

Claim Elements:	U.S. Patent No. 6,436,880 B1 (Frenier)	U.S. Patent No. 10,072,205 B2 (Reyes)	Borchardt, <i>Chemicals Used in Oil Field Operations</i> , 1989
1. A method for stimulating an existing well in a nano-darcy shale formation comprising:	ABSTRACT This invention relates to the stimulation of hydrocarbon wells and in particular to acid fluids and methods of using such fluids in treating a subterranean formation having low permeability. 6.49 The efficiency of a matrix treatment depends primarily upon removing or bypassing regions of low permeability that restrict productivity. This restriction is generally shown by an overall diminished production level or a sharper-than expected decline in production. Pressure transient analysis is a common technique for estimating the extent of damage. What is claimed is: 1. A well treatment fluid composition. 8. A method of matrix-acidizing a sandstone or carbonate subterranean formation,	ABSTRACT Methods for treating a subterranean formation can comprise: providing a treatment fluid comprising an aqueous carrier fluid, an acid, and a chelating agent comprising an amino-polycarboxylic acid, the treatment fluid having a pH below that at which the carboxylic acid groups of the chelating agent are substantially protonated and the chelating agent is ineffective for complexing a metal ion; introducing the treatment fluid into a subterranean formation comprising a carbonate mineral; reacting the acid with the carbonate mineral, such that the acid at least partially spends and the pH of the treatment fluid rises; and once the pH of the treatment fluid rises above a pK, value for one or more of the carboxylic acid groups, complexing a metal ion with the chelating agent. The invention claimed is: 1 . A method comprising: providing a treatment fluid comprising an aqueous carrier fluid ... introducing the treatment fluid into a subterranean formation comprising a carbonate mineral.... 2 . The method of claim 1 , wherein the carbonate mineral comprises calcite , dolomite , or any combination thereof. 3 . The method of claim 2 , wherein the subterranean formation comprises a chalk formation. 13 . The method of claim 12, wherein the subterranean formation comprises a chalk formation .	Page 3 Chemicals of various types are used in every stage of drilling, completing, and producing oil and gas wells. This review describes these chemicals, why they are used, and recent developments. These chemicals include common inorganic salts, transition metal compounds, common organic chemicals and solvents, water-soluble and oil-soluble polymers, and surfactants. As existing fields become depleted, use of chemistry to maintain production via well stimulation, more efficient secondary recovery operations, and enhanced oil recovery become ever more important. Page 3 While geochemistry plays a role in the discovery of oil and gas and production chemicals are used to break produced oil-water emulsions and as friction reducers in pipelines, this review will be restricted to the chemistry and chemicals involved in drilling, completing, stimulating, and operating production and injection wells and in enhanced oil recovery. Page 13 Matrix acidizing is the injection of acids into the formation at a pressure below the formation parting pressure (the pressure at which natural fractures are forced open by injected fluids). Properly designed, the injected acid enters the flow channels of the formation and flows radially outward from the wellbore dissolving mineral fine particles in the flow channels. Minerals forming the flow channel walls also react with the acids. These processes increase formation permeability near the wellbore. The end result Page 20 A chelating agent such as ethylenediamine tetraacetic acid can aid in dissolving calcium sulfate deposits. Page 30 Chelating and sequestering agents have been used to reduce the adverse effect of divalent (316) and multivalent metal ions on polyacrylamide solution viscosity (321,322). Page 17 Precipitation of Fe(III) compounds from acid solutions as the pH increases above 2.2 is a particular problem. Complexing agents that have been used include 5-sulfosalicylic acid and citric acid (136); dihydroxymaleic acid (137); ethylenediaminetetraacetic acid (138); lactic acid (138); blends of hydroxylamine hydrochloride, citric acid, and glucono-delta-lactone (139); nitriloacetic acid; blends of citric acid and acetic acid; lactic acid; and gluconic acid (140). Page 18 Ethylenediaminetetraacetic acid and similar complexing agents have been used to remove scale from formation surfaces near wellbores.
