LF-4.4 Selective Methane Oxidation Over Promoted Oxide Catalysts

CONTRACT INFORMATION

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OBJECTIVES

The objective of this research is to selectively oxidize methane to C_2 hydrocarbons and to oxygenates, in particular formaldehyde and methanol, in high space time yields under milder reaction conditions than heretofore employed over industrially practical catalysts. In particular, air, carbon dioxide, or oxygen, rather than nitrous oxide, is being used as the oxidizing gas in a continuous flow reactor system and a wide range of reaction conditions, e.g. temperature, pressure, and gas hourly space velocity, is being explored to maximize the space time yields of the desired products. All of the investigated processes are catalytic and aimed at minimizing gas phase oxidation reactions.

BACKGROUND INFORMATION

Saturated linear hydrocarbons, particularly methane, are major components of natural gas and of the gas produced by certain gasifiers. While methane makes an excellent gaseous fuel, it is desirable to convert it to higher molecular weight products for transportation, storage, and for utilization as chemical feedstocks. The desired reactions are shown below for methane only:

$$CH_4 + 0.5 O_2 \rightarrow CH_3OH \qquad [1]$$

$$CH_4 + O_2 \rightarrow CH_2O + H_2O$$
 [2]

$$2CH_4 + O_2 \rightarrow C_2H_4 + 2H_2O \qquad [3]$$

$$2CH_4 + 0.5 O_2 \rightarrow C_2H_6 + H_2O.$$
 [4]

Another reaction of potential interest is

 $2CH_4 + 2CO_2 \rightarrow C_2H_4 + 2CO + 2H_2O.$ [5]

After Keller and Bhasin published their research results for methane coupling over a decade ago (1), many laboratories have been striving to develop efficient methane conversion catalysts and technologies. At present, there is no commercial technology for processes of the type represented by Equations [1]-[5] above, despite the sizeable patent and open literature on this subject. Various aspects of the state of the art of methane oxidation, including early developments, have been reviewed by Foster in 1985 (2), Gesser et al. in 1985 (3), Pitchai and Klier in 1986 (4), Scurrell in 1987 (5), Lee and Oyama in 1988 (6), Hutchings et al. in 1989 (7), Amenomiya et al. in 1990 (8), Lunsford in 1990 and 1991 (9,10), Mackie in 1991 (11), and Hamid and Moyes in (1991) (12). Therefore, the literature will not be extensively reviewed here.

PROJECT DESCRIPTION

While the catalytic oxidative coupling paths [3] and [4] show considerable promise, it is evident from patent examples that the process conditions are still quite severe, in particular that the reaction temperature, in the range 650-800°C, is still too high. Reactions leading to oxygenates (Equations [1] and [2]) are more difficult to conduct selectively, but they have been identified as being very desirable, particularly the oxidation to methanol At the same time, the standard free (13). energy of all the oxidations [1]-[4] is negative over a wide range of temperatures, establishing a thermodynamic driving force for these reactions even at room temperature should an effective catalyst be found. More practical considerations led us to seek a desirable temperature range of 350-650°C. The lower limit of 350°C is based on experience with the dehydration of most oxide catalysts, which lose water at temperatures \leq 350°C. The upper limit of 650°C is in the range of temperatures at which uncontrolled free radical reactions will occur and often will lower the selectivity by driving the oxidation process to CO and CO₂. Hence, it is desirable to investigate and develop catalysts that promote partial oxidations of methane to C₂⁺ hydrocarbons, methanol, or formaldehyde in the temperature range of 350-650°C.

Oxide catalysts were chosen for this research that are surface doped with small amounts of acidic dopants. It was proposed that, for example, the very basic Sr/La_2O_3 catalyst that is active in the formation of methyl radicals, and therefore of C_2^+ products (14,15), can be doped with Lewis acidic oxides or other acidic groups to increase further its activity and selectivity to C_2 products.

The research being carried out under this U.S. DOE-METC contract is divided into the following three tasks:

- Task 1. Maximizing Selective Methane Oxidation to C_2^+ Products Over Promoted Sr/La₂O₃ Catalysts.
- Task 2.Selective Methane Oxidation to
Oxygenates.
- Task 3. Catalyst Characterization and Optimization.

Task 1 deals with the preparation, testing, and optimization of acidic promoted lanthana-based catalysts for the synthesis of C_2^+ hydrocarbons. Task 2 aims at the formation and optimization of promoted catalysts for the synthesis of oxygenates, in particular formaldehyde and methanol. Task 3 involves characterization of the most promising catalysts so that optimization can be achieved under Tasks 1 and 2.

RESULTS

PART 1. Methane Oxidation Over Silica

In our previous studies with Cu/Fe oxide and zeolite dual redox methane activation catalysts, the effect of the quartz beads that are used to dilute the catalysts being tested for the selective oxidation of methane to oxygenates was investigated (16,17). It was found that the ability of the quartz beads to activate methane below 700°C was very low. However, above 700°C, appreciable conversion of methane and oxygen was observed, and the principal oxidation product consisted of the **C**₂ hydrocarbons. At the same time, there was a significantly increasing selectivity towards CO relative to CO₂ and CH₂O.

Since many supported metal oxide catalysts being studied for selective oxidation of methane utilize silica as a support (4,11,18-24), including the Pd/SiO₂ catalyst investigated during the previous project (17), the reactivity and selectivity of two common silica supports was determined. It had been shown that silica itself has discernible activities for methane oxidation to formaldehyde (20,22,25-29). Kasztelan and Moffat (22) have shown that up to 4.5% of the methane co-fed with O_2 can be converted at 593°C at relatively high contact times, but selectivity to formaldehyde was poor (8%) and no formaldehyde was detected with N_2O as oxidant. In addition to using silica, Kastanas et al. (25) reported a detailed study on partial oxidation of methane over Vycor and on quartz walls of reactor tubing. In the temperature region employed (620-720°C), C₂ hydrocarbons were observed as coproducts. Parmaliana et al. (28) recently reported that precipitated and sol-gel silicas have higher activities than MoO₃ catalysts supported on silica (Cabosil and gel), and it was noted that high temperature treatment (1000°C) of the silica catalyst was very beneficial for methane conversion. Therefore, the catalytic activity of

a number of silicas was investigated for converting methane to products under our reaction conditions that are directed toward using lower reaction temperatures.

Experimental

Fumed silica (Cabosil) and silica gel (Grace 636 gel) obtained from Aldrich with surface areas of 385 and 480 m²/g, respectively, have been used in this research. Catalytic testing was carried out with a fixed-bed continuous-flow 9 mm OD (7 mm ID) quartz reactor using 0.100-0.125 g of catalyst. The system had two independently controlled inlet gas lines, and a standard reactant mixture of $CH_4/air (1.5/1)$ was at under ambient pressure.

The principal products analyzed by online sampling of the exit gas using gas chromatography were CO₂, C₂ (C₂H₆ + C₂H₄), $C_3 (C_3 H_8 + C_3 H_6)$, CO and H_2O . Condensable water-soluble products, i.e. formaldehyde in particular, were collected in two water-filled scrubbers in series, the first was kept at room temperature and the second at 0°C. Formaldehyde was quantitatively determined by the modified Romijn's iodometric titration method (30), which has been well-established as a reliable method for determining small amounts of formaldehyde in aqueous solutions. In the present research, the carbon mass balance was always better than 90% and usually better than 95%.

Results

The pure silica gel was tested for the activation of methane in the temperature range of 630-780°C, and the experimental results are given in Table 1. The data in this table were obtained after designing the reaction conditions (CH₄/air mixture flow rates and temperatures) so that the methane conversions were at a

TABLE 1. Methane Conversion, Formaldehyde Space Time Yields, and Product Selectivities Over the Pure SiO_2 Gel Catalyst with $CH_4/Air = 1.5/1$ Reactant at Ambient Pressure and Different Reaction Temperatures and Gas Hourly Space Velocities (GHSV)

<u>Temp.</u> (<u>°C)</u>	GHSV (ℓ/kg/hr)	CH₄ Conv. (mol%)	CH ₂ O Yield (g/kg/hr)	CH ₂ O Sel.*	C ₂ Sel.ª	CO ₂ Sel.ª	CO Sel.ª
630	8,000	0.91	25.8	49.0	4.6	6.8	39.7
680	17,500	1.53	77.7	40.2	6.4	5.0	48.3
730	70,000	1.36	267.0	38.8	11.4	8.4	41.4
780	280,000	1.20	549.2	21.2	33.1	3.7	41.5

^aProduct Selectivity in Carbon atom%.

comparable level. It is evident that the overall selectivity to CO and CO₂ did not vary considerably with the reaction temperature at relatively constant methane conversions. On the other hand, lower reaction temperatures enhanced the selectivity toward clearly formation of formaldehyde over the synthesis of C_2 hydrocarbons, while the total selectivity toward the C_2 hydrocarbons was increased by increasing the reaction temperature. It is also seen that increasing the GHSV of the reactants greatly increased the space time yield of CH₂O. The productivity of nearly 550 g CH₂O/kg catal/hr at 780°C and GHSV = $280,000 \ell/kg$ catal/hr is a very high yield, but these reaction conditions are such that the methane conversion level is low.

The same sequence of experiments was carried out with the Cabosil silica and similar trends were observed, with some notable differences. In particular, the Cabosil was less active than the silica gel, and much less CO was observed. For example, at 730°C and GHSV = $70,000 \ \ell/kg/hr$ the methane conversion was

only 0.31 mol%, and the formaldehyde space time yield was 75.7 g CH₂O/kg catal/hr. The observed selectivities were 46.0% CH₂O, 39.1% C_2 hydrocarbons, 14.9% CO₂, and 0% CO.

The apparent activation energies of CH_4 conversion to products, the formation of CH_2O , and the formation of C_2 products were calculated from the data obtained in the 630-780°C temperature range for both samples of silica. The results are given in Table 2.

TABLE 2. Apparent Activation Energies (± 5 kcal/mol) for Methane Conversion and C₂ Hydrocarbon and CH₂O Formation Over Silica Catalysts (reaction conditions given in Table 1)

Catalyst	Appare: CH	tion Energy CH ₂ O	
Cabosil	34	57	26
Silica gel	47	68	41

The influence of temperature on the apparent activation energies is consistent with the observed selectivities, e.g. increasing selectivity toward the C2 product with increasing reaction temperature. In addition, insight into mechanistic considerations is provided. For example, the apparent activation energy is significantly lower for CH₂O generation compared to that for C_2 formation, and this indicates there are significant mechanistic differences in the pathways leading to the formation of these products. In addition, if formaldehyde were formed in the gas phase by the reaction of methyl radicals and oxygen, the overall activation energy for formaldehyde formation would be at least equal to that of methane conversion. However, the apparent activation energies for formaldehyde formation are appreciably less than those observed for methane conversion. This suggests that formaldehyde is formed by a surface reaction over the silica catalysts. The apparent activation energies should include terms for surface reactions, which could give the lower values observed. On the other hand, the C_2 hydrocarbon formation proceeds in many cases via gas phase methyl radical coupling (31,32). The apparent activation energy for C₂ products are 57 kcal/mol over the Cabosil and 68 kcal/mol over the silica gel catalyst. These values are much higher than the activation energies for methane conversion, which implies that the methyl radical desorption processes are difficult ones.

To attain a better understanding of the silica support/catalyst system for methane oxidation, the methane conversions and the product selectivities were determined over a wide range of the reactant flow rate. In this experiment, a constant, but high, reaction temperature of 780°C was utilized with the silica gel catalyst. The methane conversion levels, the space time yields of formaldehyde, and the product selectivities, where C_2 = ethane + ethene, are given in Table 3.

Because of the range of high space velocities employed, blank tests with the empty reactor were carried out, and they showed that contributions from reactor wall and gas phase reactions were negligible. Table 3 shows that at very high flow rates, very high productivities of formaldehyde were obtained. At the higher flow rates (short contact times) a linear dependence on the methane conversion is obtained, indicating that these experiments were in the differential reactor regime where there is no diffusion limitation.

In Figure 1, the product selectivities are plotted against the methane conversion level (mol%). The C_2^+ product selectivities plotted here are the individual ethane (C_2) and ethene (C_2^-) selectivities. It appears that the C_2H_6 and CH_2O products exhibit parallel behavior, i.e. decreasing selectivities with increasing methane conversion levels, which corresponds with decreasing reactant gas flow rate and increasing residence time over the silica. This indicates that these two products are primary products, while the carbon oxides are secondary products.



FIGURE 1. Product Selectivity as a Function of the Methane Conversion Level at 780°C with $CH_4/Air = 1.5/1$ Reactant. The Reaction Conditions are Given in Table 3.

TABLE 3. Methane Conversion, Formaldehyde Space Time Yields, and Product Selectivities Over the Pure SiO_2 Gel Catalyst with $CH_4/Air = 1.5/1$ Reactant at Ambient Pressure and 780°C with Different Gas Hourly Space Velocities (GHSV).

GHSV (ℓ/kg/hr)	CH₄ Conv. (mol%)	CH ₂ O Yield (g/kg/hr)	CH ₂ O Sel.ª	C ₂ Sel.*	CO ₂ Sel.ª	CO Sel.ª
35,000	5.96	147.5	9.8	19.5	11.5	59.2
52,500	4.95	234.3	13.5	18.0	8.9	59.6
70,000	3.96	307.0	15.0	19.0	7.3	58.7
105,000	3.09	352.3	14.9	19.8	5.5	59.8
140,000	2.65	344.7	13.2	21.8	5.5	59.5
210,000	1.59	487.0	19.1	30.5	3.7	48.8
280,000	1.20	549.2	21.2	33.1	3.7	41.5
420,000	1.00	726.2	23.3	35.3	2.8	38.6
560,000	0.68	812.8	28.0	38.8	3.2	30.0

^aProduct Selectivity in Carbon atom%.

Conclusions

Silicas that are sometimes utilized as supports for oxide catalysts being investigated for selective methane conversion to C_2^+ hydrocarbons (ethane and ethene) or to oxygenated products such as formaldehyde and methanol exhibit catalytic activity without the presence of surface-held promoters. It was shown that the silicas have high selectivities toward partial oxidation products, and the space time yields of formaldehyde are very high under optimum reaction conditions, e.g. low temperatures and low conversions.

Short residence times enhanced both the C_2^+ hydrocarbons and formaldehyde selectivities over the carbon oxides even within the

differential reactor regime at 780°C. This suggests that the formaldehyde did not originate from methyl radicals, but rather from methoxy complexes formed upon the direct chemisorption of methane at the silica surface at high temperature. Very high formaldehyde space time yields (e.g. 812 g/kg catal/hr at the gas hourly space velocity = $560,000 \ell(NTP)/kg$ catal/hr) could be obtained over the silica gel catalyst at 780°C with a methane/air mixture of These yields greatly surpass those 1.5/1. reported for silicas earlier, as well as those over many other catalysts. However, the methane conversion levels were < 1% at the high GHSV where high space time yields were achieved.

The experimental results indicate that there are two different, possibly parallel,

mechanistic pathways for the conversion of surface activated methane into formaldehvde and C_2^+ products over silica. This has been discussed in greater detail elsewhere (33), where it is proposed that the first involves conversion of surface methoxy species into formaldehvde and the second involves desorption of surface-held methyl groups as gas phase methyl radicals that subsequently couple to form C_2H_6 . These two pathways have different apparent activation energies that are reflected in the temperature dependence observed in the product selectivity trends.

<u>PART 2</u>. Methane Oxidation Over Sr/La_2O_3 Catalysts

The basic 1 wt% Sr/La_2O_3 catalyst has been shown to be a very active methane coupling catalyst (14,15). AMOCO Oil Co. has prepared a large batch of this catalyst for further investigation and has provided a portion of this catalyst to us for catalytic testing.

To determine the degree of reproducibility of catalyst testing of the AMOCO Oil Co. Sr/La₂O₃ catalyst, three different researchers tested four different portions of the catalyst. The catalytic tests of the 1 wt% Sr/La₂O₃ catalyst were carried out with a CH₄/air = 1/1 reactant mixture at 1 atm and with GHSV = 70,000 ℓ/kg catal/hr over the range of temperatures of 500-700°C. It was found that this catalyst was active at 500°C, and it is shown in Figure 2 that catalytic behavior of the Sr/La_2O_3 catalyst was reproducible and that no deactivation was observed.

In this figure, the open data points were obtained while increasing the temperature, while the solid data points were obtained while the temperature was decreased in a stepwise manner. The conversion at 500°C is very sensitive to the reaction temperature since the methane oxidation reaction, once initiated, is highly exothermic. Thus, the data points indicated for 500°C have appreciable scatter, and the data points indicating $\approx 10-13\%$ conversion could actually be for a somewhat higher temperature than 500°C.

