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(72) Inventeurs/Inventors:
PURDY, CLAY, CA;
THATCHER, DARREN, CA;
GARNER, JOHN, CA;
ULMER, BRUCE, CA

(73) Propriétaire/Owner:
FLUID ENERGY GROUP LTD., CA

(74) Agent: BURNET, DUCKWORTH & PALMER LLP

(54) Titre : COMPOSITIONS D'ACIDES SYNTHETIQUES UTILISABLES COMME SUBSTITUTS D'ACIDES CLASSIQUES
DANS L'INDUSTRIE PETROLIERE ET GAZIERE

(54) Title: SYNTHETIC ACID COMPOSITIONS ALTERNATIVES TO CONVENTIONAL ACIDS IN THE OIL AND GAS
INDUSTRY

(57) **Abrégé/Abstract:**

A synthetic acid composition for use in oil industry activities, said composition comprising: urea and hydrogen chloride in a molar ratio of not less than 0.1:1; and an amino acid, and optionally, a phosphonic acid derivative.

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(71) Applicant: **FLUID ENERGY GROUP LTD.** [CA/CA];
#104-214-11th Avenue SE, Calgary, Alberta T2G 0X8
(CA).(72) Inventors: **PURDY, Clay**; #20 Chinook Place SW, Medi-
cine Hat, Alberta T1A 8S1 (CA). **THATCHER, Darren**;
Box 5859, High River, Alberta T1V 1P6 (CA). **GARNER,**
John; PO Box 2682, Stony Plain, Alberta T7Z 1Y2 (CA).
ULMER, Bruce; 18 Willowood Court, Stony Plain, Al-
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DUSTRY(57) Abstract: A synthetic acid composition for use in oil industry activities, said composition comprising: urea and hydrogen chlor-
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SYNTHETIC ACID COMPOSITIONS ALTERNATIVES TO CONVENTIONAL ACIDS IN THE OIL AND GAS INDUSTRY

FIELD OF THE INVENTION

This invention relates to compositions for use in performing various applications in the oil & gas industry, more specifically to synthetic acid compositions as alternatives to conventional acids.

BACKGROUND OF THE INVENTION

In the oil & gas industry, stimulation with an acid is performed on a well to increase or restore production. In some instances, a well initially exhibits low permeability, and stimulation is employed to commence production from the reservoir. In other instances, stimulation is used to further encourage permeability and flow from an already existing well that has become under-productive.

Acidizing is a type of stimulation treatment which is performed above or below the reservoir fracture pressure in an effort to restore or increase the natural permeability of the reservoir rock. Acidizing is achieved by pumping acid into the well to dissolve typically limestone, dolomite and calcite cement between the sediment grains of the reservoir rocks.

There are three major types of acid applications: matrix acidizing, fracture acidizing, and spearhead breakdown acidizing (pumped prior to a fracturing pad in order to assist with formation breakdown (reduce fracture pressures, increase feed rates), as well as clean up left over cement in the well bore or perforations. A matrix acid treatment is performed when acid is pumped into the well and into the pores of the reservoir formation below the fracture pressure. In this form of acidization, the acids dissolve the sediments and mud solids that are inhibiting the permeability of the rock, enlarging the natural pores of the reservoir (wormholing) and stimulating flow of hydrocarbons. While matrix acidizing is done at a low enough pressure to keep from fracturing the reservoir rock, fracture acidizing involves pumping highly pressurized acid into the well, physically fracturing the reservoir rock and etching the permeability inhibitive sediments. This type of acid treatment forms channels or fractures through which the hydrocarbons can flow known as wormholing.

There are many different mineral and organic acids used to perform an acid treatment on wells. The most common type of acid employed on wells to stimulate production is hydrochloric acid (HCl), which is useful in stimulating carbonate reservoirs.