providing a treatment mixture containing between about 0.1% and 95% by weight metal complexing agent at a pH of between about 0 and 10;	An acidic fluid that is useful in stimulation and workover operations, and in particular, for the control of iron in acidizing operations, the removal of alkaline earth carbonate scale in scale removal operations, and matrix or fracture acidizing operations, comprises an acid, such as hydrochloric acid; water, and a hydroxyethylaminocarboxylic acid. Preferred hydroxyethylaminocarboxylic acids are hydroxy ethylethylenediaminetriacetic acid (HEDTA) and hydroxy ethyliminodiacetic acid (HEIDA). Also disclosed herein are methods of controlling iron, removing alkaline earth carbonate scale, or matrix or fracture acidizing, involving the use of the acidic fluid. What is claimed is: 1. A well treatment fluid composition, comprising: a first acid in an amount from about 15 wt % to about 28 wt % of the composition; water; and hydroxyethyliminodiacetic acid (HEIDA) or a salt thereof.	The invention claimed is: 1 . A method comprising: providing a treatment fluid comprising an aqueous carrier fluid , an acid , and a chelating agent comprising methylglycine diacetic acid , the treatment fluid having a pH of 1 or lower.... 11.21 In various embodiments, the concentration of the chelating agent in the treatment fluid may range between about 0.1% to about 40% of the treatment fluid by weight . In some embodiments , the concentration of the chelating agent in the of the treatment fluid by weight, or between about 1% to about 10% of the treatment fluid by weight , or between about 5% to about 15% of the treatment fluid by weight , or between about 0.5 % to about 5% of the treatment fluid by weight , or between about 10% to about 25% of the treatment fluid by weight , or between about 10% to about 40% of the treatment fluid by weight, or between about 30% to about 40% of the treatment fluid by weight.	

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injecting the treatment mixture into the well at a pressure less than a fracture pressure of the nano-darcy shale formation until at least some of the treatment mixture exits the well and contacts the nano-darcy shale formation;	9. A method of acid-treating a subterranean formation, comprising: injecting a well treatment fluid composition via a wellbore into a subterranean formation, the well treatment fluid composition comprising: a first acid in an amount from about 15 w % to about 28 w %; water, and hydroxyethyliminodiacetic acid (HEIDA).	1.29 Acidizing operations may be used to stimulate a subterranean formation to increase production of a hydrocarbon resource therefrom . Introduction of the acidizing fluid to the subterranean formation may take place at matrix flow rates without fracturing of the formation matrix , or at higher injection rates and pressures to fracture the formation (i.e. an acid - fracturing operation) . 9.14 Illustrative carbonate formations that may be acidized using the treatment fluids and methods described herein include, for example, limestone and chalk formations. Chalk formations are to be distinguished from other types of carbonate formations due to their high porosity, but generally low permeability values. Specifically, chalk formations can be highly porous, but the pores may lack interconnectivity Claim 1. ...introducing the treatment fluid into a subterranean formation comprising a carbonate mineral ... Claim 11. ...providing a treatment fluid comprising an aqueous carrier fluid, an acid , and a chelating agent comprising methylglycine diacetic acid, the treatment fluid having a pH of 1 or lower, such that the carboxylic acid groups of the chelating agent are protonated and the chelating agent is ineffective for metal ion complexation; introducing the treatment fluid into a subterranean formation comprising a carbonate mineral, the treatment fluid being introduced into the subterranean formation at a pressure greater than or equal to a fracture gradient of the subterranean formation, so as to form a fractured formation....	Page 13 Matrix acidizing is the injection of acids into the formation at a pressure below the formation parting pressure (the pressure at which natural fractures are forced open by injected fluids). Properly designed, the injected acid enters the flow channels of the formation and flows radially outward from the wellbore dissolving mineral fine particles in the flow channels. Minerals forming the flow channel walls also react with the acids. These processes increase formation permeability near the wellbore. The end result is to increase well productivity without increasing the produced water:oil or gas:oil ratios.
maintaining the treatment mixture in contact with the nano-darcy shale formation for a contact time of between about 1 minute to 100 days, thereby allowing the metal complexing agent to bind with at least some naturally-occurring metals contained within the nano-darcy shale formation; and	7.22Matrix Acidizing Treatment The well treatment fluid compositions of the present invention can be used in matrix acidizing of subterranean formations surrounding wellbores. Such matrix acidizing methods generally involve pumping the acid-containing well treatment composition down the wellbore and out through perforations into the target formation.... After the composition has been injected into the formation, optionally the well can be shut in for a period of time to allow more complete reaction between the acid and the formation material. The desired result of the treatment is an increase in the permeability of the formation, for example by the creation or enlargement of passageways through the formation, and therefore an increase in the rate of production of formation fluids such as oil and gas	Claim 1. ...reacting the acid with the carbonate mineral in the presence of the chelating agent at or below the pH at which the chelating agent is ineffective for metal ion complexation , such that the acid at least partially spends and the pH of the treatment fluid rises as the acid reacts; and once the pH of the treatment fluid rises above a p _k value for one or more of the carboxylic acid groups, complexing a metal ion with the chelating agent, wherein the chelating agent decreases a rate of dissolution of the carbonate mineral	Page 25 The most commonly used crosslinkers are Al(III) and Cr(III) compounds(199). The injected fluid preferentially enters the thief zone. The well is shut in to allow crosslinking to occur. After 1-7 days depending on the treatment, normal injection operations are resumed.

