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Permeability Alteration of Sandstone Using A High-Energy Liquid Compound

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ABSTRACT

This study was done to determine the technical feasibility of the thermal alteration of sandstone by the in situ burning of a high-energy compound. A proprietary liquid monopropellant was burned in several sandstone cores to effect an increase in permeability. This report summarizes the results of preliminary tests.

Attempts were made to burn the propellant in 13 different cores, each saturated with the combustible liquid. Burning was complete in three of the cores, while in three other cores burning was only partial. The increase in permeability for the three completely burned cores ranged from 109 per cent to 384 per cent and showed an average increase in air permeability of 216 per cent. Results of these tests, based on recorder response, indicated a maximum uniform heating of the rock matrix to a temperature of about 455°C.

INTRODUCTION

Most gas-storage and gas-producing reservoirs have adequate capacity but would benefit from improved deliverability. During peak demand periods, the lack of formation permeability adjacent to the wellbore often limits the flow of gas. By altering the permeability of the sandstone around the wellbore, productivity can be increased.

References and illustrations at end of paper.

Sandstones are composed primarily of crystal phases or modification of silica. There are seven principal crystalline phases of silica, but the three most common ones are quartz, tridymite and cristobalite. Quartz, the phase most generally found in nature, can be converted to tridymite or cristobalite by heat. The stable forms of these silicas are: quartz below 867°C, tridymite to 1,470°C and cristobalite to the liquid form at 1,723°C. Within each of these crystal modifications there are reversible changes or inversions which can be effected by the rapid cooling or heating of the crystal through a fairly definite temperature value. For example, the low-high inversion of quartz occurs at 573°C. During the heating and also during the modification of silica crystals there are changes in volume. The density of quartz is 2.65, that of tridymite is 2.26 and that of cristobalite is 2.32. The transformation of quartz to tridymite causes an increase in volume of 17.? per cent. In most volume changes, fracturing or spalling takes place. In addition to its effect on silica, heat can effect not only the dissociation of carbon dioxide from carbonates but also the complete irreversible dehydration of clays. A manifold increase in permeability of sandstone should be obtained by heating.

Somerton, et al., have indicated that increases in permeability of sandstone can be obtained by the application of heat at temperatures in the range of 700 to 900°C.[2-3] The beneficial effect of the presence of certain salts was also shown.

The supplying of heat into a reservoir can be considered in several ways. A fuel such as a liquid hydrocarbon could be injected into the formation adjacent to the wellbore. Hot air or air after ignition could then be injected until in situ combustion of the fuel was completed. There are other ways of adding heat to a formation. The in situ combustion of a high-energy fuel-oxidant liquid was one method considered by Bureau of Mines engineers. A literature survey did not reveal that research in this field had ever been considered or performed. A study was made to determine the technical feasibility of heating sandstone by in situ burning of a high-energy compound to effect an increase in permeability. This report summarizes the results of preliminary tests.

EXPERIMENTAL PROCEDURES AND RESULTS

Background

Heat must be liberated in a large enough quantity to produce a temperature rise sufficient to produce the desired reaction in the cementing material and the outer shell of each sand grain. The heat required to raise the temperature of one cc of a typical sandstone, having a porosity of 15 per cent, from 25°C to 900°C, is about 510 calories; and for a 20-per cent porosity sandstone the heat required is about 480 calories. Therefore, a fuel-oxidant mixture would have to contain more energy per cc of liquid as the porosity of the sandstone decreases. Applying these values to actual cases, a fuel-oxidant liquid would have to contain about 3,400 calories/cc to heat a 15-per cent porosity sandstone to 900°C while one containing only 2,400 calories/cc is required to heat a 20-per cent porosity sandstone to 900°C.