Also, HCl can be combined with hydrofluoric acid (HF) to form a mud acid, and used to dissolve quartz, sand/silica Argillaceous mudstones, bioturbated limestones, siliceous organic rich mudstones and mixed siliceous mudstones and limestones and clay from the reservoir. In order to protect the

integrity of the well and its components, corrosion inhibitor additives are introduced to the acid system to prohibit the acid from breaking down or corroding the steel (or combination metal-alloy) casing in the well. Also, a sequestering agent can be added to block the formation of gels or precipitate of iron, which can clog the reservoir pores during an acid job as well as a non-emulsifier (demulsifier) to allow the acid and oil (produced fluids) to separate or break. After an acid job is performed, the spent acid and sediments are removed from the reservoir in a process called back flush, or by mechanical means if the reservoir pressure is not sufficient to overcome the hydrostatic pressure of the column of fluid in the wellbore on its own

Some of the major challenges faced in the oil & gas industry from using hydrochloric acid include the following: extremely high levels of corrosion (which is countered by the addition of 'filming' corrosion inhibitors that are typically themselves toxic and harmful to humans, the environment and equipment) reactions between acids and various types of metals can vary greatly but softer metals, such as aluminum and magnesium, are very susceptible to major effects causing immediate damage. Hydrochloric acid produces Hydrogen chloride gas which is toxic (potentially fatal) and corrosive to skin, eyes and metals. At levels above 50 PPM (parts per million) it can be Immediately Dangerous to Life and Health (IDLH). At levels from 1300-2000 parts per million (PPM) death can occur in 2-3 minutes.

The inherent environmental effects (organic sterility, poisoning of wildlife etc.) of acids in the event of an unintended or accidental release on surface or downhole into water aquifers or other sources of water are devastating which can cause significant pH reduction of such and can substantially increase the toxicity and could potentially cause a mass culling of aquatic species and potential poisoning of humans or livestock and wildlife exposed to/, or drinking the water. An unintended release at surface can also cause a hydrogen chloride gas cloud to be released, potentially endangering human and animal health. This is a common event at large storage sites when tanks split or leak. Typically if near the public, large areas need to be evacuated post event. Because of its acidic nature, hydrogen chloride gas is also corrosive, particularly in the presence of moisture.

The inability for acids and blends of such to biodegrade naturally without neutralizing the soil results in expensive cleanup-reclamation costs for the operator should an unintended release occur. Moreover, the toxic fumes produced by mineral & organic acids are harmful to humans/animals and are highly corrosive and/or explosive potentially, transportation and storage requirements for acids are restrictive and taxing in such that you must typically haul the products in acid tankers or intermediate bulk containers (IBC) that are rated to handle such corrosive-regulated products, blending exposure dangers for personnel exposed to handling..

Another concern is the potential for spills on locations due to high corrosion levels of acids causing storage container failures and/or deployment equipment failures i.e. coiled tubing or treatment iron failures caused by high corrosion rates (pitting, cracks, pinholes and major failures). Other concerns include: downhole equipment corrosion causing the operator to have to execute a work-over and replace down hole pumps, tubing, cables, packers etc.; inconsistent strength or quality level of mineral & organic acids; potential supply issues based on industrial output levels; high levels of corrosion on surface pumping equipment resulting in expensive repair and maintenance levels for operators and service companies; the requirement of specialized equipment that is purpose built to pump acids greatly increasing the capital expenditures of operators and service companies; and the inability to source a finished product locally or very near its end use; transportation and onsite storage difficulties.

Typically, acids are produced in industrial areas of countries located far from oil & gas applications, and up to 10 additives can be required to control various aspects of the acids performance adding to complications in the handling and shipping logistics. Having an alternative that only requires minimal additives is advantageous.

Large price fluctuations with typical mineral and organic acids based on industrial output causing end users an inability to establish long term costs in their respective budgets; severe reaction with dermal/eye tissue; major PPE requirements (personal protective equipment) for handling, such as on site shower units; extremely high corrosion rates and reaction rates as temperature increases causing the product to “spend/react or become neutral” prior to achieving its desired effect such as penetrating an oil or gas formation to increase the wormhole “pathway” effectively to allow the petroleum product to flow freely to the surface. As an example, hydrochloric acid or mud acid is utilized in an attempt to free stuck drill pipe in some situations. Prior to getting to the required depth to solubilize the formation that has caused the pipe/tubing to become stuck many acids spend or neutralize due to increased bottom hole temperatures and increased reaction rate, so it is advantageous to have an alternative that spends or reacts more methodically allowing the slough to be treated with a solution that is still active, allowing the pipe/tubing to be pulled free.

