**UNIVERSIDAD POLITECNICA DE MADRID
E.T.S. DE INGENIEROS DE CAMINOS, CANALES Y PUERTOS**

**CHARACTERIZATION OF THE THERMO-HYDRO-
MECHANO-CHEMICAL BEHAVIOUR OF
UNCEMENTED RESERVOIR QUARTZ SAND AT HIGH
TEMPERATURE AND PRESSURE**

TESIS DOCTORAL

MIRIAM MARTIN RUIZ

Licenciada en Geología

Madrid 2019

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Título de Tesis

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EL PRESIDENTE

LOS VOCALES

EL SECRETARIO

RESUMEN

Uno de los principales objetivos en la caracterización de yacimientos de petróleo es la determinación de la compresibilidad, habida cuenta de que ésta no sólo influye directamente en la producción del crudo, sino que una estimación inadecuada puede dar lugar a problemas medio ambientales tales como subsidencias. En el caso de producción mejorada de petróleo por métodos térmicos, tales como los denominados por los acrónimos SAGD (Steam Assisted Gravity Drainage), CSS (Cyclic Steam Stimulation), SF (Steam Flooding) o WF (Water Flooding), que emplean la inyección bien de vapor o de agua en el yacimiento con objeto de mejorar la movilidad del crudo, el reto es mayor, dado que bajo ciertas condiciones, llevan aparejados procesos Termo-Hidro-Químico-Mecánicos que pueden generar cambios en la compresibilidad, porosidad y permeabilidad del yacimiento.

En la presente tesis se ha estudiado el efecto de la temperatura (25-250°C), la tensión (hasta 50MPa) y la composición del agua en la compresibilidad de muestras de arenas de cuarzo no cementadas procedentes de un yacimiento de crudo pesado en Venezuela. Se han realizado una serie de ensayos enfocados al estudio de los siguientes procesos acoplados: Ensayos Termo-Hidro-Químicos, ensayos Termo-Mecánicos y ensayos Termo-Hidro-Químico-Mecánicos.

Los resultados revelan que en condiciones secas la temperatura no afecta a la compresibilidad y que los procesos responsables son, en caso de bajas temperaturas, una rotura crítica rápida de granos tipo “Hertz”, que pasa a rotura subcrítica por corrosión bajo tensión con el incremento de la temperatura debido a la presencia de inclusiones fluidas en los granos. En el caso de muestras saturadas (con salmuera), la temperatura desempeña un papel importante en la compresibilidad, porosidad y permeabilidad debido a la solubilidad de las arenas de cuarzo, cuya actividad es fuertemente dependiente de la temperatura, pH y composición del agua. Los procesos responsables a nivel de grano son, en caso de bajas temperatura, la rotura por corrosión bajo tensión, que dan paso a fenómenos de disolución por presión en el contacto de los granos con el aumento de la temperatura.

Por último, se ha implementado un modelo numérico en el software MATLAB que da cuenta de la deformación vertical y evolución de la porosidad y permeabilidad debido a procesos de disolución por presión cuyos resultados ajustan con los datos experimentales.

Es importante señalar que para el estudio de las muestras ha sido necesario el desarrollo de un método que permitiera mantener su fábrica. Dicha metodología ha sido patentada.

ABSTRACT

The assessment of compressibility is one of the key objectives regarding the characterisation of an oil reservoir, not only because it strongly affects oil production, but also because a lack of proper judgement may lead to environmental problems (subsidence) during production. In particular, the use of thermal Enhanced Oil Recovery (EOR) technologies, such as Steam Assisted Gravity Drainage (SAGD), Cyclic Steam Stimulation (CSS), Steam Flooding (SF) or Water Flooding (WF) which use injection of either steam or water into the reservoir to improve the oil recovery, is much more challenging, as such technologies entail, under certain conditions, complex Thermo-Hydro-Mechano-Chemical processes that modify the compressibility, porosity and permeability of the reservoir.

In this regard, we have studied the effect of temperature (25-250°C), stress (up to 50MPa) and water composition on the compressibility of samples of uncemented quartz sand, as well as the associated processes that occur at grain scale. The sand samples were extracted from a heavy oil reservoir in Venezuela and subjected to a series of tests, focused on the analysis of the following coupled processes: Thermo-Hydro-Chemical tests, Thermo-Mechanical tests and Thermo-Hydro-Mechano-Chemical tests.

The results show that at dry conditions the temperature has a negligible effect on the compressibility, which can be attributed to critical rapid Hertzian crack growth at low temperature that leads to subcritical crack growth by stress-corrosion when the temperature rises due to the presence of fluid inclusions within the grains. In the case of saturated conditions (with brine), temperature proved to have a strong effect on compressibility, porosity and permeability, as a result of the dissolution of quartz sands, being its activity heavily dependent on the water composition, pH and temperature. Thus, compressibility and changes in the porosity and permeability can be attributed to stress-corrosion at low temperatures that lead to the phenomenon of pressure-solution at the grain contact when the temperature rises.

Finally, a numerical model has been implemented in MATLAB software. The model accounts for the vertical deformation and the evolution of the porosity and permeability caused by processes of pressure-solution. The results match fairly well with the experimental data.

It is noteworthy that a novel procedure aimed at keeping the fabric of samples after the tests for a detailed observation has been developed and patented.

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Dedicated to Enrique, Marco, and Saúl

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List of notation

A_i	is an experimental factor (m s^{-1})
A	is the relative grain surface area
α	is the ratio (c/R)
a_c	is the a smallest value of the area
α	is the thermal expansion coefficient
b	is the geometry of the crack tip (J mol^{-1})
c	is the initial pre-existing flaw length
c_α	is the creep coefficient
c_c	is the compression index
C_{eq}	is the silica solubility (silica concentration in equilibrium)
C_{int}	is the silica concentration in the contact area
C_n	is the coordination number
C_{n_yield}	is the coordination number at the yield point
C_{pore}	is the silica concentration in the pores
c_s	is the swelling index
D	is the depth (m)
d	is the mean linear grain size
d_c	is the contact area diameter
d_o	is the initial horizontal grain size
d_{oz}	is the initial vertical grain size
d_p	is the initial vertical grain size
d_z	is the vertical grain size
δ	is the elastic grain shortening
e	is the void ratio
e_o	is the initial void ratio
E	is the Young's modulus
E_m	is the heat of fusion of quartz (kJ mol^{-1})
$\dot{\epsilon}$	is the strain rate for diffusion creep
$\dot{\epsilon}_{diss}$	is the strain rate for pressure-solution
F_n	is the normal force applied considering two particles
F_{n_s}	is the normal force applied considering a soil aggregate

Φ	is the porosity
γ_s	is the fracture surface energy (J m^{-2})
ΔH_i	is the activation enthalpy (J mol^{-1})
k_{ad}	is the adsorption coefficient (molal^{-1})
k_i^+	is the dissolution rate constant of the quartz for individual cations ($\text{mol/m}^2\text{s}$)
k^+	is the dissolution rate constant of the quartz ($\text{mol/m}^2\text{s}$)
k^-	is the precipitation rate constant of the quartz ($\text{mol/m}^2\text{s}$)
K_{IC}	is the fracture toughness
L	is the length
L_o	is the initial length
m	is the molal concentration of cation
M	is the relative mass of the fluid
M_{diss}	is the dissolved mass
M_{diff}	is the diffused mass
M_{prec}	is the precipitated mass
ν	is the Poisson's ratio
$\theta_{Si-O}^{H_2O}$	is the fraction of Si-O reacting with molecular water
θ_{Si-O}^{OH-}	is the fraction of Si-O reacting with hydroxyl ions
ρ_g	is the grain density
R	is the grain radius
R_m	is the universal gas constant ($\text{J mol}^{-1}\text{K}^{-1}$)
σ	is the total stress
σ_c	is the critical activation stress
σ_{ef}	is the effective stress
σ_{ef_cr}	is the critical effective stress that cause crushing of a particle embedded in a soil matrix
σ_{f_gr}	is the Griffith failure stress for mode I
σ_{int}	is the intergranular stress
σ_{int_cr}	is the critical intergranular stress that cause crushing of a particle embedded in a soil matrix
σ_t	is the tensile stress
σ_{t_s}	is the tensile stress in a particle embedded in a soil matrix

T	is the temperature (Celsius degree)
T_k	is the experimental temperature (Kelvin degree)
T_h	is the temperature of homogenization
T_m	is the temperature of fusion of quartz (Kelvin degree)
V_m	is the molar volume of the quartz ($\text{m}^3 \text{mol}^{-1}$)
V_p	is the pore volume
V_{rem}	is the removed volume
V_s	is the volume of solid
V_{s_in}	is the initial volume of solid
V_t	is the total volume
V_{SIO}	is the fracture rate due to stress-corrosion (m s^{-1})
ω	is the interfacial thickness of water

Chapter 1

Introduction

1.1 Motivation

One of the main objectives concerning the characterisation of oil reservoirs refers to the assessment of the compressibility of the reservoir formation since it significantly influences the oil production and may even generate major environmental problems. Examples are the Lake Maracaibo in Venezuela, where levees had to be built along the lake shore because the surrounded towns had sunk 10-12 m as the production of petroleum from uncemented sands reservoirs with large compressibility caused subsidence; or in the North Sea where production platforms in oilfields from chalk formations with large compressibility has resulted in subsidence as well.

Moreover, if it deals with the so-called Enhanced Oil Recovery (EOR) technologies for the oil production, such as Steam Assisted Gravity Drainage, SAGD, Cyclic Steam Stimulation, CSS, Steam flooding, SF, or Water Flooding, WF, the challenge is higher. That is because, such technologies are based on the injection of steam or hot water into the reservoir to reduce the in situ oil viscosity and, therefore, to increase oil production. Such technologies, due to the increase in temperature and the water composition, are likely to generate specific chemical and thermo-hydro-mechano-chemical processes that might not be appropriately accounted for and whose effects may affect significantly the reservoir compressibility, porosity, permeability, oil production and even bring about environmental problems caused by subsidence or jeopardise the

integrity of the wells and the surface facilities.

However, the majority of the research on oil sands studies their response from the point of view of the geomechanics behaviour (Dusseault, 1977; Agar, 1984; Kosar, 1989; Dusseault, 2001; Oldakowski, 2013), leaving aside the chemical coupled processes.

1.2 Objectives

The objective of the present research is the study of the compressibility response of a quartz sand formation (Morichal Fm.) to define a micromechanical model that accounts for the Thermo-Hydro-Mechano-Chemical behaviour considering: (i) oil production alone; and (ii) due to the phenomena generated at particulate level by the injection of steam (Enhance Oil Recovery). For that purpose the following experimental aspects are determined to be studied:

- Determination of the over consolidation ratio (OCR) of the sand formation.
- Effect of the grain size and the morphology on the compressibility at dry conditions.
- Effect of the temperature on the compressibility at dry and brine-saturated conditions.
- Effect of the temperature on the preconsolidation stress.
- Chemical effect of the water on the quartz sand solubility as a function of the temperature, pH and composition.

1.3 Scope of the thesis

The present research is part of a comprehensive feasibility study concerning EOR applications in an oilfield of heavy oil. The drilling well area lies at the easternmost end of the Orinoco Belt in Venezuela, at the Carabobo area. The reservoir is at approximately 1000 m of depth and is composed mainly of uncemented quartz sand.

In particular, this dissertation has addressed the compressibility of the reservoir (at effective stresses up to 50 MPa), at macroscopic and particulate level, as well as the phenomena that arise and the consequences on compressibility when steam is injected (at temperatures up to 300°C) into the samples. Heavy oil considerations are beyond the scope of this research.

The work has been addressed with the support of a partnership contract between the Repsol Technology Center (CTR) and the Technical University of Madrid (UPM). It has been mainly carried out at the CTR and in the Department of Continuum Mechanics and Structures, (UPM).

Also, the author spent a three-month stay at the Particulate Media Research Laboratory at the School of Civil and Environmental Engineering of the Georgia Institute of Technology (Atlanta) under the supervision of Dr J. Carlos Santamarina as a part of her research.

The vast majority of the experiments have been carried out at the facilities of the Repsol Technology Center. Some others have been conducted with the support of external laboratories. The following list summarises the laboratories involved:

- CTR, Laboratory of cement: Sand cleaning y grain size distribution.
- CTR, Laboratory of oil refining: Grain size distribution by laser.
- CTR, Pilot plants: Tests in a batch reactor.
- CTR, Laboratory of Geology: Study of fluid inclusions and SEM observation.
- CTR, Laboratory of EOR: Core-flooding tests.
- CTR, Laboratory of Petrophysics: Micro CT-scan.
- CTR, Analytical services: Chemical analysis and SEM observation.
- Geotechnical Laboratory of the University of Civil Engineering of A Coruña: Oedometric tests and grain size distribution.
- Geotechnical Laboratory, CEDEX, attached to the Public Works Ministry: Grain size distribution tests.
- Weatherford Laboratories: Aquathermolysis tests.

As the thermo-hydro-mechano-chemical coupled characterisation is a complex problem to tackle, it has been found that uncoupled tests are still valid, as they have proved their usefulness to help to weigh the significance of each contribution alone in such a complex relationships. Thus, firstly, in chapter 2, we present the geological and petrographical characterization of the sand formation under study. In chapter 3, we present the study of the effect of the temperature, pH and composition of the water on the solubility of the quartz sands by means of autoclave reactor tests for different residence times, pressures and temperatures (100, 200 and 300°C). In chapter 4, we present the study of the mechanical compressibility at dry conditions of the reservoir quartz sand by means of oedometric tests monitored with acoustic emissions. The test covered a broad range of effective stresses (0.5 to 50 MPa) and temperature (room temperature to 250°C). In addition, a novel procedure to determine the over consolidation ratio of the sand samples based on fluid inclusions within the syntaxial cement is presented. In chapter 5, we present the study of the mechano-chemical coupled behaviour of the quartz sands as a function of the temperature, stress and water composition. In that way, the possible chemical reactions caused by the injection of steam/water on the mechanical compressibility have been analysed in a coupled manner by means of saturated-brine tests performed at constant effective stress of 14 and 18 MPa, and 60 and 150°C. For a detailed observations of the samples after the tests it has been necessary to develop a novel procedure aimed at keeping their fabric. The procedure has been patented and entitled “*Fabric preservation of uncemented sand samples*”. Finally, in chapter 6 we present a numerical model implemented that accounts at a phenomenological level for pressure-solution, as it has been found that it is ultimately the main process responsible for creep strains. Conclusions and future works are summarised in chapter 7.

1.4 Terminology

A noteworthy remark refers to those expressions that, depending on whether they are used on the scope of petroleum engineering, geomechanics, soil mechanics or geological disciplines, take on a different meaning. Thus, for the sake of clarifying the two expressions below are used throughout this dissertation with the following

meanings.

A *non-consolidated material* refers to a completely different meaning in the scope of petroleum engineering and soil mechanics. Petroleum engineers define as *no consolidated* those reservoirs formed by uncemented particles. However, in the scope of geomechanics, it refers to a soil that its current in-situ stresses are the highest undergone since its deposition. Henceforth the geomechanical term is adopted.

The terms *compaction and consolidation* are used in the field of geology and soil mechanics with a slight difference in their meaning as well. Thus, according to Allen, D.R. and Chilingarian, G.V. (1975), Table 1.1, the broader geological meaning will be adopted since the definitions in soil mechanics are much narrower in the scope, so it can be easily fit into the geological or petroleum engineering field and because compaction includes consolidation as used by soils engineering.

Table 1.1 Compaction and consolidation definitions from soil mechanic and geology/petroleum engineering disciplines (after Allen, D.R., and Chilingarian, G.V., 1975).

<i>Geology-Sedimentology usage</i>	<i>Soils Engineering usage</i>
<u>Compaction</u>	
<i>A lessening of sedimentary volume owing to overburden loading, grain rearrangement, etc.</i>	<i>An increase in bulk specific weight (or bulk specific gravity) caused by mechanical or hydraulic means such as vibrating, loading or wetting.</i>
<u>Consolidation</u>	
<i>The acquisition of structural competency by sediment owing to a reduction in volume, induration, cementation, etc.</i>	<i>The lessening of the volume of a porous material (such as clay) by the expulsion of pore water upon the application of load.</i>

Chapter 2

Geological and Petrographical Characterization

2.1 Overview

The drilling well area is located at the Easternmost end of the Orinoco Belt, the Carabobo area (formerly known as Cerro Negro), highlighted in Figure 2.1. The depth of the reservoir is at about 1000 meters, in the Morichal Formation which is mostly composed of uncemented quartz sand.

Morichal sands consist of a fluvial to deltaic sequence at the base of the early Miocene Oficina Formation (Morichal Member) that constitutes the reservoir rock of The Orinoco Heavy Oil Belt field. The Belt comprises an extension of 70 km from north to South and about 650 km from East to West, following the course of the Orinoco River, and is located within the so-called Maturín Basin, a peripheral foreland basin at the northeast of Venezuela (Roure et al., 1994; Chevalier et al., 1995; Passalacqua et al., 1995; Hung, 1997).

Figure 2.1 Northeastern Venezuela map showing the location of the Orinoco Heavy Oil Belt in the Venezuela foreland basin (Yoris et al., 1997). (A-A' cross-section is shown in figure 2.2).

2.2 Maturín Basin and Orinoco Heavy Oil Belt

The Maturín Basin is located on Venezuela's continental margin and is associated with the subduction zone of the Lesser Antilles (Fig. 2.2). The earthquake records in the area indicate that the South American Plate is subducting under the Caribbean Plate (Russo et al., 1993). The collision started during the Eocene period, being most intense over the Miocene Age when the greater amount of sediments (braided, meandering and distributary channels deposits) filled the basin.

Figure 2.2 Tectonic map of northeastern Venezuela. The interaction between the oceanic Caribbean Plate and the continental South America Plate. A-A' cross-section of the subduction zone (Jácome, M.I et al., 2003. Simplified after Ysaccis and Audemard, 2000).

The downward deflection of the crust caused by the subduction of the South American plate caused the Maturín Basin development. Figure 2.3 shows a geological cross section of the basin where the oil fields and API gravity are depicted. The API gravity is used to classify oils as light, medium, heavy, or extra heavy, as is shown in table 1.1. A detailed explanation of API gravity is provided in Appendix I.

Table 2.1 Oil Classification

<i>Oil classification</i>	<i>API</i>
Light	> 31.1
Medium	22.3 - 31.1
Heavy	< 22.3
Extra Heavy	< 10.0

Even though Morichal reservoir sands are saturated at present by low-density heavy oil (1376-2592 cp) with high viscosity (typically 8.4 API), the oil was originated as light oil at the source rock, located in the deep Cretaceous Formations north of the basin. During the later Miocene, the oil probably migrated up a few thousand kilometres towards the southern margin of the basin, period during which it might have evolved to heavy oil by microbial action.

Note that the depth of the primary light oil fields are about 2-4 kilometres, whereas the heavy oil is encountered at shallow depths, less than 2 kilometres.

By the time the migrating oil filled the existing reservoir formation, the diagenetic processes could have ceased, in such a manner that only early diagenetic features developed, which is possibly the cause of the lack of cementation in the studied reservoir.

Figure 2.3 Geologic cross section of Maturin basin (adapted from Erlich and Barret, 1992).

Regarding the temperature gradient in the basin, as a result of the tectonic activity, the geothermal gradient has been found to be higher than the average value in the crust (25 °C/km). According to García Lugo (2011), the geothermal gradient in the Orinoco Heavy Oil Belt (about 32°C/km) can be estimated as follow; where D (m) is the depth, and T (°C) is the temperature. Figure 2.4 displays graphically the gradient.

$$T = 0.032 * D + 25.58 \quad (2.1)$$

Figure 2.4 Orinoco Oil Belt geothermal gradient (from García Lugo, R.A, 2011).

2.3 Petrophysical characterisation

The sand employed in this dissertation was extracted from an oil well sited in Venezuela by means of tricone drill bits, assisted by mud injection drilling, and collected in a barrel. The sand was drilled from 1000 meters deep, at the Carabobo unit, from the so-called Morichal Member of the Miocene Oficina Formation, a succession of deltaic deposits (braided, meandering and distributary channels deposits) superposed and separated by shale levels characterises the formation.

The sand deposits were originated from the erosion of the adjacent granitic and gneissic rocks of the Precambrian Guayana Shield. Hence, the mineralogical content corresponds to a quartz arenite (Fig. 2.5), with 95% of quartz, 2-3% of feldspars and 2-3% of clay minerals and mica.

Figure 2.5 Classification of sandstones (adapted from Dott 1964).

With the aim of preventing any distortion in the experimental results of the tests of this dissertation, the oil sand samples were pre-conditioned prior to test as follows: acid-washed (36 wt. % HCl), rinsed (deionised water), alcohol-washed (96 wt. % ethylic alcohols) and oven-dried. So that the tests were conducted on free oil sands.

In order to characterize the sand, we conducted eight grains size distribution by sieving which curves are shown in figure 2.6. According to these data and from a geotechnical point of view, the sand may be classified as a fine uniform sand ($C_u=2-3$) with a D_{50} from 100 to 300 μm ,

Figure 2.6 Particle size distribution of sand samples for tests (Middle Morichal).

Some particle size fractions resulting from sieving were kept separated in order to study their characteristics independently. Figure 2.7 shows 24 scanning electron microscope images taken for the different sieved sand fractions.

As it can be noted, the coarser fraction is dominated by subrounded grains whereas grains with angular shapes prevail in the finer fractions, which is more apparent from the 140 μm sieve size.

Such a feature could infer a morphology evolution due to the breakage of the coarser grains as a result of burial compaction. The evolution may be characterised by the path displayed in figure 2.8, on the sphericity-roundness chart of Krumbein and Sloss, (1957).

1.190 μm (# 16)

600 μm (# 30)

Figure 2.7 Scanning electron microscope images of Middle Morichal sand for tests.

420 μm (# 40)

210 μm (# 70)

Figure 2.7. (Cont.) Scanning electron microscope images of Morichal sand for tests.

150 μm (# 100)

105 μm (# 140)

Figure 2.7. (Cont.) Scanning electron microscope images of Morichal sand for tests.

74 μm (# 200)

53 μm (# 270)

Figure 2.7. (Cont.) Scanning electron microscope images of Morichal sand for tests.

Figure 2.8 Evolution of the roundness and sphericity by burial compaction of Morichal sand grains (sphericity-roundness chart of Krumbein and Sloss, 1950).

Careful observation by scanning electronic microscope (SEM) of these oil-free sand particles give evidence of authigenic quartz faces growth, incipient cracking and dissolution pits in concave surfaces of quartz grains, (see Figure 2.10). In addition, a detailed optical microscope petrography study of some thin sections from a frozen core (from previous studies of REPSOL, out of the scope of this work) shows syntaxial cement overgrowth as well, long and concave-convex contacts, chains of concatenated grains and broken grains, as are displayed in Figure 2.9.

All these features are characteristics of the burial diagenesis realm (mesodiagenesis) and will be dealt with in chapter 4.

Figure 2.9 Diagenetic features in a thin section of Morichal sand observed by an optical microscope.

Figure 2.10. Diagenetic features of Morichal sand particles observed by SEM.

Figure 2.10. (Cont.) Diagenetic features of Morichal sand particles observed by SEM.

Chapter 3

Thermo-Hydro-Chemical Characterization

3.1 Introduction

The so-called Enhanced Oil Recovery (EOR) technologies, such as Steam Assisted Gravity Drainage (SAGD), Cyclic Steam Stimulation (CSS), Steam flooding (SF) or Water Flooding (WF), are based on the injection of steam or hot water into the reservoir to reduce the in situ oil viscosity and, therefore, to increase the oil production. However, such technologies are likely to trigger some chemical processes that might not be appropriately accounted for, such as chemical reactions on the quartz sand surface.

In addition, the effect of the high increment of temperature and the water composition, along with the high effective stresses within reservoir may lead to complex coupled phenomena such as stress-corrosion and pressure solution that ultimately may affect the compressibility of the reservoir (see chapter 5), and in which the kinetic reactions of quartz (dissolution and precipitation) play a crucial role.

It is in this context that the coupled effect of temperature and water composition on the quartz reservoir sands has been studied in the current research to gain insight on the kinetic reactions of quartz.

3.2 Quartz solubility

Although quartz is considered one of the most stable minerals at ambient temperature its solubility and dissolution rate strongly depends upon the temperature, pH, and water composition (examples are geothermal brines).

Thus, over the last 50 years, both experimental and theoretical studies on the characterisation of quartz surface chemistry and reactivity in aqueous solutions have been carried out for a better understanding of the factors that control the kinetics of the dissolution, which has been found to be due to changes in superficial charge and interfacial reactions.

