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A SOLUTION TO PROPPANT DISSOLUTION IN HYDROTHERMAL ENVIRONMENTS

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INTRODUCTION

The chemistry of silica may be one of the most widely studied subjects in the world. In Ilers[1] "The Chemistry of Silica" there are over 3000 references. Perhaps it has been so widely studied partially because it is one of the most abundant materials on earth and partially because its behavior is so enigmatic.

The concern with silica in this paper relates to its use as a gravel packing material in wells which produce from an unconsolidated formation or as a proppant used to provide a high permeability fracture path to the wellbore in lower permeability consolidated formations.

In gravel packed wells which produce heavy oil from incompetent formations the practice of injecting steam to enhance production is widespread. It has been found that under the conditions at which steam is injected, that is, pH 11 or higher and at temperatures up to 600°F, quartz sand dissolves fairly rapidly.[2] Attempts to alleviate this problem by substituting other materials for sand have been described.[3,4]

High alumina sintered bauxite has been suggested by one author;[3] a second author obtained contradictory results.[4] Additional studies show that siliceous formations also dissolve but at a lower rate because of impurities in the system[1,5].

Present studies agree with the work of the second author showing that bauxite is not only soluble to a considerable extent in high pH water, but that it also reprecipitates and fills in void spaces, decreasing the permeability of the pack.

Specially graded quartz sand is the primary proppant used in fracturing operations to stimulate production in lower permeability, competent formations. Bauxite type materials are used in deeper, harder formations to provide long term, high fracture permeability. Fracturing techniques using both sand and bauxite(6-8) to stimulate production in geothermal formations have been described.

There is no reason to assume that successful fracture treatments in geothermal wells cannot be accomplished. There may be no reason to be concerned that the quartz proppant should dissolve because one would assume that formation water from a sandstone formation would be saturated with silica. There is evidence that high temperature decreases the strength of quartz proppants.(6)

A review of "Compilation of Data on Fluids from Geothermal Resources in the US" showed silica contents from 4 ppm to 1416 ppm in water samples from different formations and fields.[9] The average concentration was in the range of 200 to 300 ppm. There appeared to be no correlation between pH of the water or total dissolved solids and the silica content. Analytical methods were not described, sampling procedures varied widely, and there was no description of formation composition.

Reprecipitation of silica from highly saturated formation water on to new silica surfaces is a real possibility.[1] Also it is unlikely that the formation water would be saturated with alumina in most instances so the possibility of dissolving bauxite exists.

A description of a new proppant which avoids the shortcoming of both sand and bauxite will be described in the following sections.

EXPERIMENTAL

A schematic of the test equipment used in this study is shown in Figure 1. Equipment includes a reservoir of deionized water which has been adjusted to pH 11 with reagent grade sodium carbonate. Carbon dioxide was excluded by utilizing a trap containing ASCARITE carbon dioxide absorbent. Upstream and downstream backpressure regulators were used to maintain a differential pressure of 60 PSI across the system, with an absolute system pressure of about 1200 PSI. The regulation equipment was protected by the cold water heat exchangers both up and down stream.

Test samples were contained in a section of 0.375 in. diameter tubing. Both the sample holder and the heat exchange coil were submerged in a thermostatically controlled fluidized sand bath. The entire system was initially constructed of wetted 316 stainless steel parts. Later studies utilized high temperature wetted parts made of monel.

Weight loss data were obtained by weighing oven-dried, loaded test cells before and after the tests. Note that this method does not account for any fines which are generated during the test and retained in the test cell, but only material which is actually produced from the cell.

A computer data acquisition system was used to determine permeability of the packs and to obtain 20 ml eluent samples on an hourly schedule. Fluids were analyzed for Si, Al, and Zr.

DISCUSSION

The initial objective of this study was the evaluation of commercially available proppants (Table I) useful as gravel packing materials for cyclic steam injection wells. These proppants were also to be considered for fracturing geothermal wells. This evaluation was to determine, under realistic conditions, the life expectancy of the packing material.

