

GHGT-10

## Impact of Acid Gas Exposure on Cap Rock Integrity Properties at Apache Zama EOR & Storage Project

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### Abstract

The Apache Canada operated Zama oil field in north-western Alberta, Canada has been the site of acid gas injection for the simultaneous purpose of enhanced oil recovery (EOR), H<sub>2</sub>S disposal, and storage of CO<sub>2</sub> since October 2005 (Figure 1). Figure 2 is a schematic of the well utilization and relative spatial distribution for the Zama F Pool EOR scheme; this is one of several pinnacle reefs within the Zama acid gas EOR project. Well 103/01-13 is the initial EOR production well, 102/08-13 is a producing EOR well that was drilled and completed in 2008, and 100/01-13 is the Pool acid gas injection well. The 1967 discovery well 100/08-13 has been plugged back from the original Keg River completion to the shallower Slave Point FFF gas zone. The Slave Point FFF completion has been depleted and is now utilized as a monitoring well for potential wellbore leakage from the underlying Keg River F Pool. The Muskeg anhydrite provides the primary cap rock seal for the reservoir; this massive thick low permeable anhydrite section also contains dolostone inclusions.

In conjunction with Apache Canada Ltd., the Plains CO<sub>2</sub> Reduction Partnership (PCOR), with the support of RPS Energy Canada and Natural Resources Canada conducted monitoring, verification, and accounting (MVA) activities at the site from October 2005 to September 2009. This project is part of the U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL) Regional Carbon Sequestration Partnership Program and has been recognized by the Carbon Sequestration Leadership Forum as being uniquely able to fill technological gaps with regard to geological storage of CO<sub>2</sub>. Complementary to the MVA activities, the subject three tests are being conducted to further understand the implications of injecting acid gas into a carbonate reef structure and the impact on the cap rock integrity.

A competent cap rock is characterized as having high compressive strength, so as to physically be resistant to the prevailing reservoir pore pressure, and, of low enough permeability so as to inhibit flow of reservoir fluid through the cap rock itself. A breakdown of the cap rock could result from exceeding the fracture resistance or strength of the cap rock leading to potentially significant leakage, or by exceeding the threshold intrusion pressure (capillary breakthrough) leading to what would likely be insignificant fluid leakage or seepage. Desired cap rock parameters have been defined through the design of both gas storage reservoirs and sour gas disposal reservoirs. It is generally accepted that optimally a competent cap rock should have a Threshold Injection Pressure (TIP) of 7,000 kPa (1,000 psi) combined with an absolute liquid permeability of 1 nanoDarcy (10<sup>-6</sup> mD)<sup>[1,2]</sup>. In practice, an absolute liquid permeability of 0.001 mD is typically accepted as the highest acceptable cap rock permeability, and lower values of TIP may be acceptable as long as the absolute permeability is low enough and other project parameters such as pressure and fluid type are also acceptable.

This paper documents how the structural integrity and leak resistance of the Zama Muskeg cap rock-quality anhydrite and dolostone is impacted before and after exposure to acid gas-rich brine (65% CO<sub>2</sub> & 30% H<sub>2</sub>S). The three tests

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undertaken for study assist in making an informed estimation of the potential for leakage through the cap rock by quantifying the impact that acid gas-saturated brine has on the threshold intrusion pressure, or ability of the acid gas-saturated brine to invade the reservoir brine saturated rock, as well as establishing a threshold intrusion pressure for the acid gas-saturated brine. Most importantly, the cap rock strength parameters are directly compared before and after exposure to acid gas-rich brine at reservoir conditions to demonstrate that a minimal reduction in compressive strength occurs and rock compressive strength remains well above the acid gas EOR and CO<sub>2</sub> storage scheme operating parameters.

