

Multifunctional Nanocomposites for Oil and Gas

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ABSTRACT

Currently, wireline, mechanical, and hydraulic mechanisms are used to operate completion tools, and "dumb" materials are used in completion and stimulation operations. "smart" materials, or materials that automatically sense and respond to their environment, are enabled using nanotechnology and hierarchical design principles. These engineered "smart" materials offer potential for new tools and activation mechanisms by responding to changes in temperature, Ph, or fluid environment to provide an engineered response. Response can include shape change, dissolution/reaction, chemical release, and change in state (eg, fluid to solid). Limited applications have been developed in temperature-activated dissolvables, leachable tracer systems, and swellable packers. These, as well as emerging, more advanced materials and applications such as switchable sand control screens and targeted deliver of energy and force will be discussed in this presentation.

Keywords: nanocomposites, multifunctional materials, completion tools, materials for oil and gas, magnesium

1 INTRODUCTION

Currently, less than 35% of all known and proven oil and gas reserves are economically recoverable. In fact, the largest source of additional oil and gas over the next decade will not be new fields, but enhanced extraction from known oil and gas deposits. Each 1% increase in oil recovery amounts to over 25 billion barrels of oil. New technologies are needed to enhance completions, stimulation, and oil recovery by controlling crack network formation and pressure distributions during recovery operations. Development of smart, "switchable" materials-materials that have a response triggered by a change in local environment, can be enabling in managing formation and fracture conductivity in different reservoir lithologies.

Controlling structure and chemistry at the nanoscale is an enabling technology for high performance multifunctional, or "smart" materials. Nanomaterials have high surface area, so that interface or surface-area driven processes such as catalysis, reaction, or dissolution occur quickly, and can be controlled by controlling the surface or interfacial area by both particle size, and amount. By controlling multiple parameters, multifunctionality (eg

strength and dissolution rate) can be controlled with some independence to produce designer materials with a specific set of properties.

Powdermet and its subsidiaries, licensees, and spin-outs such as Terves Inc, has been working to exploit these capabilities by designing multifunctional materials over the last several decades. This has led to a portfolio of currently commercially available and emerging materials being used in aerospace and defense, and more recently oil and gas completion and stimulation applications.

Specific multifunctional materials that are currently in early commercial, or are emerging include; Tervalloy™ dissolvable high strength metals, LocProp™ triggerable sand control screens, ExoProp™, high strength expandable materials, AcoustiFlow™, acoustic enhancement agents.

2 LOCPROP™ PUMPABLE SAND SCREENS

Water injection wells used for secondary and tertiary oil recovery have a high failure rate, requiring frequent intervention or stimulation. The primary failure is a loss of injectability- leading to unacceptable increases in injection pressure and low flow rates. This is particularly cumbersome and costly in offshore wells, where the cost of intervention and workover to restimulate or clean up a well is excessive. A major cause is transfer of fines and sand between zones, and during completions. The problem is exasperated when thermal EOR techniques, such as Huff-n-puff or cyclic steam injection are used. Technology advancement is required to improve performance of single point injection wells, water injection wells, and thermal enhancement wells for offshore application.

Many formations being developed consist of unconsolidated or loosely consolidated sandstone. In these formations, high closure forces an use of high pressure gradients are not achievable. Current techniques for stabilizing these formations, including gravel packing with large proppant, injection of polymer adhesives have proven to be of limited success, or cause secondary issues that create additional problems. Using engineered multifunctional materials, Powdermet has developed a "pumpable screen" consisting of environmentally responsive coatings on the surface of pumpable powders (sand, ceramic beads) that can be easily pumped, and which then crosslinks and forms a rigid screen under the conditions encountered in unconsolidated water injection

wells. Previous materials have been primarily developed for higher temperature, or higher closure force applications (eg, procured epoxy's) to prevent flowback of proppants used in stimulation treatments, or are active materials that can set-up and plug the pipeline or during transport (eg, two part epoxy's).

