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# Environmentally Friendly Filtercake Removal System

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## Abstract

Chelating agents are chemicals that have been widely used in the oil and gas industry to control undesirable effects of metal ions. Chelate-based fluids have been successfully implemented in numerous well stimulations to control iron precipitation during acidizing and as filter-cake breaker fluids in a variety of formations.

A family of novel biodegradable polyacidic chelate-based (NPC) breaker fluid systems has been developed for treating oil and gas wells in a wide temperature range and in environmentally sensitive locations. The enhanced filter-cake breaker systems were engineered with a target of achieving improved biodegradation, reduced toxicity and a smaller environmental footprint while offering less corrosion potential than conventional treatment with hydrochloric acid (HCl). Maintaining a high reaction rate with di-valent metal ions is critical for efficient filtercake removal. The new products can provide significant improvements in the range and scope of applicability relative to what is available in the industry.

Laboratory effort focused on solubility of the products in various densities and valencies of the carrier fluids, carbonate dissolution rates, and corrosion potential prevention. The new breaker fluid systems have been fully investigated for their performance and characteristics in dissolution of filtercakes in the laboratory, establishing basic guideline to minimize operational challenges in terms of corrosion, usage volumes, fluid preparation, and conformance to discharge regulations in various environmentally-sensitive locations.

The technology represents a combination of many of the traditionally advantageous properties of the chelates with the effect of the unique chemical environment.

## Introduction

Conventionally, filter-cake cleanup solutions are achieved by utilizing acids, chelating agents, oxidizers, enzyme treatments, or combinations of these materials. Acid-based systems may be challenging to control in a downhole environment: it is difficult to treat entire interval due to rapid acid reaction that generates wormholes. For filter-cake breakers systems the main challenge becomes how to slow the reaction rate so as to cover the entire interval and remove all of the filter cake present. An additional challenge is to simulate downhole conditions in the laboratory for proper breaker system engineering.

Other difficulties associated with treating open-hole sections with acid-based filter-cake systems include the following:

- Some clay minerals are sensitive to low pH and the introduction of a low pH fluid may damage the formation.
- Corrosion problems are extremely aggravated at elevated temperatures.
- Meanwhile, at lower temperatures (i.e., 150°F or below), acid-based breaker systems are not believed to be effective at breaking polymers and implementing these systems is both time-consuming and costly in low temperature ranges.
- Separate breaking systems (i.e., acids and enzymes) are used to break the cake and the polymers (Ewing 1983).
- Recently, the industry has also had issues using breaker materials for effective calcium carbonate removal with minimal environmental impact.

As an alternative to acid-based systems, chelating agents such as EDTA, HEDTA, DTPA, and NTA have been used, but for these chelating agents, the common issue is environmental and safety concerns. While considered safe, EDTA and HEDTA are not readily biodegradable. On the other hand, while NTA is readily biodegradable, it is potentially hazardous to humans and therefore creates handling and environmental discharge concerns (Rainey 2003). Other chelants such as NPC have been identified as readily biodegradable, but are more limited in their ability to dissolve calcium carbonate and control iron. Some of the chelating agents also have solubility problems in certain brines. Laboratory studies of chelate solubility in brine are detailed in the Solubility Study section.

Metal chelating materials have been used as iron control agents in acidizing treatments for many years. There are several disadvantages associated with use of the various commercially available products, including low solubility and high toxicity. These complexes serve as models for the in-depth evaluation of various chelating agents over a broad range of temperatures and fluid compositions and have been characterized with respect to solubility and thermal stability in spent acid fluids. The experimental results show loss of solubility of calcium complexes as well as thermal decomposition of ferrous complexes at relatively low temperatures. Implications of these results will be discussed below. The problems are exacerbated in sour environments where iron sulfide precipitation occurs at a very low pH (Brezinski 1999).

Commonly filter-cake residue is removed by displacing the open hole section with a clean up fluid (often referred to as a breaker fluid) that attacks the filtercake. In some situations, such as wells with gravel packed completions or other types of screen/slotted liners, ensuring that the treatment effectively contacts the filtercake on the wellbore face can present challenges. For example, in the case of completions in unconsolidated formations, where it is often desirable to gravel pack an interval but before the filtercake is completely removed, because gravel pack may limit contact of the breaker fluid with a filtercake. Another challenge is facing the industry to design a delay in reaction breaker solution in order to dissolve the filtercake uniformly from entire interval. When degrading a filtercake with a breaker fluid, the breaker fluid may not have completely covered the entire interval of exposed formation, causing premature flowing of production fluids or the loss of breaker fluids into the formation from one portion of the interval before another portion has even been exposed to breaker fluid.

Optimizing the breaker fluid concentration, determining the appropriate carrying fluid, and addressing environmental and corrosion concerns were targets in laboratory investigation.