The interfacial tension (IFT) test was carried out to determine the IFT between the injected Zama acid gas and formation brine. The IFT governs fluid distribution and retention within porous media and the threshold entry pressure (or capillary entry pressure) for intrusion of acid gas saturated brine into the brine-saturated low-permeability cap rock. The lower the IFT value, the easier it will be for the injected brine or gas to penetrate and potentially move through the cap rock. IFT is one factor to be considered when the safe storage or EOR operating pressure of a reservoir is determined, and in turn the reservoir pressure is a factor in the potential storage capacity. Current industry technical documentation indicates that CO<sub>2</sub> and H<sub>2</sub>S saturated brine IFT's decrease with increasing pressure, while increasing temperature and brine salinity have the opposite effect<sup>[3,4,5]</sup>. It has also been observed that H<sub>2</sub>S–brine IFT can be 30%–40% of that for CO<sub>2</sub>–water IFT<sup>[6]</sup>. It is widely postulated that an acid gas (H<sub>2</sub>S + CO<sub>2</sub>)-rich brine may result in a further decrease in the IFT between the water and the acid gas and how it affects the intrusion pressure characteristics of the cap rock.

The TIP is the pressure that the injected fluid can first begin to infinitesimally displace the original reservoir brine within the cap rock matrix. Two tests were carried out to measure a threshold intrusion pressure (TIP) for the Zama acid gas-rich brine; one test utilized an anhydrite sample, and one a dolostone sample. TIP data for anhydrite, dolomite, and other rock in the presence of CO<sub>2</sub> saturated brines are reported; however, no data are available as they relate to CO<sub>2</sub>/H<sub>2</sub>S acid gas saturated brine mixtures.

The third set of tests compare cap rock mechanical properties including compressive strength of the anhydrite and dolostone before and after exposure to acid gas-rich brine. There is existing mechanical property data determined from Zama core recovered prior to acid gas brine exposure, and in this case, the project has documented an in-situ rock stress test prior to acid gas exposure, but there is limited, if any specific data following acid gas-saturated brine exposure. In order to measure this, four matching pairs of vertical core plugs were cut from existing full diameter anhydrite and dolostone cap rock core. One sample from each pair provided the baseline rock mechanics data through pre-exposure rock strength testing. The second sample from each pair was exposed to acid gas saturated brine for 30 days. After 30 days, the same set of rock mechanics tests provides contrasting post-exposure strength parameters.

These three measureable parameters and other related data provide valuable information to CCS (carbon capture and storage) stakeholders, including project operators and regulators who co-operate to establish maximum project operating pressures. Extension of the understanding and definition of the long-term integrity and strength of cap rock in the presence of acid gas saturated brine, and demonstration that the cap rock integrity is not severely reduced when exposed to acid gas-saturated brine provides several potential benefits; 1) regulators may allow licensed operating pressures to be increased which in some cases result in improved miscibility and EOR recovery and increased CO<sub>2</sub> storage capacities, 2) dissemination of this information will benefit public awareness programs, and, 3) associations dealing in the accrediting of CCS sites for geological storage will be assured that injected volumes of CO<sub>2</sub> will remain stored over the project lifespan.