Laboratory screening conditions were selected to be representative. Most of the initial testing utilized a fluid temperature of 550°F and pH of 11. A fluid velocity of about 4 cm/min was generally used, however, this varied during the tests since a constant pressure differential was maintained. Three days of injection proved to be sufficient duration for the evaluation of most materials.

The weight loss results of some of the materials evaluated are shown in Table II. Sand gave the highest weight loss value, losing 77% of its weight in three days. It was found that this weight loss is proportional to fluid pH, temperature, and throughput volume, Figure 3 is a scanning electron micrograph of the sand sample after the three day test. Notice the smooth surfaces and the absence of any fines, indicating complete and uniform surface dissolution.

Several alumina based proppants, which are reported to have superior crush resistance at high temperatures are available for fracturing operations. These were evaluated and found to indeed be more stable than sand under the harsh conditions of cyclic steam treatments. Results of stability tests on five popular, high performance proppants which have been used for gravel packing cyclic steam injection wells are reported in Table II. The analyses of these materials are given in Table I. Weight loss results after three days of flowing hot water ranged from 37-60%. While this is an improvement over sand, it was considered unsatisfactory for two additional reasons. First, the material cost is very high (10-15 times) when compared to sand, and second, it was observed that pack permeability decreased dramatically. This is shown for IMS-2 in Figure 2.

The unexpected loss in permeability has also been observed in field operations using these type proppants. Figure 4 is a photograph of the sample as it was removed from the flow cell after a three day test. Copious quantities of fines were evident. Some actual consolidation of the pack can be observed. Figure 5 is a micrograph of this material showing an amorphus material being partially responsible for the consolidation of the pack. A crystalline overgrowth is also evident. The crystalline material shown in Figure 6 was identified as analcite ($NaAlSi_2O_6 \cdot H_2O$).

The unexpected occurrence of fines was observed with all the alumina and zirconia based materials. Some of these are shown in Figure 7-10. These results suggested that the use of high strength proppants for gravel packing cyclic steam injection wells or for use in geothermal applications may not be desirable. It has not been determined yet whether the fines formed during degradation of the packing material invade the formation and do permeability damage, nor how deep this damage may occur.

The poor performance of these high strength proppants led to the study of noncommercial materials as possible gravel packing solids. Many materials were evaluated and several were found to possess thermal stability properties. Most of these were eliminated because of poor control over particle size distribution and/or cost considerations. For example, nickel plated sand (Table II) proved to be highly resistant to the test conditions, however cost is prohibitive.

One material emerged as a product of choice. It is low cost, can be sieved to meet most any required size distribution, and is highly resistant to dissolution and fine formation under the test conditions. This material is identified in this paper as SRG

(Steam Resistant Gravel) in Table II. Photomicrographs in Figures 11-13 show the effect of 3 and 14 days of flowing 550°F water. There were no visible fines generated from this treatment as shown by (1) the micrographs and (2) the effect on permeability (Figure 2). Weight loss data show 8% decrease in weight. This occurs rapidly, and no additional loss was observed. This corresponds to a 5-10% silica contamination in the material. It is believed that silica contamination exists as small inclusions since small craters are apparently formed by the dissolution of this silica as shown in Figures 11-13.

This material is somewhat more angular than sand, but usually can meet the API minimum recommended sphericity and angularity requirements for gravel packing. Its acid solubility is very similar to that of sand, which permits performance of HCl and HF acid stimulation treatments through gravel packs of this material.

CONCLUSIONS.

1. Sand dissolves rapidly in pH 11, 550°F water but fines formation was not observed and permeability damage did not occur in the pack.
2. High strength, alumina and zirconia based proppants are not stable under test conditions used, losing 37-60% of their weight in three days. They also formed copious quantities of fines and showed severe permeability damage to the pack.
3. A new material (SRG) has been found to have a low loss of weight even after long exposure. There was no evidence of fines formation nor permeability damage. This material is 30-50% the cost of the high strength proppants.