## Materials

Technical grade calcium carbonate powder was obtained from Excalibar Minerals, Houston, Texas. Sodium bromide and sodium chloride brines were obtained from Albemarle, Baton Rouge, Louisiana. Potassium formate was purchased from Cabot, The Woodlands, Texas. Soltrol 170 having a 0.79 g/mL density was obtained from Chempoint, Bellevue, Washington. All the chelate reagents including tetra ammonium and tetra sodium salts of ethylenediaminetetracetic (EDTA), NPC, and EGTA were obtained from AkzoNobel, Chicago, Illinois. The sodium salts of iminodisuccinat and polyaspartic acids were obtained from Lanxess, Pittsburg, Pennsylvania. Berea Sandstone was used as received from Cleveland Quarries, Cleveland, Ohio. The 35-micron aloxide disks were purchased from Fann Instruments, Houston Texas. Acid precursors were used as received from Esther Chem Ltd, Leebrook, Staffordshire. Mild carbon steel corrosion coupons were obtained from Fann Instruments, Houston, Texas. An in-house built manual return permeameter was used for the return permeability tests.

## Experimental Methods

Testing the miscibility of the breaker systems was performed by adding a known volume percent of the test breaker (5%, 10%, or 20%) to the volume of the test brine needed to total 100 ml in a 4-oz jar. The jars were then sealed and swirled to mix the components. Observation of the compatibility of the components was noted, and then the jars were placed in a static oven at 150°F for 16 hours. Thereafter, another observation was again made of the miscibility of the components and the pH of each mixture was measured.

Calcite-dissolving capacity of the breaker systems was determined by drying a known amount of the technical grade calcium carbonate in an oven for 2 hours. A 2.5-g portion of the carbonate was stirred into a 50-mL solution of the test fluid and allowed to stand for one hour and subsequently filtered with a 1-micron fiber glass filter paper. The residue was dried for an hour and the percent of the dissolved carbonate was calculated by difference in weight between the starting material and what remained on the filter paper.

The corrosion effect of the filter-cake breakers was evaluated by completely immersing a mild carbon steel corrosion test coupon in the test solutions at the required temperature. Duplicate coupons were used in each test in different jars. The coupon was placed in a glass vessel so that the coupons were in a vertical position and the test fluid was then added. All tests were run at a volume-to-surface area ratio of about 20 ml/square inch. After seven days the coupons were removed from the oven, cleaned and dried. The corrosion rate was then determined by weight loss and calculated as mm/year.

The drill-in fluids were made in-house as needed by mixing required additives and polymers in addition to bridging materials in a blender for 60 minutes. The fluids were rolled in the oven at 150°F for 16 hours. The fluids were removed from the oven, cooled and remixed for 10 minutes. The fluids were used to make the filtercake by filtering for 2 hours through the aloxide disks at 500psid and the required temperature. To remove the filtercake, the cell was opened after cooling and the remaining drill-in fluid was carefully poured out and replaced with breaker systems of known volume percent in the appropriate brine.

For the return permeability test, the following procedure was used with the required breaker fluid solution and drill-in fluid:

1. A 1-in. diameter core plug was cut out of a low-permeability Berea Sandstone block (about 20% porosity).
2. The core plug was inserted into the containment sleeve of the manual return permeameter (MRP). The pressure chamber was sealed and the temperature maintained at approximately 110°F, while maintaining confining pressure at 2,500 psi. Once the temperature and overburden pressure stabilized, the Soltrol 170, filtered to 0.45 micron, was produced through the core at 4 ml/min against approximately 200 psi back-pressure.
3. After establishing constant permeability with flow of the Soltrol 170, the flow was stopped.
4. The initial and final permeability values were calculated using Darcy's Law for linear flow:

$$K = \frac{(Q\ \mu\ L)\ (14700)}{(60\ \Delta p\ A)}$$

*Where:*

K = permeability in mD
Q = flow rate, cc/min
M = viscosity of the fluid @ 100°F = 1 cP

L = length of core plug, cm
14700 = conversion factor (atm to psi and darcy to millidarcy)
60 = conversion factor from cc/min to cc/sec
$\Delta P$ = pressure drop, psi
A = cross sectional area of core plug, $cm^2$

5. The damage phase involved three separate steps: 1) introducing a drill-in fluid into the core cell, thereby displacing the Soltrol 170; 2) filtering the drill-in fluid through the core at 500psid for two hours to deposit the filtercake while collecting the filtrate; and 3) displacing the drill-in fluid from the test lines and chamber by pumping Soltrol 170 at 10 ml/min for 15 min.
6. Once the displacement of the drill-in fluid was complete, the production of Soltrol 170 was resumed until a constant permeability was obtained by applying the same procedure used for the initial permeability.
7. The flow was consequently stopped and a breaker fluid solution was introduced by the same method used for the drill-in fluid to place the fluid in the core chamber. Flow of the breaker fluid was allowed to pass through the core and then stopped after one pore volume of the fluid was collected. The system was left to soak in the breaker fluid for 16 hours at the test temperature.

## Results and Discussions

**Biodegradation.** Unlike cleanup materials containing mineral acids, the non-acidic nature of chelating systems helps lower the safety risk to personnel and the environment, and helps avoid corroding downhole hardware, including screens, packers, and tubulars. However, some chelating agents, particularly EDTA and DTPA, may not be safe from an environmental standpoint. Biodegradation is specifically important in determining the extent of environmental impact and investigation of the biodegradation of chelating agents could be challenging due to complexity of downhole conditions and interactions with formation fluids. The most commonly used EDTA-type chelating agent could be degraded by chemical/photochemical methods.

