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Integration and Testing of Hot Desulfurization and Entrained Flow Gasification for Power Generation Systems

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Texaco, Inc.<br>Montebello Research Laboratory Montebello Research Laboratory  $\mathbb{R}^n$  in  $\mathbb{R}^n$  in  $\mathbb{R}^n$ **P.O.** Box 400 i\_{\extend{in figure for figure  $\frac{1}{2}$  figure  $\frac{1}{2}$  figure  $\frac{1}{2}$  is the figure of  $\frac{1}{2}$ **Montebello, CA 90640 i**,*a* **i1992** 

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## **CONTRACT INFORMATION**

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# **OBJECTIVES**

PHASE V - TEST INTEGRATED PDU

The objective of this project is to develop hot gas cleanup processes for incorporation into the Texaco Coal Gasification Process (TCGP). Both in-situ and external hot gas desulfurization have been investigated from a technical and economical perspective.

### **BACKGROUND INFORMATION**

The Texaco gasifier is a pressurized, entrained bed, slagging gasifier in which a coalwater slurry, or other hydrocarbon-containing liquid feed, is reacted with either oxygen or air. The product synthesis gas is cooled either by heat exchangers or by direct quench with water,

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depending on the end use. Currently, gas<br> **•** Develop and demonstrate in-situ<br>
desulfurization of synthesis gas in an<br>
desulfurization of synthesis gas in an contaminants are removed by conventional desulfurization of synthesis gas in an entertiods that require the gas to be cooled to entrained flow gasifier using both air and methods that require the gas to be cooled to entrained flow gasification.<br>
entrained flow gasification.<br>
Solution and the 120 system gasification. ambient temperature or below. As in the 120 MW TCGP-based Cool Water IGCC electric power plant, sulfur emissions are reduced to **•** Develop and demonstrate a high efficiency 10% of the New Source Performance Standards integrated system on a process 10% of the New Source Performance Standards (NSPS). Economic studies indicate that, compared to a conventional pulverized coal include coal preparation, gasification, plant with stack gas cleanup, a TCGP-based sulfur removal, particle and trace element plant with stack gas cleanup, a TCGP-based sulfur removal, particle and *IGCC* system is 15% more efficient and has *removal* and a gas turbine. IGCC system is 15% more efficient and has comparable investment costs.

efficiency can be further increased if the hot which DOE/<br>
synthesis gas is fed to a combustion turbine These were: synthesis gas is fed to a combustion turbine without cooling the gas to ambient temperature. Howeve<sup>-</sup>, gas contaminants such as sulfur still • Test advanced instruments developed by have to be removed. Desulfurization can be **METC** for coal conversion processes. have to be removed. Desulfurization can be accomplished either in-situ, by including a sulfur sorbent with the coal-water slurry feed to <br>the gast fier, or externally, by contacting the gas<br>removal sorbents that could be used the gasifier, or externally, by contacting the gas removal sorbents that could be used<br>with a sorbent downstream of the gasifier external to the gasifier. Development of with a sorbent downstream of the gasifier external to the gasifier. Development of vessel. In-situ desulfurization could provide the these sorbents would provide a backup to vessel. In-situ desulfurization could provide the these sorbents would provide a back<br>lowest investment cost and simplest design, the in-situ desulfurization approach. lowest investment cost and simplest design, while external desulfurization has the potential for very high sulfur removal and the production A contract (Cooperative Agreement) with<br>of a salable by-product. A significant amount the DOE/METC was awarded on September 30, of a salable by-product. A significant amount the DOE/METC was awarded on September 30, of work has been done by other investigators in 1987 for conducting an extended (5 years) cost of work has been done by other investigators in 1987 for conducting an extended (5 years) combined areas of in-situ and external desulfurization shared test program. The work was divided the areas of in-situ and external desulfurization shared test program. The work was divided<br>using either a fluidized bed or a moving bed into five phases, with each phase originally using either a fluidized bed or a moving bed gasifier. However, prior to this study, little work had been done to study hot desulfurization phases are defined as shown on the<br>in conjunction with an entrained bed gasifier schedule/milestone chart. The first two phases in conjunction with an entrained bed gasifier such as that used in the TCGP.

