

# **DISSOLUTION OF BARITE SCALE USING CHELATING AGENTS**

A Thesis

by

**ANIKET VISHWANATH SHENDE**

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**

May 2012

Major Subject: Petroleum Engineering

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## ABSTRACT

Dissolution of Barite Scale Using Chelating Agents. (May 2012)

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Barium sulfate scaling can cause many oilfield problems leading to loss of well productivity and well abandonment. Currently, diethylene triamine pentaacetic acid (DTPA) is used, along with synergist oxalic acid and potassium hydroxide, to remove the scale by dissolution. However, the chemical factors affecting this reaction are not known fully, leading to mixed results in terms of treatment effectiveness. This thesis investigates the effect of these factors, by analyzing the change in barite dissolution due to intrinsic factors like variations in formulation composition and extrinsic factors like presence of competing ions. The dissolution reaction is carried out, by taking the barite powder and chelant solution in a teflon round bottom flask and measuring the barite dissolved periodically, with an ICP-OES. The effect of different factors is studied by varying each factor individually and plotting the changes in solubilities.

These lab tests show that solubility of barite (0.01mM in water), ideally, increases with increasing concentrations of chelating agents, even going as high as 239 mM. However experimental or field constraints lead to significant decrease in dissolution,

especially at higher chelant concentrations. Thus, field tests to determine most effective chelant concentrations must precede treatment design. Lab tests also show that combination of DTPA with weaker chelating agents like ethylene diamine tetraacetic acid (EDTA), L-glutamic acid, N,N-diacetic acid (GLDA) or methyl glycine diacetic acid (MGDA) reduces barite dissolution and should be avoided during treatment design. Addition of synergists to the formulations, initially improves dissolution performance, especially for moderate chelant concentrations, but proves detrimental and hence must be avoided, over longer treatments. Finally, presence of competing ions in seawater, calcium sulfate and calcium carbonate, can significantly reduce barite dissolution and must be carefully studied for each formation-fluid system before design of treatments.

Thus, this project sets a framework to identify the best chelant formulation and estimate its dissolution profile to ensure, a more informed treatment design for barite scale removal.

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## TABLE OF CONTENTS

	Page
ABSTRACT .....	iii
ACKNOWLEDGEMENTS .....	v
TABLE OF CONTENTS.....	vi
LIST OF FIGURES .....	viii
LIST OF TABLES .....	x
CHAPTER	
I INTRODUCTION AND LITERATURE REVIEW .....	1
1.1 Barium Sulfate Scales.....	2
1.2 Scale Treatments .....	3
1.3 Chemical Means of Scale Removal.....	3
1.4 Mechanism of the Reaction.....	5
1.5 Activators .....	6
1.6 Competing Ions .....	7
II EXPERIMENTAL METHODS AND PROCEDURE.....	8
2.1 Materials.....	8
2.1.1 Scaling powders .....	8
2.1.2 Chelant formulations .....	8
2.2 Establishing Procedure.....	9
2.2.1 Size of particles.....	9
2.2.2 Stirring rate .....	11
2.2.3 Selection of initial amount of barite.....	14
2.2.4 Selection of base .....	17
2.2.5 Final procedure .....	17
2.3 Analytical Procedures .....	18
III INTRINSIC FACTORS AFFECTING CHELANT PERFORMANCE .....	19
3.1 Effect of DTPA Concentration.....	19
3.1.1 Effect of different initial concentrations of DTPA, without agitation.....	20

CHAPTER	Page
3.1.2 Effect of different initial concentrations of DTPA, with agitation.....	22
3.2 Combination of Chelating Agents .....	30
3.2.1 Combination of EDTA and DTPA.....	31
3.2.2 Combination of DTPA and MGDA .....	34
3.2.3 Combination of DTPA and GLDA .....	37
3.3 Effect of Synergists .....	39
3.3.1 Effect of oxalic acid .....	39
IV EXTRINSIC FACTORS AFFECTING CHELANT PERFORMANCE.....	43
4.1 Effect of Seawater on Barite Dissolution.....	43
4.2 Effect of Calcium Sulfate Scale .....	46
4.3 Effect of Calcium Carbonate Scale .....	48
V CONCLUSIONS.....	51
REFERENCES .....	53
VITA.....	57



## LIST OF FIGURES

FIGURE		Page
1	a) EDTA and b) DTPA structures show the carboxylic acid arms, which when activated pick up chelate ions.....	4
2	Similar barite dissolution profiles are observed for different stirring rates of barite above 20 rpm .....	12
3	Barite dissolution remains similar between 1 to 10 gm of initial barite taken.....	16
4	Barite dissolution initially increases with DTPA concentration and then remains steady.....	21
5	Dissolution profiles of barite dissolution at different initial concentrations of chelants show increase in dissolution as concentration increases.....	23
6	Dissolution significantly improves with time for higher concentrations of DTPA.....	25
7	Dissolution profiles improve with higher DTPA concentrations, longer treatment times and more accessibility.....	26
8	Increase in dissolution at higher concentrations and longer times is due to more progress of reversible reaction.....	28
9	Dissolution profiles for different ratios of chelating agents shows increase in dissolution as concentration of DTPA increases.....	32
10	Dissolution profiles due to addition of MGDA to DTPA show wide variation.....	36
11	Dissolution profile for GLDA+DTPA, showing similar trend to that of MGDA+DTPA.....	38
12	Addition of oxalic acid beneficial initially for 0.1M DTPA, but detrimental for 0.5M DTPA.....	40
13	Seawater reduces dissolution capacity of DTPA, especially at higher concentrations.....	45

FIGURE		Page
14	DTPA dissolves mixed scale containing barite and calcium sulfate in ratio of Ca/Ba of 4.45 for 0.1M DTPA.....	47
15	Dissolution profile decreases due to presence of calcium sulfate for 0.5M DTPA.....	48
16	Dissolution profile for 0.5M DTPA shows significant decrease in dissolved barite in presence of calcium carbonate scale.....	49

## LIST OF TABLES

TABLE		Page
1	Chelating agents used in experiments.....	9
2	Barium dissolved at different times for different stirring rates.....	11
3	Dissolution for different initial amounts of barite.....	15
4	Barium dissolved by different concentrations of DTPA in static mode	20
5	Barite dissolution due to different chelant concentrations.....	22
6	Barium dissolved by higher concentrations of DTPA at longer time duration.....	24
7	Mole ratios in which chelating agents were mixed.....	31
8	Barite dissolution for different combinations of EDTA and DTPA....	32
9	Different combinations of DTPA and MGDA are taken to study the effect of MGDA on barite dissolution.....	35
10	Barite dissolution due to different combinations of DTPA and MGDA	35
11	Molar ratios for combinations of GLDA and DTPA.....	38
12	Dissolution caused by oxalic acid.....	41
13	Composition of seawater.....	44
14	Dissolution profile for 0.5M DTPA in seawater.....	45
15	Dissolution profiles for calcium sulfate scales.....	47
16	Dissolution profile for 0.5M DTPA in presence of calcium carbonate	49

## CHAPTER I

### INTRODUCTION AND LITERATURE REVIEW

Scale is defined as the secondary deposition of organic or inorganic chemical compounds caused by the presence or flow of fluids in a system (Vetter 1976). When we drill a well, we disturb the thermodynamic and chemical equilibrium established in the formation over a period of many years (Frenier 2001). The scales are precipitated as a consequence of the system adjusting to a new equilibrium. This disturbance can be in the form of change of pressures, temperatures, mixing of incompatible waters or reactions of inappropriate chemicals (Chilingar , Mourhatch and Al-Qahtani 2008). Precipitation of scales can occur in any point in the petroleum production process like formation, tubing, transfer lines, treatment equipment and storage vessels.

Scales can be classified as organic and inorganic compounds based on the nature of constituents. Inorganic scales are primarily metal salts formed in the presence of water and include carbonate, sulfate and sulfide scales. The common sulfate scales are barite, celestite, anhydrite and gypsum. These scales are sulfate salts of the alkaline earth metals. Since they have many similar physical properties and periodic chemical properties, many times, they are precipitated together.

These scales interfere with fluid flow. Scales enhance corrosion and may also foster bacteria. They cause decrease in effective area available for flow of oil leading to the increase in required bottomhole pressures. Scales may damage equipment like pumps,

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This thesis follows the style of *SPE Journal*.

separators, etc. Radium Sulfate scales if formed are radioactive and hence care must be taken to contain their radioactivity. Thus, scaling can cause many problems in the oilfield leading to loss of well productivity and sometimes, well abandonment. So, research is required to address these problems and design effective scale treatments.

### **1.1 Barium Sulfate Scales**

Of all the scales in the oil industry, barium sulfate scales are the most easily precipitated due to the very low solubility (2.3 mg/L at STP) of barite in water (Chilingar, Mourhatch and Al-Qahtani 2008). Barite scales are typically grayish in color. Though pure barite is white, the scales may have impurities or organic materials trapped in them giving them a blackish tinge. Specific gravity of barite is around 4.5. The scales are fairly hard with Mohr hardness in the range 2.5-3.5.

Barium sulfate scales are precipitated due to comingling of incompatible waters. Seawater having 2400mg/L to 4800mg/L sulfate ions, when mixed with formation waters rich in barium ions leads to formation of barium sulfate (Gates and Caraway 1964). Depending on the pH, temperature and pressure, the salts tend to reach a point of super saturation leading to a metastable condition which leads to phase separation (ionic salts convert from dispersed phase to crystals). The salts precipitate by nucleation and crystal growth (Clemmit, Ballance and Hunton 1985). Once these crystals are formed, they tend to adhere to form layers or blocks which causes major interference with fluid flow. Besides this process, barium sulfate can also be precipitated due to change in thermodynamic, hydrodynamic and kinetic parameters (Vetter 1975). Scale treatments have to be designed considering all these factors.

## 1.2 Scale Treatments

Scale treatments include scale inhibition, sulfate ion exchange and scale removal. The most effective way of avoiding scaling is by using chemical scale inhibitors which prevent or delay scale formation at substoichiometric levels in solution. Nucleation inhibitors like polymers PAA, PVS, etc disrupt and redissolve the scale protocystals formed due to supersaturation and prevent deposition. Crystal growth inhibitors like DETPMP adsorb on or interact with the crystal growth sites (growing edges or spirals) and retard the crystal growth. Intermediate inhibitors like PPCA operate by both the above mechanisms. (Inches, Doueiri and Sorbie 2006)

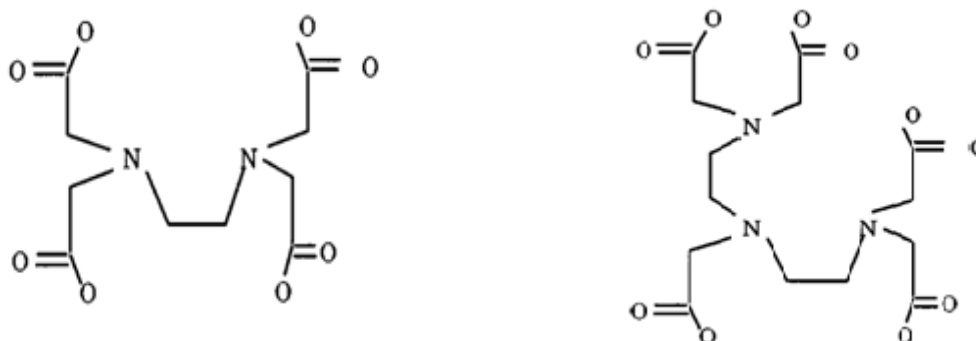
If inhibitors cannot be used, scale formation can be prevented by removing the sulfate ions from seawater by approaches like membrane distillation, nanofiltration, reverse osmosis in conjunction with liquid phase precipitation (Bader 2006). These approaches can sometimes be the most economical, quick and energy efficient solutions.

However, if scale formation cannot be prevented, or if the strategy to prevent its formation fails, scale deposits need to be removed either with mechanical means like milling, jetting, ultrasound or chemical means like sequestration with a chelating agent. Mechanical means are effective in the well bore, but are not of much use, if deposits are in the formation. Chemical removal treatments are considerably less expensive than mechanical methods and effective for scale removal from the formation.

## 1.3 Chemical Means of Scale Removal

Barite scales in oil field were first identified by Moore (1914). Featherstone (1959) analyzed the different factors influencing the precipitation of  $\text{BaSO}_4$ . Shaughnessy and

Kline (1983) gave graphical representations of thermodynamics of scale deposition. Barium sulfate scale is insoluble in most mineral acids like hydrochloric acid, nitric acid, etc. Though it can dissolve in sulfuric acid, it precipitates back. Hence the only way to dissolve the barite scale is by using complex organic acids called chelating agents or chelants. These chelating agents are ethylamine molecules having multiple carboxylic acid arms which can pick up barium molecules from solid state and bring them into the solution. Common chelating agents include diethylene triamine pentaacetic acid (DTPA) and ethylene diamine tetraacetic acid (EDTA). **Fig. 1** shows the chemical structure of these chelants with their constituent ethylamines and acetic acid arms.



**Fig.1. a) EDTA and b) DTPA structures show the carboxylic acid arms, which when activated pick up chelate ions.**

Rhudy (1993) studied efficiency of different chelants in reservoir cores. Paul and Fieler (1992) found many new chemical formulations. These formulations were tested in the first successful chemical barite removal job in North Alwin region of North Sea (de Vries and Arnaud 1993). Lakatos, Lakatos-Szabo and Kosztin (2002a) extended study to 5 new chelants and found that the barium sulfate dissolution capacity of various

chelating agents was in the order DTPA >1,2-PDTA >CDTA > EDTA. Putnis, Putnis and Kowacz (2008) studied barite dissolution by different concentrations of DTPA and concluded that barite dissolution increases with DTPA concentration until 10mM and then decreases. However, the limitations imposed by experimental conditions were not identified clearly. Hence, impact of constraints like accessibility of scales, soaking times and treatment volumes on barite dissolution, needs to be analyzed properly. Recently, biodegradable agents like L-glutamic acid, N,N-diacetic acid (GLDA) or Methyl Glycine Diacetic acid (MGDA) have been used for solving many oilfield problems. But their low stability constants for barium sulfate discourage their use for barite removal. This project studied the effect of addition of these chelants to DTPA to gain insight into chelant interaction mechanisms.