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<u>TABLE I</u>

Typical Analysis for Gravel Packing Materials Tested

Typical Analysis	Ottawa Sand	IMS-1	IMS-2	IMS-3	HS-1	HS-2	SRG
Al_2O_3	0	55-60	39	75	-	77	0
$Al_6Si_2O_{13}$	0	40-45	54	24	-	22	0
$Al(OH)_3$	0	<1	<1	1.4	-	1	0
Amorphous	0	0	7	0	60	0	0
Spinnel	-	-	-	-	-	-	90-95
SiO_2	>98	-	-	-	-	-	5-10
ZrO_2	-	-	-	-	40	-	-

IMS = Intermediate strength proppant.
HS = High strength proppant.
SRG = Steam resistant gravel.

<u>TABLE II</u>

Weight Loss of some Evaluated
Gravel Packing Materials

Test Material	Injection Volume (Liters)	Weight Loss (%)
Ottawa Sand	13.6	77
IMS-1	13.1	60
IMS-2	11.6	56
IMS-3	14.5	41
HS-1	14.3	37
HS-2	13.1	48
Nickel Plated Sand	15.1	3
SRG	15.1	8
SRG	70.6	8

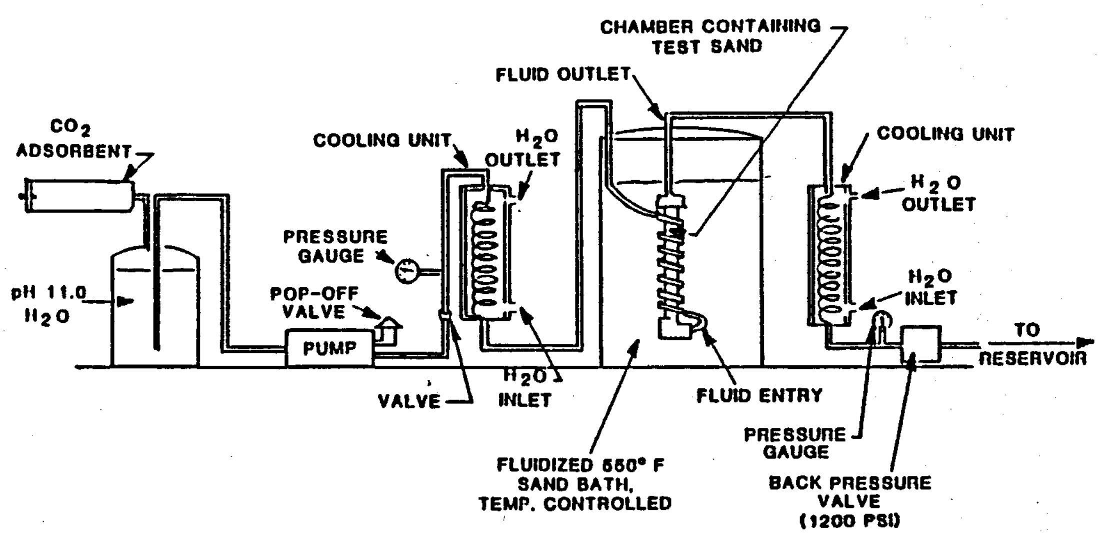

Figure 1: Schematic of Test Equipment for Injecting pH 11, 550°F Water Through a Pack of Test Solids.

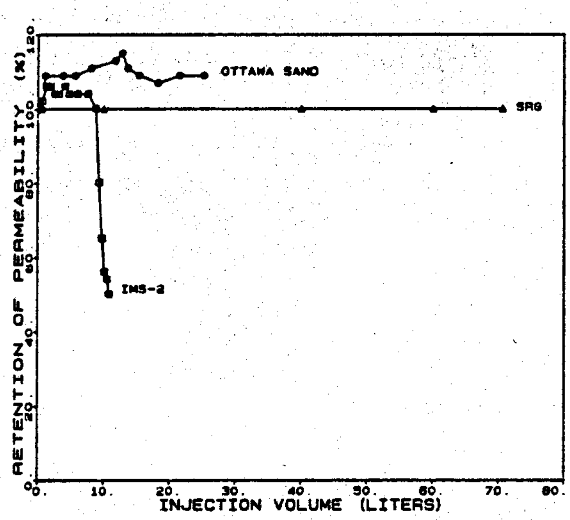

Figure 2: The Effect of Injection Volume of pH 11, 550°F Water on Pack Permeability