power generation from coal, Texaco submitted and summarized in our 1989 Contractors an unsolicited proposal in July 1986 to develop Review Meeting paper (Robin, *et al.* 1989). an unsolicited proposal in July 1986 to develop Review Meeting paper (Robin, *et al.* 1989)<br>and demonstrate the integration of high Completion of the Phase II work has taken and demonstrate the integration of high Completion of the Phase II work has taken<br>temperature desulfurization with the TCGP. longer than initially expected, partly because of temperature desulfurization with the TCGP. longer than initially expected, partly because<br>The main goals of the proposed program were: difficulties experienced during the PDU tests The main goals of the proposed program were:

- 
- development unit (PDU) scale which would<br>include coal preparation, gasification,

In addition, secondary goals were proposed Studies also indicate that process thermal which would help further major research in<br>ciency can be further increased if the hot which DOE/METC was already involved.

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corresponding to approximately one year. The phases are defined as shown on the cover proof of concept and process selection for the integrated system, with the following three phases covering the design, construction and PROJECT DESCRIPTION operation of the integrated PDU.

To help achieve the goal of clean, low cost<br>
To help achieve the goal of clean, low cost<br>
All of the Phase I work has been completed<br>
and summarized in our 1989 Contractors

and partly because the initial scope of work for operating difficulties. Zinc based mixed metal<br>Phase II has been modified as more has been oxides were also evaluated in external Phase II has been modified as more has been learned. These modifications have involved a desulfurization tests. Data were obtained for significant expansion of the process optimization several formulations at a variety of inlet studies and the inclusion of additional PDU temperatures, sulfur loadings and space studies and the inclusion of additional PDU testing.

### RESULTS

The research efforts in this program can be **Zinc Titanate Regenerable Fixed Bed.**<br>grouped into two areas: 1) the PDU test Sorbent durability is critical to the economic program, which is supported by theoretical studies and bench scale tests, and 2) the process optimization (economics) studies.<br>These two areas form an integrated research program, with the experimental data forming the order for the sorbent replacement cost not to basis for the optimization studies, and with the dominate the plant operating cost. Most of the basis for the optimization studies, and with the results of those studies guiding the ongoing results of those studies guiding the ongoing previous data on zinc titanate durability have<br>PDU test program. (A sketch of the PDU been obtained with bench scale equipment an PDU test program. (A sketch of the PDU been obtained with bench scale equipment and configuration can be found in the 1989 review simulated syngas for a limited number of cycle paper.) The progress to date in both of these areas is summarized below.

We previously reported the results of the initial theoretical studies and bench scale tests in For this reason we designed and built a<br>which we investigated potential sorbents that regenerable fixed bed which allows us to ex which we investigated potential sorbents that regenerable fixed bed which allows us to expose could be used to remove sulfur either in the one cubic foot of zinc titanate to multiple cycles gasifier (in-situ sorbents), or downstream of the gasifier (external sorbents). We also have gasifier (external sorbents). We also have diagram was shown in our 1991 Contractors reported the results of both air and oxygen Review Meeting paper (Robin, *et. al.* 1991). blown gasification PDU test runs using the most promising sorbents (Robin, *et. al.* 1990 and promising sorbents (Robin, *et. al.* 1990 and gasification PDU, was tested for the first time<br>Robin, *et. al.* 1991). Two cycles were

in-situ desulfurization tests. Iron, the most<br>promising in-situ sorbent, was limited to a with fresh L-3140 pellets; and five cycles were promising in-situ sorbent, was limited to a with fresh L-3140 pellets; and five cycles were maximum of 50 to 60% sulfur removal. Calcium was evaluated as an external sorbent in 1991. Table 1 summarizes the averaged d**at**a both entrained and fixed bed reactors. Although for the initial test (cycles A-1 and A2) a<br>as much as 80% desulfurization was achieved, five-cycle test (cycles B-1 through B-5). as much as 80% desulfurization was achieved, steady state data were never obtained because of

velocities during single sulfidation (half-cycle) tests. Z**i**nc titanate (ZnTi), the most promising sorbent, achieved sulfur removal levels greater than 99%.

