A COMPARISON OF IRON CONTROL TECHNIQUES

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ABSTRACT

Matrix acidizing is often undertaken to improve the permeability of reservoir rock. When excessive quantities of ferric (Fe^{+++}) ions are taken into solution by matrix acidizing, iron deposition and permeability reductions can occur after acidization. Sources of iron include (1) iron oxides from tubular goods, (2) pipe scale and (3) iron in mineralogical form such as siderite, pyrrhotite, magnetite, hematite and pyrite. Preventing iron deposition in matrix acidizing is essential to a successful acid treatment.

This paper details a relatively new technique for controlling the precipitation of ferric compounds in matrix acidizing by incorporating a reducing agent/chelator blend. This new method is compared to three older techniques commonly used in iron control: buffering the pH, chelating, and a combination of buffering and chelating. Using standard wet chemical methods, the sequestering capabilities of the various iron control methods are evaluated at various values of pH and temperature. The effect of calcium ions on iron-sequestering capacity is also demonstrated in the paper.

INTRODUCTION

The acidizing of oil wells in the petroleum industry has been used as a viable method for increasing the permeability of tight formations and removal of plugging materials since the 1930's. Early patents demonstrated the growing interest in acidizing oil wells as a means of increasing their output. They discussed the use of organic and inorganic acid and mixtures of the two in acidizing operations. The technology used to acidize oil wells also produced new problems. Normally insoluble iron compounds can be dissolved by treating acids and then redeposited in the formation when the pH of the spent acid rises above 2. An answer to the problem was found in the addition of iron sequestering agents. Since the early days of acidizing, a number of iron control systems have been developed.

IRON DEPOSITION

Iron exists in 3 oxidation states (valences): +2, +3 and +6. The most common oxidation states are +2 and +3. Iron in the +2 (ferrous) state normally precipitates at a pH of about 7.0. Iron in the +3 (ferric) state, however, will precipitate at a pH of about 2.2. Because ferric compounds begin to precipitate at a pH range of 2 to 3, the damaging effects due to iron precipitation in spending acid under down-hole conditions are readily apparent. To demonstrate how ferric iron can precipitate under down-hole acidizing conditions, the following simplified chemical reactions are presented:

$$1)\quad Fe(OH)_3 + CaCO_3 + 5HCl \rightarrow CaCl_2 + FeCl_3 + CO_2 + 4H_2O \qquad (1)$$

or

$$Fe_2O_3 + CaCO_3 + 8HCl \rightarrow CaCl_2 + 2FeCl_3 + CO_2 + 4H_2O$$

$$pH\ 2 \Rightarrow 6$$

$$2)\quad FeCl_3 \dashrightarrow Fe(OH)_3 \dashrightarrow Fe_2O_3 \qquad (2)$$

The preceding chemical equations show how hydrochloric acid reacts with iron hydroxide and calcium carbonate to form ferric chloride and calcium chloride. The pH of the solution will increase as the hydrochloric acid is consumed. After the acid is "spent," the pH remains slightly acidic. At this point, the acid continues to consume calcium carbonate but the overall cleanout efficiency of the acid has been lowered. The last set of chemical formulas represent an evolution of ferric chloride to ferric oxide. The down hole temperature causes this reaction to take place more rapidly as a direct function of temperature increase.

Iron can come from three major sources in well acidizing. The first possible source is from tubular goods. Iron corrosion of tubular goods can take place both as long or short term corrosion due to injected acid, bacterial growth or trace amounts of oxygen, hydrogen sulfide, or other corrosion sources. The second is from iron based pipe scale. The third source is from the formation. The five most common mineral sources of iron located in oil bearing formations are (1) pyrite (FeS_2) (2) pyrrhotite (FeS) (3) siderite ($FeCO_3$) (4) magnetite (Fe_3O_4) and (5) hematite (Fe_2O_3). Practically all forms of iron found under down hole conditions are soluble in hydrochloric acid. The oxidation state of an ion is dependent on the oxidizing or reducing properties of the surrounding environment. In air, which is an oxidizing environment, ferric iron is predominate whereas in a reducing or anaerobic environment, ferrous iron is predominate. The use of oxidation potentials can illustrate that ferric iron occurring from rust dissolution is converted to ferrous iron in the presence of metallic iron from the tubing.

$$Fe^{o} + Fe^{+++} \xrightarrow[\text{(anaerobic reduction)}]{} Fe^{++} + e \qquad (3)$$

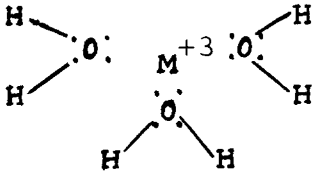
Thus, iron due to corrosion is not generally a problem because that iron is generally in the +2 (ferrous) state. Iron from the formation can be a problem if the mineral going into solution in acid is in the +3 (ferric) state. The iron containing mineral tends to stay in the +3 (ferric) state because there is no metallic iron to bring about a transition to the +2 state. Iron (+3) remaining in this state can cause potential depositional problems if the pH begins to rise. Fortunately, most producing formations do not contain large amounts of iron (+3) to cause major producing problems. These formations respond well to treatments containing iron-control additives. Occasionally, formations will have iron levels that exceed the solubility of the treating acid. Such situations are rare, however, and treatment with iron control agents is marginally effective. In such cases, the iron (+3) in solution is often 20,000 ppm or greater.