#### **1.4 Mechanism of the Reaction**

Dunn, Daniel and Shuler (2001) and Putnis, Putnis and Kowacz (2009) established mechanism of reaction. Solid-fluid heterogeneous reactions can be studied in two ways. They can be simulated with mathematical modeling and computer simulations various, to gain insights into reaction mechanisms. Else, they can be analyzed experimentally with contact and non contact atomic force microscopy, to better understand surface chemistry.

Solid-Fluid type reactions (non-porous solids) consist of multiple steps including bulk diffusion of fluid particle to the boundary layer of solid surface; diffusion through boundary layer to the solid surface; adsorption; chemical reaction; desorption of products from solid and diffusion through the boundary layer into bulk solution. The



slowest step in this multiple step chemical reaction controls the rate of the overall reaction and hence is called the rate determining step. Mechanism can be diffusion controlled or reaction controlled if the slowest step is diffusion or chemical reaction, respectively. The activation energy of barite dissolution by DTPA is 9.59kcal/mol and EDTA is 9.31 kcal/mol (Putnis, Putnis and Kowacz 2009). Activation energy values below 3.6kcal/mol indicate a significant contribution from the mass transport kinetics. Due to high activation energy and strong temperature dependence of reaction, particles find diffusion much easier than chemical reaction. Hence, chemical reaction is rate controlling step.

Two main mechanisms have been proposed when the fluid is chelating agent formulation and the solid is barite. First mechanism (Dunn, Daniel and Shuler 2001) states that the chelant particle physically moves to barite surface and the mechanism proceeds exactly as described above. However, recent findings indicate this may not be the only mechanism. Putnis, Putnis and Kowacz (2009) suggested that dissolution proceeds with barite molecule physically diffusing into the chelant solution and getting picked up by chelating agent. Thus, dissolution occurs due to the combination of these two mechanisms.

### **1.5 Activators**

Lakatos, Lakatos-Szabo and Kosztin (2002b) studied catalysts for EDTA. Catalyst or activator is any chemical species which improves the rate of reaction without itself getting consumed. Though catalysts cannot shift equilibrium, they can provide an alternative pathway and reduce reaction times for reversible reactions. Lakatos,

Lakatos-Szabo and Kosztin (2002b) found out that except the oxalic acid, all other organic acids like malonic acid, maleic acid, succinic acid and tartaric acid, instead of having positive impact, reduce the dissolution capacity of EDTA. Oxalic acid, on the other hand, has no impact on dissolution. This finding conflicts with the results presented by Paul and Fieler (1992) which show 0.5M oxalic acid significantly improves the dissolution capacity of EDTA and DTPA. Hence, this project also studies the effect of activators on barite dissolution.

### **1.6 Competing Ions**

Once the formulation composition is fixed in terms of DTPA concentration, chelant combinations and activator, the effect of external environment is studied. Barite dissolution will occur in seawater. Hence the dissolution reaction is carried out in seawater to quantify the decrease in dissolution due to presence of magnesium and calcium ions in seawater. Also, barite may be co-precipitated with other scales like calcium sulfate and calcium carbonate. Thus, these calcium ions will also compete with barium ions for chelant molecules. Hence, dissolution is significantly affected in presence of these scales. This behavior is also studied in this project.

Thus, this project will analyze the effect of different intrinsic chelant properties and extrinsic environmental factors on barite dissolution.

## CHAPTER II

### EXPERIMENTAL METHODS AND PROCEDURE

#### 2.1 Materials

The chemicals used in these experiments are barium sulfate, calcium sulfate, calcium carbonate, chelating agents, bases, and activators.

##### 2.1.1 Scaling powders

Barium sulfate powder is obtained from Noah Technologies Corporation, San Antonio, Texas. Calcium sulfate powder is obtained by reacting calcium chloride dihydrate with sodium sulfate. These powders are separated into size fractions 45-70 microns, 70-105 microns, and 105-150 microns using sonic sifters. Then, they are washed repeatedly, and air dried to remove fines as fines interfere with barium solubility measurements.

##### 2.1.2 Chelant formulations

Chelant formulations were prepared by dissolving the respective amounts of chelating agents in deionized water, and regulating the pH. **Table 1.** shows the chelating agents used in these experiments, and their manufacturers. For optimum activity of chelating agents the pH has to be maintained between 11-13 ( Lakatos, Lakatos-Szabo and Kosztin 2002b) by adding sodium hydroxide (NaOH) or potassium hydroxide (KOH). These were supplied in granular form by Sigma-Aldrich. Oxalic acid used in these experiments is obtained in powder form from Sigma-Aldrich.

**Table 1. Chelating agents used in experiments.**

<b>Chelant</b>	<b>Product Name</b>	<b>Common Name</b>	<b>Company</b>
Ethylene Diamine Tetraacetic Acid	Dissolvine Z-S	EDTA	AkzoNobel
Diethylene Triamine Pentaacetic Acid	Dissolvine DZ	DTPA	AkzoNobel
L-glutamic acid N,N-diacetic acid	Dissolvine GL-47-S	GLDA	AkzoNobel
Methyl Glycine Diacetic acid	Trilon M	MGDA	BASF

## 2.2 Establishing Procedure

Several different procedures have been used in literature, to study barium sulfate dissolution. Literature survey shows a wide variation of parameters and hence the results. Experiments have been done with initial amount of barite ranging from 0.4gm (Dunn, Daniel and Shuler 1999) to 10gm (Nasr-El-Din, Al-Mutairi and Al-Hajji 2004). Barite particles from 1micron to 400 microns ( Lakatos, Lakatos-Szabo and Kosztin 2002a) have been used. Results for final dissolution have been reported in % dissolved, ppm, mg/l, and mM. Mixing has been done by shakers, paddle stirrers or magnetic stirrers. Due to these wide variations of initial conditions, sometimes diametrically opposite conclusions have been drawn. So, final procedure of experiment was established after considering impact of barite particle size, rpm of stirrer, and amount of initial barite.

### 2.2.1 Size of particles

In 100ml Teflon round bottom flasks, 50 ml of 0.1M DTPA is taken at a pH of 12. 3 gm of barite in size range 45-75 microns, is added to this solution, and stirred with a magnetic stirrer at 20rpm. 2ml samples is withdrawn periodically, diluted to 50ml, and

analyzed for barium concentration using ICP-OES spectrometer. This procedure is repeated for other size ranges of barite powder. The barium concentration gives the solubility of barite in water. The amount of barium in water as given by ICP is plotted vs the time at which the sample was taken. This graph is called the dissolution profile, and it quantifies chelant performance. Good chelant formulations have more favorable dissolution profiles i.e. the barium concentration in water rises quickly to a high value. Poor chelant formulations have low dissolution profiles i.e. they dissolve less barite in given time or they take much higher time to dissolve same amount of barite. The most interesting aspect of dissolution profile is the amount of barium in the solution at the end of experiment i.e. 11 hours. This is the maximum amount barite that can be dissolved by that formulation in 11 hours.

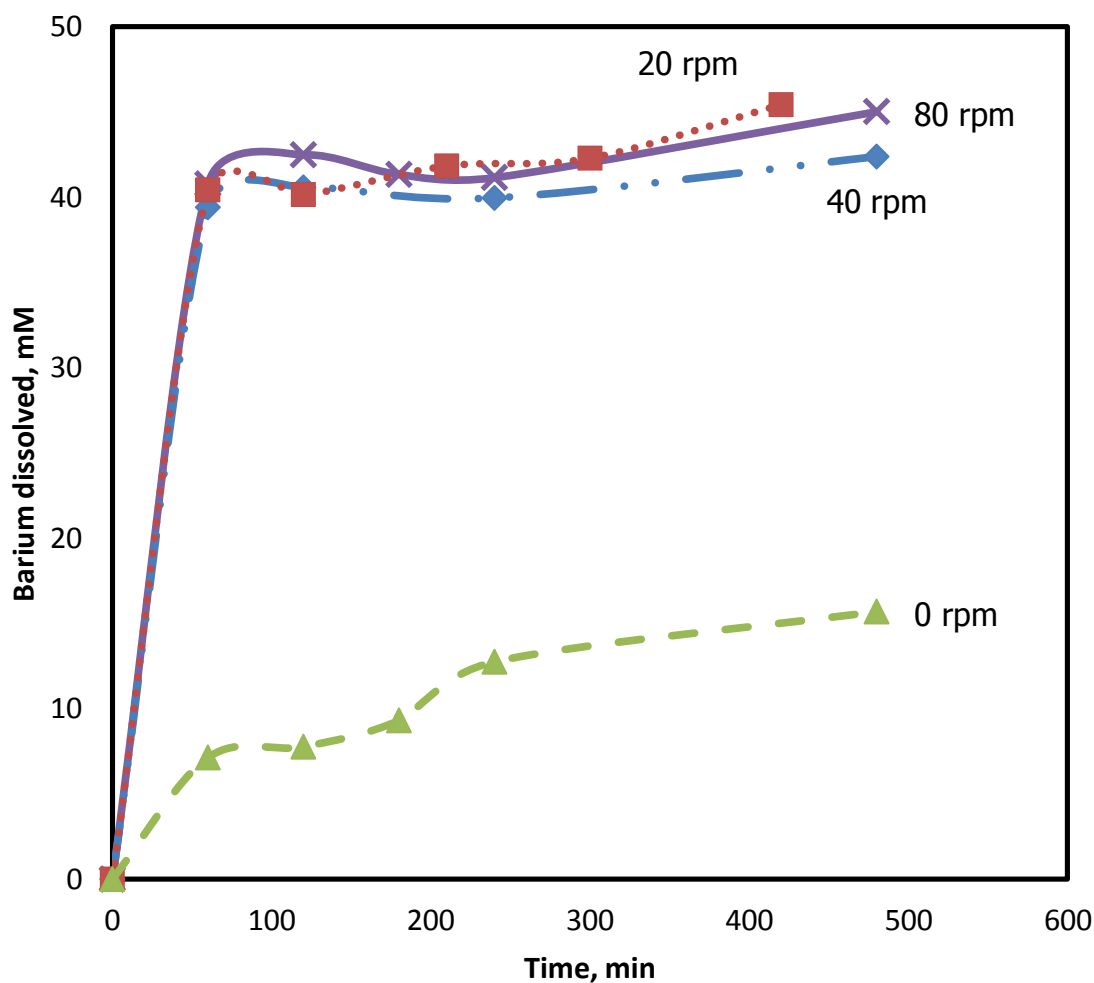
In this experiment, dissolution profiles are similar for all cases, with final dissolution after 11 hours being 43.7mM, 40.40mM, and 45.44 mM for 45-75 microns, 75-105 microns, and 105-150 microns size ranges respectively. Thus, barite dissolution does not depend on size of barite particles, in this general size range. This also follows from the conclusion that barite dissolution is a rate dependent reaction (Dunn, Daniel and Shuler 1999) as chemical reaction is much slower than dissociation of reactants and products. However, if the size range is drastically different, then the dissolution profiles will be different. Thus, dissolution profile may be different for a continuous scale film or for barium sulfate blocks. However literature survey shows that above size ranges are the most commonly used ranges for lab tests. Hence, size range of 105-150 micron is selected for future experiments.

### 2.2.2 Stirring rate

Different stirring rates and stirring mechanisms have been used in lab tests in literature. Thus, the effect of stirring rate on dissolution of barite is studied by varying the stirring rate from 0 to 80 rpm, and plotting the dissolution profiles. When the stirring rate is 0, i.e. no stirrer is present the barite particles settle at the bottom of the round bottom flask. When stirrer speed is increased to 20 rpm, all powder is suspended. Thus, the above procedure is repeated to test the dependence of dissolution of barite on stirring rate. 3 gm barite is taken with 0.1M DTPA. Solution is stirred at rates 0, 20, 40, and 80 rpm. Sampling and elemental analysis is done as earlier, to obtain results shown in **Table 2**, and plotted in **Fig. 2**.

**Table 2. Barium dissolved at different times for different stirring rates**

Time, min	mM Ba in 0 rpm	mM Ba in 20 rpm	mM Ba in 40 rpm	mM Ba in 80 rpm
0	0	0	0	0
60	7.14	40.44	39.42	40.78
120	7.77	40.16	40.58	42.50
180	9.31	41.84	-	41.35
240	12.75	42.30	39.96	41.17
480	15.70	45.44	42.39	45.04



**Fig.2. Similar barite dissolution profiles are observed for different stirring rates of barite above 20 rpm**

Initially, we have taken 3gm or 250 mM barite in the solid state. There is negligible barite in the solution as barite has a very low solubility. As time proceeds, chelating agent is dissolving solid barite, i.e. concentration of solid powder is decreasing, and the amount of barite in the solution is increasing. We are plotting the dissolution profile i.e. amount of barium in the solution with time. So, initially all curves start from zero. The

nature of this increase can be analyzed, to decide the effectiveness of the chelant formulation. When we place 3gm of barite powder in 50ml 0.1M DTPA, and stir it at 80 rpm, as the dissolution profile shows, 45.04 mM of barium sulfate is dissolved after 480 min. For the same procedure at 40 rpm, and 20 rpm, 42.39 mM, and 45.44 mM of barium sulfate is dissolved. Finally, if the same reactant mixture is taken, and no stirring is provided, 15.7 mM of barium sulfate are dissolved in the same time interval. Thus, if no stirring is provided, the dissolution reduces to almost one third the value for when stirring is provided. This can be explained in terms of accessibility. When no stirring is provided the barite powder settles down. Thus, at any given time, only the top layer is exposed to DTPA. Thus, dissolution occurs in that layer only. When the stirring is increased to 20 rpm, the barite powder is well mixed. Thus, all barite particles are floating in the solution, and are thus accessible to the DTPA molecules. Thus, dissolution increases to 45 mM. If the stirring rate is increased further, there is no change in the dissolution profile as already the accessibility is at the maximum limit. Thus, increasing the stirring rate just makes the particles move faster, without changing the dissolution profile. This is consistent with the observation stated before that barium sulfate dissolution is a rate controlled reaction in which dissociation does not play a dominant role. For all future experiments where agitation is used, the stirring rate of 40 rpm is chosen.