- *Structure of quartz surface*

The structure of the α -quartz (natural quartz which structure is stable up to 573°C) consists of silicon atoms in tetrahedral coordination surrounded by four oxygen atoms, (Fig. 3.1).

Figure 3.1 Structure of α -quartz.

It has a relatively simple surface chemistry that concludes with superficial oxygen atoms, as is shown in Figure 3.2, with a site density in the surface of about 8 sites/nm², which depends on the type of crystal plane developed (de Leeuw et al., 1999).

Figure 3.2 Surface of α - α quartz.

- *Surface complexes at the quartz-water interface*

It is broadly agreed that the breakdown of SiO_2 surface came from nucleophilic attack (by H_2O or OH^-) of the solvent according to the general first-order reactions 3.1 and 3.2.

- Silica interaction with molecular water:

- Silica interaction with ionized water or hydroxide group:

A nucleophile is a chemical species that donates an electron pair to an electrophile to form a chemical bond in relation to a reaction; where the electrophile is a reagent attracted to electrons. It should be noted that the water molecule is a weak nucleophile compared to the more aggressive charged hydroxide (Casey et al., 1990). In addition, a water molecule is characterised by strong dipolar behaviour owing to the electronegative and electropositive character of oxygen and hydrogen ions. Thus, the variable interlayer charge modifies the properties of near-surface water which may be related to the reactivity of quartz surface structures and, therefore, to the kinetics of dissolution (Dove, 1994).

Neutral silanol groups $>\text{SiOH}$ are the primary superficial species responsible for the superficial electric charge and the dissolution behaviour in aqueous solutions, which

are formed by the neutralisation of the superficial oxygens by the adsorption of a proton, Figure 3.3.

Figure 3.3 Silanol group at α -quartz surface.

In the absence of cations, these groups may undergo protonation (proton adsorption) or deprotonation (hydrolysis) in acid or basic solutions, respectively. As a result, the following acid-basic complex reactions occur.

Additionally, in aqueous alkali solution, the surface complexes generated incorporate the existing cation, (eq. 3.5), so the distribution of the surface complexes would describe an average electronic state resulting from proton, cation and hydroxyl ion interaction with the undersaturated oxygens at the mineral surface (Prigogine and Fripiat, 1974).

Consequently, the kinetics of quartz dissolution is dependent upon the formation of acid-base surface complex and the interaction of the solvent with these complexes.

- Effect of the temperature on the kinetics of quartz dissolution

Several experiments have been conducted in deionised water to determine the effect of temperature on silica dissolution (Keenan et al., 1969, Fournier y Potter, 1982b; Rimstidt and Barnes, 1980; Tester et al., 1994; Rimstidt, 1997).

The results proved that the solubility rises exponentially with temperature: the equilibrium concentration is approximately 6 ppm at room temperature and reaches a maximum value of about 700 ppm at 340°C (Rimstidt and Barnes, 1980), see Figure 3.4.

Table 3.1 shows the results obtained by Fournier and Potter (1982b) where enthalpy values for saturated vapour obtained previously by Keenan et al. (1969) are included.

Table 3.1 Temperature, enthalpy (from Keenan et al., 1969) and quartz solubility (From Fournier and Potter, 1982b).

No.	T °C	H J/g	SiO ₂ mg/kg	No.	T °C	H J/g	SiO ₂ mg/kg	No.	T °C	H J/g	SiO ₂ mg/kg
1.	20	84.0	6.1	18.	190	807.6	230.1	35.	360	1760.5	707.7
2.	30	125.8	8.1	19.	200	852.5	263.0	36.	370	1890.5	573.0
3.	40	167.6	10.7	20.	210	897.8	298.5	37.	374	2099.3	299.6
4.	50	209.3	14.0	21.	220	943.6	336.4	38.	370	2332.1	125.0
5.	60	251.1	18.2	22.	230	990.1	376.4	39.	360	2481.0	60.4
6.	70	293.0	23.5	23.	240	1037.3	418.3	40.	350	2536.9	35.4
7.	80	334.9	30.0	24.	250	1085.4	461.8	41.	340	2622.0	22.1
8.	90	376.9	37.9	25.	260	1134.4	506.2	42.	330	2665.9	14.1
9.	100	419.0	47.4	26.	270	1184.5	551.0	43.	320	2700.1	9.2
10.	110	461.3	58.6	27.	280	1236.0	595.3	44.	310	2727.3	6.0
11.	120	503.7	71.8	28.	290	1289.1	638.2	45.	300	2749.0	3.9
12.	130	546.3	87.1	29.	300	1344.0	678.4	46.	290	2766.2	2.5
13.	140	589.1	104.7	30.	310	1404.3	714.2	47.	280	2779.6	1.6
14.	150	632.2	124.6	31.	320	1461.5	743.6	48.	270	2789.7	1.0
15.	160	675.6	147.1	32.	330	1525.3	763.6	49.	260	2796.9	0.6
16.	170	719.2	172.1	33.	340	1594.2	770.1	50.	250	2801.5	0.4
17.	180	763.2	199.8	34.	350	1670.6	756.2	51.	240	2803.8	0.2

Figure 3.4 Solubility of quartz (concentration, ppm SiO₂) in deionised water at saturated solution vapour pressure as a function of temperature (From Rimstidt, 1997).

- *Composition of the solute on the kinetics of quartz dissolution*

The composition of the aqueous solutions has a strong influence on the water molecules and hydroxide ions distribution at the quartz-water interface. Therefore, many studies have focused on the effect of alkali cations in solution (Dienert and Wandenbulcke, 1923; Sasaki, 1952; Van Lier et al., 1960; Weigel, 1964; Kamiya and Shimokata, 1976; Bennet, 1991; Dove and Crerar, 1990; Dove and Nix, 1997), giving as a result that the interactions of the silica with alkali cations increase the silica dissolution rate constant, causing a significant silica concentration in solutions at high temperatures waters (Keenan et al., 1969; Gallei and Parks, 1972; DeJong and Brown, 1980; Fournier y Potter, 1982; Geerlings et al, 1984; Mortier et al, 1984; Fisk and Michalske, 1985; Foley, 1986; Dove and Rimstidt, 1994; Du et al 1995; Rimstidt 1997; Dove and Nix, 1997). That is because the alkali cations, attracted by the negative charge of the quartz, promote enlarged zones of adsorption (Fig. 3.5) that improve the accessibility of the water to the quartz surface, (Dove et Crerar, 1990; Dove and Nix,

1997), and in turn, to the dissolution rate constant increases.

The reaction rate would be directly proportional to the number of sites and the frequency at which the cations are adsorbed onto these sites, increasing the accessibility of water molecules (Dove and Crerar, 1990).

Figure 3.5 Optimized bond lengths and angles for static molecular models in absence or presence of sodium (Gibbs et al., 1987; Gibbs, pers.comm.).

In this regard, Ba, Ca-Na, Mg, K, Na, and Li cations have proven to be the most influencing cations on quartz dissolution rate (Dove and Nix, 1997; Dove, 1999). Figure 3.6 shows the significance of this effect as a function of temperature.

Figure 3.6 Arrhenius diagram showing the temperature dependence of quartz rates in alkali water (from Dove et al., 1990).

In the case of aqueous solutions with mixed cations, the dissolution rate is governed exclusively by the cations with higher adsorption coefficient, irrespective of their dissolution rate constants.

Table 3.2 summarises the main physical properties of the most common cations on natural waters obtained under 200°C and neutral pH (Dove, 1999).

As can be noted, magnesium ion has the closest rate-regulating control (due to its higher adsorption coefficient) among the common solutes found in natural waters, followed by Ca, Ba, Na, and K.

Table 3.2 Physical properties for dissolution of quartz of the most abundant cations on natural waters at 200°C and neutral pH (from Dove, 1999).

<i>Cation</i>	<i>dissolution rate constant</i>		<i>Adsorption Coefficient</i>	
	$k_i^+ \text{ (mol/m}^2\text{s)}$		$k_{ad} \text{ (molal}^{-1}\text{)}$	
<i>Mg</i>	$10^{-6.85 \pm 0.2}$	(1.41x10 ⁻⁷)	$10^{3.7 \pm 0.3}$	(5011,87)
<i>Ca</i>	$10^{-6.35 \pm 0.2}$	(4.47x10 ⁻⁷)	$10^{3.35 \pm 0.3}$	(2238,72)
<i>Ba</i>	$10^{-6.05 \pm 0.2}$	(8.91x10 ⁻⁷)	$10^{2.68 \pm 0.3}$	(478,63)
<i>Na</i>	$10^{-6.28 \pm 0.1}$	(5.25x10 ⁻⁷)	$10^{1.78 \pm 0.2}$	(60,26)
<i>K</i>	$10^{-6.28 \pm 0.1}$	(5.25x10 ⁻⁷)	$10^{1.78 \pm 0.2}$	(60,26)

As a result, the reaction rate in a solution with mixed cations is proportional to the population of the alkali cations at the surface of quartz and their corresponding adsorption constant, $K_{ad,i}$. Consequently, the reaction rate, r , may be obtained by the expression 3.6 (Dove, 1999).

$$r = k_i^+ \theta_i + k_{ii}^+ \theta_{ii} \quad (3.6)$$

where k_i^+ and k_{ii}^+ are the dissolution constants for the quartz dissolutions in an aqueous mixed cations solution, and θ_i and θ_{ii} are the fractions of the total sites affected by each cation as $>\text{SiO-cation}_i$ and $>\text{SiO-cation}_{ii}$ (for example: $\theta_{>\text{SiO-Na}^+}$ and $\theta_{>\text{SiO-Ca}^{2+}}$) and can be obtained from the expressions 3.7, (Dove 1990).

$$\theta_i = \frac{K_{ad,i} m_i}{1 + K_{ad,i} m_i + K_{ad,ii} m_{ii}} \quad ; \quad \theta_{ii} = \frac{K_{ad,ii} m_{ii}}{1 + K_{ad,ii} m_{ii} + K_{ad,i} m_i} \quad (3.7)$$

where m_i and m_{ii} are the molal concentration of the deemed cations.

- *Effect of pH on the kinetics of quartz dissolution*

Numerous studies have been developed to study the effect of the pH on Kinetics of quartz dissolution (Bauman, 1955; Weigel, 1964; Schwartzentruber et al., 1987; Knauss and Wolery, 1988; Brandy and Walther, 1990; House and Orr, 1992; House and Hickenbotham, 1992). It has been found that the pH in the aqueous solution governs the way that the water molecules are oriented toward the quartz surface. Hence, silanol groups can interact with water either by electrostatic water orientations (high pH) or by hydrogen bonds (low pH).

At high pH (basic solutions), the silanol groups can be negatively charged by the deprotonation in water with a sufficiently low proton concentration, Figure 3.7. The negative surface charge produces a strong electric field in the vicinity of the surface that orient several monolayers of interfacial water molecules with their dipolar moment facing to the quartz surface (Du et al., 1994).

Thus, the increment of the susceptibility of the Si-O-Si bonds reaction with OH^- is attributed to the proton orientation toward the oxygen bonds (Dove and Rimstidt, 1994) due to their negative charge (DeJong and Brown, 1980; Geerlings et al., 1984; Foley, 1986). Experimental studies show that the oxygen bonds on the quartz surface are prone to absorb water molecules so that the solubility increase (Gallei and Parks, 1972; Mortier et al., 1984; Fisk and Michalske, 1985).

Figure 3.7 Quartz-water interface at high pH (from Dove, 1994).

On the contrary, at low pH (acid solutions), the quartz surface is neutral. Therefore the interfacial molecules of water tend to form hydrogen bonds with their oxygen facing the quartz surface, as shown in Figure 3.8, opposite to the orientation expected for the high pH. Consequently, the interfacial zone presents abundant water that has weak nucleophiles properties and a limited corrosive effect (Du et al., 1994). As a result, the dissolution rate is low, and the quartz dissolution is limited by slow reactions with slightly weak nucleophilic molecular water (Dove, 1994).

Figure 3.8 Quartz-water interface at low pH (from Dove, 1994).

At intermediate pH, quartz surface is partially ionised, so interfacial water molecules reduce its ordering, creating either hydrogen bonds or oxygen oriented to quartz surface (Du et al., 1994). In this case, alkali cations play a crucial indirect role, as they increase the dissolution rates by the enlargement of the absorption zone what promote the dissolution mechanism by hydroxyl ion, Figure 3.9. It is worth highlighting that the water employed for conducting the tests in this dissertation has this pH.

Figure 3.9 Quartz-water interface at intermediate pH (from Dove, 1994).

3.3 Aquathermolysis tests

Aquathermolysis test is an experiment designed to determine the physico-chemical reactions between the crude and the steam at high temperatures. The tests have focused on simulating the effect of the steam injection on the reservoir to assess the reduction of oil viscosity and the production CO_2 and H_2S . In this regard, sand samples with water/crude ratio equivalent to that into the reservoir were subjected to 275°C for a month. Table 3.3 summarises the conditions in the tests, and Figure 3.10 depicts a scheme of the tests.

Table 3.3 Aquathermolysis tests conditions. $275^\circ\text{C} - 30$ days.

	<i>Test 1</i>		<i>Test 2</i>	
	<i>Reactor 1</i>	<i>Reactor 2</i>	<i>Reactor 1</i>	<i>Reactor 2</i>
<i>Total volume test (cc)</i>	500	500	500	500
<i>Crude (gr)</i>	55	55	100	100
<i>Distillated water (gr)</i>	33.6	33.6	87.4	87.4
<i>Brine (gr)</i>	21.4	21.4	12.6	12.6
<i>Quartz Sand core volume (cc)</i>	170	170	100	100

Figure 3.10 Aquathermolysis test scheme.

It should be noted that the sand particles are embedded in a mixture of oil, brine and distilled water. Besides, the generation of H_2S during the tests yield to an acid environment.

The particles of sand have been observed after the tests by scanning electronic microscope (SEM). Evidence of the effect of dissolution, as a result of the temperature and water-oil presence, have been found. The particles of sand are strongly affected by dissolution irrespective of the presence of heavy oil or acid pH.

The effect of the dissolution seems to be more significant on the syntaxial overgrowth cement than on the detrital grains itself.

Figure 3.11 shows six SEM images of the corrosion features observed after the aquatermolysis tests at the surface of the quartz sand in comparison with equivalent original grains.

These results represent a reliable probe of the possible dissolution phenomena in the reservoir sand during enhanced oil recovery by steam or hot water injection.

Original Samples

Post-test Samples

Figure 3.11 Pre and post-aquathermolysis tests SEM images of quartz sand particles.

3.4 Reactor tests

On the basis of the quartz solubility phenomena aforementioned, 6 reactor tests have been designed to study the effect of the temperature, the resident time and the solvent state (steam or hot water/brine) on the solubility of the quartz sand and derived processes.

In this regard, with the aim of assessing this phenomenon, synthetic water with the same reservoir composition and pH was prepared.

3.4.1 Experimental Methods and Material

The tests have been carried out in an autoclave reactor in a pilot plant at the Repsol Technology Center.

A series of tests for the solubility study were performed submerging reservoir quartz sand (free of oil and impurities, described on chapter 2) into the synthetic water with an equivalent reservoir composition (see Table 3.4) and pH, 7.7.

Since the composition contains a high concentration of salts, it will be henceforth termed brine.

Table 3.4 Water composition for tests (considering mg/kg = mg/L).

<i>Anions</i>	<i>mg/kg</i>	<i>Cations</i>	<i>mg/kg</i>
HCO ₃ ⁻	1797,90	Na ⁺	11295
CO ₃ ²⁻	2,13	K ⁺	223,8
SO ₄ ²⁻	4	Mg ²⁺	238,5
Cl ⁻	20034,30	Ca ²⁺	837,5
F ⁻	-	Sr ²⁺	0
OH ⁻	-	Ba ²⁺	4,650
NO ₃ ⁻	1,6	Fe ²⁺	0

The tests have been carried out at different temperatures, residence times (duration of the tests) and solvent states. Table 3.5 summarises the conditions of the tests.

Table 3.5 Experimental conditions of the reactor tests.

<i>Test</i>	<i>Temperature (°C)</i>	<i>Resident time (days)</i>	<i>Solvent state</i>
1	200	22	100 % liquid phase
2	200	8	50% liquid+ 50 % vapour
3	200	4	100 % liquid phase
4	300	4	50% liquid+ 50 % vapour
5	300	4	50% liquid+ 50 % vapour
6	100	4	100 % liquid phase

In addition to the cleaning procedure of the sand described on chapter 2 and due to the presence of a certain amount of calcium (from the drilling mud) in the finer fractions, the sand was re-washed by dichloromethane and hydrochloric acid solution to prevent any likelihood of disturbance in the results. Figure 3.12 shows six SEM images of the sand after the re-washing procedure.

The calcium concentrations before and after the re-washing procedure have been checked by micro-X-Ray Fluorescence (see figures 3.13 and 3.14).

As can be noted, the calcium content after the re-washing processes is negligible.

Figure 3.12 SEM images showing sands particle after the re-washing procedure.

Figure 3.13 Micro-X-Ray Fluorescence images and composition of the sand samples after hydrochloric acid, water, and ethylic alcohol washing procedure.

Figure 3.14 Micro-X-Ray Fluorescence images and composition of the sand after the dichloromethane re-washing procedure.

- *Tests procedure*

The autoclave reactor consists of a 400 ml stainless steel-316 vessel with a magnetic stirrer, an inlet of Nitrogen (N_2) controlled by a pressure reducer on the top lid, two manual valves to charge and vent the system, a connection to discharge the liquid on the bottom and mechanical safety elements (a 60-bar rupture disc and a 50-bar pressure safety valve, PSV). Figure 3.15 depicts a simple layout. An external jacket controlled by thermocouples heats the system.

Figure 3.15 Reactor system scheme.

In order not to damage the sand particles during the stirring of the fluid, it was decided to install a 43-micron mesh catalytic basket to house the sand particles. Its design guarantees the solution circulation through the mesh and within the particles, as shown in Figure 3.16.

Figure 3.16 Catalytic basket.

Nitrogen was injected through the connection on the top of the reactor to reach the target liquid pressure established for each test. Most of the experiments were run at pressures above the saturation vapour pressure of the brine so that the fluid remained in the liquid phase.

Three tests below vapour pressure were developed, so two phases, steam and fluid brine, coexisted during the tests, (see Table 3.4). These tests were planned with the purpose of assessing the effect of biphasic dissolution that may coexist during the steam injection and its further condensation.

The reactor vessel was filled with 230cc (100°C tests) or 120cc (in this case for the 200 and 300°C tests) of brine. Approximately 2 grams of the reservoir sand free of the oil and the impurities were placed into the catalytic sampler which was assembled to the stirrer of the reactor, as is shown in the layout of Figure 3.17.

The system was pressurised with N_2 , and then both, the agitation and a heating ramp up to the operational temperature were started. The testing timing starts once the target temperature is reached.

Figure 3.17 Autoclave reactor.

- Brine collected from an external sampler

The resulting brine of the experiment named as test 1 was collected on an external sampler previously filled with 1380cc of deionised water with the purpose of diluting the expected extent of silica in dissolution and prevent any precipitation.

Once the test was complete, the connection from the reactor to the external sampler was heated up to the testing temperature to prevent silica precipitation during the discharge. Finally, when the discharge was finished, the sampler was disconnected from the reactor, and both reactor and sampler were left to cool down at room temperature up to 45 °C.

As a consequence of the shape of the connection between the external sampler and the reactor, the total water recovering failed, and just a partial amount of the tested water was discharged correctly (nearly half). Therefore, it was decided to use the reactor itself as the sampler for the subsequent tests.

Figure 3.18 Autoclave reactor system with the external sampler.

- Tests 2 to 6

Tests 2 to 6 have been carried out following the same procedure as test 1 but by the use of the reactor as the sampler itself to prevent any problem on the recovery of the brine. Once the tests were completed, the reactor was left to cool down to 40°C and the resulting brine and precipitates were analysed.

3.4.2 Material Precipitated Over the sand sampler

After testing, the catalytic sampler mesh became clogged and covered by a brownish muddy substance. Figure 3.19 displays some detailed SEM images.

Figure 3.19 SEM images of the catalytic sand sampler mesh after tests and sampler.

The analysis of the composition reveals that the precipitated substance is free of Fe, Ni or Cr, being its main constituents silica and carbonate, see Figure 3.20. That fact leads to believe that the precipitated material is a by-product of the reaction between silica and brine, while no interaction is observed with the reactor.

Figure 3.20 Chemical composition of the substance precipitated on the basket mesh after testing.

3.4.3 Material Precipitated Inside of the sand sampler

The residual sand after testing shows some sand grains covered by needles-like precipitates or even by a crust of needles, (see Fig. 3.21). The main components are silicon, magnesium, and calcium with a low concentration of iron, nickel, and zinc which are assumed to come from the reactor itself, (see Table 3.6).

Figure 3.21 Resulting sand inside the sand sampler after the test.

Table 3.6 Experimental conditions of the reactor tests.

	<i>P-1</i>	<i>P-2</i>	<i>P-3</i>	<i>P-4</i>
	% atom	% atom	% atom	% atom
<i>C</i>	22.21	23.51	40.14	19.11
<i>O</i>	53.96	51.40	41.89	63.11
<i>Na</i>	-	-	2.71	0.91
<i>Mg</i>	8.73	6.88	2.40	0.59
<i>Al</i>	0.22	0.23	0.08	-
<i>Cl</i>	-	-	3.32	0.76
<i>Si</i>	11.87	9.75	3.91	13.71
<i>Ca</i>	1.37	1.08	5.44	1.75
<i>Mn</i>	0.08	-	-	-
<i>Fe</i>	1.35	1.03	0.07	0.05
<i>Ni</i>	0.11	0.12	-	-
<i>Zn</i>	0.09	-	-	-

3.4.4 Material Precipitated Outside the sand sampler

The brine from the reactor exhibited after testing a certain amount of white silica gel floating (silica re-precipitated) and small solid particles (as sandy-like precipitates) at the bottom of the vessel, Figure 3.22.

Figure 3.22 Silica gel and solid particles precipitated on the reactor water after the tests.

The precipitated particles on the water after testing had a macroscopic sandy-like aspect that in the microscopic observation reveals features related with rapid precipitation, such as a lack of homogeneity, botryoidal textures and a wide range of particle sizes up to about 400 μm , see Figure 3.23.

These characteristics along with their chemical composition based on a mixture of magnesium, calcium silicates, calcium carbonate, sodium salts, iron, nickel, and chromium, suggest that these particles might be caused by the interaction among the brine, the silica sand, and the reactor, resulting in a crust on the reactor wall. As a consequence, the crust could have trapped some of these metallic elements during the precipitation. Table 3.7 summarises the chemical composition obtained from four samples analysed.

Table 3.7 Experimental conditions of the reactor tests.

	<i>P-1</i>	<i>P-2</i>	<i>P-3</i>	<i>P-4</i>
	% atom	% atom	% atom	% atom
<i>C</i>	45.83	50.32	48.74	58.85
<i>O</i>	41.66	39.02	40.30	21.08
<i>Mg</i>	4.33	1.80	4.05	-
<i>Si</i>	5.28	2.77	5.36	4.09
<i>Ca</i>	0.69	3.18	0.44	4
<i>Fe</i>	1.26	0.74	0.67	3.98
<i>Ni</i>	0.49	0.73	-	1.24
<i>Ge</i>	0.47	0.35	0.45	2.06
<i>Cr</i>	-	-	-	1.41
<i>Bo</i>	-	-	-	3.3

Figure 3.23 Precipitated particles in water after the tests.

Figure 3.23 (Cont.). Precipitated particles in water after the tests.

3.5 Determination of the silica concentration

The amount of silica and particles precipitated (on the reactor and catalytic basket) in the brine after testing has been determined by ICP-OES technique (Inductively Coupled Plasma - Optical Emission Spectroscopy), quantified by the method of standard additions. The determination of silica concentration requires following the succeeding process.

Firstly, the brine was evaporated in a platinum capsule. Then, the solid residue is fused to dissolve the silicon by a mixture of lithium tetraborate and lithium fluoride (Spectraflux 120 A, 1.5 grams) at 950°C for 15 minutes; the resulting paste is dissolved afterwards by tartaric and hydrochloric acid. Finally, the reactor and the catalytic basket are cleaned in an ultrapure-water ultrasounds bath for 10 minutes. Additionally, the reactor was cleaned with a water solution with a NaOH 0.2M concentration. Then, both the ultrapure-water and the sodium hydroxide solution from the cleaning processes were also analysed following the same procedure aforementioned. The concentrations obtained are listed in tables 3.6 and 3.7.