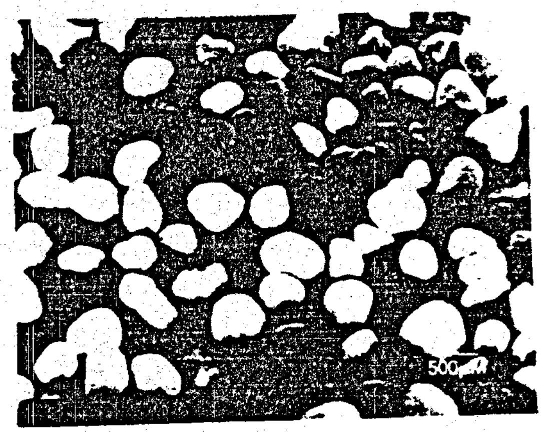

Figure 3: Ottawa Sand After Flowing 550°F Water for 3 Days.

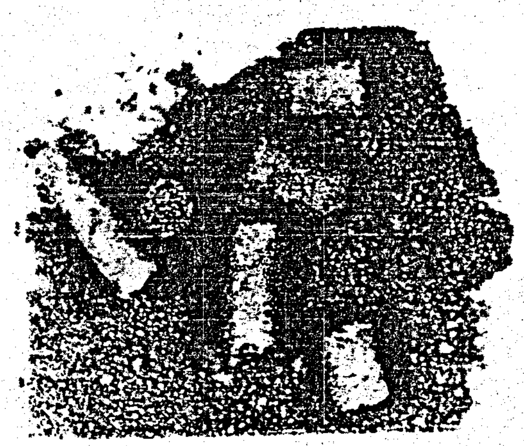

Figure 4: IMS-2 Sample as Removed from Test Cell After 3 Day Exposure to 550°F Water

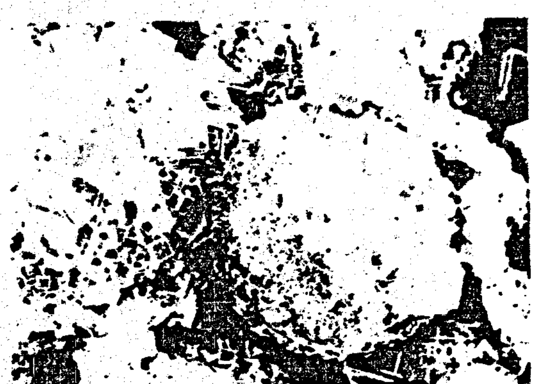

Figure 5: SEM of IMS-2 From Figure 4.

Figure 6: Crystalline Overgrowth From Figure 5 Identified as Analcite.

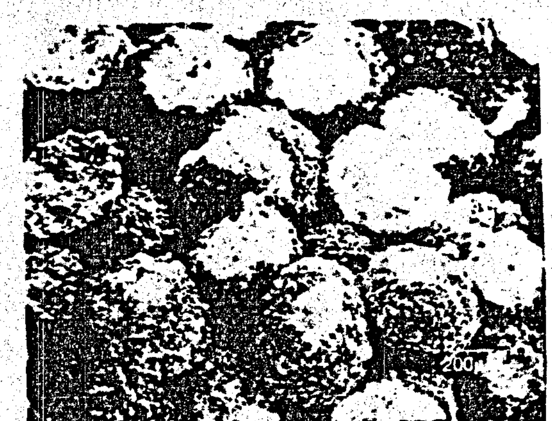

Figure 7: IMS-1 After 3 Day Exposure to 550°F Water.