It is notable that methane was converted to products over the Sr/La_2O_3 catalyst at temperatures as low as 500°C. This contrasts with the typical steam reforming reaction of methane over commercial Ni-based catalysts that is carried out at $\approx 850°$ C. At temperatures higher than 550°C under the reaction conditions employed here, over 70% of the oxygen was consumed. Thus, at the higher temperatures studied, the conversion level of CH₄ was limited by the availability of the O₂ reactant.



i

FIGURE 2. Methane Conversion and C_2^+ Yield (mol%) Over 1 wt% Sr/La₂O₃ Catalyst with CH₄/Air = 1/1 at Ambient Pressure and GHSV = 70,000 ℓ/kg catal/hr.

The %yields of total C_2 products as a function of temperature under these reaction conditions, i.e. CH₄/air = 1/1 at 1 atm and with GHSV = 70,000 ℓ /kg catal/hr, are shown in Figure 2. The % yield is defined as the product of the total C₂ selectivity (mol% ethane + ethene) and the total conversion of methane (mol%). Once again, the data indicates that the Sr/La₂O₃ catalyst is quite reproducible and stable.

<u>PART 3</u>. Oxidative Coupling of Methane Over Sulfate-Doped Sr/La₂O₃ Catalysts

Since the formation of surface carbonates might be at least partially responsible for deactivation of basic catalysts under some methane conversion reaction conditions, the catalytic behavior and/or stability of the very basic Sr/La₂O₃ might be enhanced by acidic doping. On the analogy of earlier findings that sulfate ion strongly enhanced the acidic properties of iron oxide (34), as well as alumina and titania (35), sulfate was used in our present study as an acidic surface dopant to improve the catalytic performance of the 1 wt% Sr/La₂O₃ catalyst.

Experimental

The 1 wt% Sr/La_2O_3 catalyst with a surface area of 6.5 m²/g was obtained from Amoco Oil Co. under their Natural Gas University Research Program. The sulfated Sr/La_2O_3 catalysts were produced by the incipient wetness impregnation technique. The appropriate amount of $(NH_4)_2SO_4$ was dissolved in deionized water, the measured quantity of Sr/La_2O_3 was added, and the slurry was continuously stirred with a magnetic stirrer until dryness was achieved. This was followed by drying the solid overnight at 120°C and calcination in air at 600°C for 6 hr. Prior to catalytic testing, the samples were activated *in* situ under air (or O_2) flow at 500°C for 1 hr unless stated otherwise. The gases used in this study were zero grade purity and were used without further purification

Catalytic testing was carried out in the fixed-bed continuous-flow 9 mm OD (7 mm ID) quartz reactor using 0.1000 g of catalyst, as previously described.

Results and Discussion

Effect of Sulfate Concentration. The effect of sulfate content on the catalytic behavior of the 1 wt% Sr/La₂O₃ catalyst was examined at 500°C, CH₄/air = 1/1, $p_{(total)}$ = 1 atm, and GHSV = 70,000 ℓ /kg catal/hr. The content of sulfate added to the 1 wt% Sr/La₂O₃ varied as 0, 0.5, 1.0, 2.0, and 4.0 wt% SO₄²⁻ of the total weight of catalyst. The 1 wt% SO₄²⁻/1 wt% Sr/La₂O₃ showed the largest promotional effects on the methane conversion (Figure 3) and C₂⁺ selectivity (Figure 4).



FIGURE 3. Effect of Sulfate Content on Methane Conversion at 500°C Over the 1 wt% Sr/La_2O_3 Catalyst (0.1000 g) with a CH₄/Air = 1/1 Reaction Mixture at a Total Pressure of 1 atm and GHSV = 70,000 ℓ/kg catal/hr.



FIGURE 4. Effect of the Sulfate Content on the C_2^+ Selectivity Observed at 500°C Over the 1 wt% Sr/La₂O₃ Catalyst. The Experimental Parameters are given in Figure 3.

From these figures, it can be seen that adding an acidic sulfate promoter to the catalysts to a 1 wt% level increased the overall conversion of methane and selectivity to C_2 hydrocarbons by factors of 1.5-2.0. The sulfate doping of the catalyst also increased the %yields of the C₂ hydrocarbon products, where the %yield is defined as the product of the total C₂ selectivity [C mol% ethane + ethene] and the total conversion of methane [mol fraction]. Thus, adding 1 wt% SO_4^{2-} to the catalyst increased the %yield at 500°C from 3% to 7.5-11%, e.g. the catalyst showing 45% C₂ selectivity in Figure 4 exhibited a %yield for the C_2 hydrocarbons of 9%. At this reaction temperature, all sulfated catalysts exhibited higher methane conversions and C₂ selectivities than the non-sulfated Sr/La_2O_3 catalyst.

Effect of Reaction Temperature. The effect of temperature on the catalytic activity of the 1 wt% $SO_4^{2^-}/1$ wt% Sr/La_2O_3 catalyst was

determined and compared with the nonsulfated The sulfate-promoted catalyst, catalyst. compared to the nonsulfated one, again showed a large increase for methane conversion at 500°C, as indicated in Figure 5. Upon increasing the temperature stepwise to 700°C, the conversion levels increased. However, the extent of the promotional effect decreased with increasing temperature, and practically no effect at reaction temperatures >650°C was observed. At the high CH, conversion levels, the reactant oxygen was nearly or totally depleted (>85-90%), which limited the oxidative reactions with This, as well as other factors, methane. contributed to the converging catalytic behavior.



FIGURE 5. Effect of Temperature on Methane Conversion in the Range of 500-700°C. (a) 1 wt% Sr/La_2O_3 with Increasing Reaction Temperature (▲), and then Subsequently Decreasing the Reaction Temperature Stepwise from 700°C to 500°C (×); (b) 1 wt% $SO_4^2/1$ wt% Sr/La_2O_3 with Increasing Reaction Temperature (=), and then Subsequent Decreasing the Reaction Temperature (\Box). Weight of Catalyst = 0.1000 g; Reactant CH₄/Air = 1/1; Total Pressure = 1 atm; and GHSV = $70,000 \ \ell/kg$ catal/hr.

Upon sequentially decreasing the temperature after reaction the 700°C experiment, the former promoting effect was not observable even at 500°C. Plots of the C_2^+ selectivities and C_{2+} %yields exhibited the same behavior as the conversion curves in Figure 5. In those plots, not shown here, the presence of the sulfate anion caused a large promoting effect at 500°C, where the C_{2+} selectivity and C_{2+} yield increased from 32.2 to 45.1% and from 3.4 to 8.0%, respectively. However, the disappeared promotional behavior after completing the temperature cycle. In both cases, the %yield of C₂ hydrocarbons was ≈2.4% for the final 500°C tests.

A new pretreatment of the tested catalyst in air at 500°C for one hour did not restore the former enhanced activity obtained at 500°C. One possible explanation of this instability is the high O_2 conversion (>85-90%) at the higher reaction temperatures, resulting in a reducing environment that could transform the sulfate to a volatile component. This would result in the loss of the acidic surface dopant. In addition, the thermal treatments utilized during the catalytic testing could have altered the surface areas of the catalysts.

Both of these possibilities were examined as causes of the loss of the enhanced catalytic properties of the sulfated catalyst that were observed for the moderation temperature reaction conditions. The pretreated sulfated catalyst had an initial BET surface area of 16.2 m^2/g and a sulfate content of 0.93%. After the catalytic testing sequence that reached 700°C, the catalyst had a lower surface area of 8.2 m^2/g and a sulfate content of 0.36%. The corresponding surface areas of the pretreated and tested Sr/La_2O_3 catalyst were 10.4 and 7.0 m^2/g , respectively. Thus, there was a loss of both sulfate and surface area induced by the high temperature testing. The final surface areas of the catalysts after high temperature testing were similar.

Effect of Reactant Flow Rate at Moderate Temperature. The 1 wt% $SO_{4}^{2-}/1$ wt% Sr/La_2O_3 catalyst was pretreated for these experiments in air at 500°C for 1 hr, and then the methane conversion reaction was carried out at 550°C with a constant reactant gas composition of $CH_4/Air = 1/1$. The reaction started with a GHSV = $70,175 \ \ell/kg$ catal/hr, which was then decreased stepwise. As the GHSV was diminished to 17,120 ℓ/kg catal/hr, the CH₄ conversion gradually decreased from 15.38 to 6.79 C-mol% (Figure 6A), the C_2^+ selectivity decreased from 35.50 to 5.01 C-mol% (Figure 6B), but the CO_x selectivity increased from 62.63 to 94.68 C-mol%. The C_2^+ %yield, of course, also decreased rapidly, i.e. from 5.46 to 0.34 C-mol%. Upon decreasing the GHSV further to 5,388 ℓ/kg catal/hr, the CH₄ conversion surprisingly increased to 8.27 Cmol%, while the C_2^+ selectivity and %yield decreased further (shown in Figure 6B). In this case, nearly complete conversion of methane to CO_x (99.4 C-mol%) was obtained, i.e. the catalyst was practically deactivated towards C_2^+ formation.

When the flow rate was increased stepwise, the catalytic behavior changed in the opposite direction to that described above. As shown in Figure 6 (A and B), the conversion level of methane and the C_2^+ selectivity increased with increasing GHSV. In each case, a hysteresis in behavior was observed, where neither the initial methane conversion nor total C_2 selectivity was achieved upon returning to the initial reactant gas flow of GHSV = 70,175 ℓ/kg catal/hr. After completing the gas flow cycle, the CH₄ conversion, the C_2^+ selectivity, and the %yield of C_2^+ hydrocarbons had increased to 11.27, 18.31, and 2.06 C-mol%, respectively, while the CO_x selectivity decreased to 80.00 C-mol%. Thus, the C_2^+ selectivity was $\approx 50\%$ of the initial value, while the C₂⁺ %yield was less than half of the original yield obtained at the initial flow rate of GHSV = $70,175 \ell/kg$ catal/hr.



FIGURE 6. Effect of Total Reactant Flow Rate on [A] Methane Conversion and [B] C_2^+ Hydrocarbon Selectivity at 550°C Over the 1 wt% SO₄²⁻/1 wt% Sr/La₂O₃ Catalyst (0.1000 g) with CH₄/air = 1/1 at a Total Pressure of 1 atm, and with (a) Decreasing (\blacksquare , solid line) and (b) Increasing (\square , dashed line) Flow Rates. GHSV was Changed in a Stepwise Manner From 70,175 to 5,388 ℓ /kg catal/hr and then the Procedure was Reversed.

Reactivation via Higher Temperature Treatment. After the experiments described above wherein the gas flow was systematically decreased and then increased to its original value (70,175 ℓ/kg catal/hr), the catalytic performance was in a partially deactivated state compared with the initial activity and selectivity (Figure 6). To overcome this deactivated state. the temperature was increased stepwise at constant GHSV beginning at 550°C. By increasing the temperature to 580°C, the CH, conversion slowly increased (Figure 7A), and then upon increasing the temperature further to 585°C the methane conversion suddenly jumped to a much higher activity. Further increasing the reaction temperature from 585°C up to 600°C caused only gradual increases in CH. conversion, where the methane conversion was ≈19%.

sudden increase in The methane conversion at 585°C was accompanied by an even more pronounced increase in C_2^+ selectivity, as shown in Figure 7B. At 600°C, the C_2 selectivity was $\approx 43\%$. The CO. selectivity pattern was the mirror image of the C_2 selectivity behavior shown in Figure 7B. Upon decreasing the temperature stepwise to 550°C, both the CH₄ conversion and C_2 selectivity decreased somewhat but tended to stabilize at ≈15% and 37%, respectively. These values compare with 15.38% and 35.50% levels observed for the initial test with the fresh catalyst, as shown in Figures 6A and 6B. Thus, the catalyst was regenerated by this higher temperature treatment under reaction conditions. However, Figures 7A and 7B show that lowering the reaction temperature below 550°C led to deactivation of the catalyst in terms of both CH₄ conversion and C₂ selectivity.

These changes in activity and selectivity appear to be interrelated to the partial pressure of CO_2 over the catalyst. It is now being established by a number of research groups that



FIGURE 7. Effect of Temperature on [A] the Conversion of CH₄ and [B] C₂⁺ Selectivity Over the Partially Deactivated 1 wt% SO₄²⁻/1 wt% Sr/La₂O₃ Catalyst (0.1000 g) with CH₄/Air = 1/1 at a Total Pressure of 1 atm and GHSV = 70,175 ℓ/kg catal/hr. The Reaction Temperature was Increased Stepwise from 550 to 600°C (\blacksquare , solid line), and then (after the Recovery of the Catalytic Performance) it was Decreased to 530°C (\square , dashed line).

basic catalysts are susceptible to carbonate formation on the catalysts and that this carbonate layer can directly affect the resultant catalytic properties. Indeed, chemical analysis of this catalyst after the described GHSV and temperature cycles showed that the catalyst contained 15.35% carbonate. Sulfate analysis showed that the sulfate promoter was not lost from the catalyst (0.87% SO₄²⁻) under the moderate reaction conditions that were employed during this testing program, where the temperature never exceeded 600°C.

Stability Test of the $SO_4^{2-}/Sr/La_2O_3$ Catalyst. The 1 wt% $SO_4^{2-}/1$ wt% Sr/La_2O_3 catalyst was tested under steady state conditions to demonstrate its stability under the moderate reaction conditions being utilized in this research. The sample was pretreated using the standard method of heating at 500°C in flowing air (GHSV \approx 35,000 ℓ/kg catal/hr) for 1 hr. The methane conversion reaction was then carried out at 550°C in the reactant gas mixture of CH₄/air = 1/1 with GHSV = 70,040 ℓ/kg catal/hr.

As shown in Figure 8, the catalyst was stable under these conditions. During the entire 25 hr experiment, the conversion of CH₄ was ≈ 20 C-mol%, while the C₂⁺ selectivity was 50 C-mol%. The C₂⁺ space time yield was 10 mol of C₂⁺ hydrocarbons/kg catal/hr, corresponding to some 290 g/kg catal/hr.

The C_2^{-}/C_2 (ethene/ethane molar ratio) and CO_2/CO ratios also remained quite constant during the test. The CO_2/CO ratio remained steady at ≈ 2.2 . The average C_2^{-}/C_2 ratio was 0.71, but this ratio shifted in time from an initial value of 0.74 to 0.68. This shift might also be reflected in the O_2 conversion level, which after a short initial period of increasing slightly, decreased during the last 21 hr of the test by a few C-mol% (curve d in Figure 8).



FIGURE 8. Stability Test at 550°C of the 1 wt% SO₄²⁻/1 wt% Sr/La₂O₃ Catalyst (0.1000 g) with CH₄/Air = 1/1 at a Total Pressure of 1 atm and GHSV = 70,040 ℓ /kg catal/hr: (a) CH₄ Conversion (**II**); (b) Conversion of Oxygen (**IX**); (c) CO_x Selectivity (+); (d) C₂⁺ Product Selectivity (**II**); and (e) Yield of C₂⁺ Hydrocarbon Products (A).

Effect of the CH₄/Air Reactant Ratio on the Catalytic Activity and Selectivity. While the reactant gas flow was kept constant (GHSV = 70,040 ℓ/kg catal/hr) at the reaction temperature of 550°C, the CH₄/air ratio was increased stepwise from 1.01 to 40.77 over the SO₄²⁻/Sr/La₂O₃ catalyst. As the amount (and partial pressure) of methane increased relative to oxygen, the conversion of methane decreased significantly, i.e. from ≈15 to less than 0.5 Cmol% as shown in Figure 9. The drop in the activity was especially large upon increasing the CH₄/air ratio from 1 to ≈3, which yielded about a 4.5-fold decrease in the conversion of methane to products.

During the reverse process of decreasing the CH_4/air ratio, the CH_4 conversion increased in basically a reversible manner, as

shown by dashed curve b in Figure 9. Some deactivation was apparent at low reactant ratios, but it was rather small. This approximate reversibility is in marked contrast with the results obtained in the prior experiments at 550°C where the reactant gas flow rate (GHSV) was systematically decreased from 70,175 to 5,388 ℓ/kg catal/hr and then stepwise increased back to the original value while maintaining the CH₄/air reactant ratio at a constant value of 1 (see Figure 6). In that case, deactivation of atleast 20-25% was observed at all flow rates. As shown in Figure 9 for the current experiment, the CH, conversion exhibited much less deactivation upon completion of cycling the methane/air ratio.



FIGURE 9. Effect on the Conversion of CH₄ at 550°C Over the 1 wt% $SO_4^{2^-}/1$ wt% Sr/La₂O₃ Catalyst (0.1000 g) as the CH₄/air Reactant Ratio was (a) First Increased (II, solid line) and (b) then Decreased (II, dashed line). The Flow Rate was Constant with GHSV = 70,040 ℓ/kg catal/hr at a Total Pressure of 1 atm. The CH₄/air ratio was changed stepwise from 1.01 to 40.77 and then the procedure was reversed.

