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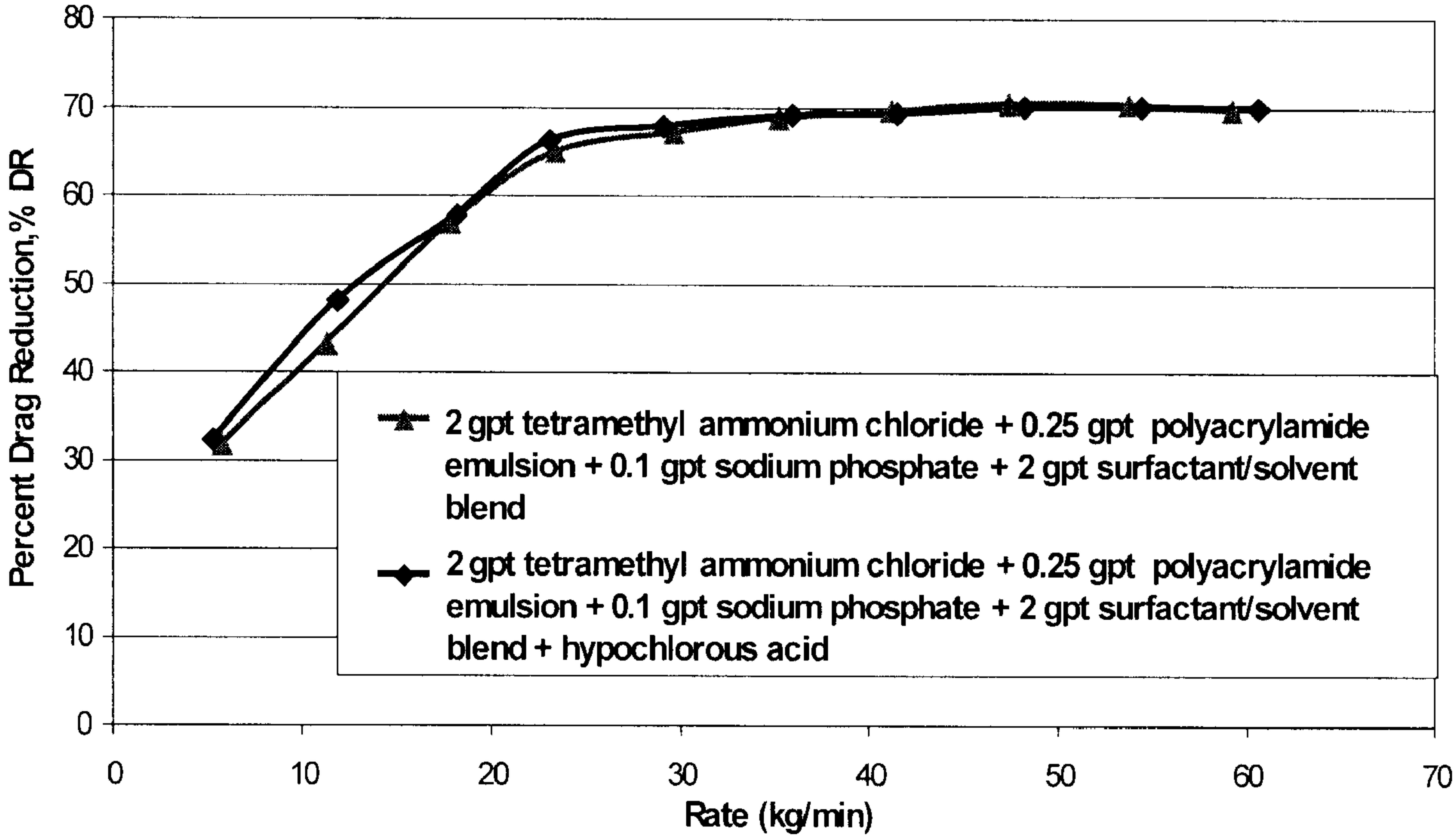
(54) Title: ENVIRONMENTALLY FAVORABLE AQUEOUS SOLUTION FOR CONTROLLING BACTERIA IN THE WATER USED FOR FRACTURING



(57) Abrégé/Abstract:

Method and apparatus for treating a subterranean formation including forming a fluid comprising hypochlorous acid and introducing the fluid to the subterranean formation, wherein the fluid exhibits a pH of about 4.0 to about 7.5 and wherein bacteria is at least 25 percent less present in the fluid than if no hypochlorous acid were in the fluid. Method and apparatus for treating a subterranean formation including forming a fluid comprising hypochlorous acid, a pH modifying agent, and a viscosity modifying agent, introducing the fluid to the subterranean formation, and fracturing the subterranean formation, wherein the fluid has a viscosity that is within 2 percent of the viscosity it would have if no hypochlorous acid were present. A composition of a fluid for use in the oil field services industry including hypochlorous acid, pH modifying agent, and viscosity modifying agent.

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Abstract

Method and apparatus for treating a subterranean formation including forming a fluid comprising hypochlorous acid and introducing the fluid to the subterranean formation, wherein the fluid exhibits a pH of about 4.0 to about 7.5 and wherein bacteria is at least 25 percent less present in the fluid than if no hypochlorous acid were in the fluid. Method and apparatus for treating a subterranean formation including forming a fluid comprising hypochlorous acid, a pH modifying agent, and a viscosity modifying agent, introducing the fluid to the subterranean formation, and fracturing the subterranean formation, wherein the fluid has a viscosity that is within 2 percent of the viscosity it would have if no hypochlorous acid were present. A composition of a fluid for use in the oil field services industry including hypochlorous acid, pH modifying agent, and viscosity modifying agent.

ENVIRONMENTALLY FAVORABLE AQUEOUS SOLUTION FOR CONTROLLING BACTERIA IN THE WATER USED FOR FRACTURING

BACKGROUND

[0001] Hydraulic fracturing uses fluid additives such as slickwater additives. The demand for this type of well services has increased over the past decade, especially because of its successful application for shale gas. Horizontal wells are often standard, requiring as much as 4.2 million gallons of water per well in as many as 6 to 9 fracture stages. Additive packages are tailored to save money. Because of environmental concerns and fresh water availability, the flowback and produced water are collected and used for subsequent fracture treatments. Produced water is a perfect environment for sulfate reducing bacteria (SRB) and acid forming bacteria (AFB) due to its anaerobic nature (<2ppm oxygen content) and high nutrient content (organics, free iron, etc.). Reuse of water introduces enough oxygen through regular pumping operations to allow aerobic bacteria to grow – mostly slime forming bacteria (SFB). The oxygen content is high enough for aerobic bacteria to grow but too low to kill anaerobic bacteria. The oxygen content will cause the anaerobic bacteria to stay in a biostatic state which does not kill them but prevents them from multiplying.

[0002] As soon as the bacteria find an environment that is conducive to their growth, they will become active again and start multiplying. The anaerobic environment in the formation is ideal for growth of bacteria like SRBs and AFBs. The aerobic environment of the wellbore is conducive for SFBs. The growth of SRBs will not only lead to Health and Safety (H&S) concerns due to increased sour gas or hydrogen sulfide (H_2S) production but also to a slow souring of the reservoir. This also increases operation expenses because of corrosion (H_2S pitting, stress cracking etc) in surface and subsurface tubulars. Other challenges in production can be related to AFBs (pitting) and SFBs (emulsion like materials may form).

[0003] Various different methods can be applied to prevent bacteria growth and reduce operational expenses related to corrosion prevention, remediation of corrosion effects, and remediation of emulsion like produced fluids. Common biocides are quaternary amines, glutaraldehyde, tetra-kis-hydroxylmethylphosphonium sulfate, and tetrahydro 3,5-dimethyl-1,3,5-thiadiazinane-2-thione. The issues with tradiational non-oxidizing biocides like those described above are that they each have compatibility issues with common additives in stimulation fracturing treatments (e.g. quat amines are not compatible with quaternary and zircontate crosslinked fluids fluids or anionic friction reducing polymers) and that they are very toxic. Despite the treatment of water with these biocides, post-fracture treatment reservoirs souring has been reported. The re-growth of SRB under reservoir conditions may lead to reservoir souring. An effective, low cost, environmentally friendly biocide that is compatible with other fluid additives and is easily transportable is needed.

FIGURES

[0004] Figure 1 is a bar graph of free active chlorine as a function of hydrochlorous acid concentration for three time periods.

[0005] Figure 2 is a bar graph of bacterial population as a function of time for three types of bacteria when a fluid comprises a friction reducer.

[0006] Figure 3 is a bar graph of bacterial population as a function of time for three types of bacteria when a fluid comprises a biocide.

[0007] Figure 4 is a bar graph of bacterial population as a function of time for three types of bacteria when a fluid comprises a hypochlorous acid.

[0008] Figure 5 is a photograph comparing produced water before and after addition of hypochlorous acid.

[0009] Figure 6 is a chart illustrating the percent drag reduction as a function of rate that compares a fluid comprising a viscosity modifying agent with and without hypochlorous acid.

[00010] Figure 7 is a chart illustrating viscosity as a function of time for the fluid identified by Table 2 and varied concentrations of hypochlorous acid.

[00011] Figure 8 is a chart illustrating viscosity as a function of time for the fluid identified by Table 3 and varied concentrations of hypochlorous acid.

[00012] Figure 9 is a chart illustrating viscosity as a function of time for the fluid identified by Table 4 and varied concentrations of hypochlorous acid.

[00013] Figure 10 is a chart illustrating viscosity as a function of time for the fluid identified by Table 5 and varied concentrations of hypochlorous acid.

SUMMARY

[00014] Embodiments of the invention relate to a method and apparatus for treating a subterranean formation including forming a fluid comprising hypochlorous acid and introducing the fluid to the subterranean formation, wherein the fluid exhibits a pH of about 4.0 to about 7.5 and wherein bacteria is at least 25 percent less present in the fluid than if no hypochlorous acid were in the fluid. Embodiments of the invention relate to a method and apparatus for treating a subterranean formation including forming a fluid comprising hypochlorous acid, a pH modifying agent, and a viscosity modifying agent, introducing the fluid to the subterranean formation, and fracturing the subterranean formation, wherein the fluid has a viscosity that is within 2 percent of the viscosity it would have if no hypochlorous acid were present. Embodiments of the invention relate to a composition of a fluid for use in the oil field services industry including hypochlorous acid, pH modifying agent, and viscosity modifying agent.

