (19)
ZINC FERRITE	16	GUPTA AND GANGWAL (9)
DISPERSED Ni IN AL_2O_3	168-722	JHUNJHUNWALA AND SWISHER (20)

CONCLUSIONS AND RECOMMENDATIONS

1. It was possible to obtain a wide variety of properties in zinc titanate sorbents by varying the chemical composition and sintering temperature
2. In rank order, the best combination of properties were obtained with the following formulations:

   (a) $50\%Zn_2TiO_4-50\%TiO_2$, made from 2 micron powders, sintered at 1000°C.
   (b) $50\%Zn_2TiO_4-50\%TiO_2$, made from 0.3 micron powders, sintered at 900°C.
   (c) $75\%Zn_2TiO_4-25\%TiO_2$, made from 0.3 micron powders, sintered at 700°C.
3. Materials sintered at very high temperatures had the highest strength but poorest reactivity because of low porosity.
4. Materials sintered at low temperatures sometimes had low chemical reactivities. The degradation could be due to structural changes that should be studied further.
5. Crush strength values more than four times that of other investigators were achieved, while maintaining good reactivity.
6. Testing in fixed and fluidized bed reactors of the most promising formulations should proceed as planned.

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PROJECT MANAGEMENT REPORT
June 1 through August 31, 1993

Project Title: **AN ATTRITION-RESISTANT ZINC TITANATE SORBENT FOR SULFUR**

Principal Investigator: J. H. Swisher
Department of Mechanical
Engineering and Energy Processes
Southern Illinois University
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Carbondale, Illinois 62901
618-453-7005
Project Manager: F. I. Honea, Illinois Clean Coal Institute

COMMENTS

The two technical milestones scheduled for completion during the fourth quarter were materials characterization and TGA measurements. The characterization work conducted during the project included X-ray diffraction, optical transmission microscopy, scanning electron microscopy, and energy dispersive X-ray analysis. Results obtained by all these techniques are mentioned in the final technical report. TGA measurements were carried out on 15 sorbent formulations using 1% H_2S in H_2 as the sulfidizing gas and the 3 best formulations using simulated coal gas. Therefore both of the scheduled technical milestones were completed.

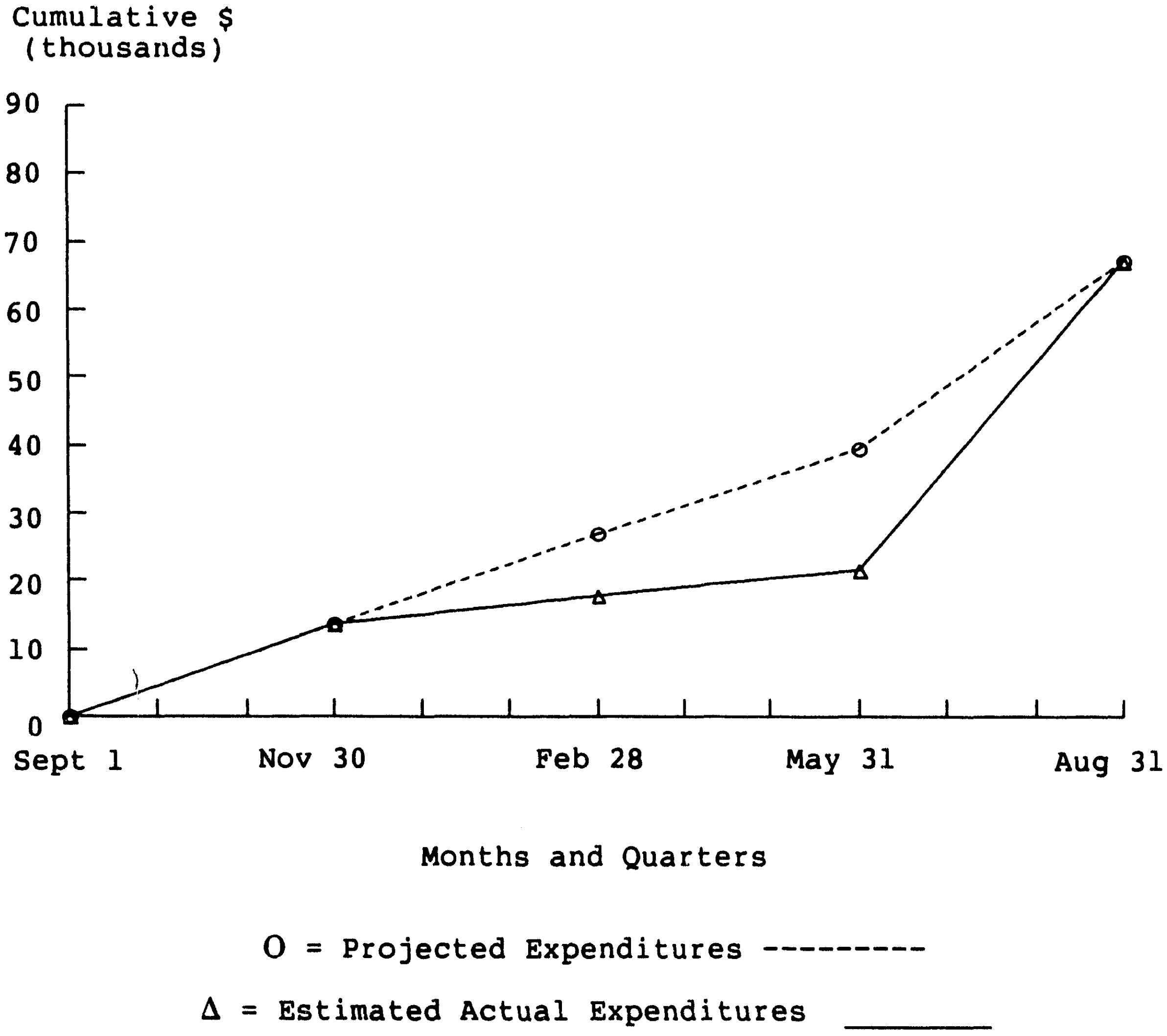
Projected and Estimated Expenditures by Quarter

