

SACS2 EUROPEAN RESEARCH PROJECT

WORK PACKAGE 7 (WP7)

Petroacoustics of poorly consolidated reservoir rocks saturated with CO₂/ Methane/Brine Mixtures

FINAL TECHNICAL REPORT

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Introduction

The quantitative interpretation of time-lapse seismic monitoring relies on a sufficiently accurate estimation of the fluid substitution impact on seismic velocity in the reservoir. The theoretical basis of this quantification is the well-known Gassmann model which relates the elastic moduli of the fluid saturated rock (bulk modulus: K_{sat} and shear modulus: μ_{sat})

- to the porosity (ϕ)
- to the moduli of the dry rock (bulk: K_{dry} and Shear μ_{dry}) bulk modulus of the rock forming mineral (K_g).
- to the saturating fluids bulk modulus (K_{fl}),

Assuming the validity of Gassmann's formula, and assuming that the three independent mechanical parameters (K_{sat} , μ_{sat} and K_g) of the rock are known, the impact of fluid saturation can be computed. In order to do this, we need:

- 1) to check the validity of Gassmann's formula,
- 2) to measure the rock parameters and
- 3) to compute the compressibility and density of the saturating mixtures.

The work in WP7 was focused on these three points.

In this report, we will follow the initial work proposal section:

A) Petroacoustics, corresponding to points 1 and 2

B) Thermodynamics, corresponding to point 3

A - Petroacoustics

1 - Accurate verification of Gassmann's formula.

The accurate verification of the Gassmann's formula and the measurement of necessary mechanical parameters on core samples are less trivial than it could seem. The conventional way is to measure P and S wave velocity in the sample in two contrasted states of saturation: dry and fully brine-saturated. But this method has two major drawbacks: 1) It is well known that dry state corresponds to a very peculiar mechanical situation in rocks with grain contacts (like sandstone) and 2) This method gives only two points to draw the K_{rock} vs. K_{fl} curve and any experimental uncertainty induces critical consequences on the result.

In order to solve these difficulties we developed an experimental protocol in order to prepare the measurements on SACS core samples.

1-1 Measurement principles and experimental set-up

Principles

- The basis of the method is to substitute liquids of different K_{fl} without modifying the sample acoustic measurement set-up in order to monitor precisely the slightest changes in P and S-wave velocity.
- To allow a good fluid substitution, we have better to use miscible displacement (i.e. to displace the saturating liquid by a liquid perfectly miscible).
- But on the other hand, as we know the importance of the residual water (S_{wi}) on the acoustic properties of sandstone, we would have better to perform this fluid substitution while keeping the irreducible water saturation and thus, to use liquid non-miscible with water.
- Last, but not least, as an argillaceous fraction could always be found in sandstone we have to avoid the use of any liquid reacting with clay minerals.

We performed several experiments to check these points. Although the confining pressure has a major impact on acoustic properties, we worked in 'room conditions' (to avoid long immobilization of confinement cells) but always keeping in mind the necessity to adapt the method to confined measurements for real reservoir samples.

Experimental set-up

We used two types of outcrop sandstone:

- Vosges sandstone, medium grain, slightly argillaceous, medium porosity (20%), high permeability (1,5 D). Sample VS 1.
- Meule sandstone, fine grain, argillaceous and micaceous, medium porosity (20%), medium permeability (150 mD). Sample MS 1 and MS 2.

To monitor the impact of fluid interaction with rock matrix, we used also a reference sample of Estailades limestone (30 % porosity, 300 mD permeability sample - no chemical interaction between calcite and the saturating liquids). Sample L 1

A sketch of the experimental set-up is shown on figure 1

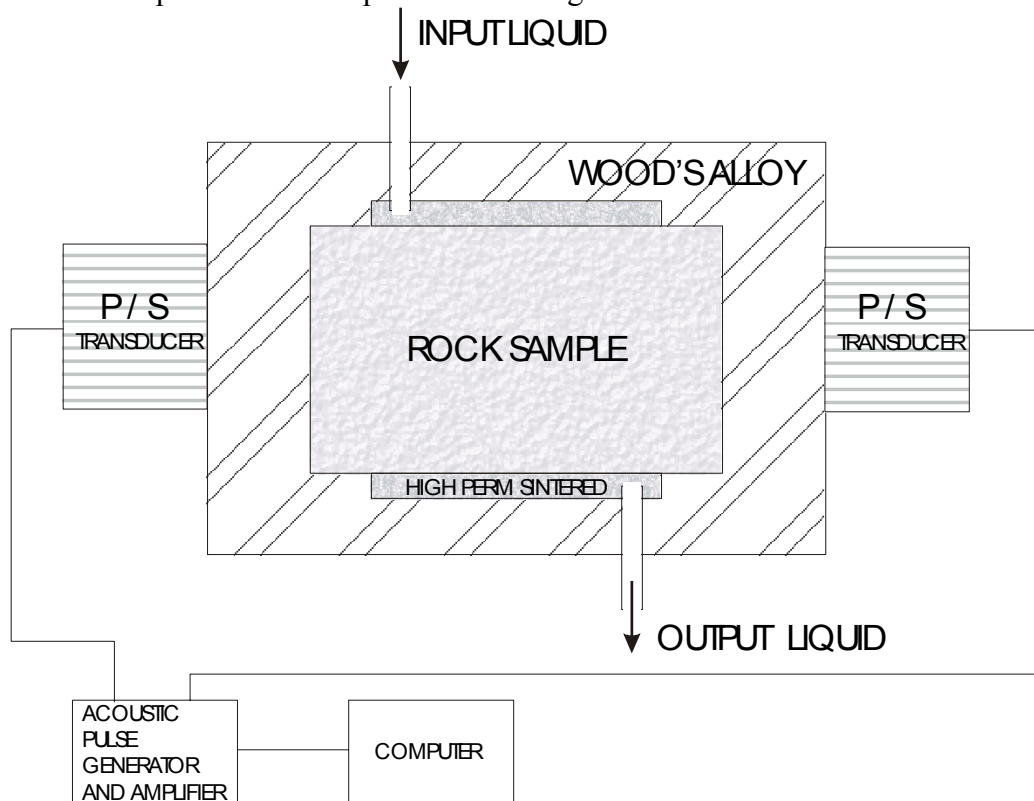


Figure 1: Sketch of the experimental set-up

The sample is imbedded in Wood's alloy (melting point 70°C) which allows a perfect acoustic coupling between transducers and rock sample. The liquid substitution was performed by low rate, low pressure displacement of at least 5 pore volumes.

The P and S-waveform are recorded, an absolute velocity measurement is performed by first break pick-up at a given saturation state and the other velocity are computed by signal correlation. This method allows a precise detection of very slight velocity variations.

By measuring precisely the specific gravity (ρ) and the sound velocity (V) of the liquid, we can easily compute the bulk modulus ($K = \rho V^2$). We tested several liquids and liquid mixtures in order to use bulk modulus between 0.8 GPa (Pentane) and 3.2 GPa (Ethylene glycol). Bulk modulus of brine at room condition is around 2.3 GPa and is practically zero for air.

Mixture of Ethanol and Ethylene glycol provides a continuous variation of K_{fl} between 1.1 GPa and 3.2 GPa. Unfortunately these mixtures react with clay minerals.

The experiment start with an acoustic measurement of the 'dry' air saturated sample. The sample is then vacuum evacuated and fully saturated with desaerated KCl brine (to protect clay mineral) or tap water (limestones). For the 4 samples used, various displacements were performed:

- MS1: monophasic miscible displacement of Ethanol, 3 different mixtures of Ethanol-Ethylene glycol, pure Ethylene glycol.
- MS2: diphasic displacement of water by kerosene, the viscosity contrast between kerosene and water being low, the resulting irreducible saturation is rather high (50%), then miscible displacement of the movable non-wetting phase: heptane, hexane, pentane. For diphasic saturation state, the saturating mixture bulk modulus (K_{fl}) is computed as the weighted harmonic mean of the two liquids bulk modulus)
- VS2: diphasic displacement of water by high viscosity (400 cP) Vaseline oil ($S_{wi}=25\%$), then miscible displacement of the movable non-wetting phase: low viscosity (1cP) oil, Pentane, Trichloroethylene, Aniline.
- L1 : reference limestone sample : All the previously described sequences (the diphasic water displacement was performed first using kerosene then medium viscosity (200 cP) Vaseline oil ($S_{wi}=40\%$),