Preliminary Ignition Tests

Initial attempts to burn the propellant inside cores met with no success due largely to ignitor problems. Finally a successful burn was obtained on an Upper Torpedo sandstone core in a nitrogen atmosphere of 500 psig. This core had been saturated by imbibition from the top down followed by a gas pressure of about 5 psig. It is estimated that the saturation was about 50 to 60 per cent. Thermocouple TC-2, buried 1-1/4 ins. from the top of the core, reacted sharply 30 seconds after ignition and indicated an initial temperature of 468°C. During the next few minutes the temperature, although a little erratic, remained around 400°C. Thermocouple TC-3, buried 1-1/4 ins. below the first thermocouple, did not respond sharply but rose steeply to 288°C and then began to decline gradually.

This core was resaturated in the same manner as before. This time the liquid was imbibed quickly and about 50 per cent more liquid remained in the core. After ignition, TC-2 registered a temperature of about 600°C. The lower thermocouple, TC-3, did not respond.

A thermocouple was used in both runs to check ignition. In the first run this thermocouple, TC-1, located about 1-1/2 ins. above the core, registered only 260°C and then declined over the next 60 seconds to 52°C. In the second run the thermocouple rested on top of the core and registered a temperature of 982°C. This temperature remained almost this high for the next 4 min., declining to only about 927°C.

Neither porosities nor permeabilities were determined for this core. An analysis of the recordings and observations indicated the existence of at least two problem areas:

1. Saturation - Saturation of the core should be accomplished in a vacuum system. It appeared that in the first run the lower part of the core was not so thoroughly saturated as the upper part, and saturation should have been greater.

2. Vaporization - In the second run the core apparently acted as a wick and some of the liquid [or vapors] did not burn in place, but rose and burned near the top surface. Based on the analysis of the preliminary test, subsequent burning tests were performed in a pressurized N environment after the cores had been saturated in an evacuated vacuum chamber.

Fuel-Oxidant Mixture

The combustible mixture used was a proprietary compound [G-2]* especially formulated by Explosives Corporation of America to burn in rock. It has a specific gravity of 1.17 and a viscosity of between 2 and 4 cp. Its other physical and chemical properties are presently unknown to the authors.

Sample Preparation

All of the sandstone cores used, with the exception of quarried Berea and Bandera, were

*This term is used for identification purposes only and does not indicate endorsement by the Bureau of Mines.

obtained from outcrop formations in northeastern Oklahoma. The cores were 1-1/2 in. in diameter and approximately 4 in. long. They ranged in porosity from 15 to 30 per cent and in permeability from 15 to 2,000 md.

Some of the cores were cut from large blocks and trimmed to length; others were cored directly from outcrops. They were not cleaned in any manner. A thin coat of silicate material was bonded to the cylindrical wall, and permeabilities and porosities were determined. Chromel-alumel thermocouples were embedded in holes drilled radially to the center of the core. The first thermocouple was 1 in. from the top of the core while a second one was 2 ins. from the top. The core was wrapped with plastic tape and encased in a thin-walled stainless steel tube, using a small amount of flame-retardant plastic at each end. Enough tubing and plastic extended above the core to allow extra propellant to be pooled on top of the core. One core was sealed at the bottom. The cores were then saturated with the propellant under vacuum for a period varying from one hour to overnight [15 hours].

A thermite-type ignitor was placed on top of the core. From 5 to 10 ml of propellant was poured on top of each sample. A check thermocouple was placed just above the ignitor, and the assembly suspended inside a vessel pressured with nitrogen. The propellant was ignited and the response of the three thermocouples was recorded. The cores were then removed from the vessel and visually examined to see if combustion had proceeded to the bottom. If combustion had not occurred internally or had not been complete, the core was placed in water. If burning had proceeded to completion, the permeability was determined.

Two cores were saturated overnight [15 hours]; all other cores were saturated for one hour. In Test 8, the core was not resaturated for the re-run.

In all tests the system was pressured to 500 psig except Tests 3, 5 and 7. In Test 5 there was a pre-ignition at atmospheric pressure, and in Tests 3 and 7 the pressure was only 400 and 390 psig, respectively. Pressurization was accomplished with nitrogen from a standard 2,000-psig cylinder.

Thermocouples are designated as TC-1, TC-2, or TC-3 depending on whether they were placed above the core, buried 1 in. from the top of the core or buried 2 ins. from the top of the core respectively.