Several in depth experiments were developed by Smith[1] to study the ratio of iron +2 to +3 under down hole conditions. He determined the ratio to be approximately 5 parts ferrous iron (+2) to 1 part ferric iron (+3). This was studied both in the laboratory and in the field. This ratio may differ from well to well but can be predicted by core analysis and by monitoring the total iron in spent-acid returns. (Divide the total iron by 5 to determine the concentration of sequestrant to be added to the treating acid). The ratio of 5:1 is a good starting point to use when trying to determine the proper concentration of iron sequestrant to be added to a treatment fluid. This level of iron sequestrant offers to minimize the expense while keeping the ratio of iron sequestrant to calcium level low to prevent calcium by-product deposition.

CHELATION

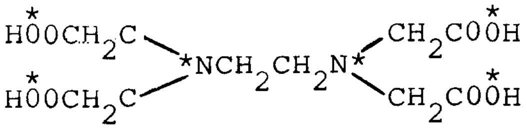
Chelation Chemistry

The term, "chelation" was derived from the Greek word <u>chele</u> meaning crab's claw. To better understand the chelation of iron, it is necessary to learn about the nature of metal ions and how they behave in solution. When iron-compounds are in solution, they exist as positively charged, free-moving ions. The positive charge of the metal ion surrounds itself with negatively charged ions or polar compounds present in the solution. The number of coordination sites (negative charges) may vary from complex to complex but is generally 2, 4 or 6. The negatively charged positions present in a metal complex are the centers of activity and are the portion of the molecule that tie up metal ions. In liquids, a metal ion is surrounded by a reactive layer formed by the aqueous solution.



(4)

When chelators are added with a stronger affinity for these active sites, the layer of aqueous molecules are displaced and the metal ion acquires a new set of properties.



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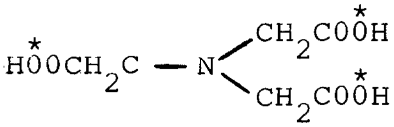
<u>Ethylenediaminetetraacetic acid (EDTA)</u>



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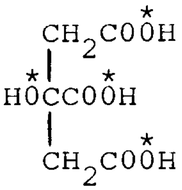
Nitrilotriacetic acid (NTA)



(7)

Citric acid

*Metal complexing sites.

Solubility

The solubility of a chelator is important in that it is the major factor that determines the maximum concentration of that chelator which can be put into solution at a given pH. Citric acid and its sodium salts are highly soluble, are not effected by pH, and will not precipitate in acids or in spent acid systems. The acid form of ethylenediaminetetraacetic acid (EDTA) is low in solubility below a pH of 3. The acid form of nitrilotriacetic acid (NTA) is relatively low in solubility below a pH of approximately 6. Because the chelating ability of the sodium salts of EDTA and NTA in an aqueous environment changes with pH and because the different salt forms have varying solubilities, the solubility figures for EDTA and NTA will vary with the pH. The solubilities of EDTA, NTA and their sodium salts versus pH are shown in Figure 1, which demonstrates that EDTA and its salts are low in solubility below a pH of 3, and that NTA and its salts have limited solubility in the pH range between 1 and 6. If the concentrations in Figure 1 are exceeded in a low pH range, precipitation of those complexing agents can be expected.

Stability Constant

Physical chemists can determine the tendency for a chelating agent to complex with a particular metal by use of the Stability Constant. The Stability Constant is derived through the following equilibrium equations using molar concentrations:

$$\text{M} + \text{Chelator} \rightleftharpoons \text{M Chelator}$$

$$\frac{\text{M Chelator}}{(\text{M})\quad(\text{Chelator})} = \text{K} = \text{Stability Constant} \qquad (8)$$

To obtain numbers that are easily used, the constant K is usually expressed as its logarithm. In the above equation, the constant K is expressed as the ratio of chelated metal ion to free metal ion, thus the larger the value of K, the more stable is the chelating agent. Referring to Figure 2, it is evident that the ferric ion forms a stable complex with EDTA, NTA, and citric acid. Figures 3 and 4 show the conditional stability constants for EDTA and NTA. The conditional stability constant (KM'L' (ML')) tends to take into account the effects of the OH^- and H^+ radicals on the metal ion, metal chelate and the chelator. This equation proves to be a better expression of the stability of a metal complex rather than the traditional stability constant. The conditional stability constant is defined as the following:

$$KM'L' \quad (ML)' = \frac{[(ML)']}{[M'] \, [L']} \qquad (9)$$

$[M']$ equals the total metal in solution that is not chelated.
$[L']$ equals the total unchelated chelator in solution.
$[(ML)']$ equals the total complexed metal in solution.