Sorbent durability is critical to the economics of hot gas desulfurization using mixed metal oxides. Our economics calculations for fixed<br>bed desulfurizers indicated that a sorbent lifetime of several hundred cycles is needed in order for the sorbent replacement cost not to simulated syngas for a limited number of cycles.<br>Obtaining data with actual PDU syngas (containing trace metals, halides, etc.) under realistic operating conditions is necessary if PDU Test Program accurate predictions of process performance and economics are to be made.

one cubic foot of zinc titanate to multiple cycles<br>of sulfidation and regeneration. A process flow Review Meeting paper (Robin, *et. al.* 1991).<br>The fixed bed, which is integrated with our in September 1991. Two cycles were completed using L-3140, a 1.5 Zn*/*Ti molar Calcium, sodium and iron were evaluated in ratio sorbent from United Catalysts Inc. (UCI).<br>in-situ desulfurization tests. Iron, the most Following this initial test, the bed was reloaded completed during November and December<br>1991. Table 1 summarizes the averaged data

Cycle Number <sup>(1)</sup>	$A-1$	$A-2$	$B-1$	$B-2$	$B-3$	$B-4$	$B-5$
Average Sulfidation Temperature, "F	1080	1040	1090	970	1015	1030	925
Maximum Sulfidation Temperature, °F	1180	1110	1170	1040	1050	1080	1008
Sulfidation Space Velocity <sup>(2)</sup> , dry, NTP, $hr^{-1}$	2880	3010	3840	5520	5510	5900	5900
Sulfidation Pressure, psig	331	341	335	336	324	321	330
Total Sulfur Capture, g-moles	151	109	128	138	128	120	114
Sorbent Utilization, % (mole S/mole Zn)	73	53	67	72	66	62	64
Average Regeneration Temperature <sup>(3)</sup> , <sup>o</sup> F	1010	1100	1140	1260	1280	1260	1270
Maximum Regeneration Temperature, °F	1390	1290	1270	1390	1400	1400	1320
Regeneration Space Velocity <sup>(3)</sup> , dry, NTP, hr <sup>-1</sup>	2730	3020	3580	3390	2980	3060	2910
Regeneration O <sub>2</sub> Partial Pressure, psia	3.45	4.55	2.75	1.75	1.44	1.19	0.59
Regeneration $O_2$ Concentration, mol%	1.57	1.37	1.07	1.08	0.98	1.04	0.45
Total Regeneration $O_2$ Fed, g-mole	406	474	392	216	246	204	84
Total $SO_2$ Produced During Regeneration <sup>(4)</sup> , g-mole (calculated from energy balance)	103	155	140	126	135	110	50

Table 1. Zinc Titanate Regenerable Fixed Bed Averaged Test Data

 $(1)$ During cycles A-1 through B-4, a 19-element ceramic candle filter was used to dedust the syngas upstream of the fixed bed. During cycle B-5, a cyclone was used.

 $(2)$ The sulfidation space velocity was increased during test B in order to shorten cycle length so that more cycles could be obtained during the test.

The average regeneration temperature was increased during test B in order to increase the regeneration kinetics and reduce the  $O_2$ requirement. Also, the O<sub>2</sub> partial pressure was decreased in order to reduce the likelihood of sulfate formation.

 $(4)$ SO, produced during regeneration was measured using an on-line mass spectrometer and a UV process gas analyzer. However, the data obtained by these instruments do not appear to be as reliable as the calculated SO<sub>2</sub> production obtained from an energy balance around the bed. Cycle B-5 regeneration was incomplete. When the sorbent was analyzed after shutdown, 56 g-mole sulfur was found remaining in the bed.

The sorbent utilization decreased from cycle  $A-1$  to cycle  $A-2$ . This can be explained by noting that cycle A-1 regeneration was incomplete. However, the residual sulfur was removed during the cycle A-2 regeneration. Overall, 99% of the sulfur fed to the reactor during cycles A-1 and A-2 was recovered as  $SO<sub>2</sub>$  during regeneration.