1-2 Experimental results

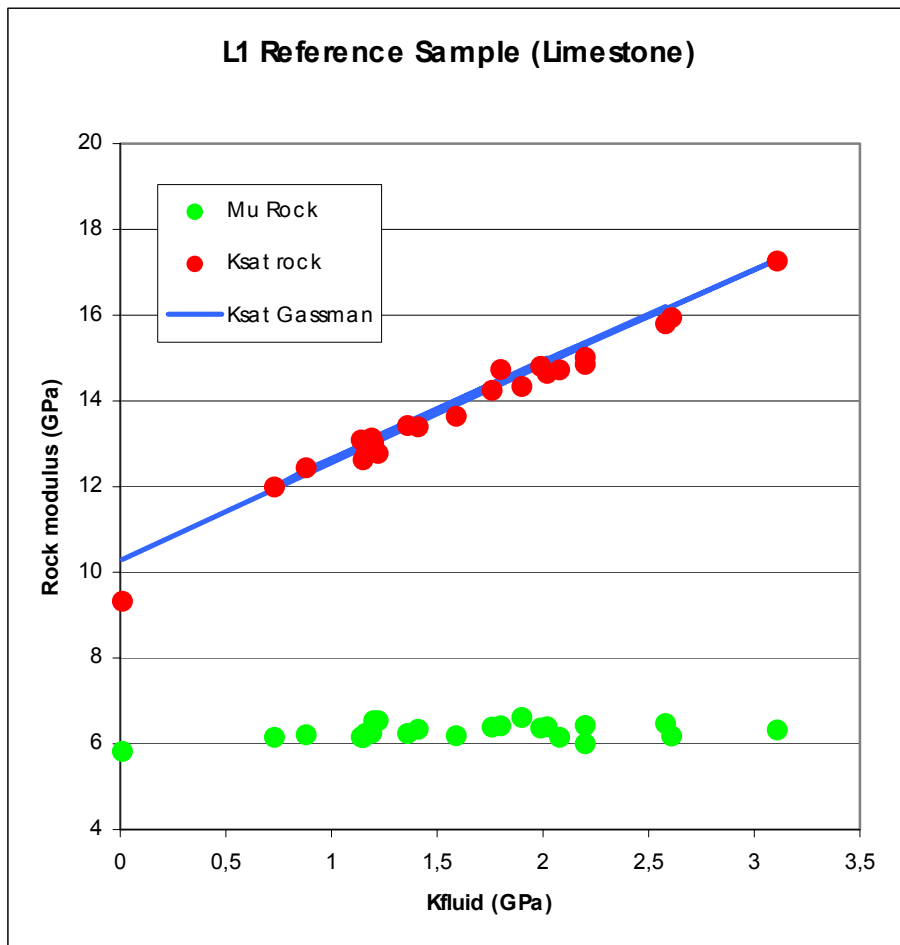
The experimental results for each samples are presented on plots (figures 2 to 5) giving the rock Bulk and Shear moduli as functions of the Bulk modulus (K_{fl}) of the saturating liquid. The nature of saturating fluid for any experimental point, could be found searching for the corresponding K_{fl} on the table below the graph.

The results for the reference sample are really good. 17 measurements corresponding to liquids of K_{fl} varying between 0,73 and 3,11 GPa exhibit a nearly perfect agreement with the Gassmann's formula prediction. The Gassmann values were computed using $K_{grain} = 70$ GPa (calcite) and, for K_{dry} , the value of the intersection with Y axis of the linear regression of experimental values, excluding the air saturated value because of the well known problem with 'dry' samples, particularly in experiments at atmospheric pressure.

- We have an exceptional example of experimental validation of Gassmann's formula.
- This experimental verification is valid for both monophasic and diphasic saturation state (and thus, we validate the method of weighted harmonic mean of liquids bulk modulus).
- The method allows a precise experimental measurement of Gassmann' parameters on core sample (K_{dry} and K_{grain} , derived from the slope of the regression line).

The results on the limestone sample are particularly good because there is no chemical reaction between the rock matrix and the various liquids used in the experiment. We have to check the validity of the method for sandstone containing clay minerals.

Reference Sample L1 (figure 2), Estailades Limestone:



MONOPHASIC

Fluid	Vacuun	Pentane	Heptan	Ethanol	1 cP oil	kerozene	200 cP oil	water	Ethyleneglyc
Bulk modulus G	0	0,73	0,88	1,15	1,16	1,41	1,8	2,2	3,11

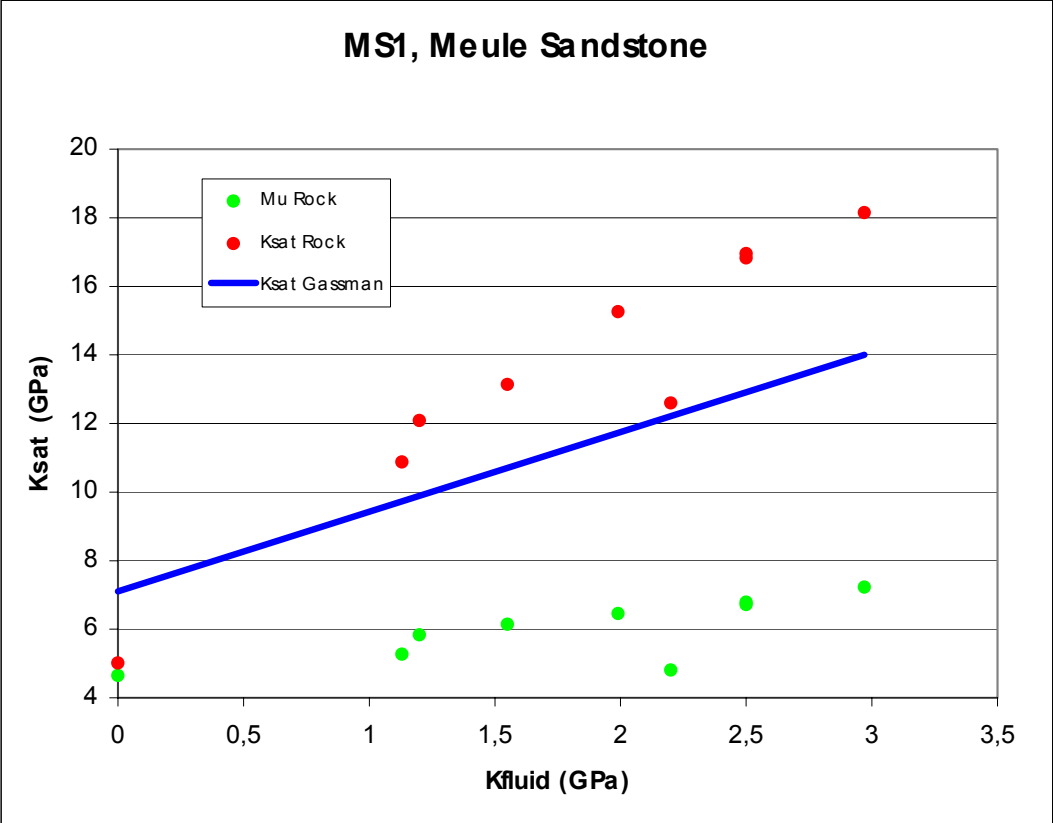
Fluid	Mixture of Ethylene-glyc and Ethanol		
Bulk modulus G	1,59	2,08	2,61

DIPHASIC

Water plus						
Fluid	Hexane	Trichloro	Kerozer	Kerozer	200 cP	Aniline
Fluid saturation	40%	40%	40%	21%	40%	40%
Bulk modulus G	1,2	1,9	1,76	1,99	2,02	2,58

Figure 2: L1 Reference Limestone Bulk and Shear Modulus vs. Saturating Fluid Modulus

MS1 (figure 3), Meule Sandstone, Monophasic displacement, Reactive liquids:



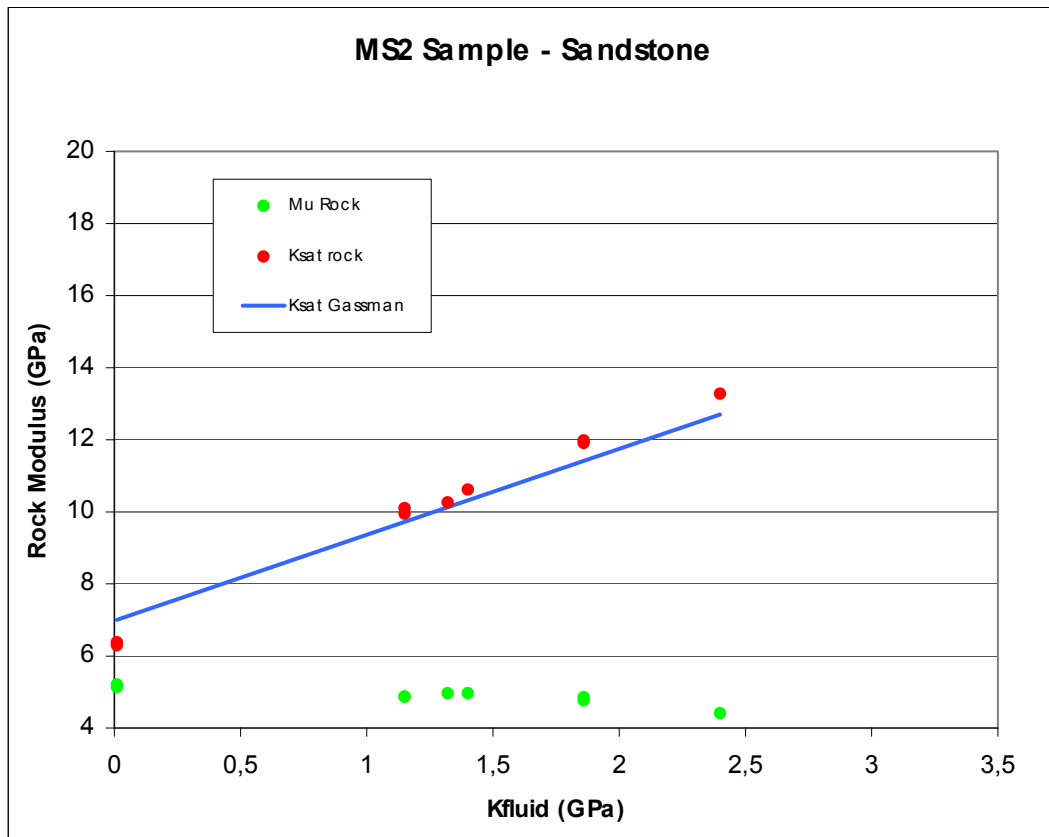
MONOPHASIC

Fluid	Vacuum	Ethanol	Ethanol-Ethyleneglycol Mixtur	Brine	Ethy.Glyco		
Bulk modulu	0	1,2	1,5	1,9	2,5	2,4	2,97