As the CH₄/air ratio was varied, the C₂⁺ selectivity showed surprising behavior. As the reactant ratio was initially increased from 1.01 to 3.45, the selectivity toward C₂⁺ hydrocarbons decreased very rapidly from \approx 32 to 13 C-mol%, as shown in Figure 10A. As the CH₄/air ratio was further increased to 40.77, the C₂⁺ selectivity reversed and increased quite linearly to over 50 C-mol%. The CO_x selectivity was the mirror image of the C₂⁺ selectivity.

The subsequent stepwise decrease in the CH₄/air reactant ratio resulted in rather reversible behavior. However, at the lowest ratios some loss of C₂⁺ selectivity was observed. As shown in Figure 10A, the final C₂⁺ selectivity obtained upon returning to the CH₄/air = 1.01 ratio was $\approx 85\%$ of the initially observed selectivity with the fresh catalyst.

It is noted here that as the CH₄/air ratio increased, the methane conversion decreased, as shown in Figure 9, and the formation rates of both the C_2 hydrocarbons and the CO_x products were quite small at high methane/air ratios. This is also reflected in the %yields of The %yield of the C_2^+ the products. hydrocarbon products decreased very rapidly with increasing CH₄/air ratio, as shown by in Figure 10B, and this is a reflection of the conversion level of CH₄ (see Figure 9). While the CH₄/air ratio increased from 1.01 to 3.24, the %yield of CH, decreased by more than a factor of 10 (from 4.81 to 0.45 C-mol%). When CH₄/air ratio reached its largest the experimental value (40.77), the methane % yield was only 0.25 C-mol%.

Decreasing the CH₄/air ratio at 550°C as the second part of the cycle of the experiment, it was shown that the productivity of the catalyst was nearly reversibility, as indicated in Figure 10B. However, some deactivation was evident at low reactant ratios, e.g. at the final ratio of CH₄/air = 1.01, the %yield of the C₂⁺ hydrocarbons was \approx 72% of the original value.





Analysis of the Catalysts. Additional experiments have been carried out with the sulfated catalysts, e.g. additional temperature programming studies and variation of pretreatment conditions. These have been described in our quarterly technical progress reports and will be included in our final technical report, but they will not be described in detail here. They give further evidence that the formation and decomposition of surface carbonate on these catalysts play an important role in controlling the activity and selectivity under the reaction conditions employed here. Surface and bulk analyses of these catalysts are being carried out, and some of the results are presented in Table 4, and some of these have been given previously in the text.

The analyses after the brief pretreatment of the sulfated catalysts at 800°C that were carried out in air or under helium indicate that sulfate was not lost from the catalysts and that the surface areas were maintained. After experiments carried out under reductive environments with reaction temperatures higher than 600°C, this was not the case. For catalysts analyzed to-date that were utilized under those reaction conditions, it was found that sulfate was lost from the catalyst and that the surface areas had decreased significantly. In addition, appreciably increased levels of carbonate were generally observed in those catalysts. Further chemical analyses are being carried out, and analyses by laser Raman spectroscopy, including in situ experiments are being carried out.

IABLE 4. Chemical and Surface Analysis of Sr/La_2O_3 -Based Ca	atalysts
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Sample	Sulfate (wt%)	Carbonate (wt%)	BET Area (m ² g ⁻¹)
(A) Before Reaction			******
1 wt% Sr/La ₂ O ₃		3.30	10.36
1 wt% SO_4^2 /Sr/La ₂ O ₃	0.93	4. 3	16.17
(B) Pretreatment only at 800°C	C (for 1 hr in Air or	He); no reaction	
1 wt% $SO_4^{2^-}/Sr/La_2O_3$ (Air	r) 0.96		15.18
1 wt% SO_4^2 /Sr/La ₂ O ₃ (He	.) 0.93		13.15
(C) After Reaction $(500 \rightarrow 700)$	→ 500°C; GHSV =	70,000 e kg ⁻¹ hr ⁻¹ ;	$CH_4/Air = 1/1)$
1 wt% Sr/La ₂ O ₃		7.50	7.03
1 wt% SO_4^2 /Sr/La ₂ O ₃	0.36	5.35	8.20
(D) After Special Reaction at $CH_4/Air = 1/1$)	550°C with Low GF	ISV (70,000 → 5,400	e kg ⁻¹ hr ⁻¹ ;
1 wt% $SO_4^{2-}/Sr/La_2O_3$	0.87	15.35	
Notes: (1) The chemical ana	lysis were carried or	ut by Galbraith Lab	oratories, Inc.

(2) The BET areas were measured with a Micrometrics Gemini-2360 instrument.

FUTURE WORK

Our research will proceed according to our work plan and will be carried out under the three designated tasks that are described in the **PROJECT DESCRIPTION.** During Year 2 of this research, we will finish work under Task 1 with the acid promoted Sr/La_2O_3 that we have shown to be a very active and selective catalyst for the oxidative coupling of methane to ethane and ethene under moderate reaction conditions. During this phase of the research, the role of CO₂ in directing the activity and selectivity of these basic catalysts will be delineated. Reaction conditions to overcome the deactivating effects of CO₂ will be determined.

Under Task 2, the objective is to direct methane conversion to the selective formation of oxygenates, especially methanol and formaldehyde. This will involve studying new catalysts and determining the influence of reaction conditions, such as pressure and gas phase additives, on enhancing the selectivity toward oxygenates. Insight into the surface chemistry that directs synthesis pathways to oxygenates will be provided. Research under Task 3, which catalyst characterization involves and optimization of the more promising catalysts, will continue to be carried out with the best industrially practical catalysts that we obtain.

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Further details of this research are provided in quarterly progress reports DOE/MC/29228-1 (January 1993) through -4 (September 1993).

REFERENCES

- G. E. Keller and M. M. Bhasin, <u>J. Catal.</u>, 73, 9 (1982).
- 2. N. R. Foster, <u>Appl. Catal.</u>, 19, 1 (1985).
- 3. H. D. Gesser, N. R. Hunter, and C. B. Prakash, <u>Chem. Rev.</u>, 85(4), 235 (1985).
- 4. R. Pitchai and K. Klier, <u>Catal. Rev.-Sci.</u> Eng., 28, 13 (1986).
- 5. M. S. Scurrell, Appl. Catal., 32, 1 (1987).
- 6. J. S. Lee and S. T. Oyama, <u>Catal.</u> <u>Rev.-Sci. Eng.</u>, **30(2)**, 249 (1987).
- G. J. Hutchings, M. S. Scurrell, and J. R. Woodhouse, <u>Chem. Soc. Rev.</u>, 18, 251 (1989).
- 8. J. H. Lunsford, <u>Catal. Today</u>, 6, 235 (1990).
- 9. J. H. Lunsford, in "Natural Gas Conversion" (Studies in Surface Science and Catalysis, Vol. 61), ed. by A. Holmen, K.-J. Jens and S. Kolboe), Elsevier, New York, 3 (1991).
- 10. J. C. Mackie, <u>Catal. Rev.-Sci. Eng.</u>, 33, 169 (1991).
- Y. Amenomiya, V. I. Birss, M. Goledzinowski, J. Galuska, and A. R. Sanger, <u>Catal Rev.-Sci. Eng.</u>, 32, 163 (1990).
- 12. H. B. A. Hamid and R. B. Moyes, <u>Catal.</u> <u>Today</u>, **10**, 267 (1991).
- F. M. Dautzenberg, in <u>Preprints, Symp.</u> on <u>Methane Activation, Conversion, and</u> <u>Utilization, PACIFICHEM '89</u>, Intern. Chem. Congr. of Pacific Basin Societies,

Honolulu, HI, Paper No. 170, pp 163-165 (1989).

- 14. J. M. DeBoy and R. F. Hicks, <u>Ind. Eng.</u> <u>Chem. Res.</u>, 27, 1577 (1988).
- J. M. DeBoy and R. F. Hicks, <u>J. Catal.</u>, 113, 517 (1988).
- K. Klier, R. G. Herman, S. DeTavernier, and J. I. DiCosimo, "Methane Oxidation Over Dual Redox Catalysts," Quarterly Technical Progress Report DOE/MC/26039-7, 25 pp (Oct. 1990).
- 17. K. Klier and R. G. Herman, "Methane Oxidation Over Dual Redox Catalysts," In "Proceedings of the Natural Gas Research and Development Contractors' Review Meeting (May 1992)," ed. by R. D. Malone, H. D. Shoemaker, and C. W. Byrer, DOE/METC-92/6125 (DE92001278, pp 251-265 (1992).

- H.-F. Liu, R.-S. Liu, K. Y. Liew, R. E. Johnson, and J. H. Lunsford, <u>J. Amer.</u> Chem. Soc., 106, 4117 (1984).
- K. J. Zhen, M. M. Khan, C. H. Mak, K. B. Lewis, and G. A. Somorjai, <u>J. Catal.</u>, 94, 501 (1985).
- 20. N. D. Spencer, J. Catal., 109, 187 (1988).
- 21. N. D. Spencer and C. J. Pereira, <u>J.</u> <u>Catal.</u>, 116, 399 (1989).
- 22. S. Kasztelan and J. B. Moffat, <u>J. Chem.</u> <u>Soc., Chem. Commun.</u>, 1663 (1987).
- S. Ahmed and J. B. Moffat, <u>J. Catal.</u>, 118, 281 (1989).
- Q. Sun, J. I. Di Cosimo, R. G. Herman, K. Klier, and M. M. Bhasin, <u>Catal.</u> <u>Letters</u>, 15, 371 (1992).

LF-4.5 Steady-State and Transient Catalytic Oxidation and Coupling of Methane

CONTRACT INFORMATION

Contract Number	DE-AC03-76SF00098
Contractor	Lawrence Berkeley Laboratory
	One Cyclotron Road
	Berkeley, CA 94720
Contractor Project Manager	Dr. Heinz Heinemann
Principal Investigators	Dr. Heinz Heinemann
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METC Project Manager	Mr. Rodney D. Malone
Period of Ferformance	August 1, 1992 to September 30, 1993

Schedule and Milestones

Four papers have been published on the mechanisms and site requirements for the oxidative coupling of methane to ethane and ethylene [1-3] and on the synthesis of thin catalytic films [12] during fiscal 1993. These publications also describe a unique inhibiting effect of water on the rate of undesired full oxidation pathways during oxidative coupling. Five quarterly reports have been written and submitted during the covered period [4]. These findings and recently reported models of surface and gas phase reactions of methane [5,6] suggest the use of membrane reactors and of cyclic methane decomposition schemes in order to avoid deleterious full oxidation reactions and to increase C_2 yields above 25%. In fiscal 1994, we will proceed with the testing of proton-conducting membranes that we have recently fabricated. We will also continue our emerging effort in cyclic decomposition of methane and scavenging of fragments on supported metal catalysts.

OBJECTIVES

This project addresses the conversion of methane and other components in natural gas using catalytic materials in packed-bed and membrane reactors. Our strategy is to identify catalytic sites responsible for selective methyl radical generation, in order to prevent direct oxidation of methane to CO_2 , and to separate reactive products (ethane and ethylene) from

 O_2 using membrane or cyclic reactors, in order to prevent their sequential oxidation to CO_2 . A CRADA between LBL, Orion ACT, and DOE went into effect on January 1, 1992 and covers most of the work reported here.

BACKGROUND INFORMATION

Oxidative coupling of methane is widely known to produce ethane and ethylene as

primary products and CO and CO₂ in both primary direct oxidation of methane and secondary combustion of C₂ products; these reactions combine methyl radical generation on oxide surfaces with coupling and oxidation of hydrocarbon free radicals in the gas phase. Full oxidation reactions also occur on surfaces during desired radical generation steps and lead to high yields of undesired CO₂.

We have previously reported that the oxidative coupling of methane to higher hydrocarbons occurs at temperatures below 600°C on Ca-Ni-K oxides. We have shown previously that water enhances the C_2 selectivity on Ca-Ni-K by inhibiting the oxidation of methane and of C₂ products to CO and CO₂. We propose that its role is to decrease the concentration of sites capable of multiple exchange between gas phase and lattice oxygen and extend these findings to Li/MgO catalysts. These sites, where oxygen availability appears to be high, appear to be responsible for deleterious total oxidation pathways on these materials.

RESULTS

Effects of Added Water on the Oxidative Coupling of Methane on Li/MgO.

Li/MgO materials have been widely studied for the oxidative coupling of methane at relatively high temperatures [7], where secondary gas phase reactions of desired C_2 products decrease their yields. Lower temperatures do not appear to increase C_2 yields because direct catalytic oxidation of methane becomes competitive with the formation of methyl radicals.

We have studied the reactions of CH_4/O_2 mixtures at low temperatures (550-

650°C) on Li/MgO in the presence and absence of added water. The presence of water is essential for the formation of C₂ products at these low reaction temperatures. Water inhibits oxidative reactions of methane that lead to the formation of CO and CO₂ products. For example, the hydrocarbon selectivity increases from 5 to 30 % when water is added to the CH_4/O_2 reactants at 600°C (Table 1). The selectivity increases even though the water also increases the level of methane conversion and thus the likelihood of secondary oxidation of primary C_2 products. The rate of the reaction also increases slightly, causing the CH₄ conversion to increase from 14 to 18% when water is added to the reactant mixture (Table 1). These effects occur without any direct involvement of water in steam reforming reactions, which would have led to higher selectivities to CO and CO₂ products. The presence of water allows the use of these metal oxide catalysts in low-temperature schemes for the oxidative coupling of methane.

The effect of water becomes weaker at higher reaction temperatures (Table 1), where oxidative coupling selectivity appears to be higher because of a smaller contribution of surface-catalyzed full oxidation of the methane reactant. This is consistent with our proposal, suggested by the findings reported below, which show that water inhibits surface-catalyzed oxidation steps by modifying the density and nature of oxygen species on metal oxide surfaces.

X-Ray photoelectron studies of selective and unselective preparations of Li/MgO and MgO preparations showed that high surface densities of oxygen species having a XPS binding energy of 534.1 eV. These oxygen surface species differ markedly in their binding energy from lattice oxygen (BE=532.4 eV) and appear to be responsible for oxygen activation

Temperature	Steam	Conversion (%) CH₄	Selectivity (%)		
(°C)			CO _x ^b	Hydrocarbons	C ₂ '/C ₂
550	Yes	6	85 (0)	15	<0.2
600	Yes	18	70 (0)	30	0.6
600	No	14	95 (2)	5	0.3
650	Yes	19	77 (3)	23	0.8
650	No	16	81 (2)	19	0.2

Table 1. Effect of Steam on Reactions of Methane with Oxygen on Li/MgO Catalysts

^a Methane, $1.5 \text{ cm}^3 \cdot \text{min}^{-1}$; O₂, $0.5 \text{ cm}^3 \cdot \text{min}^{-1}$; H₂O, $3.3 \text{ cm}^3 \cdot \text{min}^{-1}$.

^b Amount of carbon monoxide in brackets; CO_x selectivity is the sum of CO and CO_2 in gas phase and CO_2 on catalyst due to the formation of carbonate.

and for the formation of methyl radicals on MgO surfaces.

Active Surface Sites for Oxidative Coupling on Ca-Ni-K Oxides and Li/MgO

These effects of added water on Li/MgO catalysts resemble those we previously reported on Ca-Ni-K oxide catalysts [1], which also convert methane to CO_x and C_2 species at temperatures around 600°C. This resemblance led us to study both types of materials using temperature-programmed isotopic exchange (TPIE) and temperature-programmed desorption (TPD) of water and CO_2 on these materials [3].

TPIE studies were carried out by exchanging ¹⁶O-containing metal oxide catalysts with H_2 ¹⁸O at 680°C until no further exchange was noted. These isotopically labeled solids were then exposed to unlabeled ¹⁶O₂ at room temperature and the temperature was increased linearly to 750°C at 10°C/min. The kinetics of exchange between surface and lattice oxygen and gas phase O₂ were measured by monitoring the concentrations cf ¹⁸O¹⁶O (single exchange) and ¹⁸O₂ (multiple exchange) in the gas phase [3]. TPIE profiles for single exchange $({}^{18}O{}^{16}O)$ and double exchange $({}^{18}O{}_2)$ oxygens are shown in Figure 1 for Li/MgO and in Figure 2 for Ca-Ni-K. The appearance of these exchange products did not result from oxygen desorption from the labeled oxide precursors, as shown by the absence of gas phase oxygen species during heating of these samples in an inert He stream. On Li/MgO, two types of kinetically-distinct surface oxygen species give rise to single exchange and result in noticeable desorption maxima at 550 and 660°C



Figure 1 TPIE of ¹⁸O in Li/MgO with gas phase ¹⁶O₂. (a) single exchange; (b) multiple exchange.

(Figure 1). Multiple exchange TPIE profiles show only a single maximum at about 500°C. About 20% of the available oxygen species are capable of multiple exchange reactions. Significant exchange between gas phase oxygen and Li/MgO occurs only above 400°C, a temperature range also required for detectable amounts of methane oxidation and oxidative coupling products.