Both Figures 3 and 4 demonstrate that the ferric ion forms a very stable complex with EDTA and NTA over a wide pH range. The use of stability constants illustrates that other ions in solution such as calcium, magnesium, barium or strontium have little or no effect on the stable ferric ion complex of EDTA, NTA and citric acid. The log K constants are representative of a series whereby the ions with lower values are displaced by ions with higher values. The ferric ion does, however, tend to form insoluble metal hydroxides when the pH rises. The solubility of the ferric ion will then markedly decrease:

$$Fe^{+++} + 3 \ OH^- \rightarrow Fe(OH)_3 \qquad (10)$$

Although the ferric ion is chelated at a lower pH, the competition between chelator and hydroxide ion is reduced at the lower pH's, however, when the pH rises, the ferric ion reaches a point where the chelating agent can no longer keep the ferric ion in solution. At a higher pH level, the hydroxide ion preferentially binds with the iron and the ferric ion precipitates. EDTA, NTA and Citric Acid all chelate ferric ions on a mole to mole ratio. NTA is the only chelator of the 3 that can form a 2 to 1 chelator to ferric ion complex. The molar ratio is important when selecting a chelator, for if all else is equal, then the complexing agent with the lowest molecular weight would be the most cost effective. The greater the temperature, the lower is the stability constant, however the stability of a chelating agent is not usually affected to any great degree until the temperature is in excess of 400^oF.

The Effect Due to pH

Next to the stability constant, the pH of a system is the single most important factor that influences the metal/chelator equilibrium. Most metal complexes are stable over a wide pH range and can withstand a considerable pH drop. Other factors can cause metal or complex precipitation by pH such as solubility of the chelator, metal hydroxide formation, etc.

Effects Due to Other Ions in Solution

EDTA and NTA are not generally effected by salt formation (calcium, barium or strontium), however, citric acid can form insoluble salts when an excess of chelator to ferric ion is used in the presence of calcium, barium, or strontium ions, which could cause possible formation damage. High concentrations of anions generally have little effect on metal chelators with the exception of sulfide, which tend to form metal sulfides that are extremely insoluble. Thus, chelators are less effective as metal-complexing agents when sulfide ions are present as a general rule.

Buffers and Buffer/Chelator Combinations

The addition of buffering agents to slow the reaction rate of inorganic acids on carbonaceous rocks was patented by Esso Production in 1966. The patent states that low molecular weight organic acids slow the reaction rates of inorganic acid thereby allowing a greater time for the acid to penetrate the formation. Many organic acids such as formic acid, acetic acid, hydroacetic acid, and chloroacetic acid have been used, but generally, acetic acid is the accepted buffering agent today. Acetic acid buffers (Figure 9B) at a pH of 2 to 4 which is in the range where ferric hydroxide begins to precipitate. Acetic acid is primarily used to slow the reaction of hydrochloric acid on carbonaceous rocks and secondly, as a buffering agent. Acetic acid is a poor chelator of iron and will chelate iron only at low temperatures (100°F and below). Because of this, chelating agents are generally added to sequester iron above 100°F. The most commonly used chelator is citric acid (Figure 10A,B). Citric acid and acetic acid are very effective at temperatures below 125°F, above this temperature the effectiveness of the combination drops off sharply.

REDUCING AGENTS AND REDUCING AGENTS/CHELATOR COMBINATIONS

The use of reducing agents is a relatively new concept. The idea is to reduce any ferric ions to ferrous ions. This is done in an attempt to hold more iron in solution. Most organic reducing agents will also chelate iron. Figure 13A shows that reducing agents chelate iron well at higher temperatures. The amount of iron in solution drops in the first few hours at elevated temperatures but is redissolved by the reduction of iron +3 to iron +2. It is easy to understand that the higher the temperature, the faster this reaction takes place. A problem with using reducing agents is that they can be expensive. The blending of chelating agents with reducing agents can make their use more cost effective. Figure 14A shows that a blend is not as effective as a reducing agent alone, in an absolute sense, but well above the level of iron held in solution by EDTA, NTA, citric acid, acetic acid and citric acid/acetic acid combinations. Reducing agents by themselves scavenge oxygen and can be used solely as oxygen scavengers. One of the major drawback to reducing agents are their ability to reduce other chemicals. They should not be used with oxidizing agents. Most stimulation chemicals such as acid inhibitors, surfactants, etc. are not effected. Hydrochloric acid generally will not affect the reducing ability of organic reducers. They are effected more by chemicals that can be reduced (oxidizers, iron, etc.) to a lower oxidation state.

EXPERIMENTATION

The following experiment was designed to compare the various iron control techniques under, as close as possible, the conditions encountered during the acidizing of an oil well.

Procedure

The stability of 7 systems at 3 different temperatures (75°F, 125°F, 200°F) in the presence of an excess of limestone chips was determined as follows:

A 100 milliliter sample of 15% HCl, 1000 ppm (parts per million) ferric iron, and 1000 ppm chelating agent was placed in a 600 (tall) milliliter beaker. The experiment was performed using units of parts per million to better compare each chelator one on one with the ferric iron. A large excess (50 grams) of limestone chips was introduced, then each beaker was placed into either a 75, 125 or 200°F water bath depending on the test. Watch glasses were placed on top of each beaker to prevent evaporation during the test. Loss due to vigorous CO_2 evolution resulting from HCl reacting with the limestone chips was not a problem.