Figure 3: MS1 Sandstone Bulk and Shear Modulus vs. Saturating Fluid Modulus

The liquids used in this experiment (Ethanol, Ethylene glycol and mixtures) modify the mechanical properties of the clays minerals, inducing a ‘stiffening’ of the rock. The increase in Shear modulus is clear and the K_{sat} points are well above the Gassmann line. One can notice that the Gassmann values are computed (as for other samples) using for K_{dry} the value corresponding to the intersection with Y-axis of the experimental K_{sat} regression. Strangely, the K_{dry} value seems to be the right one: notice the good position of the point corresponding to brine. This K_{dry} value is nearly equal to the one measured on adjacent sample MS2, using non-reactive liquids. We have no explanation to this observation, which is most probably coincidental.

MS2 (figure 4), Meule Sandstone, Diphasic displacements, Non-reactive liquids:



MONOPHASIC

Fluid	Vacuum	KCl brine
Bulk mod	0	2,4

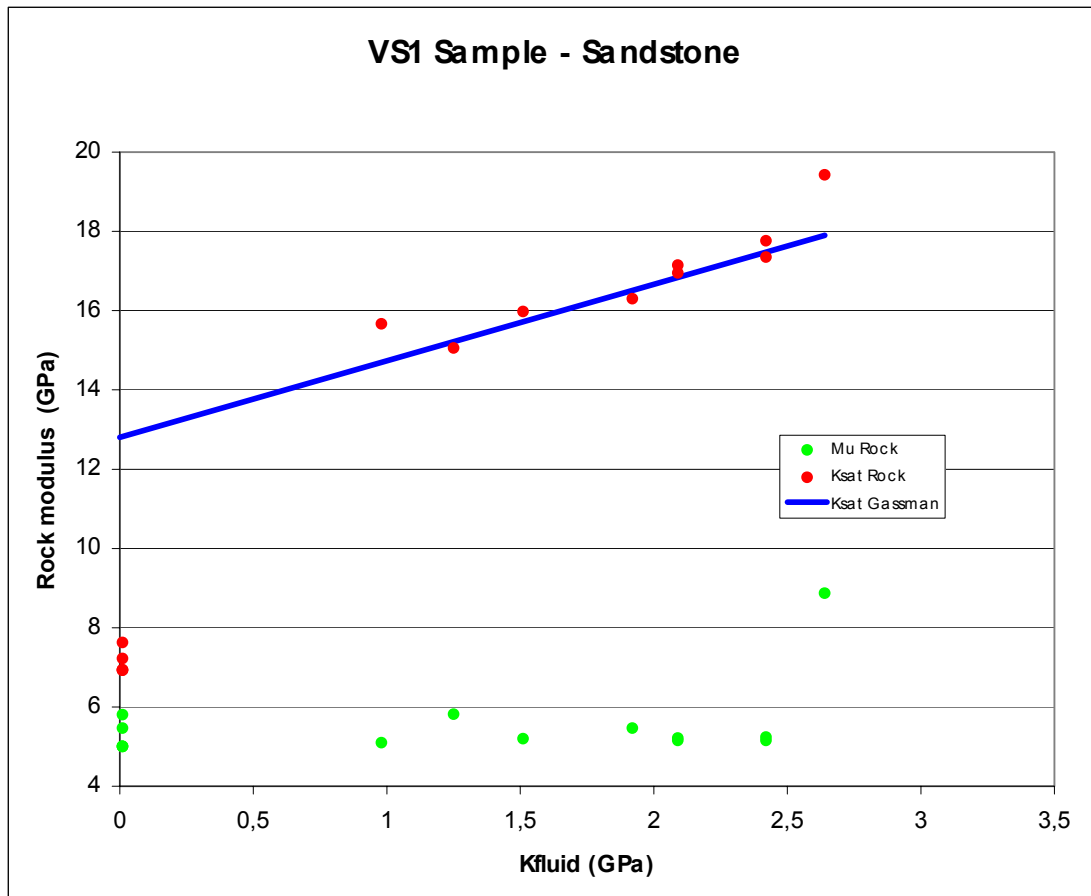
DIPHASIC

KCL Brine plus				
Liquid	Pentane	Hexane	Heptane	Kerozene
Fluid saturation	48%	48%	48%	48%
Bulk modulus GPa	1,15	1,32	1,4	1,86

Figure 4: MS2 Sandstone Bulk and Shear Modulus vs. Saturating Fluid Modulus

The results, in that case, are very good; the hydrocarbon liquids used in the experiment have no effect on the clay mineral. More over, the extremely high amount of ‘residual’ brine (52%!) does not modify the ‘Gassmann behavior’ of the experimental results. This is a convincing evidence of the Gassmann’s formula validity in the case of diphasic (non-miscible) saturating mixtures.

VS2 (figure 5): Diphasic displacements, Non-reactive and Reactive liquids:



MONOPHASIC

Fluid	Vacuum	Ethanol	KCl brine
Bulk modulus	0	1,25	2,4

DIPHASIC

KCL Brine plus					
Liquid	Pentane	1 cP Oil	Trichloroethy	400 cP Oil	Aniline
Fluid saturation	63%	63%	63%	63%	63%
Bulk modulus GPa	0,98	1,51	1,92	2,09	2,64

Figure 5: VS1 Sandstone Bulk and Shear Modulus vs. Saturating Fluid Modulus

The experimental results exhibit a rather good fit with the computed Gassmann's values, except for Aniline. Aniline reacts with clays and iron oxides minerals and despite the fact that the clay and iron minerals content of this sandstone is low (< 5%) and that 'irreducible' water (not miscible with Aniline) is abundant, there are obviously some effects. The increase in Shear modulus (and on K on a lesser extend) is very detectable.

The difference between the K_{dry} value deduced from the experimental regression and the K_{dry} value measured on the 'dry' sample is extremely high. This is not surprising for this unconfined experiment on sandstone where the grain joints are very marked, because of the syntactic quartz cementation.

Conclusion of section 1.

The main result of this section is an extremely precise and convincing experimental verification of the validity of Gassmann formula on sandstone samples saturated with monophasic liquid and diphasic mixtures of liquids.

Moreover, we set up an experimental method enabling to define, in the laboratory, the Gassmann's parameter on core samples. We suggest choosing the following procedure of diphasic fluid substitution:

- Saturation with KCl brine to protect the clays mineral
- Non-miscible displacement with very viscous oil to establish an irreducible water saturation
- Miscible displacement with hydrocarbon liquids such as Pentane, Hexane, Heptane for the lower K_{fl} and kerosene and low viscosity oil for the higher K_{fl} .

Using this method, we can measure the saturated rock bulk modulus (K_{sat}) for K_{fl} ranging from 0,85 GPa (diphasic Pentane) up to 2.4 GPa (brine). Unfortunately the liquids with highest Bulk modulus investigated are either water miscible and/or reacting with clay and iron oxide minerals, it seems thus difficult to find a way to extend the experimental curve toward higher than brine K_{fl} . But this does not seem necessary for a good definition of the Gassmann's poroelastic parameters of the core samples.

2) Petroacoustics characterization of sandstone under confining pressure

Introduction

In order to perform, on core samples, a precise laboratory petroacoustics characterization including measurement of Gassmann's poroelastic parameters, necessary to a quantitative interpretation of seismic monitoring of CO₂ aquifer sequestration, we designed a new method based on saturating fluid substitution. The principle of the method was developed during experiments at atmospheric pressure, presented in the previous section.

.Confining pressure is necessary for knowing the parameters in reservoir condition and for measuring the sensitivity of the seismic velocity to confining pressure (Hertz coefficient).

In this report, we present

- the parameters necessary to a petroacoustics characterization of a reservoir sample.
- the experimental method to measure these parameters.