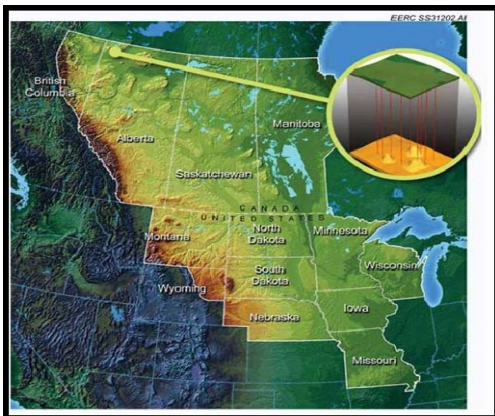


Figure 1: Apache Zama Field Location

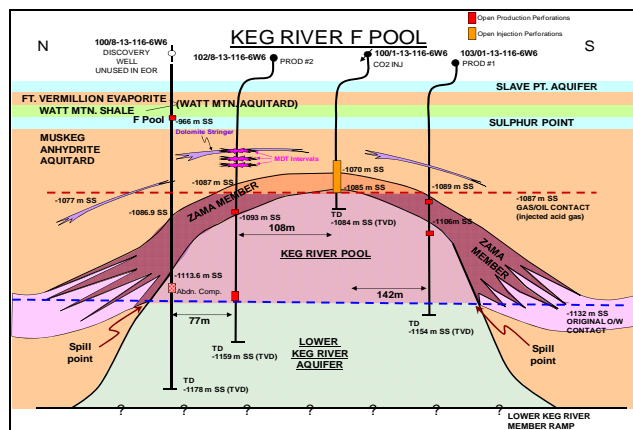


Figure 2: Zama Keg River F Pool EOR Scheme

Testing determined that the IFT and TIP for the acid gas-brine appear to be similar to that of a CO<sub>2</sub>-brine, and that the rock compressive strength was reduced just 4% to 372,710 kPa (54,058 psi) by exposure to acid gas. The remaining compressive strength remains well above that required to contain the Zama acid gas EOR & Storage project operating pressures. Supporting this is the evidence that previous in-situ (in wellbore, at reservoir conditions) testing with the Schlumberger MDT Stress Tool showed that application of the maximum available MDT tool pressure of approximately 30,800 kPa (4,475 psi) above the maximum permitted pool operating pressure of 16,600 kPa could not fracture the anhydrite. Testing of the interbedded dolomite layer initiated a micro-fracture at a pressure of 40,200 kPa (5,834 psig) and indicated an average fracture closure pressure of 31,550 kPa (4,575 psig). This pressure is still almost 2 times the maximum approved Zama F Pool EOR operating reservoir pressure; a single digit reduction of these strength values through acid-gas exposure is not significant.

Key Words: CCS, CO<sub>2</sub>, H<sub>2</sub>S, acid gas, cap rock integrity, CO<sub>2</sub> storage, MVA, IFT, TIP, compressive strength

## 1. CO<sub>2</sub>/H<sub>2</sub>S Acid Gas-Brine Interfacial Tension

The potential for fluid to invade and travel through reservoir or cap rock quality strata is a function of the IFT for the original and injected fluids, the absolute cap rock permeability to fluid, the relative permeability<sup>[7]</sup>, initial cap rock wettability state and the reservoir pressure and temperature conditions. The Zama acid gas-brine interfacial tension (IFT) measurements were conducted using the pendant-drop method developed originally by Hauser and his colleagues<sup>[5]</sup>. A general schematic of the HP/HT IFT apparatus is shown in Figure 3 and Figure 4. IFT Testing utilizing the Pendant Drop Method was carried out by Weatherford Laboratories in Calgary, Alberta as per the following general test procedure;

- I. Synthesize 30% H<sub>2</sub>S -65% CO<sub>2</sub> -5% CH<sub>4</sub> acid gas. Table 1 summarizes the calculated gas properties for this mixture and Figure 1 illustrates the complex PVT properties associated with this mixture.
- II. Synthesize test brine based on the formation brine composition.
- III. Conduct IFT measurements of the acid gas mixture and brine at reservoir pressure and temperature. Standard API salinity/density charts were utilized to verify the reservoir brine density. Equation of state modeling was utilized to verify the gas density.
 

• Reservoir Overburden Pressure:	68,162 kPag (9,886 psig)
• Test (reservoir) Temperature:	70°C (158°F)
• Test (reservoir) Pressure:	15,255 kPag (2,212 psig)
• Acid gas composition:	30% H <sub>2</sub> S -65% CO <sub>2</sub> -5% CH <sub>4</sub>
• Brine:	Synthetic Keg River formation water
• Brine DTS:	186,975 ppm
- IV. Condense acid gas in a 660 cc cylinder to the test pressure 15,250 kPag and raise cylinder to test temperature (70°C).
- V. Fill the 660 cc cylinder with 300-400 cc of formation brine; place the cylinder with the brine in the oven at the test temperature.
- VI. Allow the acid gas flow through the brine from the bottom at the test temperature in order to saturate the brine with the acid gas.
- VII. Measure density of the upper phase and transfer the upper gas phase into a visual cell.
- VIII. Measure density of the lower phase and push the liquid into the gas in the visual cell by using a pendant drop needle. Capture an image of the liquid drop and calculate IFT.