Samples of each solution were taken at 1 hour intervals for a period of 4 hours at which time the test was terminated. Each sample was filtered and diluted. The samples were then analyzed for iron content using an Instrumentation Labs Inductively Coupled Plasma Spectrophotometer.

Acetic acid was tested at a concentration of 10,000 ppm because of its primary use as a buffer rather than a chelator of iron. This amount is equal to 10 gallons per 1000 gallons of solution, a commonly used concentration in the acidizing of oil wells.

A blank was tested to compare the other seven systems to a system with no iron control present.

Conclusion

In summary, this comparison of iron control techniques lead us to the following conclusions:

A. Iron deposition during the acidizing of oil wells is the result of insoluble ferric hydroxide formed as the pH rises. Iron is solubilized during the acidizing process primarily from iron in mineral form. It is the deposition of this iron that the addition of iron sequestrants are needed to prevent.

B. All the iron control methods tested prevented the deposition of iron. Each system had advantages and disadvantages.

Ethylenediaminetetracetic Acid (EDTA)

1. Doesn't form insoluble calcium salts.

2. Forms stable complexes with iron compounds and is not affected by other metal ions in solution.

3. Effective at temperatures up to 200°F.

4. The acid form is not soluble at a low pH. The sodium salts tend to decrease in solubility at lower pH's.

5. On a mole to mole basis, EDTA tends to be more expensive than the other chelators tested.

Nitrilotriacetic Acid (NTA)

1. Doesn't form insoluble calcium salts.

2. Forms stable complexes with iron compounds, and is not affected by other metal ions in solution.

3. Effective at temperatures up to 200°F.

4. All forms tend to have low solubility at low pH's.

5. Can form di-complex with iron, thereby needing double the amount to complex iron in solution.

6. NTA is less expensive than EDTA but more expensive than citric acid.

Citric Acid

1. When sufficient quantities are used, citric acid is effective at temperatures up to 200°F.

2. If quantities are used above those needed to chelate the iron present in solution, precipitation as the calcium citrate salt can occur.

3. Citric acid is more cost effective than EDTA and NTA.

Acetic Acid

1. Will not precipitate as calcium acetate.

2. Soluble over wide pH range.

3. Effective only to about 80°F.

Citric Acid/Acetic Acid Mixtures

1. Very effective at temperatures below 150°F.

2. At temperatures up to 200°F this system is only as efficient as the concentration of the citric acid in the system.

3. If quantities are used above those needed to chelate the iron present in solution, precipitation as the calcium citrate salt will occur.

Reducing Agents

1. Effective at temperatures up to 200°F.
2. More effective at higher temperatures - the higher the temperature the faster Iron 3 is reduced to Iron 2.
3. More effective at lower concentrations - tends to keep iron in solution longer because of the reducing properties present in reducing agents.
4. Tends to reduce chemicals that can be reduced.
5. More expensive than traditional chelators but is less expensive on an iron maintained in solution basis.

Reducing Agent/Chelator Blends

1. Effective at temperatures up to 200°F.
2. More effective at higher temperatures - the higher the temperature the faster Iron 3 is reduced to Iron 2.
3. More effective at lower concentrations - tends to keep iron in solution longer because of the reducing properties present in reducing agents.
4. Tends to reduce chemicals that can be reduced.
5. Slightly more expensive than traditional chelating agents but less expensive than organic reducing agents.

C. Many physical factors should be considered when selecting an iron control additive such as bottom hole temperature, acid spending time, forms of iron present, and concentration of the iron in the formation. The choice of an iron control additive should take into account current chemical technology to determine the best system for the specific conditions existing down hole.

D. Iron control additive should be used in moderation and should only be used when needed. If used freely, iron control additives can cause potential damage to the formation.

ACKNOWLEDGMENTS

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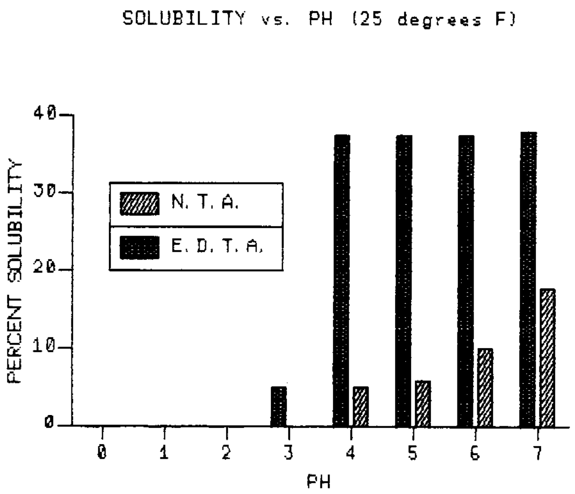

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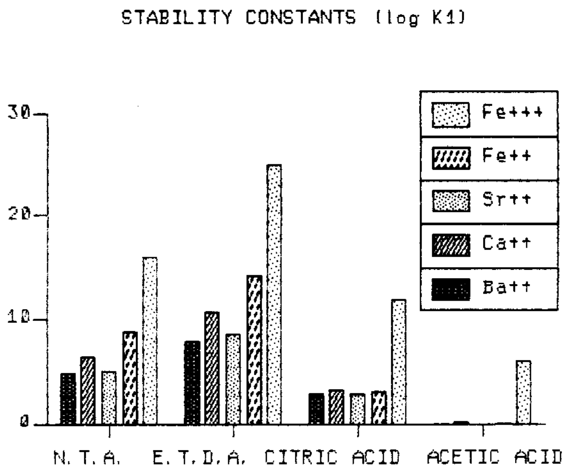

