Analysis and Modelling of In Situ Geochemical Reactions in Oil Fields Based on Produced Brine Chemistry Data

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ABSTRACT

Management of mineral scale precipitation is one of the major challenges faced by the oil industry. Total costs of scale prevention can exceed £1 million for a field or even sometimes for a single well. Identification of the injection water fraction in the produced brine stream is of importance to production chemists involved in mineral scale prevention. This data is required to determine the onset and the severity of barium sulphate precipitation, one of the most challenging flow assurance issues in the oilfield due to the very low solubility of the mineral.

This body of work develops a solution to the problem of how to determine the injection water (IW) fraction in the produced brine. A robust and accurate method for calculating IW fraction in produced water samples is presented. The method has been named the "Reacting Ions" method. The Reacting Ions method is based on interactions between ions during reactions, by correctly taking account of ion losses that will occur due to precipitation. The proposed new method allows injection water fraction to be calculated from concentrations of the ions involved in reactions, which has never been done before. In addition, the new method incorporates as a limiting case the Ion Track method - the most widespread method currently used in the industry. The Reacting Ions method removes the limitation that only conservative ions can be used to track injection brine in produced water.

This Reacting Ions method is applied to a synthetic produced water case, generated using a reservoir simulator, where the "correct" IW fraction is known, and a very good match is achieved, even when significant noise is applied to the synthetic data. An additional outcome of the synthetic case tests is that conventional use of sulphate in the Ion Track method leads to a late detection of injection water breakthrough, while the Reacting Ions method based on barium and sulphate is significantly more accurate. Delayed detection of injection water breakthrough can lead to the onset of scaling before preventative measures have been taken.

The Reacting Ions method was applied in the analysis of produced brines for more than 100 wells in several regions of the North Sea. Results of the study presented here show that the method is generally more effective in detecting IW fractions than conventional ion tracking techniques, especially at low IW fractions soon after breakthrough occurs. Using barium and sulphate, the new Reacting Ions method benefits from near zero end-point concentrations of

these two ions that is typical for North Sea brines, and is consequence of the low solubility of barite.

The more accurate identification of IW fraction has led to the development of three applications that use the Reacting Ions method. In the first, the relative ion deviations are used to identify whether an ion is conservative, precipitating or part of a dissolution reaction. This information can be applied by production chemists to predict possible types of mineral scale occurring. The second application assists in detecting which formation or formations the well is producing from, which gives incremental information about the reservoir itself. In the third, a method to analyse squeeze treatment response is proposed. The impact of scale inhibitor placement on the ion concentrations is evaluated, and thus a judgement can be made regarding the overall effect of the squeeze treatment in stopping the identified scale reactions from happening. All three new applications were successfully applied to field data.

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I am standing near the end of the most significant challenge I ever had to face. It's said every end is a new beginning. Yes, I feel that, I am eager to move further, not to delay for a single moment. However one stop I could not miss. This stop is for you, for those who were around me. Not only my research would not have been completed, but I owe you my deepest gratitude for everything that I will reach in my life further.

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NOMENCLATURE

Ca	Calcium ions
CO_2	Carbon dioxide
Conc.	Concentration
g	Grams
HCO_3^-	Bicarbonate ion
K^+	Potassium
l	Litre
M	Molar concentration
mg	Milligram
MIC	Minimum inhibitor concentration
ml	Milli litre
M.wt	Molecular weight
Na^+	Sodium ion
ppm	Parts per million
t	Time
V_w	Volume of water
V_T	Total volume
^oC	Degree centigrade
~	Approximately
%	Percentage
RI	the Reacting Ions method
IT	the Ion Track method
PCA	Principal Component Analysis
CUSUM	Method of Cumulative Sums
IW	injection water
IWf	injection water fraction
FW	formation water
C_{fw}	formation water concentration
C_{iw}	injection water concentration
$\tilde{C}$	observed/measured ion concentration
$\overline{C}$	conservative ion concentration
K^a	Stochiometric coefficient for ion A
K^b	Stochiometric coefficient for ion B
WCT	Watercut
E_{rel}	Random relative error
E_{abs}	Random absolute error
SQZ	Inhibitor squeeze treatment

CHAPTER 1 INTRODUCTION

This introductory chapter provides the basic information that the reader will need to understand before continuing to the kernel of the thesis – the Reacting Ions method. Such issues as the background of oilfield mineral scale formation, what the research topic is, and how the research topic was developed are covered.

1.1. Background

When water is discussed in the context of the oil industry, it is usually being considered as an injection fluid, as a waste fluid as produced water (PW), and as the main cause of corrosion in tubing.

In the history of the development of the oil industry, water was not thought of as one of the key factors during production. Moreover, it was not until 1938 ([1] and [2]) that the existence of water in oil reservoirs was generally accepted.

Now it is widely recognised that hydrocarbons in reservoirs are coupled with subsurface waters. Subsurface waters play an important role in hydrocarbon migration and accumulation. The properties of these subsurface waters can vary significantly. Chemical compositions may range from fresh waters, evaporated sea water, to highly concentrated brines. The first dozen brines in a database of North Sea brines arranged alphabetically show a range of salinities from near seawater to greater than 200,000 mg/l TDS (Table 1.1). Water deep in reservoirs can be present as a result of trapping during sedimentation or infiltration of meteoric water ([2],[3]), or a combination of both mechanisms. Subsurface waters/brines are in place with hydrocarbons for a significant geological time — typically of order millions of years. Over such time the subsurface waters come to chemical equilibrium with the rock and the hydrocarbons.

Table 1.1 Formation Water compositions (FAST research group, 2009).

Field	Na^+	Ca^{2+}	Mg^{2+}	K^+	Sr^{2+}	Ba^{2+}	Fe^{2+}	Cl^-	$SO4^{2-}$	HCO_3^-
Aare	15900	5300	360	790	1120	800	74	38800	8	
Alba	14100	650	130	110	35	65	0	23000	0	0
Anglia	67840	21000	3410	1470	770	1		151949	505	145
Argyll	25450	3110	295	535	430	5.2	18	45080	275	295
Balmoral	29950	3120	615	375	755	300	0	54200	0	290
Banff	25210	2600	345	585	135	100		45173		
Beatrice	22700	2500	320	160	216	44	0.5	41950		350
Beryl	20680	20080	405			0	27	68070	405	435
Birch	35650	2000	200	2150	450	1000	0	63500	0	0
Brae	21460	550	170	740	26	550	0	33740	600	0
Brage	17526	1567	284	0	315	96	0	30593	0	0
Brent	12160	370	50	550	70	95	0.7	19500		308

As a result of the field/reservoir depletion during production, subsurface water moves along with the hydrocarbons and is often produced in a mixture that may contain a range of metals, rock particles, sand, hydrocarbons precipitates etc. The amount of produced water tends to increase with field lifetime. Produced water as a waste fluid is related to the fact that during oil production, water from the reservoir should be separated from the hydrocarbons and disposed of.

The dominant use of water in the oil industry is as an injection fluid. Waterflood is a method of secondary recovery in which injection water (IW) is pumped via injection wells into reservoirs to displace oil and provide pressure support ([4],[5]). Waterflooding is one of the main oil recovery processes. It has being applied in many reservoirs around the world. In the early 1970s one-third to one-half of the production in the United States came from fields into which water was injected ([2]). The principles of waterflooding have been reviewed in most standard reservoir engineering texts books and in special waterflood monographs ([6],[7]).

The potential problems associated with waterflood include poor sweep efficiency due to variable permeability and/or viscous fingering, and early water breakthrough that may cause production and surface processing problems.

Waterflooding is often designed without regard to the composition of the brine injected. In offshore developments seawater is often used as an injection water as it is the most readily available. Chemical equilibrium is distorted when a mix of injected and subsurface (formation) waters is moving through the reservoir, or as a result of pressure/temperature changes. As a consequence, mineral scale can precipitate and form a blockage. Mineral scale (hereafter simply referred to as scale) is normally defined as a deposition of inorganic minerals from a brine ([8], [9], [10], [11] etc). Precipitation of such deposits is not a problem in itself, but the tendency of scaling deposits to precipitate on surfaces causes major damage. Solids may adhere to the rock, may plug sand screens, block perforations, tubing, pumps, create emulsions, and damage sub-surface safety valves.

Formation of mineral scale can be a major problem in oil extraction. It creates blockages and formation damage which leads to significant cost for industry in maintaining productivity of the wells, flow rate through the production facilities and/or to treat such damage through application of chemical inhibitors. Remoteness makes mechanical removal of any scale expensive. Some scale deposits can incorporate radioactive materials and removed scale must be treated as low radioactive waste. The reported typical cost of the most common scale mitigation procedure - squeeze treatment - in the North Sea is in the range of £30,000 – £70,000 for conventional treatments excluding deferred oil costs ([12], [13]). Total costs of scale mitigation procedures can exceed £1 million for a field or sometimes even for a well. Frenier ([14]) reports estimations for the economic impact of scale at more than $1.4 billion (£850 million) each year. Graham and Mackay ([15]) cite more than 4 million barrels of production is lost annually in the United Kingdom sector of the North Sea (predominantly due to barium sulphate, but by no means exclusively).

1.2. Research Area and Research Objective

Hydrocarbons and aqueous solutions produced from petroleum reservoirs vary in amounts and ratios that change with time. Changes in fluids, temperatures and pressures during the reservoir's life cycle cause different types of scaling. In field conditions naturally occurring scales frequently are found as mixed deposits.

Local equilibrium is disturbed when a well starts to flow, and as a result solids may start to precipitate. Inorganic deposits are called "scales", organic deposits are referred to as "waxes" or "asphaltenes".

1.2.1 Mechanisms of Scale Formation

There are several mechanisms that lead to scale formation. One of the most important properties is supersaturation. The degree of supersaturation controls the extent of salt precipitation. In simple terms supersaturated brine contains more ions than is thermodynamically stable, and precipitation may occur. When scale precipitates, the system is returned to chemical (thermodynamic) equilibrium. The speed or reaction kinetics of the process is affected most of all by the temperature. However, degree of supersaturation does not give any indication of the amount of scale deposition that is possible.

1.2.2 Solubility

Water is a naturally and universally occurring solvent. Subsurface waters are usually solutions containing a number of ions. Contact with minerals present in the rock can lead to dissolution of some compounds. In addition, water usually contains dissolved gases. As conditions change many of the dissolved compounds may become insoluble to some degree and precipitate from the water to form scale.

Solubility is defined as the limiting amount of solute which can be dissolved in a solvent under certain conditions ([16]). Water has a limited capacity for keeping these compounds in solution.

The main parameter that governs scale precipitation is the saturation ratio. The saturation ratio of a compound reflects the degree of its supersaturation. If the saturation ratio is greater then one, precipitation can occur. Saturation ratio can be expressed as a function of ion activities and solubility product.

Species activities are often simplified to their concentrations if the scaling salt is dissolved in a solution. The solubility product is, again, usually simplified as the product of ion concentrations under equilibrium conditions. Composition is defined as the amount of the solute in a certain volume of solution. Depending on units, concentration can be called molarity if units are moles per volume, molality if units are moles per mass of solvent, or the most widespread unit is mg/l, which takes into account mole weight of the component.

Solubility products (solubilities) of various scales at different pressures, temperatures, pH etc form a complex subject, which is discussed in a variety of sources, and is out of the scope of this work.

1.2.3 Types of Mineral Scale

The major categories of mineral scales are carbonates, sulphates, sulfides and silicates. The oil industry focuses on two major types of scales – carbonates and sulphates.

Pressure drops are the primary cause of carbonate scaling. A pressure drop below the water bubble point pressure leads to evolution of carbon dioxide. As the solubility of the carbonate declines, the scale forms. The most common type of carbonate scale is calcium carbonate.

$$Ca(HCO_3)_2 \longleftrightarrow CaCO_3 + CO_2 + H_2O \tag{1.1}$$

Carbonate scaling potentials become high with increasing water cut and lower well pressures.

Sulphate scales are precipitated mostly by the mechanism of mixing of incompatible waters. Brines are called chemically incompatible if minerals precipitate as a result of their mixing. High barium and strontium levels in the formation water will result in a high sulphate scaling tendency when mixed with injection water which is rich in sulphate.

$$Ba_2(Sr_2, Ca_2) + SO_4 \longleftrightarrow BaSO_4(SrSO_4, CaSO_4) \tag{1.2}$$

A comprehensive list of scaling deposits may be compiled from many literature sources ([17], [2], [3], [18]). Deposits often reduce flow and may even cause loss of the well. Scale deposits reduce the volume available for flow, and the additional pressure drop caused by scale buildup can be very large. Detailed description of the mechanisms and types of formation damage is out of the scope of this work. A comprehensive description of formation damage and its causes can be found in a book by Civan ([18]).

This work focuses on prediction of barium sulphate scale. Barium sulphate is a significant cause of production loses in the North Sea area ([8]). This type of scaling is largely caused by mixing of formation water with incompatible injection water during the waterflood ([8]). Barite solubility is very low: of the order of 10^{-5} moles/kg. Ion concentrations become the main factor controlling the severity (solubility) of barium sulphate scale. Barium sulphate solubility has a modest dependency on temperature, with a maximum around 100^{o}C. Another property of sulphate scales is that they have a low dependency on pH ([19], [20], [21], [22] et al).

1.2.4 Amount of Mixing

The sulphate concentration in seawater which is often used as an injection water in offshore developments, is very high and can reach 2700-3000 mg/l. If there are high levels of barium and strontium ion concentrations in the formation water, then this results in a high sulphate scaling tendency when the brines are mixed.

To be able to model and predict scaling tendencies in a reservoir, information concerning the degree of mixing is required. The resulting concentration of any ion is a function of the degree (proportion) of mixing and the reacted amount.

The proportion of mixing can be defined as fraction of the injection water in the mix.

$$IWf = \frac{InjectionWaterVolume}{TotalVolume} = \frac{V_i}{V} \tag{1.3}$$

A zero value for injection water fraction (IWf) means that there is only formation water in the mix, while a value of one means that the mix is 100% injection water.

The amount of injection water/formation water (IW/FW) mixing that has taken place is one of the main parameters that determines the severity of barite scaling. If the amount of mixing and pressure/temperature conditions are known, then the barium sulphate scaling tendency may be calculated using any of the commercially available thermodynamic simulators (MultiScale, PHREEQC), see example in Figure 1.1. Thus, the injected water fraction in the produced brine mix is an important value to determine.

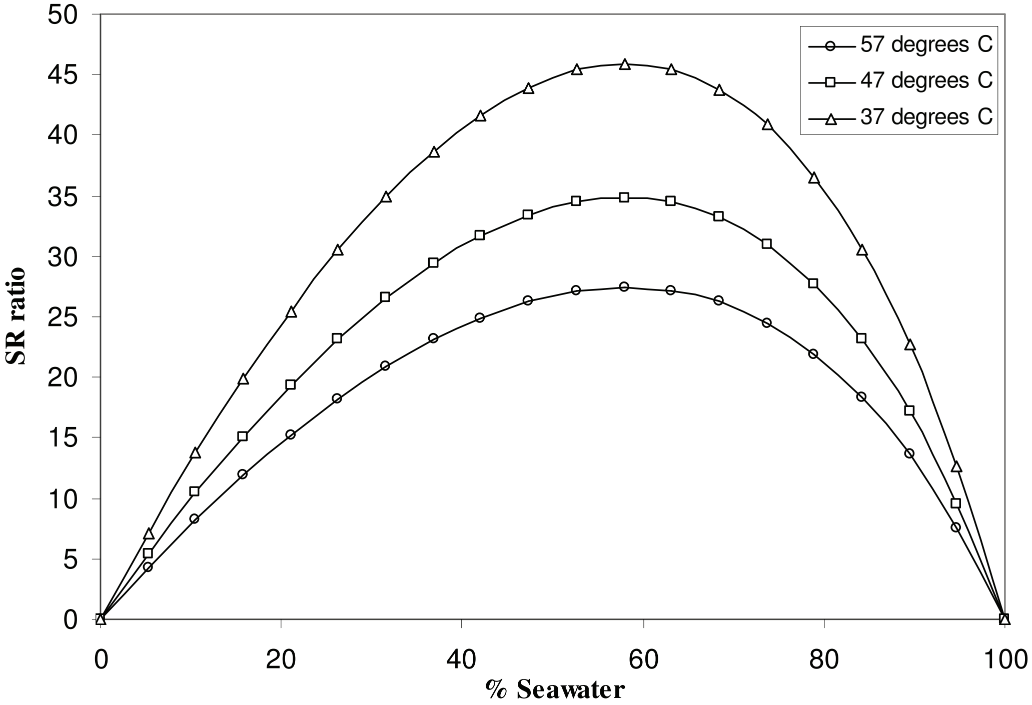


Figure 1.1 Effect of temperature on barium sulphate supersaturation ratios (SR) (predicted by Multiscale) for different Seawater fractions for a formation water with a barium concentration of 200 mg/l.

Conditions that allow scale to form can be predicted, but the exact location where scale forms is more difficult to determine. The full-field modelling of barite scale in the reservoir requires the solution of the flow equations, the equations for the thermodynamic equilibrium, and the equations for geochemical reactions. This implies conditions for the choice of modelling software. Some simulators, such as Schlumberger Eclipse (the de-facto reservoir simulation standard in the oil industry), are capable of solving the flow equations fast, but are limited in terms of scaling reactions ([25]). One of the limitations with software designed specifically for geochemical reactions, such as MultiScale by Scale Consult AS/Petrotech (chemistry database is specifically focused on reservoir conditions), Geochemist's Workbench by Rockware (with chemistry database limited to atmospheric pressure conditions, which is not suitable for reservoir simulations), PHREEQC by USGS (which uses a widely validated database at reservoir conditions), is that none of them provide dynamic capabilities other than 1D reactive-transport flow modelling. Two full-field simulators capable of modelling scale precipitation CMG STARS (kinetic model), and Petroleum Experts Reveal (which uses PHREEQC chemical database) are used in this work. Despite the fact that CMG STARS uses a kinetic model without thermodynamics, it is suitable to model Barite precipitation ([28]). Another product of CMG – GEM is excluded from the list here on the grounds that even though it provides better options to model reactions, the chemistry database does not consider high pressure environments (such as equilibrium constants from the Geochemists Workbench software, [29]).

However, the next problem with full-field simulations is that our ability to model scale precipitation in situ and in the well is linked to our ability to accurately determine the IW fraction at production wells. The research question of this work is the amount of mixing that has occurred in the produced brine. Chapter 2 develops the theme of the importance of IW fraction for barite scale prediction in more detail.

The main objective of this PhD thesis is to develop an efficient method for the petroleum industry to identify the fraction of injection water in the produced brine.

1.3. Thesis Content

The thesis is organised in seven chapters. Chapter 2 gives a broad overview of the methods currently available to perform IWf calculations. Despite the fact that there is only a limited number of articles present in the literature, three main approaches – radioactive tracers, the Ion Track method, and statistical tools (Principal Component analysis) are covered. Use of radioactive tracers is seen as the most preferable, because it allows great flexibility as several wells and several brines can be tagged separately. However, radioactive tracers are expensive, and complex procedures are required for design, delivery, implementation, and measurements. Due to high costs, radioactive tracers are often performed in pulses; that approach limits use of radioactive tracers except for detecting IW breakthrough. IW fraction cannot be to measured continuously on the basis of the injection of pulsed radioactive tracers. The limitations of the Ion Track method, the most commonly used method in the industry, are also analysed in Chapter 2. These limitations come from the nature of linear extrapolation. Statistical tools used to measure IW fraction include Principal Component analysis and the CUSUM method. The application of Principal Component analysis is reviewed based on a published example and is compared with the Reacting Ions method.

The derivation of the Reacting Ions method is presented in Chapter 3, the final section of that chapter covering the testing of the method (with different amounts of noise) with a synthetic model, where injection water fractions are controllable and known independently of the method. Two new benefits of using the injection water fraction are presented in Chapter 4, followed by the successful field applications in Chapter 5. The development in Chapter 6 explores the opportunity that the Reacting Ions method now allows to measure squeeze treatment response, a measure of squeeze treatment efficiency, based on an accurate calculation of IW fraction. This chapter establishes a link between determination of IW fraction and the application of scale inhibitor squeeze treatments, another very important issue in the industry. Correct and accurate IW fraction is required to evaluate squeeze treatment efficiency, and to measure actual response of ion concentration to the placement of scale inhibitor. Chapter 7 is the conclusion to this thesis. The thesis outline shown in Figure 1.2 describes the structure of the thesis.

Chapter 1	Background of the research problem. The importance of injection water fraction for modelling barium sulphate scale formation.
Chapter 2	Review of the available methods (Ion Track, Multivariate analysis, CUSUM).
Chapter 3	The Reacting Ions method description and formulation. Sensitivity studies under different conditions.
Chapter 4	New applications of IW fraction. Identifying ions participating in reactions and detecting which formation a well is producing from.
Chapter 5	Field applications of the Reacting Ions method.
Chapter 6	Measuring squeeze treatment response as an indicator of squeeze efficiency (using the injection water fraction).
Chapter 7	Conclusion and results.

Figure 1.2 Thesis outline.

CHAPTER 2 METHODS OF INJECTION WATER DETECTION

This chapter covers materials relevant to the subject being explored, and determines which literature makes a significant contribution to the understanding of the topic of mineral scale, and calculations of injection water fraction in the produced brine in particular.

2.1. Overview of sources

Despite the fact that during the past 50 years much information has become available on the topic of mineral scale precipitation (Figure 2.1), there is only a limited number of sources (the total number barely exceeds 10-15, depending on the criteria of which publications to count) investigating the problem of measuring the fraction of injection water in produced brines.

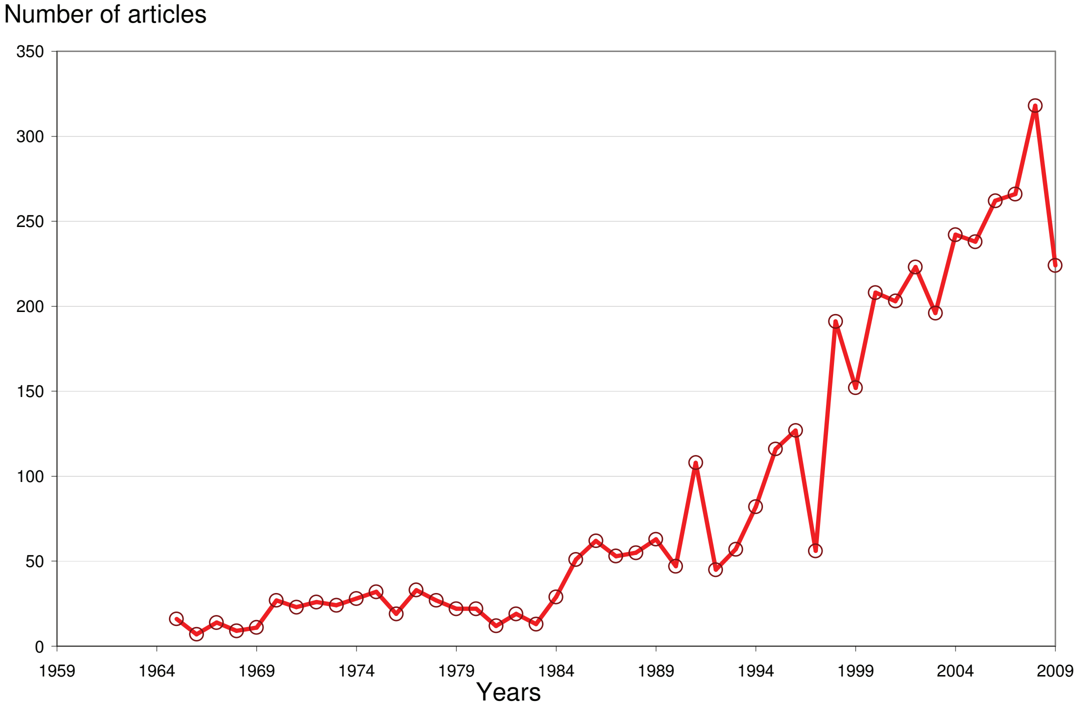


Figure 2.1 Number of articles on topic of mineral scale per year in the Society of Petroleum Engineers (onepetro.org) knowledge base.

2.2. Chapter Content

This chapter has been organised in the following way. First it begins with the fact that oilfield water is associated with and is adjacent to the oil in reservoirs for millions of years. Water is a very good natural solvent and dissolves minerals from the rock it resides in. Over such long time periods mineral components (ions) dissolve in the water until it reaches equilibrium (rates of dissolution and precipitation become equal) marker "A" in the Literature Review Structure diagram (Figure 2.2).

When oil from the reservoir is recovered, the equilibrium is disturbed. Disturbed chemical/thermodynamic equilibria may lead to the precipitation of scale (Marker B, Figure 2.2). Two general types of scale are often considered – mineral and organic. Mineral scale causes significant expense for the oil industry (see Chapter 1 for more details). It can cause health and safety problem (malfunction of sub surface safety valves), can block flow in the production system, and can be difficult to remove due to low solubility and/or poor access (e.g. subsea wells). Carbonate and sulphate scales are the most common types of mineral scale.

Carbonate scales occur primarily as a result of pressure drop. Carbonate scale is more soluble than barium sulphate, and can be dissolved using acid treatments.

Sulphate scales usually result from the mixing of chemically incompatible brines, such as formation water and seawater. An injection agent for offshore developments is often seawater since this is the most readily available option. However, seawater contains about 3000 mg/l sulphate. Formation waters are often rich in barium (and/or strontium and calcium). As a result of mixing of these brines in the reservoir, sulphate scales may precipitate. Sulphate scale is a major problem for offshore developments as barium sulphate, in particular, is almost insoluble except in the presence of chelating agents (marker C, Figure 2.2). Barium sulphate's solubility product in brine is very low, and varies very little in the range of common reservoir temperatures and pressures (70-150^{o}C). No mechanism is currently known that could significantly alter the solubility of $BaSO_4$ ([19]), so prevention often relies on chemical inhibition. Solubility product is a function of ion activities, which are functions of ion concentrations. Concentrations of ions change when several brines are mixed (Marker D, Figure 2.2). When a reservoir is waterflooded, injection water mixes with formation water. The degree of mixing (the fraction of injection water in a mix with formation water) is called "injection water fraction" (Marker E, Figure 2.2). The resulting concentrations of ions in the mix are a function of injection water fraction. Thus injection water fraction is therefore an important parameter to determine.

Injection water fraction can be calculated using two approaches. The first is to use the physical properties of the produced mixture, such as density and resistivity. The second method involves analysis of the produced water chemical composition.

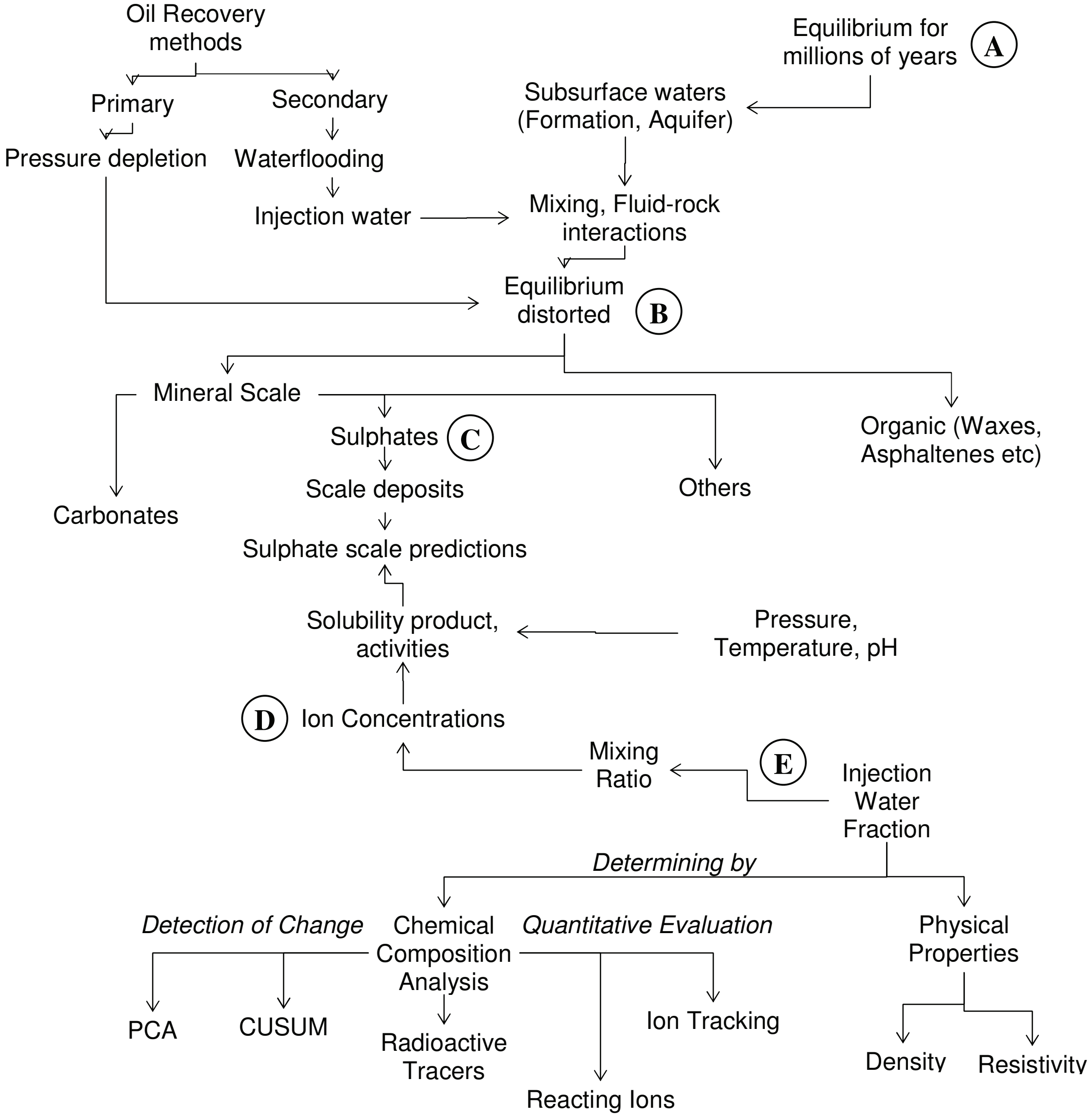


Figure 2.2 Process summarised diagram.

2.3. Existing methods for detecting fraction of injection water

The presence of some “marker” property in a brine is the only chemical way of distinguishing it from another brine. Brines are waters with high concentrations of dissolved salts. Brine properties that can be used for the purposes of detecting marked brine are temperature, resistivity, ion concentrations, pH, density etc.

2.3.1 Temperature and Resistivity logs

Normally the temperature of the injection fluid (10-30^{o}C) differs from that of the formation brine (70-150^{o}C). However, it cannot be used as a reliable property for distinguishing brines. Injection fluid travels through the reservoir, warming as it goes, and the temperature difference between fluids becomes negligible with time.

Previous studies ([30], [31]) have reported the use of density to distinguish drilling mud from formation brines, with drilling muds typically significantly denser than the formation brines. However, changes in produced water density as a result of mixing with injection water will not be detected accurately, especially at low mixing ratios. The reason for this is the loss of mass due to in situ scale precipitation. Also, some measurement errors for other ions can mask real changes in the desired ion concentration, since by definition density includes the total mass of all components. The low injection water fractions are of especially high interest for production chemists as they allow monitoring and detecting injection water breakthrough; moreover, the mass of barite scale that can precipitate is generally highest at IW fractions less than 10%. All this makes density unsuitable for use as parameter for calculation of injection water fractions.

Resistivity and magnetic properties would be attractive options as they allow the use of non-intrusive measurements; however, there are no consistent results reported in the literature. Bottom hole resistivity logging is time-intensive and costly, and it can affect production. Resistivity measurements of produced water samples can be misinterpreted if there are other sources that lead to changes in resistivity, for example if corrosion has occurred in the tubing some iron will remain in solution.

2.3.2 Tracers

The most straightforward approach used in many industries to distinguish fluids is to tag one of them with a special chemical marker. Special chemical species introduced to the fluid to measure flow paths and amounts are called tracers ([32]).

Tracers have a long history of use for tagging water. The pioneering work of Slithcer ([33]) was performed over one hundred years ago in 1901. It was the first direct field measurement of the rate of ground water flow. Electrolyte was used as a tracer and the parameter measured was electric current between wells. Slithcer ([33]) conducted a natural gradient two-well test and correctly attributed the shape of the breakthrough curve to the dispersion; moreover, he was the first person who identified the potential to use temperature as a tracer ([34]).

In many literature sources where tracers are mentioned, usually radioactive tracers are implied. Both radioactive and chemical tracers may behave similarly, although having different chemical/physical properties. The most common types of tracers are radioactive ones. Radioactive isotopes used to tag compounds proved itself as suitable for many purposes in biomedicine, chemistry, physics, oil industry etc. Radioactive isotopes are used to tag chemical tracers, and so provide analytical options of high selectivity and sensitivity.

This work, however, does not set out to describe tracer technology in depth. A considerable amount of literature has already been published on tracers. Tracers are a powerful tool to enhance knowledge about the reservoir and advantages of its application, even taking into account high costs and complex design issues. Tracers help to investigate anomalies, flow channels and barriers. Tracers are the best option that can be used in terms of mineral scale to distinguish between waters from different injection wells in the same field. Any experience involving use of tracers adds valuable knowledge available to the reservoir engineer.

In recent years, the most wide ranging work published is “Tracers in the Oil Field” by Zemel ([32]). This is the most comprehensive and deep piece of work ever done in the area of oilfield tracers. In this work, almost every aspect of tracer application is covered, starting from the development of suitable materials for the purpose of tracing water. Zemel tracks the full history of materials used, including everything from sticks, dyes, and mushroom spores to chemical and radioactive tracers.

For the purpose of tracing water while monitoring scaling problems, two main requirements have been identified by Zemel ([32]) as major contributing factors for a water tracer to be considered ideal. A special chemical marker must follow the path and travel at the same velocity as the water in which it is injected, and it must be easy to identify and measure quantitatively ([32]). The ability to identify the water source is basic to the use of tracers for all the purposes: it is based upon the assumption that the movement of the tracer reflects the movement of the injected water ([32]).

The main advantage of radioactive tracers is that different tracers can be added to the flow in different injection wells, and this makes it possible to obtain not only information on water sources, but in some cases (if pulse injection is not used) to calculate quantitative values of water flow in the reservoir. However, it should be noted that not every compound is suitable for these purposes. Many organic and inorganic candidates have been tested in history ([33]; [35]; [36]; [37]; [38]; [37]; [39], [40]; [41], [42]; [43]). Some of them showed poor results; the tracers either did not survive or showed long delays in appearing relative to the carrier fluids (retardation).

Lake ([5]) defines ideal tracers as those that should be displaced at the velocity of the injected water. However, one problem identified by Zemel, which prevents tracers from being considered as ideal, is that the survival time of tracers is related to the properties of the reservoir. Rock usually has a negative charge and contains high concentrations of clays, which have high cation-exchange capacities. If the tracer ions are positively charged, then they can exchange with the cations adsorbed on the reservoir surfaces. A similar effect can occur if some of the tracer is soluble in the oil phase. Therefore the tracer ions can be delayed relative to water. Even if tracer is delayed, it may arrive at the producer at some point. However, the tracer would not be conservative, which means the tracer participates in reactions and is no longer ideal, since some or all may never be produced.

The main advantage of using radioactive tracers is that radioactivity itself provides a very sensitive analytical method for detection. On the other hand, there are disadvantages that preclude tracers from routine use. Generation of radioactive isotopes, delivery, controlled injection, monitoring, analysis and disposal requires special measures to avoid radioactive contamination, and as consequence this makes the whole procedure very expensive and technically extremely complex.

2.3.3 Ion tracking

Ion tracking (sometimes referred to as Ion Track) is the name for the standard interpolation technique used to calculate the fraction of Injected Water in produced brine. There is no direct authorship of that method as it is quite straightforward; however, Schmidt and Thingvoll ([44]) may be cited. It is based on the concentration differences between formation and injection brines. One of the critical issues with the Ion track is that it can only effectively handle two brines in solution as it is a linear function of ion concentration. The usefulness of the method relies on the fact that some ions can be treated as ideal tracers (chloride, sodium etc), which means they do not participate in geochemical reactions (conservative), they follow injection water without delays, and their concentration differences are high enough to overcome measurement errors. If those requirements are met, then measured concentration of the conservative ion may be used as an indicator of mixing ratio.

The amount of mixing may be defined as fraction of injected water in the mix (Figure 2.3).

$$IWf = \frac{InjectionWaterVolume}{TotalVolume} = \frac{V_i}{V} \qquad (2.1)$$

$$IWf \subset [0;1]$$

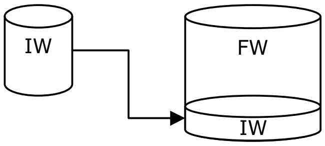


Figure 2.3 Schematic of brines mixing.

Based on a mass conservation law, the mixing of two brines is linear, and therefore the concentration of any conservative ion is a function of the initial ion concentrations and the extent of mixing.

By *initial ion concentrations* we refer to the average concentration of ions in water samples taken from the formation and from the injection brine stream.

C_{iw} – Initial ion concentration in injection brine

C^{fw} – Initial ion concentration in formation brine

The term "conservative ion concentration" refers to the concentration of any ion that is only the result of conservative mixing of brines, with no reactions occurring.

A conservative ion concentration is dependent only on the mixing proportion and the initial ion concentration in participating brines. The first assumption used here is that in the absence of any reaction, brines mix by linear law. This means that if there is no reaction occurring, then the observed ion concentration is equal to the sum of fractions of initial ion concentrations:

$$\overline{C} = \sum C_i \cdot F_i \tag{2.2}$$

Where

C_i – concentration of ion in brine *i*,

F_i – fraction of brine *i* in a mix, so $\sum F_i = 1$

For the most common oilfield cases, where two brines (Injection and Formation) mix:

$$\overline{C} = C_{iw} \cdot IWf + C_{fw} \cdot FWf = C_{iw} \cdot IWf + C_{fw} \cdot (1 - IWf) \tag{2.3}$$

where

$\overline{C}$ – conservative ion concentration

C_{iw} – initial ion concentration in Injection brine

C_{fw} – initial ion concentration in Formation brine

IWf – Injected Water fraction

FWf – Formation Water fraction *FWf=(1-IWf)*

For example, at time *t* there is a mixing of formation brine with an injected water (Figure 2.4). If the fraction of IW is 30% (*IWf=0.3*), the initial barium concentration in the injected water is 10 mg/l ($C_{iw} = 10$) and 50 mg/l in the formation water ($C_{fw} = 50$), then the resulting conservative barium concentration will be 38 mg/l (see Eq.(2.3)):

$$\overline{C} = C_{iw} \cdot IWf + C_{fw} \cdot (1 - IWf) = 10 \cdot 0.3 + 50 \cdot 0.7 = 38$$

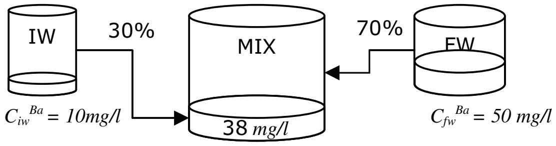


Figure 2.4 Schematics of injection and formation brines mixing.

If no reaction occurs then the observed ion concentration is a conservative one. It is a linear combination of initial ion concentrations, and therefore injection water fraction can be calculated from the conservative ion concentration:

$$\overline{C} = C_{iw} \cdot IWf + C_{fw} \cdot (1 - IWf) \Rightarrow \overline{C} - C_{fw} = IWf(C_{iw} - C_{fw}) \tag{2.4}$$

$$IWf = \frac{\overline{C} - C_{fw}}{C_{iw} - C_{fw}}$$

Equation (2.4) is the main equation of the Ion Track method. Ion Track is just a linear interpolation between concentrations of ion in formation and injection waters (Figure 2.5).

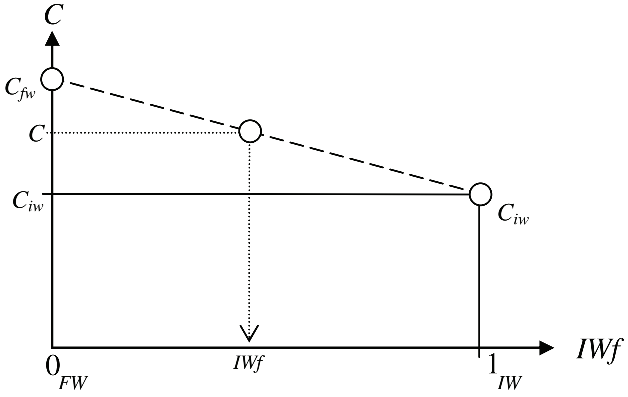


Figure 2.5 Illustration of the Ion Track method.

The main advantage of this method which makes it widely used in industry, is its simplicity and ease of interpretation. However, there are some limitations. The first one is the limited number of conservative ions which can be used in oil field applications with high enough concentration differences between injection and formation brines. Those ions are chloride, sodium and bromide. The second issue arises from analysis errors which can hide small changes in IW fractions. The last issue is that Ion Track can effectively handle only two brines in a mix.

2.3.4 Multivariate Analysis

The time series of observed ion concentrations are a set of cross-correlated variables. Any change in an ion concentration in produced water samples is the result of mixing and geochemical reactions that have taken place.

Plotting variations of ion concentration over time is the simplest way to analyse produced water. A limitation of this approach is that changes in ion concentration may occur for several reasons, such as measurement errors, dilution, well operations, reservoir effects, ion-exchange reactions etc. Analysis of several time series usually enhances the interpretation of the data or even may produce significantly new information (Figure 2.6).

Considerable time is required for handling and interpreting large data sets, especially when each variable (ion concentration time series) must be inspected.

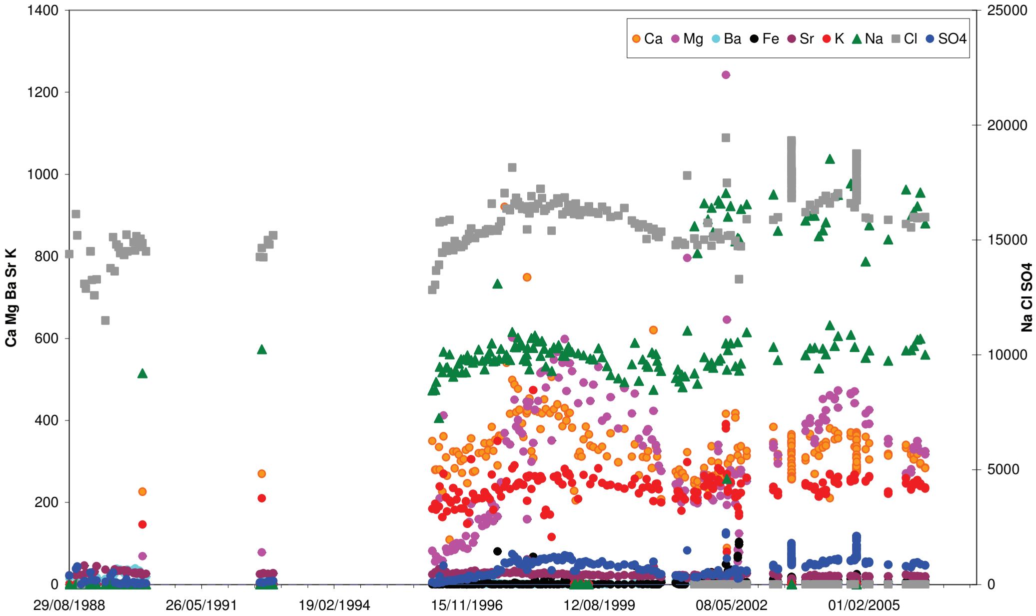


Figure 2.6 Well Y produced ion concentrations over time.

The use of statistical methods can help in systematic analysis of produced water compositions. Multivariate data analysis and its fundamental method Principal Component Analysis (PCA) helps to reduce the multi-dimensional space to make data manageable, as well as reducing the time required for analysis.

PCA was developed by Pearson ([45]), and the method involves a mathematical procedure that transforms a number of possibly correlated variables into a smaller number of uncorrelated variables called principal components. PCA finds linear combinations of the variables (the so-called principal components) that correspond to directions of maximal variance in the data. The first principal component accounts for as much of the variability in the data as possible, and each succeeding component accounts for as much of the remaining variability as possible ([46]). A detailed description of the PCA method, defined as an orthogonal linear transformation that transforms the data to a new coordinate system, is out of the scope of this work.

Despite the fact that the PCA method is well known and has a great history of applications in many areas (financial markets, handwritten zip code classification ([47]), human face recognition ([48]) etc), its application in the area of oilfield scale has not been a widespread practice. Currently, there are only several reported implementations of PCA for scaling problems by Schmidt ([44]), Coleman ([49]), Webb ([50]), and Scheck ([51]).

Application of Multivariate analysis (PCA method) for injection water breakthrough detection was recently published by Scheck and Ross ([51]). Shell UK Production Chemistry unit observed a decline in barium concentrations in several wells and suspected scaling. However, Environmental Scanning Electron Microscopy/Energy Dispersive X-Ray showed no scale formation and the reservoir model did not support the possibility of IW breakthrough.

Ion Tracking (single ion analysis) was not able to help support a clear conclusion and the authors relied fully on the application of the PCA method to state that seawater breakthrough occurred in those wells. Subsequently undertaken scale dissolver and squeeze treatments led “to significant production gain” ([51]). The analytical technique was applied for more wells, which resulted in a reduction of the number of scale squeeze treatments from 18 to 6.

The paper highlights the effect for the Shell U.K. operations from the use of the Principal Component Analysis method together with Environmental Scanning Electron Microscopy/Energy Dispersive X-Ray.

A serious weakness with this argument, however, is whether Shell UK benefited from using only the PCA. Scheck and Ross failed to fully acknowledge whether the general approach to measure injection water fractions was more accurate compared to single ion analysis.

The key problem with the Principal Component Analysis is that the analyst has to decide the meaning of Principal components. Scheck and Ross ([51]) in the “case study 1” argue that PCA1 (the first Principal Component) is heavily influenced by chloride, sulphate and magnesium (but no supporting data tables are provided, unfortunately). Based on that, they develop the conclusion that PCA1 is a function of injection water fraction. Plotting PCA1 versus time clearly indicates a steep change occurring at a specific time, which they attribute to seawater breakthrough.

Principal Component Analysis is an important tool as it offers a way to compress the data with minimal information loss and the principal components are uncorrelated. However, there are a number of well documented disadvantages as well. A particular disadvantage is that principal component is a linear combination of all variables and weights of variables in the linear combination are often non-zero ([52]). This often makes it difficult to interpret the derived PCs, therefore the issue with applying PCA for scaling problems is that there is no definite meaning for the principal components. Analysts in most cases assume the first principal component as an injection water fraction on the basis that the first principal component explains most of the variation in the data.

