Steel Corrosion Control in Highly Corrosive Wet Coal-Bed Methane Wells Using a Passive Iron/Sulphur Complex Layer Created Using Organic Sulphur Salts.

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Abstract

Water in some CBM wells (Mannville Coal Beds) can cause severe corrosion to steel parts below the water surface when containing high amounts of chlorides, acids or other corrosive components. Current corrosion inhibitor chemicals cannot handle water that can corrode through steel in 30 days or less. A new approach is to create an iron/sulphur passive layer on the steel to protect it. Creating this layer is done by adding a solid organic sulphur salt based on carbon disulphide that is water soluble and sinks in the well, evenly distributing its CS_2 *component to react with the steel to produce the passive layer. The layer protects all steel parts that corrode beneath the water surface without any* H_2S *generation of any kind. Laboratory studies have shown an estimated six fold reduction in iron loss from standard carbon steel when exposed to 30,000 ppm chloride solution with potential for a much greater steel lifespan.*

Introduction

The exploitation of coal bed methane in some of the coal formations in Alberta has brought significant challenges in terms of corrosion of steel parts in wet wells. These wells can contain brines with levels of chlorides over 30,000 ppm as well as carbon dioxide and other acid generating components. The use of standard corrosion inhibition chemicals, such as water insoluble quaternary amines, cannot slow corrosion down enough (average 40 days before coiled tubing failure) for the economic exploitation of gas from these long lasting, but slow flowing wells. A new approach is needed to achieve long term steel survival. Based on passive layer coatings using water soluble organic sulphur salts, the Corrxan Process has the potential to increase steel life span six fold or longer from current levels.

Passive Sulphur Coatings

Use of organic sulphur compounds to create corrosion resistant layers on iron and steel parts immersed in water have been studied for decades.[1,2,3,4,5] Even studies on the interaction of H_2S on steel revealed a passive coating/corrosion cycle where iron sulphide is plated on steel, creating a corrosion resistant layer, only to be restriped by the acidic H_2S and re-precipitated back on over and over again.[6] While potential for resistance to acid corrosion was clear, resistance to chloride corrosion which interacts with steel in an entirely different way was not so clear.

Chlorides absorb into steel surfaces, creating complex iron/chloride ions which are water soluble. Any coating that is used to stop this kind of corrosion must have the ability to stop the migration of chloride ions towards the steel. Quaternary amines adsorb onto the surface after the chlorides have absorbed, changing the charge on the steel from positive to negative. This is why the amines are only temporary, require continuous additions, and only slow, not stop, corrosion.

Organic sulphur salts act entirely differently. Once the chloride has ionized the iron in steel to make it soluble, the sulphur reacts quickly and directly with the iron ion to produce a water insoluble compound that immediately precipitates onto the steel surface. The organic sulphur salt also contains organic chains (isopropyl, butyl, amyl, etc) that produce a hydrophobic layer that pushes water and its corrosive components (acid and especially chlorides) away from the steel surfaces. Chlorides cannot diffuse through this layer for further attack on the steel.

Corrxan Chemicals has developed such an organic sulphur salt for use in wet gas wells with high chloride levels.

The Corrxan Process

There are a number of ways to introduce sulphide ions into water. It has been shown that H_2S in sour gas in pipelines and wells does form sulphide protective layers on the steel.[6] Using H_2S when it isn't in the gas in the first place is impractical and the solubility of H_2S in water is very low. A more effective way, in terms of a solid salt that dissolves in water, is to add sulphur using an organic sulphur salt, designated as CX131(patent pending). Interaction of CX131 solutions with steel holding tanks have shown to provide a high level of corrosion protection to the tanks. It is also a salt that is very susceptible to mechanical pelleting processes, making a solid, hard pellet (useful if adding additional solid or liquid chemicals for delivery into the well) that readily dissolves in water (useful for distribution of chemicals throughout a gas well).

CX131 is fully soluble in water, producing a pH of about 8.5 at a 1% solution. Unlike H_2S, CX131 can distribute a significantly higher concentration of sulphide into the gas well water and counteract some of the acidification of the water.

The Sulphide Coating

Experiments have shown that iron coatings reach 4 to 10 microns in thickness with H_2S supplying the sulphur.[6] Iron/CX131 coatings, with their organic chains, can create a passive barrier with fewer molecular layers. Due to the size of the molecules, however, the layer would still be in the 4 to 10 micron range. The organic chains push water and aqueous corrosive ions away from the steel surface, effectively reducing corrosion rate considerably. Figure 1 illustrates the molecular interactions of iron and CX131.

