An improved proppant and method of use are shown for use in wellbore operations in which a well is hydraulically fractured with a suitable fluid to create fractures in a surrounding subterranean formation where the proppant is used to hold the fracture open and provide a conduit for the production of fluids or gases. The improved proppant has associated therewith a chemically active adjunct material designed to react with the fracturing fluid, with the surrounding subterranean formation or with a fluid produced from the subterranean formation. The chemically active adjunct material may be an ion exchange resin which reacts with any multivalent ions released into solution by reaction of the fracturing fluid with the surrounding formation or with any multivalent ions dissolved in formation fluids, in order that these fluids being produced from the well will not contain these ions, requiring more exotic treatment procedures on the well surface.
WELL BORE OPERATIONS USING REACTIVE PROPPANT

CROSS REFERENCE TO RELATED APPLICATIONS


BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] The present invention relates to well bore production, stimulation and related operations, and to such operations where a proppant is used in fracturing, or in frac pack, gravel pack and sand control operations and, more specifically, to well flowback operations which occur at the conclusion of such production and stimulation operations.

[0004] 2. Description of the Prior Art

[0005] Hydraulic well fracturing treatments are well known and have been widely described in the technical literature dealing with the present state of the art in well drilling, completion and stimulation operations. In a typical hydraulic fracturing operation, the subterranean well strata is subjected to tremendous pressures in order to create “fractures” of the strata to enable an increased flow of oil or gas reserves, ultimately to be produced to the well surface. These fracturing treatments typically employ a “proppant” in order to prop open the fractures which result from the fracturing treatment. Proppants or “propping agents” have been widely used in the past to maintain permeability in oil and gas wells. Proppants are materials that can be dispersed in a carrier liquid and pumped into oil or gas wells under pressure during a fracturing process. Proppants can “prop” open fractures in the rock formation surrounding the wellbore and thus preclude such fractures from closing. As a result, the amount of formation surface area exposed to the wellbore can be increased, enhancing recovery rates. Proppants can also add mechanical strength to the formation and thus help maintain flow rates over time.

[0006] In some instances in the prior art, proppants have been used to provide additional functionality to cover such uses as tracking or tracing the proppant pack or to provide information on the properties or progression of the fracturing operation. For example, Nguyen et al. (U.S. Patent Application Publication No. US 2008/0274510 A1) describes the use of a particular conductive polymer and/or conductive filler phase in a polymer coated proppant to determine formation parameters via an electric field-based remote sensing procedure. In another example, Ayoob et al. (U.S. Pat. No. 7,082,993 B2) describes the use of active or passive devices to characterize fracture parameters. Barron et al. (U.S. Patent Application Publication 2009/0288820) is another recent publication which describes the use of “proppants having added functional properties” which allow them to be used to “track and trace the characteristics of a fracture in a geologic formation” (see Abstract). These tracking or mapping proppant applications did not appear to react with the surrounding formation or formation fluids to achieve some specific result. Certain of these applications required the presence of an external stimulus or the application of heat or, in some cases, the pumping of a companion material.

[0007] In addition, these rather exotic uses of “functional proppants” have failed to address certain more fundamental problems associated with the traditional well fracturing processes, however, such as the problem of contaminated flow back water produced from the well at the conclusion of the fracturing operation.

[0008] In large volume hydraulic fracturing treatments, the primary treatment fluid is water. In some instances, some 1-5 million gallons of fresh water, or more, may be used in such a hydraulic fracturing treatment. Additives such as gelling agents, clay stabilizers, friction reducers, and scale inhibitors are often added. These chemicals are generally compatible with fresh water or water containing single valent ions such as hydrogen, sodium, potassium, or ammonium. When the water contains multivalent ions such as calcium, magnesium, or iron then incompatibilities can occur.

[0009] Most mineral surfaces such as carbonates, sandstones, and shales are ionically active. Depending on the specific composition when exposed to water containing single valent ions, the surface of the mineral adsorbs the ion releasing the corresponding ion to the solution.

[0010] If fresh water is being pumped, then hydrogen is the active ion. A 2% KCl solution has an abundance of potassium (K). Any mineral surface containing bivalent ions such as Ca++ or Mg+++ will replace the surface cation with the concentrated ion in solution. If, by way of example, a 2% KCl solution is used to treat a shale formation with predominately Ca++ surface ions, the result will be a decrease in K+ and an addition of Ca++ in the flow back water.