The target of investigation was to identify a biodegradable and environmentally friendly filter-cake breaker miscible in multivalent brine carrier fluids. The best candidate from the chelating family based on eco-toxicological test data was NPC (**Table 1**). In addition NPC is highly soluble in carrier fluids with a wide range of pH and densities. **Fig. 1** represents the biodegradation ratio in percent over standard 28-day biodegradation test. Over 80% of the NPC was degraded. The biodegradability of the NPC will comply with most worldwide environmental regulations.

**Calcium Carbonate Dissolution Study. Table 2** shows the results of the carbonate dissolving capacity and miscibility studies of various chelating agents and mineral acids on a 2.5g sample of calcium carbonate in fresh water. As expected, most of the chelates and the mineral acid were miscible with fresh water and displayed different reactivity with the carbonate that is in relation with their individual dissociation constants. The dissolving capacity of NPC is lower than the dissolving capacity of EDTA and dilute mineral acid, but the slower dissolution of carbonate by the NPC breaker fluid observed in the laboratory could be an advantage over the mineral acids in situations where delayed filter-cake dissolution is desired in the field. The miscibility and carbonate dissolution tests were also performed using 20% of the NPC in different brines. **Table 3** shows that 80 to 90% of the dissolving capacity of the mineral acid was achieved with NPC breaker fluid solution without cloudiness, separation, or precipitation of the salt from the brines.

A 20% NPC breaker in various concentration of sodium bromide was used to evaluate the effect of the brine concentration on the dissolving capacity of NPC at 150°F for 16 hours. It was expected that reducing the amount of available free water in the brine would reduce the rate of dissociation of the acid functionalities on the breaker, which would reduce the amount of complexed calcium ion. **Fig. 2** shows that the NPC breaker fluid dissolved more than 80% carbonate at low concentration and a little less than 45% at high concentration of the brine.

**Solubility Study.** The use of most available filter-cake breakers like the acid precursors with the formate brines has become a concern in the oil and gas industry due to incompatibility and solubility with formates. Therefore, a miscibility test of NPC with formate brines was evaluated and compared to other available alternative breaker fluids. **Table 4** shows that chelating agents NPC and EDTA are totally soluble in all concentrations of the non-buffered potassium formate brine while the solubility of the acid precursor decreased with increased concentration of the brine.

Moreover, various chelating agents were tested for solubility in wide pH range and test results are illustrated in the **Fig. 3**. NPC demonstrated greater solubility in acidic and alkaline environment when compared to NTA and EDTA chelating agents. The pH observed for the NPC fluids can be attributed to the higher pKb values relative to the EDTA. Solution pH of the acid precursor test fluids reduced more in the lower formate concentrations with more available free water due to hydrolysis at 150°F. The mineral acid was not soluble in the brines, but did disperse evenly in them. After static testing at 150°F, there was still a haze to the fluids and some slight separation at the top of the fluid level. In the 13.0 lb/gal brine, there were crystals formed on the bottom of the jars.

The American Electrochemical Society defines corrosion as the “destruction of the metals by chemical or electrochemical reaction with its environment.” The destruction of the metals by corrosion occurs by:

1. direct chemical attack at elevated temperatures and in a dry environment, and
2. electrochemical process at lower temperatures in water-wet or moist environment.

Corrosion occurs because metals tend to revert to a more stable form in which they were found in nature initially, i.e., oxides, sulfates, sulfides, or carbonates. Inasmuch as the corrosion mechanism is the same for all metals and alloys, differing only in degree, it is useful to examine the corrosion effects on the metal the fluid it will come in contact with in downhole conditions (Bertness 1989). As described above, breaker fluids were previously tested to optimize a break-through time, calcium carbonate dissolution, and brine solubility. The next investigation step was corrosion potential.

The corrosion rate was measured by percent weight loss. The reacted (buffered) fluids in general have a low corrosion rate. However, when the breaker was not buffered, the corrosion could be severe. This could create a damaging situation downhole if the breaker did not contact a sufficient amount of carbonate filter cake to fully react. Extreme cases of corrosion in non-buffered fluids were tested on standard corrosion coupons at 10% and 20% concentration levels of the breaker fluids in 11.0 lb/gal NaBr, and static at 105°F and 150°F. The results of the tests are shown in **Tables 5 and 6** indicating that NPC is less corrosive than the alternative acid precursor breaker at both concentration levels and temperatures tested.

Also, the increase in the corrosion rate is reduced with an increase in concentration of the breaker and temperature in comparison to the acid precursor breaker. **Fig. 4** shows the photograph of the standard corrosion coupons in 10% of the NPC in sodium bromide at 105 and 150°F.

The formulation of the drill-in fluid used for filter-cake deposition is shown in **Table 7**. The yield point value was 25 lb/100 $ft^2$ and 8mL of total filtrate was collected at 150°F under 500psid for 30 minutes, which is typical of a good drill-in fluid that forms a filtercake of acceptable integrity. As mentioned in the experimental section, dissolution of filtercake by the NPC is determined after the cake has been deposited on 35-micron aloxide disk for 2 hours. Then a 20% breaker solution is introduced into the cell after removing the drill-in fluid.