The usefulness of the cleaning procedure by the method mentioned above was checked by a SEM observation of the mesh of the catalytic basket after the cleaning procedure. As it can be observed in the images shown in Figure 3.24, the sandy-like material that previously clogged the mesh was adequately removed.

Figure 3.24 Catalytic basket mesh after the cleaning process by NaOH 0.2M.

Table 3.8 Silica concentration after the reactor tests.

<i>Test</i>	<i>Test Conditions</i>	<i>Si mg</i>	<i>Si ppm</i>	<i>SiO₂ ppm</i>	<i>Comments</i>
1	200°C 22 days	8	69	149	Just only 37 ml of water from the reactor were recovered in the sampler. It is not possible to determine the whole of silica in solution
2	200°C 8 days	23	193	412	50% liquid+ 50 % vapour
3	200°C 4 days	50	413	884	100 % liquid phase
4	300°C 4 days	41	339	724	50% liquid+ 50 % vapour
5	300°C 4 days	50	419	896	50% liquid+ 50 % vapour
6	100°C 4 days	15	122	262	100 % liquid phase

Table 3.9 Silica concentration after reactor tests related to the active phase.

<i>Temperature</i>	<i>Liquid Phase</i>		<i>Biphasic</i>	
	<i>SiO₂ concentration (ppm)</i>	<i>Loss of sand (SiO₂) over initial mass (%)</i>	<i>SiO₂ concentration (ppm)</i>	<i>Loss of sand (SiO₂) over initial mass (%)</i>
100°C	262	2,1	No data	-
200°C	890	7,1	415	3,3
300°C	No data	-	724-896	5,8-7,2

3.6 Results

It has been found that the silica solubility is strongly dependent on the temperature, water composition and solvent phases existing in the tests. Figure 3.25 plots the results obtained with the reactor tests as well as the one for distilled water in liquid phase reported by Fournier and Potter 1982, and J. D. Rimstidt, 1997. As can be noted, the amount of silica dissolved in the tests conducted by the use of the reservoir brine is considerably higher than the one reported in the literature for distilled water. Hence, in distilled water, the solubility of the silica reaches a maximum value at 300°C of about 700 ppm whereas, in the reservoir water, the concentration is sharply increased due to the cation content up to a value of about 900 ppm at just 200°C. In the case of the tests conducted at a vapour saturation of roughly 50%, the values obtained of the solubility of the silica are lower but, in any case, higher than the ones obtained for distilled water.

Figure 3.25 Silica solubility.

Finally, the quartz dissolution rate constant for the studied conditions (water composition, pH and temperature) has been estimated at around 2.2×10^{-7} (mol/m² s). Table 3.10 shows the parameters for the determination on that value.

Table 3.10 Determination of the dissolution rate constant for the predominant cations in the reservoir water.

	Mg	Ca	Ba	Na	K
concentration of ion (mg/L) (from table 3.4)	238,5	837,5	4,65	11295	223,8
Peso molecular	24,305	40,078	137,34	22,989	39,098
concentration of ion (molal)	0,009812796	0,02089675	3,3858E-05	0,49132194	0,00572408
dissolution rate constant (k_i^+) (mol/m ² s) (from Table 3.2,Dove 1999)	1,41254E-07	4,4668E-07	8,9125E-07	5,6234E-07	5,6234E-07
Equilibrium adsorption coefficient (K_{ad}) (molal ⁻¹)	5011,87	2238,72	478,63	60,25	60,25
Fraction sites as >SiO-ión (from equation 3.7)	0,387465498	0,36856921	0,00012767	0,23324183	0,00271735
Reaction rate for the reservoir water (mol/m ² s) (from equation 3.6)	2,19365E-07				

Although the magnesium exhibits the highest coefficient of adsorption for the reactive cations in the water of the reservoir, the dissolution rate constant will be controlled by the reactivity of those cations with higher concentration, i.e. the calcium and the sodium.

3.7 Conclusions

The reactor tests developed at 100, 200 and 300°C have shown the significance of the thermo-hydro-chemical effect of the water composition, the temperature and the fluid state (liquid or biphasic) on the quartz sand solubility.

Once the reactor, the catalytic basket and the brine cooled down, some sandy-like material were observed as a result of the reprecipitation of the silica dissolved.

The silica concentration has been determined by ICP-OES technique (Inductively Coupled Plasma - Optical Emission Spectroscopy) and quantified by the method of standard additions. Table 3.8, 3.9 and Figure 3.25 show the amount of silica obtained, which increase sharply with the temperature.

The effect of the water composition is noteworthy. Thus, the silica concentrations in the tests conducted by the use of the reservoir brine are considerably higher (about 900 ppm at just 200°C) than the one reported in the literature for distilled water (700 ppm at 300°C). In addition, the tests conducted at a vapour saturation of roughly 50%, the values obtained of the solubility of the silica are lower but, in any case, higher than the ones obtained for distilled water.

Finally, the quartz dissolution rate constant for the studied conditions has been estimated at around 2.2×10^{-7} (mol/m² s). Table 3.10 shows that, in this case, the dissolution rate constant is controlled by the reactivity of those cations with higher concentration, i.e. the calcium and the sodium, 837.5 and 11295 mg/L respectively.

Both, the silica concentration and the dissolution rate constant are necessary input data for the phenomenological numerical model implemented and described in Chapter 6.

Chapter 4

Geomechanical Characterization

4.1 Introduction

The effect of temperature on grain crushing and the subsequent strain response of soils subjected to high stresses is an issue that deserves a profound insight. Unlike conventional geotechnics, some emerging problems in geotechnology must deal with the concurrence of high stresses and temperatures. Examples of such problems are thermal oil recovery, long-term isolation of CO₂, the storage of radioactive wastes and unconventional foundations or structures.

There are a significant number of studies focused either on quartz sand compressibility or on crushing of single particles. Initial void ratio, grain shape and size are considered as the key factors to understand the compressibility of sand (Roberts and De Souza, 1958; Lee and Farhoomand, 1967; Vesic and Clough, 1968; Miura and Yamanouchi, 1975; Hardin, 1985; Coop and Lee, 1993; Hagerty et al.1993; Yamamuro et al., 1996; Lade et al., 1996; McDowell and Bolton 1998; Nakata et al., 1999, 2001a, 2001b). At high stresses there is a certain stress level beyond the oedometric curve exhibits a significant slope change, which would denote an increase in the compressibility trend related with the onset of particle crushing (Coop and Lee, 1993; Miura and Yamanouchi, 1975; Lo and Roy, 1973, Vesic and Cough, 1968; Lee and See,

1967; Bishop et al., 1965). Likewise, fast-loading compaction tests are proven to generate intense crushing irrespective of the stress level (Borg et al., 1960; Zhang et al., 1990; Menendez et al., 1996; Chuhan et al., 2002; Karner et al., 2003, 2005).

Hence, 33 oedometric tests at dry conditions and a wide range of temperatures (from 25 to 250°C) have been carried out in this research. The micro and macromechanical response derived from these results are described and analysed in this chapter.

In addition, as the maximum overburden stress undergone by the reservoir (*preconsolidation stress*) has an extraordinary effect on production, a novel method to determine its overconsolidation ratio has also been developed in this research.

It is worth to underlining (from the mechanical point of view) that one of the main features of heavy oil sands is that the sand grains are uncemented and the oil only works as a binder element. Therefore, undisturbed heavy oil sand samples are somewhat difficult to obtain mainly due to the oil expansion caused by gas exsolution when the cores are extracted up to the surface. Additionally, the core handling, transport and oil removal cause changes in their original properties that may yield major scatter in their deformability and compressibility characterisation.

Figure 4.1 plots several proposals of relationships between Young's Modulus and the effective confining pressure. It can be inferred from this figure the poor agreement among the authors. Error connected to soil disturbance might have well played a part on it.

Figure 4.1 Young Modulus versus confining effective stress (from Oldakowski, 2013).

Likewise, the compressibility values given for the Orinoco Belt and Athabasca Heavy Oilsands, displayed in Figure 4.2, present also a remarkable scattering.

Figure 4.2 Orinoco Oil Belt and Athabasca Oil sand compressibility values from different authors.

Given the above, it becomes apparent that the deformational characterisation based on the extraction and core preservation has to be handled with care. Otherwise, it may lead to an overestimation or underestimation of the deformational properties of reservoir rocks.

It is therefore that as the OCR, grain morphology, grain size distribution and porosity presumably are the most influential factors on the compressibility of oil sands, a series of oedometric tests have been carried out to assess their relative effect on its compressibility.

The results are described below.

4.2 Determination of the reservoir preconsolidation stress (OCR)

One of the main goals concerning the characterisation of reservoirs refers to the assessment of the compressibility of the formation since it significantly influences oil production. Generally speaking, reservoirs undergo pressure depletion due to the extraction of the fluid in its pores that ultimately may cause the pore volume to decrease. The reservoir compressibility behaviour during production, considering merely a mechanical point of view, is strongly dependent on the maximum overburden stress (preconsolidation stress) and consequently, on its overconsolidation ratio (OCR). The so-called overconsolidation ratio refers to the relationship between the in situ effective vertical stress ($\sigma_{ef_current}$) and the maximum one (σ_{ef_max}) reached during its geologic history, equation 4.1.

$$OCR = \frac{\sigma_{ef_max}}{\sigma_{ef_current}} \quad (4.1)$$

The term overconsolidated reservoir relates to those reservoirs that have experienced higher vertical effective stress than the current one at a given depth and its OCR is characterised by a value higher than 1. On the contrary, a reservoir whose in situ effective stress is the maximum throughout its geologic history is termed normally consolidated, and its OCR equals to 1.

The role of the overconsolidation ratio in the compressibility of the reservoir can be illustrated by means of an oedometric curve. Thus, Figure 4.3 depicts a common oedometric curve with two points, A and B, which represent different in-situ stress state of a hypothetical reservoir. Both scenarios sustain the same vertical effective stress but with different void ratios as a result of their geologic history. The reservoir at the stress level represented by the point A reached this state merely by burial whereas the reservoir represented by the point B did it by burial and subsequent uplift or surface erosion, so a preconsolidation stress was reached sometime in the past.

Therefore, the point A is plotted on the so-called normal virgin line which represents a normally consolidated material, and the point B is plotted on the so-called unload-load curve which represents an overconsolidated material.

It is worth noting that the expected compressibility of the reservoir for both scenarios would be distinctly different. In the case of the scenario represented by point A (normally consolidated, $OCR=1$), a significant value of compression would be expected during production as a result of the reduction of the pore pressure. However, in the case of point B, the reservoir compression might be negligible, as compared with point A, until it reaches its preconsolidation stress (the maximum stress that it has sustained in the past).

In practice, the OCR of the reservoir entails major consequences not only concerning production but to environmental issues as well. A normally consolidated reservoir (point A), stores a certain amount of “pseudo-elastic” energy that contributes to the oil recovery, the so-called compaction drive energy. However, due to the compressibility of the reservoir, an intensive production over time is likely to cause extensive land surface subsidence, and therefore, environmental consequences that have to be considered.

Conversely, for heavily overconsolidated sand reservoirs (point B) neither subsidence nor drive energy would be expected, unless its effective stress increases clearly over its preconsolidation stress.

Subsequently, the preconsolidation stress will determine the maximum overburden stress that the reservoir may undergo without porosity change.

Figure 4.3 Settlement associated with the reservoir consolidation behaviour. Point A represents a normally consolidated reservoir and the point B represents a reservoir overconsolidated.

As a result, the preconsolidation stress and overconsolidation ratio knowledge play an essential role for a close estimation of the reservoir compressibility behaviour. However, the preconsolidation stress, or maximum vertical effective stress undergone by the reservoir, cannot be directly measured and it has to be estimated indirectly. In the case of the Orinoco Heavy Oil Belt, an OCR in the range of 1.3-1.5 is proposed as a consequence of the judgement of superficial erosion, equivalent to about 275-460 metres (Dusseault, 2001; Treballe et al., 1993). Under these conditions, the effective stress increment to reach the preconsolidation stress and, consequently, necessary to count with drive compressibility would be about 4-5 MPa, what would take place when an accumulated production of about 2% is reached (Treballe et al., 1993).

Hence, the information provided by the geologic history and diagenetic features derived from the burial of sediments is very useful to assess the maximum overburden stress level reached.

4.2.1 Compaction evolution

The process of diagenesis is commonly divided into three major stages, eodiagenesis, mesodiagenesis and telodiagenesis (after Schmidt and Macdonald, 1979). Eodiagenesis starts just after deposition, so is often termed early diagenesis, and encompasses processes that take place from deposition and into the shallow burial realm up to a maximum depth of about 1-2 km with temperatures ranging between 30 to 70°C (based in a usual geothermal gradient, Morad et al., 2000). Mesodiagenesis develops during the burial realm so is often termed burial diagenesis. It is encountered at 1-2 km and in many cases, includes sediments of a wide range of meter of burial (about 100 to 1000), with maximum temperatures of 200 to 250°C. Finally, Telogenesis occurs after burial in uplifted rocks.

Taylor (1950) proposed four types of grain-to-grain contacts as a function of increasing effective stress (overburden stress) during burial, namely: punctual or tangential contacts, long contacts, concave-convex contacts and sutured contacts.

Grain contacts start off as punctual or tangential contacts just after deposition and turn into long contacts by burial and compaction. During this stage, compaction evolves

by rotation, fracturing and ductile deformation of grains, resulting in uncemented and clean sands. This diagenetic phase covers from the eodiagenesis to the so-called immature stage of the mesodiagenesis (Schmidt and Macdonald, 1979). In addition, it is worth noting that the initial porosity of coarse sand is not considerably reduced by compaction until the stress is high enough to crush the grains (Fraser, 1935). In this context, Ottawa sand compressibility values for a range of high stresses (from about 7 to 70 MPa) proved to be more compressible than clay, owing to grain breakage. Moreover, it has been found that neither the original grain size distribution nor the grain shape (that the sand had right after deposition) is maintained in deep-buried sands with low void index (Roberts and De Souza, 1958). Consequently, the medium grain sizes will tend to get smaller and more angular by compaction.

With further burial, beyond the mere mechanical compaction (mentioned above), the rise of the temperature and pressure cause the increase of the grain-to-grain contact area reducing the intergranular stress as a result. Also, favoured by the connate water held at the contacts (as an adsorbed film or as menisci) grains start to dissolve at the contacts generating concave-convex surfaces. The chemical gradient generated between the grain contacts due to the silica dissolved within and the pores promote material transport by diffusion towards the pores where ultimately is reprecipitated, as so-called syntaxial cement.

It is commonly accepted that dissolution-diffusion-reprecipitation phenomena in quartz sands are common from about 1.5 kilometre depth which correspond to the semi-mature stage of mesodiagenesis, where chemical compaction essentially occurs through the dissolution of sand grains at contacts (Schmidt and McDonald, 1979). In this regard, several authors suggest that syntaxial quartz cement tends to occur in diagenetic conditions at temperature usually in the range of 80 to 100°C (Lander and Walderhaug 1999; Bjørlykke and Egeberg, 1993; Walderhaug 2000; Giles et al., 2000) or even about 120°C for subsequence episodes, which equate to higher depths (Walderhaug 1996; Oelkers et al. 2000).

If the pressure keeps increasing, grain-to-grain contact dissolution continues, and grain boundaries become irregular or sutured.

All these phenomena increase the bulk density by compaction through intensification in packing which results in a loss of porosity.

Figure 4.4 illustrates a typical grain-to-grain evolution through progressive burial. This appraisal of burial history at grain level in conjunction with some principles of geomechanics seems to be of the greatest importance on the assessment of the preconsolidation stress level and critical quality parameters for uncemented reservoirs. Reservoir permeability, porosity, pore size distribution, pore shape, grain interlocking (and hence dilatancy) and the specific surface cannot be accounted for without the bearing of such approach.

Figure 4.4 Grain-to-grain contact evolution as a function of depth and temperature.

4.2.2 Determination of the Overconsolidation ratio (OCR) by fluid inclusions

As mentioned above, OCR determination has to be estimated by indirect methods that may encompass those relating to the geological processes. In this context, the features derived from the diagenetic evolution previously discussed may be a useful tool to determine the overburden stress level reached by the reservoir, i.e. grain-to-grain contact morphology, grain shape or syntaxial cement overgrowth, among other.

It is well known that during syntaxial cement growth some diagenetic paleofluids may get trapped inside microscopic vacuoles that may experience phase change if any entrapment conditions (pressure and/or temperature) are modified.

These little volumes of paleofluids, known as fluid inclusions, are considered as a useful source of information for evaluating diagenetic environments, as they were trapped just at the sample temperature and pressure conditions and, therefore, may provide valuable information about its geologic history.

It is on this assumption that a novel study based on fluid inclusions on the syntaxial cement of the reservoir quartz sands has been developed with the aim of assessing the temperature at which they were formed. From this value and, relying on the Orinoco Belt geothermal gradient described in chapter 2, the maximum overburden stress reached by the reservoir, i.e. the preconsolidated stress, (its OCR) has been determined.

Since the reservoir sands are not cemented, small wafers of sand particles embedded in polycarbonate of 100 μm thickness with high-quality doubly-polished plate have been prepared as a first step. Then, a detailed observation using an optical microscope was carried out with the purpose of identifying and selects some suitable fluid inclusions (preferably biphasic) within the scarce syntaxial cement present on the detrital quartz grains.

As a result, some biphasic, liquid+vapour (L+V), fluid inclusions of about 5 μ m in size were identified and selected for a further temperature determination.

Figure 4.5 shows some examples of the fluid inclusions selected.

Figure 4.5 Fluid inclusions in syntaxial cement of quartz sand.

Figure 4.6 (cont.) Fluid inclusions in syntaxial cement of quartz sand.

As syntaxial cement frequently precipitates in optical continuity with the original grain, its identification by optical microscope has to be verified by cathodoluminescence technique that ensures its reliability (Guscott and Burley, 1993). Figure 4.6 shows some of the precipitates over detrital quartz studied with the characteristics short-lived bottle-green or blue luminescence colours common in syntaxial quartz cement (Ramseyer K., 1988).

Figure 4.7 Syntaxial cement over detrital quartz observed by SEM-cathodoluminescence.

Once some fluid inclusions on syntaxial cement were identified and selected, their entrapped temperature was determined by microthermometry. The microthermometry technique is a useful method to determine the temperature for a phase change in fluid inclusions by the process of heating and cooling of the sample.

Thus, since a fluid inclusion represents a chemically closed system and its volume remains constant since its entrapment, the minimum entrapment temperature by heating can be obtained. In that way, the minimum entrapment temperature (termed homogenization temperature, T_h), is that at which the vapour phase in the fluid inclusion condenses fully liquid. Figure 4.7 depicts this process.

Figure 4.8 Change of phases within a fluid inclusion by heating. Temperature of homogenization.

4.2.3 Results

The microthermometry study has been carried out by means of a calibrated Linkam slide for fluid inclusions analysis with a precision of $\pm 2^\circ\text{C}$ in heating. The fluid inclusions studied were contained in either, the syntaxial cement and the detrital quartz itself. They are aqueous, biphasic (L+V, with a vapour phase of about 5%), and in the case of the ones in the detrital quartz includes lighter oil.

The homogenization temperatures obtained are distinctly different in each case (see Table 4.1): the homogenization temperatures of samples from the syntaxial cement are in the range of 90°C , whereas those from the detrital quartz, in the range of 150°C . It should be noted that the results are notably higher than the temperature recorded in

situ, about 60°C, at around 1100 meters depth. The results of the syntaxial cement can be considered in good agreement with the onset of the formation temperature of the quartz syntaxial cement, while the results of the detrital quartz may correspond to the oil formation temperature within the source area before oil migration.

Assuming that the fluid inclusion on the syntaxial cement was trapped at a temperature higher than the current temperature it can be inferred that the reservoir was subjected to higher overburden stress sometime in the past and, according, the reservoir should be considered as slightly overconsolidated. This overburden may be due to the existence of superficial terrain that was eroded during its geologic history, (Dusseault, 2001; Treballe et al., 1993).

Table 4.1 Homogenization temperature of fluid inclusions on Morichal quartz sand.

SAMPLE	DEPTH (m)	FLUID INCLUSION SET	TEMPERATURE (°C)
Syntaxial cement	1100	1	92
		2	90
		3	85,5
Detrital quartz sand	1100	1	150
		2	148

Subsequently, the obtained homogenization temperature of the fluid inclusions within the syntaxial cement have been plotted on the Orinoco's Belt geothermal gradient line with the aim of estimating the reservoir preconsolidation stress and OCR, see Figure 4.8. According to the figure, the equivalent formation depth related to the temperature of the syntaxial cement overgrowth, around 90°C, lies approximately at 2000 m. Consequently, as changes of specific weight, in this case, have a minor effect on stress, the OCR becomes the ratio of the formation depth over the current depth (i.e. 2000/1100); i.e., $OCR \cong 1.8$. These results are in good agreement with those reported in the literature (Dusseault, 2001; Treballe et al., 1993) and provide a reasonable prospect of its potential applicability.

Figure 4.9 Equivalent entrapped depth for the fluid inclusions on the Morichal sand.

Table 4.2 OCR as a function of Th of fluid inclusion on syntaxial cement on Morichal sand.

<i>Current depth (m)</i>	<i>Th (°C)</i>	<i>Cement formation depth (m)</i>	<i>OCR</i>
1100	89	2000	1.8
1100	90	2000	1.8
1100	92	2100	1.9

4.2.4 Compressibility model

Note that the method of fluid inclusion designed and tested in this dissertation not only provides an appropriate technique to determine the overconsolidation ratio of sands but also, it is a useful technique to develop a compressibility model (just considering mechanical conditions, primary recovery).

Two types of laboratories tests are necessary to characterize a sand reservoir: on one hand, the novel method of fluid inclusions described above (that provides a fairly

good judgement on the OCR).; on the other hand, a set of oedometric tests from whatever initial void ratio, vertical stress higher (say, twice as high) than the in situ, and load-unload-reload cycles.

Thus, it would be simplest to assess the formation deformation response known the in-situ porosity ($\text{void ratio} = \text{porosity} / (1 - \text{porosity})$) and effective stress, as it is shown in Figure 4.9.

The compressibility behaviour during primary production would follow the course of the respective formation stress state given.

Figure 4.10 Compressibility Model of the reservoir during primary recovery.

4.3 Compressibility of quartz sand at dry conditions

The research of the quartz sand compressibility at dry conditions has been addressed by the study of a series of oedometric tests at high stresses (up to 50 MPa) and a wide range of temperatures, from 25 to 250°C. Tests were carried out at the Geomechanics Lab of School of Civil Engineering of A Coruña.

Three basic features have been analysed:

- The effect of the grain size and morphology on compressibility.
- The effect of the temperature on compressibility.
- The effect of the temperature on preconsolidation stress and compressibility.

Many available studies focused either on the one-dimensional and isotropic quartz sand compressibility or on crushing of single particles. In a number of them the initial void ratio, grain shape and size are considered as the key factors to govern the compressibility of sand (Roberts and De Souza, 1958; Lee and Farhoomand, 1967; Vesic and Clough, 1968; Miura and Yamanouchi, 1975; Hardin, 1985; Coop and Lee, 1993; Hagerty et al. 1993; Yamamuro et al., 1996; Lade et al., 1996; McDowell and Bolton 1998; Nakata et al., 2001). The same sources reveal that at high stresses there is a stress threshold beyond which the oedometric curve exhibits a significant slope change, what would denote an increase in the compressibility that, in turn, would be connected to the onset of particle crushing (termed yield point or yield stress). Above this stress level, the compression line tends towards a normal compression line (Coop and Lee, 1993; Miura and Yamanouchi, 1975; Lo and Roy, 1973, Vesic and Cough, 1968; Lee and See, 1967; Bishop et al., 1965). In addition, it has been found that the oedometric modulus of oil sands is rather similar for room temperature, 100, 200 and 300°C as long as the sample is heated under effective null stress (Kosar, 1989). Besides, the unloading values are about twice that of the obtained in the loading stages.

Likewise, fast-loading compression tests would result in significant compaction due to the same grain crushing phenomena (Borg et al., 1960; Zhang et al., 1990; Menendez et al., 1996; Chuhan et al., 2002; Karner et al., 2003, 2005).

Similar processes have been invoked in the realm of the diagenetic compaction of natural sediments (Brzesowsky et al., 2011, 2014; Karner et al., 2008; Chester et al., 2004, 2007; Schutjens et al., 1991; Wong, 1990), in the behaviour of cataclastic zones (Heard and Carter, 1968; Hirth and Tullis, 1992).