The general limitation of the PCA is that it provides only visual indication of changes (variations) in observed ion concentrations. To overcome that, the authors compared the approximated current values with theoretical and state current level of IWf is about 8-10%.

2.3.5 Testing Principle Component Analysis versus the Ion Track and the Reacting Ions methods

This section presents a comparison of PCA with the Ion track and the Reacting Ions methods. Direct comparison is not possible, since the resulting score values of the first principal component, which accounts for the greatest change in the data, is a linear combination of all variables used in PCA. Those values are too high to be plotted on the same plot along with the injection water fractions. This is the reason why scaled first principal component (PC1) was used. Scaling was performed in the range between minimum and maximum values of PC1. It is assumed that scaled PC1 represents a profile of the changes in IWf.

The first test was performed on a synthetic case with no noise added to observed samples. Sodium, chloride, sulphate, barium, potassium, and magnesium ion concentrations were used in Principal Component Analysis. The first principal component took 100% proportion of variance in data. The profile of the first principal component matches IW fractions calculated with Ion Track and the Reacting Ions methods (Figure 2.7).

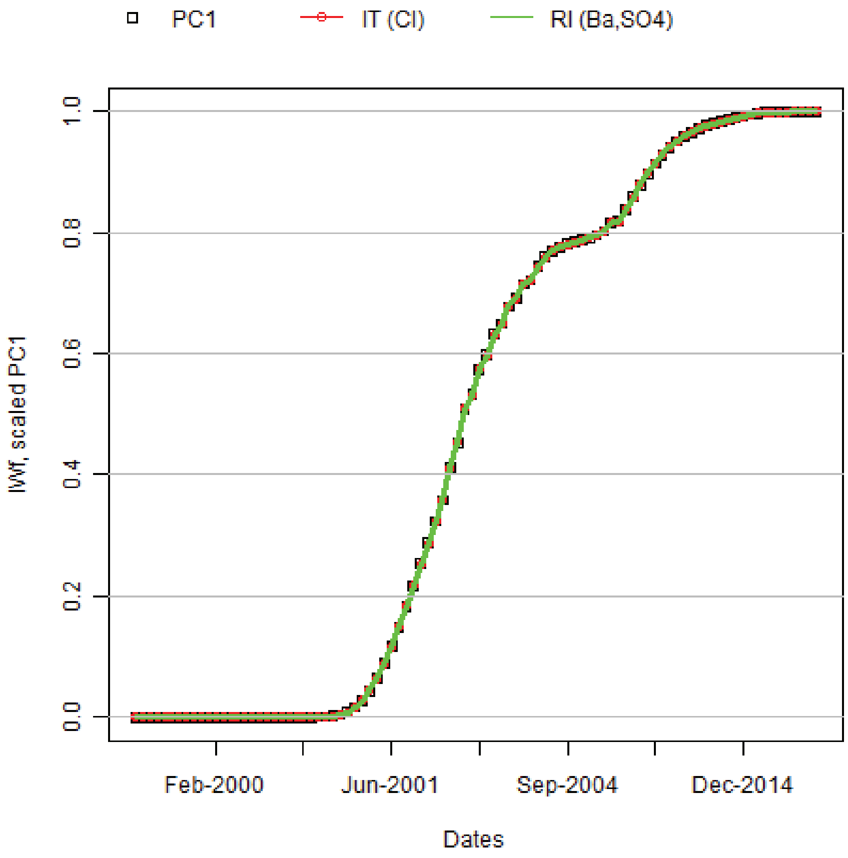


Figure 2.7 Results of scaled scores of Principal Component analysis, injection water fraction calculated by Ion track method based on chloride (red) and the Reacting Ions method based on barium and sulphate (green) for a synthetic case with no noise added versus date.

In the second scenario random 5% of relative and 5 mg/l of absolute noise were added to the observed ion concentrations from the synthetic case to simulate field conditions. After the PCA was performed over the data, the first two principal components covered 98% of variations in the data (Table 2.1). PC1 took 91% and was selected as parameter representing IW fraction. Scaled PC1 was plotted together with IW fractions calculated by Ion Track method and the Reacting Ions method (Figure 2.8).

Table 2.1 Proportion of variance explained by principal components.

	PC1	*PC2*	*PC3*	*PC4*	*PC5*	*PC6*
Proportion of Variance	0.915	0.0681	0.0159	5.50E-04	0.00004	0
Cumulative Proportion	0.915	0.9835	0.9994	1.00E+00	1	1

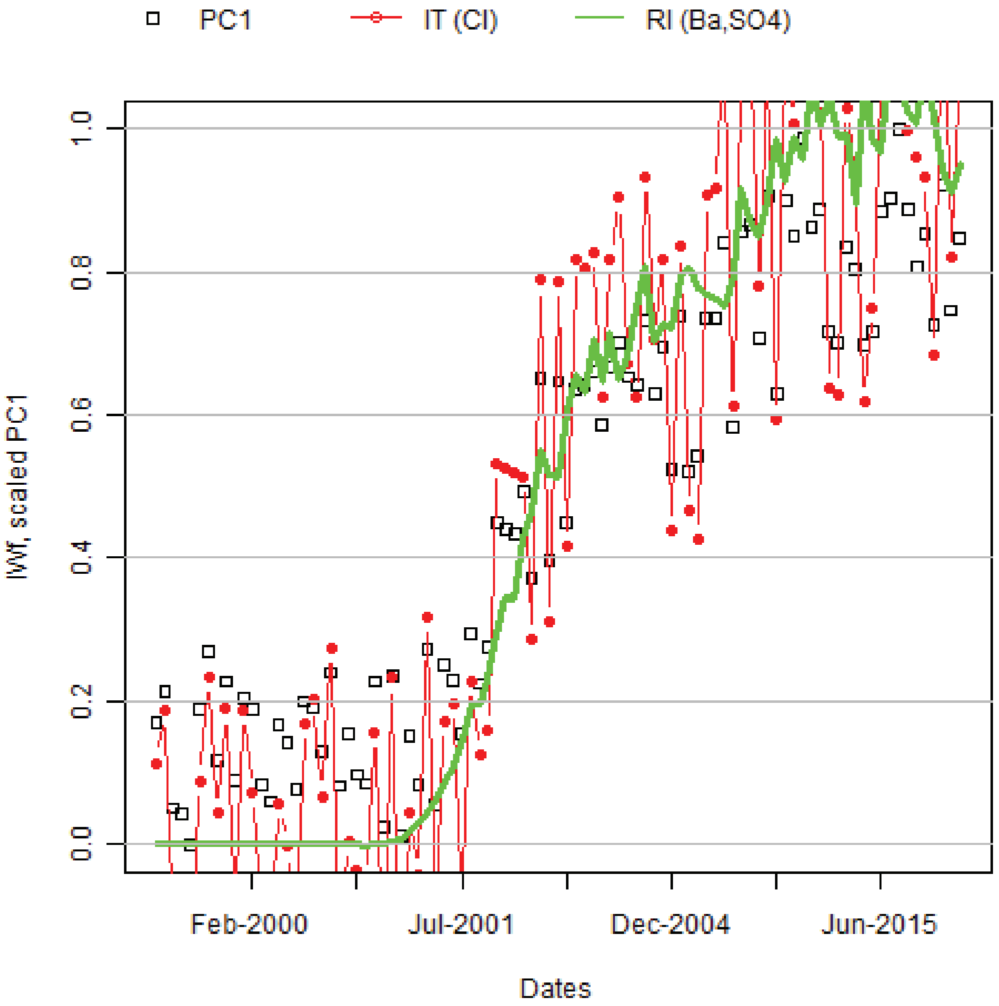


Figure 2.8 Results of scaled scores of Principal Component analysis, injection water fraction calculated by Ion track method based on chloride (red) and the Reacting Ions method based on barium and sulphate (green) for a synthetic case with 5% noise added versus date.

Principal component analysis potentially can be used to monitor changes in IW fractions over time; however, this method is as noisy as the Ion Track (it is based on analysis concentrations of a group of ions, and if chloride and sodium are in the list, noise associated with them affects results). The analyst should also make a subjective decision whether the first principal component reflects behaviour of IW fraction, and values of the first principal component cannot be used as measure of IW fractions.

2.3.6 Cumulative Sum Analysis

The Cusum method is a statistical tool for continuous monitoring of data to detect large shifts. It was introduced by Page in 1954 ([53]).

$$S_m = \sum_{i=1}^{m} \left(\overline{X}_i - \mu \right) \tag{2.5}$$

where

$\overline{X}_i$ - mean of the sample,

μ - target (mean) value.

Pioneering work by Schmidt and Thingvoll ([44]) introduced the CUSUM method for the mineral scale problems. This paper compares conventional approaches (radioactive tracers, Ion Track method) with the statistical approaches. The method of cumulative sums was used to detect seawater breakthrough time. The authors identify a consistent decline in Ba CUSUM values starting from 7 July 1989 (Figure 2.9), which was attributed to injection water breakthrough. That conclusion was supported by radioactive tracer data. Schmidt and Thingvoll ([44]) work benefits from the comparison of direct methods of measurement, when IW breakthrough was detected by radioactive tracers, with statistical analysis of the array of produced concentrations. Another good finding discussed by Schmidt and Thingvoll is that magnesium is not good indicator for injection water breakthrough or a good parameter for calculating low injection water fractions. They explain this by possible ion exchange reactions with calcium in the reservoir. One thing, however, the authors failed to spot is that sulphate is not a good parameter for low injection water fractions also as in the presence of barium it reacts and barite precipitates (see Chapter 3 for more details and test).

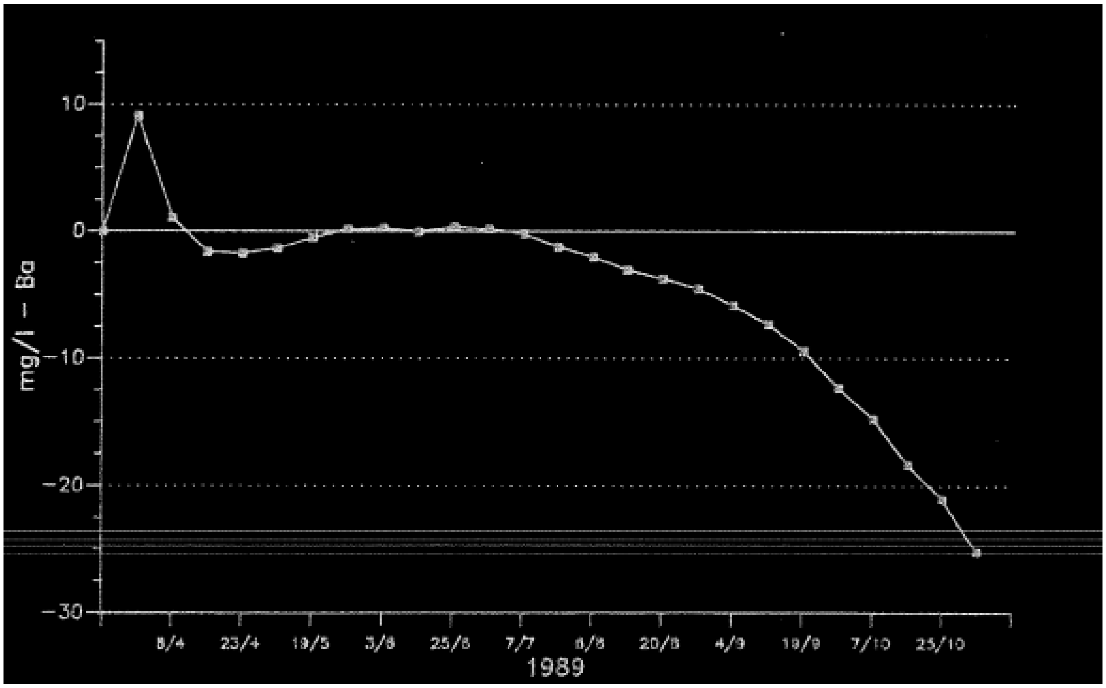


Figure 2.9 Barium CUSUM plot for Well A (from Schmidt, Thingvoll, 1990).

The advantage of this method is that it includes information based on trends in previous samples, making it more obvious to detect. However, the CUSUM method is a tool for visualising changes and it cannot give quantitative values of injection water fraction; it can only assist in detecting the time of injection water breakthrough.

2.4. Overview of examples of the analyses of produced water chemical composition

Analyses of ion concentrations in the produced brine in order to detect possible scaling has been performed on a routine basis in the industry for several decades. Some successful applications are discussed here.

One paper, that leads to a series of significant developments in the analyses and modelling of scaling reactions in the reservoir, has to be mentioned first. A paper published by White et al. in 1999 ([54]) identified lower than expected barium levels in many wells in the Alba field. This raised the question of where scale deposition is occurring – deep in the reservoir or near wellbore. Sorbie and Mackay ([55]) took into consideration this work by White et al. ([54]) and identified from a theoretical standpoint where brine mixing should be expected, and suggested that significant scale deposition may occur deep within the reservoir. The paper became a corner-stone, as the authors not only considered, but also modelled all of the principal mechanisms of brine mixing in waterflood displacements. One of the main conclusions of that paper related to this thesis is that in order to estimate how much barite in situ precipitation might occur in reservoirs, the researcher must be able to model the appropriate displacement processes incorporating the correct level of dispersive brine mixing in the reservoir formation. In other words injection water fraction is of vital importance.

In another paper showing detailed analysis of the produced brines, Mackay et al. ([56]) analysed water samples from Gyda field and successfully used the technique to qualitatively distinguish brines based on ion ratios. It should be mentioned that change in ion ratios between injection and formation brines is governed by non-linear law and could not be used as a quantative parameter to calculate IW fraction. This, however, was not specifically addressed in that paper. Further analysis by Mackay et al. noted unusual significant sulphate stripping and the cause suggested was precipitation of calcium sulphate. The strength of the article is that the conclusion of calcium sulphate precipitation was supported by reactive transport calculations.

Wright et al. ([57]) presents a study evaluating sulphate concentrations as a controlling factor in the scaling tendency of sulphate minerals. The authors report a simplified approach in which they assume that wells are producing a mix of two types of water: formation water and an ‘equilibrated’ mixture of formation/seawater (termed ‘mixing zone’ water, which has been equilibrated deep in the reservoir). One interesting statement that should be credited to Wright et al. is that each fluid type has the opportunity to change its composition even before mixing occurs. The seawater waters can change their composition as a result of reactions with formation and formation water can change its composition due to change of pressure near the wellbore. As a result mixing is more likely to occur between equilibrated seawater and formation brines, and not between pure seawater and formation water. However, the problem with the presented simplified approach of mixing formation and ‘mixing zone’ waters is that the authors fail to take into account sulphate scale precipitation near or in the well; in other words the main limitation of this work is that the authors assume that the mix of formation brine with the ‘mixing zone’ water has no scaling potential and can be further treated as a conservative mixing, which often is not true.

Houston et al. ([58]) investigates the analysis of produced water chemistry in a field in the North Sea. One particular advantage of this publication is that through continuous study of the produced water samples the evidence of a number of other geochemical reactions occurring in the reservoir was highlighted (except sulphate scaling). These conclusions were based on the construction of linear mixing lines (initially proposed by White et al. in 1999 [54]) and estimating the deviation of the observed concentrations in the water samples from those lines. However, this approach is similar to the Relative Ion deviations proposed in this thesis, which was developed independently from the publication by Houston et al. in 2006 ([58]). An interesting observation was also presented by Houston et al., that based on the injection water fraction and production rate for each well it is possible to calculate well production profile. Well production profiles were different for each well that lead to the conclusion that the permeability of the reservoir is not homogeneous and injected water flows more quickly to some wells than others. This could be treated as a first application of the injection water as a natural inter-well tracer.

2.5. Summary

This chapter has given an account of the methods of injection water fraction calculations currently available to the industry. None of them, except the Ion Track method and volumetric analysis of produced radioactive tracers, can give a quantitative value of injection water fraction in the produced water sample.

CHAPTER 3 THE REACTING IONS METHOD

This chapter presents the Reacting Ions method. The aim of the first subsection is to present general definitions, and to establish the base assumptions, terms, entities, and notations. The significant new development presented in the second subsection is that this approach may be used accurately even in situations where scale deposition deep in the reservoir impacts the brine composition at the production wells, *and where we use the concentrations of components that are involved in the in situ scaling reactions.*

3.1. History of Development

The motivation for the development presented in this thesis came from difficulties encountered identifying injection water fraction at the production wells of a certain North Sea field being studied. Data for conservative (non-reacting) ion concentrations were incomplete, and this lack of information made it difficult to identify the true injection water fraction using the conventional method called Ion Track (Ion Track is described in Chapter 2).

The Reacting Ions method was developed. It is a byproduct of the research initially aimed at modelling geochemical reactions in a full-field reservoir model. The effect of IW front advance in the reservoir model of Field X, and the amount of precipitation it causes was to be investigated. In order to simulate this, artificial water tracers were added into the given simulation model of Field X using the ECLIPSE software.

The field model (Figure 3.1) was quite complex: it had three main phases — oil, water and gas; moreover the VAPOIL (vaporised oil) and DISGAS (dissolved gas) options were activated. Faults, vertical well flow profiles, and two PVT regions add more complexity to the task, and increased the overall run time.

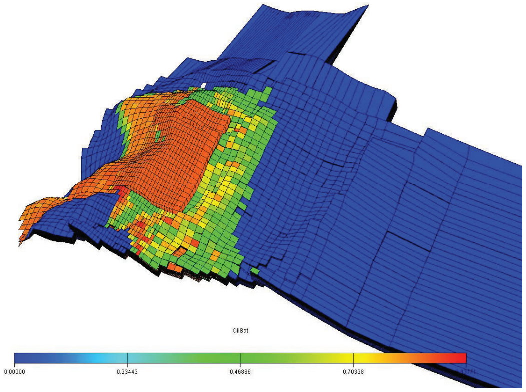


Figure 3.1 Field X reservoir model.

Produced water ion composition data were available for Field X, and therefore it was possible to compare modelled injection (sea) water fractions with observed field data. Unfortunately, there was a lack of analysis of chloride (and sodium) concentrations in the produced brines (see Table 3.1), which led to the question of which ion to choose as the base ion for determine IW fraction.

Table 3.1 Field X, well C produced water ion concentrations.

DATO	*WC %*	*BHP*	*Na*	*Ca*	*Mg*	*Ba*	*Fe*	*Sr*	*K*	*Cl*	*SO4*	*HCO3*
13-Sep-98					1020	1.8		35.6			2100	
11-Dec-98	0.7	214.0			119	59.5		126			7	
26-Jan-99	1.0	218.7										
15-Mar-99	1.1	224.3										
18-Mar-99					134	94		151			6	
1-May-99					125	77.7		141			8	
4-May-99	2.0	226.9										
17-Jul-99					139	38.9		138			17	
9-Aug-99	8.5	222.5										
19-Aug-99					215	5.2		106			320	
12-Sep-99	0.6	187.3			276	4.9		91			530	
14-Sep-99												
5-Oct-99	0.5	233.9			794	3.8		77.1			1700	
7-Oct-99												
9-Oct-99												
9-Oct-99	0.4	221.8										
26-Oct-99	21.4	220.3										
3-Nov-99					541	5.5		66.7			1200	
7-Dec-99	27.7	219.3										
4-Jan-00					675	1.4		58.3			1400	
26-Feb-00	27.6	217.1										
2-Mar-00					625	0.7		67.1			1200	
20-Apr-00					605	2.6		54				
29-Apr-00					638	0.4		70.6			1200	
14-May-00					530	3		64				
27-May-00	27.0	220.8			565	2.7		58				
10-Jun-00					600	3.4		68				
29-Jun-00												
29-Jun-00	25.7	222.0			632	1.8		75.9			1200	
2-Jul-00	26.0	225.6										
26-Jul-00					476	0		65				
17-Aug-00	28.7	223.9										
31-Aug-00					587	18		70				
31-Aug-00					611	0.5		78.2			1100	
16-Sep-00					594	0.7		74.8				

Injection water fractions were calculated using the Ion Track method (see Chapter 2) based on the magnesium and sulphate ion concentration (those ions were chosen as the most representative ions for seawater in the absence of chloride and sodium data). The modelled injection water tracer results were compared with those calculated from samples where injected water fractions were based on magnesium and sulphate.

Despite the reasonable match between observed and modelled water production (Figure 3.2, Figure 3.4), there was a poor match between modelled and calculated Injected Water fractions (Figure 3.3, Figure 3.5).

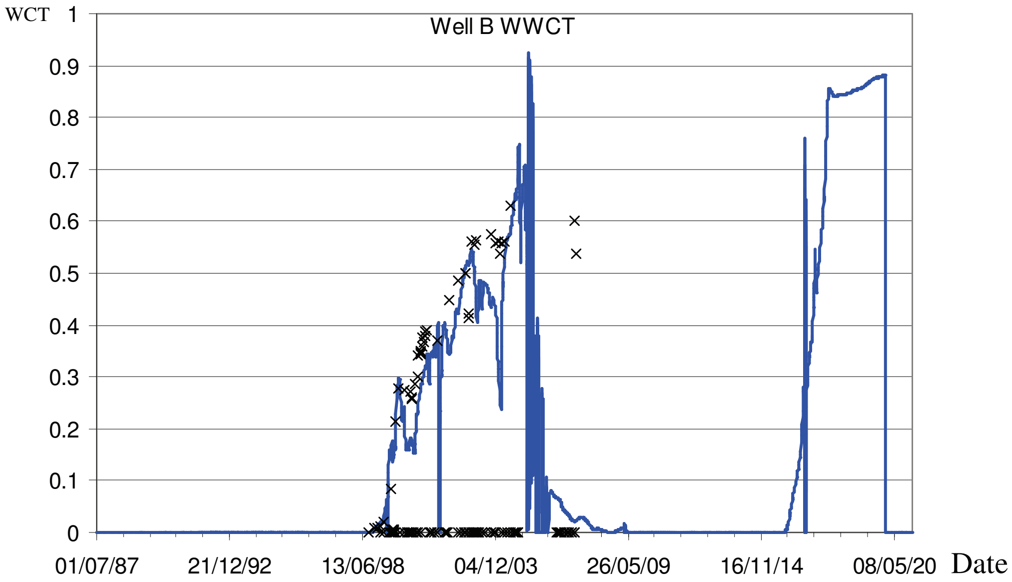


Figure 3.2 Modelled and observed watercut in well B.

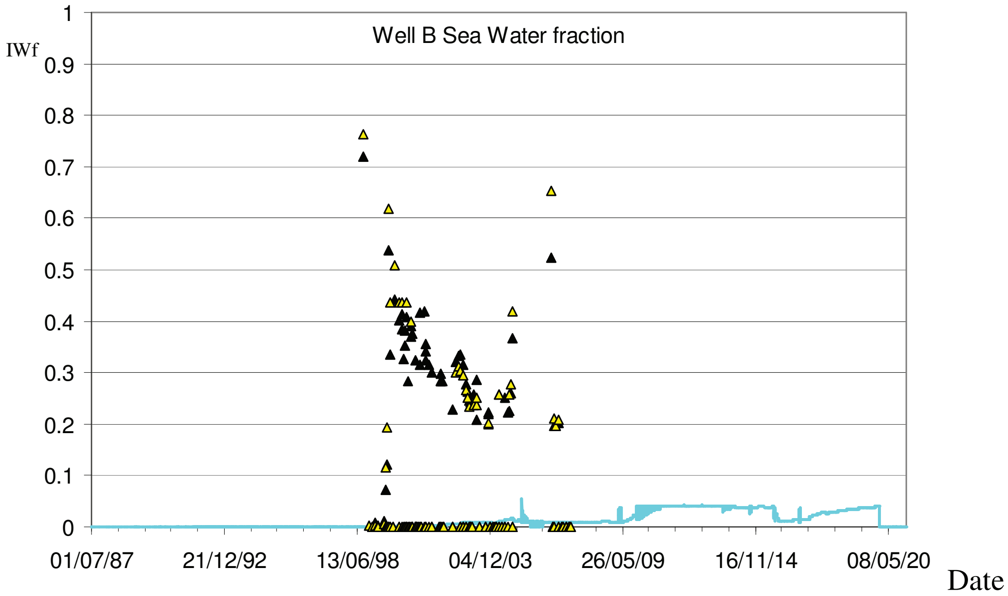


Figure 3.3 Modelled and observed Injection water fractions in well B.

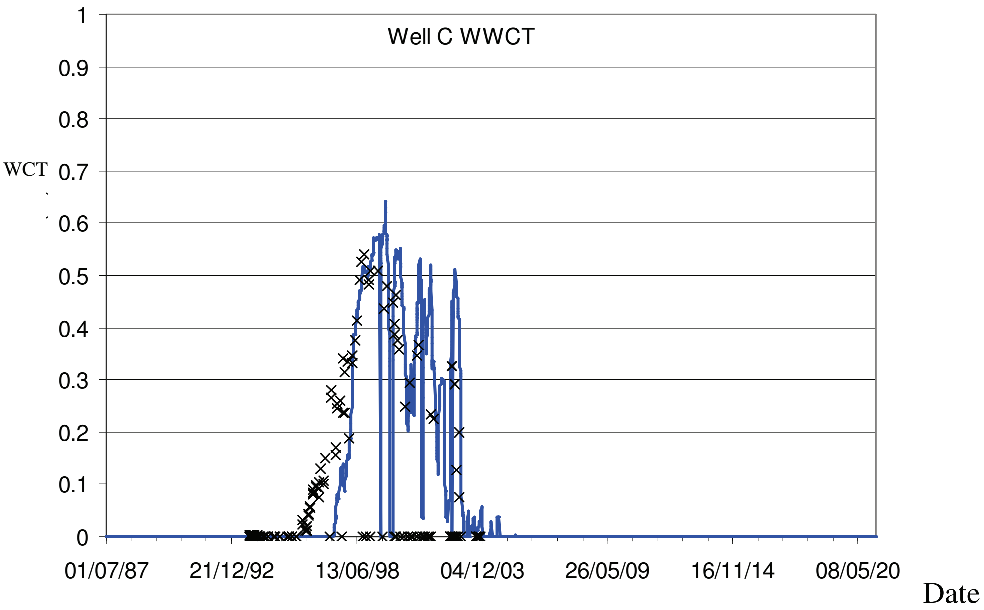


Figure 3.4 Modelled and observed watercut in well C.

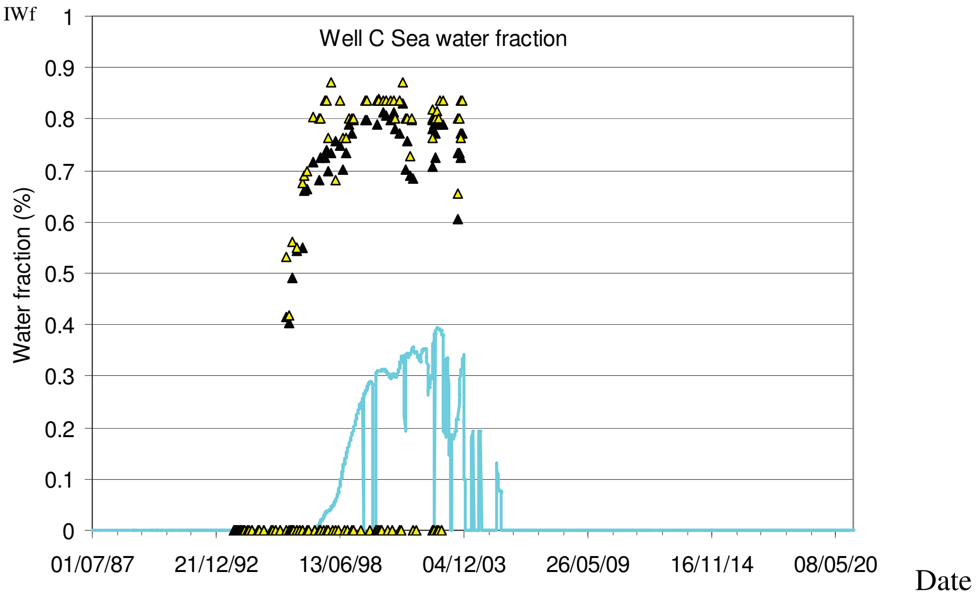


Figure 3.5 Modelled and observed Injection water fractions in well C.

Chloride values are often considered the most reliable ion to calculate injection water fractions. In the absence of chloride data magnesium and sulphate were used. However precise analysis indicated the significant mismatch in IW fractions calculated based on the different ions for some wells (Figure 3.6).

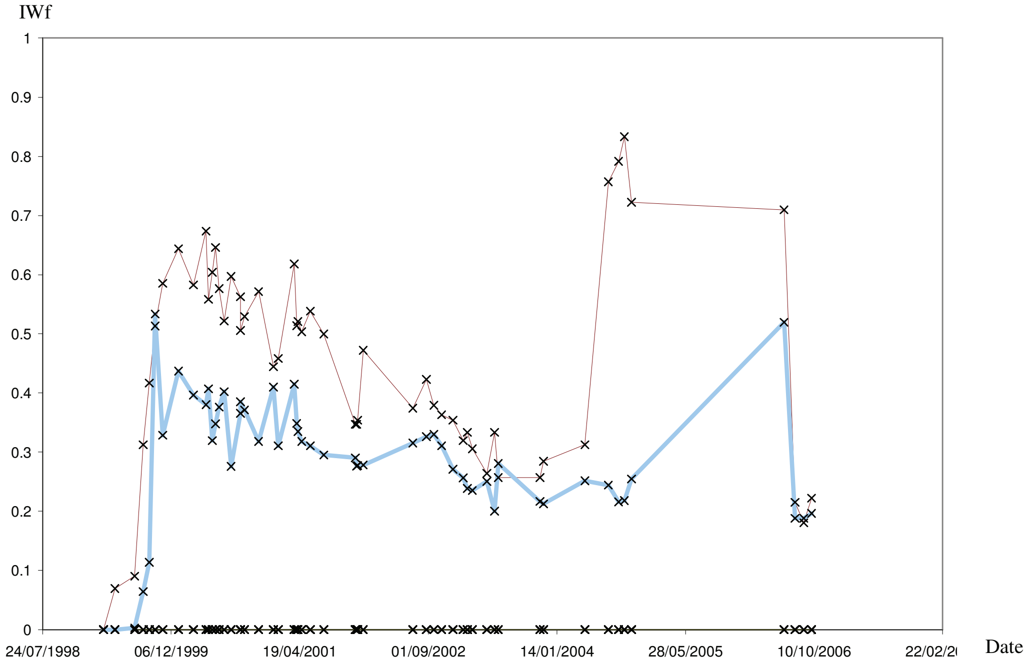


Figure 3.6 Well Z injection water fractions calculated based on magnesium (red) and sulphate (blue).

Several attempts were made to improve the Field X dynamic model to obtain a better match of injection water, but results were poor. On the other hand, there was no consistency in the calculated injection water fractions based on different ions. This made it impossible to have confidence in the derived injection water fractions, or to use those values as an objective function for Field X reservoir model history matching.

The need for a method to calculate injection water fraction that is more robust than the conventional Ion Track method was thus identified. It is clear that this new analytic technique is required especially in scenarios where chloride is not measured, or it is not measured with the frequency with which barium, strontium and sulphate are measured.

3.2. General definitions

Mixing of two brines is a common scenario in the petroleum industry when brine is injected for pressure support and to sweep oil, and it mixes *in situ* with formation brine. Cases of more than two brines in a mix can be simplified as multiple mixes of brine pairs. For example if three brines A,B, and C participate in mixing, this complex process may be conveniently presented as brine A and B mixing first, and then the resulting mixed brine is mixed with brine C.

The Reacting Ions method uses as input the concentrations of the dissolved mineral species in aqueous solutions. By ion concentrations we refer to the average mass concentration of ions in water samples taken from production wells.

Mixing of two brines without any reactions occurring is considered as "conservative mixing" (see Chapter 2). In the case of conservative mixing of injected water (IW) and formation water (FW), then the resulting (observed) concentration of any ion in the mix is simply a function of the degree (or proportion) of IW/FW mixing and the initial ion concentrations in the IW and FW.

For a conservative ion, the Ion Tracking method is based on the assumption that the injection and formation brines mix by a linear mixing law (Chapter 2). Thus, the observed concentration of the chosen ion, $\overline{C}$, in a general form is given by the expression 2.2.

In the case of conservative mixing, the injected water fraction, *IWf*, is calculated from the well known expression (2.4):

$$IWf = \frac{\overline{C} - C_{fw}}{C_{iw} - C_{fw}} \tag{3.1}$$

In cases where the ion is involved in a chemical reaction, then it is evident that the observed ion concentration, $\tilde{C}$, will be different from the corresponding conservative ion concentration, $\overline{C}$. In fact, the observed ion concentration, $\tilde{C}$, is the conservative ion concentration altered by the extent of the reaction:

$$\tilde{C} = \overline{C} + X \tag{3.2}$$

Where

X – some unknown reacted amount. In the case where precipitation X is a negative value, as for scale formation reactions, it is more convenient to use Eq (3.2) as

$$\tilde{C} = \overline{C} - R \tag{3.3}$$

3.3. Description of Reacting Ions Method

In this section, the Reacting Ions method is explained for the case of mixing of two brines – injected water (IW) and formation water (FW), in which two ions A and B participate in one scaling reaction:

$$K^A \cdot A_{(aq)} + K^B \cdot B_{(aq)} \rightarrow \underset{(solid)}{A_{k^A} B_{k^B}} \qquad (3.4)$$

Where, K^A, K^B – stoichiometric number of moles participating in the reaction, e.g.

$$1 \cdot Ba^{2+}{}_{(aq)} + 1 \cdot SO_4^{\ 2-}{}_{(aq)} \rightarrow BaSO_{4(solid)}$$

In each instance of the scaling reaction, K^A moles of ion A and K^B moles of ion B are consumed in accordance with Equation (3.4).

At some later time of observation *t*, unknown molar amounts of ions A and B are lost due to the fact that these ions are involved in the scaling reaction. The molar amounts of the ions lost equals the product of the total number of occurrences of the reactions, $N_{r,}$ and the loss of ions in each instance of the reaction K^{ion}, where the total number of occurrences of the reactions N_r is unknown to the analyst (observer):

$Reacted(t) = N_r \cdot K^A$ or in concentration units $Reacted = N_r \cdot K^{ion} \cdot M^{ion}$ (3.5)

where

M^{ion} is the conversion coefficient from moles to the concentration units.

Following the definition of the reactive concentration (3.2), the observed ion concentrations can now be shown to be given by the following expressions:

ion A observed concentration (3.6)

$$\tilde{C}^A = \overline{C}^A - (N_r \cdot K^A \cdot M^A)$$

ion B observed concentration (3.7)

$$\tilde{C}^B = \overline{C}^B - (N_r \cdot K^B \cdot M^B)$$

Despite the fact that the number of occurrences of the reaction, N_r, is unknown, it is the same for ion A as for ion B, because both participate in the same reactions; that is:

$$\frac{\tilde{C}^A - \overline{C}^A}{K^A \cdot M^A} = -N_r \tag{3.8}$$

And

$$\frac{\tilde{C}^B - \overline{C}^B}{K^B \cdot M^B} = -N_r \tag{3.9}$$

and hence we can equate Equations (3.8) and (3.9) as follows:

$$\frac{\tilde{C}^B - \overline{C}^B}{K^B \cdot M^B} = \frac{\tilde{C}^A - \overline{C}^A}{K^A \cdot M^A} \tag{3.10}$$

which, in turn leads to:

$$\tilde{C}^B \cdot K^A \cdot M^A - \tilde{C}^A \cdot K^B \cdot M^B = \overline{C}^B \cdot K^A \cdot M^A - \overline{C}^A \cdot K^B \cdot M^B \tag{3.11}$$

Adding the expression for the conservative ion concentration, Equation (2.3) above to Equation (3.11), allows us to rewrite the equation for the fraction of injection water, *IWf*, as follows:

$$\begin{aligned}
&\tilde{C}^B \cdot K^A \cdot M^A - \tilde{C}^A \cdot K^B \cdot M^B = \\
&\left(C_{IW}{}^B \cdot IWf + (1-IWf)\cdot C_{FW}{}^B\right)\cdot K^A \cdot M^A - \left(C_{IW}{}^A \cdot IWf + (1-IWf)\cdot C_{FW}{}^A\right)\cdot K^B \cdot M^B \\
&= \left(C_{IW}{}^B \cdot IWf - C_{FW}{}^B \cdot IWf\right)\cdot K^A \cdot M^A - \left(C_{IW}{}^A \cdot IWf - C_{FW}{}^A \cdot IWf\right)\cdot K^B \cdot M^B + \\
&+ C_{FW}{}^B \cdot K^A \cdot M^A - C_{FW}{}^A \cdot K^B \cdot M^B \\
&= IWf\left(\left(C_{IW}{}^B - C_{FW}{}^B\right)\cdot K^A \cdot M^A - \left(C_{IW}{}^A - C_{FW}{}^A\right)\cdot K^B \cdot M^B\right) + \\
&C_{FW}{}^B \cdot K^A \cdot M^A - C_{FW}{}^A \cdot K^B \cdot M^B
\end{aligned} \tag{3.12}$$

$$\begin{aligned}
&\tilde{C}^B \cdot K^A \cdot M^A - \tilde{C}^A \cdot K^B \cdot M^B - C_{FW}{}^B \cdot K^A \cdot M^A + C_{FW}{}^A \cdot K^B \cdot M^B = \\
&Wf\left(\left(C_{IW}{}^B - C_{FW}{}^B\right)\cdot K^A \cdot M^A - \left(C_{IW}{}^A - C_{FW}{}^A\right)\cdot K^B \cdot M^B\right)
\end{aligned}$$

$$IWf = \frac{\left(\tilde{C}^B - C_{FW}{}^B\right)\cdot K^A \cdot M^A - \left(\tilde{C}^A - C_{FW}{}^A\right)\cdot K^B \cdot M^B}{\left(C_{IW}{}^B - C_{FW}{}^B\right)\cdot K^A \cdot M^A - \left(C_{IW}{}^A - C_{FW}{}^A\right)\cdot K^B \cdot M^B}$$

The startling significance of this is that all the terms on the right hand side are known or can be measured, and so the fraction of injection water in the produced brine stream may be calculated using conservative or reacting ions. Previously it had been assumed that if ion concentrations had been significantly altered as a result of in situ reactions, then they could not be used for this calculation.

This method means that a wider range of the measured ion concentrations may be used in calculating injection water fraction. This also has implications for the accuracy of the calculation.

It should be noted that in a situation where one of the ions is absent, and hence the reaction cannot occur, the calculation reduces to the Ion Track method in Equation (2.4).

3.3.1 The Reacting Ions Method for Two or More Reactions

A more complex scenario exists if ion A participates in two or more reactions:

$$\begin{array}{lll} A^{+} & + & B^{-} \\ + & & \\ C^{-} & & \end{array}$$

In this case the stoichiometric equations are:

$$K^{A} \cdot A_{aq}{}^{+} + K^{B} \cdot B_{aq}{}^{-} \rightarrow \left(A_{k^{A}} B_{k^{B}}\right)_{sol} \quad \text{and} \tag{3.13}$$

$$K^{A} \cdot A_{aq}{}^{+} + K^{C} \cdot C_{aq}{}^{-} \rightarrow \left(A_{k^{A}} C_{k^{C}}\right)_{sol} \tag{3.14}$$

The resulting observed concentration of ion A can be shown as the conservative ion concentration altered by the loss from both reactions (3.13) and (3.14). The total loss of the ion is shown in Equation (3.5):

$$\tilde{C}^{A} = \overline{C}^{A} - \sum \text{Reacted} = \overline{C}^{A} - \left(Nr_1 \cdot K_1^{A} \cdot M^{A}\right) - \left(Nr_2 \cdot K_2^{A} \cdot M^{A}\right) \tag{3.15}$$

Where the lower index is for the reaction number, and the top index is the ion index. $Nr_1 \cdot K_1^{A}$ and $Nr_2 \cdot K_2^{A}$ - number of moles of ion A lost in reaction (A+B) (3.13), and A+C (3.14)

for ion B (3.16)

$$\tilde{C}^{B} = \overline{C}^{B} - \left(Nr_1 \cdot K_1^{B} \cdot M^{B}\right)$$

and for ion C (3.17)

$$\tilde{C}^{C}=\overline{C}^{C}-\left(Nr_2\cdot K_2^{C}\cdot M^{C}\right)$$

Equations (3.16) and (3.17) become:

$$\frac{\tilde{C}^{B}-\overline{C}^{B}}{K_1^{B}\cdot M^{B}}=-Nr_1 \tag{3.18}$$

$$\frac{\tilde{C}^{C}-\overline{C}^{C}}{K_2^{C}\cdot M^{C}}=-Nr_2 \tag{3.19}$$

Substituting Nr_1 from (3.18) and Nr_2 from (3.19) into (3.15) gives: (3.20)

$$\tilde{C}^{A}=\overline{C}^{A}-\left(\tilde{C}^{B}-\overline{C}^{B}\right)\cdot\frac{K_1^{A}\cdot M^{A}}{K_1^{B}\cdot M^{B}}-\left(\tilde{C}^{C}-\overline{C}^{C}\right)\cdot\frac{K_2^{A}\cdot M^{A}}{K_2^{C}\cdot M^{C}}$$

Using (2.3) in (3.20) gives (3.21)

$$\left(\tilde{C}^{A}-C_{fw}^{A}\right)-\left(\tilde{C}^{B}-C_{fw}^{B}\right)\frac{K_1^{A}\cdot M^{A}}{K_1^{B}\cdot M^{B}}-\left(\tilde{C}^{C}-C_{fw}^{C}\right)\frac{K_2^{A}\cdot M^{A}}{K_2^{C}\cdot M^{C}}$$

$$=IWf\left(\left(C_{iw}^{A}-C_{fw}^{A}\right)-\left(C_{iw}^{B}-C_{fw}^{B}\right)\cdot\frac{K_1^{A}\cdot M^{A}}{K_1^{B}\cdot M^{B}}-\left(C_{iw}^{C}-C_{fw}^{C}\right)\cdot\frac{K_2^{A}\cdot M^{A}}{K_2^{C}\cdot M^{C}}\right)$$

and finally

$$IWf=\frac{\left(\tilde{C}^{A}-C_{fw}^{A}\right)-\left(\tilde{C}^{B}-C_{fw}^{B}\right)\frac{K_1^{A}\cdot M^{A}}{K_1^{B}\cdot M^{B}}-\left(\tilde{C}^{C}-C_{fw}^{C}\right)\frac{K_2^{A}\cdot M^{A}}{K_2^{C}\cdot M^{C}}}{\left(C_{iw}^{A}-C_{fw}^{A}\right)-\left(C_{iw}^{B}-C_{fw}^{B}\right)\cdot\frac{K_1^{A}\cdot M^{A}}{K_1^{B}\cdot M^{B}}-\left(C_{iw}^{C}-C_{fw}^{C}\right)\cdot\frac{K_2^{A}\cdot M^{A}}{K_2^{C}\cdot M^{C}}} \tag{3.22}$$

Or, in the general form, if ion A participates in *n* reactions:

$$IWf=\frac{\left(\tilde{C}^{A}-C_{fw}^{A}\right)-\sum_{ion}^{n}\left(\left(\tilde{C}^{ion}-C_{fw}^{ion}\right)\frac{K_i^{A}\cdot M^{A}}{K_i^{ion}\cdot M^{ion}}\right)}{\left(C_{iw}^{A}-C_{fw}^{A}\right)-\sum_{ion}^{n}\left(\left(\tilde{C}_{iw}^{ion}-C_{fw}^{ion}\right)\frac{K_i^{A}\cdot M^{A}}{K_i^{ion}\cdot M^{ion}}\right)} \tag{3.23}$$

here *ion* – is index of the ion-partner of A in reaction *i* (e.g. B in reaction 1, C in reaction 2).

3.4. Testing of the Reacting Ions Method

A synthetic reservoir simulation model was developed to test the validity of the Reacting Ions method and to compare it directly with the Ion Tracking method. The advantage of a synthetic model is that all parameters are completely known and are controllable. Consequently, the Reacting Ions method can be tested in various circumstances, and results may be compared with the known "true" solution. This is the best approach for testing this method since, in a real field system, the IW fraction cannot be determined with a high degree of confidence in all field scenarios.

The CMG STARS software ([26]) was used to model chemical reactions in a reservoir with a simple 2D vertical cross-sectional geometry with 50 x 1 x 10 cells, where each cell has dimensions 40m x 200m x 25m (Δx, Δy, Δz). Two wells, one injector and one producer, were located at the opposite ends of the grid as shown in Figure 3.7.

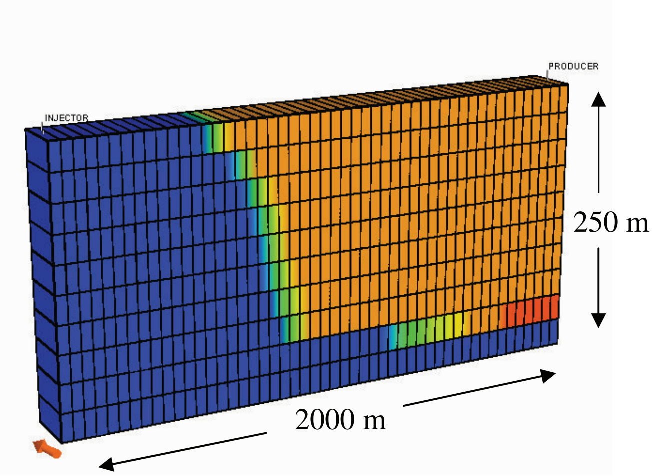


Figure 3.7 Synthetic reservoir model.

In order to check the stability and the robustness of both methods of calculating injection water fraction, sensitivity tests were performed. However, if we were to take the exact simulated produced water compositions knowing everything about the system, we would find that either Ion Tracking or the Reacting Ion method would give us identical (and exactly correct) values for the injected water fraction, IWf. Therefore, the core idea of the testing is to add different amounts of noise to initial parameters and then to compare the impact on the output calculated IW fractions. For each observed ion concentration from the synthetic model, the following noise function was applied:

$$\tilde{C}^{(ion)} = C_{correct} \cdot E_{rel} + E_{abs} \tag{3.24}$$

Where

$C_{correct}$ - modelled ion concentration

E_{rel} - random relative error, $E_{rel} \subset [-e_r; e_r]$ (e.g. random value in [-1%;1%])

E_{abs} - random absolute error, $E_{abs} \subset [-e_a; e_a]$ (e.g. random value in [-5mg/l; 5mg/l])

1%, 5% and 10% levels of random noise were added into the modelled (observed) data to simulate typical errors in measurements.

