



Drew Industrial Division

ASHLAND CHEMICAL COMPANY, DIV. ASHLAND OIL, INC.
One Drew Plaza, Boonton, New Jersey 07005

RECOVERY FROM
LOW pH EXCURSIONS IN COOLING WATER SYSTEMS

by

Ross K. Fuller, Manager, Customer Technical Services

Ronald J. Delavan, Industry Specialist

May 24, 1986

INTRODUCTION

Of all the upsets, or excursions, that can occur in an open recirculating cooling water system, perhaps the most common and potentially most harmful, is a decrease in pH. The causes of excessive pH reduction are numerous and include acid overfeed, airborne sulfur dioxide from boiler stack gas and process leaks.

Although there are cooling systems running without the addition of acid, by and large, the majority of large systems in industrial and utility plants use acid to control pH. Thus, there always exists the possibility of overfeeding acid. It is important to recognize that proper planning and preparation can minimize the effects of low pH excursions. These adverse effects include metal loss and fouling by corrosion products.

Typically a great deal of time, care and effort is taken to establish an effective cooling water treatment program and to maintain control of the program. In spite of efforts by plant personnel, low pH excursions can occur due to human error and equipment failure and malfunction. It is essential that control of the water treatment program be regained as quickly as possible with a minimum amount of damage. With that purpose in mind this paper is designed to serve as a guide for recovery from low pH excursions in cooling systems. The recovery planning and procedures are based on experience at oil refineries and chemical and petrochemical plants. The cooling water treatment supplier should always be consulted during the development of the recovery procedures and should be present during recovery and repassivation.

THEORETICAL CONSIDERATIONS

It is usually believed that the lower the pH, the greater the corrosion rate of most metals and alloys used in cooling systems. That is true for yellow metals but is not necessarily so for ferrous metals whose corrosion rates increase significantly in solutions with either high or low pH's. First, consider the case of aerated cooling water that contains no corrosion inhibitor.

Uhlig¹ stated that within the range of about pH 4 to 10, the corrosion rate is independent of pH, and depends only on how rapidly oxygen diffuses to the metal surface. Regardless of the observed pH of water within this range, the surface of iron is always in contact with an alkaline solution of saturated hydrous ferrous oxide, the observed pH of which is about 9.5. Within the acid region (pH < 4), the ferrous oxide film is dissolved, the surface pH falls, and iron is more or less in direct contact with the aqueous environment.

Uhlig supports those statements with data from Whitman, Russell and Altieri,² shown in Figure I which illustrates the amphoteric nature of iron.

The correlation between pH and free mineral acidity for pH's below 4.5 is detailed in Table I which illustrates that unbuffered free mineral acidity is present below about pH 4.5. Below this is the range of major concern with low pH excursions.

In the case of cooling water treated with a corrosion inhibitor, the passivated film reduces corrosion to an acceptable level (usually less than 3 mpy) within a pH range defined by the specific inhibitor and certain operating parameters, peculiar to each system. In the event of a low pH excursion, the passivated film is destroyed at some pH value, generally about pH 5. Below pH 5, the corrosion rate will increase to some value and will not change significantly as the pH decreases, until the pH reaches the 4.0 to 4.5 range where the corrosion rate begins to increase rapidly. Because unbuffered free mineral acidity exists in systems operating in pH conditions of less than 4.5, equipment failure may occur within a relatively short period of time. Corrosion rates are estimated to be over 1,000 mpy for mild steel in the pH range below 2.5.

RELATIONSHIP BETWEEN pH RANGE AND DEGREE OF CONCERN

In the event of a low pH excursion, the degree of concern increases with a decrease in pH. The first (I) level of concern is minor and occurs when the pH depression is less than one pH unit below the lower control point. In this case, the operator can usually determine the cause and make the necessary corrections. These usually include adjusting the acid feed pump and checking and recalibrating the pH, monitoring and/or control equipment.