Comparing to previous literature, different results have been observed for different types of mixing. If paddle type stirrers (Putnis, Putnis and Kowacz 2008) are used, lower values have been observed possibly because paddles only stir the solution, and not the



barium sulfate powder. If shakers are used (Lakatos, Lakatos-Szabo and Kosztin 2003), amount dissolved is same, but equilibrium is achieved after 1-5 days as compared to roughly 11 hours in our case. Again, this can be attributed to more accessibility of suspended barite particles as compared to static particles that are periodically shaken. Thus, dissolution of barite does not depend on rpm of magnetic stirrer, but strongly depends on accessibility of barite scale. This effect of accessibility is studied by taking two cases; static case, when no agitation is provided, and dynamic case, when agitation is provided at 40 rpm.

### **2.2.3 Selection of initial amount of barite**

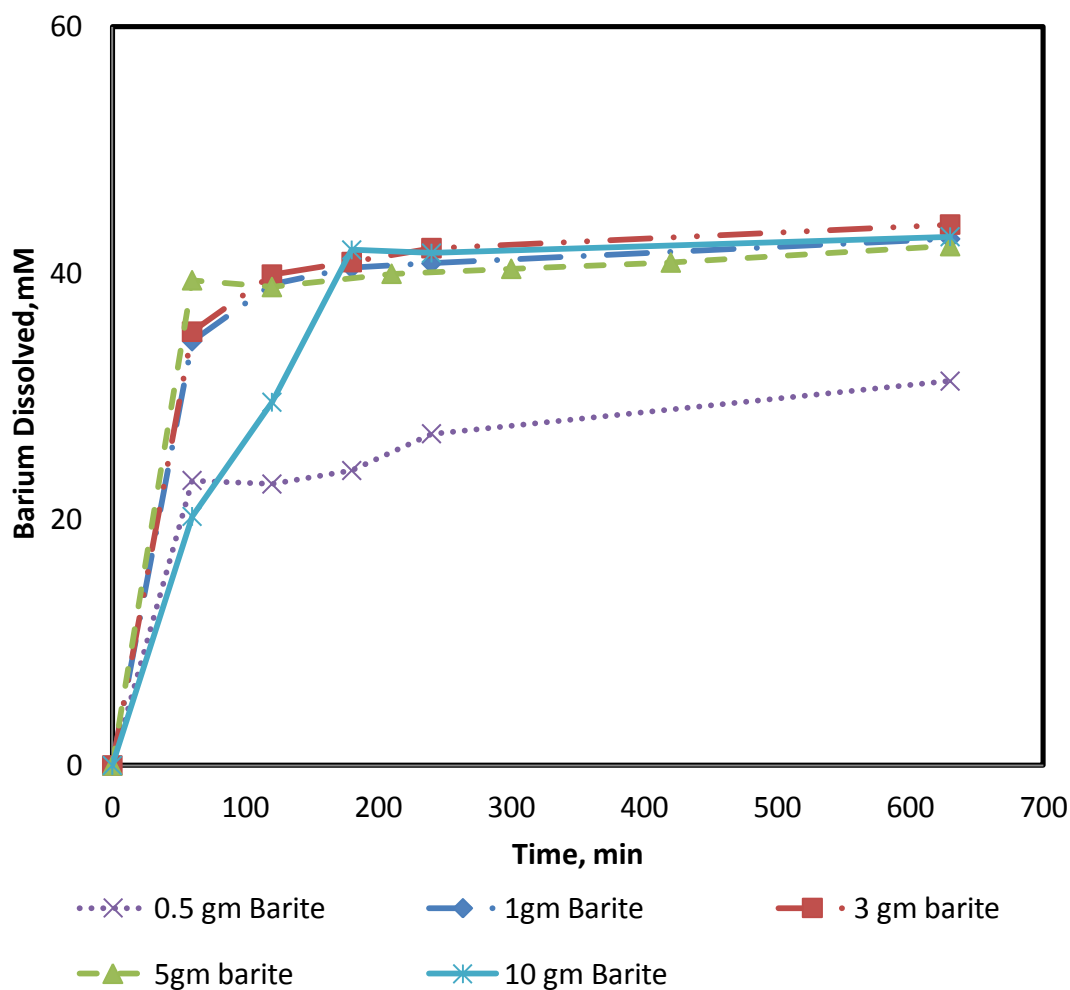
In real field conditions, the amount of scale deposited will determine the treatment design. This influence can be studied by taking different quantities of barium sulfate scale as reactants in the lab tests. So, the above procedure is repeated for 5 different initial amounts of barite. 0.5 gm (44 mM), 1 gm (89 mM), 3 gm (257 mM), and 5 gm (429 mM), and 10 gm (890 mM) barite is added to 100 mM DTPA at pH 12, and amount of barite dissolved is observed by ICP-OES. Since the stoichiometry dictates that 1 DTPA molecule can dissolve only 1 barite molecule, 100 mM DTPA can dissolve maximum 100mM barite at infinite time. **Table 3.** gives the dissolution profile of 0.1M DTPA for these different initial concentrations of barite.

**Table 3. Dissolution for different initial amounts of barite**

<b>Time, min</b>	<b>mM Ba due to 10gm</b>	<b>mM Ba due to 3 gm</b>	<b>mM Ba due to 1 gm</b>	<b>mM Ba due to 0.5gm</b>
0	0	0	0	0
60	20.24	35.24	34.47	23.16
120	29.51	39.87	39.07	22.86
180	41.88	40.89	40.42	23.96
240	41.62	42.03	40.78	26.95
630	42.96	43.94	42.77	31.22

<b>Time, min</b>	<b>mM Ba due to 5 gm</b>
0	0
60	39.42
120	38.87
210	39.95
420	40.86
630	42.19

This can be analyzed graphically, when the profile is plotted in **Fig. 3**.



**Fig.3. Barite dissolution remains similar between 1 to 10 gm of initial barite taken**

Thus, when 0.5 gm of barite is taken initially, 31.22 mM of barium is dissolved by 0.1M DTPA in 630 min. If 1 gm of barite powder is taken initially, then the barium dissolved after 630 min is 42.77 mM. If the amount of barite taken initially is increased to 3 gm, 5 gm, and 10 gm, the barium dissolved is 43.94, 42.19, and 42.96 mM respectively. Thus, amount of barite dissolved is roughly around 0.04 M or 0.5gm for all the initial concentrations of the powder excluding 0.5 gm. Thus, like all reversible

reactions, extent of barite dissolution is dependent on initial concentration of barite only when it is significantly lesser than (limiting condition) the molar concentration of DTPA. For other cases, the barite concentration can be treated as excess for kinetic calculations.

#### **2.2.4 Selection of base**

Chelating agents, being weak acids, their activity increases with increase in basicity of the solution. Thus, the reactivity of the acids can be controlled by pH. The reactivity of these acids is maximum, when pH is between 11, and 13. Thus, bases like potassium hydroxide, sodium hydroxide, sodium carbonate, etc can be added to ensure pH remains between 11 and 13 throughout the reaction. The most common bases used for DTPA are potassium hydroxide and sodium hydroxide. Putnis, Putnis and Kowacz (2008) has shown that potassium hydroxide gives the most favorable dissolution profiles and hence, it is used for regulating pH in our experiments.

#### **2.2.5 Final Procedure**

Thus, after all above considerations, the final procedure for future experiments has been designed as follows:

1. Take 50 ml water in a 100 ml teflon round bottom flask
2. Put sufficient KOH to maintain pH in the range of 11-13. After complete dissolution, prepare the required chemical formulation.
3. Sieve barite to isolate 45-75, 75-105, 105-150 micron fractions. Wash it with deionized water and then with alcohol. Take 3 gm of the air dried barite and put it in the solution. Stir the mixture uniformly with a magnetic stirrer at 40 rpm. Take care to ensure laminar flow.

4. Using a syringe take out 2ml of the mixture periodically. Dilute sample to desired volumes and using ICP-OES, measure the concentrations of barium in the solution for each volume.

### **2.3 Analytical Procedures**

For analyzing the concentrations of barium and calcium, an emission spectrophotometric technique, ICP-OES has been used. In ICP-OES electrons of elements are excited to a higher energy state and then allowed to fall back to the ground state. Energy emitted by these electrons when they fall back to the ground state is measured by a spectrophotometer. Each element emits energy at specific wavelengths peculiar to its chemical character. The intensity of the energy emitted at the chosen wavelength is directly proportional to the concentration of that element in the analyzed sample. Thus, by determining which wavelengths are emitted by a sample and by determining their intensities, the elements present and their concentrations can be identified.

This procedure is now used to evaluate the intrinsic and extrinsic factors that affect barite dissolution.

## **CHAPTER III**

### **INTRINSIC FACTORS AFFECTING CHELANT PERFORMANCE**

Once the procedure is established, it is used to analyze the intrinsic and extrinsic factors that affect barite dissolution. The 3 main intrinsic factors that affect chelant performance are the 3 aspects of chelant composition namely DTPA concentration, presence of chelant combinations and presence of synergists. These factors are studied in detail in this chapter. Thus, the impact of DTPA concentration is assessed, by varying the concentration of DTPA from 0.001M to 0.5 M and comparing the dissolution profiles or chelant performance. The effect of chelant combinations is analyzed by taking different combinations of DTPA and EDTA, MGDA and GLDA. Finally, effect of synergist is studied by adding 0.5M oxalic acid to DTPA and comparing dissolution results with that DTPA alone.

#### **3.1 Effect of DTPA Concentration**

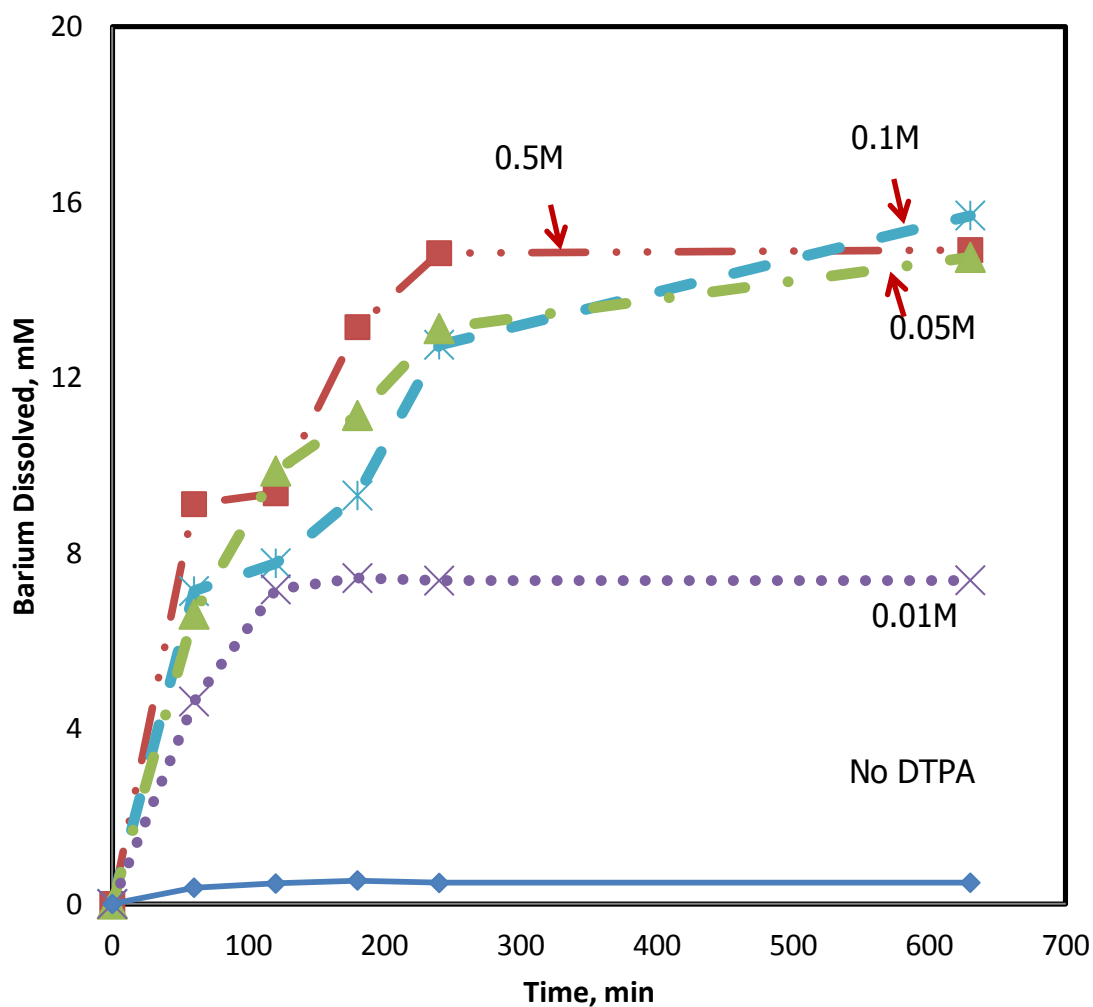
To a large extent, amount of barite dissolved finally, depends on initial concentration of chelating agent. To analyze this effect, dissolution profiles for different concentrations of DTPA are observed. Generally the chelant solution is bull headed and the well is shut in for the treatment time. Sometimes chelant is flown continuously, making the formation act as a static mixer. Thus, dissolution profiles are created for both the static and dynamic cases.