Often the most sensitive ions to use are barium and sulphate since these ions are highly reactive in each other's presence. The presence of the one ion in excess molar concentration largely precludes the presence of the other ion under conditions of thermodynamic equilibrium because of the very low solubility of barium sulphate. Typically, barium concentration in injection water is effectively zero if the injection water is seawater (SW). Correspondingly, if significant barium is present in the formation water, the sulphate concentration in the FW will be very low. Initially, when even only a little mixing of formation and injection brines has occurred, both barium and sulphate will have participated to some extent in the reaction to precipitate the mineral scale $BaSO_4$. This may lead to only a small change in concentration in *absolute* terms. However, there may be a significant change in *relative* terms. This method considers changes in both ions, and therefore the IW breakthrough can be detected with a high degree of accuracy, particularly as the barium concentration will change whether or not there is in situ precipitation.

Barite precipitation was modelled in STARS with the standard reaction as in Equation (3.4)

$$Ba_2 + SO_4 \longleftrightarrow BaSO_4$$

Chloride, as a conservative ion, was chosen as the base ion for the Ion Tracking method to calculate the IW fraction, since in the model it was not included in any reactions to simulate natural conservative behaviour of chloride ions. Initial brine compositions are shown in Table 3.2. The injection water is normally seawater, and the formation water composition is from a North Sea field, where the formation brine is moderately fresher than seawater.

Table 3.2 Formation water (FW) and injection water (IW) compositions for the synthetic model.

	Na	*Ca*	*Mg*	*Ba*	*Fe*	*Sr*	*K*	*Cl*	*SO4*	*HCO3*
FW	9 000	250	50	60		25	200	14 300		1 050
IW	11 000	400	1 300			8	400	19 300	2 800	160

Modelled produced ion concentrations over time are presented in Figure 3.8. Calcium, magnesium, barium, and strontium concentrations are plotted on the primary vertical axis, sodium, chloride, and sulphate on the secondary vertical axis.

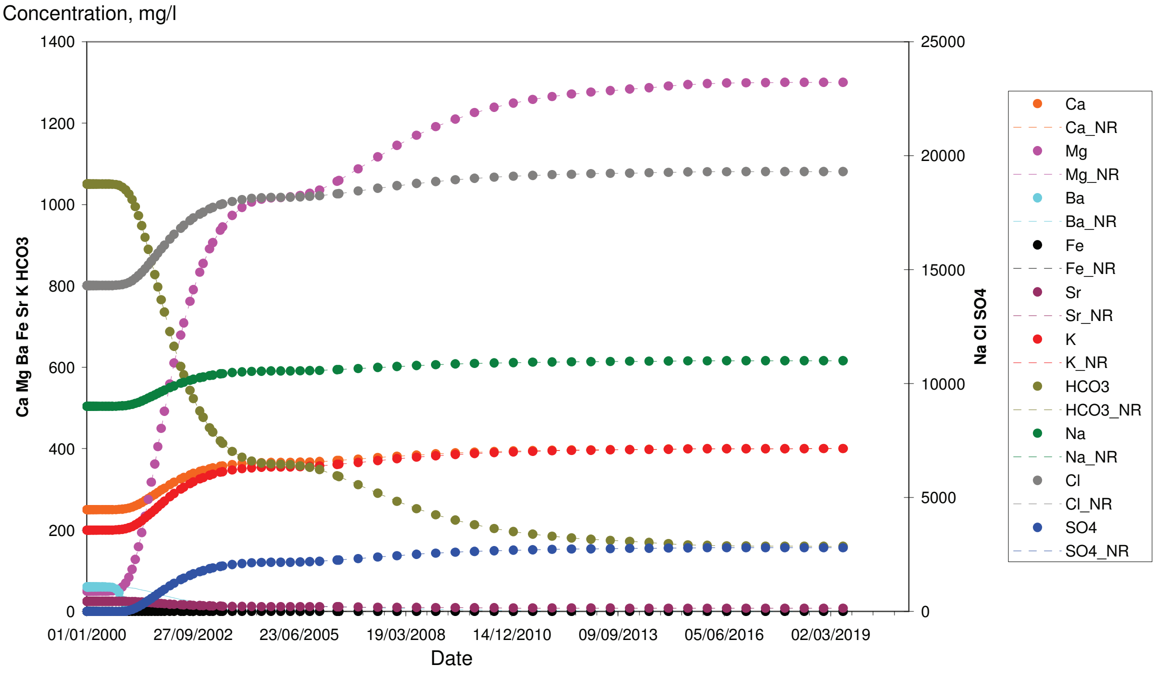


Figure 3.8 Simulated produced ion concentrations with $BaSO_4$ reaction taking place.

The important change in ion concentrations due to reactions is hard to identify when it is plotted in concentration units. However, the relative change plots (for more details see section Relative Ion Deviations in Chapter 4) are more convenient in order to analyse the change in ion concentrations from the conservative (no reaction) concentrations.

Conservative chloride was chosen as the base ion for Ion Track method to calculate the IW fraction. Chloride is typically used in the industry when the Ion Track method is employed. Figure 3.9 shows the Ion Deviations, where it may clearly be seen that there is a drop in barium and some reduction in sulphate concentrations at low values of injected water fraction, and no change in the other ions, which proves that they are conservative.

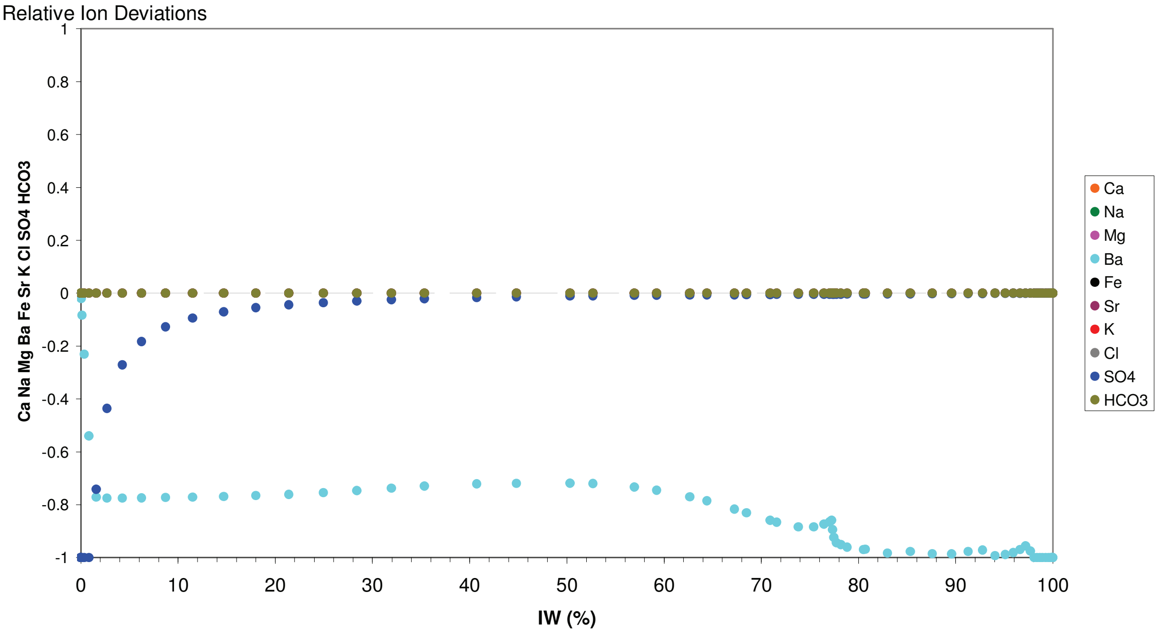


Figure 3.9 Relative Ion deviations from conservative concentrations versus injection water fraction for the synthetic model.

Below are the same ion deviations plotted against time (Figure 3.10).

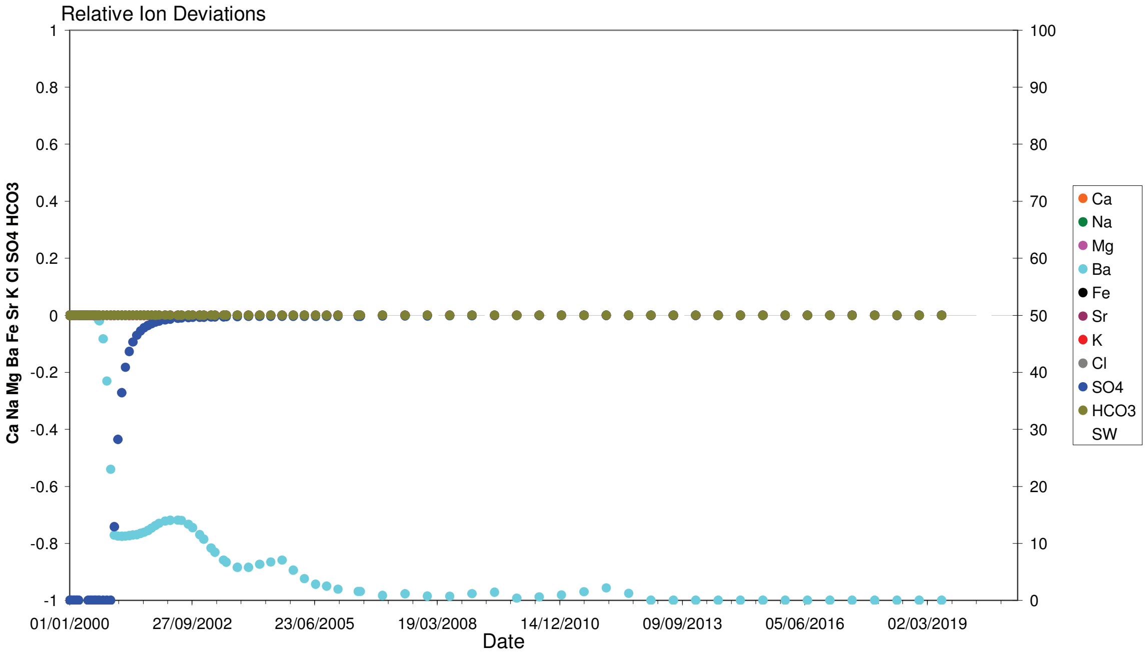


Figure 3.10 Relative Ion deviations from conservative concentrations versus time.

In order to check the stability and the robustness of both methods of calculating injection water fraction (Ion Track and Reacting Ions), sensitivity tests were performed.

The core idea of the testing is to add different amounts of noise to initial parameters and then to compare the impact on the output calculated IW fractions. 1%, 5% and 10% percent random noise with 5 mg/l of absolute noise was added in turn to the modelled (observed) data to simulate errors in measurements. Noise was added in accord with Equation (3.24) presented above.

3.4.1 Case with one reaction and 1% of noise in the observed data

Here 1% of random noise with 5mg/l of absolute noise is introduced into the measurement system. The resulting measured ion concentrations are presented in Figure 3.11.

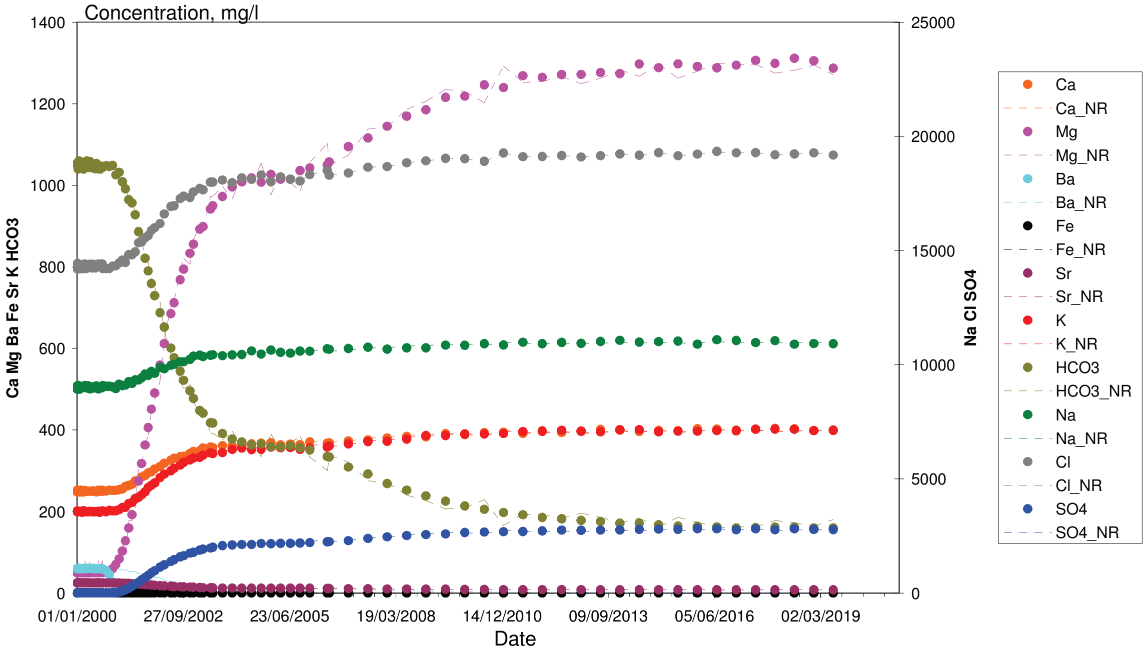


Figure 3.11 Ion concentrations observed with 1% noise introduced.

Chloride is taken as the base ion for the conventional Ion Track method with 1% noise in the data; reacting barium and sulphate were used for the Reacting Ions method. Figure 3.12 illustrates the calculated IW fractions (on vertical the axis) plotted against time. The solid blue line is the true case (synthetic IW fraction from model), red dots show the conventionally calculated Ion Track values, and the green line is the new Reacting Ions method.

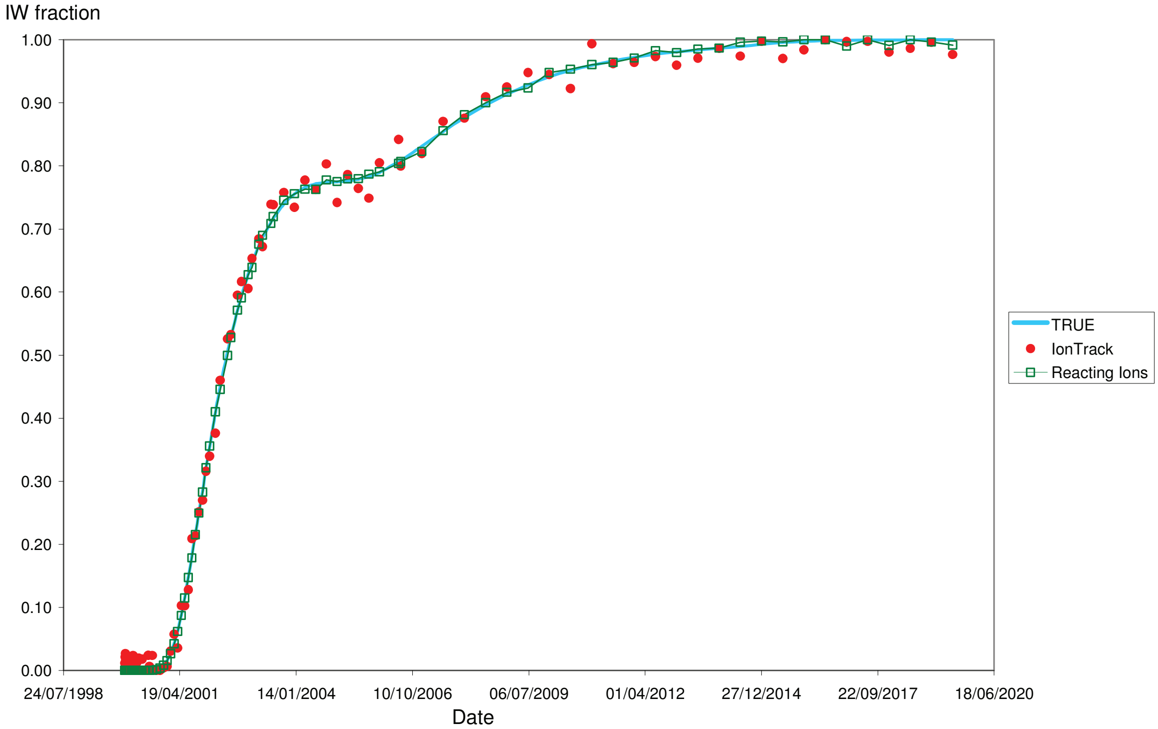


Figure 3.12 Modelled and calculated IW fractions for synthetic dataset with 1% noise.

To highlight the impact of scatter on the Ion Track method at IW breakthrough, the date range 1999-2002 is expanded and is shown in Figure 3.13. *This figure clearly demonstrates that the new RI method is more accurate for calculating IW fraction and particularly IW breakthrough when there is the possibility of 1% scatter in the observed data.*

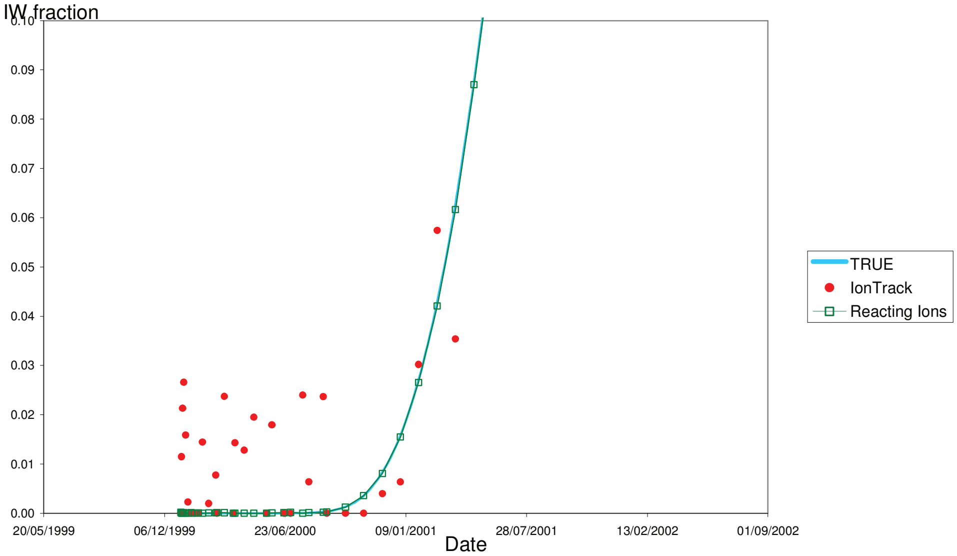


Figure 3.13 Zoom of the modelled and calculated IW fractions for synthetic dataset with 1% noise.

When sulphate (a reacting ion) was taken as the base ion, the conventional Ion Track method actually shows improved robustness to the noise compared to chloride (Figure 3.14). Moreover, the results of the Ion Track method and the Analytic solution match each other. The explanation is that when there is an excess of sulphate, the loss of sulphate in the barium sulphate reaction is negligible. Therefore the sulphate in the Ion Track method behaves almost as a conservative ion. The RI method uses the barium and sulphate reaction to calculate IW fractions, at 20% of IWf the majority of barium ions are consumed by the reaction, and the method therefore depends fully on sulphate concentrations at this point. This is why the analytic solution gives approximately the same fractions as the Ion Track method based on sulphate.

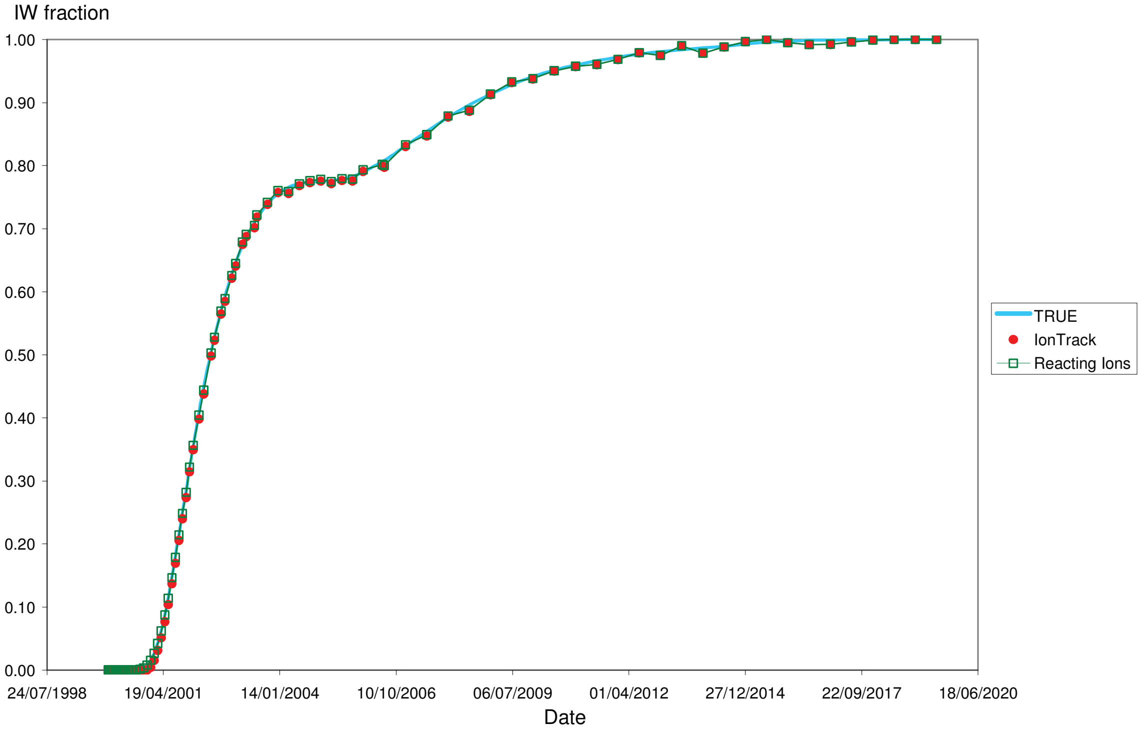


Figure 3.14 IW fraction when sulphate is used as the base ion for the Ion Track method with 1% of noise present in the system.

However, if we consider the region of IW breakthrough in detail, as in Figure 3.15, the Ion Tracking method using sulphate as the base ion indicates a later breakthrough time than is actually the case. Under the same conditions, the Reacting Ions method is much more accurate, being more responsive to IW breakthrough. The reason is that at low IW fractions sulphate is the limiting ion. At the time of IW breakthrough, the Reacting Ions method depends much more heavily on the barium concentration.

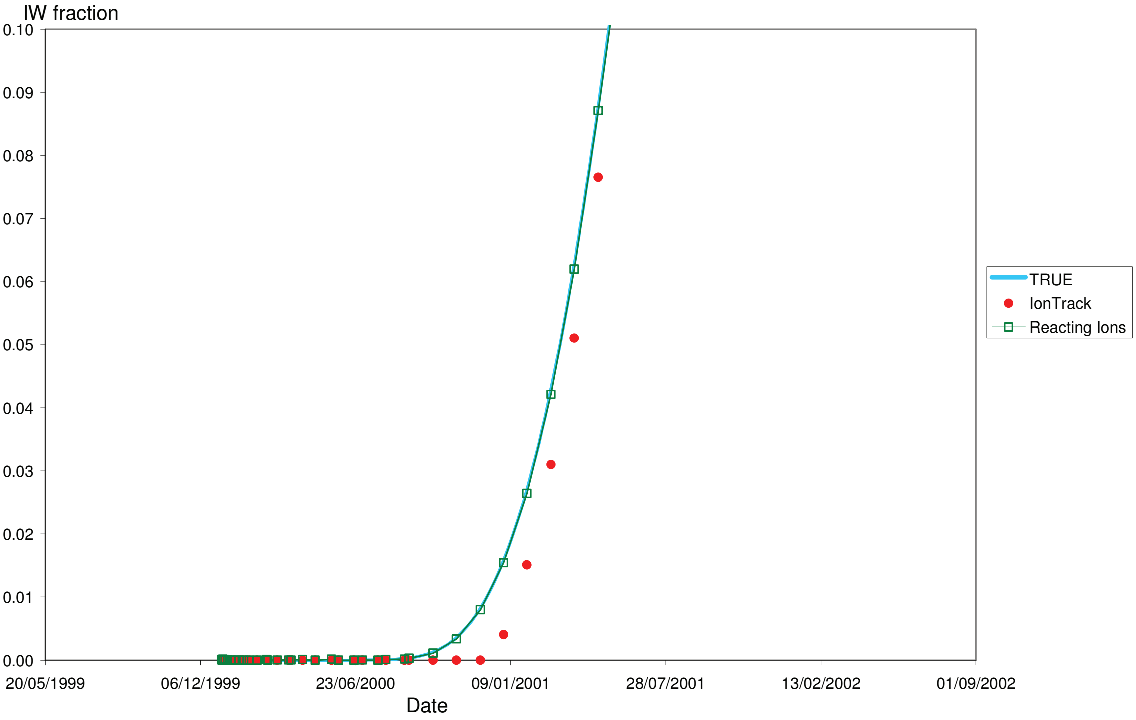


Figure 3.15 Zoom of the low IW fraction region, when sulphate is used as the base ion for the Ion Track method.

Therefore, the Reacting Ions method is more accurate than the Ion Tracking method, which if based on sulphate *may not detect IW breakthrough* until months after the event. Although the risk of $BaSO_4$ precipitation does not occur until sulphate (rather than IW) breakthrough takes place, detecting IW breakthrough earlier would allow preventative measures (such as a scale inhibitor squeeze treatment) to be deployed earlier, and this may have a significant impact on safeguarding hydrocarbon production from the well.

3.4.2 Case with one reaction and 5% of noise in observed data

Figure 3.16 presents results for the case where 5% of the relative noise and 5 mg/l of absolute noise is added to the true measurements of the ion concentrations. The conventional ion tracking method based on chloride, say, is very inaccurate at low

IW fractions, particularly where there is not a significant compositional difference between formation and injection brines. Such levels of scatter in analysis are commonly observed. The resulting errors may potentially be quite significant relative to the small change in concentration that may occur on IW breakthrough.

The modelled ion concentrations with 5% of relative noise and 5 mg/l of absolute noise added are plotted in Figure 3.16:

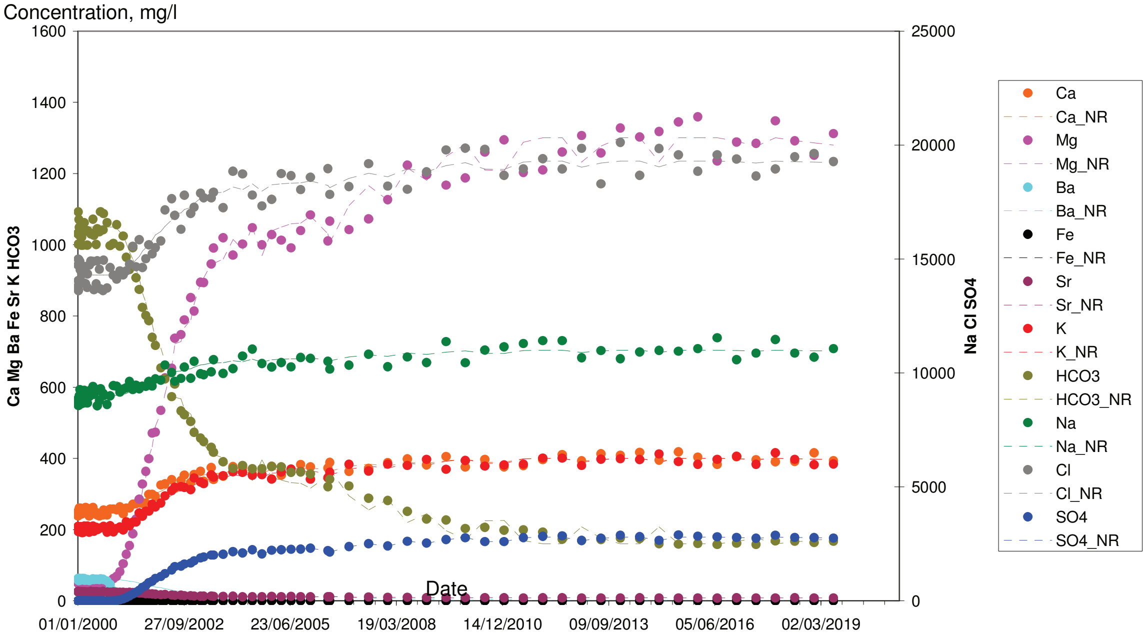


Figure 3.16 Modelled Ion concentrations with 5% noise added.

Figure 3.17 illustrates the IW fractions when chloride is used as the base ion, where the solid blue line is the true case (modelled IW fraction), red dots represent the Ion Track method, and the green line is the newly developed Reacting Ions solution. As may be clearly seen, with 5% noise chloride gives significant scatter, which affects the ion track results, whereas the analytic solution gives a much more accurate result.

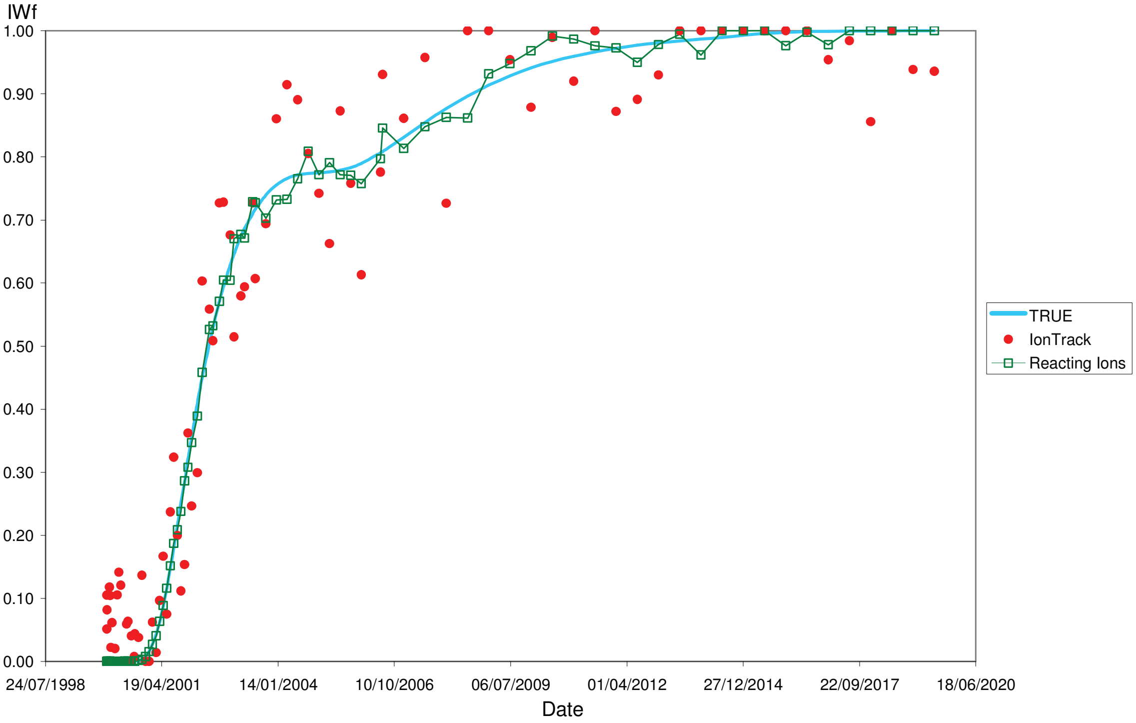


Figure 3.17 Modelled and calculated IW fractions for synthetic dataset with 5% noise.

With 5% noise added the IW fraction calculated by the Ion Track method with sulphate as the base ion matches the IW fraction calculated by the Reacting Ions method (Figure 3.18) as was explained for the case with 1% noise. However, the Ion Track method again gives a later breakthrough time (about 6 months, see Figure 3.19):

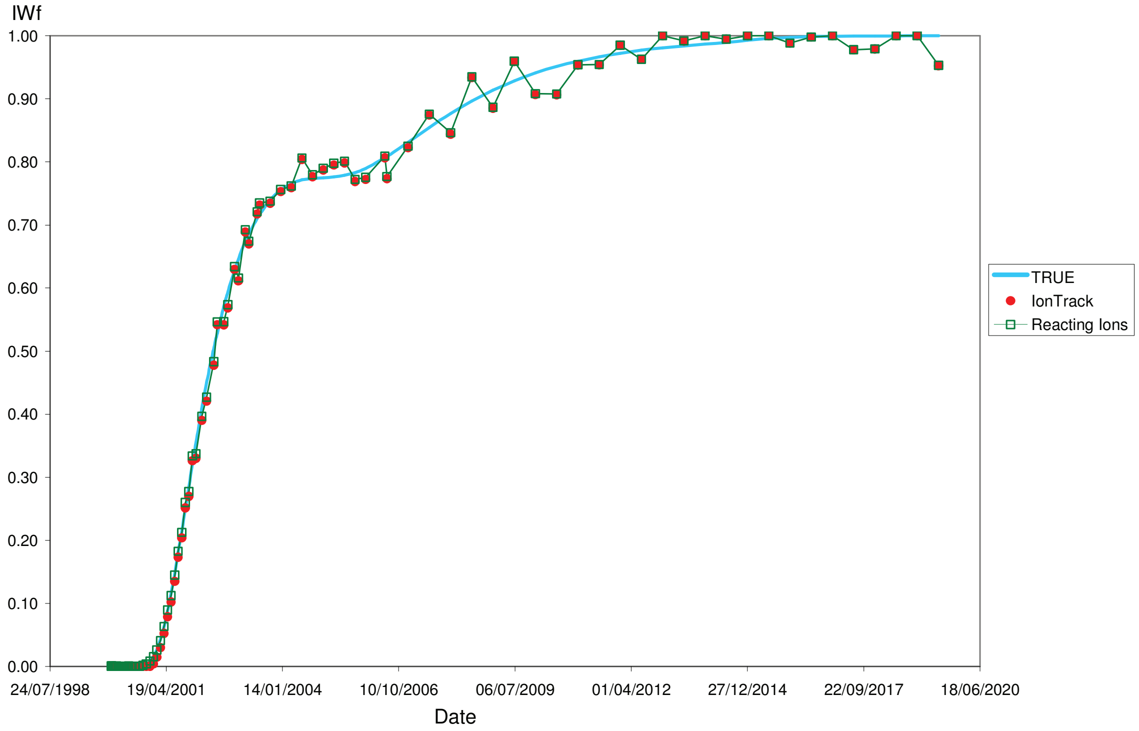


Figure 3.18 Sulphate is used as the base ion in the Ion Track method for the case with 5% noise added.

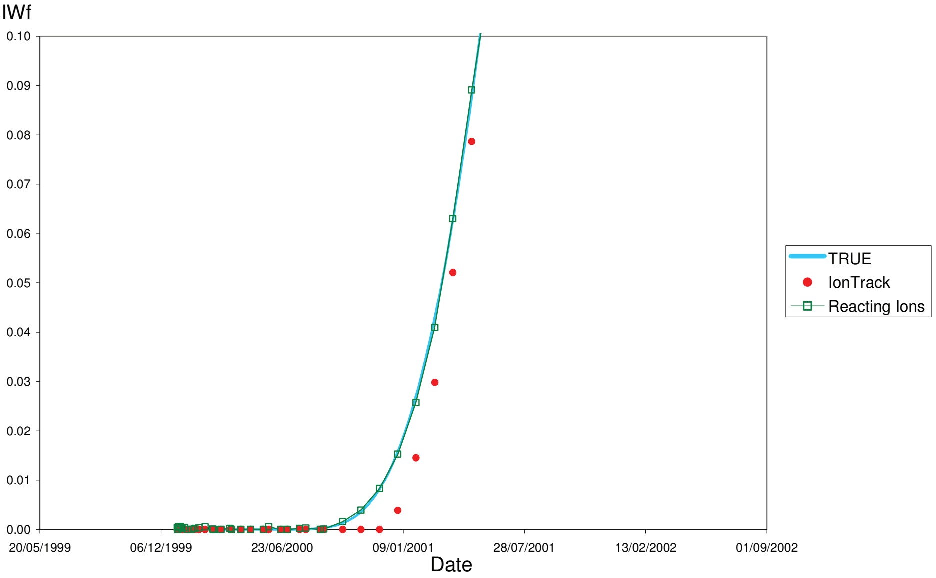


Figure 3.19 Zoom of the low IW fraction region, when sulphate is used as the base ion in Ion Track method.

With respect to the Ion Tracking method, it was demonstrated that in the presence of even moderate levels of scatter and noise (5%), it is more accurate to use reacting ions (such as sulphate) instead of the conservative chloride ion, given there is a much bigger differential between the sulphate concentrations in the two brines than the differential between the chloride concentrations in the two brines. In addition, in field scenarios where chloride is not measured, or it is not measured with the frequency with which barium, strontium and sulphate are measured, this new Reacting Ions technique may prove very useful.

3.4.3 Case with one reaction and 10% of noise in observed data

Here 10% noise is introduced into the system. The ion concentrations observed are shown in Figure 3.20:

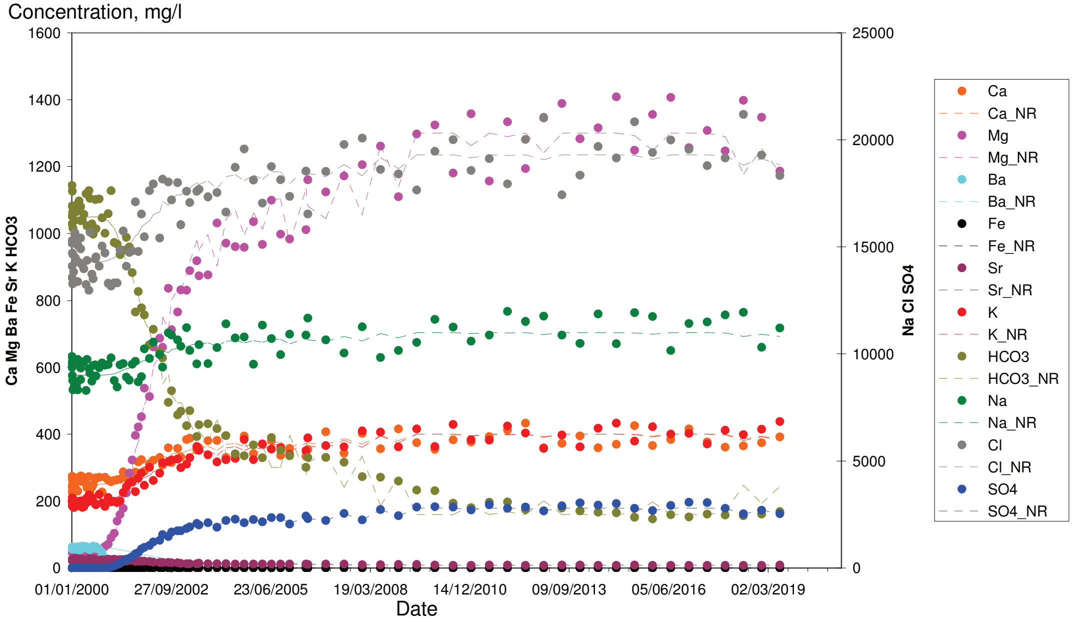


Figure 3.20 Ion concentrations observed with 10% noise introduced.

When chloride is taken as the base ion for the Ion track method, the trend in the results is similar to the case of 1% and 5% noise (Figure 3.21):

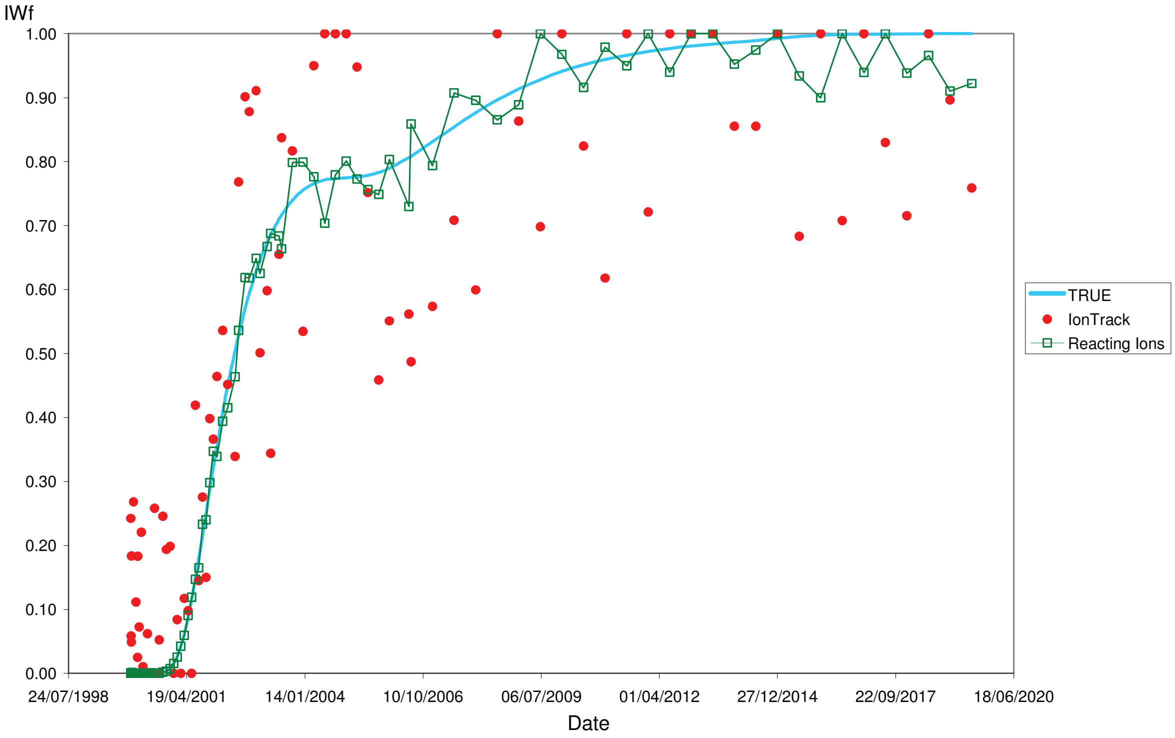


Figure 3.21 Modelled and calculated IW fractions for synthetic dataset with 10% noise.

When sulphate is taken as the base ion, conclusions are again the same as for the 1% and 5% noise cases (Figure 3.22):

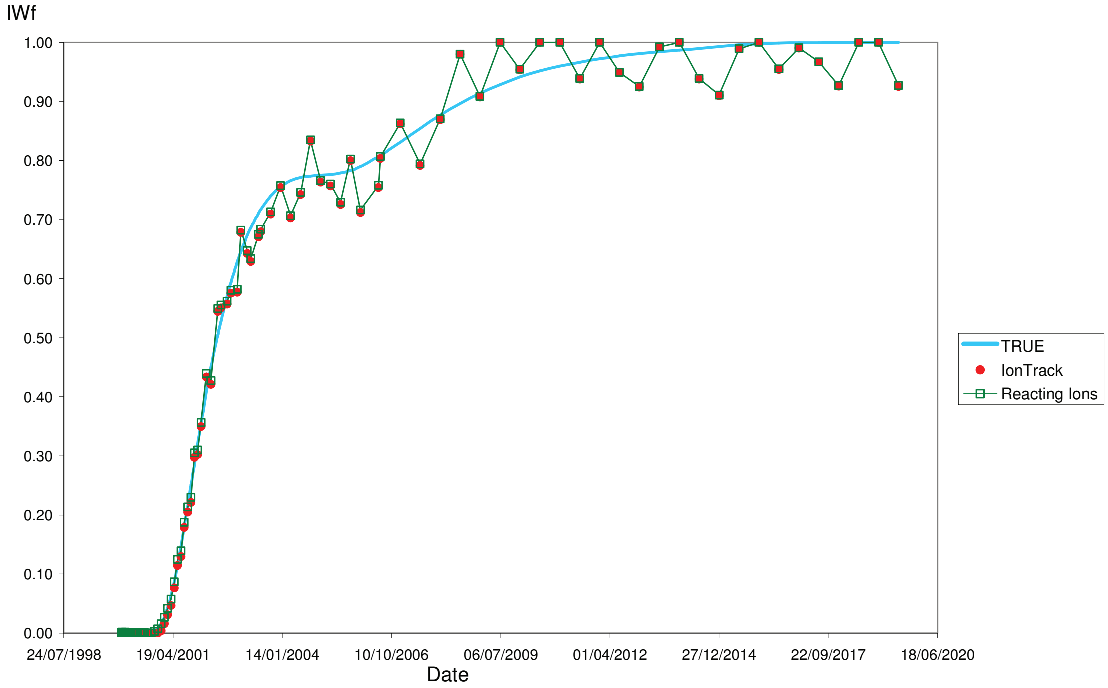


Figure 3.22 Sulphate used as base ion in the Ion Track method.

3.4.4 Ions participating in two or more reactions

The synthetic model was modified to perform the two reactions of $BaSO_4$ and $SrSO_4$ precipitation. Figure 3.23 presents produced ion concentrations for the case of two reactions.

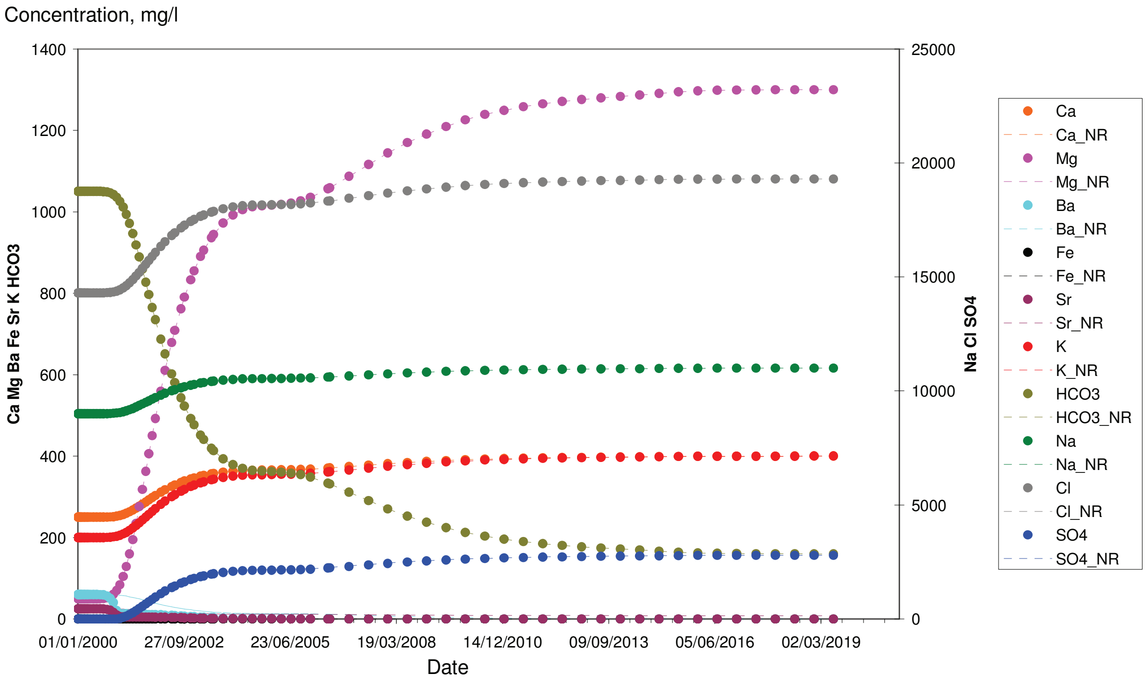


Figure 3.23 Synthetic dataset. Produced ion concentrations after $BaSO_4$ and $SrSO_4$ reactions.