Multiple exchange occurs on Li/MgO during a single surface sojourn and not by sequential single exchange processes. In fact, the multiple exchange process appears to occur at even lower temperatures than single exchange. This single-step multiple exchange process occurs on active sites with kinetic access to more than one oxygen atom, such as peroxide sites present on metal oxide surfaces. McCarty [9] has recently suggested the involvement of both superoxide (O_2^-) and peroxide (O_2^{-2}) anions in reactions of methane on metal oxides. Oxygen reactivity and availability appear to be greater in peroxide species, suggesting the involvement of these sites in multiple exchange pathways and in deeper oxidation reactions of methane.

Single and multiple exchange sites are also present on Ca-Ni-K oxides catalysts, but their relative abundance is more difficult to detect because sequential single exchange steps also lead to ${}^{18}O_2$ products on these catalysts. Also, the TPIE profiles depend on the method of catalyst synthesis. At least three types of sites catalyze single exchange reactions on Ca-Ni-K oxides (Figure 2), with TPIE maxima at 430, 580, and >750°C. Multiple exchange TPIE products also reveal three kinetically distinct processes with maxima at 450, 520, and >720°C. After sequential single step processes are taken into account, we find that about 7% of the available exchange sites promote singlesojourn multiple exchange reactions.



Figure 2. TPIE of 18 O in Ca-Ni-K oxides with gas phase 16 O₂. (a) single exchange; (b) multiple exchange.

The presence of water appears to inhibit the extent of multiple exchange occurring on Li/MgO and Ca-Ni-K oxide catalysts. It also inhibits full oxidation reactions during the oxidative coupling of methane at low temperatures. We suggest that water can catalyze the decomposition of peroxide anions (O_2^{-2}) by stabilizing surface OH⁻ surface species that act as intermediates in the formation of highly mobile charge carriers such as O⁻, which are likely to lead to both single exchange and single H-abstraction from CH₄ molecules. At higher temperatures, peroxide decomposition can apparently occur without the assistance of adsorbed water species, and the effect of water on oxidative coupling selectivity is much less marked than at lower temperatures.

Characterization of Ca-Ni-K Oxide Powders

These studies have been complemented with detailed surface characterization of CaNiK

materials, specifically the surface density and location of K, and its essential role in the oxidative coupling reaction. X-Rav Photoelectron Spectroscopy (XPS) studies show that K species segregate to the surface of Ca-Ni oxides in oxidative environments at usual oxidative coupling reaction temperatures. The required K promotion of oxidative coupling reactions on Ca-Ni oxides requires segregation of K to their surface and their strong interaction with the underlying oxide in order to prevent alkali loss during pretreatment and catalytic Magnetochemical characterization reactions techniques have also been used to determine the structure and oxidation state of Ni cations within the oxide lattice in Ca-Ni-K catalysts

Reaction-Transport Models of Oxidative Coupling and Predicted Benefits of Membrane Reactors.

Computer simulations using recently reported detailed reaction-transport models of oxidative coupling reactions [5,6] confirm previous suggestions that selective methyl radical generation sites are necessary but not sufficient to achieve high C₂ yields. Increasing turnover rates or site densities increase C₂ yields by increasing gas-phase methyl radical concentrations probability and the of bimolecular coupling reactions. Such sites. however, also activate ethane and ethylene to C₂ radicals that undergo facile oxidation in homogeneous gas-phase reactions. Thus, C₂ yields above about 25% in conventional reactors require not only sites that form methyl radicals from methane without total oxidation pathways but also sites that can activate methane without catalyzing similar C-H abstraction steps in ethane and ethylene molecules. This type of selectivity is unlikely to occur because of the structural and chemical similarities between methane and ethane.

Homogeneous C_2 oxidation reactions inhibited by lowering can be oxygen concentrations, but this approach also limits the availability of the required stoichiometric oxygen reactant and the driving force for the catalytic generation of methyl radicals. The required stoichiometry can be maintained by introducing oxygen continuously as it is consumed along the reactor, while maintaining a low and constant oxygen concentration in the reactor gas phase. This approach depends on the availability of surface sites that activate methane to methyl radicals with low kinetic dependence on oxygen concentration, so that homogeneous oxidation pathways can be selectively inhibited compared with methyl radical generation steps as we decrease the oxygen concentration.

Figure 3 illustrates the improved C_2 yields predicted as oxygen transport membranes lower local oxygen concentrations near catalytic sites and in the contacting gas phase. C_2 yield improvements become significant only when the oxygen kinetic dependence for the catalytic methyl radical generation step becomes less than one. Then, gas phase oxidation reactions are influenced more strongly by lower oxygen concentrations than the desired surfacecatalyzed methyl radical generation steps.

Hydrogen Transport Membranes for the Oxidative Coupling of Methane

An alternate approach that totally excludes contact between the hydrocarbon and oxygen components of the stoichiometric reaction mixture is the use of hydrogen transport membranes. Metal oxides with high protonic and electronic conductivity are especially appealing because they avoid the extensive fouling inherent in the use of metal membranes (e.g., Pd). One side of the membrane would catalyze hydrogen abstraction



Figure 3. Simulated effect of oxygen concentration on C₂ yields in tubular membrane reactors at 800°C and 67 kPa CH₄ [membrane catalyzes formation of methyl but not ethyl radicals; kinetic order in oxygen for methyl radical generation (n); Curve B (n=1); C (n=0.5); D (n=0)]



rigure 4. Catalytic Membrane Reactors Using Proton Conductors

H Abstraction from CH₄ by Surface O⁻.

 CH₄ + O⁻ → CH₃· + OH⁻

 Proton (H+/OH⁻) Transport Across Membrane

 Flux = -D_{H+}(Δ[H+]/Δx)

 O Regeneration by O₂.

 OH + 1/2 O₂ → 2 O⁻ + H₂O

 Hole (h :/O⁻)Transport Across Membrane.

 Flux = -D_{h+}(Δ[h+]/Δx)

Figure 5. Reaction Pathways Involved in Non-Electrochemical Activation of Methane in Proton-Conducting Membrane Reactors

steps and the formation of methyl radicals and hydrogen atoms from methane. Hydrogen atoms would move across the membrane under a concentration gradient imposed by the CH_4 activation step and react with O_2 or other hydrogen acceptor species on the opposite side of the membrane (Figures 4 and 5).

Recent reports suggest that these reactor configurations allow the selective conversion of methane to C_2 hydrocarbons but conversions were limited by the slow transport of protons and holes across relatively thick membranes [10]. Our objective is to demonstrate the feasibility of this approach, to develop techniques for the synthesis of thinner disks and films (<0.5 mm), required for faster proton transport, and to combine these membranes with catalyst films in order to optimize the catalytic chemistry at each side of the proton conducting membrane.

We have recently prepared $SrM_{0.9}Y_{0.1}O_{2.95}$ (M=Ce, Zr) perovskites in the form of thin disks (1 mm) suitable for use in a membrane reactor that we have recently designed and constructed in our laboratory. These materials allow the selective transfer of the abstracted H-atoms from one side, where the CH₄ activation occurs, to the opposite side, where they are oxidized to provide the thermodynamic driving force for the overall conversion reaction, without allowing direct contact between hydrocarbons and O₂.

Initial membrane fabrication procedures involved spin coating alcohol solutions of mixed metal alkoxides onto porous alumina disks. These synthesis procedures failed to produce membranes of uniform thickness. Dried and calcined forms of these membranes showed extensive defects and porosity within the metal oxide film even after densification; these supported membranes were also difficult to seal against the reactor.

Synthesis procedures were developed in order to produce thicker unsupported metal oxide disks. These membranes were prepared by calcining mixtures of SrCO₃, ZrO₂, and Y₂O₃ at 1000°C in order to form mixed oxides with X-ray diffraction lines and compositions SrZr0.9Y0.102.95 corresponding to in perovskite structures. The resulting powder was then pressed into a disk and sintered by heating in air first to 1300°C in order to make a disk preform and then to 1600°C overnight in order to densify the materials and eliminate internal porosity and bypass channels. The density of the resulting material was 85% of the theoretical solid density, with the top and bottom of the disk much closer to this theoretical density

A thin sample of this disk was obtained by cutting a 1 mm slice off the end of this disk and mounting it within the reactor using a zirconia-based ceramic paste. The membrane developed a small (2 x 0.1 mm) crack during reaction, allowing some intermixing of the two reactants streams during testing. Additional slices of the same disk are being prepared for In addition, we have found that testing. preforms where Zr has been replaced with Ce $(SrCe_{0.9}Y_{0.1}O_{2.95})$ sinter to disks with 90% of the theoretical density at lower densification temperatures (1500°C). These lower temperatures may ultimately allow the use of graphite as a membrane barrier in order to block remaining channels across the membranes. Both Zr and Ce forms of these perovskites materials are being prepared for measurements of oxidative coupling catalytic activity and proton conductivity.

Membrane and Catalytic Films of Metal Oxides.

We are also studying alternate methods for the fabrication of coherent thin films in order to decrease the ultimate thickness of the membrane materials well below the 1 mm thickness presently attainable. These methods can also be used to deposit thin films of catalytic materials on the surface of metai oxides and thus remove the need for catalyzing the methane activation reaction and the hydrogen oxidation reactions on the actual metal oxide used as the membrane material.

Specifically, we have demonstrated the formation of Ca(1-x)NixO solid solution films using pulsed laser deposition from sintered targets of NiO and CaO. This technique involves the vaporization of a target by a pulsed laser beam, the formation of plasma plume, and the deposition of the plume materials on a heated substrate. The resulting films were approximately 150 nm thick and showed X-ray diffraction patterns corresponding to crystalline bulk materials with sodium chloride structures. This technique allows the formation of coherent films of varying stoichiometries and thickness, which cannot be formed directly by thermal treatment of NiO and CaO powder precursors.

This techniques was also used successfully to prepare Ca-Ni-K oxide films with K contents spanning the entire range of catalytically relevant compositions. The pulsed laser deposition prevents the extensive loss of species volatile K that occurs during conventional thermal synthesis of these materials at high temperatures.

These synthesis techniques are quite general and can be applied to the synthesis of most metal oxide materials. In particular, we will attempt to extend this pulse laser deposition techniques to the synthesis of protonconducting oxides in thin film configurations and of catalytic films of optimum composition for the non-oxidative generation of methyl radical on one side of the membrane and for the oxidation of hydrogen using O_2 on the opposite side. Additional control of film density, adhesion to substrate, and oxide orientation may be obtained using ion-assisted pulsed laser deposition, a technique under active research in our laboratory.

Cyclic Decomposition of Methane and Scavenging of Hydrogen or Hydrocarbon Fragments

The separation between the CH_4 and O_2 stoichiometric reactants can occur spatially, as it does in our proposed catalytic membrane configuration, or temporally, as in recently reported cyclic schemes for the sequential decomposition of methane to surface carbides on metals surface followed by hydrogenation of these species to C_2 hydrocarbons using gas phase H_2 [11]. In these schemes, the coupling is thermodynamically driven by changes in temperature between the two cycles, rather than by providing an oxidative pathway for the removal of the hydrogen reaction products.

We have recently started an experimental program to examine the feasibility of alternate cyclic schemes for methane conversion on supported metal catalysts. Three specific approaches differing significantly from those described in reference [11] are being examined:

1. Decomposition of methane to CH_x surface species and oxidative removal using O_2 to form H_2 and CO mixtures with high selectivity.

2. Decomposition of methane on metal surfaces to form CH_X species and scavenging of such

species by alkylation of hydrocarbons such as ethylene, ethyne, or benzene.

3. Decomposition of CH₄ on metals, suboxides, or alloys that form stable interstitial hydride compounds (e.g., Zr_2Fe , Pd, Ga, La and W oxides, ...) and scavenging of the interstitial hydrogen in a subsequent cycles by transfer to hydrogen acceptor species.

FUTURE WORK

1. Develop thin film deposition techniques and other fabrication techniques for membranes with higher proton fluxes.

2. Determine catalytic and proton conduction properties of $SrM_{0.9}Y_{0.1}O_{2.95}$ (M=Ce, Zr) perovskites

3. Develop rigorous reaction-transport models of methane activation under non-oxidative (pyrolysis) conditions

4. Explore potential of proposed approaches for cyclic methane decomposition followed by scavenging of the CH_x or H reaction products.

5. Exploit magnetochemical techniques for the characterization of the structure and oxidation state of transition metal cations within catalytic oxide films.

REFERENCES

1. Ginter, D.M., Magni, E., Somorjai, G.A., and Heinemann, H., "Oxidative Coupling of Methane on CaNiK Oxide Catalysts", Catal. Lett. <u>16</u>, 197 (1992).

2. Chang, Y. F., Somorjai, G.A., and Heinemann, H., "Oxidative Coupling of

Methane over Mg-Li Oxide Catalysts at relatively Low Temperatures", J. Catal. <u>141</u>, 713 (1993).

3. Chang, Y. F., Somorjai, G.A., and Heinemann, H., "A Temperature-Programmed Isotope Exchange Study of Ca-Ni-K and Mg-Li Oxide Catalysts for Oxidative Coupling of Methane", J. Catal. <u>142</u>, 697 (1993).

4. LBL Reports: LBL-32857; LBL-33241; LBL-33769; LBL-34250; LBL-34616.

5. Reyes, S.C., Iglesia, E., and Kelkar, C.P., "Kinetic-Transport Models of Bimodal Reaction Sequences I. Homogeneous-and Heterogeneous Pathways in Oxidative Coupling of Methane", Chem. Eng. Sci. <u>48</u>, 2643 (1993).

6. Reyes, S.C., Iglesia, E., and Kelkar, C.P., "Kinetic-Transport Models and the Design of Catalysts and Reactors for the Oxidative Coupling of Methane", Catal. Lett. <u>19</u>, 167 (1993)

7. Lunsford, J.H., in "Natural Gas Conversion" (A. Holmen, K.J. Jens, and S. Kolboe, Eds.) p. 3. Elsevier, Amsterdam, 1991.

8. Pereira, P., Lee, S.H., Somorjai, G.A., and Heinemann, H., Catal. Lett. <u>6</u>, 255 (1990)

9. McCarty, J.G., in "Direct Methane Conversion by Oxidative Processes" (Wolf, E.E., Ed.) p. 320. Marcel Dekker, New York, 1992.

10. Nozaki, T., Yamazaki, O., Omata, K., and Fujimoto, K., "Selective Oxidative Coupling of Methane with Membrane Reactor" Chem. Eng. Sci. <u>47</u>, 2945 (1992).

11. Koerts, T., Deelen, M.J., and van Santen, R.A., J. Catal. <u>139</u>, 101 (1992).

12. Perry, D.L., Mao, X., and Russo, R.L., "Ca-Ni-K Oxide Catalytic Thin Films Prepared by Pulsed Laser Deposition", J. Mater. Res. <u>8</u>, 2400 (1993)

Session NG -- Natural Gas Technology

Session NG-1

Hydraulic Fracturing Technology

NG-1.1 Fracturing Fluid Characterization Facility (FFCF)

CONTRACT INFORMATION

Contract Number	DOE Cooperative Agreement #DE-FC21-92MC29077
Contractor	University of Oklahoma School of Petroleum & Geological Engineering 100 East Boyd, Sarkeys Energy Center T301 Norman, OK 73019 (405)325-2921
Contractor Project Manager	Ronald D. Evans
Principal Investigators	Jean-Claude Roegiers John Fagan
METC Project Manager	Karl Frohne
Period of Performance	September 1, 1993 to June 30, 1995

Schedule and Milestones

FFCF PROGRAM SCHEDULE

	MAJOR TASKS	1993	1994	1995
		SOND	JFMAMJJASOND	JFMAMJ
I.	Design Modifications for High Pressure Simulator			
II.	Design, Fabrication and Installation of the Mechanical/Hydraulic Systems for the Low Pressure Simulator (LPS)			
III.	Design, Fabrication and Installation of the Computational/Instrumentation/Data Acquisition and Control Hardware and Software for the LPS			
IV.	Interim Research and Development Activities			
	A. Rheological Studies			
	B. Instrumentation and Experimental Support.			
V.	Development of a Strategy/Plan for Soliciting On- Going Support for FFCF.			
VI.	FFCF Building Construction			
	A. Site preparation, utilities and construction			
	B. Drill, case, cement, test and equip a 4500 feet well.			
VII.	Develop a Systematic Plan for Relocating High Pressure Simulator to New Building.			
VIII.	Verification and Testing of Low Pressure Simulator			
IX.	Reporting and Documentation			

OBJECTIVES

The objectives of this project are:

- 1. Design and fabricate a large scale experimental apparatus for characterizing proppant laden fracturing fluids.
- 2. Investigate rheological properties and proppant transport characteristics of various fracturing fluids used for stimulating oil and gas bearing formations.
- 3. Develop new information for characterizing the behavior of fracturing fluids under conditions more representative of the behavior in actual fractures.