### 3.1.1 Effect of different initial concentrations of DTPA, without agitation

To consider the effect of concentrations of DTPA, the procedure described in chapter II, is repeated without any agitation for concentrations of DTPA from 0.01 or 10 mM to 0.5M or 500 mM. Highest DTPA concentration taken is 0.5M, as preparation of more concentrated DTPA solutions becomes challenging. The dissolution profiles are obtained for different concentrations of DTPA as shown in the **Table 4 and Fig.4.**

**Table 4. Barium dissolved by different concentrations of DTPA in static mode**

Time min	mM Ba in 500mM	mM Ba in 100mM	mM Ba in 50mM	mM Ba in 10 mM	mM Ba in DIwater
0	0	0	0	0	0
60	9.12	7.14	6.61	4.62	0.37
120	9.36	7.77	9.87	7.17	0.47
180	13.15	9.31	11.14	7.43	0.54
240	14.84	12.75	13.12	7.37	0.48
630	14.91	15.70	14.74	7.38	0.48



**Fig.4. Barite dissolution initially increases with DTPA concentration and then remains steady**

Thus, in 11 hours, 500mM of DTPA dissolves 14.9 mM barium sulfate for the experimental procedure described earlier. Similarly, 100 mM DTPA dissolves 15.7 mM barium sulfate. Barium sulfate dissolved by 50m M, 10mM and only base are respectively 14.74mM, 7.38 mM and 0.48mM. As can be seen from the dissolution profiles, the dissolution of barium sulfate caused by different concentrations of DTPA is



widely different. Thus, dissolution has a strong dependence on the concentration of chelating formulations. Also, dissolution increases with concentration of DTPA, until 0.05M and then remains almost constant. This behavior and its causes are discussed in detail in future sections.

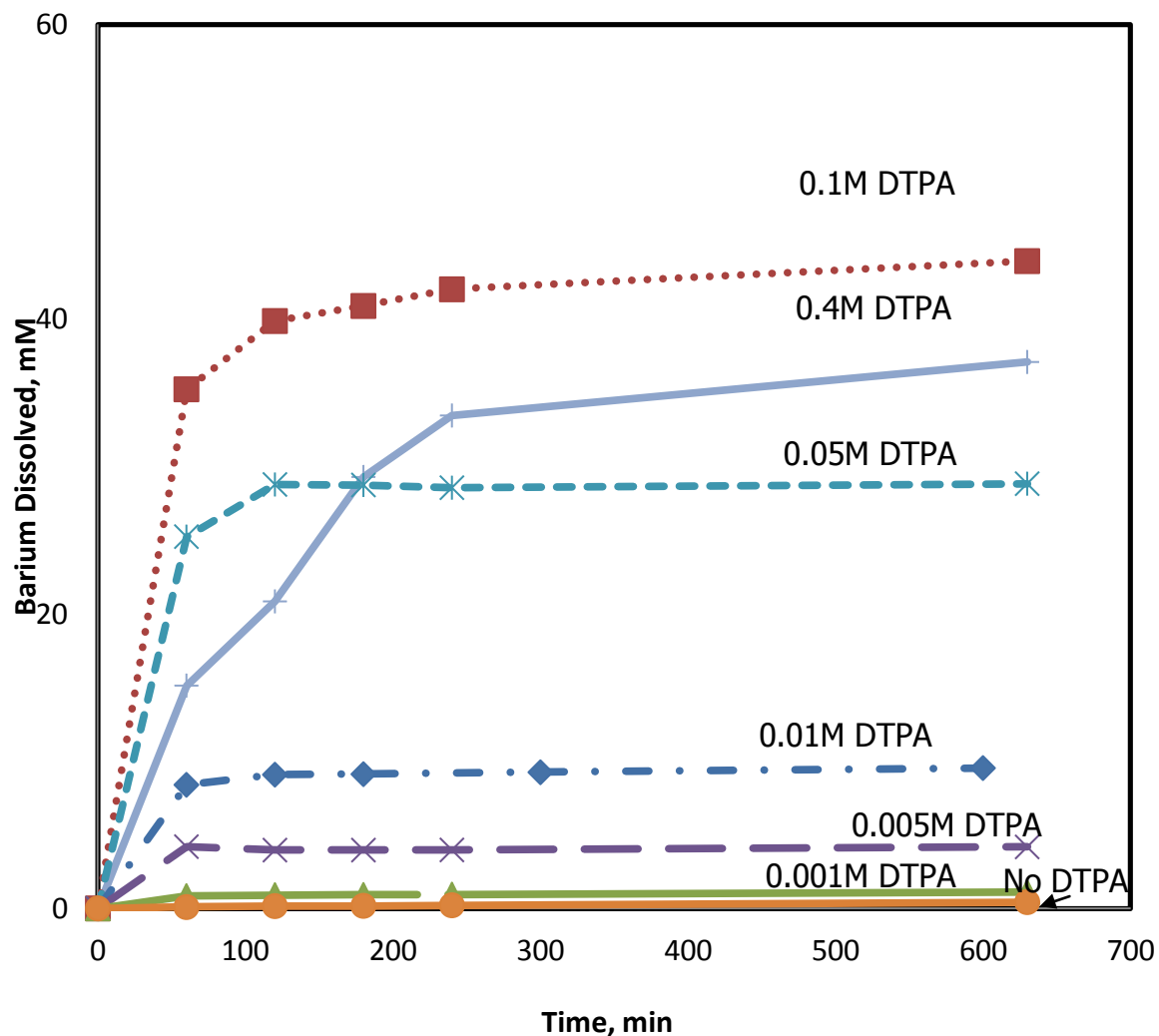
### 3.1.2 Effect of different initial concentrations of DTPA, with agitation

To study the effect of chelating agent concentrations in well mixed solutions, agitation is provided using a magnetic stirrer rotating at 40 rpm. Thus, all the experiments and calculations done above are repeated, this time including the effects of agitation. So, barite dissolution caused by different concentrations of chelating agents, is measured to create dissolution profiles for each concentration as shown in **Fig. 5** and **Table 5**.

**Table 5. Barite dissolution due to different chelant concentrations**

Time min	mM Ba in 500mM	mM Ba in 100mM	mM Ba in 50mM	mM Ba in 10mM	mM Ba in 5mM	mM Ba in 1mM
0	0	0	0	0	0	0
60	15.13	35.24	25.24	8.02	4.19	0.84
120	20.84	39.87	28.78	8.17	3.96	0.90
180	29.28	40.89	28.74	8.38	3.96	0.92
240	33.46	42.03	28.56	8.51	3.97	0.94
630	37.09	43.94	28.83	8.80	4.17	1.11

Thus, in 11 hours, 0.5M of DTPA dissolves 37.09 mM barium sulfate for the experimental procedure described earlier. Similarly, 0.1M DTPA dissolves 43.94 mM barium sulfate. Barium sulfate dissolved by 0.05M, 0.01M, 0.005M, 0.001M and only base are respectively 28.83 mM, 8.8 mM, 4.17 mM, 1.11 mM and 0.43mM.



**Fig.5. Dissolution profiles of barite dissolution at different initial concentrations of chelants show increase in dissolution as concentration increases**

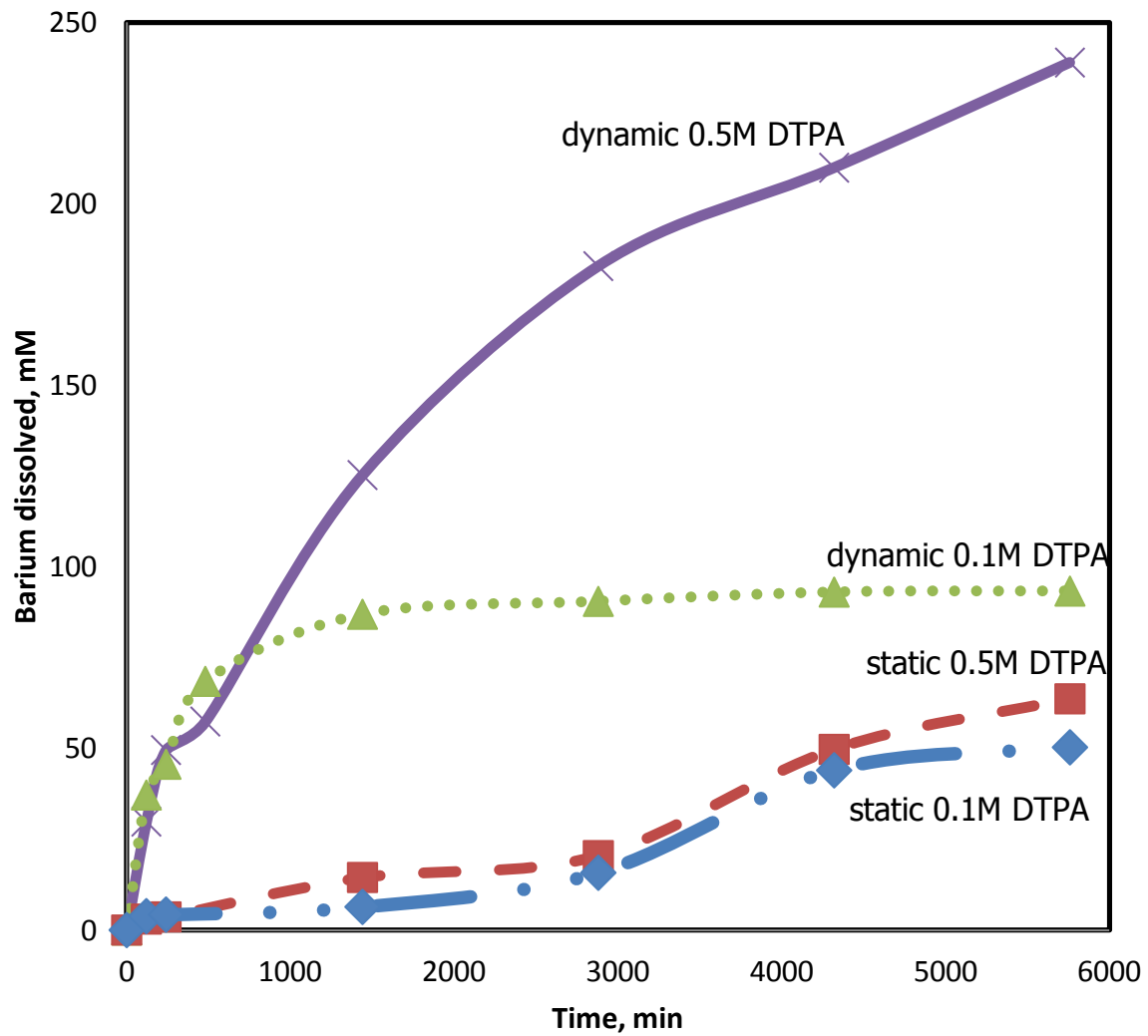
Similar to the pattern of dissolution profiles for the static case, the dissolution of barium sulfate caused by different concentrations of DTPA is widely different. Thus, dissolution has a strong dependence on the concentration of chelating formulations even for well mixed solutions. Also, for higher concentrations of DTPA, the amount of

dissolution is almost thrice that of the corresponding concentrations in the static case. Thus, it is always beneficial to provide some form of agitation as it greatly increases the extent of reaction and enhances dissolution. This increase in dissolution is not that apparent for lower concentrations of DTPA. This shows that the agitation increases accessibility of barite to DTPA and this leads to increase in dissolution. This point was discussed at length while determining the experimental procedure.

For all concentrations of DTPA below 0.1M, steady state is eventually observed, in both static and dynamic cases. But for 0.1M and 0.5M DTPA, true steady state is not observed in 11 hours, as reaction is not complete. So, to study true final dissolution in 0.1M and 0.5M DTPA, the reaction is allowed to continue for a much longer time of 4 days and results are shown in **Table 6** and **Fig. 6**. Fig. 6 shows that increasing the time for reaction, greatly increased the final dissolution for both static and dynamic cases.

