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(54) **STABILIZED PIPE SCALING REMOVER AND INHIBITOR COMPOUND**

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(57) **ABSTRACT**

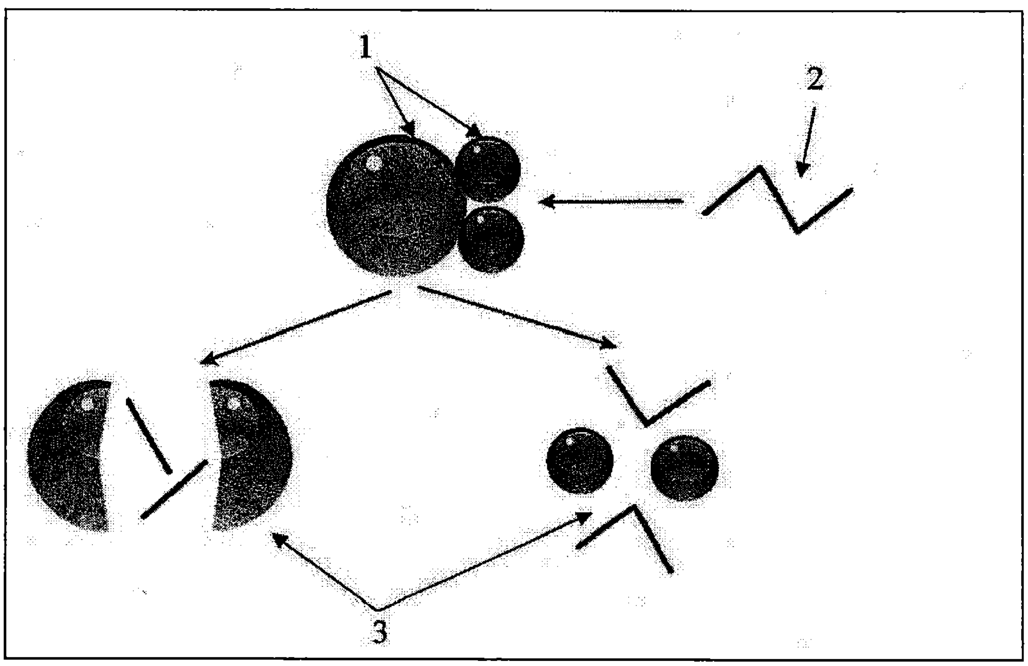
This invention refers to a stabilized pipe scaling remover and inhibitor compound, where a useful formulation is presented for the dissolution of scaling such as barium sulfate, calcium sulfate, calcium carbonate, magnesium carbonate, barium carbonate and ferric oxide.

This formulation is made up by a stabilized group of organic and inorganic acids, in addition to amines or alcohols of a high molecular weight which make it a low-corrosion, highly-effective fluid.

The possible fluids to be obtained from this document ensure the least amount of damage to the pipes used for its transportation and are friendly to different polymer materials. They progressively attack buildup scaling by solubilizing it in an aqueous medium and breaking down the carbonate ion.

Its use in the oil industry is as scale inhibitor, inorganic scale inhibitor, or scale formation inhibitor (when applied in solution). When used for dissolving scaling, it causes a gradual decomposition which allows for the fluid to enter over longer distances with a better action, along the solid with which it becomes in contact.

The product interferes by anion-cation interaction on ions with precipitation potential, inhibiting them, producing a group of agglomerations with a low molecular weight and high stability, which allows it to stay in the core of the solution in which it is located without forming insoluble agglomerates.