The second (II) level of concern is moderate and occurs when the pH is below level I and above pH 4.5. Destruction of the passivated films begins to occur in this range. In addition to action taken for level I, acid and chlorine feed should be stopped. Soda ash may be used to bring the pH back into the control range. The corrosion inhibitor should then be slug fed to attain a concentration that is twice normal. This high level should be maintained for one week.

The third (III) level of concern is defined as major and occurs when the pH falls to the 4.5 to 2.5 range. In this range, free mineral acidity is present and accelerates corrosion, thereby dissolving considerable amounts of iron. When pH falls this low, all chemical feeding is stopped and control of pH must be regained as quickly as possible preferably with soda ash. Recovery should include the addition of an iron dispersant to minimize deposition of hydroxides of iron as the pH rises through the 4.0 to 4.5 range. Care must be taken to minimize iron fouling.

The fourth (IV) and greatest level of concern occurs when pH values of less than 2.5 are observed. All the care used in level III above is required, plus the judicious addition of caustic soda to raise the pH up to the 2.5 to 3.0 range, but not above 3.0, to minimize precipitation of ferric hydroxide. Then use soda ash to raise the pH to about 4.5. The first reaction of many plant operators to a pH excursion is to pour in, or slug, caustic soda to bring the pH back into range. This may bring the pH to the desired level quickly but it can also precipitate voluminous amounts of iron hydroxides, especially if the pH has been below about 4.5.

RECOVERY PROCEDURES

Metal loss and fouling can be minimized with proper planning. Each plant must establish its own corrective procedure based upon a number of local factors and do so for each of the pH ranges mentioned above. Prompt and corrective action will minimize the amount of corrosion, corrosion products and fouling that can occur. Points that must be considered include whom to call for assistance, what each person is responsible for, and where and how much remedial chemicals to stock.

To help plant personnel select the appropriate countermeasures, a decision scheme can be established similar to the example shown in Figure 2. The chart and attendant procedures are written with the assumption that the pH excursion is caused by acid feed being out of control. However, with slight modifications for local conditions, the procedures can also be used for excursions caused by process leaks or airborne sulfur dioxide. Detailed instructions are included in Procedures I through IV. In addition, check lists detailing necessary chemical procurement and minimum inventory are given in Tables II and III.

After control of pH is attained, the metal in the system is very active and repassivation must be started immediately to minimize corrosion and the formation corrosion products.

SUMMARY

Timely implementation of preplanned procedures in the event of a low pH excursion will minimize corrosion and subsequent fouling by deposition of metal hydroxides.

After recovery from a low pH excursion, repassivation generally takes longer for systems using organic corrosion inhibitors than for those using chromate, molybdate, phosphate and/or zinc based inhibitors. However, by following the prescribed procedures, the passivated film formed by both organic and other corrosion inhibitors can be reestablished and corrosion brought under control with minimum fouling and within a minimum practical time frame.

TABLE I

CORRELATION BETWEEN pH AND FREE MINERAL ACIDITY

<u>pH</u>	<u>Free Mineral Acidity as Ca CO₃</u>
4.5	1.8
4.0	5
3.5	16
3.0	50
2.5	160
2.0	500
1.5	1600
1.0	5000

TABLE II

CHECK LIST TO PREPARE FOR A pH EXCURSION

	<u>Name</u>	<u>Plant Phone</u>	<u>Home Phone</u>
Plant Personnel to be Notified	_____	_____	_____
	_____	_____	_____
	_____	_____	_____
Name of Chemical Supplier	_____		
Telephone Number(s) of Supplier	_____		(Day & Off Hours)
Warehouse Telephone Numbers	_____		(Day & Off Hours)
Inhibitor #1; Name	_____		
Warehouse Supply Number	_____		
Inhibitor #2; Name	_____		
Warehouse Supply Number	_____		
Oil and/or Particulate Dispersant; Name	_____		
Warehouse Supply Number	_____		
Soda Ash ($\text{Na}_2 \text{CO}_3$)	_____		
Warehouse Supply Number	_____		
50° Be Caustic Soda	_____		
Warehouse Supply Number	_____		
Volume In System	_____		
Circulation Rate	_____		