DETAILED DESCRIPTION

[00015] At the outset, it should be noted that in the development of any such actual embodiment, numerous implementation-specific decisions must be made to achieve the developer's specific goals, such as compliance with system related and business related constraints, which will vary from one implementation to another. Moreover, it will be appreciated that such a development effort might be complex and time consuming but would nevertheless be a routine undertaking for those of ordinary skill in the art having the benefit of this disclosure. The description and examples are presented solely for the purpose of illustrating the preferred embodiments of the invention and should not be construed as a limitation to the scope and applicability of the invention. While the compositions of the present invention are described herein as comprising certain materials, it should be understood that the composition could optionally comprise two or more chemically different materials. In addition, the composition can also comprise some components other than the ones already cited.

[00016] In the summary of the invention and this description, each numerical value should be read once as modified by the term "about" (unless already expressly so modified), and then read again as not so modified unless otherwise indicated in context. Also, in the summary of the invention and this detailed description, it should be understood that a concentration range listed or described as being useful, suitable, or the like, is intended that any and every concentration within the range, including the end points, is to be considered as having been stated. For example, "a range of from 1 to 10" is to be read as indicating each and every possible number along the continuum between about 1 and about 10. Thus, even if specific data points within the range, or even no data points within the range, are explicitly identified or refer to only a few specific, it is to be understood that inventors appreciate and understand that any and all data points within the range are to be considered to have been specified, and that inventors have disclosed and enabled the entire range and all points within the range.

[00017] Embodiments of the present invention relate to the use of hypochlorous acid as an effective biocide for use in operations related to recovering hydrocarbons from subterranean formations, such as fracturing operations, especially those fracturing operations that use fluid additives for viscosity modification. That is, embodiments of this invention relate to the use of hypochlorous acid for killing and managing microbes in water used for fracturing including slickwater fracturing. For example, hypochlorous acid can be delivered in a dilute and stable form, such as by using EXCELYTE^{TM} composition, which is commercially available from Benchmark of Houston, Texas. Calcium hypochlorite may be selected for some embodiments. It also will form hypochlorous acid upon exposure to water.

Hypochlorous Acid

[00018] Generally, when chlorine is added to water, hypochlorous acid is formed according to the equation:

$$Cl_2 + H_2O \leftrightarrow HOCl + HCl$$

[00019] Hypochlorous acid has outstanding bactericidal power. This is generally attributed to its ability to diffuse through cell walls and thereby reach the vital parts of the bacterial cell. A widely accepted theory credits the death of the cell to a reaction between hypochlorous acid and enzyme. The hypochlorite ion has little if any bactericidal effect since its negative charge impedes penetration of the cell wall.

[00020] The bactericidal power of a solution of chlorine, a hypochlorite, or a chloramine is directly proportional to the hypochlorous acid concentration of the solution. The percent available chlorine as un-dissociated hypochlorous acid is therefore the true measure of the bactericidal effectiveness of a solution containing one of the chemicals of the available chlorine family.

[00021] The available chlorine family is comprised of the group of chemicals which, when dissolved in water, yield solutions of hypochlorous acid. These compounds may be further subdivided into those which contain free available chlorine and those which contain combined available chlorine.

[00022] Oxidizing power of a hypochlorite and/or hypochlorous acid solution is attributable to the amount of active oxidant, measured as Free Available Chlorine (FAC), irrespective of pH. Organic chloramines are also a source of FAC, where the low rate of hydrolysis of dissolved organic chloramines to give hypochlorite and/or hypochlorous acid contributes little to the rate of oxidation while maintaining the total oxidizing power, which relates to the amount of organic chloramines present. Thus, organic chloramines and other reagents that contribute to FAC supply more hypochlorite and/or hypochlorous acid as these oxidizers are depleted.

[00023] Hypochlorous acid is 25 to 100 times more effective than bleach as a disinfectant without being corrosive. The key active ingredient, hypochlorous acid, is a naturally occurring molecule synthesized from an electrolyzed solution of salt and water. When exposed to atmospheric conditions, it quickly degrades into saltwater, therefore not leaving ecological damage at field locations.

[00024] Unlike bleach (sodium hypochlorite), hypochlorous acid does not fully dissociate and has a neutral pH. (around 7.5). In aqueous solutions, hypochlorous acid partially dissociates into a salt (the hypochlorite ion), therefore its use in oil field service application does not leave an undesirable ecological footprint. In contrast, the most commonly used oxidizers do not sterilize and completely kill bacteria. Hypochlorous acid, on the other hand, reacts quickly with any organic-based or readily oxidizable materials (Fe, H_2S) present in the water. Further, hypochlorous acid is noncorrosive compared to other biocides.

[00025] In some embodiments, hypochlorous acid will have a concentration of about 1 to 8,500 ppm in a fluid. The pH of hypochlorous acid influences the free available chlorine concentration. The relationship between pH and the degree of dissociation acid is illustrated by Table 1. Hydrolysis increases rapidly as the pH rises above neutrality.

Table 1 — Dissociation of Hypochlorous Acid as a Function of pH at 25°C

pH	% HOCl Undissociated
5.0	99.6
6.0	96.5
7.0	73.0
7.4	50.0
8.0	21.0
9.0	2.7
10.0	0.3

[00026] Hypochlorous acid may be commercially manufactured using several methods. In some embodiments, hypochlorous acid may be made by exposing water containing sodium chloride to an electrolytic cell. It can also be made in a more concentrated form in the field by using a buffer, such as citric acid to lower the pH of a sodium hypochlorite solution in water. Finally, in some embodiments, hypochlorous acid may be generated by dissolving chlorine gas in water.

[00027] Hypochlorous acid can also be formed by introducing sodium hypochlorite into a solution that has a pH that can be synthesized from an electrolyzed solution of salt and water, or generated by lowering the pH of a hypochlorite solution to a pH below 7.5, often tailored to have a pH of 4 to 7. For example, a continuous process that includes continuous addition of sodium hypochlorite and pH modifying agent such as a weak acid such as on the fly mixing in oil field service applications may be selected. PH modifying agents such as weak acid, a buffer and/or a strong acid may be used to tailor the pH. In some embodiments, the preferred pH modifying agent may comprise water-soluble organic acids with twelve or fewer carbon atoms. The weak acid is an acid that exhibits a pKa of less than 6. Weak acids include potassium dihydrogen phosphate, phthalic acid, phthalates such as potassium hydrogen phthalate and related acid salts, chelates, citric acid, sulfamic acid, ascorbic acid, octanoic acid, nonanoic acid, propionic acid, erythorbic acid, succinic acid, glutaric acid, adipic acid, polyacrylic acid, maleic acid, cyanuric acid, orthophosphoric acid, acetic acid, and sodium, potassium, and calcium salts of these acids. A weak acid, a buffer, or a combination thereof may be used to tailor the pH. In some embodiments, the preferred weak acid may comprise water-soluble organic acids with twelve or fewer carbon atoms. The preferred weak acid exhibits a pKa of less than 6. Weak acids include,

[00028] In some embodiments, a pH modifying agent may include a strong acid that does not contain a halogen, such as sulfuric, nitric, or phosphoric acid may be used in very dilute concentration, such as nanomolar concentration. Other buffers, buffer solutions, or buffer systems may be selected.

[00029] The pH modifying agent may be selected to activate upon the passage of time or temperature, such that the hypochlorous acid is present in solution after the solution containing sodium hypochlorite and pH modifying agent is pumped into a wellbore. Generally, however the hypochlorous acid is manufactured, the pH modifying agent may be selected to modify the pH of the fluid over a tailored time or temperature. Agents most likely to be effective include polylactic acid, polyglycolic acid, or similar hydrolytic polyesters. Delay may be enhanced by isolating the agent in an oil phase and the sodium hypochlorite in the water phase in some embodiments, the acid may be encapsulated. Upon temperature and downhole mixing, delayed formation of hypochlorous acid may be achieved. Fumeric acid encapsulated in wax may also be selected.

[00030] In any event, however the hypochlorous acid is formed, to maintain the hypochlorous acid concentration within a fluid, the fluid may be tailored to exhibit a pH of 4.0 to 7.5 using a weak acid. In some embodiments, the preferred weak acid may comprise water-soluble organic acids with twelve or fewer carbon atoms. A weak acid is an acid that exhibits a pKa of less than 6. Weak acids include potassium dihydrogen phosphate, thallic acid, phthalates, chelates, citric acid, sulfamic acid, ascorbic acid, octanoic acid, nonanoic acid, propionic acid, erythorbic acid, succinic acid, glutaric acid, adipic acid, polyacrylic acid, maleic acid, cyanuric acid, orthophosphoric acid, acetic acid, and sodium, potassium, and calcium salts of these acids. In some embodiments, a strong acid that does not contain a halogen, such as sulfuric, nitric, or phosphoric acid may be used in very dilute concentration, such as nanomolar concentration. Other buffers, buffer solutions, or buffer systems may be selected.

[00031] Additional chemicals may be added to a hypochlorous acid composition to stabilize the hypochlorous acid concentration and/or to reduce the reactivity of the bacteria's residual enzymes. Dichloroisocyanuric acid, cyanuric acid, sulfamic acid, potassium iodate, ethylenediaminetetraacetic acid, or a combination thereof may be selected for some embodiments.

