A process for treating an underground formation, which process comprises: (a) introducing into the underground formation a treatment fluid comprising an organic acid precursor; (b) heating a zone within the formation, which zone contains at least a portion of the organic acid precursor, to a temperature which is above the natural formation temperature and sufficient to increase the rate of hydrolysis of the organic acid precursor; and (c) allowing the organic acid precursor to hydrolyze to produce an organic acid in an amount effective to acidize the underground formation.
The process of the present invention is generally applicable to the production of oil, gas or water from wells drilled into underground reservoirs. It is also applicable to injection wells.

During drilling, workover and production operations there are numerous situations where the production rate of an oil, gas or water well following these operations is limited due to the presence of formation damage. Types of damage include, but are not limited to, the presence of polymer-containing filter cakes including drilling mud filter cakes, fluids (including hydraulic fracturing fluids) filtrates or residues including polysaccharide-containing filter cakes, fluids, filtrates or residues; particulate materials such as fluid loss control agents, bridging agents and rock fines, biofilms, scales and asphaltenes. Damage may arise as a result of drilling, production, injection, workover or other oilfield operations.

Damage can be near wellbore, for example the presence of drilling mud or fracturing fluid filter cake, or damage may be present deeper into the formation, for example mineral scale deposited in natural or induced fractures or in the rock matrix. The effective removal of damage, especially near wellbore damage such as filter cake, can significantly increase the production rate of hydrocarbon or water producing wells penetrating underground formations. The effective removal of damage can also increase the injectivity of injection wells.

Treatment with acid (acidizing) has been used for many years to treat damage in underground formations and stimulate the rate of oil or gas production.

If acids can be delivered sufficiently far into the formation, acidizing may also be effective in stimulating undamaged formations, particularly carbonate formations, by increasing the permeability of the rock matrix around the wellbore. For example, increasing the permeability of a radial zone around a vertical or other wellbore will increase the rate of fluids production (or injection rate) in a situation where there is no near wellbore damage. The efficient delivery of acids into fractures such as induced fractures or natural fractures or natural fracture networks can also increase the conductivity of the fractures allowing higher rates of fluid production or injection.

Acids may also be used to break acid-sensitive gels such as crosslinked guar-borate gels used in hydraulic fracturing and other oilfield applications. Efficient breaking of gels is generally required to obtain maximum production after such treatments. Acid may also be used to break mixed metal hydroxides or complexes of mixed metal hydroxides with materials such as bentonite.

However, conventional acids have several drawbacks. They react rapidly with acid-soluble materials which can prevent effective placement of reactive acid deep into carbonate formations or throughout long horizontal wells, resulting in poor zonal coverage. Conventional acids are also hazardous in use. To improve zonal coverage the use of high pressure, high rate injection is often attempted, which increases the hazards associated with the use of such acids.

One approach which can improve zonal coverage has been the use of solutions of carboxylic acid esters which hydrolyse at high formation temperatures to produce a carboxylic acid downhole (U.S. Pat. No. 3,630,285). Preferably, the formation temperature for this process is greater than about 150°C. Because the acid is produced predominantly after placement of the fluid improved zonal coverage can be achieved. The preferred esters used in U.S. Pat. No. 3,630,285 were ethyl acetate and methyl formate. These compounds have the disadvantage of low flash points and have other health and safety drawbacks such as some degree of toxicity.

U.S. Pat. No. 3,630,285 indicates that ester hydrolysis generally proceeds too slowly. It considers the possible use of strong acids and alkalis to increase the rate of hydrolysis of the esters, but then discounts the use of such catalysts downhole, due to the fact that carbonate (limestone) formations will rapidly neutralise the catalytic effects of these materials.

U.S. Pat. No. 5,678,632 teaches the use of enzymes to increase the rate of hydrolysis of esters, providing a highly effective means of generating carboxylic acids in-situ for acidizing without using extremes of pH and extending the range of downhole temperatures over which useful rates of hydrolysis of esters can be obtained.

The use of certain types of non-enzyme catalysts to increase the rate of hydrolysis of esters and achieve effective acidizing has been taught in WO 01/02698. Non-enzyme catalysts taught included metal ions such as transition metal ions, organic molecules including amino acids, peptides, monosaccharides, oligosaccharides, nucleic acids, peptide nucleic acids and derivatives of organic molecules and combinations thereof.

The enzymes and non-enzyme catalysts of U.S. Pat. No. 5,678,632 and WO 01/02698 are typically used at relatively low concentrations of up to a few percent of enzyme concentration or 1 to 10 mM non-enzyme catalyst. The solution containing the ester and enzyme or non-enzyme catalyst is made up in a suitable aqueous fluid such as fresh water, produced water or seawater.