4.3.1 Experimental Methods and Material. Oedometric compression tests

The tests were performed with a 24.5 mm-thick AISI-304L-SST ring in which a 40 mm OD thin-walled (1.3 mm) Al-6063-T5 sample holder was introduced. Compression was transmitted through two perforated SST platens that fit into the sample holder. On top and bottom of the sample holder, two drilled 1 mm-thick SST lids, together with two sheets of filter paper guarantee the integrity of the sample during handling. Two band heaters connected to a PID temperature controller and a PT100 located in the middle of the cell wall sensor for the tests performed above room temperatures were used. Temperature calibration was carried out by an additional PT100 sensor.

Axial load was applied by a hydraulic cylinder connected to an ISCO-260HP syringe pump. Temperature, axial displacement with two-averaged LDT-type transducers and axial load, were recorded. Figure 4.10 displays a scheme of the device employed.

The oven-dried quartz sand samples have 37.40 mm in diameter and an average height of 12 mm, and they were loaded in its loosest state. Under these conditions, the initial porosity ranges from 42 to 47%. The typical weight of each sample was ~18.5 g, leading to an initial dry density of 1.40 g/cm³.

Experiments were performed under dry conditions (to avoid chemical couplings) but allowing air drainage.

The procedure of sample preparation is described in Figure 4.11.

Figure 4.11 Oedometric test scheme.

<p>A perforated steel metal disc fitted to a metal ring and a filter paper is placed on its surface.</p>
<p>The sand sample is sieved, and afterwards, the required amount of sand for filling up the ring at its loosest initial state is weighed and placed into the ring.</p>
<p>Another filter paper and perforated steel metal disc are placed on the sand. Then, the sand sample height is estimated by the measure of the free length of the metal ring.</p>

Figure 4.12 Procedure of sample preparation for the oedometric test.

<p>The steel ring with the sand sample is placed into the test cell.</p> <p>- Bottom of the cell:</p>
<p>- Top of the cell:</p>
<p>LVDTs, ultrasonic sensors and lateral protections for high-temperature tests are placed around the cell.</p> <p>Before testing, a preconsolidation pressure of 0.2 MPa is applied for the sake of sample homogenization.</p> <p>The temperature sample is increased up to the target temperature test before loading.</p>

Figure 4.11 Procedure of sample preparation for the oedometric test (cont.).

As tests were programmed to be run at high temperatures, some calibration tests without sand sample were carried out previously. Figures 4.12, 4.13, and 4.14 plot the vertical displacement evolution recorded as a function of the applied temperature.

Figure 4.13 Pressure vs temperature at calibration tests. (Supplied by the Geomechanics Laboratory of the University of A Coruña).

Figure 4.14 Vertical displacement at calibration tests. (Supplied by the Geomechanics Laboratory of the University of A Coruña).

Figure 4.15 Vertical displacement versus applied load at calibration tests. (Supplied by the Geomechanics Laboratory of the University of A Coruña)

As a result, it has been proven that the different elements that comprise the system (discs of Al-6063, positioning reference block of Al-6063, compression platens of steel AISI-316, refractory ceramic blocks to protect the load cell, etc.) respond to temperature with a thermal expansion coefficient consistent with the expected, considering a theoretical linear expansion coefficient for the steel AISI 316 of $16 \times 10^{-6} \text{ m/m}^\circ\text{C}$.

As is shown in figure 4.15, the thermal expansion in the first stage of the test was 0.176 mm over the initial length of 140.2 mm (taking the temperature rise from 25 to 109.3°C as reference) while for the last stage, the thermal expansion was 0.284 mm for a temperature increase of 109.3 to 223.1°C .

So, the linear thermal expansion coefficient, α , obtained by the expression 4.2, corresponds to $15 \times 10^{-6} \text{ m/m}^\circ\text{C}$ and $18 \times 10^{-6} \text{ m/m}^\circ\text{C}$ (for the first and second loading stages, respectively).

$$\alpha = \frac{L}{L_0 \Delta T} \quad (4.2)$$

Regarding the mechanical deformation (platen compression) with temperature, the following values were obtained: 0.613 mm from 0.1 to 50 MPa at 109°C and 0.534 mm from 0.1 to 50 MPa at 223.1°C . This minor difference, about 0.09 mm, is considered as a consequence of the fitting between the O-rings and the parts.

In any case, even though this vertical deformation difference could give rise to a non-recoverable axial displacement, both thermal and mechanical effects are, in both cases, negligible as compared with the deformations expected by the sand.

Figure 4.16 Detailed recording of the vertical displacement as a function of temperature in the calibration test. (Supplied by the Geomechanics Laboratory of the University of A Coruña)

4.3.2 Effect of the Grain Size and Morphology on the Compressibility

Uniform, coarse and fine sands have been reconstituted from the Morichal's original sieved sand fractions (Fig. 4.16) with the purpose of assessing the effect of the grain size and morphology on compressibility.

Main sand characteristics and nomenclature tests are as follows:

- **EDO-AM-C** (Grain size distribution coarser than the original sample). It is a uniform ($C_u=1.9$) and well-graded sand ($C_c= 1.2$) with a D_{50} of 350 μm . As it can be observed in Figure 4.16, the main particle size fractions correspond to 210 μm (63 % content) with a sub-angular to angular morphology and without particles lower than 105 μm (see Figure 4.16 and 4.17).
- **EDO-AM-U** (Grain size distribution more uniform than the original sample). It is a uniform ($C_u=1.6$), well-graded sand ($C_c= 1.3$) with a D_{50} of 275 μm . The mean particle size fraction corresponds to 150 μm (76 % content) with a sub-angular - angular morphology. There are no particles smaller than 105 μm , just as in the coarser sand (see Figure 4.16 and 4.17).
- **EDO-AM-F** (Grain size distribution finer than the original one). A D_{50} of 180 μm characterises it. Since it lacks particles smaller than 74 μm (Fig. 4.16) is not possible to define its uniformity and gradation characterisation (C_u and C_c respectably). The mean particle size fraction corresponds to 150 μm (63 % content) with a sub-angular to angular morphology (see Figure 4.16 and 4.17).

Tests were performed by 18 loading/unloading steps (1/2/3/4/6/10/15/20/25/30/10/1/30/50/30/15/5/1 MPa). Each one lasting around 6 hours, so the completion occurred after 108 h (4.5 days). For the different step duration, within the range of duration of the steps considered, it has not been observed any significant

time-dependent effect.

Figure 4.18 Reconstituted grain size distribution samples for compressibility study.

4.3.2.1 Results

Macroscopic observation

Vertical strain, effective stress and acoustic emissions (AE) throughout the tests were recorded, and give an idea about the macroscopic behaviour during the sample consolidation.

As shown in Figure 4.18, the resulting oedometric curves reveal a somewhat similar pattern at stresses higher than 10 MPa (in both load and unload curves) irrespective of the grain size distributions or initial void ratio. As usual, consolidation is interpreted regarding vertical deformation versus effective vertical stress (in logarithmic scale).

A detailed analysis based on both one-dimensional vertical deformation together with AE recorded data, shows three distinct stages of compression during load:

- *Stage I:* From the beginning of the test to about 10 MPa for the coarser sand and around 20 MPa for the uniform and finer one.
- *Stage II:* At the stress range of 10-20 MPa the oedometric curves bend slightly to a steeper path. Besides, the acoustic emissions counts increase at that load step. It is worth noting that the curvature path for the finer sand shifts more softly to the steeper slope as the obtained for the coarser and uniform sand.
- *Stage III:* From about 10-20 MPa the slope of the curves increases as a result of the compressibility increase, keeping constant up to the end of the test.

a)

b)

Figure 4.19 a) Oedometer curve for EDO-AM-C, EDO-AM-F and EDO-AM-U tests at 25° C b) Estimation of the yield point.

Figure 4.20 AE data for EDO-AM-C, EDO-AM-F and EDO-AM-U tests at 25° C. (Supplied by the Geomechanics Laboratory of the University of A Coruña), and estimation of the deformation stage.

The acoustic emissions recorded suggest that particle crushing occurs in coincidence with the onset of loading ramps, from about 10-20 MPa. This phenomenon ceases during the unloading stages until regaining the previous preconsolidation stress at the reloading steps. The intensity in crushing is significant on the coarser sand while in the finer one AE counts are scarce. Below 6 MPa, particle crushing is negligible with barely AE counts.

Unfortunately, in the test carried out on the coarser sand the data acquisition system failed to record the AE from 30 MPa.

Figure 4.20 displays a summary of the evolution of effective stress and vertical deformation over a period just as the oedometric curves versus loading stages.

Microscopic observation

The analysis of the grain size distribution of post-test sands reveals that the grain breakage has a remarkable effect on coarser sand whereas on the finer one is reduced (as it has been noticed on acoustic emissions data). Fines content increases a 7 to 12% while the D_{50} reduces a 15 to 37%. Table 4.3 summarises these results.

Table 4.3 D_{50} reduction and fines content increase in the sand samples tested.

Sample	D_{50} Decrease	Fine content Increase
Coarser	37 %	12%
Uniform	21 %	9 %
Finer	15 %	7 %

Coarser sand experiences an increase of about 12 % in the fines content, reducing its D_{50} about 37 % from 350 to 200 μm . The initial main fraction 200 μm reduces to 60 μm and the second main fraction, 150 μm , reduces to 30 μm , as it is shown in Figures 4.21.

Uniform sand experiences an increase of about 9 % in the fines content, reducing its D_{50} about 20 % from 250 to 200 μm . The initial main fraction, 150 μm , reduces to 60 μm , as it is shown in Figures 4.22.

Finally, finer sand experiences an increase of about 7 % in the fines content, reducing its D_{50} about 15 % from 200 to 170 μm . The initial main fraction, 150 μm , reduces to 80 μm , as it is shown in Figures 4.23.

Figure 4.21 EDO-AM-C, EDO-AM-F and EDO-AM-U tests at 25°C.

Figure 4.22 Grain size distribution before and after testing for coarser sand.

Figure 4.23 Grain size distribution before and after testing for uniform sand.

Figure 4.24 Grain size distribution before and after testing for finer sand.

Grain size distribution after tests for the coarser and the uniform-sand tend to become equivalent, (Fig. 4.24) but do not reach the initial fines content of the finer sand, as the latter originally contained 9% of the finer fraction that the others lack.

Figure 4.25 Comparison of the grain size distributions after testing for the sands tested.

4.3.2.2 Discussion

The oedometric curves obtained can be split into three stages, regarding particle behaviour, over a wide range of stresses, Figure 4.25.

Figure 4.26 Stages of particle behaviour in the oedometric tests over a wide range of stresses.

Unlike conventional oedometric curves, the stretch with shifting curvature observed in the sand at high pressures marks the onset of grain crushing. Different authors have identified this vague threshold as “yield point or yield stress” (Hagerty et al. 1993; McDowell and Bolton, 1998; Nakata et al., 2001a and 2001b; McDowell and Humphereys 2002; Chuhan et al., 2003; Mesri and Vardhanabhuti, 2009). The curves evolve toward a steeper “degenerated-by-crushing” normal compression line. The change in the curvature of the curves point to a particle breakage onset in oilsand was found from 7 MPa (Kosar, 1989). The compaction occurring at stresses lower than the yield point is dependent on the initial sample conditions (void ratio, grading, and grain morphology) and it is typically attributed to particle rearrangement (i.e. intergranular sliding and rotation, and pore collapse) and the elastic deformation of the grains. Both processes gradually increase the stiffness of the quartz aggregate with minor grain damage up to the yield point. However, at higher stresses, particle movement is strongly hindered, and phenomena at particle-level can only explain any further strains.

Particle rearrangement, Stage I

The curvature in this stage accounts for primary compaction which is controlled mainly by the particle rearrangement up to the maximum particle packing is reached. Despite the highly constrained conditions of the oedometric cell (radial strains prevented), the maximum packing (maximum density) is ultimately reached as long as the vertical stress is raised up to an intermediate level (6~10 MPa).

Applied stresses (including boundary effects) are transmitted, as discrete forces, through granular chains within the soil skeleton. Thus, the less uniform the grain size distribution the stiffness the respond is expected, since the coarser fractions embedded in the soil matrix is more stressed, delaying the compression, and ultimately it is likely to break. Figure 4.26, from Drescher and De Josselin de Jong experiments (1972) with photosensitive discs and, more recently, Figure 4.27 from Gent et al. (2001), show the interaction and force field/paths spread by the contacts.

Hence, the curvature and the slope during this stage depend on the original grain size distribution, grain morphology, and initial void ration.

Figure 4.27 Drescher and De Josselin de Jong (1972) experiments. Intergranular forces distribution through photosensitive discs.

Figure 4.28 Intergranular forces distribution through photosensitive pentagonal discs: a) due to the self-weight; b) adding a concentrated load. (adapted from Gent et al., 2001).

Yield point, Stage II

Once the maximum particle packing is reached, the potential grain movement turns completely frustrated and blocked. As a result, no further strains can be developed but caused by particle crushing.

The phenomenon of the breakage of a particle embedded in a soil matrix and the effective stress that causes it may be explained and developed in accordance with the fracture mechanic theories below.

Theory of Hertzian fracture and effective stress of breakage

According to Hertzian Theory, deformation between two grains can be explained as the deformation of two contacting elastic spherical bodies. The contact area is circular, and its radius depends on the normal force applied, F_n , the grain radius, R , Young's modulus, E , and Poisson's ratio, ν , by the expressions 4.3, and Figure 4.28 (adapted from Gallagher, 1976):

$$\frac{d_c}{2} = \left(\frac{3 F_n (1-\nu^2) R}{4 E} \right)^{1/3} \quad (4.3)$$

Figure 4.29 Radius of the contact area caused by Hertzian forces.

In turn, the intergranular stress generated at the grains contact, σ_{int} , can be expressed in terms of the applied force spread over the contact area:

$$\sigma_{int} = \left(\frac{F_n}{\pi \left(\frac{d_c}{2} \right)^2} \right) \quad (4.4)$$

Moreover, the maximum tensile radial stress at the contact, σ_t , reaches its maximum value at the edge of the circular contact area where bring about circumferential cracks, see Figure 4.29. The development of this kind of breakage follows the Mode-I of cracking (Huber 1904).

$$\sigma_t = \frac{(1-2\nu)\sigma_{int}}{2} \quad (4.5)$$

Figure 4.30 Hertzian maximum tensile radial stresses (from Yasuhara and Elsworth, 2008).

Figure 4.30 shows two SEM images taken after the core-flooding tests carried out at 150 °C and reservoir stress conditions (addressed in chapter 5). As can be seen, the patterns of fractures fully fit the fracture mechanics theory described.

Figure 4.31 Circumferential fracture pattern on quartz sands particles.

Even though relevant efforts have been made during the last decade in the field of granular media to establish the relationship between the macroscale ("Terzaghiian" effective) stresses and the microscale (particulate level) stresses, the simplified expression 4.6 for monosized spheres suffices for the purpose of the current research (Santamarina, 2001; Mavko et al, 2009). The total normal load exerted at the contact of a particle embedded in a soil matrix, F_{n_s} , can be expressed as a function of the grain size, d , the effective stress applied, σ_{ef} , and the void ratio, e .

$$F_{n_s} = \sigma_{ef}(d)^2 \frac{\pi(1+e)^2}{12} \quad (4.6)$$

So, both the microscopic and the macroscopic behaviours can be connected, and the tensile stress on a particle embedded in a soil matrix, σ_{t_s} , due to the effective macroscopic stress can be obtained by the equation 4.7 (Nakata, 2001b). In this case, the intergranular stress refers to the one caused by the normal load calculated by equation 4.6.

$$\sigma_{t_s} = \sigma_{int} \left(\sqrt[3]{\frac{(1+e)\pi}{6}} \right)^2 \quad (4.7)$$

Note that, unlike the relationship between the macroscopic, F_n , and the microscopic stresses for two particles, in this case, the microscopic stresses for particles embedded in a soil matrix are not just a function of the particle sizes, but also a function of the void ratio of the soil aggregate at the stress level considered.

Thus, going one step further, the porosity of the soil, and in turn, its void ratio, gives an average number of contacts points per particle, known as coordination number, C_n .

Field (1963) suggested a simple relationship between the coordination number and the porosity, equation 4.8, by the study of granular assemblies of rounded stones of different sizes and grading.

$$C_n = 12(1 - n) = \frac{12}{1+e} \quad (4.8)$$

For porosities over 0,35, this expression is in good agreement with typical packing arrangements and other available formulae, as shown in Figures 4.31 and 4.32.

Figure 4.32 Coordination number versus porosity in random sphere packs, from Smith et al. (1929), Manegold and von Engelhardt (1933), Murphy (1982), and Garcia and Medina (2006). HCP = hexagonal close-packed; SH = simple hexagonal; and SC = simple cubic. The thin lines approximately indicate ± 1 standard deviation from the data of Smith et al. (1929).

Figure 4.33 Ordered packing arrangements, porosity, and coordination number.

It is worth noting that the coordination number for dense sands is around 7.7 (assuming a maximum density of 1700 kg/cm^3 around to approximately 36% of porosity) and for loose (poured) sand is about 6.5 (assuming a minimum density of 1400 kg/cm^3 equivalent to around 45% of porosity).

As the coordination number increases with the decrease of the void ratio (Field, 1963 and Oda, 1977), the tensile stress on a particle embedded in a soil matrix decreases as well:

$$\sigma_{t_s} = \sigma_{int} \left(\sqrt[3]{\frac{2\pi}{C_n}} \right)^2 \quad (4.9)$$

Lastly, the determination of the effective stress that causes the crushing of a particle embedded in a soil matrix has to assume the premise that the breakage of grains will occur as long as the stress intensity factor on the tip of the crack equals the value of the fracture toughness. Therefore, for a Mode-I of breakage, the stress intensity factor, K_I , follows the equation 4.10 (Frank and Lawn, 1967), where c , is the length of a pre-existing flaw.

$$K_I = K_{IC} = 1.12 \sigma_t \sqrt{\pi c} \quad (4.10)$$

Atkinson et al. (1980) studied the fracture toughness of the quartz at different temperatures and obtained a characteristic value of $0.31 \text{ MN m}^{-3/2}$ at 20°C .

Besides, the length of the pre-existing flaw is related to the grain radius by the parameter α , which has the same value, 3.6×10^{-5} , for most porous soils (Zhang, 1990). As α is the ratio of the initial flaw length over the grain radius, it is worth noting that the coarser the particle, the higher the likelihood of flaws, and consequently of the particle crushing.

$$\alpha = \frac{c}{R} \quad (4.11)$$

Thus, combining equations 4.9 and 4.10, the critical intergranular stress that causes crushing of particles embedded in a soil matrix can be derived:

$$\sigma_{int_cr} = \frac{K_{IC}}{1.12 \sqrt{\pi R 3.5 \cdot 10^{-5}} \left(\sqrt[3]{\frac{2\pi}{c_{n_yield}}} \right)^2} \quad (4.12)$$

Moreover, again, the microscopic and the macroscopic behaviours can be connected by the equation 4.13, which gives the macroscopic critical effective stress for the crushing of the particles embedded in a soil matrix at the maximum packing, i.e. the yield point.

$$\sigma_{ef_cr} = 1.17 \cdot 10^{-2} \frac{\sigma_{int_cr}^3 \pi^2 c_{n_yield}^2 (1-\vartheta^2)^2}{E^2} \quad (4.13)$$

Thus, the effective stress that causes the crushing of the particles depends on the particle size. Thus, the effective critical stress increases inversely with the size of the particles, as shown in table 4.4, as long as the sand is at a dense state (a coordination number around 7.7, at the yield point). These observations fit pretty well with the acoustic emissions recorded.

Table 4.4 Effective stress for crushing.

<i>Test</i>	<i>Particle size (μm)</i>	σ_{ef_c} (MPa)
Coarser	$D_{50} = 350$	8
	Predominant fraction= 210 (63%)	17
More uniform	$D_{50} = 275$	12
	Predominant fraction= 150 (76%)	30
Finer	$D_{50} = 180$	22
	Predominant fraction= 150 (63%)	30

Particle crushing and interparticle slips, Stage III

From the moment on the overloaded particles starts to break, a crushing knock-on effect is brought out (see Figure 4.33), and the compressibility curve shifts to a steeper “degenerated-by-crushing” virgin compression line due to particle crushing and interparticle slip.

Figure 4.34 Grain crushing evolution as a result of the intergranular stress distribution.

Uniform granular material composed of large particles would crush more readily than other composed of smaller ones of the same material (Lee and Farhoomand, 1967; Hagerty et al., 1993; Hardin, 1985; Lade et al., 1996; McDowell and Bolton, 1998). Likewise, angular particles would crush more easily than rounded particles (Lee and Farhoomand, 1967; Hagerty et al., 1993; Lade et al., 1996), as they result in more stresses since their asperities will enhance the locking effect preventing their packing. Besides, uniform soils exhibit more crushing than well-graded soils having the same maximum size (Lee and Farhooman, 1967; Lade et al., 1996).

As a result, sand from different grain size distributions under the same loading conditions would tend to equal coarser fractions to “equivalent finer” particles sizes distributions which coordination number would allow spread out the load preventing the particle breakage. So, grain sizes distributions would evolve during compaction by crushing and interparticle slip until reach a minimum particle size distribution able to withstand the load applied without crushing.

From that moment on, the compressibility beyond the yield point seems to be equivalent irrespective of the initial void ratio, as can be noticed in Figure 4.34 from data reviewed from the literature.

Figure 4.35 Oedometric curves of quartz sand at high stresses and room temperature (from Golightly 1990; Nakata et al. 2001; and Leleu and Valdes 2006).

4.3.3 Effect of Temperature on the Preconsolidation Stress

Three oedometric tests have been performed to assess the effect of temperature on the preconsolidation stress. The tests have been carried out on oil-free reservoir sand under the following conditions (Fig. 4.35):

Figure 4.36 Conditions of the oedometric tests for the study of the effect of the temperature on preconsolidation stress.

4.3.3.1 Results

Figure 4.36 displays the results of the 3 oedometric tests. Note a certain lack of overlapping of the unloading-loading stress paths with a heating stage in between.

It has been noted a slightly higher stiffness (lower slope) at stage I in the EDO-2C (rearrangement stage), which is supposed to be caused by the sample preparation.

This offset of the strain paths can be attributed mainly to the thermal expansion of the metallic parts of the oedometer, previously recognised in its calibration.

Thus, in the EDO-1-C, the thermal expansion associated to the temperature rise from 25 to 100 °C is approximately 0.21 mm while for the same range of temperature in the calibration of the system was 0.18 mm. The difference of 0.03 mm should be attributed to the sand expansion itself, negligible at any rate.

Figure 4.37 Oedometric curves, EDO-1-C (25-100°C), EDO-2-C (25-200°C) and EDO-3-C (25-100-200°C).

In any case, such lack of overlapping does not disturb the preconsolidation stress, and the loading path from the maximum stress reached in previous steps is retaken in the subsequent load stages.

Again, as in previous oedometric tests, oedometric curves reach a maximum packing ($C_n \cong 7.3-7.8$) at nearly 10 MPa (yield point), from where the compressibility evolves similarly irrespective of temperature or initial void ratio, (see Figure 4.37). The

average compression index reached $c_c=0.29$ and the average swelling index $c_s=0.03$ is characteristic of the whole range of unloading. These results compare reasonably well with those available in the literature (Mesri and Vardhanabhuti, 2009; Roshankha, 2014).

Figure 4.38 Oedometric curves, EDO1-C, EDO2-C and EDO3-C at 25-100-200°C.

4.3.3.2 Discussion

As it has been seen in the previous section, in this case, it can also be drawn for the tests developed that beyond the yield point, the temperature has neither effect on sand compressibility (c_c around 0.3) nor preconsolidation stress (around 10 MPa) regardless of initial void ratio.

Both load and unloading-loading curves follow a similar pattern despite the processes of heating-cooling during the tests.

The processes at particle level that underlies that phenomenon are attributed to those described in the previous section, particle crushing, and interparticle slip.

Considering that the grain size distribution is characterised by a D_{50} of 250 μm ,

the effective stress that causes the crushing of these particles (calculated by the equation 4.13) is again in the range of 10-15 MPa (around 13 MPa).

4.3.4 Effect of Temperature on the Compressibility

Twenty-three oedometric tests at dry conditions and a range of temperature from 25 to 250 °C have been performed on oil-free sands and 2 additional tests on oil sand (15% oil cont.) at 25 °C. Table 4.6 summarises their temperature conditions.