TABLE III

Inventory and Feed Rates

For Worst Case Condition

<u>Name</u>	<u>Minimum Inventory</u>	<u>Maximum Feed Rate</u>
Inhibitor #1	_____	_____
Inhibitor #2	_____	_____
Iron Dispersant	_____	_____
Oil and/or Particulate Dispersant	_____	_____
Soda Ash (Na ₂ CO ₃)	_____	_____
50° Be Caustic Soda	_____	_____
Biocide	_____	_____

The following formulae can be used to estimate chemical requirements:

SLUG:

$$\text{Pounds of Product} = \frac{\text{desired product concentration (ppm)} \times \text{system volume (gallons)}}{120 \times 1,000}$$

CONTINUOUS:

$$\text{Pounds of Product per day} = \frac{\text{desired product concentration (ppm)} \times \text{makeup (gal. per day)}}{\text{Cycles of concentration} \times 120 \times 1,000}$$

See TABLES IV and V for alkaline chemical needs.

TABLE IV

Soda Ash Requirements to Raise pH
From 2.5 to 4.5 for 100,000 Gallons Water

<u>From pH</u>	<u>50° Baume^(a) Caustic Soda Gallons</u>	<u>Soda Ash (Na₂CO₃) Pounds</u>
2.5	Not recommended	130
3.0	because of danger	41
3.5	of over feed	14
4.0		3

(a) 50° Be Caustic Soda: 50.0% NaOH; 6.36 lbs. NaOH/Gallon; Sp. Gr. 1.525.

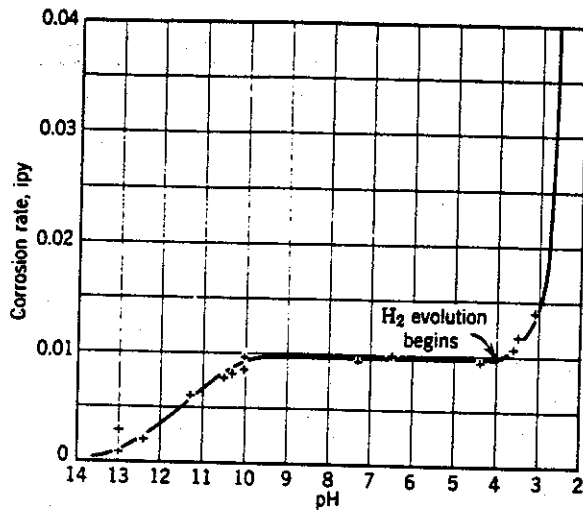
TABLE V

Fresh Caustic Soda (a) Requirements
To Bring pH Up To 2.5 For 100,000 Gallons Of Water

<u>From pH</u>	<u>Gallons</u>
0.5	1600
1.0	500
1.5	150
2.0	37

(a) 50° be Caustic Soda: 50.0% NaOH; 6.36 lbs. NaOH/Gallon; Sp. Gr. 1.525.