WO04/007905 A1 teaches that compounds with a carboxylate functionality can also increase the rate of acid production from esters.

As well as esters, other organic acid precursors may be used for in-situ acidizing processes. The use of orthoesters, anhydrides, polyesters and polyorthoesters as alternatives to esters has been taught. For example, the use of polyesters in oilfield acidizing has been taught in WO2005/095755.

The period required for sufficient acidizing to occur is determined by several factors, including the type and concentration of organic acid precursor used, solvent composition, availability of water, pH, formation temperature and amount and type of any enzyme or other catalyst used to increase the rate of acid production.

There is a need for further methods by which the rate of production of acid from certain organic acid precursors can be increased in certain situations.

For example, at formation temperatures in the range 60-100°C, precursors of formic acid might hydrolyse too quickly, but precursors of acetic acid, even in the presence of suitable catalysts, might take a few days to produce acid. If a method was available to achieve controlled acidizing over a shorter period, for example 3 to 24 hours, this would be attractive to operators wishing to minimise expensive rig time.

It is an object of the present invention to provide further simple and effective processes for increasing the rate of hydrolysis of organic acid precursors to facilitate acidizing
of underground formations based on the in-situ production of organic acids within a reduced timescale.

[0019] It is a further object of the present invention to provide simple and effective processes for acidising underground formations in combination with one or more polymer breakers, where desired. Additionally, the present invention provides processes and chemicals that are generally low hazard and environmentally acceptable. It is yet another object of the present invention to provide processes that can achieve acidizing at a predictable rate with excellent zonal coverage.

[0020] Accordingly, the present invention provides a process for treating an underground formation, which process comprises:

(a) introducing into the underground formation a treatment fluid comprising an organic acid precursor;

(b) heating a zone within the formation, which zone contains at least a portion of the organic acid precursor, to a temperature which is above the natural formation temperature and sufficient to increase the rate of hydrolysis of the organic acid precursor; and

(c) allowing the organic acid precursor to hydrolyse to produce an organic acid in an amount effective to acidise the underground formation.

[0021] The process of the present invention is intended to achieve controlled and effective acidizing for purposes such as increasing the rate of production or injectivity of wells drilled into the formation, increasing the permeability of the formation, for example the permeability of the rock matrix or of induced or natural fractures or fracture networks, treating filter cake, including following a gravel packing operation, and treating biofilm.

[0022] The process of the present invention may produce acid in an amount effective to dissolve acid soluble material in the underground formation. Such material includes calcium carbonate and other carbonates. It may also be used to break acid-sensitive gels such as crosslinked guar-based gels used in hydraulic fracturing and other oilfield applications or to disrupt acid sensitive materials such as mixed metal hydroxides and complexes of mixed metal hydroxides with materials such as bentonite. The process may also be used in any other downhole application where the in-situ production of acid may be useful.

[0023] Where the process of the present invention is used to treat filter cakes following gravel packing operations, the treatment fluid may be used as the base fluid for a gravel packing operation, or be introduced after gravel packing.

[0024] The formation may be a hydrocarbon reservoir, for instance a gas or oil reservoir. Alternatively the reservoir may be a water reservoir. When it is a hydrocarbon reservoir the process of the invention may further include recovering a hydrocarbon from the treated reservoir. The hydrocarbon may be gas or oil. Likewise, when it is a water reservoir, the process of the present invention may further include recovering water from the treated reservoir.

[0025] Typically the reservoir is, or includes, carbonate or sandstone rock structures. The organic acid precursor may be any organic acid precursor that hydrolyses in the presence of water to produce an organic acid. One or more organic acid precursors may be used. When there is more than one organic acid precursor, these may be different. Organic acid precursors useful in the process of the present invention include esters, orthoesters, anhydrides, polyesters and polyorthoesters. The organic acid precursor may be in the form of a liquid, a colloid, a gel, a semi-solid or a solid.

[0026] The organic acid precursor may be dissolved or dispersed in water. Where appropriate, it may be mixed, dissolved or dispersed in a non-aqueous solvent such as a mutual solvent, hydrocarbon or organic solvent. The organic acid precursor may also be incorporated into an emulsion such as a water-in-oil emulsion or oil-in-water emulsion or into a micellar dispersion (also referred to as a microemulsion or transparent emulsion). In most applications the use of a water-soluble organic acid precursor such as an ester, or a solid organic acid precursor such as a polyester, in an aqueous treatment fluid will be preferred. Where a solid organic acid precursor is used it may be in any physical form that can be introduced into the formation.