[0011] There will also be a resultant change in anion concentration due to solubilities. For example, if the formation contains Ca(SO)4, i.e., (calcium sulfate) then some of the mineral will dissolve producing Ca++, K+, Cl−, and SO4− ions in solution. These ion exchange reactions create changes in the quality of the flow back water being produced from the well. In most cases, the flow back water must either be treated to improve quality, or must be disposed of in some way. There are, therefore, significant problems associated with the contaminated flow back water produced in hydraulic fracturing operations.

[0012] According to the Petroleum Technology Transfer Council, a recent study suggests that approximately 35,000 hydraulic fracture treatments will be pumped per year through 2025 and that 75% to 79% of all new gas production in the U.S. will be produced from wells that have been hydraulically fractured. Assuming 35,000 hydraulic “frac” treatments per year at 100,000 barrels of frac water, this translates into some 3.5 billion barrels of frac water that will flow back to the surface every year to 2025 and will need to be treated.

[0013] At the present time, a number of different means are being utilized to handle the need for fracturing water, as well as disposing of used flow back water. Water is transported from the gas well to the disposal well typically done by air-polluting, road-damaging trucks. A single well may have more than 100 water-haulers servicing the well during a hydraulic fracturing operation. Traffic accidents, associated spills, and driver/passenger injuries are a further risk. Frac water is oftentimes purchased from municipalities near the drilling site for a cost that may be on the order of $1.50 per barrel. The cost to remove the frac flowback water and to dispose of the water (deep hole injection or above ground storage pits) is presently on the order of approximately $4.00 per barrel, so that the total cost for transport to and from the...
well is approximately $5.50 per barrel. Assuming that the gas driller is using 100,000 barrels to frac a well, the cost of water acquisition/transportation/disposal per well is on the order of $500,000 for such a theoretical scenario.

[0014] It is significant to note that while the various ionic reactions discussed above have the potential of producing various deleterious effects in flow back water, i.e., resulting in contaminated flow back water, these ionic reactions are also reversible. This principal of the reversible nature of such ionic reactions is the same principal which is used in commercially available home water softeners. The typical home water softener has a bed of ion exchange resin that is exposed to sodium chloride. When water enters the consumer’s home and contains calcium and/or magnesium ions, the water flows through the resin bed and the calcium and magnesium ions are adsorbed onto the resin, releasing Na+ into the water. After all the Na+ ion is expended, then a brine of very high NaCl concentration is back flowed through the resin bed, removing the calcium and magnesium and restoring the Na+ concentration. The back flow is discharged to the local sewer system in the typical home water softener system.

[0015] There exists, therefore, a need for a method for improving the quality of flow back water of the type produced in well bore fracturing and stimulation operations, which method would eliminate the need for many of the more expensive water treatment processes presently employed.

[0016] A need exists for such a method which could be economically employed as a part of the typical well bore fracturing or stimulation treatment and which would improve the quality of flow back water by an “in situ” treatment process, rather than requiring extensive above ground treatment processes and equipment.

[0017] A need exists for such a treatment procedure which would be simple in design and relatively economical to implement based upon the same type principles as those used in commercially available home water softeners.

SUMMARY OF THE INVENTION

[0018] The present invention has, as its primary object, to overcome many of the deficiencies associated with prior art techniques for dealing with well flow back water which have been described above.

[0019] One object of the present invention is to include an appropriate “functional adjunct material” for traditional proppant used in well bore operations, so that the proppant is “reactive” with the surrounding subterranean formation, or with formation fluids in order to achieve a specified end result. The particular end result can vary, but one particularly preferred end result is the capture of specific unwanted multivalent ions or cations present in well flow back water. In one particularly preferred version of the invention, an adjunct such as an ion exchange resin would be included as one of the components which is added to the frac treatment as proppant or in conjunction with proppant. The ion exchange resin could be added, for example, as a coating for sand or bauxite if a higher strength is needed for the particular well bore treatment. Theoretically, a bed of ion exchange resin would then exist in the created fractures and, as the treatment water is flowed back to the surface, any unwanted multivalent ions or cations will be captured and remain in the subterranean well bore location. The returned water could be filtered to remove any fines and any oil separated and the water would be ready for the next treatment stage or in a more traditional water quality treatment process, such as reverse osmosis, ultra filtration, etc. The improved quality of the flow back water would greatly lessen the burden on the traditional surface equipment and processes used to produce an environmentally acceptable end product.