**Table 6. Barium dissolved by higher concentrations of DTPA at longer time durations**

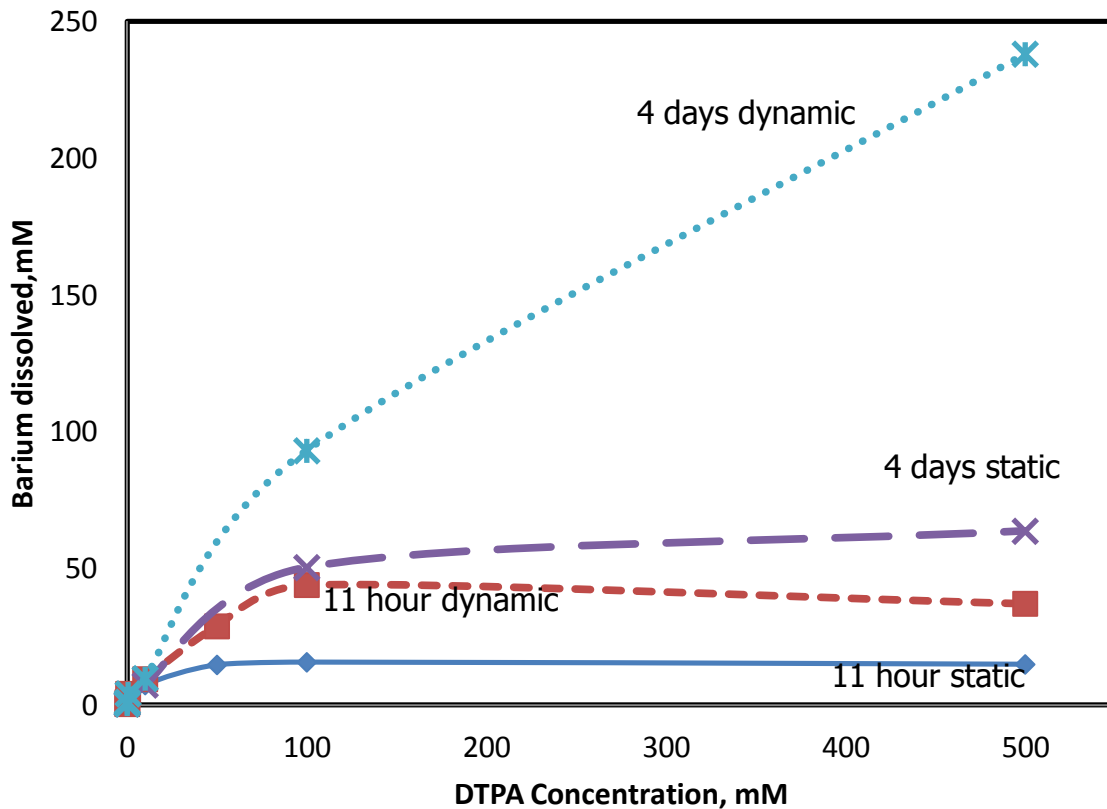
Time min	Static case		Dynamic case	
	mM Ba in 500mM	mM Ba in 100mM	mM Ba in 500mM	mM Ba in 100mM
0	0	0	0	0
120	3.02	3.82	29.86	37.19
240	3.63	4.25	49.57	45.66
480	5.75	-	57.43	68.50
1440	14.47	6.38	125.31	86.97
2880	20.49	15.78	182.85	90.51
4320	49.75	43.99	209.95	93.07
5760	63.69	50.32	238.92	93.35



**Fig.6. Dissolution significantly improves with time for higher concentrations of DTPA**

Fig. 6. shows that for all cases steady state has been attained at the end of 4 days, though for dynamic case of 0.1M DTPA, equilibrium is achieved in a day. Also, that there is no difference in dissolution for different concentrations for static case. But, for dynamic case, dissolution increased a lot with time and concentration. Initially, 3 gm or 257 mM

of barite was taken in solid state and 0.5M DTPA has dissolved most of it at the end of 4 days. In order to better analyze these results, the maximum dissolution at the end of 11 hours and 4 days for each concentration of DTPA are plotted together in **Fig. 7**.



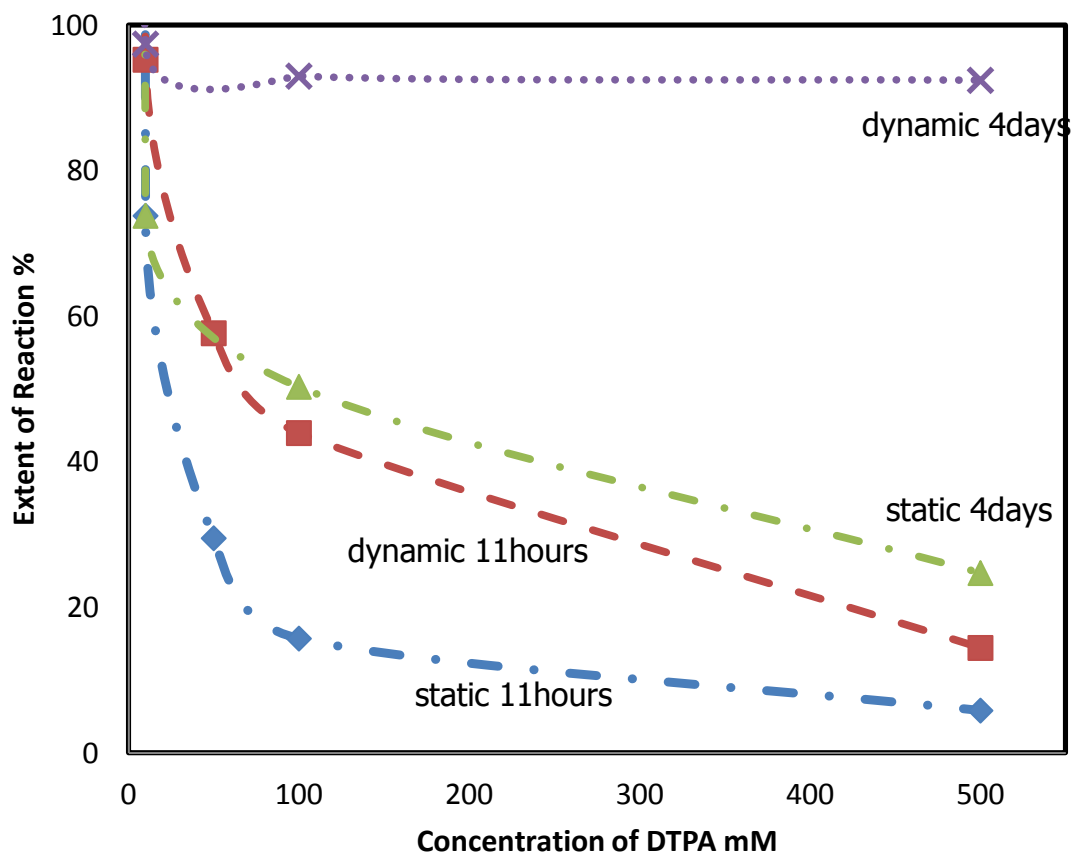
**Fig.7. Dissolution profiles improve with higher DTPA concentrations, longer treatment times and more accessibility**

Putnis, Putnis and Kowacz (2008) conducted similar experiments and found out that as DTPA concentration increases, barite dissolution increases and reaches a peak of 6mM at 10mM of DTPA. If DTPA concentration is increased still further, the barite dissolution decreases. Putnis concluded that this dissolution behavior could be caused

by two factors. At high concentrations, the DTPA molecules could cause crowding at barite surface leading to steric hindrance and reducing overall activity of reaction. Or they could form cluster structures in the bulk solution, away from barite, reducing accessibility to barite. Putnis et al. had used 0.0429M barite and 100 ml solution. Also, they had used a paddle stirrer. In our experiments, we have used a magnetic stirrer to uniformly suspend all the barite particles throughout the solution. This eliminates causes for second reason in Putnis' case. Also, we have taken 50 ml chelant solution and 0.257M of barite initially. Thus, a lot more contact area is available to chelant molecules eliminating steric hindrance and any causes for first reason in Putnis's case. Thus, we obtain four unique cases which can be analyzed in Fig. 7. In the static case after 11 hours, barite dissolution increases with DTPA concentration and then remains same above 50mM DTPA. If more time is allowed to lapse, after 4 days in the same static case, significantly higher dissolution is achieved. Also, dissolution goes on increasing with DTPA concentration even until 500mM. Thus, the only reason, static case after 11 hours, was showing low dissolution values was because reaction had not progressed far enough and if sufficient time is allowed, especially for higher DTPA concentrations, much higher barite dissolution can be observed. Now, if we include agitation, almost complete barite dissolution is observed at the end of 4 days for 500mM DTPA. Thus, if constraints of low scale accessibility, short soaking time and dilute volumes are removed, significantly higher barite dissolution can be achieved.

Another important factor for consideration is the extent of reaction, which is the percent of total reaction that is completed in the time interval. Since barite dissolution by

a chelating agent is a reversible reaction, the extent of reaction is 100% only after a relatively long time. Since stoichiometric ratio for barite dissolution by DTPA is 1:1 for DTPA: barite, 0.1M dissolves should dissolve 0.1M barite.



**Fig.8. Increase in dissolution at higher concentrations and longer times is due to more progress of reversible reaction**

Thus, as seen in **Fig. 8** out of 10mM barite that can be dissolved by 10mM DTPA in static case, it has dissolved 7.4 mM at the end of 11 hours, showing reaction is 74% complete. Similarly, out of 100mM barite that can be dissolved by 100mM DTPA in

dynamic case, it has dissolved 93mM, showing reaction is 93% complete. Reaction progress is more when DTPA concentration is less, agitation is provided and time is increased from 11 hours to 4 days. 500mM DTPA in dynamic case can dissolve 500mM barite. But since only 257 mM of barite are added and 238 mM are dissolved, reaction is assumed 92% complete. Thus, progress is high for 0.5mM DTPA as it is in excess of barite taken. Thus, 100mM and 500mM DTPA give maximum dissolution in dynamic case after 4 days. So, these two cases are considered for all future experiments.

Extent of reaction decreases as the concentration of DTPA goes on increasing. At lower concentrations of DTPA, conditions are much closer to ideal conditions and hence, equilibrium is shifted more towards the product side. So, extent of reaction is higher. Also, lower concentrations of DTPA are more efficient than higher concentrations for barite dissolution. But, lower concentration solutions may mean more volumes of solutions, more energy in mixing and higher sizes of mixing apparatus. Thus, this increase in efficiency may not translate to reduction in costs and from economic point of view; it may still be beneficial to have highest concentration of chelant solutions to be pumped downhole.

With regards to time of reaction, as concentration of chelant increases, the time for attainment of equilibrium increases. For concentrations of chelants lower than 0.01M, equilibrium has been achieved within the first two hours. For higher concentrations of DTPA, equilibrium needs much more time. Thus, as treatment is designed for higher concentrations of chelant, more soaking time should be allowed for completion of reaction. However, a positive observation is that majority of the reaction occurs in the



first few hours. Thus, soaking time should be decided not based on consideration of equilibrium directly, but when 60-70% of equilibrium value has been attained.

These times are the shortest times possible as in the lab tests, all effects of dissociation have been eliminated. The barite is in the form of powder with uniform particle size, kept suspended in the solution with a stirrer. In the field, it may be in the form of solid blocks or much coarser particles. It may have oil or organic coating. It may be contaminated with other scales. It may also contain fines, clay particles, bacteria, etc. Also, during soaking, the solution may be essentially static. Thus, there will not be any stirring or circulation. Due to this, reaction may take much longer to attain equilibrium. Also, amount of barite dissolved will be much lower.

These tests are not for the purpose of finding the amount of barite dissolved or the time required for dissolution. The purpose of lab tests is to compare the reactivity of different formulations and identify the best formulation. Thus, from the above graphs, the important concept to be grasped is that substantially higher barite dissolution is observed in 0.5M DTPA after 4 days of reaction time with maximum accessibility. But, if the constraints of concentrations, time and accessibility are left in place, barite dissolution is affected.

### **3.2 Combination of Chelating Agents**

DTPA is the most efficient chelant for barite dissolution and all formulations need to contain it. The value of this formulation could be enhanced further by adding other chelants, which though weaker in barite dissolution, could have other complimentary qualities like low costs, favorable environmental profiles or higher reactivity to different

scale/contaminant. Thus, the effect of combinations of DTPA with EDTA, MGDA and GLDA is studied.

### 3.2.1 Combination of EDTA and DTPA

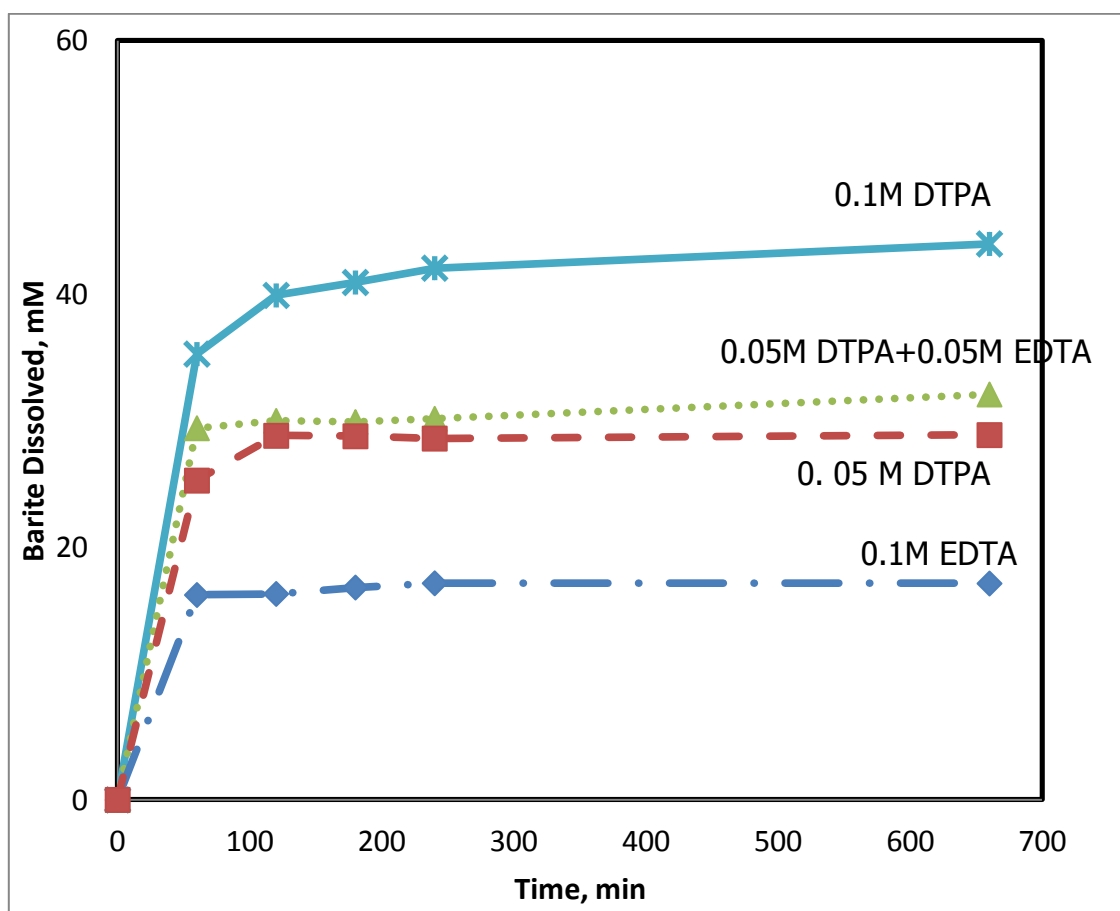
Ethylene diamine tetraacetic acid and diethylene triamine pentaacetic are two of the best known chelants for barite scale dissolution. DTPA having 5 acetic acid arms dissolves barite much more effectively than EDTA which has four acetic acid arms. Thus, DTPA is widely used in the industry for barium sulfate dissolution. However EDTA is much cheaper than DTPA. Also, its lower size causes less stearic hindrance, especially for inaccessible scale deposits. Hence, it is also widely used in the industry. Hence, the properties of formulations which had both EDTA and DTPA were studied. Thus, both chelating agents could complement each other and retain high dissolution profiles while reducing cost of chemicals. For this reason, EDTA and DTPA were mixed and their dissolution was observed. Experimental procedure developed above was followed. EDTA and DTPA were mixed in ratios shown in **Table 7** and gave dissolution profiles in **Table 8** and **Fig. 9**.

