Distinguished Lecturer Program

Primary funding is provided by

The SPE Foundation through member donations and a contribution from Offshore Europe

The Society is grateful to those companies that allow their professionals to serve as lecturers

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Distinguished Lecturer Program

Stimulation Fluids – Myths, Reality and Environmental Stewardship through Better Chemistry

Dan Daulton

Enhanced Production

Pressure Pumping

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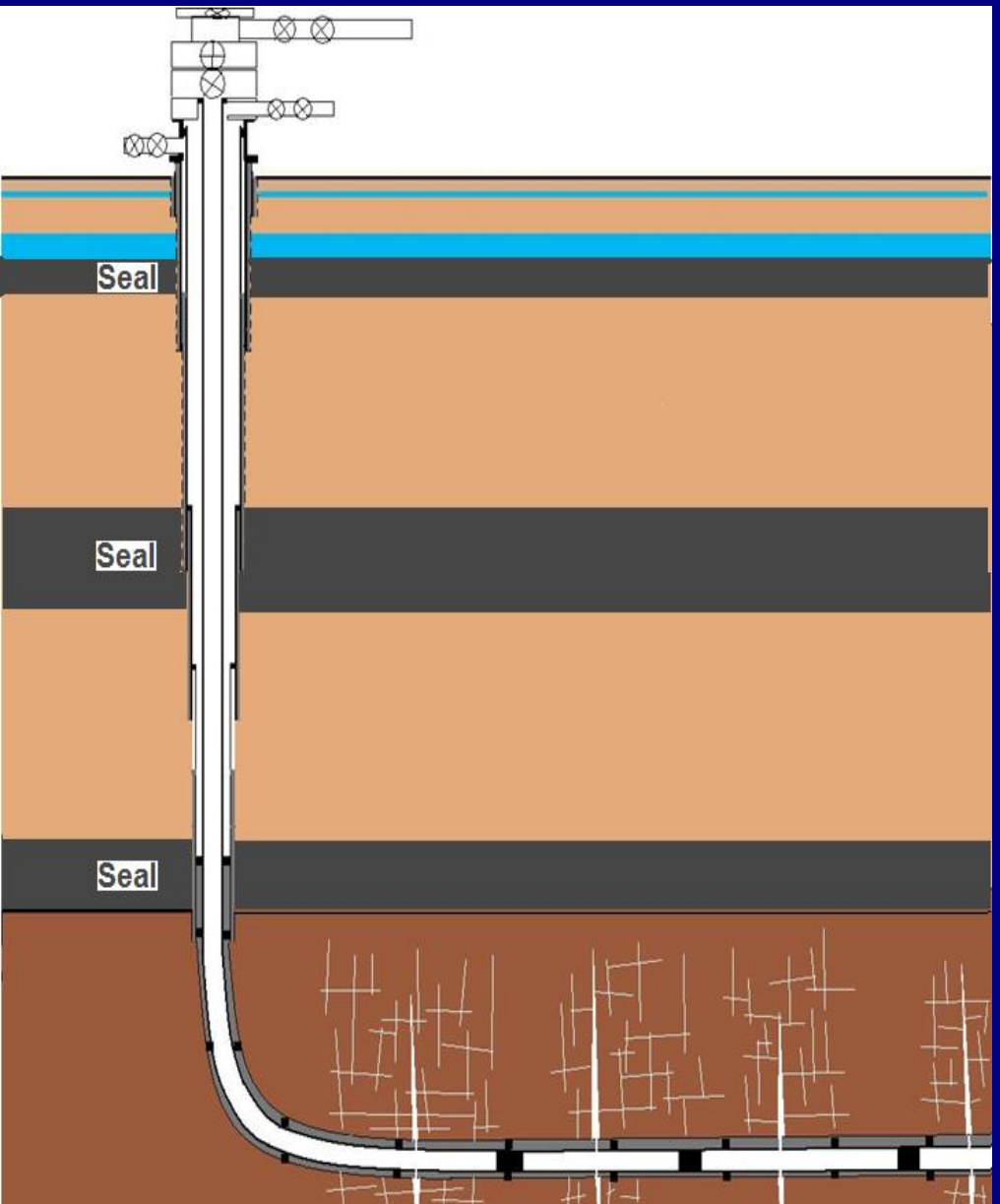
Agenda

- Industry Myths or Realities
  - Fracturing “out of sight, out-of mind”
  - “Your fracturing chemicals are secret or unregulated”
  - “Your frac chemicals are dangerous and unregulated”
  - “You use a lot of water”
- Industry Environmental Stewardship
  - Stimulation Chemicals Evaluation/Utilization

Well Integrity / Zonal Isolation



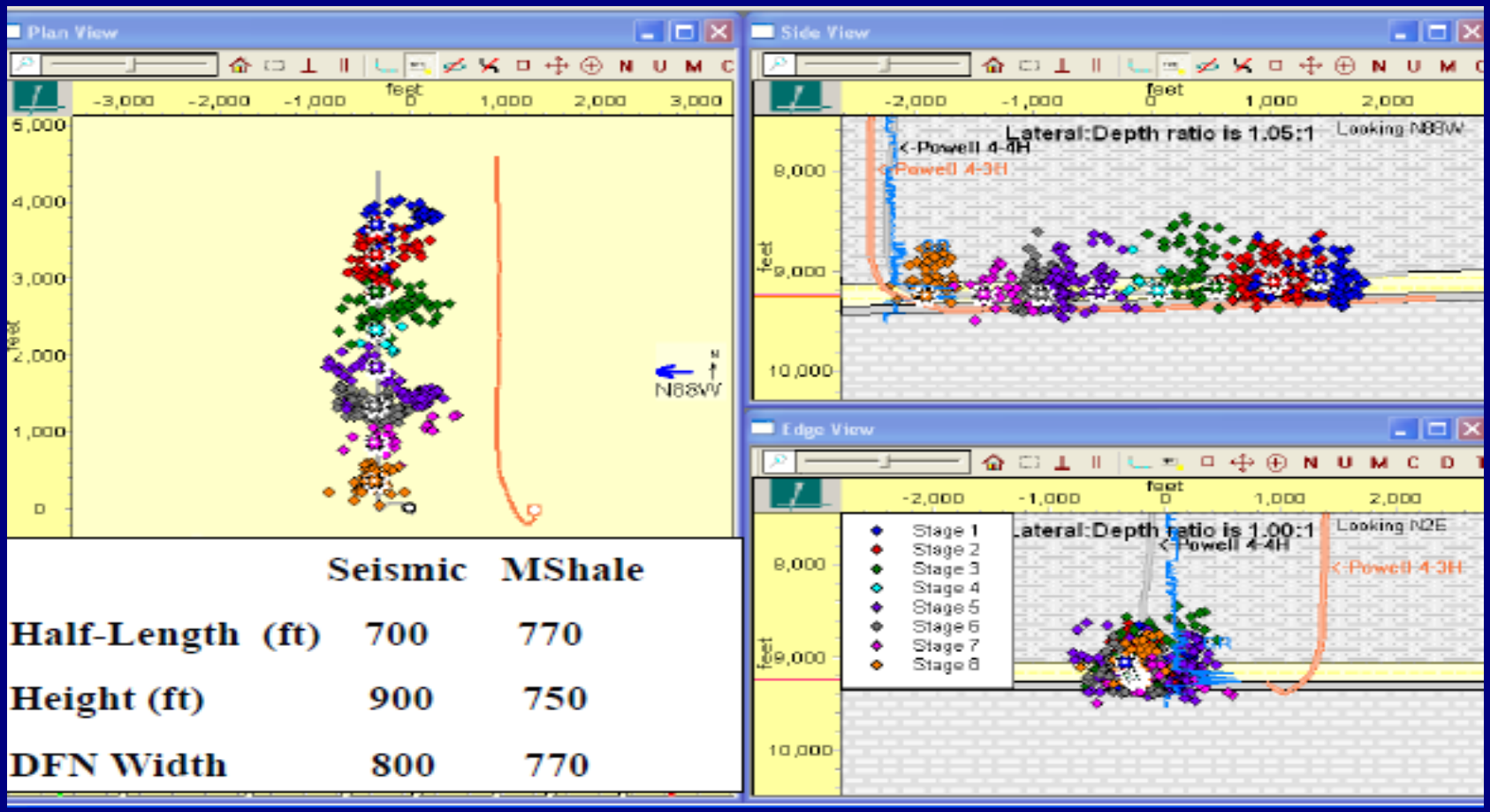
- Natural barriers
- Manmade barriers
  - Proper well construction

As an industry we focus on long-term well integrity as a key objective

Courtesy George King., Apache Corp

Myth or Reality? “Out of Sight-Out of Mind”

Information in the industry exists to show accurate measurements where hydraulic fractures are created