[00032] The method can also include contacting the aqueous medium with an enzyme activity minimizer including a metal. In an embodiment, the metal can include a heavy metal compound in the aqueous medium including oilfield produced water. In an embodiment, the heavy metal can include zirconium compound. Zirconium containing chemicals may be used to reduce the reactivity of residual bacteria enzymes. Examples of zirconium containing chemicals that act as enzyme activity minimizer include zirconium nitrate, zirconyl chloride, zirconium phosphate, zirconium potassium chloride, zirconium potassium fluoride, zirconium potassium sulfate, zirconium pyrophosphate, zirconium sulfate, zirconium tetrachloride, zirconium tetrafluoride, zirconium tetrabromide, zirconium tetraiodide, zirconyl carbonate, zirconyl hydroxynitrate, zirconyl sulfate, zirconium complexed with amino acids, zirconium complexed with phosphonic acids, hydrates thereof and combinations thereof. Organo-zirconium compound examples include zirconium acetate, zirconyl acetate, zirconium acetylacetonate, zirconium glycolate, zirconium lactate, zirconium naphthenate, sodium zirconium lactate, triethanolamine zirconium, zirconium propionate, hydrates thereof and combinations thereof. Zirconium dichloride oxide may be selected for some embodiments.

Other Fluid Additives

[00033] The carrier fluid, such as water, brines, or produced water, may contain other additives to tailor properties of the fluid. Rheological property modifiers such as friction reducers, viscosifiers, emulsions, stabilizers, solid particles such as proppant or fibers, or gases such as nitrogen may be included in the fluid. The fluid may include viscosity modifying agents such as guar gum, hydroxyproplyguar, hydroxyelthylcellulose, xanthan, or carboxymethylhydroxypropylguar, diutan, chitosan, or other polymers or additives used to modify viscosity for use in the oil field services industry . Water based fluids may include crosslinkers such as borate or organometallic crosslinkers. In some embodiments, the fluid may contain viscosity modifying agents that comprise viscoelastic surfactant. Viscoelastic surfactants include cationic, anionic, nonionic, mixed, zwitterionic and amphoteric surfactants, especially betaine zwitterionic viscoelastic surfactant fluid systems or amidoamine oxide viscoelastic surfactant fluid systems.

Applications

[00034] The fluid may be used as a fracturing fluid, drilling fluid, completions fluid, coiled tubing fluid, sand control fluids, cementing operations fluid, fracturing pit fluid, or onshore or offshore water injector fluid, or any other fluid that is introduced into a subterranean formation primarily for the recovery of hydrocarbons. The fluid is introduced to the subterranean formation by drilling equipment, fracturing equipment, coiled tubing equipment, cementing equipment, or onshore or offshore water injectors. During, before, or after the fluid is added to a subterranean formation, the formation may benefit from fracturing, drilling, controlling sand, cementing, or injecting a well.

[00035] An oil field services application of a hypochlorous acid fluid may include delivery of the fluid to the following mechanical equipment. Hypocholorous acid fluid may be delivered to the low pressure side of the operation, that is, into any low pressure hose, connection, manifold, or equipment; before or during treatment. Examples of the location for addition include into pond, pit, or other water containment source; into inlet hose/manifold of water tanks (upstream of water tanks); frac tanks – all together or separate; into water tanks (frac tanks) themselves; into hose/manifold of outlet side of water tanks; into batch mixing unit; into hose/manifold in between batch mixing unit and blender; into blender itself; into exit side of blender (upstream of fracturing pumps); hose/manifold; directly into low pressure side of pump manifold (missile). Hypochlorous acid fluid may be delivered to the high pressure side of an operation including into any high pressure iron, anywhere. Pumps that may be used, either solo or combined, include positive displacement pumps, centrifugal pumps, and additive pumps. The hypochlorous acid fluid may be added to the water stream in any way. (i.e. pour from a bucket, pump it into the water, etc.).

[00036] Delivering the components to form the hypochlorous acid fluid to the mechanical equipment in the field must be selected based on the source of the acid. Commercially available hypochlorous acid, such as EXCELYTE^{TM}, is delivered premixed into any size storage containers. It may be added to the system with any way into any of the above points of addition. Sodium hypochlorite may be combined with a weak acid on the fly or by batch mixing. In on the fly applications, the material may be added by separate add lines – one for bleach, one for acid/buffer (any order); by a combined system - concentrated mixture of bleach and acid/buffer; or by a slurry system – combined mixture of water, bleach and acid/buffer. In batch mixing applications, the components may be mixed together before or during the fracturing job and stored in any type of container. It may be added to the system with any way into any of the above points of addition. In some embodiments, hypochlorous acid may kill or retard the reproduction of microorganisms. In some embodiments, hypochlorous acid in the fluid will result in a fluid with at least 25 percent less microorganisms or at least 25 percent less bacteria than if no hypochlorous acid were present.

Examples

[00037] The following examples are presented to illustrate the preparation and properties of fluid systems, and should not be construed to limit the scope of the invention, unless otherwise expressly indicated in the appended claims. All percentages, concentrations, ratios, parts, etc. are by weight unless otherwise noted or apparent from the context of their use.

[00038] Several analytical tools were selected to confirm the effectiveness of hypochlorous acid, its compatibility with other fluid additives, and its stability over time with optional stabilizing additives.

Water Quality - Water analysis (produced water)

[00039] The type of water used in this study was produced water from the Piceance Basin, which is considered to be among the dirtiest, recycled, produced water with poor quality. The sample water was provided to us by a supplier and yielded a pH of 8.0 and a TDS of 142,000 ppm. Titrimetric methods were used to determine the anions present while Inductively Coupled Plasma spectrometry was used for the detection of cations in the sample water.

Free Available Chlorine (FAC) Demand Test

[00040] The chlorine exists in the water as hypochlorous acid (free available chlorine, FAC). Chlorine is effective against all microorganisms and any readily oxidizable organic matter. If there is a lot of organic matter in the fracturing water, the chlorine will be consumed (or spent) and will be unavailable for killing the bacteria. Therefore, it is necessary to have a residual of FAC in the water to be effective as a biocide. The FAC demand test determines the dosage of hypochlorous acid necessary to treat the water and kill the bacteria in the frac water. The FAC demand test was used to determine the dosage of hypochlorous acid necessary to treat and kill the bacteria downhole. The FAC of the sample water was determined at several time points up to 45 minutes using various concentrations of hypochlorous acid. 5% (*v/v*) of hypochlorous acid was found to be the lowest effective concentration that showed a positive FAC residual necessary to sanitize and kill the microorganisms present in the produced water. Figure 1 shows data collected on a Piceance Basin water sample. As can be seen, 5% (*v/v*) or 50 gpt hypochlorous acid was the lowest effective concentration that showed a positive result of FAC residual which was necessary to sanitize and kill the bacteria. Consequently, 50 gpt was used as the concentration for all subsequent testing regarding hypochlorous acid.

[00041] Bottle tests were used to evaluate the biocidal efficacy of hypochlorous acid against the three types of bacteria mentioned above as well as compare its performance with friction reducer and commonly used biocide, gluteraldehyde. The bacterial population was measured at time points up to seven days.

Effect of Friction Reducer on Bacterial Population

[00042] Figure 2 shows the effect of a viscosity modifying agent, that is, a friction reducer has on biological activity. As can be seen that friction reducer had little or no effect on the bacterial population. 0.25 gal/Mgal polyacrylamide emulsion was added to the Piceance Basin water sample for a period of seven days to see its effect on the biological activity. The above figure shows that the friction reducer had little or no effect on the bacterial population.

Effect of Gluteraldehyde on Bacterial Population

[00043] Figure 3 shows that gluteraldehyde is not very effective in killing bacteria in Piceance River water containing 0.25 gpt of friction reducer. Note a 2 log reduction in the population of SRB after 24 hours (a 3 log reduction is desirable). However, after 7 days there was re-growth of bacteria. 0.25 gal/Mgal gluteraldehyde was added to the produced water sample along with 0.25 gal/Mgal friction reducer to evaluate the effect of gluteraldehyde on bacterial activity for seven days. The above figure shows that gluteraldehyde in the presence of friction reducer was not effective in killing the bacteria in the water sample; however, there was a 2 log reduction in the SRB population after 24 hours. After seven days, regrowth of bacteria was apparent, suggesting the possibility of sour wells after fracturing treatment.

Effect of Hypochlorous Acid on Bacterial Population

[00044] Figure 4 shows the hypochlorous acid is very effective in killing all bacteria in the Piceance River water. After 7 days, the bacterial counts were blow detectable limits and no regrowth was apparent. 50% (*v/v*) hypochlorous acid was added to the produced water sample containing 0.25 gal/Mgal friction reducer to evaluate the effect of hypochlorous activity on bacterial activity for seven days. Within five minutes, the bacterial population was significantly reduced from 10^6 cells/mL to 10^1 cells/mL. After 24 hours, the SRB population was not detectable and regrowth was not apparent after seven days.

Compatibility with Slickwater Additives and Piceance River Water

[00045] Visual tests were performed to illustrate that there were no incompatibilities between viscosity modifying additives and hypochlorous acid. Also, bottle tests were performed. Bottle tests (deionized water and produced water) were performed with deionized water and produced water, separately. 5% (*v/v*) hypochlorous acid was added to a series of individual bottles with slickwater additives, including clay stabilizer, scale inhibitor, friction reducer and a microemulsion. The compatibility of hypochlorous acid and the slickwater additives were observed at time 0 and 5 minutes. No incompatibilities were observed between the slickwater additives and hypochlorous acid in deionized water. Before adding hypochlorous acid to the produced water, there was a strong rotten egg odor in the water sample indicating the presence of SRB. After the five minute treatment of hypochlorous acid, a color change was observed and the rotten egg odor was eliminated. Additionally, the pH remained stable for all fluids tested. Figure 5 shows addition of hypochlorous acid to the produced water eliminated rotten odor and color changed to a lighter shade. The pH remained stable after the hypochlorous acid treatment. Apparently, the hypochlorous acid is very effective in improving the quality of produced water by oxidizing the contaminants.