2- 1. The parameters for petroacoustics characterization:

Hertz Coefficient (h), Drained Bulk Modulus (K_{dry}) and Grain Bulk Modulus (K_{grain})

2-1-1 *Impact of effective pressure: Hertz Coefficient*

Seismic velocity in rocks depends on effective pressure and in some case (loose, argillaceous sandstone) the impact could be very important. The cause of this effect is well known: the micro-cracks or grain-contacts, which tend to close down under effective pressure and thus increasing the rock stiffness.

It is rather easy to characterize the effective pressure impact on velocity using the Hertz coefficient (h), which is the exponent of the exponential relationship, observed between the velocity (V) and the effective pressure (P):

$$V = kP^h$$

This relationship is generally well verified when dealing with effective pressure higher than 2 to 5 MPa corresponding to reservoir conditions.

The name Hertz coefficient was chosen because Hertz computed the value of this parameter for a packing of non-cemented isogranular spheres (in that case the value of h is 1/6).

Experimentally, to get h we just need to measure the slope of the line V vs. P in a bi-logarithmic scale.

2-1-2 *Impact of saturating fluid, Gassmann's equation: K_{dry} and K_{grain}*

In order to use the Gassmann's equation for field application, we need to know the rock undrained bulk modulus (K_{dry}) i.e. the modulus when the rock is saturated with a zero bulk modulus fluid ($K_f = 0$). We have to point out that this definition (saturating fluid $K_f = 0$) does not correspond to a low pressure gas saturation, because in that case, the capillary forces related to the remaining adsorbed water have a major impact. On figure 7, the difference in recorded

waveforms in the "wet air" and "vacuum dry" saturation states are an illustration of this problem.

The Gassmann's equation links the rock drained (K_{dry}) and undrained (K_{sat}) bulk modulus through the following parameters:

- related to the rock: porosity (ϕ) and rock forming mineral bulk modulus (K_{grain}).
- related to the saturating fluid: bulk modulus (K_{fl}).

One can show (see for instance Rasolofosaon and Zinszner, Revue IFP, N°2, 2002) that this formula could be simplified as a linear relationship valid for porous (reservoir) rocks:

$$K_{sat} \approx K_{dry} + (\beta^2 / \phi) K_{fl}$$

with β , Biot's coefficient, such as $\beta = 1 - (K_{dry} / K_{grain})$.

Knowing the P and S wave velocity (V_p and V_s) and the rock specific gravity (ρ), it is easy to compute K_{sat} :

$$K_{sat} = \rho[V_p^2 - (4/3)V_s^2]$$

and thus to draw the line K_{sat} vs. K_{fl} . The ordinate when X is zero, equals K_{dry} and the slope of the line is β^2 / ϕ .

As the porosity is always known with great accuracy, it is easy to compute the Biot's coefficient and to derive an experimental value for K_{grain} . One can show that the K_{grain} value computed that way is very sensitive to experimental uncertainty, a very small fluctuation of the K_{sat} vs. K_{fl} slope inducing a strong variation of the K_{grain} value. We have thus a way to check the validity of our measurement, if the K_{grain} is known from the rock petrography and if this petrography is simple (clean sandstone, limestone).

2-2. Experimental method

2-2-1 Pressure Cell

In the pressure cell (Fig 6), the rock cylinder (40 mm in diameter and between 40 to 80 mm in length) is covered by a Viton jacket in order to isolate the sample from the confining liquid (oil). Inside the measuring heads we have piezo-electric double -P wave and S wave-transducers (half-circle ceramics) giving good wave forms, when the investigated medium is not too attenuating (see Fig. 7). The maximum confining pressure is 70 MPa (around 10,000 PSI).

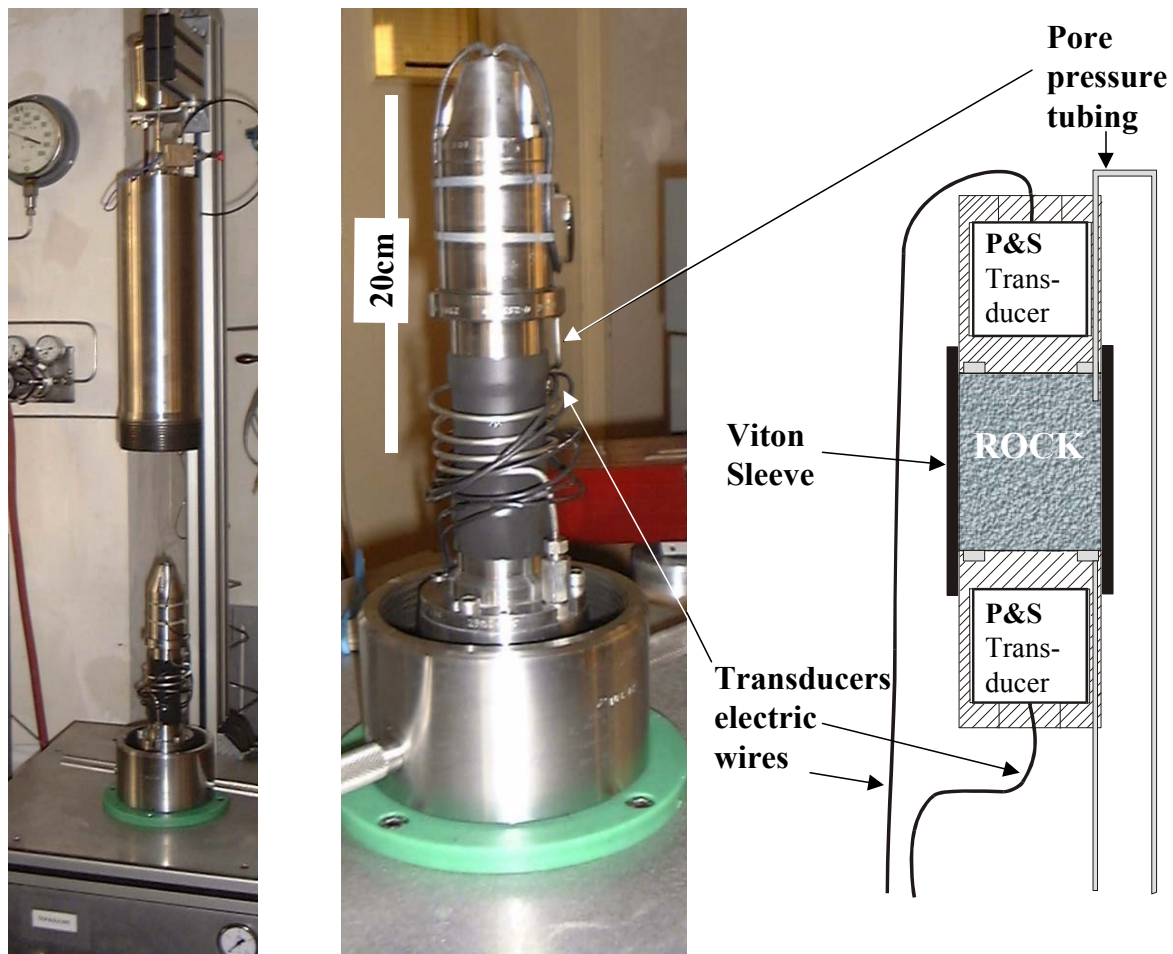


Figure 6: Pressure cell for petroacoustics measurements, photographs and sketch.

It is of major importance to control the pore pressure and to be able to change the saturating fluid inside the sample. Thus, we keep a hydraulic continuity between the sample and the exterior, using sintered steel plates and thin tubing (Fig. 7).

2-2-2 *Waveform recording set-up*

We use a conventional acoustic set up made of

- an electric pulse transmitter (to induce acoustic pulse in the emitting ceramic).
- an amplifier and an oscilloscope receiving the transmitted signal.
- a computer recording the waveforms.