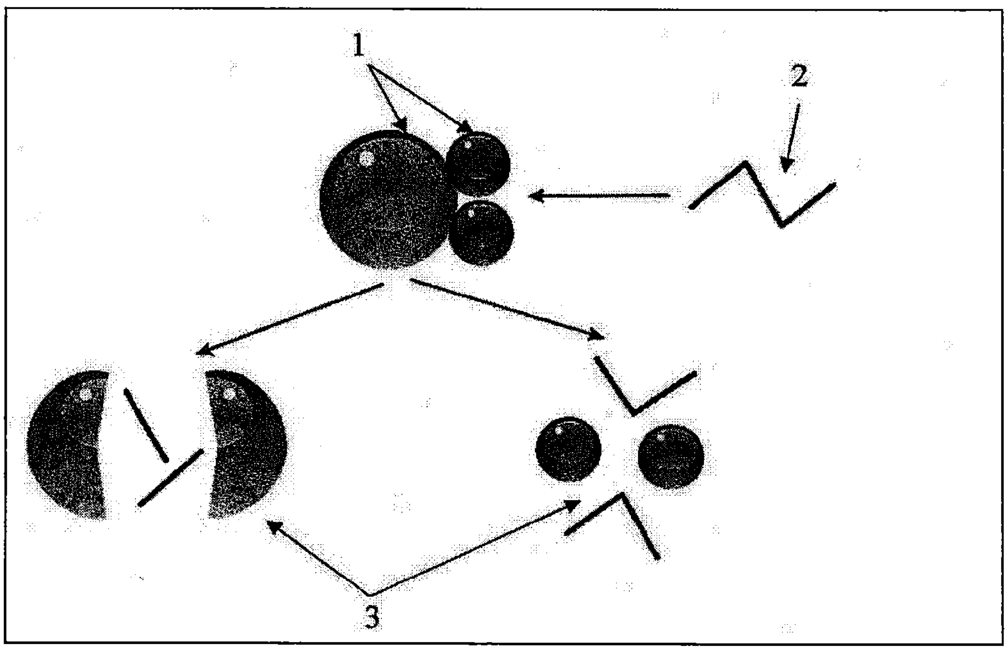


Figure 1

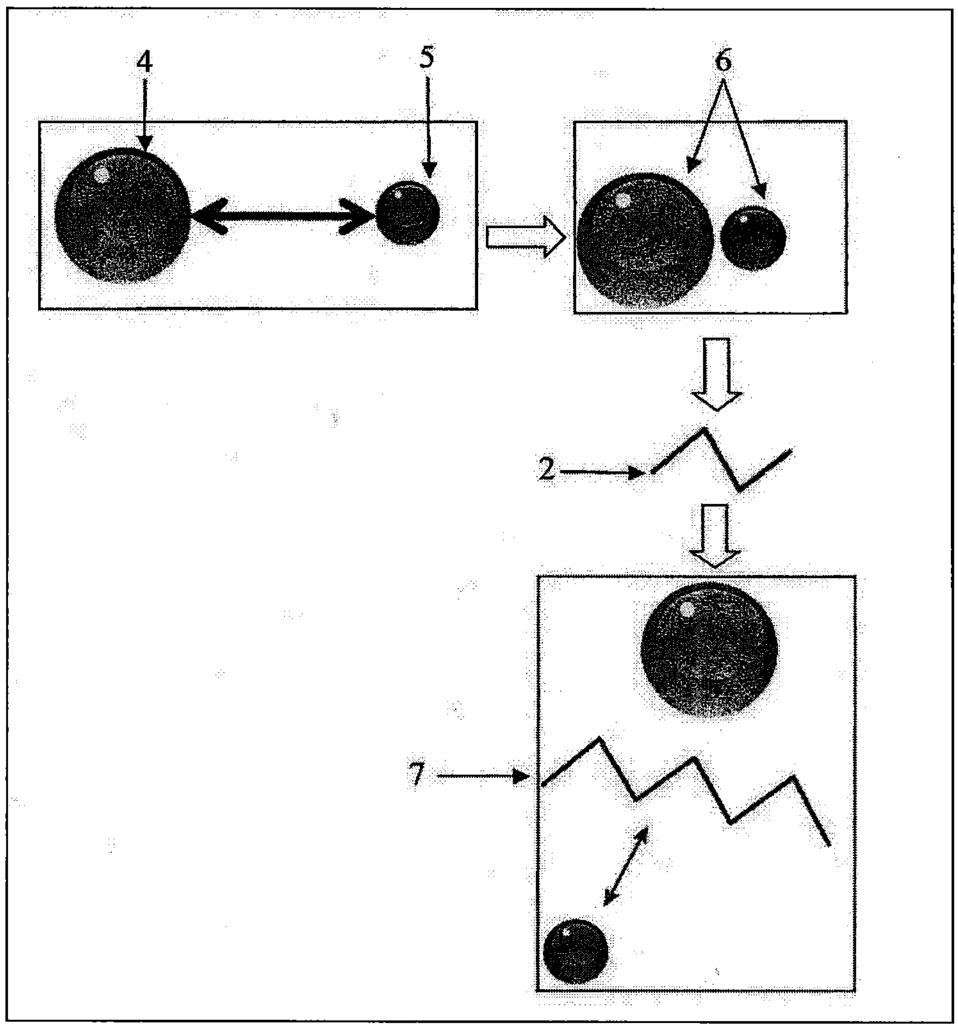


Figure 2

STABILIZED PIPE SCALING REMOVER AND INHIBITOR COMPOUND

INVENTION BACKGROUND

[0001] When an oil or gas well produces water (generally with a large content of dissolved salts), there is a possibility for scaling to form. This may also occur in deposits where water injection is used as an improved recovery system, or when using gas with high CO2 content and other contaminants. The most common scaling formed is barium sulfate or calcium carbonate.

[0002] Buildup of mineral sediments or incrustations may form in pipes both on the surface and in the bottom of the well, or even inside the porous medium in the formation of the oil deposit itself, which causes serious backup problems or even full blockages in pipes.

[0003] The techniques within the oil industry for eliminating scaling must be quick, not harmful with the formation and to the environment. Chemical use techniques are the most common because they are the most economical; when scaling is formed by carbonates, hydrochloric acid (HCl) is the most widely used to dissolve and remove scaling, but this acid loses its effectiveness with the precipitated calcium sulfate or other incrustations, in addition to having special care for its use. Although there are methods used where a solvent is utilized together with washers containing normal or viscoelastic surfactants, these are very selective products, making it necessary for versatile formulations for different scaling types.

[0004] HCl, as mentioned before, is the most widely used chemical compound for eliminating this type of scaling due to its cost, but it is also the acid with the fastest reaction, and therefore, a fast depletion of its effect, reason for which formulations which react gradually are recommended, in order to have a greater reach within a formation.

