THERMAL STABILITY OF VARIOUS CHELATES THAT ARE USED IN THE OILFIELD

A Thesis

by

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Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

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December 2012

Major Subject: Petroleum Engineering

ABSTRACT

Acid treatment, especially at high temperatures, is very challenging since HCl is really corrosive to the metal equipment. The use of HCl is associated with face dissolution, corrosion, and iron precipitation. Organic acids are weak and less corrosive than HCl but they have a limitation, which means that they can't be used at high concentrations. The next option would be chelating agents. Chelating agents are used in well stimulation, iron control during acidizing, and removal of inorganic scales. Chelates such as ethylenediaminetetraacetic acid (EDTA), N-(hydroxyethyl)-ethylenediaminetetraacetic acid (HEDTA), L- glutamic acid-N, N diacetic acid (GLDA), and nitrilotriacetic acid (NTA) are used in high-pressure/high-temperature oil and gas wells. GLDA is environmentally friendly, which makes it favorable. One of the concerns with these chelates is their thermal stability at high temperatures because if they degrade at high temperatures, they may lose their functionality.

This study describes the thermal stability of these chelates, thermal degradation products, and some methods to improve their stability. The thermal stability is determined by measuring the concentration before and after heating using a complexometric titration utilizing $FeCl_3$ as a titrant. The degradation products are identified using Mass Spectrometry (MS).

A series of experiments were run in the lab at varying temperatures (300 to 400°F) up to 12 hours, and the results shows chelates are not stable at temperatures greater than 350°F. Furthermore, chelates with two nitrogen atoms are more stable than those with

one nitrogen atom. Iminodiacetic acid (IDA), acetic acid, and $\boldsymbol{\alpha}$-hydroxy acids are the decomposition products. There is a layer of black deposition after the chelates are heated, which is analyzed using Scanning Electron Microscope (SEM). Some coreflood tests are conducted using these degraded chelates to investigate the effect of these solid precipitates on the permeability of carbonate and sandstone cores.

Increasing ionic strength and raising pH results in a higher thermal stability. Some salts such as, NH_4Cl, KCl, Csformate, and NaBr are added to chelate solutions to enhance stability.

DEDICATION

This thesis is dedicating to my beloved family especially Jamshid Sokhanvarian who opened my eyes through the path of wisdom, which is the greatest thing in the world to me.

Also, this thesis is dedicated to Ehsan for all his support in this part of my life. Finally, this thesis is dedicated to Dr. Nasr-El- Din who helped me in finishing this journey.

ACKNOWLEDGEMENTS

First and foremost, I would like to thank my adviser Dr. Nasr-El-Din for all his generous support and guidance through my research. I can never pay you back for all the help.

I would like to acknowledge my committee members, Dr. Schubert and Dr. El-Halwagi for their guidance and support throughout the course of this research.

Thanks also go to my friends and colleagues and the department faculty and staff for making my time at Texas A&M University a great experience. Finally, many thanks to AkzoNobel company for funding this projects and Texas A&M for providing facility and resources.

NOMENCLATURE

DTA	Differential Thermal Analysis
EDTA	Ethylenediaminetetraacetic acid
GC	Gas Chromatography
GLDA	L- glutamic acid-N, N diacetic acid
HEDTA	N-(hydroxyethyl)-ethylenediaminetetraacetic acid
ICP	Inductive Coupled Plasma
MGDA	Methylglycinetetraacetic acid
MS	Mass Spectrometry
NTA	Nitrilotriacetic acid
SEM	Scanning Electron Microscope

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1. INTRODUCTION

1.1 Matrix acidizing

Matrix acidizing has been used to remove near-wellbore damage by creating channels or wormholes in carbonate formations to improve well performance. Hydrochloric acid (HCl) has been used extensively as a stimulation acid. One of the major challenges associated with conventional stimulation fluids like HCl is its corrosivity toward metal surfaces and equipment. It is especially hard to control HCl corrosion rate at elevated temperatures due to technical difficulties and cost (Wang et al. 2009). Hydrochloric acid is cheap and powerful in dissolving rock, in addition to the fact that the reaction products are usually soluble. However, the carbonate/HCl reaction is so fast that it leads to weak penetration and face dissolution, especially at elevated temperatures (Buijse et al. 2004). Through the use of emulsions or micro-emulsions, HCl can be retarded to prevent rock deconsolidation. Furthermore, reducing the contact area between the acid and the rock improves deep penetration of live acid.

At very high temperatures (greater than 400°F) where corrosivity and reaction rate of HCl become more challenging, an alternative option is to choose a less aggressive acid type, such as acetic or formic acid. These organic acids have a lower reaction rate than HCl, providing deep penetration (Buijse et al. 2004). However, organic acids are more expensive per unit volume than HCl and can’t be used at high concentrations. Typically, acetic and formic acid concentrations should not exceed more than 13 and 9 wt%, respectively. Precipitation is because of the limited solubility of these acids’ salts (especially calcium formate), which may precipitate at higher acid concentrations (Al-Khaldi et al. 2009).

In addition, organic acids' reaction with calcite is reversible and thermodynamically limited because of the presence of the reaction products. In the other words, the reaction path is controlled by the diffusion of the reaction products away from the rock surface (Fredd and Fogler 1998b).

Chelating agents are aminopolycarboxylic acids, which are capable of binding with metal atoms. These chemicals have been used extensively in the oilfield for different purposes such as iron control, inorganic scale removal, and well stimulation. In oilfield chemical treatments, chelates are added to the acid that is used in the stimulation treatment to prevent solids precipitation as acid spends on the formation (Ali et al. 2002). Ethylenediaminetetraacetic acid (EDTA) is an alternative fluid that has the ability to stimulate the carbonate porous media by means of sequestering the metal components of a carbonate matrix. The dissolution may be enhanced at low pH through the combination of hydrogen ion attack and chelation. At the Prudhoe Bay field of Alaska, conventional HCl treatment led to high decline rates in calcium carbonate ($CaCO_3$) removal and then precipitated in the perforation and near-wellbore region of the sandstone formation. Na_2EDTA was successful in removing $CaCO_3$ scale as well as in removing calcium (Ca), barium (Ba), and strontium (Sr) scale from reservoir cores (Fredd and Fogler 1998a; Rhudy 1993; Shaughnessy and Kline 1983; Tyler et al. 1985). While Crowe (1985) concluded that EDTA can be used to control ferrous and ferric hydroxide precipitation up to 350°F and its efficiency actually improves above 250°F because it acted as a reducing agent, Brezinski (1999) claimed that EDTA is not stable as an iron control agent in HCl/carbonate spending tests in the presence of H_2S based on the Eq. 1 :

$Fe (HEDTA) + H_2S \rightarrow FeS + H_3EDTA$ ………………………………………… (1)

He suggested using sulfide control chemicals to avoid FeS precipitation (Crow 1985; Brezinski 1999).

Sodium salts of HEIDA and HEDTA can be used as a replacement in all formulation types that require EDTA. HEDTA can control precipitation of Fe^{+3} species better than EDTA because it has higher solubility in HCl than EDTA and is much more biodegradable in standard laboratory tests. (Frenier et al. 2003; Frenier et al. 2000).

Frenier et al. (2001) defined two different mechanisms involving for high and low pH chelates, which is shown in Eq. 2 and 3, respectively.

$CaCO_3 + 2 H^+ \rightarrow Ca^{2+} + CO_2 + H_2O$ ………………………………………...… (2)

$CaCO_3 + Na_3HEDTA \rightarrow NaCaHEDTA + Na_2CO_3$ …..………………………… (3)

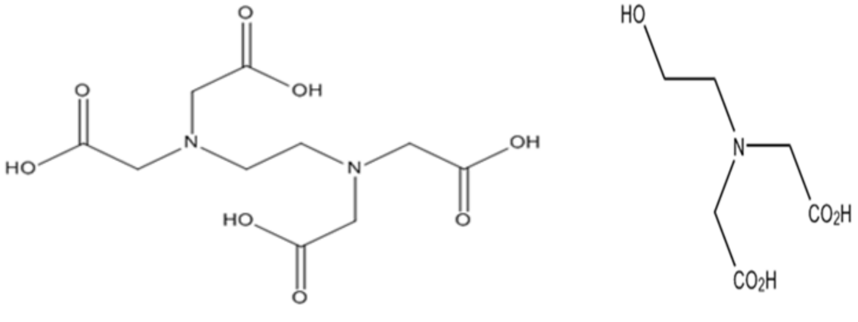
Both equations are effective at low-pH, while at pH 12 only Eq. 3 is dominant. This is essentially the same mechanism as for EDTA, but Eq. 2 becomes increasingly important and dominant as the pH is lowered below 4. These low-pH solvents appear to be very operative and efficient matrix fluids at high temperatures where EDTA is insoluble in acid at pH values < 4 and HCl (and organic acids) are too aggressive to produce expeditious wormholes at typical flow rates for most matrix treatments (Frenier et al. 2001).

GLDA is used as an environmentally friendly fluid with an optimum injection rate for Pink Desert limestone (high permeability) and Indiana limestone (low permeability) that are 3 cm^3/min and 1 cm^3/min, respectively. In addition, no face dissolution problems are associated with using GLDA at low injection rates, which had been seen with using HCl. GLDA is highly soluble even in 28 wt% HCl where other conventional chelates like HEDTA have limitations (Mahmoud et al. 2010; LePage et al. 2011).

1.2 Chelating agent structures

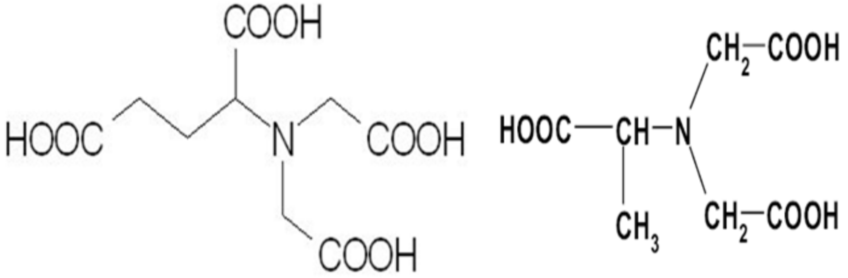
Aminopolycarboxylic acids (APCAs) are the compounds that consist of several carboxyalkyl groups bound to one or more nitrogen atoms. Their ability to form stable, water-soluble complexes with a broad range of metal ions makes them versatile in different applications (Means et al. 2003).

Various chelates are used in oilfield treatment such as ethylenediaminetetraacetic acid (EDTA), methylglycinediacetic acid (MGDA), L-glutamic acid, N, N-diacetic acid (GLDA), hydroxyethyliminodiacetic acid (HEIDA), and hydroxyethylethylenediaminetriacetic acid (HEDTA).



Ethylenediaminetetraacetic (EDTA)

N-(hydroxyethyl)-
ethylenediaminetetraacetic acid (HEDTA)



L- glutamic acid-N, N diacetic
acid (GLDA)

Methylglycinetetraacetic acid
(MGDA)

Fig. 1—Structures of chelating agents (after Fernier et al. 2001)

GLDA is a chelating agent that contains a single nitrogen atom, and has a singular structure because a major portion of it is derived from monosodium glutamate (MSG). Monosodium glutamate is achieved from corn sugar fermentation and is considered a renewable raw material. Furthermore, the carbon source in EDTA is fossil-based, but in GLDA it is biologically-based, which makes it the only chelating agent with green carbon atoms (Kolodynska 2010; LePage et al. 2011). HEDTA and HEIDA are hydroxyaminocarboxylic acids, of which the most considerable typical feature is their very high solubility of the free acids in aqueous solutions. Furthermore, HEIDA is very biodegradable (Frenier et al. 2001).

1.3 Environmental concerns

The main characteristic of chelating agents, metal binding, which makes them favorable in so many areas, at the same time is an important concern from the environmental point of view. The four main environmental concerns are:

1. Negative impact on the wastewater treatment plant operation
    - At environmentally relevant concentrations, no adverse impacts have been reported so far from wastewater treatment plants for EDTA.
2. Toxicity effect of APCAs on aquatic and mammalian organisms
    - EDTA is only weakly toxic toward humans (indeed, it is used as an antidote and is acceptable as a food additive in some countries).
3. Eutrophication induced by the nitrogen atom in APCAs
    - Nitrogen loading from EDTA is not significant enough for any direct eutrophication.
4. Metal mobilization

Metal mobilization by EDTA will not be significant at an environmental concentration. On the other hand, pH variation has a huge impact on concentrations of heavy metal ions. Thus, heavy metals adsorbed in groundwater aquifers in calcareous regions characterized by pH values >7 can be remobilized by the presence of Fe (III) EDTA, which is an important EDTA species in many rivers. On the other hand, in aquifers with lower pH values (<7), the dissolution of the mineral and the formation of Fe (III) EDTA occur due to the reaction between Me (II) EDTA chelates with iron (hydr) oxides. The liberated metal from the original EDTA adsorbs to the surface and leads to immobilization. Hence, under such circumstances, no remobilization, but the immobilization of toxic metals should be anticipated (Anderson et al. 1985; Alder et al. 1990; Ngwack and Sigg 1997; Bucheli-Witschel and Egli 2001; Means et al. 2003).

Biodegradability of chelates

Biodegradation is the conversion of a complex organic compound into one or more simpler elements, which can be separated into three categories:

1. Eventual biodegradation
    - The elements comprising the original compound are liberated in an inorganic form (e.g. as CO_2, H_2O, salts, NH_3).
2. Secondary degradation
    - Original compounds decompose to smaller compounds which have the same primary characteristics.
3. Elementary degradation
    - The characteristic properties of the original compound are no longer obvious.

These classifications may also be applied to other types of degradation such as photolysis, radiolysis, and thermal breakdown (Alexander 1973; Means et al. 2003). Actually, microbial attack on the metal chelate or on the free ligand in equilibrium with it initiates the chelate degradation (Bucheli-Witschel and Egli 2001). HEIDA can be degraded by activated sludge from sewage and it will have no chelation ability anymore (primary degradation), whereas acid EDTA and HEDTA keep their chelating capacity.

While MGDA degraded 90 to 100% within 14 days, EDTA didn't show any degradation after 30 days (Bucheli-Witschel and Egli 2001; González et al. 2011). Biodegradation tests in wastewater treatment plants and the environment for GLDA showed the degradation value of > 60% within 28 days, which exceeded standards for ready biodegradability (van Ginkel 2007).

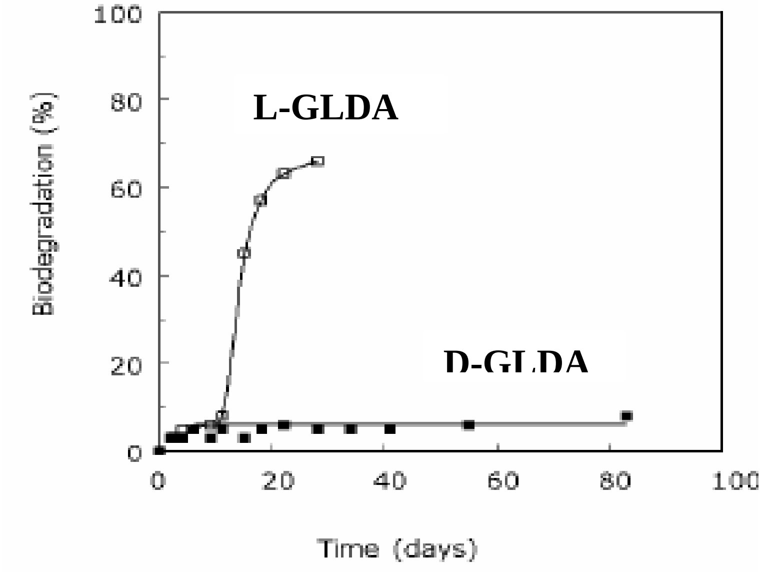


Fig. 2—L-GLDA (open points) rapid degradation of about 72% in 30 days makes it more environmentally safe than D-GLDA (closed points) (From Kolodynska and Hubicki 2009).

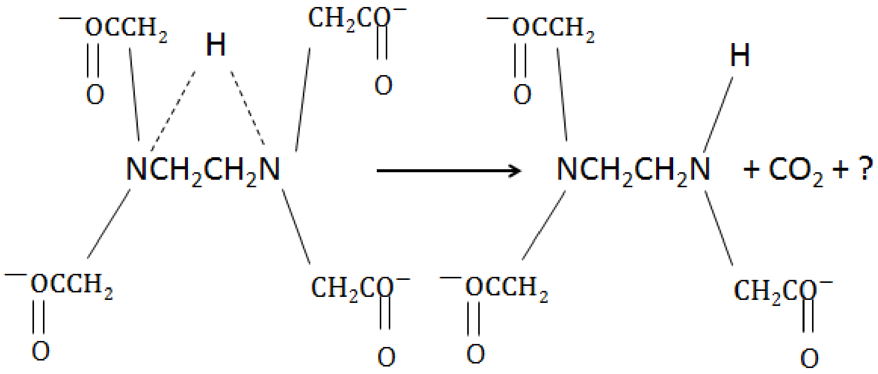
HEIDA, GLDA, and MGDA, which are biodegradable, contain one nitrogen atom, while EDTA and HEDTA, which remained undecomposed, carry two nitrogen atoms (Bucheli-Witschel and Egli 2001).

2. THERMAL DECOMPOSITION OF CHELATES

Chelates are used in high-pressure/high-temperature oil and gas wells. One of the concerns with these chelates is their thermal stability at elevated temperatures. Therefore, it is essential to determine thermal stability of these expensive chemicals.

Studying the hydrolytic stabilities of these chelates is necessary and to do so, it is essential to specify if the chelate which is present in the reaction time is actually the same as introduced into the solution (Martell et al. 1975).

EDTA is stable up to 200°C. Eq. 4 depicts the decomposition path and the relation of a proton with the $EDTA^{4-}$ structure that causes the CH_2CO_2 group to split in a stepwise reaction.



…… (4)

Decomposition proceeds until the entire $EDTA^{4-}$ is degraded into smaller compounds. Such compounds may have undesirable effects in any application since they may lose the chelation property. The hydrogen bridging structure causes decomposition and it can be prevented by complexing nitrogen with a strong Lewis acid like Li (**Table 1**). Thermal degradation of H_4EDTA increases as the solutions pH decreases.

TABLE1—ESTIMATED TIMES FOR ONE-HALF OF THE INITIAL CONCENTRATIONS OF $EDTA^{4-}$ AND NTA^{3-} AQUEOUS SOLUTIONS TO DECOMPOSE AT 200°C

Salt	Initial solution concentration, M	Initial pH at room temperature	$t_{1/2}$, hr
Na_2H_2EDTA	0.25	4.5	3
Li_4EDTA	0.13	9.8	13
H_4EDTA	0.24	2.8	1
Na_2HNTA	0.2	8.3	>10000
Na_3NTA	0.2	9.9	>10000
H_3NTA	0.3	2	12

The infrared spectroscopy (IR) spectrum of EDTA at 200°C is the same as the original, which confirms its stability up to 200°C. At 260°C, EDTA starts to crack (**Fig. 3**). Its degradation path after 30 minutes leads to the formation of HEIDA and IDA as species 1 and 2, respectively. HEIDA hydrolyzes and yields ethylene glycol (species 3), and then it decarboxylates to form N-methyl amine and dimethylamine (Eq. 5). After some time at 260°C (**Fig. 4c**), the original decomposition products of EDTA yields the different substituted methylamines due to decarboxylation. The thermogravimetric (TG) plot confirmed 59%, 60 %, 74 %, and over 90% weight loss at temperatures of 240 °C, 260 °C, 300 °C, and 600 °C respectively.

At temperatures above 200°C, the chelation ability of EDTA is dependent on HEIDA and IDA, which are the elementary degradation products (Esteban et al. 1983; Martell et al. 1975; Venezky and Moniz 1970).

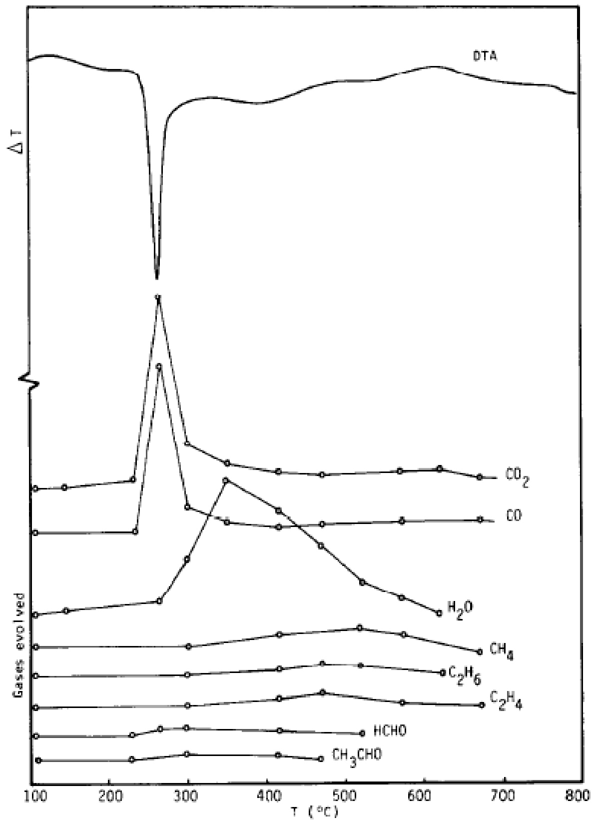
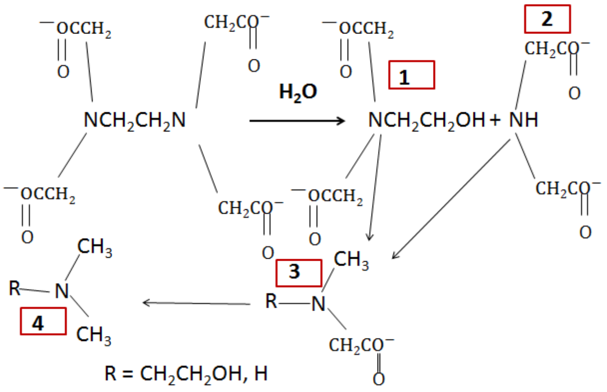


Fig. 3—DTA and GC of EDTA. Decomposition starts at 260°C by releasing CO and CO_2 (from Esteben et al. 1983)



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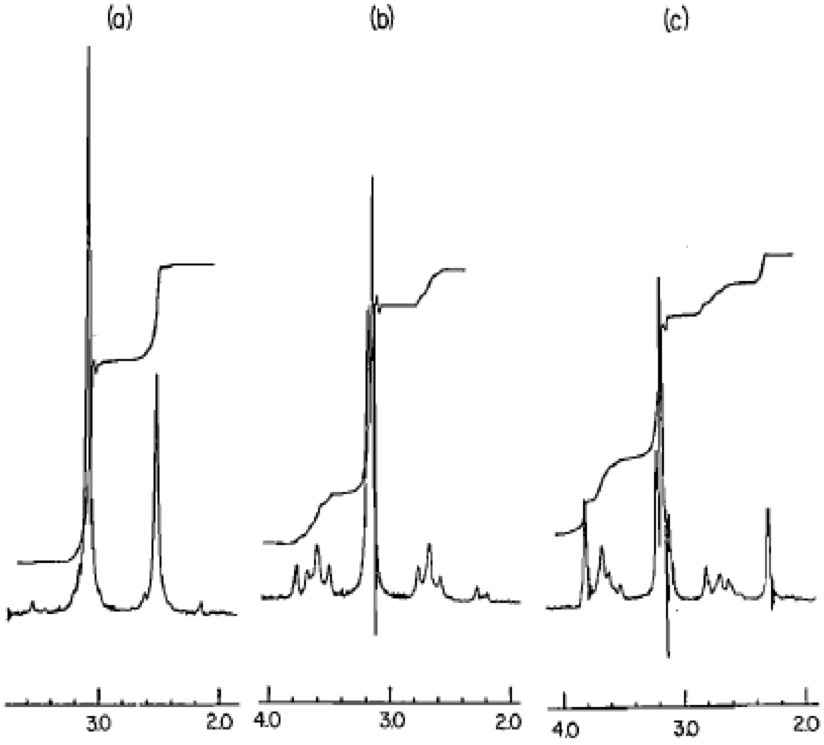

Fig. 4—NMR spectra of EDTA samples heated at 260°C at (a) *t*=0, (b) *t*=0.5 hour, (c) *t*=7.5 hours. The two singlets in 2:1 ratio corresponding to the acetate methylenes and ethylene bridge protons of EDTA (a) have disappeared and were replaced by two closely spaced singlets at 3.1 to 3.2 p.p.m., and two triplets at 2.7 and3.6 p.p.m. relative to TMS (from Martell et al. 1975)

Additionally, the split of EDTA molecules to HEIDA and IDA via hydrolysis at 175°C in an Alkaline environment (pH=9.4) has a half-life of about 4 hours (Motekaitis et al. 1982).