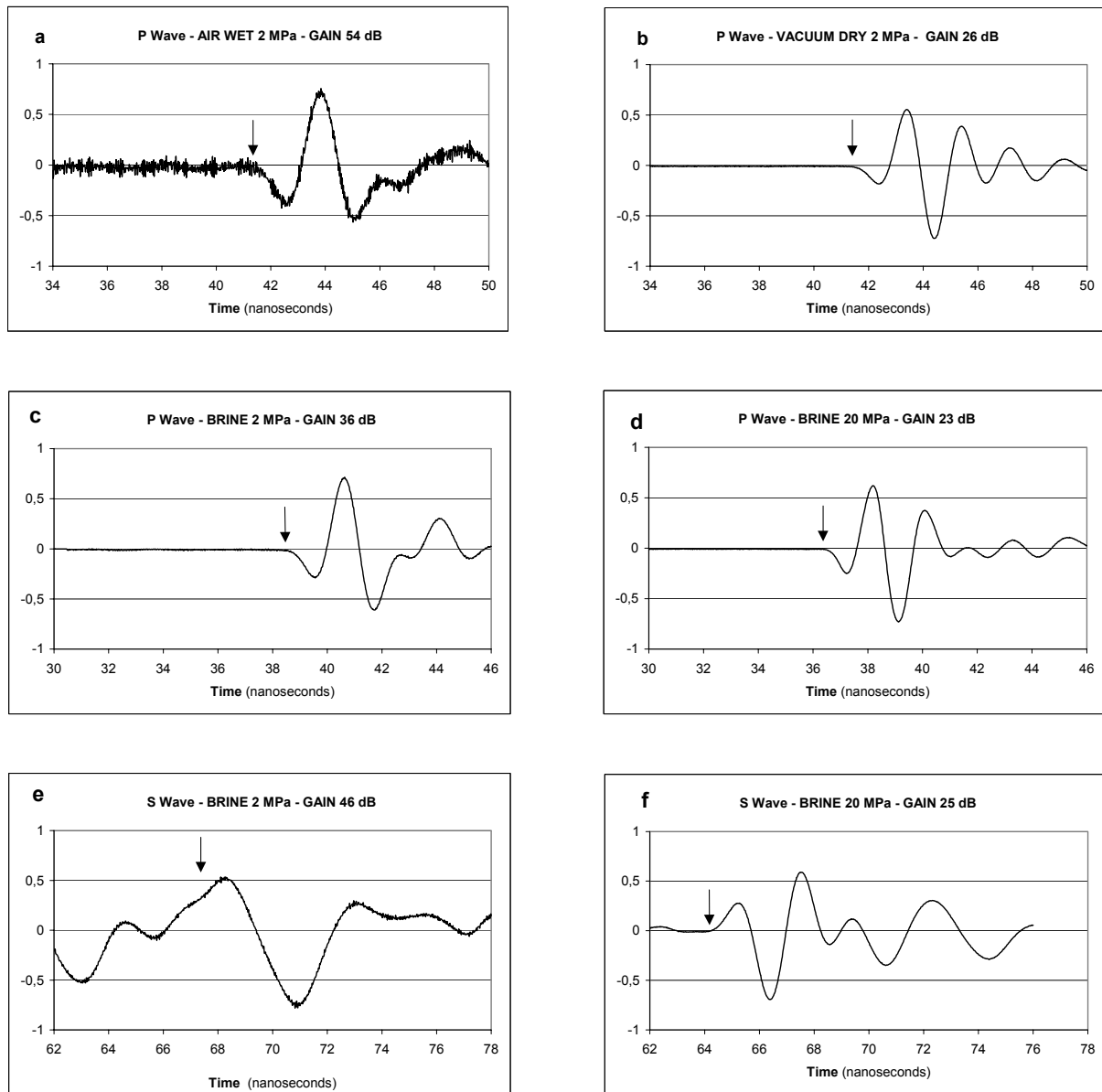


Figure 7: Example of acoustic waveforms recorded with the pressure set-up, on the same sandstone sample.

a) and b): P wave, Effective pressure 2 MPa. Notice the contrasted situation (gain) between the vacuum dry signal (no attenuation) and the air wet signal (attenuation).

c) and d): P wave, Brine saturated, effective pressure 2 and 20 MPa.

High quality P waveforms, the first break picking method (arrows) gives good results. Notice that at the same effective pressure (2 MPa) the brine saturated sample (**c**) is much more attenuating than the vacuum dry sample (**b**)

e) and f): S wave, Brine saturated, effective pressure 2 and 20 MPa.

Under high effective pressure (low attenuation, **f**), the S-Waveform is of very good quality and allows a reliable first break picking. At low effective pressure (**e**), due to higher attenuation, the S-wave first break picking energy could be lost in the noise.

2-2-3 Saturation method.

The basic point, in our experiment, is to compute the rock bulk modulus (K_{sat}) for various state of saturation with fluids of different bulk modulus (K_{fl}). As we plan to work on sandstone, which generally contains some clay materials, we have to be careful to avoid any modification of this clay. The best way is to use brine with a convenient salt content (for instance KCl at 20 g/liter) and to keep the "residual water" i.e. the water bounded to the rock by capillary forces.

For routine work on sandstone we suggest the following sequence of saturations:

- wet air,
- 100% brine
- S_{wi} (irreducible saturation) by non-miscible viscous displacement using viscous oil (viscosity ranging between 10 and 1000 cP, according to the rock permeability)
- miscible displacement of the viscous oil by less viscous hydrocarbon liquids (kerosene, pentane, etc.).

2-2-4 Computation of P , S wave velocity, K_{dry} and K_{grain} , Experimental Results

At any step of the experiment, the P and S waveforms are recorded and the velocity computed either from first break picking (the most conventional way) or from signals correlation. The specific gravity ρ and P wave velocity of the saturating liquids are also measured, allowing a precise computation of K_{fl} (for liquids, $K_{fl} = \rho V_p^2$).

That way is rather easy:

- to draw the line $\log(V)$ vs. $\log(P_{eff})$ and thus compute the Hertz Coefficient h equal to the slope of this line.
- to draw the line K_{sat} vs. K_{fl} and thus derive K_{dry} and K_{grain} as explained section 1.

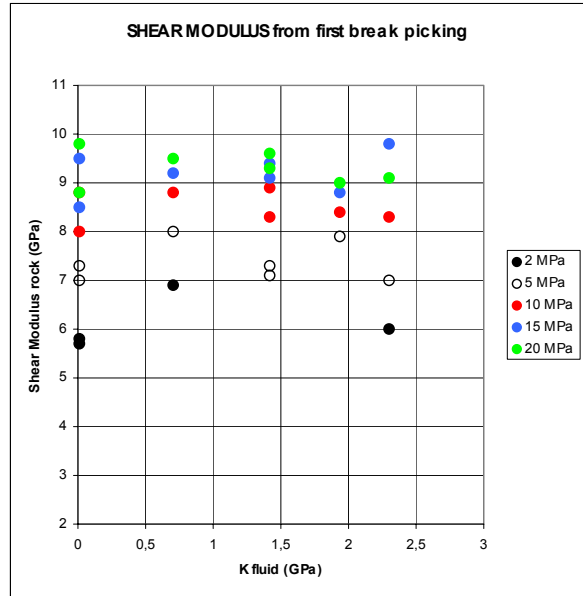
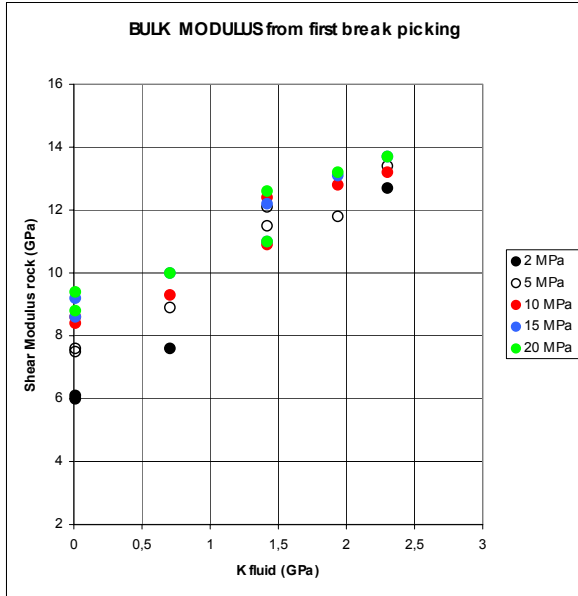
The results could be summarized on a plot like the one shown on Fig. 8.

Conclusion of section 2

The laboratory method presented in this section was developed in the scope of SACS2 project, in order to improve the prediction of the impact of CO₂ injection on seismic characteristics of the reservoir rock. This method gives very good results in the case of normally consolidated sandstone and allowed presenting a non-disputable laboratory verification of the validity of the Gassmann's equation for several types of porous sandstone, under confining pressure.

This method is very efficient but need to be adapted to the case of unconsolidated sand. Actually, many of aquifers suitable for CO₂ sequestration will be of the type found in Sleipner Utsira formation, i.e. loose sand where coring is difficult and laboratory samples handling extremely difficult. The same difficulties are encountered for any petrophysics measurement: permeability, capillary pressure etc, but are more pronounced for petroacoustics (a careful preservation of the initial rock microstructure is needed).

Considering its great importance for practical applications, the problem of petrophysics of unconsolidated reservoir rocks deserves a greater care.



Loose Sandstone slightly shaly

GASSMANN'S PARAMETERS

Effective	Press. MPa	2 MPa	5 MPa	10 MPa	15 MPa	20 MPa
Including	Beta		0,82	0,76	0,75	0,74
	Dry Kdry GPa		7,5	8,4	8,8	8,9
	Value Kgrain GPa		43	35	35	34
Excluding	Beta		0,83	0,77	0,75	0,74
	Dry Kdry GPa		7,5	8,3	8,9	9
	Value Kgrain GPa		45	37	35	34
Average	Shear Mod.		7,3	8,5	9,2	9,3

Porosity 27%

Permeability 400 mD

Grain Density 2660 kg/ m3

VP/VS 1,69
(Mod. Average 10-20 MPa)

HERTZ'S COEFFICIENTS *1000

EFFECTIVE PRESSURE RANGE: 5 to 20 MPa

Fluid	Air Wet	Dry Vacuum	Brine	Polyal	Kerozene	Pentane	Average	Av. Liquids
Hertz VP	54	97	46	44	53	55	44	42
Hertz VS	66	111	91	48	99	63	60	59
1/2 Hertz K	34	84	10	41	11	47	28	28

Figure 8: Example of petroacoustics results under confining pressure.