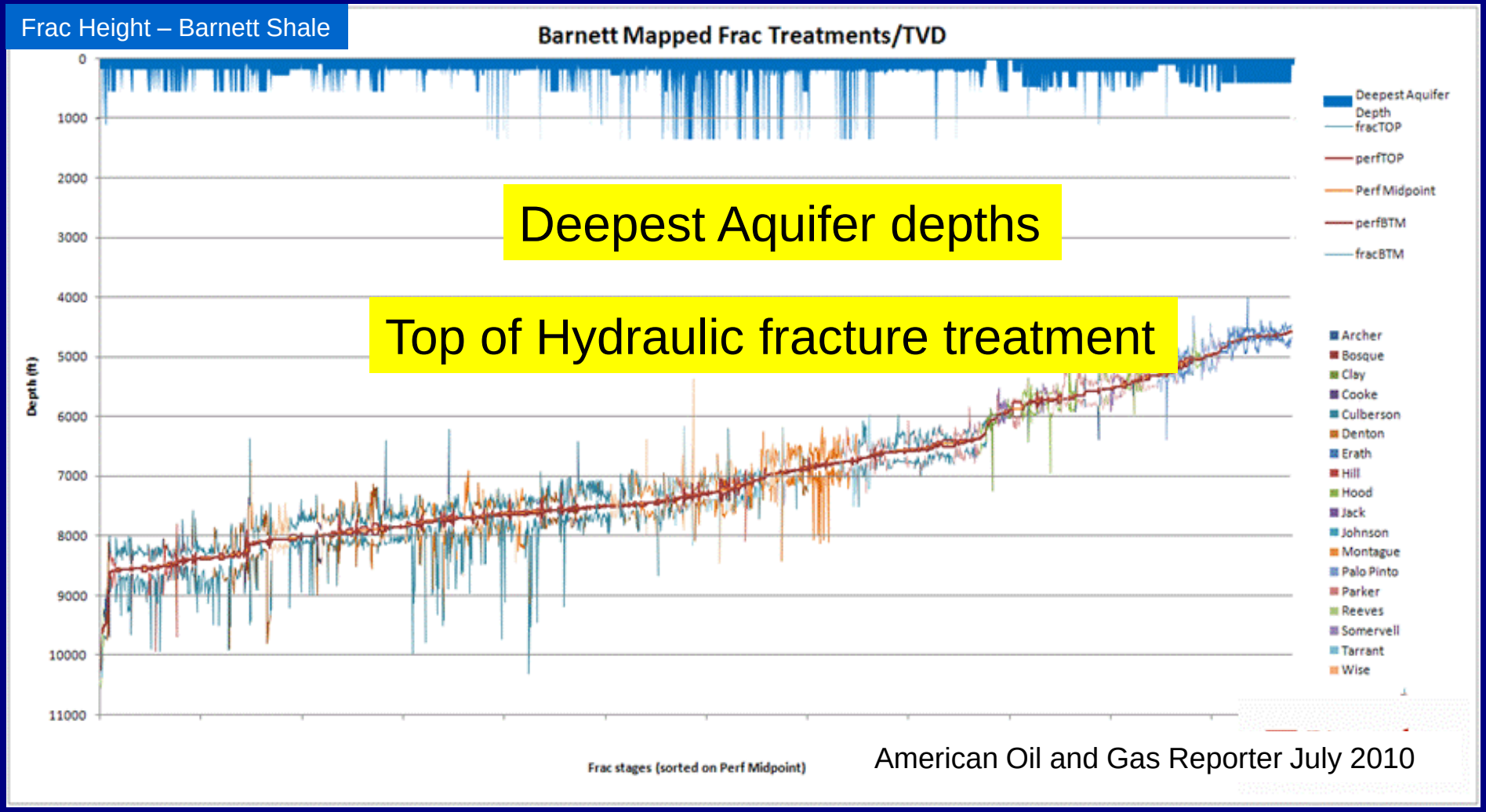


	Seismic	MShale
Half-Length (ft)	700	770
Height (ft)	900	750
DFN Width	800	770

Microseismic mapping Woodford Shale

Myth or Reality? "Out of Sight-Out of Mind"

Frac Height – Barnett Shale

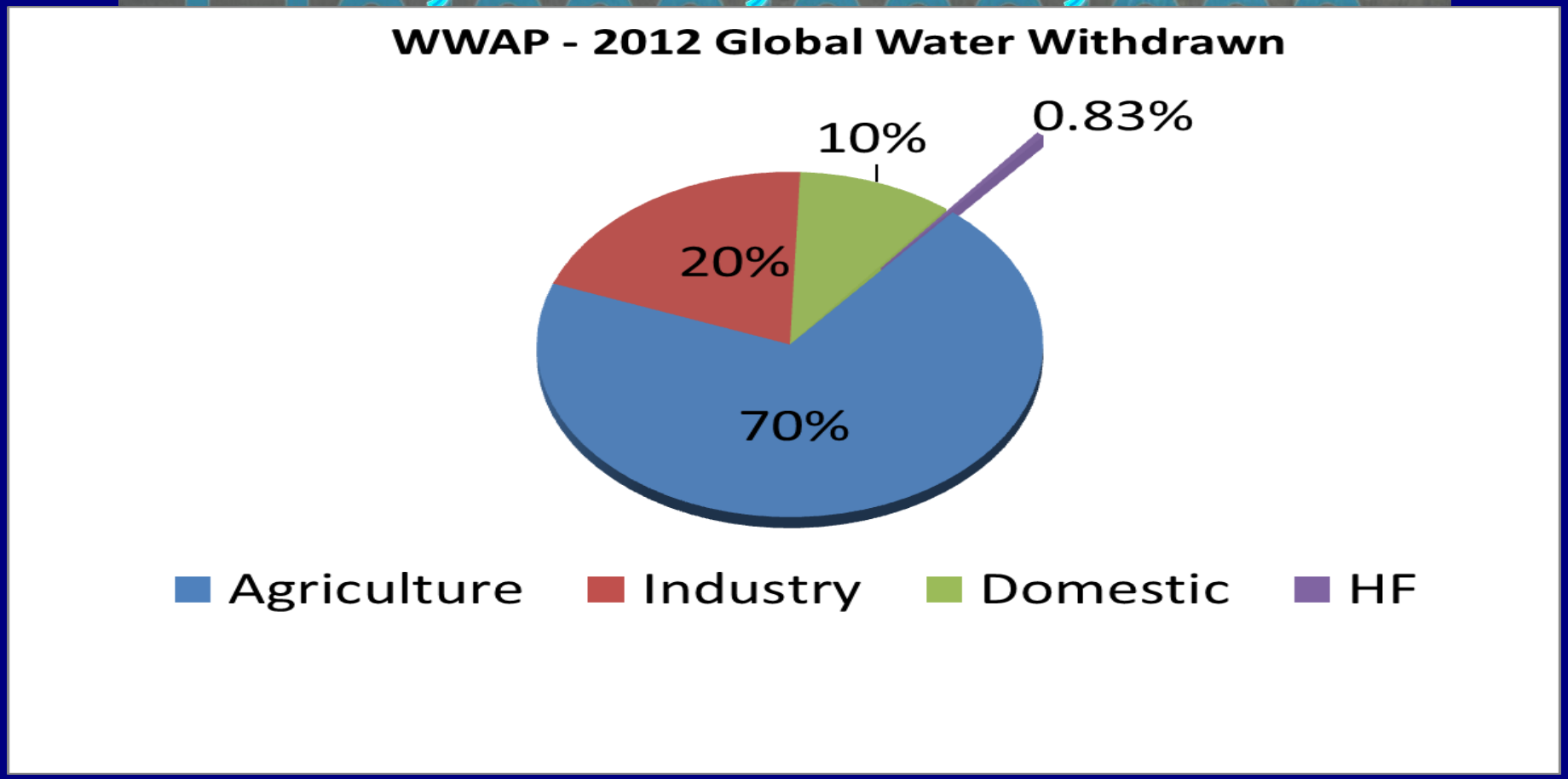


American Oil and Gas Reporter July 2010

http://nwis.waterdata.usgs.gov/nwis/inventory

Myth or Reality – “we use a lot of freshwater”

140,000,000,000*

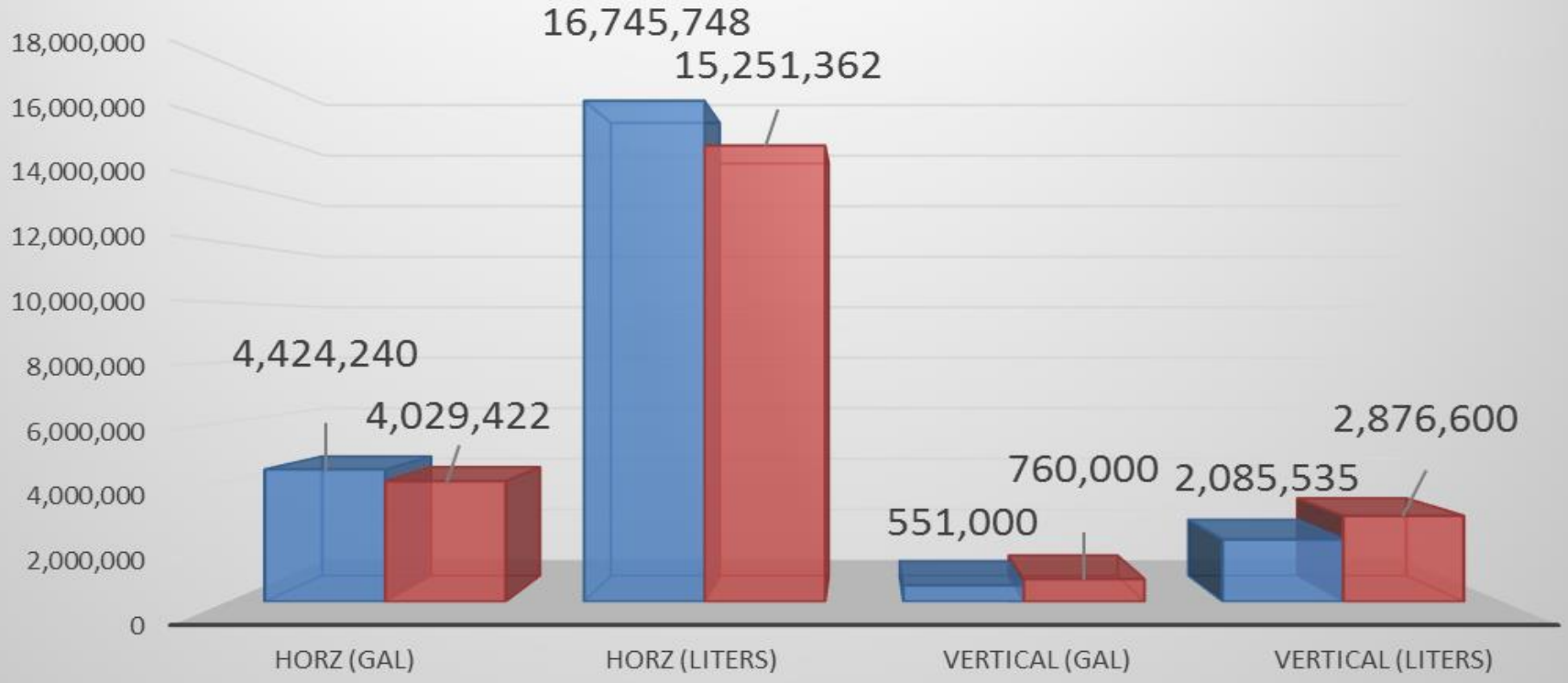


*Draft Plan to Study the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources
Office of Research and Development, U.S. Environmental Protection Agency
Washington, D.C. February 7, 2011