Summary of Results

One liquid monopropellant and sandstone cores from five different formations were used in this study. Attempts were made to burn the propellant in 13 different cores, each saturated with the combustible liquid. Burning was complete in three of the cores, while in three other cores burning was only partial. Table 1 summarizes the results of permeability, porosity and burning tests. The increase in permeability for the three completely burned cores ranged from 109 per cent to 384 per cent. Results of several tests, based on recorder response, indicate a maximum uniform heating of the rock matrix to a temperature of about 455°C. Flash temperatures inside the core of over 1,100°C were recorded.

Individual Tests

Tests 2, 3 and 4 [Torpedo sandstone cores] are considered to be successful burns. Tests 6, 10 and 13 are considered to be partially successful, while the remainder of the tests [1, 5, 7, 8, 9, 11, 12 and 14] were failures.

Successful Burns

Test 2 - A good burn was obtained on Torpedo 31 core. A fresh mixture of propellant was used in this test. Five ml of propellant was placed on top of the saturated core just before it was lowered into the pressure vessel. A small amount, perhaps up to 2 ml, dripped out the bottom of the core after weighing and before burning. The ignitor thermocouple TC-1 gave an initial response of +1,230°C and continued above 1,095°C for the duration of the run of about 20 min. At 37 seconds after ignition, TC-2 registered a maximum of 635°C and in 4 seconds dropped to 455°C then gradually dropped to ambient in 18-1/2 min. When the flame front reached thermocouple TC-3, at 62 seconds after ignition, the temperature rose to 1,055°C and then declined to 455°C. From this point the temperature gradually decreased to ambient in 17 min.

Fig. 1 is a portion of the recorder tracing for Test 2. TC-1 was touching the top of the core and was initially covered with the propellant. When the ignitor was fired, the initial temperature was roughly 600°C. Apparently, the ignition momentarily pushed the liquid to one side, but then some liquid returned and cooled the thermocouple to 300°C. Almost immediately thereafter the temperature T_1 rose to over 1,230°C [the recorder limit] and fluctuated from approximately 1,000°C to over 1,230°C for the duration of the test. The exact cause for the way this thermocouple reacted is not known. Normally, based on other tests, this temperature should have peaked quickly and then declined rapidly to ambient.

Examination of this core, Torpedo 31,

revealed that the upper half contained many fractures which probably accounted not only for the erratic response of TC-1 but also for the high permeability obtained after burning. These fractures did not follow any consistent pattern but rather meandered and crossed one another quite haphazardly.

The two buried thermocouples gave similar responses in that they peaked quickly and just as quickly fell to an indicated uniform rock temperature of 455°C. It is interesting to note that in the other two successful burns the indicated uniform rock temperature was approximately the same.

As seen from Fig. 1, T_1 and T_2 are quite different in the maximum value obtained. T_2 is only 650°C while T_3 is 1,055°C. This may represent an actual flash temperature, a flame front of this magnitude, or it may be that there was enough extra propellant around each thermocouple to give that high a temperature only at the thermocouple drill holes. Future testing will be necessary to determine the nature and magnitude of the flame front.

Test 3 - A fresh mixture of propellant was used to saturate Torpedo 32 core. About 5 ml of propellant was pooled on top of the core prior to lowering it into the pressure vessel. The ignitor thermocouple [TC-1] gave an initial response of 790°C which decreased to 205°C within 6 seconds. The reading from this thermocouple then gradually decreased to ambient temperature during a period of 8-1/2 min. TC-2 gave a reverse polarity response at about 20 seconds after ignition. It took 60 seconds to reverse the thermocouple wires, at which time a temperature of 345°C was recorded. After 11-1/2 min. this had declined to ambient. At 50 seconds after ignition, TC-3 gave a sharp response of 730°C. Apparently, the flame front was traveling a little more slowly through the second inch of core, than through the first inch. The temperature at the point of reading dropped to 425°C in about 1/2 second, but then gradually and uniformly decreased to ambient in about 14 min. Only one small fracture was found near the top of the core in Torpedo 32. Most of the increase in permeability of this core is due to thermal alteration.