BACKGROUND INFORMATION

Many numerical simulators have been developed to simulate hydraulic fracturing treatments.¹ Although these simulators usually have sound theoretical bases, out of necessity they must incorporate assumptions and approximations to allow solutions to be generated or to account for unavailable data.² Evaluation of the consequences assumptions of the and approximations has not yet been conclusive because controlled experiments on a scale necessary for the evaluation have not been possible. In addition, most fundamental data relating to fluid behavior and proppant transport in fractures have been obtained from laboratory-scale studies, and there is uncertainty about scaling data from such tests to field-scale applications.³ To attempt to resolve these issues, the Gas Research Institute, (GRI) and the U.S. Department of Energy (DOE) are jointly supporting construction and operation of a large slot flow apparatus at the University of Oklahoma.^{4,5} This paper discusses the capabilities of this apparatus and presents results from initial measurements with the apparatus.

PROJECT DESCRIPTION

The FFCF Project has as its main focus the design, fabrication, and construction of a high pressure simulator (HPS) and a low pressure simulator (LPS) to be used to experimentally investigate the rheological properties and transport characteristics of proppant laden fracturing fluids. A discussion of each apparatus is provided as well as the auxiliary equipment, and data acquisition and control systems associated with the simulators.

The High Pressure Slot Flow Apparatus (HPS)

Figure 1 shows the apparatus installed at the University of Oklahoma. The apparatus is designed to operate at pressures to 1200 psi and temperatures to 250°F, and has an instrumented slot flow channel that is 7 ft high by 9.3 ft long and is adjustable to any gap width to 1.25 in. One wall of the flow channel consists of 12 separate, movable steel platens which are 28 in. square and are laid out in a 3 by 4 matrix. The opposite wall is a continuous, 6 in. thick steel slab. The position of each of the movable platens is controlled by hydraulic actuators so that the gap between each platen and the opposite wall can be adjusted. arrangement individually This minimizes variations in the width of the flow channel that might be caused by deformation of the supporting structure at high pressures and high temperatures.

Each of the movable platens is covered by a 1 in. thick, replaceable facing, and the opposite wall is covered by a matching 3 by 4 matrix of identical, replaceable facings. These facings simulate rock surfaces and can be made with desired permeabilities. Therefore, by changing the facings different permeabilities and different surface properties, such as roughness, and topology, can be investigated for their effects on flow behavior and proppant transport. Behind each facing is a system of fluid collection channels which route fluid loss to a measuring point outside the apparatus, so that when permeable facings are installed on the walls the effects of fluid leakoff can also be investigated.

The flow path through the apparatus is shown schematically in Figure 2. Fluid inlet is through an inlet manifold into 22 equally-spaced inlet tubes, which are 3 in. long by 0.5 in. diameter. These tubes can be used to simulate flow entering a fracture through perforations. Bored plugs can be inserted into the inlet tubes to reduce the ID of the inlets to any desired diameter, and solid plugs can be inserted to prevent flow through any desired inlet. Thus a wide range of inlet configurations can be obtained. Fluid outlet from the apparatus is through 22 outlet tubes into an outlet manifold.

The Low Pressure Slot Flow Apparatus (LPS)

In order to investigate convective settling and proppant/fluid encapsulation in a quantitative manner a much larger (slot height and length) experimental apparatus in currently being This experimental apparatus will designed. contain many of the features of the HPS but will operate at a much lower pressure (300psig). The dimensions of the slot (fracture) will be approximately 15 feet in height, 40 feet in length with a variable slot width of 0.10 in - 1.25 in. A design schematic of the LPS is shown in Figure 3. The control system architecture of the LPS is shown in Figure 4.

Auxiliary Equipment

Auxiliary equipment for each apparatus consists of equipment for mixing fluids and slurries, equipment of pumping the fluids and slurries through the apparatus, and equipment for heating fluids and the apparatus. (See Figure 5)

Pumping equipment consists of a model 6P10 Moyno® pump and a model 5M Deming®

centrifugal pump. The Moyno pump has an infinitely variable speed drive and can deliver up to approximately 140 gal/min at 600 psi. The centrifugal pump serves to boost the suction of the Moyno pump, as an aid in fluid preparation, and as an injection point for crosslinker during tests with crosslinked and proppant-laden crosslinked fluids. Two model 260D ISCO metering pumps (not shown) can be used to inject crosslinker into the suction of the centrifugal pump.

Fluid mixing and storage vessels include a 55 gal stainless steel tank equipped with a threebladed Lightnin® air mixer, a 200 gal ribbon blender, and a 1000 gal polyethylene storage tank (not shown). Fracturing fluids and slurries are prepared either in the 55 gal tank or in the 200 gal ribbon blender. The 1000 gal storage tank serves as a large volume source of linear gel for continuous, single-pass crosslink tests. The double-pipe heat exchanger can be used for temperature control of the test fluids.

Figure 6 shows a schematic layout of the auxiliary equipment used for tests at high pressures. Pumping equipment consists of a triplex plunger pump and a Galigher 4 x 6 centrifugal pump. The triplex pump can deliver 200 gal/min at the 1200 psi maximum operating pressure of the apparatus. The trifugal pump is used to boost the suction of the triplex pump, as an aid in fluid mixing, and as an injection point for crosslinker.

Two 50-bbl fluid-mixing and storage tanks are located on a trailer unit. Each tank is equipped with an individually-controlled, hydraulically-driven agitator. Two 330-sack bulksand storage tanks are located on a second trailer. Sand can be transferred pneumatically from these tanks to prepare slurries for investigating the properties and behavior of proppant-laden fluids.

Instrumentation

Characterization of flow through the apparatus requires measurement of pressure drops,

flow rates, gap widths and temperatures. Instrumentation to accomplish these measurements is:

- 1. Honeywell model STD 120 differential pressure transducers which are accurate to better than 0.1%.
- 2. A Micro Motion® model DL200 mass flowmeter that measures volumetric flow rates to 0.2%.
- 3. Linear voltage displacement transducer (LVDTs) that measure the displacements of the pistons in the hydraulic actuators and thus measure platen displacements and Displacements are the gap width. measured from an initial gap width that is set by gage blocks. The accuracy of these measurements is estimated to be on the order of the accuracy of the LVDTs which are accurate to 0.002 in. To confirm the accuracy of the gap width measurements, two LVDTs that span the gap, and thus measure the gap width directly have been installed.
- 4. Thermistors located in the flow channel (intrusive), and mounted at the facing/fluid interface, 0.25 in. back from the interface, and 0.50 in. back from the interface in each wall facing, so that the fluid temperature and the heat flux to the fluid can be measured.

In addition, laser Doppler velocimeters (LDVs) are located at nine platens so that the fluid velocity can be measured at nine locations. Three of these LDVs are mounted on translating stages so that velocity profiles across the gap can also be measured. The LDVs are TSI SUREPOINT[™] Laser Probes which operate at 780 nm with 30 mW power. A more complete discussion of LDVs can be found in reference 6.

In the HPS, a system of transmitting fiber

optic bundles mounted in the facings on one side of the apparatus, combined with receiving fibers on the other side of the apparatus provides a "vision system" for monitoring proppant concentration in the apparatus and for monitoring bed formation. Addicional information about the HPS vision system can be found elsewhere.^{5,7} In the LPS the fiber optics bundles will be replaced with instrumentation strips which will be used to illuminate the slot.

Data Acquisition

Figure 7 is a flow diagram for data acquisition. The system can acquire up to 30 channels of temperature data and 7 channels of differential-pressure data. Data from the temperature and differential-pressure transducers are conditioned and converted to digital signals by an analog/digital (A/D) conversion array, then sent to a personal computer (PC) where temperatures and pressures are calculated. Filtering and calculation of moving averages in the PC reduce signal noise. Data are then processed for display and logged by the main computer. The display shows temperature and pressure surfaces in the apparatus, and thus provides a visual image of the progress of a test. A signal processor (PC) validates

signals from the LDV's, and converts the signals to velocities that are displayed on a monitor and logged by the main computer. Data from the mass flowmeter are interfaced to still another PC and logged by the main computer.

Experimental Considerations

To verify operations of the apparatus with the associated control systems and auxiliary equipment, and to evaluate the measuring systems, a series of verification tests with fluids having known properties were conducted. Comparison of the results of these tests with the known properties allows evaluation of the operation of the apparatus and subsystems. This section presents results from the first of the verification tests. A corn syrup solution (a Newtonian fluid), and a 60 lb/Mgal HPG solution (a non-Newtonian fluid) were used for these tests. Some of the results presented in this paper have been previously reported in reference 8.

Procedures

- 1. Newtonian Fluid. A solution of nominally three volumes of corn syrup in one volume of water was mixed, and the low pressure pumping system (Figure 5) was used to recirculate the solution through the apparatus at a series of flow rates for each of several different gap widths. There was no attempt to control the fluid temperature during these measurements, so, because of fluid heating caused by pumping, the fluid temperature increased during the measurements. Pressure drops, flow rates, fluid velocities, and temperatures were continuously measured and logged. Samples of the solution were taken from the mixing tank and subsequently run on a model 50 Fann viscometer to determine the viscosity-temperature behavior of the solution.
- 2. Non-Newtonian Fluid. A solution of nominally 60 lb of HPG/Mgal of water was mixed, and the low pressure pumping system (Figure 5) was used to recirculate the solution through the apparatus at a series of flow rates for each of several different gap widths. Cooling fluid circulating through the double pipe heat exchanger kept the test fluid nominally at constant temperature. Pressure drops, flow rates, fluid velocities, and temperatures were continuously measured and logged. Samples of the solution were taken from the mixing tank and subsequently run on a

Fann 50 viscometer to determine the viscosity-shear rate behavior of the solution.

Results

1. Newtonian Fluid. Figure 8 shows the flow rate schedule and resulting pressure drops for the measurements at a gap width of 0.75 in. Similar results were obtained for gap widths of 0.50 in. and 0.25 in. From the measured pressure drops, flow rates, and gap widths, viscosities for each gap width were calculated according to the relations

$$\mathbf{t}_{w} = \Delta P B / L \tag{1}$$

$$\gamma_a = 3Q/2HB^2 \qquad (2)$$

$$\eta = \tau_{w} / \gamma_{a}$$
 (3)

Figure 9 compares viscosities obtained at all gap widths with the apparatus to viscosities obtained from a sample of the solution with a Fann 50 viscometer. An average temperature measured by the mass flowmeter is used to correlate data from the large apparatus. This average temperature is expected to be accurate to within $\pm 1^{\circ}$ F. As shown in Figure 9. agreement between viscosities from the apparatus and viscosities from the Fann 50 is generally within $\pm 10\%$. The cause for the few discrepancies is not known. However, the most probably cause is an error in measuring the gap width, with an error of 0.01 in. being sufficient to account

for the discrepancies. Confirmation of the gap width by direct measurement in future tests should reduce the uncertainty of gap width measurements, so more reliable results can be expected from future tests.

Figure 10 compares velocity profiles across the gap obtained from LDV measurements with the profile

$$v = \frac{3Q}{4BH} [1 - (y/B)^2]$$
 (4)

predicted for laminar flow through the gap. Agreement between both the shape and magnitude of the measured and predicted profiles is very good at a gap width of At a gap width of 0.50 in., 0.75 in. measured and predicted velocities agree up to the centerline, but beyond the centerline they are offset about 0.08 in. The cause for this discrepancy is not known, but it does not appear any in other measurements, so it may be caused by a systematic error in location for these particular measurements. The good results obtained at the 0.75 in. gap width indicate that detailed information about velocities in the gap can be obtained.

2. Non-Newtonian Fluid. Figure 11 shows the flow rate schedule and resulting pressure drops for the measurements at a gap width of 0.50 in. Similar results were obtained at gap widths of 0.25 in. and 0.75 in. From these results apparent viscosities were calculated from Equations 1 through 3. Figure 12 compares apparent viscosities from the slot flow apparatus and data from the Fann 50 viscometer. Data from the Fann 50 are represented by the power law model

$$\eta_a = \tau_w / \gamma_a = K \gamma_a^{n-1}$$
 (5)

and have been corrected from the concentric cylinder geometry of the Fann 50 to the slot flow geometry of the measurements from the apparatus according to

$$K_a = K_v \left(\frac{2n + 1}{3nS}\right)^n \tag{6}$$

where

$$S = (1 - \beta^2)/n(1 - \beta^{2/n})$$
(7)

and

$$\beta = \tau_{bob} / \gamma_{cup}$$
 (8)

The temperature of these measurements was 70.5 ± 0.6 °F. In this case, the agreement is to within $\pm 10\%$ and further indicates satisfactory operation of the equipment and the measuring systems. Figure 13 compares velocity profiles across the gap obtained from LDV measurements with the profile

$$v = \frac{Q(2n + 1)}{2BH(n + 1)} \left[1 - (y/B)^{(n + 1)/n}\right]$$
⁽⁹⁾

predicted for laminar flow of a power-law fluid through the gap between parallel plates. The power-law parameter, n, required for the prediction was obtained from the measurements on a sample of the solution with a Fann 50 viscometer. Agreement in both the shape and magnitude of the measured and predicted profiles is again good (all measured values are within $\pm 10\%$ of predicted values) and gives further evidence that detailed information about velocities in the gap can be obtained.

Figures 14-16 shows a plot of apparent viscosity versus shear rate for a 60lb Titanium crosslinked HPG fluid. Data was obtained at different fracture widths. From the data presented in Figures 14-16 the displacement of the curves of data for different gap (fracture) widths can be interpreted as suggesting wall slip or differences in fluid structure. Investigation of these differences is continuing.

Figures 17-18 show plots of perforation friction as a function of flow rate and variation of perforation coefficient as a function of perforation size for various fracturing fluids. From the data in Figure 18 fluid structure plays an important role in predicting pressure drop through perforations.

FUTURE RESEARCH

Future research will focus upon the following activities:

- 1. Design, fabricate, and install the Low Pressure Simulator (LPS).
- 2. Rheological and Proppant Transport Research Using the High Pressure Simulator (HPS)

- Convective settling and encapsulation and their effects upon proppant transport
- Dynamic fluid loss studies and correlation with laboratory scale experiments
- Characterization of crosslinked fluids and crosslinked slurry rheology
- Investigate fluid dynamics through perforations
- Develop a verification test plan for the LPS
- Theoretical modeling of transport of proppant laden non-Newtonian fluids
- 3. Develop a strategy/plan for soliciting future support for the FFCF.
- 4. Develop a verification and testing program for the LPS.

In addition to these future research endeavors a building to house the HPS, LPS, and associated equipment will be constructed at the University of Oklahoma. Completion of the building for occupancy is scheduled for the last quarter of 1994. In addition a 4500-5000 ft. vertical shear well is proposed to be drilled, completed and instrumented near the new FFCF building. Although funds are not currently available for such a well it is believed the cost of this well can be raised from industry. Further, efforts will also be directed toward dismantling the HPS, moving and reassembling it in the new building. Some effort will have to be devoted to conducting selected flow tests to insure the HPS is still functioning correctly after its relocation.

CONCLUSIONS

From the above descriptions and results it can be concluded that:

- 1. A slot flow apparatus for investigating hydraulic-fracturing fluid flow, proppant transport, and leakoff, on a scale much larger than previously reported, is now operational at the University of Oklahoma.
- 2. Initial tests with a Newtonian fluid and with a non-Newtonian fluid show that the apparatus and associated instrumentation are working satisfactorily. Viscosities obtained from the slot flow apparatus for both the Newtonian fluid and the non-Newtonian fluid generally agree to within $\pm 10\%$ of data obtained from a laboratory rotational viscometer.
- 3. LDV measurements with a Newtonian fluid and with a non-Newtonian fluid show that detailed information about velocities in the slot can also be obtained.
- 4. A much larger low pressure simulator is being designed which can be used to provide industry with new and valuable information for characterizing the behavior of fracturing fluids under conditions that are more representative of their behavior in fractures than previously possible.

NOMENCLATURE

B =half width of the gap

H = height of the flow channel

K = power law consistency index

 K_a = power law consistency index for slot flow

 K_{ν} = power law consistency index for concentric cylinders

- L =length over which a pressure drop is measured
- n =power law flow index

 ΔP = pressure drop

Q = volumetric flow rate

 r_{bob} = bob radius for concentric cylinder rheometer

- $r_{cup} = \operatorname{cup} \operatorname{radius}$ for concentric cylinder rheometer
- S = defined by Equation 7
- v = fluid velocity
- y = gapwise distance, from centerline
- $\beta = r_{bob}/r_{cup}$
- γ_a = nominal shear rate
- η = shear viscosity
- η_a = apparent shear viscosity
- $T_{\rm w}$ = shear stress at the wall

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MTS Systems Corporation designed, built, and installed the apparatus and has participated in the project since its inception.