B) Thermodynamics

Introduction

The goal of the thermodynamics study is to provide the CO₂ - methane compressibility (isothermal, isentropic) and density for temperatures and pressures in the range encountered in the reservoir. The work is a continuation of the study performed by SINTEF during SACS1 project. In this last work, many equations of state have been examined to allow restitution of the volumetric properties of pure CO₂. The first set of equations is classical cubic equation (Peng and Robinson, Soave-Redlich-Kwong) with volume translation. These equations show high deviations (up to 20 %) near the critical point. Best results are obtained with second set of equations derived from Lee and Kesler form, the deviation near the critical point is close to 6 %. At least, a specific equation for CO₂ has been tested which gives the less deviation (1%). The mixtures of methane and CO₂ have also been examined, the best results have obtained with the Lee-Kesler-Duan form, but this equation is not continue through the critical point.

3-1) Thermodynamic work

3-1-1) Pure CO₂

For the SACS project, the temperature range is close to the critical one, so we need an equation of state giving good results near the critical conditions. We have examined the case of pure CO₂, then mixtures of CO₂ and CH₄ and then mixtures of CO₂, CH₄ and N₂. In the case of pure CO₂, the specific IUPAC equation of state¹ is used as a reference as seen by SINTEF previously. These results have been compared to the ones obtained from two others equations of state: Peng and Robinson² and Soave-Benedict-Webb-Rubin³. The first one is a classical cubic equation of state and does not give satisfying results for the liquid volumes or near the critical point. Whereas the second one is not a cubic equation and some of these parameters are fitted on critical curve.

$$Z = \frac{P}{\rho RT} = 1 + B\rho + C\rho^2 + D\rho^4 + E\rho^2(1 + F\rho^2)\exp(-F\rho^2)$$

Volumes of pure CO₂ is well computed with SBWR, the mean square deviation is about 0.8 % in the temperature range of 10 to 40°C and a pressure range from 1 up to 100 bar. The maximum deviation is about 6 % close to critical point. In conclusion, the SBWR equation has been chosen to model the volumetric properties of such mixtures.

¹ ANGUS S., ARMSTRONG B., de REUCK K., International Thermodynamic Table of the Fluid State : Carbon Dioxide, 1973, IUPAC, London.

² PENG D-Y., ROBINSON D.B., A new two-constant equation of state, *Ind. Eng. Chem., Fundam.*, 1976, **15**, p. 59-64.

³ SOAVE G., A noncubic equation of state for the treatment of hydrocarbon fluids at reservoir conditions, *Ind. Eng. Chem. Res.*, 1995, **34**, p. 3981-3994.

From the expression of molar volume, it should be possible to derive the isothermal and isentropic compressibility:

$$\beta_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

$$\beta_s = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_s$$

Figure 9 shows the isothermal compressibility in function of pressure for eight temperatures from 0 °C up to 150 °C obtained with the IUPAC equation.

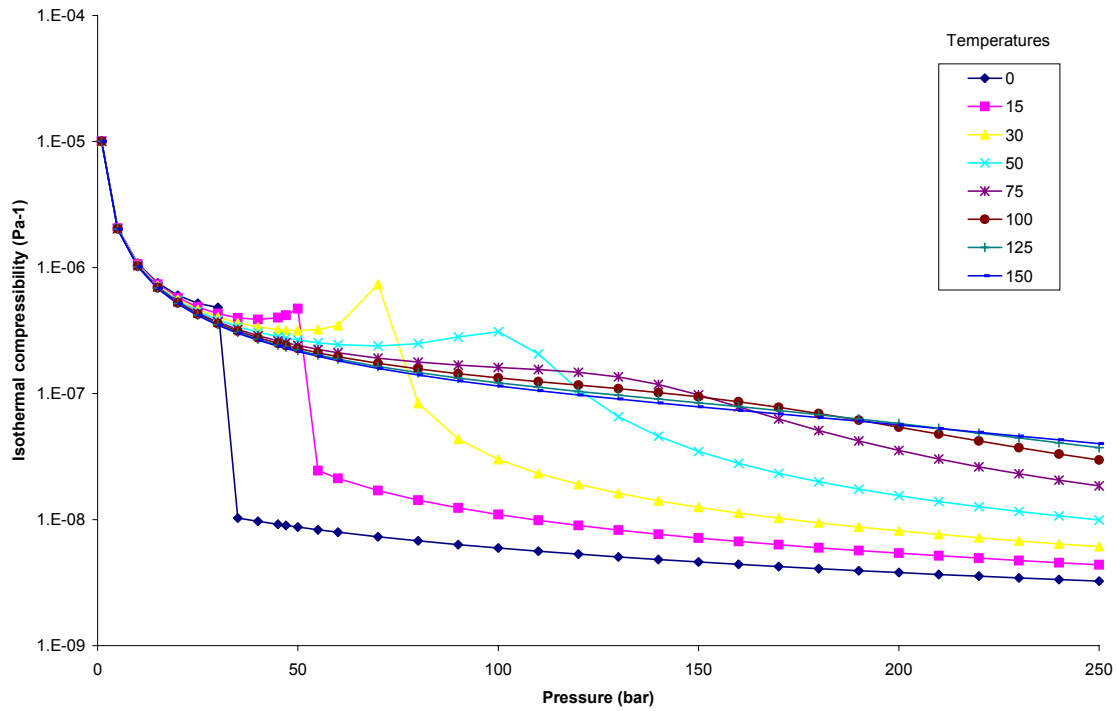


Figure 9: Isothermal compressibility function of pressure and temperature (IUPAC equation)

At low pressure, the temperature has no influence on the isothermal compressibility and the value is given by the ideal gas equation: $\beta_T = 1/P$. When the pressure comes close to the vapor pressure, the compressibility shows a divergence. This divergence is greater when the temperature is near the critical temperature. Indeed for the critical temperature, the compressibility becomes infinity. It should be notice that these results have been obtained with the analytical form of the IUPAC equation, which is not the best near the critical region. If we use the specific critical form of the IUPAC equation, we obtained the same results as shown in figure 10. Therefore, in this work, we can use indifferently both forms of equation.

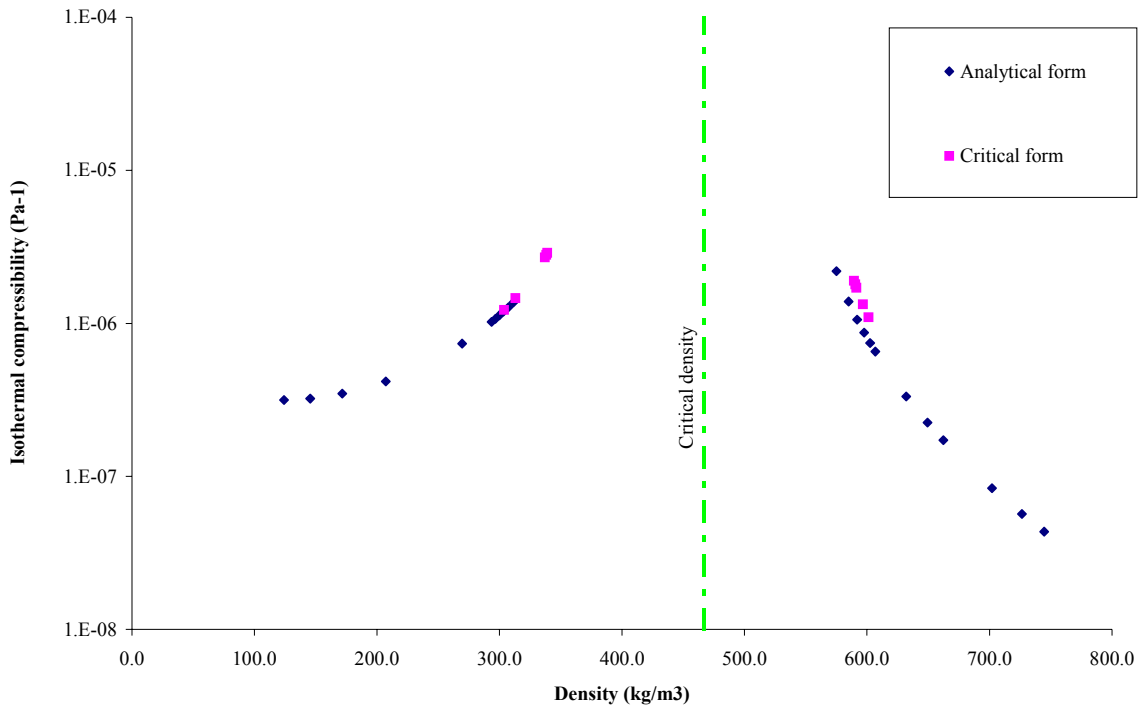


Figure 10: Isothermal compressibility of CO₂ in the critical region
Comparison between the analytic and critical forms.