Quarter*	Types of Cost	Direct Labor	Materials and Supplies	Travel	Major Equipment	Other Direct Costs	Indirect Costs	Total
Sept. 1, 1992 to Nov. 30, 1992	Projected	10,573	1,200	300	0	500	1,258	13,831
	Estimated Actual	9,704	1,300	400	0	1,100	1,251	13,755
Sept. 1, 1992 to Feb. 28, 1993	Projected	21,146	2,000	300	0	900	2,435	26,781
	Estimated Actual	13,022	1,474	400	0	1,516	1,641	18,053
Sept. 1, 1992 to May 31, 1993	Projected	31,719	2,500	300	0	1,350	3,587	39,456
	Estimated Actual	15,400	2,300	400	0	1,700	2,000	21,800
Sept. 1, 1992 to Aug. 31, 1993	Projected	54,228	3,000	700	0	3,300	6,123	67,351
	Estimated Actual	54,228	3,000	700	0	3,300	6,123	67,351

*Cumulative by quarter.

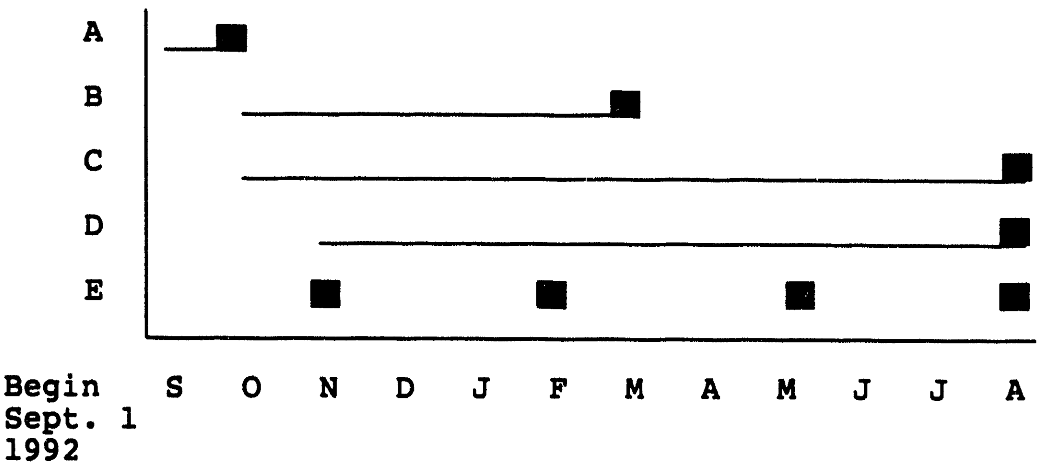
COSTS BY QUARTER

An Attrition-Resistant Zinc Titanate Sorbent for Sulfur



Total Illinois Clean Coal Institute Award $67,351

SCHEDULE OF PROJECT MILESTONES



Milestones:

A. Phase identification
B. Sorbent preparation
C. Materials characterization
D. TGA measurements
E. Technical and project management reports