Myth or Reality – “we use a lot of freshwater”

2011 & 2012 water use averge per well

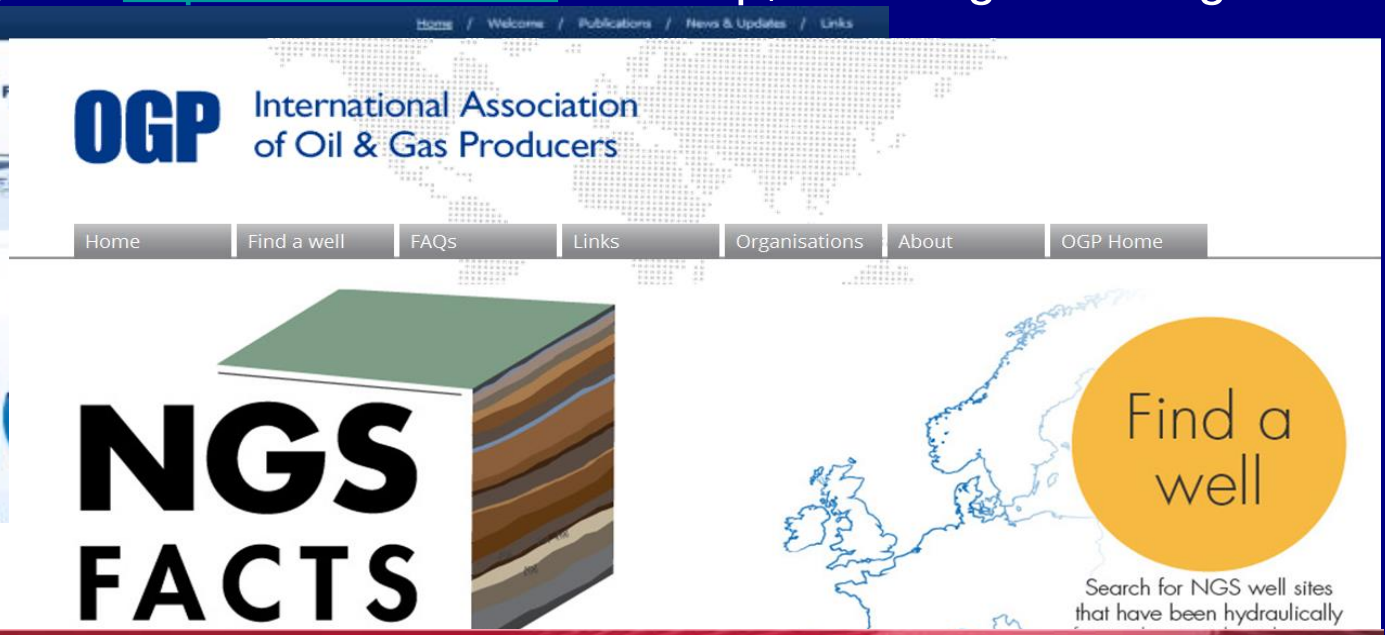
Year	Horz wells	Vertical wells	Total wells
2011	4931	2407	7338
2012	8428	5528	13956

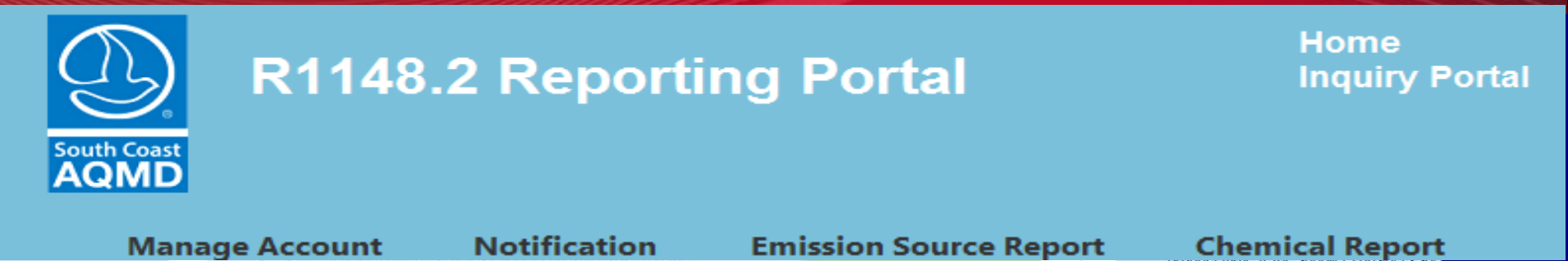


Source: GWPC – FracFocus.org

Myth or Reality? "Your Chemicals Are Secret"

http://fracfocus.org and http://fracfocus.ca/ and http;//www.ngsfacts.org





Report Overview

Fracture Date	4/21/2012
State:	CO
County:	Weld
API Number:	05-123-27303
Operator Name:	Noble Energy Inc
Well Name and Number:	Duke J04-33

Hydraulic Fracturing Fluid Product Component Information Disclosure

Fracture Date	4/21/2012
State:	CO
County:	Weld
API Number:	05-123-27303
Operator Name:	Noble Energy Inc
Well Name and Number:	Duke J04-33
Longitude:	-104.79272
Latitude:	40.42571
Long/Lat Projection:	NAD83
Production Type:	Gas
True Vertical Depth (TVD):	7,439
Total Water Volume (gal)*:	293,622

Trade Name	Supplier	Purpose	Ingredients	Chemical Abstract Service Number (CAS #)	Maximum Ingredient Concentration in Additive (% by mass)**	Maximum Ingredient Concentration in HF Fluid (% by mass)**	Comments
Water	Operator	Carrier	Water	7732-18-5	100.00%	82.10784%	
HCl, 10.1 - 15%	Baker Hughes	Acidizing	Hydrochloric Acid	7647-01-0	15.00%	0.02432%	
			Water	7732-18-5	85.00%	0.13780%	
Frac-Cide 1000	Baker Hughes	Biocide	2,2-Dibromo-3-Nitrilopropionamide	10222-01-2	100.00%	0.00151%	
GBW-5	Baker	Breaker	Ammonium Persulfate	7727-54-0	100.00%	0.00235%	SmartCare Product
						.00040%	SmartCare Product
						.00020%	
						.00751%	
						.00188%	
						.00131%	
						.00065%	
						.01109%	
						.01110%	SmartCare Product
						.00555%	
						.05812%	SmartCare Product
						.02325%	
						.00018%	
						.00001%	
						.00003%	

Ingredients	Chemical Abstract Service Number (CAS #)	Maximum Ingredient Concentration in Additive (% by mass)**	Maximum Ingredient Concentration in HF Fluid (% by mass)**	Comments
	7732-18-5	100.00%	82.10784%	
chloric Acid	7647-01-0	15.00%	0.02432%	
	7732-18-5	85.00%	0.13780%	
bromo-3-Nitrilopropionamide	10222-01-2	100.00%	0.00151%	
nium Persulfate	7727-54-0	100.00%	0.00235%	SmartCare Product
nium Persulphate	7727-54-0	60.00%	0.00040%	SmartCare Product
lline Silica Quartz	14808-60-7	30.00%	0.00020%	
nium Persulphate	7727-54-0	80.00%	0.00751%	
lline Silica	7631-86-9	20.00%	0.00188%	
esium Oxide	1309-48-4	60.00%	0.00131%	
esium Peroxide	14452-57-4	30.00%	0.00065%	
zardous Ingredients	Trade Secret	100.00%	0.01109%	
ium Carbonate	584-08-7	60.00%	0.01110%	SmartCare Product
ium Hydroxide	1310-58-3	30.00%	0.00555%	
e Chloride	67-48-1	75.00%	0.05812%	SmartCare Product
	7732-18-5	30.00%	0.02325%	
tic Aldehyde	Trade Secret	30.00%	0.00018%	
ormic Acid	64-18-6	60.00%	0.00037%	
opropanol	67-63-0	10.00%	0.00006%	
ethanol	67-56-1	5.00%	0.00003%	
ganic Sulfur Compound	Trade Secret	5.00%	0.00003%	
kylalkylated Fatty Acid	Trade Secret	30.00%	0.00018%	
uaternary Ammonium Compound	Trade Secret	30.00%	0.00018%	
opyl Alcohol	71-23-8	30.00%	0.02042%	
ethanolamine	102-71-6	100.00%	0.06808%	
Propyl Zirconate	23519-77-9	30.00%	0.02042%	
isopropanolamine	122-20-3	10.00%	0.00178%	
conium Sodium Hydroxy Lactate omplex	113184-20-6	30.00%	0.00535%	
troleum Distillates	64742-47-8	30.00%	0.01352%	SmartCare Product
odium Thiosulfate	7772-98-7	100.00%	0.00671%	
troleum Distillates	64742-47-8	60.00%	0.25100%	SmartCare Product
tric Acid	77-92-9	60.00%	0.00042%	SmartCare Product
lycerine	56-81-5	30.00%	0.00984%	
Oxyalkylated Alcohol	Trade Secret	5.00%	0.00164%	
Polyethylene Glycol	25322-68-3	5.00%	0.00164%	
Crystalline Silica (Quartz)	14808-60-7	100.00%	8.24043%	
Crystalline Silica (Quartz)	14808-60-7	100.00%	8.39202%	
Amphoteric Surfactant	Trade Secret	40.00%	0.04210%	SmartCare Product

Ingredients shown above are subject to 29 CFR 1910.1200(i) and appear on Material Safety Data Sheets (MSDS). Ingredients shown below are Non-MSDS.