Calculated IW fractions are plotted in Figure 3.24 For the Ion Track method chloride is used as the base ion, whereas the Reacting Ions uses sulphate, barium and strontium.

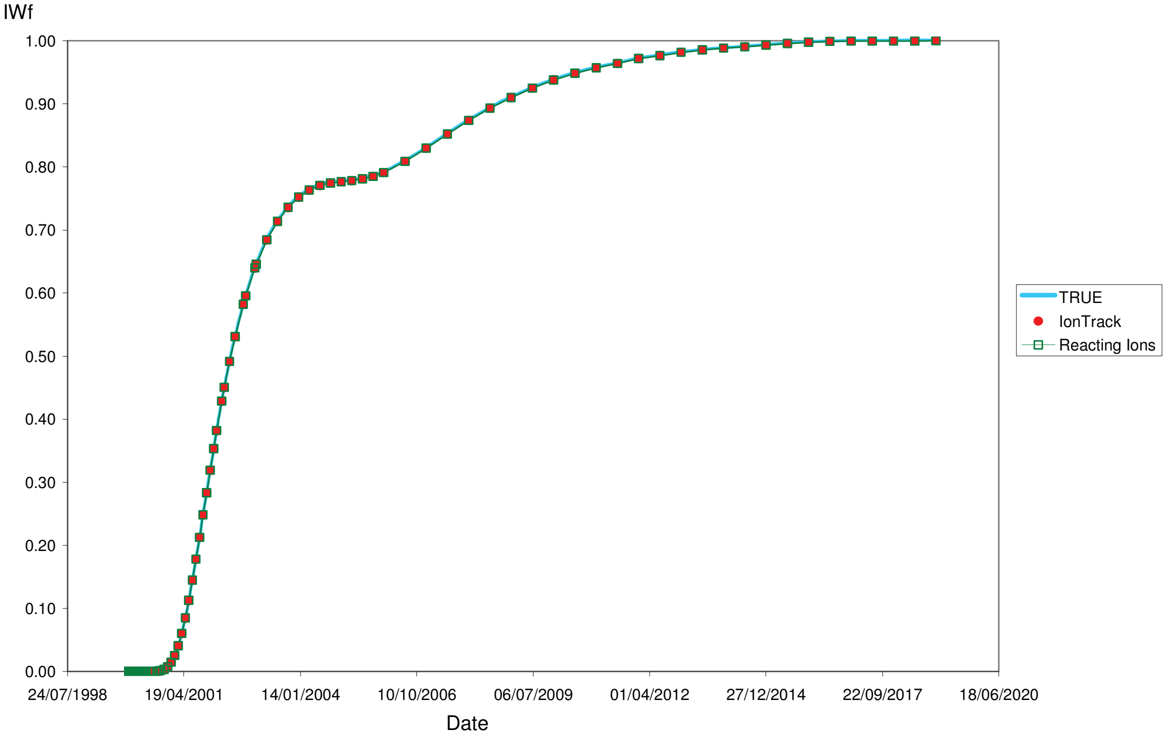


Figure 3.24 Synthetic dataset. Without noise applied both methods show a perfect match with true injection water fraction.

3.4.5 Two reactions with 1% noise added

Chloride, as the most typical conservative ion, is chosen as the base ion for the Ion Track method with 1% of noise applied to the modelled dataset. Figure 3.25 illustrates the IW fractions when chloride is used as the base ion. It shows scatter for the low IW fractions and therefore incorrect identification of IW breakthrough time.

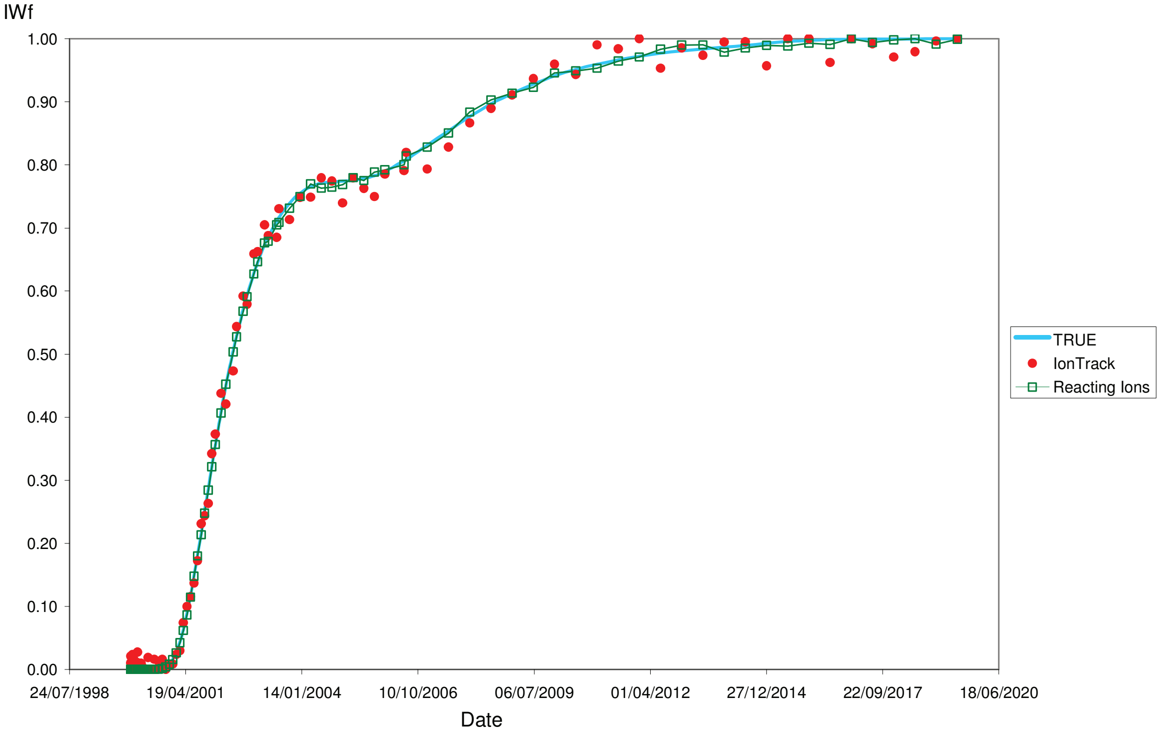


Figure 3.25 Modelled and calculated IW fractions for synthetic dataset with 1% noise.

According to the IW fractions calculated by the Ion Track method with each ion taken as base ion (Figure 3.26), we observe that the IW fraction based on reacting sulphate is approximately the same as the IW fraction calculated based on conservative chloride. Excess of sulphate over barium and strontium explains the fact that sulphate behaves like a conservative ion.

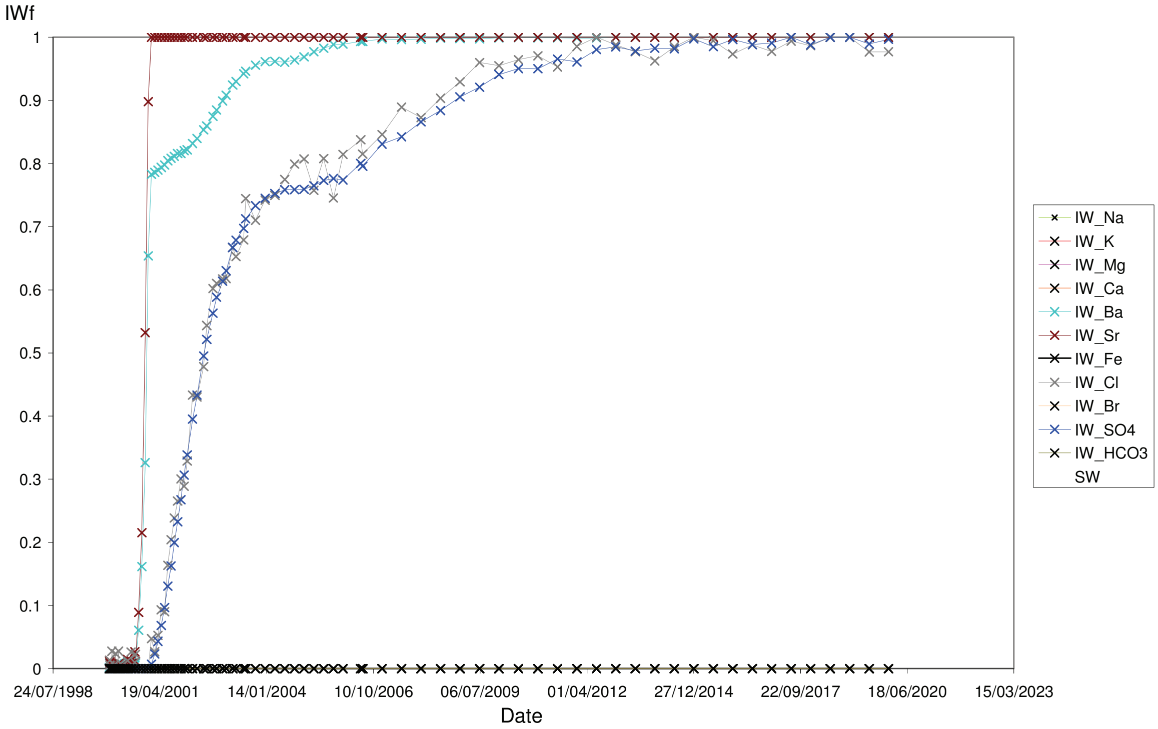


Figure 3.26 IW fractions calculated by Ion Track method where each ion in turn is taken as the base ion.

Two cases were investigated further, each of them with 1%, 5% and 10% of noise applied. The first case was a comparison of the Reacting Ions method versus the Ion Track method where both sulphate and chloride are taken as base ions, and the second case where the Reacting Ions method versus Ion Track method with only sulphate used as the base ion.

Sulphate and chloride are taken as base ions with equal weights (Figure 3.27). Scatter at the low IW fractions is clearly seen for the Ion Track method.

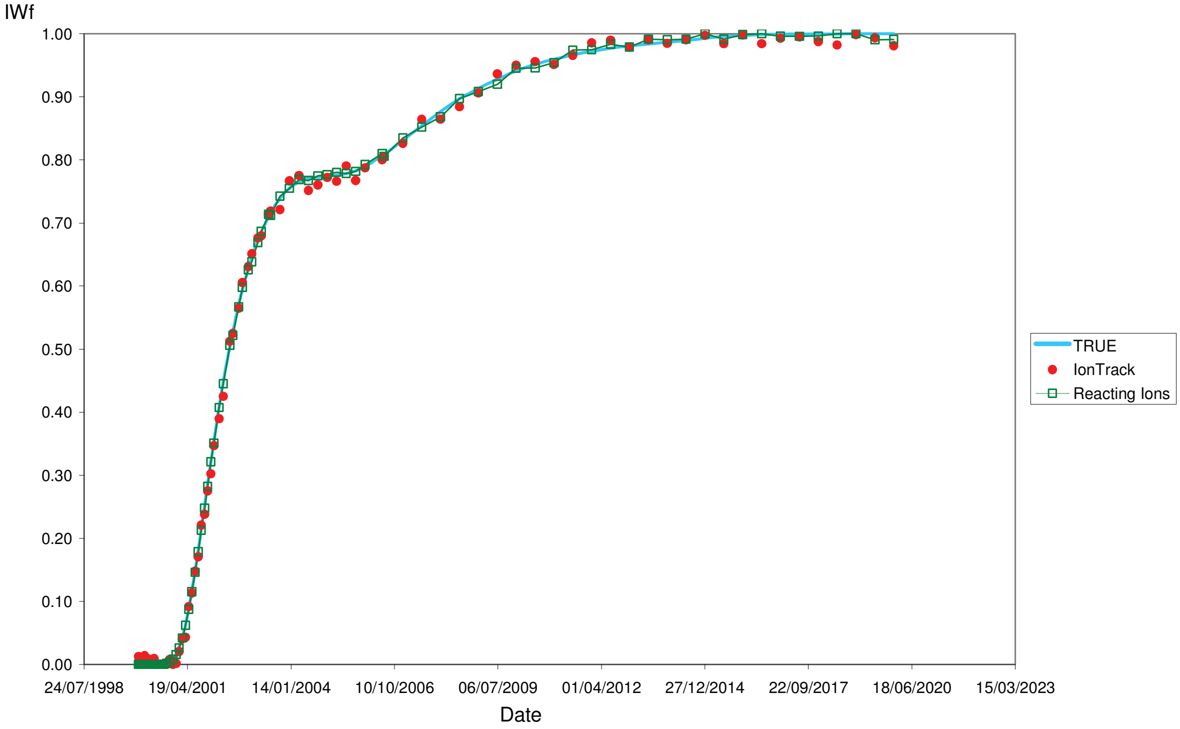


Figure 3.27 Sulphate and chloride are taken as base ions for the Ion Track method.

Sulphate (a reacting ion) is taken as the base ion for the Ion Track method. At the large scale it is difficult to detect the scatter at low IW fractions, but the zoomed region shows late IW breakthrough time for the Ion Track method (Figure 3.28).

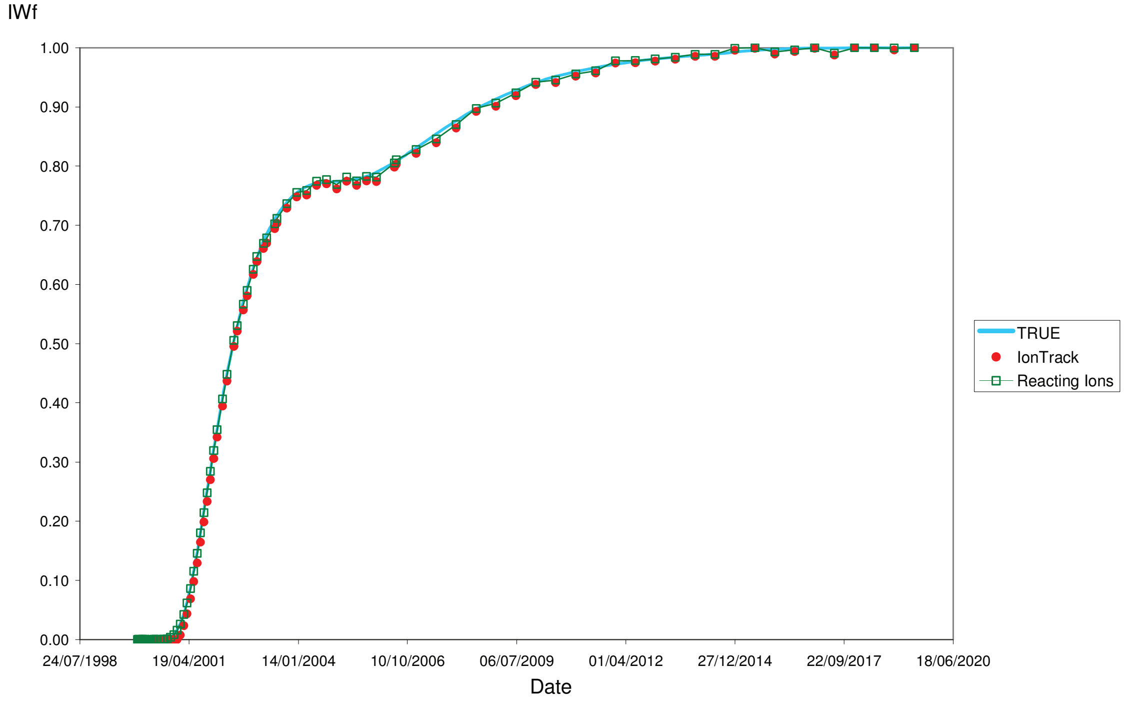


Figure 3.28 Sulphate is taken as base ions for the Ion Track method.

Ion Track gives later IW breakthrough (about 6 month later) when sulphate is taken as the base ion. The Reacting Ions method (based on barium, strontium and sulphate) exactly matches and overlaps the true IW fraction (Figure 3.29).

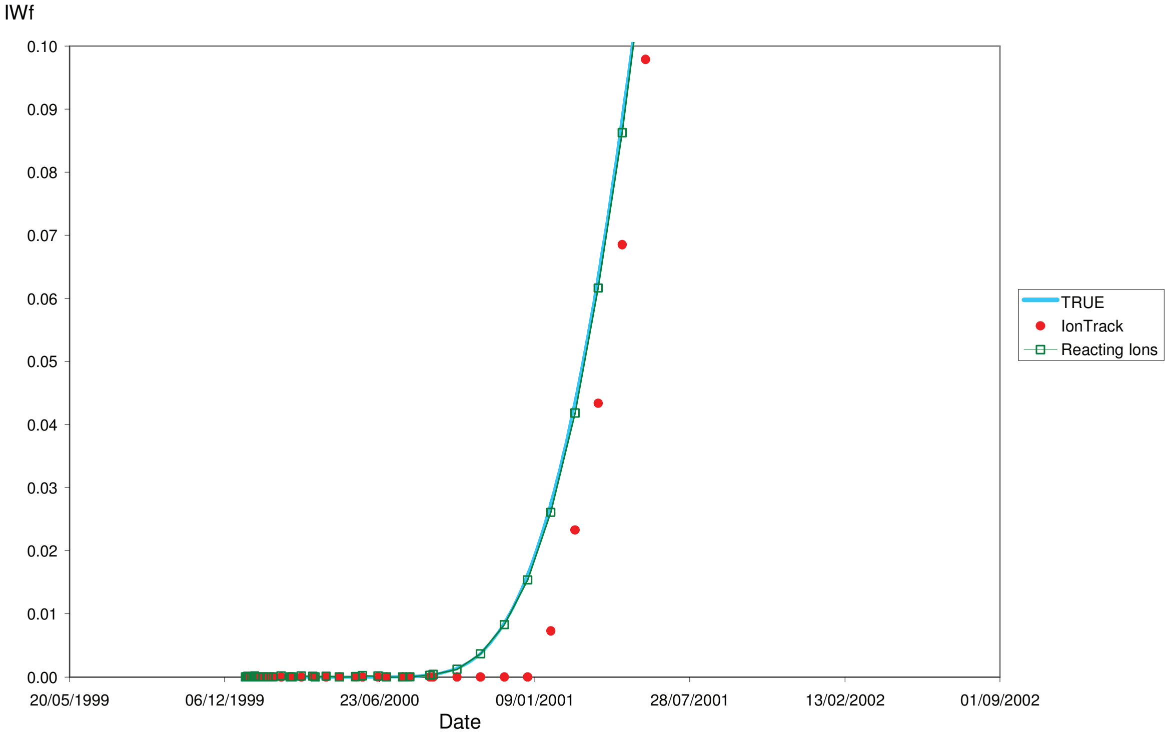


Figure 3.29 Zoom of the low IW fraction region, when sulphate is used as base ion in Ion Track method.

3.4.6 Two reactions with 5% noise added

5% random noise was introduced into the system with two reactions. The base ion for the Ion Track method is chloride, and the IW fraction calculated by both approaches is shown below (Figure 3.30).

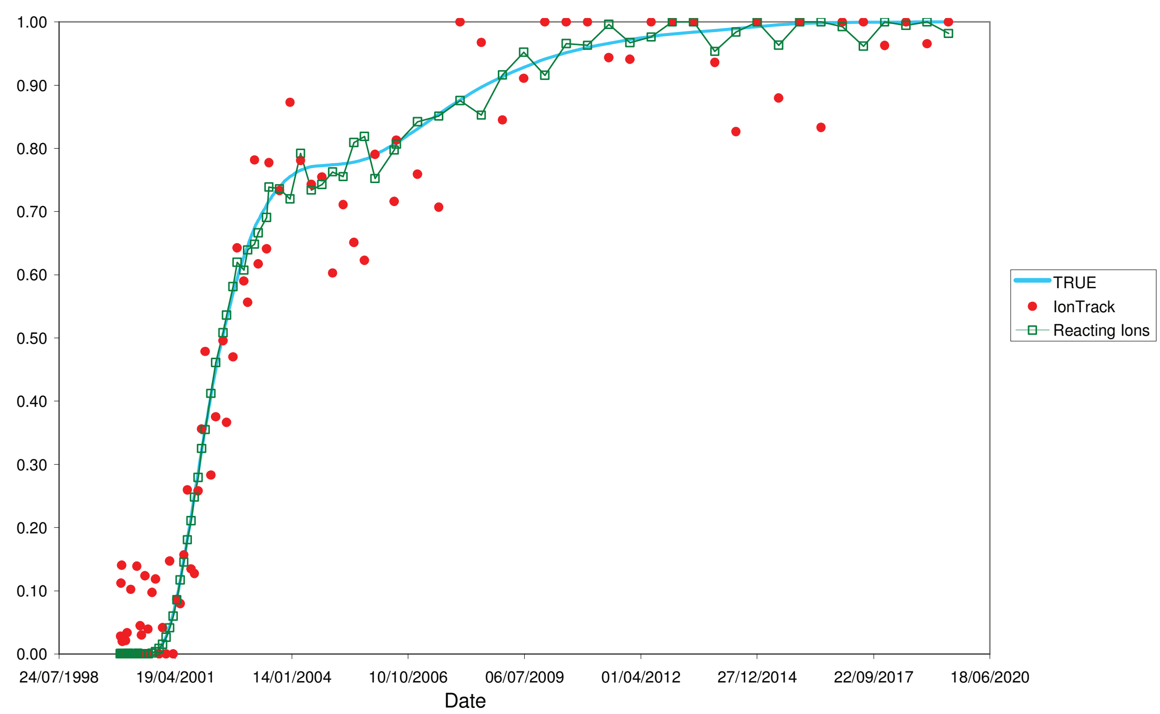


Figure 3.30 Modelled and calculated IW fractions for two reactions in synthetic dataset with 5% noise.

Sulphate (reacting ion) and chloride are taken as base ions (Figure 3.31). It is clear that the analytic method gives a more accurate solution for low IW fractions.

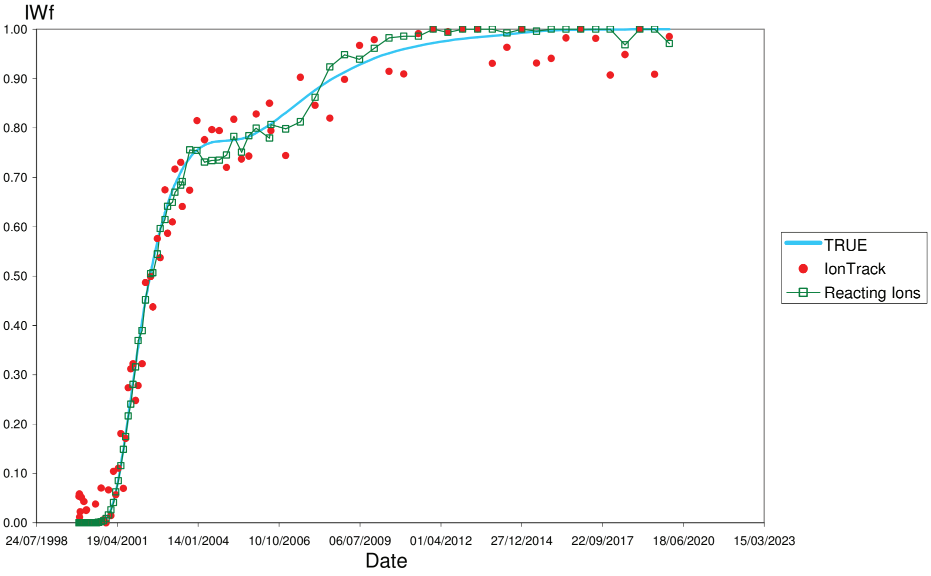


Figure 3.31 Sulphate and chloride are taken as the base ions for Ion Track method.

Figure 3.32 illustrates the case where sulphate is taken as the base ion for the Ion Track method. A zoom into the region of low IW fraction (Figure 3.33) shows late breakthrough using the Ion Track method.

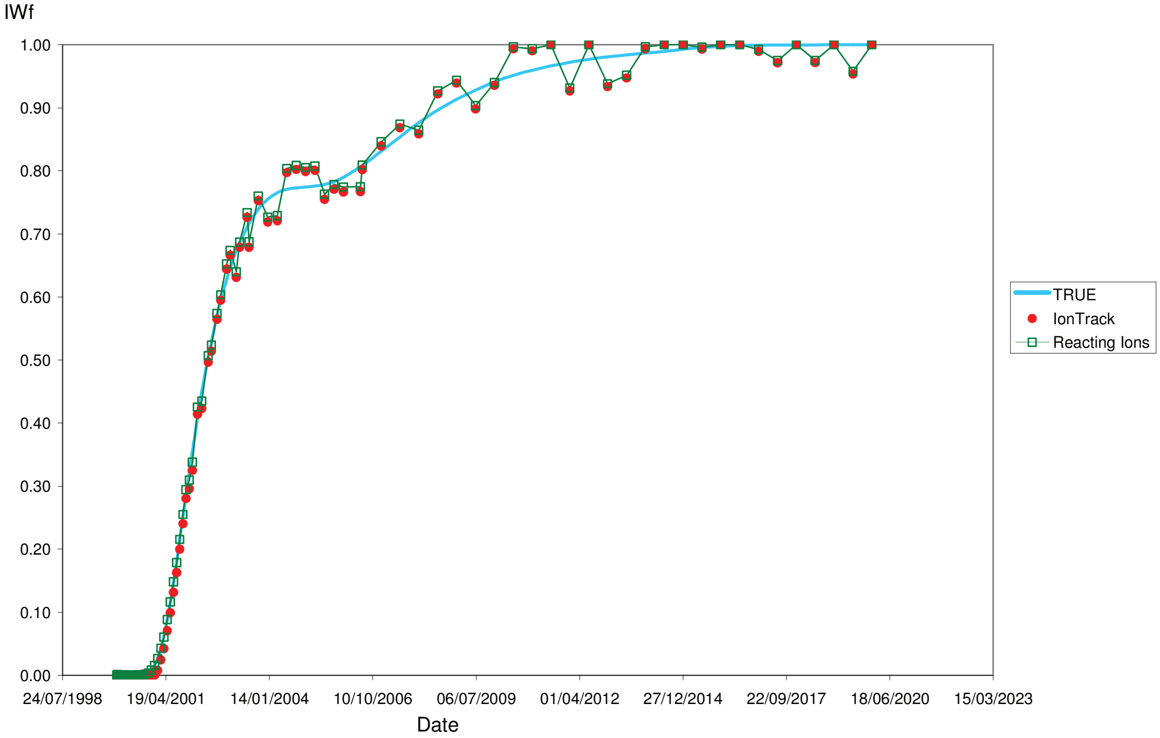


Figure 3.32 Sulphate is taken as the base ion for the Ion Track method.

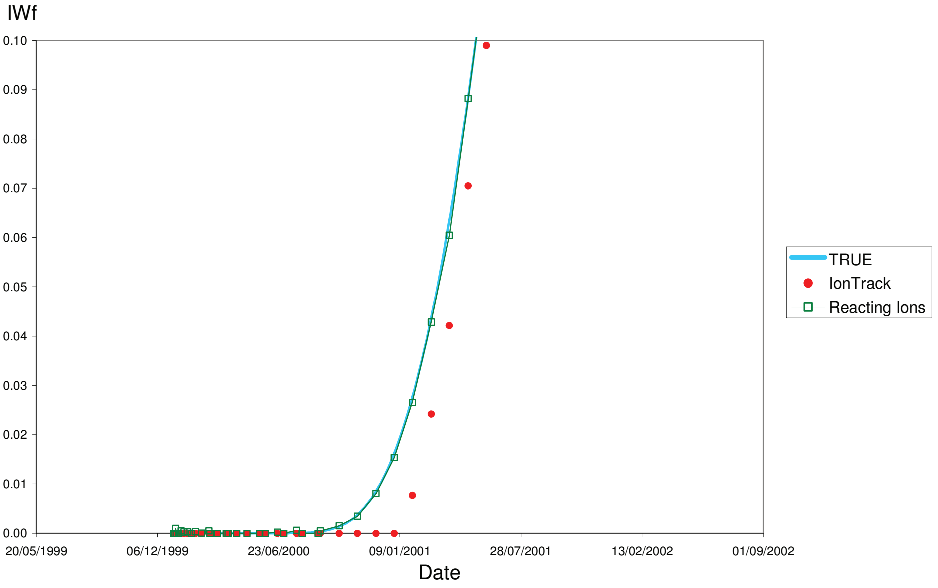


Figure 3.33 Zoom of the low IW fraction region, when sulphate is used as the base ion in Ion Track method.

3.4.7 Two reactions with 10% noise added

Finally, 10% random noise was introduced into the system. The base ion for the Ion Track method is chloride (Figure 3.34).

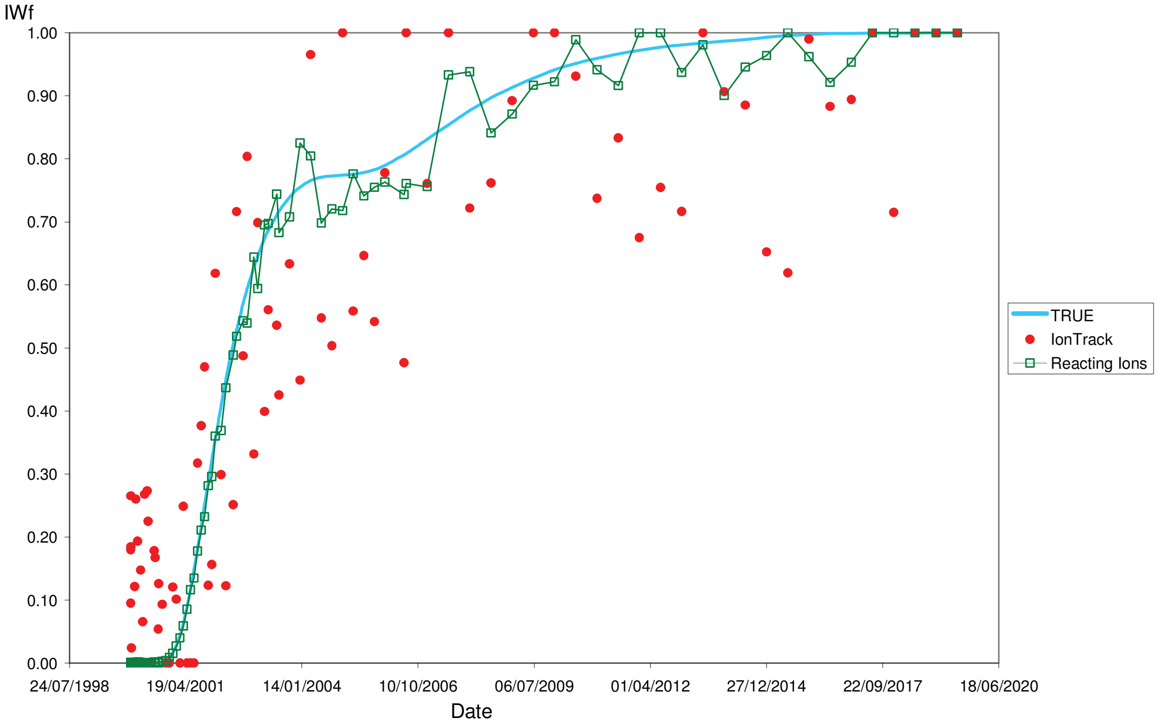


Figure 3.34 Modelled and calculated IW fractions for synthetic dataset with two reactions and 10% noise.

The results of using sulphate and chloride as base ions with equal weights are shown in Figure 3.35, whereas when sulphate alone is taken as the base ion the results are as in Figure 3.36.

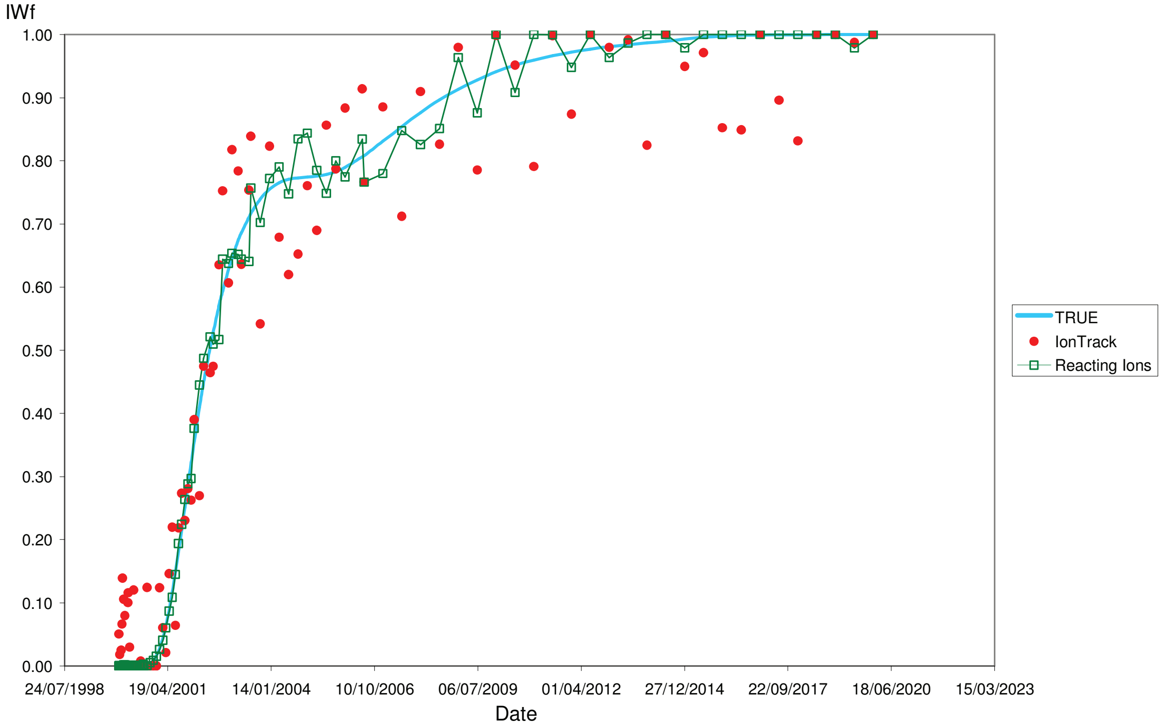


Figure 3.35 Sulphate and chloride are used as the base ions in the Ion Track method for the case of 10% noise added.

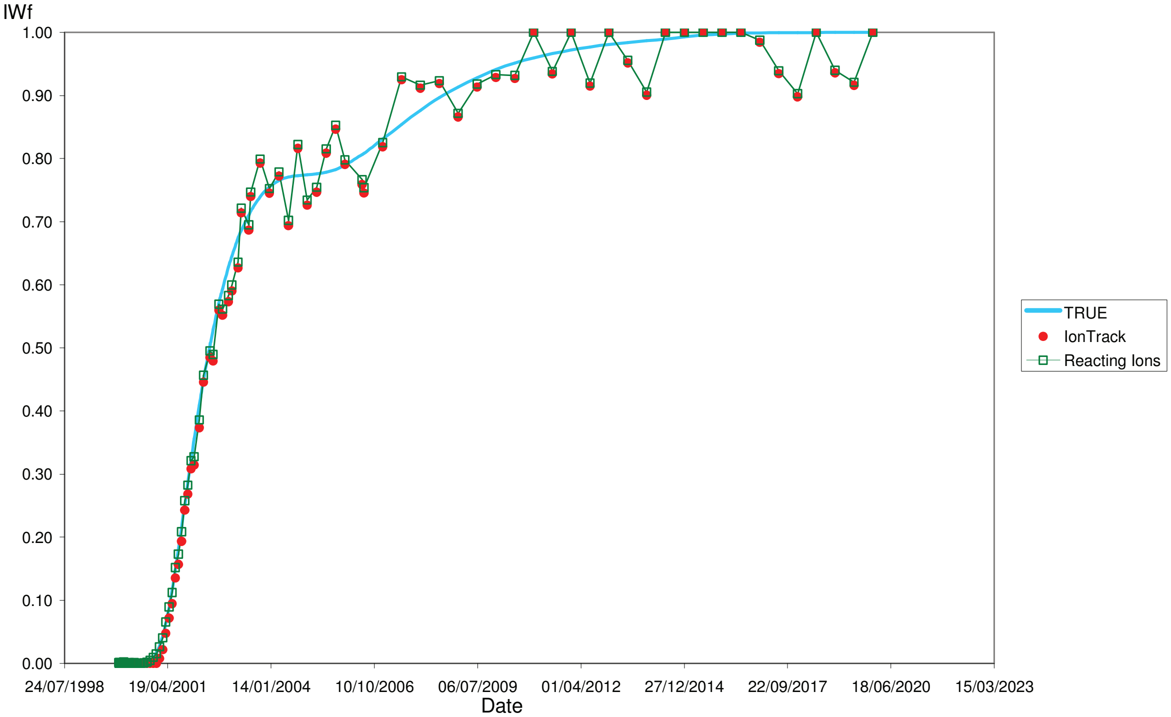


Figure 3.36 Sulphate alone is taken as the base ions for the Ion Track method.

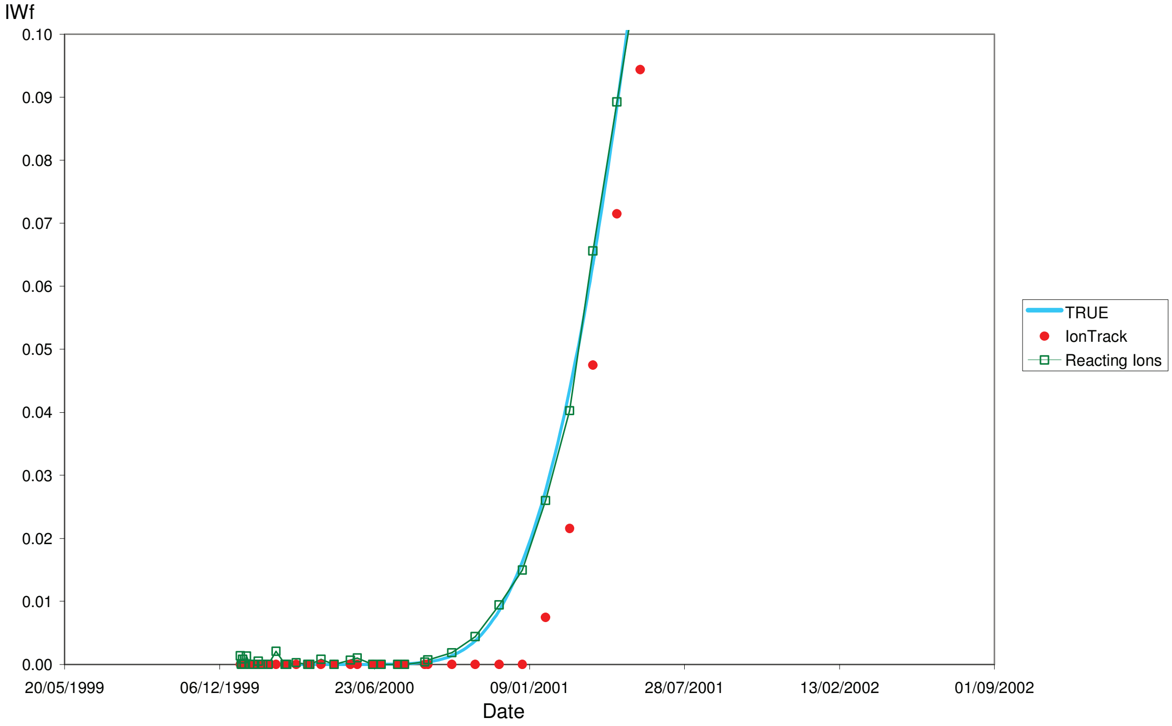


Figure 3.37 Zoom of the low IW fraction region, when sulphate alone is used as base ion in the Ion Track method.

Again, a zoom in to the period around injection water breakthrough shows that the new Reacting Ions method (for two reactions) is much more accurate for identifying injection water breakthrough than the Ion Track method based on sulphate (Figure 3.37).

3.5. Summary

The Reacting Ions method presented in this chapter was successfully tested on a synthetic model. Testing scenarios were combined from three noise levels 1%, 5%, and 10% with case of one reaction ($BaSO_4$) and two reactions ($BaSO_4$, $SrSO_4$). In each of the testing scenarios the Reacting Ions method proved itself robust and more accurate in detecting injection water breakthrough. More testing scenarios were run during the field applications phase presented in the Chapter 5.

CHAPTER 4 NEW APPLICATIONS BASED ON THE INJECTION WATER FRACTION

Recent developments in the area of oilfield scale management have led to a renewed interest in the methods of detection injection water breakthrough ([51]).

The time of injection water breakthrough is one of the main indicators production chemists monitor for. After injected water breaks through, the risk of scaling significantly increases and scale mitigation procedures should be planned. Timely detection of IW breakthrough can significantly reduce costs and well work over time, and the risk of a well scaling up. IW fraction and breakthrough time may only be ascertained from the produced water samples, therefore the analytical methods to calculate injection water fractions discussed in this thesis (in Chapters 2 and 3) may be applied to identify when a scale inhibitor squeeze treatment should be deployed, for instance.

So far, however, there has been little discussion about applications of injection water fraction tracking techniques other than as the indicator of seawater breakthrough. In this chapter new applications that follow on from accurate knowledge of injection water fraction are presented.

The calculated IW fraction may be applied to:

1. Quickly and accurately identify when seawater breakthrough has taken place and therefore remedial action to prevent scale damage needs to be implemented.
2. Identify which ions are involved in reactions, and the degree of relative ion deviations; identify ion exchange reactions.
3. Detect which formation or formations a well is producing from.

Note that for the above mentioned applications, injection water fraction can be determined by methods other than the Reacting Ions method. However, the improved accuracy of the Reacting Ions method has made these applications viable options in the production chemist's toolkit.

4.1. Detecting ions participating in geochemical reactions

Information regarding the degree of the various ions' involvement in reactions can significantly help production chemists to choose the right scale mitigation strategies. To identify which are the reacting ions and what types of reactions are taking place in the reservoir and/or the near well-bore area, an observed ion concentration should be compared with the concentration of that ion should there be no reactions occurring. Therefore, the measured/observed ion concentrations in water samples should be compared with the conservative ion concentrations.

The reader should recall that the conservative concentration referred to is the expected ion concentration should there be only mixing, with no scaling reactions taking place. If the observed ion concentration is less than its conservative value, generally it means that a scaling reaction results in loss of this ion. If the observed ion concentration is equal to the conservative value, then this represents no net reaction. If the observed ion concentration is greater than the conservative value, then this corresponds to a dissolution reaction.

Increases or decreases in ion concentrations relative to the conservative values may also occasionally be attributed to ion exchange processes.

A "Relative Ion Deviation" is defined, which indicates the degree of ion deviation from the conservative value (4.1).

$$D = \frac{\text{Observed}}{\text{Conservative}} - 1 = \frac{\tilde{C}}{\overline{C}} - 1 \qquad (4.1)$$

where $\tilde{C}$ - observed ion concentration

$\overline{C}$ - conservative ion concentration.

Relative Ion Deviation values are in the range $[-1;\infty)$. A zero values of "Ion Deviation" indicates that the observed ion concentration is equal to the conservative ion concentration, and therefore the ion is either not reacting, or the net change in ion concentration is zero (e.g. 10 moles of ion A is lost in reactions type A+B↔AB but 10 moles are gained in dissolution a reaction such as AC↔A+C). Negative values represent precipitation or losses due to ion exchange and positive values represent dissolution or gains due to ion exchange.

Figure 4.1 presents the results of a synthetic simulation in which barium (light blue dots) precipitation occurs in a reaction with sulphate (typical barite formation).

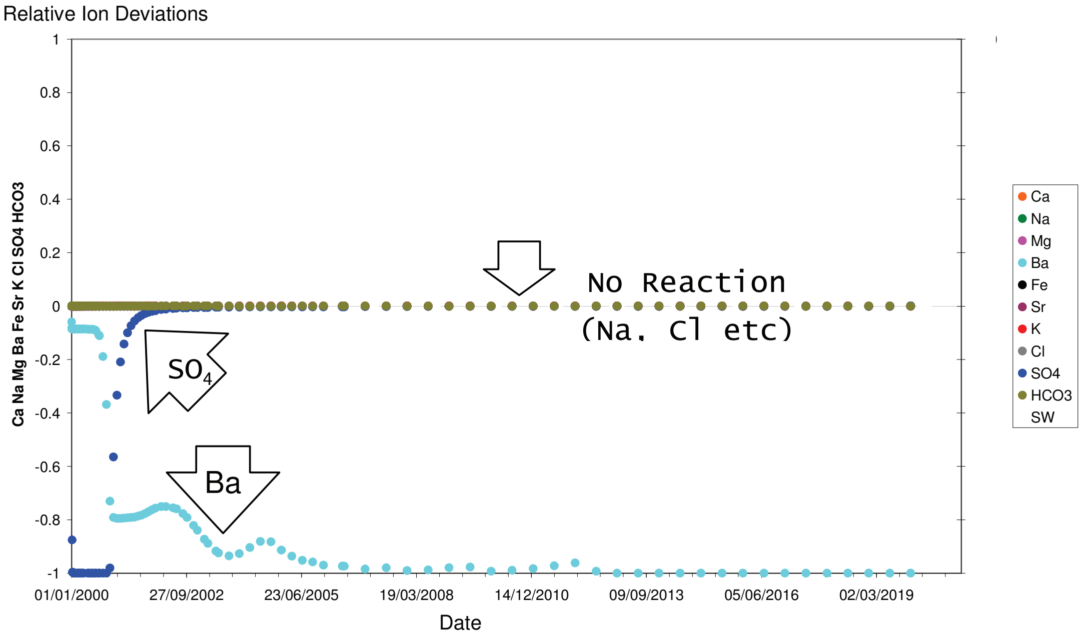


Figure 4.1 Relative ion deviations vs time based on synthetic case.

Typical ion relative deviation profiles do not depend on initial concentrations, volumes of water produced, time, etc, because ion deviation values are calculated in relative terms (injection water fractions and fraction of difference between observed and conservative concentrations are relative values). Kinetics (the speed of the reaction or reaction rate) and the type of reaction are the only parameters that affect ion deviation profiles. Figure 4.2 presents the difference in relative ion deviation profiles for the two cases of reservoir temperatures of 37^{o}C (100F) and 93^{o}C (200F).