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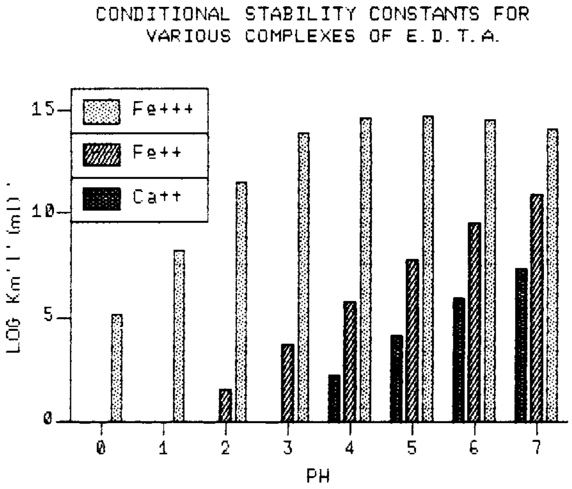

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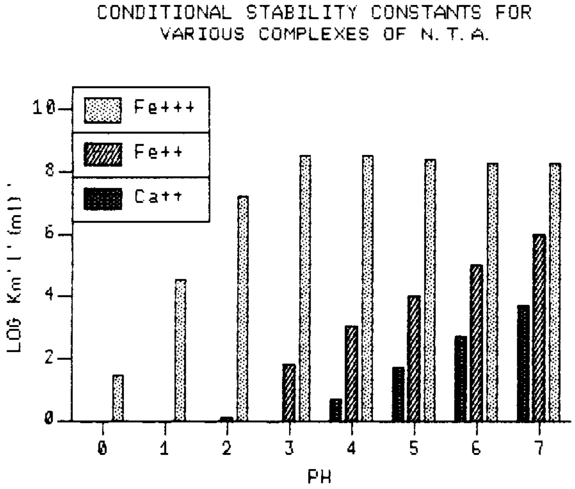

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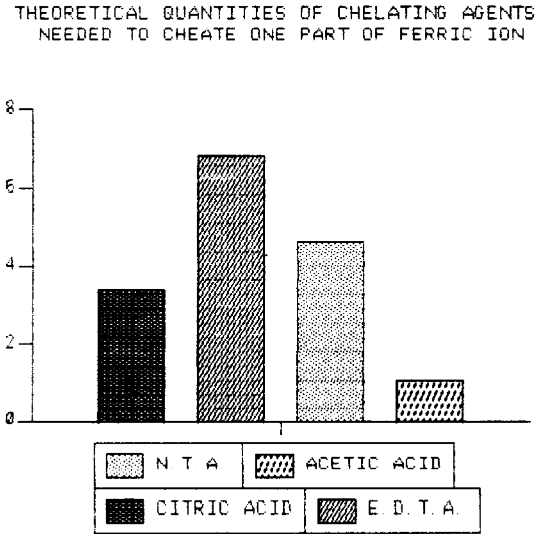

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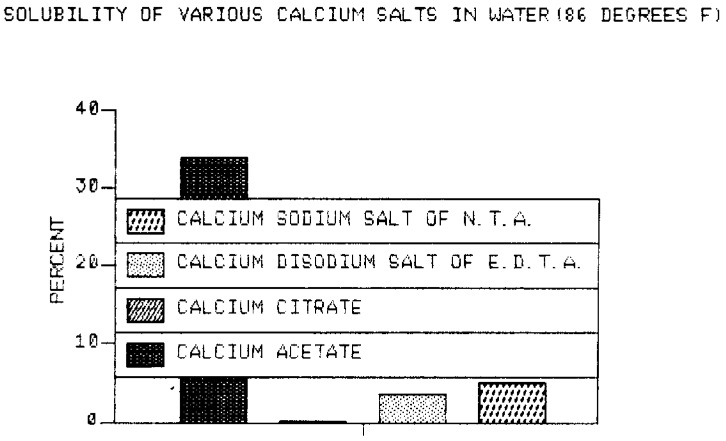

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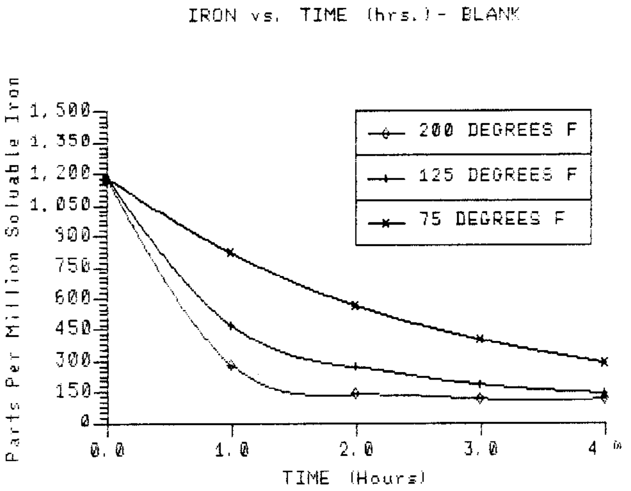
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Figure 7A