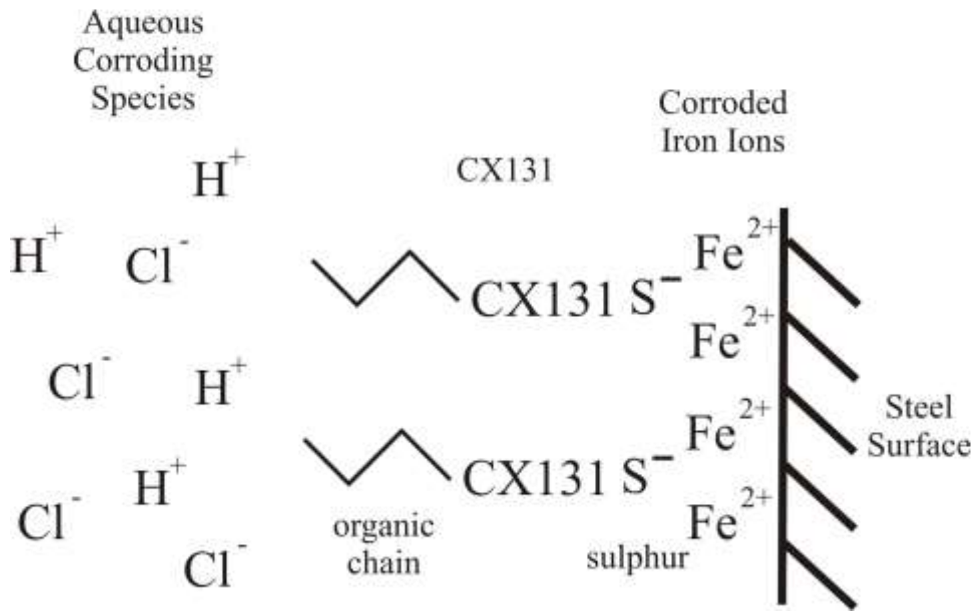

Figure 1. Representation of Iron/CX131 Layer on Steel

Iron/CX131 coatings are very stable molecules as well. Where the original CX131 salt will decompose in water environments over a four day period back to its original components, iron/CX131 coatings have been found to resist decomposition. In environments where high chloride levels can dissolve steel at a rate of approximately 0.15 mm/day at a high corrosion active site, iron/CX131 coatings were found to oxidize at a sixth of that rate and the oxidization would only involve removing the organic chains from the complex, leaving the iron/sulphur part intact on the steel surface. By continually adding CX131 to the matrix, the passive layer can be continually regenerated, increasing the lifespan of steel considerably more. Eventually, addition of CX131 would cease to be necessary.

Experimental Work

A number of experiments were undertaken to establish the ability of CX131 to protect steel from chloride corrosion.

Preliminary Coating Experiments

Two lengths of carbon steel pipe (two feet in length) were each placed into a 1000 mL graduated cylinder containing water prepared to be similar to high chloride well water (Table 1). The water level is set so the pipe has a two to three inch length above the water surface. In one of the cylinders, three 5 mm pellets of CX131 (0.5 grams each) were added. Every three days, the cylinder water was replaced and another 3 pellets of CX131 were added to the one cylinder. This procedure was continued for 30 days.

Table 2 shows the pH measurements over the course of the test.

Application in Gas Wells

In gas wells, xanthate would need to be added in sufficient strength to produce the initial coating capable of long term corrosion inhibition. Distribution of CX131 in the water is also affected by the pellet dissolution rate. A pellet would be required to travel the entire depth of the well in order to effectively treat all metal parts. Studies done with 5 mm pellets show that at 20°C, it takes approximately 18 minutes and 30 seconds to dissolve and a drop rate of about 6.7 meters per minute, indicating that 125 meters of water can be treated. This data gives only an approximation as other factors, such as CX131 concentration already in the water, can change the dissolution rate. Another factor is temperature. An experiment with elevated temperatures is shown in a graph in figure 2. As temperature increases, dissolution rate increases. Once about 60°C is reached, the dissolution rate acceleration increases. The addition of tripolyphosphates as an anti-scaling/binding agent has the effect of slowing dissolution rate