**Table 7. Mole ratios in which chelating agents were mixed.**

<b>Expt No</b>	<b>Mol of EDTA</b>	<b>Mol of DTPA</b>	<b>Ratio EDTA:DTPA</b>
1	0	0.1	0
2	0.05	0.05	1:1
3	0.1	0	Infinity

**Table 8. Barite dissolution for different combinations of EDTA and DTPA**

Time min	Mm Ba in 0.1MEDTA only	mM Ba in 0.05M DTPA + 0.05M EDTA	mM Ba in 0.1M DTPA only	mM Ba in 0.05M DTPA only
0	0	0	0	0
60	16.20	29.38	35.24	25.24
120	16.28	29.96	39.87	28.78
180	16.79	29.87	40.89	28.74
240	17.12	30.12	42.03	28.56
660	17.10	32.04	43.94	28.83



**Fig.9. Dissolution profiles for different ratios of chelating agents shows increase in dissolution as concentration of DTPA increases.**

0.1M EDTA by itself dissolves 17mM barite and 0.1M DTPA by itself dissolves 44 mM. If chelant combination of 0.05M DTPA and 0.05M EDTA is to be considered beneficial for barite dissolution, it should dissolve more barite than 0.1M DTPA. For 1:1 ratio, amount of barite dissolved (32mM) is midway between 17mM and 44 mM. As demonstrated earlier, with decreasing concentration of chelants, the efficiency of dissolution increases. Thus, 0.05M DTPA instead of dissolving 22 mM (i.e. half the amount of barite dissolved by 0.1M DTPA) actually dissolves 28 mM. Thus, amount of barite dissolved by 0.05M EDTA and 0.05 M DTPA together is less than the sum of the amounts dissolved independently by 0.05M EDTA or 0.05M DTPA. In other words, even if 1:1 formulation contains 0.05M DTPA and 0.05M EDTA, the extent of reaction is similar to 0.1M chelant rather than two 0.05M chelants. The only similarity between 1:1 formulation and the individual 0.1M chelants is they have the same no of moles of chelant species or same no of molecules of chelants. Thus, extent of reaction is related to the number of molecules of chelant species rather than their nature. From this we could assume that if any other acid with lower stability constant for barite than DTPA, is added to DTPA, it will always lead to decrease in total barite dissolution. This will be proven in future experiments.

As stated in the introduction, two main mechanisms have been proposed for dissolution of barium sulfate by chelating agent. First mechanism states that the chelant particle physically moves to barite surface, grabs the barium ion and then moves back into the bulk solution. Second mechanism states that barium ion dissociates into the bulk solution by itself due to the concentration gradient from bulk solution to boundary layer

and gets picked up by chelant molecule. Two cases exist and the above results can be explained for each case.

When barium ions desorb from the barite surface and go into the bulk solution, they have to pass through the boundary layer and then through some part of bulk solution. If there is less hindrance in their path more barium molecules will travel and also barium molecules will travel more distances. Thus, even chelant molecules farther away from the surface will be involved with dissolution and dissolution will be high. As number of chelant molecules increases, there will be more crowding in the above paths of barium molecules. Due to this blocking, barium molecules may find it difficult to dissociate freely into the bulk solution. Thus, extent of reaction will reduce.

When dissolution is only dependent on surface reaction, the surface area occupied by each chelant species becomes critical. When more number of molecules are present, there may be steric hindrance. Also, after chelants pick up barium, they may find it difficult to dissociate back into bulk solution due to crowding in the boundary layer. This will reduce extent of reaction in case of surface mechanism.

### **3.2.2 Combination of DTPA and MGDA**

MGDA is a new environmentally friendly chelating agent from BASF. Since it is biodegradable, it can improve the environmental profile of the chelant formulation. The procedure from chapter II is used to determine the effect of addition of MGDA to DTPA. **Table 9.** shows the different combinations of DTPA and MGDA, analyzed for understanding the dissolution behavior of chelant combinations. **Table 10.** and **Fig. 10** shows the resultant dissolution profiles.

**Table 9. Different combinations of DTPA and MGDA are taken to study the effect of MGDA on barite dissolution**

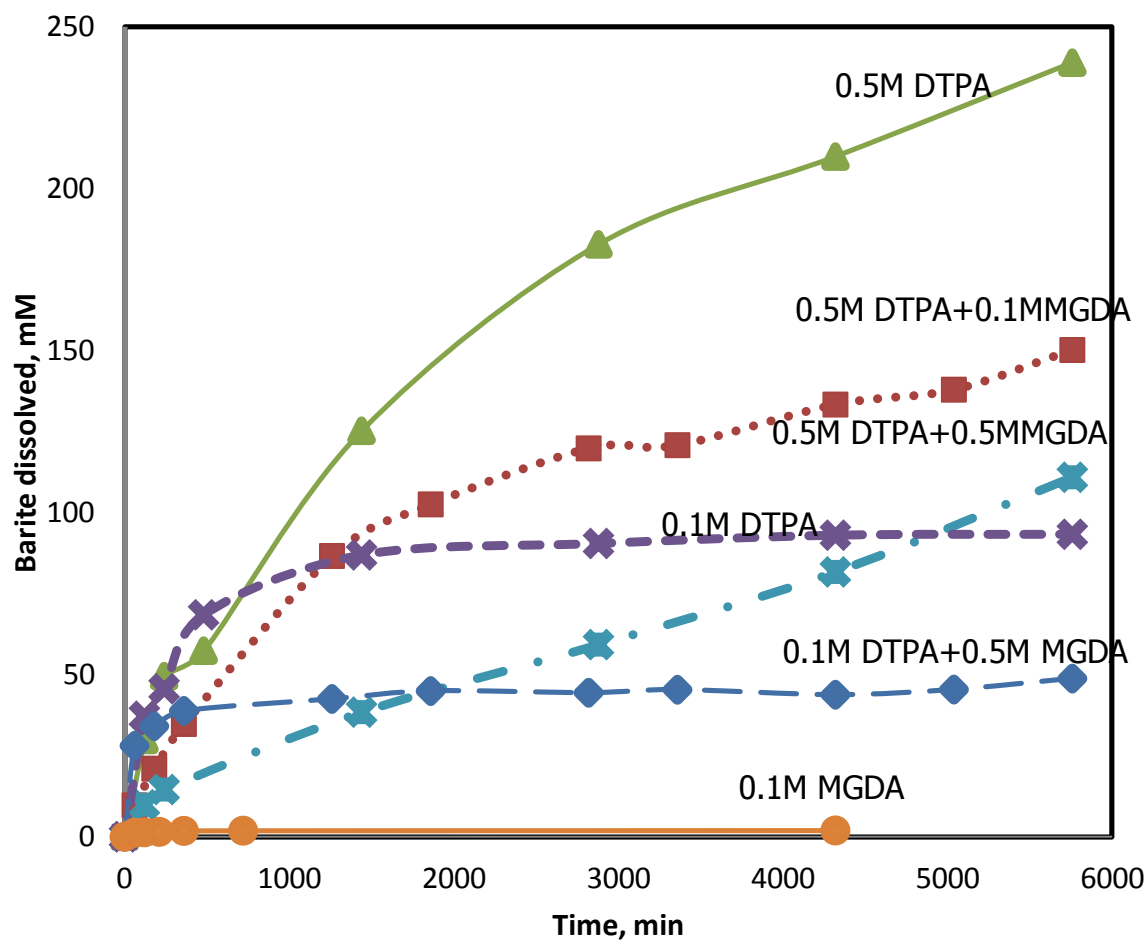
Concentration of MGDA, M	Concentration of DTPA, M	Molar ratio
0.5	0.1	5:1
0.1	0.5	1:5
0.5	0.5	1:1
0.1	0	infinity
0	0.1	0
0	0.5	0

**Table 10. Barite dissolution due to different combinations of DTPA and MGDA**

Time min	mM Ba in 0.1M MGDA	Time min	mM Ba in 0.5M DTPA+ 0.5M MGDA
0	0	0	0
60	1.26	120	1.66
120	1.35	240	5.54
210	1.50	1440	56.51
360	1.81	2880	94.03
720	1.87	4320	128.04
4320	1.92	5760	162.77

Time, min	mM Ba in 0.1M DTPA+ 0.5M MGDA	mM Ba in 0.5M DTPA+ 0.1M MGDA
0	0	0
60	28.08	9.69
180	34.11	21.00
360	38.83	34.80
1260	42.52	86.66
1860	44.96	102.59
2820	44.43	119.87
3360	45.36	120.86
4320	43.81	133.39
5040	45.42	137.99
5760	48.81	150.24



**Fig.10. Dissolution profiles due to addition of MGDA to DTPA show wide variation**

MGDA is a very weak barite dissolution agent and has a low stability constant for barium. Thus, 0.1M MGDA by itself dissolves only 3 mM of barite. There are two reasons for the weakness of any dissolution agent. Either the molecules find difficulty collecting the barium ions or they find difficulty retaining the ions. Since MGDA has only one nitrogen atom and only one chelating arm as compared to 5 of DTPA, it is very weak for dissolution of barium ions. This is quantified by its low stability constant for barite. Thus, no increase in dissolution is expected by addition of MGDA to DTPA.

However, contrary to expectation, a significant decrease was observed, on addition of 0.1 MGDA to 0.5M DTPA. When 0.5M MGDA is added to 0.5M DTPA, the drop in dissolution increases further. Thus, MGDA is inhibiting the dissolution process. When 0.5M MGDA is added to 0.1M DTPA, dissolution almost halves, but the drop in dissolution is less as compared to loss due to addition of 0.5M MGDA to 0.5M DTPA. Thus, addition of MGDA is significantly decreasing barite dissolution.

This inhibition can be explained in terms of both the mechanisms. Thus, in case of surface mechanism, the MGDA molecules near the surface reduce accessibility and prevent DTPA from contacting the barite scale, reducing dissolution. In bulk mechanism, the MGDA molecules are hindering smooth dissociation of DTPA molecules in solution and hence, preventing chelant-ligand interactions.

Thus, addition of any chelating agent in the formulation can lead significant loss of barite dissolution for DTPA and must be avoided. Similar procedure is repeated for GLDA to confirm conclusions.

### **3.2.3 Combination of DTPA and GLDA**

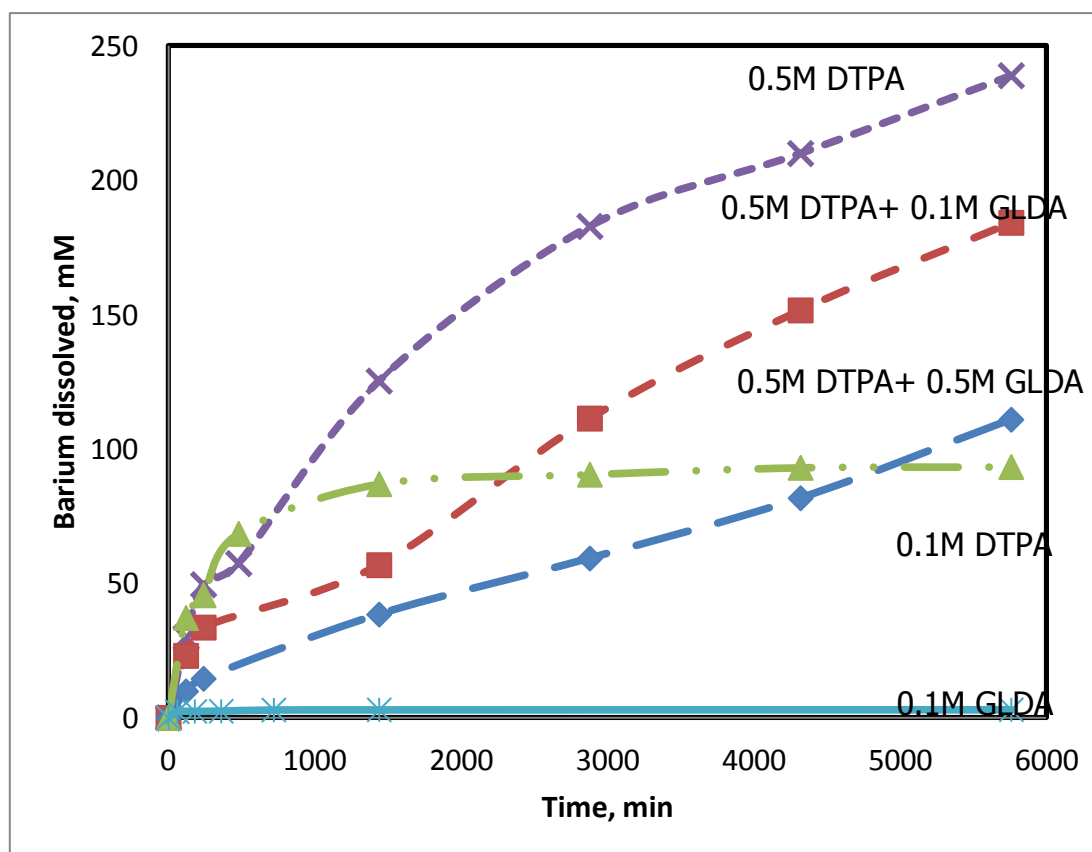
GLDA is another environmentally friendly chelating agent. It is produced by AkzoNobel. It has similar structure to MGDA and consequently is a weak chelating agent by itself. Different combinations of GLDA are added to DTPA as given in **Table 11**.