We have also determined these compressibilities with the SBWR equation. The deviation between IUPAC and SBWR is about 2.6 % for temperature range between 0 to 150 °C and pressure range up to 250 bar. The maximum deviation is 30 % close the critical point. Figure 11 shows these deviations.

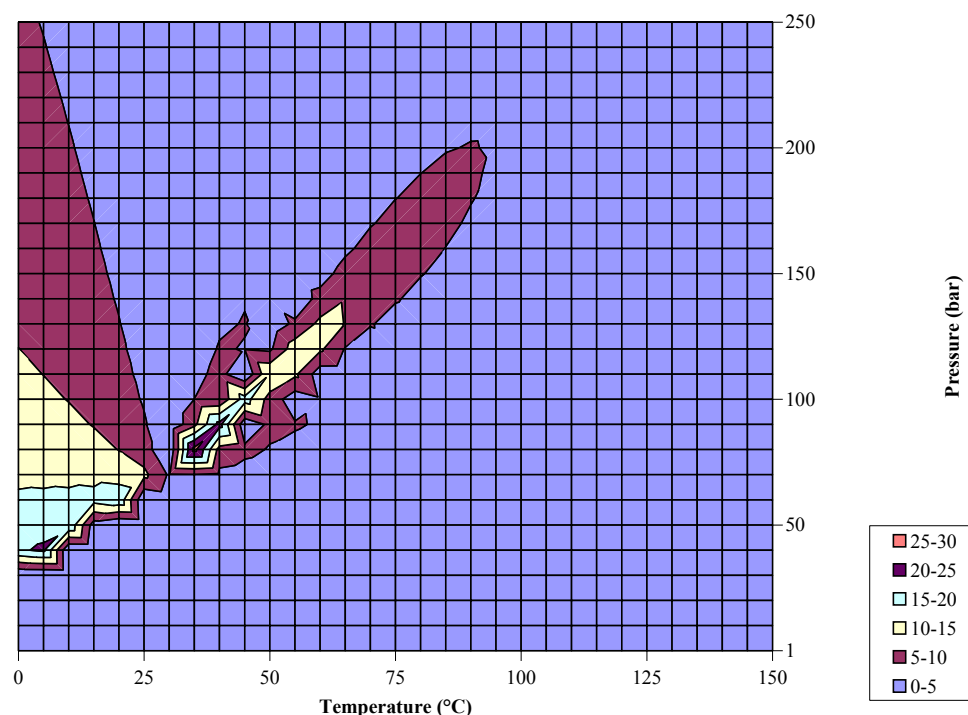


Figure 11: Deviation (%) about isothermal compressibility of CO₂ between IUAPC and SBWR equation

In conclusion, the IUPAC and SBWR equations should be used to determine density of pure CO₂ in the desired temperature and pressure range as well as compressibility. As in the next step, we will examine mixture, we propose to use SBWR equation, which is enable to perform mixture properties.

3-1-2) Mixture of CO₂ and methane

In the case of reinjection, the gas is not only composed by CO₂, but contains some methane which could be present up to 5 molar %. We use liquid-vapor data of Xu et al.⁴ and Brian et al.⁵ to fit the binary parameter of SBWR equation. The temperature range of these data is 20 to 30 °C. The value of binary parameter is 0.0592. Then we should calculate the phase envelope of mixture of CO₂ and methane. Figure 12 gives these diagrams for four compositions of CO₂ and CH₄.

⁴ XU N.,DONG J.,WANG Y.,SHI J., *J. Chem. Ind. Eng.(CHINA)*, 1992, **43**, p. 640

⁵ BIAN B.,WANG Y.,SHI J., *Fluid phase Equilib.*, 1993, **90**, p.177.

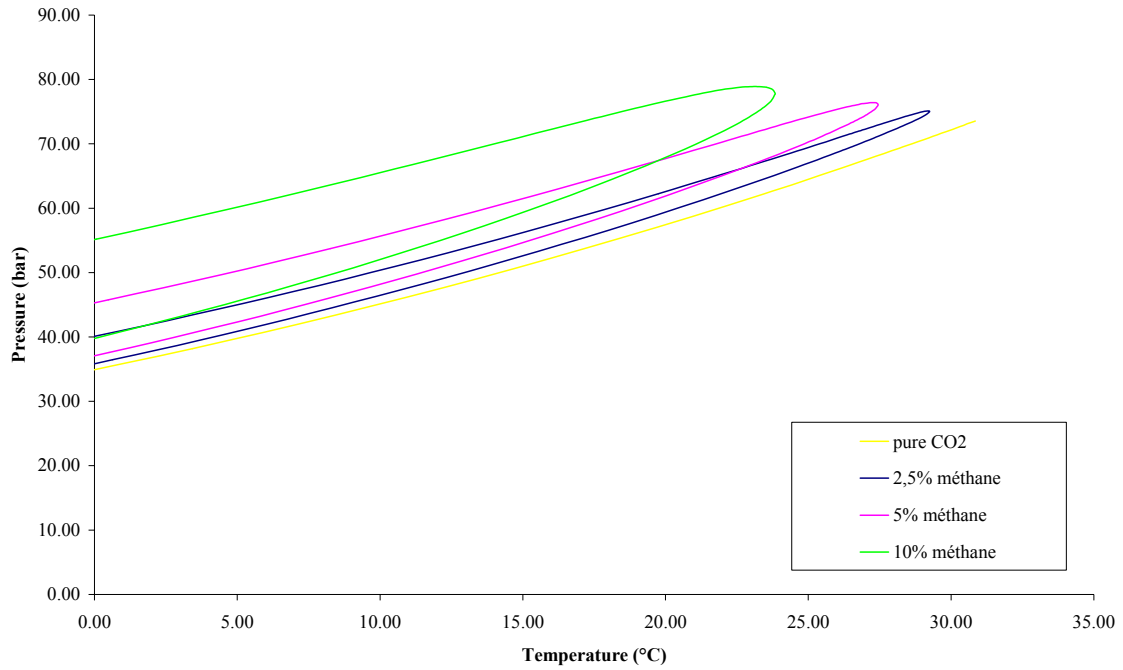


Figure 12: Phase envelope for four mixtures of CO₂ and methane (molar %)

We have compared the volumes given by the SBWR model to experimental values of Hwang et al.⁶. Figure 13 shows model density against experimental density for a mixture of CO₂ and CH₄ (90 % molar of CO₂) at four temperatures in our temperature range.

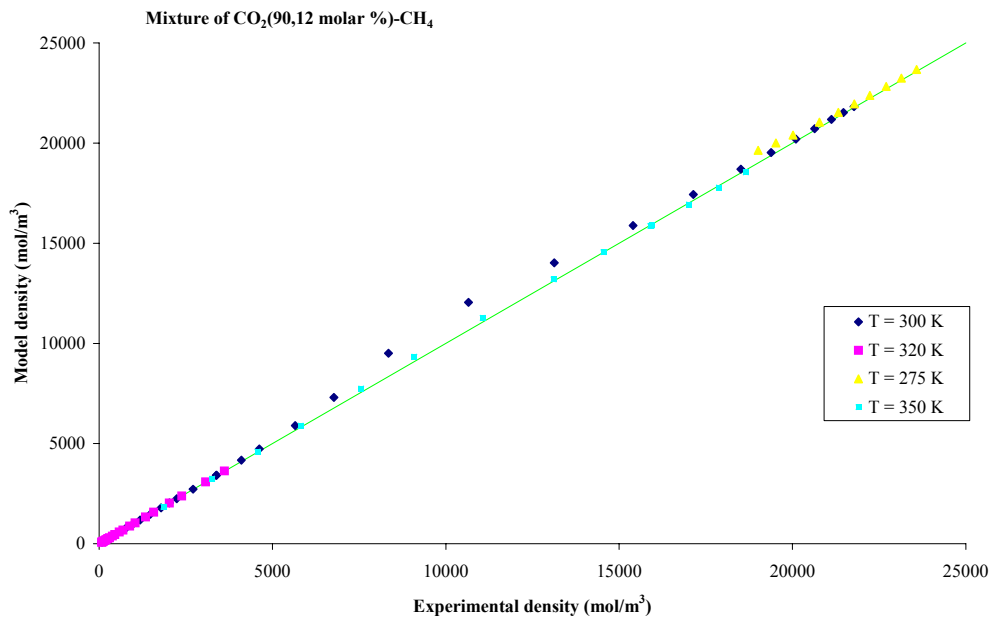


Figure 13: Comparison of Model Density and Experimental Density

⁶ HWANG C., Duarte-Garza H., EUBANK P., HOLSTE J., HALL K., GAMMON B., MARSH K., Thermodynamic properties of CO₂+CH₄ mixtures, 1995, GPA RR-138

We see that the values of the model are very close to the experimental one; for 81 experimental data points, the mean square deviation is about 1.1%. Isotherm at 300 K shows the large deviation and then we read the results in details, we can observe that the data with high deviation corresponding to temperature and pressure conditions close to the critical point of the mixture. So, not taking into account these five data points near the critical point, the deviation is no more than 0.6 %. So we can conclude that the SBWR model allows us to reproduce the density of the interesting mixture of CO₂ and CH₄. Comparing to the LK-Duan proposed by Sintef, this model has the advantage to be continue near the critical point.