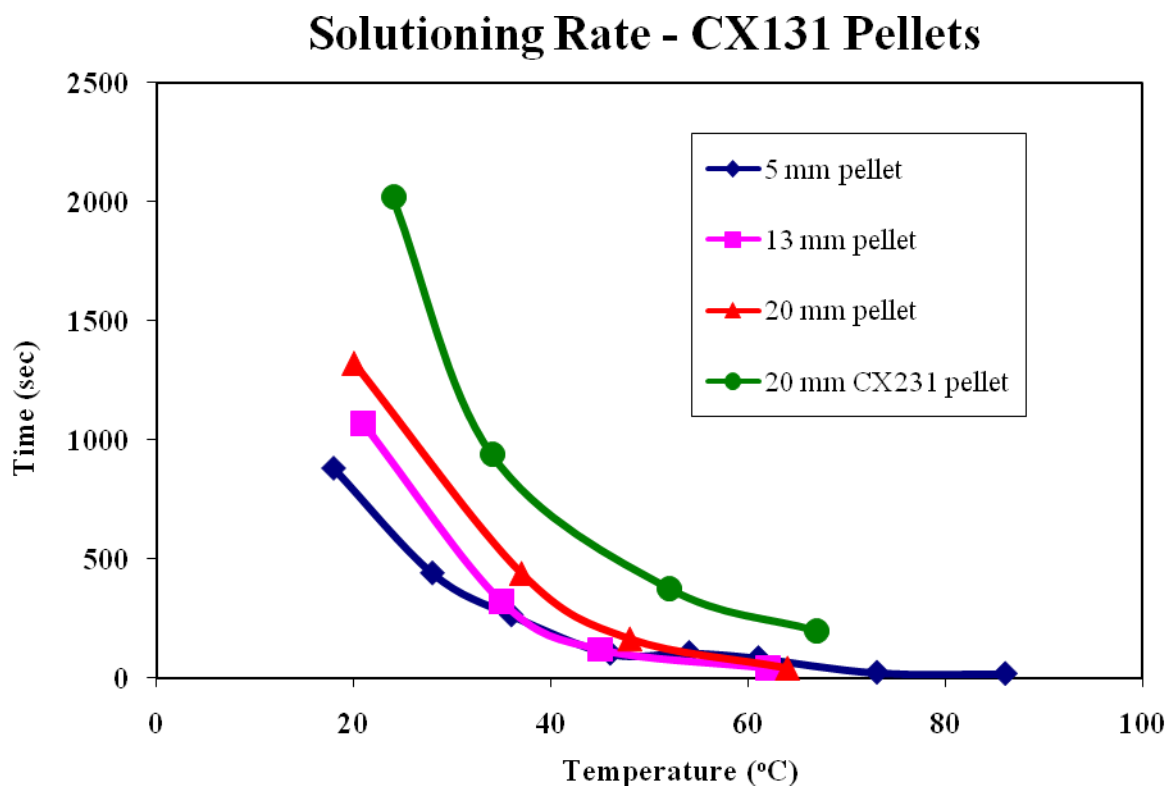

Figure 2. Temperature Effects on CX131 Dissolution

In order to be effective, a pellet of xanthate should reach close to the bottom of a well before it is totally dissolved. Sink rates of the 5 mm by 11 mm pellets average about 11 cm/s, or a pellet needs approximately 15 minutes for every 100 metres of well water. Calculating pellet sizes based on pellet surface areas and correlated with the data with the 5 mm pellet, it was determined that a 15 mm diameter by 20 mm length pellet would be required to treat 100 metres of well water at 40°C to 50°C (assumption: pellets will sink at the same rate regardless of size, has not been proven. Gas flow through the water will affect sink rate as well).

Scaling

The CX131 pellets are an effective delivery system for other chemicals into well water. The well simulation water contains over 1000 ppm of calcium and magnesium ions which tend to form hard scaling carbonates that can plug up pipes and pumps. Tripolyphosphates are effective in precipitating calcium and magnesium as gels which are easily pumped out of the well. Introducing tripolyphosphates into the water as a solution comes up against the mixing problem in gas wells. CX131 can easily be blended with a small amount of tripolyphosphates when manufactured. The CX131 then become a delivery system to disperse the tripolyphosphates throughout the well water. The use of CX131, which will raise the pH, will require tripolyphosphates as the higher pH will create more scaling problems. However, raising the pH also reduces acid corrosion.

Tests with tripolyphosphate content in CX131 pellets also showed a previously unknown benefit. 20 mm pellets that normally dissolve in about 41 seconds in 60°C water as pure CX131, took 3 minutes and 17 second to dissolve with a 12% tripolyphosphate content. Suddenly, the dispersion depth in a well is greatly increased. Tripolyphosphate also turns out to be an excellent binding agent for CX131 when making the 20 mm pellets.

Gas Well Simulations

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