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APPLICATION OF STABILIZED HYDROGEN PEROXIDE FOR THE REMOVAL OF IRON POLYSULFIDE DEPOSITS

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ABSTRACT

Hydrogen Peroxide is a strong oxidizing agent that could be used for the effective removal of the iron sulfide species. Because Hydrogen Peroxide is catalytically decomposed into oxygen and water by the presence of metal ions, the full potential benefits of the peroxide are not achieved. The efficacy and safety of a several commercially available stabilized peroxide systems are examined. two examples of real world cleaning are given, including, in place cleaning of aluminum cryogenic cold boxes and the removal of iron polysulfide's from twisted tube exchanger using peroxide and ultrasonic chemical cleaning.

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INTRODUCTION

Hydrogen Peroxide would seem like an obvious choice for use in industrial cleaning. It is a strong oxidizing agent, that when it reacts leaves only water as a residue, it is relative in expensive, and is readily available.

Hydrogen Peroxide has one really big problem; it is unstable in the presence of transition metal ions. Peroxide plus small amounts of dissolved iron or copper or manganese or silver will catalytically break down back into water and oxygen. (eq. 1)

$$2H_2O_2 \rightarrow 2H_2O\ (l) + O_2\ (g) \qquad (1)$$

The reaction is very exothermic and rapid. The resulting release of heat and gas (both oxygen and steam) can have catastrophic consequences.

The intention to use hydrogen peroxide to remove iron sulfides and polysulfides can be described by two reactions.

$$2FeS + 9H_2O_2 + 2H^+ \rightarrow 2Fe^{3+} + 2SO_4^{2-} + 5H_20 \qquad (2)$$

$$2FeS_2 + 15H_2O_2 \rightarrow 2Fe^{3+} + 4SO_4^{2-} + 14H_20 + 2H^+ \qquad (3)$$

The release of ferric ions for both cases may then set off the catalyzed decomposition reaction described in equation 1. The resulting decomposition is counterproductive as the loss of peroxide will prevent it from taking part in the desired reactions.

The reaction rate for decomposition is controlled by ferric ion concentration, hydrogen ion concentration and the concentration of hydrogen peroxide. The paper by Eary[i] gives the reaction rates as following the equation:

$$-\left(\frac{d[H_2O_2]}{dt}\right) = k\frac{[H_2O_2][Fe^{3+}]}{[H^+]} \qquad (4)$$

Equation 4 would suggest that controlling both the free ferric ion and the pH will have a substantial effect in controlling the reaction.

Stabilizers have been used to control the decomposition reactions typically these are substances to control the free metal ions in the concentrated solution.[ii] [iii] [iv]

There are little or no attempts described in the literature to stabilize the peroxide against high concentrations of metal as would be expected in cleaning operations. All of the described systems are for the prevention of peroxide decomposition in storage.

EXPRIMENTAL

To determine the effect of pH, stabilizers and temperature on the peroxide decomposition rates we measured the rate of oxygen generation. This was done by placing the test solution in an Erlenmeyer flask and then adding a small amount of either iron sulfide (FeS) or Iron Pyrite (FeS_2). The gasses generated were then captured and the volume of gas generated over time measured. All tests were performed using reagent grade peroxide diluted to 5% by weight. The solutions were preheated in a water bath before adding the iron sulfides. All rates are reported in moles/second of O_2 generated.

RESULTS

The results for the FeS are given in the table below.

Table 1: effect of FeS on Decomposition rate

	Experiment stabilizer		**Commercial Stabilizer**	
pH	**40°C**	**60°C**	**40°C**	**60°C**
2	3.46E-06	1.74E-05	2.84E-06	1.53E-05
2.5	4.33E-07	1.35E-05	4.74E-06	6.49E-06
3	6.29E-07	1.36E-05	3.03E-07	1.06E-06
3.5	5.37E-07	9.28E-06	9.34E-07	1.96E-06
4	6.62E-07	8.32E-06	4.71E-07	2.92E-06
7	1.78E-06	1.02E-05	1.67E-06	9.51E-06
11	4.25E-05	0.000207	1.91E-05	6.36E-05

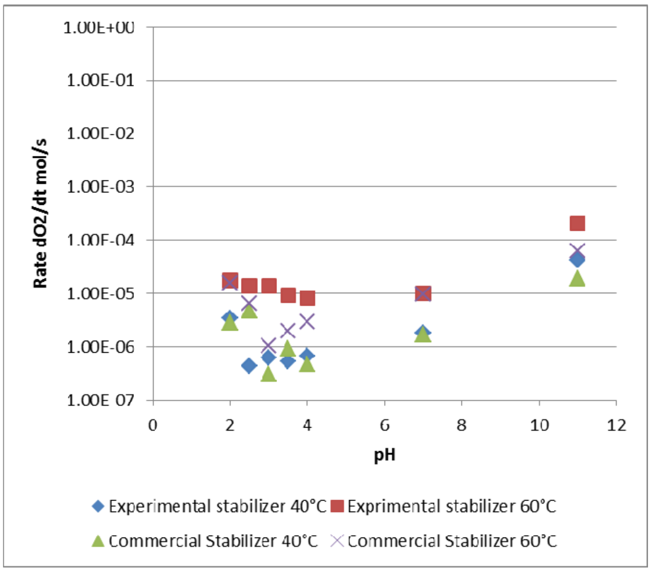

Figure 1 Effect of pH on decomposition rate for two different stabilizers.