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removing the treatment mixture from the well after the contact time, thereby removing the bound naturally-occurring metals from the non-darcy shale formation and thereby improving the hydrocarbon production of the well relative to the hydrocarbon production immediately prior to performance of the method.	7.39 Parametes such as pumping rate, pumping time, shut-in time, acid content, and additive package, must be determined for each particular treatment since each of these parameters depends upon the extent of the damage, formation geology (e.g., permeability), formation temperature, depth of the producingzone, etc. A well-treatment designer of ordinary skill is familiar with the essential features of matrix acidizing treatments.	1.35 During an acidizing operation an acid-soluble material in the subterranean formation can be dissolved by one or more acids to expand existing flow pathways in the subterranean formation, to create new flow pathways in the subterranean formation, and/or to remove acid-soluble precipitation damage in the subterranean formation. The acid-soluble material being dissolved by the acid(s) can be part of or formed from the native formation matrix or can have been deliberately introduced into the subterranean formation in conjunction with a stimulation or like treatment operation (e.g., proppant or gravel particulates). Illustrative substances within the native formation matrix that may be dissolved by an acid include, but are not limited to, carbonates , silicates and aluminosilicates. Other substances can also be dissolved during the course of performing an acidizing operation, and the foregoing substances should not be considered to limit the scope of substances that may undergo acidization. 5.19 [R]elated benefits may also be realized when removing a carbonate material from a predominantly siliceous formation. In this regard, the treatment fluids described herein may be used to dissolve a carbonate material in a siliceous formation during a first acidizing stage, such that calcium ions are removed from the formation....	Page 18 Ethylenediaminetetraacetic acid and similar complex-ing agents have been used to remove scale from formation surfaces near wellbores.
2. The method of claim 1 wherein the metal complexing agent is citric acid.	3.39 U.S. Pat. No. 4,888,121, Compositions and Method for Controlling Precipitation When Acidizing Sour Wells, discloses an acidizing composition that includes an acid such as CHI; an iron sequestering agent such as citric acid, EDTA, or nitrilotriacetic acid (NTA); and a sulfide modifier such as formaldehyde. This composition is stated to inhibit precipitation of ferric hydroxide, ferrous sulfide, and free sulfur, during the well acidizing treatment.	4.5 One of ordinary skill in the art will recognize that there are fairly well established pH ranges over which a chelating agent can be expected to effectively complex a metal ion. The pH range over which metal ion complexation may effectively take place can be dependent on a number of factors including, but not limited to, the chemical structure of the chelating agent, the functional groups present in the chelating agent, and the particular metal ion being complexed . Nevertheless, one of ordinary skill in the art will understand these issues and be able to determine if a particular metal ion is being effectively complexed by a given chelating agent. 4.16 in a chelating agent that contains carboxylic acid groups, complexation of a metal ion may occur when one or more of the carboxylic acid groups are in a deprotonated state.	Page 17 Precipitation of Fe(III) compounds from acid solutions as the pH increases above 2.2 is a particular problem. Complexing agents that have been used include 5-sulfosalicylic acid and citric acid (136); dihydroxymaleic acid (137); ethylenediaminetetraacetic acid (138); lactic acid (138); blends of hydroxylamine hydrochloride, citric acid, and glucono-delta-lactone (139); nitriloacetic acid; blends of citric acid and acetic acid; lactic acid; and gluconic acid (140).
3. The method of claim 1 wherein the metal complexing agent is ethylenediaminetetraacetic acid (EDTA).	3.39 U.S. Pat. No. 4,888,121, Compositions and Method for Controlling Precipitation When Acidizing Sour Wells, discloses an acidizing composition that includes an acid Such as CHI; an iron Sequestering agent Such as citric acid, EDTA, or nitrilotriacetic acid (NTA); and a sulfide modifier such as formaldehyde. This composition is Stated to inhibit precipi-tation of ferric hydroxide, ferrous sulfide, and free sulfur, during the well acidizing treatment.	10.59 In some embodiments , as an alternative to aminopolycarboxylic acid chelating agents, traditional chelating agents such as, for example, ethylenediaminetetraacetic acid (EDTA)... may be included in the treatment fluids described herein.	Page 17 Precipitation of Fe(III) compounds from acid solutions as the pH increases above 2.2 is a particular problem. Complexing agents that have been used include 5-sulfosalicylic acid and citric acid (136); dihydroxymaleic acid (137); ethylenediaminetetraacetic acid (138); lactic acid (138); blends of hydroxylamine hydrochloride, citric acid, and glucono-delta-lactone (139); nitriloacetic acid; blends of citric acid and acetic acid; lactic acid; and gluconic acid (140).