During cycles B-1 through B-5, there was less variation in sorbent utilization between cycles. Regeneration B-5 was incomplete, and 56 g-moles of sulfur were found remaining in the sorbent throughout the bed. If this residual sulfur is included, 98% of the sulfur fed to the reactor during cycles B-1 through B-5 is accounted for either as SO<sub>2</sub> produced during regeneration or as residual sulfur.

Following each test, the sorbent was removed in eight sections for sampling and inspection. Pellet cracking and spalling was apparent throughout both beds, with the exception of the sulfidation outlet, where little



### Table 2. UCI L-3140 Sorbent Analysis For Cycles A-1 Through A-2

<sup>(1)</sup> UNUSED = sample in "as received" condition; TOP = sulfidation inlet, regeneration outlet; BOTTOM = sulfidation outlet, regeneration inlet

 $(2)$ Digits represent relative presence of each phase

 $(3)$ Zinc Sulfide/Zinc Titanate =  $ZnS/(2ZnO*3TiO<sub>2</sub> + 2ZnO*TiO<sub>2</sub>)$ 

 $(4)$ Average of six tests

DCP = Direct Current Plasma Spectrometry;  $XRF = X-Ray$  Fluorescence Spectrometry; ICP = Inductively Coupled Plasma Spectrometry

sulfidation and regeneration occurred. The degradation was more severe in the bed exposed to five cycles, where  $3 w t \%$  of the sorbent passed through a 14-mesh screen (1.4 mm) openings). Samples from each section were analyzed for residual sulfur, crystal phases, crush strength, pore volume, surface area and zinc and titanium content. Sulfate was also analyzed for; but none was found in any of the samples. The data for the two- and five-cycle tests are shown in Tables 2 and 3, respectively.

Table 2 shows that the crush strength of the sorbent decreased by as much as 46% in one section. From the DCP, XRF and ICP data, it is not clear whether or not the Zn/Ti molar ratio changed significantly during the two-cycle test. However, Table 3 shows that the sorbent exposed to five cycles suffered an average decrease of 7% in the Zn/Ti molar ratio, as detected by both XRF and DCP. Also, the crush strength decreased by as much as  $40\%$  in one section.

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Sorbent Bed Position <sup>(1)</sup>	Unused	Top							Bottom
Sample No.	$\bf{0}$	$\mathbf{1}$	$\mathbf{2}$	3	4	5	6	7	8
wt% Sulfur	0.09	14.3	14.3	9.41	6.78	3.37	0.49	0.17	0.14
Phases <sup>(2)</sup>									
ZnS	$\bf{0}$	4	4	$\overline{2}$	$\boldsymbol{2}$	$\mathbf{2}$	$\bf{0}$	$\bf{0}$	$\bf{0}$
2ZnO•3TiO <sub>2</sub>	$\mathbf{1}$	$\overline{2}$	$\mathbf{2}$	$\overline{2}$	1	1	1	1	1
$2ZnO\bullet TiO2$	3	$\mathbf{1}$	$\mathbf{1}$	2	3	3	3	3	3
ZnO	$\bf{0}$	$\bf{0}$	$\bf{0}$	$\bf{0}$	$\bf{0}$	$\bf{0}$	$\bf{0}$	$\bf{0}$	$\bf{0}$
TiO <sub>2</sub>	$\bf{0}$	$\overline{c}$	$\overline{2}$	1	1	$\bf{0}$	$\mathbf 0$	$\bf{0}$	$\bf{0}$
(3) Zinc Sulfide Zinc Titanate	$\bf{0}$	1.3	1.3	0.5	0.5	0.5	$\bf{0}$	$\bf{0}$	$\bf{0}$
Crush Strength <sup>(4)</sup> , lb	25.0	27.0	----	15.0	17.0	22.0	20.0	32.0	20.0
Pore Volume, cc/gm	0.40	0.32	0.31	0.32	0.33	0.34	0.36	0.37	0.38
Surface Area, $m^2/gm$	3.1	6.2	5.8	3.1	4.0	1.9	1.7	2.5	2.1
Zn/Ti molar ratio, DCP	1.51	1.39	1.38	1.41	1.36	1.39	1.37	1.39	1.36
Zn/Ti molar ratio, XRF	1.47	1.42	1.38	1.40	1.37	1.36	1.34	1.36	1.42