**Fig. 5** shows the state of the filtercakes on the disk after soaking in the breaker fluid for 16 hours at 150°F. It is obvious that the cake integrity has been compromised by the dissolution of the calcium carbonate in the cake by the breaker, making it possible for the fluid in the cell to flow through the disk. In comparison to the alternative, the acid precursor, the NPC was able to remove about the same amount of the filtercake from the disk but the removal in the case of NPC is spread out more than the removal of the by the acid precursor, which is indicative of achieving uniform filtercake removal and less wormhole effect by using a NPC breaker fluid compared to the acid precursor breaker.

To simulate the performance of the breaker solution in the downhole applications, a 20% NPC in 11.0 lb/gal sodium bromide was used in a multiple step return permeability test using a manual return permeameter on a low permeability Berea sandstone core plug (see experimental section for details of the return permeability test method). **Fig. 6** illustrates the initial permeability obtained from the core plug before and after damaging the core as well as after treatment with the breaker fluid and restarting the flow of the Soltrol 170 at a constant flow rate of 4 mL/min. The permeability returned to 86% of the initial value after damaging with the drill-in fluid. Thereafter, the breaker was pumped through the core plug at a slow rate of 2 mL/min, 200 psi, and collected one pore volume of fluid before stopping the flow. The return permeability after the breaker cleanup for 16 hours is calculated to be 94% of the initial permeability.

## Conclusions

3. A novel polyacidic chelate (NPC) has been shown to have excellent solubility and can be used in various field applications as a single breaker component or in combination with alternative breakers.
4. The solubility of several organic acid precursors in formate brines can be challenging and NPC was shown to be the best candidate in terms of solubility, clean-up efficiency, and environmental impact.
5. NPC has excellent biodegradation values and toxicity characteristics, which makes it an excellent candidate for breaker fluid solutions in environmentally-sensitive locations.
6. Due to low corrosion potential, NPC is an excellent solution for breaker fluids when long break-through time is required for specific operational needs.

## References

1. Use 9 pt New Times Roman font for references. Press Tab, followed by reference number, then Tab again, and then type reference info. This will make the references indented properly.
2. Farmer, P., Miller, D., Pieprzak, R., J., and Woods, R.: “Exploring the Subsalt.” Oilfield Review v. 8, No.1, (Spring 1996) 50 – 64.
3. Dunn, M.D., Crane, L.R. and Thomas, R.L.: “North Slope Drilling Practices – Ever Adapting to New Challenges.” AADE-05-NTCE-07, AADE National Technical Conference, Houston, April 5-7, 2005.
4. Alotabi M.B. “An Optimized Method to Remove Filter Cake Formed by Formate Based Drill-in Fluid in Extended Reach Wells.” Paper SPE 109754 presented at the Asia Pacific Oil and Gas Conference and Exhibition, Jakarta, Indonesia, 30 October-1 November, 2007.
5. Brezinski M.M. “Chelating Agents in Sour Well Acidizing: Methodology or Mythology” Paper SPE 54721-MS presented at the European Formation Damage Conference, The Hague, Netherlands, 31 May-1 June 1999,
6. Bertness, T. “Corrosion in Drilling and Production Operations.” In Developments in Petroleum Science, Volume 19, Part 2, ed. G.V. Chilingarian, J.O. Robertson, Jr. and S. Kumar, Chap. 8, 238-317. Amsterdam: Elsevier Science Publishers,1989.
7. Ewing, B. A Synergistic Chelation System for Acidizing in the Presence of High Iron Concentrations. Paper SPE 11795 presented at the SPE Oilfield and Geothermal Chemistry Symposium, Denver, Colorado, 1-3 June, 1983.
8. Frenier, W. “Acidizing Fluids Used to Stimulate High Temperature a Wells Can be Inhibited with Organic Chemicals.” Paper SPE 18468 presented at the SPE International Symposium on Oilfield Chemistry, Houston, Texas, 8-10 February 1989.
9. Rainey M. “A Biodegradable Chelating Agent is Developed for Stimulation of Oil and Gas Formations.” Paper SPE 80597 presented at the SPE / EPA / DOE Exploration and Production Environmental Conference, San Antonio, Texas, 10-12 March 2003.

## Tables

### TABLE 1. SUMMARY OF ECO-TOXICOLOGICAL TEST ON NPC

| Biodegradability Test | Result | Date |
|---|---|---|
| NPC in the Closed Bottle test (OECD 301 D) | Readily biodegradable; 76% at day 28 | 08/05/07 |
| Closed Bottle Test with NPC | Readily biodegradable; >60% at day 14 | 10/18/07 |
| The active toxicity of NPC to Rainbow trout (Oncorhynchus mykiss;OECD 203) | 96-h LC50>100mg/l;96-h NOEC≥100mg/l | 08/02/94 |
| The active toxicity of NPC to Daphnia magna (OECD 202) | 48-h EC50>100mg/l; 48-h NOEC≥100mg/l | 02/13/95 |
| NPC: Algal inhibition test (OECD 201) | 72-h EC50>100mg/l; 72-h NOEC≥100mg/l | 08/29/95 |

### TABLE 2. MISCIBILITY AND COMPLEXATION EVALUATION OF 10% V/V BREAKER IN FRESH WATER WITH 2.5g OF BARACARB 5 (STATIC AT 150°F FOR 16 HOURS).