Test 4 - Although a good burn was obtained on Torpedo 33 core, a different type of temperature reaction was noticed. Fresh propellent was used to saturate this core. The bottom end of this core was sealed with a silicate preparation, and saturation was only about 55 per cent. Nine ml of propellant was placed on top of the core. A temperature in excess of 1,230°C was observed at TC-1. Nineteen seconds after ignition, TC-2 responded to a maximum temperature of 455°C and then gradually declined to ambient in 13 min. Thirty-eight seconds after [illegible] ature of 480°C which immediately dropped to 455°C and declined gradually for 55 seconds. The temperature then rose moderately to 1,150°C and continued at a constant value for 32 seconds, at which time it fell moderately to 475°C in 4 min., at which time the test was terminated.

In this test the response from TC-3 was unusual. The temperature peaked in 1/2 min., gradually falling off for 1 min. The temperature then peaked again at a value over twice the initial peak and remained constant for 1/2 min. before gradually declining. The bottom end of this core had been sealed with a silicate preparation prior to the burning test. After burning, this core was examined under a microscope and a fine fracture was seen to extend from the bottom through the lower thermocouple hole. There was no trace of this fracture beyond about 1/2 in. above TC-3. This fracture must have been caused by the heating and at the time the flame front had substantially passed TC-3. At that time hot and/or burning vapors began to escape upwards through the fracture causing a high temperature to be recorded by TC-3. The response from TC-2 was normal. Fig. 2 shows a slice of Torpedo core 33 taken from between the two thermocouple holes after the burning test.

Partial Burns

Partial burns were obtained only on Prue Sandstone cores. Prue core 51 was burned a little over half its length. This core was not fractured in any way, and a test on the burned portion gave a permeability of slightly over 40 md, for an increase of 208 per cent. The other two Prue cores were fractured to some extent at the lower end, but the burned parts were not fractured. In all cases the burned portion was changed in color from light brown to black. This could possibly be a carbon deposit, although it is believed to be caused by the color change of an iron compound. Future chemical analyses should indicate the cause of this and other color changes.

Test 6 - The core for this test, Prue 51, was placed in a fresh batch of propellant and saturated under a vacuum for 15 hours. Prior to lowering the assembly into the pressure vessel, a pool of 5 ml of propellant was placed on top of the core. When the core was removed after the burning test, some propellant was observed to be dripping from the bottom.

At ignition, the temperature T_1 above the core rose sharply to 480°C, fell erratically to 65°C, rose at a moderate rate [12 seconds] to +1,230°C for one second, and then fell moderately for 10 seconds to 565°C. It then rose gradually to 620°C in 28 seconds. The temperature gradually declined to the end of the test. Thirteen seconds after ignition, the temperature

T_2 rose sharply to 830°C, dropped steeply to 315°C, and then dropped gradually to the end of the test. Twenty-nine seconds after ignition the temperature T_3 rose gradually for 17 seconds to 110°C and then rose sharply to 650°C. It dropped fairly sharply to 275°C and gradually declined to the end of the test. Fig. 2 shows a slice of this core taken from near the lower thermocouple hole.

Test 10 - A fresh mixture of propellant was prepared, and Prue core 54 was saturated overnight. Prior to placement of the core inside the pressure vessel, 5 ml of propellant was placed on top of the core. Although the bottom of the core was wet with propellant after removal, burning did occur over part of the core. Thermocouple TC-1 registered a temperature of 660°C. T_2 after 20 seconds began to rise slowly for 80 seconds to 175°C and then, even more slowly, declined to ambient. The response of this thermocouple was probably the effect of conducted heat, the flame having died somewhere between the ignition end and TC-2. There was no response from TC-3.

Test 13 - Surplus propellant from a previous overnight saturation was used in the saturation of Prue core 53. Actual saturation time was reduced below the normal one hour. The resultant saturation was low, and it is believed that only the two ends were saturated. Prior to firing, a pool of 10 ml of propellant was placed on top of the core. A slightly different type of ignitor was used in this test, and Test 14. The ignitor was composed essentially of magnesium metal. A slight burning inside the core was obtained. T_1 was 995°C. T_2 rose, probably because of heat conduction, to 115°C after 2-1/2 min.

