ZetaPro™
Enhanced Conductivity, Fines Control, Increased Production
What is ZetaPro™?

• New and unique patent pending chemical solution
  (Inner Salt of Very low Molecular weight Polymer that when added to aqueous solutions coats rapidly any metal oxide or anionic substrate like proppant, sand or coal)
• Enhances conductivity of proppant pack
• Minimizes fines migration
• Enhances fluid load recovery
• Enhances production and reduces water cut
• CaCO$_3$ Scale prevention
• Changes the zeta potential of solid surfaces
• Alters the Zeta Potential to optimum range
• Provides a strengthened attraction between the particles to optimally align proppant, sand particles or coal fines
Zeta Potential Theory

Zeta potential is defined as the electrokinetic potential between a surface of a particle and the bulk phase of the suspending liquid. It is typically used to measure colloidal systems.

- Zeta potential is a function of, or can be modified by:
  - Surface charge on the solid surface or particle
  - Surfactants that adsorb on the particle
  - Nature and composition of the surrounding medium including brine content.

- High zeta potential of > absolute value of 20mv, system stays dispersed
- Lower zeta potential, solids coagulate or flocculate
Zeta Potential of Silica and Coal with ZetaPro™

- Zeta Potential in the range of -20 and +20 mV is sufficient to aggregate particles, thereby stopping fines migration into and through the proppant pack.

- Optimal alignment and attraction of the particles to each other enhances conductivity and control of fine migration.
How ZetaPro™ Works

- Alters the zeta potential of solid surfaces to the optimum range (between -20 & +20 mV)
- Creates an uneven or random charge distribution on the surface of the solid particles.
  - Locations with high attraction (Van der Waals and electrostatic)
  - Locations with high electrostatic repulsion

Untreated

Untreated

Treated

Agglomerated material with high conductivity that stays in the formation
R&D Testing

- Zeta Potential
- Expansion of sand packs
- Conductivity through sand packs
- Gas rates core testing
- Load recovery core testing
- Effect of overtreatment
- Fine migration
- Scale treatment
Sand Packs Illustrate Effect of ZetaPro™
Effect of ZetaPro™ on Conductivity of 20/40 mesh Frac Sand

+40% improvement over untreated sand

ZetaPro™ at 6 gal/1000 lbs sand
Effect of ZetaPro™ on Conductivity of 20/40 mesh Frac Sand

At concentration of ZetaPro™ greater than 6 gal/1000 lb sand no further increase in flow rate was observed through the 20/40 sand column.
Effect of ZetaPro™ on Long-term Conductivity of Frac Sand

2 lb/ft² 20/40 Frac Sand, ZetaPro® at 6 gal/1000 lbs sand @ 150°F in 2% KCl between Ohio Sandstone, 50 hours

- untreated
- treated

Closure Stress (psi) vs. Conductivity (millidarcy-foot)

Conductivity: untreated (2770) vs. treated (3545) with an increase of +28%.

Graph showing the increase in conductivity for treated sand compared to untreated sand at different closure stresses.
Effect of ZetaPro™ on Long-term Conductivity of Lightweight Ceramic Proppant

2 lb/ft² 20/40 Lightweight Ceramic Proppant, ZetaPro™ at 6 gal/1000 lbs proppant @ 150ºF in 2% KCl between Ohio Sandstone. 50 hours

$$\text{Closure Stress (psi)}$$

$$\text{Conductivity (millidarcy-foot)}$$

untreated
treated

$$\{+48\%\}$$
Core Flow Testing

Improved Gas Rates with ZetaPro™

- Initial Permeability to N₂: 54 mD
- Overburden Pressure: 1000 psi
- Temperature: 72°F
- ΔP across core: 10 psi

The graph compares the gas rate and cumulative gas production for treated and untreated sandstone samples. The data shows improved gas rates with ZetaPro™ treatment.
Core Flow Testing

Improved Load Recovery of injected fluids when using ZetaPro™

![Graph showing brine cumulative production for treated and untreated sandstone]

- **treated sandstone**
- **untreated sandstone**
No damage observed when sand pack was treated with 4 pore volumes of 2% KCl with more than 8 times the recommended ZetaPro™ loading.