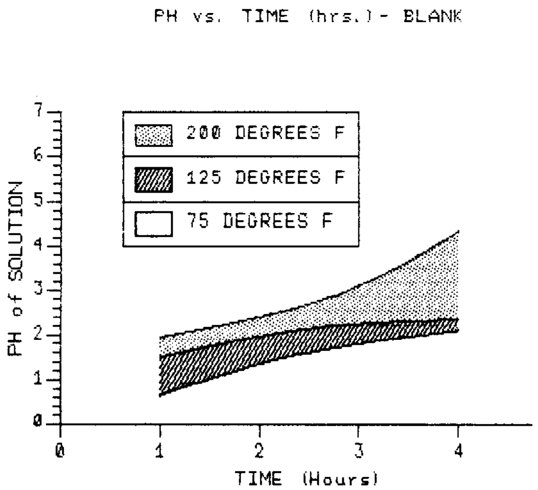
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Figure 7B

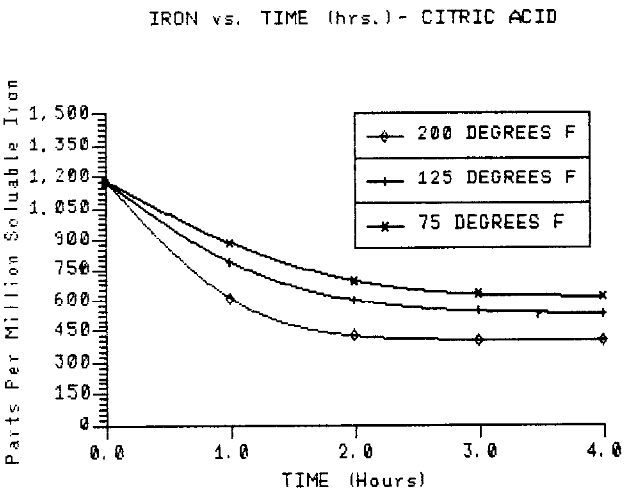
IRON vs. TIME (hrs.) - CITRIC ACID

Figure 8A

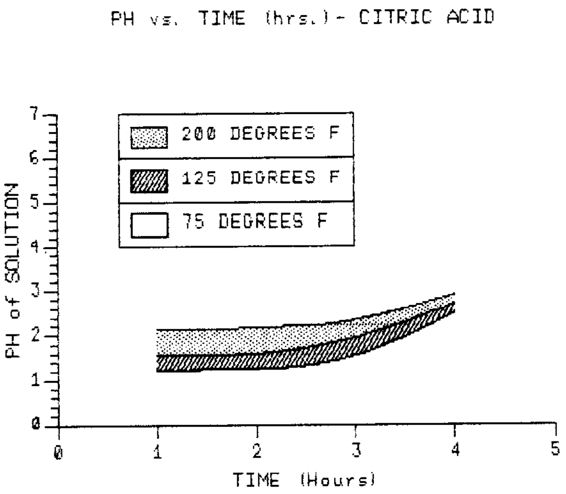
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Figure 8B

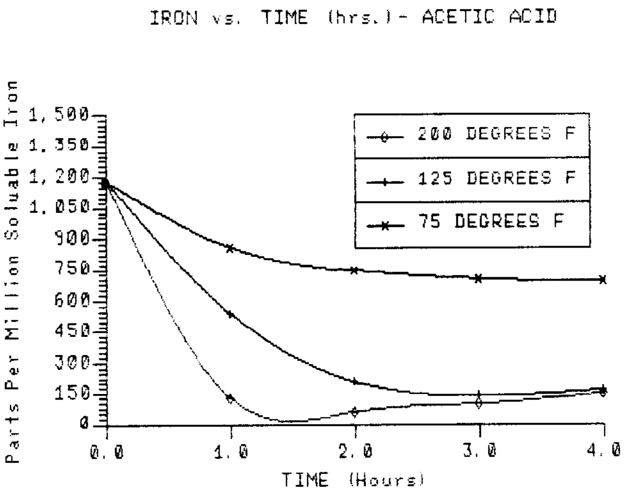
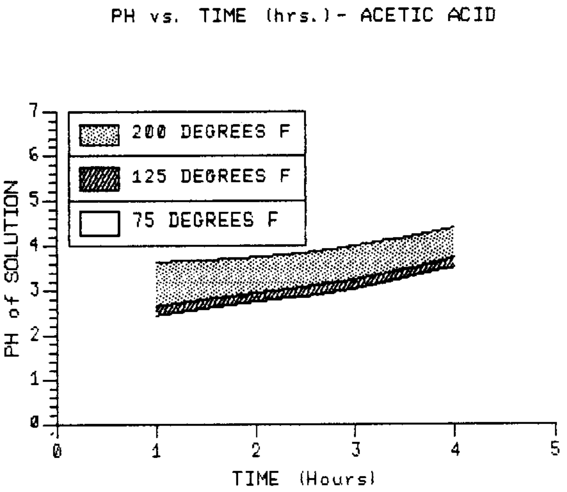