[0020] In the preferred form to be described in greater detail in the discussion which follows, the novel method of the present invention thus deals with a method of stimulating oil, gas, or water wells where a hydraulic fracturing fluid is used to create and propagate a hydraulic fracture and is used to transport a proppant to prop the fracture. In the preferred method of the invention, the proppant is reactive, rather than being relatively inert, as was the case of sand, bauxite, and other traditionally employed well proppants. A review of the traditional technical literature related to well fracturing operations discusses the use of such proppants as sand, walnut hulls, aluminum pellets, glass beads, ceramic beads, resin coated sands. All of these materials are generally understood to be inert. To the best of Applicant’s knowledge, no one has previously claimed the use of a reactive proppant that is placed by itself or in conjunction with normal proppants to specifically react with components of well fluids, or with the surrounding formation in order to improve the quality of the well water flow back fluids ultimately recovered from the well bore following the fracturing treatment.

[0021] One application of the method of the present invention would be to pump ion exchange resin beads as proppant or in conjunction with proppant to react with any multivalent ions released into solution by reaction of the fracturing fluid with the formation or with any multivalent ions dissolved in formation fluids, in order that these fluids being produced from the well will not contain these ions, requiring more exotic treatment procedures on the well surface. Specific ion exchange resins can be selected depending on the chemical species which is being attempted to be removed or reduced in the flow back water.

[0022] The method of the invention is intended to encompass the concept of pumping a reactive proppant as part of a traditional well fracturing treatment, where the reaction of the proppant or a chemical constituent of the proppant would be designed to achieve a specific functional result, namely to improve the quality of flow back water being produced to the surface of the well.

[0023] Thus, a novel method is shown for hydraulically fracturing a well with a suitable fluid to create fractures in a surrounding subterranean formation, the fluid containing a well proppant to hold the fracture open and provide a conduit for the production of fluids or gases. The improvement comprises the use of a proppant which has associated therewith a chemically active adjunct material designed to react with components of the fracturing fluid, with the surrounding subterranean formation or a fluid produced from the subterranean formation. The preferred chemically active adjunct material is an ion exchange resin which can be a component of the proppant or applied, as by a coating to the proppant. Preferably, the proppant is coated with an ion exchange resin.

[0024] Additional objects, features and advantages will be apparent in the written description which follows.

DETAILED DESCRIPTION OF THE INVENTION

[0025] The present invention has as a primary objective to provide a means for the recapture and reuse of flow back water from a hydraulic fracturing treatment and to improve the overall quality of such flow back water “in situ” down-hole, prior to the water being returned to the well surface. As
explained in the background discussion above, such flow back water typically contains an excessive amount of calcium, magnesium, and iron, along with trace amounts of a number of other elements. The multivalent ions in the flow back water react with common fracturing fluid additives such as friction reducers, oxygen scavengers, corrosion inhibitors, scale inhibitors, and biocides. The resulting reaction products thus make the flow back water unusable in a new fracturing operation. Several techniques are currently being investigated to remove these contaminants and allow the water to be used. These include reverse osmosis, ultrafiltration, distillation, among others. These processes tend to be complicated and require expensive equipment and techniques.

[0026] In the typical fracturing operation conducted in the prior art, the proppant pumped is inert. Current and common proppants include sand, walnut hulls, bauxite, aluminum pellets, and glass beads to name a few. A good proppant will be of uniform size with greater than about 90% being between 16 mesh and 50 mesh. It will be resistant to fine generation and have a low density for transport, for example, a specific gravity around 1.18. The above listed and other of the prior art proppant materials are, by in large, all inert. Recently resin coated proppant has been introduced into the fracturing industry, and the resin coating may be reactive, but typically only with itself. For example, the resin may cure to bond together to prevent proppant flowback or provide more fracture closure resistance.