When used to treat scaling issues on surface due to water/fluid precipitation, acids are exposed to humans and mechanical devices as well as expensive pumping equipment causing increased risk for the operator and corrosion effects that damage equipment and create hazardous fumes. When mixed with bases or higher pH fluids, acids will create a large amount of thermal energy (exothermic reaction) causing potential safety concerns and equipment damage, acids typically need to be blended with fresh water (due to their intolerance of highly saline water, causing precipitation of minerals) to the desired concentration requiring companies to pre-blend off-site as opposed to blending on-site with water thereby increasing costs associated with transportation.

Typical mineral acids used in a pH control situation can cause degradation of certain polymers/additives/systems requiring further chemicals to be added to counter these potentially negative effects, many offshore areas of operations have very strict regulatory rules regarding the transportation/handling and deployment of acids causing increased liability and costs for the operator. When using an acid to pickle tubing or pipe, very careful attention must be paid to the process due to high levels of corrosion, as temperatures increase, the typical additives used to control corrosion levels in acid systems begin to degrade very quickly (due to the inhibitors “plating out” on the steel) causing the acids to become very corrosive and resulting in damage to equipment/wells. Acids are very destructive to most typical elastomers found in the oil & gas industry such as those found in blow out preventers (BOP’s)/downhole tools/packers/submersible pumps/seals etc. Having to deal with spent acid during the back flush process is also very expensive as acids typically are still at a low pH and toxic. It is advantageous to have an acid blend that can be exported to production facilities through pipelines that, once spent or applied, is commonly a neutral pH greatly reducing disposal costs/fees.

Acids perform many actions in the oil & gas industry and are considered necessary to achieve the desired production of various petroleum wells, maintain their respective systems and aid in certain functions (i.e. freeing stuck pipe). The associated dangers that come with using acids are expensive and tasking to mitigate through controls whether they are chemically or mechanically engineered.

Eliminating or even simply reducing the negative effects of acids while maintaining their usefulness is a struggle for the industry. As the public demand for the use of cleaner/safer/greener products increases, companies are looking for alternatives that perform the required function without all or most of the drawbacks associated with the use of conventional acids.

US Patent no. 4,466,893 teaches gelled acid compositions comprising a gelling agent selected from the group consisting of galactomannans such as guar gum, gum karaya, gum tragacanth, gum ghatti, gum acacia, gum konjak, shariz, locus, psyllium, tamarind, gum tara, carrageenan, gum kauri, modified guar such as hydroxypropyl guar, hydroxyethyl guar, carboxymethyl hydroxyethyl guar, carboxymethyl hydroxypropyl guar and alkoxyated amines. This patent teaches that presence of urea has a marked impact on the viscosity of the gelled acid and the gelled acid compositions are used in fracking activities.

US2014/041690 discloses a purportedly new compound made by dissolving glycine in water, in a weight ratio of approximately 1:1 to 1:1.5. The solution obtained is subsequently mixed until the glycine is essentially fully dissolved in the water. Once dissolution is complete, hydrogen chloride gas is dissolved in the solution to produce the new compound, which is referred to as hydrogen glycine.

US 5,135,668 teaches that corrosion inhibitors used in oil production offshore are highly cationic but the use of such cationic based corrosion inhibitors for offshore oil platforms are becoming less acceptable for environmental reasons. The description states that one method of overcoming the environmental concerns. By being cationic, they are attracted to metal surfaces, controlling acid type corrosion. When these cationic corrosion inhibitors find their way into the seawater, they are attracted to a particular type of algae which are a part of a food-chain for mussels. The description states that inhibiting corrosion in oil production fluids can be attained by adding to the oil production fluids an effective amount of betaine or certain ampholytes to circumvent the problems caused by typical cationic corrosion inhibitors.

US 4,308,168 teaches a method for inhibiting corrosion of metal by contacting the metal with a volatile alkyl ester of an amino acid. The description states that compositions containing these alkyl esters of amino acids can have activity as anti-corrosion inhibitor. It is further stated that the compositions can be either fluid or semi-fluid depending on their content. The compositions may also be porous materials such as zeolite, silica gel, paper board, kraft paper, cloth, etc.