Halliburton Services has participated in the project since its inception, has supplied the auxiliary equipment, and its employees have provided many valuable suggestions and much valuable assistance.

RESPEC Corporation has also participated in the project since its inception and has provided valuable suggestions relating to quality assurance and project organization.

REFERENCES

- Gidley, J.L., Holditch, S.A., Nierode, D.E., and Veatch, R.W. Jr.: <u>Recent Advances in</u> <u>Hydraulic Fracturing</u>, Society of Petroleum Engineers, Richardson, TX, 1989, chapters 4 and 5.
- 2. Warpinski, N.R., Moschovidis, Z.A., Parker, C.D., and Abou-Sayed, I.S.:
"Comparison Study of Hydraulic Fracturing Models: Test Case-GRI Staged Field Experiment No. #," SPE 25890, Denver, CO, April, 1993.

- Medlin, W.L., Sexton, J.H., and Zumwalt, G.L." "Sand transport Experiments in Thin Fluids," SPE 14469, Las Vegas, NV, Sept., 1985.
- 4. RFP90-211-0367: "Fracturing Fluid Characterization," GRI, Chicago, IL, April, 1990.
- 5. Fracturing Fluid Characterization Facility, Annual Report, Aug., 1991 - Dec., 1992, The University of Oklahoma, Norman, OK, Dec., 1992.

- Mears, R.B., Sluss, J.J. Jr., Fagan, J.E., and Menon, R.K." "The Use of Laser Doppler Velocimetry (LDV) for the Measurement of Fracturing Fluid Flow in the FFCF Simulator," Proceedings of the SPE 68th Annual Technical Conference and Exhibition, Houston, TX, Oct. 1993, SPE Paper No. 26619,
- "Concepts and Objectives of the Fracturing Fluid Characterization Facility (FFCF)," <u>IN</u> <u>FOCUS - Tight Gas Sands</u>, GRI, Chicago, IL, Dec., 1991.
- Rein, R.G., Gord, D.L. and Shah, S.N., "Description of a Large, High Pressure Slot Flow Apparatus for Characterizing Fracturing Fluids," Proceedings of the SPE 68th Annual Technical Conference and Exhibition, Houston, TX, Oct. 3-6, 1993, SPE Paper No. 26524.



Figure 1. The High Pressure, Slot Flow Apparatus



Figure 2. Schematic of Flow Simulator Showing Fluid Flow Paths





Figure 3. Design Schematic of Low Pressure Simulator



Figure 4. Control System Architecture for LPS



Figure 5. Low Pressure Fluid Pumping and Mixing Equipment



Figure 6. High Pressure Fluid Pumping and Mixing Equipment



Figure 7. Flow Diagram for the Data Acquisition System



Figure 8. Flow Data for 3:1 Corn Syrup in 0.75 Inch Gap Width



Figure 9. Viscosity vs. Temperature for 3:1 Corn Syrup Solution



Figure 10. Velocity Profiles for a 3:1 Corn Syrup Solution



Figure 11. Flow Data for 60 lb/Mgal HPG Solution in 0.5 Inch Gap Width



Figure 12. Apparent Viscosity vs. Shear Rate for 60 lb/Mgal HPG



Figure 13. Velocity Profiles for 60 lb/Mgal HPG Solution



Figure 14. Apparent Viscosity vs. Shear Rate for a 60 lb. Crosslinked HPG Fluid with with 1/4 Inch Wellbore Perforations



Figure 15. Apparent Viscosity vs. Shear Rate for 60 lb. crosslinked HPG Fluid with 3/8 Inch Wellbore Perforations.



Figure 16. Apparent Viscosity vs. Shear Rate for a Crosslinked HPG Fluid with 1/2 Inch Wellbore Perforations.



Figure 17. Perforation Friction as a Function of Flow Rate (0.25" Width & Four 0.25" Perfs)



Figure 18. Perforation Coefficient vs. Perforation Size

NG-1.2 Introduction to the GRI/DOE Field Fracturing Multi-Site Project

CONTRACT INFORMATION

DOE Cooperative Agreement Number GRI Contract Number	DE-FC21-93MC30070 5093-221-2553
Contractor	CER Corporation 950 Grier Drive Las Vegas, NV 89119 (702) 361-2700
Contractor Project Manager	Richard E. Peterson
Principal Investigators	Michael L. Middlebrook, CER Norman R. Warpinski, Sandia Michael P. Cleary, RES Paul T. Branagan, B&A

METC Project Manager

Period of Performance

Schedule and Milestones



CY 1993 to 1995 Project Schedule

Karl H. Frohne

July 28, 1993 to July 27, 1996

OVERALL OBJECTIVE OF THE PROJECT

The objective of the Field Fracturing Multi-Sites Project is to conduct field experiments and analyze data that will result in definitive determinations of hydraulic fracture dimensions using remote well and treatment well diagnostic techniques. In addition, experiments will be conducted to provide data that will resolve significant unknowns with regard to hydraulic fracture modeling, fracture fluid rheology and fracture treatment design. These experiments will be supported by a well-characterized subsurface environment, as well as surface facilities and equipment that are conducive to acquiring high-quality data.

It is anticipated that the primary benefit of the project experiments will be the development and widespread commercialization of new fracture diagnostics technologies to determine fracture length, height, width and azimuth. Data resulting from these new technologies can then be used to prove and refine the 3D fracture model mechanisms. It is also anticipated that data collected and analyzed in the project will define the correct techniques for determining fracture closure pressure. The overall impact of the research will be to provide a foundation for a fracture diagnostic service industry and hydraulic fracture optimization based on measured fracture response.

BACKGROUND INFORMATION

Project Justification

Research work performed by the Gas Research Institute (GRI) and the U.S. Department of Energy (DOE) over the past several years has been directed at acquiring comprehensive data sets before, during and after hydraulic fracture treatments on a number of wells. Researchers have made significant advancements in several areas from these data, including formation evaluation, modeling fracture propagation processes, diagnosing the azimuth and height of the created fracture, and modeling production from a hydraulically-fractured natural gas reservoir. Significant advancements have also been made in developing and applying technology to define the stress characteristics of various rock layers, measuring important parameters before, during and after a fracture treatment, and using that information in a hydraulic fracture propagation model to predict the shape and extent of the resulting hydraulic fracture.

Although advances have been made, several important questions remain. Fracture propagation models being used by industry today can vary widely in their results for given input parameters due to various assumptions about the in-situ hydraulic fracturing process. In addition, fracture diagnostic systems developed thus far are capable of determining only fracture azimuth and, possibly, height. There is no proven diagnostic technique available for accurately determining fracture length. These deficiencies in fracture diagnostics and modeling provided the basis for GRI and DOE to collectively sponsor a research project having the research objectives stated above.

Characteristics of the Proposed Experimental Site

The site proposed for the field-fracturing Multi-Sites Project (i.e., M-Site) hydraulic fracture experimentation is the former DOE Multiwell Experiment (MWX) site located near Rifle, Colorado, as shown in Figure 1. This site presently includes three closely-spaced wells (MWX-1, MWX-2 and MWX-3), as shown in Figure 2.

All of the proposed M-Site experimentation will occur in several sandstone units, shown in Figure 3 and referred to in this report as the A, B and C Sands, present in the upper Mesaverde Group between 4,130 and 5,000 ft. These shallower sandstone units are desirable for multiple reasons:

- the fluvial and paralic depositional environments of the upper Mesaverde were conducive to deposition of thick, laterally-continuous sandstone bodies;
- the previous MWX project did not perform any hydraulic fracture stimulations above 5,500 ft, thereby preserving the subsurface laboratory;



Figure 1. Location of the Field Fracturing Multi-Site Project



Figure 2. Closely-Spaced Well Initially Drilled as Part of the Multiwell Experiment



Figure 3. Upper Mesaverde Sandstone Units Targeted for Research in the Multi-Site Project

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- few (if any) wellbore obstructions (e.g., bridge plugs, fishes) exist above 5,500 ft in the existing MWX wells;
- shallower target intervals decrease operational costs associated with conducting experiments; and
- 5) shallower depths promote the acquisition of higher quality data from surface-deployed instrumentation.

The fluvial and paralic sections of the upper Mesaverde, which includes the A, B and C Sands, in this area of the Piceance Basin is characterized by thick, blanket-like (i.e., laterally continuous) as determined by well log correlations and outcrop investigations. These sandstone units are also characterized as low permeability. For example, the average dry core permeability of the sandstone unit between 4,290 and 4,366 ft in MWX-2 is 0.107 md and the average porosity is 5.2 percent as determined from core analyses. The uppermost Mesaverde sands are interpreted to have very high water saturations (up to 100 percent). Gas saturations, however, begin to increase with increasing depth below 4,500 ft as determined from existing core and log analyses.

There are abundant data which currently exist as a result of MWX research within the proposed test interval which will be used to the advantage of the Multi-Sites Project:

This entire proposed interval, from 4,170 to 5,550 ft, was continuously cored in the MWX-1 well. This core is now stored at Sandia National Laboratories and is available for continued analysis, if required. Routine and special core analyses have already been performed on much of this core to determine rock mechanical and reservoir properties. Mineralogic, petrographic and sedimentological analyses have also already been performed and results documented. A portion of the upper Mesaverde target interval was also cored in the MWX-2 well.

- Thirteen cased-hole stress tests have already been performed in the MWX-2 well between 4,170 ft and 5,502 ft.
- Multiple overlapping runs of high-quality wireline log data exists for this interval and are archived at CER. The log and core data have been compiled into a depth-shifted, digital database which is maintained at CER.
- Seismic data in the form of high-resolution 3D, vertical seismic profile and cross-bore-hole is available.

There are additional data and information below the proposed test interval which will be useful to M-Site research. These data and information include the following:

- Hydraulic fracture azimuth was determined to be N78°W based on 7 different techniques implemented in the deeper Mesaverde in the MWX wells.
- 3D fracture modeling was previously performed on a hydraulic fracture treatment at 5,530 ft, so there is information on model behavior.
- Natural fractures associated with significant over-pressuring are known to occur primarily below 5,500 ft (i.e., below the proposed interval).
- Through work in 10 separate completion intervals, there were no indications of any near-wellbore effects during fracturing experiments. Thus, fracture treatment modeling is not expected to be hindered.

From a logistical point of view, the Multi-Site Project is suitable with regard to proximity to oil field services and airports. The M-Site is located 9 miles from Rifle, Colorado (see Figure 1). Grand Junction is 60 miles from the site via Interstate 70. Access from the interstate to the site is by a county-maintained paved road.

Verification of Site Suitability

All indications were positive that the MWX wells and the character of the subsurface formations were suitable for fracture diagnostics experimentation. However, a series of technical assessments were planned and executed before proceeding with full-scale project development to confirm the site suitability from various perspectives. These assessments included: 1) evaluation of confining stresses of the sandstone units; 2) assessment of wellbore (cement and casing) integrity; and 3) capability of remotely detecting seismic signals during a mini-frac.

The site suitability assessments performed involved the use of existing stress data from the MWX wells and the acquisition of new seismic and fracture treatment data collected during field operations conducted in September and October 1992. These assessments indicated the following:

- Wellbore and cement conditions of the MWX-2 and MWX-3 wells were suitable for acquiring high-quality seismic signals with low ambient noise levels.
- Log-derived stress data calibrated with in-situ stress test data indicate that a stress contrast ranging from 500 to 1,000 psi exists between the target sandstone units and the bounding lithologies. This stress contrast was considered suitable for limiting excessive fracture height growth.
- There were no unusual occurrences (e.g., nearwellbore effects) in pressure responses which inhibited 3D fracture modeling of the mini-frac treatment.
- Remote-wellbore monitoring during the minifrac injections was clearly able to identify over 1,000 microseisms. Limited analysis of these data indicated that the seismic signals can be

spatially located and used for mapping the hydraulic fracture.

Based on these positive assessments, it was concluded that the MWX site is suitable for conducting additional comprehensive M-Site fracture diagnostics and fracture model verification experiments. Complete documentation of the field operations and results is found in CER and others, 1993.

Contractor Team

The contractor team organized by GRI and DOE to execute the research project and interpret the results includes CER Corporation, Sandia National Laboratories (SNL), Resources Engineering Systems (RES), Branagan & Associates (B&A), and James E. Fix & Associates (F&A). Each organization's responsibilities are listed in Table 1.

Table 1. Contractor Team

Organizatio	on Responsibility	
CER	Site operations and data acquisition systems	
SNL	Fracture diagnostics	
RES	Hydraulic fracture modeling	
B&A	Design of data acquisition systems	
F&A	Geophysical consultant	

DESCRIPTION OF PROPOSED RESEARCH EXPERIMENTS

Experiments are planned for 3-year period from 1993 to 1995, as shown in the project schedule (see Contract Information). These experiments will use combinations of the existing MWX wells and wells which will be drilled. An overview of the experiments to be conducted using the existing and new wellbores is described in the following sections.

MWX Wellbores - Comprehensive A Sand Experiments

The objective of the MWX A-Sand seismic experiments is to determine hydraulic fracture azimuth, height and length, as a function of various fluid viscosities and net pressure. The experiment will involve several mini-frac injections using MWX-3 as the treatment well and the A Sand as the treatment zone. The primary data acquisition equipment, to be run in the MWX-2 well, will be seismic instrumentation (five triaxial accelerometers) on a fiber optics wireline. Fracture pressure data will also be acquired and used to model the mini-frac treatment. However, 3D fracture modeling will not necessarily be constrained by the fracture diagnostics data at this early stage of the project. In addition, a determination of the velocity structure of the upper Mesaverde will be performed to more accurately interpret the seismic data acquired during this and subsequent experiments.

These MWX-based fracturing experiments represent an intermediate step preceding the more comprehensive data acquisition planned for 1994. The data collected in the MWX experiments, however, will be applied as follows:

- demonstrate the utility of a commercially-available 5-level seismic receiver for enhanced microseismic monitoring of hydraulic fracture dimensions;
- begin validation of current treatment-well diagnostic technology (h/z, noise polarization);
- begin validation of current mechanisms used in 3D fracture models; and
- 4) contribute to the finalization of a new observation well design (see Monitor Well discussion below) with regard to the optimum spacing and total number of second instruments to be cemented in place.

Monitor Well and Geophysical Instrumentation Arrays

The objective of this phase of the Project is to drill and case a specially-designed offset well (i.e., Monitor Well) that will be used to emplace an array of seismic and earth tilt instrumentation. Comprehensive fracture diagnostics experiments can then be performed using a combination of the Monitor Well and MWX-3 as monitoring wells and the MWX-2 as the treatment well. The Monitor Well is necessary because comprehensive seismic experimentation, which has the potential for clearly defining the dimensions of a hydraulic fracture, requires an instrumentation array beyond that which can be fielded on a wireline retrievable system. These instrumentation arrays must be coupled to the formation, i.e., cemented in place, and properly located (vertically and horizontally) to be effective in acquiring meaningful data.

Figure 4 diagrammatically illustrates instrumentation and diagnostics arrays to be initially deployed at M-Site. The Monitor Well instrumentation arrays shown in the figure are to be cemented in place in the annular space between the 9-5/8-in. casing and 2-3/8-in. tubing strings. These arrays will be fundamental to fracture diagnostics data acquisition. The instrumentation cemented in place across the B and C Sand intervals will consist of the following:

- six inclinometers to be used for fracture closure experimentation; and
- a minimum of 16 and possibly as many as 64 triaxial seismic instruments for use in mapping hydraulic fracture microseisms and cross-well imaging.

Instrumentation will be secured to the casing string and adequately protected with centralizers when placing them in the hole. Cabling from the instrument arrays will run to the surface and into a data acquisition trailer positioned on the location. Figure 5 illustrates the approximate position of the monitor well, its data acquisition trailer and other infrastructure at the M-Site.



Figure 4. Instrumentation and Diagnostics Arrays to be Grouted in the Monitor Well



Figure 5. Layout of M-Site Infrastructure

Monitor/MWX Wells - B Sand Experiments

Fracture diagnostics will be the primary focus of this phase of the project which is anticipated to be performed in mid-1994 (see Project Schedule). Several mini-frac injections will be designed to achieve increasing hydraulic fracture length and height using MWX-2 as the treatment well. This fracture diagnostics plan is conceptually illustrated in Figure 6. These treatments, performed in the B Sand, would also have a progression of fluid types (from slick water to gel) pumped at multiple rates. Seismic data collected by the fracture diagnostics monitoring instruments cemented in the Monitor Well and wirelineretrievable seismic instruments in MWX-3 will be recorded during each treatment by the high-speed data acquisition system. The microseismic monitoring system will be capable of detecting, identifying, locating and displaying seismic sources as a function of time. The loci of source locations will be an ellipsoid that defines the extent of the active rock failures. The dimensions, orientation and geometry of the seismically active zone will provide a measurement of the fracture to be compared to the results of the post-fracture history match of various 3D fracture models. The accelerometer instrumentation in the Monitor Well will have continued use throughout the remaining phases of the M-Site project.