[0027] The organic acid precursor will hydrolyse at a predictable rate in the presence of even a small amount of water to generate an organic acid. The organic acid precursors will preferably be low hazard and toxicity with a high flash point and high environmental acceptability. Generally they will also be biodegradable to an acceptable extent.

[0028] The organic acid precursor is typically an ester, for instance an ester of a carboxylic acid or of a hydroxy carboxylic acid. Esters have been taught in U.S. Pat. No. 5,679,636 to U.S. Pat. No. 5,829,466 to U.S. Pat. No. 6,702,023 and to U.S. Pat. No. 6,763,888 are suitable for use in the present invention. They include esters of an aliphatic carboxylic acid of formula R-CONH wherein R is selected from the group consisting of hydrogen, an alkyl group having from 1 to 6 carbon atoms and —R— CO2,H wherein R is a bond or an alkylene group having from 1 to 6 carbon atoms, the alkyl or alkenylene group being unsubstituted or substituted by halogen or hydroxy.

[0029] Esters of short chain carboxylic acids including ethanoic and methanoic acid (acetic and formic acid) are particularly suitable. The calcium and magnesium salts of these acids have good solubility in water, formate brines, acetate brines and many other brines, which is advantageous when the acid produced by the process of the present invention is used to dissolve calcium carbonate, magnesium carbonate, calcium magnesium carbonate (dolomite) or other acid soluble calcium or magnesium salts.

[0030] Ester of hydroxy carboxylic acids such as glycolic and lactic acid are also particularly suitable. For example hydroxyacetic acid can dissolve calcium sulphate. Where the acid has a hydroxy substituent, the ester may be a cyclic ester such as a lactone. Esters of chelating compounds such as malonic acid, oxalic acid, succinic acid, ethylenediaminetetraacetic acid (EDTA) nitrosoacetic acid (NTA) citric acid or hydroxyacetic acid as taught in U.S. Pat. No. 6,702,023 and U.S. Pat. No. 6,763,888 may also be used. If a base is present and the chelating acid is neutralised, it will be understood that salts of such chelating acids may also act as dissolved agents for acid soluble materials as taught in U.S. Pat. No. 7,021,377. Where acid soluble materials are described in the current description, this also refers to material soluble in solutions of salts of chelating acids and agents.

[0031] The ester should be at least slightly water soluble. Preferably the ester should be soluble to at least 1% w/v in water and most preferably soluble to at least 5% w/v in water. Preferably 5% to 20% w/v ester will be used but concentrations of ester higher than 20% w/v may be used in some cases.

[0032] In general it has been found that 5% to 10% w/v ester is sufficient to give good increases in permeability or good removal of filter cake damage. The solubility of some
esters may be reduced in high salt concentration fluids such as heavy brines, compared to their solubility in water.

[0033] In such cases an ester which is completely soluble in the base fluid to a sufficient concentration will normally be selected. In some situations, it may be desirable or necessary to use an emulsion of an ester in the treatment fluid.

[0034] The alcohol portion of the ester may be monohydric or polyhydric. The degree of esterification of polyhydric alcohols will affect the solubility of the ester in water and other solvents such as hydrocarbons. For example, partial esters of polyhydric alcohols can be used in which case the unesterified hydroxyl groups serve to increase the water solubility of the ester, compared to fully esterified polyhydric alcohols.

[0035] In one embodiment the ester is a carboxylic acid ester of 1,2,3-propanetriol, ethylene glycol, diethylene glycol or triethylene glycol. Suitable esters include but are not limited to ethylene glycol monoformate, diethylene glycol diformate, glycerol monoformate, glycerol triacetate, glycerol diacetate, butyl lactate, propyl lactate and ethyl lactate.

[0036] The organic acid precursor is alternatively a polyester, for instance an aliphatic polyester. Any polyester that hydrolyses in the presence of water to produce an organic acid may be used. Suitable polyesters include those which comprise one or more of lactic acid, lactide, glycolic acid, glycolide, caprolactone and (optionally) other compounds which may condense with lactic acid, lactide, glycolic acid, glycolide or caprolactone.

[0037] Suitable monomers include but are not limited to hydroxy carboxylic acid or hydroxy-carboxylic acid compounds trisubacids such as citric acid, dibasic acids such as adipic acid, and diols such as ethylene glycol and polyols. They also include difunctional molecules such as 2,2-(bis-hydroxymethyl) propionic acid.