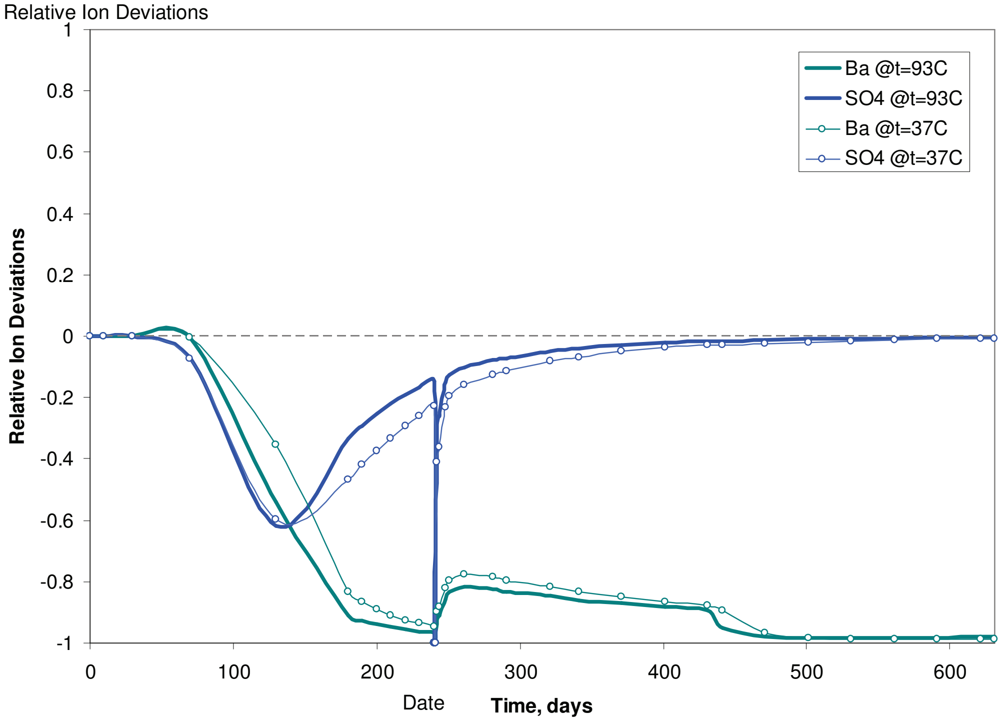


Figure 4.2 Relative ion deviations for barium and sulphate at different temperatures for the synthetic case.

All of the many relative ion deviations calculated for field cases and for modelled synthetic reactions involving barite precipitation are characterised by the initial decrease in sulphate Relative Ion deviations, especially at low IW fractions (Figure 4.1, Figure 4.2). This is explained by the fact that at low IW fractions, sulphate is the limiting ion, and there is an excess of barium in the produced water mix. Therefore, most of the sulphate is consumed due to precipitation of barite. With an increase in IW fraction, more sulphate is available for the scaling reactions, and so more barium is consumed. Above some IW fraction when sulphate and barium concentrations are equivalent in molar units, sulphate is in excess and a major loss of barium is observed due its reaction with the sulphate (Figure 4.1, Figure 4.2). However, the analyst should expect some non-zero barium concentration even in samples with high IW fraction as the thermodynamic equilibrium can be reached before all the barium is consumed.

Strong evidence of the involvement of barium and sulphate ions in reactions, based on the calculations of Relative Ions Deviations, is evident for the field data shown in Figure 4.3.

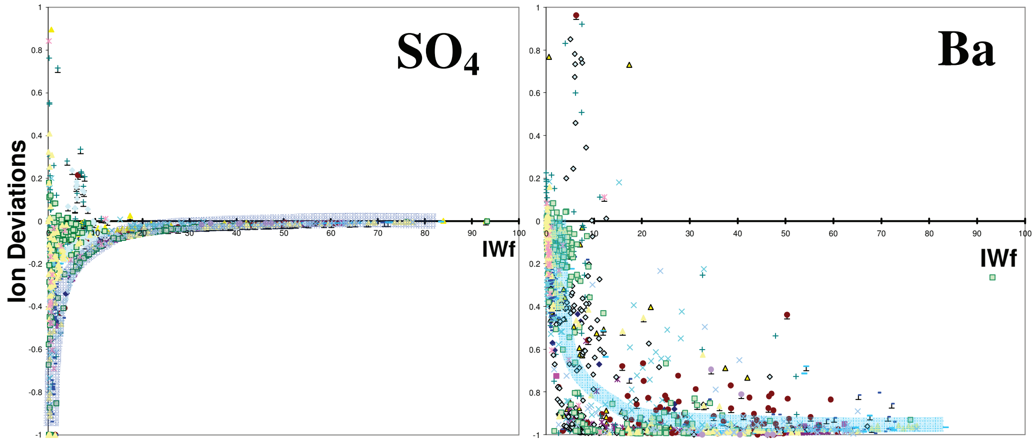


Figure 4.3 Sulphate and barium relative ion deviations for field data plotted against IW fraction.

The application of Relative Ion Deviations to specific field data is discussed in more detail in Chapter 5.

4.2. Identifying which formation(s) a well is producing from using IW fractions

4.2.1 General definitions

Formation water compositions may vary between geological formations due to different depositional environments, diagenetic effects, mineralogies and other issues related to the reservoir environment. Chloride is normally present in formation water and is a conservative ion, which means that it does not react with any other ion in the formation or injection brines. Its concentration is high enough to allow us to use it to distinguish between formation and injection brines (using the Ion Track method). However, the relative noise in the analysis may be high, which can make it less accurate for identifying low injection water fractions.

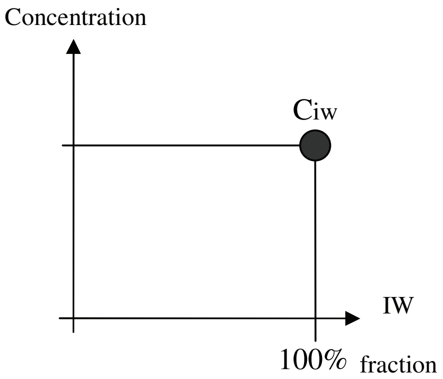
The chloride concentration in the injection water is generally well known. On the other hand, formation water samples are more difficult to acquire, as generally they can only be obtained from exploration wells or during initial well tests before the start of production. Also, these samples may be contaminated with drilling brine, etc.

Produced water samples are generally more reliable, although there may still be issues associated with scatter, contamination, preservation, etc. However, in general there will be a larger number of produced water samples than formation water samples. The greater the number of produced water samples, the more representative will be the evaluation of formation water composition.

Since chloride is a conservative ion, its concentration in each produced water sample will be equal to its conservative concentration plus or minus some noise added due to sampling, preservation, analysis, etc. If the IW fraction is known (measured or calculated) for a given produced water sample, and if the chloride concentration is measured, then the chloride concentration in the formation water can be back-calculated from a linear equation of conservative mixing, assuming the chloride concentration in the injection brine is known (4.2).

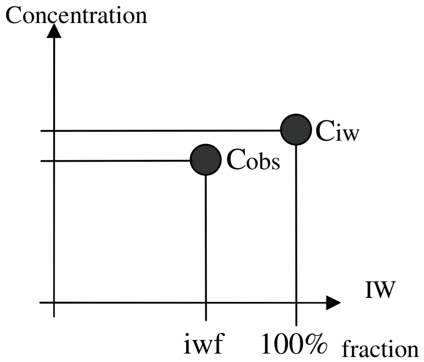
$$C_{fw} = \frac{C_{obs} - C_{iw} \cdot iwf}{1 - iwf} \qquad (4.2)$$

The step by step process is illustrated in Figure 4.4:



1st step

Cl concentration
in IW is measured

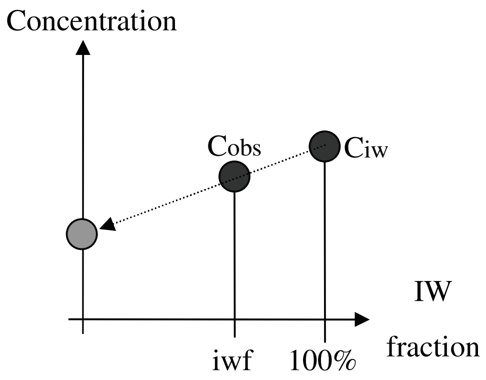


2nd step

Cl concentration in
produced water is
measured

and

IW fraction is calculated



3rd step

Cl concentration in Formation Water

is back-calculated by linear extrapolation to 0% IW fraction

Figure 4.4 Method for back-calculating formation water chloride concentrations.

4.2.2 Synthetic tests

A synthetic model was built to test the validity of the method for back-calculating formation water conservative ion concentrations. The Petroleum Experts Reveal ([66]) reservoir simulator was used to model chemical reactions in a two-layered 3D reservoir. The reservoir consists of two formations/layers separated by impermeable shale. The top layer is less permeable (180 mD) than the bottom one (200 mD). The formation brine compositions are based on field examples and are shown in Table 3.2.

Table 4.1 Formation waters (FW1, FW2) and injection water (IW) compositions for the synthetic model.

ppm	*Na*	*K*	*Mg*	*Ca*	*Ba*	*Sr*	*Fe*	*Cl*	*Br*	*SO4*	*HCO3*
FW1	16355	533	212	1331	65	0	0	28698	0	0	0
FW2	17750	565	240	1150	71	0	0	30637	0	7	0
IW	10768	399	1292	412	0	8	0	19353	0	2712	142

This section explores the situation where a well was producing from formation A (FW1) for 400 days and then it was reperforated to produce from formation B (FW2). The aim of the test was to check whether that sequence can be detected by analysing the produced ion concentrations only. Two scenarios were assessed: brine analyses without noise and with some random noise added (in line with Equation 3.24). Figure 4.5 and the expanded area in Figure 4.6 illustrate the case where no noise was added to the observed produced water samples. Initial concentrations of chloride in formation brines are marked with grey lines.

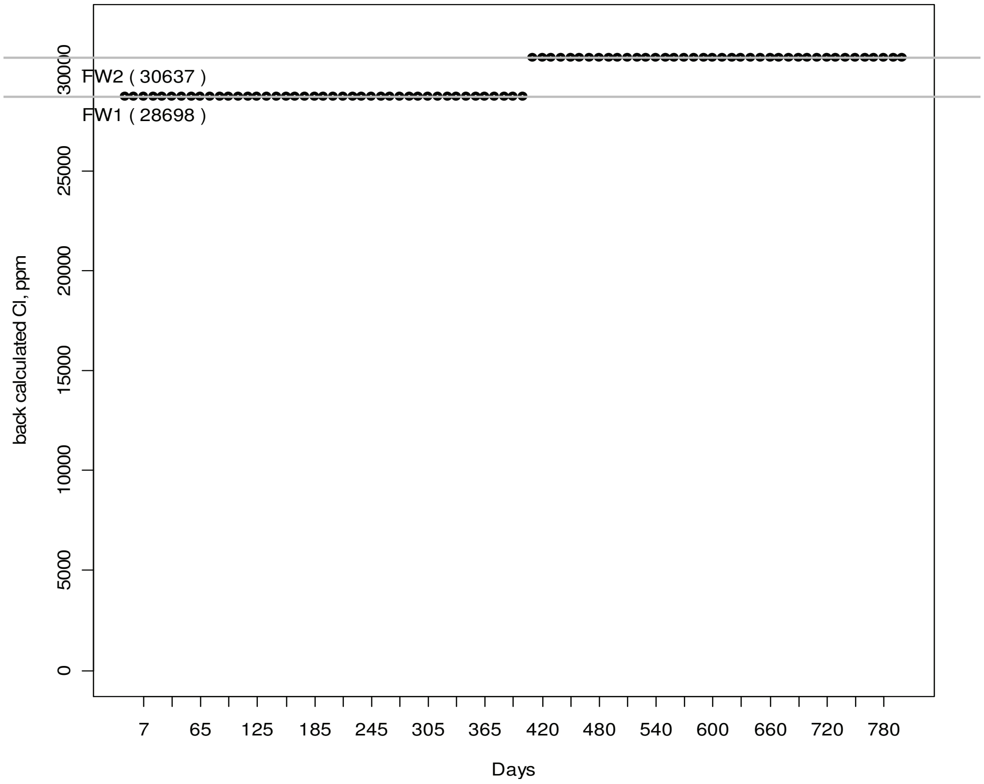


Figure 4.5 Back-calculated chloride concentration in the formation water for synthetic case without noise versus days of production.

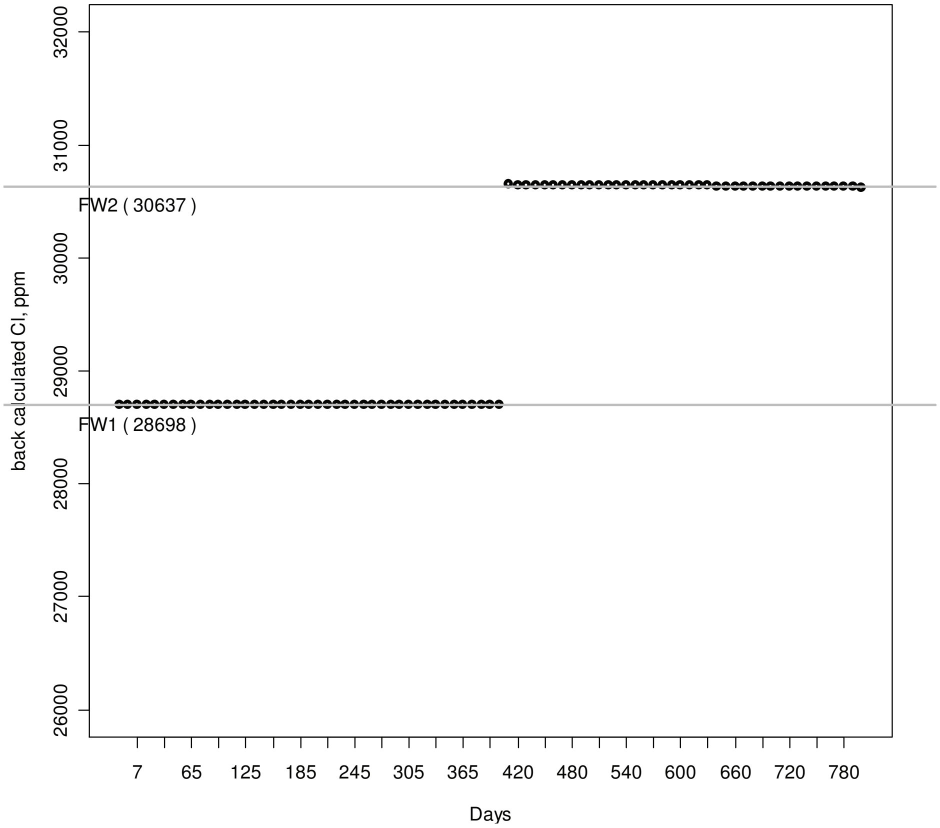


Figure 4.6 Zoom of the back-calculated chloride concentration in the formation water for synthetic case without noise.

From the modelled results it can be observed that the method gives accurate and exact results detecting which formations the well was producing from.

The next step in testing the approach proposed was to see how noise impacts the results. Random relative noise of 2% (Figure 4.7, zoom in Figure 4.9) and 5% (Figure 4.9) with 5 mg/l of absolute noise was added to the produced water samples.

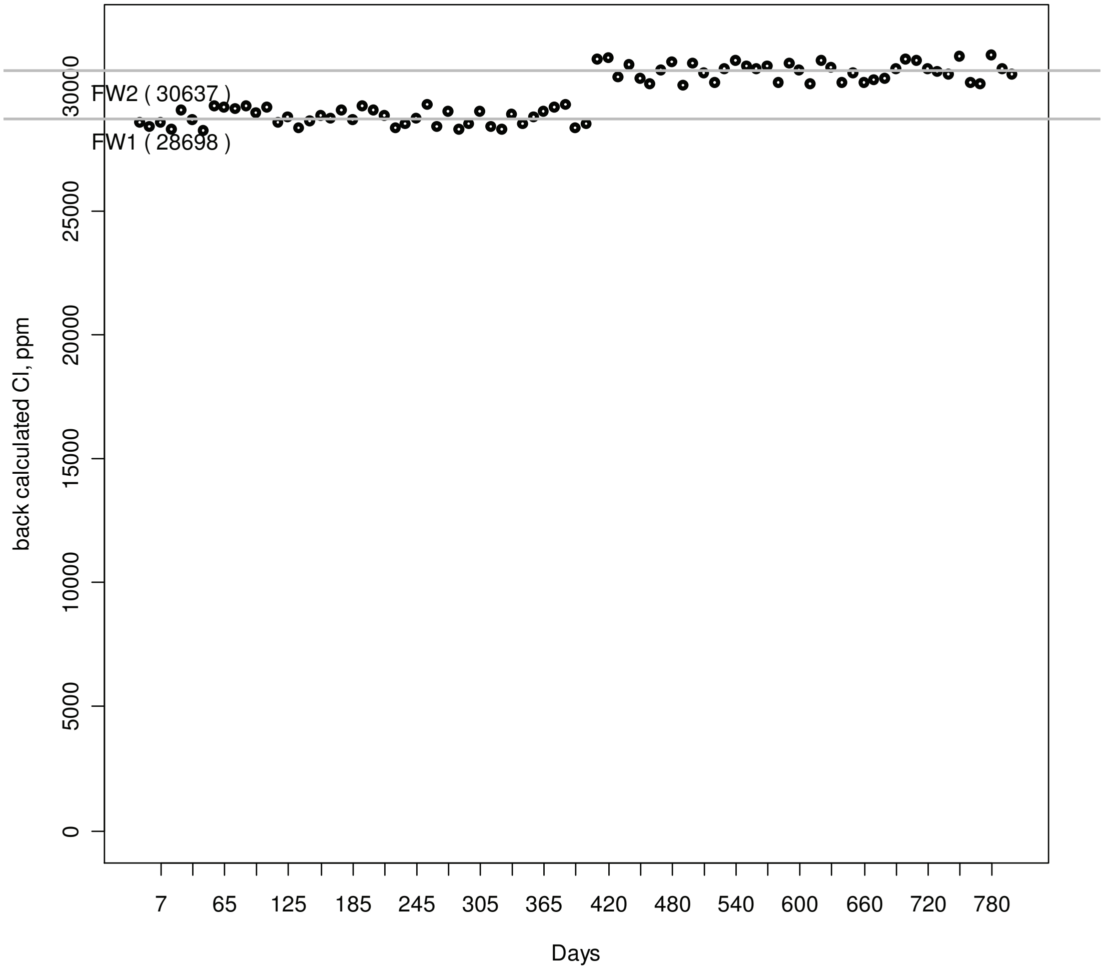


Figure 4.7 Back-calculated chloride concentrations in the formation water for synthetic case with 2% relative noise.

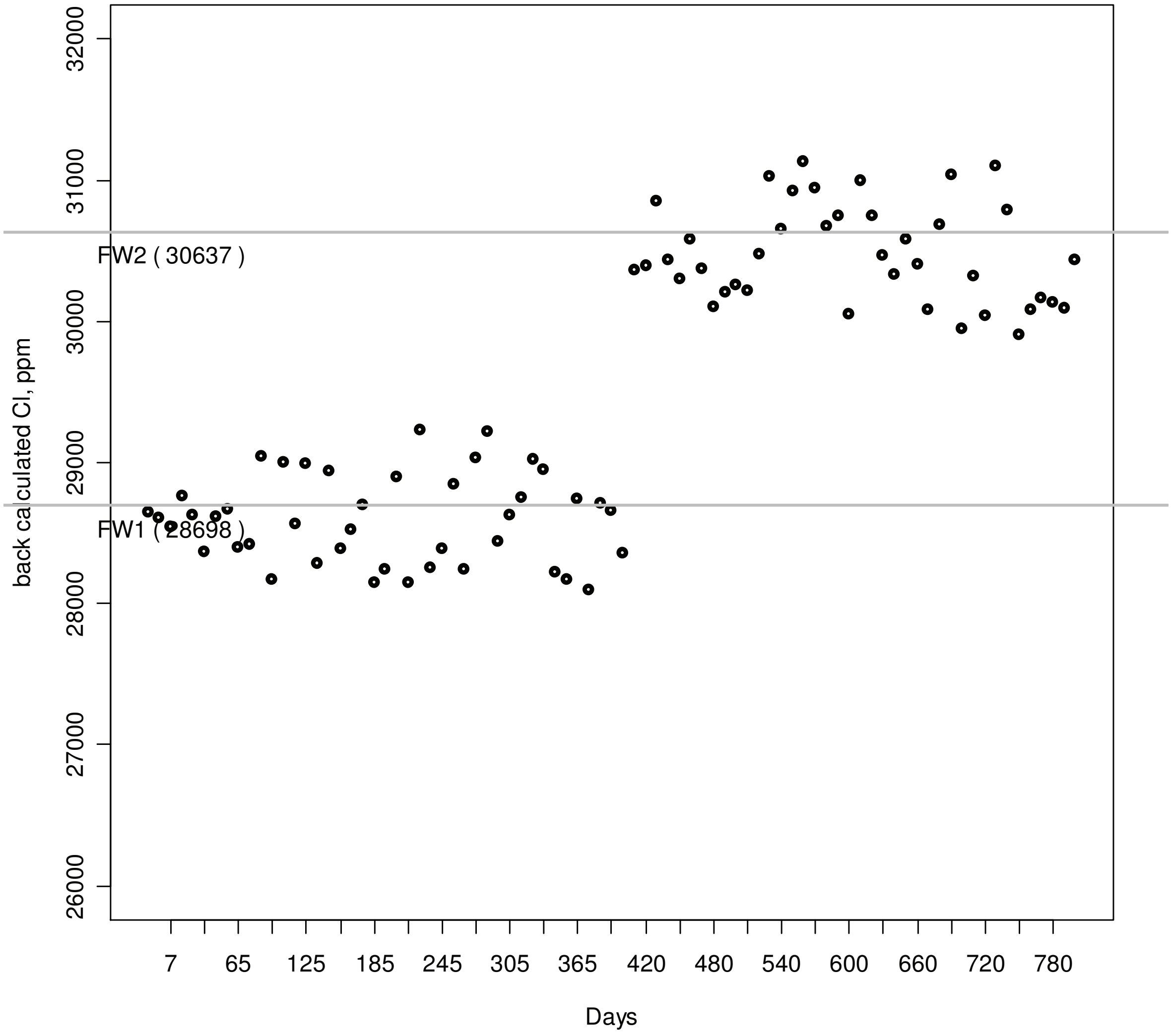


Figure 4.8 Zoom of the back-calculated chloride concentration in the formation water for synthetic case with 2% of relative noise.

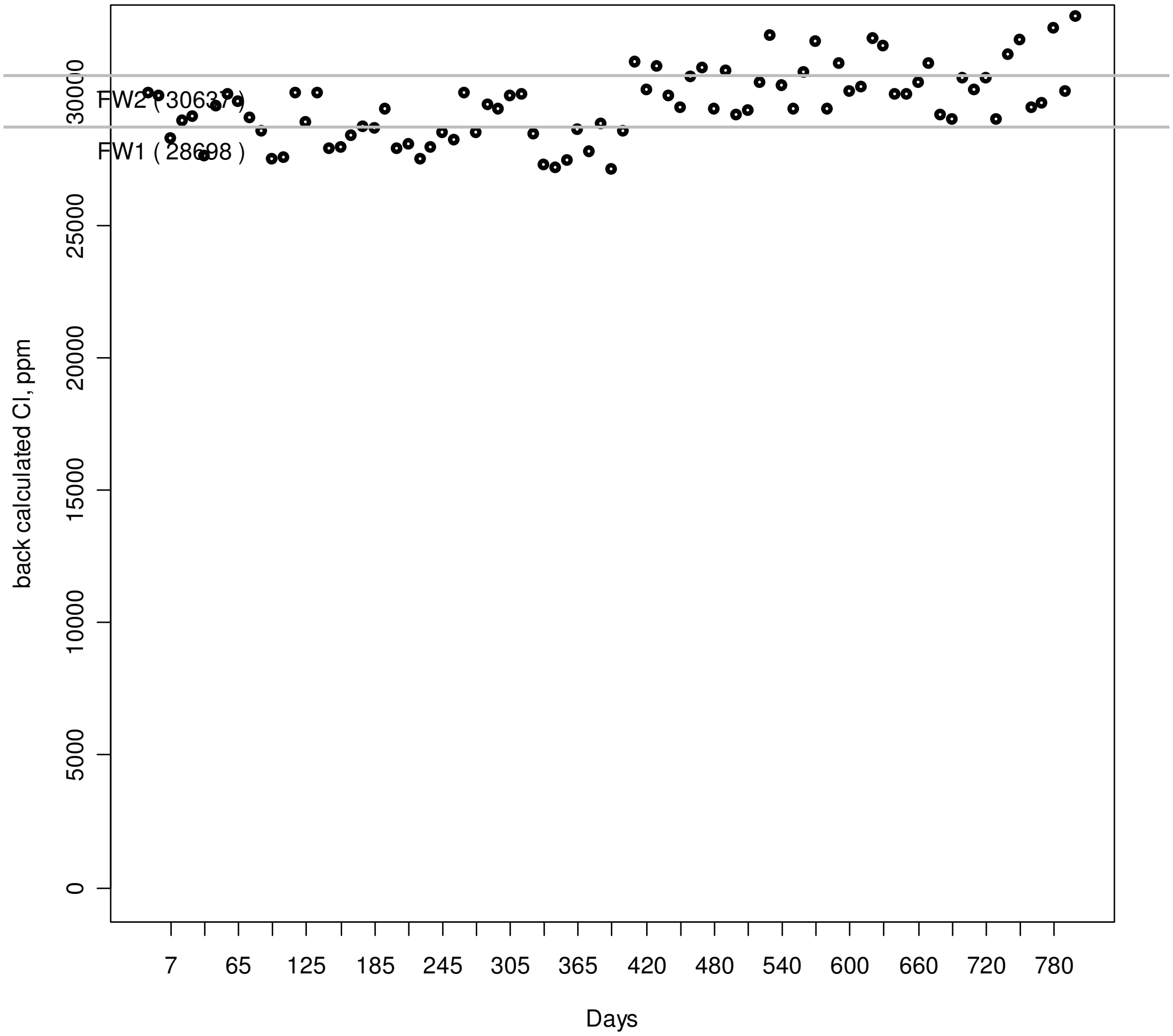


Figure 4.9 Back-calculated chloride concentrations in the formation water for synthetic case with 5% relative noise.

The amount of noise present in the produced water samples becomes the main parameter reducing the accuracy of the method to detect producing formations. Specific to the conditions of the synthetic case, with given formation water compositions (Table 3.2), 2% of relative noise is still acceptable to distinguish formations with confidence (Figure 4.8), while 5% of relative noise creates more uncertainty and definite conclusion is difficult to make. The following section presents this approach appied to field data.

4.2.3 Field examples

The next two figures (Figure 4.5 and Figure 4.11) show back-calculated chloride concentrations in the formation water for produced water samples from two wells. The solid line represents the chloride concentration measured in the original formation water sample. Both plots show that the back-calculated values are consistent and very close to the initial chloride concentration in the formation water. Such agreement can be achieved only if two conditions are valid – (a) the injection water fraction calculated for each produced water sample is correct, and (b) the well was producing from one formation only.

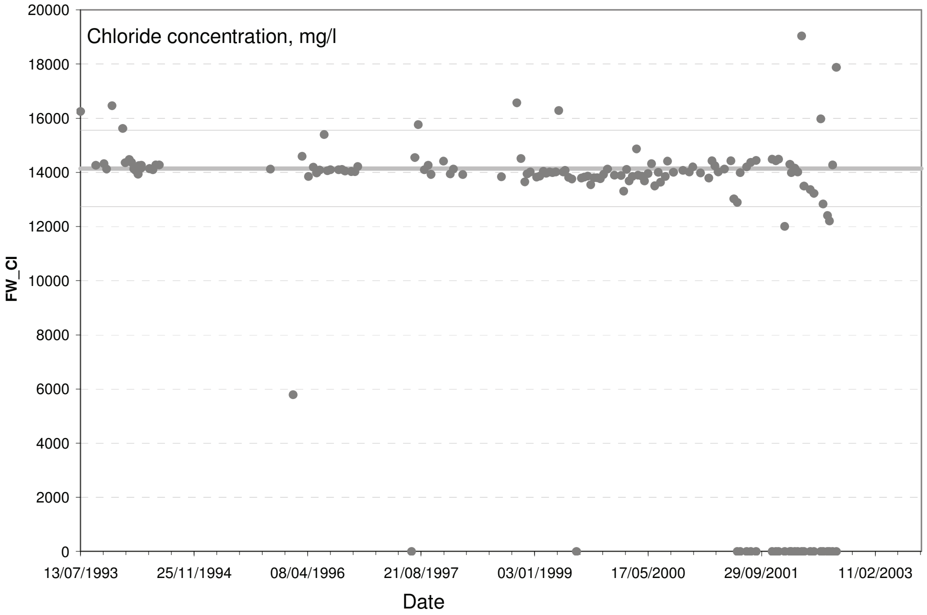


Figure 4.10 Back-calculated chloride concentration in the formation water for produced water samples for well X.

A second well shows similarly consistent results, although samples are taken with greater lab/measurement error.

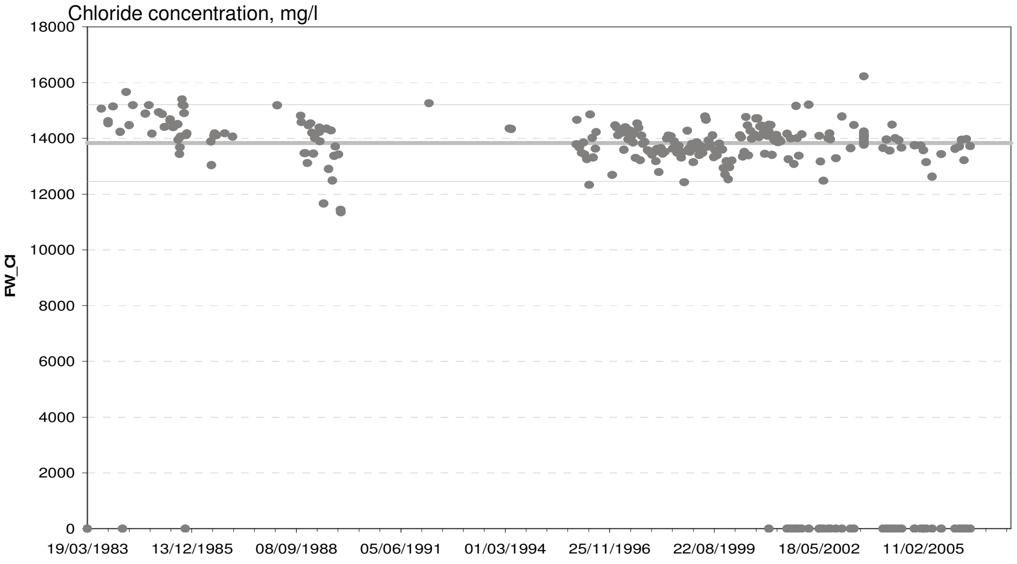


Figure 4.11 Back-calculated chloride concentration in the formation water for produced water samples for well Y.

However, other wells showed behaviour that suggested production from different formations, with different formation water compositions, as in Figure 4.12. This well is reported as producing from Formation A, but the distribution of back-calculated chloride concentrations is grouped along the concentration that belongs to Formation B. Thus IW fraction method may be used to detect which formation the well is producing from.

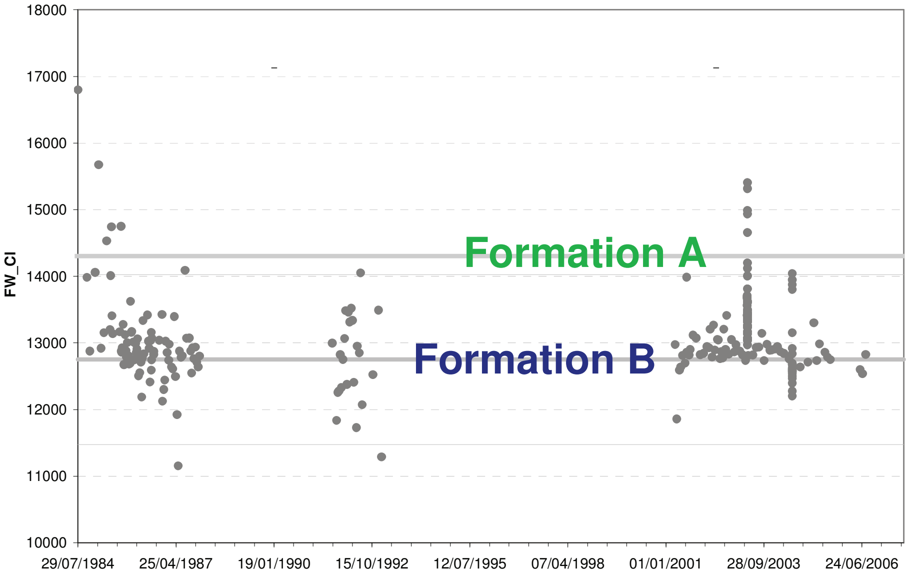


Figure 4.12 Back-calculated chloride concentration in the formation water for produced water samples for well Z.

The well is reported as producing from Formation A, but the back-calculated chloride concentrations suggest it is actually producing from Formation B.

Using this technique to back-calculate the chloride concentration in formation water, the engineer can identify which formation the well is producing from. In the case of mixing between two formation waters the approach can be used to determine the proportion of mixing, and hence how much brine is being produced from each formation, given the well's total water flow rate. In situations where it is not possible to run production logs, this could to valuable information for reservoir engineers trying to manage fluid distribution in the reservoir.

CHAPTER 5 FIELD APPLICATIONS OF THE REACTING IONS METHOD

The Reacting Ions method had been tested on a synthetic dataset, as presented in Chapter 3, and proved to be at least as robust and accurate as other techniques, especially in detecting IW breakthrough.

The method has been tested on data from a great number of wells (over one hundred). The majority of the wells were from oilfields in the North Sea. It was found that due to the errors in the measured chloride concentrations the conventional ion tracking method led to more scattered identification of IW fractions and less clearly determined breakthrough times. The Reacting Ions method led to a more consistent evaluation of IW fraction and hence a more reliable estimate of when IW breakthrough had occurred.

This section describes the field application of the Reacting Ions method.

5.1. General Approach Used

Data from each field was subjected to the same procedure. Initially the brine compositions given by the operator or taken from the published source on that field are used to calculate the injection water fraction. The next step is to examine plots of Relative Ion Deviations against the injection water fractions, where the injection water fractions are calculated by the Reacting Ions method. Ion concentrations for each sample as a function of injection water fraction and back-calculated chloride concentrations are shown to identify any trends. If some unexpected behaviour is observed, the process involves reviewing the brine compositions or splitting the dataset into subsets for different scenarios (Figure 5.1).

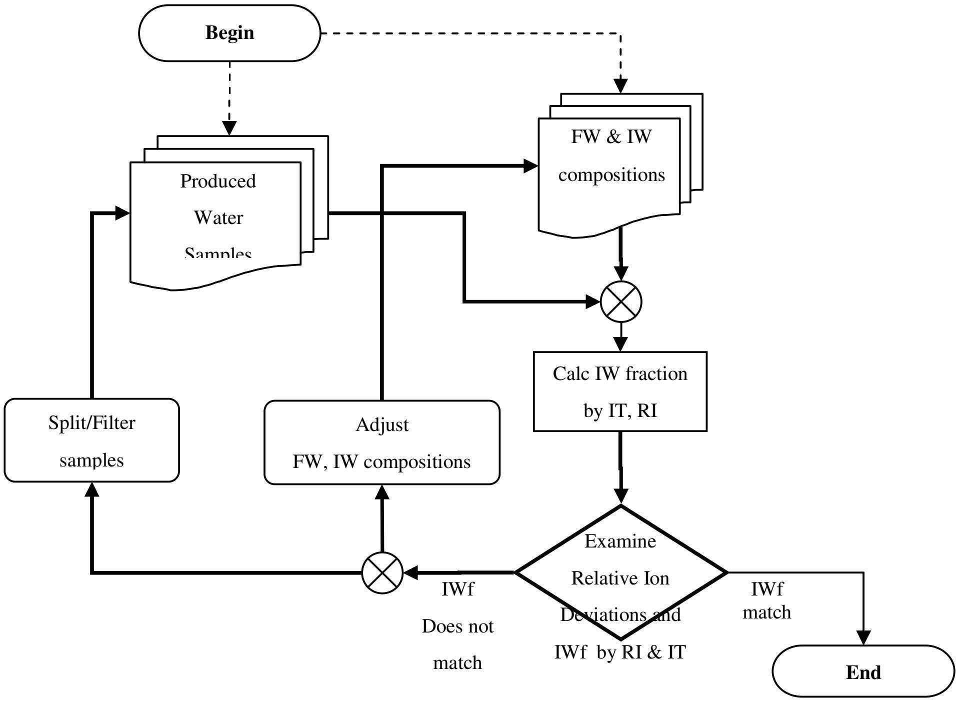


Figure 5.1 Approach used during calculations of IW fractions.

In some cases the following technique was used to correct the formation brine composition. The highest barium concentrations correspond with the greatest probability that the sample contains exclusively formation water. Produced water samples were sorted in order of decreasing barium concentrations and the highest barium sample were selected to determine the formation water composition. However, it must be bourn in mind that this method is not 100% reliable in that the sample with the highest barium concentration may already represent a mix of formation water with injection water, and so does not represent a pure formation water sample. However, this should be identifiable from consideration of all the ions and comparison with known data.

5.2. Field Test of the Reacting Ions Method

In the first stage of this study, the Reacting Ions method was tested on a synthetic dataset and the method proved to be both robust and accurate, especially in detecting IW breakthrough. The Reacting Ions method was applied to the field data under conditions where measurement errors, contamination and preservation issues may have an impact. IW fraction and breakthrough time may only be ascertained from the produced water samples that were made available, and therefore the analytic methods presented in Chapter 2 and Chapter 3 were applied to determine the IW fractions.

The following examples show typical IW fraction distributions, with a case where the injection water fraction calculated by Ion Track and Reacting Ions methods are significantly different, a case where both methods are in a good agreement, and a case where at first glance both methods appear to show a good match, but on closer inspection the injection water breakthrough is identified late when using the Ion Tracking method.

IW fractions were calculated based on the conventional ion tracking method using the chloride ion as a marker, and based on the Reacting Ions method using the reacting barium and sulphate concentrations. Sample initial brine compositions are presented in Table 5.1. In the following plots (Figure 5.2, Figure 5.3, and Figure 5.4), the IW fraction, expressed as a percentage on the vertical axis, is plotted against time, which is on the horizontal axis. The IW fraction scale is taken from 0 to 10% (30% for well B) to study in more detail the behaviour around the time of IW breakthrough. Red dots represent the results of the conventional ion track method (IT) using chloride, and the green line is the result of using the Reacting Ions (RI) method based on barium and sulphate.

Table 5.1 Initial brine compositions. Field B.

mg/l	*Na*	*K*	*Mg*	*Ca*	*Ba*	*Sr*	*Fe*	*Cl*	*Br*	*SO_4*	*HCO_3*
FW	9000	200	50	250	60	75		14300		0	1050
IW	11000	400	1300	400	0	8		20500		2800	160

Figure 5.2 shows a typical case where there is a significant difference in the IW breakthrough prediction between the Reaction Ions method and the conventional ion tracking method based on chloride. The green band highlights the results of the Reacting Ions method to show a more consistent and smooth growth of IW fraction in Well A (Figure 5.2). Application of the conventional ion tracking method for this particular well produces data with a high degree of scatter.

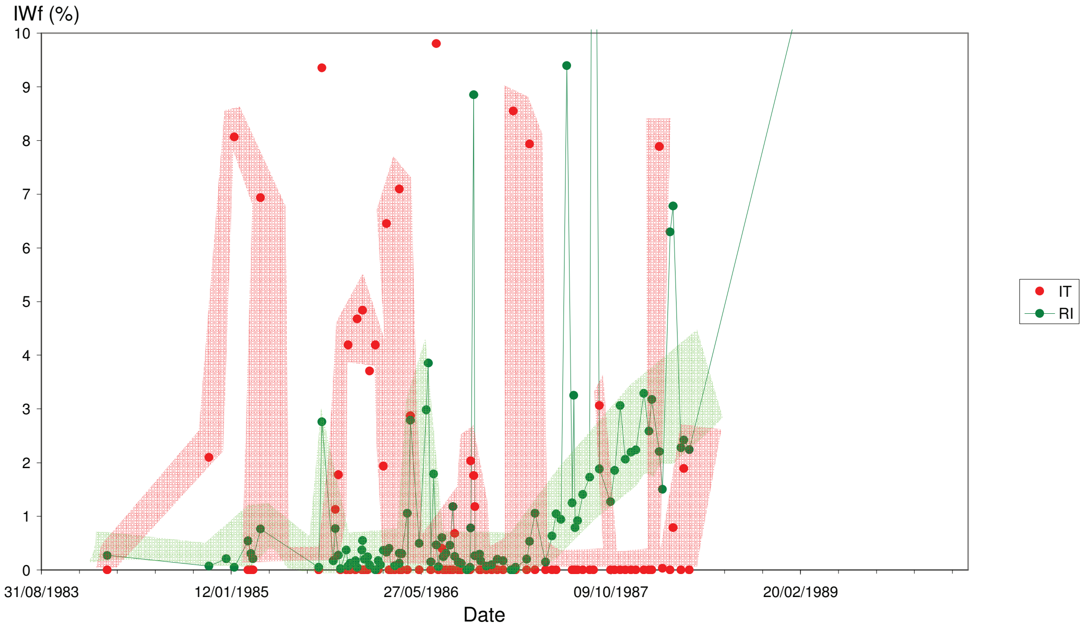


Figure 5.2 Injected water fraction calculated by conventional ion tracking and by Reacting Ions methods for Well A.

Figure 5.3 (Well B) and Figure 5.4 (Well C) present two cases where injection water fraction calculated by the Ion Tracking and the Reacting Ions methods in general match each other quite closely. However, injection water breakthrough fractions and timings in Figure 5.4 do differ significantly. Injection water breakthrough time for Well C, based on calculations using the Ion Tracking method, is delayed by several months compared with data from the Reacting Ions method.

Figure 5.3 Injected water fraction calculated by conventional ion tracking and by Reacting Ions methods for Well B.

This conclusion is based on the first produced water sample with IWf greater than zero calculated with Ion Track method based on chloride.

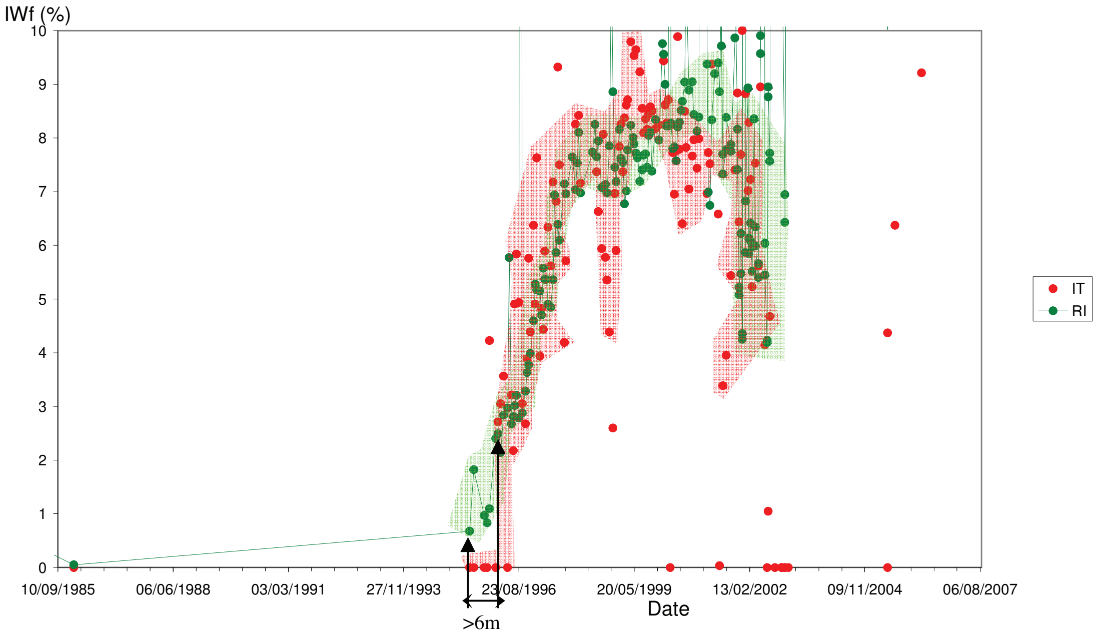


Figure 5.4 Injected water fraction calculated by conventional ion tracking and by Reacting Ions methods for Well C.

In general, when the data from all the wells in the study were considered, it was found that due to the errors in the measured chloride concentrations the conventional ion tracking method led to more scattered identification of IW fractions and less clearly determined breakthrough times. However, the Reacting Ions method led to a more consistent evaluation of IW fraction and hence a more reliable estimate of when IW breakthrough occurred. While each of the wells analysed has its own distribution of IW fractions versus time, the common factor amongst these wells is that the Reacting Ions method results in smoother and more consistent determination of IW fraction behaviour, especially at low IW fractions (close to breakthrough time). In cases where chloride is measured accurately the difference between the two methods becomes less evident, particularly at IW fractions greater then 30%.

5.3. Application of Relative Ion Deviations to Field B

Relative ion deviations (that is, the relative deviation of observed ion concentrations from the conservative values) are a good indicator of the processes that are occurring down-hole.

Data were taken from produced water sample compositions of Field B in the North Sea. To investigate trends in ion behaviour and to identify whether there were any location related trends, relative ion deviations were calculated and then grouped according to the four sectors of this particular field. Different sectors of the field may vary in mineralogy, temperature and pressure, all of which can affect brine compositions and precipitation reaction rates, etc.

Relative ion deviations are plotted on the vertical axis as a function of changing injection water fractions (horizontal axis). Plotting relative ion deviations versus relative injection water fraction eliminates the time effect and makes trends easier to identify and compare.

The profile of sulphate relative ion deviations (Figure 5.5) is similar to the profile for the synthetic dataset (Chapter 4, Figure 4.1). The sulphate concentration declines at low IW fractions due to the reaction with other ions (barium in the first instance) and subsequently, at higher than ~30% IW, the sulphate appears to be almost conservative (since it is in large molar excess compared to Ba in this IW% region).