Effects of Hypochlorous Acid on Friction Reducer

[00046] A friction loop consisting of a ½" and a ¾" pipe was used for drag reduction measurements. Synthetic water was prepared based on the water analysis of the Piceance Basin produced water sample. Fifteen liters of the source water, along with the slickwater additives and hypochlorous acid, were stirred using an overhead stirrer at 1000 rpm for two minutes before being added to the friction loop for evaluation. Before analysis, the differential pressure gauges were purged and the pump was primed prior to recording the data for the test. The test fluid was then pumped for about 10 seconds at incremental intervals of about 6 Kg/min and the percent drag reduction was calculated. The figure below shows the friction loop results of the slickwater additives and hypochlorous acid measuring the percent drag reduction as a function of flow rate (Kg/min). Varying the viscosity modifying additives with and without hypochlorous acid shows no incompatibilities as illustrated by Figure 6. Figure 6 shows the friction loop results of slickwater additives and hypochlorous acid. Data are plotted as the percent drag reduction as a function of flow rate (Kg/min). Hypochlorous acid had no effect on the slickwater additives. This shows that the viscosity difference due to the presence of the hypochlorous acid in about 2 percent or less.

Hypochlorous Acid in Combination with Common Fracturing Fluids

[00047] The compatibility of hypochlorous acid was evaluated with common fracturing fluids currently used in field operations. The biocide was used at concentrations of 0 gal/Mgal, 10 gal/Mgal, and 50 gal/Mgal. The fluid compositions are listed in Tables 2-5. Fluids were tested at 150 degF for a period of one hour. The mixing procedure for the fracturing fluids is as follows: 500 mL of deionized water was placed into a Waring blending cup; subsequently, the biocide was added and allowed to mix for 20 seconds. The gelling agent was then added and allowed to mix for 10 minutes, after which the linear gel viscosity was checked and compared to the hydration chart (see below). The remaining additives were then added to the solution and the vortex was allowed to close (after the addition of the crosslinker). Rheology profiles of the four fluids may be found in figures 7 to 10 which illustrate the experimental results generated using the fluids of tables 2-5. The fluids did not result in a significant loss in viscosity when the biocide concentration was increased from 0 gal/Mgal to 50 gal/Mgal. Additionally, the fluid is still viable and capable of transporting proppant.

[00048] Common Fracturing fluids that may be utilized with hypochlorous acid are listed in the following tables

Table 2. Fluid formulation 1

Additive	Concentration	
Tetramethyl ammonium chloride (TMAC)	2 gpt	
Slurried guar	6.25 gpt	
Borate crosslinker	3 gpt	
Hypochlorous acid	0, 10, 50 gpt	

Table 3. Fluid Formulation 2

Additive	Concentration	
Tetramethyl ammonium chloride (TMAC)	2 gpt	
Slurried guar	6.25 gpt	
Boric acid	5.5 ppt	
Sodium Hydroxide	10 ppt	
d-Sorbitol	2 gpt	
Hypochlorous acid	0, 10, 50 gpt	

Table 4. Fluid Formulation 3

Additive	Concentration	
Tetramethyl ammonium chloride (TMAC)	2 gpt	
Slurried guar	6.25 gpt	

Sodium Borate	1.3 gpt	
30% Sodium Hydroxide	0.5 gpt	
Hypochlorous acid	0, 10, 50 gpt	

Table 5. Fluid Formulation 4

Additive	Concentration	
Polyvinyl acetate/ polyvinyl alcohol copolymer	6.7 gpt	
Erucic amidopropyl dimethyl betaine	40 gpt	
Hypochlorous acid	0, 10, 50 gpt	

Table 6. Linear Gel Viscosities at Increased Biocide Concentrations

Biocide Concentration (gpt)	*Temperature (F)*	*Viscosity (511, sec^{-1})*
0	71.2	19
10	74.1	18.5
50	68.7	18

Neutralization of hypochlorous acid

[00049] Using 100 mL of 3% (v/v) hypochlorous acid, 29 mL of 5% (v/v) acetic acid was added to obtain a pH of 6.5 from an initial pH value of 8.48. The FAC residual of was over 1000 ppm. Additionally, in a separate experiment, 22 mL of 1M sodium citrate was added to the hypochlorous acid solution to obtain a pH of 6.5. The FAC value was then found to be 24 ppm.

[00050] Bottle tests were used to evaluate the stabilization of hypochlorous acid with the following chemicals: dichloroisocyanuric acid (DCCA) and cyanuric acid (CA). Cyanuric acid is known to stabilize the rate of decomposition of hypochlorous acid in ultraviolet conditions. Over a period of four days, a set of bottles with the following components were left open: 1) hypochlorous acid, 2) hypochlorous acid + 30 ppm CA, 3) hypochlorous acid + 50 ppm CA, 4) hypochlorous acid + 30 ppm DCCA, and 5) hypochlorous acid + 50 ppm DCCA. At the time of preparation, the initial pH and FAC were taken and recorded (see table below). The test points were then taken again after 1 day and four days. For all solutions prepared, the pH was stable (within 5% of the hypochlorous acid) after the addition of DCCA and CA. Additionally, the FAC residual value for all solutions decreased by 5%, with the DCCA-containing solutions obtaining a consistently higher FAC residual than hypochlorous acid.

	Time = 0		Time = 1 day		Time = 4 days	
	pH	FAC (ppm)	pH	FAC (ppm)	pH	FAC (ppm)
Hypochlorous acid	6.80	726	6.86	692	7.18	628
Hypochlorous acid + 30 ppm CA	6.51	660	6.76	646	7.13	587
Hypochlorous acid + 50 ppm CA	6.47	670	6.77	637	7.16	580
Hypochlorous acid + 30 ppm DCCA	6.62	739	6.75	705	7.13	639
Hypochlorous acid + 50 ppm DCCA	6.79	739	6.99	705	7.20	639

Hypochlorous acid solution made from sodium hypochorite.

[00051] A tank is filled with 400 gallons of city water. To this is added 20 gallons of 12% sodium hypochlorite solution. This result in a 0.6% solution of sodium hypochorite. To this is added an excess of citric acid until the pH of the resulting solution reaches pH equal to 6.5. This stock solution is then added on the fly to the fracturing treatment. The concentration of the stock solution added to the fracturing fluid was 0.2 to 0.6 gallons per thousand gallons. Using 100 mL of 1% (*v/v*) hypochlorous acid (10000 ppm), 12.8 mL of 5% (*v/v*) acetic acid was added to obtain a pH value of 7.0 from an initial pH of 9.7. The active concentration (FAC residual) of the resultant solution was then found to be 8500 ppm. After one hour, the active concentration remained the same. In 24 hours, the active concentration decreased by 3.5% to 8210 ppm. Similarly, 55.2 mL of 0.1M succinic acid solution was added to 100 mL 1% (*v/v*) hypochlorous acid to obtain a pH value of 7.0. The active concentration was found to be 6040 ppm after titration.

Field test

[00052] A fracturing treatment using hydrochlorous acid lasted two days. Four stages, at 2 hours per stage, were pumped using a total of 1.86 million gallons of water. 1.6M pounds of proppant were used. In total, 19k gallons of hydrochlorous acid was pumped. The concentration of acid that was required (10 gpt) also required bulk storage and high rate additive pumps. A 12,000 gallon fluid module (modified frac tank) was placed next to the water frac tanks. An additive skid with 2 large wakeisha pumps, capable of 45 gpm, added hypochlorous acid at a rate of 42 gpm. Hypochlorous acid was pumped from the bulk module tank and into the 250 bbl batch mixing tank.

[00053] The particular embodiments disclosed above are illustrative only, as the invention may be modified and practiced in different but equivalent manners apparent to those skilled in the art having the benefit of the teachings herein. Furthermore, no limitations are intended to the details herein shown, other than as described in the claims below. It is therefore evident that the particular embodiments disclosed above may be altered or modified and all such variations are considered within the scope and spirit of the invention. Accordingly, the protection sought herein is as set forth in the claims below.

CLAIMS

What is claimed is:

1. A method of treating a subterranean formation, comprising:

   forming a fluid comprising hypochlorous acid; and

   introducing the fluid to the subterranean formation;

   wherein the fluid exhibits a pH of about 4.0 to about 7.5; and

   wherein microorganisms are at least 25 percent less present in the fluid than if no hypochlorous acid were in the fluid.

2. The method in claim, 1 wherein the hypochlorous acid has a concentration of 1 to 8,500 ppm.

3. The method of claim 1 or 2, wherein the fluid is introduced to the subterranean formation by drilling equipment, fracturing equipment, coiled tubing equipment, cementing equipment, or onshore or offshore water injectors.

4. The method of claim 3, wherein the introducing the fluid to a subterranean formation comprises introducing the fluid in a low pressure portion or a high pressure portion of the fracturing equipment.

5. The method of claim 1, wherein the introducing the fluid to a subterranenan formation further comprises fracturing, drilling, controlling sand, cementing, or injecting a well.

6. The method in claim 1 or 2, wherein the fluid is made at the wellsite by adding sodium hypochlorite to a volume of water and then adjusting the pH to about 4.0 to about 7.5.

7. The method in claim 6, wherein a pH modifying agent is added to the fluid to adjust the pH to 4.0 to 7.5.

8. The method of claim 7, wherein the pH modifying agent is potassium dihydrogen phosphate, phthalic acid, phthalates, chelates, citric acid, sulfamic acid, ascorbic acid, octanoic acid, nonanoic acid, propionic acid, erythorbic acid, succinic acid, glutaric acid, adipic acid, polyacrylic acid, maleic acid, cyanuric acid, orthophosphoric acid, acetic acid, and/or sodium, potassium, and/or calcium salts of these acids.

9. The method of claim 1, wherein a pH modifying agent is added to the hypochlorous acid to adjust the pH to about 4.0 to about 7.5.

10. The method of claim 9, wherein the pH modifying agent is potassium dihydrogen phosphate, phthalic acid, phthalates, chelates, citric acid, sulfamic acid, ascorbic acid, octanoic acid, nonanoic acid, propionic acid, erythorbic acid, succinic acid, glutaric acid, adipic acid, polyacrylic acid, maleic acid, cyanuric acid, orthophosphoric acid, acetic acid, and/or sodium, potassium, and/or calcium salts of these acids.

