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Tech Watch: Covalently bound selenium has potential for hydraulically fractured wells

New coating could provide environmentally friendly alternative to biocides.

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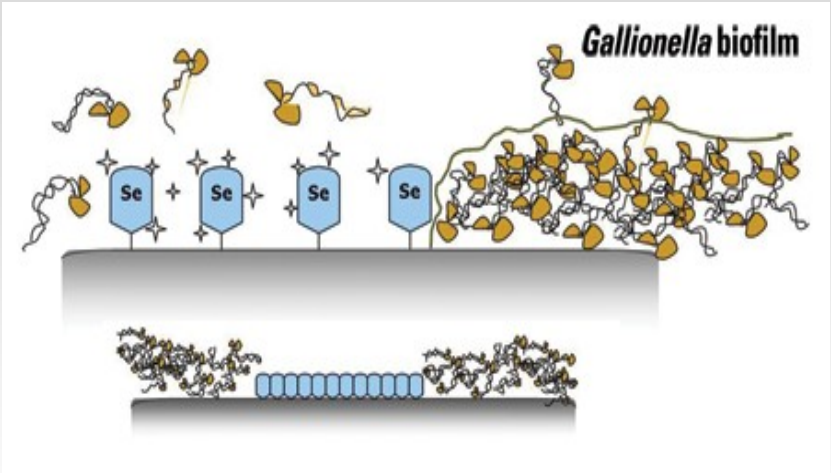
Hydraulic fracturing, a method pioneered by Halliburton, involves sending high-pressure fluid containing sand through a well bore deep in an oil/gas-bearing shale formation to cause fractures. This is followed by injection of proppants typically composed of ceramic beads, sand, or other materials that are lodged inside the shale deposit to keep the fracture open. The fractured shale allows free flow of natural gas and oil into the well bore.



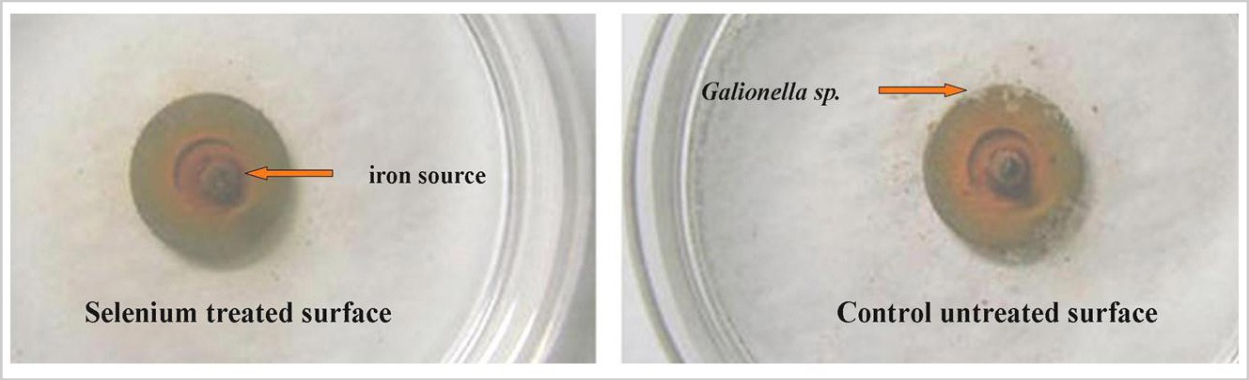
Se is attached permanently to a surface using patented processes and yet continues to be biologically active. Upon contact with an Se-treated surface, the reactive oxygen released by Se kills bacteria, thereby preventing biofilm formation. (Images courtesy of Poseidon Sciences Group).

Anaerobic iron and sulfate-degrading bacteria rapidly proliferate in the fracturing fluids, causing corrosion of the pipes and clogging of the proppants. Biocides typically are included in the fracturing fluid to inhibit bacterial growth. However, over the years, there has been overwhelming public concern about the environmental impact associated with hydraulic fracturing and, in particular, the possible contamination of aquifers and nearby streams by biocides and other chemicals present in the fracturing fluid.

Considering the economic and strategic value of extracting US oil and gas reserves, an alternative technology needs to be developed as soon as possible to alleviate this environmental concern. A biocidal approach still is the best method to keep iron bacteria (*Gallionella*) and sulfate-reducing bacteria (*Desulfovibrio*) from clogging the wells and corroding the pipes. However, biocidal material should be environmentally friendly and must not freely diffuse away from the well bore.