Table 3. UCI L-3140 Sorbent Analysis For Cycles B-1 Through B-5

 $(1)$ UNUSED = sample in "as received" condition;  $TOP =$  sulfidation inlet, regeneration outlet; BOTTOM = sulfidation outlet, regeneration inlet

 $(2)$ Digits represent relative presence of each phase

<sup>(3)</sup> Zinc Sulfide/Zinc Titanate = ZnS/(2ZnO $\cdot$ 3TiO<sub>2</sub> + 2ZnO $\cdot$ TiO<sub>2</sub>)

 $(4)$ Average of six tests

 $(6)$  $DCP = Direct Current$  Plasma Spectroscopy;  $XRF = X-Ray$  Fluorescence Spectroscopy

We had planned to continue testing the same batch of L-3140 for a total of 20 cycles. However, given the level of decrepitation after only five cycles, we decided to test other ZnTi formulations in order to find a more durable sorbent. Consequently, we designed the last test run of this program to simultaneously compare the durability of four different ZnTi formulations. Alternating layers of the four formulations were placed in the fixed bed so that they could be exposed to the same set of operating conditions over multiple cycles. The four sorbents included L-3140  $(Zn/Ti=1.5)$  and

L-3787M  $(Zn/Ti=2)$  from UCI, and TRZ-14  $(Zn/Ti=0.8)$  and TRZ-21  $(Zn/Ti=1.1)$  from Research Triangle Institute (RTI). Since the L-3140 had cracked during the previous tests, it was used as a control sample against which the other sorbents could be compared. The two RTI formulations and the UCI L-3787M were spherical pellets with nominal diameters of five millimeters. The UCI L-3140 extrudates were nominally five millimeters in diameter and 15 millimeters long. These sorbents were exposed to a total of six cycles during July and August 1992.

The sorbents were inspected following the fragments from the surface of the shperical first cycle. Both the L-3787M and TRZ-14 pellets. These fragments had the appearance showed no visible signs of decrepitation.<br>
Approximately 10% of the TRZ-21 sorbent peeled from the surface. The characteristic pellets showed some signs of spalling. As of these flakes was less than 0.5 mm. Some before, a significant quantity of the L-3140 pellets, which still retained the initial, general

Following the inspection, the sorbents were<br>replaced in the fixed bed and subjected to an replaced in the fixed bed and subjected to an Following the inspection of these sulfided additional four-and-a-half cycles. After the pellets, the sorbents were replaced in the reac sixth sulfidation, the fixed bed reactor was so that they could be regenerated. The final cooled down and the sorbents were inspected in regeneration and the data analysis from this cooled down and the sorbents were inspected in regeneration and the data analysis from this the sulfided state. All four formulations had experiment were not available when this part the sulfided state. All four formulations had experiment were not available when this paper<br>cracked and spalled. was prepared. The results will be reported to

The UCI L-3787M suffered the least amount of degradation. Approximately 40 **Ceramic Candle Filter Testing.** A ceramic percent of the L-3787M pellets were broken, 50 cross flow filter was operated for a total of 345 percent of the L-3787M pellets were broken, 50 cross flow filter was operated for a total of 345 percent had cracks which penetrated an hours during several PDU test runs. Any viable 10 percent showed no visual signs of cracking. <br>The whole, uncracked pellets appeared to have particulate removal device, to limit emissions The whole, uncracked pellets appeared to have particulate removal device, to limit emission<br>retained their crush strength, as they could not and to protect the combustion turbine from retained their crush strength, as they could not and to protect the combustion turbine from<br>be crushed between two fingers. None of the erosive particles. Several different internal be crushed between two fingers. None of the erosive particles. Several different internal<br>cracked material passed through a 14-mesh configurations have been tried in the filter, and cracked material passed through a 14-mesh screen. **a** considerable amount of operating experience

of the L-3140 extrudates, and roughly  $50$ percent of the pellets were broken. However, the level of degradation was less than the degradation that was observed in the December 1991 five-cycle test.