4. The method of claim 1 wherein the metal complexing agent is acetic acid.	2.51 In response to this “radial penetration' problem, organic acids (e.g., formic acid, acetic acid) are sometimes used, since they react more slowly than mineral acids such as HCl.	Claim 6 . The method of claim 1, wherein the acid is selected from the group consisting of hydrochloric acid, hydrobromic acid, formic acid, acetic acid, methanesulfonic acid, and any combination thereof.	Page 13 Sodium bicarbonate and sodium carbonate are used to attain basic pH while weak acids: acetic, fumaric, formic, and adipic, are generally used to obtain acidic pH values. Organic acids used in carbonate rock acidizing include formic, acetic, sulfamic, and chloroacetic acids. Precipitation of Fe(III) compounds from acid solutions as the pH increases above 2.2 is a particular problem. Complexing agents that have been used include ... blends of citric acid and acetic acid; lactic acid; and gluconic acid.

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5. The method of claim 1 wherein the metal complexing agent includes at least one of ethylenediaminetetraacetic acid (EDTA), propylenediaminetetraacetic acid (PDTA), nitrilotriacetic acid (NTA), N-(2-hydroxyethyl)ethylenediaminetriacetic acid (HEDTA), diethylenetriaminepentaacetic acid (DTPA), hydroxyethyliminodiacetic acid (HEIDA), cyclohexylenediaminetetraacetic acid (CDTA), diphenylaminesulfonic acid (DPAS), ethylenediaminedi(o-hydroxyphenylacetic) acid (EDDHA), glucoheptonic acid, gluconic acid, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, phthalic acid, terephthalic acid, aconitic acid, carballylic acid, trimesic acid, isocitric acid, citric acid, or any salt or derivative of any of the previously listed compounds.	5.37 The compositions and methods of the present invention include hydroxyethylaminocarboxylic acids. By “hydroxy ethylaminocarboxylic acid” is meant a compound comprising at least one carboxylic acid moiety and at least one >N-CH-CH-OH (“hydroxyethylamino”) moiety. (It should be noted that compounds wherein the nitrogen can form either two single bonds to other atoms or one double bond to a single atom in the remainder of the compound are included within the definition). Preferred examples of hydroxyethylaminocarboxylic acids include hydroxyethyl ethylenediaminetriacetic acid (HEDTA), hydroxyethyliminodiacetic acid (HEIDA), or a mixture thereof. HEDTA comprises three carboxylic acid moieties and one hydroxy ethylamino moiety, whereas HEIDA comprises two carboxylic acid moieties and one hydroxyethylamino moiety. Hydroxyethylaminocarboxylic acids provide a number of benefits to the well treatment fluids of the present	4.5 One of ordinary skill in the art will recognize that there are fairly well established pH ranges over which a chelating agent can be expected to effectively complex a metal ion. The pH range over which metal ion complexation may effectively take place can be dependent on a number of factors including , but not limited to , the chemical structure of the chelating agent , the functional groups present in the chelating agent , and the particular metal ion being complexed . Nevertheless , one of ordinary skill in the art will understand these issues and be able to determine if a particular metal ion is being effectively complexed by a given chelating agent. 4.16 in a chelating agent that contains carboxylic acid groups, complexation of a metal ion may occur when one or more of the carboxylic acid groups are in a deprotonated state.	Page 17 Precipitation of Fe(III) compounds from acid solutions as the pH increases above 2.2 is a particular problem. Complexing agents that have been used include 5-sulfosalicylic acid and citric acid (136); dihydroxymaleic acid (137); ethylenediaminetetraacetic acid (138); lactic acid (138); blends of hydroxylamine hydrochloride, citric acid, and glucono-delta-lactone (139); nitriloacetic acid; blends of citric acid and acetic acid; lactic acid; and gluconic acid (140).
6. The method of claim 1 wherein the treatment mixture comprises:			
between about 0.1% and 95% by weight metal complexing agent;	6.30 In addition to being effective as iron control agents, hydroxyethylaminocarboxylic acids have the advantage of being effective in acidizing treatment of a formation without the use of a first acid. In addition, they can readily remove scale from tubing and the well bore. In Such an aqueous composition, a Small amount of a mineral acid, an organic acid, or a base can be added to provide pH control of the composition. Typical concentration ranges for such an aqueous composition are as follows (percentages are by weight): hydroxyethylaminocarboxylic acid 1-30% pH controller 0.1-15% other additives O. 1-5% water 50-95%	11.21 In various embodiments , the concentration of the chelating agent in the treatment fluid may range between about 0.1 % to about 40 % of the treatment fluid by weight . In some embodiments, the concentration of the chelating agent in the treatment fluid may range between about 0.1% to about 5% of the treatment fluid by weight , or between about 1% to about 10% of the treatment fluid by weight, or between about 5% to about 15% of the treatment fluid by weight, or between about 0.5% to about 5% of the treatment fluid by weight, or between about 10 % to about 25% of the treatment fluid by weight , or between about 10% to about 40% of the treatment fluid by weight , or between about 30% to about 40% of the treatment fluid by weight.	