[0005] The application of scaling treatment is varied according to the location, and goes from solely pumping the dissolving product in a duct or well to a mixture with organic, inorganic solvents and surfactant agents, by using flexible piping, capillary piping or in the same gas injection for Pneumatic Pumping, and the most appropriate is the most convenient in accordance with the problem at hand.

[0006] The chemical inhibition process involves the inhibitor molecules' preferential absorption in these buildup locations. In consequence, the crystal will stop developing when the inhibitor's molecules have occupied all these active zones. Inhibitors act by controlling the scale deposits when they chemically interact with the crystal nucleation locations and substantially reduce their development rates, by altering their surfaces, the latter are known by the name of initiation inhibitors. They also act by sequestering the ions that precipitate and form scaling.

[0007] A scale inhibitor must satisfy several conditions in order to have a prolonged use, among them:

[0008] Be compatible (not to form reaction products with other system chemicals which causes its inactivation).

[0009] Be thermally stable (especially to the conditions in the bottom of the well) and hydrolytically stable for long terms.

[0010] Bacteriologically not sensitive.

[0011] Modify the size of crystals (form a tendency to disperse).

[0012] Delay or block the scaling precipitation process to a low concentration.

[0013] Must not promote emulsions.

[0014] Must be able to be monitored in the return fluids.