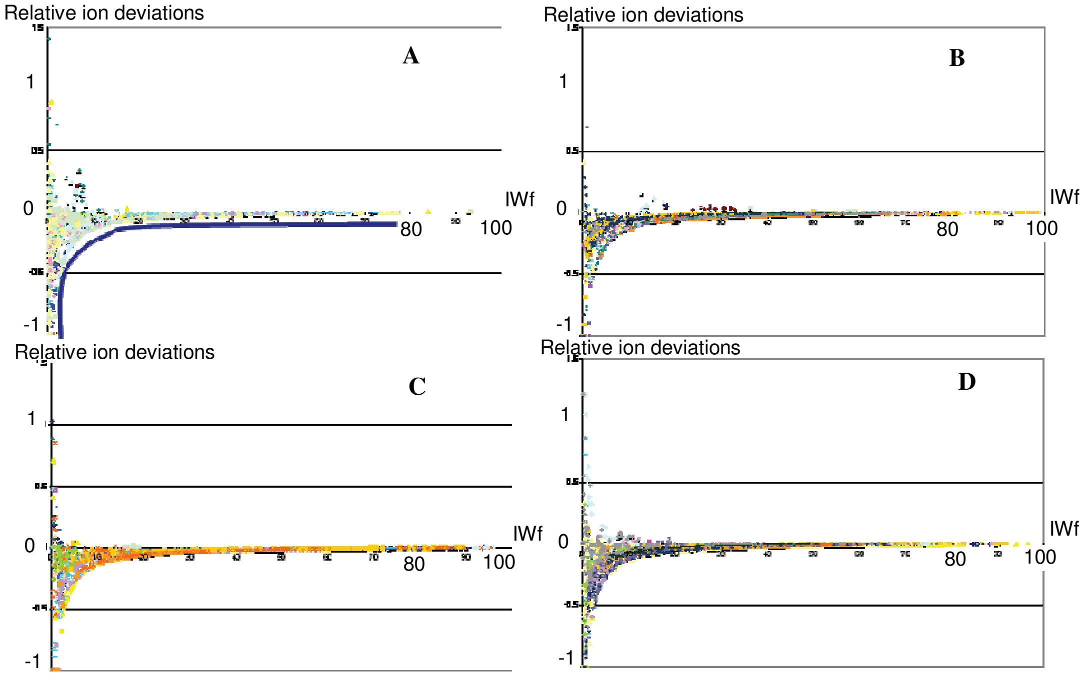


Figure 5.5 Sulphate relative ion deviations grouped by regions of the field. Profiles are as expected.

Although the general barium behaviour presented in Figure 5.6 is similar to the trend observed from the synthetic model, much of the data appears more scattered, and some points may be found outside the main trend. The explanation is as follows: barium concentrations are predominantly much lower than sulphate concentrations, and measurement errors, especially at points where zero barium is expected due to high sulphate concentrations, lead to severe spikes in relative ion deviations. In this data, all outliers are reported, as are values from samples that have been preserved with ethylene diamine tetra-acetic acid (EDTA), a commonly used barium sulphate dissolver. These latter samples include some very high barium concentrations, consistent with dissolution of scale crystals that may have been carried through with the produced water.

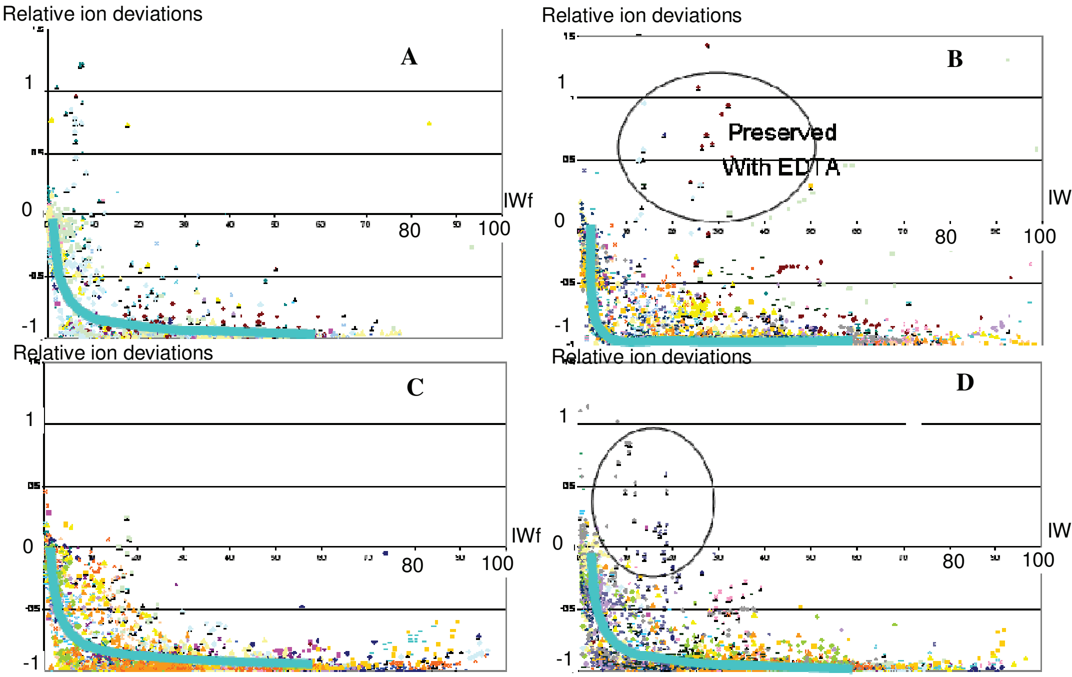


Figure 5.6 Barium relative deviations identify significant precipitation of barium.

The magnesium relative ion deviation vs. IW % is shown in Figure 5.7. As the injection water fraction increases, magnesium reacts and is removed from solution (possibly precipitating with sulphate, or by cation exchange, or by dolomitisation), but with further increases in IW fraction magnesium is found to dissolve.

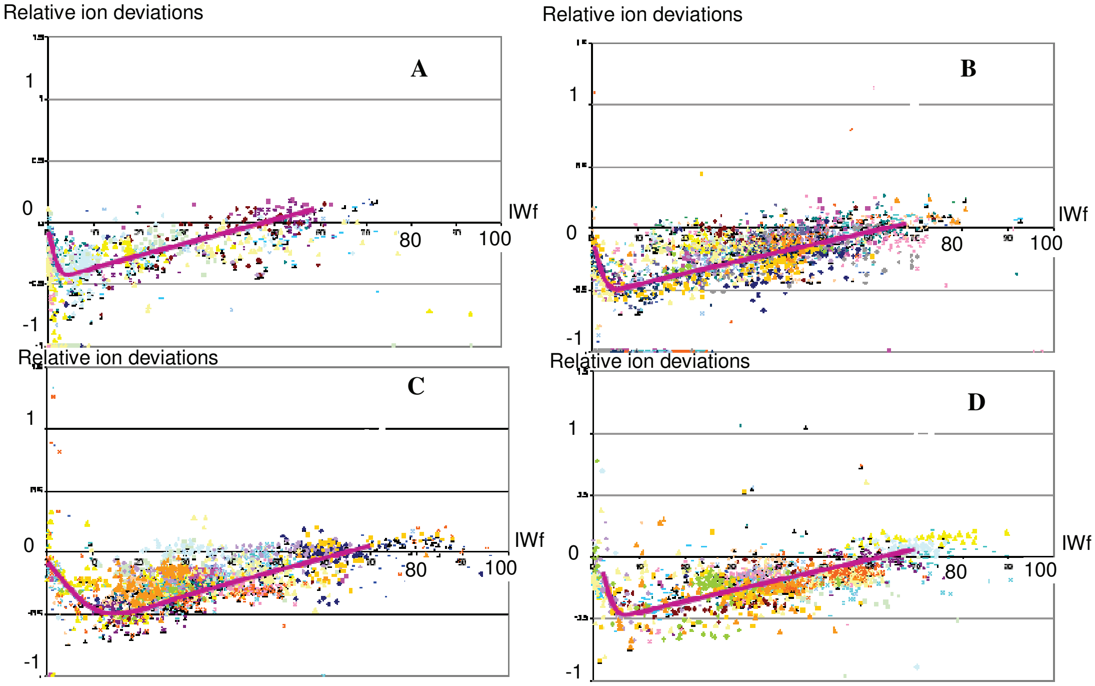


Figure 5.7 Magnesium relative ion deviations suggest precipitation and dissolution.

Scattered calcium relative ion deviations could not be used to inter whether calcium-magnesium ion exchange occurred or not. Calcium relative ion deviations did not show a trend or any consistent behaviour and are not presented here. Poor quality of calcium values could be a consequence of poor measurements or calcium carbonate scale precipitation.

Sodium (Na+) should be a conservative ion, which means that it is expected that it does not react with any other ion in the formation or injection brines, other than to form the very soluble sodium chloride, except possibly by some ion exchange reactions. Thus, it was not expected that the plot of sodium concentrations or ion deviation trends would show evidence of any reactions. This proved to be the case, as shown for most samples in Figure 5.8. The sodium relative ion deviations are grouped around the zero deviation line, which means that the observed sodium ion concentrations are equivalent to the conservative ion concentrations. The second implication of this is that the calculation of IW fraction is correct. Samples marked with black underlines are preserved with EDTA and should be ignored, since this chelating agent contains sodium.

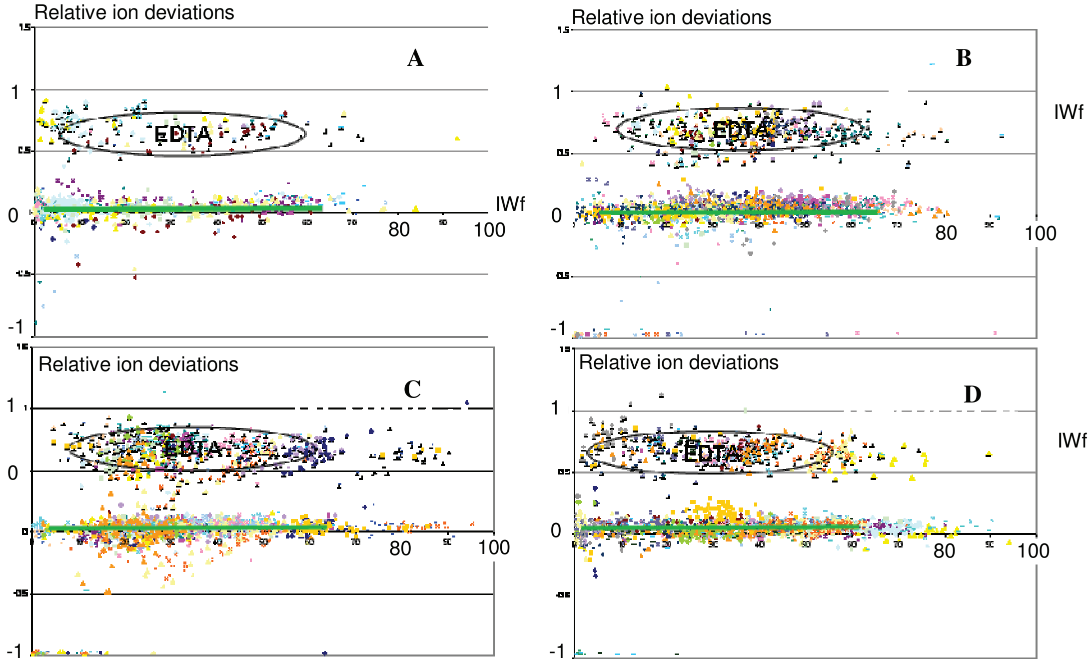


Figure 5.8 Sodium relative ion deviations proof sodium as conservative ion.

Application of the Reacting Ions method to this North Sea field indicates that for this particular field SO_4, Ba and Mg are all reacting to some extent. However, it is anticipated that the IW fraction may be calculated with a high degree of confidence based on the profiles of relative ion deviations (all of them uniformly similar to the theoretical). In general, identification of which ions are reacting can help production chemists better understand reservoir geochemical reactions and to design scale mitigation strategies more effectively.

5.4. Well X analysis

Well X is reported as producing from Formation B, for which the initial brine compositions are presented in Table 5.2. Measured concentrations of ions from produced water samples are presented in Figure 5.9.

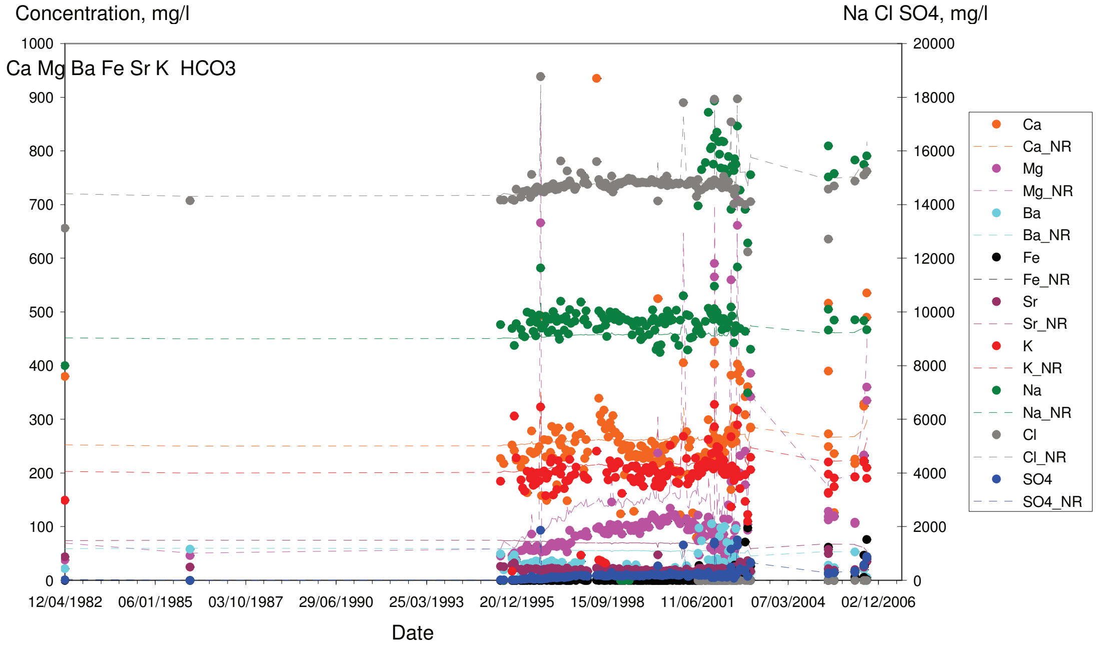


Figure 5.9 Observed ion concentrations vs time (data points), and equivalent values should there be no reactions (NR – dotted lines).

Table 5.2 Well X initial brine compositions.

mg/l	*Na*	*K*	*Mg*	*Ca*	*Ba*	*Sr*	*Fe*	*Cl*	*Br*	SO_4	HCO_3
FW	9000	200	50	250	60	75		14300		0	1050
IW	11000	400	1300	400	0	8		20500		2800	160

The Reacting Ions method based on barium and sulphate was used to calculate the IW

Fraction.

The first step in the well analysis is to make sure that initial conditions are taken correctly. Injection water composition for most systems is well known. However, formation water composition may be more uncertain. In this case, the chloride concentration in formation water was back-calculated according to the approach described in Chapter 4. It is consistent throughout the well's operating life and on average is equal to the initial concentration in the formation reported (Figure 5.10).

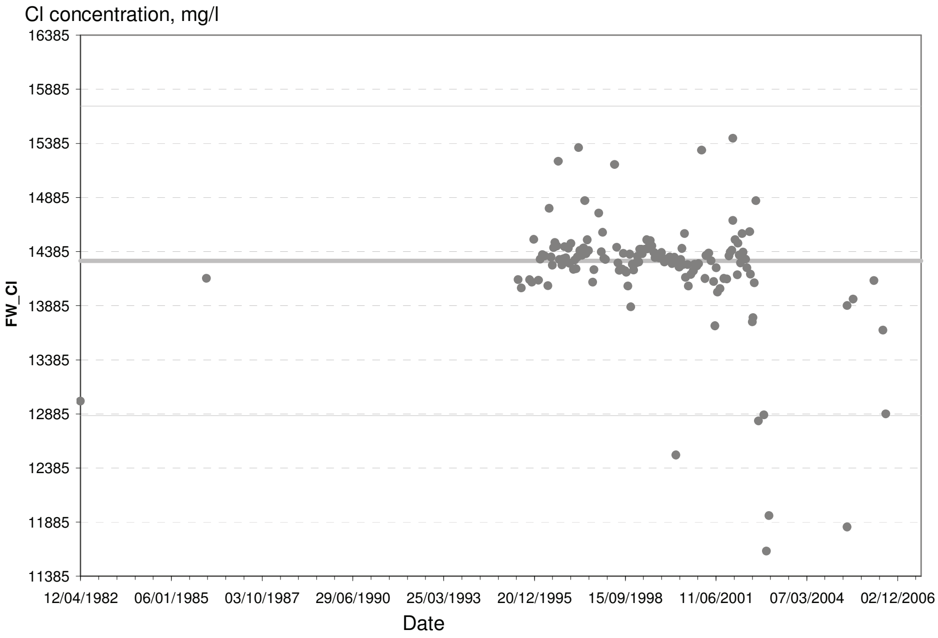


Figure 5.10 Expanded area of back-calculated chloride concentration in formation water.

The consistent back-calculated chloride concentration indicates that the IW fraction based on the conventional Ion Tracking method with chloride should be close to the IW fraction calculated with the Reacting Ions method.

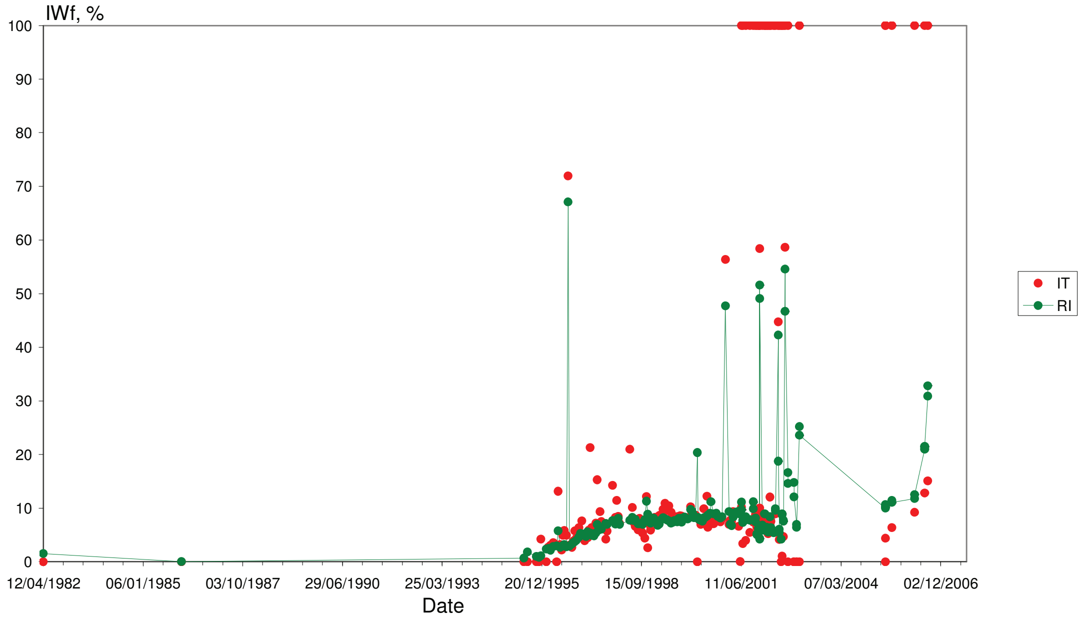


Figure 5.11 Injection water fractions calculated by Ion Track and Reacting Ions method.

Indeed, the IW fractions based on the two methods are close to each other on a full scale plot (Figure 5.11), but the Reacting Ions method is still better at predicting injection water breakthrough time (expanded region of IW breakthrough is shown in Figure 5.12).

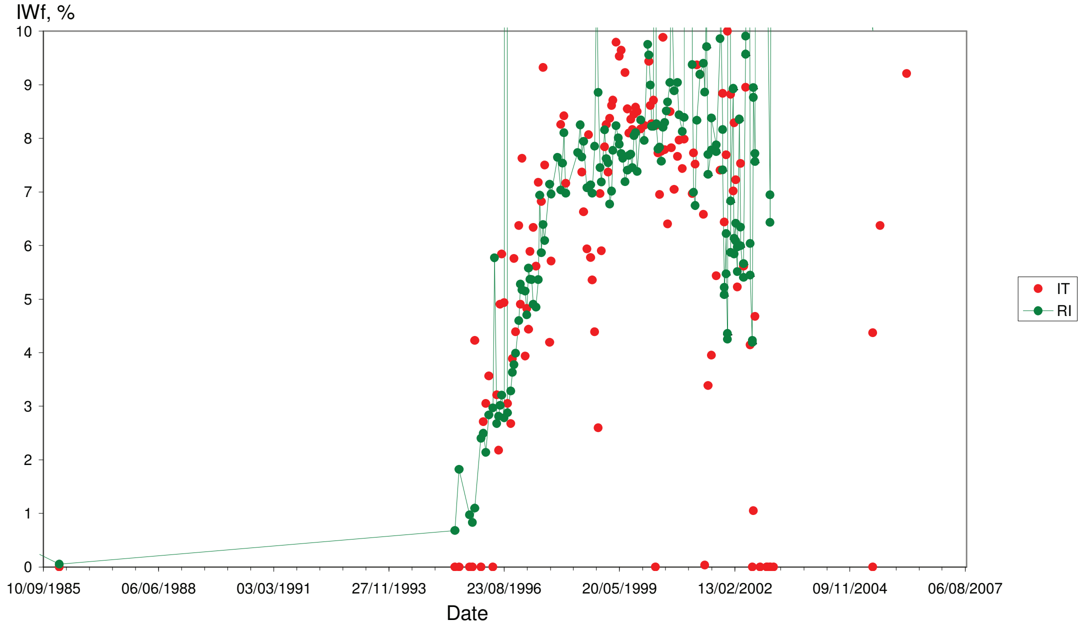


Figure 5.12 Expanded area of injection water breakthrough.

Barium, strontium, magnesium, calcium and sulphate are reacting, according to the ion deviations plotted in Figure 5.13.

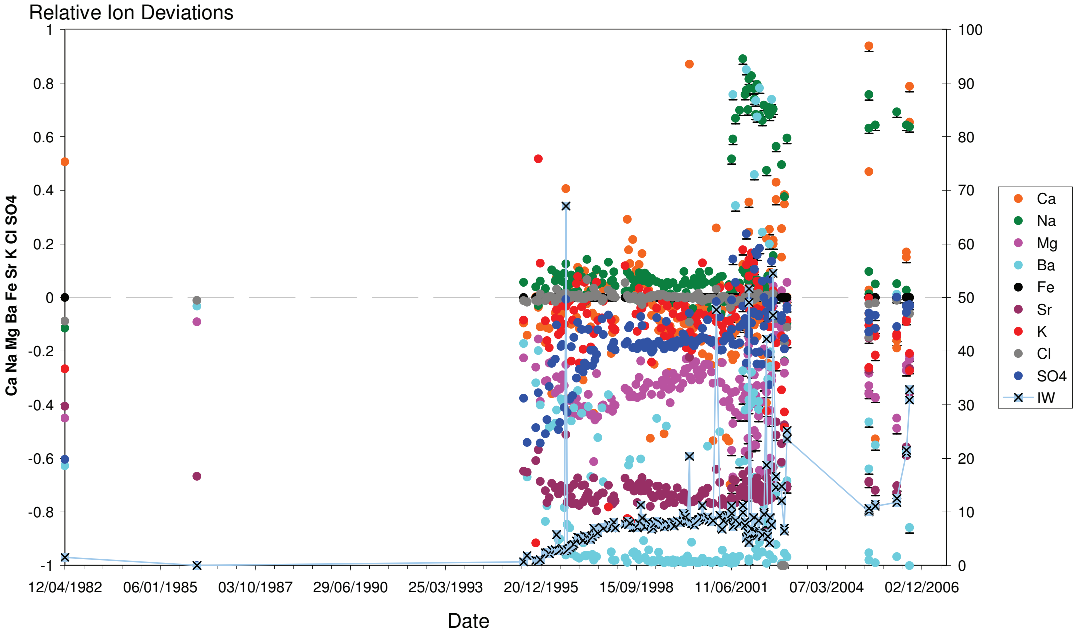


Figure 5.13 Relative Ion Deviations vs time.

Sodium and chloride do not react as they are conservative ions (Figure 5.14).

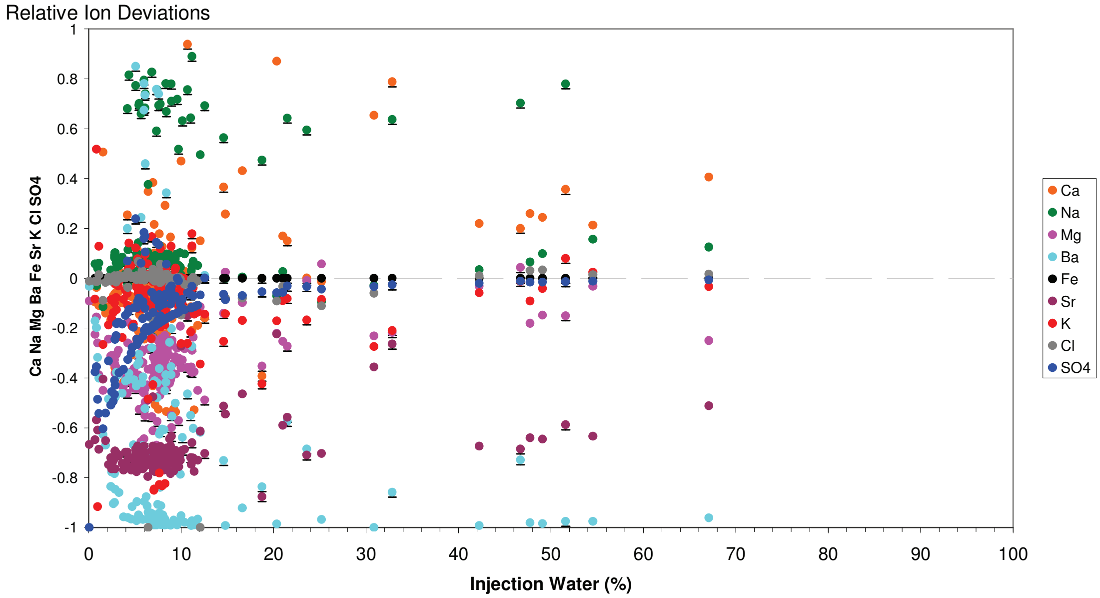


Figure 5.14 Relative Ion Deviations plotted against injection water fraction.

The Reacting Ions method was successfully applied to the field data. Reliable values of injection water fractions were calculated, which were supported by the values of Ion Track calculations based on Chloride. Injection water breakthrough was detected more accurately comparing with the date based on Ion Track (on Chloride). Ions participating in geochemical reactions were also identified.

5.5. Field G

This case illustrates a scenario where barium, strontium and sulphate were identified as reacting ions during the examination of the Relative Ion Deviations plot. The possibility of the formation of BaSO4 and SrSO4 scales was assumed. The assumption of these reactions is supported by the fact that injection water fraction calculated with the Ion Track method based on conservative ion chloride and injection water fraction from the Reacting Ions method based on three reacting ions - barium, strontium and sulphate - show a good match. Scale prediction calculations made using MultiScale, developed by Scale Consult AS/Petrotech, also suggested BaSO4 and SrSO4 scale precipitation (saturation ratios greater than 1). However, MultiScale was not able to solve the precipitation completely. The reason is probably due to high ion concentrations, many precipitating salts or a very complex system.

Well G33 from Field G was considered for analysis. Initial brine compositions supplied for Field G are shown in Table 5.3. The measured ion concentrations from produced water samples are shown in Figure 5.15.

Table 5.3 Initial Brine compositions for Field G.

mg/l	*Na*	*K*	*Mg*	*Ca*	*Ba*	*Sr*	*Fe*	*Cl*	*Br*	SO_4	HCO_3
FW	14 500	355	320	1 200	15	320		26 000		20	
IW	12 250	390	1 310	410		8		21 685		2 740	

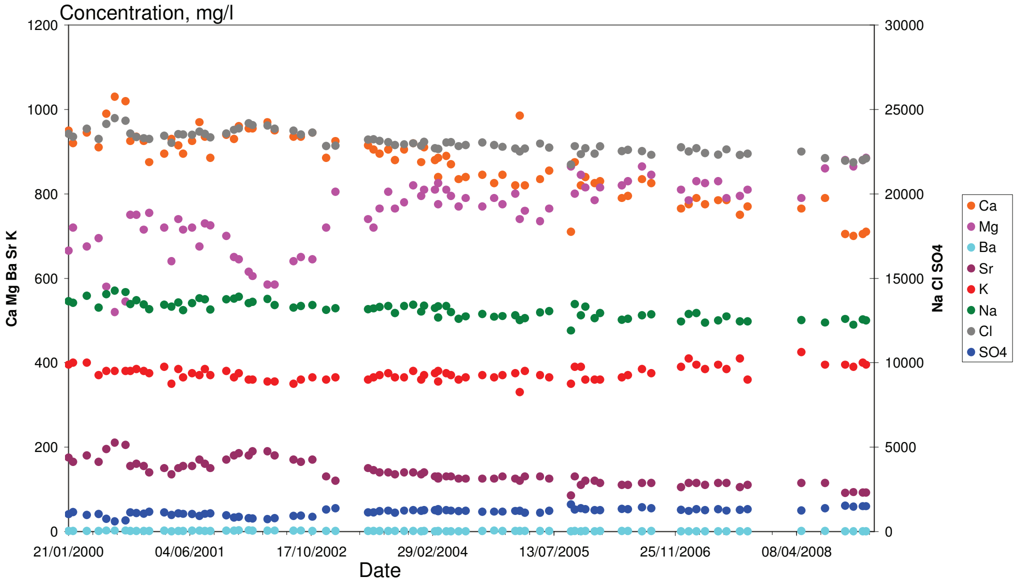


Figure 5.15 Well G33 observed Ion Concentrations plotted versus Time.

The Reacting Ions method was run with the initial formation and injection water compositions (Table 5.3). Injection water fraction was calculated using Ion Track based on chloride and the results were compared with the results of using the Reacting Ions method based on barium and sulphate. The Ion Track method was selected to give the Relative Ion deviation plots. When the resulting plots were examined, three issues attracted attention. First, there is a significant difference between injection water fractions calculated by the Ion Track and by the Reacting Ions methods (Figure 5.16).

Figure 5.16 Injection water fractions by Ion Track (based on chloride) and Reacting Ions (based on barium and sulphate) versus Time.

The second and third issues are the unexpected behaviour of barium and strontium (Figure 5.17). Note that as injection water fraction approaches 100%, there is an unusual decrease in sulphate deviations (tending towards zero from below), which is expected to be at least on the 0 line, and an increase in strontium and barium deviations (tending upwards away from zero) indicating unusual strontium and barium dissolution.

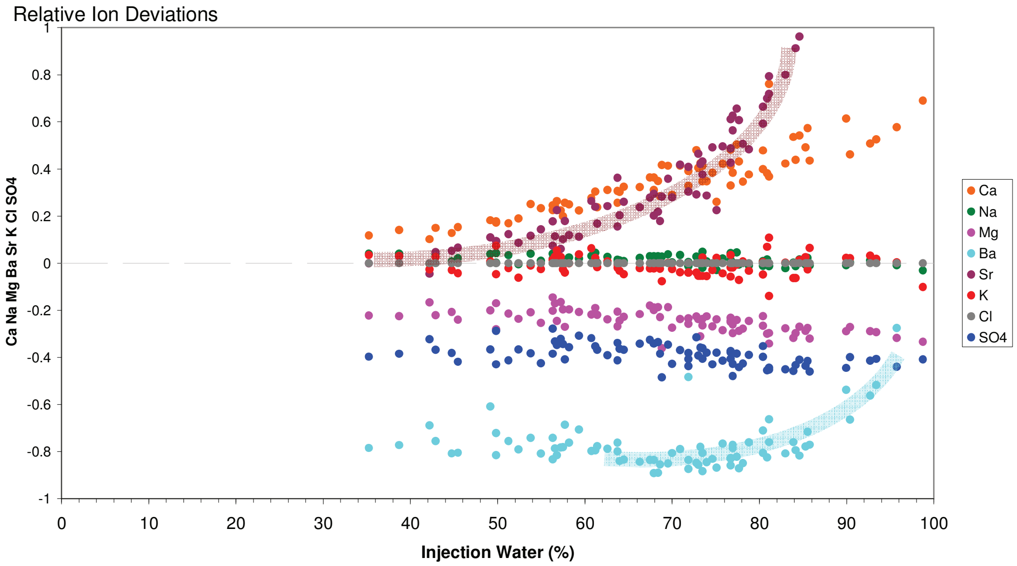


Figure 5.17 Relative Ion Deviations versus injection water fraction based on Ion Track Method.

An increase in barium relative deviations at high IW fractions is suggested in some cases: this may be explained by the application of scale squeeze treatments. However, if scale inhibitor placement affected scaling reactions and that was a cause that changed the trend of barium and strontium relative ion deviations, then sulphate relative ion deviations would be affected as well. In this case sulphate does not show any change, thus it was considered that the squeeze treatment was not the cause of abnormal barium and strontium behaviour. Also, the strontium relative ion deviations suggest a strong indication of dissolution (high strontium concentrations), which is not expected in the given environment and suggests either a wrong IW fraction has been calculated and/or an incorrect initial concentration of strontium in the formation or injection brines.

However, plots of the other (conservative) ions, such as sodium (which is not reacting according to the Relative Ion Deviations plot), are supporting evidence that the calculation of the injection water fraction based on chloride is correct.

This apparently contradictory evidence indicated further investigation was required.

5.5.1 Modifications made

By analysis of data from various wells, ordering the data in terms of decreasing barium concentration, the barium concentration in the formation brine was changed from 15 mg/l to 45 mg/l, and in the injection brine the sodium and chloride concentrations were changed to 11,000 mg/l (from 12,250 mg/l) and to 19,300 mg/l (from 21,685) mg/l, respectively. The resulting brine compositions are presented in Table 5.4, with amended values marked in bold.

Table 5.4 Adjusted brine compositions.

mg/l	*Na*	*K*	*Mg*	*Ca*	*Ba*	*Sr*	*Fe*	*Cl*	*Br*	*SO_4*	*HCO_3*
FW	14 500	355	320	1 200	**45**	320		26 000		20	
IW	**11 000**	390	1 310	410		8		**19 300**		2 740	

The injection water fractions were calculated based on the new formation and injection water compositions (Table 5.4). The resulting Relative Ion Deviations calculated based on the injection water fraction calculated by the Ion Track method still indicate that strontium is reacting (Figure 5.18), but this time the values are decreasing, indicating precipitation rather than dissolution.

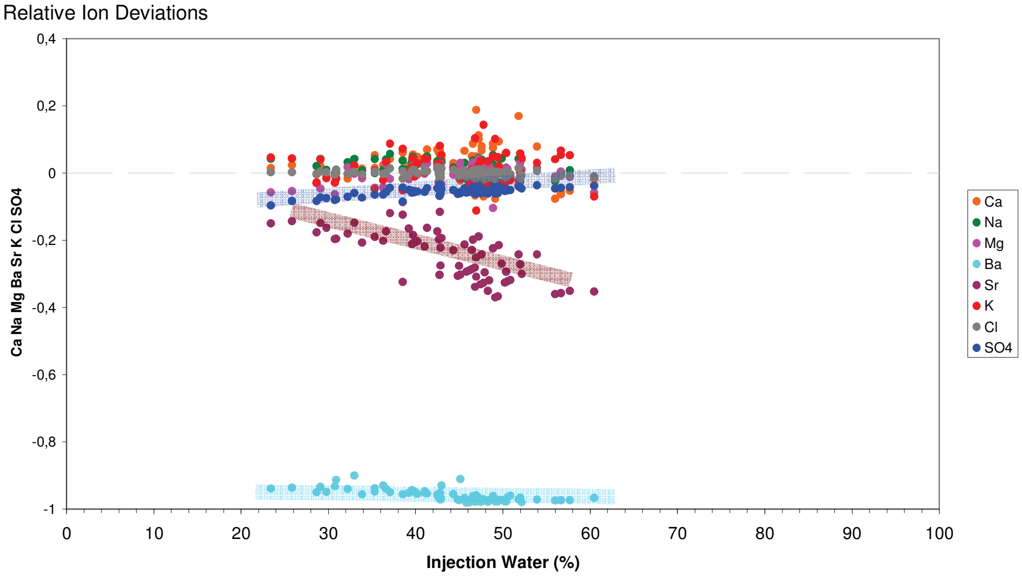


Figure 5.18 Relative Ion Deviations versus injection water fraction for revised formation water composition.

Strontium is known to be the second most preferable ion after barium to participate in scaling reactions with sulphate. The solubilities of barium sulphate and strontium sulphate are extremely low in the oilfield environment, and thus they are expected to precipitate rather than dissolve. Note that after the updated formation water composition is applied, strontium is now decreasing (indicating precipitation), and barium is no longer rising. Also the data lies in the range 22% - 62% injection water fraction, not in the higher and larger range 35% - 99%, as previously.

Based on this evidence of strontium precipitation, strontium was included in the Reacting Ions method for injection water fraction calculations. As a result of using the updated formation water composition, the injection water fraction calculated with the Ion Track method based on the conservative ion chloride and the calculation of injection water fraction from the Reacting Ions method based on three reacting ions - barium, strontium and sulphate - shows a very good match (Figure 5.19).

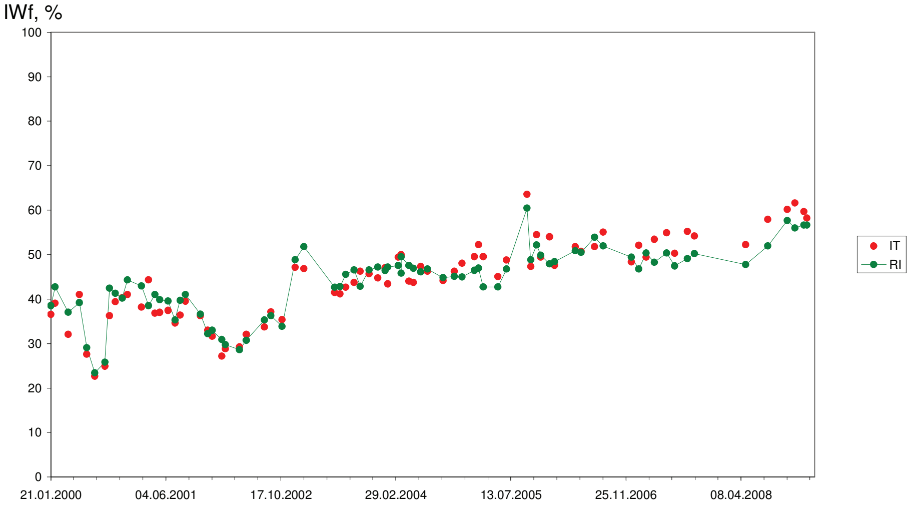


Figure 5.19 Injection water fractions versus Time.

Application of the Reacting Ions method for this well in Field G led to a re-interpretation of the formation water composition that should be used for calculating injection water fraction. Subsequent calculation of the injection water fraction using the conventional Ion Track method and the Reacting Ions method led to a good match between the two methods, despite the differences in the methods and their use of different ions for the calculation of injection water fractions. Finally, precipitation of strontium sulphate and barium sulphate may be inferred from the barium, strontium and sulphate trends in the Relative Ion deviations plots.

5.6. Field V

In this example injection water fraction calculations for two wells (V2 and V9) from the same field are presented. Initial formation and injection water compositions were given by the operator and are presented in Table 5.5.

Table 5.5 Field V initial brine compositions.

mg/l	*Na*	*K*	*Mg*	*Ca*	*Ba*	*Sr*	*Fe*	*Cl*	*Br*	SO_4	HCO_3
FW	4 920	119	23	919	5	50		9 080		31	559
IW	10 890	460	1 368	428		7		19 766		2 960	140

Wells V2 and V9 produced water sample concentrations are shown in Figure 5.20 and Figure 5.21.

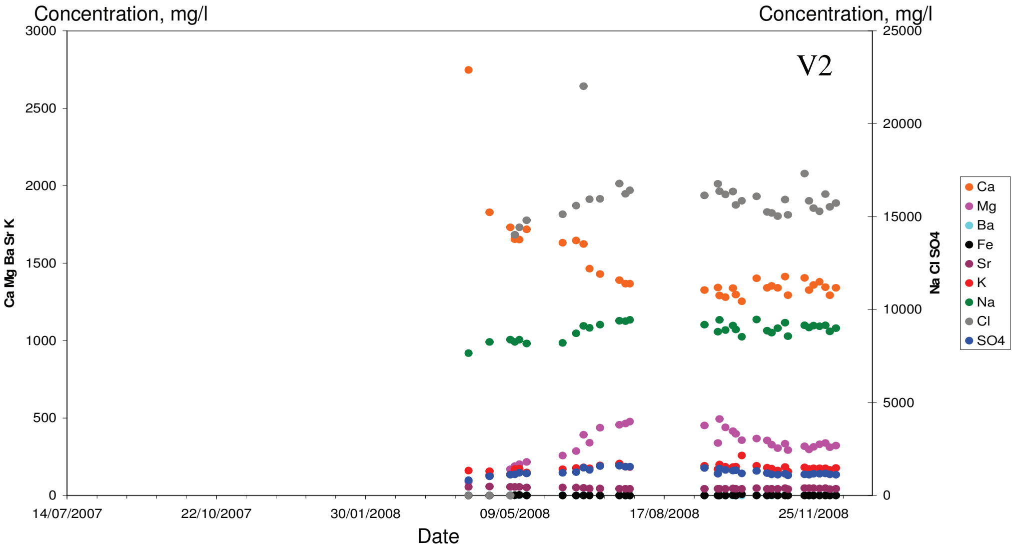


Figure 5.20. Well V2 produced water samples versus time.

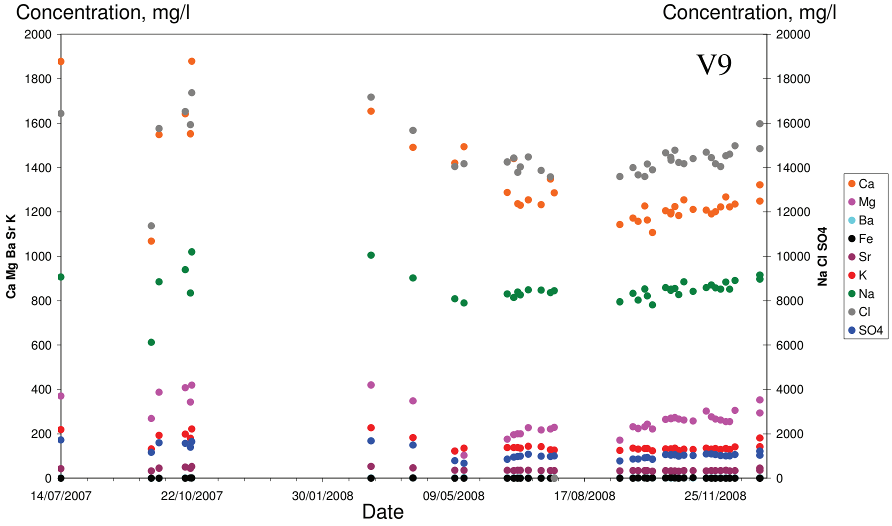


Figure 5.21 Well V9 produced water samples versus time.

The initial formation and injection water compositions (Table 5.5.) were used in the Reacting Ions calculations. The conventional Ion track method based on chloride and the Reacting Ions method based on barium and sulphate were used for the IW fractions calculations. This same approach was used for both wells.

The injection water fractions calculated by the Ion Track and Reacting Ions methods for both wells did not show a good match (Figure 5.22 and Figure 5.23).

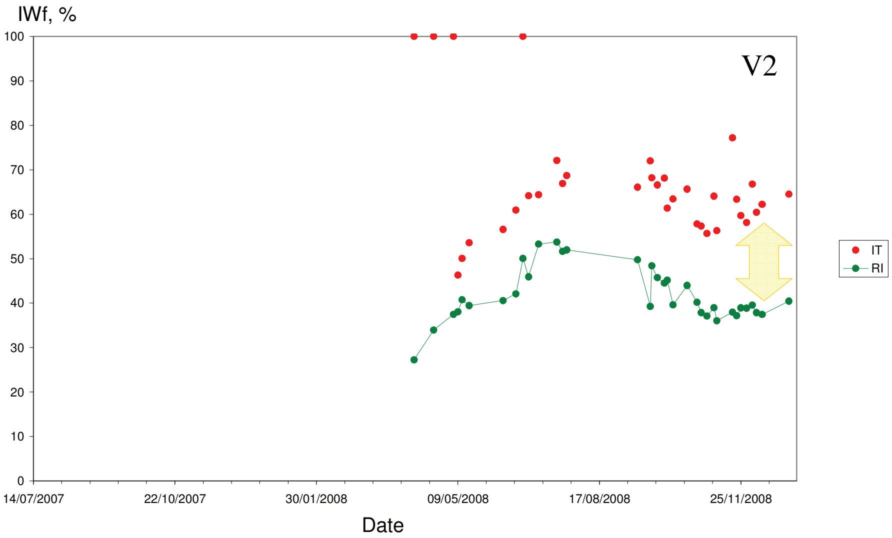


Figure 5.22 Well V2 injection water fraction versus time calculated with the Ion Track (IT) and the Reacting Ions (RI) methods.

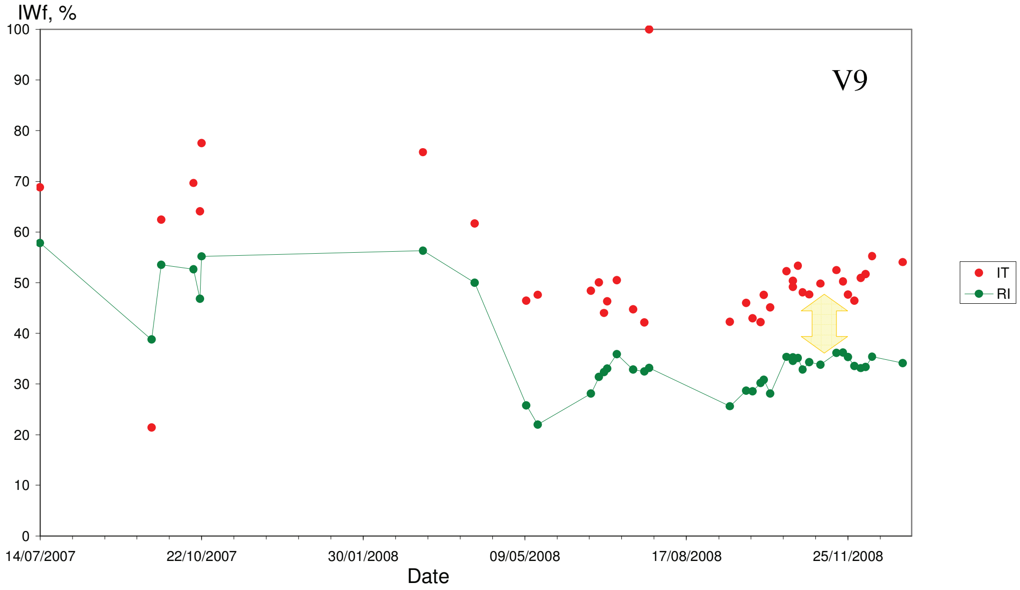


Figure 5.23 Well V9 injection water fraction versus time calculated with the Ion Track (IT) and the Reacting Ions (RI) methods.