As an alternative, Powdermet has developed a low temperature low pressure crosslinking coating that, when applied to particles, can create a free-flowing system that sets up and cures in mildly acidic conditions at temperatures around 60C. Specifically, LocProp is a low-temp, controlled curable thermoplastic-coated proppant that sets to form an in-situ sand control filter matrix. Designed to prevent proppant flow through in water injection wells, and flowback in production wells, this proppant extends fracture conductivity lifetime with reduction in fines generation and self-healing capability.

This activator free immobile proppant is frac-fluid and breaker compatible, and optimally performs in reservoir temperatures from 100-260F. This patent-pending product is an activated thermo-plastic coating that creeps to form good contact under mild pressure, and acts as a "living polymer", having an environmentally controlled tackiness and crosslinking ability. Typical product features include:

- Mesh size: 16/20 and 20/40
- Sphericity: 0.9
- Roundness: 0.9
- Absolute density: 2.7 g/cc
- Bulk density: 1.57 g/cc

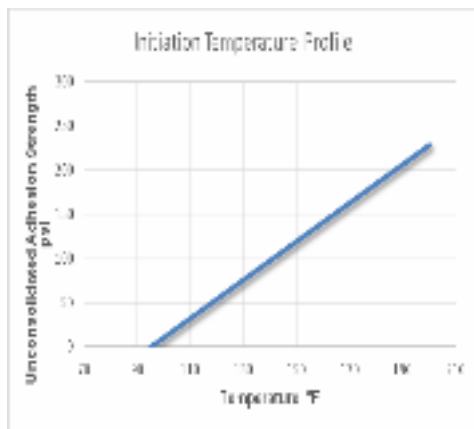


Figure 1: unconstrained cohesive strength as a function of thermal exposure for LocProp pumpable sand screens

3 TERVALLOY™ DISSOLVABLE METALS

In carbonate and shale reservoir lithography, the formations are fractured, or "stimulated" to improve flow. These tight formations have only become economic with the development of horizontal drilling and hydraulic fracturing technologies. However, even with stimulation, the formations must be constantly drilled and stimulated, as the wells typically lose 80% of their production in the first two years. This phenomena, along with the reduced price of oil, is placing increasing demands on the industry to reduce costs and improve efficiencies in drilling, completion, and stimulation operations.

The development of improved completion technologies, including sliding sleeve, open hole packers, and swellable packers has driven completion times and costs down dramatically over the last 10 years. This has resulted in a dramatic increase in stages fractured, from only a few in the early 2000's to more than 20 on average, and as many as 150 stages/well currently. One of the innovations driving down completion costs is the development of dissolvable materials that eliminate the need to recover or drill-out flow isolation stages.

Tervalloy is a high strength, nano-engineered magnesium composite that is engineered to degrade in a highly controlled and repeatable manner in completion fluids (brines, slickwater, completion fluid). Use of these dissolvable materials can reduce completion costs by several hundred thousand dollars or more for each well, by eliminating the need for coiled tubing workover rigs, and reducing completion time and fluid use by 30-50% or more.

Terves Inc licensed Powdermet technology to create a patent pending reactive magnesium metal matrix composite (MMC) that exhibits controlled dissolution rates. These cast and extruded magnesium composites have shown tensile yield strengths as high as 48ksi with ductilities over 5%. Previous high strength magnesium alloys are based on rare earth additions and rapidly solidified alloys, however these formulations are extremely costly, and do not exhibit the desired controllable dissolution rates. Terves has demonstrated new alloys that have the desired strength and dissolution properties using the addition of fillers through ultrasonic casting and semi-solid mixing. 15 initial active metal formulations were extruded at an 8:1 extrusion ratio at different temperatures and soak times.

Properties of the engineered degradable alloys ranged from 20ksi to 45.6ksi in yield with ultimate tensile strengths from 36ksi to 52.5ksi. Elongation of samples ranged from 5-21% however typical elongation was 5-12%. Dissolution were controlled over a wide range to meet targeted dissolution for common completion brines between 30 and 80 mg/cm²/hr.