IRON vs. TIME (hrs.) - ACETIC ACID

Figure 9A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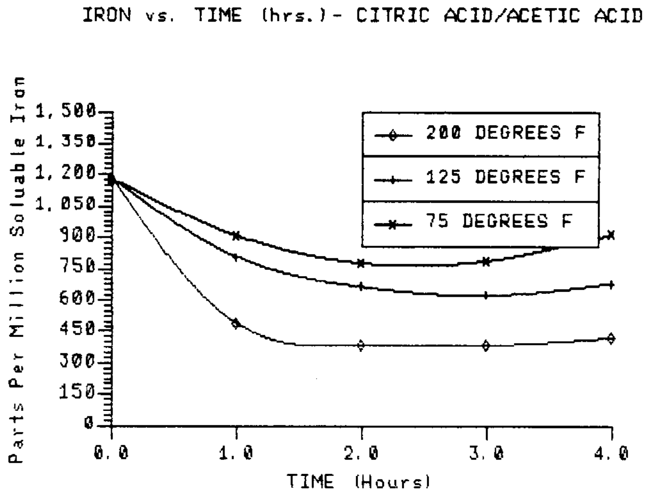

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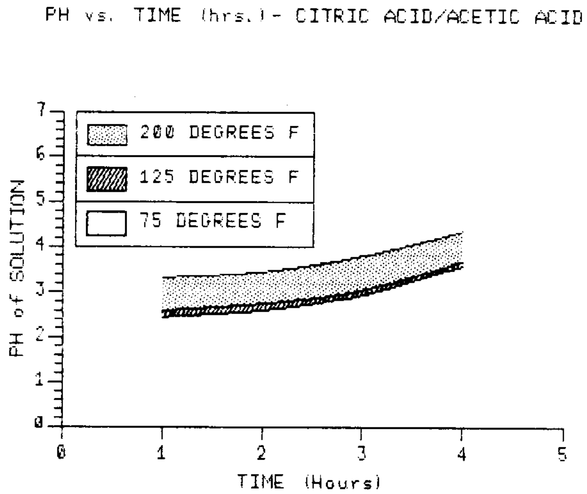

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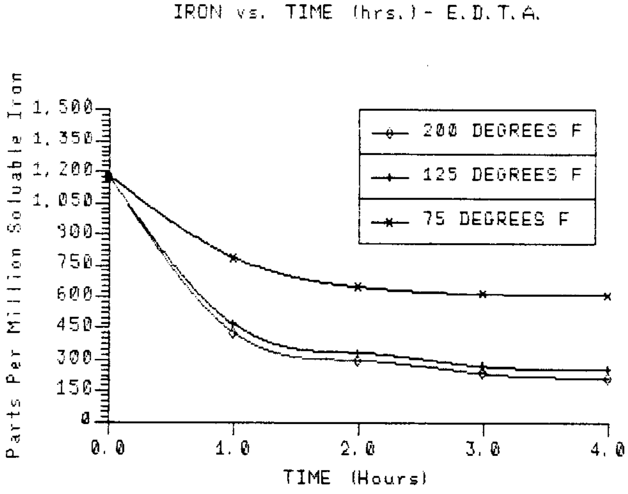

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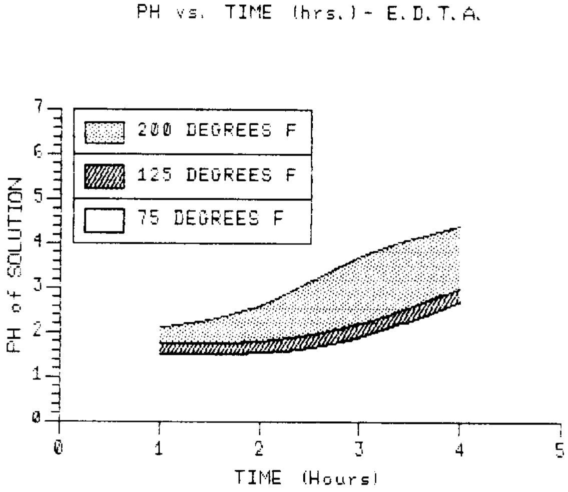

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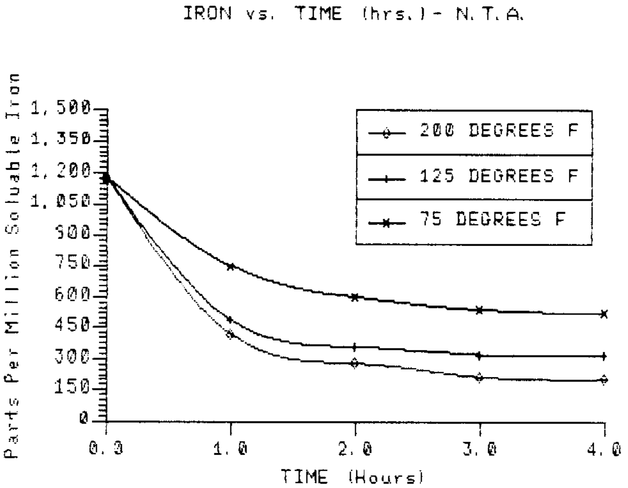