[0015] On the other hand, the inhibitor's maximum efficiency is threatened by:

[0016] Salinity and pH of the water going in contact with the inhibitor.

[0017] The water's chemical composition, water's magnesium content and dissolved iron must be low.

[0018] Presence and type of suspended solids (the inhibitor, is not yet "smart" and acts upon everything soluble traveling in the medium).

[0019] System's temperature.

[0020] In order to obtain a successful inhibition, there must be then a sufficient concentration of inhibitor molecules accompanying the fluid extracted from the well. This condition may be assured only if the inhibitor is held in the formation and gradually desorbed along with the produced fluid.

INVENTION DESCRIPTION

[0021] The characteristic details of this new stabilized pipe scaling remover and inhibitor compound are clearly described in the description and figures below.

[0022] FIG. **1** depicts in an illustrative fashion the manner in which the compound subject to this invention works in eliminating calcium carbonate scaling.

[0023] FIG. **2** depicts in an illustrative fashion the manner in which the compound subject to this invention works in inhibiting scaling formation.

[0024] FIG. **1** depicts calcium carbonate formations (**1**) present in pipes. Natural water contains dissolved salts which differ in ion concentration and variety, where said calcium carbonate ($CaCO_3$) (**1**) is generally present in this type of water in its ionized form, formed by calcium ions (Ca^{2+}) and carbonate ions (CO_3^{2-}) produced from the reaction $Ca^{2+}+CO_3^{2-}\rightarrow CaCO_3$. Calcium carbonate (**1**) may precipitate from the solution due to causes such as:

[0025] Solution saturation by some of the ions.

[0026] Increase in temperature.

[0027] Carbonate ions may come from the atmospheric CO_2 or from mixing with other gases, reacting with the Ca^{2+} ions forming calcium carbonate (**1**) which precipitates. This way the reaction $CO_2+H_2O\rightarrow CO_3^{2-}+2H^+$ explains the formation of carbonic acid, which is possible in high pH; and although the latter is very unstable, the carbonates that get to form due to its presence end up being very stable, staying in the solution as long as the conditions are the adequate.

[0028] The solution's pH also has an influence on the calcium carbonate's solubility because an acid pH destroys the carbonate ions, causing an inverse reaction (CO_2+H_2O→CO_3^{2-}+$2H^+$). The presence of CO2 increases this salt's solubility.

[0029] Upon adding a stabilized acid mixture (**2**), compound of this invention, compounds (**3**) that are highly soluble in water are obtained, this way eliminating the calcium carbonate precipitates (**1**).

[0030] One can observe in FIG. **2** the manner in which the formation of scaling may be inhibited. The existing interaction between calcium ions (**4**) and carbonate ions (**5**) bring about the formation of calcium carbonate precipitate (**6**), but when adding the stabilizing compound (**2**) subject to this invention, the inhibition of precipitable anion-cation interaction is achieved (**7**).

[0031] The influence of the pH may be evaluated if the temperature and hardness of water is known by the Langelier Saturation Index:

$$IL=pH-pH_s$$

where pH_s is the pH calculated for a Ca^{2+} concentration to arrive at the saturation. The Langelier Saturation Index is interpreted with the Stiff-Davis analysis: negative values indicate that there will not be precipitation; and if on the contrary, it ends up being positive, scaling water will result.

[0032] Another highly-precipitable ion is Calcium Sulfate, generally present when finding dissolved sulfate ion and calcium ion, as follows:

$$Ca^{2+}+SO_4^{2-}\rightarrow CaSO_4$$

[0033] In addition to ferric oxide (Fe_2O_3), the reaction occurs due to the oxidation of iron according to:

$$Fe^{2+}\rightarrow Fe^{3+}+e^-$$

and

$$O_2+4H^++4e^-\rightarrow 2H_2O \text{ or } O_2+2H_2O=4e^-\rightarrow 4OH^-$$

[0034] The compound of this invention has various formulations formed by the components described in Table 1.