2.1 Thermal behavior of sodium salts of EDTA

The first step, which was losing water, started below 200°C (endothermic effect in DTA curve below 200°C) and is shown in **Figs. 5** and **6**. The endothermic effect corresponds to the first decarboxylation of acid groups decreases from NaEDTA to Na_3-EDTA is in the range of 200 to 300°C followed by the release of CO_2, CO, and H_2O. At temperatures of 300 to 500°C, the second decarboxylation process is followed by cracking, and CO_2, CO (lesser amount), NH_3, and traces of hydrocarbons are observable. The maximum amounts of CO and CO_2 are summarized in **Table 2.**

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TABLE 2—TEMPERATURES (°C) AT WHICH MAXIMUM AMOUNTS OF CO AND CO2 ARE RELEASED. THE TEMPERATURES LIMIT INCREASES FROM NaEDTA to Na_4EDTA.

	NaEDTA	Na_2EDTA	Na_3EDTA	Na_4EDTA
CO_2	240-375	250-400	270-420	420
CO	240	240	270-420	

The amounts of CO_2, which are liberated from the first and second decarboxylation depend on the number of –COOH and –COO^- groups, respectively (Esteban et al. 1983).

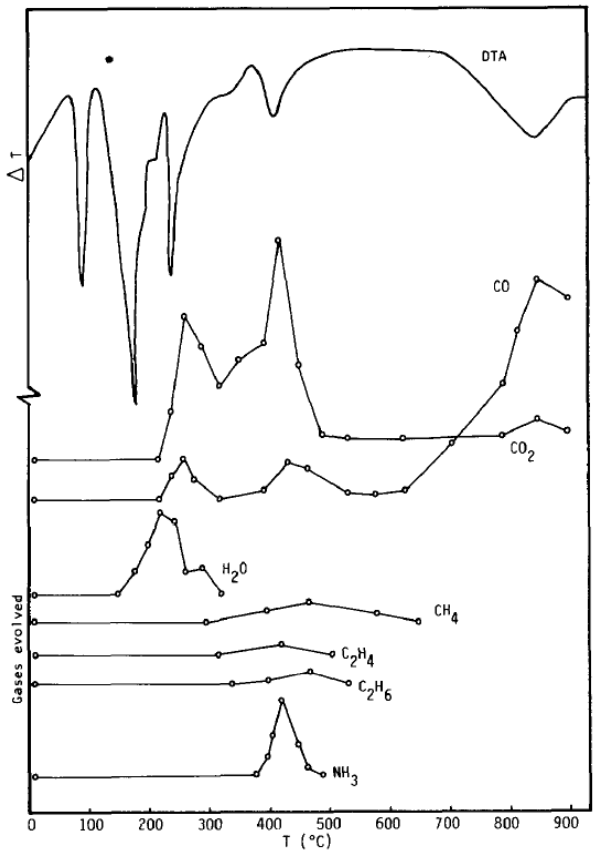


Fig. 5—DTA and GC of Na_3EDTA. Water loss started below 200°C. The first decarboxylation step is between 200 to 300°C by releasing CO and CO_2 (from Esteben et al. 1983).

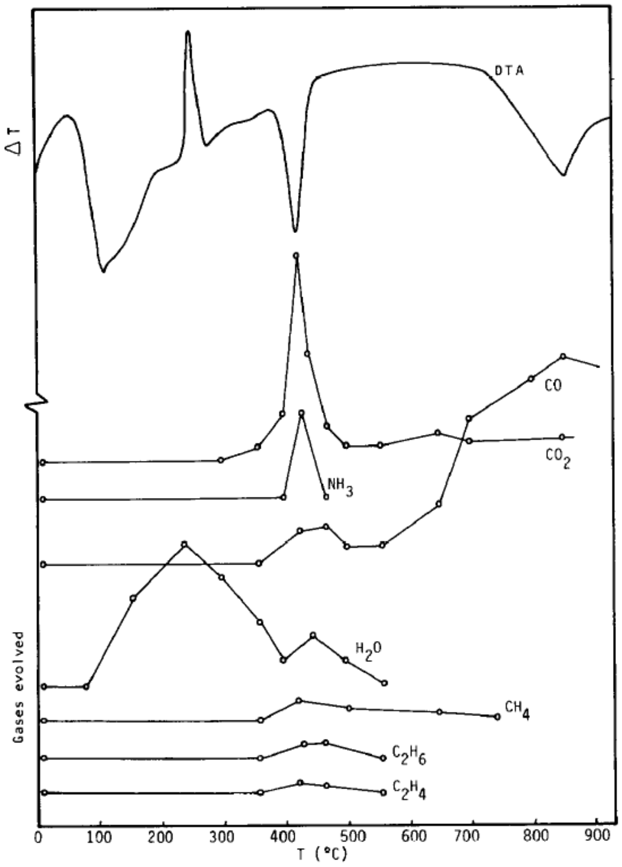


Fig. 6—DTA and GC of Na_4EDTA. Water loss started below 200°C. The first decarboxylation step is between 200-300°C by releasing CO and CO_2 (from Esteben et al. 1983).

Except Na_4EDTA, which demonstrates only the second decarboxylation, the other sodium salts of EDTA showed the two decarboxylation steps. Compounds that lose carboxyl groups in a single step are thermally more stable than those that decompose by two-step decarboxylation (Esteban et al. 1983; Venezky 1967).

2.2 EDTA-Metal complexes

A solution of 1.5 mole of EDTA and Fe (III) with a pH=9.3 after heating at 175°C converts to a yellow green solution of 1 mole of Fe (II) EDTA and 0.5 mole of an oxidized reaction product. The same solution with a 1:1 mole ratio at 175°C leads to precipitation of one-third of Fe (III) as Fe_2O_3 (Eq. 6 and 7).

$$2\text{Fe (III) EDTA} \longrightarrow 2\text{Fe (II) EDTA} + \frac{1}{2}Fe_2O_3 + \text{EDTA}_{\text{decomp}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

$$3\text{Fe (III) EDTA} \longrightarrow 2\text{Fe (II) EDTA} + \frac{1}{2}Fe_2O_3 + \text{EDTA}_{\text{decomp}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (7)$$

Then, a sample with a molar ratio 10:1 EDTA to Fe (III) at pH 9.3 at 135°C for 3 hours leads to the formation of ethylenediaminetriacetic acid (ED3A) as a result of catalytical oxidation of EDTA coordinated to Fe (III), as can be seen in Eq. 8 and 9. (Motekaitis et al. 1980).

$$2\text{Fe(III)EDTA} + \text{EDTA} \rightarrow 2\text{Fe(II)EDTA} + \text{ED3A} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (8)$$

$$\text{Fe(II)EDTA} \xrightarrow{O_2} \text{Fe(III)EDTA} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (9)$$

This cycle continues until either the oxygen or the reducing agent (EDTA) becomes exhausted. While this redox reaction makes EDTA very unstable at temperatures just above the boiling point of water, the Fe (II) chelate that is formed is stable up to 24 hours. Metal complexes prevent EDTA from hydrolytic degradation, as is shown in **Table 3**.

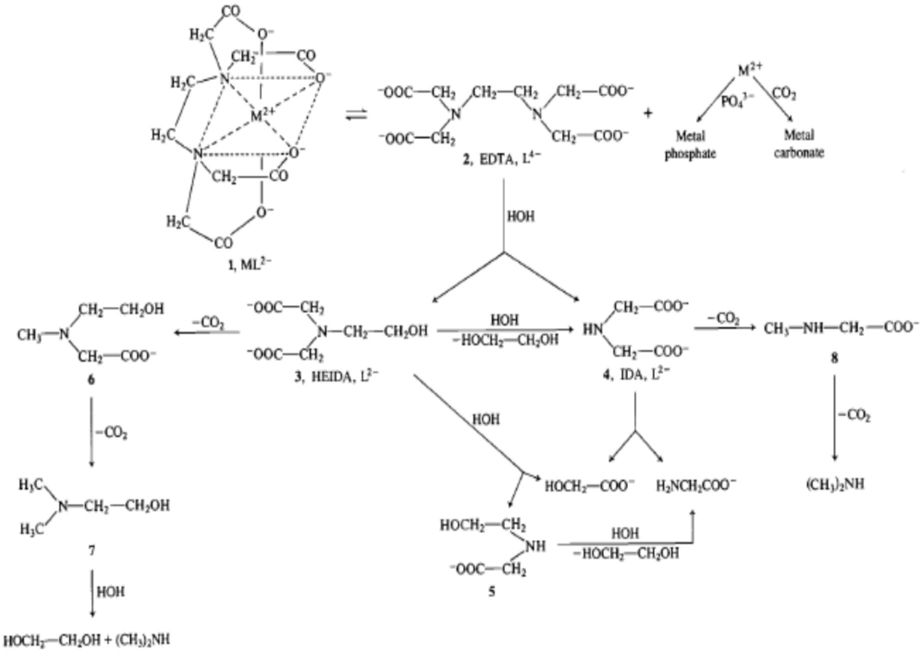
TABLE 3 - FIRST ORDER RATE CONSTANTS FOR DECOMPOSITION OF EDTA AND ITS METAL CHELATES AT pH_0 = 10.4 AT VARIOUS TEMPERATURES

Metal Ion	T (˚C)	k_{obs} (h^{-1})	Analytical Method
None	190	0.37	Nmr
Ca^{2+}	310	0.27	Titrimetric
Ca^{2+}	320	1.1	Titrimetric
Mg^{2+}	307	0.50	Titrimetric
Fe^{2+}	310	0.31	Gas chromatographic
Fe^{2+}	310	0.30	Spectrophotometric
Zn^{2+}	308	0.22	Nmr
Ni^{2+}	310	0.075	Nmr

Free EDTA degrades rapidly at 190°C and pH=10.4 with a half-life of 1.9 hours. The following is the order of thermal stability in metal complexes

None (Sodium salt) > Mg^{2+} > Ca^{2+}~ Fe^{2+} ~Zn^{2+} >> Ni^{2+}

A Pyrex liner in an autoclave increases the decomposition of EDTA chelates of Mg (II) and Ca (II) because of the formation of insoluble Ca (II) and Mg (II) silicates that probably adsorbed on to the glass surface. In addition, phosphate can play a major role as a catalyst in decomposition of EDTA chelates of Zn (II), Ca (II), and Mg (II) because of the formation of insoluble Zn (II), Ca (II), and Mg (II) phosphates. Proposed degradation path for EDTA chelates of divalent metal ions at 300°C is dempnstrated in Eq. 10. Final reaction products at 300°C are carbon dioxide, ethylene glycol, dimethylamine, glycine, glycolic acid (specie 3), hydroxyethyliminodiacetic acid (HEIDA), iminodiacetic acid (IDA) at 200-230°C.



… (10)

2.3 Effect of oxygen on the thermal decomposition of EDTA and its salts

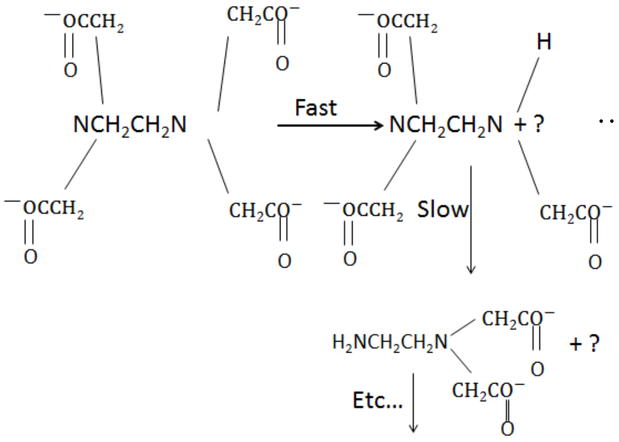
Oxygen induces the decomposition of EDTA in a way that the dissolved oxygen becomes activated at temperatures near 180°C. In testing one part of oxygen equivalent resulted in 50 to 100 parts of $EDTA^{4-}$ becoming valueless in the prevention of scales in a boiler. On the other hand, in the case of deoxygenated water, free $EDTA^{4-}$ and its metal complexes were stable for 2 hours at temperatures up to 251°C so the chelation ability of $EDTA^{4-}$ is deactivated in solution at temperatures above 149°C because of the dissolved oxygen. Although $EDTA^{4-}$ acts as an oxygen scavenger at temperatures above 180°C, adding sodium sulfite to make-up water that contains $EDTA^{4-}$ is advisable because using $EDTA^{4-}$ as an oxygen scavenger is not economical (Venezky 1967).

Estimation of half-lives under different solution treatments are summarized in **Table 4**.

TABLE 4—SOLUTIONS, SEALED UNDER REDUCED PRESSURE, USED TO STUDY THE THERMAL DECOMPOSITION OF EDTA^{4-} IN AQUEOUS SOLUTIONS AT 200°C

Compound	Solution Concentration (M)	pH	Solution Treatment Before Sealing	Estimated $t_{1/2}$ (hr)
Na_4EDTA	0.15	9.9	Air saturated	4
Na_4EDTA	0.15	9.9	Undegassed	5
Na_4EDTA	0.15	11.4	Degassed	15
Li_4EDTA	0.08	9.8	Air saturated	4
Li_4EDTA	0.10	9.8	Degassed	13

The effect of O_2 on the thermal degradation of Na_4EDTA and Li_4EDTA that is the fast reaction (Eq. 11) is substantial, but the Li or Na (weak Lewis acids) do not affect the thermal decomposition rate of aqueous solutions of EDTA^{4-} under the basic environment of their experiment.



………………. (11)

The first step in the above reaction is rapid and followed by a slower step (second stage), which is the loss of CH_2CO_2 from the nitrogen. Later, reinterpretation about the decomposition of $EDTA^{4-}$ leads to the fact that it occurs through the hydrolysis of the ethylenic C-N bond (Martell et al. 1975; Venezky 1971).

2.4 Thermal behavior of NTA

The structure of NTA^{3-} does not form a bridge structure. NMR (Nuclear Magnetic Resonance) is used to illustrate the nature of decomposition products. For NTA^{3-} , the single PMR peak corresponds to the methylenic protons can be utilized to monitor the thermal decomposition rate in aqueous solution. The Na_2HNTA solutions (pH=8.34) showed the desirable single peak initially at 107 Hz (**Fig. 7**). The pmr spectra for Na_3NTA solutions (pH=9.98) comprise of robust sharp resonance at 150 Hz and a weak peak at 83 Hz (**Fig. 8**). ‘‘The latter peak is attributed to an impurity in the technical-grade reagent used. The impurity present may be a strong Lewis acid, which would cause a peak downfield from the uncomplexed peak (150 Hz) similar to the shift noted for Mo (VI)-NTA complexes. Because the peaks attributed to uncomplexed NTA^{3-} showed little effect after heating the Na_3NTA and Na_2NTA solutions at 200°C for up to 672 hours, the traces of impurities which may have been present were not considered to be detrimental to the observed results" (Venezky and Moniz 1970).

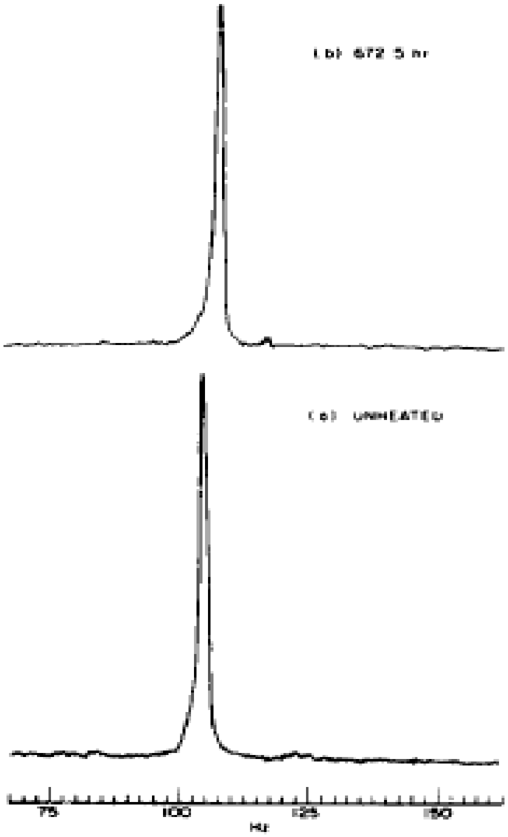


Fig. 7—NMR spectra of degassed solution of Na_2HNTA (0.2M) sealed under reduced pressure and heated to 200°C (From Venezky and Moniz 1970).

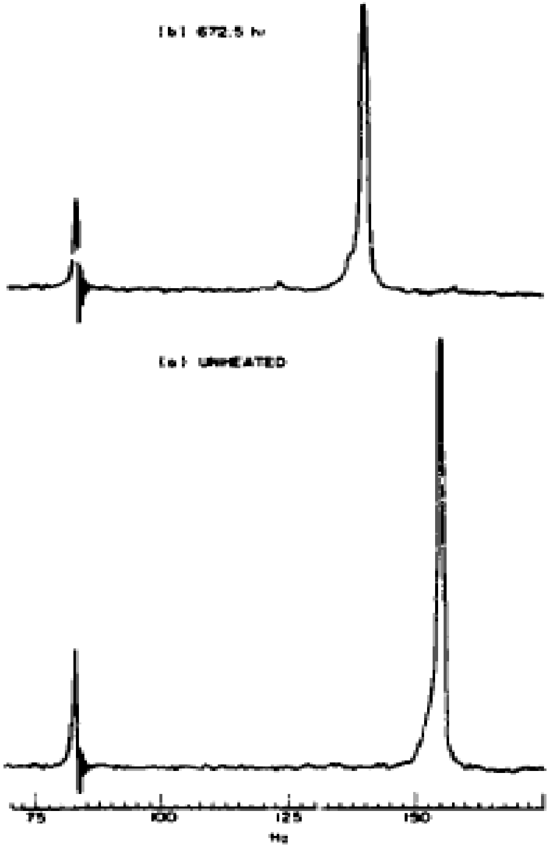


Fig. 8—NMR spectra of degassed solution of Na_3NTA (0.2M) sealed under reduced pressure and heated to 200°C (From Venezky and Moniz)

The decomposition rate of H_3NTA is the same as Li_4EDTA, the most stable of $EDTA^{4-}$ solutions studied. In acidic medium, the apparent Second-order kinetics similar to the Li_4EDTA solutions, demonstrates a strong hydrogen bonding between the acid molecules and the nitrogen in amine group which may be required as an intermediate structure for the stepwise decomposition of H_3NTA. Therefore, acid solutions (pH = 2) induce thermal decomposition rate of NTA the same way it did in $EDTA^{4-}$ but the low concentration of hydrogen (pH=8) leads to a slow degradation rate (Venezky and Moniz, 1970).

2.5 Thermal behavior of transition metal complexes of NTA

NTA-Iron (III)

NTA degraded via reduction of Fe (III) to Fe (II) and left the solid $Fe^{II}_3 (NTA)_2 \cdot H_2O$ at temperatures greater than 496°F, and is followed by the formation of magnetite as the final product at higher temperatures. The pmr spectrum of the solution at 554°F for 2 hours confirmed the existence of small but almost equal amounts of both deacetylation (IDA) and decarboxylation products (MIDA), which demonstrates deacetylation is as important as decarboxylation in contrast to the degradation of Na_3NTA (decarboxylation is the main mode). Fe (III) oxidized the NTA ligand with the formation of IDA, formaldehyde, and CO_2.

NTA-Iron (II)

It decomposed just by decarboxylation, and the degradation product, $Fe (OH)_2$, became unstable near 566°F decomposed to magnetite, which acted as a catalyzer in further degradation of NTA. The ^1H NMR spectrum of solutions indicated just MIDA (decarboxylation product) and no IDA (deacetylation product). In non-acidic medium, deacetylation occurs when the ligand is oxidized by a metal ion. Thus, IDA can be detected when the reaction is occurred under air (iron (III) is formed) (Booy and Swaddle 1977a&b).

2.6 Thermal degradation of GLDA, EDTA, NTA, and HEDTA

Thermal stability of GLDA, NTA, MGDA, HEDTA, and some salts of EDTA have not been studied in detail. Kołodynska and Hubicki suggested that the thermal stability of GLDA is high at temperatures greater than 300°C since there was no significant degradation, but their work was qualitative (Kołodyńska and Hubicki 2009). The thermal stability of GLDA and HEDTA at temperatures of 300 and 350°F in different pH are almost in the same range (LePage et al. 2011). The thermal stability of GLDA is favorably affected by solutions which have high ionic strength like brines (Mohamed et al. 2010).

To the best of our knowledge, thermal stability of GLDA, an environmentally friendly chelating agent, has not been studied so far in detail. The objectives in this study are to: investigate thermal stability of chelates, identify the thermal decomposition products and their impact on the permeability of carbonate and sandstone cores, and improve the thermal stability by the addition of some organic and inorganic salts.

3. EXPERIMENTAL WORK, RESULTS, AND DISCUSSION

3.1 Material

The chelating agents that are used to accomplish this project are GLDA, NTA, EDTA, MGDA, and HEDTA. All the chemicals were provided by Akzonobel Company. The properties of the chelates are summarized in the **Table 5**.

TABLE 5—PHYSICAL PROPERTIES OF DIFFERENT CHELATING AGENTS

Chemical	pH	Density (g/cm$_3$)	Concentration (wt%)	MW (gram/mol)
NaH_3GLDA	3.92	1.263	36.78	285.0
Na_4GLDA	13.75	1.405	40.00	350.0
$NaKH_2GLDA$	3.92	1.255	39.39	323.1
NH_4H_3GLDA	4.03	1.222	39.70	282.0
NaH_2HEDTA	3.92	1.217	40.80	300.0
NaH_2MGDA	4.21	1.220	31.60	230.2
$(NH4)_2EDTA$	5.72	1.192	45.88	318.0

3.2 Equipment

Measuring density and pH

The density of the fluid will be measured at room temperature and 1 atmosphere. We will use a Paar densitometer model DMA-35 (**Fig. 9**). The pH of the chelates will be measured using an Oakton pH 510 meter, which is calibrated with three solutions with the pH of 4, 10, and 12 before use (**Fig. 10**).

Fig 11—Paar densitometer

Figure 9—Paar densitometer

Fig. 12—An Oakton pH 510 meter

Figure 10—An Oakton pH 510 meter

Cylinder

- Put a chelate in the Teflon liner and close it with the piston plug.
- Place the Teflon liner in the steel aging cell.
- Pressurize the aging cell to a desired pressure.
- Check to make sure that there is no leaking.