Cracking and spalling in the RTI approximately 180 hours were logged on the formulations was most severe, with over 14% candle filter. Inlet dust loadings were general formulations was most severe, with over 14% candle filter. Inlet dust loadings were generally of the TRZ-21 passing through a 14-mesh 1000 to 2000 wppm, as measured during runs in screen. It appeared that similar levels of September, November and December 1991 degradation had occurred in the TRZ-14. Both The outlet gas samples appeared dust free, RTI sorbents had lost significant crush strength, although the impactor collection plates appeared as it was relatively easy to crush them between to contain debris from the process piping. The two fingers. Unlike the UCI L-3787M sorbent, performance and operating character which typically broke into two or three large candle filter did not appear to differ which typically broke into two or three large candle filter did not appear to differ pieces, the RTI sorbents lost many small, thin, significantly from that of the cross flow filter. pieces, the RTI sorbents lost many small, thin,

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first cycle. Both the L-3787M and TRZ-14 pellets. These fragments had the appearance of showed no visible signs of decrepitation. Small pieces of an egg shell which had been Approximately 10% of the TRZ-21 sorbent peeled from the surface. The characteristic size<br>pellets showed some signs of spalling. As of these flakes was less than 0.5 mm. Some before, a significant quantity of the L-3140 pellets, which still retained the initial, generally<br>pellets had cracked. spherical shape, were missing from 10 to 20 of spherical shape, were missing from 10 to 20 of these small flakes.

additional four-and-a-half cycles. After the pellets, the sorbents were replaced in the reactor sixth sulfidation, the fixed bed reactor was so that they could be regenerated. The final was prepared. The results will be reported to METC as soon as they are available.

percent had cracks which penetrated an hours during several PDU test runs. Any viable unknown distance below the surface, and only IGCC power plant using hot gas cleanup will IGCC power plant using hot gas cleanup will<br>need this filter, or some other high temperature has been gained. The ability of the filter to Multiple, deep cracks were observed in all function essentially as an absolute filter has the L-3140 extrudates, and roughly 50 been demonstrated.

In August 1991, a nineteen-element candle<br>array was substituted for the eight cross flow elements inside the Westinghouse filter vessel. Between September 1991 and August 1992, 1000 to 2000 wppm, as measured during runs in September, November and December 1991. degradation had occurred in the TRZ-14. Both The outlet gas samples appeared dust free,<br>RTI sorbents had lost significant crush strength, although the impactor collection plates appeared as it was relatively easy to crush them between to contain debris from the process piping. The two fingers. Unlike the UCI L-3787M sorbent, performance and operating characteristics of the

The Phase II process optimization studies regenerated with pure, rather than diluted, air.<br>were intended to provide guidance for the The more concentrated SO<sub>2</sub> regeneration off-ga were intended to provide guidance for the The more concentrated  $SO_2$  regeneration of f-gas design of the integrated PDU by revealing those streams resulting from these changes meant that design of the integrated PDU by revealing those streams resulting from these changes meant that<br>hot gas cleanup configurations having the smaller, less costly sulfur recovery units could hot gas cleanup configurations having the **smaller**, less costly sulfur recovery units could greatest potential for commercialization as part be used. Design improvements to the reactors greatest potential for commercialization as part be used. Design improvements to the reactors of a Texaco-based grass roots IGCC plant. The using once-through, non-regenerable sorbents of a Texaco-based grass roots IGCC plant. The using once-through, non-regenerable sorbents<br>results of the first nine study cases were were also made in an attempt to improve the **results** of the first nine study cases were were also made in an attempt to improve the reported in our 1990 Contractors Review sulfur removal efficiency of these units. **M**ee**ting pap**e**r (Robin,** *et*. *al*. **1990**). The**s**e studies, which were first attempts at integrating The key results of this second group of hot gas cleanup with Texaco's gasification economics cases are summarized in Table 4 process, showed that IGCC power plants based<br>on the Texaco gasifier using hot gas cleanup are<br>given in the footnotes to the table; and costs are on the Texaco gasifier using hot gas cleanup are<br>more efficient than similar plants using more efficient than similar plants using expressed in terms of mid-91 dollars. Case 1 is<br>conventional cold gas cleanup. Improvements the cold gas cleanup base case against which all conventional cold gas cleanup. Improvements the cold gas cleanup base case against which all<br>in overall plant heat rates of up to 400 Btu/kWh the hot gas cleanup cases are compared in terms were calculated. However, all of the plants were more expensive to build and operate than the cold gas cleanup base case.