When FeS is used at pH<3 some of the gas generated is H_2S. The same test was performed with a limited quantity of iron pyrite (FeS_2).The results are given below. The peroxide the solution contained two different commercial stabilizers stabilizer and the pH was adjusted to 3.5. The uncontrolled peroxide was a dilution of 30% H_2O_2 to 5% in distilled water. In the FeS2 case the stabilizer used was the final commercial stabilizer applied in field.

Table 2: gas evolution rate with FeS_2

Temperature	Rate (mol/s)	
°C	Stabilized	Uncontrolled
45	2.41E-04	1.53E-01
60	4.29E-04	8.04E-01

DISCUSSION

The experimental results show several important factors influencing the decomposition reaction.

1. pH follows the Rate law giving by Eary above pH 4
2. The presence of stabilizers can limit the decomposition.
3. Different iron sulfides give different decomposition rates. FeS and FeS_2 do not react the same.

APPLICATION EXAMPLES

Stabilized hydrogen peroxide has been used commercially for several years. The exact mechanism of its function hasn't been well understood. (This paper describes some of our recent work in deciphering the mechanisms). Two recent examples of the usage are as follows:

Example 1: Aluminum Cold Box Exchanger

This heat exchanger is located in a straddle plant. The Inlet gas passes through a mole sieve bed to remove water then to the aluminum exchangers to cool the gas to cryogenic temperatures permitting the later separation of C_2+ hydrocarbons as well as CO_2. The exchange had been cleaned unsuccessfully several times.

Analysis of the deposit showed it was composed of a mixture of heavy hydrocarbons and iron sulfides. Previous cleaning procedures attempted to remove just the organic portion of the deposit. It was decided to try a combination of degreasing followed by treatment with stabilized peroxide. The results of the cleaning procedure were deemed a success with a 60% reduction of the pressure drop across the exchanger.

Example 2: Crude overhead vapor exchanger

A Hastalloy C276 exchange in a crude unit was determined to have a highly pyrophoric scale composed of iron polysulfides. The scale was difficult to remove by water blasting because of the tight tube pitch and the hardness of the scale. (Not to mention the propensity of the deposit to catch fire). The exchanger was cleaned using a stabilized peroxide solution in an ultrasonic cleaning bath.

Figure 1: Exchanger Prior to cleaning

Figure 2: Bath during Cleaning

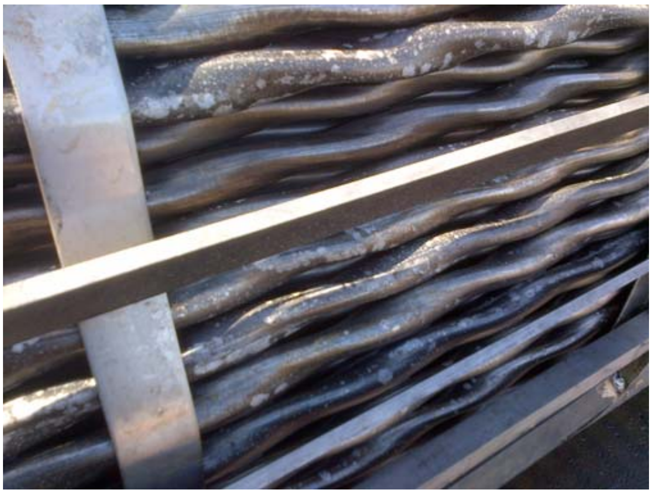

Figure 3: Exchanger after cleaning

The exchanger was completely clean. No iron sulfide or polysulfide residues remained after the cleaning was completed. Some oxygen generation occurred during the cleaning process probably due to UV exposure. The white spots shown are small shallow pits revealed by the cleaning process.

Excess foam as shown in Figure 2 was thought to be due to a combination of the presence of hydrocarbons in the tube side of the exchanger and the effect of UV light on peroxide generating an excess of oxygen and CO_2.

CONCLUSIONS

Hydrogen Peroxide decomposition can be successfully reduced by the addition of stabilizers and careful pH control. By maintaining the pH in the control region of 3 – 4 the amount of oxygen generated can minimized and the reaction between the peroxide and sulphides directed toward removal of the sulphide.

REFERENCES

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