Steel stainless aging cells

The OFITE aging cell (Schroeder 1989) is a pressure vessel that enables samples to be subjected to temperatures higher than the boiling point of water and still be maintained in a liquid state (**Fig. 11**). The cells may be used for static temperature exposure or in a dynamic mode in a roller oven with a preset minimum aging time of 16 hours. Aging cells are typically constructed of stainless steel (grade 303 or grade 316) and are used for high temperatures testing (up to 600°F).

Teflon liners

We will use Teflon liners (**Fig. 12**) model 175-60 for aging cells. These liners are suitable for temperatures above 300°F. They also protect steel aging cells from corrosion. We will put a chelate into a Teflon liner and then put the Teflon liner in the aging cell. The sample will be pressurized by a nitrogen source.

Figure 11—Steel aging cell

Figure 12—Teflon liner with a t-screw

Static heating

We will use 5-roller ovens (173-00/173-00-1 model, **Fig. 13**) in the static mode. The oven temperature range is 100 to 450°F.

- Set a desired temperature.
- Put the pressurized aging cell in the preheated oven.

- Record the time for the desired duration.

Fig. 16—5-roller oven

Figure 13—5-Roller oven

Titration based on $FeCl_3$

We will use a new analytical method that is based on a $FeCl_3$ solution.

- Prepare the 0.1M standard solution ($FeCl_3$) by adding 27g of $FeCl.6H_2O$ to deionized water containing 1ml HCl, and dilute to 1L.
- Prepare the buffer solution (pH 3) and the tiron, which is the color indicator.
- Put 100 mL of distilled water in the beaker.

- Add 10 mL buffer, 1 mL tiron, and 1 mL of chelate.
- Put the beaker on the stirrer.
- Start to add $FeCl_3$ solution until reaching to the endpoint color.
- Subtract the initial volume of $FeCl_3$ from the final volume.
- Calculate the concentration from the formula below

$$\textbf{Conc.} = \frac{Conc.of\ FeCl_3 * MW\ of\ chelate * consumed\ vol.of FeCl_3}{10 * density\ of\ chelate}$$

Scanning electron microscope (SEM)

Scanning electron microscopy (SEM) is a type of electron microscopy, which is imaging the surface of sample by scanning it using a high-energy beam of electrons in a raster scan pattern. The interaction of electrons with the atoms that make up the sample will produce signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity **(Fig. 14).**

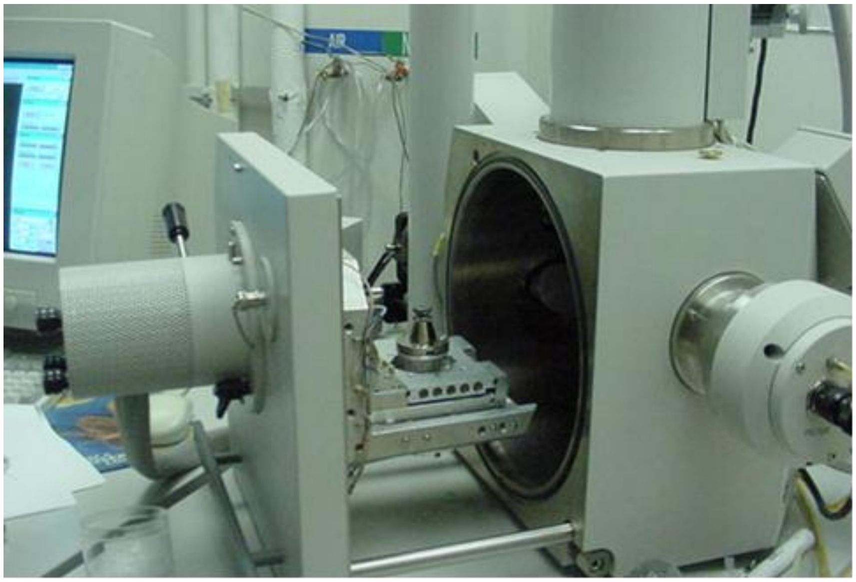


Figure 14—Mini SEM

Mass spectrometry (MS)

Thermal decomposition products were determined by comparing the results of solutions before and after heating. An MDS Sciex API QStar Pulsar with electrospray ionization (ESI) instrument was used in –ve mode. This method is qualitative and gives molecular weight over charges vs. intensity. The MDS Sciex API QStar Pulsar with Electrospray Ionization (ESI) is a hybrid quadrupole/time-of-flight instrument **(Fig. 15).**

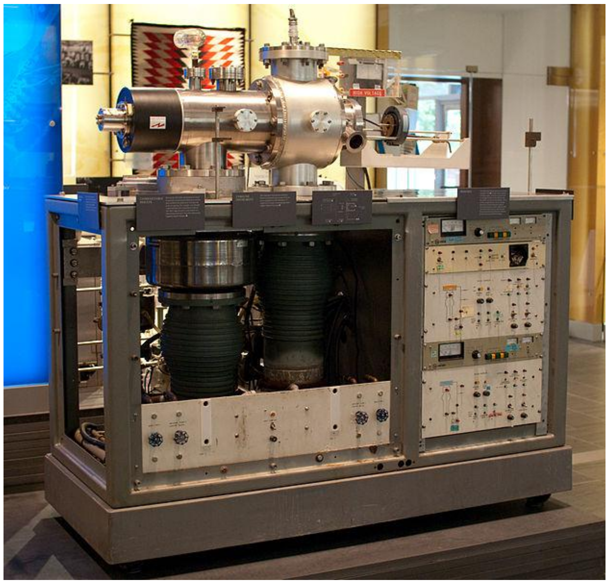


Figure 15—MS with electrospray ionization

3.3 Results and discussion

The purpose of this study is to measure the thermal stability of various chelates that are used in the oilfield, determine the thermal degradation products and their effect on the permeability of carbonate and sandstone cores, and improve the stability of chelates at high temperatures application.

Thermal stability of mono salts of GLDA, and HEDTA

The trend of stability vs. time for sodium salt of GLDA at 300, 350, and 400°F up to 12 hours is shown in **Fig. 16**. NaGLDA maintains its stability up to 80% at 300°F and 12 hours. As we increase the temperature to 350 & 400°F, there is a sharp drop in thermal stability of this chelate by time, where at 300°F, the decline trend is not clear. The thermal stability vs. time for NaKGLDA is demonstrated in **Fig. 17**. The degradation starts at 350°F and after 4 hours of heating. Thermal stability decreases comparing to 350°F as the temperature increases to 400°F, but the thermal stability difference between the two temperature ranges decrease with time. Thermal stability vs. time for NH_4GLDA also shows the decomposition trend starts at 350°F (**Fig. 18.**)

The thermal stability of NaHEDTA at 300 to 400°F is depicted in **Fig. 19.** NaHEDTA is highly stable (above 90%) up to 12 hours of heating at 300°F. The thermal stability of NaHEDTA sharply decreases by increasing the temperature to 350 and 400°F; however, this downward stability drift with NaHEDTA is less noticeable than NaGLDA. **Figs. 20, 21,** and **22** show the comparison of thermal stability of GLDA with HEDTA at 300, 350, and 400°F up to 12 hours, respectively. At 300°F, both chelates behave the same, except for the 12 hour period that NaHEDTA remains 20% more stable than NaGLDA. By going to 350°F, NaHEDTA has a higher thermal stability than GLDA after 4 and 6 hours of heating; however, for 12 hours of heating, NaGLDA is 5% more stable than NaHEDTA. At 400°F, NaHEDTA retains more thermally stable than NaGLDA up to 12 hours of heating. It should be noted that the difference between the thermal stability percentages decreases by time.

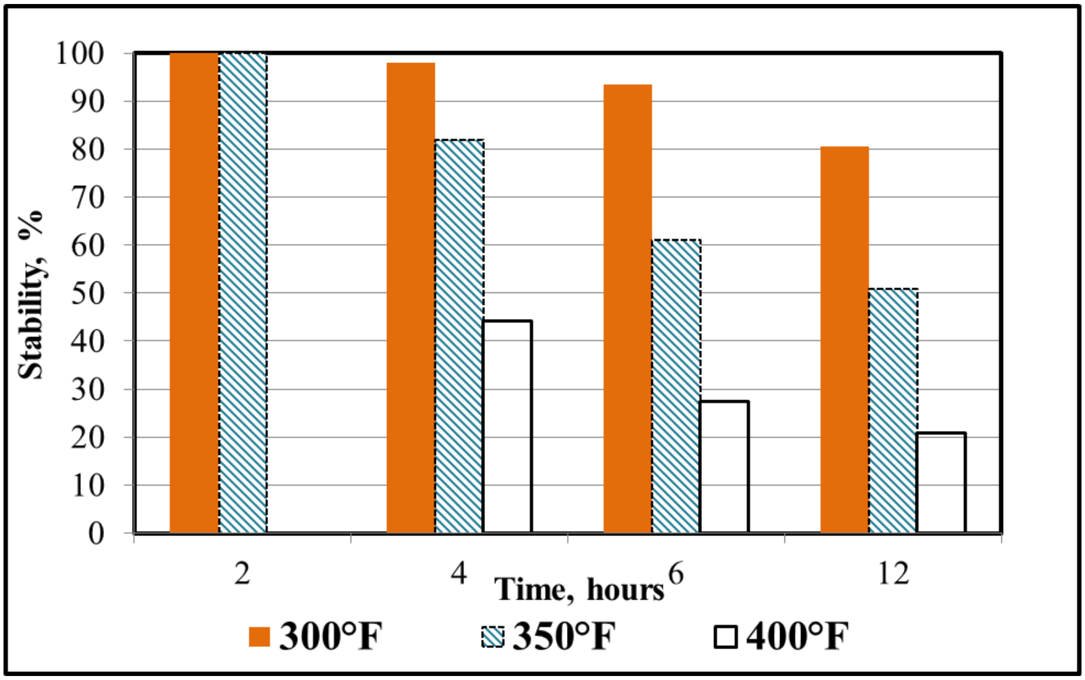


Figure 16—Thermal stability of NaH_3GLDA (pH 3.8) at 300 to 400°F up to 12 hours

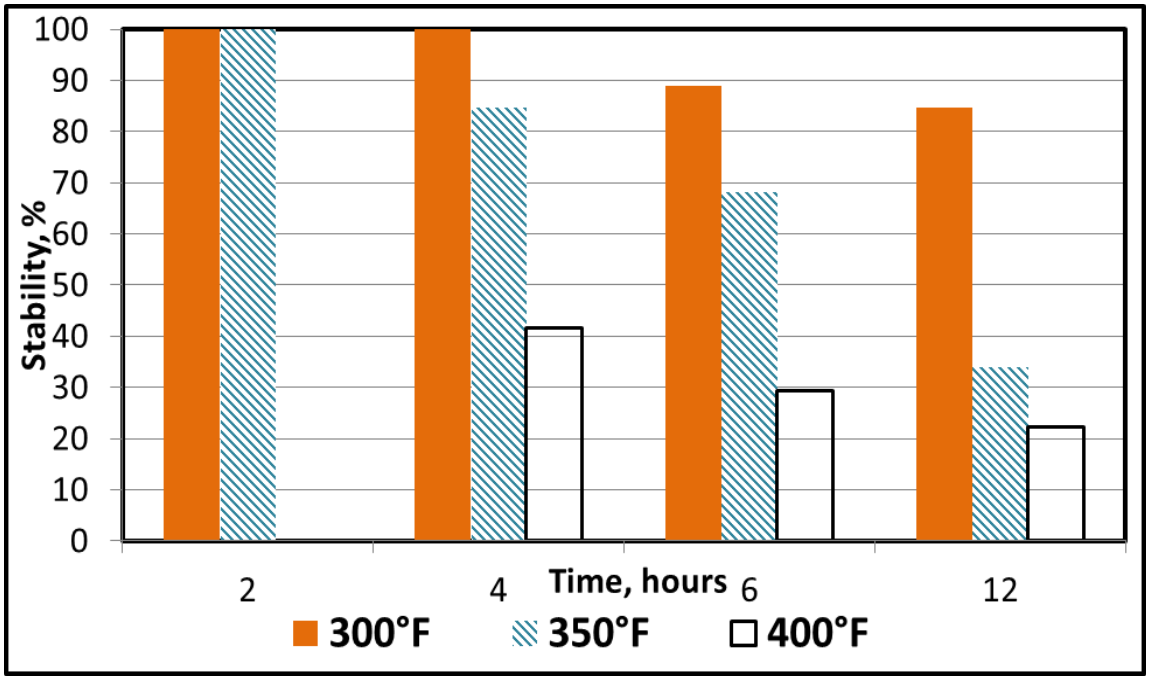


Figure 17—Thermal stability of $NaKH_2GLDA$ (pH 3.6) at 300 to 400°F up to 12 hours

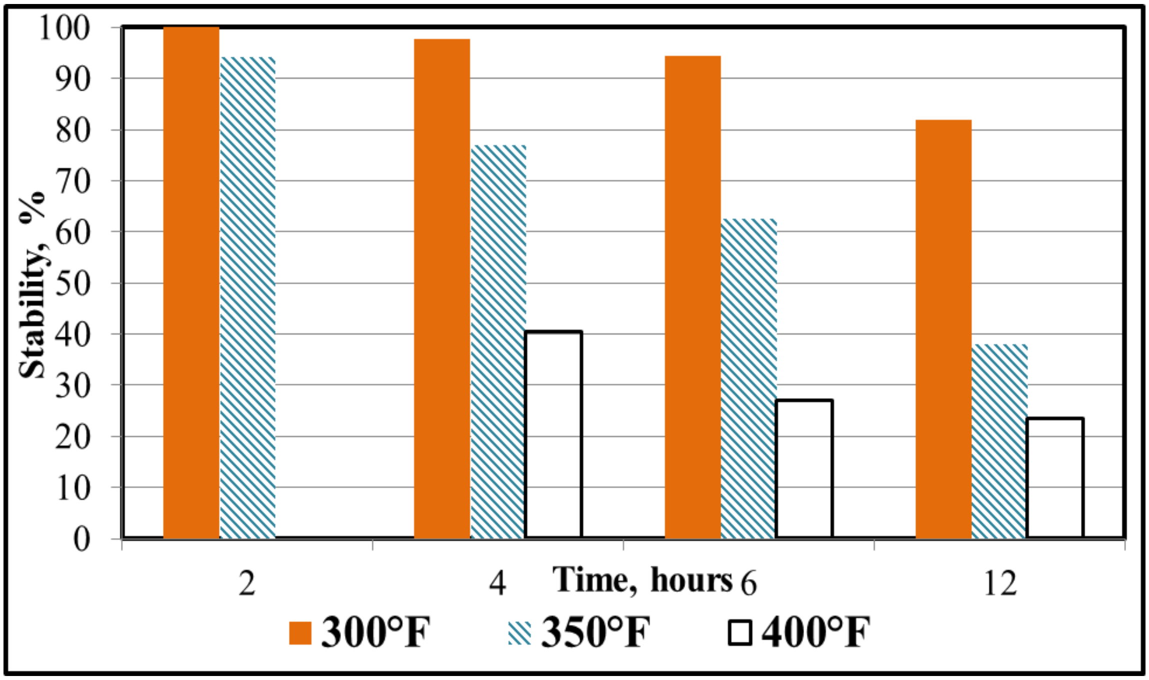


Figure 18—Thermal stability of NH_4H_3GLDA (pH 3.6) at 300 to 400°F up to 12 hours

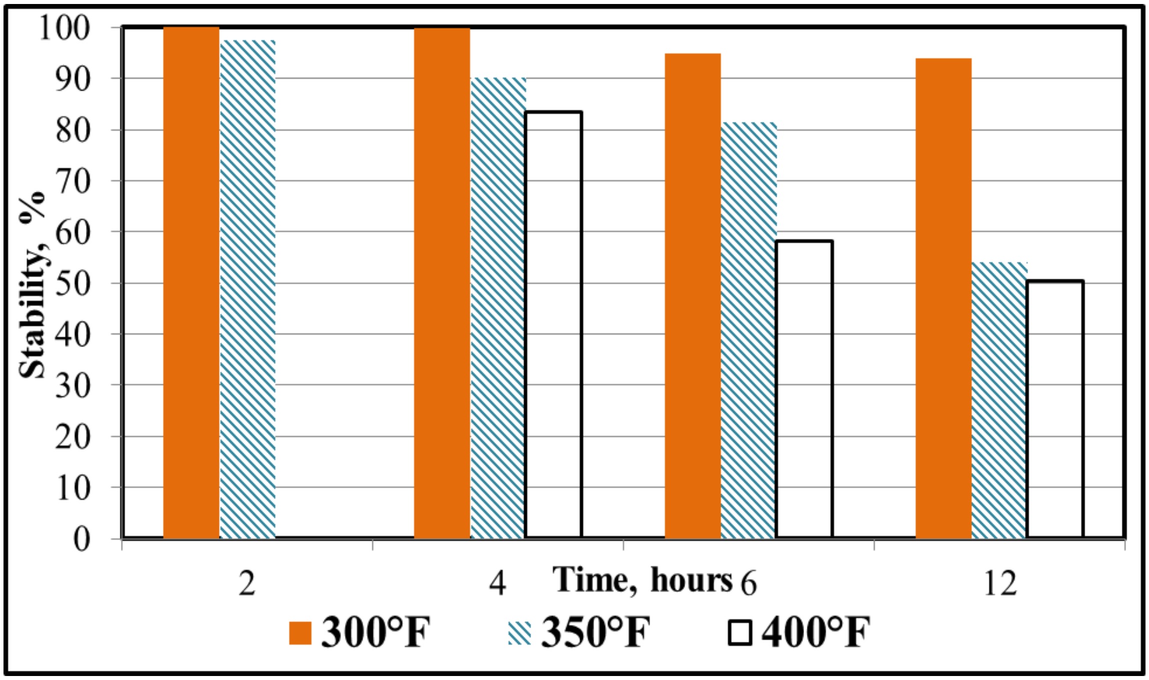


Figure 19—Thermal stability of NaH_2HEDTA (pH 3.9) at 300 to 400°F up to 12 hours

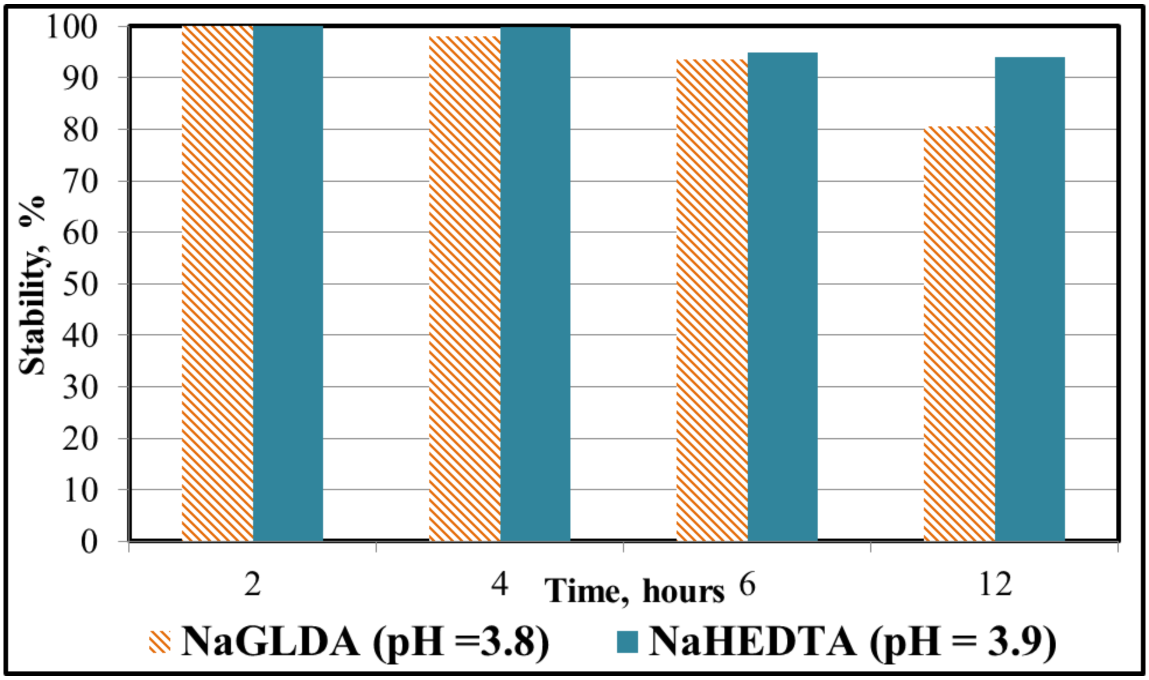


Figure 20—Comparison of thermal stability of NaH$_2$HEDTA (pH 3.9) with NaH$_3$GLDA at 300 up to 12 hours

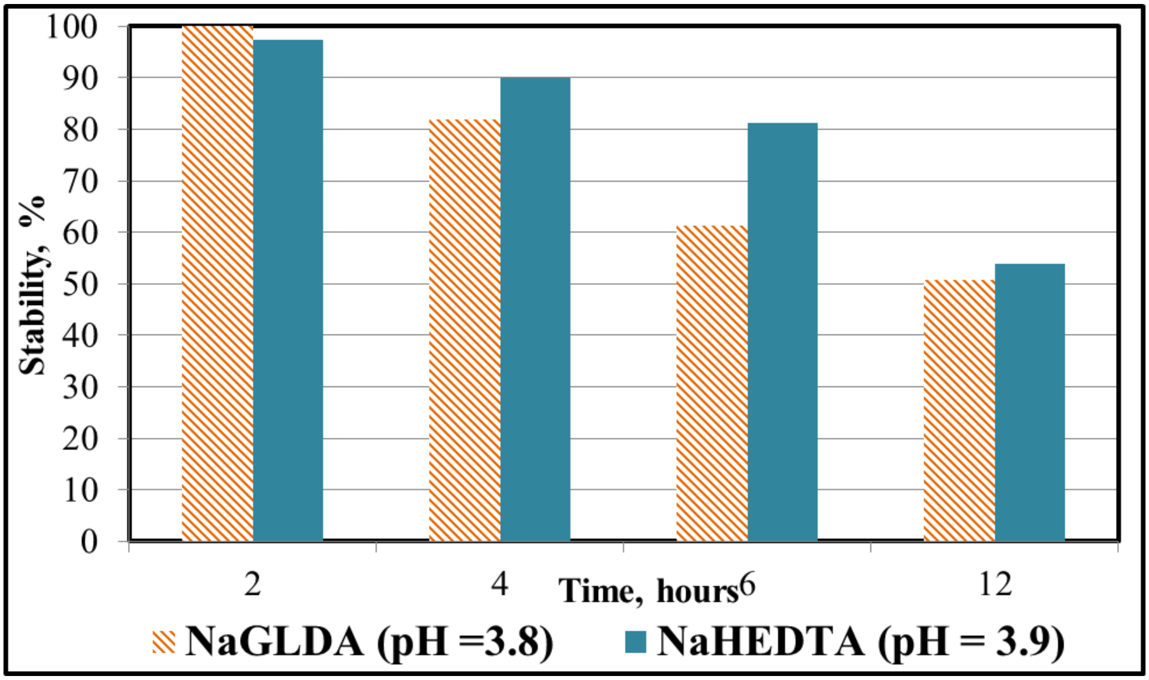


Figure 21—Comparison of thermal stability of NaH_2HEDTA (pH 3.9) with NaH_3GLDA at 350°F up to 12 hours

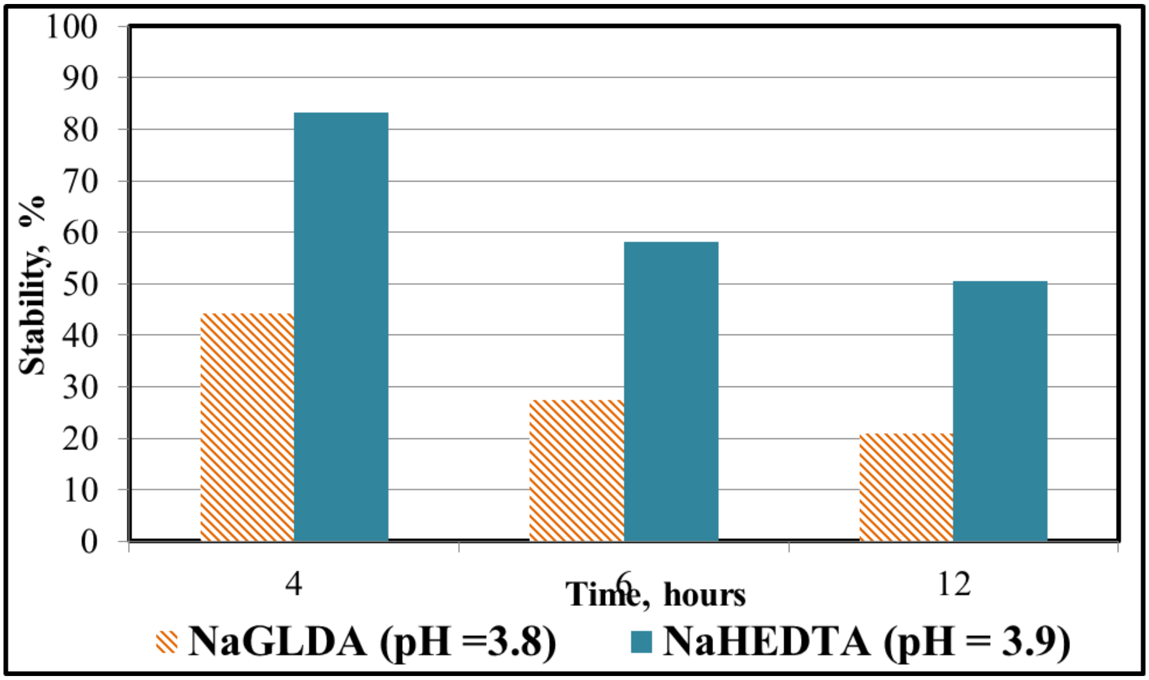


Figure 22—Comparison of thermal stability of NaH_2HEDTA (pH 3.9) with NaH_3GLDA at 400 up to 12 hours

Solid precipitates in the solution of chelates after heating

There are black solids dispersed in the chelate solutions immediately after heating or after passing some time. As these depositions may affect the permeability of formation, we need to analyze them. The black solids in the degraded chelate solutions of NH_4GLDA, NaKGLDA, and NaHEDTA are shown in **Figs. 23**, **24**, and **25** along with the pictures before heating, respectively. **Figs. 26**, **27**, and **28** are the SEM spectra of NH_4GLDA, NaKGLDA, and NaHEDTA, respectively. There is mainly carbon and oxygen that form the precipitates, which are shown in **Tables 6 through 8** for NH_4GLDA, NaKGLDA, and NaHEDTA, respectively. **Figs. 29**, **30**, and **31** are the SEM images of NH_4GLDA, NaKGLDA, and NaHEDTA. It should be noted that solid precipitates occur more with NH_4 salt of GLDA.