US 5,171,477 teaches a method for inhibiting corrosion in aqueous systems which employ amino acid as chelants in concentrations which are corrosive to metal surfaces in contact with the aqueous system. It is stated that the method comprises the incorporation of a corrosion inhibitor, 1-hydroxyethane-1,1-diphosphonic acid (HEDPA). The concentration of HEDPA is sufficient to provide for corrosion inhibition and said concentration can range from 0.5% to 10% on the basis of the concentration of amino acid present.

US 5,300,235 teaches amine derivatives which are compounds of formula (I) where the compound contains at least one $(CH_2)_{1-4} COOH$ group; or a salt thereof are useful in inhibiting corrosion of metals in oil- and gas-field applications. The compounds also show low toxicity to marine organisms. The amine derivatives are obtained by the amidation of a di- or a polyamine with a fatty acid, followed by a reaction with either acrylic acid, ester or halocarboxylic acid.

US 6,447,717 B1 teaches that the carbon dioxide induced corrosion of ferrous metals in aqueous systems can be inhibited by treatment with corrosion inhibiting amino thiol and amino disulfide compounds. The description states that certain inhibitors considered to be particularly effective are the natural amino acids cysteine and cystine and their decarboxylated analogues cysteamine and cystamine. The description also discloses purportedly novel corrosion inhibiting compositions comprising a combination of amino thiol or amino disulfide compounds with acidic amino acid polymers.

US 3,699,052 teaches compositions containing amino acids and other components to inhibit corrosion and which are non-toxic to lower mammalian and aquatic lifeforms. The compositions contain, in essence, an amino acid or derivative thereof, an inorganic acid ester, such as an ester of phosphoric acid, a chelating agent, and a water soluble metal ion, such as copper or zinc.

EP 1 080 067 teaches compounds of formula (1), wherein R is the α -side chain of an amino acid, R1 is a straight or branched chain alkyl or alkenyl residue containing 1 to 30 carbon atoms or a cycloalkyl or aryl residue having from 5 to 12 carbon atoms; R2 is hydrogen or aryl or a straight chain alkyl or alkenyl residue having from 1 to 30 carbon atoms or together with R is the α -side chain of an amino acid; X is a linking moiety and Y is a suitable backbone moiety on which to append the N-acylated amino acid moieties via X linkages; and n is a number between 1 and the total number of available reactive substituents on Y. The description states that the compounds are efficient corrosion inhibitors and/or scale formation for use in systems in contact with aqueous media and/or hydrocarbon media in contact with water. The description also states a preferred product consists of acylated aspartic or glutamic acid anhydride or suitable activated ester product which is further reacted with a suitable nucleophilic group.

Despite these compositions, there is still a need for simpler, effective compositions for use in the oil industry which can be used over a range of applications which can decrease a number of the associated dangers/issues typically associated with acid applications to the extent that these acid compositions are considered much safer for handling on worksites, as well as much safer to manufacture/blend.

SUMMARY OF THE INVENTION

Compositions according to the present invention have been developed for the oil & gas industry and its associated applications, by specifically targeting the problems of corrosion, logistics/handling, human/environmental exposure and formation/fluid compatibilities, manufacturing/blending as well as controlling overall costs.

It is an object of the present invention to provide a synthetic acid composition which can be used over a broad range of applications in the oil and gas industry and which exhibit advantageous properties over known compositions.

According to one aspect of the present invention, there is provided a synthetic acid composition which, upon proper use, results in a very low corrosion rate of oil and gas industry tubulars/equipment.

According to another aspect of the present invention, there is provided a synthetic acid composition for use in the oil industry which is biodegradable.

According to a preferred embodiment of the present invention, there is provided a synthetic acid composition for use in the oil industry which has a methodically spending (reacting) nature that is linear as temperature increases, non-fuming, non-toxic, and has a highly controlled manufacturing process, ensuring a consistent end product strength

According to a preferred embodiment of the present invention, there is provided a synthetic acid composition for use in the oil industry which has a pH below 1.

According to a preferred embodiment of the present invention, there is provided a synthetic acid composition for use in the oil industry which has minimal exothermic reactivity.