between 1 and 10,000 parts per million (ppm) of a corrosion inhibitor;	claim 6. The composition of claim 1, further comprising a corrosion inhibitor. claim 7. The composition of claim 6, wherein the corrosion inhibitor comprises a quaternary ammonium compound and at least one of an unsaturated oxygen compound or a reduced sulfur compound.	11.34 In additional embodiments, the treatment fluids described may further comprise any number of additives that are commonly used in downhole operations including, for example, silica scale control additives, surfactants, gel stabilizers, anti-oxidants , polymer degradation prevention additives, relative permeability modifiers, scale inhibitors, corrosion inhibitors, foaming agents, defoaming agents, antifoaming agents, emulsifying agents, de-emulsifying agents , iron control agents, proppants or other particulates, particulate diverters, salts, acids, fluid loss control additives, gas, catalysts, clay control agents, dispersants, flocculants, scavengers (e.g., H ₂ S scavengers, CO ₂ scavengers or O ₂ scavengers), gelling agents, lubricants, breakers , friction reducers, bridging agents, viscosifiers, weighting agents, solubilizers, pH control agents (e.g., buffers), hydrate inhibitors, consolidating agents, bactericides, catalysts, clay stabilizers, breakers, delayed release breakers, and the like.	Page 6 Corrosion inhibitors are used to reduce the corrosion of surface equipment, surface casing, and the drill string by drilling and well treatment fluids. Many different corrosion inhibitors have been used. These include amine salts such as ammonium sulfite - bisulfite blends, zinc carbonate, zinc chromate, hydrated lime, fatty amine salts of alkylphosphates, cationic polar amines, ethoxylated amines, and tertiary cyclic amines. Commercial products are usually proprietary blends of chemicals. Page 14 Earlier corrosion inhibitors limited the maximum strength of the acid to 15% by weight. Improved corrosion inhibitors (see below) have made the use of higher acid concentrations, such as 28% HCl more common. More dilute solutions may initially be injected in sandstone acidizing to reduce the formation of insoluble sodium and potassium fluorosilicates by displacing saline formation water before injection of hydrochloric acid.

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between 1 and 10,000 ppm of a biocide;	5.56 The composition can also include one or more additives that are compatible with the acid composition, Such as surfactants, corrosion inhibitors (Such as the alkylphenones described in U.S. Pat. Nos. 5,013,483 and 5,096,618), stabilizers, solvents, iron reducing agents, viscosity modifying agents, wetting agents, emulsifiers, non-emulsifiers, and pH control agents. Many such additives are well known in the art.	See 11.34 above.	Page 6 Bactericides are used to control bacterial growth which can cause corrosion, plugging of the fomation face, and alteration of drilling fluid rheological properties. Paraformaldehyde, glutaraldehyde, sodium hydroxide, lime derivatives, dithiocarbamates, isothiazolones, and diethylamine have all been used.
between 1 and 10,000 ppm of a colloidal silica deposition inhibitor;	5.56 The composition can also include one or more additives that are compatible with the acid composition, such as surfactants, corrosion inhibitors (such as the alkylphenones described in U.S. Pat. Nos. 5,013,483 and 5,096,618), stabilizers, solvents, iron reducing agents, viscosity modifying agents, wetting agents, emulsifiers, non-emulsifiers, and pH control agents. Many such additives are well known in the art.	See 11.34 above.	
between 1 and 500 gallons per thousand gallons (gpt) of a mutual solvent; and	5.56 The composition can also include one or more additives that are compatible with the acid composition, Such as surfactants, corrosion inhibitors (such as the alkylphenones described in U.S. Pat. Nos. 5,013,483 and 5,096,618), stabilizers, solvents, iron reducing agents, viscosity modifying agents, wetting agents, emulsifiers, non-emulsifiers, and pH control agents. Many such additives are well known in the art.	See 11.34 above.	Page 16 Mutual solvents have been used to reduce surfactant adsorption on formation minerals, particularly oil-wetting surfactants (131). Ethylene glycol monobutyl ether is the most commonly used mutual solvent. Page 20 Oil-soluble corrosion inhibitors may be dissolved by organic solvents such as xylene or toluene containing a mutual solvent, most often ethylene glycol monobutyl ether, EGMBE (167). Aqueous fluids containing 5-10% EGMBE can be used to dissolve cationic surfactants.