11. The method in claim 1 or 2, wherein the fluid further comprises a viscosity modifying agent.

12. The method of claim 1 or 2, wherein the fluid further comprises an enzyme activity minimizer.

13. The method of claim 12, wherein the enzyme activity minimizer is zirconium nitrate, zirconyl chloride, zirconium phosphate, zirconium potassium chloride, zirconium potassium fluoride, zirconium potassium sulfate, zirconium pyrophosphate, zirconium sulfate, zirconium tetrachloride, zirconium tetrafluoride, zirconium tetrabromide, zirconium tetraiodide, zirconyl carbonate, zirconyl hydroxynitrate, zirconyl sulfate, zirconium complexed with amino acids, zirconium complexed with phosphonic acids, zirconium acetate, zirconyl acetate, zirconium acetylacetonate, zirconium glycolate, zirconium lactate, zirconium naphthenate, sodium zirconium lactate, triethanolamine zirconium, zirconium propionate, hydrates thereof and combinations thereof.

14. A method of treating a subterranean formation, comprising:

forming a fluid comprising hypochlorous acid, a pH modifying agent, and a viscosity modifying agent;

introducing the fluid to the subterranean formation; and

fracturing the subterranean formation

wherein the fluid has a viscosity that is within 2 percent of the viscosity it would have if no hypochlorous acid were present.

15. The method of claim 14, wherein the viscosity modifying agent is a friction reducing polymer.

16. The method of claim 14 or 15, wherein the pH modifying agent is potassium dihydrogen phosphate, phthalic acid, phthalates, chelates, citric acid, sulfamic acid, ascorbic acid, octanoic acid, nonanoic acid, propionic acid, erythorbic acid, succinic acid, glutaric acid, adipic acid, polyacrylic acid, maleic acid, cyanuric acid, orthophosphoric acid, acetic acid, and/or sodium, potassium, and/or calcium salts of these acids.

17. The method of claim 14, 15, or 16, wherein the fluid is introduced to the subterranean formation by drilling equipment, fracturing equipment, coiled tubing equipment, cementing equipment, or onshore or offshore water injectors.

18. The method of claim 17, wherein the introducing the fluid to a subterranean formation comprises introducing the fluid in a low pressure portion or a high pressure portion of the fracturing equipment.

19. A composition of a fluid for use in the oil field services industry, comprising:

hypochlorous acid;

viscosity modifying agent; and

pH modifying agent.

20. The composition of claim 19, wherein the pH modifying agent is potassium dihydrogen phosphate, phthalic acid, phthalates, chelates, citric acid, sulfamic acid, ascorbic acid, octanoic acid, nonanoic acid, propionic acid, erythorbic acid, succinic acid, glutaric acid, adipic acid, polyacrylic acid, maleic acid, cyanuric acid, orthophosphoric acid, acetic acid, and/or sodium, potassium, and/or calcium salts of these acids.

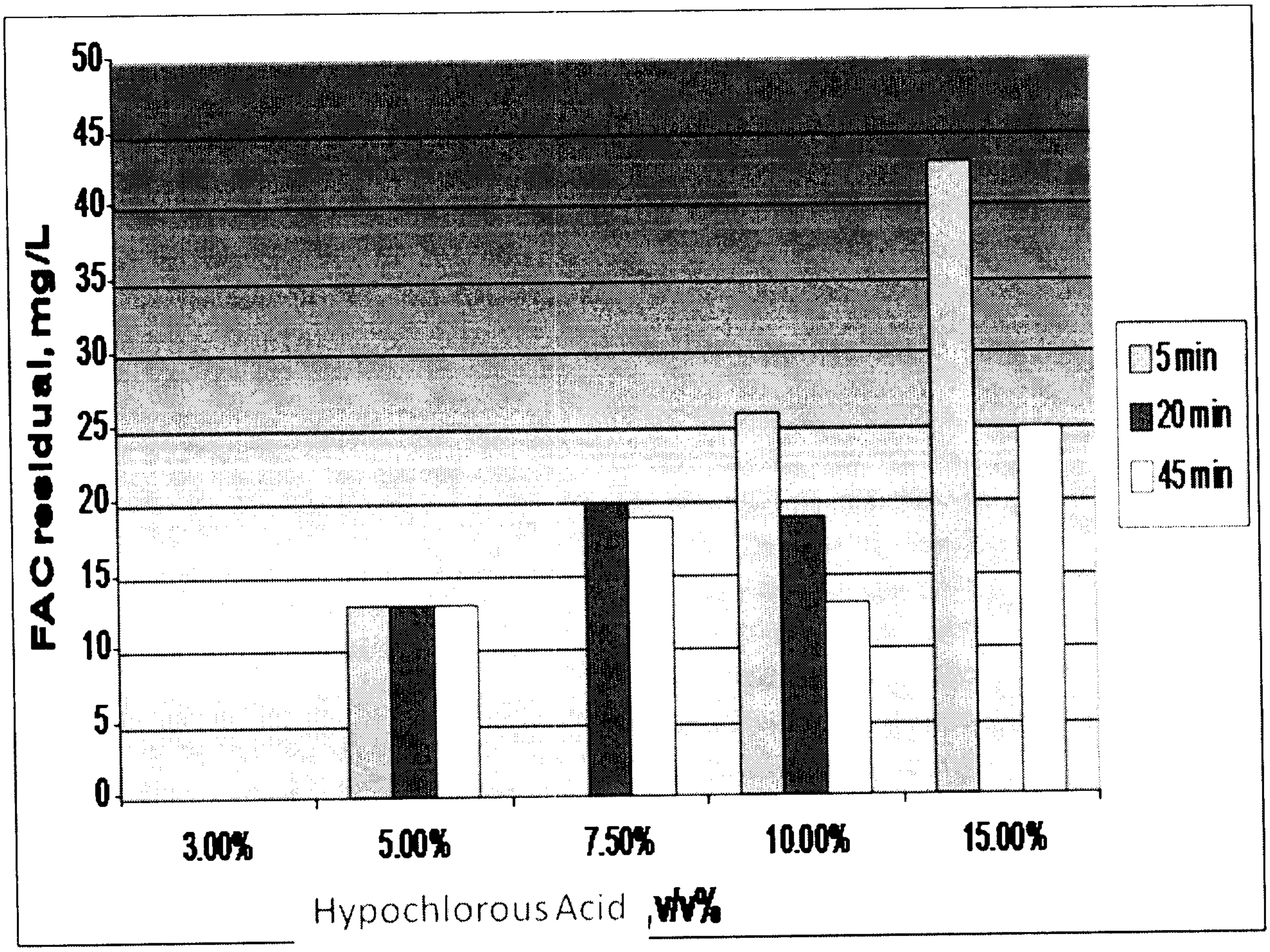

FAC residual, mg/L
50
45
40
35
30
25
20
15
10
5
0
3.00%
5.00%
7.50%
10.00%
15.00%
Hypochlorous Acid ,v/v%
5 min
20 min
45 min