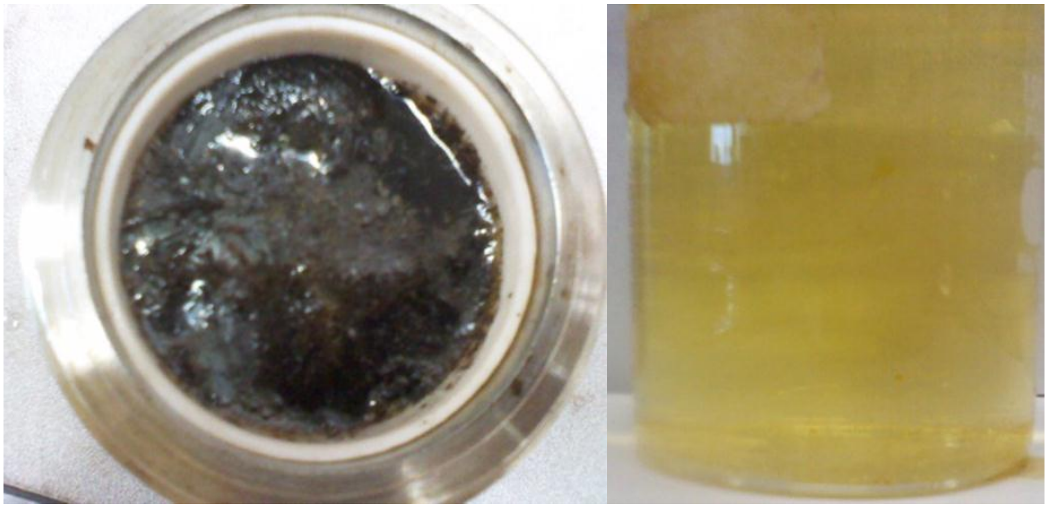


Figure 23— NH_4GLDA after heating at 400°F for 6 hours and before heating

Figure 24— NaKGLDA after heating at 400°F for 6 hours and before heating

Figure 25— NaHEDTA after heating at 400°F for 12 hours and before heating

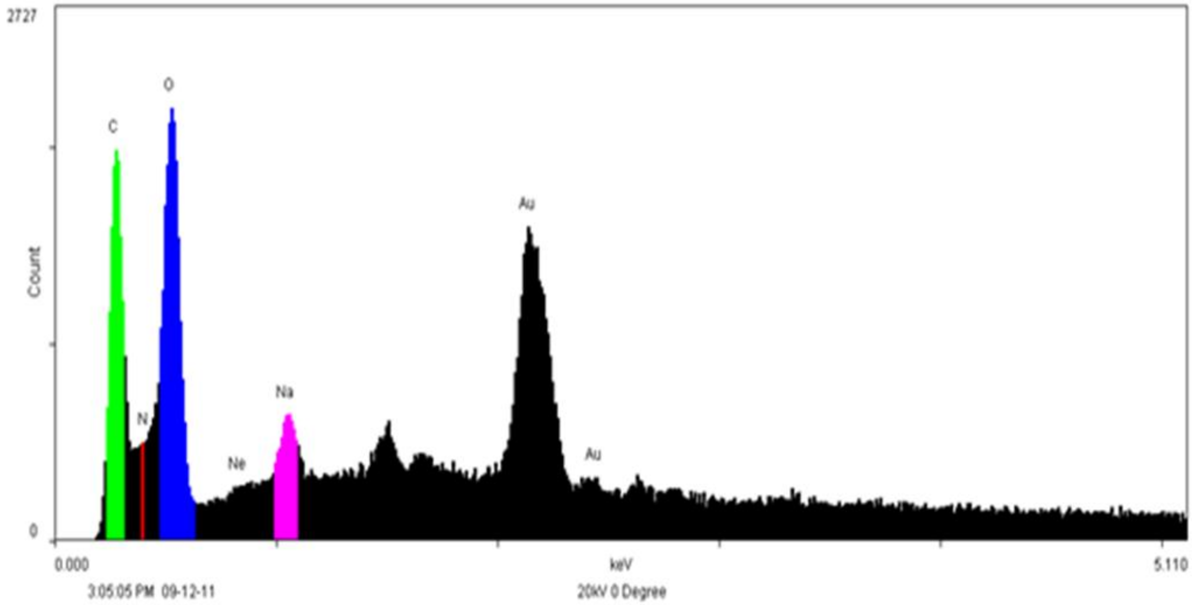


Fig. 26—SEM spectrum of solid precipitates in NH_4GLDA solution after heating for 6 hours at 400°F

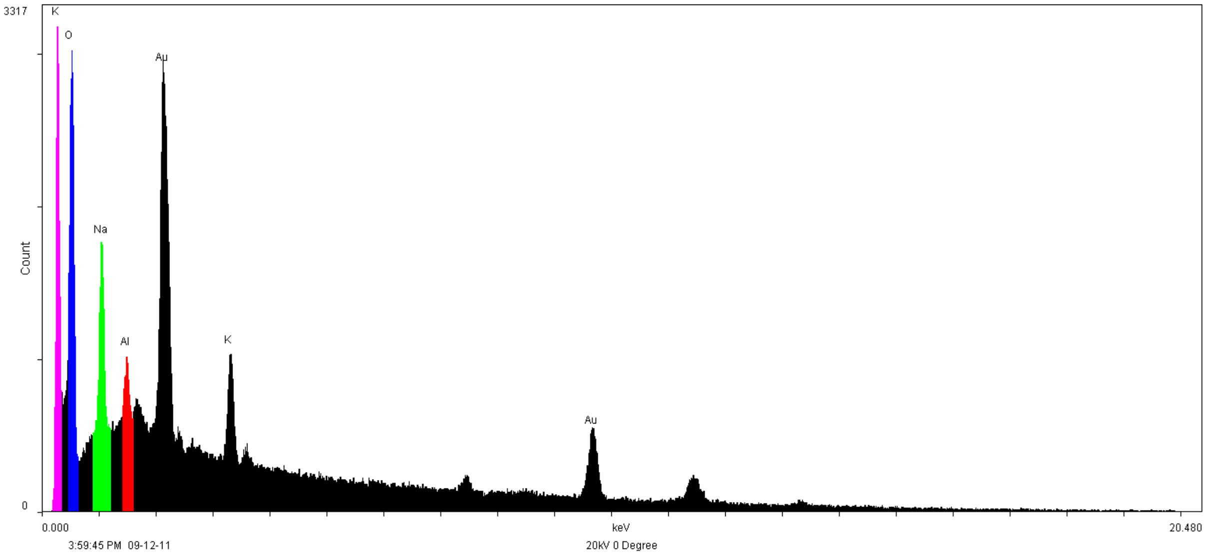


Fig. 27—SEM spectrum of solid precipitates in NaKGLDA solution after heating for 6 hours at 400°F

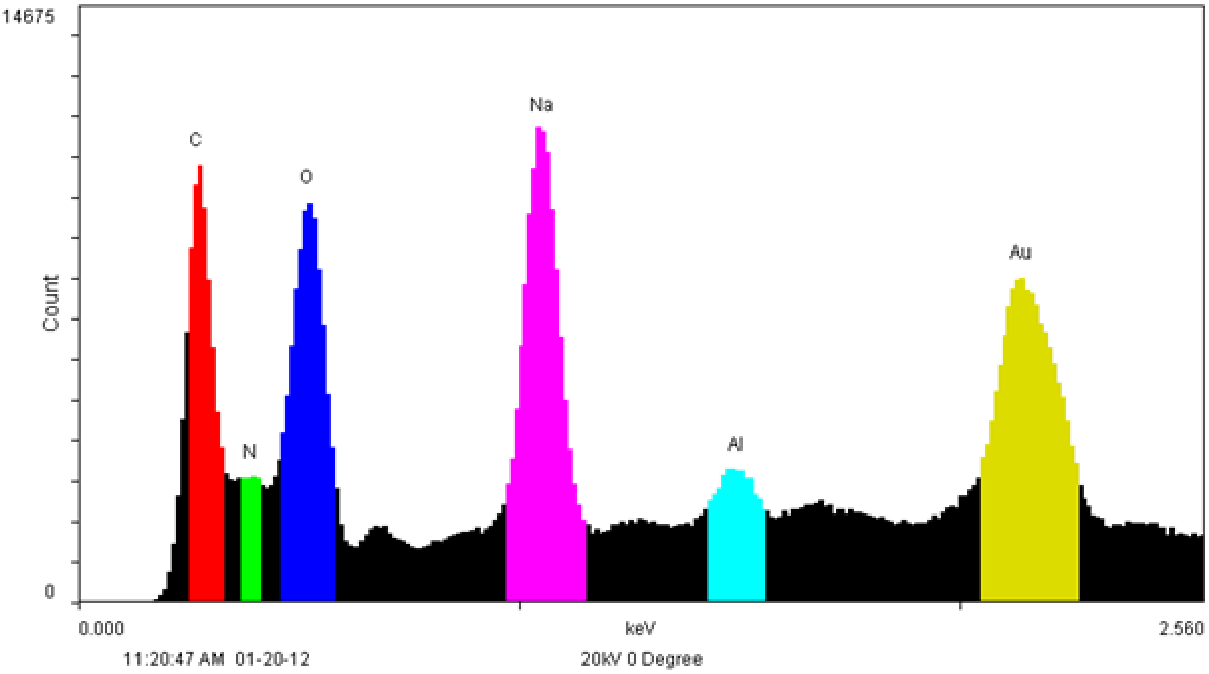


Fig. 28—SEM spectrum of solid precipitation dispersed in NaHEDTA after heating for 12 hours at 400°F

TABLE 6—ELEMENTS CONSISTING SOLID PRECIPITATION OF NH_4GLDA at 400°F AFTER 6 HOURS

Elements	Concentration, wt%
C	53.75
N	14.02
O	27.02
Na	1.13
Mg	0.1

TABLE 7—ELEMENTS CONSISTING SOLID PRECIPITATION OF NaKGLDA at 400°F AFTER 6 HOURS

Elements	Concentration,wt%
C	50.11
O	34.63
Na	2.77
K	0.53
Al	0.44

TABLE 8—ELEMENTS CONSISTING SOLID PRECIPITATION OF NaHEDTA at 400°F AFTER 12 HOURS

Elements	Concentration, wt%
C	31.2
N	14.9
O	42.9
Na	10.5
Al	0.6

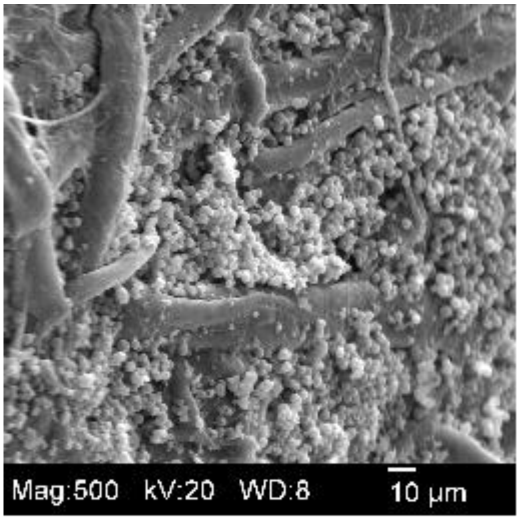


Fig. 29—SEM image of solid precipitates in NH_4GLDA solution after heating for 6 hours at 400°F

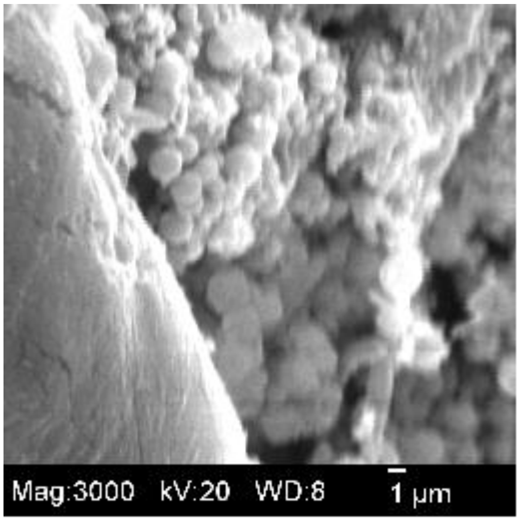


Fig. 30—SEM image of solid precipitates in NaKGLDA solution after heating for 6 hours at 400°F

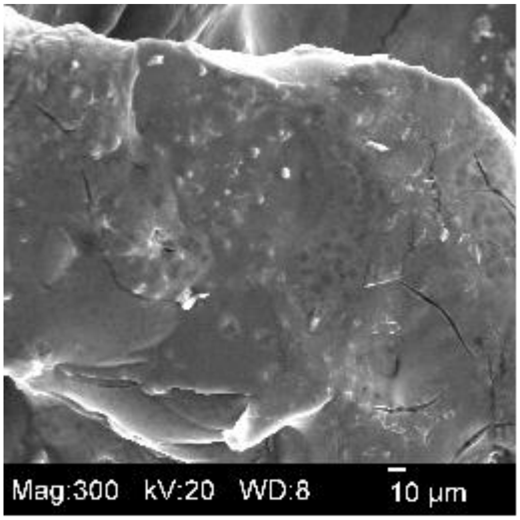


Fig. 31—SEM image of solid precipitates in NaHEDTA solution after heating for 12 hours at 400°F

Thermal stability of di-salts of GLDA, NTA, and EDTA

The thermal behavior graph of $(NH_4)_2$GLDA is shown in **Fig. 32**. It can be seen that this chelate remains 83% stable up to 12 hours at 300°F; however, by increasing the temperature to 350°F, a sudden decline in thermal stability trend by time is visible, until at 12 hours, there is just 36% of the chelate left. Rising the temperature from 350 to 400°F doesn't have a significant impact on the thermal stability of this chelate, since at 400°F after 12 hours of heating, the thermal stability is almost the same as at 350°F. The temperature effect on the thermal stability of $(NH_4)_2$EDTA is demonstrated in **Fig. 33** , and it is clear that the temperature rise doesn't affect the thermal stability of this chelate up to 4 hours of heating ,however, by going to 6 & 12 hours of heating, the thermal stability declines sharply. Na_2NTA has a high thermal stability since at 300 & 350°F up to 12 hours, it remains stable above 90%, and at 400°F the decreasing trend in thermal stability is barely noticeable (**Fig. 34**).

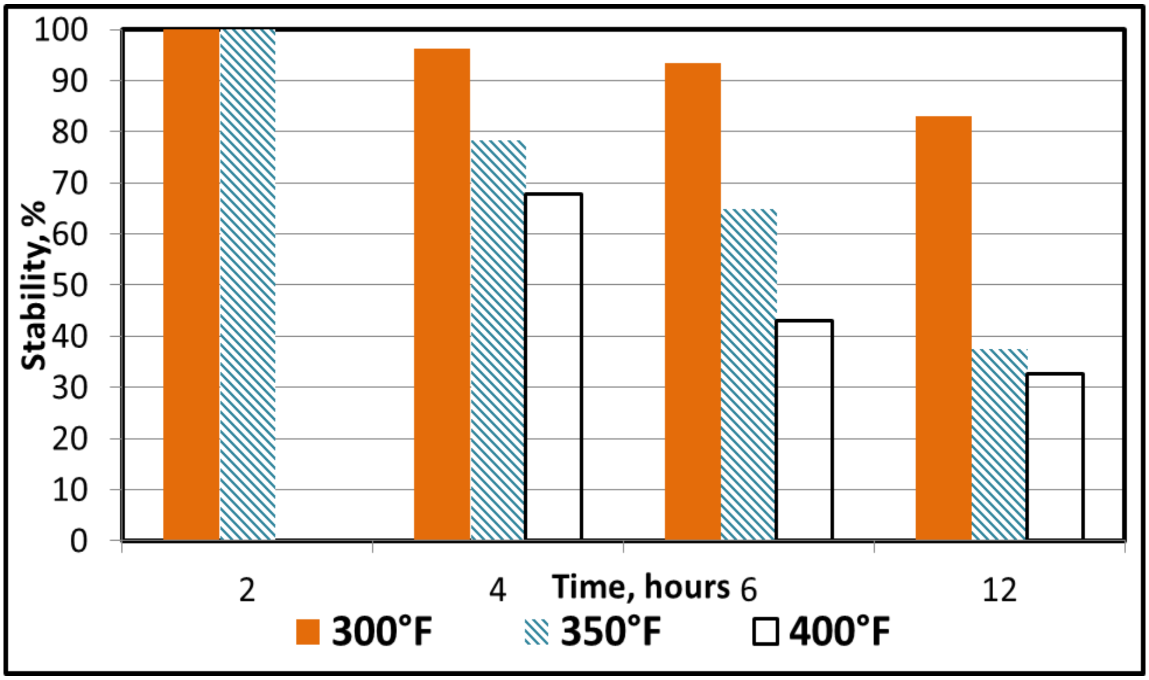


Figure 32—Thermal stability of $(NH_4)_2GLDA$ (pH 5.1) at 300 to 400°F up to 12 hours

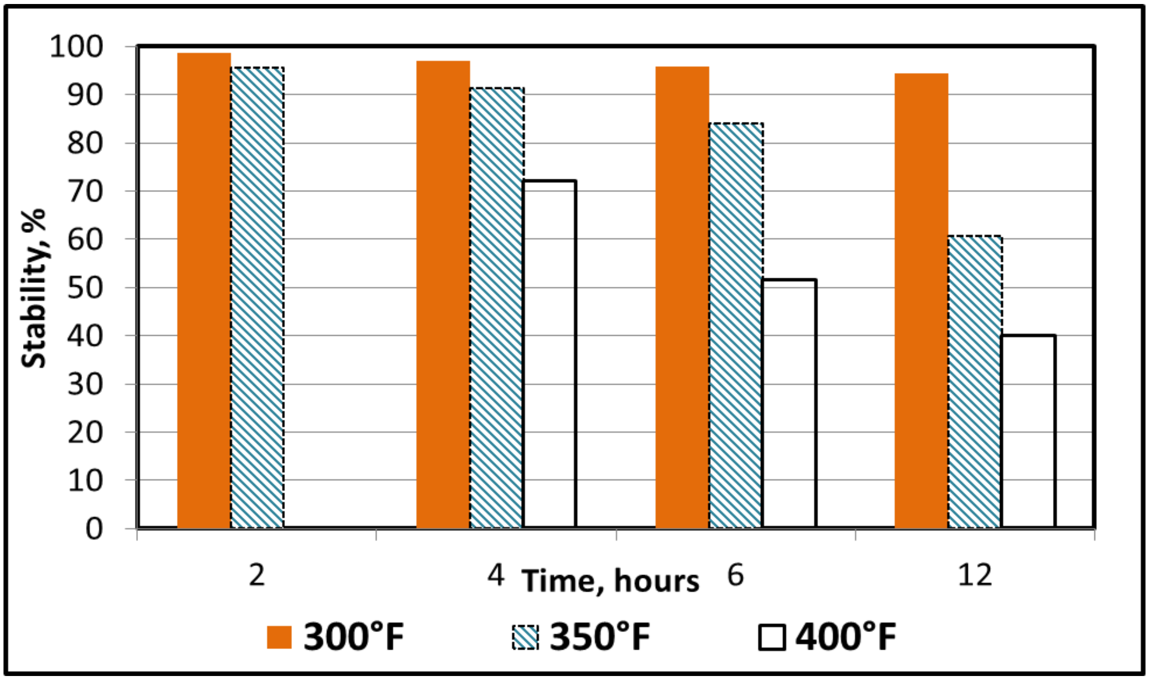


Figure 33—Thermal stability of $(NH_4)_2EDTA$ (pH 5.6) at 300 to 400°F up to 12 hours

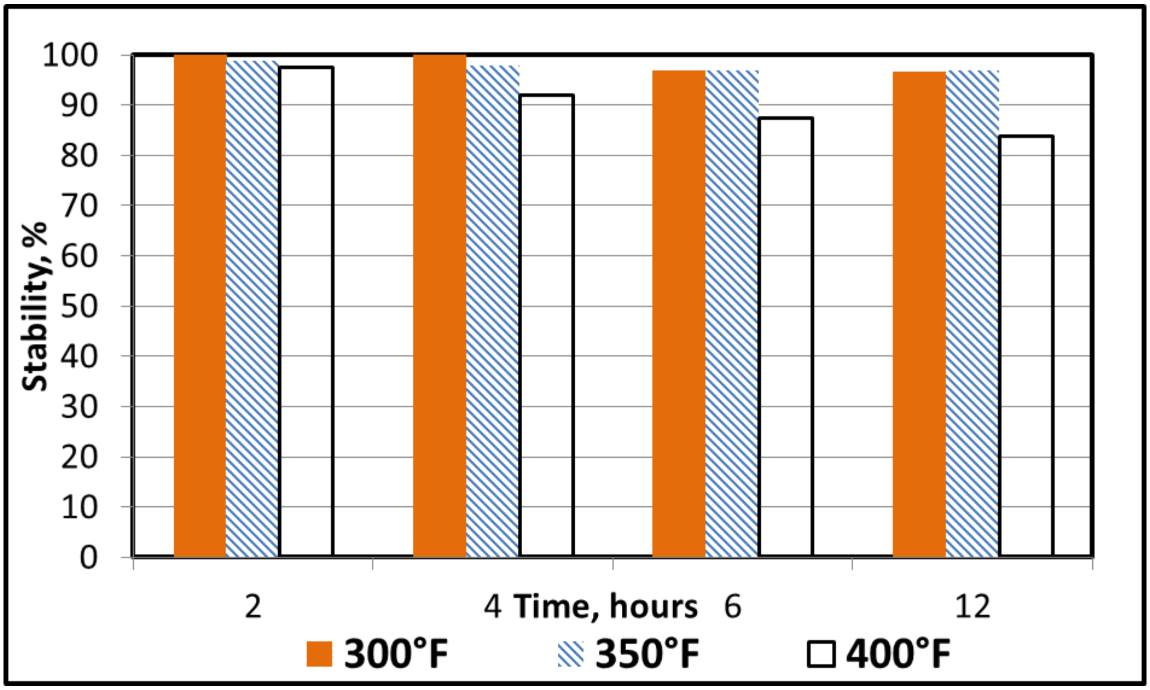


Figure 34—Thermal stability of Na_2NTA (pH 7.3) at 300 to 400°F up to 12 hours

Comparison of thermal behavior of diammonium salt of SALT GLDA with diammonium salt of EDTA

EDTA and GLDA both behave the same at 300°F up to 6 hours, but as it is shown in **Fig. 35**, after 12 hours of heating EDTA is 12% more stable. By increasing temperature to 350°F, higher thermal stability of EDTA is obvious from 4 hours in **Fig. 36.** Thermal stability of both chelates is demonstrated in **Fig. 37.** After observation of these results, we can conclude that EDTA that has two nitrogen atoms is more stable than GLDA with one nitrogen atom. Furthermore, the black precipitates are only associated with GLDA, which can be seen in **Fig. 38**.

