Engineered Response Materials for Oil and Gas

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ABSTRACT

Currently, wireline, mechnical, 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, multifuctional 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 ovet the next decade will not be new fields, but enhanced extraction from known oil and gas deposits. Each 1% inrease 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 reovery 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 multifuctional, 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 commerial, 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 re-stimulate 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, Terves has developed a low temperature low pressure crosslinking coating that, when applied to particles, can create a free-flowing system that sts 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 hermos-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

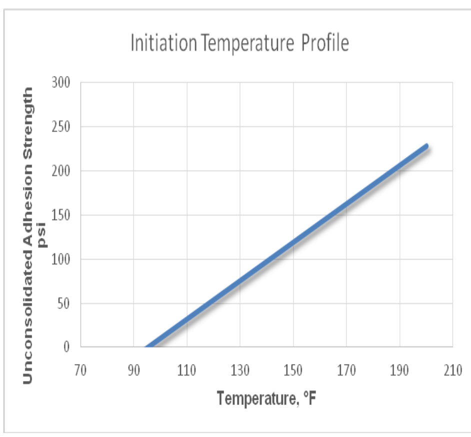

Figure 1: unconstrained cohesive strength as a function of thermal exposue for LocProp pumpable sand screens

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 facturing technologies. However, even with stimulation, the formations must be constantly drilled and stimulated, as the wells typicaly loose 80% of their production in the first two years. This pheomena, 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 mproved 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 recuce completion costs be several hundred thousand dolaars 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 yeild 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 involve the processing of highly flammable/explosive magnesium alloy powders while providing limited ductility. 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/cm^2*hr or about 0.3 mm/hr.

Newly developed Tervalloy alloys include Tervalloy-HD (high ductility), offering 16-20% elongation to failure, and Tervalloy-MMC, high hardness erosion resistant dissolvable materials suitable for use in seats and grips.

4 TERVALLOY ALLOYS FOR OFFSHORE

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

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 $CaCl_2$ 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 $CaCl_2$ brines, TA-6, TA-7 and TA-9.

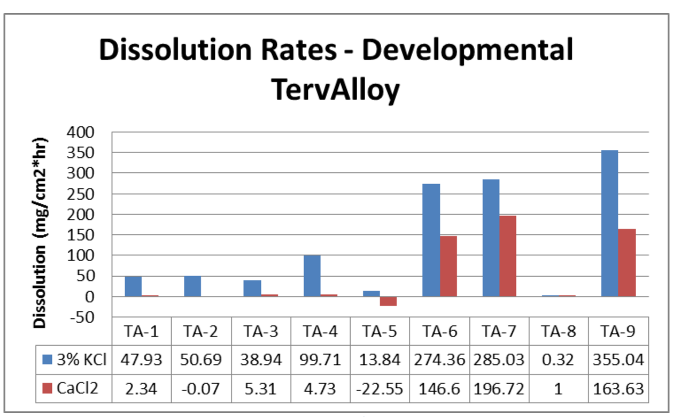

Figure 1. Dissolution Rates of Developmental Alloys

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

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

5 EXALON™ EXPANDABLE STRUCTURAL MATERIALS AND XOPROP™ EXPANDABLE PROPPANTS

Terves has recently introduced Exalon™ expandable polymers that enablke the in-situ controlled delivery of force. These patent-pending materials differ from conventional swellable polymers in that they have GPa modulus values (2-40GPa range), and activate quickly due to the use of specific engineered phase changes. Typcal expansions of 15-40% are ontained, along with the ability to deliver 3-15,000 psig force. Targeted applications include self-doploying centralizers, refrac sleeves, and loss control sleeves.

A pumpable version of Exalon materials, tradenamed XOProp™, is being developed for extending natural fractures and counteracting closure forces in tight formations, reducing rate of decline and enhancing oil recovery by over 20% in a typicl shale formation.

6: RESPONSE™ COATINGS AND ELEMENTS

To extend the application of engineered response materials, and allow for controlled activiation, Terves has developed a series of RESPONSE™ coatings that act as thermal or chemical "switches", controlling timing of the activiation of Tervalloy and Exalon materials. Resoonse coatings have been developed in the following formulations:

- Response-T **T**ime delay
- Response-P **P**ermanent
- Response-TR **T**empe**ra**ture trigger
- Response-C **C**hemical trigger
- Response Element- dissolvable elastomer

Response coatings and materials alloy for interventionless activiation by either formation response, or via pumping.

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Response-T time delay coatings delay dissolution or reaction by 4-24 hours, enabling acid pumping or preventing reaction while running a tool. Response-P Permanent coatings are used to prevent reaction from a coated surface, for example on a sealing surface to force dissolution from the bore only in a bridge plug.

Response-TR temperature trigger coatings prevent reation until a specified temperature is achieved, after which the coatings become permeable and dissolution or other reactions occur. This can prevent reaction while pupming occurs, only starting dissolution or reactionm once formation temperatures are achieved, for example.

Response-C Chemical triggered coatings are activated by specific chemicals, such as chlorides, salts, amines, Ph, etc, that can allow activiation of the engineered response upon circulating or pumping a trigger. This allows reactions to be controlled and activiated through pumping.

Response-Elements are dissolvable elastomer composites that are combined with various response activiating mechanisms, with the baseline Response elements being time and temperature triggered and designed for low temperature (50-60C) operation. These elastomers eliminate resigual sealing materials for bridge plugs.

7 SUMMARY

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