According to a preferred embodiment of the present invention, there is provided a synthetic acid composition for use in the oil industry which is compatible with most existing industry additives.

According to another aspect of the present invention, there is provided a synthetic acid composition for use in the oil industry which has high salinity tolerance. A tolerance for high salinity fluids, or brines, is desirable for onshore and offshore acid applications. Typical acids are blended with fresh water and additives, typically far offsite, and then transported to the area of treatment as a finished blend. It is advantageous to have an alternative that can be transported as a concentrate safely to the treatment area, then blended with a high salinity produced water or sea water, greatly reducing the logistics requirement typical with conventional acid systems. A typical acid system could precipitate salts/minerals heavily if blended with fluids of an excessive salinity level. Brines are also typically present in formations, thus having an acid system that has a high tolerance for brines greatly reduces the potential for formation damage or emulsions down-hole during or after product placement/application.

According to another aspect of the present invention, there is provided a synthetic acid composition for use in the oil industry which is immediately reactive upon contact/application.

According to another aspect of the present invention, there is provided a synthetic acid composition for use in the oil industry which results in less unintended near wellbore erosion due to the controlled reaction rate. This, in turn, results in deeper formation penetration, increased permeability, and reduces the potential for zonal communication during a typical 'open hole' mechanical isolation application treatment. As a highly reactive acid, such as hydrochloric acid, is deployed into a well that

has open hole packers for isolation (without casing) there is a potential to cause a loss of near-wellbore compressive strength resulting in communication between zones or sections of interest as well as potential sand production, and fines migration. It is advantageous to have an alternative that will react with a much more controlled rate or speed, thus greatly reducing the potential for zonal communication and the above potential negative side effects of traditional acid systems.

According to another aspect of the present invention, there is provided a synthetic acid composition for use in the oil industry which provides a controlled and comprehensive reaction.

Accordingly, the product would overcome many of the drawbacks found in the use of compositions of the prior art related to the oil & gas industry.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The description that follows, and the embodiments described therein are provided by way of illustration of an example, or examples, of particular embodiments of the principles of the present invention. These examples are provided for the purposes of explanation, and not limitation, of those principles and of the invention.

According to an aspect of the invention, there is provided a synthetic acid composition comprising:

- urea & hydrogen chloride in a molar ratio of not less than 0.1:1; preferably in a molar ratio not less than 0.5:1, more preferably in a molar ratio not less than 1.0:1; and
- an amino acid.

According to a preferred embodiment of the present invention, the composition further comprises a metal iodide or iodate. More preferably, the iodide is selected from the group consisting of: cupric iodide, potassium iodide, lithium iodide and sodium iodide.

According to a preferred embodiment of the present invention, the composition may also include a phosphonic acid or derivatives, preferably alkylphosphonic acid or derivatives thereof and more preferably amino tris methylene phosphonic acid and derivatives thereof.

According to a preferred embodiment of the present invention, the composition further comprises an alcohol or derivatives thereof, preferably alkynyl alcohol or derivatives thereof, more preferably propargyl alcohol (or a derivative of).

Urea is the main component in terms of volume and weight percent of the composition of the present invention, and consists of a carbonyl group connecting with nitrogen and hydrogen. When added to

hydrochloric acid, there is a reaction that results in urea hydrochloride, which traps the chloride ion within the molecular structure. This reaction greatly reduces the hazardous effects of the hydrochloric acid on its own, such as the fuming effects, the hygroscopic effects, and the highly corrosive nature (the Cl^- ion will not readily bond with the Fe ion). The excess nitrogen can also act as a corrosion inhibitor at higher temperatures. Urea and hydrogen chloride in a molar ratio of not less than 0.1:1; preferably in a molar ratio not less than 0.5:1, and more preferably in a molar ratio not less than 1:1. However, this ratio can be increased depending on the application.