TABLE 1

Formulation components of this invention's compound

Percentage	Element Description
0 to 12%	Inorganic Salt
0 to 45%	Organic monocarboxylic acid
0 to 45%	Organic di or tricarboxylic acid
0 to 15%	Inorganic acid
0 to 15%	Salt derived from an organic carboxylic acid
0 to 15%	Corrosion inhibitor
0 to 92%	Potable or sea water

[0035] The organic monocarboxylic acid may be formic acid (HCOOH) or acetic acid (CH3COOH). The organic di or tricarboxylic acid is formed by any organic acid which contains two three or more carbonyl groups bonded to a hydroxyl radical (—COON) such as citric acid or oxalic acid. The inorganic acid refers to hydrochloric acid (HCl) or Nitric acid (HNO3). The salt derived from an organic carboxylic acid is any one with the formula:

$$R—COO^{-+}Me$$

where R is any radical which may also contain one or more carboxyl groups and Me is any alkaline or alkaline earth metal.

[0036] The corrosion inhibitor is composed by a mixture of amines or alcohols of a high molecular weight.

[0037] Scaling Formation Inhibition Experiments.

[0038] Formulation 1.

[0039] For the formulation 1 described in Table 2 a scaling formation inhibitor is shown with the components mentioned in Table 1:

TABLE 2

Formulation 1.

Formulation 1	CITRIC ACID SOLUTION AT 20% 10 NaCl 10% SODIUM CITRATE 2% NITRIC ACID

[0040] Additionally, 2 highly-scaling solutions were prepared with different ion concentration in accordance with what is shown in Table 3.

TABLE 3

Concentration in milliequivalents/liter of cations and anions in synthetic water

Name	Na+	Ca++	Mg++	Fe++	Cl−	HCO3−	SO4=	CO3−
Solution 1	934.47	122	127.48	1.86	1076.53	8.08	1	1.2
Solution 2	3893.94	1472	671.66	46.9	5946.5	67	50	21

[0041] Mixtures were made with these 2 solutions prepared in Table 3 in different ratios as described in Table 4.

TABLE 4

Parts in the mixture of mixtures from Solution 1 and Solution 2		
Mixture	Solution 1 from Table 3	Solution 2 from Table 3
1	10	90
2	25	75
3	50	50
4	75	25
5	90	10

[0042] Theoretical Analysis of Precipitates

[0043] The theoretical precipitate was calculated for each mixture. The mixture of the two solutions which contain different concentrations of the same ion will give a final concentration of this ion, which is calculated as follows:

$$C_f=(x_A)(C_A)+(x_B)(C_B)$$

Where C_f, X and C are the concentration of the ion in the final solution, the fractions of the solution taken in order to make the mixture and the concentration of the ion in the corresponding solution, respectively.

[0044] The Langelier Stability Index was calculated in accordance with:

$$IS=pH-pH_s$$

Where IS, pH, pH_s are the stability index, pH of the solution and pH of the solution saturated with calcium carbonate, respectively.

[0045] The pH_s parameter is calculated as follows:

$$pH_s-(9.3+q_{SDT}+q_T)-(q_{Ca}{}^{2+}+q_{Ak})$$

[0046] From where the following parameters stem out:

$$q_{SDT}=\frac{-1+\log STD}{10}$$

$$q_T=(-13.12)(\log[T+273])+34.55$$

$$q_{Ca}^{2+}=-0.4+\log D$$

$$q_{Ak}=\log Ak$$

[0047] Where SDT, T, D and Ak are the total dissolved solids in mg/L, the temperature in ° C., the calcium hardness as calcium carbonate in mg/L and the total alkalinity as calcium carbonate in mg/L, respectively.