			2-Bromo-3-Nitrilopropionamide	1113-55-9		0.0000120739%	
			2-Mercaptoethyl Alcohol	60-24-2		0.0000213364%	
			Acetyl Triethyl Citrate	77-89-4		0.0110928825%	
			Alcohols, C12-14, Ethoxylated Propoxylated	68439-51-0		0.0209168305%	
			Aliphatic Hydrocarbon	Trade Secret		0.0104978776%	
			Alkylene Oxide Block Polymer	Trade Secret		0.0037642286%	
			Alkyoxylated Amine	Trade Secret		0.0032805650%	
			Ammonium Chloride	12125-02-9		0.0012484628%	
			Ammonium Lactate	515-98-0		0.0017835468%	
			Ammonium Sulfate	7783-20-2		0.0005350641%	
			Carboxymethyl Guar Gum, Sodium Salt	39346-76-4		0.1673346444%	
			Crystalline Silica	14808-60-7		0.0209168305%	
			Cured Acrylic Resin	Trade Secret		0.0020793914%	
			Dibromoacetonitrile	3252-43-5		0.0000015092%	
			Diethylene Glycol	111-46-6		0.0000006096%	
			Fumaric Acid	110-17-8		0.0209168305%	
			Iron	7439-89-6		0.0001341543%	
			Isotridecanol, Ethoxylated (TDA-6)	9043-30-5		0.0209168305%	
			Isotridecanol, Ethoxylated (TDA-9)	9043-30-5		0.0209168305%	
			Magnesium Carbonate	7757-69-9		0.0003270011%	

			Oxyalkylated Alcohol	Trade Secret	5.00%	0.00164%	
			Polyethylene Glycol	25322-68-3	5.00%	0.00164%	
Sand, White, 20/40	Baker Hughes	Proppant	Crystalline Silica (Quartz)	14808-60-7	100.00%	8.24043%	
Sand, White, 30/50	Baker Hughes	Proppant	Crystalline Silica (Quartz)	14808-60-7	100.00%	8.39202%	
GasFlo G2, 330 gal tote	Baker Hughes	Surfactant	Amphoteric Surfactant	Trade Secret	40.00%	0.04210%	SmartCare Product

Ingredients shown above are subject to 29 CFR 1910.1200(i) and appear on Material Safety Data Sheets (MSDS). Ingredients shown below are Non-MSDS.

			2-Bromo-3-Nitrilopropionamide	1113-55-9		0.0000120739%	
			2-Mercaptoethyl Alcohol	60-24-2		0.0000213364%	
			Acetyl Triethyl Citrate	77-89-4		0.0110928825%	
			Alcohols, C12-14, Ethoxylated Propoxylated	68439-51-0		0.0209168305%	
			Aliphatic Hydrocarbon	Trade Secret		0.0104978776%	
			Alkylene Oxide Block Polymer	Trade Secret		0.0037642286%	
			Alkyoxylated Amine	Trade Secret		0.0032805650%	
			Ammonium Chloride	12125-02-9		0.0012484628%	
			Ammonium Lactate	515-98-0		0.0017835468%	
			Ammonium Sulfate	7783-20-2		0.0005350641%	
			Carboxymethyl Guar Gum, Sodium Salt	39346-76-4		0.1673346444%	
			Crystalline Silica	14808-60-7		0.0209168305%	
			Cured Acrylic Resin	Trade Secret		0.0020793914%	
			Dibromoacetonitrile	3252-43-5		0.0000015092%	
			Diethylene Glycol	111-46-6		0.0000006096%	
			Fumaric Acid	110-17-8		0.0209168305%	
			Iron	7439-89-6		0.0001341543%	
			Isotridecanol, Ethoxylated (TDA-6)	9043-30-5		0.0209168305%	
			Isotridecanol, Ethoxylated (TDA-9)	9043-30-5		0.0209168305%	
			Magnesium Carbonate	7757-69-9		0.0003270011%	

Report Overview – EU system style

HYDRAULIC FRACTURING FLUID CONSTITUENTS

Chemical substance in fracturing fluid[2]	Chemical Abstract Service Number (CAS Number)[3]	Maximum Chemical substance Mass % in Hyd Fracturing Fluid[4]	Comments
Water		74.1650%	
Carbon Dioxide	124-38-9	16.7266%	
Ceramic materials and wares, chemicals	66402-68-4	5.7234%	
Potassium chloride	7447-40-7	1.4945%	
Crystalline silica	14808-60-7	1.1731%	
2-butoxyethanol	111-76-2	0.2428%	
Guar gum, carboxymethyl 2-hydroxypropyl ether, sodium salt	68130-15-4	0.1494%	
Hydrochloric acid	7647-01-0	0.1166%	
Sodium bromate	7789-38-0	0.0583%	
1,2-ethanediylbis[oxy]]bis-Methanol	3586-55-8	0.0408%	
1-Propanaminium, 3-amino-N-(carboxymethyl)-N,N-dimethyl-, N-coco acyl derivs., chlorides, sodium salts	61789-39-7	0.0339%	
Sodium diacetate	126-96-5	0.0311%	
Formic acid	64-18-6	0.0278%	
Polyethylene glycol monohexyl ether	31726-34-8	0.0171%	
Propan-2-ol	67-63-0	0.0133%	
Tetrasodium ethylenediaminetetraacetate	64-02-8	0.0073%	
Reaction product of: acetophenone, formaldehyde, cyclohexylamine, methanol and acetic acid	224635-63-6	0.0068%	
Ethyleneglycol	107-21-1	0.0034%	
Alkyl quaternary ammonium bentonite	71011-24-0	0.0033%	

Chemical substance in fracturing fluid[2]	Chemical Abstract Service Number (CAS Number)[3]	Maximum Chemical substance Mass % in Hyd Fracturing Fluid[4]	Co
Potassium iodide	7681-11-0	0.0023%	
Magnesium nitrate	10377-60-3	0.0017%	
Hydroxypropyl cellulose	9004-64-2	0.0012%	
Tridecyl alcohol polyethoxylate	68015-67-8	0.0011%	
Methanol	67-56-1	0.0008%	
Dicoco dimethyl quaternary ammonium chloride	61789-77-3	0.0007%	
5-Chloro-2-methyl-3(2H)-isothiazolone and 2-methyl-3(2H)-isothiazolone	55965-84-9	0.0007%	
Sodium Glycolate (impurity)	2836-32-0	0.0006%	
Ethoxylated tall oil	65071-95-6	0.0005%	
Acetophenone	98-86-2	0.0004%	
Heavy aromatic naphtha	64742-94-5	0.0003%	
Prop-2-yn-1-ol	107-19-7	0.0003%	
Formaldehyde	50-00-0	0.0003%	
Sodium hydroxide	1310-73-2	0.0002%	
Trisodium Ethylenediaminetetraacetate (impurity)	150-38-9	0.0002%	
Disodium Ethylene Diamine Tetra Acetate (impurity)	139-33-3	0.0002%	
Acetic acid	64-19-7	0.0002%	
Non-crystalline silica	7631-86-9	0.0002%	
Trisodium nitrilotriacetate (impurity)	5064-31-3	0.0001%	
Potassium hydroxide	1310-58-3	<0.0001%	
Naphtalene (impurity)	91-20-3	<0.0001%	
1,2,4 Trimethylbenzene (impurity)	95-63-6	<0.0001%	

Report Overview – W AU system style

B. PRODUCT LIST

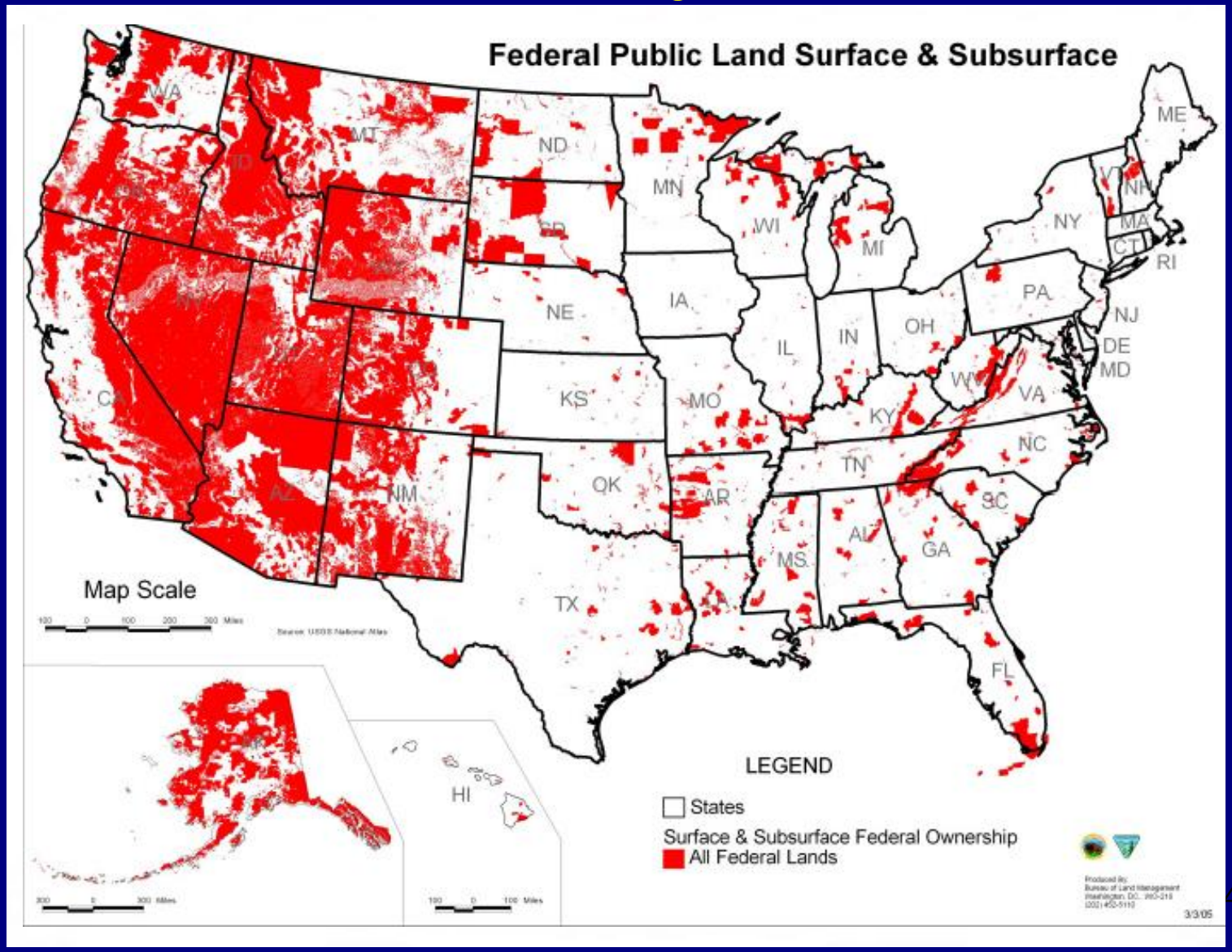
Product name	Supplier	Purpose	% Product in system fluid	Ecotoxicity info	MSDS attached
Water	Bore water	Base fluid	87.64%	Bore water sourced on site.	N/A
Sud-Chemie Bentonil THR	Sud-Chemie Australia Pty Ltd	Drilling mud	5.28%	Acute toxicity (Bentonil THR): Bentonites are natural unmodified clays. Acute toxicity (Silica crystalline quartz as ingredient): Fish LC_{50}(96hr): >10,000mg/l (*Brachydanio rerio*, zebra fish) Crustacean EC_{50}(24hr): >1000 mg/L (*Mysidopsis bahia*) Chronic toxicity (Silica crystalline quartz as ingredient): Silica is a IARC Group 1 Carcinogen, respiratory (IARC) Biodegradation / bioaccumulation (Bentonil THR): Low bioaccumulation expected**	Y
GEM CP	Halliburton	Shale stabiliser	2.05%	Acute toxicity (GEM CP): LD_{50} (oral): >2000 mg/kg (rat) Fish EC_{50}: 86ppm (*Abra alba*) Crustacean TLM(48hr): 356 mg/L (*Acartia tonsa*) Algae EC_{50}: 465 mg/L (*Skeletonema costatum*) Chronic toxicity (GEM CP): No known carcinogenic properties or chronic impacts. Biodegradation / bioaccumulation (GEM CP): BOD (28day): 76% of COD	Y
Magnacide	Baker Hughes Australia Pty Ltd	Biocide	1.02%	Acute toxicity (Magnacide): Oral LD_{50}: 29 mg/kg (rat) Fish LC_{50}(96hr): 24ppb (*Oncorhynchus mykiss*) Crustacean LC50(96hr): 500 ppb (*Mysidopsis bahia*) Algae EC_{50}(120hr): 27 ppb (*Skeletonema costatum*) Chronic toxicity (Magnacide): Studies do not indicate carcinogenic (rat, dog) or mutagenic (rat, Salmonella strains) properties (WHO, 2005). Biodegradation / bioaccumulation (Magnacide): Studies indicate not bioaccumulative (fish, shell fish, mammals, birds, lettuce) (WHO, 2005). Degradation half-life (freshwater): 6-10 hrs. Degradation half-life (aerobic soil-water): 4.2 hrs.	Y
Etc….					
Total			**~100%**		