**Table 11. Molar ratios for combinations of GLDA and DTPA**

Expt No.	Concentration of GLDA, M	Concentration of DTPA, M	Molar ratio
1	0.5	0.5	1:1
2	0.1	0.5	1:5
3	0.1	0	infinity
4	0	0.5	0
5	0	0.1	0

The procedure is repeated exactly similar to MGDA and the dissolution profiles are plotted as shown in Fig. 11.



**Fig.11. Dissolution profile for GLDA+DTPA, showing similar trend to that of MGDA+DTPA**

Thus, after analyzing results for addition of EDTA, MGDA and GLDA to DTPA, it can be concluded that chelant combinations are detrimental to barite dissolution and should be avoided in treatments.

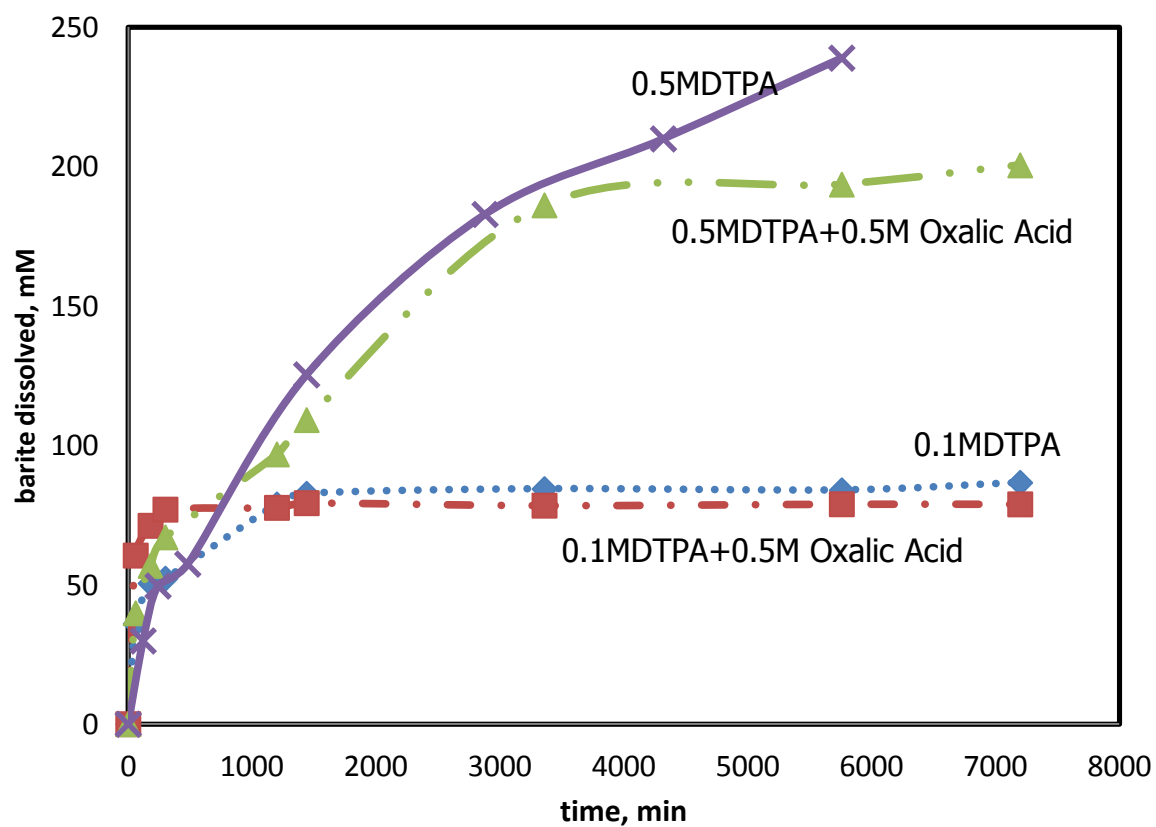
### **3.3 Effect of Synergists**

Paul and Fieler (1992) identified new synergists or activators which increased the dissolution capacity of chelant formulations. Synergists are similar to catalysts and can decrease reaction time, thereby increasing barite dissolved in given time. Generally, many weak organic acids having chelation capabilities have been tried as synergists. Of all these synergists, oxalic acid has been shown to be the best synergist for DTPA Paul and Fieler (1992).

#### **3.3.1 Effect of oxalic acid**

There is some debate in the literature over effectiveness of oxalic acid as a synergist for barite dissolution. Paul and Fieler (1992) show that oxalic acid is an effective synergist for 0.5M DTPA and thus, synergists should be added to chelant formulations. However, Lakatos, Lakatos-Szabo and Kosztin (2002) showed that oxalic acid does not significantly increase dissolution for 0.1M EDTA and thus, synergists should not be added to chelant formulations. However, since the procedures employed by both of them were not consistent, it is difficult to correlate the results. Thus, using the procedure developed in chapter II, the effect of oxalic acid on barite dissolution is studied. First of all, only 0.5M oxalic acid is taken with 1M and 5M potassium hydroxide and dissolution for each is calculated. However, no significant dissolution is observed in either case. Thus, oxalic acid by itself is not effective in barite dissolution. Then, 0.5M oxalic acid is

added to 0.1M and 0.5M solutions of DTPA containing potassium hydroxide for pH regulation. The dissolution profiles are tabulated in **Table 12** and plotted in **Fig. 12**.



**Fig.12. Addition of oxalic acid beneficial initially for 0.1M DTPA, but detrimental for 0.5M DTPA**

**Table 12. Dissolution caused by oxalic acid**

<b>Time, min</b>	<b>mM Ba in 0.1M DTPA+ 0.5M Oxalic Acid</b>	<b>mM Ba in 0.5M DTPA+ 0.5M Oxalic Acid</b>
0	0	0
60	60.48	39.77
180	71.18	56.80
300	76.97	67.03
1200	77.61	96.78
1440	79.29	109.09
3360	78.40	186.13
5760	78.90	193.57
7200	78.86	200.47

Thus, 0.1M DTPA dissolves 79 mM with oxalic acid and 87 mM without oxalic acid. There is a slight decrease in dissolution due to presence of oxalic acid. However, adding oxalic acid decreases the equilibrium time from 1200 min to 180 min. Thus, if possible a continuous treatment could be devised where oxalic acid would increase dissolution for the short residence times of chelant formulation. However, if treatment times are high, oxalic acid should not be added especially for high concentrations of DTPA. For 0.5M DTPA and oxalic acid, dissolution is 200 mM or 0.2M. Since 3 gm barite is added or 257 mM barite is present initially, 0.5M DTPA with oxalic acid dissolves 75% of the barite. However, equilibrium is only achieved after 3360 hours. Also, DTPA individually dissolves much higher barite. Thus, if long treatment times are possible, 0.5M DTPA should be added alone. If short treatment times are desired, a chelant solution containing 0.1M DTPA and oxalic acid could be continuously circulated.

Thus, after determining the procedure for lab tests, the effect of intrinsic factors like DTPA concentration, chelant combinations and synergists are analyzed. It is seen that

0.5M DTPA dissolves maximum barite scale after long time intervals, in presence of agitation and in absence of any other chelant or synergist.

Thus, after fixing the composition of chelant formulation, extrinsic factors are identified and their effect on barite dissolution is studied.

## CHAPTER IV

### EXTRINSIC FACTORS AFFECTING CHELANT PERFORMANCE

Having finalized the chelant formulation, the next step is to identify extrinsic factors that affect barite dissolution. When this chelant formulation is put into the formation, it encounters formation and seawater. Possibly, seawater is already being used for preparing the chelant. Thus, the effect of seawater on barite dissolution needs to be studied further. Another set of extrinsic factors have to deal with the solid scale in the formation. There are many scales that precipitate together. Generally, calcium sulfate scales precipitate along with barite as calcium belongs to the same group in the periodic table and has similar chemical properties. Calcium sulfate is more soluble than barite. Thus, if calcium sulfate scale is present along with barite, the calcium ions will compete with barium ions for the chelant molecules. Thus, again dissolution is expected to drop in presence of calcium sulfate scale. Finally, calcium carbonate may also be found with barite, either as scale or as limestone formation. It may also compete with barite for dissolution and affect chelant performance. Thus, the effect of extrinsic factors on barite dissolution using chelant formulations is analyzed in context of seawater, calcium sulfate scale and calcium carbonate scale.

#### **4.1. Effect of Seawater on Barite Dissolution**

The procedure developed in chapter II is repeated, just replacing deionized water by seawater. Synthetic seawater is prepared according to **Table 13**.

**Table 13. Composition of seawater**

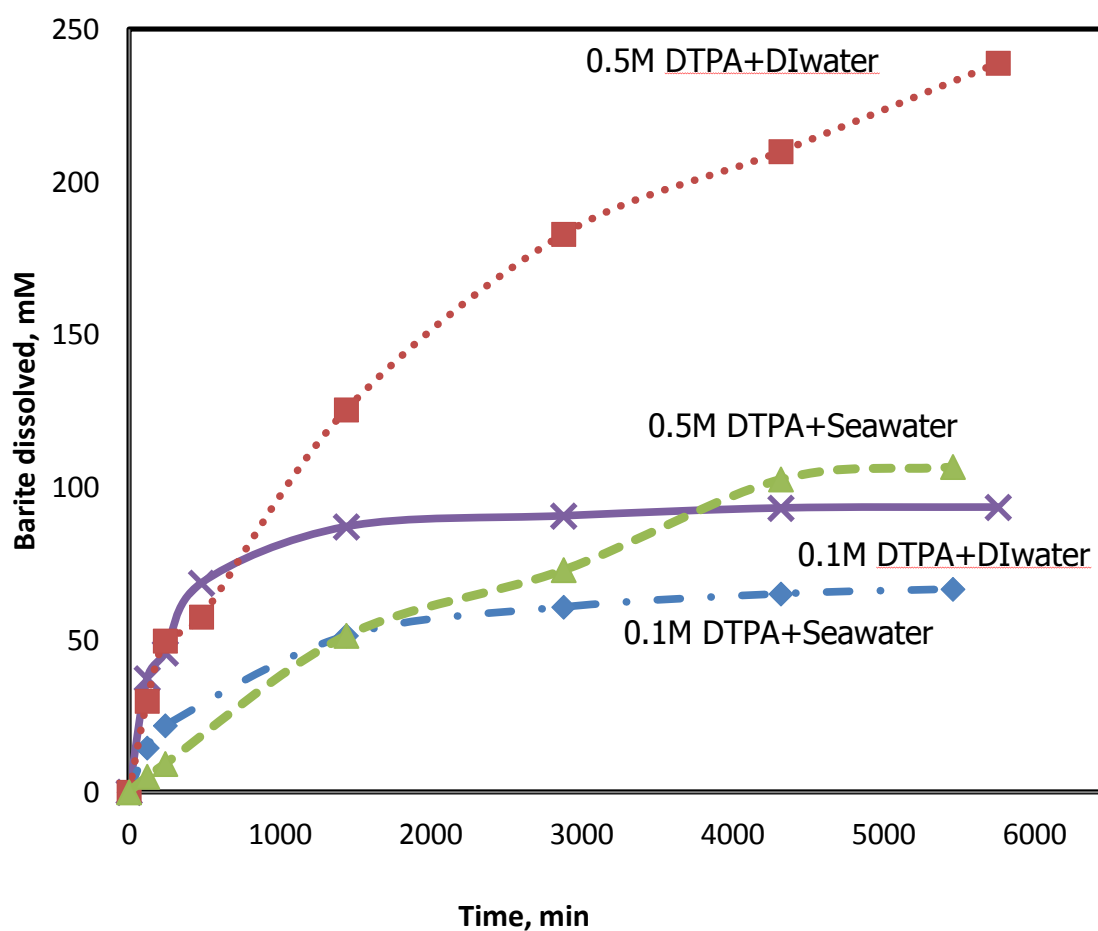
Salt	Concentration, g/l
NaCl	38.39
CaCl <sub>2</sub> ·2H <sub>2</sub> O	2.44
MgCl <sub>2</sub> ·6H <sub>2</sub> O	19.06 (.09M)
Na <sub>2</sub> SO <sub>4</sub>	5.26
NaHCO <sub>3</sub>	0.27

When the chelant formulation is put into seawater, magnesium hydroxide and calcium carbonate precipitate out due to their very low solubility. This deposition of magnesium hydroxide and calcium carbonate, on decreasing pH is observed commonly in alkaline flooding and desalination. Thus, even before treatment design, this problem needs to be addressed first. Chelating agents are active between pH of 11-13. Seawater is always going to be present near barite scale. If seawater pH falls as is inevitable on mixing with chelant formulation, magnesium hydroxide and calcium carbonate will be deposited first, before barite dissolution begins. Thus, barite removal treatment could end up depositing a newer scale.