Table 1 compares the Zama Acid Gas-Brine data point to other CO<sub>2</sub> and H<sub>2</sub>S IFT and tip data at similar temperatures and pressures as reported by D.B. Bennion et al <sup>[3,4,6,5]</sup>. The Zama Acid Gas-Brine data point suggests that the 65% CO<sub>2</sub> content is dominating the IFT as it is most similar to other CO<sub>2</sub>-Brine values. H<sub>2</sub>S alone appears to have a more dramatic impact on IFT; however, it would be desirable to have more H<sub>2</sub>S-Brine IFT values to compare to.

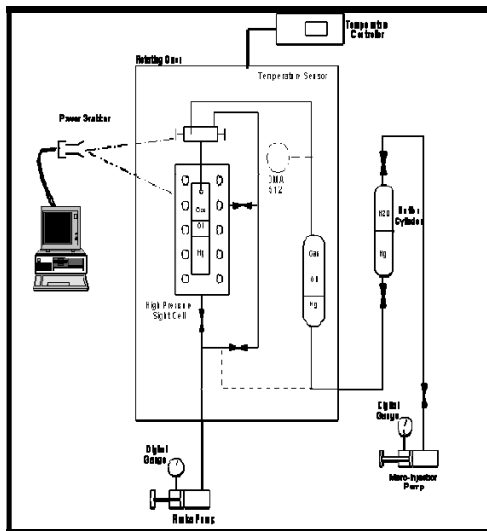


Figure 3: Reservoir Condition IFT Apparatus

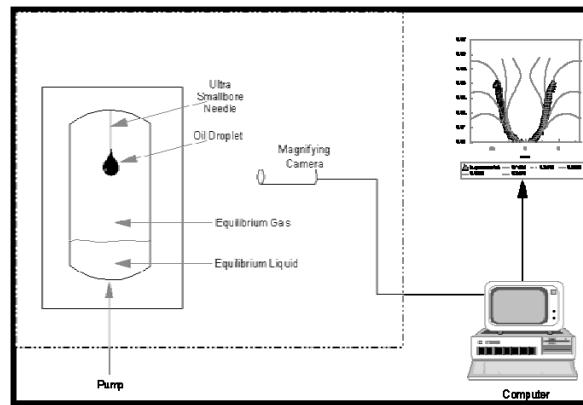


Figure 4: HPHT Pendant Drop System

## 2. CO<sub>2</sub>/H<sub>2</sub>S Acid Gas Threshold Intrusion Pressure

The Keg River anhydrite and dolostone cap rock is consistently described as a dense, high strength, high quality cap rock. Exceeding the gas threshold intrusion pressure (TIP) of a competent cap rock provides the potential for fluid seepage into and through a cap rock but this leakage rate is not expected to be significant for a proven cap rock. Full diameter core from the Zama well 100/06-24-116-06W6M was utilized for this study; this existing 39 m section of full diameter core was originally drilled in 1967. Figure 5 provides an example of one of the chosen dolostone sections from a depth of 5012 m. Almost the entire length of this core was non-reservoir rock and provided several very good anhydrite and dolostone sample opportunities. This location is very near to Zama 05-02-116-06W6M Muskeg cap rock core section previously utilized to provide a the measurement of the Muskeg anhydrite permeability, relative permeability and interfacial tension. Reference <sup>[5]</sup> presents a comparative permeability value of 0.000354 mD for the Zama Muskeg anhydrite as shown in Table 1.