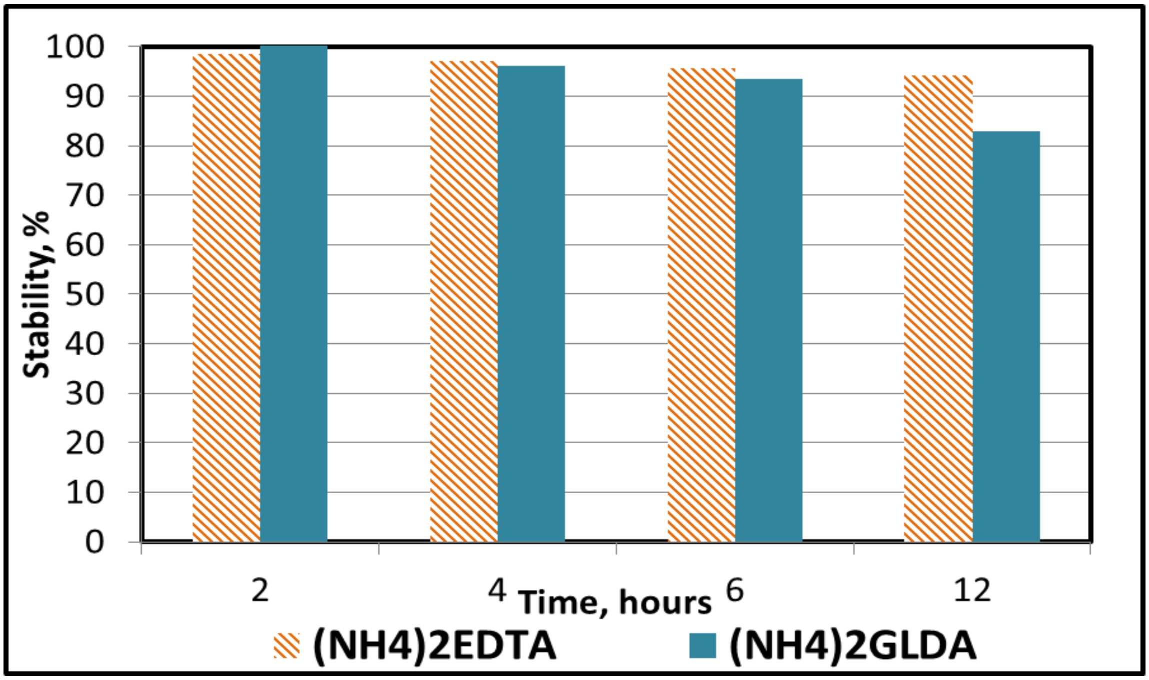


Figure 35—Thermal behavior of $(NH_4)_2$EDTA and $(NH_4)_2$GLDA at 300°F up to 12 hours

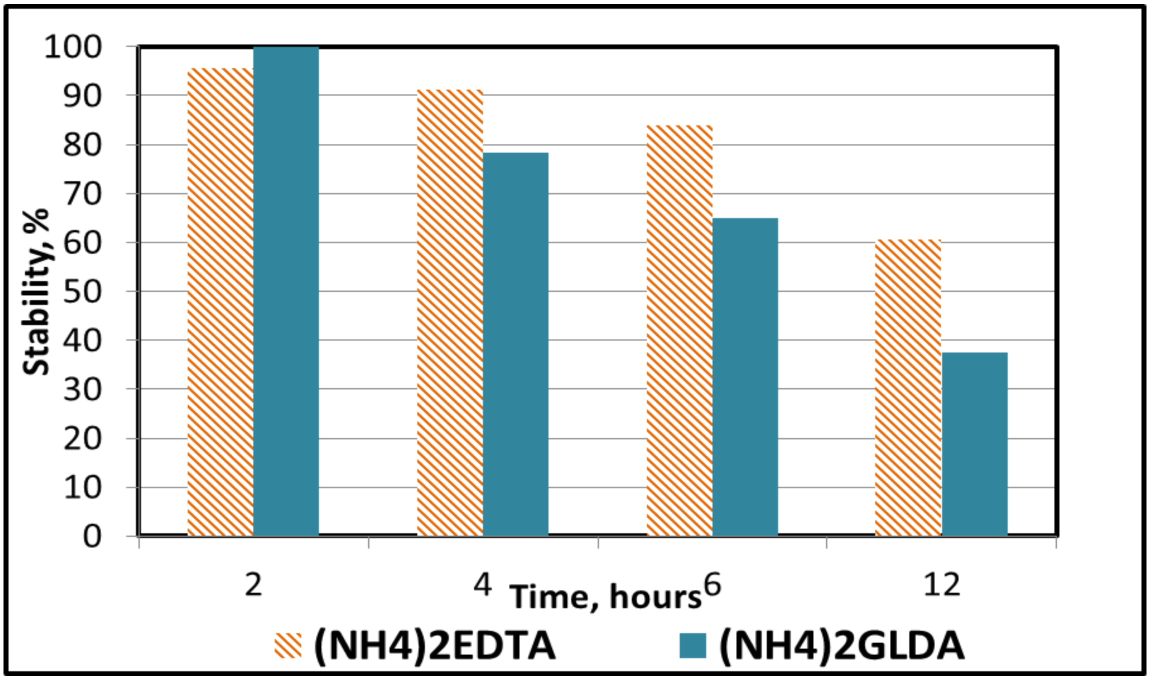


Figure 36—Thermal behavior of $(NH_4)_2$EDTA and $(NH_4)_2$GLDA at 350°F up to 12 hours

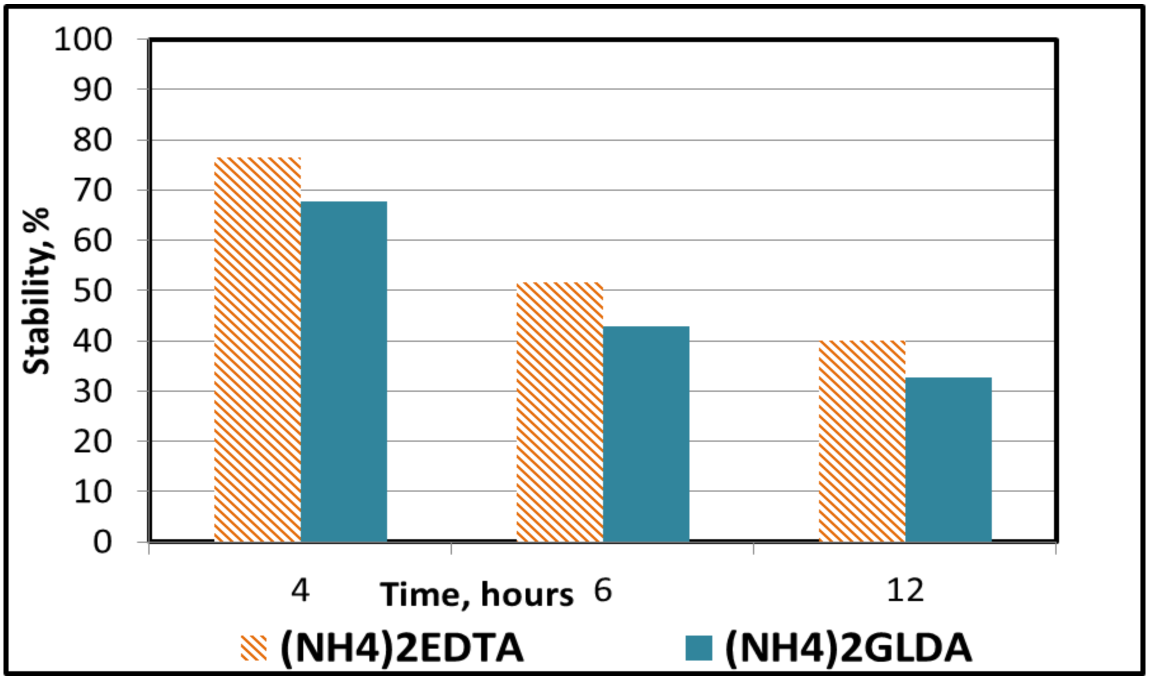


Figure 37—Thermal behavior of $(NH_4)_2$EDTA and $(NH_4)_2$GLDA at 400°F up to 12 hours

Figure 38—Black precipitates dispersed in the solution of $(NH_4)_2$GLDA after heating at 400°F for 6 hours

Effect of pH on thermal stability of GLDA, HEDTA, and EDTA

We increased the pH of NH_4GLDA that was provided from AkzoNobel by adding NH_4OH based on the following calculation to investigate the impact of pH on stability. The original concentration of NH_4GLDA is 39.7 wt%, and we obtained the number of moles from dividing it by its molecular weight (280.2 g/mole). We need to add the exact mole of NH_4OH to have $(NH_4)_2$GLDA at the end.

Number of moles in 39.7 wt% of NH_4GLDA = 39.7/280.2 = 0.142 mole. Thus, we need exactly 0.142 mole of NH_4OH. Thermal stability percent enhancement is less noticeable in a longer period of heating, which means that even the disalt of GLDA can't stand high temperature for a long time, as can be seen in **Fig. 39 a and b**.

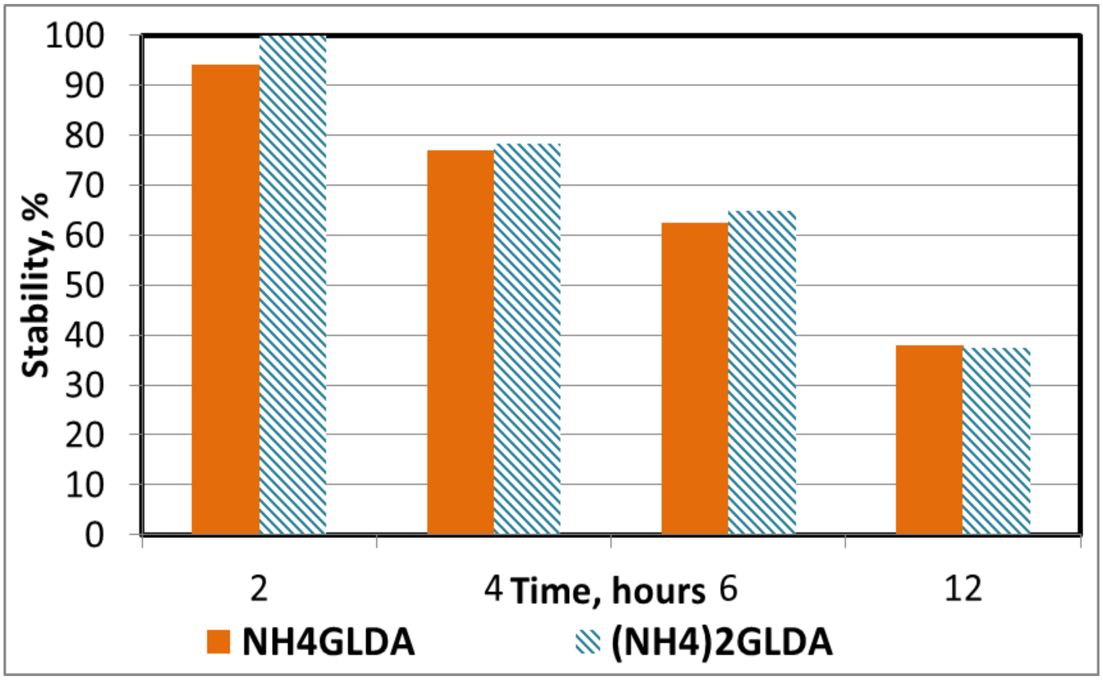


Figure 39 a—Comparison of thermal stability of NH_4GLDAwith $(NH_4)_2$GLDA at 350°F up to 12 hours

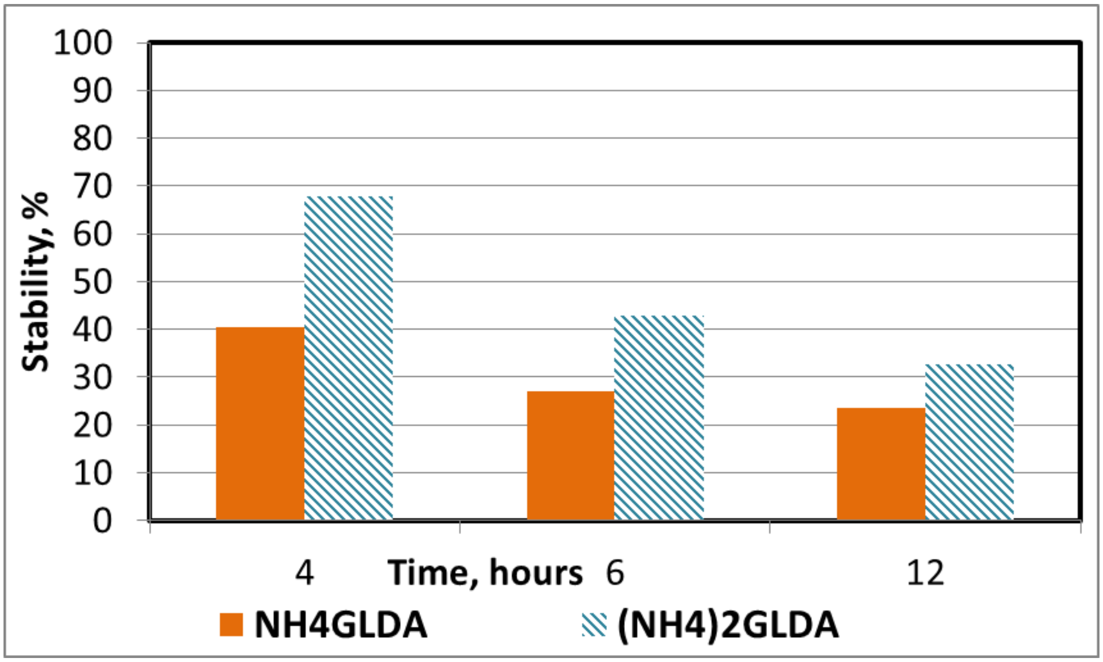


Figure 39 b—Comparison of thermal stability of NH_4GLDAwith $(NH_4)_2$GLDA at 400°F up to 12 hours

Solutions of NH_4GLDA with different pH

The chelate solutions with pH of 3.6, 4, and 8 were heated at 300°F and the stability vs. time is shown in **Fig. 40.** As with almost all other chelates at 300°F that they are stable, the effect of pH is not noticeable. However, when the temperature goes up to 350 and 400°F, GLDA with pH 8 is more stable than those two with pH around 4 **(Figs. 41 & 42).** It should be noted that like other chelates, the thermal stability difference between chelates with different pH decreases by increasing time and temperature.

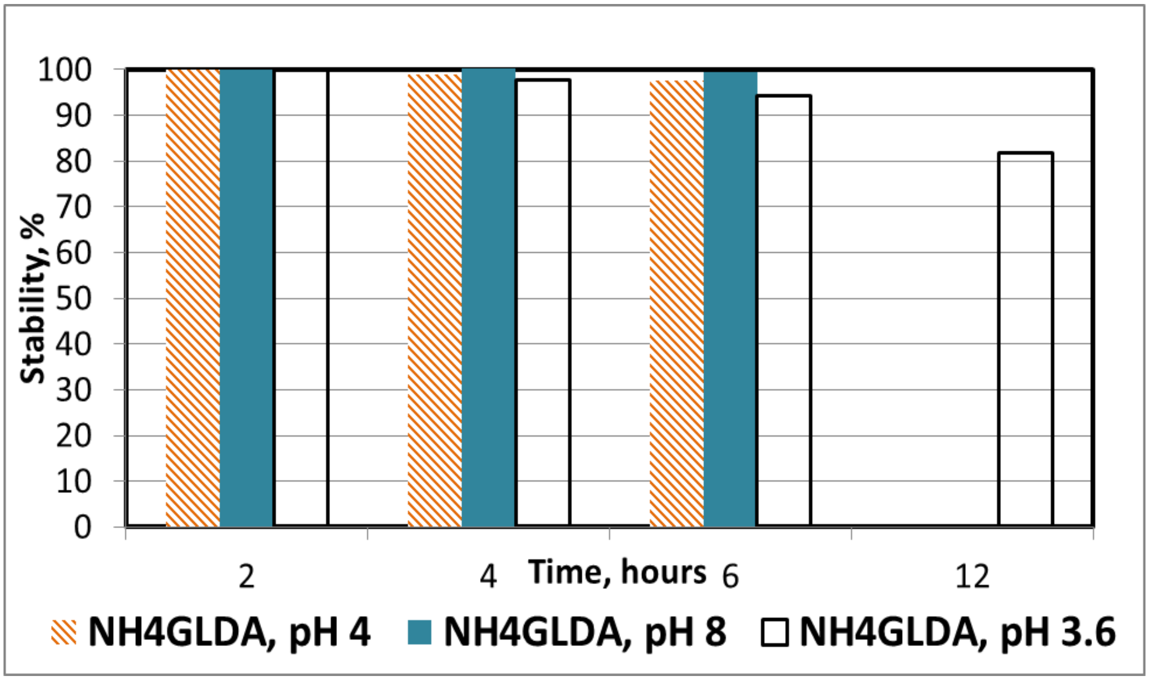


Figure 40—Thermal stability of NH4GLDA solutions with three different pH at 300°F up to 12 hours

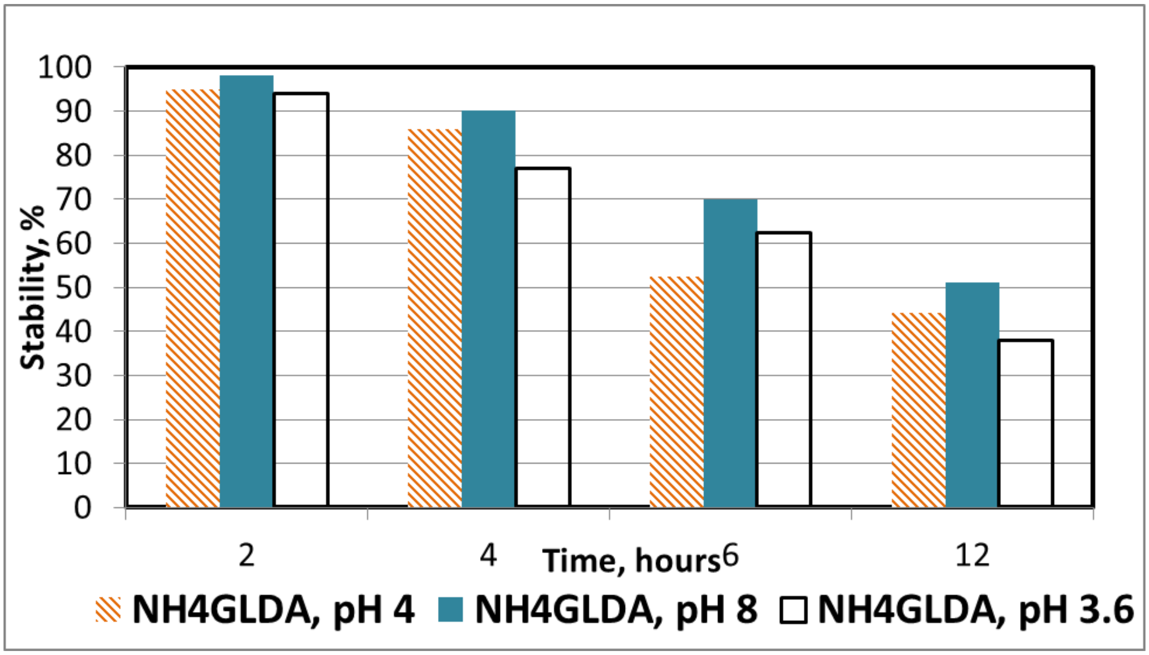


Figure 41—Thermal stability of NH4GLDA solutions with three different pH at 350°F up to 12 hours

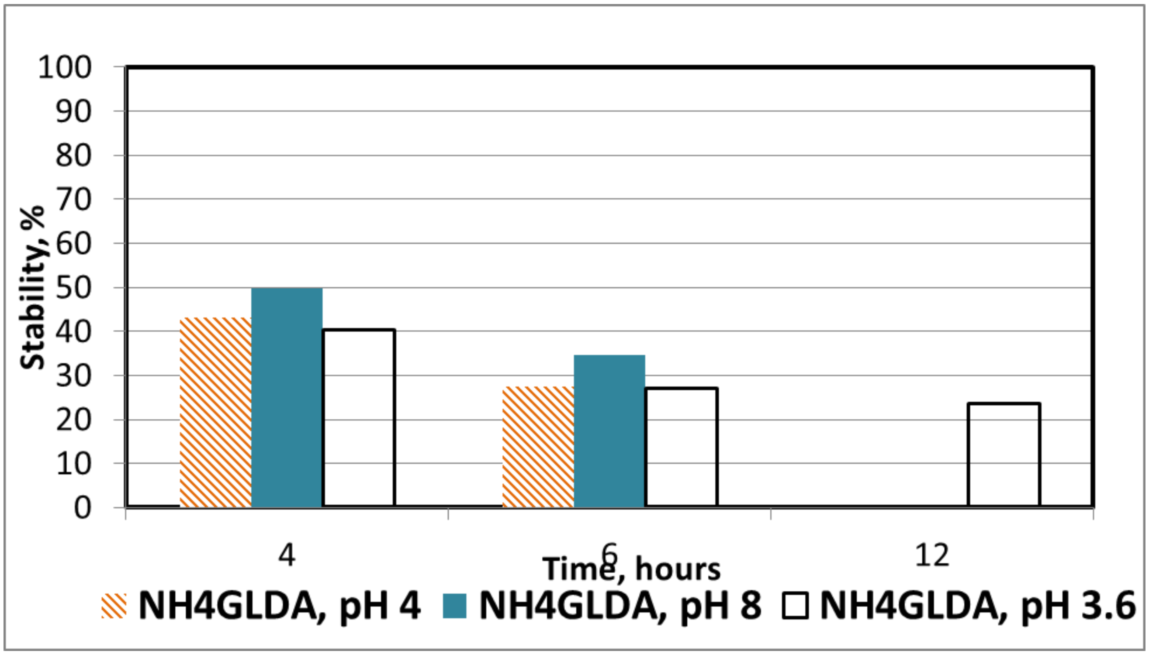


Figure 42—Thermal stability of NH4GLDA solutions with three different pH at 400°F up to 12 hours

Raising the pH of HEDTA from 3.9 to 13 improves the thermal stability significantly. Na_3HEDTA with pH 13 remains almost 100% stable at 300 to 400°F up to 12 hours. The results can be seen in **Fig. 43**. Resonance stabilization may be the cause of higher stability with high pH chelates. At 350 and 400°F, as the stability of low pH HEDTA decreased by time, the high pH HEDTA remains almost 100% stable, which is depicted in **Figs. 44 and 45**.