Table 4.5 Temperature for the oedometric tests at dry conditions

Sample	T (°C)	Sample	T (°C)
EDO 1-25	25	EDO 1-60	60
EDO 2-25	25	EDO 1-100	100
EDO 3-25	25	EDO 2-100	100
EDO 4-25	25	EDO 3-100	100
EDO 5-25	25	EDO 4-100	100
EDO 6-25	25	EDO 1-150	150
EDO 7-25	25	EDO 2-150	150
EDO 8-25	25	EDO 3-150	150
EDO 9-25	25	EDO 4-150	150
EDO 10-25	25	EDO 1-200	200
EDO 1-50	50	EDO 2-200	200
EDO 2-50	50	EDO 1-250	250
EDO 3-50	50		

They have been developed following the same loading-unloading steps as those described for the grain size and morphology study, (1 / 2 / 3 / 4 / 6 / 10 / 15 / 20 / 25 / 30 / 10 / 1 / 30 / 50 / 30 / 15 / 5 / 1 MPa), each one lasting 1.5 to 6 hours.

4.3.4.1 Results

Macroscopic observations

Oedometric curves from tests developed are shown in Figure 4.38 and Figure 4.39. Even though a strict procedure for placement of the sand at its loosest state was followed, some scattering in the initial void ratio could not be avoided, with departing values from 0.65 to 0.95. Yet, all of the curves follow a fairly similar pattern (both throughout load and unload-reload cycles). Therefore, it can be inferred that the strain-strength relationship at macroscopic scale remains unchanged with temperature.

Figure 4.39 Oedometric curves for temperature from 25 to 250 °C, under dry conditions. Void ratio vs effective stress.

Figure 4.40 Oedometric curves for temperature from 25 to 250 °C, under dry conditions. Vertical strain vs effective stress.

As it has been described in the preceding section, oedometric curves follow three stages that account for different responses at the particle level, stage I, II and III, as shown in Figure 4.40. Given that the initial grain size distribution in the samples tested is alike, the macroscopic response of the particle rearrangement at stage I, the deformability is equivalent regardless of temperature and initial void ratio. Furthermore, it can be assessed that the yield point (stage II) occurs at approximately 10 MPa, irrespective of temperature as well, and neither the initial void ratio of the samples nor temperature have significant effects on the compressibility beyond the yield point (stage III). Thus, for an interval stress range between 10 to 50 MPa, compression indexes average, C_c , are approximately 0.305, in good agreement with the results presented by Mesri and Vardhanabhuti (2009) and the ones obtained by Roshankha (2014). The oedometric parameters obtained for each test, (oedometric modulus, compressibility, and swelling modulus) are summarised in table 4.7 and graphically in Figure 4.41.

Figure 4.41 Deformational stages during oedometric tests at a temperature from 25 to 250 °C and dry conditions.

As it can be noted, the temperature does not have any effect on sand compressibility.

The coordination number at that stage II, yield point, for the tests carried out correspond to around 7 to 7.5, which is in good agreement for dense sands, 7.7, and the tests reviewed from the literature (Golightly, 1990; Nakata et al., 2001; Leleu and Valdes, 2006). Besides, the compressibility beyond the yield point is equivalent irrespective of the initial void ratio.

It is worth also noting that the value for loose (poured) sand, 6.5, agrees to the initial void ratio, $e_o \approx 0.824$ in the oedometers tests.

Table 4.6 Oedometric parameters of sand samples free of oil.

TEST	LOAD			UNLOAD		
	Cc	Em (MPa)	mv (kPa ⁻¹)	Cs	Em (MPa)	mv (kPa ⁻¹)
EDO 1-25	0.310	224	5.27E-06	0.038	876	6.46E-06
EDO 2-25	0.279	251	4.53E-06	0.035	967	7.06E-06
EDO 5-25	0.273	263	4.03E-06	0.033	1075	2.73E-06
EDO 6-25	0.288	240	4.78E-06	0.033	1004	2.04E-06
EDO 7-25	0.286	249	4.71E-06	0.030	1692	1.29E-06
EDO 8-25	0.291	235	4.85E-06	0.038	1150	1.40E-06
EDO 9-25	0.299	220	4.84E-06	0.039	1102	1.48E-06
EDO 10-25	0.309	204	5.43E-06	0.038	1081	1.64E-06
EDO 1-50	0.332	201	5.48E-06	0.038	1137	1.49E-06
EDO 1-60	0.257	291	4.62E-06	0.030	1156	2.05E-06
EDO 1-100	0.306	226	5.25E-06	0.032	1297	1.52E-06
EDO 2-100	0.332	201	5.48E-06	0.038	1137	1.49E-06
EDO 3-100	0.329	207	5.33E-06	0.038	1170	1.45E-06
EDO 4-100	0.332	201	5.48E-06	0.038	1137	1.49E06
EDO 1-150	0.229	365	2.84E-06	0.036	1286	5.37E-06
EDO 2-150	0.287	244	4.38E-06	0.037	1282	1.56E-06
EDO 3-150	0.332	201	5.48E-06	0.038	1137	1.49E-06
EDO 1-200	0.276	231	4.78E-06	0.037	1101	1.53E-06
EDO 2-200	0.281	271	4.30E-06	0.037	1344	1.22E-06
EDO 1-250	0.249	317	3.82E-06	0.032	1591	1.13E-06
Average	0,301	232	4,91E-06	0,036	1215	1,53E-06

LOAD

UNLOAD

Figure 4.42 Oedometric parameters for experimental temperature (25 to 250 °C), under dry conditions.

The results of the oedometric test in the original oil sand samples (15 % oil cont.) are relatively similar to those with free-oil sand (Tables 4.8 and 4.9).

Thus, comparing both results, it seems to be apparent that the 15% of the presence of oil does not have significance affection on the mechanical compressibility behaviour.

Table 4.7 Oedometric parameters for oilsand samples (15 % oil cont.).

TEST	LOAD			UNLOAD		
	Cc	Em (MPa)	m_v (kPa ⁻¹)	Cs	Em (MPa)	m_v (kPa ⁻¹)
EDO 3-25 (14.6% OIL)	0,202	221	5,71E-06	0,033	925,7	-
EDO 4-25 (14.6% OIL)	0,248	302	4,12E-06	0,024	1631	9,50E-07
Average	0,225	261,5	4,92E-06	0,028	1278,3	9,50E-07

Table 4.8 Comparison of oedometric parameters for oil sand samples and sand samples free of oil.

TESTS	LOAD			UNLOAD		
	Cc	Em (MPa)	m_v (kPa ⁻¹)	Cs	Em (MPa)	m_v (kPa ⁻¹)
Oil sands	0,225	261,5	4,92E-06	0,028	1278,3	9,50E-07
Free oil sands	0,305	228,1	4,97E-06	0,036	1219,5	1,52E-06

Microscopic observation

The results of post-test grain size distribution are illustrated in Figure 4.42, proved to be highly insightful, as it becomes apparent the intense crushing (complete splitting) of the sand particles at room temperature, whereas it is negligible in those samples tested at higher temperatures. The fines content at room temperature increases from 5 to 15% on average, and D_{50} reduces in some cases by more than 50%.

Figure 4.43 Grain size distributions post-test on oedometric tests up to 50 MPa and 25 to 250 °C.

The recorded AE data further confirm this observation. Figure 4.43 illustrates the distribution of the AE counts of three 1.5-h time-step experiments performed respectively at 25, 100 and 150°C. It is worth observing the extraordinary reduction in the number of AE counts when the temperature increases.

It is also interesting to note that, at the lower loading steps (up to ~10 MPa), and even during unloading, AE activity is more severe at lower than at higher temperature. Most of this activity is highly concentrated during each load ramps. Once the target stress is reached, the AE decay with time following pseudo-exponential damping, so, although peak activity coincides with the load-rising ramp, there is a continuously decreasing activity during the steady-loading segments. Above 10 MPa (stage II), the AE are much more intense.

This behaviour matches the dominant processes governing the compression of sand at the corresponding stress level. Hence, grain rotation and local crushing would enhance further rearrangement and packing of sand at low loads (stage I) while grain crushing would prevail at higher ones (stage III). According to this experimental data and for the tested sand, grain crushing is not expected at stress levels below 6 MPa.

Figure 4.44 Acoustic emission recorded data for the oedometric tests at 25, 100 and 150 °C. (Supplied by the Geomechanics Laboratory of the University of A Coruña).

On the other hand, the lack of affection of the soil compressibility as the temperature is raised, and in particular, the interplay of the attenuation of AE and the reduction of fines generation is an issue that needs deeper insight and is addressed in the next section.

4.3.4.2 Discussion

As it has been seen, the macroscopic sand compressibility beyond the yield point remains unaffected by the temperature increase whereas the AE activity decays and hardly any changes in the particle size distribution after the tests at higher temperatures are observed.

Consequently, grain-scale mechanical crushing alone seems to fail to account for the sources that result in the same compressibility at higher temperatures. Therefore, additional sources have been investigated.

Fracture parameters

As shown in Figure 4.40, (Pabst, 2013) the elastic parameters of quartz decrease with temperature within the range studied. As the variation of Poisson's ratio with temperature is negligible (Atkinson and Avdis, 1980), only the change of Young's modulus is considered to determine the following fracture parameters.

Figure 4.45 Variation of the elastic parameters with temperature (from Pabst, 2013).

According to Griffith (1920), who studied the rupture of solids, the fracture toughness can be obtained through the equation 4.14, by the relation between Young's modulus and the critical strain energy release rate, G_c , defined as the energy dissipated during fracture per unit of newly created surface area. Characteristic values from 0.307 to 0.593 $\text{MN m}^{-3/2}$ are given by Atkinson and Avdis (1980) for a range of temperatures from 20 to 200°C.

$$K_{IC}^2 = G_c \frac{E}{(1-\nu^2)} \quad (4.14)$$

In turn, the critical strain energy release rate can be obtained through the equation 4.15 where γ_s is the energy required for breaking atomic bonds per unit surface area created by the crack (fracture surface energy). Brace and Walsh (1962) measured the fracture surface energy of quartz at different temperatures, which range from 0.46 to 1.77 for temperatures from 20 to 200°C, see Table 4.10.

$$G_c = 2\gamma_s \quad (4.15)$$

As the energy required for breaking atomic bonds increases with temperature, then the critical strain energy release rate increases accordingly.

Failure stress and critical stress required for the crushing of particles embedded in a soil matrix

The failure stress derived from Griffith's work is given through the equation 4.16.

$$\sigma_f = \sqrt{\frac{G_c E}{\pi c}} \quad (4.16)$$

The value of the initial flaw or crack length, c , can be estimated according to the relation previously given in equation 4.11 for α . Table 4.10 shows the values calculated for 20, 150 and 200°C. As can be noted, the failure stress increases with temperature.

Table 4.9 Failure stresses as a function of the temperature.

T (°C)	E (GPa)	γ_s (J m ⁻²)	G_c (J m ⁻²)	σ_f (MPa)
20	95.6	0.46	0.92	2.49E+03
150	94.5	0.75	1.50	3.16E+03
200	93.5	1.77	3.54	4,83E+03

On the other hand, Table 4.11 depicts the stresses required for the crushing of particles embedded in a soil matrix due to the contact area of sand grains as a function of the temperature (assuming the fracture mechanics and stresses distribution explained in section 4.3.2.2).

It is worth noting that the tangential stress required for the crushing of particles embedded in a soil matrix are in the same range than those obtained by Griffith's equations, given in Table 4.10.

Table 4.10 Critical stresses that cause particle crushing as a function of the temperature.

T (°C)	e	E (GPa)	K_{Ic} ($MN\ m^{-3/2}$)	$dc/2$ (μm)	$\sigma_{t,s}$ (MPa)	σ_{int_cr} (MPa)	σ_{ef_cr} (MPa)
20	0.6	95.6	0.31	8,04E-06	2,32E+03	2,61E+03	12.64
	0.7			7,72E-06	2,32E+03	2,51E+03	9.92
150	0.6	94.5	0.387	9,75E-06	2,89E+03	3,13E+03	25.18
200	0.72	93.5	0.593	1,5E-05	4,44E+03	4,76E+03	69.28

The effective critical stress increases exponentially with temperature, as shown in Figure 4.45. So, the relation between the critical intergranular and effective stresses for the grain breakage tend to be reduced, in particular for the temperature range considered, from 2 to 1 order of magnitude, see Table 4.12.

Figure 4.46 Effective stress that causes crushing as a function of the temperature.

Table 4.11 Relation between intergranular and effective stress as a function of the temperature.

$T (^{\circ}\text{C})$	$\sigma_{\text{int}}/\sigma_{\text{ef}}$	
20	2,53E+02	$\sigma_{\text{int_cr_20C}}=1000*\sigma_{\text{ef_cr}}^{0,401}$
150	1,58E+02	$\sigma_{\text{int_cr_150C}}=1000*\sigma_{\text{ef_cr}}^{0,396}$
200	6,86E+01	$\sigma_{\text{int_cr_200C}}=1000*\sigma_{\text{ef_cr}}^{0,368}$

Grain size susceptible to crush

The grain sizes likely to crush for a given effective stress have been estimated for different temperatures, see Table 4.13. The estimations reveal that at higher temperatures, the grain sizes are much coarser than the range tested. As a consequence, no splitting of the sand particles in the tested sands would be expected to occur.

Table 4.12 Particle size expected to crush for the mechanical processes.

Temperature	20°C			200°C		
K_{IC}	0.31 MN m ^{-3/2}			0.59 MN m ^{-3/2}		
Yield point	10 MPa	15 MPa	20 MPa	10 MPa	15 MPa	20 MPa
Particle size	≥ 300 μm	≥ 240 μm	≥ 200 μm	≥ 1150 μm	≥ 900 μm	≥ 750 μm

However, an SEM analysis of the and grains after tests at 150°C shows incipient fractures, see Figure 4.48, which seems to strike down the principles described above.

Figure 4.47 Incipient cracks on quartz grains tested at 150°C.

Thus, the only possibility for a fracture to occur is by the concurrence of any other phenomenon participating in the crushing process.

Subcritical crack growth

A detailed study by optical microscope revealed that the quartz grains contain fluid inclusions, not only related to the syntaxial cement growth but in the detrital grains as well, Figure 4.47. These fluid inclusions are, in some cases, strongly aligned, as shows Figure 4.48.

Figure 4.48 Fluid inclusions in quartz grains.

Figure 4.49 Fluid inclusions.

Fluid inclusions, that are themselves flaws, may contribute to the crack growth by a process known as stress-corrosion. Stress-corrosion (addressed in detail in chapter 5) occurs by the chemical rupture of the Si-O bonds which contributes to weakening the tip of the flaw or crack, and steadily maintaining the propagation of the crack irrespective of the current stress level.

Stress-corrosion is the main mechanism of a kind of cracking known as subcritical crack growth. That time-dependent phenomenon promotes the crack growing even at a stress lower than the required for a catastrophic breakage, i.e. for stress intensity factor below the fracture toughness.

The incipient fractures within the grains promote further packing for the stress level applied since they become more dislocable.

Thus, at high temperatures, the subcritical cracking growth rate does not release enough amount of energy to generate sound waves (elastic stress waves), and some counts drop off as a result. Conversely, at room temperature, as the catastrophic cracking occurs once the critical effective stress for crushing is reached, the growth rate is higher, and the acoustic wave velocity gives rise to acoustic emissions.

Although this kind of cracking is usually related with the high temperature and wet conditions (coupled thermo-hydro-mechano-chemical process), in the case of the tests developed in this chapter, at dry conditions, the fluid inclusions observed are thought to assist the subcritical cracking by stress-corrosion.

Hence, the compressibility and mechanical responses of the samples tested at high and low temperatures can be explained by the same grain-scale mechanisms of cracking and interparticle slip or grain densification, though the underlying process at high temperature could be silent, i.e., without apparent acoustic emissions.

4.4 Conclusions

The studied sands show both superficial features and grain size morphology that lead to assume an early diagenetic history, yet it does not match fairly well with the current depth location. In this regard, a novel methodology to determine the range of the overconsolidation ratio (OCR) of the reservoir formation based on the determination of the entrapped temperature of fluid inclusions within the syntaxial cement overgrowth of sand particles has been developed. Then, the depth at which the syntaxial cement overgrew can be estimated by plotting the homogenization temperature on the geothermal gradient of the basin. Accordingly, the OCR of the reservoir can be readily obtained, and a preliminary assessment of its compressibility behaviour during production can be evaluated.

An OCR in the range of 1.7 for the reservoir formation at approximately 1100 meters has been obtained. This value is in good agreement with previous values reported in the literature (1.3 to 1.5), and therefore this methodology can be regarded as suitable for this purpose.

On the basis of such a satisfactory outcome, a novel methodology for assessing the formation response has been developed, as long as the in situ porosity and effective stresses are known. Based on the fluid inclusion method and carrying out some oedometric tests, the compressibility during the early stages of production (primary production) can be readily estimated, irrespective of the initial void ratio.

With regard to the effect of the grain size and morphology on the compressibility behaviour, it has been found that the grain size distribution and morphology control the yield point (stage II) and the compressibility during the stage I (rearrangement of the

particles). The acoustic emissions recorded suggest that particle crushing occurs in coincidence with the onset of loading ramps, from about 10 to 20 MPa (for coarser and finer sands respectively), and ceases during the unloading stages until regaining the previous preconsolidation stress at the reloading steps. The intensity in crushing is significant on the coarser sand while in the finer one AE counts are scarce. Hence, the grain size distribution after tests for the coarser, the finer and the uniform-sand tend to become equivalent. Coarser sand experiences an increase of about 12 % in the fines content while an increase of about 7% and 9% can be attributed to the finer and uniform sand, respectively.

That fact result on the basis of the critical stress of breakage depends on the grain size, eq. 4.12 and 4.13. Thus, the effective critical stress increases inversely with the size of the particles, as long as the sand is at a dense state (a coordination number around 7.7, at the yield point). These observations fit pretty well with the acoustic emissions recorded.

With regard to the mechanical behaviour as a function of the temperature, it has been found that the temperature does not affect the preconsolidation stress and beyond the yield point the oedometric curves obtained from the tests carried out at dry conditions are much alike, irrespective of the temperature or the initial void ratio; thus, all the oedometric curves follow a reasonably similar compression pattern ($c_c=0.294$ on average, with a coefficient of variation of 0.1).

Although the AE counts drop off and changes in the particle size distribution are negligible when the temperature is raised, the quartz grains subjected to high temperatures and stresses (150°C and 14 MPa) show incipient fractures.

A detailed study by optical microscope reveals fluid inclusions in the detrital grains, which suggests that subcritical cracking growth may well be considered the cracking process of the grains at high temperature through stress-corrosion.

Hence, the fact that the compressibility remains unaffected with the temperature can be attributed to a change in grain-scale mechanics: from critical rapid crack growth, at low temperatures, to fluid-sensitive subcritical cracking, at the higher ones.

Chapter 5

Thermo-Hydro-Mechano-Chemical Characterization

5.1 Introduction

Following the principles of poroelasticity (Detournay and Cheng, 1993; Wang, 2000), compressibility of porous media can refer to the compatibility between the stiffness of the solid skeleton (sand particles), the fluid compressibility within the porous (water, oil and gas) and the porous pressure caused by the external forces. *(It should be pointed out that the fluid phase compressibility itself is beyond the scope of this dissertation).*

In turn, as it has been addressed in chapter 3, the mere contact of quartz sand particles with an aqueous phase (water/brine) may lead to temperature-and water composition-dependent reactions that cause quartz dissolution in a certain degree.

This hydro-chemical behaviour, together with the increase in the intergranular stresses at the grain contacts during oil production may cause coupled phenomena due to physical and chemical processes which are developed to a greater or lesser extent depending on the temperature and water composition. These processes are known as stress-corrosion, and pressure-solution and their progress increase the reservoir compressibility and decrease the porosity, just as it happens in nature during the diagenetic compaction of sediments.

Sediments compaction and the time-dependent fracture processes (creep mechanisms) related to faults, cataclastic zones, earthquakes or lithosphere cracking take place in wet environments under diagenetic and low-grade metamorphic conditions, where the maximum temperature reached is around 300°C (Fig. 5.1), by mechanical and chemical coupled phenomena such as grain cracking (stress-corrosion) and stress-induced intergranular solution transfer, i.e. pressure-solution (Heard and Carter, 1968; Scholz, 1972; Anderson and Grew, 1976; Rutter and Elliot, 1976; Atkinson, 1984; Atkinson and Meredith, 1987; Scholz, 1990; Engelder, 1993; Ramsay, 1977; Angevine and Turcotte, 1983; Rutter, 1983; James et al., 1986; Palmer and Barton 1987; Tada et al, 1987; Bell and Cuff, 1989; Wong, 1990; Schutjens et al., 1991; Hirth and Tullis, 1992; Wong and Baud, 1999; Karner et al., 2008; Chester et al., 2004, 2007; Brzesowsky et al., 2011, 2014;).

As early as 1970, numerous studies at high temperature have attempted to assess compaction of quartz by pressure-solution in distilled water, alkali solutions and natural brine (Renton et al. 1969, de Boer et al. 1977, Wenwu et al. 2003, 2013). According, it is broadly accepted that quartz sand compaction by pressure-solution is strongly dependent on water composition, temperature, and stresses.

Figure 5.1 Temperature and pressure for diagenesis and metamorphism grades. (Adapted from Prof. Stephen A. Nelson, Lecture note).

- *Stress corrosion cracking*

Subcritical crack propagation under liquid water or vapour water conditions, i.e. stress corrosion cracking, is a time-dependent crack phenomenon defined for quartz by Atkinson, B.K, in 1979 in terms of fracture mechanics (Irwin, G.R., 1958). Where, the stress at the tip of a crack (K) that cause the crack growth is directly proportional to the stress intensity factor (it is assumed that $K=K_I$, mode I stress intensity factor).

In addition, the grain breakage is not controlled by the critical pressure for fracture alone, but under certain chemical conditions, it may well occur at lower stress. In fact, the rupture of the Si-O bonds (see Fig. 5.2), undoubtedly contributes to weakening the tip of the crack, and steadily maintaining the propagation of the crack, irrespective of the current stress level (fluid-sensitive subcritical cracking).

Figure 5.2 Subcritical crack growth - Stress Corrosion (from Alonso et al., 2003 adapted from Michalske and Freiman, 1982).

Following the most widely accepted interpretation, crack propagation is governed by reaction and diffusion rate as a function of the environment conditions (Fig. 5.3).

Figure 5.3 Schematic stress intensity factor-crack velocity diagram for fracture (mode I) of glasses and ceramics in chemically active environments (Atkinson, 1979).

Where K_{IC} is the fracture toughness, and K_0 is the limit of the stress-corrosion. Therefore:

- If $K=K_I \geq K_{IC} \Rightarrow$ immediate (catastrophic) crack breakage;
- If $K=K_I \leq K_0 \Rightarrow$ corrosion reaction ceases $\Rightarrow$ the crack does not propagate.

A kinetic model for subcritical fracture of quartz was given by Dove in (1995), as follow up her works on quartz solubility referred to in chapter 4. The formulation embraces the fracture mechanics theory and a mechanistically-based description of chemical, thermal, and tensile stress effect on reactivity in aqueous environments. Such a model predicts that the fracture rate increases with temperature, which is in agreement with the experimental findings by Atkinson, over a certain range of temperatures (20-80°C).

$$V_{SIO} = A_{H_2O} \exp \frac{-\Delta H_{H_2O}}{R_m T_k} \exp(b_{H_2O} K_I) \theta_{H_2O} + A_{OH} \exp \frac{-\Delta H_{OH}}{R_m T_k} \exp(b_{OH} K_I) \theta_{OH} \quad (5.1)$$

where,

V_{SiO}	fracture rate due to stress-corrosion ($m s^{-1}$)
$\theta_{Si-O}^{H_2O} + \theta_{Si-O}^{OH^-} = 1$	fraction of Si-O reacting with molecular water or hydroxyl ions (* $\theta_{OH^-}=0.00079$ and $\theta_{H_2O}=0.99921$ considering the cation content in the reservoir water (Dove, 1995)).
ΔH_i	activation enthalpy ($kJ mol^{-1}$)
R_m	universal constant of gases ($J mol^{-1}K^{-1}$)
T_k	temperature (Kelvin degree)
A_i	experimental factor ($m s^{-1}$)
b	geometry of the crack tip ($J mol^{-1}$)

Thus, developing the given equation, the fracture rates for temperatures from 20 to 200°C has been obtained (Fig. 5.4.b) for the values of K_{IC} from 0.307 to 0.594 $MN m^{-3/2}$ given in Atkinson, 1980. These results have been compared with those arrived at by Atkinson, (1979) in previous works in distilled water and, as shown in Figure 5.4.a, the log rate of fracture of the grains of quartz in the presence of reservoir water (brine) are higher than that in distilled one. Hence, this response may be attributed to the activity of the cations in the water, as already addressed in chapter 3.

a)

Figure 5.4 Strain rate of a quartz sand particle as a function of the temperature and fracture toughness. a) Distilled water (from Dove modified from Atkinson 1979), b) Results for reservoir water referred to this research

b)

Figure 5.4 (cont.) Strain rate of a quartz sand particle as a function of the temperature and fracture toughness. a) Distilled water (from Dove modified from Atkinson 1979), b) Results for reservoir water referred to this research.