It is preferable to add the urea at a molar ratio greater than 1 to the moles of HCl acid (or any acid). This is done in order to bind any available Cl^- ions, thereby creating a safer, more inhibited product. Preferably, the composition according to the present invention comprises 1.1 moles of urea per 1.0 moles of HCl. The urea (hydrochloride) also allows for a reduced rate of reaction when in the presence of carbonate-based materials. This again due to the stronger molecular bonds associated over what hydrochloric acid traditionally displays. Further, since the composition according to the present invention is mainly comprised of urea (which is naturally biodegradable), the product testing has shown that the urea hydrochloride will maintain the same biodegradability function, something that hydrochloric acid will not on its own

Phosphonic acids and derivatives such as amino tris methylene phosphonic acid (ATMP) have some value as scale inhibitors. In fact, ATMP is a chemical traditionally used as an oilfield scale inhibitor, it has been found, when used in combination with urea/HCl, to increase the corrosion inhibition, or protection. It has a good environmental profile, is readily available and reasonably priced.

Amino tris (methylenephosphonic acid) (ATMP) and its sodium salts are typically used in water treatment operations as scale inhibitors. They also find use as detergents and in cleaning applications, in paper, textile and photographic industries and in off-shore oil applications. Pure ATMP presents itself as a solid but it is generally obtained through process steps leading to a solution ranging from being colorless to having a pale yellow color. ATMP acid and some of its sodium salts may cause corrosion to metals and may cause serious eye irritation to a varying degree dependent upon the pH/degree of neutralization.

ATMP must be handled with care when in its pure form or not in combination with certain other products. Typically, ATMP present in products intended for industrial use must be maintained in appropriate conditions in order to limit the exposure at a safe level to ensure human health and environment.

Amino tris (methylenephosphonic acid) and its sodium salts belong to the ATMP category in that all category members are various ionized forms of the acid. This category includes potassium and ammonium salts of that acid. The properties of the members of a category are usually consistent. Moreover, certain properties for a salt, in ecotoxicity studies, for example, can be directly appreciated by analogy to the properties of the parent acid. Amino tris (methylenephosphonic acid) may specifically be used as an intermediate for producing the phosphonates salts. The salt is used in situ (usually the case) or stored separately for further neutralization. One of the common uses of phosphonates is as scale inhibitors in the treatment of cooling and boiler water systems. In particular, for ATMP and its sodium salts are used in to prevent the formation of calcium carbonate scale.

Alcohols and derivatives thereof, such as alkyne alcohols and derivatives and preferably propargyl alcohol and derivatives thereof can be used as corrosion inhibitors. Propargyl alcohol itself is traditionally used as a corrosion inhibitor which works extremely well at low concentrations. It is a toxic/flammable chemical to handle as a concentrate, so care must be taken during handling the concentrate. In the composition according to the present invention, the toxic effect does not negatively impact the safety of the composition.

Metal iodides or iodates such as potassium iodide, sodium iodide, lithium iodide and cuprous iodide can potentially be used as corrosion inhibitor intensifier. In fact, potassium iodide is a metal iodide traditionally used as corrosion inhibitor intensifier, however it is expensive, but works extremely well. It is non-regulated and friendly to handle.

Example 1 - Process to prepare a composition according to a preferred embodiment of the invention

Start with a 50% by weight solution of pure urea liquor. Add a 36% by weight solution of hydrogen chloride while circulating until all reactions have completely ceased. The amino acid component is then added. Circulation is maintained until all products have been solubilized.

Table 1 lists the components of the composition of Example 1 including their weight percentage as compared to the total weight of the composition and the CAS numbers of each component.

Table 1 - Composition of a preferred embodiment of the present invention

Chemical	% Wt Composition	CAS#
Water	60.0%	7732-18-5
Urea Hydrochloride	39.0%	506-89-8
Glycine	1.00%	2605-79-0

The resulting composition of Example 1 is a clear, odourless liquid having shelf-life of greater than 1 year. It has a freezing point temperature of approximately minus 30°C and a boiling point temperature of approximately 100°C. It has a specific gravity of 1.15±0.02. It is completely soluble in water and its pH is less than 1.

The composition is biodegradable and is classified as a mild-irritant according to the classifications for skin classification. The composition is non-fuming and has no volatile organic compounds nor does it have any BTEX levels above the drinking water quality levels. BTEX refers to the chemicals benzene, toluene, ethylbenzene and xylene. Toxicity testing was carried out on rats and the LD₅₀ was determined to be greater than 2000mg/kg.