Failures

As indicated earlier, a flame could not be propagated into eight of the tests. In most instances the ignitor and the surplus propellant on top of the core burned. Of the tests that were failures, Test 5 is of enough interest to discuss.

Test 5 - Torpedo core 35 was coated, first with a very thin film of highly viscous, white epoxy plastic and then with 1/4 in. of translucent epoxy plastic. This core was saturated with a fresh mix of propellant. Five ml of propellant was placed on top of the core. The ignitor was placed on the core, the wiring completed, and the assembly lowered into the pressure vessel. Just as the operator began to thread the cover, the ignitor pre-ignited. It is assumed that a critical hypergolic condition developed. After being placed under water, this core, together with its plastic coating, fractured longitudinally down the center of the core, and then the half portions fractured into halves. The largest crack measured almost 1/16 in. Fig. 2 shows a slice taken from near the top of this core.

DISCUSSION

Fourteen tests were conducted, although two of them were on the same core. There were two failures because of either ignition or preignition trouble. Because an earlier preliminary test indicated low saturations, a vacuum was drawn on the cores and the propellant was introduced via a separatory funnel. Considerable fuming of the liquid was observed and the loss of certain volatiles may have significantly altered the composition of the propellant. This loss appeared not to affect the burning within the first cores, but the continued use of the surplus liquid to saturate subsequent cores probably was the major cause in the failures of subsequent tests.

The propellant is somewhat hydroscopic, and since there was no humidity control, the propellant may have been more or less desensitized by absorption of water from the atmosphere.

Rate of burning of the propellant was not uniform, neither through the entire cores [Torpedo] nor through corresponding sections. The time required to burn through the first inch was 37, 20 and 19 seconds for cores 31, 32 and 33 respectively. For these same cores the burning rate for the second inch was 25, 30 and 19 seconds. The fastest rate of burning for the first 2 in. was observed in Torpedo core 33 which had been sealed at the bottom. The recorder tracing gave no indication of the last 2 in. of two of the cores, but on Torpedo core 33, if the erratic action of TC-3 is any indication, the burning of the last 2 in. must have taken 87 seconds.

Cores in which the propellant did not ignite and burn were placed in a water bath for a few hours. In some of the cores thus treated the propellant did not fully mix with the water and did not become desensitized. Within the next few days these cores became badly fractured. These cores had a crushed appearance, the fractures not necessarily following any bedding plane but running in all directions. It may be that the cores not only are inhibiting the propellant, but also are reacting in some way with the propellant constituents when the two are in contact over a long period of time. Fig. 2 shows how the ends of one of the Prue cores looked after being fractured. Fig. 3 shows a Berea core in which the cementing material has deteriorated and most of the core can be crumbled easily. Some of the cores were unaffected by the propellant except for possib discoloration.

CONCLUSIONS

The burning of a high-energy compound within the interstices between sand grains is technically feasible.

Preliminary tests indicate that the heat of burning significantly increased permeability. The three Torpedo sandstone cores which were successfully and completely burned showed an average increase in air permeability of 216 per cent.

Additional testing of this and other high-energy compounds is warranted and necessary to more completely evaluate this method of increasing permeability.