It is worth noting that the temperature has a key effect on the fracture rate, significantly increasing as temperature increase.

To sum up the previous discussion, the grain breakage under wet (even caused by the presence of fluid inclusions, as it has been addressed in chapter 4) conditions may take place under a moderate load by coupled thermo-hydro-mechano-chemical processes which rate depends on the temperature (see Fig. 5.5).

Figure 5.5 Rate of stress-corrosion for a 250 μm quartz grain subjected to 13 MPa of effective stress.

- *Pressure-solution*

The stress-induced intergranular solution transfer commonly termed pressure-solution takes place as a result of the increase of both the stress at the grain-to-grain contact (that cause dissolution of the grains by pressure) and the temperature. Dissolved material is transported by diffusion through the asperities at the intergranular contact area up to the pores, where it is redeposited as a function of the silica concentration. In this regard, pressure-solution phenomenon is expected to reduce the primary porosity significantly (see Fig. 5.6), and control the compaction rate (McClay, 1977; Freeman, 1986; and Wheeler, 1992;).

Figure 5.6 Porous aggregate compaction by Pressure-solution (from Yasuhara, 2003).

The process starts as soon as the intergranular stress acting on the grain-to-grain contacts outreaches the critical activation stress, σ_c , which represent the compressive stress to compensate the thermal energy deficit to displace a mole of mineral from the intergrain contacts.

Revil (1999) gave the expression to obtain it, equation (5.2), modified from Stephenson et al., (1992).

$$\sigma_c = \frac{E_m \left(1 - \frac{T_k}{T_m}\right)}{4V_m} \quad (5.2)$$

In the equation, V_m is the molar volume of the quartz and E_m and T_m are the heat and temperature of fusion of quartz, respectively.

The vertical strain rate due to the grain-to-grain dissolution can be estimated by the expression given by Yasuhara et al., (2003) modified from Revil, (1999). The compaction will continue as far as the reduction of the stress at the grain-to-grain

contact (by the increase of the contact area) down to the critical activation stress. In such condition, the compaction ceases.

$$\dot{\epsilon}_{diss} = \frac{3 V_m K^+}{R_m T d} (\sigma_{int} - \sigma_c) \quad (5.3)$$

Bearing in mind that quartz sand compaction under wet conditions is controlled by thermo-hydro-mechano-chemical interplay, a proper experimental program on compaction that accounts for time and temperature effects should also include processes within the soil and the fluid phase as a function of temperature.

Therefore, in an attempt to cast some light on this issue, a series of brine-saturated oedometric and core flooding tests have been performed at high temperature and stresses conditions.

5.2 Oedometric tests

5.2.1 Experimental Methods and Material

Six oedometric tests on oil-washed sands have been performed with the same equipment and sample preparation as those performed at dry conditions, but in this case, assisted by an injection system. Figure 5.7 shows a scheme of the tests.

Since the tests are designed for assessing the effect of the composition of the reservoir water on the quartz sand compressibility, synthetic brine with virtually the same reservoir composition have been employed (see Table 3.5).

*(**Note that calcium and sodium are the cations with the higher concentration in the reservoir, just the most reactive ones and, accordingly, the cations that basically govern the pore fluid reactivity (dissolution constant). Consequently, the dissolution constant of this brine upon quartz (for strain rate assessments) has been estimated following the guidelines of Dove (1994), Dove et al. (1990) and Dove (1999). The result, roughly $2 \times 10^{-7} \text{ mol/m}^2\text{s}$, is in good agreement with the author*

Figure 5.7 Scheme of the oedometric equipment for brine-saturated tests (Supplied by the Geomechanics Laboratory of the University of A Coruña).

Six tests have been carried out for three different water conditions, constant effective stresses and a target temperature of 150°C with the aim of assessing their compressibility response. Only one sample was tested at dry conditions for the sake of comparing its compressibility result with those at brine-saturated conditions. The silica concentration in the outflow brine, for those tests at brine-saturated conditions, has been determined as well.

1) Dry conditions and constant load: These tests were designed to study the mechanical sand compressibility at constant load (creep) and high temperature. Dry samples were subjected to vertical stress of 13.5 MPa at 150°C for 15 days. Up to reach the setting constant load, the following load sequence, each maintained for 1.5 hours, have been applied: $0.5/1/2/3/5/13.5 \text{ MPa}$.

2) *Pseudo-static brine-saturated conditions and constant load*: These tests were designed to study the effect of chemical processes (coupled hydro-mechano-chemical behaviour) on the sand compressibility at constant load (creep) and high temperature. The samples were saturated with brine and subjected to effective stress of 18 MPa at 150°C. The pore fluid (brine) was kept static for 7 consecutive periods of 24 h, yet it was renovated every day.

The phases of the experimental procedure were as follows:

- Heating and keeping the system at 60°C for 7 days. During the first day, the sample is loaded up to the vertical target stress (0.5/1/2/3/5/10/15/20 MPa).
- The temperature is again raised up to the target temperature (150°C).
- Once the thermo-mechanical stabilization is reached, brine is injected at 2.1 MPa.
- Samples of pore fluid are collected every day (from day 7).
- Finally, the sample is cooled down and dismantled.

3) *Continuous brine flow and constant load*: These tests were designed to study the hydro-mechano-chemical coupled processes on the sand compressibility under constant load (12.5 MPa, saturated with brine at 1 MPa), a high temperature (150°C) and constant brine flow throughout the tests (0.35mL/min). The tests comprised the following stages: heating the system up to the target temperature and a subsequent thermo-mechanical stabilization; loading steps of the sample up to the target vertical stress (0.5/1/2/3/5/13.5 MPa); imposing brine flow (note that a slight gradient suffices); unloading the sample using the reversed loading sequence; cooling down and dismantling.

Table 5.1 summarises the experimental conditions described above.

Table 5.1 Experimental conditions of the oedometric tests.

Test	Dry/Brine-saturated	Temperature (°C)	Applied load	Max. stress applied (MPa)	Pore pressure (MPa)	Effective stress (MPa)	Initial void ratio	Flow rate (ml/min)	Test duration
BRINE-1	<i>Brine-Saturated</i> <i>*Drained</i>	60-150	Constant	20	2	18	0.818	-	29 days
BRINE-2	<i>Brine-Saturated</i> <i>*Daily Renovated fluid</i>	60-150	Constant	20	2	18	0.801	-	15 days
BRINE-3	<i>Brine-Saturated</i> <i>*Continuous Flow</i>	60-150	Constant	21	2	19	0.696	0.35	40 days
EDO-7	<i>Dry</i>	150	Constant	13.5	-	13.5	0.885	-	15 days
EDO-8	<i>Brine-Saturated</i> <i>*Continuous Flow</i>	150	Constant	15	1	14	0.839	0.35	8 days
EDO-9	<i>Brine-Saturated</i> <i>*Continuous Flow</i>	150	Constant	13.5	1	12.5	0.92	0.35	12 days

5.2.2 Oedometric system for brine-saturated tests

In at brine-saturated conditions, the fluid was injected at 2.1 MPa using an ISCO-260HP pump fitted to a PTFE-lined floating-piston accumulator of $\sim 49 \text{ cm}^3$ of capacity. Due to its limited capacity with respect to the duration of the continuous flow of the experiments, periodic refilling was necessary by the aid of a Water 600E HPLC pump connected to a large volume of feed solution.

A backpressure regulator set at 2 MPa was installed at the outlet of the sample in order to avoid desaturation due to water evaporation upon decompression to ambient pressure, to keep the aqueous solution in the liquid state and, ultimately, to ensure a sufficiently small hydraulic gradient to keep a nearly constant pore pressure in the sample. After cooling in a coil, the circulated fluid was allowed depressurising and then collected in a beaker placed on a digital scale.

Figure 5.8 Oedometric equipment for brine-saturated tests.

5.2.3 Results

Figure 5.9 summarises the results of the oedometric tests described in section 5.2.1. It is worth noting that there is significant vertical strain during the very first days of the tests, approximately 1.5-2 days. Such early deformation is likely caused by particle rearrangement once the load is applied, and therefore, it can be considered as the mechanical part of the total vertical strain generated. Thus, once the maximum particle packing is reached (so that the particles are impeded to move), the vertical plastic strain commences.

According to the tests shown in Figure 5.9, the temperature seems to have a clear effect on the effective stress on the final vertical strain. Hence, those samples tested at 150°C reached larger strains and even a higher rate than those that during the first 7 days were set at 60°C (highlighted with a yellow band) before increasing the temperature up to 150°C.

Figure 5.9 Oedometric test at saturated brine conditions vs t dry conditions.

A detailed description and classification of the tests conducted are shown below:

- Dry conditions and constant load

Once the maximum load is reached no time-dependent strain is observed throughout the test (Fig. 5.10.a). Likewise, the grain size distribution after the test hardly exhibits any change (Fig. 5.10.b).

Figure 5.10 Oedometric tests at dry conditions, a constant load of 13 MPa and 150°C: a) Void ratio vs time; b) Grain size distribution.

Once the target load is reached, the particles are impeded to move, and the creep deformation occurs. Figure 5.10.c shows the strain rate achieved, around $1\text{e-}8\text{ s}^{-1}$.

- *Brine-saturated conditions and constant load*

Tests at brine-saturated conditions have been carried out at three different flow conditions: pore fluid drained as a result of the load applied, pseudo-static pore fluid which was renovated daily and continuous brine flow.

The chemical effects, caused by the brine composition, proved to play a relevant part on the compressibility of the quartz sand, in so high a degree that as soon as the brine is fully renovated (daily), the inelastic vertical strain is consistently reactivated at a similar rate, as it can be observed in Figure 5.11.

Figure 5.11 Inelastic vertical strain for daily renovated pore fluid tests at constant $\sigma_{\text{eff}}=18\text{ MPa}$.

In the case of the tests in which a continuous flow (0.35 mL/min) is imposed, the inelastic vertical strains of the sample increase an order of magnitude concerning the daily renovated tests.

This behaviour contrasts with the observed in the oedometric tests at dry conditions, which do not develop any creep at all once the maximum load is reached.

Figure 5.12 depicts these curves, where the vertical inelastic strain is defined as the vertical strain undergone after the mechanical strain, roughly 13%, which correspond to strain experienced during about the first 2 days of the test.

Therefore, the strain caused in the different tests during the first days (2 days) has not been included in the following figures, where only the inelastic strain have been plotted (from the 10th day onwards, in the case of the daily-renovated tests).

Table 5.2 summarises the deformations regarded as mechanical, which were removed from the curves in Figure 5.11. Thus, Figures 5.12 and 5.13 show the resulting curves.

Table 5.2 Non-plastic strain assumed in the oedometric tests.

Test	Dry/Brine-saturated	Temperature (°C)	Effective stress (MPa)	Initial void ratio	Flow rate (ml/min)	Test duration	Non-plastic Strain (%)
BRINE-1	<i>Brine-Saturated</i> <i>*Drained</i>	60 (7 days) -150	18	0.818	-	10 days	16
BRINE-2	<i>Brine-Saturated</i> <i>*Daily Renovated fluid</i>	60 (7 days) -150	18	0.801	-	10 days	14.5
BRINE-3	<i>Brine-Saturated</i> <i>*Continuous Flow</i>	60 (7 days) -150	19	0.696	0.35	10 days	18
EDO-7	<i>Dry</i>	150	13.5	0.885	-	2 days	12.5
EDO-8	<i>Brine-Saturated</i> <i>*Continuous Flow</i>	150	14	0.839	0.35	2 days	19
EDO-9	<i>Brine-Saturated</i> <i>*Continuous Flow</i>	150	12.5	0.92	0.35	2 days	14.5

Figure 5.12 Inelastic vertical strain (creep) for oedometric tests at constant load and 150°C.

In this context, data plotted in a semi-log graph fits fairly well a linear trend (Fig. 5.13), so the creep coefficient, c_α , reaches 0.12 approximately, which is 10 times as high as the coefficient for the dry conditions. (Where $c_\alpha = \frac{-\Delta\epsilon(1+e_o)}{\log \frac{t_i}{t_o}}$).

Thus, the processes that account for creep slow down exponentially over time, being the strain rate at early times in the range of $2 \times 10^{-7} \text{ s}^{-1}$, and about $5 \times 10^{-8} \text{ s}^{-1}$ by the end of the test.

Figure 5.13 Inelastic vertical strain; creep coefficient.

As shown in Figure 5.14, unlike the tests carried out at dry conditions, whose particle size distribution curves hardly undergo any changes, those tests subjected to a continuous brine-saturated flow exhibit a certain degree of grain breakage in the range of 200 to 20 μm , which entails further strains.

Figure 5.14 Grain size distribution after oedometric tests at constant load and 150°C for continuous flow and dry conditions.

The change of the parameters accounting for the grain size distribution is shown in Table 5.3. As can be noted, the change is more significant for those tests conducted at brine-saturated conditions.

Table 5.3 Grain size distribution after dry and brine-saturated tests at constant load.

	<i>Original</i>	<i>Dry</i>	<i>Brine-saturated</i>
D₅₀	194 μm	194 μm	168 μm
D₂₀	82 μm	82 μm	45 μm
D₁₀	41 μm	46 μm	20 μm
Cu	5.3	4.7	9.4
Cc	2.4	1.9	2.5

5.3 Core flooding tests

5.3.1 Experimental Methods and Material

A core flooding device is a system that allows injecting a fluid through a core of sand sample where the confining pressure and temperature are established as well. The sample is placed into a core holder (encased in a Viton jacket) inside an oven, where an ISCO pump system applies the confining pressure using a surrounded fluid.

Firstly the sample is saturated using an external water container, and afterwards, a flow rate is injected into the pore network of the sample. The pore pressure is controlled at the outlet of the sample by a back pressure regulator. Figures 5.15 and 5.16 show a layout and a picture of the device.

Figure 5.15 Layout of the core-flooding equipment.

Figure 5.16 Core-flooding device.

Tests have been carried out at 22 MPa of confining pressure (equivalent to the reference overburden pressure of the reservoir) and 9 MPa of pore pressure (the assumed in the reservoir). The back pressure regulator restores any departure from the target pore pressure. In addition, the settled pressure assures the injected fluid at liquid phase irrespective of the temperature test.

The injected fluid, in this case, synthetic brine, was prepared just with the same composition as in the reservoir, Table 3.5.

As shown in Table 5.4, reconstituted sand samples of 7 cm in length have been prepared by pouring the sand free of oil and impurities (described in chapter 2) into a Viton jacket. Initial porosity, of about 45%, has been determined from the mass of the sand and the total volume of the sample. Two sintered discs with a porosity of about 37% enclose the sand into the jacket to avoid any loss of sand during the test and assure their safety transfer into the core flooding device. *(As it was explained in chapter 4, from about an effective stress of 10 MPa a maximum sand density is expected to be reached (porosity around 36%). Under these conditions, the sintered discs will not interfere in the development of the tests).*

Then, the samples were placed inside the core flooding sample holder (Fig. 5.17) carefully in order to not alter the initial “homogeneous” distribution of the porosity.

Table 5.4 Procedure to prepare samples for the core-flooding test.

<i>Sand sample, viton jacket, sintered discs</i>
<i>Initial porosity determination and sample holder preparation</i>
<i>Sand sample preparation</i>

Figure 5.17 Core sample inside core holder.

A 6 meter 1/8" stainless-steel coil tube is connected to the outlet valve of the sample holder to house the resulting fluid for the subsequent analysis. Each turn of the coil has an internal volume of 8.5 ccs of brine, which corresponds to the resident times and flow rates given in Table 5.5.

Table 5.5 Resident times and flow rates of the injected fluid in the core-flooding tests.

<i>Residence time</i> (day)	<i>Coil</i> turn	<i>Flow rate</i> (cc/min)
1	0,5	0,002951389
2	1	0,004427083
4	1,5	0,005902778
8	2	0,005902778

The fluid volume of the samples as a function of the resident time is plotted in Figure 5.18.

Figure 5.18 Fluid samples as a function of the resident time.

Afterwards, the sampler coil tube was isolated (closing its entry and outlet valves), and detached from the system. Then, it was immediately frozen in liquid nitrogen to prevent any silica diffusion when temperature decreases or any loss of fluid when cut, Figure 5.19.

Figure 5.19 Frozen Coil after testing.

Once frozen, each turn or equivalent sample length is cut, keeping them frozen until its analysis, Figure 5.20.

Figure 5.20 Core-flooding samples.

Finally, silica concentration is determined following the procedures described below:

- Test at 60°C

The fluid in the coil tubes was carefully flushed out by means of a peristaltic pump, then washed by the injection of 25 ml of a solution of NaOH 0.2M, and finally 75 ml of

ultrapure water at room temperature, Figure 5.21.

Figure 5.21 Cleaning procedure of the coil turns by NaOH 0.2M solution and 75 ml of ultrapure water.

Both the tube content and the flushing water were evaporated in a platinum capsule. The solid residue was fused to dissolve the silicon by a mixture of lithium tetraborate and lithium fluoride (Spectraflux 120A, 1.5 grams) at 950°C for 15 minutes. The resulting paste was dissolved by tartaric, and hydrochloric acid. ICP-OES (Inductively Coupled Plasma-Optical Emission Spectroscopy) determined the content of silicon (quantified by the method of standard additions).

- Test at 150°C

As the results of the silica concentration from the tests at 60°C were minor, an enhancing method for the silicon reprecipitated analysis was implemented. With this method, the coil turns were filled up with a solution of NaOH 0.2M and immersed in a bath of water at 40°C for 12 hours. After that, it was placed in an ultrasound bath in water at room temperature for 1 hour (15 min x 4 turns so that the whole inner surface is treated equivalently), Figure 5.22.

Figure 5.22 Ultrasound water bath at 40°C for the resulting coil turns of the core-flooding tests at 150°C.

The fluid extraction, washing, evaporation, and fusion, as well as the determination of silica concentration, followed the same procedure as the test carried out at 60°C.

5.3.2 Methodology for preserving sample fabrics

Since the sand samples are uncemented a novel methodology based on the injection of a jelly solution has been developed with the aim of preserving their fabric after tests for further experiments. As a result, this procedure has resulted in a **patent** entitled ***Fabric preservation of uncemented sand samples.***

Once the tests are concluded, the mentioned jelling solution is injected while keeping the stress and temperature conditions of the tests. By this method, the sand samples preserve their inner fabric for a subsequence observation by means of CT-scan (Fig. 5.23).

Figure 5.23 Sand sample after the jellifying solution injection.

5.3.3 Results

Once the tests were concluded, and after the jellifying completion, the samples were carefully extracted by cutting the Viton jacket. Samples showed proper consistency and handling.

Their diameter showed a radial reduction of around 4% in the case of the test carried out at 60°C and about 8% for that at 150°C, and a respective elongation of nearly a 1% and 7%, see Figure 5.24.

Given that only 2 tests were successfully completed, however reasonable they may seem (and indeed they are), special cautions should be taken in extrapolating these findings to a wide-range behaviour.

Figure 5.24 Plugs diameter before and after core-flooding at 60 and 150°C.

The core-flooding tests carried out at 60 and 150°C yield much lower concentrations (14.5 ppm and 40.5 ppm, respectively, see Tables 5.6 and 5.7) as theoretically expected. It becomes evident, when compared with those obtained with the reactor tests (for instance 250 ppm at 100°C and 900 ppm at 200°C, see Table 3.5) as well as with the literature review (see Figure 3.25) that most of the silica previously dissolved sometime during the core-flooding tests re-precipitated within the pore structure or as quartz overgrowth. It is entirely a likely conclusion that the kinetic rate of precipitation is higher than the injection flow rate established through the sample.

Table 5.6 Silica content at the coil turns core-flooding tests at 60°C.

<i>Residence time</i> <i>(days)</i>	<i>Si</i> <i>(mg)</i>	<i>Sample size</i> <i>(cc)</i>	<i>Si</i> <i>(ppm)</i>	<i>SiO₂</i> <i>(mg)</i>	<i>SiO₂</i> <i>(ppm)</i>	<i>% mass loss</i>
1	<0,003±0,001	4,25	0,71	0,01	8,60	0,00000862
2	0,01±0,001	8,50	0,71	0,01	8,60	0,00000862
4	0,02±0,001	12,75	1,41	0,04	10,10	0,00003448
8	0,12±0,001	17,05	6,80	0,25	14,48	0,000215517

Table 5.7 Silica content at the coil turns core-flooding tests at 150°C.

<i>Residence time</i>	<i>Si</i> <i>(mg)</i>	<i>Sample size</i> <i>(cc)</i>	<i>Si</i> <i>(ppm)</i>	<i>SiO₂</i> <i>(mg)</i>	<i>SiO₂</i> <i>(ppm)</i>	<i>% mass loss</i>
1 day	0,08±0,011	4,25	18,59	0,17	39,55	0,000146552
2 days	0,16±0,011	8,50	19,06	0,34	40,55	0,000293103
4 days	0,20±0,002	12,75	15,37	0,42	32,71	0,000362069
8 days	0,18±0,032	17,05	10,44	0,38	22,21	0,000327586

Thus, for the sake of detecting whether any evolution in the grain-to-grain contacts, porosity changes, silica reprecipitation or any features of pressure-solution or stress-corrosion phenomena have taken place, grain size distributions before and after the tests, tomographic (Micro CT-scan) and SEM study have been carried out.

For that purpose, two mini-samples of about 0.5 cm length have been trimmed from the jellified plugs (see Figure 5.25 and 5.26). This size is suitable for the Micro CT-scan, as it is required at least 4 μm of resolution for proper observation of the grain-to-grain contacts. Figure 5.27 shows the Micro CT-scan device.

Figure 5.25 Plug samples from samples after core-flooding tests at 60 y 150°C.

Figure 5.26 Mini-plugs for Micro CT-scan observation.

Figure 5.27 Micro CT-scan device and mini-plug sample.

Meticulous observation of the sheet images reveals (Fig. 5.28) the presence of preferential breakage alignments both in the samples subjected to 60°C and 150°C. However, crushed grains are more numerous in the sample subject to 60°C, whereas the

sample subjected to 150°C exhibits more “grain indentation” and dissolution features to a greater extent. Such findings seem to underpin that at 60°C the response of the soil can be explained on the grounds of mechanics, while at 150°C mechanical and chemical processes coexist. Accordingly, both stress-corrosion and pressure-solution features are found leading to a porosity reduction of roughly 2-3%.

Figure 5.28 Features of breakage and dissolution in sand grains after the core-flooding test at 60 y 150°C. Slides observation in Micro-CT-scan.

Such porosity reduction has interpreted carefully since those samples might have experienced a slight decompression after extraction from the jacket and all the more so since unfortunately the tomography study was completed two months after testing.

Consequently, it is strongly recommended to carry out more experiments that monitor the in situ permeability and porosity under the range of stresses and temperatures of interest. Unfortunately, the refereed tests failed to prove reliable measurements of permeability and porosity as the accuracy of the sensor were not suitable for the conditions of the tests.

Finally, regarding the grain size distributions, Figure 5.29 shows the curves obtained for the original and the after tests ones. It can be noted, that the after testing curves are alike and have experienced a slight reduction of the D_{50} and D_{10} parameters of around 29.4% and 15.4% respectively with respect to the original; and the C_u and C_c increase slightly after testing, see Table 5.8.

Table 5.8 Grain size distribution after brine-saturated core-flooding tests.

	<i>Original</i>	<i>After the test at 60 °C</i>	<i>After the test at 150 °C</i>
D₅₀	0.26 μm	0.22 μm	0.22 μm
D₁₀	0.17 μm	0.12 μm	0.12 μm
C_u	1.4	1.7	1.7
C_c	0.96	1.04	1.04

Figure 5.29 Grain size distribution before and after core-flooding tests at 60 y 150°C.