C. CHEMICAL LIST

Chemicals within Drilling Mix Water S1A	CAS number	Mass fraction (%)
Water	7732-18-5	84.65%
Crystalline silica	14808-60-7	14.53%
Petroleum distillate, hydrotreated light	64742-47-8	0.19319%
Guar gum	9000-30-0	0.17459%
Polyactide resin	9051-89-2	0.14763%
Tetramethyl ammonium chloride	75-57-0	0.09164%
1,2,3-Propanetriol	56-81-5	0.04667%
Methanol	67-56-1	0.04594%
Carbonic acid, sodium salt	533-96-0	0.00910%
Sodium hydroxide	1310-73-2	0.00007%
Magnesium silicate hydrate	14807-96-6	<0.00001%
Etc…..		
Total		**~100%**

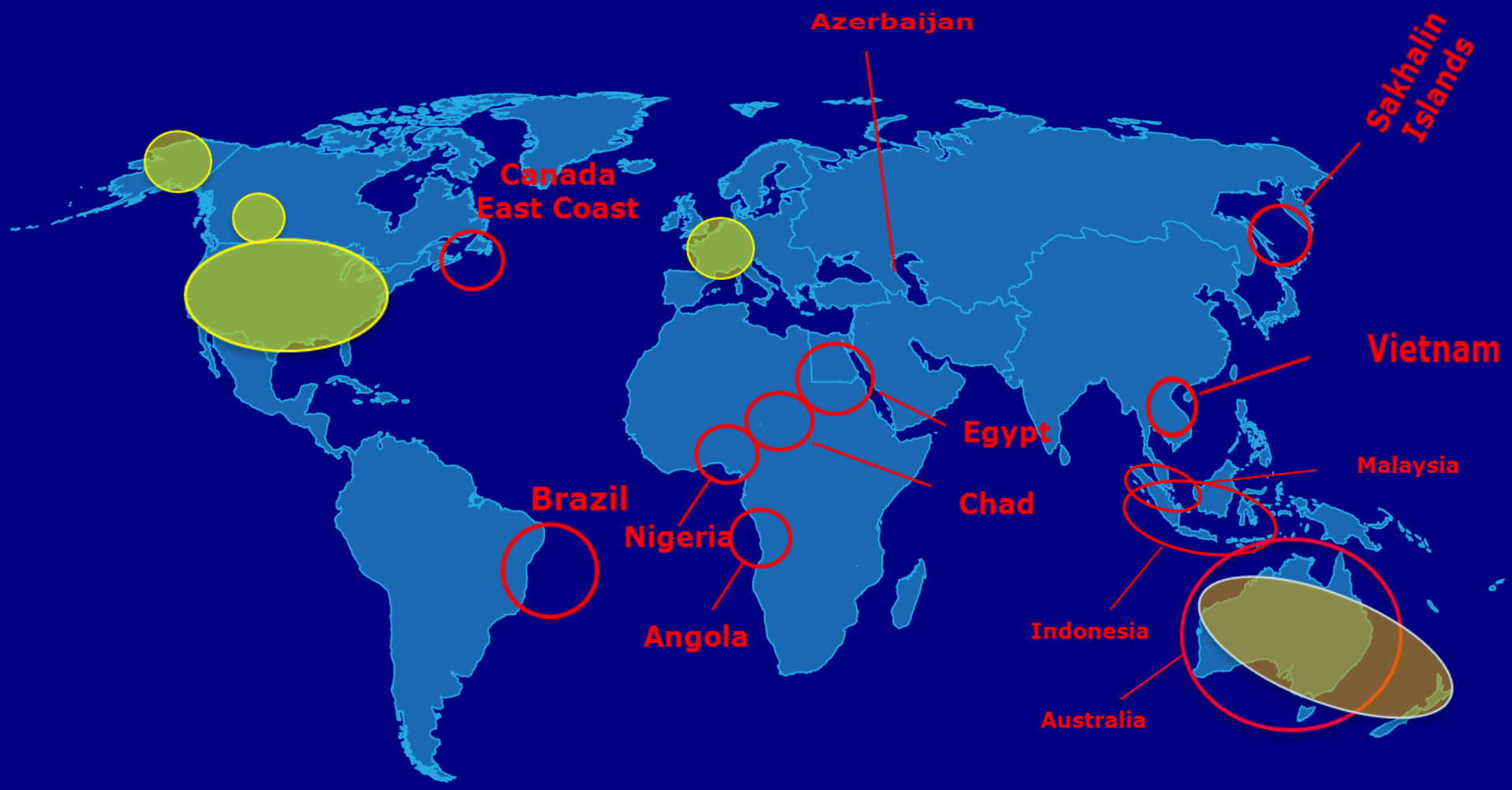
Myth or Reality?

“Your chemicals are secret or unregulated”



Myth or Reality?

“Your chemicals are secret or unregulated”



Myth or Reality? "Your chemical are dangerous"

- Gelling agents – Guar, sourced from food industry
- Clay control – KCl, choline chloride sourced from food agricultural and industry
- Buffers – potassium carbonate, calcium peroxide, calcium hydroxide, potassium hydroxide, medical, agriculture and food industry
- Friction reducers – Water treatment facilities
- Surfactants – household cleaning and personnel grooming
- Breakers – enzyme specific to breakdown only guar molecules

So what is “green” chemistry?

- Properties of an “ideal green” candidate
  - Not regulated
  - Low aquatic toxicity
  - Good biodegradation
  - Low bioaccumulation potential
  - Not toxic to humans and animals
    - Acute
    - Chronic
  - No handling issues
    - Low flammability
    - Not reactive

SPE 133517 (2010)
Product Evaluation – ”end points”

Environmental	Human Health	Physical hazards
Aquatic toxicity	Mammalian toxicity	Explosive
Bioaccumulation	Irritation/corrosion	Flammability
Biodegradation	Carcinogenicity	Oxidizer
Priority pollutants [1]	Genetic toxicity	Corrosive
VOC content [1]	Reproductive and developmental toxicity	

Globally Harmonized System of Classification and Labeling of Chemicals (GHS)

1 *EPA List Based*

Product Evaluation Score Example

Acute Aquatic Toxicity

Scoring	0	1	2	3
Exposure route	GHS Category 4	GHS Category 3	GHS Category 2	GHS Category 1
Oral (mg/kg bodyweight)	>300	>50 and ≤ 300	>5 and ≤ 50	≤ 5
Dermal (mg/kg bodyweight)	> 1000	>200 and ≤ 1000	>50 and ≤ 200	≤ 50
Inhalation-gases (ppmV)	>2500	>500 and ≤ 2500	>100 and ≤ 500	≤ 100
Inhalation-vapors (mg/l)	>10.0	>2.0 and ≤ 10.0	>0.5 and ≤ 2.0	≤ 0.5
Inhalation-dusts and mists (mg/l)	>1.0	>0.5 and ≤ 1.0	>0.05 and ≤ 0.5	≤ 0.05

"Hazard x Exposure = Risk"

Acute toxicity values are expressed as LD50 (oral, dermal) or LC50 (inhalation)

Chemical Evaluation Process Review* (CEPR)

- Objectives
  - What it is
  - What it's not
- Four Core elements
  - Highly discouraged substances
  - OSPAR HMCS pre-screen prediction tool
  - Regulatory impact assessment
  - Hazard assessment
- Confidentiality issues?