between 1 and 2000 parts per million of a surfactant.	6.9 A non-emulsifier can be used with compositions comprising CH1 or other mineral acids. The non-emulsifier is typically a surfactant, usually an anionic surfactant, which can lower or prevent the formation of an emulsion between the mineral acid and hydrocarbons present in the formation.	See 11.34 above.	Page 13 Surfactants are used to stabilize water-in-oil emulsions and to promote rapid return of injected fluids and a faster return of the well to hydrocarbon production. Page 20 Emulsion blocks within the formation can form as a result of various well treatments and are more easily prevented (by using surfactants in conjunction with well treatments, see above) than removed. Page 21 Care must be taken in all well treatment and injection operations not to alter rock wettability in an undesired manner. Use of carefully selected surfactants in well treatment fluids is a way to accomplish this. More recently well treatments that do not interrupt normal water injection operations have increased in frequency. Addition of surfactant to the injection water (144,146) can displace the oil remaining near the production well. The lower oil saturation results in an increase in the water relative permeability (145). Consequently a greater water injection rate may be maintained at a given injection pressure or a lower injection pressure. Thus smaller and cheaper injection pumps may be used to maintain a given injection rate. While the concentration of surfactant in the injection water is relatively high, the total amount of surfactant used is not great since it is necessary only to displace the oil from a 6-10 foot radius around the injection well.

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7. The method of claim 1 wherein the treatment mixture further comprises between 0.1 and 95% of acid(s) as pH modifier.	6.34 In such an aqueous composition, a small amount of a mineral acid, an organic acid, or a base can be added to provide pH control of the composition. Typical concentration ranges for such an aqueous composition are as follows (percentages are by weight): pH controller 0.1 - 15%	See Claim 6, above.	Page 6 pH control aids in reducing corrosion and scaling and in controlling interaction of the drilling fluid with formation minerals. Sodium hydroxide, calcium carbonate, sodium bicarbonate, sodium carbonate, potassium hydroxide, magnesium oxide, calcium oxide, fumaric acid, and formic acid have all been used commercially in this application.
8. The method of claim 1 wherein the injecting operation further comprises: alternately injecting a first amount of treatment mixture and a second amount of a diverting mixture into the well.	7.22 The well treatment fluid compositions of the present invention can be used in matrix acidizing of subterranean formations surrounding wellbores. Such matrix acidizing methods generally involve pumping the acid-containing well treatment composition down the wellbore and out through perforations into the target formation. Packers can be used in the wellbore to control the formation zones into which the treatment fluid is injected from the wellbore, if the well has perforations in more than one zone.	8.20 [A]t least a portion of the siliceous mineral in the subterranean formation may be removed in a separate acidizing stage with a treatment fluid comprising hydrofluoric acid or a hydrofluoric acid - generating compound.	Page 17 Diverting agents assist in distributing acid more uniformly through the perforated formation interval (141). These are usually oil soluble hydrocarbon resin particles. They may be dissolved by post-acid injection of xylene or similar solvents. Oil-soluble waxes, naphthalene, and solid organic acids such as benzoic acid have also been used (142). Best results are obtained using a broad range of particle sizes. Page 17 These precipitates plug flow channels and the cumulative effect is to reduce permeability in the most flooded portions of the reservoir diverting injectant to rock zones containing higher oil saturations. These precipitates plug flow channels and the cumulative effect is to reduce permeability in the most flooded portions of the reservoir diverting injectant to rock zones containing higher oil saturations.
9. The method of claim 1 wherein the injecting operation further comprises: injecting the treatment mixture until the pressure within the well reaches a predetermined target pressure calculated based on the fracture pressure of the nano-darcy shale formation; and	1.40 Techniques performed by hydrocarbon producers to increase the net permeability of the reservoir are referred to as “stimulation.” Essentially, one can perform a stimulation technique by: (1) injecting chemicals into the wellbore to react with and dissolve the damage (e.g., wellbore coating); (2) injecting chemicals through the wellbore and into the formation to react with and dissolve small portions of the formation to create alternative flowpaths for the hydrocarbon (thus rather than removing the damage, redirecting the migrating oil around the damage); or (3) injecting chemicals through the wellbore and into the formation at pressures sufficient to fracture the formation, thereby creating a large flow channel through which hydrocarbon can more readily move from the formation and into the wellbore. The present invention is directed to all three processes. 8.25 One of ordinary skill in the art will recognize that the well treatment compositions of the present invention can be used in the fracture acidizing of a formation. By increasing the pumping pressure (to above the minimum in situ rock stress), a matrix acidizing treatment becomes an acid fracturing treatment.	5.54 In some embodiments, the treatment fluids and methods described herein can be utilized in matrix acidizing operations described herein can be introduced to a subterranean formation below a fracture gradient pressure of the subterranean formation. 9.49 One of ordinary skill in the art will understand how to measure the fracture gradient of a subterranean formation and how to introduce a treatment fluid to a subterranean formation above or below this pressure .	Page 8 Hydraulic fracturing is a process whereby the permeability of a formation is increased by generating high permeability cracks in the rock. Particulate suspensions (usually sand slurries) are injected at sufficiently high rates (which require high injection pressures) to generate fractures in the rock which are held open by the suspended proppant in the fracturing fluid. Page 13 Matrix acidizing is the injection of acids into the formation at a pressure below the formation parting pressure (the pressure at which natural fractures are forced open by injected fluids). Properly designed, the injected acid enters the flow channels of the formation and flows radially outward from the wellbore dissolving mineral fine particles in the flow channels. Minerals forming the flow channel walls also react with the acids. These processes increase formation permeability near the wellbore. Page 14 In the third type of acidizing, fracture acidizing, acid is injected above the parting or fracture pressure of the formation. The acid reacts with the minerals on the exposed fracture face in a process called etching. With sufficient etching, the fracture does not reseal when normal well production or injection operations are resumed.