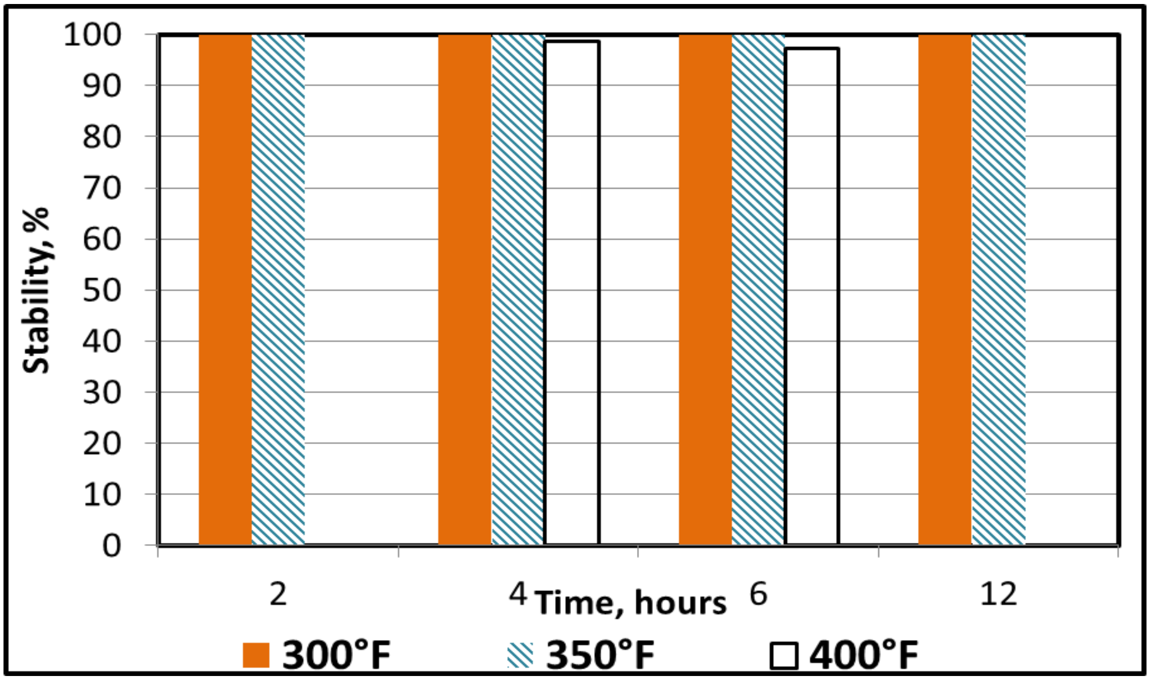


Figure 43—Thermal stability of Na_3HEDTA at 300 to 400°F up to 12 hours

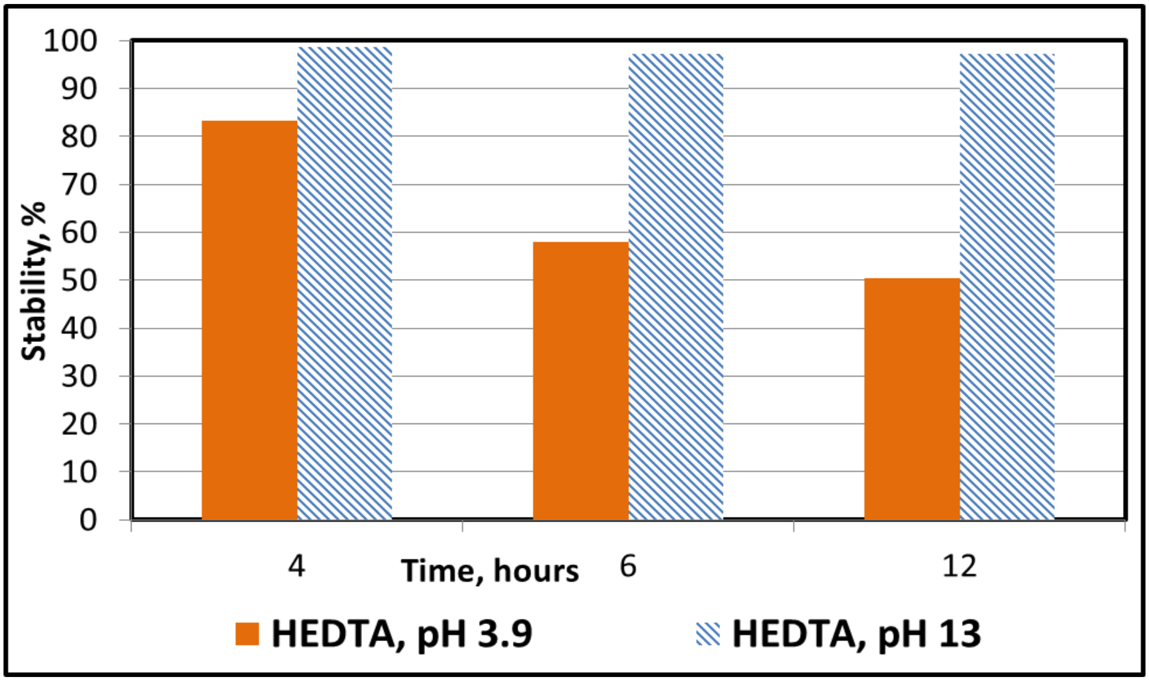


Figure 44—Comparison of thermal stability of Na_3HEDTA with NaHEDTA, pH 3.9 at 350°F up to 12 hours

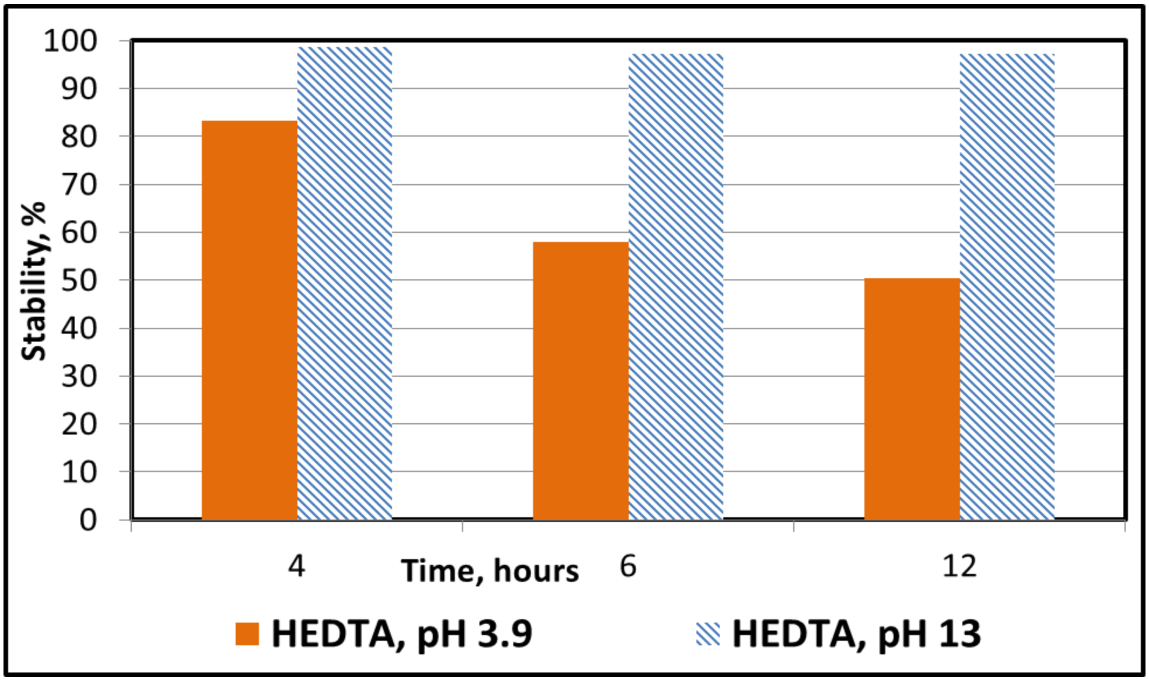


Figure 45—Comparison of thermal stability of Na_3HEDTA with NaHEDTA, pH 3.9 at 400°F up to 12 hours

The Effect of pH on thermal stability for GLDA (pH 3.8) that its stability decreases greatly by time at 350 and 400°F is shown in **Figs. 43 and 44**, respectively.

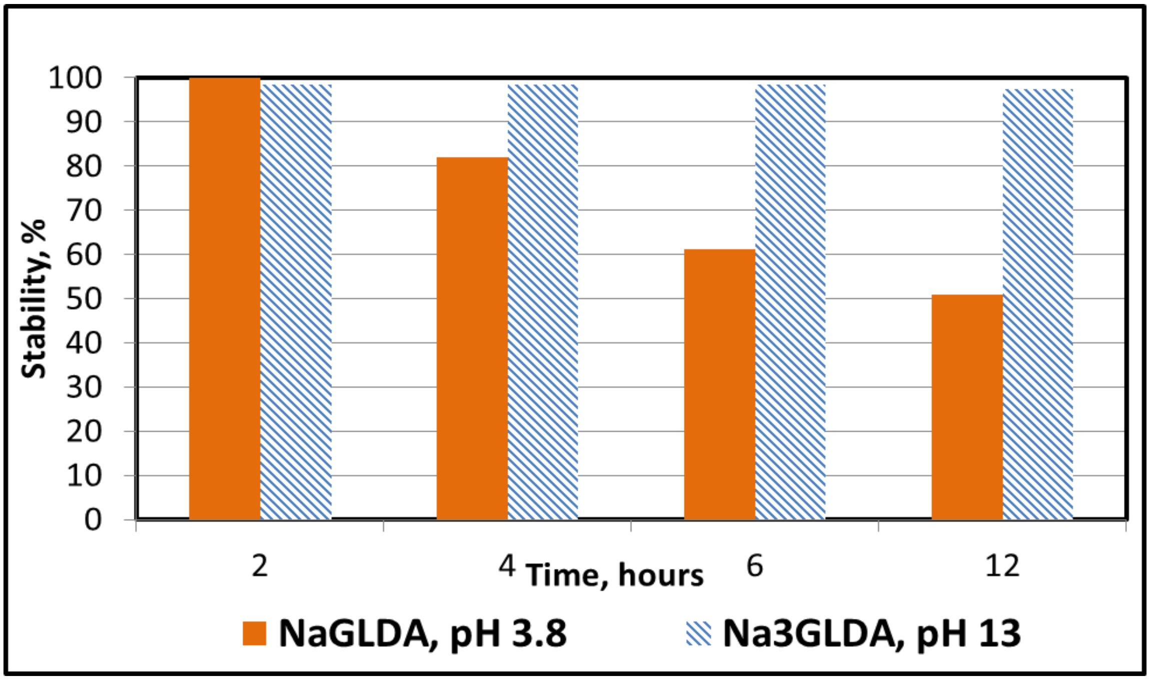


Figure 46—Comparison of thermal stability of Na_3GLDA with NaGLDA, pH 3.9 at 350°F up to 12 hours

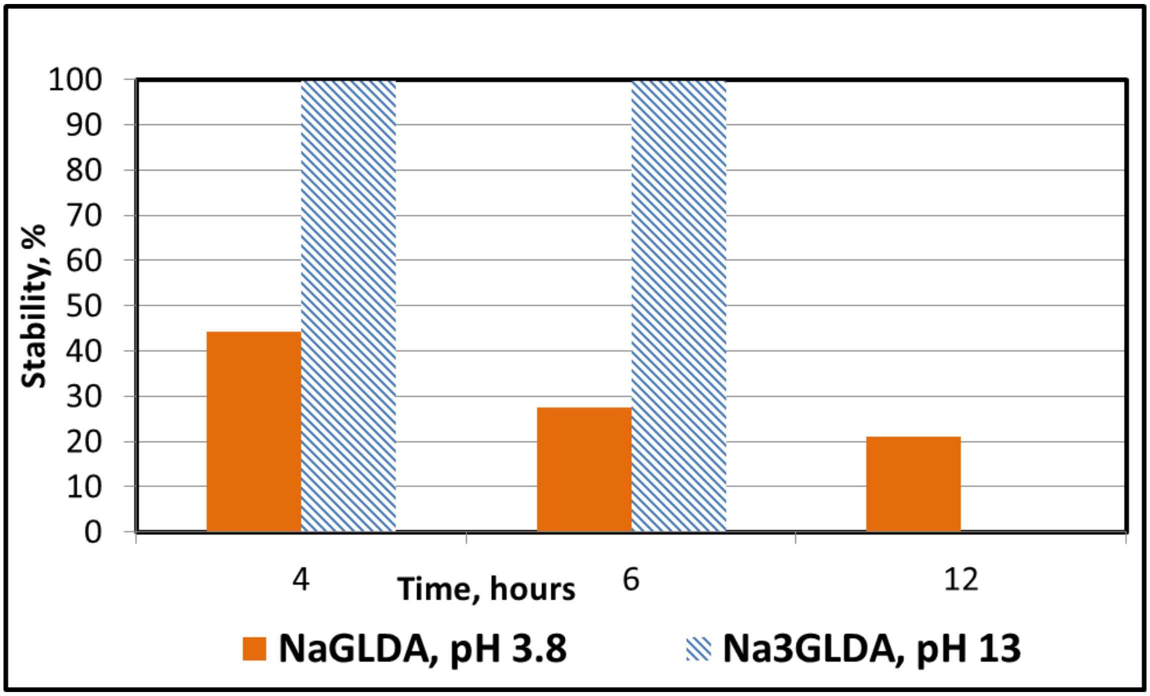


Figure 47—Comparison of thermal stability of Na_3GLDA with NaGLDA, pH 3.9 at 400°F up to 12 hours

Thermal behavior of di and triammonium salts of EDTA

DiammoniumEDTA at 300°F is above 90% stable, however, it starts to decompose at 350°F. Furthermore, triammoniumEDTA remains more stable in addition to precipitating less after heating, as can be seen in **Figs. 45 and 46**, respectively. Thermal stability percent improvement decreases by time. This latter may imply that the thermal degradation products will degrade sooner too.

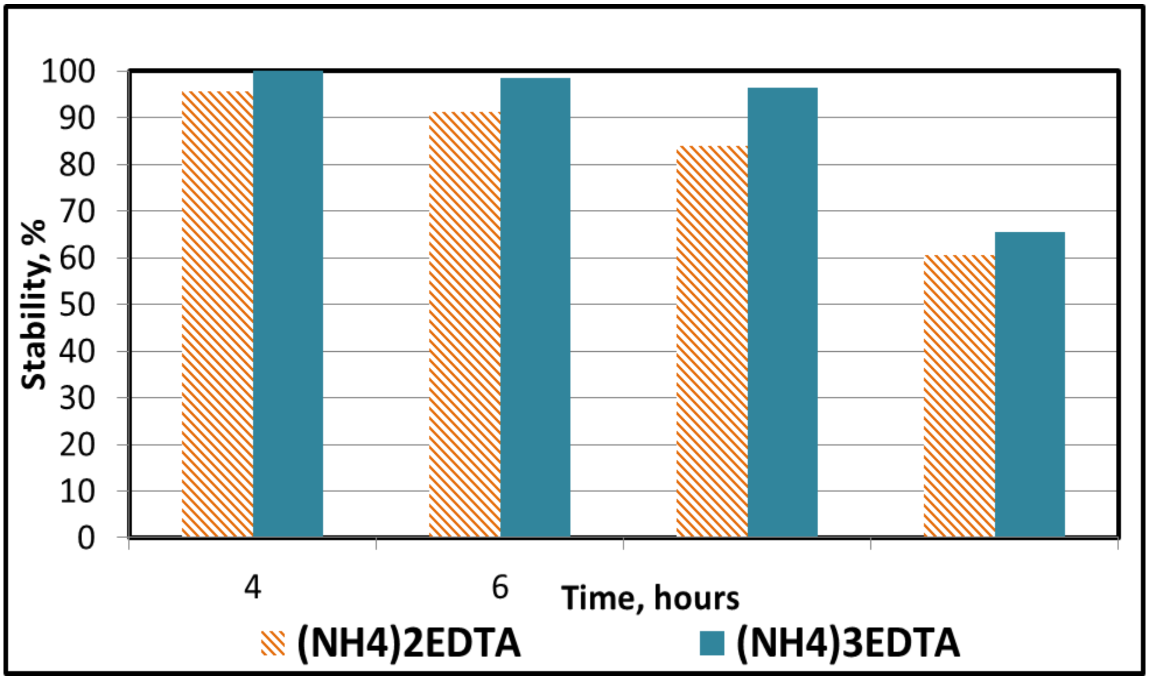


Figure 48—Thermal behavior of $(NH_4)_2EDTA$ and $(NH_4)_3EDTA$ at 350°F up to 12 hours

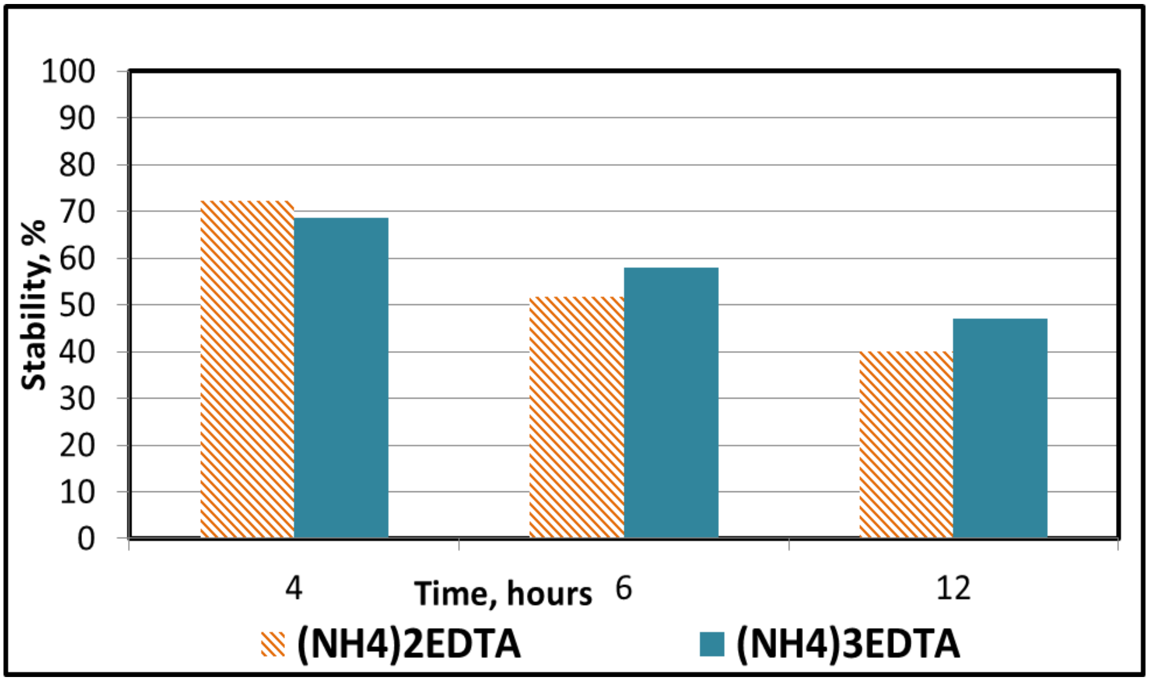


Figure 49—Thermal behavior of $(NH_4)_2$EDTA and $(NH_4)_3$EDTA at 400°F up to 12 hours

Thermal degradation products of NH_4GLDA at 400°F after 6 hours

There were some solid precipitates in the solution of NH_4GLDA after heating, which we ran SEM on, and the results were shown in previous sections. After filtration of the GLDA solution, we ran SEM in –VE mode, and since the molecule is not large enough, the atoms are not far enough from each other to be charged with more than one. Each molecule needs to lose one atom to be charged negatively so m/z of 59, actually corresponds to the molecular weight of 60, which is acetic acid. The MS method that we used is qualitative. **Figs. 50 and 51** show the results of MS in the range of 10 to 100 m/z for the GLDA before and after heating, respectively. The results of range 100 to 500 m/z can be seen in **Figs. 52 and 53** before and after heating, respectively. It's clear from the results the decomposition products also exist in the solution before heat too, but in a lower intensity. The latter may mean that chelates undergo some degree of degradation at room temperature or it may be due to impurities in their manufacturing formula.