[0048] In order to calculate the solution pH, one must initially determine the concentration of the hydrogen ion in solution:

$$[H^+]_f=(x_A)([H^+]_A)=(x_B)([H^+]_B)$$

[0049] Where $[H^+]_f$, X, $[H^+]$ are the final concentration of hydrogen ions in the mixture, the fractions of the solution taken in order to make the mixture, the concentration of hydrogen ions in each solution (obtained with $[H^+]=10^{-pH}$). The final pH of the solution will be given by:

$$pH=-\log[H^+]_f$$

[0050] Calcium sulfate milligrams are obtained by the following formula:

$$mg_{CaSO4}=68(meq_{SO4})$$

Where meq_{CaSO4}=milliequivalents of sulfate ions.

[0051] Calcium carbonate milligrams are obtained by the following formula:

$$mg_{CaCO4}=50(meq_{CO4})$$

Where meq_{CaCO4}=milliequivalents of carbonate ions.

[0052] Calcium carbonate milligrams due to bicarbonate ions are obtained by the following formula:

$$mg_{CaCO4}=100(meq_{HCO3})$$

Where meq_{HCO3}=milliequivalents of bicarbonate ions.

[0053] Maximum ferric oxide milligrams produced are:

$$mg_{Fe2O3}=1.43(mg_{Fe2})$$

Where mg_{Fe2}=milligrams of iron ions present.

[0054] Experimental Analysis of Precipitates

[0055] Mixtures were carried out in laboratory, at room temperature, in order to determine the actual solids obtained per mixture according to Table 3.

[0056] Table 5 shows the theoretical results of precipitates obtained from the formulas shown above. I.E. means Stability Index.

[0057] Table 6 shows the results of precipitations where the mixtures were left to rest for 24 hours and were subjected to a centrifuge. The experiment was repeated on Table 7 with a dosage of 1000 ppm of Formulation 1 showing results with precipitates.

TABLE 5

Theoretical results of possible precipitates in the mixture of Solution 1 with Solution 2 in different ratios by applying formulas							
Composition	Temp (° C.)	I.E.	Theoretical CaSO4 (mg/L)	Theoretical CaCO3 (mg/L)	Theoretical Fe2O3 (mg/L)	Theoretical CaCO3 by Ca(HCO3)2 (mg/L)	Pp (mg/L)
10% Sol1 + 90% Sol2	25	2.19	3,067	951	1,773	12,222	18,012
25% Sol1 + 75% Sol2	25	1.68	2,567	803	1,490	10,454	15,314
50% Sol1 + 50% Sol2	25	1.12	1,734	555	1,020	7,508	10,817
75% Sol1 + 25% Sol2	25	0.56	901	308	549	4,562	6,319
90% Sol1 + 10% Sol2	25	0.10	401	159	266	2,794	3,621

TABLE 6

Experimental results of possible precipitates in the mixture of Solution 1 with Solution 2 in different ratios obtained by laboratory analysis

Composition	Temp (° C.)	Experimental CaSO4 (mg/L)	Experimental CaCO3 (mg/L)	Experimental Fe2O3 (mg/L)	Pp (mg/L)
10% Sol1 + 90% Sol2	25	2,980	12,800	2,010	17,790
25% Sol1 + 75% Sol2	25	2,321	10,500	1,510	14,331
50% Sol1 + 50% Sol2	25	1,700	7,700	1,100	10,500
75% Sol1 + 25% Sol2	25	914	4,400	510	5,824
90% Sol1 + 10% Sol2	25	389	2,820	239	3,448

TABLE 7

Experimental results of possible precipitates in the mixture of Solution 1 with Solution 2 in different ratios by applying 1000 ppm of Formula 1

Composition	Temp (° C.)	Experimental CaSO4 (mg/L)	Experimental CaCO3 (mg/L)	Experimental Fe2O3 (mg/L)	Pp (mg/L)
10% Sol1 + 90% Sol2 + 1000 ppm F1	25	<10	,2	69	71
25% Sol1 + 75% Sol2 + 1000 ppm F1	25	<10	<2	48	49
50% Sol1 + 50% Sol2 + 1000 ppm F1	25	<10	<2	30	30
75% Sol1 + 25% Sol2 + 1000 ppm F1	25	<10	<2	<5	<10
90% Sol1 + 10% Sol2 + 1000 ppm F1	25	<10	<2	<5	<10

[0058] Formulation 2.