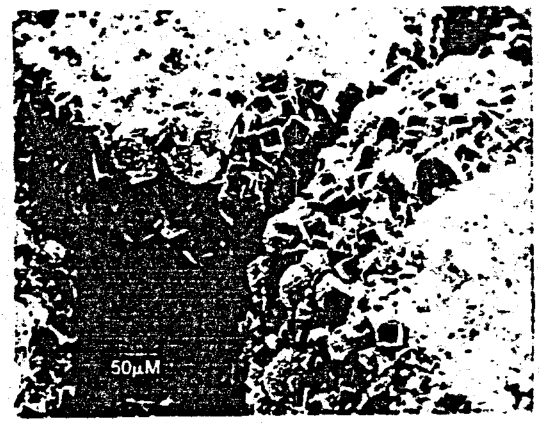

Figure 8: IMS-1 After 3 Day Exposure to 550°F Water. Higher Magnification.

Figure 9: HS-1 After 3 Day Explosure to 550°F Water.

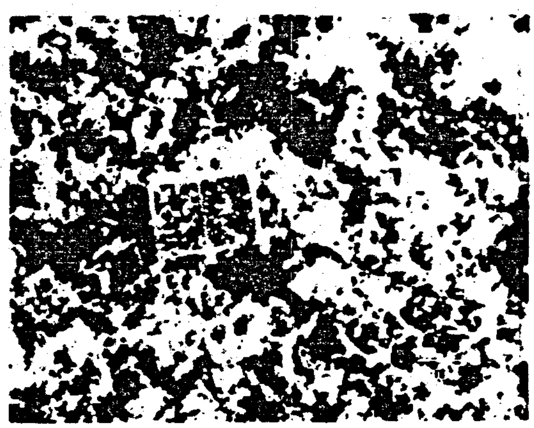

Figure 10: High magnification of Fines From 3 Day Exposure to HS-2.

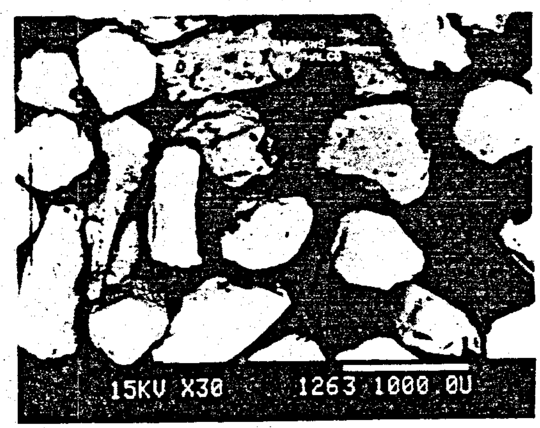

Figure 11: SRG Before Exposure to Hot Water.

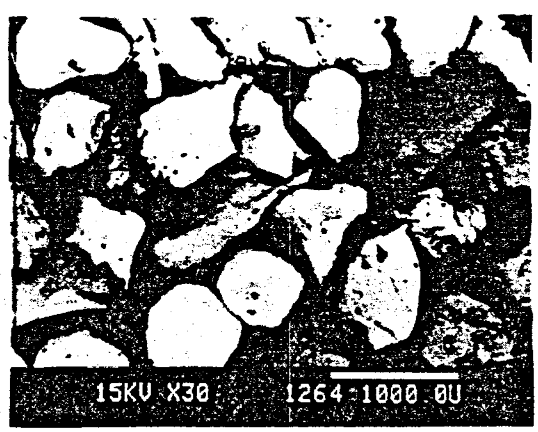

Figure 12: SRG After 3 Day Exposure to 550°F Water.

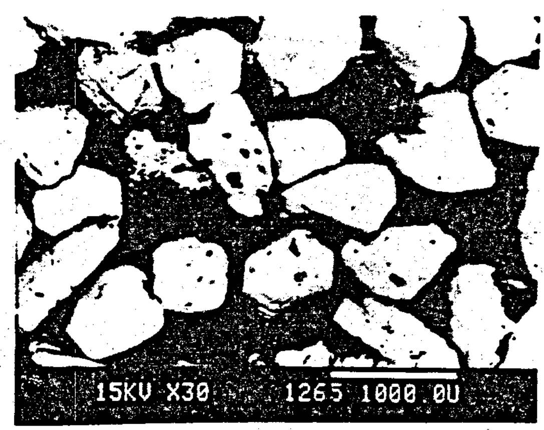

Figure 13: SRG After 14 Day Exposure to 550°F Water.