One of the potential seismic experiments to be conducted in the B Sand will be to map the shear-wave shadow. Following each injection, shear-wave shadow experiments could be performed using MWX-3 for deployment of a downhole seismic source and the Monitor Well as the seismic-signal receiver well. Execution of these seismic experiments would lead to hydraulic length and height dimensional characterization of the staged treatments being pumped from the MWX-2 well. The last fracture treatment to be pumped in the B Sand would include proppant to facilitate research to be conducted in the next phase of the project.

Intersecting Well 1 - B Sand Experiments

The goal of this phase of the project is to 1) intersect the propped hydraulic fracture created in the last B-Sand injection; and 2) perform hydraulic fracture conductivity tests between the treatment well and the intersection well. A conceptual diagram of Intersecting Well 1 cutting across the B Sand hydraulic fracture is shown in Figure 7. The drilling of Intersecting Well 1 would occur late in 1994 as shown in the Project Schedule.

The Intersecting Well 1 will be drilled on the same drilling pad as the Monitor Well. The initial part of the drilling operation would involve drilling a pilot hole to a depth of 4,750 ft. This pilot hole would be logged with a basic suite of resistivity, porosity and mechanical properties logs. With this information, the depth interval of the B Sand would be defined so that a horizontal wellbore could be kicked off of the pilot hole and directionally drilled to intersect the propped fracture emplaced in the B Sand. A coring assembly will be utilized, as the zone anticipated to include the hydraulic fracture is approached, to cut across the fractured interval and allow direct observation of the character of the fracture recovered in the core. Subsequently, borehole image log data (e.g., FMS or CAST) would be acquired through the fractured interval to fully characterize the fracture. The portion of the borehole which intersects the B Sand will be left open hole to facilitate fracture conductivity experiments as described below.

Fracture conductivity testing will be performed using the combination of the MWX-2 treatment well, propped hydraulic fracture in the B Sand and Intersecting Well 1 which has intersected the hydraulic fracture. Implementation of these experiments would potentially provide data for the verification of the following hydraulic fracture unknowns:



Figure 6. Conceptual Diagram of Fracture Diagnostics in the B Sand



Figure 7. Conceptual Diagram of the B Sand Intersection Well 1

- propped fracture width;
- permeability of the proppant pack;
- proppant convection or settling;
- proppant crushing and/or embedment; and
- pressure drop down the fracture.

In addition, with the propped fracture in place, seismic experiments will be performed to determine the propped dimensions of the hydraulic fracture.

Intersecting Well 2 - C Sand Experiments

A second horizontal wellbore is proposed to be kicked off from the existing vertical pilot hole after fracture conductivity and seismic testing is completed in the B Sand. This borehole, however, would cut across the C Sand and would be in place prior to initiation of hydraulic fracture treatments in the C Sand. This borehole would also be left open hole to facilitate subsequent fracture pressure measurements. A conceptual diagram of Intersecting Well 2 residing in the path of the propagating hydraulic fracture in the C Sand is shown in Figure 8. Intersecting Well 2 will be cored through the zone which will subsequently include the hydraulic fracture. In addition, a conventional suite of resistivity and porosity log data would be acquired to verify to the lateral variability of the unit.

An experiment will be designed, with the borehole in place in the C Sand, such that the hydraulic fracture will propagate towards and transect the Intersecting Well 2. The intent of this experiment would be to 1) measure the hydraulic pressure at the leading edge of the fracture; 2) provide a direct indication of the horizontal growth rate of the fracture wing and, thus, provide comparisons of fracture length determined from seismic and net pressure calculations; and 3) provide estimates of fracture width. Each of these data sets would assist in the verification of the calculations made in 3D hydraulic fracture models. After this initial experiment has been completed, then various other pressure monitoring and seismic experiments would be conducted using fluids injected at different rates down the treatment well, through the hydraulic fracture and recovered at the intersection well. Through execution of these fluid-only experiments, data would be gathered to evaluate:

- rheology of fracturing fluids which have been subjected to actual subsurface temperature and pressure conditions;
- estimates of the hydraulic width of the fracture;
- additional comparisons of fracture length from seismic and net pressure calculation methods; and
- pressure drop in the fracture due to varying viscosities.

The last injection pumped in the C Sand would include proppant. The following data could be gathered during this treatment:

- propped frac width estimates;
- proppant concentration and rheology of the slurry at the fracture tip; and
- pressure drop in the fracture due to sand-laden slurry (i.e., proppant drag).

DATA ACQUISITION SYSTEMS

The experiments conducted during M-Site investigations will require comprehensive electronic equipment for detecting and storing data. These systems are subdivided into conventional-speed data acquisition systems, high-speed data acquisition systems and a Local Area Network (LAN) or client server.



Figure 8. Conceptual Diagram of C Sand Experiments with Intersection Well 2

Conventional-Speed Data Acquisition Systems (DAS)

The primary objective of this segment of the M-Site project is to provide project field experimenters with easy assess to existing, on-site, low- to moderatespeed DASs and assure the acquisition of high-quality data. Three data acquisition systems are currently planned and designed to provide the following basic functions:

- uniform signal processing and conditioning;
- local-area, data-gathering focal points;
- clean and controlled hardware environments; and
- data communications linkage between satellites and the central client server.

Data gathered at these satellite systems will automatically transfer pertinent information back to the central client/server in a specific format for systematic review, analysis and archiving. Figure 9 illustrates the conventional DAS system and other related components. These computer systems will be located in the Central Computer Trailer as was shown in Figure 5.

Each of the DASs will be configured to accommodate the currently-planned experimental data that includes the following:

- downhole inclinometer signals;
- fracturing service company and project measured pressure, injection rate and fluid rheology data;
- bottomhole injection and reservoir monitoring pressures.



Figure 9. Data Acquisition Systems for Fracture Diagnostics Experiments

-184-

These systems will also include sufficient hardware and software flexibility and expandability to accommodate additional experimental data as they are incorporated into the project plan.

High-Speed Data Acquisition Systems (Hi-DAS)

The primary objective of this segment of the M-Site project is to provide project seismic and other field experimenters with a data acquisition system that combines high speed with efficiency and cost effectiveness. Sandia National Laboratories will take primary responsibility for the design and fabrication of two data acquisition systems that will serve the microseismic receiver arrays in the two project monitor wells. These two Hi-DAS systems, which are modified versions of an existing SNL/OYO field system, will provide the following basic functions:

- low-noise, high-bandwidth data acquisition sites capable of accepting as many as 96 seismic receivers per well;
- event detection and transferring of specific data across the communications link to the LAN/central client server;
- local high-density (DAT) tape storage of all raw signal data.

A Hi-DAS for the seismic array receivers in the existing MWX-3 monitor well will be situated in the DOE data acquisition/wireline trailer. This system will accommodate the expected wireline-run array of 15 seismic channels. Sufficient power, equipment racks and environmental infrastructure presently exist within this facility to accept the proposed Hi-DAS.

An existing instrument trailer is slated to be retrofitted to house the second M-Site Hi-DAS. This system will serve as the focal point for the large array of seismic receivers, up to 96, that will be grouted in place at the bottom of the Monitor Well to be drilled in 1994.

The Hi-DASs will be designed with sufficient hardware and software flexibility and expandability to accommodate moderate alterations that may arise during the course of the project. Local display software will be available such that the experimenters will be able to monitor the progress of their instruments and the acquired engineering data through a series of graphic and tabular screen displays and a variety of print media.

Central Computer/Client Server/Local Area Network Hub

A PC-based central computer system will function as the focal point for the projects Local Area Network (LAN) and client server. The purpose of this system is to provide a central hub to receive, distribute and store the large data arrays from the satellite data acquisition systems (Hi-DAS and DAS) as well as to allow each of the project experimenters easy access to all real time data. The client server will include the following basic functions:

- high-speed Novell LAN system;
- fiber optic and hardwire Ethernet connections;
- high-capacity disk storage; and
- workstations and local PCs for real-time analysis.

Data from the large microseismic detector arrays will be scanned and evaluated in the satellite Hi-DAS. If an event is considered significant, it will be transported across the fiber optic Ethernet link to the LAN client server where it will be available for further real-time analysis by the experimenters using either a work station or other project-provided PC systems. All the LAN client server data will be permanently stored on a hard drive and backed up after each experiment on DAT.

IRIG timing will be provided across links from the LAN client server to each of the DAS systems. This link will provide the required data timing identification stamp to precisely time-tie related events from any microseismic detector at any location. Precise timing between systems is critical to accurately define the location of microseismic events using travel-time triangulation.

Each of the three conventional speed DAS will be Ethernet-linked to the LAN client server which will again serve as a focal point for data distribution and storage. Service company data will be routed through a DAS where it will be formatted and shipped over the Ethernet to the LAN client server. FRACPRO or other related fracturing programs can then readily access the data from the client server.

REFERENCES

CER Corporation, Sandia National Laboratories and Resources Engineering Systems, 1993: "Multi-Site Project Seismic Verification Experiment and Assessment of Site Suitability," GRI Topical Report No. GRI-93/0050 prepared under Contract No. 5091-221-2130, February.

NG-1.3 Slant Hole Completion Test, Cozzette and Paludal Production Testing

CONTRACT INFORMATION

Contract Number	DE-AC21-90MC26024		
Contractor	CEL Corporation 950 Grier Drive Las Vegas, NV 89119 (702) 361-2700		
Contractor Project Manager	Robert L. Mann		
Principal Investigators	Robert L. Mann Mark S. Malinowsky		
METC Project Manager	Karl-Heinz Frohne		
Period of Performance	January 16, 1992, to July 31, 1993		
Schedule and Milestones			
	FY92/FY93 Program Schedule		
	FY92 FY93		
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Cozzette Testing			
Paludal Testing			

OBJECTIVES

The objectives for testing the sidetrack to the original slant hole wellbore are as follows:

1. Production test the Cozzette open-hole interval into the pipeline to determine long-term gas productivity.

2. Production test selected paludal sandstones and coals in the 60° section of the wellbore to determine long-term gas productivity.

BACKGROUND INFORMATION

The Slant Hole Completion Test (SHCT), funded by the U.S. Department of Energy, is a test well drilled to evaluate the effectiveness of directional drilling in stimulating gas productivity in tight, naturally-fractured sandstones and coals of the Mesaverde Group in the Rulison Field in northwestern Colorado. The wellsite is located in Section 34, T6S, R94W, Garfield County, Colorado, approximately 7.5 miles west of the town of Rifle. Drilling operations were completed during August 1991. The well was turned to the pipeline on January 16, 1992, producing from the unstimulated Cozzette open-hole interval at a gas rate of 3.0 MMCFD with no water. This paper discusses the results of production testing in the upper Cozzette Sandstone, and stimulation and production testing in selected sandstones and coals within the paludal Mesaverde depositional environment.

PROJECT DESCRIPTION

Cozzette 1992 Testing Operations

Production Testing (January 16 to April 21, 1992). SHCT No. 1 was turned into the pipeline at 4 p.m. January 16, 1992, at 3.048 MMCFD, 0 BOPD, and 0 BWPD at 4,750 psi FTP. Production from the upper Cozzette for the remainder of January 1992 was 17,030 MCF (14.73 psia) and 100 BW.

About February 10, 1992, the well started to produce water while flowing gas at a rate of 3 MMCFD. The initial water rate was approximately 80 BPD but gradually increased during the month to over 300 BPD at a gas rate of 3.0 MMCFD. When the gas rate was decreased to 2.0 MMCFD, the water rate dropped to about 140 BPD. Production from the Cozzette during February 1992 was 66,537 MCF (14.73 psia) and 3,154 BW. Water analyses for samples collected during February 1992 were consistent. At this time, it was not sure if the water was coming from the Cozzette Sandstone or from the Rollins Sandstone due to channeling behind casing.

The well was produced at rates between 2.5 MMCFD and 3.0 MMCFD with 350 BWPD to 380 BWPD until 9 a.m. March 16, 1992, at which time the well was shut-in for pressure buildup. The well

was returned to production at 1 p.m. March 27, 1992, at a rate of 1.0 MMCFD and 38 BWPD. Production from the Cozzette during March 1992 was 40,385 MCF (14.73 psia) and 5,264 BW.

The SHCT No. 1 was shut-in at 8 a.m. April 13, 1992, for a pressure buildup prior to conducting an isochronal test to determine open-flow potential. Production from the Cozzette during April 1992 was 25,055 MCF (14.73 psia) and 325 BW.

Modified Isochronal Test (April 17 to April 18, 1992). A modified isochronal test was performed from April 17 to 18, 1992. The pressure data was taken with Kuster gauges at 7,250 ft MD. Prior to the flow tests, the well was shut-in for four days, from April 14, 1992, to April 17, 1992, for pressure buildup. The initial bottomhole pressure was 5,415 psi. Flow and shut-in periods during the test were six hours long. The test information is presented in Table 1. Figure 1 is a delivery plot of the test information. Based on the modified isochronal test, the absolute open-flow potential for the Cozzette openhole interval is estimated to be 10.0 MMCFD.

Table 1.	SHCT No. 1 Modified Isochronal
	Test (April 17-18, 1992

Time, hours	Rate, MCFD	Bottomhole Pressure, psi	Comments
6		5,414	BHP After Shut-in
6	1,000	5,360	
6	0	5,415	
6	1,750	5,220	
6	0	5,400	
6	2,750	5,000	
6	0	5,380	
6	3,700	4,900	
48	2,500	4,950	

Pressure Buildup Test (April 21 to April 28, 1992). A pressure buildup test was conducted in the Cozzette from April 21 through April 28, 1992, with the



Figure 1. SHCT No. 1 Modified Isochronal Test

Kuster gauges located at 7,250 ft MD. The maximum bottomhole pressure recorded was 5,500 psi after a shut-in time of 177 hours. Figure 2 is a plot of the pressure buildup data in Horner time and Figure 3 is the log-log and log-log derivative plot of the same data.

Some observations can be made despite the poor quality of the data. Qualitatively, the pressure derivative appears to behave in a manner consistent with dual porosity reservoirs. If it is assumed that combined radial flow is effective at the end of the buildup, the extrapolated Horner buildup pressure would be 5,550 psi. Assuming a dry gas gradient, this is equivalent to a wellhead pressure of 4,830 psi. Analysis of this data is complicated by the fact that the depletion pattern in the Cozzette is probably not uniform due to the anisotropy of the natural fracture system. Analysis is further complicated by an unknown source of water production and the mechanics of multi-phase flow. Pressure gradients measured after the pressure buildup do not indicate a liquid column in the wellbore above the Kuster gauges at the end of the test.

Production Testing (April 29 to June 3, 1992). From April 29 to May 7, 1992, the gas production rate was maintained at 2.0 MMCFD. Wellhead pressure declined slowly to 3,899 psi, and water production stabilized at 62 to 67 BWPD. From May 8 through May 11, 1992, the gas production rate was maintained at 3.0 MMCFD. Wellhead pressure further declined to 2,948 psi, and water production increased from 187 BWPD on May 8 to 397 BWPD on May 11. From May 12 through May 16, the gas production rate was reduced to 2.0 MMCFD. Wellhead pressure stabilized at 3,180 psi, and water production ranged between 348 and 355 BWPD. May 17 through June 2, 1992, the gas production rate was reduced to 1.0 MMCFD. Wellhead pressure increased to 3,800 psi, and the water rate ranged from 27 to 62 BWPD by the end of the test period. Gas production from the Cozzette during May 1992 was 47,750 MCF (14.73 psi) and 3,597 BW.







Figure 3. Cozzette Buildup Log-Log and Log-Log Derivative

Figure 4 illustrates the Cozzette gas and water production rates from January 16 through June 3, 1992.

Water Shut-off Operations. During early June 1992, a tubing plug was set in the 2-7/8-in. tubing stub below the Baker Model DB packer to isolate the Cozzette Sandstone below the packer. The tubing string was pulled from the wellbore and a retrievable bridge plug was set, as a safety precaution, in the 7-in. casing at 8,420 ft MD.

It had been hypothesized that the produced water might be migrating into the Cozzette from formations uphole. The Cement Evaluation Tool, TDT and Oxygen Activation logs were run from 8,420 to 6,400 ft MD to determine if there was channeling and water movement behind the 7-in. casing. The Cement Evaluation Tool indicated severe channeling behind pipe over the interval logged. The Oxygen Activation log also indicated water movement behind pipe. The lower Rollins interval was perforated from 8,274 to 8,276 ft MD and squeeze cemented in an attempt to shut off any water flow down hole behind the 7-in. casing into the Cozzette. Two cement squeeze jobs were required before attaining a satisfactory squeeze pressure.