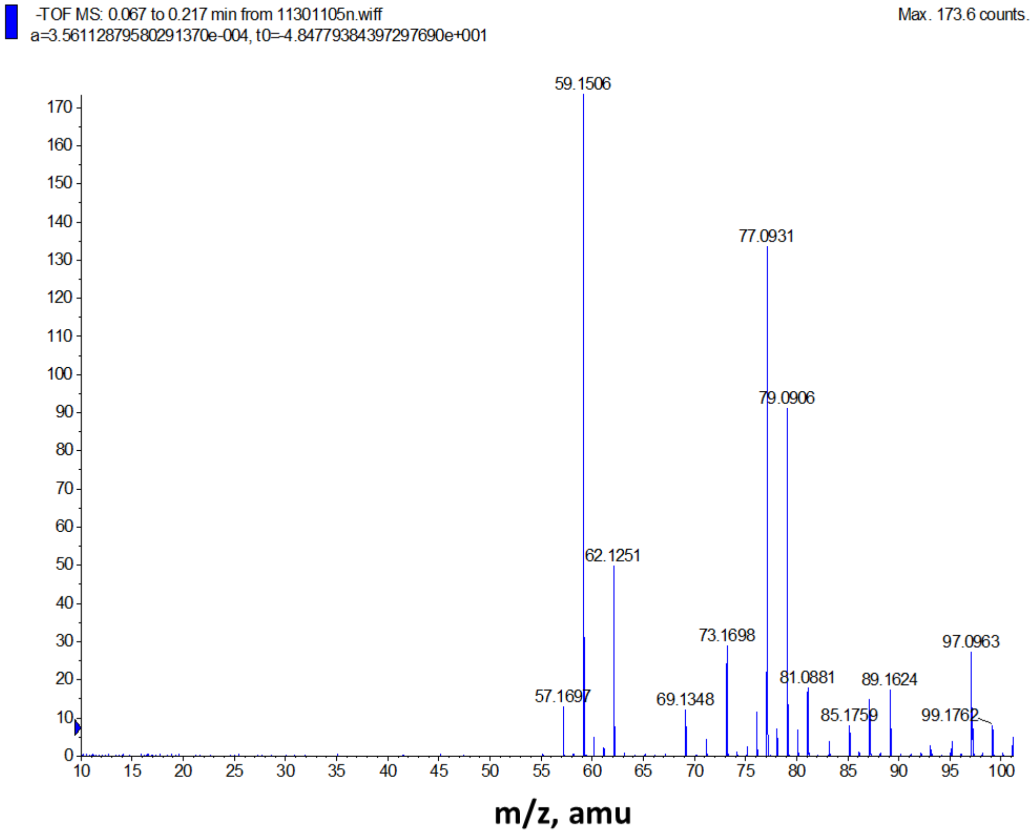


Figure 50—MS spectrum of 20 wt% NH4GLDA before heating- 10 to 100 m/z

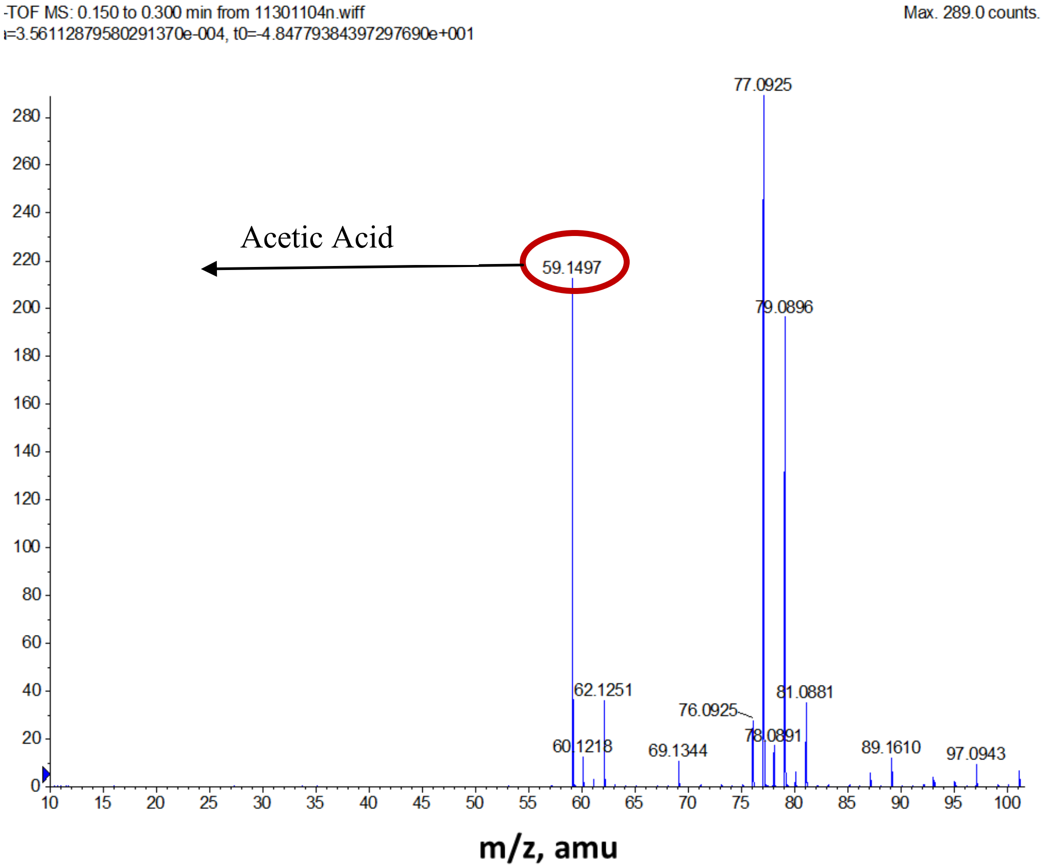


Figure 51—MS spectrum of 20 wt% NH4GLDA after heating- 10 to 100 m/z

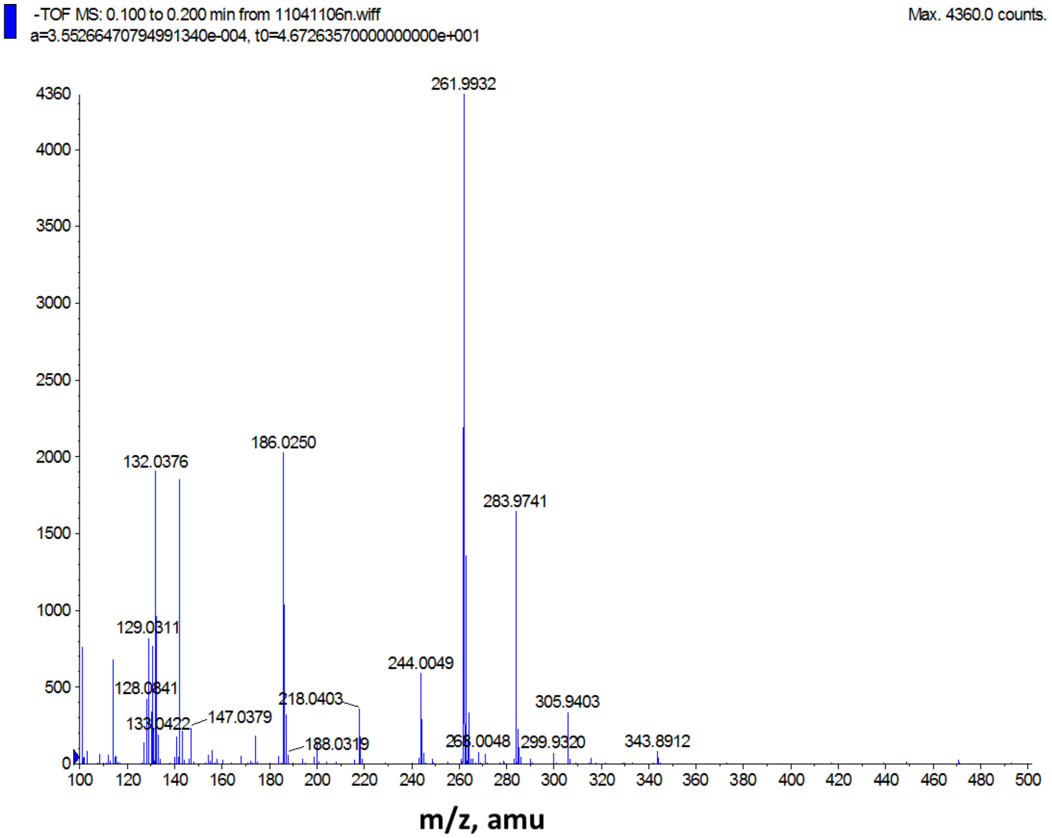


Figure 52—MS spectrum of 20 wt% NH4GLDA before heating- 100 to 500 m/z

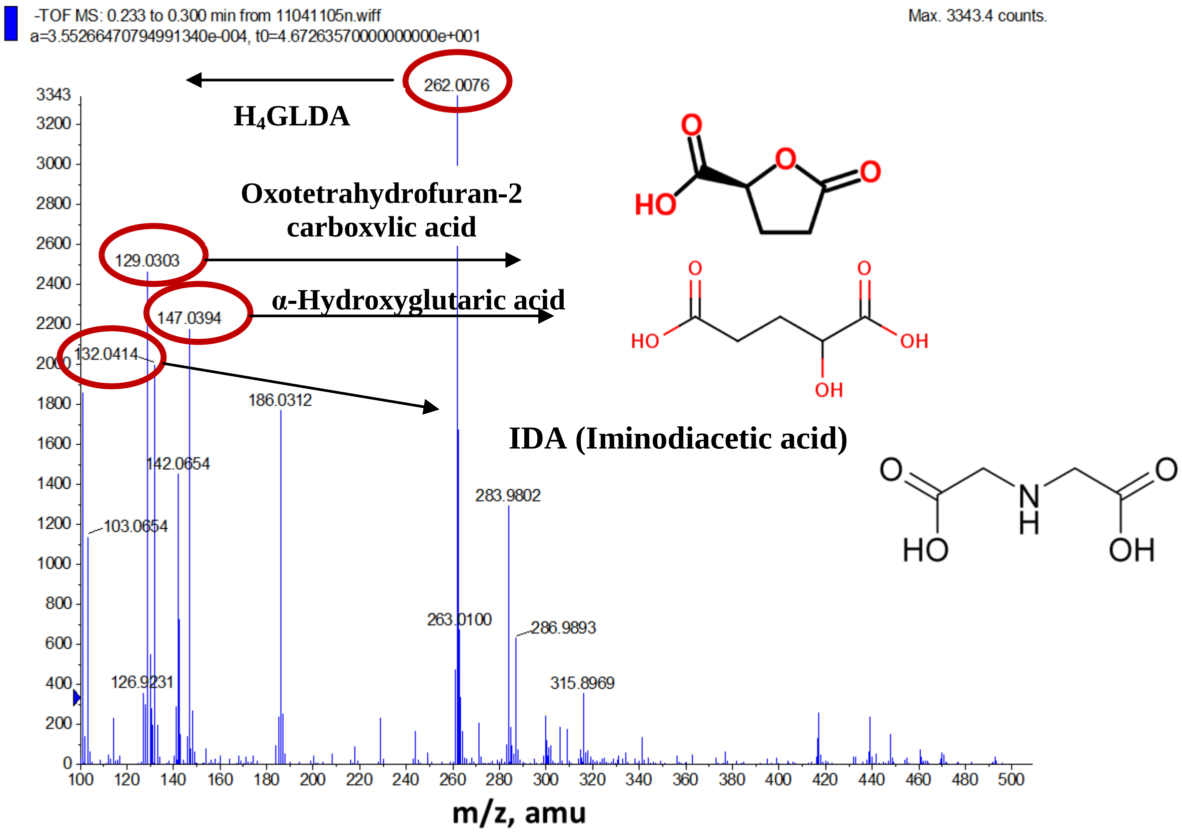


Figure 53—MS spectrum of 20 wt% NH4GLDA after heating- 100 to 500 m/z

Impact of degradation products on permeability of carbonate and sandstone cores

After we saturated the limestone core with DI water and temperature was stabilized at 325°F, The injection of GLDA at 2.5 cm^3/min was started. The pressure drop across the core started to increase, which was due to a higher viscosity of degraded GLDA than DI water (**Fig. 54**). We switched back to water after the injection of two PVs of GLDA. The pressure drop started to decrease until all GLDA residue was flushed out, as the viscosity of DI water is lower than GLDA. We stopped the injection of DI water as the pressure drop became constant and the core effluent was colorless. At the end, the final permeability of the limestone core was measured at room temperature, and found to be around 6.65 md, which was higher than its initial permeability. This means that the decomposed GLDA was able to stimulate the core. However, the inlet face of the core was partially covered with the "black precipitate" from the degraded GLDA, which lowered the injectivity and caused damage (**Fig. 55**). For the sandstone core, we saturated the core with 5 wt% NH_4Cl. GLDA was injected at 3 cm^3/min and as a result, the pressure drop increased because of a higher viscosity of GLDA (**Fig. 56**). After the injection of two PVs of GLDA, we switched back to NH_4Cl and the pressure decreased with the lower viscosity of brine. We stopped the injection until the core effluent became colorless. The final permeability of the sandstone core was 2.78 md, which was measured using 5 wt% NH_4Cl. The degraded GLDA caused damage since the initial permeability was 3.76 md

There was a thin layer of the “black precipitate” from degraded GLDA on the inlet face of the sandstone core (**Fig. 57**). The precipitate was finer than the precipitate on the carbonate core and it was very well attached on the surface. The injectivity of the core was reduced by the precipitate and formation damage was observed.

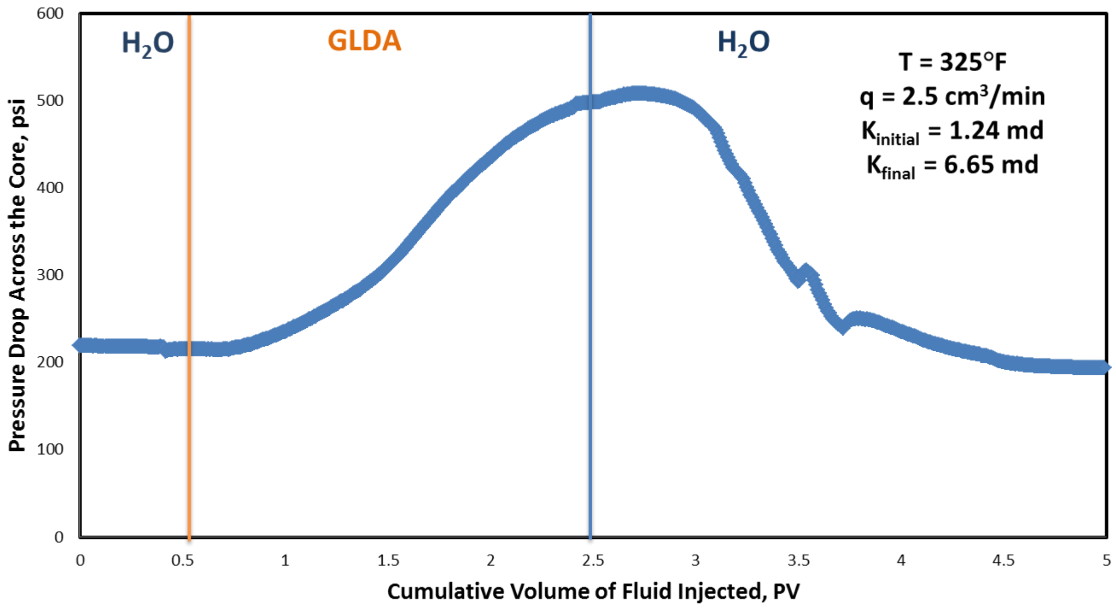


Figure 54—Pressure drop profile across the core- carbonate

Figure 55—Grey precipitates on the inlet surface of carbonate core

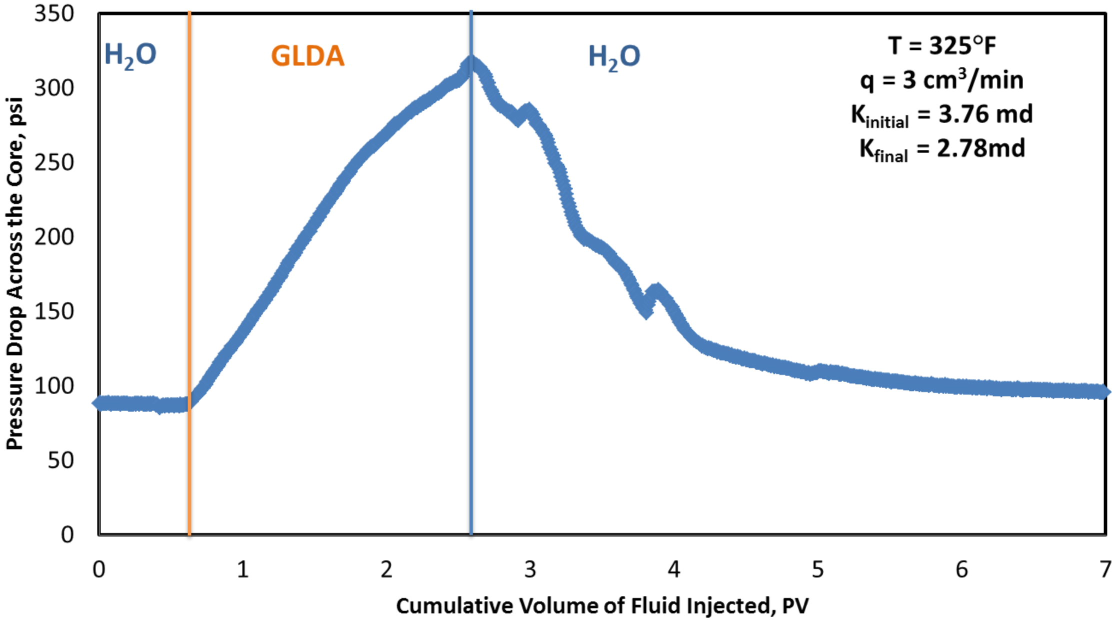


Figure 56—Pressure drop profile across the core- sandstone

Figure 57—Black precipitates on the inlet surface of sandstone core

Capability of degraded chelate in dissolving carbonate and sandstone cores

We analyzed dissolved Ca for limestone, and Mg, Al, Si, and Fe for sandstone from the effluent samples. The concentration of these elements vs. PV is shown in **Figs. 58 through 62.**

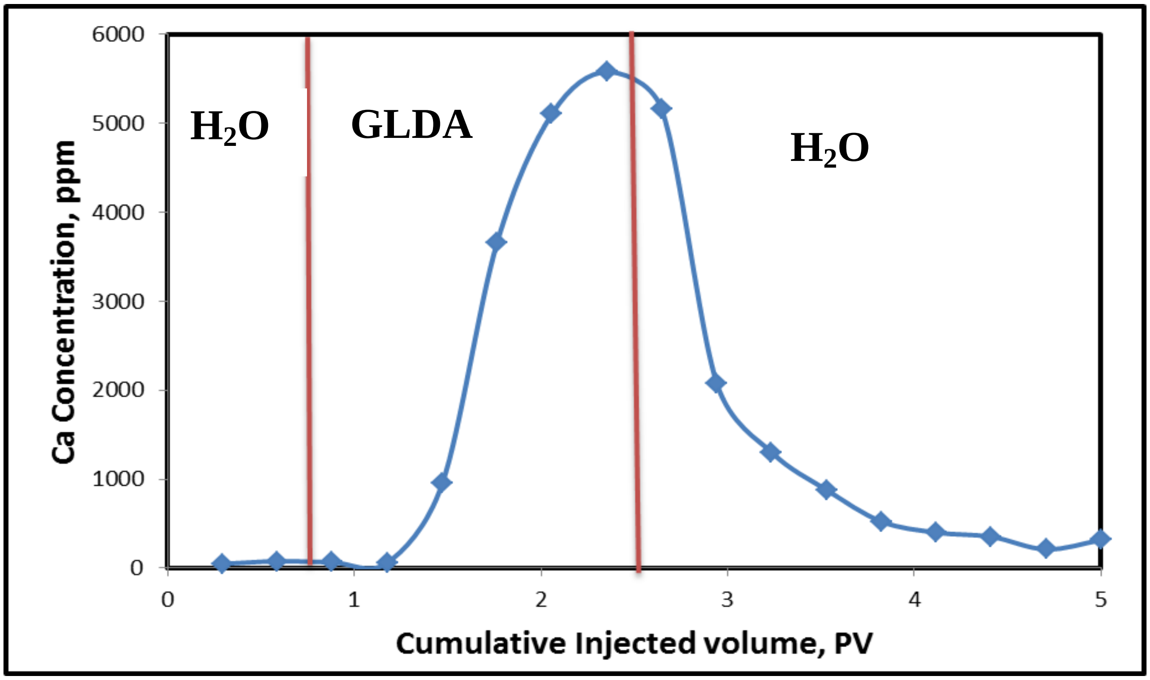


Figure 58—Concentration of dissolved Ca from limestone core using the degraded GLDA

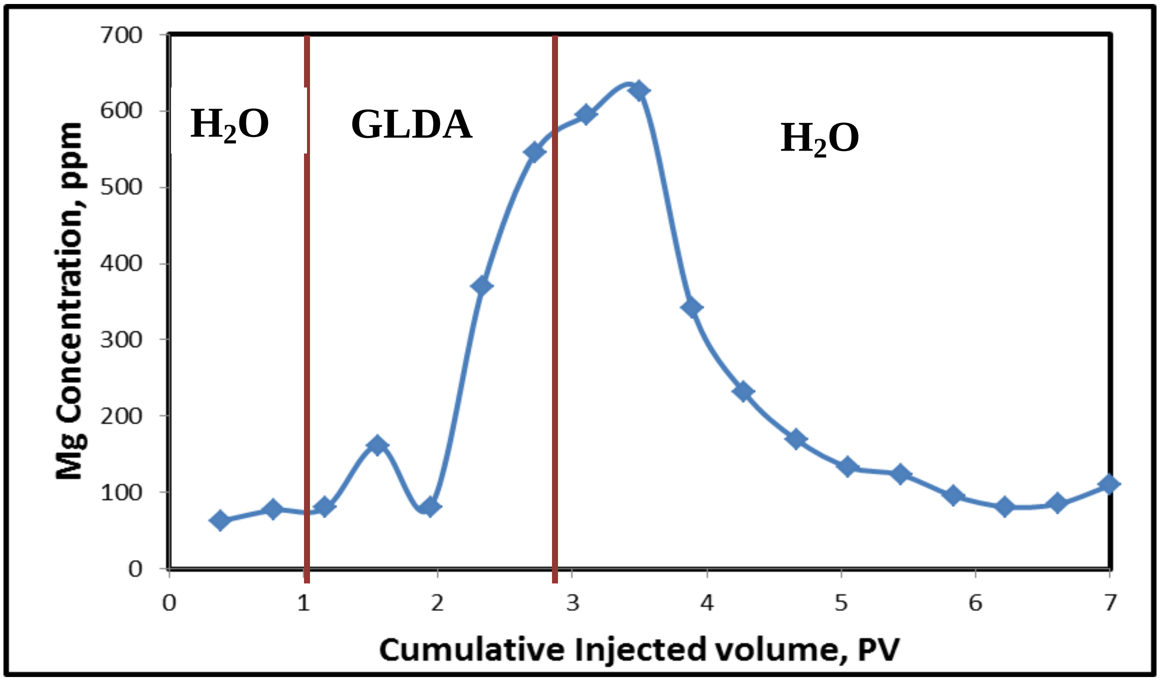


Figure 59—Concentration of dissolved Mg from limestone core using the degraded GLDA

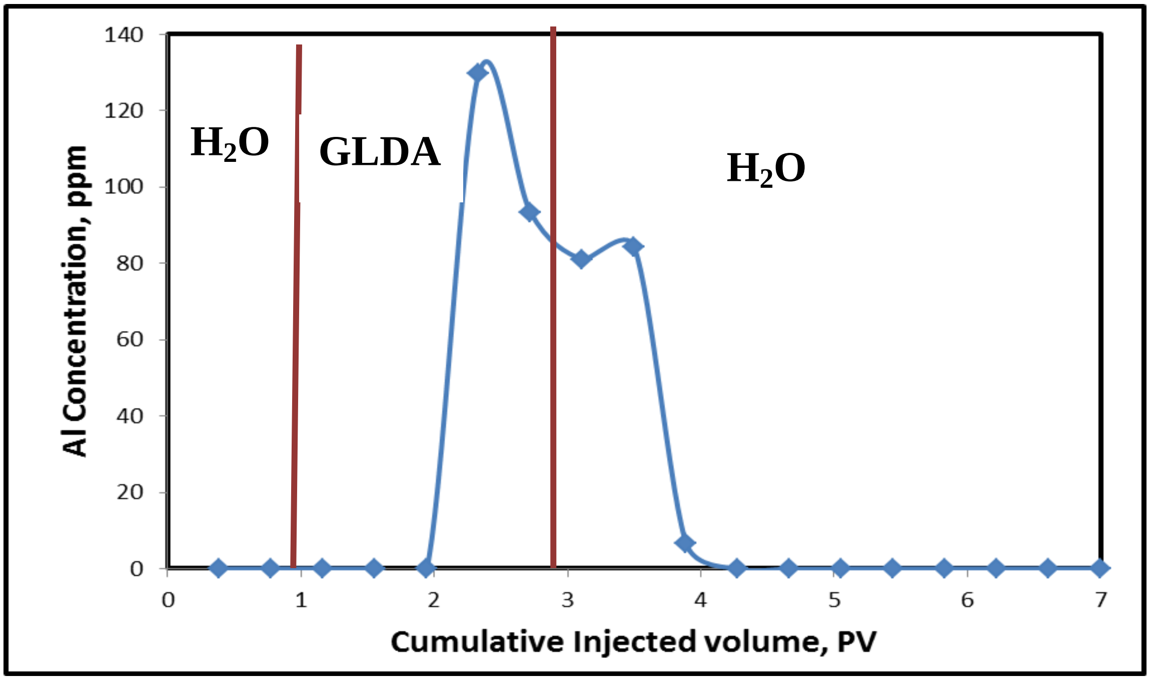


Figure 60—Concentration of dissolved Al from limestone core using the degraded GLDA