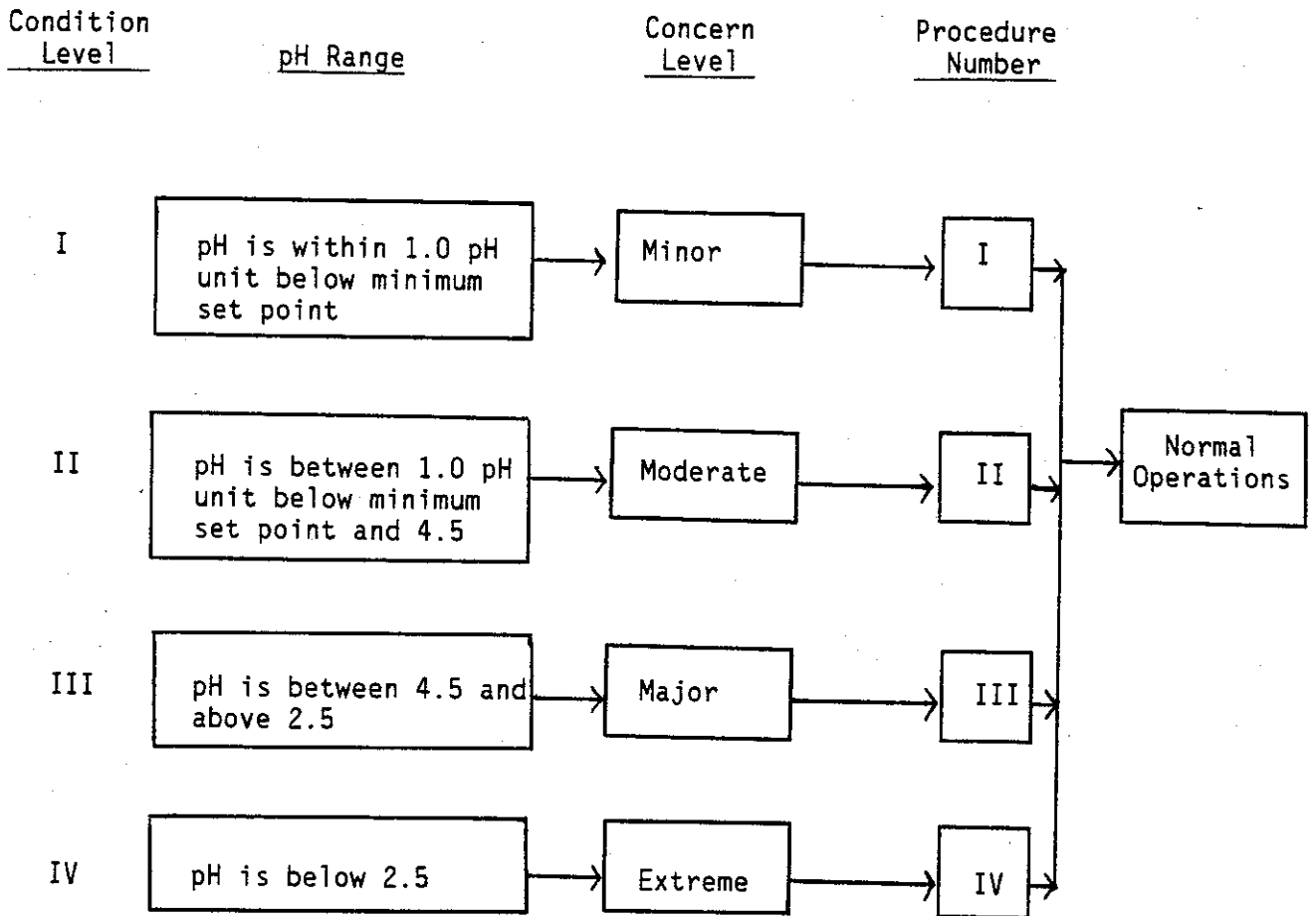
FIGURE I



Effect of pH on corrosion of iron in aerated soft water, room temperature²

FIGURE 2

Corrective Plan for Low pH Excursions
in Cooling Systems



Procedure I pH Within 1.0 Unit Below Minimum Control Point

1. Determine level of acid in day or storage tank.
2. Check for proper operation of acid feed pump.
3. Verify calibration of monitoring and/or control equipment.
4. Make necessary adjustments and/or notify supervisor.

Procedure II pH Between 1.0 Unit Below Minimum Control Point and 4.5

1. Stop acid feed pump and block off acid feed system.
2. Stop chlorination.
3. Check for proper operation of feed pump.
4. Verify proper operation of monitoring and/or control equipment.
5. Slowly sprinkle predetermined amounts of soda ash (a) to recirculating pump intake every 10 to 15 minutes after checking pH.
6. Monitor pH at headers about every 10 minutes after each addition.
7. Slug enough corrosion inhibitor to attain a concentration of about twice the normally use concentration.
8. Maintain corrosion inhibitor concentration at twice normal concentration for a minimum of one week.

(a) Liquid caustic soda can be used in place of soda ash only if absolutely necessary but its use is not recommended.