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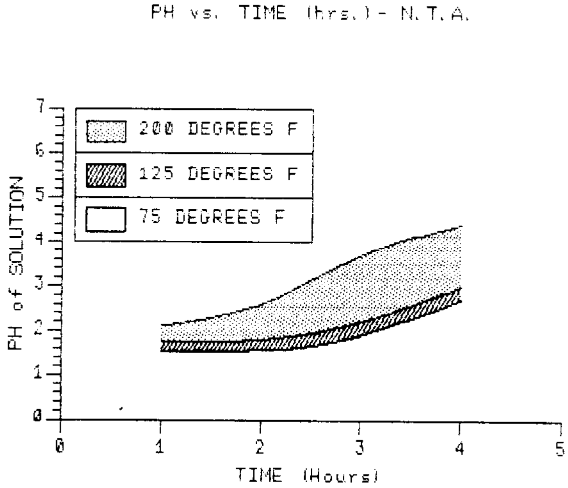

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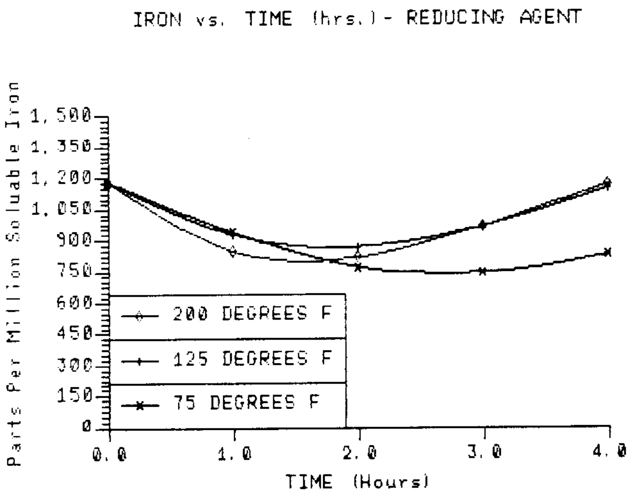

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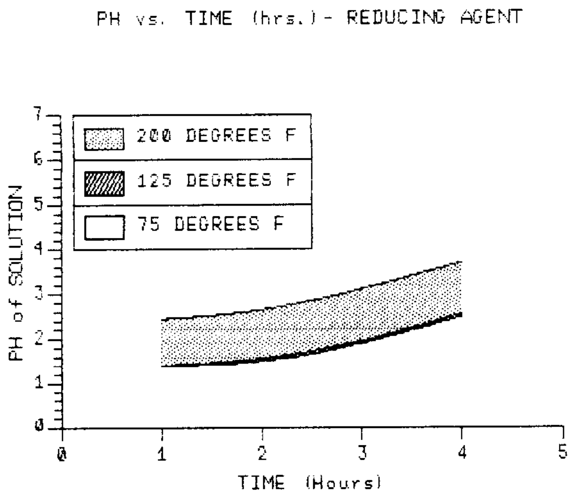

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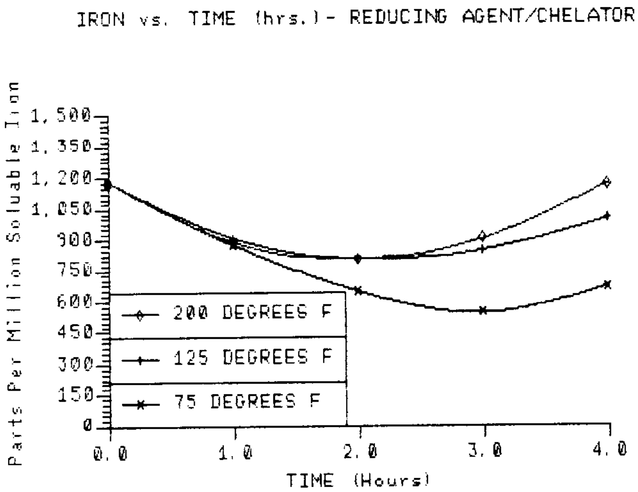

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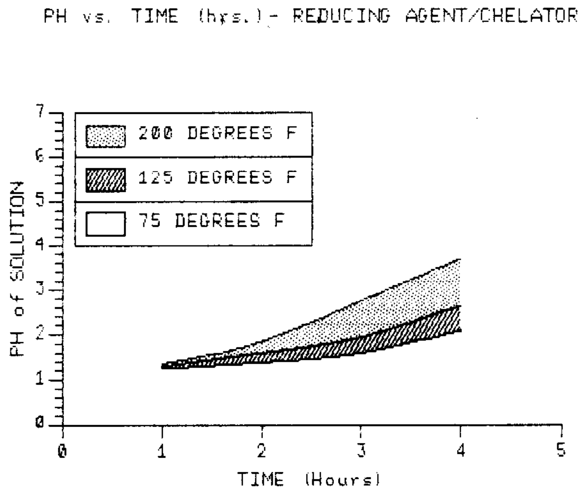

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