Figure 1

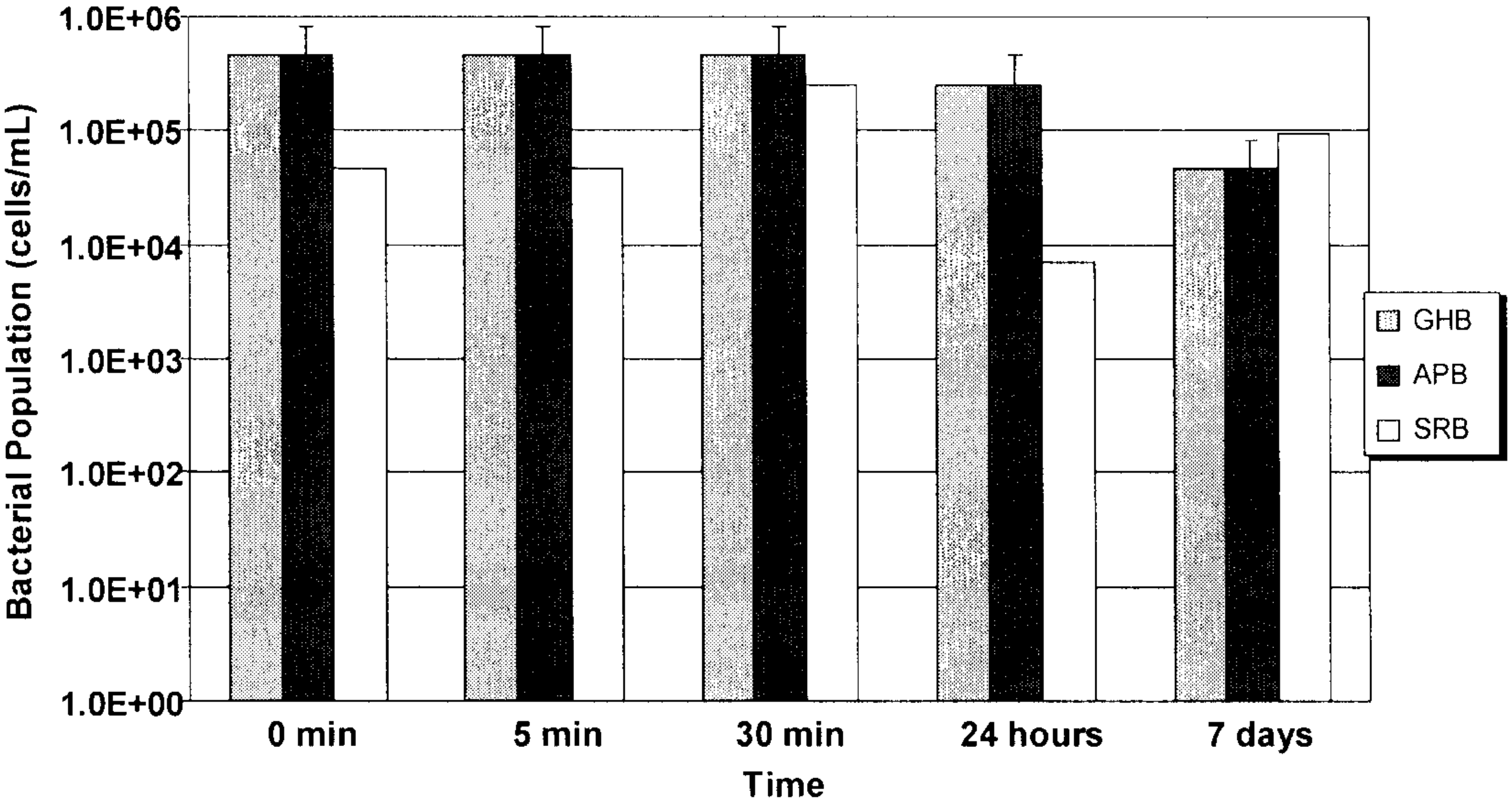


Figure 2

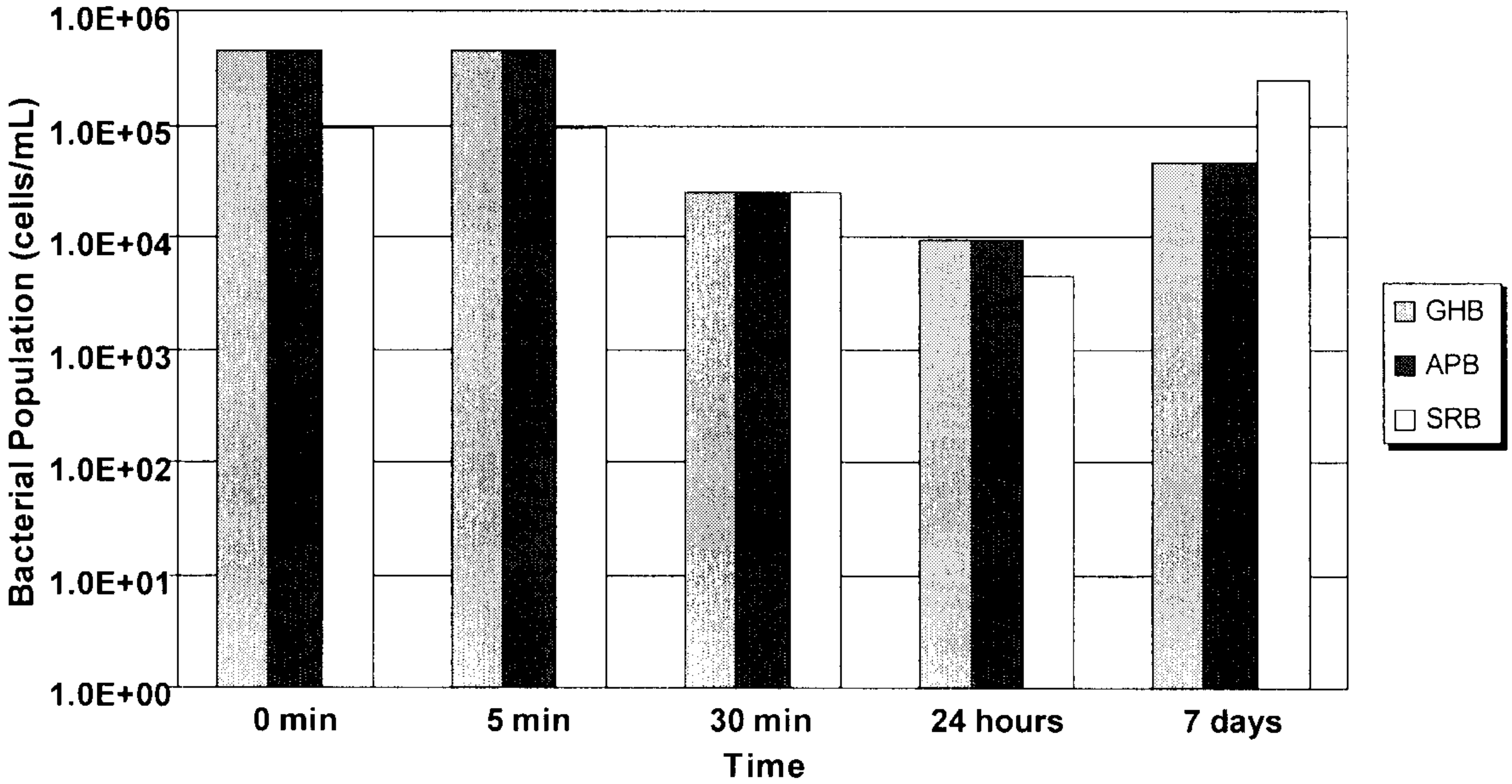


Figure 3

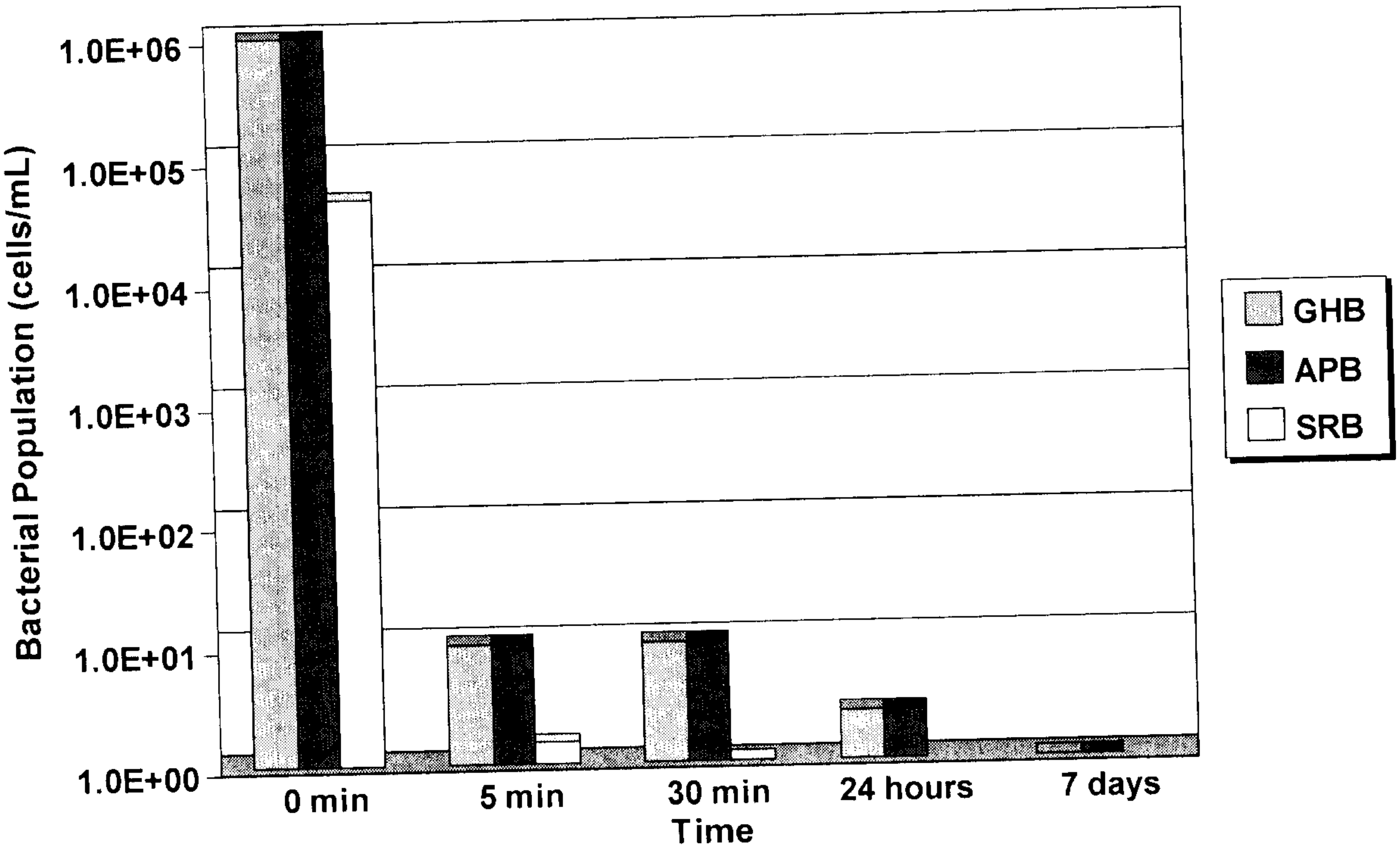


Figure 4

Produced Water at Time = 0

5 min after adding Hypochlorous acid

Figure 5

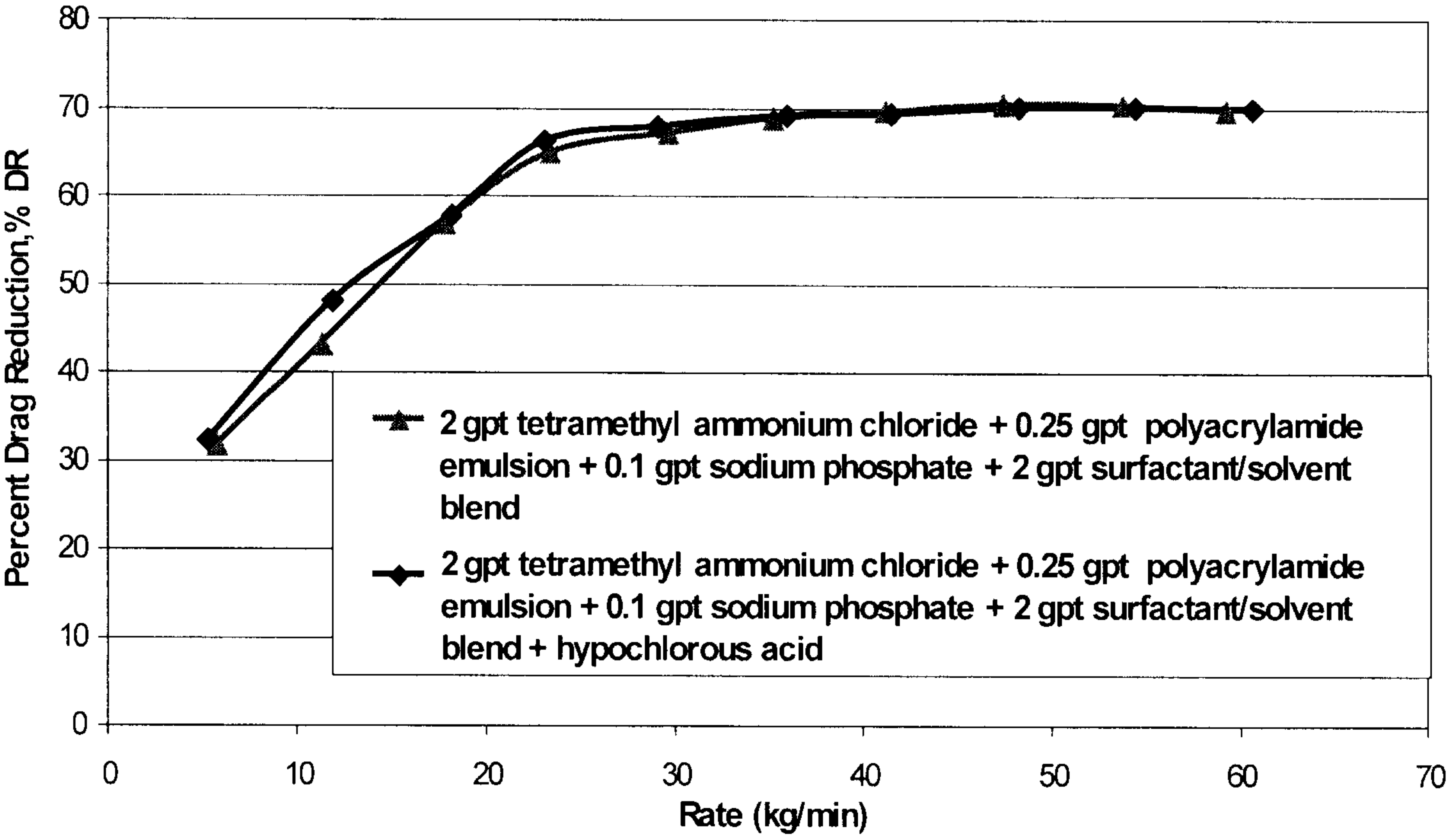

80
70
60
50
40
30
20
10
0
Percent Drag Reduction,% DR
0
10
20
30
40
50
60
70
Rate (kg/min)
2 gpt tetramethyl ammonium chloride + 0.25 gpt polyacrylamide emulsion + 0.1 gpt sodium phosphate + 2 gpt surfactant/solvent blend