| Material | pH | Miscibility with Fresh Water | Final weight of BARACARB 5 | % Carbonate complexed or dissolved |
|---|---|---|---|---|
| EDTA ammonium salt | 4.77 | miscible, no phase separation | 1.54 | 38.4 |
| EDTA Sodium salt | >12 | miscible, no phase separation | 1.62 | 35.2 |
| Polyaspartic acid, sodium salt | 10.1 | miscible, no phase separation | 2.41 | 3.6 |
| Iminodisuccinate, sodium salt | 11.3 | miscible, no phase separation | 2.37 | 5.2 |
| **NPC** | **>12** | **miscible, no phase separation** | **1.72** | **29.6** |
| Mineral Acid | 0.88 | miscible, no phase separation | 1.62 | 35.2 |
| EGTA | 11 | miscible, no phase separation | 2.32 | 9.28 |

### TABLE 3. MISCIBILITY AND COMPLEXATION EVALUATION OF 20% V/V BREAKER IN 10.2lb/gal KCl/NaBr BRINE AND 12.5lb/gal NaBr BRINE WITH 2.5g of BARACARB 5 (STATIC AT 150°F FOR 16 HOURS).

| | Material | Miscibility | Final weight of BARACARB 5 | % Complexed or dissolved |
|---|---|---|---|---|
| 10.2lb/gal KCl/NaBr | NPC | clear, no precipitate | 1.27 | 49 |
| | Mineral acid | Cloudy, no phase separation, no Precipitate | 1.12 | 55 |
| 12.5lb/gal NaBr | NPC | clear, no precipitate | 1.78 | 29 |
| | Mineral Acid | Cloudy, no phase separation, no precipitate | 1.61 | 36 |

## TABLE 4. MISCIBILITY OF VARIOUS BREAKER FLUIS SYSTEMS WITH DIFFERENT CONCENTRATIONS OF POTASSIUM FORMATE BRINE

| Additive | pH | | Initial Observation | After Static Aging |
|---|---|---|---|---|
| | Initial | Final* | | |
| **Fluid Density 11.0 lb/gal** | | | | |
| Blank | 11.9 | 11.7 | Clear | Clear |
| Acid Precursor- 5% | -- | 6.2 | Not miscible, floats on top | Clear, miscible |
| Acid Precursor- 10% | -- | 5.6 | Not miscible, floats on top | Clear, miscible |
| N-FLOW 325- 20% | -- | 5.1 | Not miscible, floats on top | Clear, not all miscible |
| EDTA Salt- 5% | -- | 9.6 | Clear, totally soluble | Clear, totally soluble † |
| EDTA Salt-10% | -- | 8.6 | Clear, totally soluble | Clear, totally soluble † |
| EDTA Salt-20% | -- | 7.0 | Clear, totally soluble | Clear, totally soluble † |
| NPC-5% | -- | 12.7 | Clear, totally soluble | Clear, totally soluble |
| NPC-10% | -- | 13.3 | Clear, totally soluble | Clear, totally soluble |
| NPC-20% | -- | 13.7 | Clear, totally soluble | Clear, totally soluble |
| Syn. Acid 5% | -- | 9.9 | Cloudy, dispersible but not soluble | Slight haze |
| Syn. Acid 10% | -- | 7.0 | Cloudy, dispersible but not soluble | Slight haze, slight insoluble |
| Syn. Acid 20% | -- | 6.0 | Cloudy, dispersible but not soluble | Slight haze, slight insoluble |
| **Fluid Density 12.0lb/gal** | | | | |
| Blank | 12.7 | 12.4 | Clear | Clear |
| Acid Precursor- 5% | -- | ** | Not miscible, floats on top | Not totally miscible, some floats |
| Acid Precursor- 10% | -- | ** | Not miscible, floats on top | Not totally miscible, some floats |
| Acid Precursor- 20% | -- | ** | Not miscible, floats on top | Not totally miscible, some floats |
| EDTA Salt- 5% | -- | 10.8 | Clear, totally soluble | Clear, totally soluble † |
| EDTA Salt-10% | -- | 9.8 | Clear, totally soluble | Clear, totally soluble † |
| EDTA Salt-20% | -- | 8.0 | Clear, totally soluble | Clear, totally soluble † |
| NPC-5% | -- | 13.3 | Clear, totally soluble | Clear, totally soluble |
| NPC-10% | -- | 14.4 | Clear, totally soluble | Clear, totally soluble |
| NPC-20% | -- | 14.7 | Clear, totally soluble | Clear, totally soluble |
| Syn. Acid 5% | -- | 11.4 | Clear, totally soluble | Very slight separation |
| Syn. Acid 10% | -- | 9.4 | Cloudy, dispersible but not soluble | Slight separation around top |
| Syn. Acid 20% | -- | 7.0 | Cloudy, dispersible but not soluble | Slight separation around top |
| **Fluid Density 13.0lb/gal** | | | | |
| Blank | 13.6 | 13.5 | Clear | Clear |
| Acid Precursor- 5% | -- | 12.7 | Not miscible, floats on top | Not miscible, floats on top |
| Acid Precursor- 10% | -- | 12.1 | Not miscible, floats on top | Not miscible, floats on top |
| Acid Precursor- 20% | -- | 12.0 | Not miscible, floats on top | Not miscible, floats on top, yellowed |
| EDTA Salt- 5% | -- | 11.4 | Clear, totally soluble | Clear, totally soluble † |
| EDTA Salt-10% | -- | 10.7 | Clear, totally soluble | Clear, totally soluble † |
| EDTA Salt-15% | -- | 9.9 | Clear, totally soluble | Clear, totally soluble † |
| NPC-5% | -- | 13.8 | Clear, totally soluble | Clear, totally soluble |
| NPC-10% | -- | 15.0 | Clear, totally soluble | Clear, totally soluble |
| NPC-20% | -- | 15.4 | Clear, totally soluble | Clear, totally soluble |
| Syn. Acid 5% | -- | 12.2 | Cloudy, dispersible but not soluble | Hazy |
| Syn. Acid 10% | -- | 11.0 | Cloudy, dispersible but not soluble | Hazy, slight separation at top, a few crystals on bottom |
| Syn. Acid 20% | -- | 7.5 | Cloudy, dispersible but not soluble | Hazy, slight separation at top, a lot of crystals on bottom |