Going green

A green technology originally was developed in the Texas Tech University (TTU) system by Dr. Ted Reid and Dr. Julian Spallholz, co-chief scientists of Selenium Ltd. and TTU professors. This proprietary technology, called SeLECT, already achieved FDA 510(k) approval for two separate Class II medical devices, and the first coated antimicrobial orthodontic products were introduced to the market in 2009 to prevent dental plaques. Selenium (Se) is a nutritional supplement typically used as a nutraceutical at a daily dose of 200 to 600 micrograms/ day. Equally important, selenium also possesses antibacterial properties through the release of reactive oxygen species such as hydrogen peroxide. When applied to industrial applications, Selenium Ltd.'s patented SeLECT technology is marketed under the SeGuard brand. Because selenium is bound permanently to the coating and yet remains bioactive, it does not have to leave the surface to exert its antimicrobial action. Thus, any leaching of SeGuard to the environment is prevented.

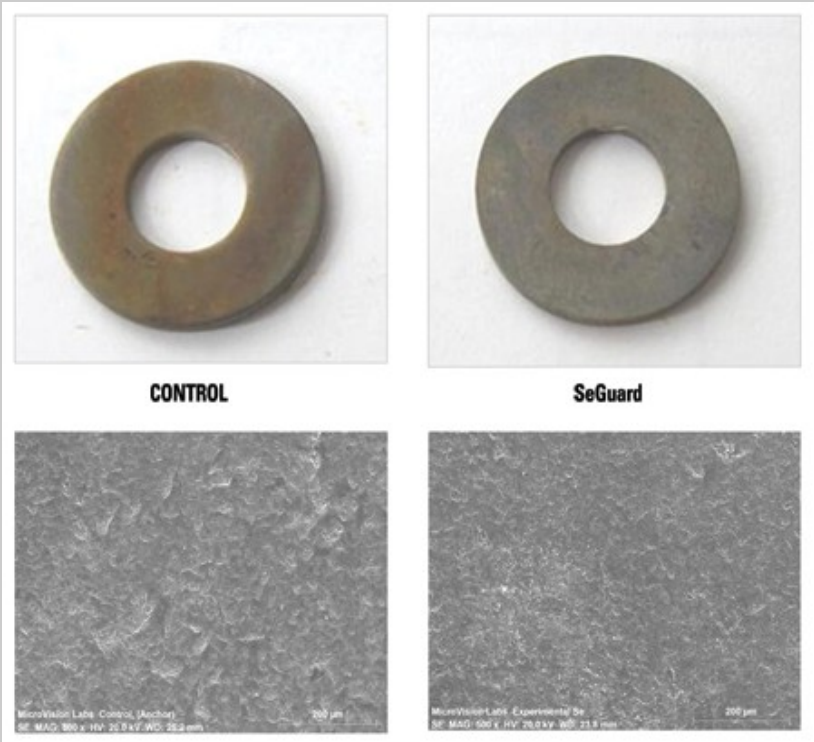


The effect of exposure of SeGuard-treated and control washers on an overgrowth of Gallionella from an iron source at the center of the washer are compared.

Poseidon Sciences and Selenium Ltd. recently entered into a strategic partnership to develop coatings containing covalently bound Se. Compared to copper or silver that typically are used in free association within the coating matrix, Se is attached permanently to a surface using patented processes and yet continues to be biologically active. Upon contact with an Se-treated surface, the reactive oxygen released by Se kills the bacteria, thereby preventing biofilm formation. This killing effect is short-range and does not extend far from the coated surface.

Se, frac fluid

Although the concept has been proven for orthodontics applications, it has yet to be demonstrated as a useful approach against bacteria associated with fluids from hydraulic fracturing operations. The culture of the iron bacteria *Gallionella sp* was undertaken at Poseidon Sciences' facilities, making it possible to develop a bioassay to evaluate the performance of SeGuard. In this method, titanium washers were coated with Se and placed in a petri dish. Titanium typically is used in medical applications because of its resistance to corrosion and was used in these studies as interim substrate to test this concept. In the middle of the open area of the washer was a piece of iron to serve as nutrient source for the added *Gallionella sp.* Controls consisted of titanium washers that were not treated with Se.



The effect of immersion of SeGuard-treated and control washers in a Gallionella-rich media on corrosion of surfaces is shown. SEM was conducted by Microvision Labs at 500 X magnification.

After immersion of the washers in a *Gallionella*-rich environment for nine days, the results showed that Se-treatment prevented the migration of Gallionella over the surface of the Se-treated washer.

A second experiment was conducted in which Se-treated and untreated washers were immersed in a *Gallionella*-rich culture for a period of 14 days at 86ºF (30°C) under anaerobic conditions. The results show that the control washers demonstrate the beginnings of corrosion compared to the Se-coated surfaces.

Future potential

Although preliminary in nature, these studies demonstrate the potential of catalytically active selenium as a biocidal alternative to conventional toxic biocides in the market today. With this validation of the biological actions of Se, a program now is in process to develop coatings technologies that would deposit selenium to iron surfaces and proppants. Se coatings could represent the next generation of non-leaching, environmentally friendly biocidal technology for the hydraulic fracturing industry in the near future.