*SPE159690 (2012)

Highly Discouraged Substances

The following substances are **HIGHLY DISCOURAGED** from being intentionally added, at any concentration, fluid or chemical products

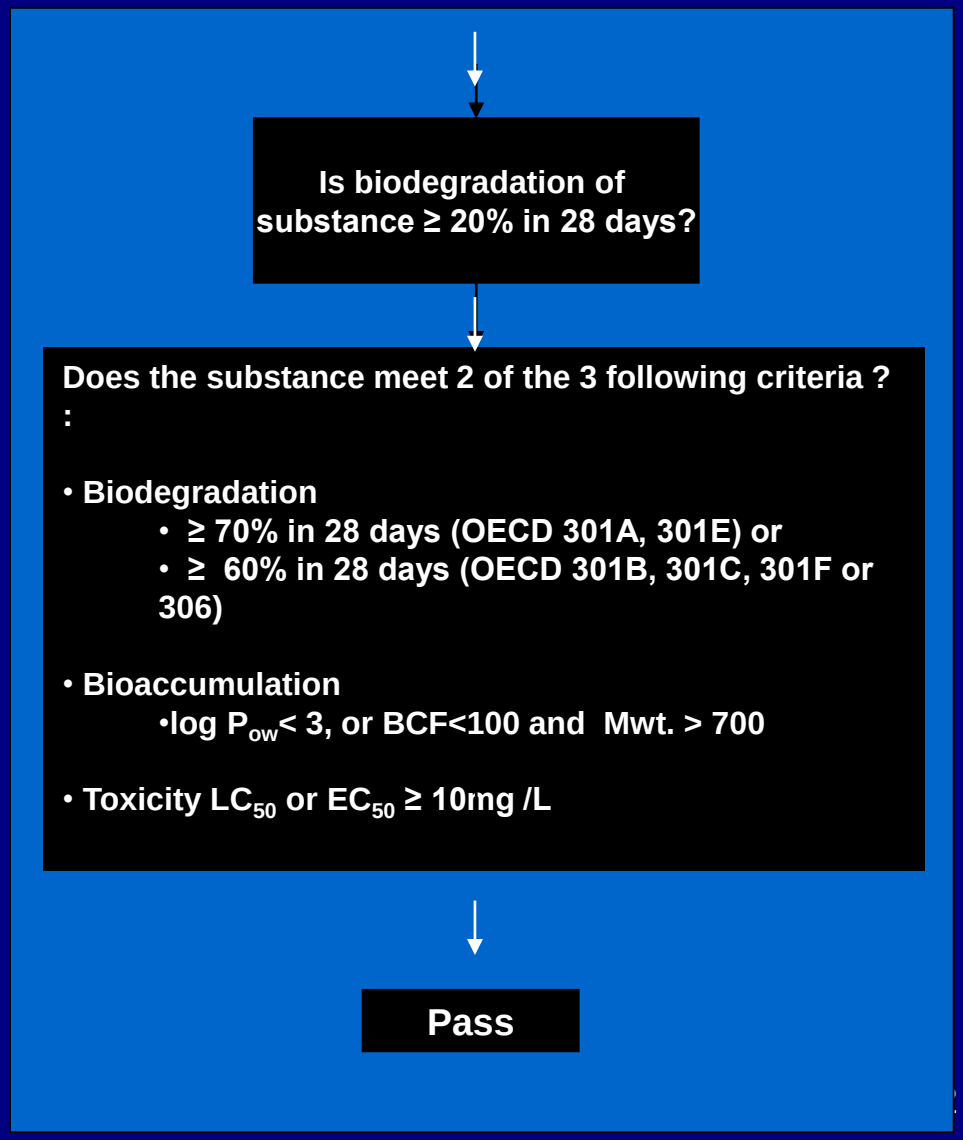
United Nations Environment Programme Persistent Organic Pollutants	
Substance	CASRN
ALDRIN	309-00-2
CHLORDANE	57-74-9
DDT	50-29-3
DIELDRIN	60-57-1
DIOXINS and FURANS	various
ENDRIN	72-20-8
HEXACHLOROBENZENE	118-74-1
HEPTACHLOR	76-44-8
MIREX	2385-85-5
POLYCHLORINATED BIPHENYLS	1336-36-3
TOXAPHENE	8001-35-2

EPA Priority Persistent Bioaccumulative & Toxic Chemicals	
Substance	CASRN
ALDRIN	309-00-2
ALKYL-LEAD compounds	various
BENZO[a]PYRENE	50-32-8
CHLORDANE	57-74-9
DIELDRIN	60-57-1
DIOXINS and FURANS	various
DDT and metabolites DDD & DDE	various
HEXACHLROBENZENE	118-74-1
MERCURY elemental and compounds	various
MIREX	2385-85-5
OCTACHLOROSTYRENE	29082-74-4
POLYCHLORINATED BIPHENYLS	1336-36-3
TOXAPHENE	8001-35-2

Table 3–GHS/CLP HAZARD PHRASES ASSOCIATED WITH CARCINOGEN, MUTAGEN, and REPRODUCTIVE TOXINS	
H340	May cause genetic defects
H341	Suspected of causing Genetic Defects
H350	May cause cancer
H351	Suspected of causing cancer
H360	May damage fertility or the unborn child
H361	Suspected of damaging fertility or the unborn child

OSPAR Pre-screen Prediction

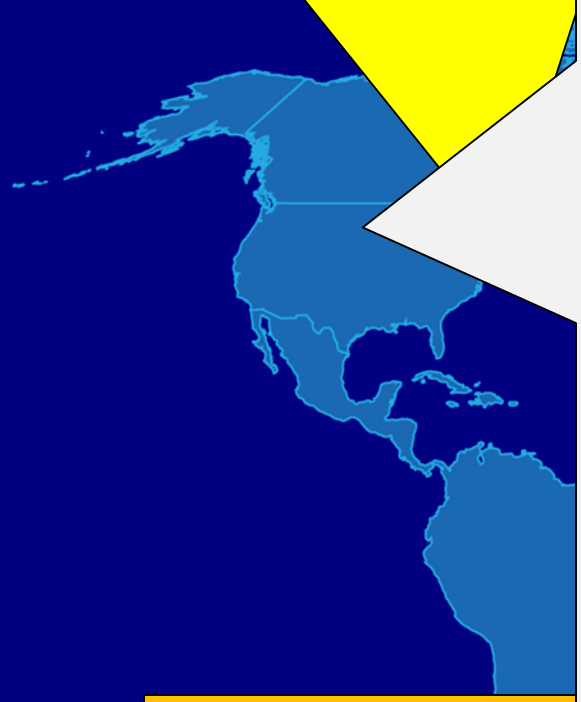
- Three key endpoints
  - Biodegradation
  - Bioaccumulation
  - Aquatic toxicity
- Not a definitive assessment
  - Strict data requirements for regulatory submittal
- Professional judgment
  - Multiple study values
  - Non-standard biodeg methods and species



Regulatory Impact Assessment

"Globally Applicable"

- International Agency Research on Cancer
- UN Environmental



- Environmental Canada
  - Toxic Substances List Schedule 1
  - Acts & Regulations Priority Substances List
- USDOT
  - Marine Pollutants
  - Environmental Hazardous Chemicals
- National Toxicology Program – Carcinogens
- USEPA
  - Safe Drinking Water Act – MCL
  - Clean Water Act Priority Pollutants
  - Hazardous Air Pollutants (HAP)
  - Volatile Organic Compounds (VOC)
- EPCRA
  - Section 302 Extremely Hazardous Substances
  - Section 313 Toxic Chemicals
- USFDA Generally Regarded As Safe (GRAS)

- Australia Air To
- Australian Drin
- Australia Natio
- ERMA New Zealand Reassessment Priority List

Chemical Hazard Evaluation

- Quantitative assessment
- Patterned after GHS
- Relevant endpoints
  - Specific scoring criteria
- Weighted scoring
  - Percent composition
  - Scaled to hazard severity
- Three-level assessment
  - Identify highest hazard category
  - Substance comparison
  - Product comparison

Toxicological
Acute mammalian toxicity
Carcinogenicity
Mutagenicity
Reproductive/developmental toxicity (DART)
Eye and Skin Irritation/Corrosion

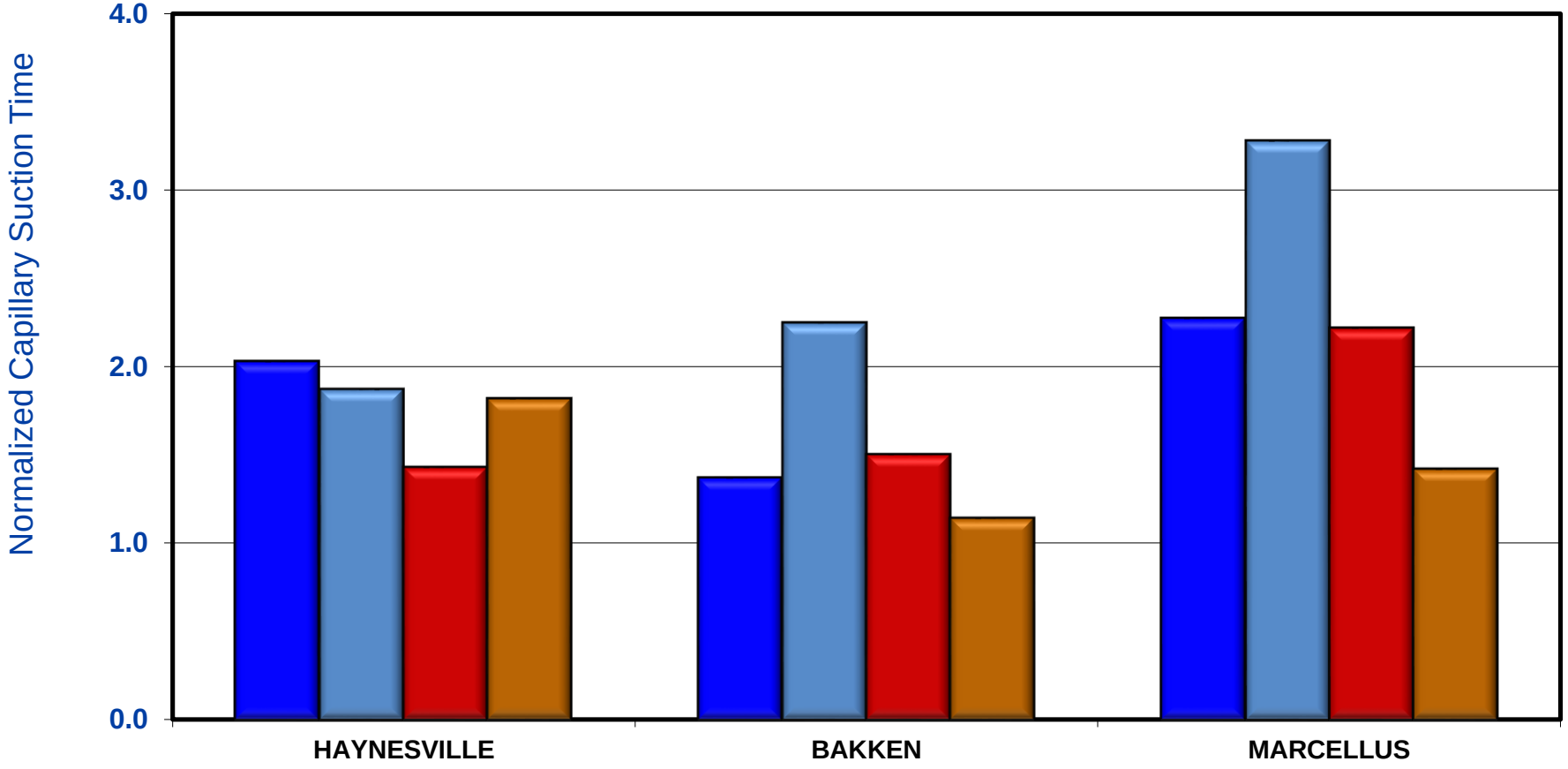
Physical
Explosive
Flammable
Oxidizing
Metal Corrosive