### TABLE 5. CORROSION TEST OF 10% NPC AND ACID PRECURSOR IN 11lb/gal NaBr ON STANDARD CORROSION COUPONS AFTER 7 DAYS

| Test Temp. °F | Product | Average Initial wt, g | Average Final wt, g | Corrosion Rate, mm/yr |
|---|---|---|---|---|
| 150 | NPC | 24.4851 | 24.1828 | 19.1 |
| | Acid Precursor | 21.2267 | 21.1064 | 23.6 |
| | | | | |
| 105 | NPC | 21.3860 | 21.0267 | 7.6 |
| | Acid Precursor | 21.4309 | 21.27 | 10.2 |

### TABLE 6. CORROSION TEST OF 20% NPC AND ACID PRECURSOR IN 11lb/gal NaBr ON STANDARD CORROSION COUPONS AFTER 7 DAYS

| Test Temp. °F | Product | Average Initial wt, g | Average Final wt, g | Corrosion Rate, mm/yr |
|---|---|---|---|---|
| 150 | NPC | 24.4496 | 24.1078 | 21.6 |
| | Acid Precursor | 21.6267 | 20.8529 | 48.9 |
| | | | | |
| 105 | NPC | 21.3714 | 21.1941 | 11.2 |
| | Acid Precursor | 21.4309 | 21.1270 | 19.2 |

### TABLE 7. FORMULATIONS FOR WBM 9.4 lb/gal DRILL-IN FLUID

| Fluid | Unit | 1.00 |
|---|---|---|
| **Products& Units** | | |
| Density | lb/gal | 9.40 |
| Water | bbl | 0.83 |
| NaCl | ppb | 96.40 |
| Defoamer | ppb | 0.01 |
| Viscosifier | ppb | 0.75 |
| NaOH | ppb | 0.50 |
| Starch | ppb | 8.00 |
| Calcium Carbonate | ppb | 40.00 |
| Sodium Sulfite | ppb | 0.50 |
| Hot-rolled at 150 °F | hr | 16.00 |
| Remixed on a Multi-mixer | min | 10.00 |
| Plastic viscosity | cP | 16.00 |
| Yield point | 100 lb/ft2 | 25.00 |
| 10 Sec gel | 100 lb/ft2 | 5.00 |
| 10 Min gel | 100 lb/ft2 | 11.00 |
| API Fluid Loss, cc/30 min | mL/min | 7.00 |

## Figures

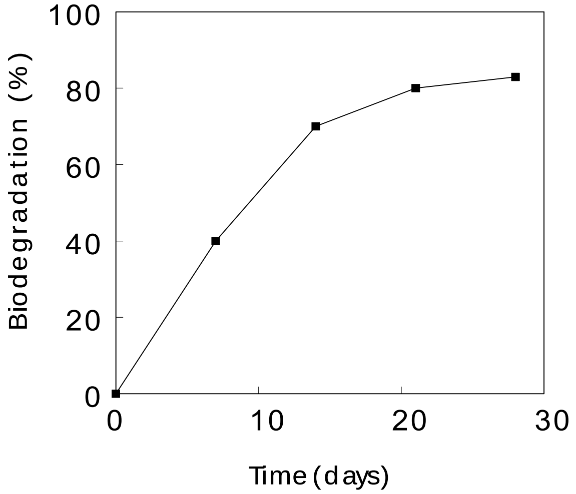

Fig. 1—NPC Biodegradation Chart.