[0038] Organic acids produced from the hydrolysis of the organic acid precursor which are useful in the process of the present invention include any organic acid which reacts with acid soluble materials downhole to produce salts of sufficient solubility to ensure substantive dissolution of the acid soluble materials takes place, for example calcium formate or calcium lactate. It is important that the dissolution of acid soluble material does not result in the deposition of another solid or other chemical form that produces a different type of damage. Sufficient water needs to be present to dissolve the salts produced by the reaction between the acid and acid soluble materials such as carbonates.

[0039] Sufficient organic acid precursor (or precursors) are provided to produce sufficient acid, when the organic acid precursor is hydrolysed, for the acid produced to have a substantive acidizing effect on acid soluble material present in the underground formation. By substantive effect it is meant that sufficient acid is produced on the hydrolysis of the organic acid precursor to give sufficient dissolution of acid soluble material, present in or adjacent to the filter cake, scale or other damage, to assist in the removal of damage or to increase the permeability of carbonate rock formations. Preferably the organic acid produced from hydrolysis of the organic acid precursor should be water soluble to at least 1% w/v and preferably higher.

[0040] The process of the present invention may be used to treat formation damage. The process of the present invention may also be used to increase the permeability of undamaged regions of an acid soluble rock matrix adjacent to a wellbore, natural or induced fracture.

[0041] Examples of situations where the dissolution of acid soluble material is desirable include the dissolution of carbonate present in a filter cake produced from a water-based or oil-based drill-in fluid, the dissolution of carbonate rock adjacent to a filter cake, the dissolution of carbonate rock adjacent to induced or natural fractures and the dissolution of carbonate scales in the wellbore, formation or tubulars.

[0042] The concentration of organic acid precursor used in the processing of the present invention will typically be at least 1% w/v but may be up to 20% w/v or higher. For applications such as treatment of filter cake a minimum of several percent w/v of acid is normally produced. The use of formulations capable of producing between 5 and 10% w/v organic acid precursor have been found to be particularly suitable for treatment of filter cakes.

[0043] Where using particulate, solid organic acid precursors, such as polyesters, the extent of any penetration into the formation will be determined, amongst other factors, by the particle size of the organic acid precursor and the size of the pore throats in the formation and this will be taken into account when designing the treatment. Solid organic acid precursors may be used in any solid configuration, including, but not being limited to spheres, cylinders, cuboids, fibres, powders, beads or any other configuration which can be introduced into the formation. They will preferably be used in the form of particles in the size range 1 micron to 4 mm, most preferably 10 microns to 1 mm. Solid organic acid precursors may also be in the form of a moulded tool or article or as a film, coating or as a fill in the annular spaces on downhole equipment such as a screen or expandable screen.

[0044] Where deep penetration is needed, solutions or other liquid forms of the organic acid precursor will normally be used.

[0045] The organic acid precursor is normally placed in the wellbore or adjacent formation following drilling of the well, for example as part of a completion or workover operation. In some cases, such as where a polyester is incorporated into a drill-in fluid, as taught by PCT/GB05/01193, it may be introduced during the drilling process.

[0046] The process of the present invention is used in the situations where the rate of hydrolysis of the organic acid precursor is not sufficient at the bottom hole static temperature (BHST) to achieve the required degree of acidizing within an acceptable or desired period of time. The process of the present invention is used to shorten the time required for the acidizing treatment. For example, at BHST, hydrolysis of the organic acid precursor (in the absence or presence of an optional catalyst) may take a longer period than the operator may desire in order for acidizing to proceed to a sufficient extent. For example it might take several days. By employing the process of the present invention and supplying heat to the zone containing the organic acid precursor, the time required to generate acid in-situ may be reduced or even substantially reduced, so that acid production takes place over a shorter period (i.e. fewer days or even over a few hours) depending on the temperature employed.

[0047] An essential feature of the present invention is that heat is supplied to the zone containing the organic acid precursor to increase the temperature to above the normal formation temperature. Heat will normally be supplied after placement of the organic acid precursor, but alternatively may be supplied before the organic acid precursor is placed in the formation or at the same time that the organic acid precursor is placed in the formation.
Heat may be supplied by any method of delivering heat to a wellbore or formation that is known to one skilled in the art of providing heat to underground formations. Such methods may include but not be limited to hot water, hot oiling, steam injection, close circuit heating, such as described in U.S. Pat. No. 4,641,710, use of exothermic chemical reactions, microwave heating, electric heating, controlled combustion or oxidation, or use of a heat exchange compressor such as described in US 2005/0034852. For convenience, heating may be achieved using a heat source which is readily moveable. When treating a short section, a single source of heat used in a single location may be sufficient. When treating long sections, for example when treating filter cake in long horizontal wells, heat will generally be applied to one section of the well at a time, unless multiple heat sources can be used. If using a single heat source to treat a long interval, the heat source will generally be placed in the wellbore and moved by methods that will be known to those skilled in the art, so that heat is supplied sequentially to different treatment zones along the interval.