the nine studies would provide clear guidance in cleanup cases are the least efficient and most<br>selecting an economically viable process expensive of all the cases shown in the table. selecting an economically viable process<br>configuration to be demonstrated in an configuration to be demonstrated in an The lower efficiencies of the air-blown cases<br>integrated PDU at Montebello. However, can be attributed to the lower efficiency of the because none of the first nine configurations<br>studied resulted in a plant which was less expensive than the cold gas cleanup base case, we proposed a second group of studies aimed at we proposed a second group of studies aimed at gasification PDU runs (Robin, *et. al.* 1990 and improving the overall economics while Robin, *et. al.* 1991). In addition, the increased maintaining, as much as possible, the calculated efficiency gains.

These studies again looked at various<br>combinations of in-situ desulfurization, external combinations of in-situ desulfurization, external The most efficient and least expensive cases<br>desulfurization using either once-through, non-<br>use zinc titanate for bulk sulfur removal. And, regenerable sorbents (such as dolomite or iron oxide) or regenerable zinc titanate sorbents, and oxide) or regenerable zinc titanate sorbents, and gained by using a less expensi*v*e once-through, gasifier. However, the expensive radiant syngas zinc titanate used as a polishing step. All of the coolers were replaced with direct contact heat cases using a non-regenerable sorbent (12, 13) coolers were replaced with direct contact heat cases using a non-regenerable sorbent (1 exchangers, and the regenerable sorbent fixed and 14) had high operating costs, which exchangers, and the regenerable sorbent fixed bed designs were replaced with either moving

**Process** O**ptimizati**o**n Studies** be**d** or **fl**ui**diz**ed bed **d**es**i**gns. **T**hese **r**e**a**c**t**or **d**e**sign** ch**ang**e**s allo**wed **t**he **sorb**e**nt to b**e  $\frac{1}{2}$  **sulfur** removal efficiency of these units.

> economics cases are summarized in Table 4.<br>Brief process descriptions for each case are the hot gas cleanup cases are compared in terms<br>of efficiency and cost.

**t**he c**old gas** c**l**ea**nup bas**e **cas**e**. All of t**he **o**x**yg**en**-blo**w**n** h**ot gas** c**l**e**anup** c**as**e**s ar**e **mor**e e**ffi**c**i**e**nt t**h**an t**he **cold gas W**e **originally** e**nvision**ed **t**h**at t**he **r**e**sults of** c**l**e**anu**p **bas**e c**as**e. The **air-blo**w**n** h**o**t **gas** can be attributed to the lower efficiency of the<br>Texaco gasifier blown with air instead of oxygen. This decreased gasification efficiency was measured during several air-blown Robin, *et. al.* 1991). In addition, the increased volume of the air-blown syngas results in larger equipment, more processing trains and increased in-plant power use.

> use zinc titanate for bulk sulfur removal. And, even though zinc titanate is expensive, little is non-regenerable sorbent, in combination with zinc titanate used as a polishing step. All of the translated into higher costs of electricity. Also,



### **Table** 4**. Process Optimization Studi**es **- Summary of K**e**y R**es**ults**

### **Case Definitions**

Case 1 is the cold gas cleanup (MDEA-based acid gas removal) case previously reported. Although this case was completed in 1989, the cost numbers shown here have been updated to mid-91 dollars for comparison with the new cases. However, it should be noted that since this case was completed, improvements have been made to Texaco's commercially available gasification technology that **hav**e **r**e**sultedinsignificantreductionsin heat rate and plant cost.**

The cases labelled 10 recover sulfur as sulfuric acid using the conventional "contact process", while the cases labelled 11 recover sulfur in the elemental form using RTI's direct sulfur recovery process. An M after the case number means that moving beds of zinc titanate were used to remove sulfur species from the syngas. An F after the case number means that fluidized beds of zinc titanate **w**e**re us**e**d to r**e**mov**e **sul**f**ur sp**e**ci**e**sfrom th**e **syngas.**

Case 12 uses in-situ desulfurization (FineOx mixed with the coal slurry feed) to capture 50% of the sulfur in the slag leaving the gasifier. Fluidized beds of zinc titanate are used to remove the remaining sulfur external to the gasifier. Sulfur removed by the zinc titanate is recovered as sulfuric acid. This case is very similar to case 10F, except that in-situ desulfurization is used in the gasifier.