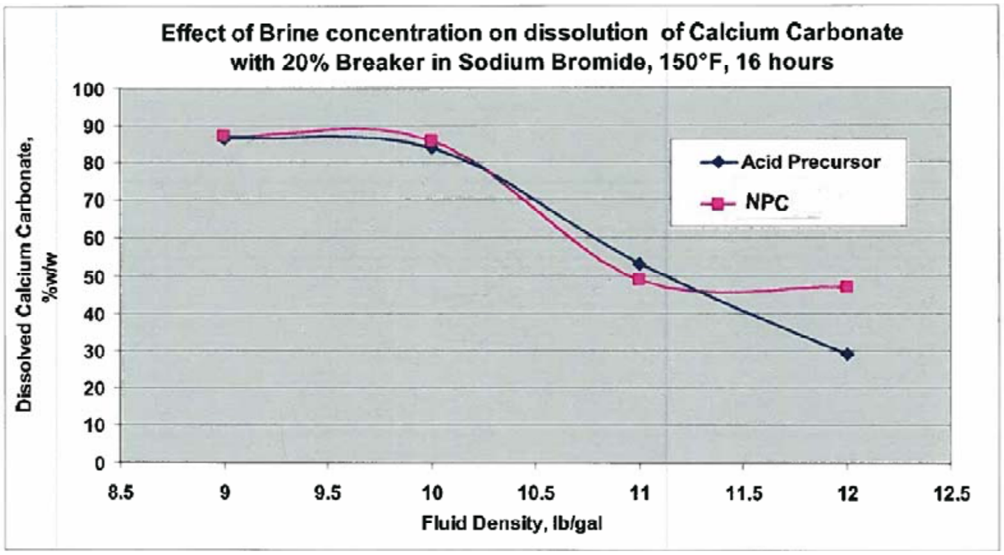

Fig. 2—Effect of Salt Concentration on Dissolution of Calcium Carbonate with 20 % Breaker in Sodium Bromide, 150˚ F, 16 hours.