Environmental
Acute aquatic toxicity
Bioaccumulation
Biodegradation

CEPR Results Clay Stabilizer

CEPR Sections	Results
Discouraged Substances	✓
22 Regulatory Lists	1
OSPAR Prescreen Prediction	Pass
Chemical Hazard Score (maximum 100)	0

Clay Control Performance



CEPR Results Surfactant A

CEPR Sections	Results
Discouraged Substances	✓
22 Regulatory Lists	9
OSPAR Prescreen Prediction	Provisional Fail
Chemical Hazard Score (maximum 100)	10

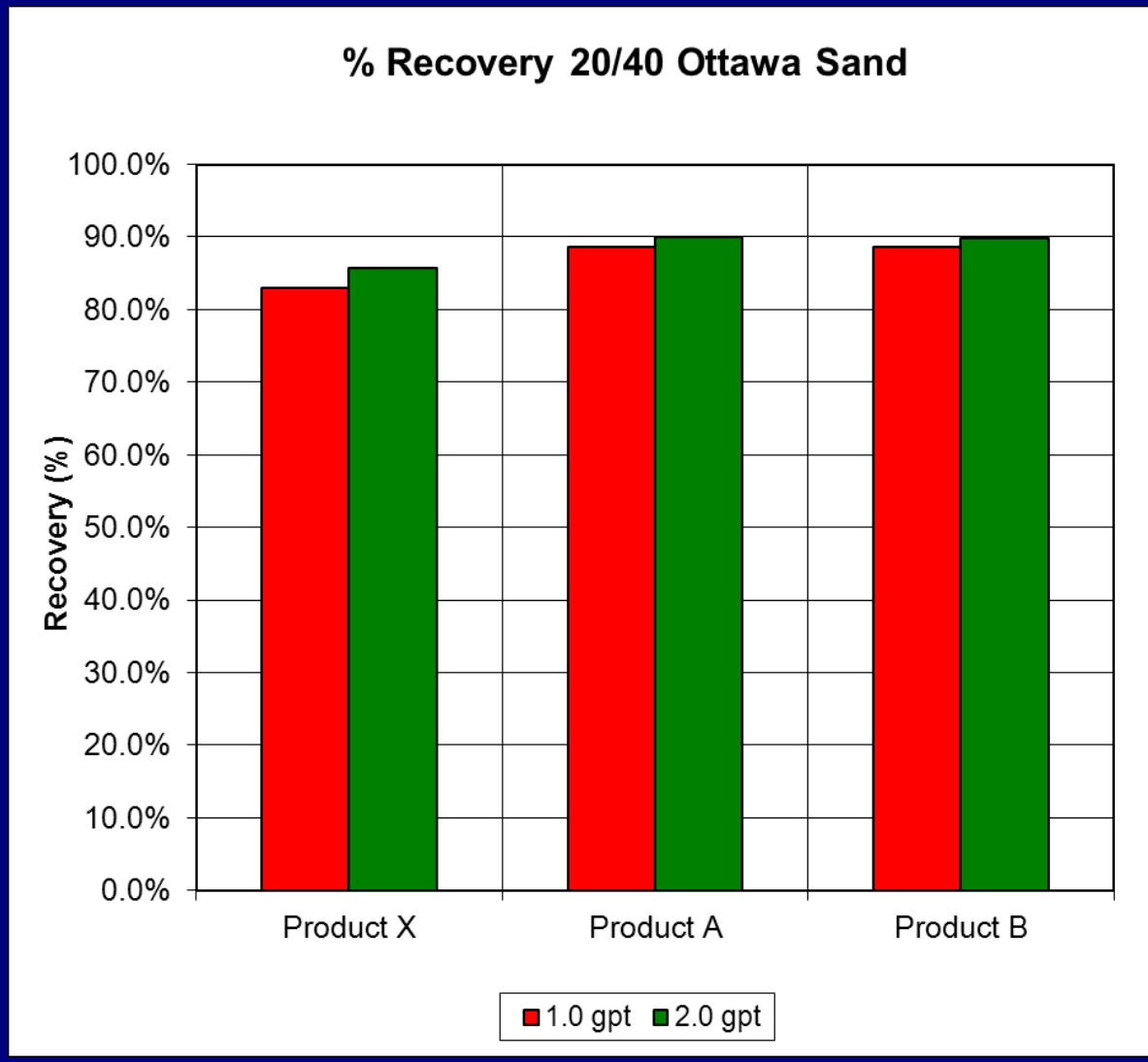
CEPR Results Surfactant B

CEPR Sections	Results
Discouraged Substances	✔
22 Regulatory Lists	2
OSPAR Prescreen Prediction	Provisional Fail
Chemical Hazard Score (maximum 100)	4

Surfactant Products Performance

Surfactant A & B

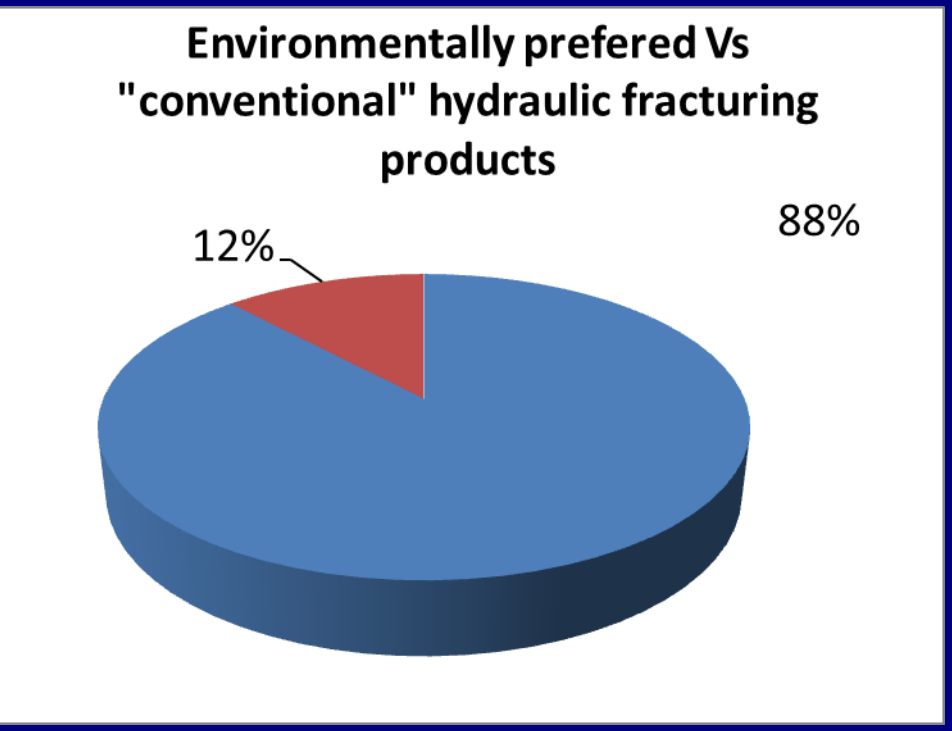
- Proprietary non-fluoro surfactant
- Biodegradable and environmentally safe
  - EGMBE
- Surfactant B MeOH