Case 13 uses an entrained bed of dolomite, injected into the syngas as a dry powder, to capture 90-95% of the sulfur as CaS. The remaining sulfur is removed in fluidized beds of zinc titanate. The spent dolomite, along with the SO, from the regeneration of the **zinc titan**\_**t**e**, i**s **oxidiz**e**dto CaS0**4 **for disposal.**

In Case 14, fine particles of iron oxide are passed once through a fluidized bed desulfurizer and a fluidized bed regenerator before being mixed with the feed coal slurry as an in-situ desulfurization additive. Total sulfur removal is about 96%. The sulfur captured by the iron oxide inside the gasifier (50%) is disposed of along with the slag, while the sulfur captured in the fluidized bed desulfurizer (46%) is recovered as sulfuric acid. All of the above cases recover 98% of the sulfur. However, at this time, we do not believe that the addition of a zinc titanate desulfurizer to raise the Case 14 sulfur recovery to 98% can be justified.

Case 15 uses four air-blown gasifier and hot gas cleanup trains compared to the previous seven cases where two oxygen-blown gasifier and hot gas cleanup trains are used. The hot syngas is desulfurized in a GE moving bed zinc titanate desulfurizer system; and sulfur is recovered as sulfuric acid. Selective Catalytic Reduction (SCR) is used downstream of the turbines to control NO, emissions.

Case 16 uses the exact same process configuration as Case 15, except that the yasifier is operated at 300 psig rather than at 480 psig. The purpose of doing cases at two different pressures is to investigate the effect of operating pressure on the economics of **IGCC pow**e**r plants bas**e**d on air-blownentrain**e**dbed ga**s**i**f**i**e**r**s**.**

use of a once-through, non-regenerable sorbent<br>solves an air pollution problem by creating a cleanup base case (in terms of efficiency and all

solves an air pollution problem by creating a cleanup base case (in terms of efficiency and all solid waste disposal problem, with its attendant the key cost numbers) used zinc titanate for bulk solid waste disposal problem, with its attendant the key cost numbers) used zinc titanate for bulk<br>long-term liability.<br>desulfurization and sulfuric acid plants for sulfur desulfurization and sulfuric acid plants for sulfur recovery. Recovering sulfur in the elemental Entrained Flow Gasification for Power<br>
form resulted in plants with operating costs only Generation Systems. In *Proceedings of the* form resulted in plants with operating costs only Generation Systems. In *Proceeding*<br>
Slightly higher than the base case. With respect Tenth Annual Gasification and Gas slightly higher than the base case. With respect *Tenth Annual Gasification and Gas* to the zinc titanate reactor design, the plants *Cleanup Systems Contractors Review* using fluidized beds were more efficient than *Meeting*, ed. V.P. Kothari and J.<br>the ones using moving beds. This difference p.15-24. DOE/METC-90/6115. the ones using moving beds. This difference p.15-24. DOE/MET<br>can be attributed largely to the power NTIS/DE90009689. can be attributed largely to the power consumption of the moving bed regenerator's<br>recycle compressor. However, it should be noted that the moving bed design is much closer<br>
to commercial demonstration than the fluidized<br>
Entrained Flow Gasification for Power to commercial demonstration than the fluidized bed design. Generation Systems. In *Proceedings of the*

The analytical work from the last PDU test 65. DOE/METC-91<br>
paring the durabilities of four zinc titanate NTIS/DE92001101. comparing the durabilities of four zinc titanate formulations in real Texaco syngas will be completed. The best hot gas cleanup process economics case (10F) and the cold gas cleanup base case (1) are being updated to include some recent process improvements. Also, cost numbers for these two cases will be recalculated in terms of 1992 dollars. The accomplishments of this research program, which is scheduled to terminate September 30, 1992, will be summarized in a Final Report. An integrated PDU will not be built.

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