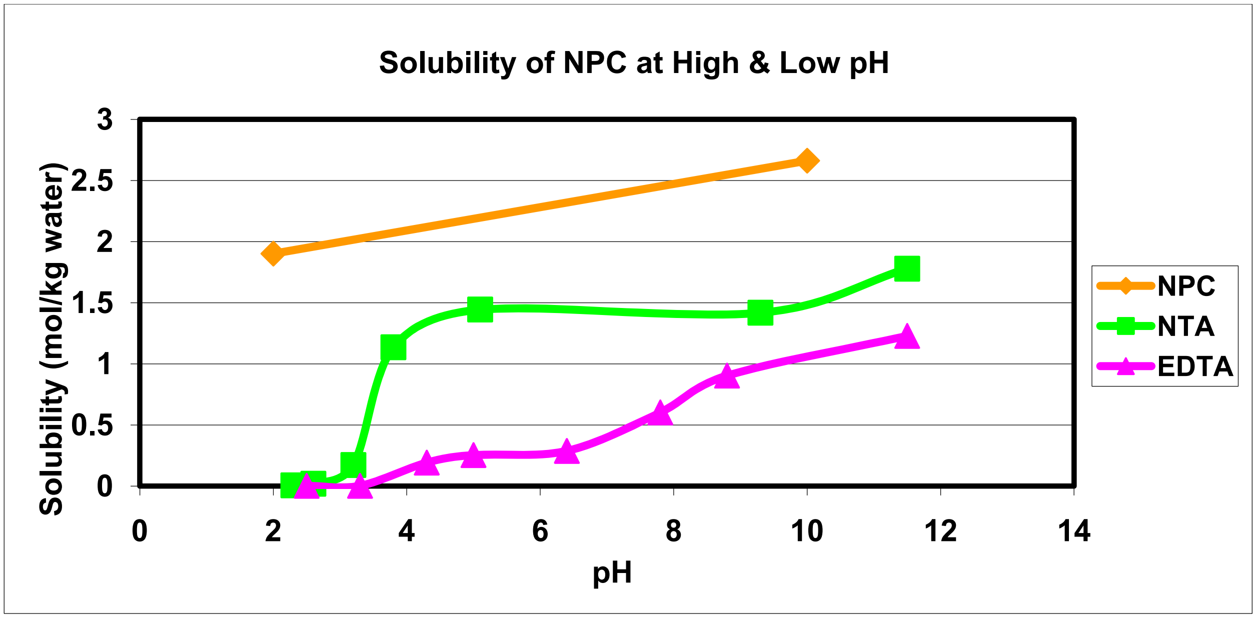

Fig. 3 Solubility Study of the Chelating Agents in Wide pH Range

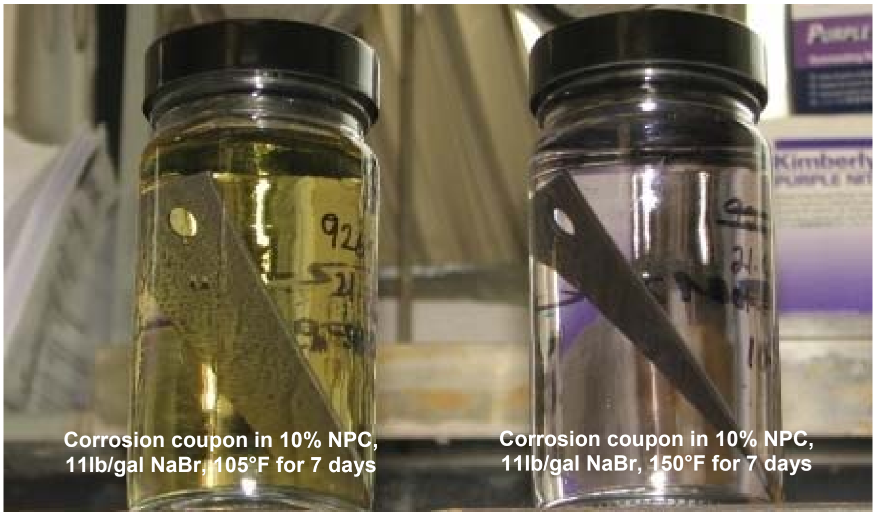

Fig. 4—Corrosion coupons in 10% of the NPC in sodium bromide at 105 and 150°F

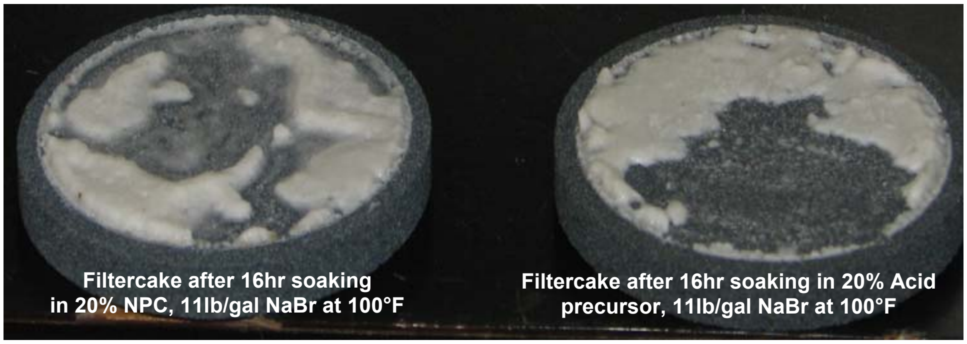

Fig. 5—Aloxide disks after 16 hr soaking in breaker fluids at 150°F and 500 psid

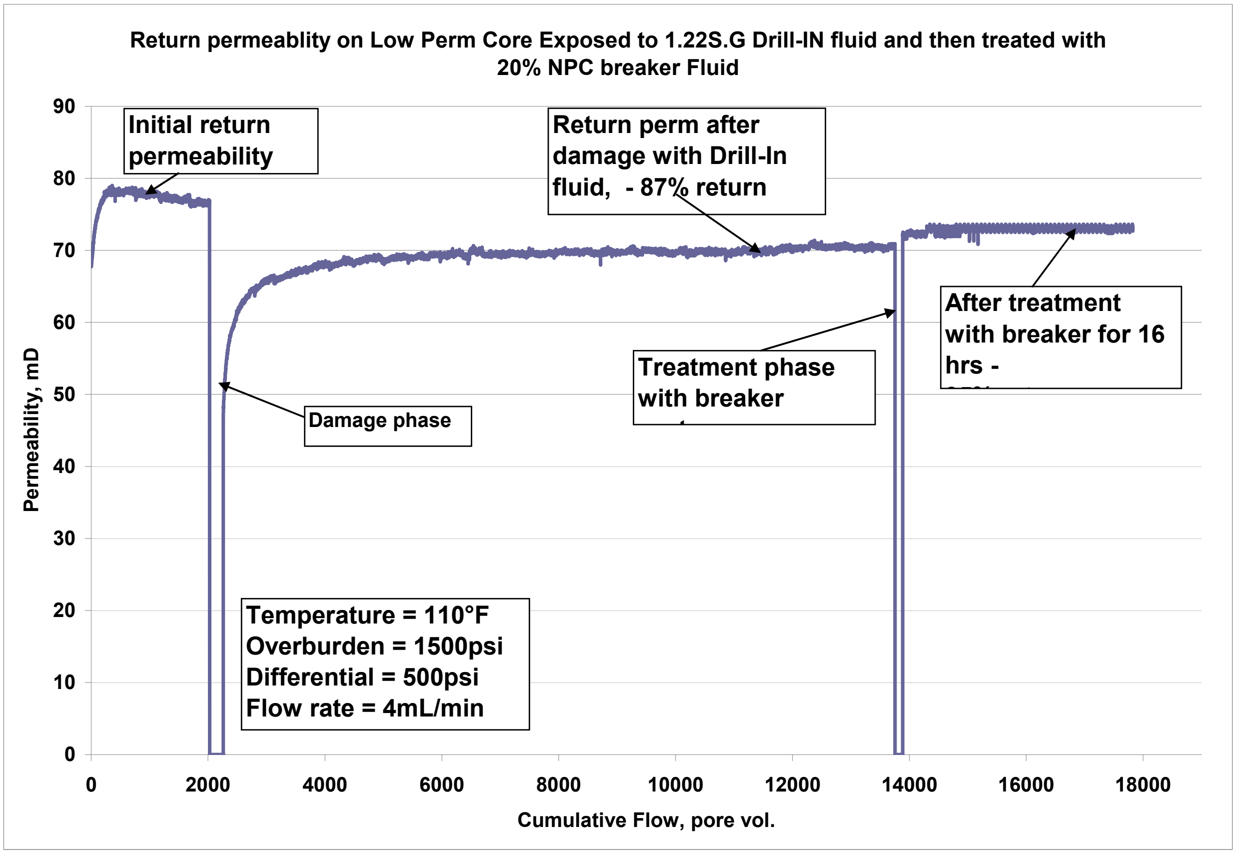

Fig. 6—Return Permeability Chart