# Paratene™ SHP

Control and Removal of Iron Sulphides and Polysulphides

Introduction

Iron sulphides and polysulphides result from the interaction of hydrogen sulphide with iron. Many Canadian oilfields have production problems directly related to the build up of iron sulphides. These problems include, plugging of water injection wells, the formation of pads in treaters, and agglomerated deposits on contactors in amine systems.

Iron Sulphide (FeS) forms from the direct reaction of H_2S with ferrous iron (Fe^{2+}) in solution. FeS is soluble in acid and will decompose into ferrous ion and H_2S in the reaction:

(1) $FeS + 2H^+ = Fe^{2+} + H_2S$
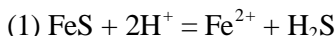
The dissolution of iron sulphide is further complicated when a high partial pressure of H_2S is present. Reaction (1) is reversible, and under high H_2S pressures, even strong acids will not encourage the iron sulphide particles to dissolve. This occurs rarely in surface equipment, but is a common problem in trying to remove FeS deposits formed in producing formations.

Iron Polysulphide (FeS_x) represents an entirely different problem. Polysulphides form because both iron and sulphur have multiple oxidation states, and can form combinations that can be either depleted or enriched in one of the two elements. The resulting crystals are not soluble in most acids (nitric being the exception), and an oxidizing agent is required to remove them.

FeS and FeS_X will react with oxidizing agents in predictable ways. For example, consider the reaction of chlorine dioxide with iron sulphide:

(2) $4FeS + 11ClO_2 = 2Fe_2O_3 + 4SO_4^{2-} + 11Cl^-$

The exact reaction of chlorine dioxide depends on pH, but in general the addition of an excess of oxidizing agent in the presence of iron sulphides will result in the formation of iron oxides and either elemental sulphur or sulphate ion.

Common Industry Oxidizing Agents

Various oxidizing agents have been considered or used to dissolve or convert iron sulphide. Several of these are listed below.

Chlorine Dioxide is a yellowish gas that can form a solution with water. Chlorine Dioxide does not act in the same manner as sodium hypochlorite, but more like hydrogen peroxide. Chlorine dioxide is toxic, and can form explosive mixtures with air. Chlorine dioxide undergoes the reactions shown in equation 2. Chlorine dioxide is also fairly corrosive.

Sodium Hypochlorite (bleach) is a powerful and common oxidizing agent. It reacts slowly with iron sulphides and forms iron oxides and elemental sulphur. Bleach is also exceptionally corrosive.

Potassium Permanganate (KMnO$_4$) is used in industrial and municipal water treating to remove H_2S and to treat iron Sulphides. The reactions of $KMnO_4$ result in the formation of elemental sulphur or

sulphate, iron oxide, and manganese dioxide. $KMnO_4$ is an effective method for dissolving finely dispersed iron sulphides or dissolved hydrogen sulphides, but works poorly on iron sulphide deposits, as it forms an insoluble layer of manganese dioxide on the surface of the deposit. The formation of manganese dioxide prevents penetration of the $KMnO_4$ to the active deposit surface, limiting the amount of the deposit that may be dissolved. The manganese dioxide formed is also an additional insoluble deposit. It can be removed by reacting it with a strong acid, but it will react with hydrochloric acid to form chlorine gas.

Hydrogen Peroxide has been used for the removal of iron sulphides and the control of hydrogen sulphide in industrial and municipal water treating. In the presence of metal ions in solution, hydrogen peroxide decomposes exothermically to form water and oxygen. This effect limits effectiveness of hydrogen peroxide in oilfield applications, as the oxygen does not react well with either the H2S or the iron sulphides.

Paratene™ SHP incorporates a stabilizer system into hydrogen peroxide. As a result, the hydrogen peroxide does not decompose in the presence of metal ions, and more hydrogen peroxide is available to react with the hydrogen sulphide and iron sulphides. Paratene™ SHP immobilizes the iron as an acid soluble salt, and prevents any reaction with the hydrogen peroxide.