These changes are accounted for the features observed in the SEM images displayed in Figures 5.30 and 5.31 which show grain breakage and dissolution pits in the sand samples after the tests and underpin the stress-corrosion proves to develop mainly at intermediate temperatures, approximately 60-100 °C, and the pressure-solution at higher ones, being more relevant over 150°C

TEST AT 60°C
GRAIN BREAKAGE

GRAIN DISSOLUTION

Figure 5.30 SEM pictures of quartz sands grain after corer-flooding tests at 60°C.

TEST AT 150°C
GRAIN BREAKAGE

GRAIN DISSOLUTION

Figure 5.31 SEM pictures of quartz sands grain after corer-flooding tests at 60°C.

5.4 Conclusions

On the basis of the results obtained, the sand compressibility at brine saturated conditions is governed by thermo-hydro-mechano-chemical coupled processes in which the chemical effect of the fluid phase is strongly dependent on its composition and temperature. These coupled processes may cause sand crushing under constant load (fluid-sensitive subcritical cracking) even if the applied stress is lower than the critical pressure of breakage.

On the other hand, pressure-solution starts once the intergranular stress on the grain-to-grain contact exceeds the critical activation stress, σ_c , (eq. 5.1). In this case, for the target experimental temperature of 150°C, the critical activation stress result in 73.12 MPa, (considering $V_m = 2.27 \times 10^{-5} \text{ m}^3/\text{mol}$, $E_m = 8.57 \text{ kJ/mol}$ and $T_m = 1883 \text{ K}$).

In addition, the vertical strain rate due to grain-to-grain dissolution (eq. 5.3) reaches a value of $6 \times 10^{-7} \text{ s}^{-1}$ at the early stages of the compaction test, assuming particles diameter, $d = 200 \text{ }\mu\text{m}$. The dissolution constant rate of the quartz, for the fluid composition, studied (reservoir brine), is assumed to be $k^+ = 2.2 \times 10^{-7} \text{ mol/m}^2\text{s}$, as it has been previously described in chapter 3.

It is interesting to note that this value is in the range of the strain rate at the early stages of the continuous flow oedometric tests, ($2 \times 10^{-7} \text{ s}^{-1}$). This similarity suggests that pressure-solution process may well be involved in the creep reported under such conditions.

This behaviour contrasts with the observed in the oedometric tests at dry conditions, which do not develop any creep at all once the maximum load is reached and the strain rate achieved is around 10^{-8} s^{-1} (Fig. 5.10.c). Thus, the chemical effects, caused by the brine composition, proved to play a relevant part on the compressibility of the quartz sand. The creep coefficient at brine-saturated conditions, c_α , reaches 0.12 approximately, which is 10 times as high as the coefficient for the dry conditions.

Moreover, the tests carried out yield much lower concentrations of silica in the brine injected after the tests (14.5 ppm at 60°C and 40.5 ppm at 150°C, see Tables 5.6 and 5.7) as the expected on the basis of the results obtained in the reactor tests (250 ppm at 100°C and 900 ppm at 200°C, see Table 3.5). That fact suggests that most of the silica

previously dissolved sometime during the tests re-precipitated within the pore structure or as quartz overgrowth.

The observation by means of the CT-scan of the samples after the tests using the novel method patented (*Fabric preservation of uncemented sand samples*) corroborated that evidence. Crushed grains are more numerous in the sample subject to 60°C, whereas the sample subjected to 150°C exhibits more “grain indentation” and dissolution pits.

Thus, on the basis of the theoretical and experimental results, both stress-corrosion and pressure-solution processes are likely to coexist in the creep processes at the experimental conditions performed, leading a porosity reduction of roughly 2-3%.

Chapter 6

Micromechanical model

6.1 Introduction

As it has been analysed in the previous chapters, the increase of temperature caused by the injection of steam or hot water in an uncemented heavy oil reservoir of quartz sands entail coupled thermo-hydro-mechano-chemical processes at particulate level, such as pressure-solution and stress corrosion (and subsequent grain rearrangement), that may lead to further compaction of the reservoir. In particular, the mechano-chemical processes are strongly dependent on water composition and temperature. Thus, the stress-corrosion proves to develop mainly at intermediate temperatures, approximately 60-100 °C, and the pressure-solution at higher ones, being more relevant over 150°C.

Furthermore, it has also been observed that stress-corrosion is a phenomenon that boosts the breakage of particles, leading to further strains just due to particle rearrangement. Thus, stress-corrosion inevitably decays as the maximum packing is approached because of the reduction of intergranular stresses (the number of contacts rises) and consequently, the pressure-solution phenomenon proves to be the key process responsible for the creep observed in the sand samples tested, caused by the dissolution of the grains at their contacts.

Therefore, with the aim of modelling the compaction of an uncemented reservoir of quartz sand subjected to the injection of steam or hot water for producing heavy oil

(scenario simulated in the oedometric tests carried out at brine-saturated conditions at 150°C, see Figure 5.11), a numerical model based only on the pressure-solution phenomena has been implemented.

It is worthwhile mentioning that the specific parameters required for the model, such as the dissolution rate constant of the quartz or the silica solubility (silica concentration in equilibrium) for the target temperature, are provided by the tests conducted in this research.

6.2 Micromechanical model

A number of theoretical models based on the pressure-solution phenomena are available in the literature. In particular, the vertical strain or the strain rate for aggregates or single particles have been studied among other by Raj (1982), Dewar and Ortoleva (1989), Lehner (1995), Schutjens (1991) or Yasuhara (2003).

In the current research, a micromechanical model (modified from the Yasuhara model) has been implemented in MATLAB software. The model is based on the physico-chemicals processes involved in the pressure-solution phenomena so that accounts for the three underlying basic processes, namely: dissolution at the grain-to-grain contact, diffusion of the dissolved matter through the intergranular aqueous film toward the pore space and precipitation of the silica in excess on the pore space.

- Theoretical bases of the model

The physical model consists of two semi-spheres in a cubic packing (initial porosity of 47%). The pore space is saturated by an aqueous solution, even in the sense that an aqueous film covers the contacts themselves.

The model considers only the vertical deformation caused by a load applied over the porous aggregate so that, the possible lateral deformations are excluded. It is supposed that at the initial conditions, the two semi-spheres are facing at punctual contact, thus, as soon as the load is applied, the intergranular stress increases significantly causing, firstly, an elastic deformation due to the Hertzian stress at the contact. Subsequently, a

plastic strain (creep) is generated owing to the grain dissolution at the contact along with the diffusion and precipitation of the mass dissolved. That is, the mass dissolved results in an increase in the silica concentration at the contact (in the aqueous film) so a chemical gradient, between the grain-to-grain contact and the pore space, is generated causing the diffusion of the dissolved matter toward the pore space through the asperities in the contact. Finally, the excess of the silica dissolved precipitates in the pore space causing a further reduction of the porosity. Figure 6.1, displays a cross-section for the representative volume described, showing the deformation caused by the applied force over a period.

Figure 6.1 Layout of the deformation of two semi-spheres due to pressure-solution.

The settings and equations considered in the model are described below.

INITIAL CONDITIONS (t=0)

- *Contact area and grain shortening due to Hertzian forces*

As described in chapter 4, according to the Hertzian Theory, the radius ($d_c/2$) of the contact area of two spheres due to an applied force (F_n) is a function of the grain radius and the Young Modulus (given in equation 4.4). Thus, the relationship between the radius and the shortening of each sphere is given by the eq. 6.1, as given in Figure 6.2.

$$\frac{\left(\frac{d_o}{2}\right)^2}{R} = \delta \quad (6.1)$$

Figure 6.2 Elastic grain shortening.

In addition, the expressions to calculate the applied force from the effective stress applied (macroscopic stress) and the resultant intergranular stress (microscopic stress) are also given in chapter 4, equations 4.3 and 4.5, respectively.

- *Volumes*

As mentioned, with the aim of facilitating further calculations, the representative volume consists of two semi-spheres in a cubic packing. Thus, the initial total volume, V_t , refer to the cube that contains the two semi-spheres (eq. 6.2), while the initial volume of solid, V_{s_in} , denotes to a whole sphere (eq. 6.3).

$$V_t = d_o^2 d_{oz} \quad (6.2)$$

$$V_{s_in} = \frac{1}{12} \pi d_{oz} (3 d_o^2 - d_{oz}^2) \quad (6.3)$$

Figure 6.3 Initial volumes for a cubic packing rearrangement.

- *Silica concentration*

Initially, the system is in equilibrium as the silica concentration in the pores, C_{pore} , along with at the contact area, C_{int} , equal the quartz solubility (maximum silica concentration in equilibrium), C_{eq} , for the temperature considered.

$$C_{eq} = C_{int} = C_{pore}$$

It is worth noting that the pressure-solution process would develop providing that the silica concentrations between the contact area and the pore space are unbalanced.

APPLIED LOAD ($t = t + \Delta t$)

Once a load is applied, the dissolution starts at the grain-to-grain contact (represented by the two semi-spheres) due to the increase of the intergranular stress, and continue as long as the intergranular stress at the contact equal the critical activation stress, σ_c , described in chapter 5 (eq. 5.3).

Note that once the process starts, the intergranular stress, σ_{int} , decreases as the contact area increases due to the dissolution process.

- Contact area diameter, d_c

The variation of the diameter of the contact area during the dissolution process, d_c , can be easily updated by the equation in Figure 6.4, which requires that the value of the resultant grain diameter due to the dissolution, d_z , as well as the cross-sectional diameter due to the precipitation, d_p , have to be previously obtained for the same period of time.

$$d_c = \sqrt{d_0^2 - d_z^2} + (d_p - d_0) \quad (6.4)$$

Figure 6.4 Radius of the contact area as a function of d_z and d evolution.

- Grain diameter during the dissolution process, d_z .

The evolution of the grain diameter during the dissolution process is given by the initial grain diameter minus the corresponding length of the removed volume by dissolution.

In that way, it is straightforward to obtain the removed volume of the spheres at

the contact due to the dissolution process by the geometrical relationships depicted in Figure 6.5.

$$V_{rem} = \frac{\pi}{3} \left(\frac{d_o}{2} - \frac{d_z}{2} \right)^2 \left(d_o + \frac{d_z}{2} \right) \quad (6.5)$$

Figure 6.5 Removed volume of the sphere due to dissolution.

Furthermore, since the shortening process depends on the diffusion of the dissolved mass along the contact area towards the porous space, the removed volume can also be determined as:

$$V_{rem} = \frac{1}{\rho_g} \Sigma \left(\frac{dM_{diffusion}}{dt} \Delta t \right) \quad (6.6)$$

Consequently, d_z , can be obtained equalling equations 6.5 and 6.6.

- Cross-sectional grain diameter due to the precipitation, d_p .

The cross-sectional grain diameter due to the precipitation, d_p (see Figure 6.1), depends on the amount of silica precipitated in the porous space, and in turn on the mass dissolved.

Thus, the grain shortening caused by the dissolution of the grains at the contact over a period can be related to the strain rate by:

$$\dot{\epsilon}_{diss} = \frac{1}{d} \frac{\Delta d}{\Delta t} \approx \frac{1}{V} \frac{dV}{dt} \quad (6.7)$$

The process of pressure-solution is governed by the closed system depicted in

Figure 6.6 and takes place as long as every phase is active. Therefore, for the sake of simplifying for further calculations, just a quarter of a sphere is necessary as the volume involved. Accordingly, the contact area is given by the equation 6.8:

Pressure-solution phases

1. Dissolution
2. Diffusion
3. Precipitation

$$\text{Contact Area} = \frac{\pi}{4d_c^2} \quad (6.8)$$

Figure 6.6 Closed system for the process of the pressure-solution and related contact area.

As a consequence, the strain rate over a period of time for a quarter of a sphere, and a one-dimensional case can be obtained by equation 6.9, where ρ_g is the density of the quartz (2650 kg/m³).

$$\dot{\epsilon}_{diss} = \frac{dM_{dissolution}}{dt} \frac{4}{\pi \rho_g d_c^2} \quad (6.9)$$

Additionally, the strain rate depends on the dissolution constant rate of the quartz, k^+ , the molar volume of quartz, V_m , the intergranular stress, σ_{int} , the critical activation stress, σ_c , the gas constant, R_m , and the temperature, T_k . Accordingly, the strain rate can be determined by the equation 6.10, modified from Yasuhara (2003), since in this case, the intergranular stress, σ_{int} , has been considered as the responsibility of the dissolution process by pressure at the grain-to-grain contact.

$$\dot{\epsilon}_{diss} = \frac{3 V_m^2 k^+ (\sigma_{int} - \sigma_c)}{R_m T_k d} \quad (6.10)$$

It is worth noting that the strain rate depends linearly with the excess of σ_{int} over σ_c . Thus, the process persists as long as the intergranular pressure keeps greater than the critical activation stress.

Finally, the expression for the mass dissolved over any period (eq. 6.11) can be obtained equalling equations 6.9 and 6.10:

$$\frac{dM_{dissolution}}{dt} = \frac{3 V_m^2 k^+ (\sigma_{int} - \sigma_c) \pi \rho_g d_c^2}{4 R_m T_k} \quad (6.11)$$

Thus, the mass dissolved result in an increase of the silica concentration at the grain-to-grain contact area that causes a chemical gradient between the pore space and the contact area, therefore. As a result, the dissolved matter commences diffusing through the contact area towards the pore space where the silica concentration increases and eventually precipitates.

Accordingly, the diffusion rate can be expressed by the equation 6.12 (from Yasuhara, 2003):

$$\frac{dM_{diffusion}}{dt} = \frac{2\pi\omega D_b}{\ln\left(\frac{d_c}{2a_c}\right)} (C_{int} - C_{pore}) \quad (6.12)$$

where D_b is the diffusion coefficient that can be assumed as 1.12×10^{-9} m²/s for the quartz; ω is the thickness of the water film trapped at the contact area; and a_c correspond to the smallest value of the area considered, which is in the range of $a_c \leq x \leq d_c/2$.

Thus, the silica concentration in the contact area is referred to as $(C_{int})_{x=ac}$ and the silica concentration in the pore space to $(C_{pore})_{x=d_c/2}$.

As a result, the amount of silica in excess in the pore space precipitates upon reaching the equilibrium value. So, the precipitation rate can be expressed by the equation 6.13 (Yasuhara, 2003):

$$\frac{dM_{precipitation}}{dt} = \frac{A}{M} k^- V_p (C_{pore} - C_{eq}) \quad (6.13)$$

Where k^- is the precipitation rate, V_p is the volume of the pore space, A is the relative grain surface area, and M is the relative mass of the fluid.

Subsequently, the resulting volume of the solid after the precipitation can be expressed as the difference between the initial volume of the solid and the amount of the remained volume of the dissolved silica in the aqueous phase within the pore volume, given by the equation 6.14.

$$V_s = \frac{1}{12} \pi d_{oz} (3 d_o^2 - d_{oz}^2) - \frac{1}{\rho_g} \Sigma \left(\left(\frac{dM_{diffusion}}{dt} - \frac{dM_{precipitation}}{dt} \right) \Delta t \right) \quad (6.14)$$

In turn, the volume of solids due to the silica dissolution and subsequently re-precipitation can also be obtained using geometrical relationships, which geometry, as depicted in Figure 6.3, is equivalent to a barrel. Thus, the equation of the volume is defined as:

$$V_s = -\frac{\pi}{3} d_p^3 + \frac{\pi}{2} d_p^2 d_0 - \frac{\pi}{6} d_0^3 - \frac{\pi}{12} d_z^3 + \frac{1}{4} \pi d_z d_p^2 \quad (6.15)$$

As a result, the resulting cross-sectional diameter, d_p , caused by the precipitation of the silica in excess in the pore space, can be obtained by equating the expressions 6.14 and 6.15.

- Pore volume and Porosity

Finally, the porosity, n , and the pore volume, V_p , can be directly obtained by the expressions 6.16 and 6.17, which express the total volume and the volume of solids according to the diameter d_z (grain shortening) for any period of time:

$$n = 1 - \frac{V_s}{V_t} = 1 - \frac{V_s}{d_o^2 d_z} \quad (6.16)$$

$$V_p = n (d_o^2 d_z) \quad (6.17)$$

- Integration of the system

As mentioned, the pressure-solution process can be considered as a closed system controlled by the complex coupled processes of dissolution, diffusion, and precipitation.

Therefore, if one of the interacting processes ceases, the whole system will stop. In this manner, it is feasible to obtain the silica concentration at the grain-to-grain contact as well as in the pore volume by the assembling of the series of equations defined.

Thus, invoking Yasuhara (2003), the evolution of the concentrations in the grain-to-grain contact, C_{int} , and the pore space, C_{pore} , can be calculated by the equation 6.18.

$$\begin{Bmatrix} C_{int} \\ C_{pore} \end{Bmatrix}_{t+\Delta t} = \begin{bmatrix} D_1 + \frac{V_p}{4\Delta t} & -D_1 \\ -D_1 & D_1 + D_2 + \frac{V_p}{2\Delta t} \end{bmatrix}^{-1} \left[\begin{Bmatrix} \frac{dM_{dissolution}}{dt} \\ D_2 C_{eq} \end{Bmatrix}_{t+\Delta t} + \frac{1}{4\Delta t} \begin{bmatrix} V_p & 0 \\ 0 & 2V_p \end{bmatrix} \begin{Bmatrix} C_{int} \\ C_{pore} \end{Bmatrix}_t \right] \quad (6.18)$$

Where, for the sake of simplifying, D_1 and D_2 refer to the equations 6.19 and 6.20 respectively.

$$D_1 = \frac{2\pi\omega D_b}{\ln\left(\frac{d_c}{2a_c}\right)} \quad (6.19)$$

$$D_2 = \frac{A}{M} k^- V_p \quad (6.20)$$

6.3 Numerical model

The algorithm for the pressure-solution process implemented in the MATLAB software is depicted in the flow chart shown in Figure 6.7. The program does n steps defined as a function of the total time of the problem. Variables d_z , d_c , d_p , σ_{int} , C_{int} and C_{pore} are computed and updated over a period, Δt , as long as the silica concentration within the pore volume equals the silica concentration in equilibrium for the temperature of the system. Or whether the intergranular stress is reduced below the critical activation value, σ_c . The system is solved by the numerical resolution of the coupled equations described above.

The input values are summarised in Table 6.1. The semi-spheres are considered made of quartz for the values assignation. An experimental time of 30 days has been considered for the length of the simulation in order to compare the numerical results with the experimental ones obtained previously in the oedometric tests subjected to 150°C and brine-saturated conditions.

Table 6.1 Input parameters for Matlab code.

<i>Input parameters</i>	<i>Values</i>
<i>Temperature, T</i>	150°C
<i>Applied stress</i>	13 MPa
<i>Grain diameter, d_o</i>	200 μm
<i>Density, ρ_g</i>	2650 kg/m ³
<i>Young Modulus, E</i>	9.5 x 10 ⁴ MPa
<i>Poisson coefficient, ν</i>	0.007
<i>Quartz molar volume, V_m</i>	2.27x 10 ⁻⁵ m ³ /mol
<i>Interfacial thickness of water, ϖ</i>	4 x 10 ⁻⁹ m
<i>Diffusion coefficient, D_b</i>	1.12 x 10 ⁻⁹ m ² /s
<i>Dissolution constant, k^+</i>	2 x 10 ⁻⁷ mol/m ² s
<i>Precipitation constant, k^-</i>	1.85 x 10 ⁻⁶
<i>Gas constant, R_m</i>	8314 J/mol k
<i>Heat of fusion, E_m</i>	8.57 x 10 ³ kJ/mol
<i>Temperature of fusion, T_m</i>	1883 k
<i>Silica solubility, C_{eq}</i>	257 ppm

Figure 6.7 Flow chart of the model.

6.4 Results

The micromechanical model has been implemented to obtain the evolution of the following parameters, which have been plotted and are summarised in Figure 6.8.

- Grain shortening, d_z .
- Contact diameter, d_c .
- Intergranular stress, σ_{int} .
- Silica concentration at the grain-to-grain contact, C_{int} , and the pore space, C_{pore} .
- Void ratio, e , and porosity, n .
- And the vertical strain.

As shown, the silica concentration at the grain-to-grain contact, C_{int} , as well as within the pore space, C_{pore} , reaches a peak value in concordance with the beginning of the dissolution-diffusion process. These values are gradually reduced, due to the precipitation of the amount of the silica dissolved in excess within the pore space, up to reach the equilibrium value for the studied temperature, 257 ppm. Consequently, both the void ratio and the porosity decrease as a result.

The intergranular stress decreases in time as the contact area between the grains increases due to dissolution. The dissolution of the grains at the contact also yields to the shortening of the grains, a fact that translates into a vertical strain.

That vertical strains decline in time up to cease as soon as the dissolution at the grain-to-grain contact concludes owing to the intergranular stress equal the critical activation stress, σ_c .

The numerical results obtained match reasonably well not only with the theoretical framework but as well with the strains recorded in the oedometric tests performed at brine-saturated conditions and 150°C, which suggests that the pressure-solution process may well be the main process responsible for the creep strains at such conditions.

Even though the true onset of creep strains can hardly be identified, it has been recognised that it may well commence sometime after the early rapid mechanical vertical strains recorded. In the case of the oedometric test edo-8, they may be just beyond the first 2 testing days.

Figure 6.8 Numerical simulation of the evolution of the main variables during the pressure-solution.

Figure 6.8 Numerical simulation of the evolution of the main variables during the pressure-solution (cont.).

Figure 6.8 Numerical simulation of the evolution of the main variables during the pressure-solution (cont.).

Figure 6.8 Numerical simulation of the evolution of the main variables during the pressure-solution (cont.).

Therefore, the numerical and experimental results can be only compared provided that the initial mechanical strains recorded in the oedometric tests be subtracted. In the case of the Matlab results, the magnitude subtracted corresponds to the elastic deformation of the grains at the contact due to the pressure applied.

Figure 6.9 depicts the curves from the numerical simulation and the experimental stretch of the curve that accounts only for the creep response.

Figure 6.9 Vertical plastic strain. Matlab vs experimental results.

It is worth pointing out that the trend of the data shows patterns in good agreement with the numerical model.

It underpins the fact that pressure-solution is the main process responsible for the creep behaviour during the oedometric tests at brine-saturated conditions and 150°C.

6.5 Conclusions

A numerical model has been implemented considering that the pressure-solution phenomenon is the main process responsible for the creep strain at long stage on sand samples subjected at constant load and brine-saturated conditions.

Thus, physico-chemicals complex processes that accounts for the three underlying basic processes, namely: dissolution at the grain-to-grain contact, diffusion of the dissolved matter through the intergranular aqueous film toward the pore space and precipitation of the silica in excess on the pore space have been coupled by the assembling of a series of equations.

The pressure-solution has been considered as a closed system controlled by these three complex coupled processes (dissolution, diffusion, and precipitation), so that if one of the interacting processes ceases, the whole system will stop.

It has been found that the trend in the numerical and experimental data at brine saturated conditions and 150°C display patterns in good agreement which underpins the idea that the processes of dissolution by pressure at the grain-to-grain contact are the phenomenon that prevails in the deformational behaviour at such conditions.

The numerical model implemented accounts for the evolution of the following main parameters:

- Vertical strain.
- Porosity and permeability as a result of the vertical deformation and the reprecipitation of the silica dissolved.
- Intergranular stress at the grain-to-grain contact.

- Diameter of the grain-to-grain contact area.
- Silica concentration at the grain-to-grain contact area and the pore space.

Finally, it is important to note that although the discussed model suffices as a phenomenological approach, advanced numerical models are required to solve upscaled problems spatially.

Chapter 7

Conclusions

7.1 Summary and Conclusions

As part of a comprehensive feasibility project on the scope of EOR applications in a reservoir of heavy oil, this study addresses the compressibility response of the sand formation (namely, Morichal sand), as a result of: (i) the oil production alone; and (ii) the phenomena generated at particulate level by steam injection.

This research contributes to the understanding of the effect of the initial stresses in the reservoir, the temperature and the water composition on compressibility and provides a thermo-hydro-mechano-chemical assessment of the deformational behaviour of the solid skeleton, mainly composed by uncemented quartz sands, regarding “drained” conditions. Considerations on the effect of the heavy oil itself (both mechanical and chemical) are beyond the scope of this research.

The factors presumed to contribute to modify the compressibility of the reservoir have been initially studied in an uncoupled way. For that purpose, a specific series of basic tests have proven to be useful for understanding the significance of each contribution in such complex behaviour.

The following main aspects have been studied:

- Effect of the initial stresses in the reservoir on compressibility.
- Effect of the temperature and stresses on compressibility.

- Effect of the water composition and temperature on the quartz sand dissolution.
- Effect of the water composition and temperature on coupled thermo-hydro-mechano-chemical processes.