Weatherford utilized standard full diameter coreflood displacement equipment to evaluate the TIP for both an anhydrite sample and a dolostone sample as per the following general test procedure. Both lithologies are expected to be of high compressive strength and low permeability as they were chosen from a long section of cap rock quality core with the anhydrite expected to be of somewhat better quality cap rock.;

- I. Mount a full diameter core sample.
- II. Pressure saturate the core with “dead” brine to reach the test pressure of 9,866 psig laboratory net overburden pressure and the reservoir P&T.
- III. Measure permeability to “dead” brine; then switch to “live” brine and measure permeability to “live” brine - both at the 300 psig delta P.
- IV. Measure the TIP with the acid gas. Begin the gas intrusion test at the first intrusion pressure (300 psig). Monitor any fluid movement at the downstream monitoring point.
- V. Monitor each pressure level as the permeability may be very low. Once movement is confirmed, maintain intrusion pressure and continue to monitor fluid production with time until “flood out” conditions.
- VI. After flood out, measure the effective gas permeability. If the maximum pressure is not reached, increase the intrusion pressure to the next pressure and monitor further.

Table 1 summarizes the TIP data for the two Zama cap rock samples and provides a comparison to two other cap rock quality samples. The TIP results indicate very good cap rock competence in the presence of acid-gas. The TIP is typically determined from the first pressure at which the acid gas can actually be forced into the rock matrix and a finite permeability can be measured. The anhydrite matrix was determined to be totally impermeable to acid gas saturated brine and the acid gas while in gas phase. In the case of the dolostone which is present as isolated stringers within the anhydrite matrix the TIP is 2070 kPa (300 psi) however at this first measurable TIP the absolute effective permeability is still much less than 0.001 mD at 0.003215 mD for acid gas saturated (live) brine and the dolostone is judged as very competent cap rock material.

Data Summary						
Fluid System	Lithology	Brine Perm. (mD)	Res. Press (kPa)	Res. Temp (°C)	IFT (mN/m)	TIP (kPa)
Zama 65% CO <sub>2</sub> 30% H <sub>2</sub> S Acid Gas-Brine	Anhydrite	0.0000000 at 2,070 kPa	15,255	70	35.97	>15,250
Zama 65% CO <sub>2</sub> 30% H <sub>2</sub> S Acid Gas-Brine	Dolostone	0.0003215 at 2,070 kPa	15,255	70	35.97	2,070
Zama 65% CO <sub>2</sub> 30% H <sub>2</sub> S Acid Gas, Gas Phase	Anhydrite	0.0000000	15,250	70		>15,250
Zama 65% CO <sub>2</sub> 30% H <sub>2</sub> S Acid Gas, Gas Phase	Dolostone	0.0000036	15,250	70		2,070
Muskeg CO <sub>2</sub> -Brine	Anhydrite	0.000354	15,000	71	39.5	
Nisku #1 CO <sub>2</sub> -Brine	Carbonate	45.9	17,400	56	34.56	58.0
Nisku #1 H <sub>2</sub> S-Brine	Carbonate	45.9	17,400	56	12.3	
Cooking Lake CO <sub>2</sub> -Brine	Carbonate	65.3	15,000	55	35.7	11.1
Calmar CO <sub>2</sub> -Brine	Shale	0.000003			27.6	72,827

Table 1: Data Summary

### 3. Rock Mechanics Analysis

Weatherford utilized a specialized soak/reactor test to evaluate the changes in the rock mechanical properties of the core samples before and after exposure to the acid gas under the reservoir conditions. Weatherford drilled 8 companion pairs of sample plugs from the FD core (Figure 5) for a total of 16 (sixteen) 1 inch OD vertical core plugs from the dolomite and anhydrite full diameter core samples as shown in Figure 6. The 1" vertical plugs were drilled at a 2:1 length to diameter ratio. All plugs were examined by white light and CT scan to validate that there were no existing or drilling induced flaws that would skew the measured strength parameters. Eight of the companion sample plugs were utilized for rock mechanics without exposure to the acid gas. The second of each companion sample plug (8 plugs) soaked in acid gas saturated brine at reservoir conditions for a period of 30 days. Following the 30 day soak period these sample plugs had the same set of rock mechanics test performed so as to provide a direct comparison the first set of non-exposed plugs. Figure 7 illustrates the 5012 m sampler pre-soak while Figure 8 illustrates the same sample post-soak. The orange coloring of the post-soak sample is similar to that reported by Kutchko<sup>[8]</sup> et al of NETL as a portion of their study of oil well cements exposed to CO<sub>2</sub> saturated brines. The color alteration is related carbonation of minerals within the samples and is well described within the NETL works.