Paludal 2 Testing Operations

Paludal 2 Squeeze Cementing Operations. After squeeze cementing to attempt to shut off the water above the Cozzette interval, work was initiated to stimulate production from the Paludal 2 interval. Because of the poor cement behind the 7-in. casing, it was necessary to block squeeze above and below the Paludal 2 interval prior to hydraulic fracture stimulation. The Paludal 2 interval was block squeezed through perforations at 7,761 to 7,762 ft MD and at 7,730 to 7,731 ft MD. Each set of perforations was successfully cement squeezed with 8 to 9 bbl of Class G cement.



Figure 4. Cozzette Gas and Water Production, January 16, 1992, to June 3, 1992

Paludal 2 Stimulation

Perforation and Breakdown. The Paludal 2 Sandstone is located in the Lower Cameo Coal section between Coal 7 and Coal 8. The Paludal 2 Sandstone was perforated at 7,732 to 7,734 ft MD (7,340 ft TVD) with 8 JSPF for a total of 16 holes. The 37-gram charges produced an average entrance hole diameter of 0.47 in. and a penetration depth of 6 to 9 in. The perforations were phased at 180° and oriented to the high and low side of the wellbore.

Following perforation, the 7-in. casing was pressured to 4,000 psi with the rig pump in an unsuccessful attempt to break down the perforations. No breakdown was achieved and minimal leakoff was observed, indicating the perforations were surrounded by good cement.

Mini-Frac. A 3-1/2-in. diameter frac workstring was run on a 7-in. treating packer to isolate the majority of the 7-in. casing from the anticipated high treating pressures during hydraulic fracture stimulation. A mini-frac was performed prior to pumping the main fracture treatment. The wellbore was pressured to 5,500 psi without breaking down the perforations, and the pumps were shut down to observe leakoff. The pumps were then engaged and the pressure increased to approximately 6,400 psi where the perforations began taking fluid. No traditional perforation breakdown was observed; the observed perforation breakdown appeared more like a fracture that was re-opening. Injection rates with 2 percent KCl water were increased to 20 BPM at 7,500 psi. At this time, a decision was made not to pump 7-1/2 percent HCl to assist with perforation cleanup since the perforations were taking fluid at reasonable rates and pressures. Prior to starting the delayed crosslink gel, 20 bbl of 2 percent KCl water was pumped. Once the crosslinked gel hit the perforations, the injection rate was increased to 25 BPM at 7,900 psi. The pumps were shut down once approximately 25 bbl of gel had passed the perforations. A 3,000 psi friction pressure drop was observed at 25 BPM; about 1,909 psi is attributed to pipe friction and 1,100 psi is attributable to perforation (and near-wellbore) friction. Another

25 bbl of crosslinked gel w is pumped at 30 BPM at 8,400 psi followed by a second shutdown. A friction pressure drop of about 3,600 psi was observed at 30 BPM of which about 2,350 psi was attributed to pipe friction and 1,250 psi to perforation friction.

The ISIP following each shut-in was approximately 5,000 psi which corresponds to a fracture gradient of 1.12 psi/ft. The anticipated minimum stress gradient around the 60° deviated wellbore was 1.14 psi/ft based on an in-situ stress gradient of 0.85 psi/ft. Since the observed and projected stress gradients were similar, and since wellbore friction was not extreme, it was decided to pump the fracture treatment as designed.

Main Fracture Treatment. The Paludal 2 Sandstone and surrounding coals in the 60° wellbore were hydraulic fracture stimulated on June 23, 1992. The treatment was conducted below a packer, down the 3-1/2-in. workstring, through 16 perforations between 7,732 and 7,734 ft MD using 5,000 lb 100 mesh sand, 76,500 lb 20/40 sand, and 30,000 lb of resincoated 20/40 sand carried in 43,512 gal of crosslinked gel. The average treating rate was 30 BPM at a surface treating pressure of 8,200 psi. The treatment was pumped according to design. The total load water to recover following the treatment, including the 67 bbl flush, was 1,192 bbl. The well was then flowed to the flare pit to cleanup through July 8, 1992.

Paludal 2 Production Testing (July 9, 1992, to January 13, 1993). The initial gas flow rates from the Paludal 2 Sandstone and surrounding coals ranged from 20 to 80 MCFD at an initial flowing wellhead pressure of 500 psi. Flowing wellhead pressure averaged 250 to 450 psi during the flow test. Figure 5 presents the daily Paludal 2 gas and water production from July 9, 1992, through January 13, 1993.

Paludal 3 & 4 Testing Operations

Paludal 3 & 4 Squeeze Cementing. Work was initiated on January 13, 1993, to complete the Paludal 3 and 4 intervals. A bridge plug was set above the





Figure 5. Paludal 2 Gas and Water Production, July 9, 1992, to January 13, 1993

Paludal 2 Sandstone perforations at 7,520 ft MD, and the Paludal 3 and 4 interval was block squeezed. The squeeze intervals were 7,510 to 7,511 ft MD and 7,385 to 7,386 ft MD. Each interval was successfully block squeezed with 8 bbl of Class G cement. A satisfactory squeeze pressure was obtained on each set of perforations.

Paludal 3 And 4 Stimulation

Perforation. On January 22, 1993, the well was perforated across the Paludal 4 Sandstone in the 60° cased wellbore at 7,386 to 7,388 ft MD (7,154 ft TVD) with 8 JSPF for a total of 16 holes. The 34-gram charge produces an entrance hole diameter of 0.50 in. and a penetration depth of 6 to 9 in. The perforations were phased at 180° and oriented to the high and low side of the wellbore using spring decentralizers.

Mini-Frac. A 3-1/2-in. frac workstring and a 7-in. treating packer were utilized to isolate the majority

of the 7-in. casing from the anticipated high treating pressures. The treating packer was set at 7,345 ft MD, and 2,800 psi was applied to the annulus using the rig pump. A breakdown and injection test using 25 bbl of 2 percent KCl water was pumped ahead of the main fracture treatment. The perforations broke down at 5,700 psi, and the remainder of the 2 percent KCl water was pumped at 15 BPM at about 7,100 psi surface pressure. The instantaneous shut-in pressure (ISIP) following the breakdown was 3,600 psi which corresponds to a fracture gradient of 0.94 psi/ft. Based on the pressures observed, the decision was made to pump the main fracture treatment as designed.

Main Fracture Treatment. The Paludal 3 and 4 Sandstone fracture treatment was initiated January 22, 1993, following completion of the mini-frac. The main fracture treatment consisted of pumping 5,000 lb of 100 mesh sand, 160,000 lb of 20/40 Ottawa sand, and 30,000 lb of resin-coated sand (tail-in) in 1,790 bbl of crosslinked gel. The maximum sand concentration placed during the treatment was 5 ppg. The average treating rate was 30 BPM at an average treating pressure of 6,700 psi. A radioactive tracer (Iridium 192 beads) was included during the sand stages to help determine the placement of the proppant. An aggressive breaker schedule was designed to break the crosslinked gel one hour following shutin. At the completion of the fracture treatment, 1,964 bbl of fluid remained to be recovered.

Flowback was initiated through the 3-1/2-in. frac workstring approximately 2-1/2 hours after the fracture treatment was completed. The well flowed on various chokes until January 26, 1993 when the well died. The 3-1/2-in. tubing was pulled, and the 2-7/8in. production tubing was run open-ended. After cleaning out sand from 7,370 to 7,500 ft MD, the tubing was landed at 7,389 ft MD, one ft below the perforations at 7,386 to 7,388 ft MD. The well was swabbed intermittently for two days before continuous flow was established. By the end of January 1993, approximately 1,158 bbl of stimulation fluid had been recovered. Following cleanup, the Paludal 4 Sandstone interval was produced into the pipeline at rates of 100 MCFD to 150 MCFD.

A post-frac gamma ray log was run from 7,200 to 7,475 ft to determine the location of the Iridium 192 radioactive tracer material pumped with the sand. The majority of the material was found across the Paludal 4 Sandstone perforations at 7,386 to 7,388 ft MD. However, significant amounts of tracer were observed at 7,372 to 7,374 ft MD, and at 7,380 to 7,382 ft MD. Small amounts of tracer were observed at 7,328 ft MD, 58 ft above the perforations, while no tracer material was observed below the perforations.

Although there was no indication from the gamma ray survey that the hydraulic fracture created in the Paludal 4 Sandstone was in contact with the Paludal 3 Sandstone at the wellbore, the Paludal 3 was perforated from 7,442 to 7,462 ft MD with 4 JSPF (19 gram, 120° phasing) in an attempt to increase gas production rates. No significant increase in production was noted from the additional perforations. The well averaged 50 MCFD to 120 MCFD from the Paludal 3 and 4 Sandstone interval for the 10 days following perforation of the Paludal 3 Sandstone.

Pressure Buildup Test (March 17 to March 24, 1993). The SHCT No. 1 was shut-in at the surface on March 17, 1993, to begin a pressure buildup test. A bottomhole shut-in could not be achieved for various reasons, and the bottomhole pressure gauge was landed in the tubing at 7,230 ft MD, 92 ft TVD above the Paludal 4 Sandstone perforations. The objective of the pressure buildup test was to evaluate the effectiveness of the hydraulic fracture treatment and determine the characteristics of the created hydraulic fracture. History matching the pressure buildup up data was performed using a single-layer, single-phase, single-porosity reservoir simulator. The following reservoir characteristics were input into the simulator.

Average Permeability	0.01 md
Matrix Porosity	10%
Water Saturation	46%
Reservoir Temperature	210° F
Reservoir Pressure	5,300 psi
Gas Gravity	0.626
Net Pay	60 ft
Depth	7,175 ft
Reservoir Size	350 ft x 4,000 ft
	(32 acres)

The reservoir properties were obtained from previous work conducted in this same interval during the Multiwell Experiment. The 20-ft thick Paludal 4 Sandstone and the 40-ft thick Paludal 3 Sandstone were modeled in this study as a single 60-ft layer. An average reservoir permeability of 0.01 md (10 times the matrix permeability) was used to simulate the presence of natural fractures. The reservoir simulator was produced at a constant bottomhole pressure of 1,150 psi for 46 days to simulate the production period following the hydraulic fracture treatment. The actual production rates for SHCT No. 1 ranged from 50 to 250 MCFD and 10 BWPD for the 46 days following fracture cleanup. These rates were similar to the post-frac production rate for MWX No. 1. The
length and conductivity of the hydraulic fracture were varied in the simulator until a reasonable match of the pressure buildup, as shown in Figure 6, was obtained. A log-log diagnostic plot of the change in pressure versus the shut-in time and the derivative is shown in Figure 7. Notice that a reasonably good match of the data is made after the first 24 hours of shut-in time.

The hydraulic fracture parameters used in the simulator to obtain the pressure match are a fracture half-length of 100 ft, fracture width of 0.6 in. and a fracture permeability of 2,000 md. Analysis of the log-log diagnostic plot shows that the well transitioned fairly quickly into formation linear flow (1/2 slope) and remained in that flow regime for the duration of the test. This quick transition into linear flow is characteristic of fractures which have a high dimensionless fracture conductivity (100 in this case) which is the result of the short fracture length.

Figure 8 is characteristic of a typical Horner plot of a hydraulically-fractured vertical well. Since the well did not reach pseudo-radial flow during the buildup, the Horner plot serves only to provide a qualitative assessment of the extrapolated reservoir pressure.

The size of the hydraulic fracture treatment in the Paludal 3 and 4 Sandstone interval in the SHCT No. 1 is very similar to that in MWX No. 1.

SHCT No. 1 MWX No. 1

Fluid Volume, gal	83,286	81,464
Total Sand, lb	195,000	193,000
Max Prop Conc, ppg	5.0	5.5
Pump Rate, BPM	30	20

The Paludal 3 and 4 hydraulic fracture in MWX No. 1 had a modeled half-length of 100 ft, and a conductivity of 104 md-ft. The similarity of these parameters to the Paludal 3 and 4 Sandstone interval modeled fracture parameters in SHCT No. 1 indicates that the induced fracture geometry was unaffected by treatment in a deviated wellbore as opposed to a vertical wellbore.

The 150-MCFD average post-fracture production performance of SHCT No. 1 was similar to that of MWX No. 1 prior to shut-in and re-entry. This supports the conclusion that hydraulic fracturing results do not improve based on stimulation from a deviated wellbore in the Paludal 3 and 4 intervals.

Paludal 3 And 4 Production Testing (January 12 to March 24, 1993)

The initial gas production rate from the Paludal 3 and 4 interval following stimulation was 400 MCFD and averaged approximately 150 MCFD during the production test. Flowing wellhead pressure averaged approximately 400 psi throughout the production test. Figure 9 presents the Paludal 3 and 4 interval daily gas and water production, following stimulation, from January 12 through March 24, 1993.

Cozzette 1993 Testing Operations

Production Testing (April 12 to June 3, 1993). On April 12, 1993 the Cozzette was returned to gas production to the pipeline at approximately 2.0 MMCFD. Gas rates between April and June 1993 generally ranged from 1.0 to 1.7 MMCFD. Water production rates increased to 140 to 180 BPD by April 26, 1993, with wellhead pressures ranging from 3,200 to 3,300 psi. Water gas ratios deteriorated during May 1993 despite efforts to hold gas rates below 1.0 MMCFD. On June 6, 1993, gas rates ranged from 350 to 425 MCFD with 251 BWPD. Figure 10 illustrates the daily gas and water production from April 12 through June 3, 1993.

Water Production Sources. Recent horizontal wells drilled in the Rulison Field have experienced significant water production as well as gas production. The SHCT No. 1 (sidetrack) in Section 34, T6S, R94W has produced as much as 600 BWPD. The Meridian 43-33 Quarter Circle well in Section 33, T6S, R94W



Figure 6. Bottomhole Pressure Vs. Shut-In Time Plot of the Actual and Simulated Buildup Data from the Paludal 3 and 4 Interval



Figure 7. Log-Log Diagnostic Plot of the Actual and Simulated Buildup Data from the Paludal 3 and 4 Interval







Figure 9. Paludal 3 and 4 Gas and Water Production, January 12, 1993, to March 24, 1993



Figure 10. Cozzette Gas and Water Production, April 12, 1993, to June 3, 1993

has produced as much as 1,800 BWPD. This water production is a very serious problem that threatens the viability of horizontal drilling as a mechanism for enhancing gas production from low-permeability reservoirs in the Rulison Field.

The nature of the water production mechanism in the Cozzette reservoir is not clearly understood. It is not known for certain whether the water produced from the Cozzette horizontal wells is, in fact, being sourced from the Cozzette. Vertical gas wells completed in the Cozzette reservoir in the Rulison Field have not experienced significant water production.

Possible sources of the Cozzette water production from the SHCT No. 1 include:

• Water migration via one or more faults penetrated by the horizontal wellbore.

- Water migration behind pipe from zones above the Cozzette.
- Water production into the Cozzette fracture system from the rock matrix.

Figure 11 illustrates the structure in the vicinity of SHCT No. 1 with produced water information and log analysis results from the Cozzette from offset wells.

CONCLUSIONS

The following conclusions result from the work completed under this contract.

• The Slant Hole Completion Test has been successful in providing good technology transfer to the oil and gas industry.



Figure 11. Structure in Vicinity of SHCT Site with Produced Water Data for the Cozzette

- The gas-producing rate from the Cozzette horizontal open-hole interval was significantly greater than from offset vertical wells.
- The source of water production from the Cozzette is not presently understood.
- Diagnosis of the water production mechanism is vital to economic exploitation of the Cozzette gas resource using horizontal well technology.
- Stimulation in a high-angle cased and cemented wellbore, such as the Paludal 2, 3 and 4 intervals in SHCT No. 1, is more difficult because of high near-wellbore stress that results in higher treating pressures.
- Low gas production potential following the Paludal 2, 3 and 4 stimulation may result from damage to the natural fracture system resulting from casing cementing operations.

• Comparison of gas production rates in SHCT No. 1 and MWX No. 1 following similar stimulations in the Paludal 3 and 4 intervals, indicate there is no advantage to a hydraulic fracture treatment in a slant wellbore when compared to a vertical wellbore.

RECOMMENDATIONS

The recommendations presented herein represent an on-going line of inquiry to resolve outstanding questions from the Slant Hole Completion Test.

- Undertake a high-angle, open-hole completion across the paludal Mesaverde interval using a slotted liner to ensure hole integrity across the highly-fractured sandstones, siltstones and coals.
- Determine the source of the Cozzette water production.

 Undertake a similar demonstration of horizontal well technology in other geologic basins containing low-permeability gas bearing formations.

REFERENCES

1. CER Corporation, 1993: "Slant Hole Completion Test, Cozzette and Paludal Production Testing, Topical Report," prepared for Morgantown Energy Technology Center under Contract No. DE-AC21-90MC26024, June 1993.

 CER Corporation, 1993: "Slant Hole Completion Test, Final Report," prepared for Morgantown Energy Technology Center under Contract No. DE-AC21-90MC26024, July 1993.

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