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upon reaching the target pressure, shutting in the well.	7.30 After the composition has been injected into the formation, optionally the well can be shut in for a period of time to allow more complete reaction between the acid and the formation material. 7.39 Parameters such as pumping rate, pumping time, shut-in time, acid content, and additive package, must be determined for each particular treatment since each of these parameters depends upon the extent of the damage, formation geology (e.g., permeability), formation temperature, depth of the producing zone, etc. A well-treatment designer of ordinary skill is familiar with the essential features of matrix acidizing treatments. For discussions of varying levels of generality, the skilled designer is referred to the following U.S. Patents: U.S. Pat. No. 5,203,413, [etc.]	6.53 reacting the acid with the carbonate mineral in the fractured formation such that the acid at least partially spends and the pH of the treatment fluid rises.	Page 19 A 6-12 hour well shut-in period is required to allow polymerization of hydroxyaluminum on formation surfaces to occur (159).
10. The method of claim 1, further comprising: injecting the treatment mixture containing a metal complexing agent in combination with hydraulic fracturing and injecting into the formation in conjunction with propagation of induced fractures, the metal complexing agent including citric acid or EDTA.	8.25 One of ordinary skill in the art will recognize that the well treatment compositions of the present invention can be used in the fracture acidizing of a formation. By increasing the pumping pressure (to above the minimum in situ rock stress), a matrix acidizing treatment becomes an acid fracturing treatment.	6.36 In other embodiments , the treatment fluid may be introduced to the subterranean formation at a pressure at or above the fracture gradient of the subterranean formation.	Page 14 In the third type of acidizing, fracture acidizing, acid is injected above the parting or fracture pressure of the formation. The acid reacts with the minerals on the exposed fracture face in a process called etching. With sufficient etching, the fracture does not reseal when normal well production or injection operations are resumed.
11. The method of claim 1 further comprising: monitoring at least one of pH and well pressure during the maintaining operation; and	7.39 Parametes such as pumping rate, pumping time, shut-in time, acid content, and additive package, must be determined for each particular treatment Since each of these parameters depends upon the extent of the damage, formation geology (e.g., permeability), formation temperature, depth of the producing zone, etc. A well-treatment designer of ordinary skill is familiar with the essential features of matrix acidizing treatments.	See 6.53 above.	Page 24 Seismic, geotomographic, controlled-source audio magnetotelluric, and pressure analyses as well as tracer chemical injection and analyses are all used to understand fluid movement within the reservoir and monitor EOR processes (191).
initiating the removing operation based on results of the monitoring operation.	7.39 Parametes such as pumping rate, pumping time, shut-in time, acid content, and additive package, must be determined for each particular treatment Since each of these parameters depends upon the extent of the damage, formation geology (e.g., permeability), formation temperature, depth of the producing Zone, etc. A well-treatment designer of ordinary skill is familiar with the essential features of matrix acidizing treatments.	See 6.53 above.	