The TIP Testing was carried out by Weatherford Laboratories in Calgary, Alberta as per the following general test procedure;

- I. Eight pairs of cylindrical plugs (1-inch diameter) were drilled from the full diameter (FD) core. Plug ends are ground parallel to within 0.001 inch. A length to diameter ratio of 2:1 is utilized to obtain representative mechanical properties. Physical dimensions of the specimen are recorded and the specimen is saturated with simulated formation brine.
- II. The specimen to be tested is placed between two end-caps and a heat-shrink jacket is placed over the specimen.
- III. Axial strain and radial strain devices are mounted in the end-caps and on the lateral surface of the specimen, respectively.
- IV. The specimen assembly is placed into the pressure vessel and the pressure vessel is filled with hydraulic oil. Confining pressure is increased to the hydrostatic testing pressure.
- V. Measure acoustic velocities at hydrostatic confining pressure.
- VI. The specimen assembly is brought into the contact with a loading piston that allows application of axial load. Increase axial load at a constant displacement rate until the specimen fails or axial strain reaches a desired amount of strain while confining pressure is held constant.
- VII. Reduce axial stress to the initial hydrostatic condition after sample fails or axial strain reaches a desired amount of strain.
- VIII. Reduce confining pressure to zero and disassemble sample.



Figure 5: Full Diameter Core from 5012 m

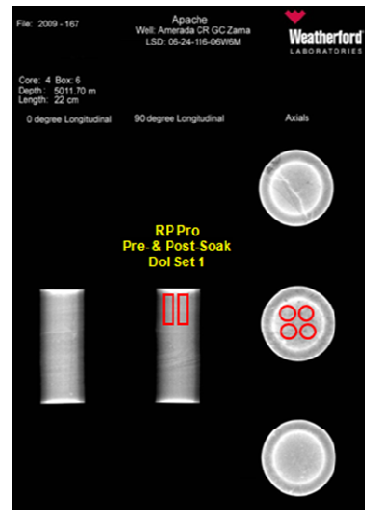


Figure 6: CT Scan of 5012 m FD Core

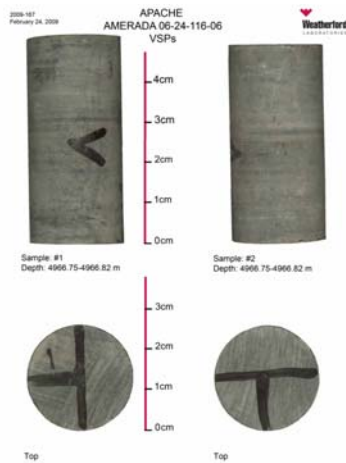


Figure 7: Pre-Soak 5012 m Companion Plug Samples

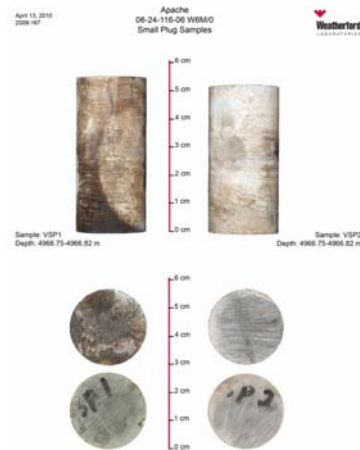


Figure 8: Post-Soak 5012 m Companion Plug Samples

Pre-soak test	
Company	RPS Energy
Project Title	Zama
WFT Project No.	CL-45467
Date	April, 2010