When using exothermic chemical reactions as a heat source the chemicals used to generate heat may be introduced to the wellbore using any convenient means, for example the drill string, coiled tubing, production tubing or by bullheading.

At least a portion of the zone containing organic acid precursor is heated to above the normal formation temperature. Heating will generally be to a temperature at least 10°C above the formation temperature and preferably to 20 to 120°C above the formation temperature. The temperature to which the organic acid precursor needs to be heated to achieve acid production within a desired time period will be well understood by those skilled in the art. For example, formic acid precursors will generally need to be heated less than precursors of other organic acids. Also, esters will generally need to be heated less than polyesters, and orthoesters less than polyorthoesters. It will be understood that a temperature gradient will be set up in the formation around the heat source. Organic acid precursor at different distances from the heat source will therefore by heated to different extents and produce acid at different rates and this will be taken into account when designing treatments.

In one embodiment, the process of the present invention further comprises introducing one or more polymer breakers into the formation to achieve polymer breaking in combination with acidizing. Polymer breakers may be selected where polymers or gels are present in the formation, for example in filter cakes including those formed from drilling muds or drill-in fluids fluids, fracturing, completion or workover fluids.

In one embodiment the polymer breaker is an oxidant (oxidative breaker). In another embodiment the polymer breaker is an enzyme. A polymer breaker component may thus be introduced into the formation in an amount effective to degrade polymers present within the formation.

Oxidative breakers used in the present invention may be any one of those oxidative breakers known in the art to be useful to react with polymers to reduce the viscosity of polymer thickened compositions or to disrupt filter cakes. The oxidative breaker is typically introduced in a treatment fluid containing the organic acid precursor component. The oxidative breaker may be present in solution or as a dispersion. Suitable compounds include persulfates, peroxides, perborates, percarbonates, perphosphates, hypochlorites, persilicates, metal cations and hydrogen peroxide adducts such as urea hydrogen peroxide and magnesium peroxide.

Preferred oxidative breakers are peroxides which can decompose to generate hydrogen peroxide. Of the oxidative breakers most preferred are percarbonates and perborates, most especially sodium percarbonate and sodium perborate.

Preferred polymer breaking enzymes used in the present invention include hydrolases and lysases, such as any one of those polysaccharide degrading enzymes known in the art to be useful to degrade (normally hydrolyse) polysaccharides and to reduce the viscosity of polysaccharide thickened compositions or to disrupt filter cakes. The polymer breaking enzymes will be selected on the basis of their known ability to hydrolyse the polysaccharide components known or believed to be contributing to the damage. Examples of suitable enzymes which may be used to break polymers include enzymes which can hydrolyse starch, xanthan, cellulose, guar, scleroglucan, succinoglycan or derivatives of these polymers. If suitable enzyme activities are available, enzymes could also be used to hydrolyse any other polymers suitable for use in drilling, workover or production operations. Appropriate enzymes for this purpose are well documented in the literature and would be well known to a person of skill in the art.

Oxidative or enzyme breakers or catalysts capable of hydrolysing other, non-polysaccharide polymers may also be incorporated into treatment fluids used in the present invention. Where a breaker is incorporated into a treatment fluid to be used in the process of the present invention, sufficient polymer breaker or gel breaker is normally included to have a substantive effect on the polymer component. The concentration of polymer breaker incorporated into the formulation will vary according to the type of breaker employed, the nature of the polymer and its concentration in the base fluid but will be of the order of 0.005 to 60 kg/m³, preferably 0.2 to 10 kg/m³.

In another embodiment, the process of the present invention further comprises introducing one or more of an enzyme catalyst, non-enzyme catalyst and carboxylate compound into the reservoir to further increase the rate of production of acid from the organic acid precursor. For example, enzyme catalysts, non-enzyme catalysts and carboxylate containing compounds that increase the rate of ester hydrolysis are taught in U.S. Pat. No. 5,678,632, WO 01/02698 and WO 04/07905.

Where an enzyme is additionally used in conjunction with the process of the present invention, to hydrolyse an organic acid precursor or as a polymer breaker, it is necessary to select an enzyme which remains active in the treatment fluid under reservoir conditions for at least as long as the catalytic activity is needed. It will be understood by those skilled in the art of using enzymes in underground formations that the enzymes may only be active in a particular temperature range. Heating of the formation to a temperature above the maximum for a given enzyme may result in its inactivation. Nonetheless, if the enzyme is active during the heating process, useful hydrolysis of an organic acid precursor or polymer breaking may be achieved.