With respect to the corrosion impact of the composition on typical oilfield grade steel, it was established that it was clearly below the acceptable corrosion limits set by industry for certain applications, such as spearhead applications or lower temperature scaling issues.

Corrosion testing

The composition according to the present invention of Example 1 was exposed to corrosion testing. The results of the corrosion tests are reported in Table 2.

Samples of J55 grade steel were exposed to various synthetic acid solutions for periods of time ranging up to 24 hours at 90°C temperatures. All of the tested compositions contained HCl and urea in a 1:1.05 ratio at a 100% concentration.

Table 2 - Corrosion testing comparison between HCl-Urea and the composition of Example 1 of the present invention

Inhibitor (%)	Initial wt. (g)	Final wt. (g)	Loss wt. (g)	Surface area (cm ²)	Density (g/cc)	Run time (hours)	Mils/yr	Mm/year	Lb/ft ²
HCl-Urea	37.616	34.524	3.092	28.922	7.86	6	7818.20	198.582	0.222
HCl-Urea	37.616	31.066	6.550	28.922	7.86	24	4140.46	105.168	0.470
HCl-Urea + glycine @ 1.0%	38.106	35.307	2.799	28.922	7.86	6	7077.34	179.765	0.201
HCl-Urea + glycine @ 1.0%	38.106	33.250	4.856	28.922	7.86	24	3069.63	77.969	0.349

This type of corrosion testing helps to determine the impact of the use of such synthetic replacement acid composition according to the present invention compared to the industry standard (HCl blends or any other mineral or organic acid blends). The results obtained for the composition containing only

HCl and urea were used as a baseline to compare the other compositions. Additionally, the compositions according to the present invention will allow the end user to utilize an alternative to conventional acids that has the down-hole performance advantages, transportation and storage advantages as well as the health, safety and environmental advantages. Enhancement in short/long term corrosion control is one of the key advantages of the present invention. The reduction in skin corrosiveness, the controlled spending nature, and the high salt tolerance are some other advantages of compositions according to the present invention.

The compositions according to the present invention can be used directly (ready-to-use) or be diluted with water depending on their use. Corrosion testing was completed on a concentrated product and dilution will amplify results.

The uses (or applications) of the compositions according to the present invention upon dilution thereof ranging from approximately 1 to 75% dilution, include, but are not limited to: injection/disposal in wells; squeezes and soaks or bullheads; acid fracturing, acid washes or matrix stimulations; fracturing spearheads (breakdowns); pipeline scale treatments, cement breakdowns or perforation cleaning; pH control; and de-scaling applications. Remove High temp applications.

The synthetic acid composition according to a preferred embodiment of the present invention can be used in the oil industry to perform an activity selected from the group consisting of: stimulate formations; assist in reducing breakdown pressures during downhole pumping operations; treat production wells; increase injectivity of injection wells; lower the pH of a fluid; remove undesirable scale on a surface selected from the group consisting of: equipment, wells and related equipment and facilities; fracture wells; complete matrix stimulations; conduct annular and bullhead squeezes & soaks; pickle tubing, pipe and/or coiled tubing; increase effective permeability of formations; reduce or remove wellbore damage; clean perforations; and solubilize limestone, dolomite, calcite and combinations thereof.

While the foregoing invention has been described in some detail for purposes of clarity and understanding, it will be appreciated by those skilled in the relevant arts, once they have been made familiar with this disclosure that various changes in form and detail can be made without departing from the scope of the invention as set out in the appended claims.