2 gpt tetramethyl ammonium chloride + 0.25 gpt polyacrylamide emulsion + 0.1 gpt sodium phosphate + 2 gpt surfactant/solvent blend + hypochlorous acid

Figure 6

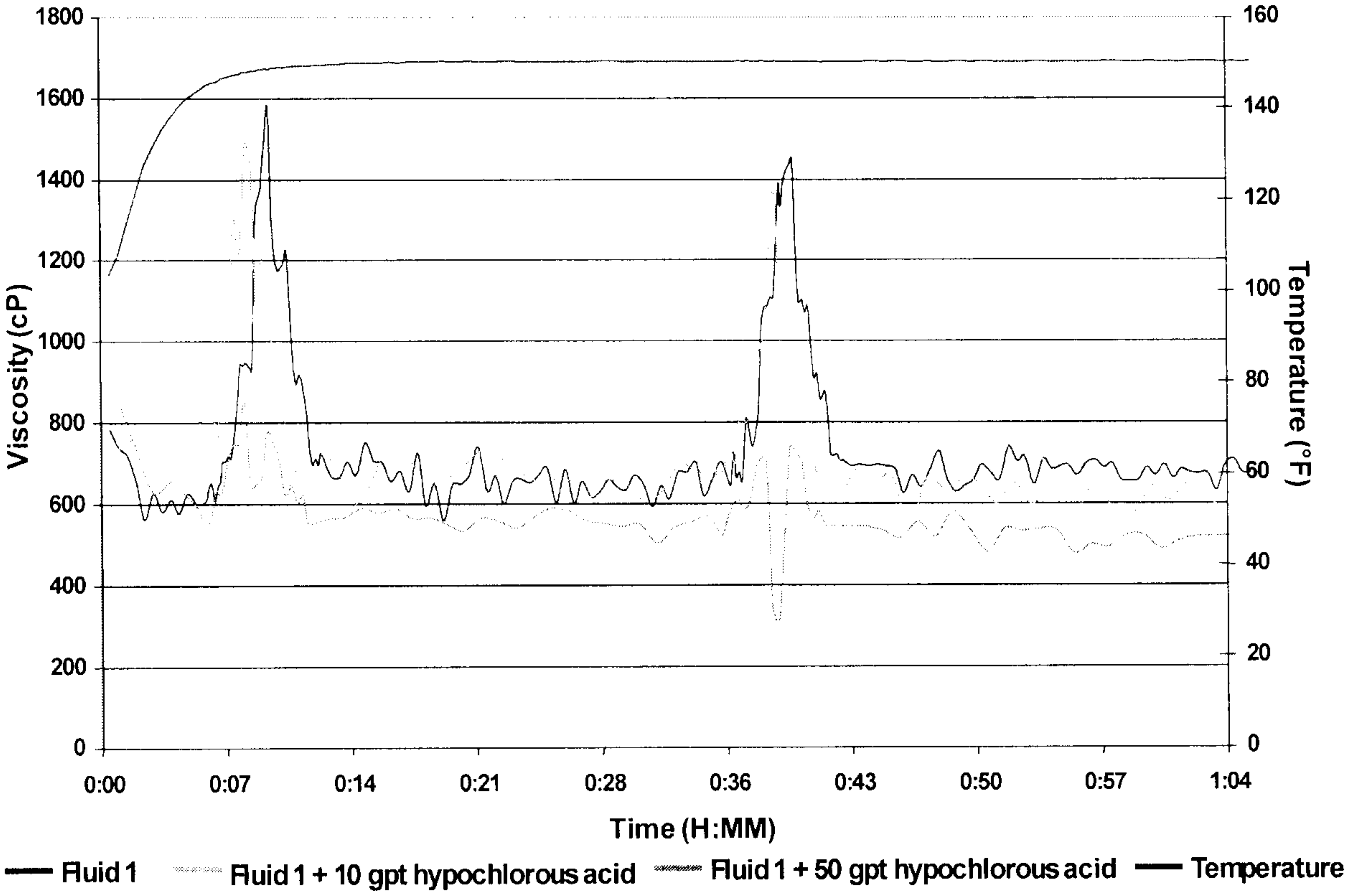

1800
1600
1400
1200
1000
800
600
400
200
0
Viscosity (cP)
160
140
120
100
80
60
40
20
0
Temperature (°F)
0:00
0:07
0:14
0:21
0:28
0:36
0:43
0:50
0:57
1:04
Time (H:MM)
Fluid 1
Fluid 1 + 10 gpt hypochlorous acid
Fluid 1 + 50 gpt hypochlorous acid
Temperature