The following conclusions can be drawn for the experimental study:

The studied sands show both superficial features and grain size morphology that lead to assume an early diagenetic history, yet it does not match fairly well with the current depth location. In this regard, a novel methodology to determine the range of the overconsolidation ratio (OCR) of the reservoir formation based on petrographic analysis has been developed. The determination of the homogenization temperature of fluid inclusions within the syntaxial cement overgrowth of sand particles provides the entrapped temperature.

Then, by plotting these values on the geothermal gradient of the basin (site of the oilfield), the depth at which the syntaxial cement overgrew can be found. Accordingly, the OCR of the reservoir can be readily obtained, and a preliminary assessment of its compressibility behaviour during production can be evaluated.

An OCR in the range of 1.7 for the reservoir formation at approximately 1100 meters has been obtained. This value is in good agreement with previous values reported in the literature (1.3 to 1.5), and therefore this methodology can be regarded as suitable for this purpose.

On the basis of such a satisfactory outcome, a novel methodology for assessing the formation response has been developed, as long as the in situ porosity and effective stresses are known. Based on the fluid inclusion method and carrying out some oedometric tests, the compressibility during the early stages of production (primary production) can be readily estimated, irrespective of the initial void ratio.

With regard to the mechanical behaviour as a function of the temperature, it has been found that the temperature does not affect the preconsolidation stress and beyond the yield point the oedometric curves obtained from the tests carried out at dry conditions are much alike, irrespective of the temperature or the initial void ratio; thus,

all the oedometric curves follow a reasonably similar compression pattern ($c_c=0.294$ on average, with a coefficient of variation of 0.1).

In addition, the curves are characterised by the following main stages:

- Stage I: This stage comprises the strains from the initial conditions up to the yield point, i.e., the maximum packing of the sand particles. It is mainly controlled by particle rearrangement and minor grain crushing, so it depends on the initial void ratio and the particle grain size distribution. If the soil is well-graded, the coarser grains or the most impeded to move are likely to develop granular chains through which the load is transmitted. Hence, the effective critical stress for breakage increases inversely with the size of the particles, eq. 4.12 and 4.13. The intensity in crushing is significant on the coarser sand while in the finer one AE counts are scarce. Hence, the grain size distribution after tests for the coarser, the finer and the uniform-sand tend to become equivalent. Coarser sand experiences an increase of about 12 % in the fines content while an increase of about 7% and 9% can be attributed to the finer and uniform sand, respectively.
- Stage II: Yield point. The maximum packing of the sand particles is dependent upon the coordination number (number of contacts per particle). That value reaches 7 -7.6 in the studied sands.
Once the soil reaches the maximum packing, in the event that the applied load exceeds its critical pressure, the sand particles start to crush evenly. That state is reached at approximately 10 MPa in the studied quartz sands.
- Stage III: The presented oedometric tests reveal that the compressibility of quartz sand beyond the yield point is not affected either by temperature or the initial void ratio; thus, all the oedometric curves follow a reasonably similar compression pattern ($c_c=0.3$ on average).

Despite the similar results in compaction and unloading results, the AE counts measured during the tests show significant variation. AE at higher temperatures 1) are most frequent at the start of each loading ramp, 2) decay in frequency exponentially with time at each loading step, 3) are rare during unloading, and 4) exhibit lower counts at higher temperatures.

Although the AE counts drop off and changes in the particle size distribution are negligible when the temperature is raised, the quartz grains subjected to high temperatures and stresses (150°C and 14 MPa) show incipient fractures.

A detailed study by optical microscope reveals fluid inclusions in the detrital grains, which suggests that subcritical cracking growth may well be considered the cracking process of the grains at high temperature through stress-corrosion.

Hence, the fact that the compressibility remains unaffected with the temperature can be attributed to a change in grain-scale mechanics: from critical rapid crack growth, at low temperatures, to fluid-sensitive subcritical cracking, at the higher one.

The effect on the solubility of the quartz sand of the composition of the reservoir water as well as the temperature has been studied in an autoclave reactor. The results yield a considerable higher silica concentration than those carried out by preceding authors in distilled water for the same range of temperatures; for instance, the silica solubility in distilled water at 300°C is approximately 700 ppm, while in the reservoir water that value reaches about 900 ppm at just 200°C.

Two chemical phenomena are found to account for this phenomenon. On the one hand, the absorption coefficient of the cations in water and on the other hand, the dissolution rate of the cations with the larger absorption coefficient. Consequently, even though the Na^+ is the principal cation in the water composition of the reservoir, the silica dissolution is controlled by Mg^{++} and Ca^{++} cations since they have the highest adsorption coefficients. For the studied case, at 150°C, the dissolution rate constant of the quartz for the water of the reservoir, brine, is regarded in the range of $2 \times 10^{-7} \text{ mol/m}^2\text{s}$.

The results prove that both the water composition and the temperature have a strong influence on promoting silica dissolution. Moreover, they also provide significant insight into their role in the comprehensive understanding of the compressibility as a result of coupled thermo-hydro-mechano-chemical processes caused by the increase in the temperature and the intergranular stresses.

Finally, as an attempt to study these phenomena in a fully coupled way, a set of

oedometric and core flooding tests at brine-saturated conditions, high stresses and temperature (60 and 150 °C) have been carried out. The tests evidence the concurrence of two coupled processes, namely, stress-corrosion and pressure-solution, identified by means of the observation of the samples after testing (core-flooding samples) by CT-scan and SEM.

It has also been found that the grain size distribution curves after the continuous flow tests increase the particle sizes in their intermediate range at intergranular stresses level below their critical pressure. It is worth noting that such changes are negligible in those tests carried out under dry conditions. Consequently, grain breakage by stress-corrosion has been regarded as the responsible process.

These results lead to the practical implication that the steam injection may damage the integrity of the gravel packs around the wells (i.e. the surrounding annulus packed outside the perforated well with prepared gravel of a specific size and designed to prevent losses of formation sand) as a consequence of the breakage by stress-corrosion of the gravels. In addition, both the breakage of the gravel packs and the formation of sand at the vicinity of the wells may give rise to the so-called sand production (i.e. the migration of sand by the flow of reservoir fluids during production). The production of sand is generally undesirable since it can restrict productivity, erode completion components (gravel packs), block wellbore access, interfere with the operation of downhole equipment, cause significant disposal difficulties and occasionally, if the production of sand is in excess, it may lead to subsidence problems at the surface.

Another relevant finding refers to the fact that the samples tested at brine-saturated conditions and high temperature (150°C), develop creep strains under constant load, which may be mainly attributed to the development of pressure-solution along with some grain crushed by stress-corrosion and rearranged. It is worth noting that in the samples tested at dry conditions such creep is neglected.

It can be inferred by the vertical strain recorded during the tests that the activity of these processes slows down exponentially over time. Thus, the strain rate at the early time of these experiments is $2 \times 10^{-7} \text{ s}^{-1}$ and decays to around $5 \times 10^{-8} \text{ s}^{-1}$ by the end of the tests. At the target experimental temperature, 150°C, the creep coefficient, c_α , is

approximately 0.12, i.e., 10 times higher than for dry conditions.

It is worth remarking that the theoretical vertical strain rate at 150°C for the grain-to-grain dissolution (pressure-solution), estimated in the range of $6 \times 10^{-7} \text{ s}^{-1}$, match fairly well with the range of the early stages of the strain rate of the tests carried out. That fact seems to underpin that the pressure-solution process may well be involved in the creep strains, with a prevailing trend at higher temperatures.

This finding leads to the following important practical consequences from the point of view of the oil production: pressure-solution may entail a reduction of porosity and, hence, permeability, as a result of the re-precipitation of the silica dissolved at the grain-to-grain contact along with the shortening of the grains.

Thus, based on the results of the experimental research, it can be concluded that the coupled hydro-mechano-chemical framework should not be overlooked in a study of the compressibility of quartz sands at brine-saturated conditions, high stresses, and temperature.

To conclude, a phenomenological numerical model considering the physico-chemical processes involved in the pressure-solution phenomena, i.e. dissolution, diffusion, and precipitation, has been implemented. The vertical plastic strain obtained is in reasonably good agreement with the experimental results at brine-saturated conditions, 150°C and continuous flow, which suggests that the pressure-solution process may well be the main process responsible for the creep consolidation at such conditions.

It is interesting to note that having in consideration the good agreement in the vertical strain, the numerical evolution of other parameters may well be taken into account for improving predictions about the in situ behaviour without testing. In this regard, the reduction estimated in the porosity by the numerical simulation reaches approximately 6.5% (for 150°C and 13 MPa of effective stresses), which would be undesirable for the oil production.

In sum, this research contributes in several ways to the understanding of the compressibility of a brine-saturated sand formation subjected at high stresses and temperatures (as a result of the injection of steam and the release of the pore pressure

due to production) and provide a basis for further research including the effect of the oil in the pore volume.

7.2 Main contributions

- Temperature does not affect the compressibility of the sands. The fact that the compressibility remains unaffected with the temperature can be attributed to a change in grain-scale mechanics: from critical rapid crack growth, at low temperatures, to fluid-sensitive subcritical cracking, at the higher ones, without acoustic emissions.
- A novel method to determine the overconsolidation ratio of sands based on fluid inclusions has been developed. The entrapped temperature of the fluid inclusions on the syntaxial cement of quartz sand is determined by microthermometry and can be correlated to the depth of entrapment by the assistance of the geothermal gradient of the area. Thus, the overconsolidation ratio can be assessed relating the depth of entrapment and the in situ depth of the sand (where the extraction of the sand occurs).
- A compressibility model for primary recovery has been proposed. The compressibility model is based on the fluid inclusions method and a set of oedometric tests from whatever initial void ratio, vertical stress higher (say, twice as high) than the in situ, and load-unload-reload cycles. In that way, once the compressibility behaviour (normal consolidated or overconsolidated sand) and the oedometer curve are defined, the changes in the void ratio or the porosity can be estimated as a result of the increase of the stress.
- An equation to determine the macroscopic critical effective stress that causes the grain crushing of the particles embedded in a soil matrix at its maximum packing has been proposed. The macroscopic stress can be related to the microscopic one by the fracture toughness of the quartz at different temperatures, and the coordination number. The critical effective stress depends on the particle size.

- A patent to preserve uncemented sand samples has been developed, entitled “Fabric preservation of uncemented sand samples” (Patentscope: WO/2018/149866). That methodology allows the handling of the samples after the tests for further observations or experiments. The fluid for the preservation can be easily removed and does not affect the original sand grains.

7.3 Further works

Finally, it should be pointed out that although the MATLAB model suffices as a phenomenological approach regarding the effect of the increase of the temperature and the water composition on the behaviour of sand particles, advanced numerical and FEM models are required to solve upscaling models that comprise the comprehensive compressibility of the reservoir. In this context, additional research is also necessary to evaluate both the chemical and the mechanical implications of the heavy oil on such complex behaviour, such as:

- Study of the presence of oil on the sand solubility.
- Study of the compressibility of original samples saturated or partially saturated with oil and brine during the injection of steam or hot water.
- Study of the effect of the temperature on the compressibility on samples saturated or partially saturated with oil.
- Study of the effect of the presence of oil on the silica reprecipitation on the pore space.
- Study of the effect of the oil on coupled processes such as stress-corrosion and pressure solution.
- Study of the Helen-Shaw flow as a result of the steam or hot water injection on samples saturated or partially saturated with oil, and its impact on the compressibility, changes on the porosity and permeability.

7.4 Publications

The present research gives, as a result, the following publications and patent:

- Martín Ruiz, M., Alvarellos Iglesias, J., Delgado Martín, J., Goicolea J.M. *Quartz sand compressibility at high stresses and temperature*. (Accepted for publishing in Acta Geotechnica Slovenica. Vol. 16, No.2.).
- Martín Ruiz, M., Alvarellos Iglesias, J., Escobar, E., Souraki, Y. *Mechanical-Chemical Constitutive Model for Unconsolidated Sands with Heavy Oil*. Conference on the Technology Centre of Repsol. Madrid (October, 2015).
- Martín Ruiz, M., Alvarellos Iglesias, J., Delgado Martín, J., Escobar, E., Goicolea J.M. *Experimental Characterization of THMC Behaviour in Granular Uncemented Media During Heavy Oil Production (EOR)*. International Conference on Coupled THMC Processes- Paris (July 2017).
- Martín Ruiz, M., Alvarellos Iglesias, J., Escobar, E. Patent: *Fabric preservation of uncemented sand samples*. (Patentscope: WO/2018/149866).

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APPENDICES

APPENDIX 1

API DENSITY

API stands for the American Petroleum Institute, which is the largest trade association of the United States in the industry of oil and natural gas. The API represents about 400 corporations in the petroleum industry and helps to set standards for production, refinement, and distribution of petroleum products. They also advocate on behalf of the industry. One of the most important standards that the API has set is the method used for measuring the density of petroleum. This standard is called the API gravity.

Specific gravity is a ratio of the density of one substance to the density of a reference substance, usually water. The API gravity is nothing more than the standard specific gravity used by the oil industry, which compares the density of oil to that of water through a calculation designed to ensure consistency in measurement. Less dense oil or “light oil” is preferable to more dense oil as it contains greater quantities of hydrocarbons that can be converted to gasoline.

Petroleum is less dense than water, and in 1916, the U.S. government instituted the Baumé scale as the standard measure for any liquid less dense than water. That, in most cases, applies to oil. The value used in this scale was 141.5 (see calculation below), but subsequent testing showed that, due to error, the actual value should be 140. The government changed the scale to 140 to correct the issue, but the use of 141.5 had become so entrenched in the oil industry that the API decided to create the API gravity scale using the old value of 141.5.

API gravity is calculated using the specific gravity of oil, which is nothing more than the ratio of its density to that of water (density of the oil/density of water). Specific gravity for API calculations is always determined at 60 degrees Fahrenheit. API gravity is found as follows:

$$\text{API gravity} = (141.5/\text{Specific Gravity}) - 131.5$$

Though API values do not have units, they are often referred to as degrees. So the API gravity of West Texas Intermediate is said to be 39.6 degrees. API gravity moves inversely to density, which means the denser the oil is, the lower its API gravity will be.

An API of 10 is equivalent to water, which means any oil with an API above 10 will float on water while any with an API below 10 will sink.

The API gravity is used to classify oils as light, medium, heavy, or extra heavy. As the “weight” of oil is the largest determinant of its market value, API gravity is exceptionally important. The API values for each “weight” are as follows:

- Light – API > 31.1
- Medium – API between 22.3 and 31.1
- Heavy – API < 22.3
- Extra Heavy – API < 10.0

These are only rough valuations as the exact demarcation in API gravity between light and heavy oil changes depending on the region from which oil came. The fluctuation as to what constitutes light crude in a given region is the result of commodity trading in oil.

Because density is a measure of weight per volume, API can be used to calculate how many barrels of crude can be extracted from a metric ton of a given oil. A metric ton of West Texas Intermediate, with an API of 39.6, will produce 7.6 barrels (at 42 gallons each). The calculation is:

$$\text{Barrels per metric ton} = 1 / [(141.5 / (\text{API} + 131.5)) \times 0.159]$$

(From Petroleum.co.uk)

APPENDIX 2

MATLAB CODE


```

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%% PRESSURE-SOLUTION %%%%%%%%%%
clear all

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%% Time %%%%%%%%%%

Time=input('Time (DAYS): ');
Dt=86400;
Ttot=86400*Time;
Nsteps=Ttot/Dt;

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%% Input parameters%%%%%%%%%

TC=input('Temperature (C): ');

Tk=(TC+274.15); % K (Sistema Internacional)

Vm=2.27*10^-5; % Molar Vol quartz. m3/mol
w=4*10^-9; % water thickness. m
Db=1.12*10^-9; % Diff. Coeff. m2*s-1
kdiss=2*10^-7; % k+ Cte diss. mol m-2 s-1.
kprec=13*1.42*10^-7; % k_ Cte prec. s-1
rg=2650; % Quartz density. kg m-3
R=8.314; % Gas Cte. J mol-1 K-1
E=95*10^9; % Quartz Young Mod. Pa
v=0.0077; % Quartz Coef. Poisson
Em=8.57*10^3; % J mol^-1;
Tm=1883; % K;

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%% Initial conditions - Hertz%%%%%%%%%

do=input('Diámetro partículas (m): ');
dz=do;
d=do;
ro=do/2;
rz=dz/2;
r=d/2;
Ro=(ro*ro)/(ro+ro);
Vs=(pi*(do^3))/6;
Vt=(do^2)*dz;
n=1-Vs/Vt;
e=n/(1-n);
Vp=n*Vs;
permeability=n*Vp/(24*pi*do);
Sog=4*pi*(rz*r);
Nu=(1-n)/Vs;
Ar=Nu*Sog;
rw=1000;
Sr=1;
Mr=Vp*rw*Sr;

```

```

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%% load applied %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

sef=input('sef (Pa): ');

Fn=do^2*sef*(pi*(1+e)^2/12);
E0=E/(2*(1-v^2));
dc=2*((3*Fn*Ro)/(4*E0))^(1/3);
rc=dc/2;
ContactArea=pi*((rc)^2);
ad=0.0001*(dc/2);
sint=Fn/ContactArea
sc=(Em*(1-(Tk/Tm)))/(4*Vm)

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%% Initial Concentration SiO2 %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

Cint0=input('Cint (kg/m3): ');
                                     % 257 ppm (0.257 kg/m3)
Ceq=input('Ceq (kg/m3): ');
Cpore0=input('Cpore (kg/m3): ');

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%% (I=1) %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

I=1;

Mdis(I)=0;
DMdis=((3*pi*(Vm^2)*(sint-sc)*kdis*rg*dc^2)/(4*R*Tk))

Mdiff(I)=0;
Mprec(I)=0;

D1=(2*pi*w*Db)/log(dc/(ad^2));
D2=kprec*Vp*Ar/Mr;

C=((([D1+(Vp/(4*Dt)) -D1;-D1 D1+D2+(Vp/(2*Dt))])^(-
1))*([DMdis;Ceq*D2]+(1/(4*Dt))*[Vp 0;0 2*Vp]*[Cint0;Cpore0])));
Cint(I)=real(C(1));
Cpore(I)=real(C(2));

Vrem=0;
B0=pi/24;
B1=0;
B2=-pi*do^2/8;
B3=((pi*do^3)/12)-Vrem;
Dz=[B0,B1,B2,B3];
x=roots(Dz);
dz=real(x(3,1));
rz=dz/2;

DP=(Mdiff(I)-Mprec(I))/rg;
Vs=((pi*do^3/6)-DP);

```

```

A0=-pi/3;
A1=pi*(0.25*dz+0.5*do);
A2=0;
A3=(-pi*dz*(dz^2/12))-(pi*do*(do^2/6))-Vs;
D=[A0,A1,A2,A3];
z=roots(D);
d=z(2,1);
dr=real(z(2,1));
r=dr/2;

Vs=(-pi*d^3/3)+((pi*dz)*((d^2)/4)-
((dz^2)/12))+((pi*do)*((d^2)/2)-(do^2)/6));
Vt=(do^2)*dz;
n=1-Vs/Vt;
e=n/(1-n);
Vp=n*Vs;
permeability=(n*Vp/24*pi*do)/(9.86923*10^-13);
%(darcy) 1darcy = 9.86923*10^-13 m^2
Sog=4*pi*(rz*r);
Nu=(1-n)/Vs;
Ar=Nu*Sog;
Mr=Vp*rw*Sr;
Maxcroarea=(pi*d^2/4)-(d^2*acos(do/d))+do*sqrt(d^2-do^2);
dc=sqrt(do^2-dz^2)+(d-do);
ContactArea=pi*(dc/2)^2;
Fn=dz^2*sef*(pi*(1+e)^2/12);

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%% Vectors %%%%%%%%%%%%%%

Porosity=[];
Time=[];
Indicehuecos=[];
Permeability=[];
dcont=[];
dzdiss=[];
Cinterface=[];
Cporo=[];
Sintg=[];
Density=[];

for I=1:Nsteps

    DMdiss=(3*pi*(Vm^2)*(sint-sc)*kdiss*rg*dc^2)/(4*R*Tk);
    Mdiss(I+1)=Mdiss(I)+DMdiss*Dt;

    DMdiff=(2*pi*w*Db*(Cint(I)-real(Cpore(I))))/log(dc/ad*2);
    Mdifff(I+1)=Mdifff(I)+real(DMdiff)*Dt;

    DMprec=((Vp*Ar*kprec*(real(Cpore(I))-Ceq))/Mr);
    Mprec(I+1)=Mprec(I)+real(DMprec)*Dt;

```

```

Vrem=(1/rg)*Mdiff(I+1);
B0=pi/24;
B1=0;
B2=-pi*do^2/8;
B3=((pi*do^3)/12)-Vrem;
Dz=[B0,B1,B2,B3];
x=roots(Dz);
dz=real(x(3,1));

DP=(Mdiff(I+1)-Mprec(I+1))/rg;
Vs=(pi*do^3/6)-DP;
A0=-pi/3;
A1=pi*(0.25*dz+0.5*do);
A2=0;
A3=(-pi/12)*(dz^3)-((pi/3)*(do^3))+DP;
D=[A0,A1,A2,A3];
z=roots(D);
d=z(2,1);
dr=real(z(2,1));

rz=dz/2;
r=d/2;
Vt=do^2*dz;
n=1-(Vs/(Vt));
e=n/(1-n);
Vp=n*Vs;
permeability=(n*Vp/24*pi*do)/(9.86923*10^-13);
Sog=4*pi*(rz*r);
Nu=(1-n)/Vs;
Ar=Nu*Sog;
Mr=Vp*rw*Sr;
Maxcroarea=(pi*d^2/4)-(d^2*acos(do/d))+do*sqrt(d^2-do^2);
dc=sqrt(do^2-dz^2)+(d-do);
ContactArea=pi*(dc/2)^2;

D1=(2*pi*w*Db)/log(dc/(ad*2));
D2=kprec*Vp*Ar/Mr;

C=([D1+Vp/(4*Dt),-D1;-D1,D1+D2+Vp/(2*Dt)]^(-1)*([DMdiss;Ceq*D2]+(1/(4*Dt))*[Vp 0;0 2*Vp]*[Cint(I);Cpore(I)]));
Cint(I+1)=real(C(1));
Cpore(I+1)=real(C(2));

Fn=dz^2*sef*(pi*(1+e)^2/12);
sint=Fn/ContactArea;

density=rg/(1+e);

```



```

    tiempo=I*Dt;
    Porosity=[Porosity;n];
    Time=[Time;tiempo];
    Indicehuecos=[Indicehuecos;e];
    Permeability=[Permeability;permeability];
    dcont=[dcont;dc];
    dzdiss=[dzdiss;dz];
    Cintp=Cint(I)*1000;
    Cporep=Cpore(I)*1000;
    Cinterface=[Cinterface;Cintp];
    Cporo=[Cporo;Cporep];
    Sintg=[Sintg;sint];
    Density=[Density;density];

end

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%% Figures %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

    figure(1)
    plot(Time/(86400),Porosity),xlabel('Time
(days)'),ylabel('Porosity')
    axis('auto');

    figure(2)
    plot(Time/(86400),Indicehuecos),xlabel('Time
(days)'),ylabel('Void Ratio (e)')
    axis('auto');

    figure(3)
    plot(Time/(86400),Permeability),xlabel('Time
(days)'),ylabel('Permeability (darcy)')
    axis('auto');

    figure(4)
    plot(Time/(86400),dcont*1e6),xlabel('Time
(days)'),ylabel('contact area diameter, dc (micras)')
    axis('auto');

    figure(5)
    plot(Time/(86400),dzdiss*1e6),xlabel('Time
(days)'),ylabel('diameter after dissolution,dz (micras)')
    axis('auto');

    figure(6)
    plot(Time/(86400),Cinterface),xlabel('Time
(days)'),ylabel('Cint (ppm)')
    axis('auto');

    figure(7)
    plot(Time/(86400),Cporo),xlabel('Time
(days)'),ylabel('Cpore (ppm)')
    axis('auto');

```

```

figure(8)
plot(Time/(86400),Sintg),xlabel('Time
(days)'),ylabel('Sint (Pa)')
axis('auto');
%hold on
%plot (Time/86400,sef),xlabel('Time (days)'),ylabel('sef
Pa')
axis('auto');

figure(9)
plot(Time/(86400),(((do-dzdiss)/do))*100),xlabel('Time
(days)'),ylabel('deformación vertical (%)')
axis('auto');

figure(10)
plot (Time/(86400),Density/1000),xlabel('Time
(days)'),ylabel('Density (g/cm3)')
axis('auto');

```