It is generally advantageous for the enzymes to be readily water soluble although the enzymes may also be active and be used in low water activity environments or two-phase systems such as emulsions or dispersions or in microemulsions. Typically, isolated enzymes are used.
Enzymes may be isolated from plant, animal, bacterial or fungal sources. The enzymes may be produced from wild-type, conventionally bred, mutated or genetically engineered organisms. The enzymes may, optionally, be chemically modified, as long as they retain or possess the desired catalytic ability. Preferably, the enzymes will be industrial enzymes available in bulk from commercial sources. Typical enzyme concentrations will be 0.05% to 5% v/v of commercial liquid enzyme preparations or about 0.005 to 0.5% v/v of dried enzyme preparation. Preferably, liquid preparations of enzymes will be used for ease of handling.

[0060] The treatment fluid containing one or more organic acid precursors is generally prepared at the surface before being introduced downhole. Suitable processes for preparing the selected treatment fluids and placing them in the formation will be well known to those skilled in the art. For example, when using an ester, a treatment fluid is normally prepared by blending the ester batchwise with suitable water, for example city (drinking) water, fresh surface or well water, produced water, sea water or a base brine. In other embodiments of the present invention, the organic acid precursors may be incorporated into a mutual solvent, mutual solvent blended with water, mutual solvent blended with water and hydrocarbon, hydrocarbons or other organic solvents. It may also be incorporated in emulsions including oil-in-water and water-in-oil emulsions or into a micellar dispersion (also referred to as a microemulsion or transparent emulsion). However, it will be understood that sufficient water needs to come into contact with the organic acid precursor to allow hydrolysis to occur during heating or in the presence of catalysts. This water may be provided in the treatment fluid at the outset, or may come from fluids introduced into the wellbore before or after the treatment fluid of from the formation. Sufficient water needs to be present to dissolve the products of the reaction of the produced organic acid with acid reactive material, for example calcium carbonate.

[0061] Optionally, other components such as catalysts to increase the rate of organic acid precursor hydrolysis and/or polymer breakers may be incorporated into the treatment fluid by suitable means. In some cases, they may be placed in proximity to the organic acid precursor using a separate fluid treatment stage. For example, when a well is drilled using a polymer, it may be hydrolyzed when a mud or drill-in fluid, as taught by PCT/GRT/01193, the organic acid precursor is incorporated into a filter cake. Displacing the liquid mud or drill in fluid to a clear brine containing a catalyst or polymer breaker will allow acidizing in conjunction with polymer breaking.

[0062] The organic acid precursor and any other components selected for incorporation into the treatment fluid will be chosen to reflect the requirements of the treatment, such as the amount of acid and rate of production of acid required. The chemical compatibility with the formation will also be considered.

[0063] The treatment fluid may also contain further chemical additives such as surfactants, mutual solvents, foaming and chelating agents if their inclusion is deemed to be beneficial and if they are sufficiently compatible with the other components of the treatment fluid and the formation fluids.

[0064] Polymer breakers, enzymes and non-enzyme catalysts may, if desired, also be used in the form of delayed release preparations, such as will be well known by those skilled in the art.

[0065] The organic acid precursor and other chemicals required for the process of the present invention will normally be technical grade to reduce the cost of the process.

[0066] If it is preferred the treatment fluid may be prepared by adding the organic acid precursor to the water on a continuous, preferably carefully controlled and monitored basis ("on the fly") while the treatment fluid is being injected into the underground reservoir.

[0067] The treatment fluids are conveniently introduced into the underground formation via a wellbore that extends into the reservoir, for instance via injection or production wells. The wellbore may be vertical, deviated, inclined or horizontal. If being introduced into a newly drilled well, particularly if being used to remove damage caused during drilling, such as filter cakes, a treatment fluid may conveniently be introduced via the drill string. This may be achieved using the mud pumps. The treatment fluid may also be introduced via coiled tubing or bullheading.

[0068] The corrosivity of a treatment fluid will be taken into account in deciding if it may be introduced into wells or the drill string without the need to add corrosion inhibitors. If required, suitable corrosion inhibitors or buffers (to raise the pH) may be added to treatment fluids. The treatment fluid will normally be introduced at below fracture pressure but may if desired be injected at above fracture pressure.

[0069] For near wellbore treatments, the volume of treatment fluid introduced into the reservoir will typically be at least equal to the wellbore volume plus an allowance for some leak off into the formation. A fluid volume of between 100% and 200% of the wellbore volume will normally be used although if a high rate of fluid loss is expected a volume up to 300% or higher of the wellbore volume may be selected.