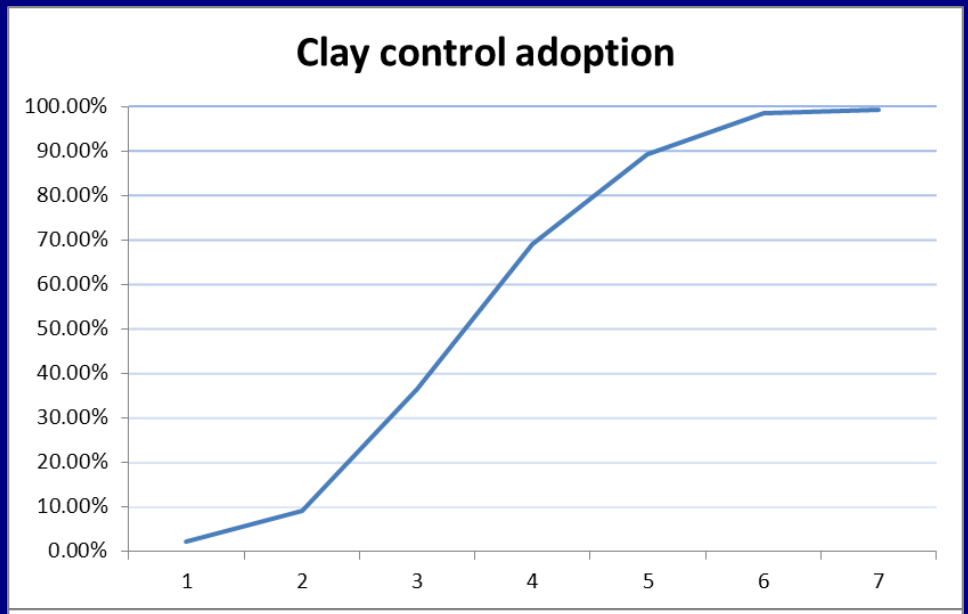


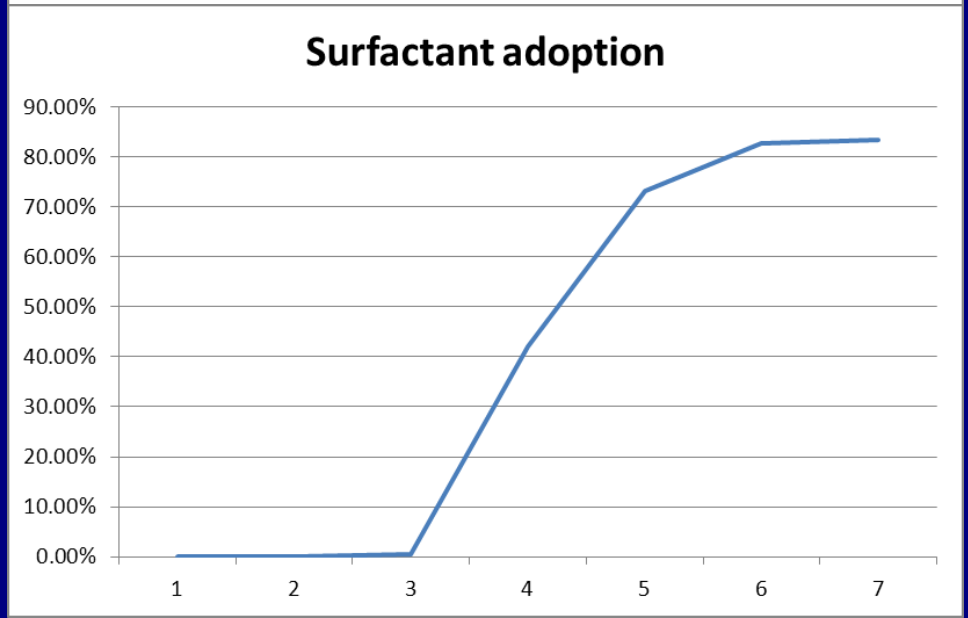
CEPR Results 15% Acetic Acid

CEPR Sections	Results
Discouraged Substances	✓
22 Regulatory Lists	2
OSPAR Prescreen Prediction	Pass
Chemical Hazard Score (maximum 100)	9 (0)

US Land Industry Adoption

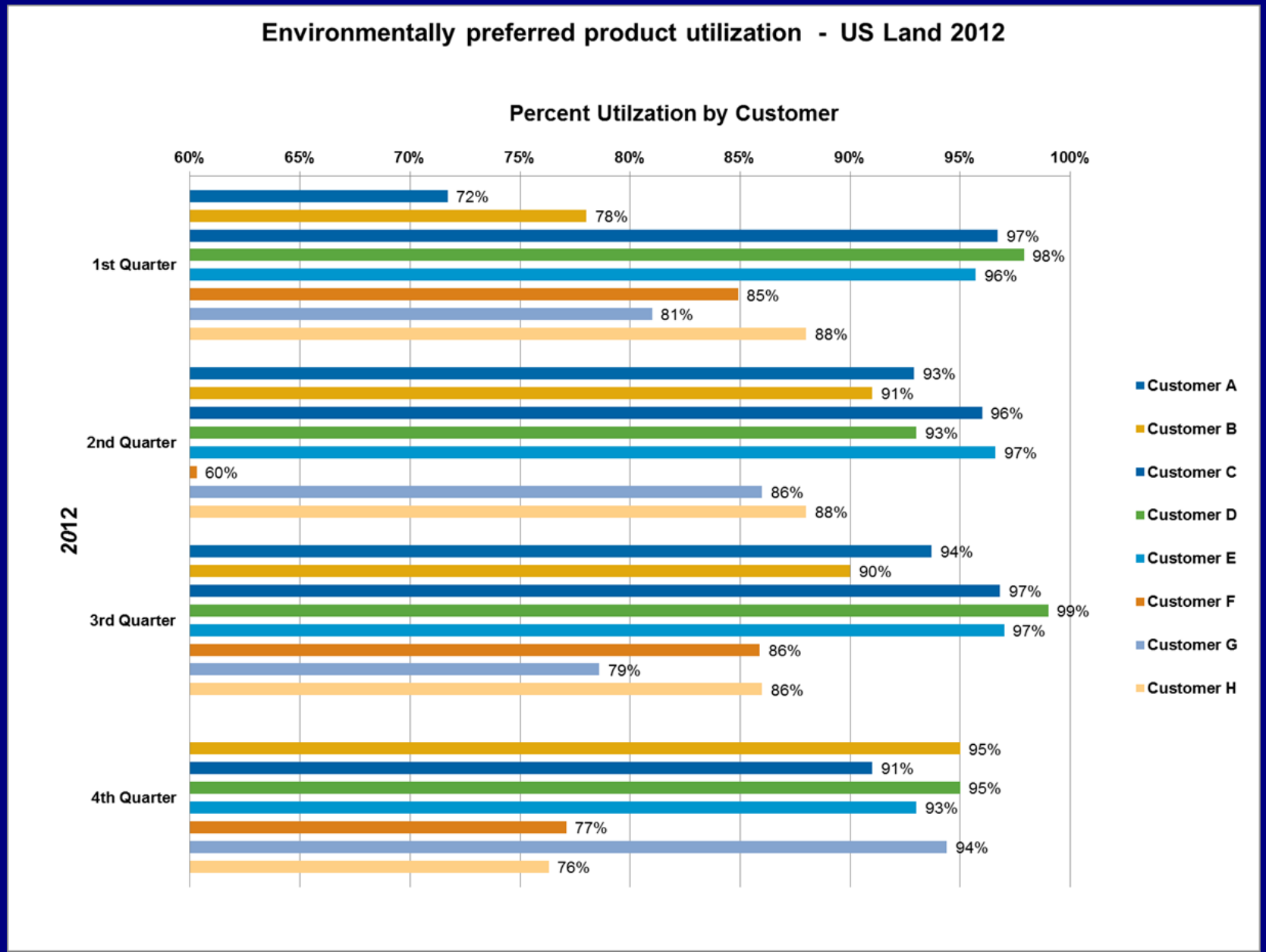




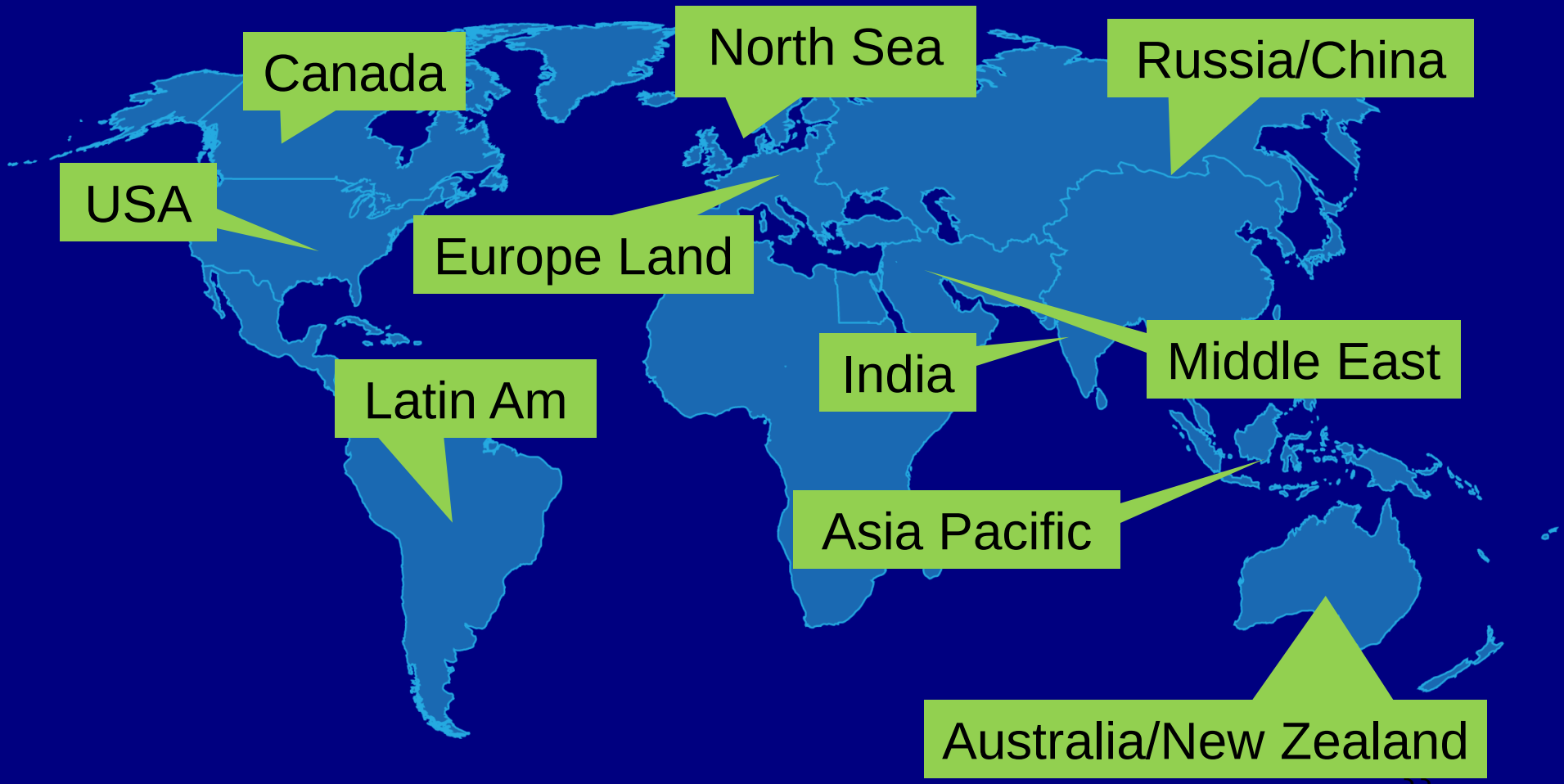


SPE 147534 Oct 2011
SPE 152068 Feb 2012

US Land Statistics



Global Expansion



Summary – Key to Future Success "Myths or Reality"

- Engage and Educate
- Ensure wellbore isolation
- Increase industry integrity
- Product development
- Equipment development
- Maintain technical focus

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