In waterflooding, this problem is solved by adding antiscalants like enhanced maleate (Patel and Milligan 2008) or organic alkali (Berger and Lee 2006). However, since most of these organic alkalis or antiscalants are chelants or other polycarboxylic acids, their addition would cause significant decline, in barite dissolution. Thus, no extra compounds were added for now. This area needs more research in the future. Thus, above procedure is repeated to study the barite dissolution by 0.5M and 0.1M DTPA in presence of seawater and results are shown in **Table 14** and **Fig. 13**.

**Table 14. Dissolution profile for 0.5M DTPA in seawater**

Time, min	mM Ba dissolved by 0.5M DTPA in seawater	mM Ba dissolved by 0.5M DTPA in seawater
0	0	0
120	14.51	5.10
240	21.81	9.29
1440	51.29	51.29
2880	60.66	72.82
4320	64.99	102.54
5460	66.53	106.62



**Fig.13. Seawater reduces dissolution capacity of DTPA, especially at higher concentrations**



Fig. 12 shows that there is a significant drop in barite dissolution in presence of seawater as compared to dissolution in DIwater, especially at 0.5M DTPA. Thus, this allowance must be included in treatment design. There are two reasons for the drop in dissolution. First, chelant is also dissolving magnesium hydroxide and hence, is not available completely to barite. In fact, of the 90 mM magnesium present in seawater, 53mM is retained in the solution in case of 0.1mM DTPA and 79mM is retained in case of 0.5 M DTPA. Thus, only 10mM magnesium is precipitated showing that chelating agent DTPA independently can also be used for suspending magnesium ions, along with barium. Another reason for decrease in dissolution is that the presence of ions in the electrolyte seawater, hinder barite dissociation into solution in the bulk mechanism. Thus, DTPA gives markedly reduced dissolution of barite in presence of seawater, but is still successful in dissolving sizable quantity of scale.

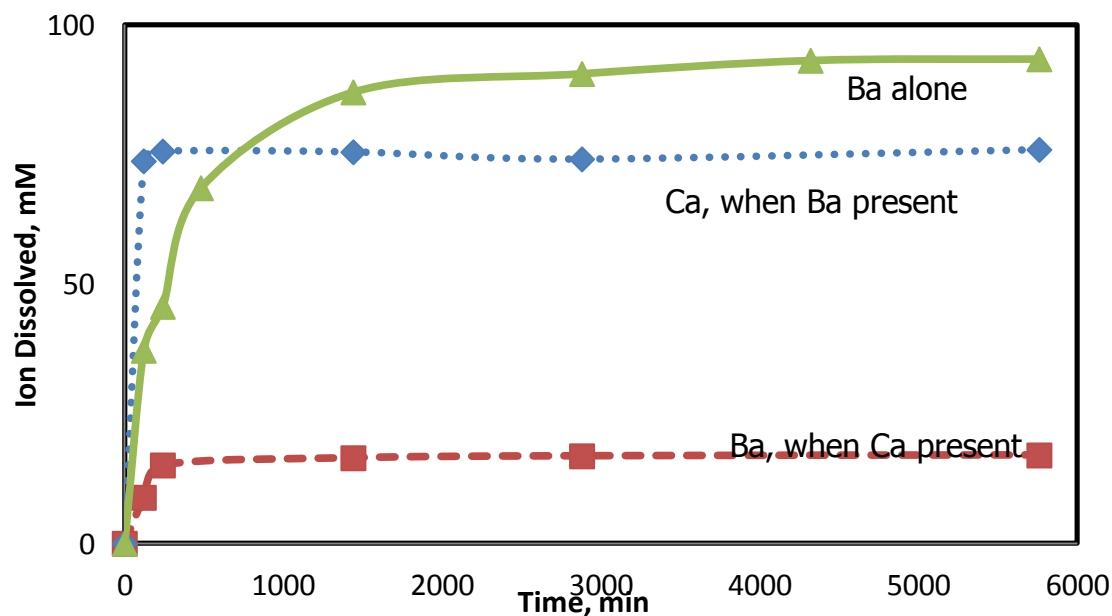
#### **4.2. Effect of Calcium Sulfate Scale**

Many times, barium and calcium are present at super saturation in the formation waters and so, barite and calcium sulfate scales get co-precipitated, in the same regions. To study the effect of this presence of competing ions, the above procedure is repeated by taking 3gm of both barite and calcium sulfate scales, instead of just barite scales. The chelant formulation contains first 0.1M DTPA and then 0.5M DTPA. Dissolution profiles are given in **Table 15** and **Figs. 14** and **15**. For case of 0.1M DTPA, almost complete reaction has occurred and 75 mM of calcium have been picked up along with 17 mM of barium. Thus, 92 mM ions have been dissolved or reaction is 92% complete. Calcium sulfate gets dissolved earlier and attains equilibrium faster. Selectivity is 4.45:1

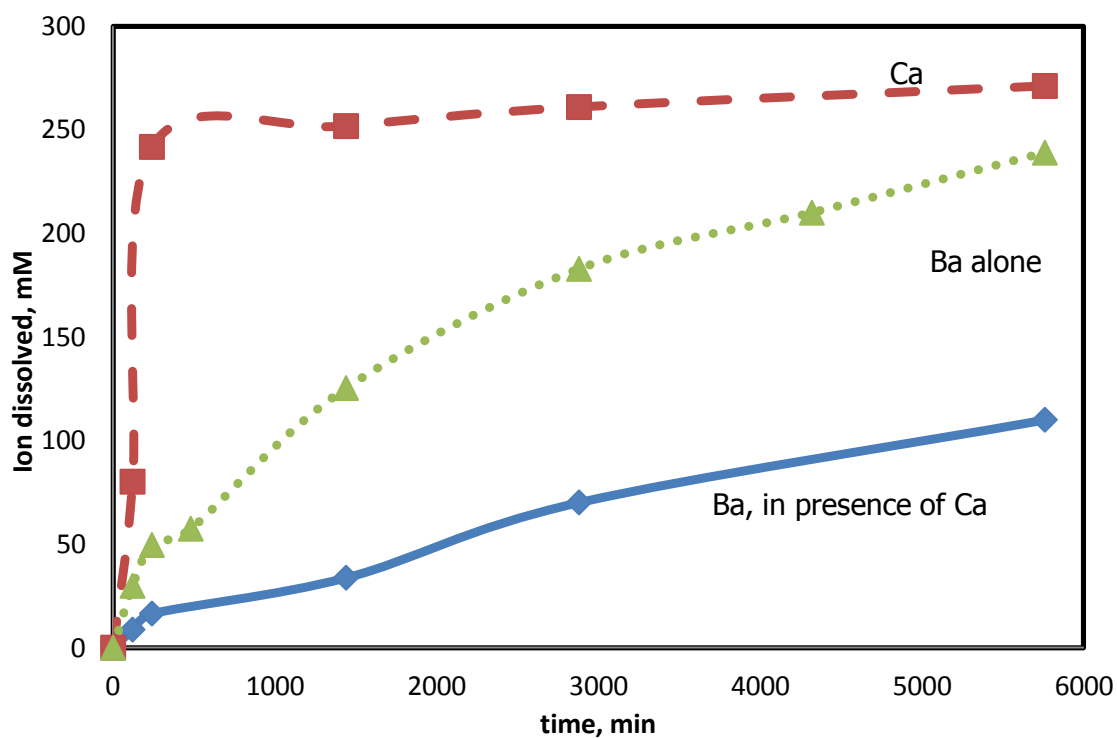
for Ca/Ba. For case of 0.5M DTPA, also barite dissolution decreases markedly with higher selectivity for calcium over barium. Thus, when calcium sulfate scales are present, it would be more efficient to treat them first and then start the barite treatment as in their presence, barite treatment is highly inefficient.

**Table 15. Dissolution profiles for calcium sulfate scales**

Time, min	0.1M DTPA		0.5M DTPA	
	mM Ba	mM Ca	mM Ba	mM Ca
0	0	0	0	0
120	8.86	73.68	8.73	80.12
240	15.09	75.57	16.47	241.69
1440	16.48	75.44	33.76	251.74
2880	16.86	74.06	70.10	260.93
5760	17.02	75.89	110.00	271.10



**Fig.14. DTPA dissolves mixed scale containing barite and calcium sulfate in ratio of Ca/Ba of 4.45 for 0.1M DTPA**



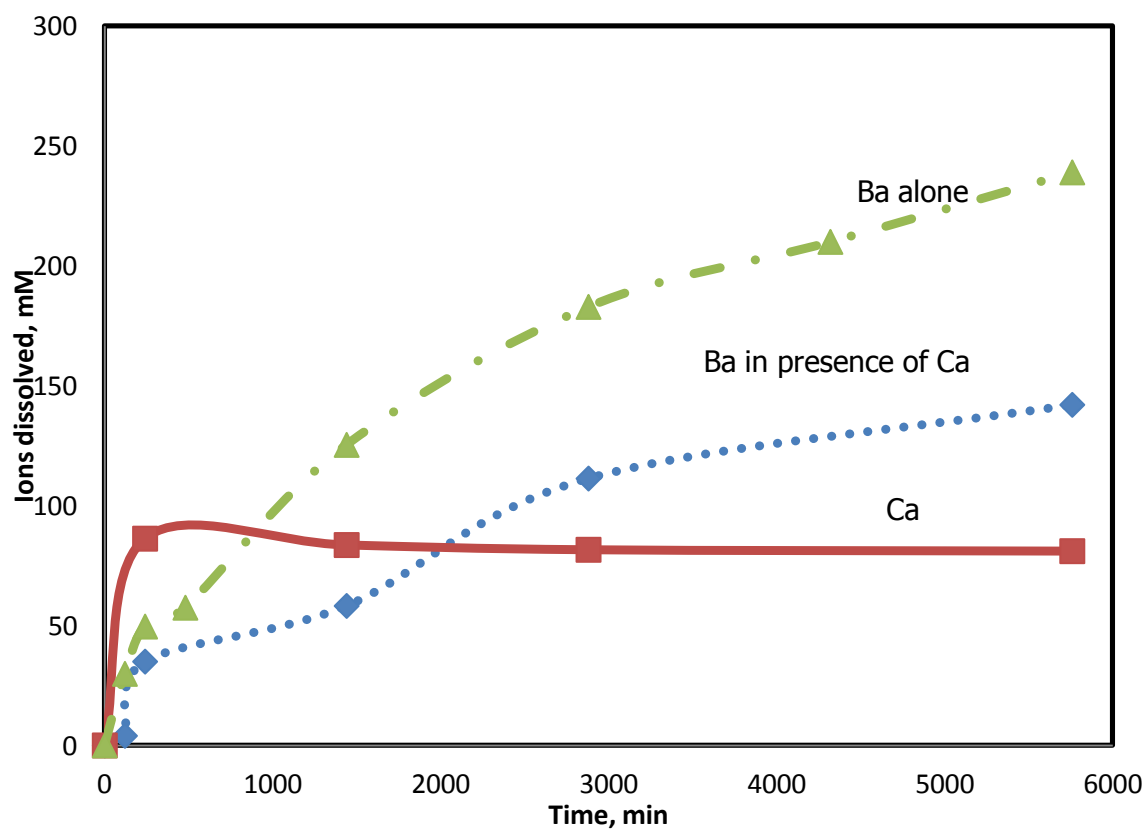
**Fig.15. Dissolution profile decreases due to presence of calcium sulfate for 0.5M DTPA**

#### 4.3. Effect of Calcium Carbonate Scale

3 gm calcium carbonate powder is taken along with 3 gm barite powder and above procedure is repeated for 0.5 M DTPA. Similar results are obtained as earlier with substantial drop in barite dissolution, but amount of calcium dissolved is lesser. Thus, DTPA is more efficient at picking up calcium sulfate than calcium carbonate. Thus, sulfate ions do play part in dissolution mechanism. Thus, if calcite is present, scale could be treated first or compensation has to be included in barite treatment design to account for presence of carbonate scale. The dissolution profile is given by **Fig. 16** and **Table 16**.

**Table 16. Dissolution profile for 0.5M DTPA in presence of calcium carbonate**

Time, min	Ca dissolved, mM	Ba dissolved mM
0	0	0
240	86.22	34.95
1440	83.56	58.16
2880	81.57	111.27
5760	81.00	142.00



**Fig.16. Dissolution profile for 0.5M DTPA shows significant decrease in dissolved barite in presence of calcium carbonate scale**

Thus, presence of competing ions, be they magnesium or calcium in seawater or calcium in the scales, calcium carbonate and calcium sulfate, causes significant decrease

in dissolution. These extrinsic factors need to be carefully considered in treatment design.

## CHAPTER V

### CONCLUSIONS

Thus, this project identifies the best possible chelant formulation and estimates the dissolution profile from lab tests, leading to a more informed and efficient treatment design to remove barite scale.

1. Barite dissolution, ideally, increases with increase in DTPA concentration, accessibility and soaking time. However, many constraints are faced during actual field treatments, which substantially decrease chelant performance. These and similar other constraints must be identified and tested, each time before treatment design
2. Barite dissolution is inhibited by the physical presence of chelant molecules. Hence, higher concentrations of DTPA are less efficient in shorter times. Also, combinations of DTPA with any chelant acid with lower stability constants inhibits barite dissolution. So, performance decreases significantly for combinations of DTPA with MGDA or GLDA.
3. Synergists like oxalic acid, increase initial barite dissolution, especially for moderate DTPA concentrations like 0.1M, but inhibit dissolution at equilibrium or longer treatment times.
4. Barite dissolution decreases in presence of seawater as competing ions magnesium and calcium reduce chelant activity towards barium and inhibit reactant dissociation. Treatment design should also account for the possibility of

precipitation of magnesium hydroxide from seawater due to the high pH chelant formulation.

5. DTPA selectively dissolves calcium ions if present, leading to significant decrease in barite dissolution. Thus, if scales contain calcium sulfate or calcium carbonate, it must be removed prior to barite removal treatment.

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