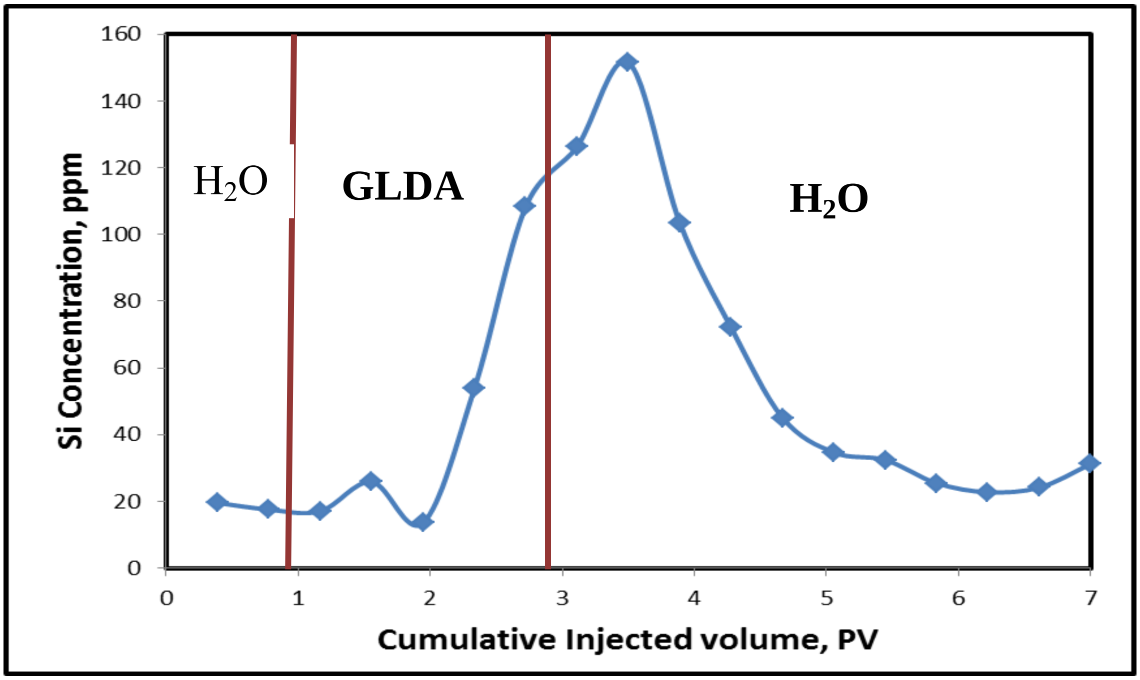


Figure 61—Concentration of dissolved Si from limestone core using the degraded GLDA

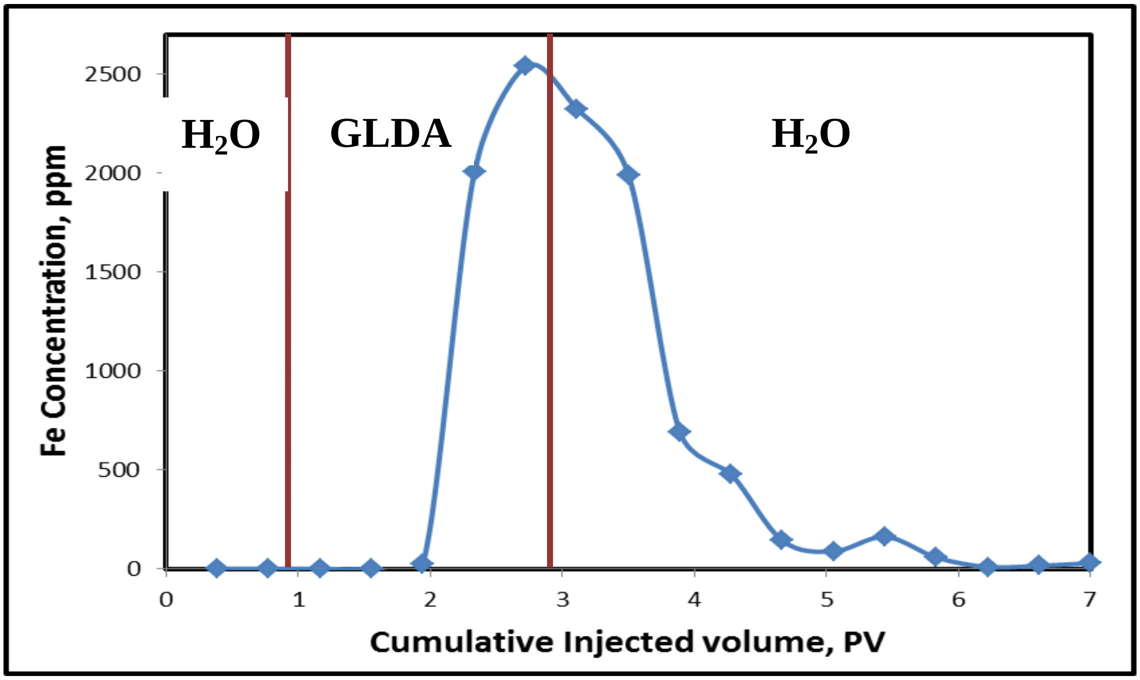


Figure 62—Concentration of dissolved Fe from limestone core using the degraded GLDA

Impact of organic and inorganic salts on thermal stability of GLDA and HEDTA-Effect of 5 wt% NH_4Cl on NaGLDA, NH4GLDA, and NaKGLDA

We investigated the impact of ionic strength. The addition of NH_4Cl improved the thermal stability of NaGLDA more than NH_4GLDA and NaKGLDA. This comparison is shown in **Fig. 63.** Thermal stability of NaGLDA, NH_4GLDA, and NaKGLDA was enhanced by 30, 7, and 10%, respectively. The Cl^- and Na^+ ions may delay degradation in these chelates by neutralizing the chelate and as a result make it less reactive.

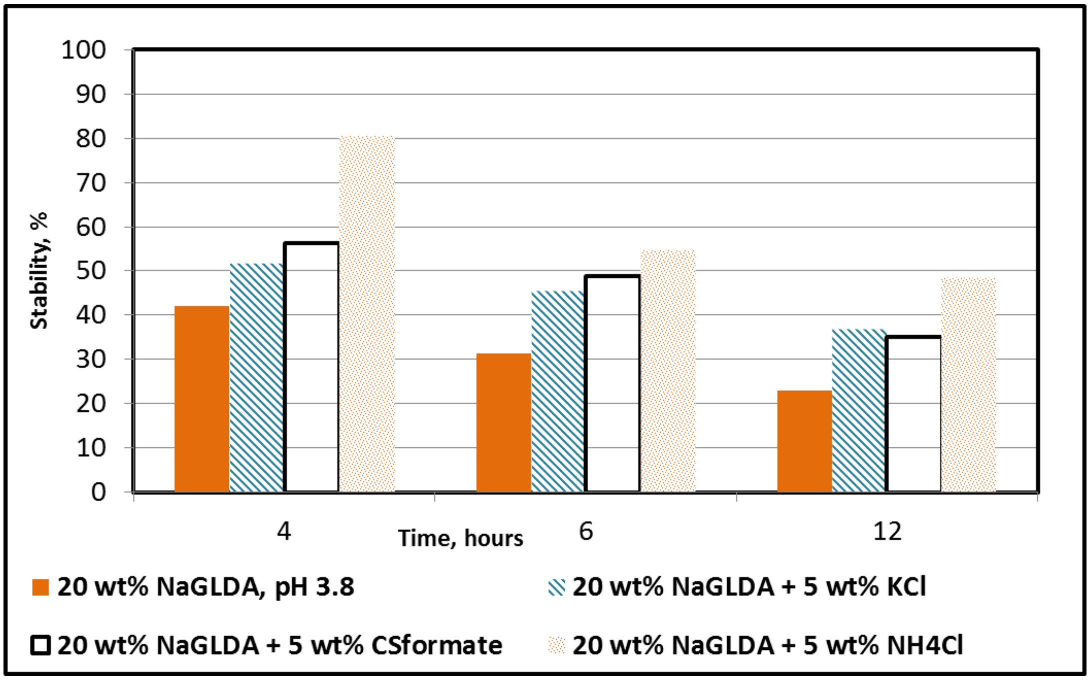


Figure 63—Effect of NH_4Cl on different salts of GLDA at 400°F up to 12 hours

We ran the same experiments with NaBr salt and we didn't observe any effect on thermal stability of NaGLDA **(Fig. 64)**. Csformate is the most effective salt in improving NaGLDA stability at 400°F.

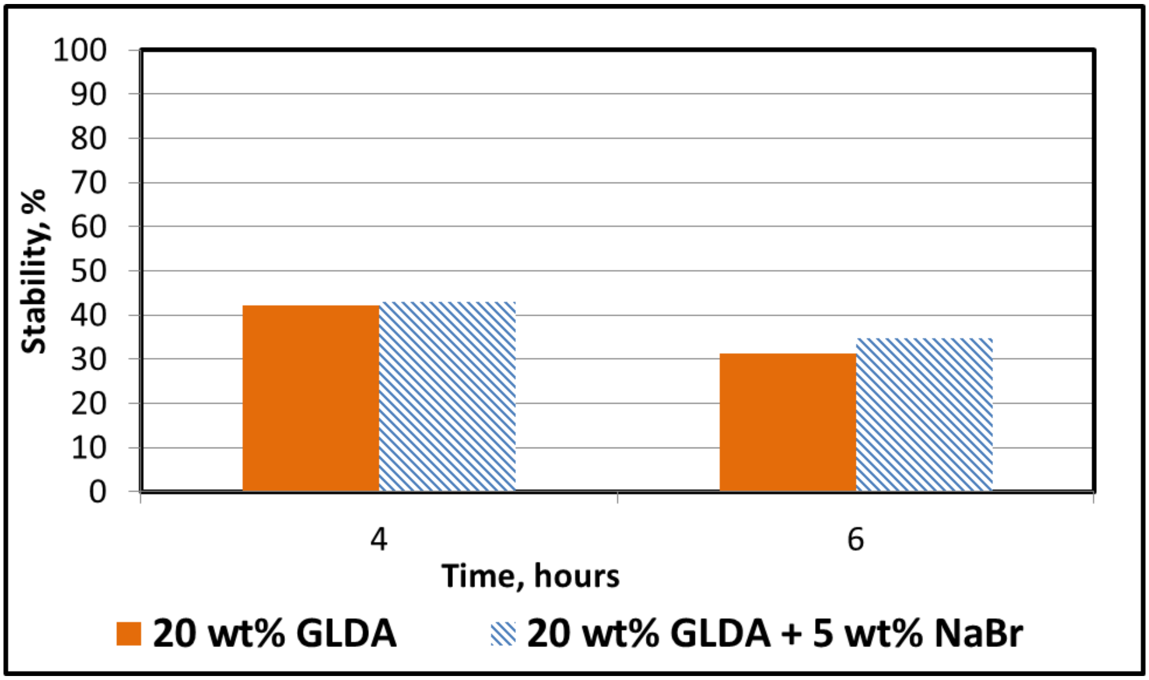


Figure 64—Effect of NaBr on thermal stability of NaGLDA at 400°F

Thermal behavior of NaHEDTA in the presence of 5 wt% Cs-Formate

HEDTA is over 80% stable at 350°F up to 6 hours but when we extend the heating time to 12 hours, its thermal stability declines significantly. The addition of 5 wt% Csformate improves its stability almost by 15% and is shown in **Fig. 65**. The impact of Csformate on thermal behavior of HEDTA is more noticeable at 400°F. HEDTA remains 100% stable up to 6 hours of heating and after 12 hours of heating, its stability drops to 80%, which is 30% enhancement compared to HEDTA solution without salt **(Fig. 66).**

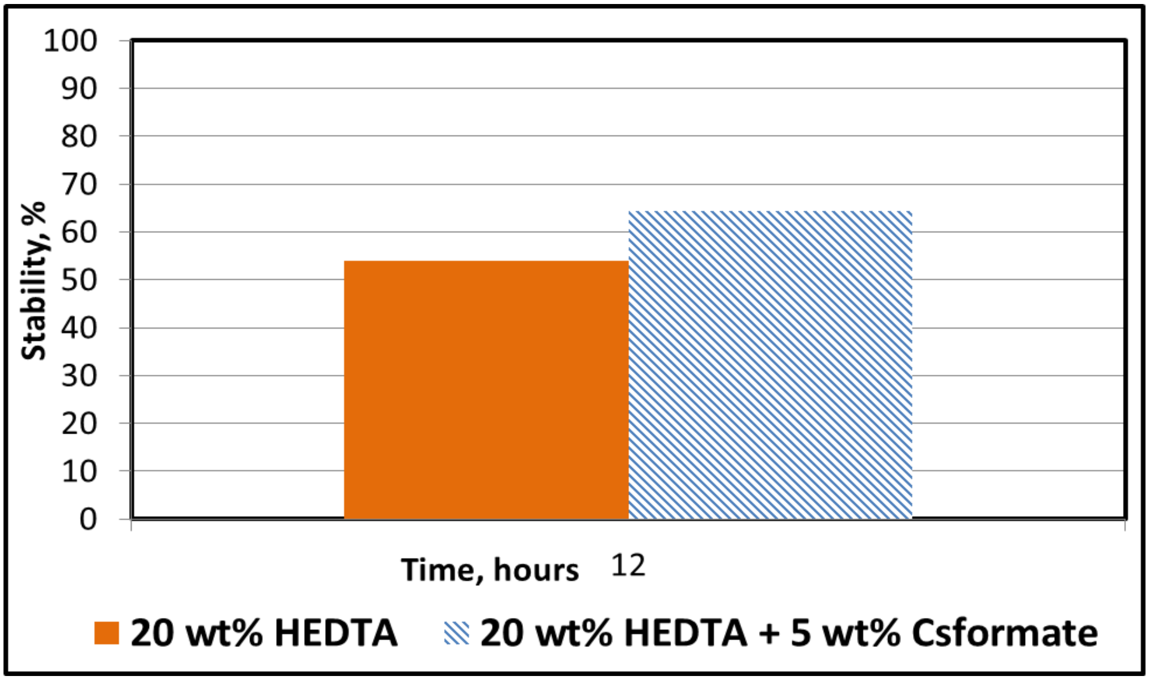


Figure 65—Effect of Csformate on thermal stability of NaHEDTA at 350°F

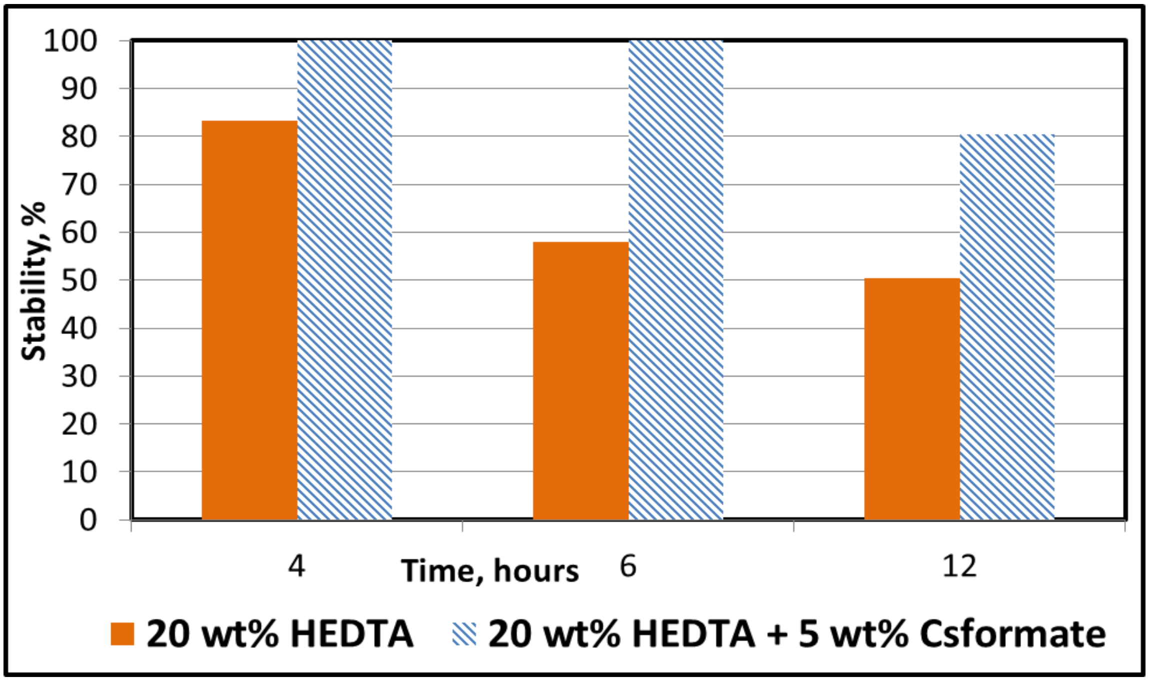


Figure 66—Effect of Csformate on thermal stability of NaHEDTA at 400°F

Thermal degradation mechanism in low pH environment

As the concentration of H^+ is high in the low pH solutions, H^+ will attack nitrogen and form a hydrogen bond that is the initiation of hydrolysis, and assist the covalent bond to break as is shown in the Fig. IDA and hydroxyglutaric acids are primary decomposition products. IDA can go under further hydrolysis at higher temperatures. This step is called secondary degradation as the degradation products are chelates and have primary properties as GLDA.

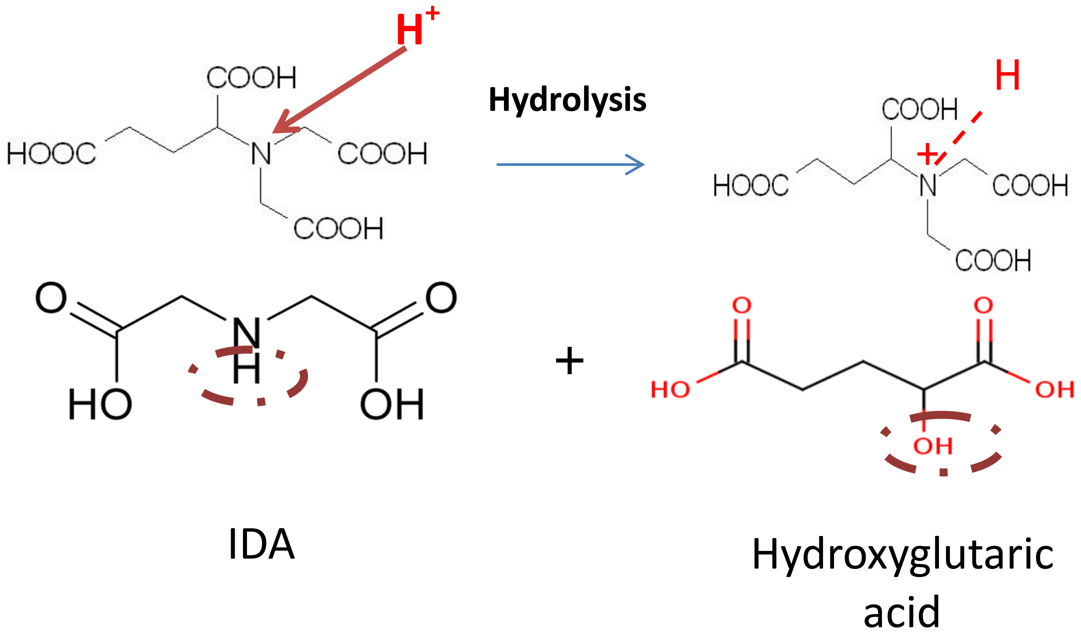


Figure 67—Thermal degradation mechanism in low pH environment

Why chelates are significantly more stable at high pH?

In high pH environment, H^+ can leave the carboxylic group more easily. In chemistry, delocalized electrons in a certain molecules or polyatomic ions can be described with resonance because the bonding can’t be showed just by one single Lewis formula. Thus, a molecule or ion with delocalized electrons is expressed by several resonance structures. The potential energy of a substance decreases as a result of electron delocalization that makes the compound more stable than any of the resonance structures. Free carboxylate anions undergo a resonance stabilization that is depicted in **Fig. 68**.

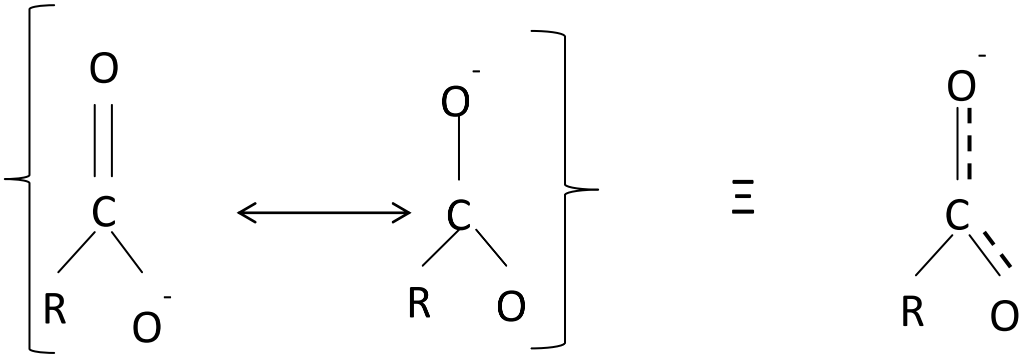


Figure 68—Resonance stabilization of carboxylate anions in high pH environment

4. CONCLUSIONS

In this study we investigated the thermal stability of different chelates with varying pH. We determined the thermal degradation products and their impact on permeability of carbonate and sandstone cores. At the end we analyzed the effect of salts on their stability by the addition of some organic and inorganic salts. The conclusions of this study are as follows:

1. Chelating agents start to decompose at 350°F
2. Chelates with two nitrogen atoms are more thermally stable.
3. There are solid precipitates associated with chelate solutions immediately after heating or by passing time after heating.
4. SEM on solid precipitates dispersed in the chelate solutions revealed the presence of C, N, and O elements.
5. Thermal degradation products found to be monosodium glutamate-monohydrate, IDA, oxotetrahydrofuran-2 carboxylic acid, hydroxyglutaric acid, and acetic acid.
6. Addition of 5 wt% salts improved thermal stability of GLDA. NH_4Cl was the most effective salt and NaBr didn't affect thermal stability.
7. 5 wt% NH4Cl didn't enhance stability of HEDTA, however, 5 wt% Cs-formate improved its stability significantly.
8. Increasing pH resulted in a significant higher thermal stability for GLDA and HEDTA.
9. Addition of salts decreases solid deposition in addition to improve thermal stability.

10. Ammonium salts of chelates precipitated a lot more than sodium salt.
11. Addition of 5 wt% NH_4Cl resulted in solid precipitates in chelate solutions after heating but Cs-formate prevents black deposition.

Recommendations

We recommend checking the thermal stability of chelates for high temperature applications with different additives before applying in the field. Different salts with different concentrations can be tested in order to determine an optimum concentration. Studying the thermal degradation mechanism in detail is useful to prevent or delay decomposition pathway.

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