No emulsions, no reduction in conductivity or expansion
Fines Migration: 2% Silica Flour in 20/40 mesh Sand Pack (12 lbs sand/gallon)

Significant Reduction of fine movement through the sand pack when treated with ZetaPro™

![Graph showing reduction in solid produced in effluents.

- Untreated: 5.0 grams/20 PV
- ZetaPro™ 3 gal/1000 lbs Sand: <0.1 grams/20 PV
- ZetaPro™ 6 gal/1000 lbs Sand: <0.1 grams/20 PV

}\+99%
Scale Prevention

Tubing Block Instrument – PMAC
Cationic and Anionic streams come together through a capillary to form scale. The instrument measures the differential pressure as the scale is formed.
Scale test Results using ZetaPro™

ZetaPro™ Composite; 75 C; 0 Back Pressure; 5.0 ml/min

- ZetaPro keeps the CaCO₃ dispersed and inhibits scale
- 250 ppm optimal dosage
ZetaPro™ Applications

- Fracturing fluid component as a normal “on-the-fly” additive to improve conductivity of a proppant pack
- Eliminate fines migration in the proppant pack, sand, or coal
- Increase fluid load recovery after fracturing
- Oil & Gas production enhancement with reduced water cut and sand production
- Surface sand control aid – convert fines to more easily removed larger particles
Effect of ZetaPro™ in coal

ZetaPro™ helps to restore aggregation of grounded coal

Coal in just Fresh water

Coal In 30 gal/Mgal of ZetaPro™
Production Enhancement – Sandstone Formations

- Over 30 wells treated to date, RRP and PCP wells in Romania
- Sand production reduced in all wells
- Water cut noticeably reduced in many of the wells
- Treatment life of greater than 1 year
- Pretreatments of wells to remove wellbore debris has been an important part of the success
ZetaPro™ applied as Squeeze

- ZetaPro is squeezed into formation
  - Typically 10% in water/2% KCl
  - Since only water dispersible, it must be kept agitated at the surface in the treatment brine
  - Keep wells shut in for more than 24 hours
  - Use annulus packer to ensure delivery
Field Data, PCP Wells

![Well 776 fluid analysis graph]

- Sand load (mg/litre) vs. Date
- Water cut (%) vs. Date
- ZetaPro Squeeze noted on graph
Field Data, PCP Wells

Well 804 fluid analysis

- Sandload (%)
- Watercut (%)

ZetaPro Squeeze

Themark Corporation
THE MARK OF EXCELLENCE
Field Data, RRP Wells

ZetaPro Squeezed into Formation
Field Data, RRP Wells

Petrom Well 134 Production Profile

ZetaPro Squeeze
Field Data, RRP Wells
Field Data, RRP Wells

Petrom Well 129 Production Profile

M³/day

2007/2008

ZetaPro Squeeze

129 #129 M³/d 129 BS&W % 129 Sand %
Surface Treatments – Sand fine Agglomeration

- 250 ppm treatment increased mean particle size by factor of 3
  - Sample 1 increased from 20 micron to 70 micron
  - Sample 2 increased from 10 micron to 35 micron
- Solids were mostly iron and carbonates
- Superior results expected on sand and more testing we are looking for additional testing sites
ZetaPro™ Summary

• Rigorous R&D testing confirmed:
  – Improved sand and proppant conductivity to gas and fluids
  – Reduced fine migration
  – No formation compatibility issues

• Field testing and use has confirmed:
  – Sand production is significantly reduced
  – Gas and Oil production is enhanced
  – Water cut is usually reduced
  – Sand fines and coal fines can be agglomerated into larger particles in surface equipment