[0070] For treatments where the target is stimulation deeper into the formation such as within induced fractures or natural fractures or natural fracture networks a volume of treatment fluid will be selected appropriate to the requirements of the treatment.

[0071] In one embodiment of the present invention, a volume of the treatment fluid which is sufficient to allow the fluid to penetrate up to several metres into a formation around a wellbore or behind a fracture face may be used. The production of acid in-situ can result in an increase in the matrix permeability of a carbonate formation to a depth up to several metres. Such treatments may be referred to as deep matrix stimulation. Using conventional acidizing it is extremely difficult to obtain a uniform effect. A much more uniform effect can be obtained using the process of the present invention if adequate heat penetration can be achieved.

[0072] The well will normally be shut in during the period of heating and optionally for some time after the application of heat ceases. Typically a period of between 0.2 hours and 48 hours will be used to heat each treated zone, depending on the formation temperature and the temperature to which the formation is heated although in some cases the period might be shorter or longer. The well is then put on or returned to production, or in the case of injection wells, put on injection.

[0073] The process of the present invention may be used in a number of different acidizing applications, such as to dissolve acid soluble material in the reservoir, to increase the rate of production or injection of wells drilled into the formation, to treat filter cake, to treat filter cake following a gravel packing operation, to treat a biofilm, to break a pH sensitive cross-linked gel or to disrupt mixed metal hydroxides or complexes of mixed metal hydroxides.
It will be understood that removal of damage or dissolution of acid-soluble material using the process of the present invention may not be complete. The treatment may however be judged a success if damage is substantially remediated, resulting in higher rates of production or injection than would be the case with no treatment.

The process of the present invention has a number of advantages.

It is a feature of the process of the present invention that the use of an organic acid precursor rather than a reactive acid avoids wormholing and improves the placement of the treatment fluid. Use of an organic acid precursor rather than a reactive acid gives the advantages described in U.S. Pat. No. 3,630,285 and U.S. Pat. No. 5,678,632 with respect to effective placement of the fluid and results in acidizing with much better zonal coverage.

To maintain this advantage in certain applications such as the treatment of long horizontal intervals, too rapid a breakthrough of filter cakes should in general be avoided. Ideally, breakthrough of filter cakes will be achieved after a period longer than that amount of time needed to place a treatment fluid throughout the zone requiring treatment. A delay in producing a substantive amount of acid and in breaking the filter cake allows even treatment of the target zone and excellent zonal coverage. In the case of the present invention, an organic acid precursor which hydrolyses at a rather slow rate at formation temperature may be selected. Increased rates of hydrolysis and acid production occur on heating to the required temperature. It will be understood that localized heating may result in localised leak-off when a filter cake or other damage is removed and this will be taken into account when designing treatments. The use of suitable fluid loss or diverting agents may be required in some circumstances. A useful combination is the use of an ester in combination with a polyester, where heating results in relatively fast acid production from the ester to dissolve acid-soluble components of the filter cake, but the polyester hydrolyses relatively slowly and can act as a fluid loss agent.

Where suitable organic acid precursors are selected, in particular where low toxicity, high flash point organic acid precursors such as esters and polyesters are used, the process of the present invention has health, safety, operational and environmental advantages.

The treatment fluids used in the process of the present invention typically start at near neutral pH. The process therefore permits the incorporation of acid incompatible gel breakers such as enzymes and oxidative breakers into fluids capable of delivering a high concentration of acid. This avoids the compatibility problems which typically arise when attempting to incorporate such breakers into highly acidic formulations based on mineral or organic acids.

The process provides a simple, effective and convenient way to acidize underground formations. In its simplest embodiment, a single fluid and a single heat source are used at one location. The process increases the rate of organic acid precursor hydrolysis to achieve acidizing within a shorter and more acceptable period of time in situations where the rate of ester hydrolysis might not otherwise be fast enough. For example, a treatment that may otherwise take 2 days might be completed in several hours. Shortening the time needed to carry out a treatment can save significant amounts of downtime and lost production. In more complex embodiments, more than one fluid may be used, more than one heat source may be used, or the heat source may be moved along long intervals.

Compared to other treatment processes where a separate conventional mineral or organic acid ("live acid") stage may be required it is a very low hazard process for the controlled rate dissolution of acid soluble materials. Handling of live acid by operators is avoided and there is generally no need for high pressure, high rate injection which is often used in conventional acidizing processes to counter the high reaction rate of live acids.

Due to the good zonal coverage that can be obtained, the process of the present invention is particularly effective for the removal of filter cakes over long horizontal intervals and in sand control completions including gravel packs, stand alone and expandable screens. Uniform cleanup of filter cakes in such situations is critical in minimising the risk of premature failure.

