SACS2 EUROPEAN RESEARCH PROJECT

WORK PACKAGE 7 (WP7)

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

EXPANDED ABSTRACT FINAL TECHNICAL REPORT

April 2002

Work Performed at Institut Français du Pétrole (IFP)

Contributors to the report:

Pascal Mougin, Patrick Rasolofosaon, Bernard Zinszner

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 $\mu_{dry})$ 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. We developed a new experimental protocol for this verification.

1-1 Measurement principles and experimental set-up

- The basis of the method is to substitute liquids of different $K_{\rm fl}$ 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 (Swi) 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 Estaillades limestone (30 % porosity, 300 mD permeability sample - no chemical interaction between calcite and the saturating liquids). Sample L 1

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.

By measuring precisely the specific gravity (ρ) and the sound velocity (V) of the liquid, we can easily compute the bulk modulus (K = ρ V²). 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, then miscible displacement of the movable non-wetting phase: heptane, hexane, pentane. For diphasic saturation state, the saturating mixture bulk modulus (Kfl) 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 (Swi=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 (Swi=40%),

1-2 Experimental results

An example of experimental result is presented on figure 1. The nature of saturating fluid for any experimental point, could be found searching for the corresponding K_{fl} on the table below the graph.



KCLBrine plus					
Liquid	Pentane	1 cPOil	Trichloroethy	400 cP Oil	Aniline
Fluid saturation	63%	63%	63%	63%	63%
Bulk mod ulus G Pa	0,98	1,51	1,92	2,09	2,64

Figure 1: 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 syntaxic quartz cementation.

2) Petroacoustics characterization of sandstone under confining pressure

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 section, 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 (Kdry) and Grain Bulk Modulus (Kgrain)

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=kph

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 bilogarithmic 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_{drv}) i.e. the modulus when the rock is saturated with a zero bulk modulus fluid (K_{fl}). We have to point out that this definition (saturating fluid $K_{fl} = 0$) 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.

The Gassmann's equation link the rock drained (K_{drv}) 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:

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

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

Knowing the P and S wave velocity (Vp and Vs) and the rock specific gravity (ρ) , it is easy to compute K_{sat} : $K_{sat} = \rho[Vp^2 - (4/3)Vs^2]$

and thus to drawn the line K_{sat} vs. Kfl. The ordinate when X is zero, equals Kdry 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 Kgrain. One can show that the Kgrain 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 Kgrain 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

Pressure Cell

In the pressure cell (Fig 2), 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. The maximum confining pressure is 70 MPa (around 10,000 PSI).

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. 2).

Saturation method.

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

- wet air,

- 100% brine

- Swi (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.).

Computation of P, S wave velocity, K_{dry} and K_{grain}

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} = ρ Vp²).

That way it is rather easy:

- to draw the line log(V) vs. log(Peff) 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. 3



Figure2: Pressure cell for petroacoustics measurements, photographs and sketch.

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. M Pa	2 M Pa	5 M Pa	10 M Pa	15 MPa	20 M Pa	Porosity	27%
Including	Beta		0,82	0,76	0,75	0,74		
Dry	Kdry GPa		7,5	8,4	8,8	8,9	Permeability	400 mD
Value	Kgra in GPa		43	35	35	34		
							Grain Density	2660 kg/m
Excluding	Beta		0,83	0,77	0,75	0,74		
Dry	Kdry GPa		7,5	8,3	8,9	9		
Value	Kgra in GPa		45	37	35	34	VP/VS	1,69
							(Mod. Average	10-20 MPa)
-	Shear Mod		7.3	8.5	9.2	9.3		

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Huid	AirWet	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 3: Example of petroacoustics results under confining pressure.

B) Thermodynamics

The goal of the thermodynamics study is to provide the CO_2 - 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.

For the project, the temperature range is close to the critical one, so we need an equation of state giving good results near the critical conditions. In the case of pure CO_2 , the specific IUPAC equation of state¹ is used as a reference. These results have been compared to the ones obtained from an other equation of state: Soave-Benedict-Webb-Rubin² which is not a cubic

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

² 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.

equation. Volumes of pure CO_2 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. From the expression of molar volume, it should be possible to derive the isothermal and isentropic compressibility:

$$\beta_{\rm T} = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_{\rm T}$$
 and $\beta_{\rm S} = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_{\rm S}$

Figure 4 shows the isothermal compressibility in function of pressure for eight temperatures from 0 °C up to 150 °C obtained with the 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. 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. 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.

In the case of reinjection, the gas is not only composed by CO_2 , but contains some methane and nitrogen which could be present up to 5 molar %. We use liquid-vapor data to fit the binary parameter of SBWR equation. Then we have compared the volumes given by the SBWR model to experimental values. We obtained respectively a mean square deviation about 1.1% for the CO_2 -CH₄ system and 0.8% for the ternary system in the temperature and pressure ranges examined.





We have shown that SBWR equation of state allows a good reproduction of the properties of these mixtures of CO_2 -CH₄-N₂ in the temperature range around 10 to 100 °C and pressure range up to 150 bar . 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 gas mixtures must contain a CO_2 concentration greater than 95% molar. The attached file Setup.exe creates directly a directory called density with inside the density.xls file.

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. Using some hypotheses for the Utsira case, we have performed 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 5 show no impedance contrast (but around 500 m - CO_2 gas phase above). In the Utsira type Pressure, Temperature conditions, we were enable 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 5: P and S-wave impedance profile computed for an Utsira type reservoir. Depth in meters Impedance in 10^{6} kg/m³ m/s