[0027] The present invention provides a method for introducing a “reactive proppant” downhole during the fracturing operation to react “in situ” with the formation or formation fluids to remove certain unwanted impurities or contaminants. One approach to achieve this result would be to pump an ion exchange resin instead of proppant or in conjunction with the proppant used in the fracturing operation. The water used in the fracturing operation would flow through the fracture and then back to the wellbore where the multivalent ions would be removed from solution by the retained proppant and the flow back water would be ready to use for the next fracturing operation.

[0028] The method of the present invention involves designing and pumping a fracturing treatment which contains the normal additives used in the industry; as well as one or more proppants selected from a variety of materials that have a sufficient size and shape to prop open the fracture and provide flow conductivity to produce from the reservoir. One of the proppant materials would contain one or more reactive proppants that would react with, for example, iron and manganese to prevent their production in water. As one example, one candidate reactive proppant material might consist of an ion exchange resin such as Dowex HCR Resin™ sold commercially by the Dow Chemical Company. This resin has a mesh size (16/50) which is the same as the size as proppant commonly used in hydraulic fracturing treatments. This resin is described in the literature as being a high capacity, gel-type, strong acid cation exchange resin with a polydispersed particle size distribution. It is based on a styrenedivinylbenzene copolymer (DVB) matrix with sulfonate functional groups. The degree of cross linkage (approximately 8% DVB content) is chosen to provide a high capacity, efficiently regenerable resin with good physical and oxidative stability for operation in a variety of water softening environments. When 1000 cubic foot of this resin is used as proppant or in conjunction with more conventional proppant, the well should be capable of flowing back a minimum of 1,000,000 gallons of treating fluid and well fluids without any appreciable multivalent ions.

[0029] Instead of using an ion exchange resin as a replacement or partial replacement for traditional proppant materials, the proppant could be treated in a variety of ways in order to allow the incorporation of the reactive adjunct which is added to produce the desired result in reacting with formation fluids, or the surrounding subterranean formation. For example, the proppant particle might therefore comprise a matrix, such as a ceramic matrix, glass matrix, or ceramic-glass matrix, and at least one functional component. The functional component could be encased by, or incorporated into, the matrix. The functional component might also be incorporated into or encased by a polymer or polymeric material, including but not limited to, a layer containing the polymer or polymeric material. The functional component of the proppant might be distributed substantially throughout the matrix (i.e., a particulate composite). The functional component can be incorporated, for example, as a discreet phase in the matrix. The functional component might also be incorporated in the proppant particle in particular zones or locations in or on the proppant, such as in one or more layers that are optionally substantially overcoated with a further layer.

[0030] The following examples are intended to be illustrative of the invention, without being limiting in nature.

**EXAMPLE 1**

Dowex MAC-3

- **Type**: Weak acid cation
- **Total Exchange Capacity**: 83.0 kgr/ft³
- **Bead Size**: 16/50
- **Particle density**: 1.18 g/ml
- **Bulk weight**: 47 lbs/ft³
- **pH range**: 5-14
- **Max operating temperature**: 250°F
- **Regenerant**: 1-5% HCl

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**EXAMPLE 2**

Dowex HCRSS

- **Type**: Strong acid cation
- **Total Exchange Capacity**: 43.5 kgr/ft³
- **Bead Size**: 16/50
- **Particle density**: 1.28 g/ml
- **Bulk weight**: 51 lbs/ft³
- **pH range**: 0-14
- **Max operating temperature**: 250°F
- **Regenerant**: 8-12% NaCl
EXAMPLE 2
Dowex HCRSS

Treatment Capacity

1000 ft² will treat 743971 gallons (17,713 bbls) gallons of 1000 ppm cation concentration

Estimate cost $60/ft² or 0.081/gallon ($3.40/bbl) of treated water

Testing Conditions:

length 6 inches
width 5 inches
depth 3 inches
Sandstone/Shale formation cut to fit into cell 2 slabs

Dimensions

length 5.5
width 4.5
depth 0.75 inches
Total liquid volume of cell — 600 mls

Testing Procedure:

Placed 250 ml formation fluid 850 ppm CaCl₂ in test cell
Added 250 ml 2% KCL with 30 grams Mac-3
30 minute sample — 513 ppm Hardness
60 minute sample — 434 ppm Hardness
90 minute sample — 188 ppm Hardness
24 hour sample — 51 ppm Hardness

Testing Procedure:

Placed 250 ml formation fluid 850 ppm CaCl₂ in test cell
Added 250 ml 2% KCL with 30 grams HCRSS
30 minute sample — 325 ppm Hardness
60 minute sample — 240 ppm Hardness
90 minute sample — 171 ppm Hardness
24 hour sample — 86 ppm Hardness

The above test results show that, in the presence of the reactive proppants of the invention, water hardness is greatly reduced, simulating the capture of multivalent ions in a subterranean formation.

