Zircadyne® 702/705 in Hydrogen Peroxide

INTRODUCTION

Hydrogen peroxide, H_2O_2, is one of the most powerful oxidizing agents known, and has increasingly become an important chemical in manufacturing plants for environmental reasons. It is used as a cleaning solvent in the electronics, pharmaceuticals, and food processing industries; as a bleaching agent for pulp and paper; and as an additive for treating solid, liquid and gaseous wastes. High Test Purity (HTP) hydrogen peroxide is also used as a fuel or propellant for rockets.

In addition to superior oxidizing power, one of the key characteristics of H_2O_2 is its instability. Hydrogenperoxide naturally decomposes to form two non-toxic products: water and oxygen. While this makes it an environmentally appealing choice for many of the applications above, the continual decomposition of hydrogen peroxide does have significant disadvantages. The effectiveness of H_2O_2 is clearly reduced as its concentration decreases, turning a valuable chemical into simple water and oxygen. Furthermore, heat is produced in the decomposition reaction, and this can create a safety hazard in combination with the buildup of oxygen. Temperature, pH, and impurity levels can all affect the rate of decomposition and must be carefully controlled. Most of the materials currently used for fabricating the equipment found in H_2O_2 applications require additional chemical stabilizers to be added to the hydrogen peroxide to prevent its breakdown. Not only does this add the cost of the extra chemicals themselves, it also adds impurities. These unwanted impurities can be significantly detrimental to the product or process streams where hydrogen peroxide is typically used and the tolerances for contamination are extremely low, such as in the semiconductor and pharmaceutical industries.

The safety and purity requirements for hydrogen peroxide make proper handling and storage critical. Corrosion in process equipment for hydrogen peroxide can lead to performance degradation, poor product quality, and potentially flammable or explosive environments. Material selection for constructing hydrogen peroxide equipment is an important factor in preventing corrosion and the effective loss of peroxide reactivity due to its decomposition. While H_2O_2 is not considered highly corrosive, it can cause problems for many metals and alloys under certain conditions. Zirconium has excellent corrosion resistance to hydrogen peroxide for almost all conditions, and most importantly, zirconium is one of the few metals whose ions do not catalyze the decomposition reaction for H_2O_2. Zirconium should be considered an ideal option for working safely and efficiently with hydrogen peroxide.

CORROSION RESISTANCE

The corrosion resistance of zirconium in hydrogen peroxide is excellent. Over a wide range of temperatures and concentrations, zirconium exhibits no measurable corrosion at all. Although only a limited amount of laboratory test data is available, zirconium has successfully been used in process equipment handling H_2O_2 at concentrations of up to 90%, with a service life of over 10 years.

TABLE 1: CORROSION OF ZIRCONIUM AT VARIOUS TEMPERATURES AND H_2O_2 CONCENTRATIONS

H_2O_2 Concentration (wt %)	Temperature (º C)	Corrosion Rate (mpy)
5	70	< 0.01
10	70	< 0.01
20	70	< 0.01
30	21 - 102	< 0.01
35	21 - 80	< 0.01
50	100	< 2.0
90	66	< 1.0

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ADVANTAGES OF ZR OVER OTHER MATERIALS

While zirconium is not widely used in H_2O_2 applications today, it has several important advantages that should make it an appealing alternative to current materials of construction, such as stainless steel. As stated earlier, zirconium does not initiate the decomposition of hydrogen peroxide. This eliminates the necessity of adding stabilizing compounds to the process solution, thereby saving money and maintaining the purity of the solution. Table 2 compares the performance of different materials in a H_2O_2 solution. The testing shows that all of the metals, except zirconium, initiated a significant buildup of gases due to the decomposition of the hydrogen peroxide. This data reinforces the improved safety aspects of using zirconium to handle H_2O_2; by reducing or eliminating oxygen formation, selecting zirconium lowers the risk and dangers of fires or explosions.