Sample No.	VSP-7
Depth (m)	5011.70
Saturation State	187 g/L KCl
Confining Pressure (psi)	8500
Bulk Density* (g/cc)	2.75
Compressive Strength (psi)	59045
Young's Modulus (x10 <sup>6</sup> psi)	10.13
Poisson's Ratio	0.40

\* saturated

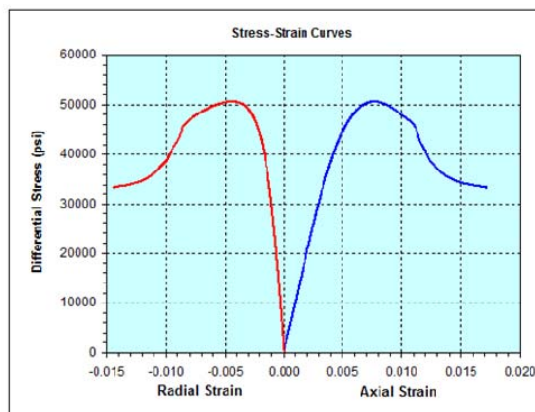


Figure 9: Pre-Soak Test 5012 m Plug Sample Test Results

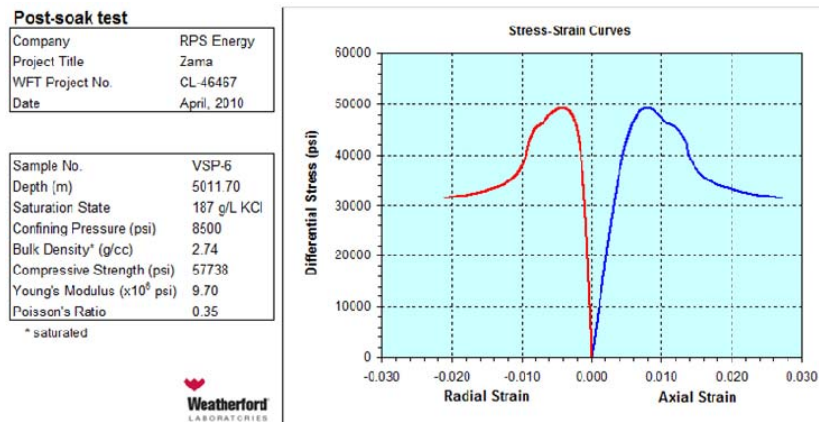


Figure 10: Post-Soak Test 5012 m Plug Sample Test Results

The rock mechanic testing included the previously described comparative Compressive Strength analysis tests as well as the comparative analysis of the Static and Dynamic Young's Modulus and Poisson's Ratio, bulk and Shear Modulus, and measurement of the Compressional and Shear Wave Velocities. Figure 9 and Figure 10 provide example of the Pre and Post Compressive Strength determinations for the 5012 m dolostone sample pair. Table 2 and Table 3 provide a summary of the individual sample results as well as the calculated comparisons of each indicator.

These results indicate that the Compressive Strength was reduced by just 3.8% on average with a range between +0.3% and -6.5%. There was minimal change in any of the remaining individual integrity indicators.

Sample No.	Depth (m)	Confining Pressure (psi)	Compressive Strength (psi)	Static Young's Modulus (x10 <sup>6</sup> psi)	Static Poisson's Ratio
Pre-Soak Test					
VSP-4 (Anhydrite)	4966.75	8500	59286	9.20	0.33
VSP-7 (Dolostone)	5011.70	8500	59045	10.13	0.40
VSP-11 (Anhydrite)	5014.40	8500	49883	7.25	0.29
VSP-15 (Anhydrite)	5047.95	8500	53744	8.13	0.28
Post- Acid Gas Soak Test					
VSP-1 (Anhydrite)	4966.75	8500	55442	9.05	0.37
VSP-5 (Dolostone)	5011.70	8500	56513	9.10	0.31
VSP-6 (Dolostone)	5011.70	8500	57738	9.70	0.35
VSP-10 (Anhydrite)	5014.40	8500	50015	7.79	0.28
VSP-13 (Anhydrite)	5047.95	8500	50583	8.39	0.34