The improved proppant and method of its use provide a number of significant advantages over the techniques used in the prior art. Rather than being inert relative to the formation and formation fluids, the proppant materials of the invention would be reactive in respect to specific reservoir conditions. Specific end results may vary, depending upon the application, but one of the preferred end results would be the capture of multivalent ions in the formation. For example, the preferred ion exchange resins would be designed to complex multivalent cations, preventing the formation of insoluble scales or other undesirable resulting conditions downhole.

The method of the invention provides a flow back fluid processing strategy that is designed to provide acceptable reuse of flow back water. The processing steps and effects which can be achieved include:

- adjusting pH to a level that is optimum for specific divalent and metal precipitation;
- use of a divalent cation additive to complex soluble ions and sediment the resulting particles;
- the removal of iron;
- performing microbiological disinfections, if needed;
- conducting final filtration steps to remove any remaining suspended solids.

The water produced by the method of the invention would be more easily recycled than typical flow back water. The recycled water could be reused in a subsequent new frac job, or used for livestock, agriculture, and industrial uses, reducing the truck traffic for water disposal and the need to inject polluted water into a deep disposal well. As the cost of water and water disposal increases, water recycling will become more cost-effective. The increased use of recycled water results in (1) reduced water usage; (2) reduced loss of water to the water cycle; (3) reduced truck traffic in and out of the hydraulic fracturing site; and (4) a reduction in the risks associated with deep well injection of the flow-back water, among other advantages. The same type advantages that can be achieved in by the use of reactive proppants in hydraulic fracturing treatments can also be achieved in frac pack and gravel pack and sand control treatments.

While the invention has been shown in one of its forms, it is not thus limited but is susceptible to various changes and modifications without departing from the spirit thereof.

What is claimed is:

1. A well treatment method wherein a well is hydraulically fractured with a suitable fluid to create fractures in a surrounding subterranean formation, the fluid containing a well proppant to hold the fracture open and provide a conduit for the production of fluids or gases, the improvement comprising:
   - the use of a proppant which has associated therewith a chemically active adjunct material designed to react with the fracturing fluid or with the surrounding subterranean formation or a fluid produced from the subterranean formation to achieve a particular specified result.

2. The method of claim 1, wherein the chemically active adjunct material is a discrete material used as a total or partial replacement for a traditional proppant material.

3. The method of claim 1, wherein the chemically active adjunct material is a treatment applied to a traditional proppant material.

4. The method of claim 1, wherein the proppant is coated with an ion exchange resin.

5. The method of claim 1, wherein the proppant is selected from the group consisting of sand and bauxite.

6. The method of claim 1, wherein the chemically active adjunct material is designed to react with any multivalent ions released into solution by reaction of the fracturing fluid with the surrounding formation or with any multivalent ions dissolved in the fracturing fluid or formation fluids, in order that these ions will be removed from any fluids being produced from the well, thereby eliminating the need for more exotic treatment procedures on the well surface.

7. An improved proppant for use in wellbore operations in which a well is hydraulically fractured with a suitable fluid to create fractures in a surrounding subterranean formation, the fluid also containing a well proppant to hold the fracture open and provide a conduit for the production of fluids or gases, the improvement comprising:
   - the use of a proppant which has associated there with a chemically active adjunct material designed to react with the fracturing fluid, with the surrounding subterranean formations;
8. The proppant of claim 7, wherein the chemically active adjunct material is designed to react with any multivalent ions released into solution by reaction of the fracturing fluid with the surrounding formation or with any multivalent ions dissolved in the fracturing fluid or formation fluids, in order that these ions will be removed from any fluids being produced from the well, thereby eliminating the need for more exotic treatment procedures on the well surface.

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