3-1-3) Mixture of CO₂-CH₄-N₂

We have used the same method for the ternary system. We have fitted the binary interaction parameter between CO₂-N₂ from the equilibrium data point of Brian et al.⁵ and Xu et al.⁷ in the temperature range about 20 to 30 °C. The parameter is equal to 0.0458. For the binary CH₄-N₂, we used a binary parameter set to zero.

Then, we have predicted the phase equilibrium of this system and density. For the density, we compare this model to the experimental data of Magee et al.⁸ who have studied a ternary composed by: 96 % CO₂, 2 % N₂ and 2 % methane. With the 39 data points, we obtained a deviation around 0.8 %. This good results show that the SBWR equation allows us to reproduce the phase equilibrium and density of mixture of CO₂-CH₄-N₂ in the temperature range around 10 to 100 °C and pressure range up to 150 bar.

3-2) Applications

3-2-1) Excel Dynamic Link Library (DLL), for density and compressibility computations

We have examined the restitution of volumetric properties of pure CO₂, CO₂-CH₄ and CO₂-CH₄-N₂ mixtures. We have shown that SBWR equation of state allows a good reproduction of the properties of these mixtures. This equation of state with its database has been introduced in an Excel sheet linked with a Dynamic Link Library (DLL). For a given set of composition, temperature, pressure, the code gives density, isothermal and isentropic compressibility factors and speed of sound. The proposed model has been examined for a temperature range between 0 up to 100°C and a pressure range from 1 to 200 bars. The gas mixtures must contain a CO₂ concentration greater than 95% molar.

The attached file Setup.exe creates directly a directory called density with inside the density.xls file. Then, the user should modify the molar composition, temperature and pressure (green area, fig.14) then click on "Calcul" and the code gives the following data (blue area): density, isothermal and isentropic compressibility factors and speed of sound.

For instance, in the case of pure CO₂, temperature: 56,85°C and pressure: 150 bar the following results are obtained (Fig. 14):

⁷ XU N., DONG J., WANG Y., SHI J., *Fluid Phase Equilibria*, 1992, **81**, p.175.

⁸ MAGGE J., HOWLEY J., ELY J., A predictive model for the thermophysical properties of carbon dioxide rich mixtures, 1994, GPA RR-136.

CO ₂	1	T (°C)	56,85
CH ₄	0	P (bar)	150
N ₂	0		

Density	ρ (kg/m ³)	625,26
Isothermal compressibility	$1/\beta_T$ (GPa)	1,93E-02
Adiabatic compressibility	$1/\beta_S$ (GPa)	7,63E-02
Speed of sound	v (m/s)	349,2

Figure 14: Example of results from Excel Sheet "Density.xls"

For this point, IUPAC tables give the following results: the density: 636.87 kg/m³ and the speed of sound: 324.1 m/s.

3-2-2) Unsuccessful search for a "thermodynamics" seismic reflector.

This Excel Dynamic Link Library enables an easy and quick computation of thermodynamics properties for varied Pressure, Temperature conditions. We take advantage of this DLL to test the hypothesis of a possible "thermodynamic" seismic reflector related to a strong contrast in impedance linked to a phase change of the saturating mixture in the reservoir. The hypotheses are:

Mixture Pure CO₂ and 10% irreducible water saturation (Swi)

Kdry = 2.7 GPa, Kg = 40 GPa, μ = 0.85 GPa

Sea bottom = -100m, Sea bottom temp. 5° C, Geothermal gradient = 0,035 °C/m

Top reservoir: 500 m, Gas/Water contact = 700m

They correspond to reasonable Utsira parameters but for the reservoir depth, for which we choose smaller values in order to increase the chance to reach the critical point.

Due to capillary pressure between CO₂ and water, we cannot use a hydrostatic pressure profile in the CO₂ saturated zone. Starting from a hydrostatic pressure at 700-m depth, we compute the density and the pressure by 10-m thickness slices. Thus, we have a representative (if not perfectly exact) density/compressibility profile enabling a Gassmann's equation computation for VP and VS (and thus of P and S impedance). The results on figure 15 show no impedance contrast (but around 500 m - CO₂ gas phase above).

In the Utsira type Pressure, Temperature conditions, we were able to point out any strong contrast of impedance related to a saturating mixture phase change the hypothesis of a possible "thermodynamics" reflector seems not to be a good one.

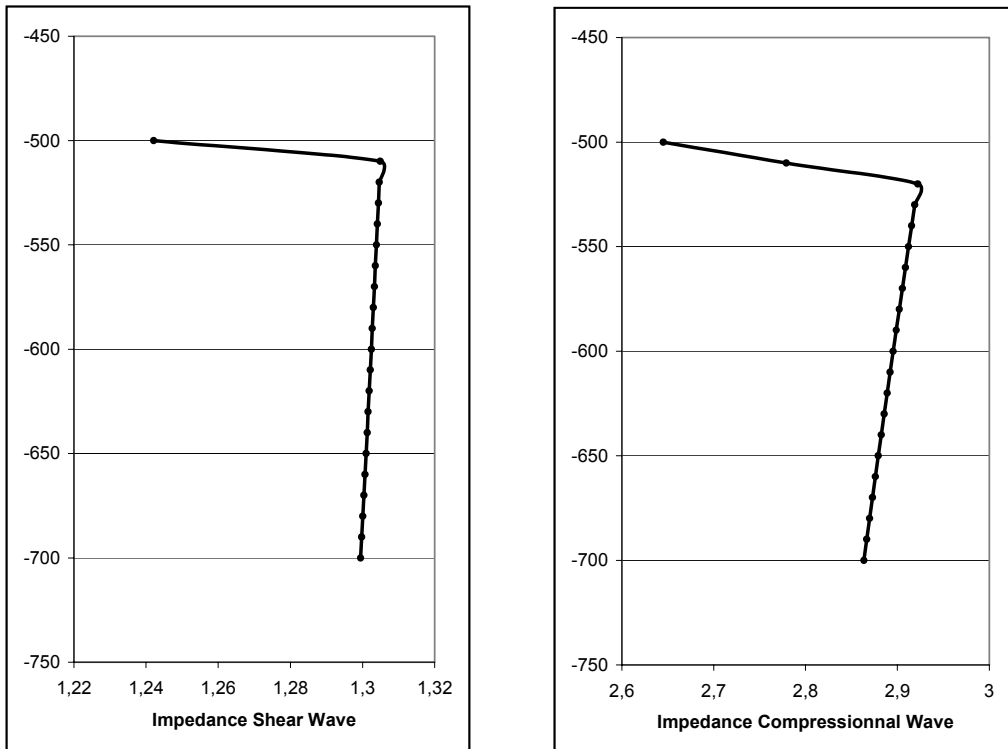


Figure 15: P and S-wave impedance profile computed for an Utsira type reservoir.
 Depth in meters Impedance in $10^6 \cdot \text{kg/m}^3 \cdot \text{m/s}$

Conclusions

During WP7 work,

- concerning **Petroacoustics**, we developed a reliable method for Gassmann's formula laboratory verification and parameters measurement of consolidated samples. The method is based on the substitution of fluids of varied compressibility. To preserve the properties of clay fraction in the sandstone, we use diphasic saturation states. The room dry sample is first saturated with brine. The brine is displaced by viscous oil (non-miscible viscous displacement), and then the viscous oil is displaced by hydrocarbon liquids of varied bulk modulus (e.g. kerosene, hexane, pentane, etc). The P and S wave velocity measurements are performed under pore and confining pressure (up to 70 MPa). This method is very successful when performed on normally consolidated samples, but the experimental difficulties in applying this method to loose sandstone, are expected to be great. The same difficulties are encountered for any petrophysics measurement: permeability, capillary pressure etc, but are more pronounced for petroacoustics (a careful preservation of the initial rock microstructure is needed).
- Concerning **Thermodynamics**, in order to provide the CO₂ - methane mixture compressibility (isothermal, isentropic) and density for temperatures and pressures in the range encountered in the reservoir (continuation of the study performed by SINTEF during SACS1 project) we used the SBWR (1995) equation, which is a version modified by Soave of the Benedict-Webb-Rubin equation (1940). We set up an Excel Dynamic Library enabling to compute the density/compressibility values for a wide range of P, T conditions and for mixtures with CO₂ concentration greater than 95% molar. Using this EDL, we checked that, in the range of depth and geothermal gradient encountered for Utsira-type aquifers, there was no chance of rapid phase change in CO₂ mixture, inducing noticeable impedance contrast.