At this point there was no reason to select one method in preference over the other, and so the Ion track method was used to calculate the Relative Ion deviation plots.

Wells V2 and V9 Relative Ion deviations indicate very strong strontium dissolution, which was not expected (Figure 5.24 and Figure 5.25).

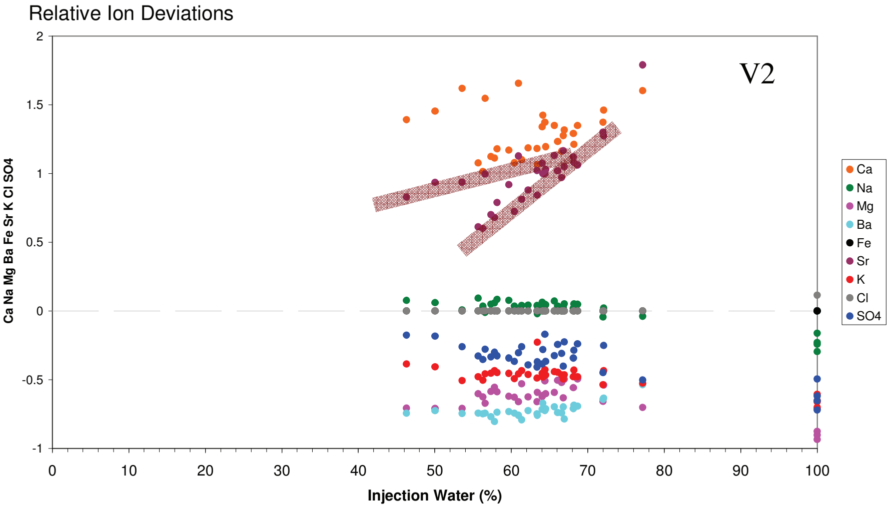


Figure 5.24 Well V2 relative ion deviations plotted versus injection water fraction.

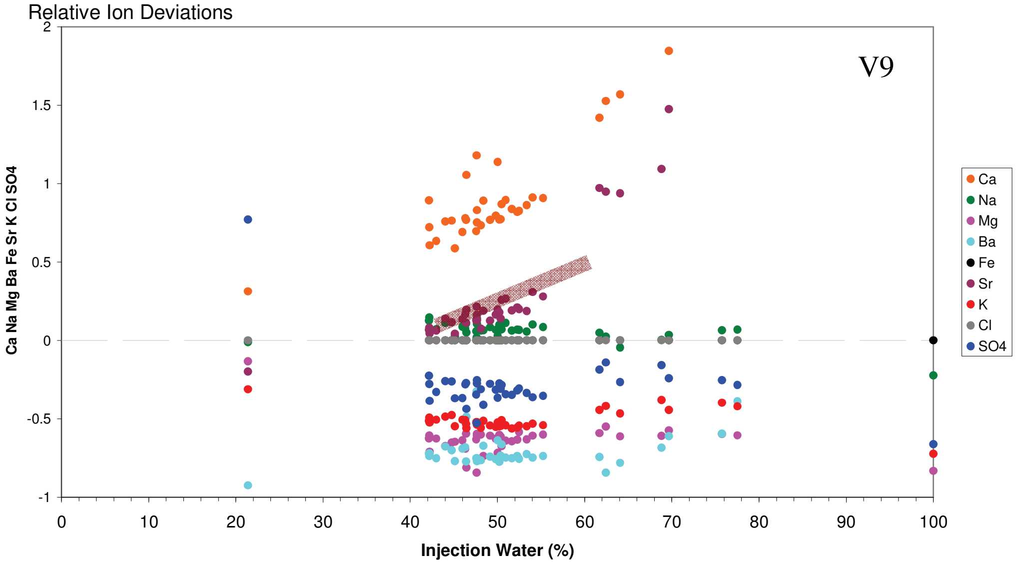


Figure 5.25 Well V9 Relative Ion deviations plotted versus injection water fraction.

Strong strontium dissolution and partial sulphate precipitation at very high injection water fractions may indicate an incorrectly calculated IW fraction and/or incorrect brine compositions.

The same procedure was applied here to analyse the produced water samples that represent the closest composition to the formation water. Data was ordered and grouped in terms of decreasing barium concentration, calcium-magnesium ratio, and date.

Several samples selected as the most representative of the end-point brine compositions were averaged. Formation and injection water compositions were thus altered to obtain a better match between injection water fractions based on the two methods. The altered values are shown in Table 5.6.

Table 5.6 Updated formation and injection brine compositions.

mg/l	*Na*	*K*	*Mg*	*Ca*	*Ba*	*Sr*	*Fe*	*Cl*	*Br*	*SO_4*	*HCO_3*
FW	6 800	50	29	1 800	10	80		11 000			559
IW	12 000	340	1 368	428		7		21 500		2 960	140

The resulting injection water fractions for both wells show a better match (Figure 5.26 and Figure 5.27).

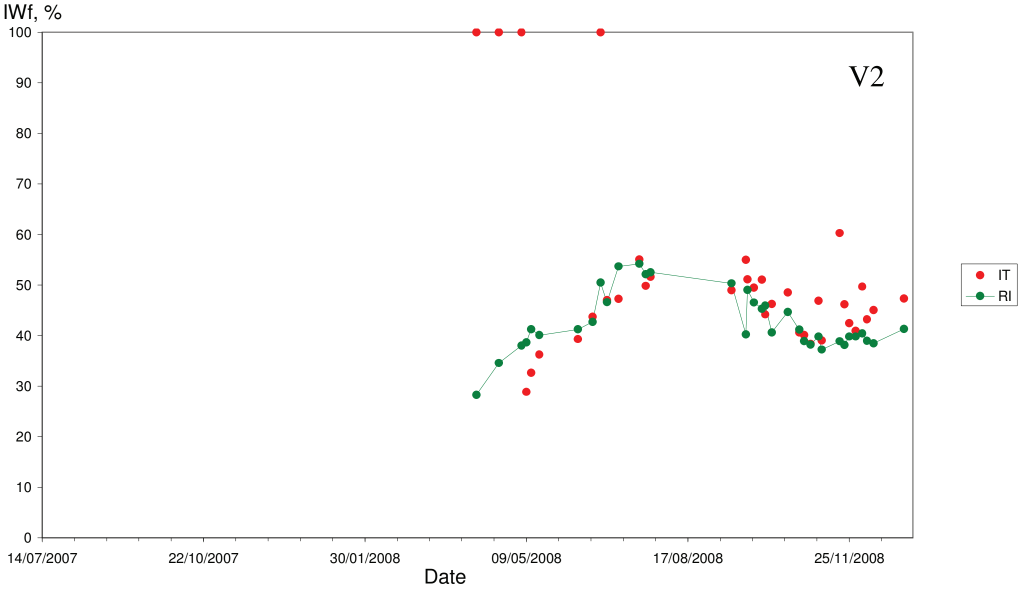


Figure 5.26 Well V2 injection water fraction versus time.

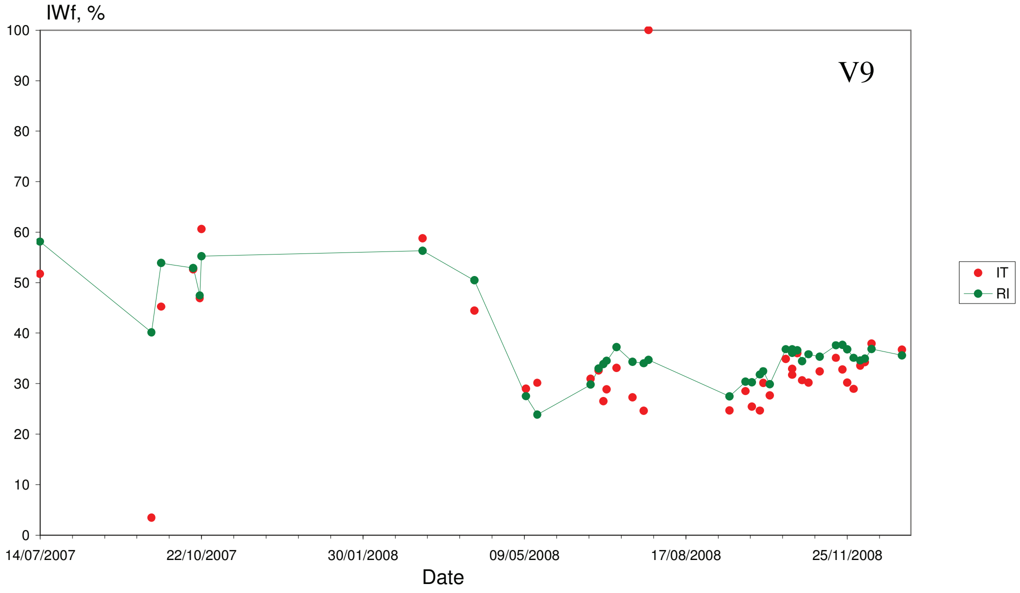


Figure 5.27 Well V9 injection water fraction versus time.

Well V2 relative ion deviations (Figure 5.28) indicate barium and magnesium decrease with an increase in calcium. This strongly indicates barium sulphate scale precipitation and calcium – magnesium ion exchange.

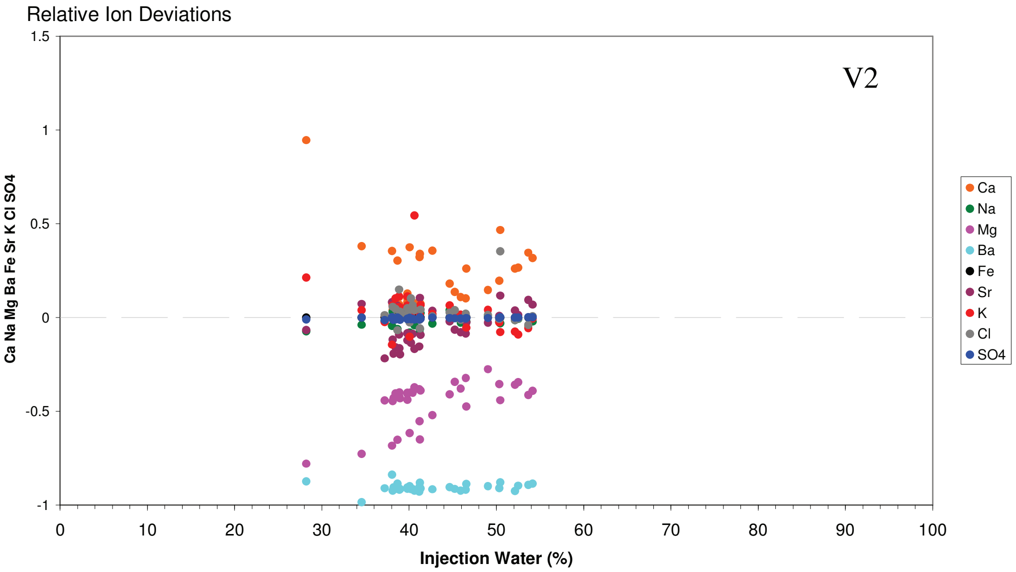


Figure 5.28. Well V2 relative ion deviations versus injection water fractions.

Application of the Reacting Ions method to Well V9 (Figure 5.29), using the updated brine compositions, indicates that for this particular well sulphate, barium, magnesium and calcium are all reacting to some extent or other, as in well V2, but that also there is evidence of strontium changes. At lower injection water fractions, strontium appears to be precipitating (probably to form $SrSO_4$), but at higher injection water fractions there may in fact be $SrSO_4$ dissolution. This behaviour of $SrSO_4$ dissolution at higher seawater fractions has been observed in other fields (Chapter 5, section 5.3).

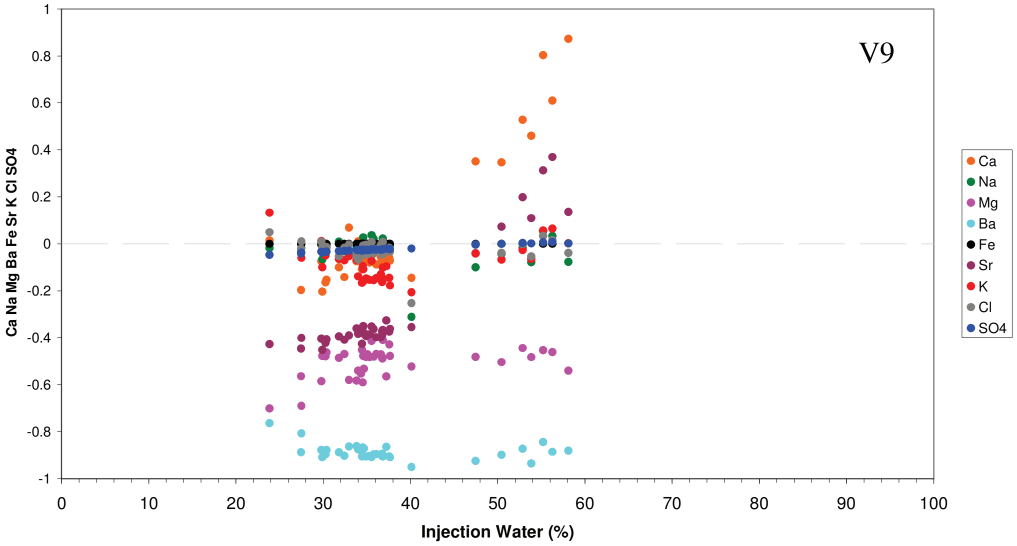


Figure 5.29 Well V9 relative ion deviations versus injection water fraction.

5.7. Field N

The formation and injection water compositions for Field N are presented in Table 5.7, and Figure 5.30 shows the observed ion concentrations for one of the wells. The injection water fraction calculations produce a significant mismatch between the Ion Track and Reacting Ions methods – see Figure 5.31.

Table 5.7 Initial Brines compositions for Field N.

mg/l	*Na*	*K*	*Mg*	*Ca*	*Ba*	*Sr*	*Fe*	*Cl*	*Br*	*SO_4*	*HCO_3*
FW	16 355	533	212	1 331	65	94	11	28 322			
IW	12 250	390	1 310	410		8		21 685		2 740	

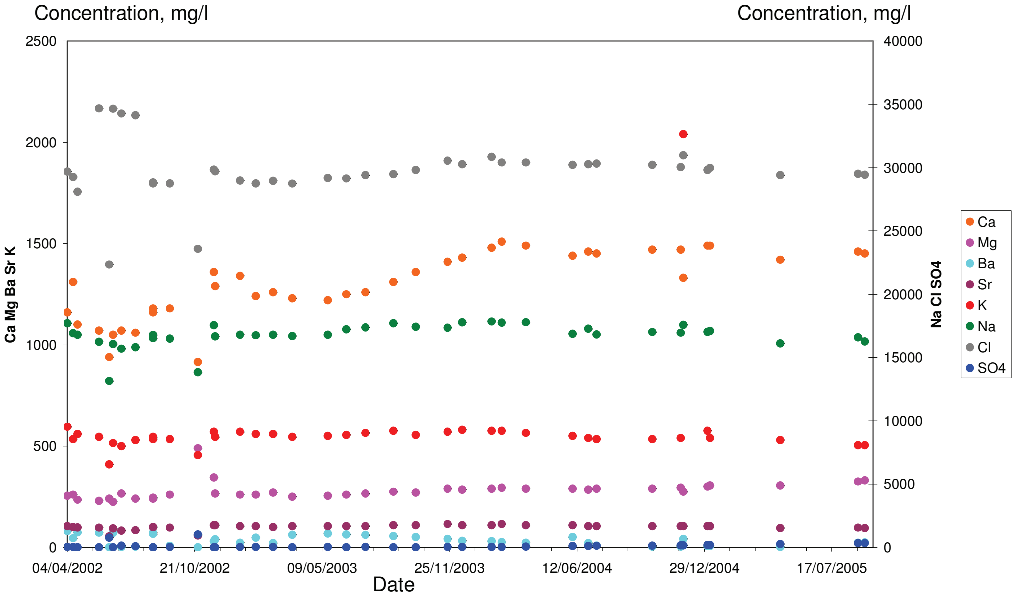


Figure 5.30 Field N observed ion concentrations.

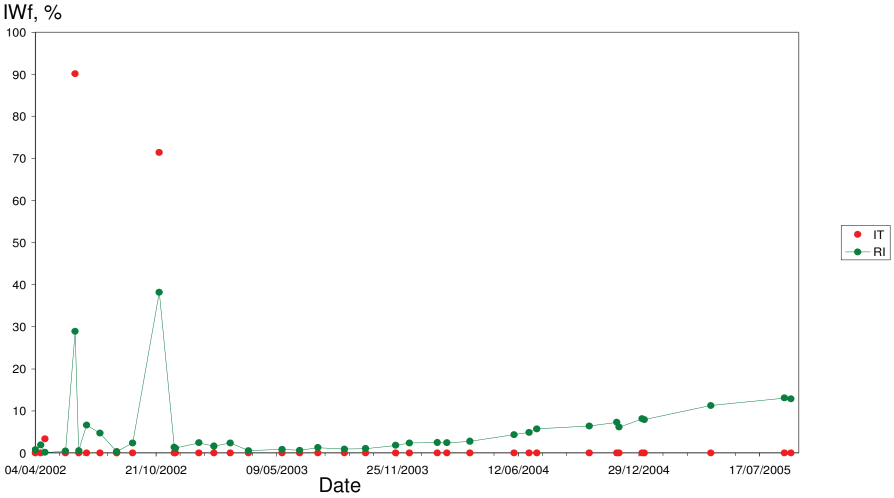


Figure 5.31 Injection water fractions calculated by the Ion Track (IT) method (based on Cl) and the Reacting Ions (RI) method (based on Ba and SO4).

In this case great care should be taken with the Ion Track method. The Reacting Ions method shows breakthrough of injection water, and this will only occur if the barium and/or the sulphate concentrations change. If there is only one formation water type, then even the smallest decrease in barium or increase in sulphate must be indicative of injection water breakthrough. Therefore the lack of response in the conventional Ion Track method here should immediately flag a risk with using only Ion Track. In the following plots (Figure 5.32 and Figure 5.33) the injection water fraction (which is used for further Relative Ion Deviation calculations) is based on the Reacting Ions method using barium and sulphate.

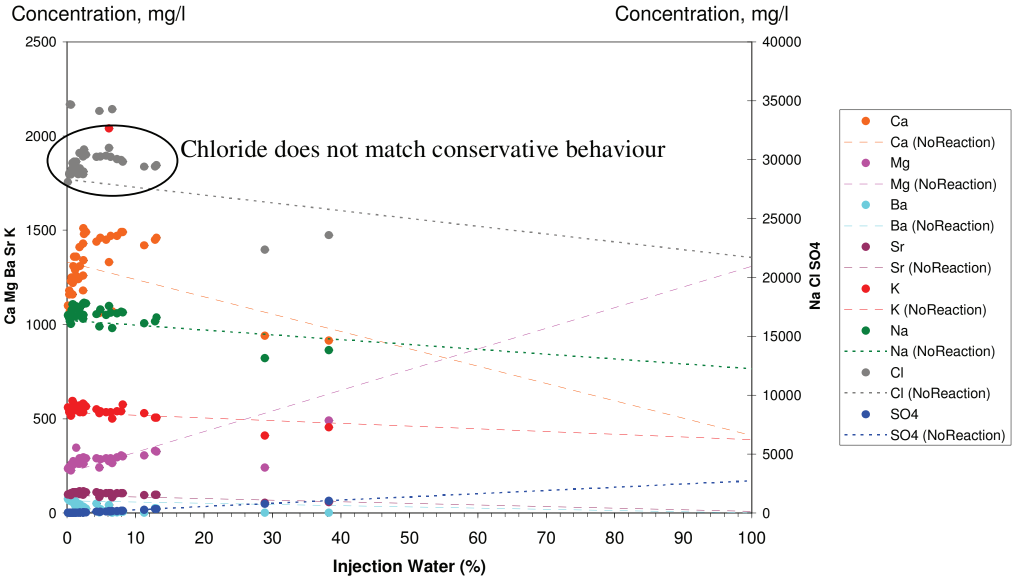


Figure 5.32 Ion concentrations plotted versus injection water fraction.

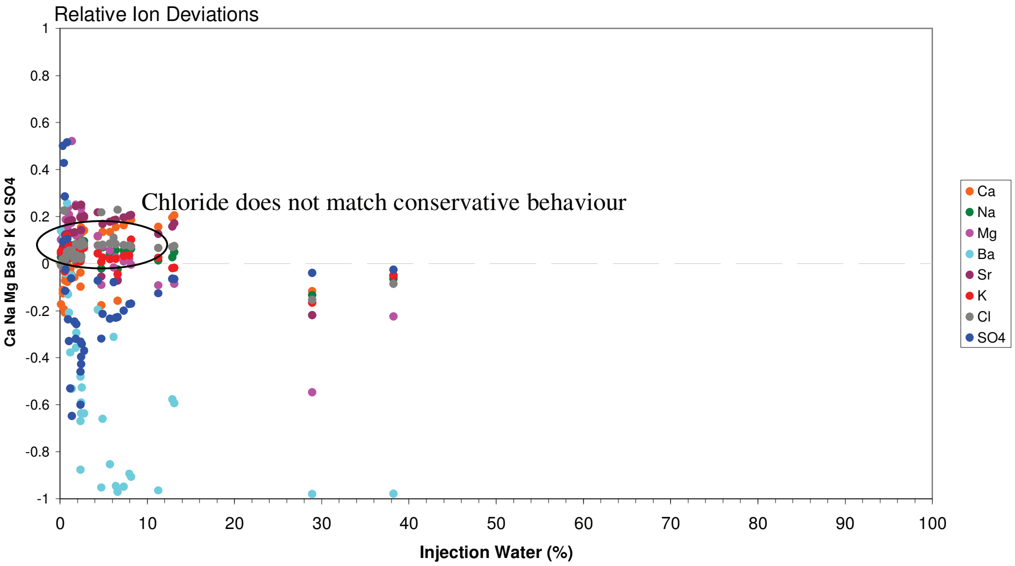


Figure 5.33 Relative ion deviations versus injected water fraction.

5.7.1 Changes applied

To match injection water fractions between the two methods, the brine compositions were reviewed (samples were sorted by decreasing barium concentrations, and the sample with the highest barium concentration was used as representative of the formation water, Figure 5.34).

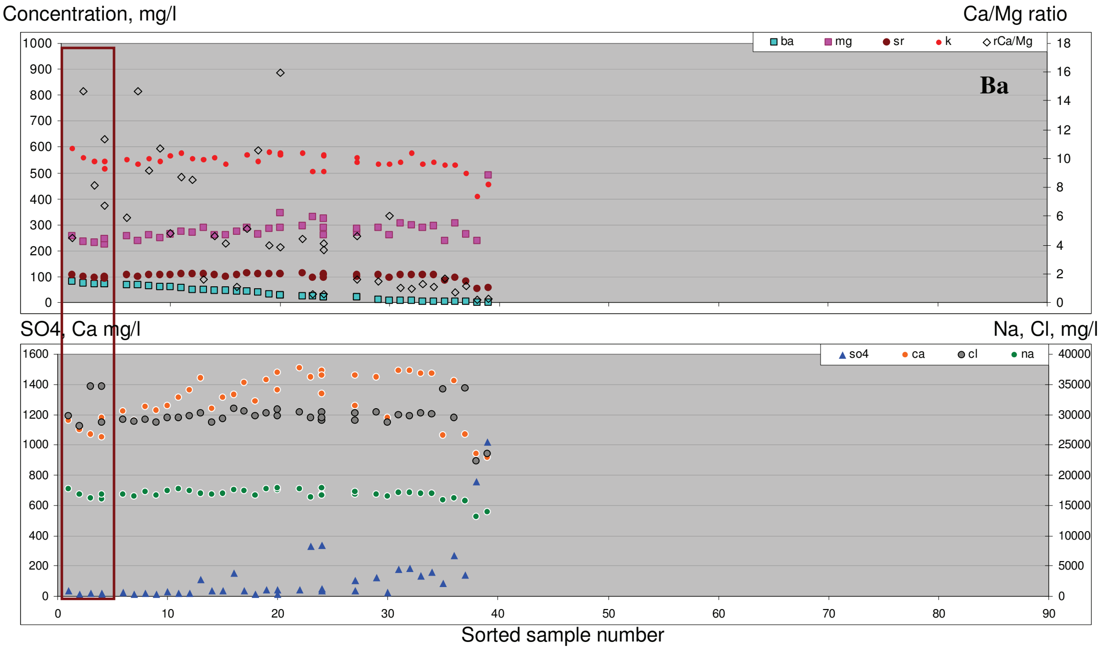


Figure 5.34 Produced water samples sorted by decreasing barium concentrations.

This process was repeated, with samples being sorted by increasing sulphate concentrations (Figure 5.35) and by decreasing Ca/Mg ratio (Figure 5.36).

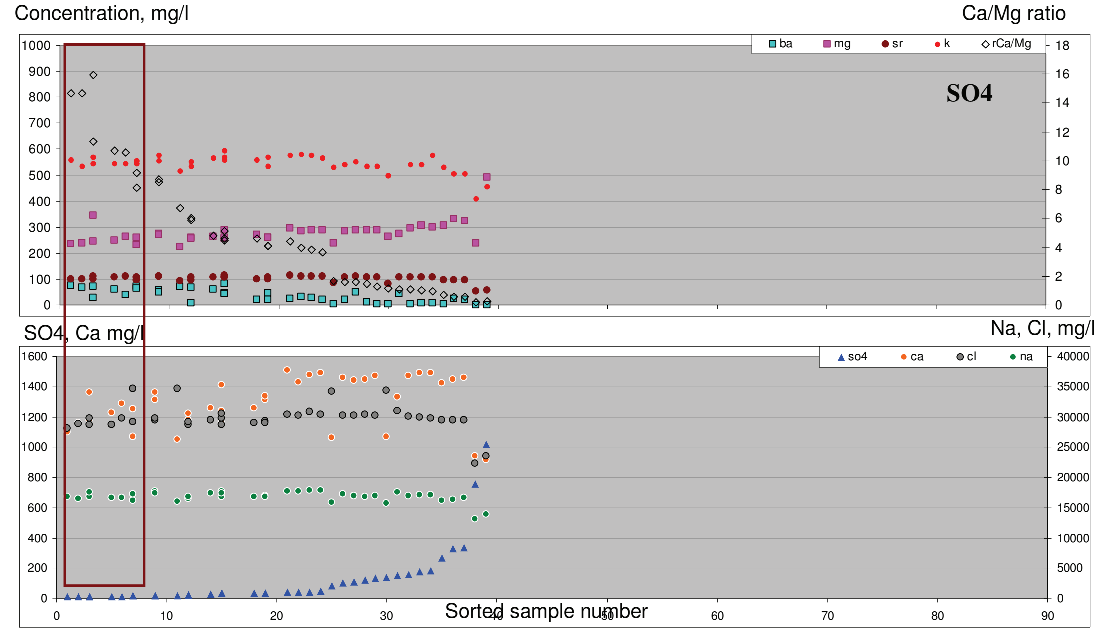


Figure 5.35 Produced water samples sorted by increasing sulphate concentrations.

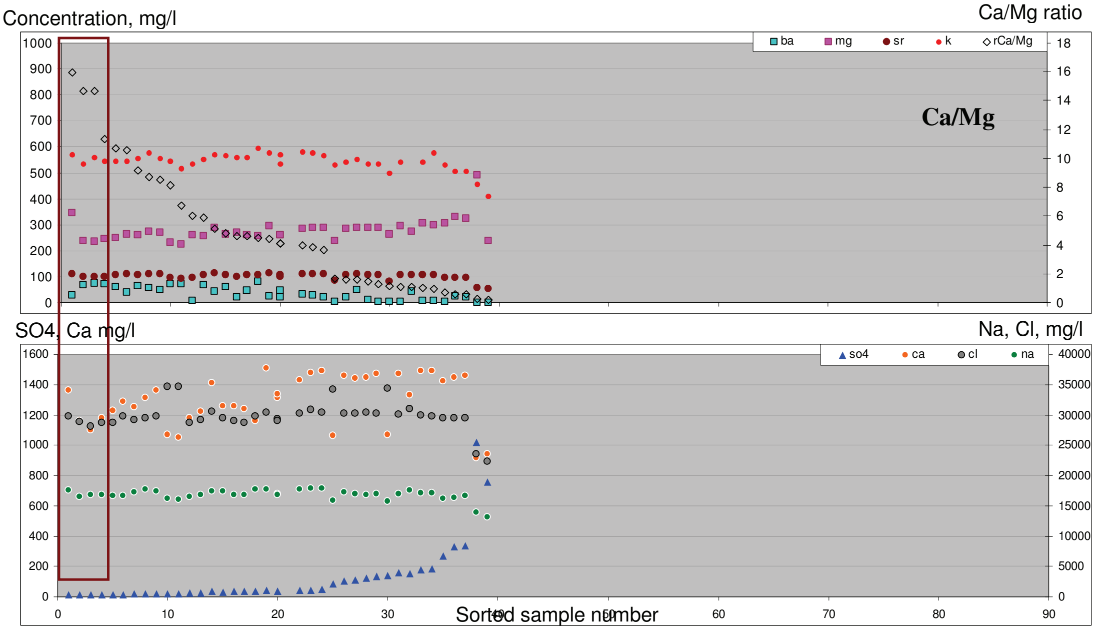


Figure 5.36 Produced water samples sorted by decreasing Ca/Mg ratio.

The mean composition of the samples that represent 100% FW was taken as the revised FW brine composition (Table 5.8).

Table 5.8 Adjusted formation and injection brines compositions.

mg/l	*Na*	*K*	*Mg*	*Ca*	*Ba*	*Sr*	*Fe*	*Cl*	*Br*	*SO_4*	*HCO_3*
FW	**17 750**	**565**	**240**	**1 150**	**81**	**105**		**30 410**		**13**	
IW	12 250	390	1 310	410		8		21 685		2 740	

However, compared to the two previous field cases where the altered brine compositions led to a good match between the injection water fractions as calculated by the Reacting Ions method and as calculated by the conventional Ion Track method, in this case there was still a significant mismatch (Figure 5.37). Figure 5.38 shows the ion concentrations vs injection water fraction, where the latter is calculated by the Reacting Ions method. The fact that for a number of ions (Na, Sr, K) the trends follow an anticipated linear relationship suggests that the calculated injection water fraction using the Reacting Ions method is at least consistent, giving further evidence for the reliability of the Reacting Ions method compared to the Ion Track method in this case. Furthermore, the overall trend of increasing injection water fraction calculated by the Reacting Ions method in Figure 5.37 is much more probable than a moderate (20%) injection water fraction that subsequently decreases, which is the case if the Ion Track method is adopted.

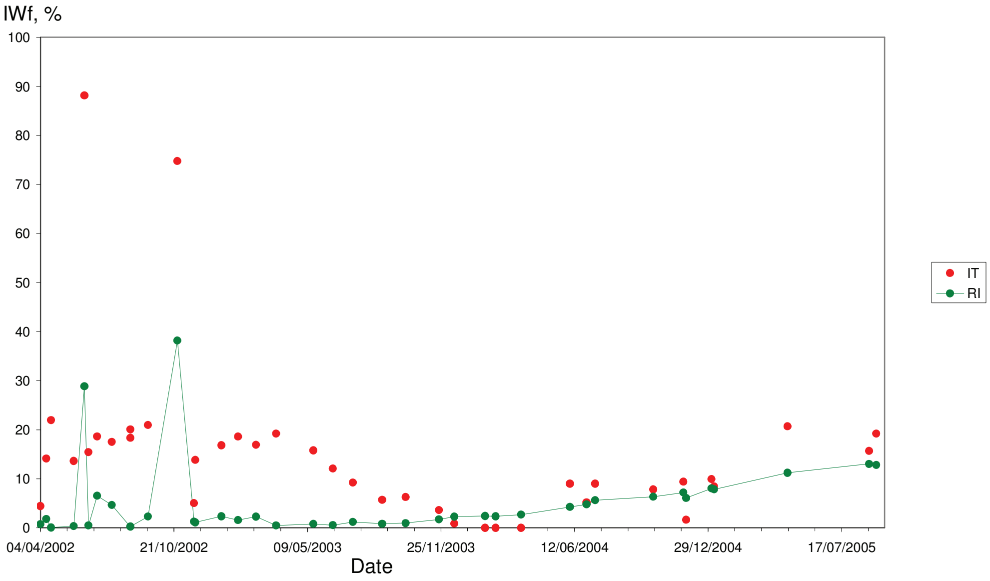


Figure 5.37 Injection water fractions by Ion Track (IT) based on Cl and Reacting Ions (RI) based on Ba and SO4 after changes in brines compositions were made.

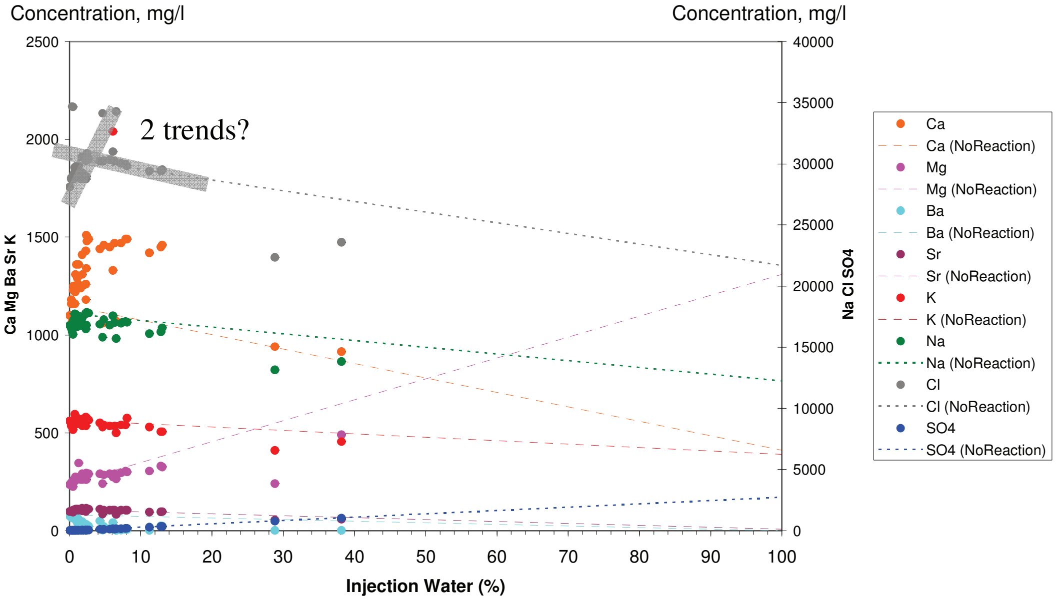


Figure 5.38 Produced water samples versus injection water fraction by Reacting Ions method.

However, if Figure 5.38 is considered there is clearly some unusual behaviour evident for some of the ions, including chloride and calcium. Concentrations of both these ions appear to increase on injection water breakthrough, before subsequently decreasing at about 3% injection water fraction. These increases are observed when the data is plotted vs. time (Figure 5.30), so cannot be attributed to incorrect formation water composition. Instead, they suggest more than one brine composition is present before injection water breakthrough (either due to different formation water compositions in different regions / layers, or due to contamination of brines during drilling and completion), or that there is some reaction taking place as a result of interaction with the injection brine which leads to an increase in the chloride and calcium concentrations – dissolution or ion exchange. This is evident from Figure 5.39, where the chloride, and *particularly* the calcium show increases when plotted as *relative* ion deviations.

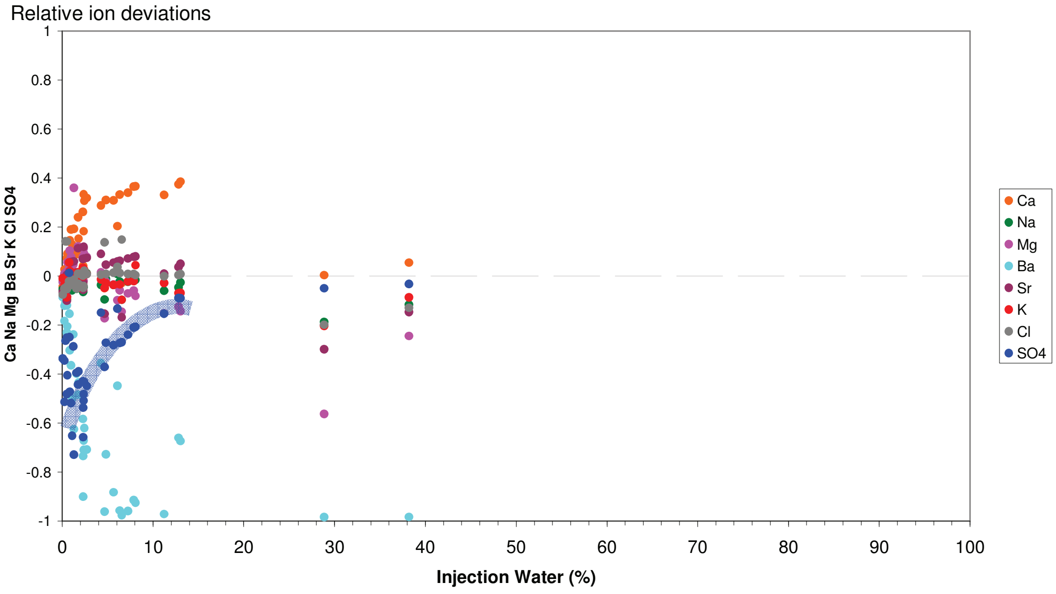


Figure 5.39 Relative ion deviations versus injection water fraction by Reacting Ions method.

Clearly this behaviour is somewhat unusual, and thus, as a check, the ion concentrations vs time and the ion deviations vs injection water fraction were plotted, where injection water fraction was calculated using the Ion Track method based on sodium and chloride (Figure 5.40). However, doing this did not eliminate the issue with high calcium concentrations, and furthermore introduced very unusual behaviour for the barium and sulphate ion deviations (Figure 5.41). The latter trends were the opposite of what is normally observed, where with increasing injection water fraction the system becomes barium limited, and thus there is an increase in the relative barium ion losses, and a decrease in relative sulphate ion losses. Here, the opposite is observed when injection water fraction is calculated using the Ion track method, and no explanation for this is evident.

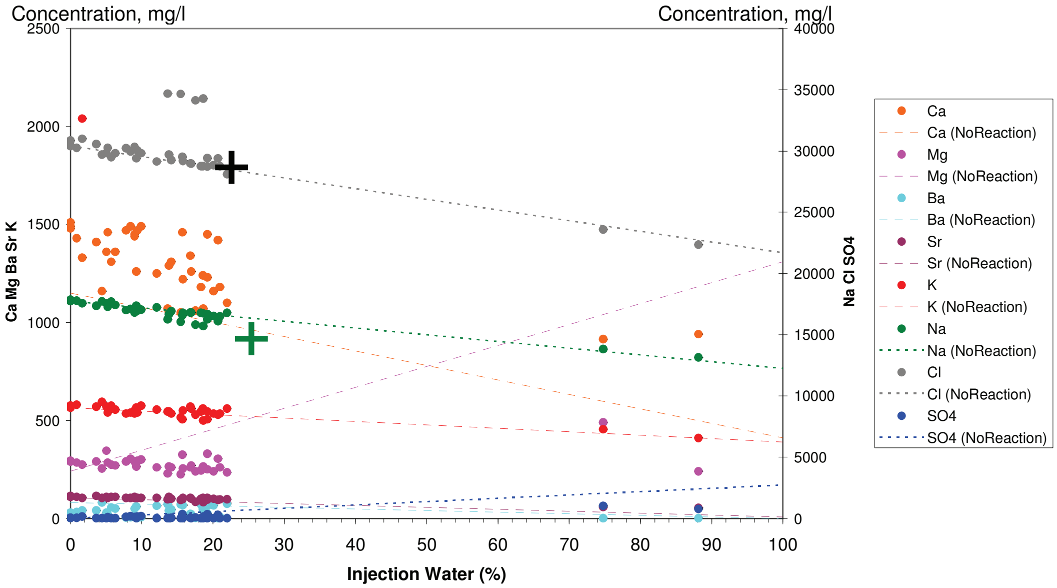


Figure 5.40 Produced water samples versus injection water fraction by Ion Track method (based on Na and Cl).

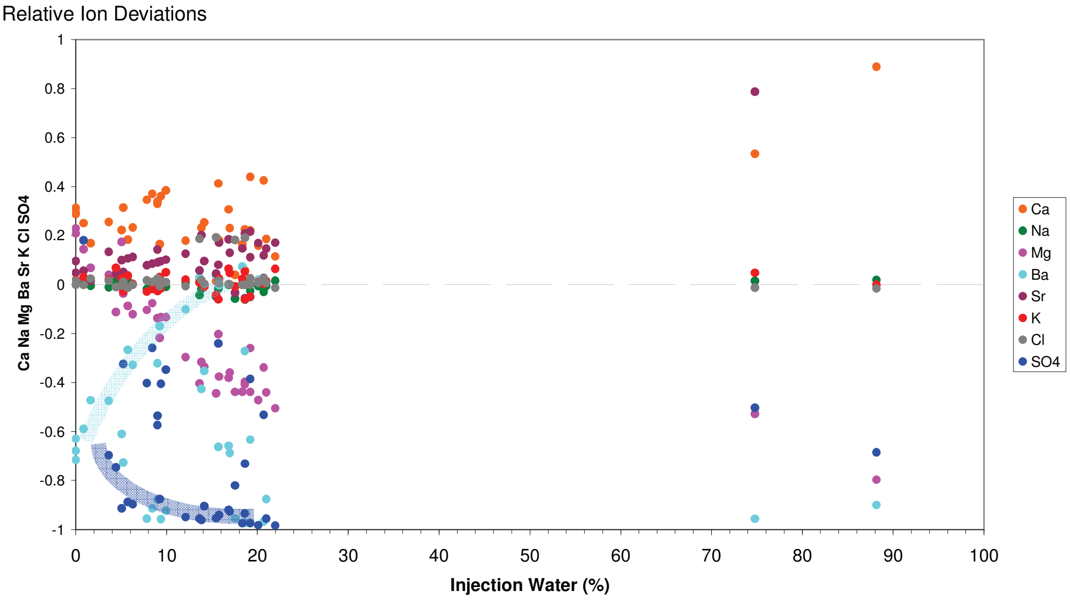


Figure 5.41 Relative ion deviations versus injection water fraction by Ion Track method (based on Na and Cl).

The above discussion suggests that the Reacting Ions method is a much more robust method for calculating the injection water fraction in this case. However, the behaviour of other ion trends requires further consideration. The back-calculated chloride concentrations (based on injection water fraction calculated using the Reacting Ions method) is shown in Figure 5.42. This data suggests that there is a relatively small, but statistically significant change in the chloride concentration associated with the formation water between the years 2002 and 2004, and that there is another change during the earliest period of production in 2002. A more in depth study of the formation layering and/or fluids used in drilling and completing the wells is warranted here.

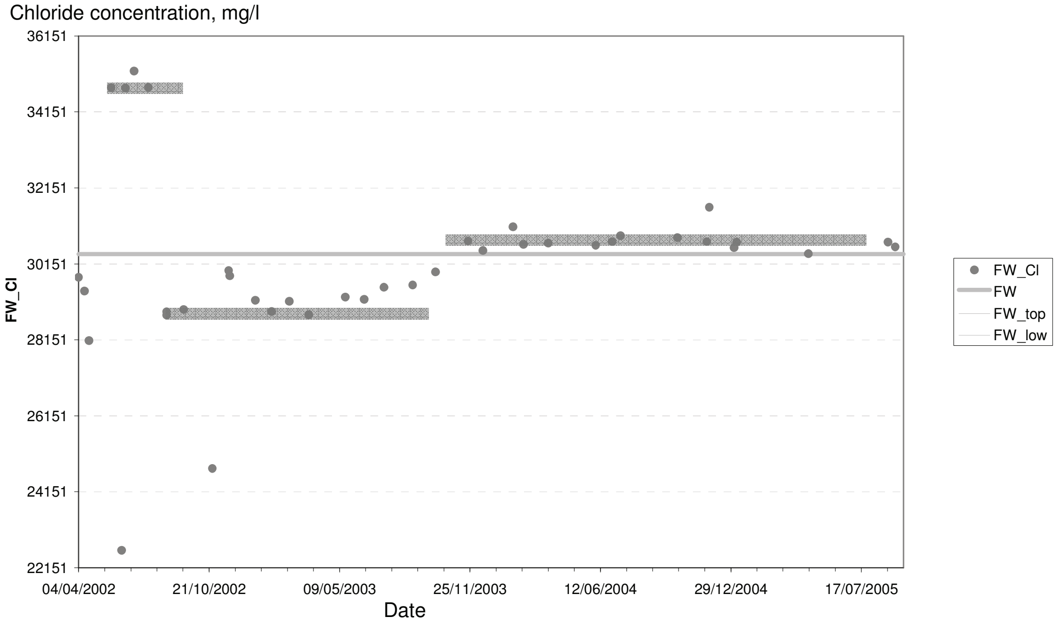


Figure 5.42 Back-calculated chloride concentration in formation water.

5.8. Summary

Following testing of the method on a synthetic dataset (Chapter 3) the Reacting Ions method was then applied to several field data sets, and as a result the Injection Water fractions were identified, with comparisons being drawn between the conventional Ion Track and the new Reacting Ions methods. In some cases the methods were shown to be equivalent, in others the Reacting Ions method was shown to be advantageous. In each case an indication is given of which ions were involved in the reactions, and the degree of relative ion deviations. This allowed investigation of whether brine mixing and potential $BaSO_4$ precipitation is occurring in situ. Evidence of $SrSO_4$ precipitation was also seen. In some cases, application of the method prompted a re-evaluation of the formation water compositions.

The Reacting Ions method was confirmed to be more robust and able to pick up injection water breakthrough earlier and reliable than the Ion Tracking method when applied to a variety of field data sets. Early, identification of injection water breakthrough can be very important for scale management, as it provides an opportunity to treat wells early before scale precipitation causes significant damage.