Applications of Paratene™ SHP

Oil and Gas Well Cleanouts

Paratene™ SHP can be applied as a batch treatment in oil and gas wells to dissolve polymer based drilling mud. The treatment volume of Paratene™ SHP depends on the extent of the problem, the geometry of the injection zone, and the porosity of the zone. Paratene™ SHP is blended as a finished product and is applied undiluted. The treatment volume of Paratene™ SHP should be pumped into the well followed by an equal volume of 15% hydrochloric acid

Water Injection Wells

Paratene™ SHP can be applied as a batch treatment in water injection wells. The treatment volume of Paratene™ SHP depends on the extent of the problem, the height of the injection zone, and the porosity of the zone. Paratene™ SHP can be applied undiluted, or diluted at 1:1 with fresh water. The treatment volume of Paratene™ SHP should be pumped into the well followed by a slug of water, followed by an equal volume of 15% hydrochloric acid.

Treaters and Flow Lines

Paratene™ SHP can be continuously applied at low concentrations to prevent the formation and accumulation of iron sulphides from forming in treaters and flow lines. The amount of Paratene™ SHP to add is determined by the concentration of H_2S and iron sulphide. The following chart can be used as a guideline to determined the recommended dosages.

Industrial Cleaning Applications

Paratene™ SHP can be applied to remove iron sulphides, iron polysulphides, polythionic acids and pyrophoric iron sulphides in industrial systems such as amine contactors, distillation towers, glycol systems, municipal water treating systems, and other systems where hydrogen sulphide may be present. To apply Paratene™ SHP the system should be filled with a solution of water and 30 – 50% of Paratene™ SHP. The solution should be heated to a temperature of 35 – 40°C and circulated for 4 –

5 hours. The amount of Paratene™ SHP required will depend on the total amount of expected deposit, and can be calculated from the graphs given for oilfield application. Additional Paratene™ SHP can be added to the system as the job progresses. Concentrations of more than 5% hydrogen peroxide must be avoided, as higher concentrations of H_2O_2 can be corrosive to carbon steel.

Relationship Between Iron and Sulphur

The ratio of hydrogen peroxide to iron sulphide is ½ mole of hydrogen peroxide per mole of iron, and 4 moles of hydrogen peroxide per mole of sulphur. Thus:

Sulphide	MW	H_2O_2 Moles	Wt H_2O_2/g sulphide
FeS	87.85	4.5	1.74
FeS$_2$	119.85	8.5	2.41
Fe$_{1-x}$S	<87.85	<4.5	<1.74

The amount of scale that can be dissolved is dependant on the relative ratio of iron to sulphur. For a high sulphur scale such as a pyrite, the relative amount of peroxide required goes up, for a low sulphur scale such as Troilite (FeS) or Pyrrhotite (Fe1-$_x$S) the relative amount of peroxide required goes down.

Sulphide	Grams sulphide dissolved Per litre of 5% SHP	Grams sulphide dissolved Per litre of 10% SHP
FeS	28.73	57.46
FeS$_2$	20.74	41.48
Fe$_{1-x}$S	>28.73	>57.46

As an example, one gram of our baseline referenced iron sulphide material with 100 ml of Paratene™ SHP (5%) will yield the following results:

Compound	Chemical Formula	Abundance
Pyrrhotite	Fe$_{(1-x)}$S	45-55%
Troilite	FeS	25-35%
Magnetite	Fe$_3$O$_4$	10-15%
Pyrite	FeS$_2$	1-5%
Iron	Fe	1-5%

The initial reaction was carried out at room temperature over night. Based on the analysis, only 80 – 85% of the sample was an iron sulphide capable of reacting with SHP. The weight of the conversion products was 1.9016 g and the amount of residue after reaction with dilute HCl (cold to dissolve only the conversion products) was 0.128 or 12.8%. The conversion of the iron sulphides was essentially complete

Corrosion on Carbon Steel

Corrosion testing for Paratene™ SHP on carbon steel resulted in a very low corrosion rate of 23 mpy. Tests were performed at 20°C, and no decomposition of the hydrogen peroxide could be observed when Paratene™ SHP was in contact with clean carbon steel for a 24-hour period.