Commercial alloys now offered include TA-50x and TA-100x. TA100x has been tested using ASTM E8-

13a for tensile testing and resulted in the following mechanical properties (average results recorded):

Ultimate Tensile Strength: 46.5 ksi
 Yield Strength (0.2% offset): 32.5 ksi
 Elongation to failure: 12%

This material was also tested for dissolution rate in a 3% KCl solution at 90°C to show that the rate at which extruded product dissolves is consistent with client specifications. These tests showed that the dissolution rate was constant at 50-60 mg/cm²*hr or about 0.3 mm/hr.

Table 1. Tensile Results of Extruded Alloys

ID	UTS (ksi)	YS (ksi)	E %
TA-1	47.1	41.1	6.5
TA-2	45	34.4	2
TA-3	44.6	33.6	12
TA-4	44.5	34.5	8.5
TA-5	50.5	41.7	8.5
TA-6	21.9	21.5	0.5
TA-7	38.4	35.5	3.5
TA-8	40.4	25.9	14
TA-9	35.5	27.6	4.5

4 TERVALLOY ALLOYS FOR OFFSHORE

As an illustration of the tailorability of nanocomposite materials, Terves was requested to develop an alloy having controlled dissolution in calcium containing brines. Calcium in the brine was found to inhibit the controlled corrosion of active magnesium composites, leading to passivation of standard materials. In response, the galvanic activity was studied extensively, and new alloys were designed to counteract the passivation effect of calcium (CaCl₂, CaBr₂) to enable use in offshore applications.

Four variations of active corrosion catalysts were varied in a magnesium matrix for a total of nine developmental composites. Each of the nine composites were tested in 3% KCl and 8.9 lb/gal CaCl₂ at 90°C for 6 hours. The dissolution results are shown below in Figure 1, demonstrating three potential alloys chemistries that dissolve in both KCl and CaCl₂ brines, TA-6, TA-7 and TA-9.

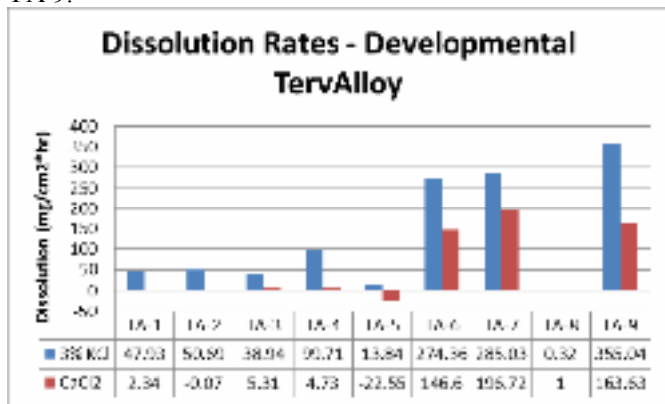


Figure 1. Dissolution Rates of Developmental Alloys

Each of the nine formulations were also sent for third party tensile testing. These results are listed in Table 1 below.

5 EMERGING DEVELOPMENTS

Powdermet is currently developing active pumpable materials that can respond to the reservoir environment to generate heat, hydrogen, sound, and force. These “controlled deposition of energy” materials are engineered nanocomposites (how fast, and with what response) that can include control coatings (when activated). One patent pending material is designed to act as a “mini-jack”, applying a large force to extend fracture networks. When added into an engineering polymer resin, this system can be used to provide formation-activated tools capable of applying tens of thousands of pounds of force to control the development of fracture networks- both initiation and extension of fractures.

Additionally, patent-pending zero-valent metal nanocomposites have been engineered and demonstrated to provide free hydrogen, as well as thermal energy *in-situ* in relatively low cost systems. Terves has developed a series of RESPONSE™ coatings that act as thermal or chemical “switches”, controlling timing of the activation of these, as well as dissolution actions of responsive materials.

6 SUMMARY

Nanotechnology and advanced materials processing has been used to develop materials that provide very controlled, engineered response to downhole environments. Commercially or field-trial level available materials provide controlled agglomeration or degradation to control flow with automated response. Emerging materials provide targeted delivery of energy and chemicals, including force, thermal energy, and chemical action (reducing, oxidizing, etc.)