Relative Changes (Pre-Soak/Post Soak)				
Sample Comparison		Compressive Strength (psi)	Static Young's Modulus (x10 <sup>6</sup> psi)	Static Poisson's Ratio
VSP-4/VSP-1		-6.5%	-1.7%	10.3%
VSP-7/VSP-5&6		-3.3%	-7.2%	-16.7%
VSP-11/VSP-10		0.3%	7.5%	-0.7%
VSP-15/VSP-13		-5.9%	3.2%	20.4%
Average Change		-3.8%	0.5%	3.3%

Table 2: Summary of Triaxial Compressive Tests

Sample No.	Depth (m)	Confining Pressure (psi)	Bulk Density (g/cc)	Ultrasonic Wave Velocity				Dynamic Elastic Parameter			
				Compressional		Shear		Young's Modulus ( $\times 10^6$ psi)	Poisson's Ratio	Bulk Modulus ( $\times 10^6$ psi)	Shear Modulus ( $\times 10^6$ psi)
				ft/sec	μsec/ft	ft/sec	μsec/ft				
<b>Pre-Soak Test</b>											
VSP-4	4966.75	8500	2.93	20859	47.94	10157	98.45	10.94	0.34	11.73	4.07
VSP-7	5011.70	8500	2.75	21560	46.38	11921	83.89	13.48	0.28	10.21	5.27
VSP-11	5014.40	8500	2.92	20533	48.70	10852	92.15	12.11	0.31	10.41	4.64
VSP-15	5047.95	8500	2.92	20795	48.09	10835	92.30	12.15	0.31	10.87	4.62
<b>Post- Acid Gas Soak Test</b>											
VSP-1	4966.75	8500	2.94	20832	48.00	10171	98.32	11.00	0.34	11.72	4.09
VSP-5	5011.70	8500	2.74	21437	46.65	11845	84.42	13.28	0.28	10.07	5.19
VSP-6*	5011.70	8500	2.74	21750	45.98	11621	86.05	12.99	0.30	10.84	4.99
VSP-10	5014.40	8500	2.94	20564	48.63	10866	92.03	12.21	0.31	10.50	4.67
VSP-13	5047.95	8500	2.93	20725	48.25	10663	93.78	11.87	0.32	10.99	4.49
<b>Relative Changes (Pre-Soak/Post Soak)</b>											
Sample Comparison				Ultrasonic Wave Velocity				Dynamic Elastic Parameter			
				Compressional		Shear		Young's Modulus ( $\times 10^6$ psi)	Poisson's Ratio	Bulk Modulus ( $\times 10^6$ psi)	Shear Modulus ( $\times 10^6$ psi)
				ft/sec	μsec/ft	ft/sec	μsec/ft				
VSP-4/VSP-1				-0.1%	0.1%	0.1%	-0.1%	0.6%	-0.3%	-0.1%	0.7%
VSP-7/VSP-5&6				0.2%	-0.2%	-1.6%	1.6%	-2.6%	3.7%	2.4%	-3.3%
VSP-11/VSP-10				0.2%	-0.2%	0.1%	-0.1%	0.8%	0.0%	0.9%	0.8%
VSP-15/VSP-13				-0.3%	0.3%	-1.6%	1.6%	-2.3%	2.0%	1.1%	-2.8%
<b>Average Change</b>				<b>0.0%</b>	<b>0.0%</b>	<b>-0.7%</b>	<b>0.7%</b>	<b>-0.9%</b>	<b>1.4%</b>	<b>1.1%</b>	<b>-1.2%</b>

\* determined after applying 45,000 psi differential stress.

Table 3: Summary of Ultrasonic Velocities and Dynamic Elastic Parameters



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