[0059] Formulation 2 was prepared as shown in Table 8 by using components from Table 1.

TABLE 8

Formulation 2, inhibitor of barium sulfate formation

Formulation 2	4% CITRIC ACID 10% ZINC ACETATE FORMIC ACID SOLUTION AT 30% 5% UROTROPINE

[0060] A mixture of 1000 mg/L of barium sulfate in distilled water was prepared in the laboratory. Subsequently, 1000 ppm of Formulation 2 were added. A complete dissolution of precipitates was observed.

[0061] Formulation 3.

[0062] Ferric oxide was used in pure state. 1 mg of ferric oxide was placed in 10 mL of water. When 1000 ppm of Formulation 1 was added, a complete dissolution of ferric oxide was observed. The same occurs by using Formulation 2.

[0063] During the experimental development of the above formulations, the following could be observed:

[0064] Precipitation process blocking.

[0065] Modification of the shape (along with smaller size) and properties of the crystals obtained in Example 1.

[0066] Did not observe adherence of solids to the walls of the containers where the experiments were carried out.

[0067] The formulations proposed herein were mixed with crude at a 50:50 and 80:20 crude-treatment ratio for the other systems. Did not observe a formation of undesirable emulsions or phases which are signs of incompatibility.

[0068] The corrosivity of a formulation was determined. The result is shown in Table 9.

TABLE 8

Corrosivity result for Formulation 1.

Formulation	30% FORMIC ACID + 4% CITRIC ACID + 10% ZINC ACETATE + 5% urotropine
COUPON No.	2
PIPE	2⅞"
SYSTEM VOLUME USED	100 ml
MEASUREMENTS COUPON (cm)	0.85 × 2 × 6.5
COUPON AREA (cm^2)	29.75
INITIAL WEIGHT (g)	86.2259
FINAL WEIGHT (g)	85.6012
WEIGHT LOSS (g)	0.6247
CORROSION (g/cm^2)	<0.03
CORROSION (lb/ft^2)	<0.05

Having sufficiently described my invention, this stabilized pipe scaling remover and inhibitor compound is considered by me as an innovation, and I therefore claim the contents of the following provisions to be exclusively owned by me:

1. A stabilized pipe scaling remover and inhibitor compound, characterized because it may include in its volume the combination of inorganic salt between 0 and 12%, organic monocarboxylic acid between 0 and 45%, organic di or tricarboxylic acid between 0 and 45%, inorganic acid between 0 and 15%, Salt derived from an organic carboxylic acid between 0 and 15%, a corrosion inhibitor composed by a mixture of amines or alcohols of a high molecular weight between 0 and 15% and potable or sea water between 0 and 92%.

2. A stabilized pipe scaling remover and inhibitor compound, characterized because just as it was described in claim **1**, the organic monocarboxylic acid is formic acid or acetic acid or a combination of both.

3. A stabilized pipe scaling remover and inhibitor compound, characterized because just as it was described in claim **1**, the organic di or tricarboxylic acid may include, but not limited to, citric acid or oxalic acid or a combination of both.

4. A stabilized pipe scaling remover and inhibitor compound, characterized because just as it was described in claim **1**, the inorganic acid may include, but not limited to, hydrochloric acid or nitric acid.

5. A stabilized pipe scaling remover and inhibitor compound, characterized because just as it was described in claim **1**, the organic salt has the same nature as mono, di or tricarboxylic acid described in claims **2** and **3**.

6. A stabilized pipe scaling remover and inhibitor compound, characterized because just as it was described in claim **1**, said compound works as dissolvent of inorganic compounds already formed, such as calcium sulfate, barium sulfate, calcium carbonate, barium carbonate and ferric oxide.

* * * * *