Figure 7

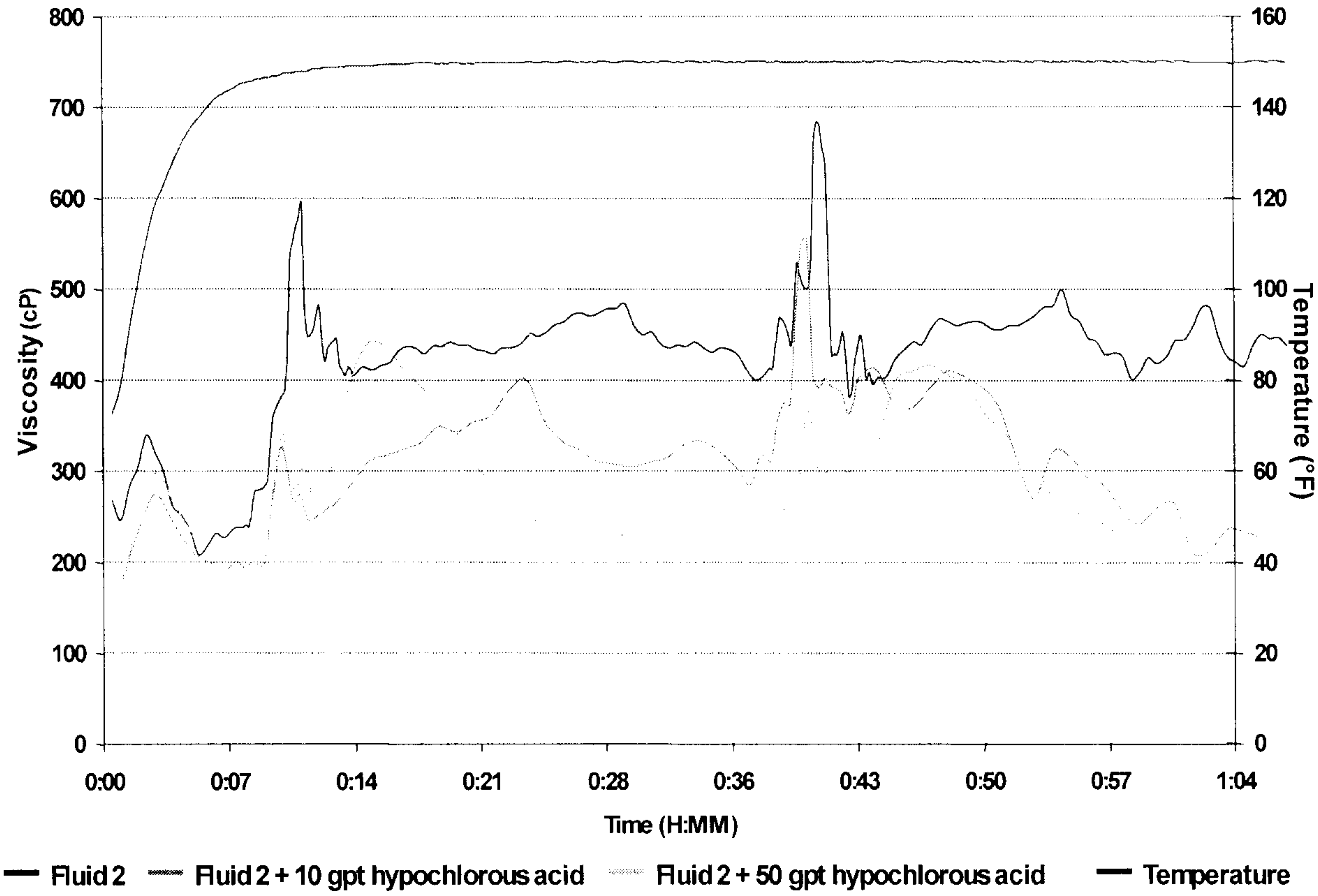
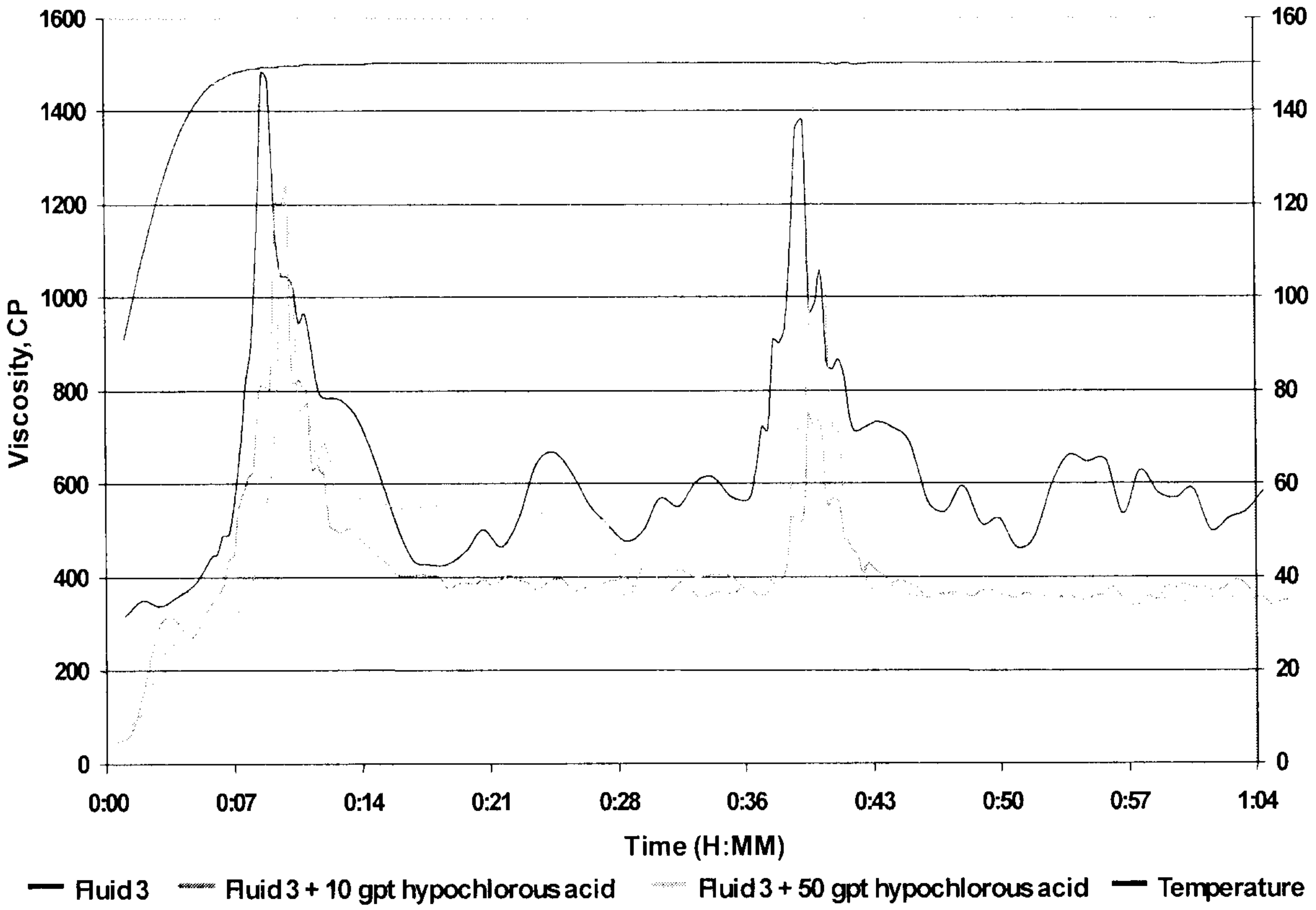

Viscosity (cP)
0
100
200
300
400
500
600
700
800
Temperature (°F)
0
20
40
60
80
100
120
140
160
Time (H:MM)
0:00
0:07
0:14
0:21
0:28
0:36
0:43
0:50
0:57
1:04
Fluid 2
Fluid 2 + 10 gpt hypochlorous acid
Fluid 2 + 50 gpt hypochlorous acid
Temperature

Figure 8


1600
1400
1200
1000
800
600
400
200
0
Viscosity, CP
160
140
120
100
80
60
40
20
0
Temperature (°F)
0:00
0:07
0:14
0:21
0:28
0:36
0:43
0:50
0:57
1:04
Time (H:MM)
Fluid 3
Fluid 3 + 10 gpt hypochlorous acid
Fluid 3 + 50 gpt hypochlorous acid
Temperature

Fluid 9

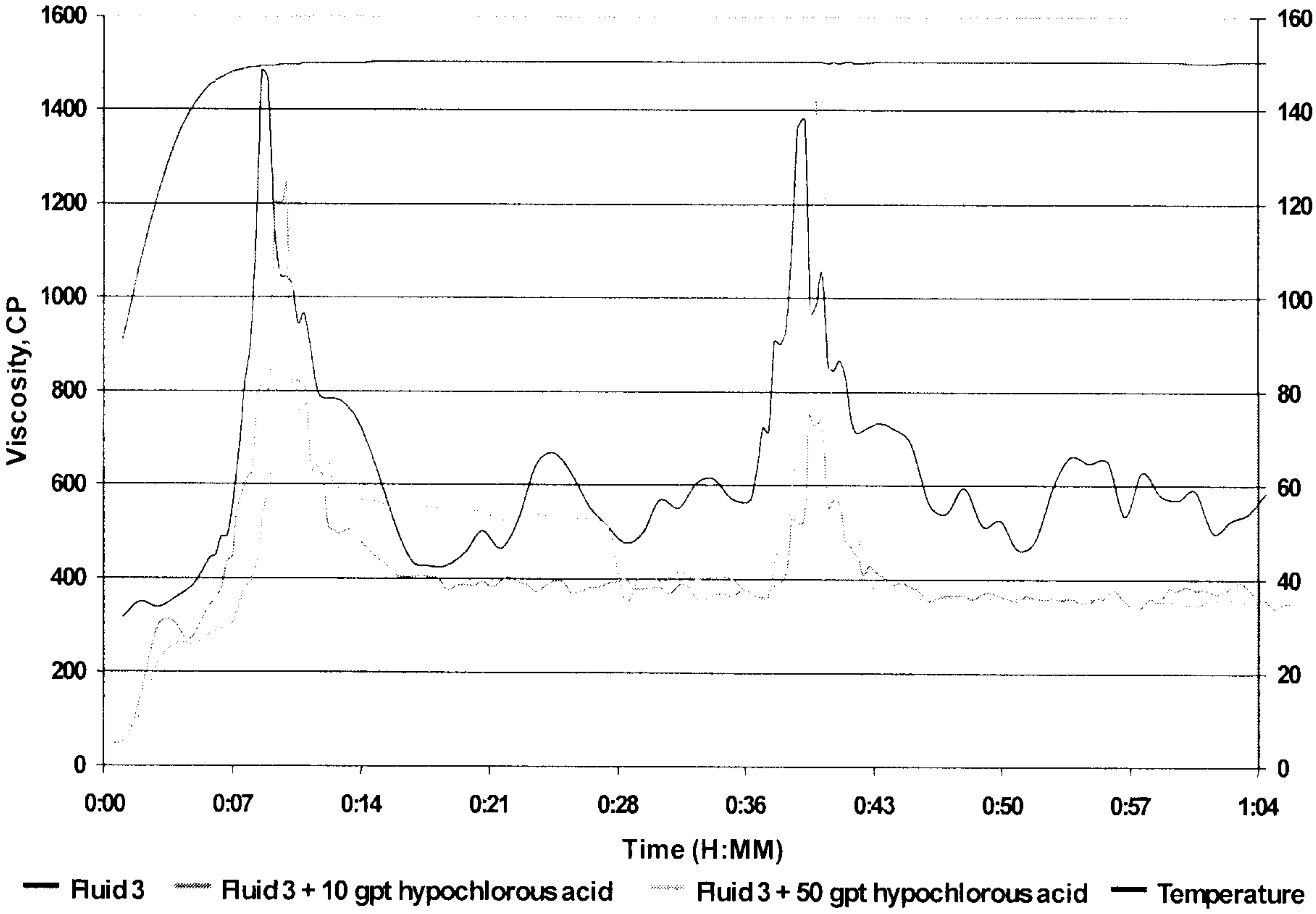

1600
1400
1200
1000
800
600
400
200
0
Viscosity, CP
160
140
120
100
80
60
40
20
0
Temperature (°F)
0:00
0:07
0:14
0:21
0:28
0:36
0:43
0:50
0:57
1:04
Time (H:MM)
Fluid 3
Fluid 3 + 10 gpt hypochlorous acid
Fluid 3 + 50 gpt hypochlorous acid
Temperature

Figure 10


80
70
60
50
40
30
20
10
0
Percent Drag Reduction,% DR
0
10
20
30
40
50
60
70
Rate (kg/min)
2 gpt tetramethyl ammonium chloride + 0.25 gpt polyacrylamide emulsion + 0.1 gpt sodium phosphate + 2 gpt surfactant/solvent blend
2 gpt tetramethyl ammonium chloride + 0.25 gpt polyacrylamide emulsion + 0.1 gpt sodium phosphate + 2 gpt surfactant/solvent blend + hypochlorous acid