TABLE 2: GAS GENERATED FROM 20-DAY EXPOSURE TO 1-LITER OF 30% H_2O_2 AT 25ºC

Metal	Volume (ml)
304 Stainless Steel	130
316L Stainless Steel	475
Iron	290
Chromium	100
Nickel	150
Aluminum	475
Zirconium	2

Another key feature of zirconium is the ability to maintain its corrosion resistance across the full range of concentrations, temperatures and pH. As seen below in Table 3, stainless steel and titanium are limited in usefulness to specific pH ranges. If there is variation in the process conditions, corrosion of one of these materials could proceed and lead to accelerated decomposition of the H_2O_2. Zirconium also has one unique characteristic that is particularly important in many hydrogen peroxide applications where product color is critical: zirconium ions are colorless, and will not visually contaminate process streams or products.

TABLE 3: CORROSION OF STAINLESS STEEL AND TITANIUM IN H_2O_2

% H_2O_2 at 70ºC	pH	Zirconium	Corrosion Rate (mpy) 316L Stainless Steel	Titanium
5	1	< 0.4	121	24
	4	< 0.4	< 0.4	7
	12	< 0.4	< 0.4	14
10	1	< 0.4	35	45
	4	< 0.4	< 0.4	22
	12	< 0.4	< 0.4	1

The combination of zirconium's attributes in hydrogen peroxide solutions makes it ideally suited for material selection in equipment with a high ratio of metal surface area to solution volume, such as piping systems, pumps, valves and heat exchangers, where there

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is a greater risk of corrosion, and the potentially damaging consequences it can produce. When ultra high purity H_2O_2 is needed, zirconium's superior corrosion resistance should make it the metal of choice in equipment fabrication.

LIMITATIONS

Although corrosion testing has not been done at all temperatures and concentrations, there are no known limitations to the use of zirconium in pure hydrogen peroxide. The presence of oxidizing chlorides in a highly acidic H_2O_2 solution may lead to localized corrosion, as pitting was observed in corrosion testing done using HCl to control the pH. There are several methods to control this form of corrosion, including proper surface cleaning by pickling, using dedicated tools for fabricating zirconium equipment, and electrochemical protection when practical.

One other impurity that always has a negative impact on the corrosion performance of zirconium is the fluoride ion. Fluoride ions present in a process solution can dramatically decrease the corrosion resistance of zirconium by forming hydrofluoric acid. Zirconium is rapidly attacked by hydrofluoric acid and fluoride solutions when the pH is less than 3. Corrosion inhibitors, such as zirconium sponge or other zirconium chemicals, may be used to form fluoride complexes and prevent corrosive attack of the zirconium equipment.

SPECIAL PRECAUTIONS

Reactive metals like zirconium can develop pyrophoric films under certain conditions in specific corrosive media. While there is no evidence of pyrophoric films forming on zirconium used in hydrogen peroxide solutions, this is a special safety concern when using zirconium. Normally zirconium corrodes uniformly and all the zirconium is converted to zirconium oxide. If corrosion rates are low, less than 5 mpy, there is time to react all the zirconium uniformly. For very high corrosion rates, above 200 mpy, the reaction rate is so high that all zirconium is also reacted.

In certain conditions, it is possible that the corrosive media will attack grain boundaries, trapping small pieces of zirconium grains in the oxide and not completing the oxidation. Under these conditions, the oxide film may be pyrophoric. To passify the zirconium, the trapped zirconium pieces need to be completely oxidized in a controlled atmosphere. This is achieved by passing hot air or steam through the equipment to make sure all the zirconium particles in the film are reacted. At 250°C, steam must flow for 30 minutes; at lower temperatures, longer treatment times are required.

SUMMARY

As outlined above, zirconium can be the best alternative for material selection in many hydrogen peroxide applications. Longer equipment life, reduced maintenance downtime, and higher purity product streams are all possible with the proper application of zirconium, making it the most cost-effective option when compared with other alloys.

Although zirconium has proven its outstanding corrosion resistance performance in a wide variety of hydrogen peroxide environments, the best way to determine zirconium's suitability for a particular environment is to perform a corrosion test. Zirconium corrosion test kits are available from ATI for use in on-line process equipment. These tests can show how zirconium will hold up under actual process conditions. ATI also has a fully capable corrosion laboratory for complete testing and detailed analysis for specific hydrogen peroxide applications.

For further information or any questions regarding the use of zirconium in hydrogen peroxide applications, please contact Technical Services at ATI.

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