Claim Elements:	U.S. Patent No. 6,436,880 B1 (Frenier)	U.S. Patent No. 10,072,205 B2 (Reyes)	Borchardt, <i>Chemicals Used in Oil Field Operations</i> , 1989
12. The method of claim 1 further wherein the metal complexing agent is selected from glutamic acid diacetic acid (GLDA), methylglycine diacetic acid (MGDA), β-alanine diacetic acid (β-ADA), ethylenediaminedisuccinic acid, S,S-ethylenediaminedi succinic acid (EDDS), iminodisuccinic acid (IDS), hydroxyiminodisuccinic acid (HIDS), polyamino disuccinic acids, N-bis[2-(1,2-dicarboxyethoxy)ethyl]glycine (BCA6), N-bis[2-(1,2-dicarboxyethoxy)ethyl]aspartic acid (BCA5), N-bis[2-(1,2-dicarboxyethoxy)ethyl]methylglycine (MCBA5), N-tris[(1,2-dicarboxyethoxy)ethyl]amine (TCA6), N-methyliminodiacetic acid (MIDA), iminodiacetic acid (IDA), N-(2-acetamido)iminodiacetic acid (ADA), hydroxymethyliminodiacetic acid, 2-(2-carboxyethylamino) succinic acid (CEAA), 2-(2-carboxymethylamino) succinic acid (CMAA), diethylenetriamine-N,N′′-disuccinic acid, triethylenetetramine-N,N′′′-disuccinic acid, 1,6-hexamethylenediamine-N,N′-disuccinic acid, tetraethylenepentamine-N,N′′′-disuccinic acid, 2-hydroxypropylene-1,3-diamine-N,N′-disuccinic acid, 1,2-propylenediamine-N,N′-disuccinic acid, 1,3-propylenediamine-N,N′-disuccinic acid, cis-cyclohexanediamine-N,N′-disuccinic acid, trans-cyclohexanediamine-N,N′-disuccinic acid, ethylenebis(oxyethylenenitrilo)-N,N′-disuccinic acid, glucoheptanoic acid, cysteic acid-N,N-diacetic acid,	OTHER PUBLICATIONS Fredd, C.N., and Fogler, H.S., “Chelating Agents as Effective Matrix Stimulation Fluids for Carbonates.” SPE 37212 (1997). 1.1 WELL TREATMENT FLUIDS COMPRISING CHELATING AGENTS 3.36 Therefore, acid treatment fluids often contain additives to minimize iron precipitation and HS evolution, for example by sequestering the Fe ions in solution using chelating agents, such as ethylenediaminetetraacetic acid (EDTA). U.S. Pat. No. 4,888,121, Compositions and Method for Controlling Precipitation When Acidizing Sour Wells, discloses an acidizing composition that includes an acid such as CHI; an iron sequestering agent such as citric acid, EDTA, or nitrilotriacetic acid (NTA); and a sulfide modifier such as formaldehyde. This composition is stated to inhibit precipitation of ferric hydroxide, ferrous sulfide, and free sulfur, during the well acidizing treatment.	18.34 Element 3: wherein the chelating agent comprises anaminopolycarboxylic acid selected from the group consisting of glutamic acid diacetic acid, methylglycine diacetic acid, B-alanine diacetic acid, ethylenediaminedisuccinic acid, iminodisuccinic acid, N-tris [(1, 2-dicarboxyethoxy) ethyl]amine, N-bis(2-(carboxymethoxy) ethyllglycine, N-bis [2-(1, 2-dicarboxyethoxy)ethy l]glycine, N-bis[2-(1, 2-dicarboxyethoxy)ethyl]aspartic acid, bis (2-(1, 2 dicarboxyethoxy)ethyl]methylglycine, any salt thereof, any derivative thereof, and any combination thereof.	Page 30 Thus, the concentration of divalent metal ions has an effect on viscosity retention at high temperature. Chelating and sequestering agents have been used to reduce the adverse effect of divalent (316) and multivalent metal ions on polyacrylamide solution viscosity (321,322).
13. The method of claim 1 further wherein the metal complexing agent is selected from acetic acid, acrylates, dihydroxymaleic acid, salts of dihydroxymaleic acid, EDTA (ethylenediamine tetraacetic acid), salts of EDTA, erythorbic acid, erythroboric acid, formic acid, gluconodeltalactone, GLDA (glutamic acid N,N-diacetic acid), salts of GLDA, HEDTA (hydroxyethylenediamine triacetic acid), salts of HEDTA, HEIDA (disodium ethanoldiglycine), salts of HEIDA, MGDA (methylglycine N,N-diacetic acid), salts of MGDA, NTA (nitrilotriacetic acid), organic metal complexers, ligands, porphyrins, pigments, peptides, saccharides, nucleic acids, phosphonic acid, polyacrylic acid and citric acid in an amount sufficient to sequester at least a portion of a metal compound.	OTHER PUBLICATIONS Fredd, C.N., and Fogler, H.S., “Chelating Agents as Effective Matrix Stimulation Fluids for Carbonates.” SPE 37212 (1997) 1.1 WELL TREATMENT FLUIDS COMPRISING CHELATING AGENTS 3.36 Therefore, acid treatment fluids often contain additives to minimize iron precipitation and HS evolution, for example by sequestering the Fe ions in solution using chelating agents, such as ethylenediaminetetraacetic acid (EDTA). U.S. Pat. No. 4,888,121, Compositions and Method for Controlling Precipitation When Acidizing Sour Wells, discloses an acidizing composition that includes an acid such as CHI; an iron sequestering agent such as citric acid, EDTA, or nitrilotriacetic acid (NTA); and a sulfide modifier such as formaldehyde. This composition is stated to inhibit precipitation of ferric hydroxide, ferrous sulfide, and free sulfur, during the well acidizing treatment.	See 18.34 above.	See Claim 12, above.