Some plant personnel recommend that no alkaline material be fed above pH 4.5 but to raise the pH only by bleedoff and makeup.

Procedure III pH Between 4.5 and 2.5

1. Stop all chemical addition and block off acid feed system.
2. Open blowdown to maximum and overflow sump, with due consideration being given to flow and/or holding capacity of the waste treatment plant. Blowdown from heat exchangers and dead lines is highly recommended. Insure maximum blowdown does not lower sump water level below pump intake.
3. Add sufficient chelant and/or sequestrant based iron dispersant to sequester soluble iron. Dosage of the iron dispersant should be predetermined based on concentrations of iron in the circulating water.
4. In raising the pH from 2.5 to 4.5, the use of soda ash is preferred over caustic soda. Slowly sprinkle predetermined amounts of soda ash to recirculating pump intake every 10 to 15 minutes until pH is up to 4.5. (See Table IV for dosage requirements.) Continue to add dissolved soda ash until pH is in preselected ranges.(a)
5. Monitor pH at return headers every 10 minutes until pH is in the preselected range.
6. Continue maximum blowdown with high level overflow until water clears, i.e., total iron is less than 3 ppm.
7. Close blowdown and makeup valves and slug enough corrosion inhibitor to attain a concentration of about twice the normal use concentration.
8. Start repassivation procedures recommended by water treatment supplier.

(a) Some plant personnel recommend that no alkaline material be fed above pH 4.5 but to raise the pH to the 5.5 to 6.5 by bleedoff and makeup only.

Procedure IV pH Below 2.5

1. Stop all chemical feed and block off acid feed system.
 2. Open blowdown to maximum and overflow sump with due consideration being given to flow and/or holding capacity of the waste treatment plant. Blowdown from heat exchangers and dead lines is highly recommended. Insure maximum blowdown does not lower sump water level below pump intake.
 3. Because of the large amounts of soda ash that would be required to raise the pH up to about 2.5 to 3.0, the slow addition of caustic to the suction side of the circulating pumps is preferred. It has been estimated that the corrosion rate in the pH range of 1.0 to 2.0 is measured in inches per year, and it drops to about a 100 mpy range in the 2.5 to 3.0 pH range, thus immediate corrective action is necessary.

Using caustic soda to raise the pH above the 2.5 to 3.0 range is not recommended because of the danger of overfeeding and exceeding the upper limit of pH control and also its tendency to precipitate iron hydroxide is greater because caustic causes higher localized pH conditions than does caustic soda.
 4. Monitor pH at return headers every 10 minutes until pH is maintained in the 2.5 to 3.0 range. Do not exceed the pH range of 2.5 to 3.0, using caustic soda.
 5. Add sufficient chelant and/or sequestrant based iron dispersant to sequester soluble iron. Dosage of the iron dispersant should be predetermined based on concentrations of iron in the circulating water.
 6. In raising the pH from 2.5 to 4.5, the use of soda ash is preferred over caustic soda. Slowly sprinkle predetermined amounts of soda ash to recirculating pump intake every 10 to 15 minutes until pH is up to 4.5. (See Table IV for dosage requirements.) Continue to add dissolved soda ash until pH is in preselected ranges.(a)
 7. Monitor pH at return headers every 10 minutes until pH is in the preselected range.
 8. Continue maximum blowdown with high level overflow until water clears, i.e., total iron is less than 3 ppm.
 9. Close blowdown and makeup valves and slug enough corrosion inhibitor to attain a concentration of about twice the normal use concentration.
 10. Start repassivation procedures recommended by water treatment supplier.
- (a) Some plant personnel recommend that no alkaline material be fed above pH 4.5 but to raise the pH further by bleedoff and makeup only.

REFERENCES

- (1) H.U. Uhlig, "Corrosion and Corrosion Control" 1971, John Wiley and Sons, Inc., pp. 98 - 100.
- (2) W. Whitman, R. Russell, and V. Altieri, Ind. Eng. Chem., 16, 665 (1924).
- (3) "Drew Principles of Industrial Water Treatment" 1984, Drew Chemical Corporation, p. 253.