CHAPTER 6 ESTIMATING SCALE INHIBITOR SQUEEZE TREATMENT RESPONSE (EFFICIENCY)

Scale inhibitor squeeze treatments are the most widespread tool of a scale control strategy to prevent scale deposition. A parameter called Squeeze Treatment Response is proposed in this section. It is used to identify the combined effect of scale inhibitor efficiency and squeeze treatment placement as an overall effectiveness of the scale inhibitor squeeze treatment.

Squeeze treatment response takes into account thermodynamic equilibrium and identifies the impact of squeeze treatments on the produced ion concentrations. Squeeze Treatment Response can also assist in the calculation of the minimum inhibitor concentration level (MIC) required to stop the scaling reaction.

In order to perform the evaluation of Squeeze Treatment Response, an accurate estimate of the IW fraction in the produced brine is required. Injection water fraction in the produced brine governs the two main parameters in Squeeze Treatment Response calculations – conservative ion concentration and, based on that, the equilibrated ion concentration.

The new application presented in this section links the two major issues in the field of mineral scale prevention. It links the issue of detecting time of injection water breakthrough and the measurement of combined effect of the scale inhibitor squeeze treatment.

6.1. Squeeze Treatment Response

The subject of mineral scale and scale inhibitor Squeeze treatments is covered in many literature sources ([56]; [59]; [60]; [61]; [62]; [64]; [65], [63] etc).

It is important for production chemists to have an indication of the efficiency of scale inhibitor squeeze treatments – in particular whether the applied chemical is preventing scale precipitation. The more reactions the inhibitor stops the higher its efficiency. Inappropriate placement of scale inhibitor during a squeeze treatment may mean that downhole zones at risk of scale damage are not adequately protected, even though the observed inhibitor concentrations at the wellhead are above the minimum threshold required for protection. The approach presented here is to measure the efficiency of the treatment based on produced water ion compositions.

Scale inhibitors are designed to stop scaling reactions from happening, the more reactions the inhibitor stops the higher its efficiency. The conventional lab approach considers a scale inhibitor efficiency (*SI_efficiency*) defined as the ratio of the difference between sampled concentration and concentration in the blank (no inhibitor *noSI*) solution, to the difference between concentration originally in solution and concentration in the blank (no inhibitor) solution (6.1).

$$SI\_Efficiency = \frac{Sampled - noSI}{(Originally\ @\ Solution) - noSI} \tag{6.1}$$

Scale inhibitor efficiency can also be considered as a ratio between the treated (non precipitated) amount of some ion (mass/concentration) vs possible or available amount for such precipitation (mass/concentration), as shown schematically in Figure 6.1.

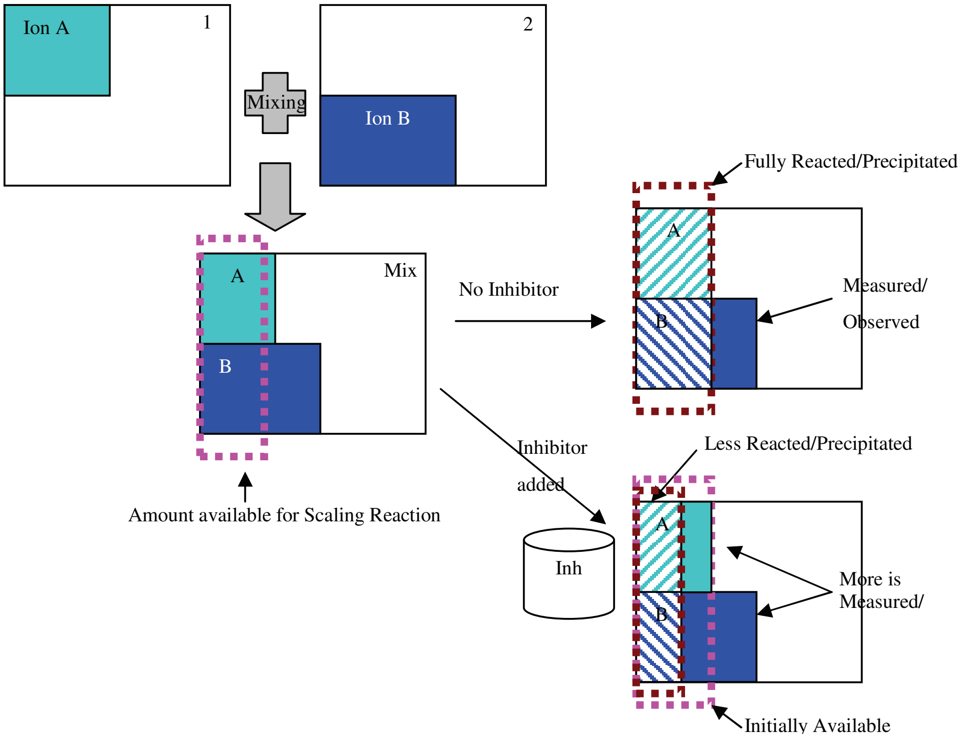


Figure 6.1 Schematic showing calculation of scale inhibitor squeeze treatment efficiency.

Comparing this with the laboratory approach, it can be seen that sampled (observed) ion concentration minus the concentration in the blank (the same brine at the same conditions, but with no SI added) is equal to the gain of ion concentration due to the effect of scale inhibitor, in other words it represents a treated amount. The difference between the concentration that was originally in solution and the blank one is actually the full amount of concentration that was lost due to precipitation, in other words this is the amount that is available for scaling if ions react in full.

In the field, the concentration that is originally in a solution is the conservative ion concentration as a result of brine mixing. The blank (or concentration if no scale inhibitor is added) is the concentration at equilibrium after scaling reactions occurred. Therefore the equation to measure scale inhibitor efficiency in the terms used in this work can be rewritten as:

$$SI\_Efficiency = \frac{Observed - Equilibrated}{Conservative - Equilibrated} \tag{6.2}$$

Scale Inhibitor efficiency is a value in the range of [0;1] or 0 to 100 percent. At the extreme, the scale inhibitor squeeze treatment would be considered to be 100% efficient if the observed ion concentration matches the conservative concentration. It is zero when the reactions occur in full (observed is equal to equilibrated – red line, calculated by the thermodynamic equilibrium, Figure 6.2).

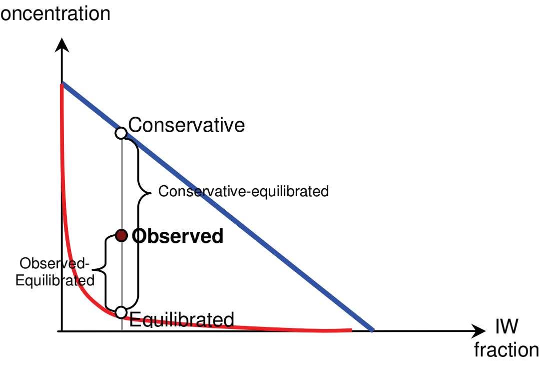


Figure 6.2 Possible ion concentration profiles as a function of injection water fraction.

One observation is required before making a transition from scale inhibitor efficiency to the efficiency of squeeze treatments. If the produced ion concentrations return towards the conservative value as the scale inhibitor concentration is increased, then we may conclude that the scale inhibitor is to some degree efficient. However, cation concentrations (barium, strontium, magnesium etc) may also come closer to their non-reacting conservative concentration due to a decrease in injection water fraction. This may occur immediately after a squeeze treatment, when the injected solutions (often made up in seawater) is displaced back into the well and replaced by formation water flowing from the reservoirs. The lower the injection water fraction in a produced brine, the less mixing occurs, and therefore we expect a lesser loss of cations due to scaling reactions and those concentrations will become closer to the conservative concentrations. Sulphate concentrations may behave similarly due to an increase in injection water fraction. This is a misconception of conservative ion concentration: conservative ion concentration is not the overall maximum possible ion concentration (which is often formation water concentration for cations and injection water concentration for sulphate), but it is the maximum possible ion concentration at given injection water fraction. Conservative Ion concentration is thus a function of initial brine concentrations (formation and injection) and the degree of mixing (refer to Chapter 2).

The conservative ion concentration is thus a function of the injection water fraction. The amount of ions lost due to the reaction itself is controlled by thermodynamics, and generally it is less than the total available, since the precipitate will have a finite solubility. The squeeze treatment response takes into account the dependency on the scale inhibitor concentration alone.

In the field (as opposed to the laboratory), the conditions that affect the ability of scale inhibitor to stop the reactions include its placement. Therefore the efficiency calculated based on field observed values should be treated as the squeeze treatment response (6.3).

$$SQZ\_response = \frac{Observed - Equilibrated}{Conservative - Equilibrated} \tag{6.3}$$

We intentionally use term “Response” instead of “Efficiency”. If scale inhibitor tested in the laboratory is known to be 100% effective at a given range of concentrations, then the squeeze treatment efficiency becomes a measure of how far the scale inhibitor has been displaced into the zone where reactions (whether due to mixing or pressure depletion) are taking place. Therefore a low squeeze treatment efficiency does not always represent low SI efficiency or poor injection strategy, it may be a consequence of the location where the reactions are taking place. In this light we propose to use a Squeeze Treatment Response as a measure of ion concentrations response to the scale inhibitor placement. The ability to perform the above calculation depends on accurate knowledge of the IW fraction, as by the Reacting Ions method.

6.1.1 Application of the Squeeze Treatment Response

Deployment of scale inhibitor squeeze treatments generally involves injection of aqueous solutions at pressures higher than the formation pressure and at temperatures lower than the formation temperature. If the pressure and temperature differences are great enough, the pumping activity may lead to the development of fractures in the near-well bore area, if the well has not already been fractured and propped.

It is quite common that squeeze treatments are specifically designed to be pumped below the fracture pressure, resulting in a uniform radial displacement of the scale inhibitor around the wellbore. However, sometimes injection of cold fluids (preflush, main slug and post flush are at temperature in the range 20^oC to 40^oC when they pass through the completions) into a hot reservoir, even at pressures lower than the hydraulic fracture pressure limit, may result in thermally induced fractures. Inappropriate placement of scale inhibitor during a squeeze treatment may mean that downhole zones at risk of scale damage are not adequately protected, even though the observed inhibitor concentrations at the wellhead are above the minimum threshold required for protection.

Therefore attention needs to be paid to the impact of squeezing fractured wells, or wells that fracture during the treatment. It is especially important to have a quantitative measure of how effective the treatment was. The “Squeeze Treatment Response” approach based on an identification of the IW fraction using the Reacting Ions method was used to measure the efficiency of the treatment analysing the produced water compositions.

Conventional scale inhibitor squeeze treatments can be modelled in some of the reservoir simulators currently available to the industry. Most squeeze treatment designs do not require complex modelling approaches. However, some complex cases, such as where a well is fractured prior to or during a treatment require more sophisticated simulators to be used. We again used the Petroleum Experts Reveal simulator for this work ([66]), which gives us the facility to model complex fracturing scenarios, such as where a fracture propagates during a treatment.

A base scale inhibitor squeeze treatment for well X was modelled, and a satisfactory match with historically observed data was obtained. Results are presented in Figure 6.3, where scale inhibitor return concentrations are plotted against the produced water volume in 1000's of barrels.

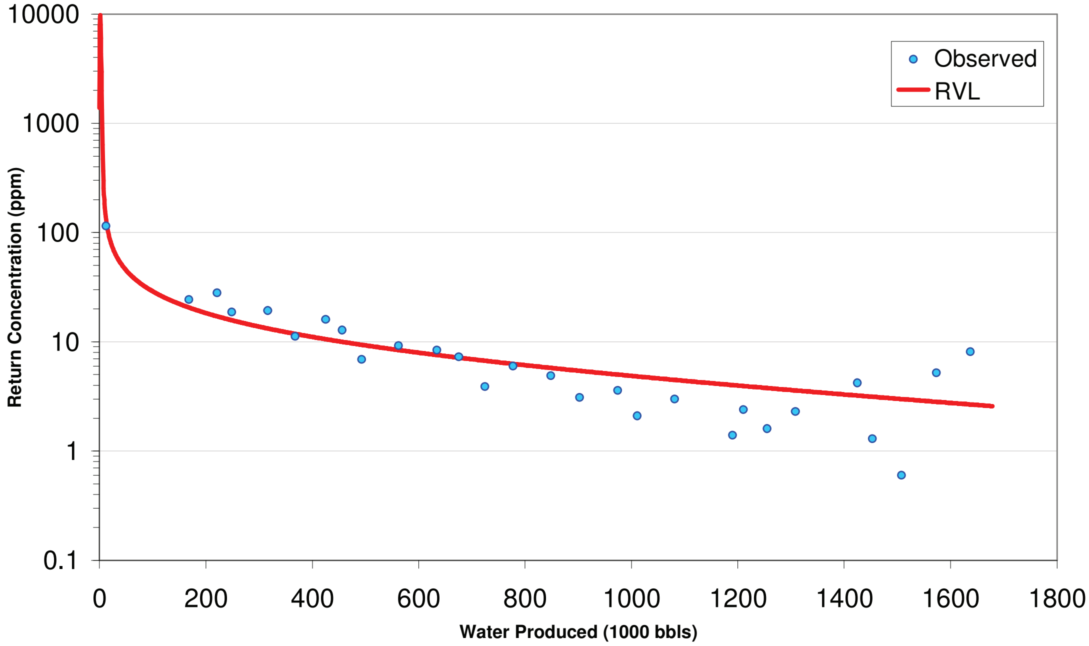


Figure 6.3 Comparison between observed field data, and simulation using Reveal (RVL). Scale inhibitor return concentrations are plotted against the produced water volume in 1000's of barrels.

A squeeze treatment in an unfractured well was compared with the case of a well that had been fractured and propped, and a well that was fractured during the treatment. The model of a squeeze treatment in well X matched to the field data was used as a base model. The only parameter that was changed is the formation height, it was decreased from 100 feet to 50 feet (Figure 6.4) to order to reduce run time. Dimensions of the other model parameters are presented in Table 6.1. The main input data used were kept the same across the three generic models. The typical squeeze treatment design was used with a standard Langmuir type isotherm, and presented in Table 6.1 and Table 6.2. The same squeeze treatment for a vertical well was modelled in each case.

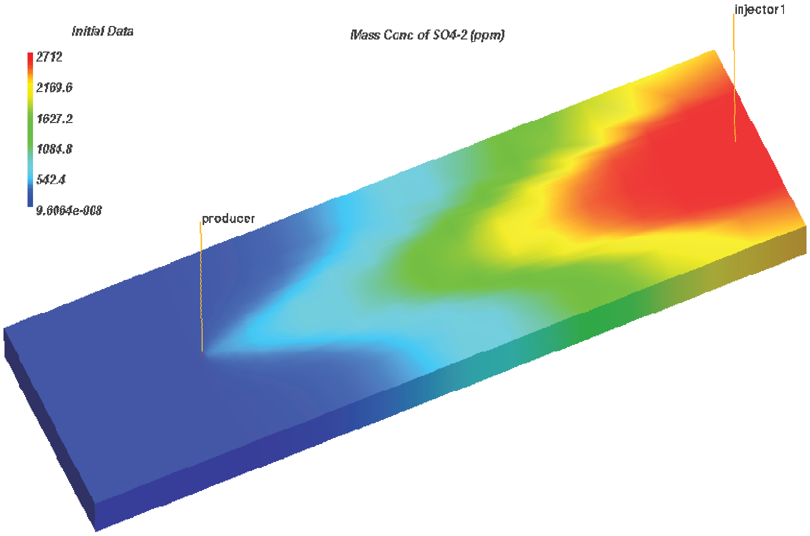


Figure 6.4 Modelled reservoir sulphate concentration before the squeeze treatment.

Table 6.1 Model parameters.

Parameter	***Value***
Model dimensions	700 ft x 200 ft x 50 ft
Average reservoir pressure	1000 psia
Permeability	200 mD
Top depth	2000 feet TVDSS

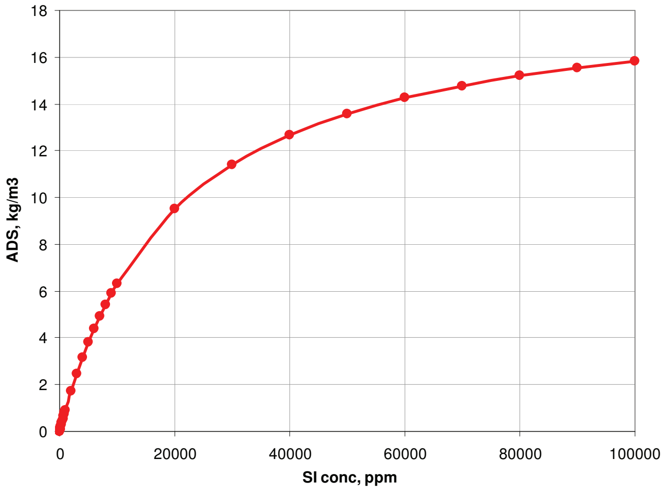
Isotherm used in modelling scale inhibitor adsorption	Langmuir type isotherm with $a=19\ kg/m^3$, and $b=5*10^{-5}$ 

Table 6.2 Squeeze treatment design.

N	*Stage*	*SI concentration*	*Duration*	*Water Rate*
1	Preflush	50 ppm	0.5 h	1.39 bbl/min
2	Main Slug	100 000 ppm	3.0 h	1.39 bbl/min
3	Postflush	1 000 ppm	8.5 h	1.39 bbl/min
4	Shut-In	-	12.0 h	-
5	Back-production	-	10 days	500 bbl/day
	Back-production	-	40 days	550 bbl/day
	Back-production	-	50 days	570 bbl/day
	Back-production	-	100 days	590 bbl/day
	Back-production	-	190 days	600 bbl/day

A number of modelling studies on the design of scale inhibitor treatments in fractured wells were considered ([67]; [59]; [68]; [60] etc). In this work, for the two cases (fractured well and for the well that fractures during the treatment) the vertically oriented fracture was designed not to extend more than 28 feet from the wellbore. Well X was assumed to be fully fractured before or right at the start of the treatment. A very high permeability (thousands of Darcies) was defined for the fracture making it highly conductive. For the case of fracturing during the treatment, the fracture was assumed to heal after the squeeze treatment finished, and thus the well would flow back radially after the treatment.

In order to compare retention of scale inhibitor, and thus squeeze treatment performance, the resulting modelled scale inhibitor return concentrations were plotted against the volume of water produced for all the three scenarios of an unfractured well, a well that is fractured prior to the treatment, and a well that fractures during the treatment (Figure 6.5).

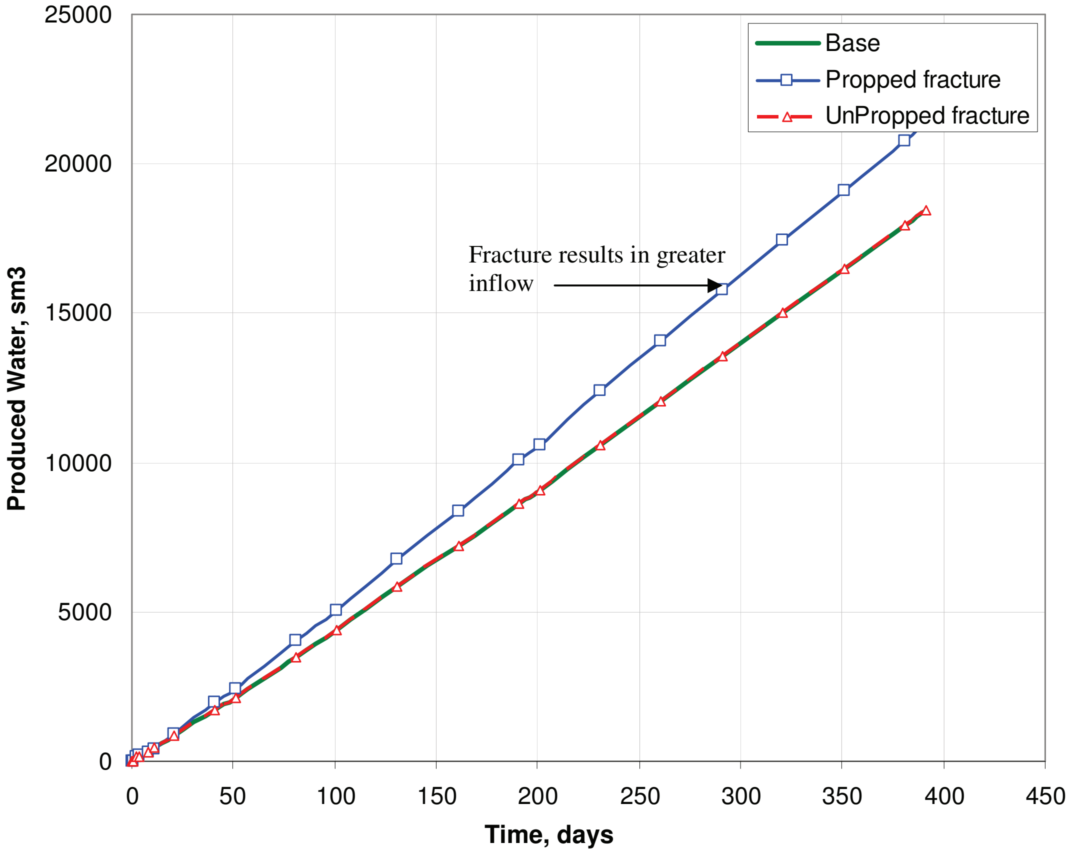


Figure 6.5 Simulated Produced Water volume for three scenarios.

When the well was fractured and propped before the squeeze treatment (blue line on Figure 6.6), the scale inhibitor was placed deeper in reservoir and therefore could adsorb onto a bigger surface area of rock. As a result the squeeze lifetime was significantly extended compared with the unfractured well scenario (green line,

Figure 6.6). The propped fractured scenario showed longer return of SI concentrations above MIC (which was set to 10 ppm). It should be bourn in mind that the fractured well will typically produce water at a higher rate than the equivalent unfractured well, and hence it is key to plot the inhibitor returns vs. volume of water produced rather than vs. time.

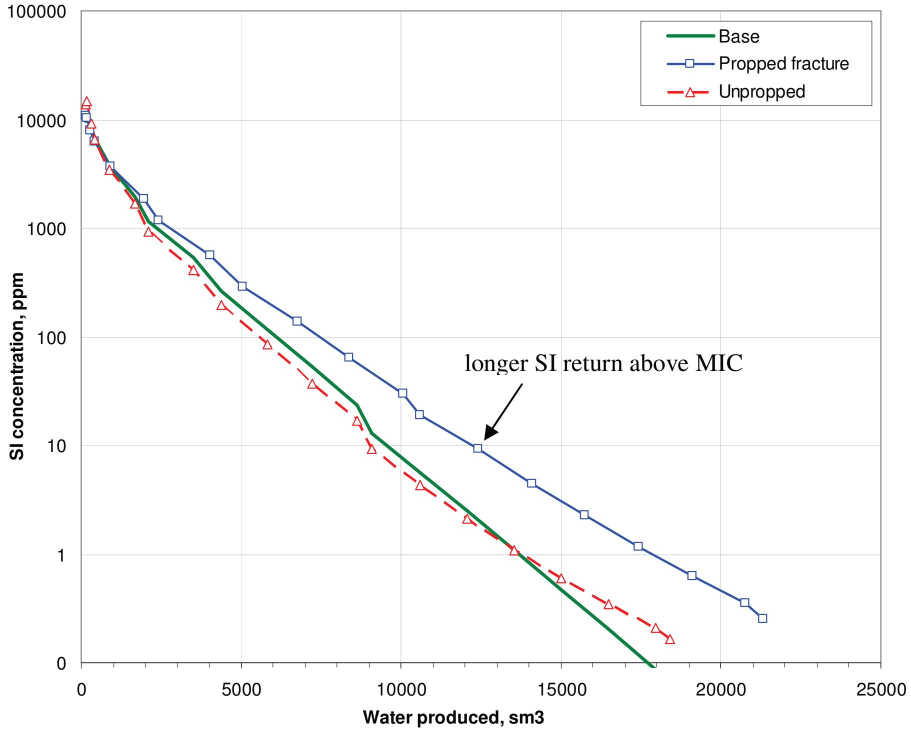


Figure 6.6 Simulated SI return concentrations.

The case where the well was fractured *during* the squeeze treatment (red line, Figure 6.6) appears to give poorer results than the fractured case. The explanation for this is as follows (refer to Figure 6.7 illustrating schematics of the placements occurring in these three scenarios): when the fracture grows at the same time as the treatment is being pumped (Propagating fracture case, Figure 6.7), care needs to be taken to ensure that the overflush is being displaced into the same volume of rock as the scale inhibitor slug has been injected into. For instance, if the fracture only starts to propagate during the postflush because this is when near wellbore cooling starts to have an effect on the local stress field, then scale inhibitor injected prior to this will have propagated radially away from the wellbore through the matrix surrounding the well (Propagating case top section, Figure 6.7), while subsequently injected overflush fluid will displace along the newly created fracture face and may "bypass" the scale inhibitor slug (Propagating case bottom section, Figure 6.7). Thus, the scale inhibitor will not have been displaced deep into the formation as would be desired to enhance adsorption on to rock surfaces, and so during the back-production stages the inhibitor will return into the well much quicker.

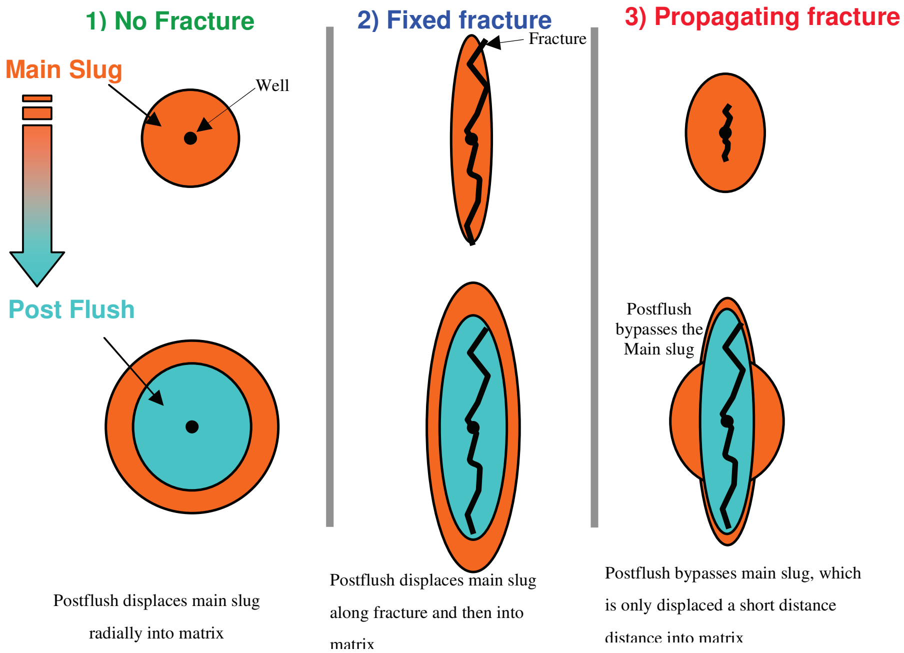


Figure 6.7 Schematics of inhibitor slug placements for three scenarios.

Produced water ion concentrations indicated higher barium return concentrations for the case when the well was fractured and propped (Figure 6.8) which indicates that propped case is more efficient.

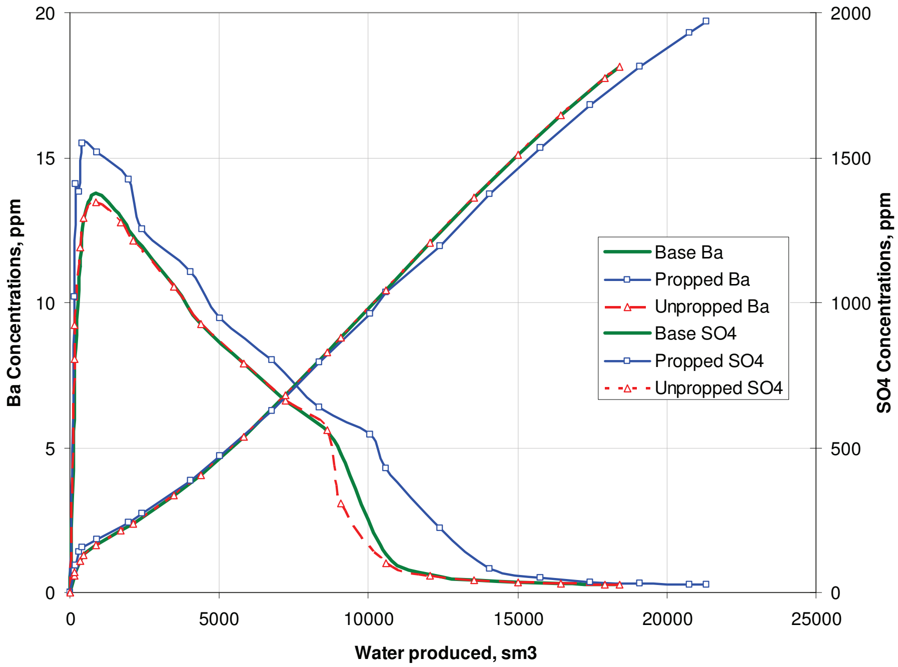


Figure 6.8 Simulated Produced Water barium and sulphate concentrations for three scenarios.

However produced barium concentrations on their own do not provide sufficient data to draw a conclusion regarding the efficiency of squeeze treatment. In general, injection water fraction profiles for different treatments can vary, and therefore a unified parameter, such as squeeze treatment response should be considered.

For the case when the squeeze well was propped, as a result of a longer period of time when scale inhibitor was present above MIC near the wellbore, the well was protected for longer and showed better squeeze treatment response, which can clearly be seen in Figure 6.9.

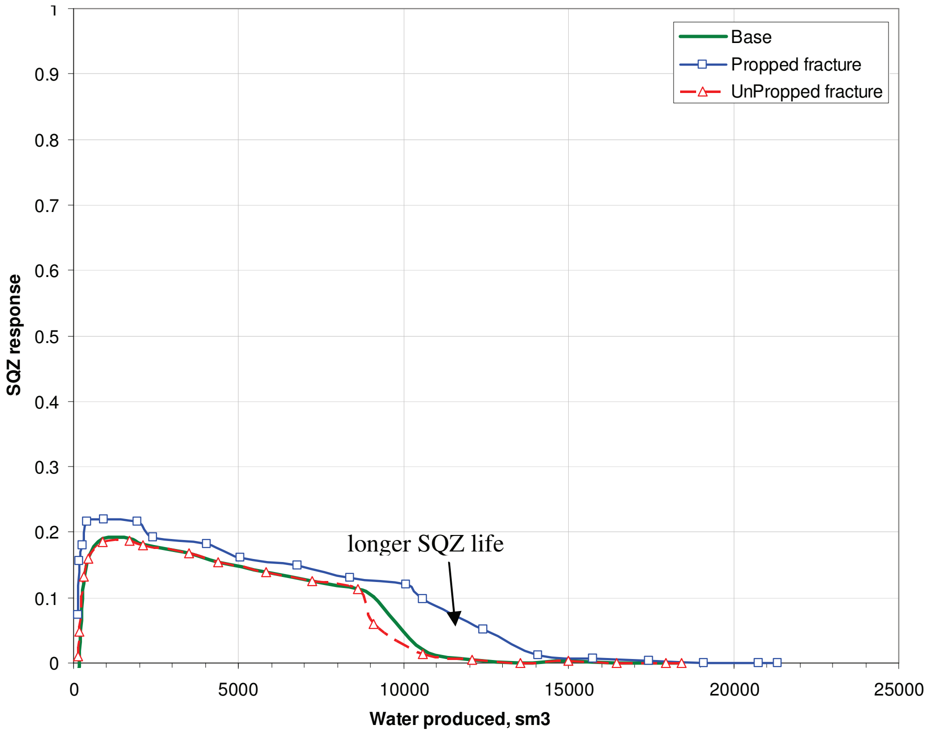


Figure 6.9 Calculated squeeze treatment responses against volume of water produced.

Developing designs for effective scale inhibitor squeeze treatments in fractured wells is a challenge, and specific attention has to be given to modelling that process. Results of the modelling suggest that fracturing a well during a squeeze treatment would not be a straightforward process. The dimensions, and especially the timing of the fracture initiation, would have to be taken into consideration, as those parameters can significantly affect the Squeeze Treatment Response, and thus the squeeze lifetime in general.

6.2. Squeeze Treatment Response and Location of Mixing

A low squeeze treatment response may result from two conditions. Firstly, if the scale inhibitor does not stop reactions at all (ineffective chemical or its concentration is not high enough). The second scenario is when the scale inhibitor cannot reach the location where the majority of the reactions are taking place. Given that most scale inhibitors are tested for efficiency before application, the second scenario is the more probable in the majority of cases where low apparent scale response is observed. If the scale inhibitor response does not increase with increasing scale inhibitor concentration, then it may be deduced that most reactions are taking place deep in the reservoir beyond the treated zone.

Thus, calculated scale inhibitor response can give an indication of the location at which reactions are taking place. If the reactions are taking place in the near well-bore area, then a squeeze will affect the majority of the reactions taking place, and therefore a change in scale inhibitor response will be observed. If all the reactions are taking place deep in the reservoir, then a squeeze treatment will not lead to any change in ion behaviour and therefore scale inhibitor response will remain the same, as illustrated in Figure 6.10.

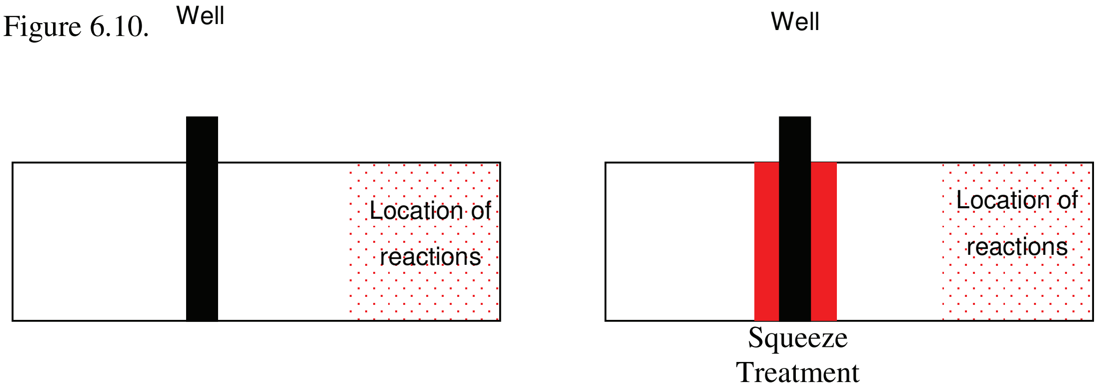


Figure 6.10 Schematic showing location of scale inhibitor squeeze treatment compared to location where scale precipitation is occurring.

Figure 6.11 illustrates the scale inhibitor response against scale inhibitor concentration for an example well, where it may be observed that the scale inhibitor response does not increase with increasing concentration. Therefore, for this particular well the conclusion may be drawn that the majority of the reactions are taking place deep in the reservoir.

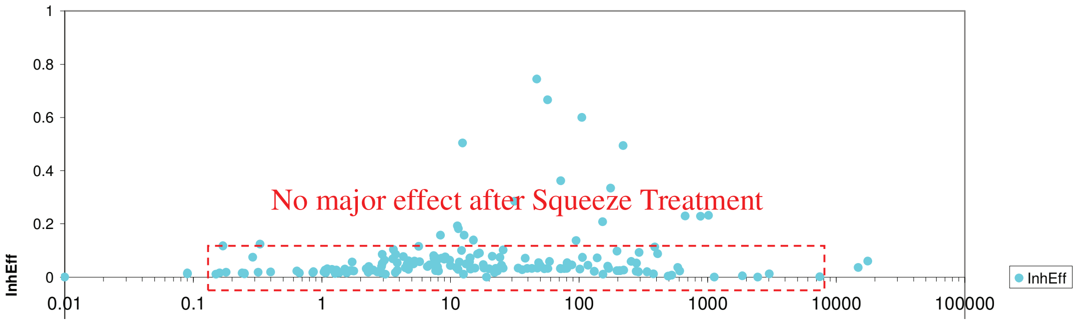


Figure 6.11 Inhibitor efficiency vs measured scale inhibitor concentration, showing that most scaling ions are lost even at high inhibitor concentrations, suggesting precipitation outside the treatment zone.

Figure 6.12 shows the case where reactions are taking place near the well bore. An example of well data for such a scenario is shown in Figure 6.13. The scale inhibitor response increases at scale inhibitor concentrations greater than 2-3 mg/l. For such a well the conclusion would be that reactions are occurring near or in the wellbore.

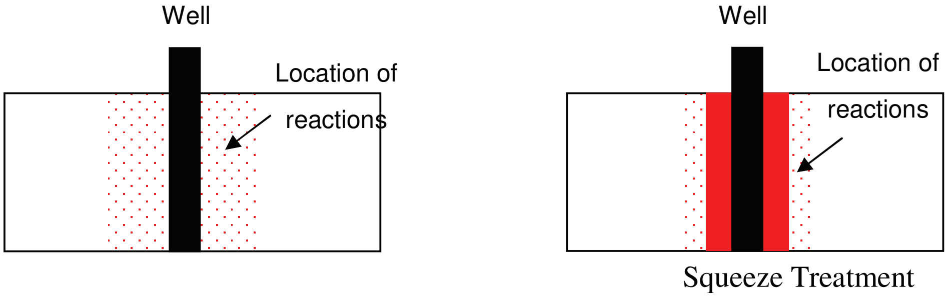


Figure 6.12 Schematic showing location of scale inhibitor squeeze treatment which coincides with the location where scale precipitation is occurring.

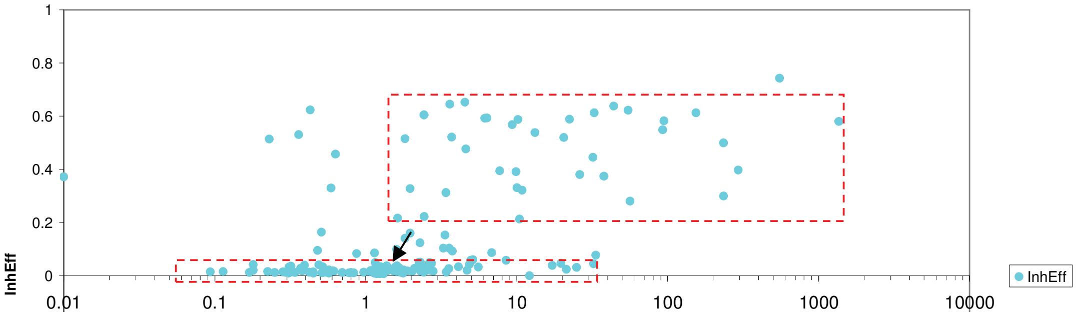


Figure 6.13 Inhibitor efficiency vs measured scale inhibitor concentration, showing that in this case fewer scaling ions are lost at higher inhibitor concentrations, suggesting precipitation inside the treatment zone.

A modelled case presents the application of Squeeze Treatment Response to identify field MIC values more clearly. In this modelled case the actual MIC was set beforehand to be 10 ppm. Analysis of the squeeze treatment response profiles indicates a significant drop when SI concentration is less then 10-11 ppm (Figure 6.14). The drop in squeeze responses at the highest scale inhibitor concentrations (around 10000 ppm) is explained by the fact that at these high concentrations it was in fact postflush fluid that was produced, which consisted of pure water and had no barium sulphate scaling tendency.

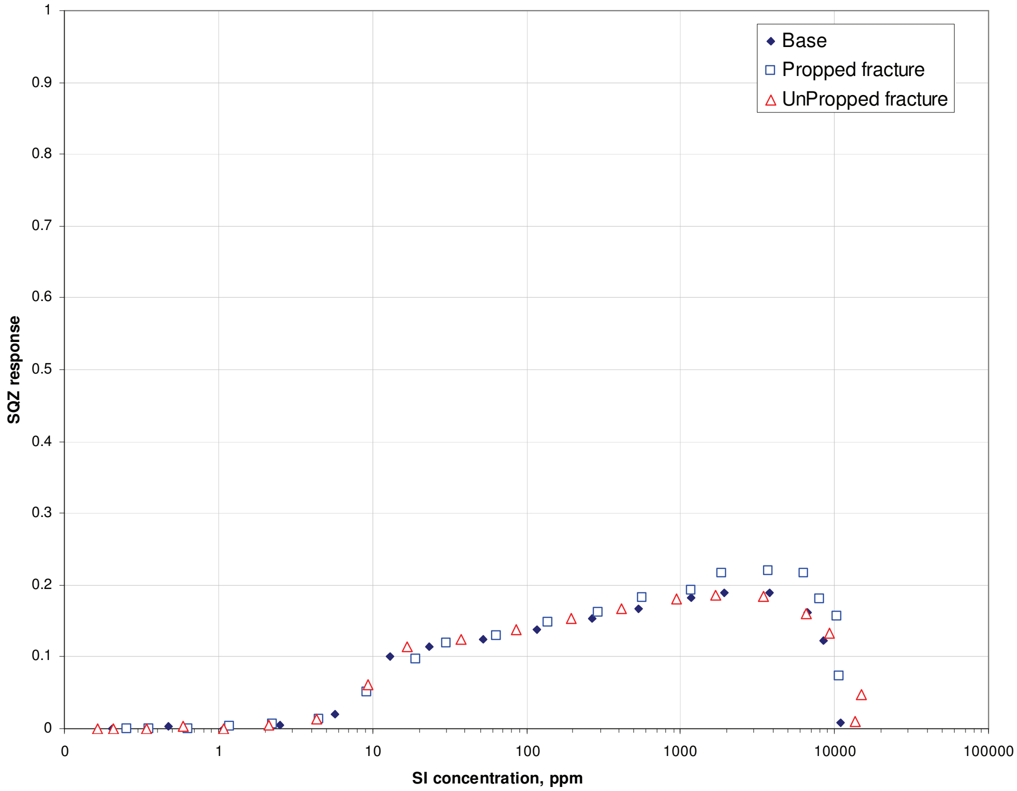


Figure 6.14 Calculated squeeze treatment responses against the SI return concentrations.

6.3. Summary

The conventional approach to measure efficiency of the scale squeeze treatments is based on the inhibitor return concentrations. The more produced water containing scale inhibitor at concentrations above the MIC level, the more efficient the treatment is considered to be. The level of inhibitor return concentrations is a function of adsorption parameters. Thus, concluding that the squeeze treatment is efficient, based solely on the return concentrations, does not take into account whether inhibitor reached the place where scaling reactions occur. The squeeze treatment response function presented here identifies the impact of squeeze treatments on the produced ion concentrations. It can be used not only to measure the success of a squeeze treatment performed, but also to determine the MIC levels and to give an indication of the location where scaling reactions are taking place.

CHAPTER 7 CONCLUSION

Our ability to model scale precipitation in situ and in the well is linked to our ability to accurately model the injection water (IW) fraction at production wells. To then match the modelled IW fraction with field data, a robust and accurate method for determining IW fractions from the field data is required. Once this condition has been met, it is possible to use the modelling techniques with a higher degree of confidence to predict future scaling tendencies at the production wells, and to help implement an appropriate scale management strategy to economically mitigate the potential effects of scale damage. The injected water fraction in the produced brine mix is thus a key value to determine.

In this thesis a new Reacting Ions method for calculating injection water fraction is developed. The method is based on interactions between ions during reactions. It proves itself as more robust than the conventionally used Ion Track method, particularly when there is noise in the data. Results of the sensitivity study presented here show that the method is more effective in detecting IW fractions, especially at low IW fractions when injection water breakthrough occurs. This method has been used to identify the injection water fraction for more than one hundred wells in several regions of the North Sea where produced water samples were available, and the timing of seawater breakthrough was identified more accurately.

Conventionally, the fraction of injected water is determined from the concentration of a conservative ion, such as chloride (Cl^-) by linear interpolation between its concentrations in the IW and the FW (see Chapter 2). Intuitively, it may seem that using ions which are known to be reacting within the reservoir (such as Ba^{2+} and SO_4^{2+}) would neither be feasible nor accurate. In this thesis, it was demonstrated that the reaction can be accounted for, particularly in a simple reaction system such as in $BaSO_4$ precipitation. Thus the Reacting Ions method for determining the fraction of IW in produced brine was developed.

The Reacting Ions method proves to be more robust than the Ion Tracking method, particularly when there is noise in the data. It was demonstrated that in the presence of even moderate levels of scatter and noise (1%) it is more efficient when using reacting ions (such as sulphate) instead of the conservative chloride ion, given there is generally a much bigger differential between the sulphate concentrations in the two brines than the differential between the chloride concentrations in the two brines.

The Reacting Ions method has the following benefits:

- It correctly takes into account ion loss due to reactions.
- It is more accurate at detecting IW breakthrough by using together the concentrations of two ions, both of which typically have very different concentrations in the end member brines. In the case of barium and sulphate this is particularly the case, as a consequence of the very low solubility of barium sulphate.
- It has been successfully tested both on a synthetic model and on field data.

In addition, by studying the relative ion deviation data over time (or injection water fraction) for the various ions present in the produced brine, we can determine whether an ion is conservative, precipitating or is part of a dissolution reaction. This information can be used to determine when to deploy a scale inhibitor squeeze treatment, and it may also be useful for scale inhibitor selection. However, to perform calculations, an accurate knowledge of the IW fraction is required, and is thus dependent on the availability of a tool such as the Reacting Ions method.

The techniques presented in this thesis were applied to various field data sets, and as a result the timing of seawater breakthrough was identified in each case. An indication is given of which ions were involved in the reactions, and the degree of relative ion deviations (Chapter 4). The scale inhibitor squeeze treatment response was proposed to measure the extent to which ion concentrations were affected only by dilution (scale inhibitor effective) and by precipitation (scale inhibitor not effective). The location where reactions were taking place (inside or outwith the treated zone) could also be estimated (Chapter 6). Additionally, a technique which identifies which formation or formations the well is producing from was proposed (Chapter 5).

7.1. Future work

One major uncertainty, however, remains to be further investigated: how applicable is the new technique when there are more than two brine compositions involved, say when there is more than one formation water type present, or where the composition of the injection water varies due to, say, the use of PWRI with seawater initially used as a top-up injection fluid to maintain voidage replacement. These types of scenario merit further investigation. There is also potential to use injection water tracking as a method to estimate the average reservoir permeability.

One of the future plans after submitting the thesis is to establish a database of produced waters from fields around the world where waterflooding has been used for recovery, and then to study what in situ reactions may have taken place during the sweep process in each of these scenarios. This will permit the development of a database of in situ reactions observed worldwide.

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