The process of the present invention may also provide deep matrix acidizing of the formation around a wellbore or fracture at the same time as removing near wellbore damage.

1. A process for treating an underground formation, which process comprises:
   (a) introducing into the underground formation a treatment fluid comprising an organic acid precursor;
   (b) heating a zone within the formation, which zone contains at least a portion of the organic acid precursor, to a temperature which is above the natural formation temperature and sufficient to increase the rate of hydrolysis of the organic acid precursor; and
   (c) allowing the organic acid precursor to hydrolyse to produce an organic acid in an amount effective to acidize the underground formation.

2. A process according to claim 1 wherein the organic acid precursor is an ester, orthoester, anhydride, polyester or poly-orthoester.

3. A process according to claim 1 wherein, in step (b), heating is achieved using hot water, hot oiling, steam injection, closed circuit heating, exothermal chemical reactions, microwave heating, electric heating, controlled combustion or oxidation, or a heat exchange compressor.

4. A process according to claim 1 which process further comprises introducing one or more polymer breakers into the formation to achieve polymer breaking in combination with acidizing.

5. A process according to claim 1 which process further comprises introducing one or more of an enzyme catalyst, non-enzyme catalyst and carboxylate compound into the formation to further increase the rate of production of acid from the organic acid precursor.

6. A process according to claim 1 wherein, in step (b), heating is provided by a source of heat which is movable within the wellbore or formation.

7. A process according to claim 1 wherein the underground formation is a hydrocarbon or water reservoir and the process further comprises recovering a hydrocarbon or water from the treated reservoir.

8. A process according to claim 7 wherein the hydrocarbon is oil or gas.

9. A process according to claim 1 wherein the organic acid precursor is an ester of a carboxylic acid or of a hydroxycarboxylic acid.
10. A process according to claim 9 wherein the ester is an ester of an aliphatic carboxylic acid of formula RCO₂H wherein R is selected from hydrogen, an alkyl group having from 1 to 6 carbon atoms and —R'—CO₂H where R' is a bond or an alkylene group having from 1 to 6 carbon atoms, the said alkyl or alkylene group being branched or unbranched and unsubstituted or substituted.

11. A process according to claim 9 wherein the ester is a carboxylic acid ester of 1,2,3-propanetriol, ethylene glycol, diethylene glycol or triethylene glycol.

12. A process according to claim 9 wherein the ester is an ester of acetic acid, formic acid, lactic acid or glycolic acid.

13. A process according to claim 1 wherein the organic acid precursor is an aliphatic polyester.

14. A process according to claim 13 wherein the aliphatic polyester comprises one or more of lactic acid, lactide, glycolic acid, glycolide, caprolactone and (optionally) compounds which may condense with lactic acid, lactide, glycolic acid, glycolide or caprolactone.

15. A process according to claim 4 wherein the polymer breaker is an enzyme.

16. A process according to claim 15 wherein the polymer breaker is an enzyme which can degrade starch, xanthan, cellulose, guar, scleroglucan or succinoglycan, or derivatives of these polymers.

17. A process according to claim 4 wherein the polymer breaker is an oxidant.

18. A process according to claim 17 wherein the polymer breaker is a persulphate, hypochlorite, peroxide, perborate, percarbonate, perphosphate, persilicate, a metal cation or a hydrogen peroxide adduct.

19. A process according to claim 1 wherein one of the preceding claims wherein the treatment fluid is introduced into the reservoir via a wellbore which extends to the reservoir.

20. A process according to claim 19 wherein the wellbore is vertical, deviated, inclined or horizontal.

21. A process according to claim 1 wherein the treatment fluid is introduced into the reservoir via the drillstring, coiled tubing or by bullheading.

22. A process according to claim 1 wherein the treatment fluid is used as the base fluid for a gravel packing operation.

23. A process according to claim 1 wherein at least one of any polymer breaker, enzyme or non-enzyme catalyst is present in the form of a delayed release preparation.

24. A process according to claim 1 wherein acid is produced in an amount effective to dissolve acid soluble material in the underground formation.

25. A process according to claim 1 wherein acid is produced in an amount effective to increase the rate of production or infectivity of wells drilled into the formation.

26. A process according to claim 1 wherein acid is produced in an amount effective to increase the permeability of the formation, treat filter cake, treat a biofilm, break a pH-sensitive cross-linked gel or disrupt mixed metal hydroxides or complexes of mixed metal hydroxides.

27. A process according to claim 1 wherein acid is produced in an amount effective to treat an induced or natural fracture or a natural fracture network.

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