CLAIMS

1. A synthetic acid composition for use in oil industry activities, said composition comprising:
 - urea and hydrogen chloride in a molar ratio of not less than 0.1:1; and
 - an amino acid selected from the group consisting of: glycine; valine, proline and tryptophan.
2. The synthetic acid composition according to claim 1, wherein the amino acid is present in a concentration ranging from 0.5 to 5.0% by weight of the total composition.
3. The synthetic acid composition according to claim 2, wherein the amino acid is present in a concentration ranging from 0.75 to 2.0% by weight of the total composition.
4. The synthetic acid composition according to claim 3, wherein the amino acid is present in a concentration ranging from 1 to 1.5% by weight of the total composition.
5. The synthetic acid composition according to any one of claims 1 to 4, wherein the amino acid is glycine.
6. The synthetic acid composition according to any one of claims 1 to 5, wherein the urea and hydrogen chloride are in a molar ratio of not less than 0.5:1.
7. The synthetic acid composition according to claim 6, wherein the urea and hydrogen chloride are in a molar ratio of not less than 1.0:1.
8. The synthetic acid composition according to any one of claims 1 to 7, further comprising a phosphonic acid derivative.
9. The synthetic acid composition according to claim 8, wherein the phosphonic acid derivative is an aminoalkylphosphonic salt.
10. The synthetic acid composition according to claim 9, wherein the aminoalkylphosphonic salt is amino tris methylene phosphonic acid.
11. The synthetic acid composition according to any one of claims 1 to 10, wherein the composition further comprises a metal iodide or iodate.

12. The synthetic acid composition according to claim 11, wherein the metal iodide or iodate is selected from the group consisting of: is cuprous iodide, potassium iodide, lithium iodide and sodium iodide.
13. The synthetic acid composition according to any one of claims 1 to 12, wherein the composition further comprises an alcohol or derivative thereof.
14. The synthetic acid composition according to claim 13, wherein the alcohol or derivative thereof is an alkynyl alcohol or derivative thereof.
15. The synthetic acid composition according to claim 14, wherein the alkynyl alcohol or derivative thereof is propargyl alcohol or a derivative thereof.
16. The synthetic acid composition according to claim 10, wherein the aminoalkylphosphonic salt is present in a concentration ranging from 0.25 to 1.0% w/w.
17. The synthetic acid composition according to claim 16, wherein the aminoalkylphosphonic salt is present in a concentration of 0.5% w/w.
18. The synthetic acid composition according to claim 14, wherein the alkynyl alcohol or derivative thereof is present in a concentration ranging from 0.01 to 0.25% w/w.
19. The synthetic acid composition according to claim 18, wherein the alkynyl alcohol or derivative thereof is present in a concentration of 0.1% w/w.
20. The synthetic acid composition according to any one of claims 11 and 12, wherein the metal iodide is present in a concentration ranging from 100 to 1000 ppm.
21. The use of a synthetic acid composition according to any one of claims 1 to 20 in the oil industry to stimulate formations.
22. The use of a synthetic acid composition according to any one of claims 1 to 20 in the oil industry to assist in reducing breakdown pressures during downhole pumping operations.
23. The use of a synthetic acid composition according to any one of claims 1 to 20 in the oil industry to treat wellbore filter cake post drilling operations.

24. The use of a synthetic acid composition according to any one of claims 1 to 20 in the oil industry to assist in freeing stuck pipe.
25. The use of a synthetic acid composition according to any one of claims 1 to 20 in the oil industry to descale pipelines and/or production wells.
26. The use of a synthetic acid composition according to any one of claims 1 to 20 in the oil industry to increase injectivity of injection wells.
27. The use of a synthetic acid composition according to any one of claims 1 to 20 in the oil industry to lower the pH of fluids.
28. The use of a synthetic acid composition according to any one of claims 1 to 20 in the oil industry to remove undesirable scale in surface equipment, wells and related equipment and/or facilities.
29. The use of a synthetic acid composition according to any one of claims 1 to 20 in the oil industry to fracture wells.
30. The use of a synthetic acid composition according to any one of claims 1 to 20 in the oil industry to complete matrix stimulations.
31. The use of a synthetic acid composition according to any one of claims 1 to 20 in the oil industry to conduct annular and bullhead squeezes & soaks.
32. The use of a synthetic acid composition according to any one of claims 1 to 20 in the oil industry to pickle tubing, pipe and/or coiled tubing.
33. The use of a synthetic acid composition according to any one of claims 1 to 20 in the oil industry to increase effective permeability of formations.
34. The use of a synthetic acid composition according to any one of claims 1 to 20 in the oil industry to reduce or remove wellbore damage.
35. The use of a synthetic acid composition according to any one of claims 1 to 20 in the oil industry to clean perforations.

36. The use of a synthetic acid composition according to any one of claims 1 to 20 in the oil industry to solubilize limestone, dolomite, calcite and combinations thereof.