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TABLE 1 -- RESULTS OF PROPELLANT BURNING TESTS

Test	Formation and Core Number	Porosity [per cent]	Liquid Saturation [per cent]	Initial Permeability [md]	Permeability after Burning [md]	Increase in Permeability [per cent]	Maximum Temperature Recorded, [°C] [1] TC-1	TC-2	TC-3
1	Prue 50	-	-	-	-	-	-	-	-
2	Torpedo 31	28.1	86.0	593	2,868	384	1,230	635	1,055
3	Torpedo 32	29.1	87.3	1,026	2,143	109	790	345	730
4	Torpedo 33	29.2	54.5	979	2,510	156	1,230	455	1,150
5	Torpedo 35	27.3	109.7	2,900 [2]	-	-	-	-	-
6	Prue 51	22.7	73.3	13	40 [3]	208	1,230	830	650
7	Bigheart 22	25.0	92.1	2,133 [4]	-	-	620	-	-
8	Bigheart 22	25.0	92.1	2,133 [4]	-	-	495	-	-
9	Berea 42	19.6	85.2	402	-	-	1,205	-	-
10	Prue 54	23.6	-	18 [4]	- [5]	-	660	175	-
11	Berea 43	19.0	82.0	410	-	-	1,230	-	-
12	Bigheart 21	24.8	71.9	1,455	-	-	855	-	-
13	Prue 53	20.9	28.8 [6]	15	- [7]	-	995	115	-
14	Bandera 10	17.3	-	17	-	-	-	-	-

[1] Termocouples are designated TC-1, TC-2 and TC-3 depending on whether placed above, buried in upper part, or buried in lower part of the core, respectively.
[2] Cast in epoxy plastic. Epoxy effected complete cure of silicate cover causing a by-passing of gas around core.
[3] Combustion died at 55 to 60 per cent of core length. Above values represent test on top 2 in. of core. Permeability of entire 4 in. was 21 md.
[4] Possible gas leak around core.
[5] Burned for approximately 5/8 in. Bottom end of core badly fractured.
[6] Saturation limited to the ends of the core.
[7] Burned for approximately 3/4 in. Bottom end of core fractured.

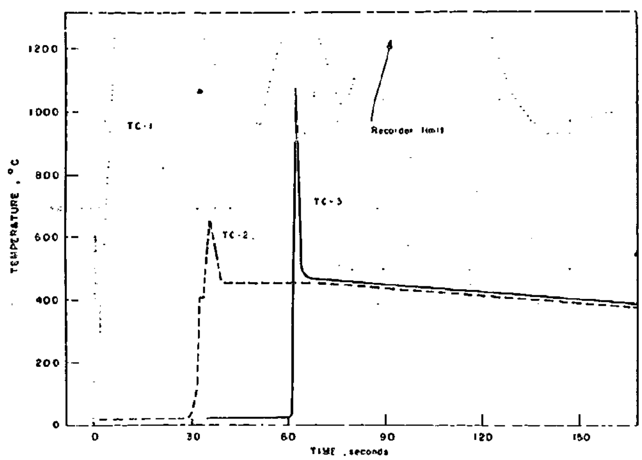

Fig. 1 - Temperature Response at Designated Locations

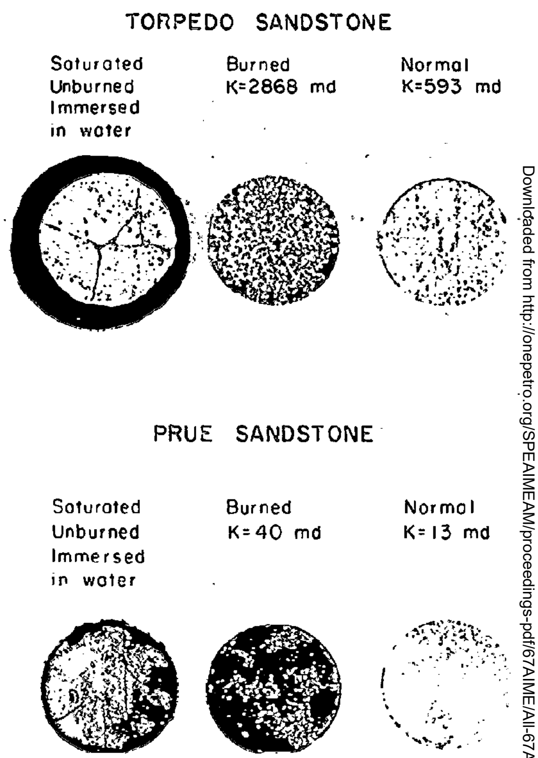

Fig. 2 - Comparison of Normal Sandstone With Both Burned and Fractured Specimens

Fig. 3 - Berea Sandstone Core After Having Been Saturated With Propellant