Formulation of Corrosion Inhibitors

Yun Chen and Wenzhong Yang

Abstract

Corrosion inhibitors are widely used in the production process due to their significant effect. In this chapter, the formulation of typical corrosion inhibitors in acid solution, near-neutral solution, alkaline solution, and oil and gas systems will be discussed, respectively. Firstly, the importance of pickling corrosion inhibitors for thermal equipment in industrial production in different situations is discussed in the “Inhibitors for acid solution” section, and the types of pickling inhibitors are mainly applied in different kinds of acid media, such as sulfuric acid, hydrochloric acid, nitric acid, phosphoric acid, hydrofluoric acid, citric acid, and sulfamic acid. Secondly, in the “Inhibitors for near-neutral solution” section, the cooling water inhibitors principally include chromate, stabilized phosphate, alkaline zinc/organic, molybdate, all organic, soft and lean water, and environmental and closed-loop programs. The hot-water inhibitor is also mentioned here. Then in the “Inhibitors for alkaline solution” section, boiler water inhibitor, oxygen scavenger, and corrosion inhibitors for condensate line are talked over. Finally, in the “Inhibition for oil and gas systems” section, drilling fluid, fracturing acidizing, oil and gas well, and oil field which produced water treatment inhibitors are introduced here. The corrosion inhibition mechanism and development trend of inhibitors are also discussed.

Keywords: inhibitors for acid solution, inhibitors for near-neutral solution, inhibitors for alkaline solution, inhibition for oil and gas systems

1. Introduction

Pickling is widely used in various production processes, such as for pickling and rust removal of metal pipes, plates, and wires, and products in the metallurgical and mechanical industries, scale cleaning of heat exchange equipment, heat transfer equipment, and cooling equipment in various industrial sectors, especially for pickling of thermal equipment such as boilers in the electric power sector. It is meaningful using pickling, for example, from a socioeconomic point of view, fuel consumption due to fouling can be reduced; from the perspective of environmental protection, fuel exhaust and atmospheric pollution are reduced; from a safety point of view, thermal equipment such as boilers and heat exchangers can be used well. As we know, various types of dirt are gradually formed in the process, and the poor thermal conductivity of the dirt causes the local temperature of the furnace tube to rise, which reduces the strength of the steel and often causes a pipe burst accident and affects the operation of the boiler. Therefore, pickling plays a very important role in the boiler operation of power plants. In addition, the use of industrial circulating cooling water technology to increase the
concentration of running water can save a lot of industrial water. In circulating cooling water, in order to avoid corrosion and scaling of equipment, it is often necessary to add water stabilizer. Also, in the process of crude oil and natural gas collection, the current drilling and oil recovery technology requires fracturing and acidification of limestone oil and gas fields with high concentration of hydrochloric acid solution. As the 15–28% hydrochloric acid solutions are often used in the oil wells, the corrosion problem of tubing and oil production equipment is serious in deep well acidification technology due to the high temperature in the well. Therefore, metal materials and products are subjected to various environments during production, storage, transportation, and use. Metal products are easy to vary from different degrees of corrosion. Corrosion problems in tubing and oil production equipment are serious, sometimes causing fracture accidents, resulting in construction failure.

Corrosion inhibitor is an anticorrosion chemical; it can be added to the corrosive environment to cause physical and chemical interaction with the metal surface, thereby significantly reducing the corrosion of the metal material. At the same time, the use of the corrosion inhibitor does not require special equipment, nor does it need to change the properties of the metal. Compared with other anticorrosion methods, corrosion inhibitors are easy to use, cost-effective, and widely used in industrial production and social life. Therefore, it is widely used in various industrial processes, such as pickling, cooling water systems, acidification of oil and gas wells, water injection in oil fields, storage and transportation of metal products, and so on. With the advancement of society and the enhancement of human environmental awareness, the development and application of corrosion inhibitors have received more and more attention. In recent years, countries around the world have paid great attention to the research and application of corrosion inhibitors, which can be used alone or in combination with other anticorrosion materials.

Herein, in view of the current requirements, the characteristic formulation of corrosion inhibitors in acid solution, near-neutral solution, alkaline solution, and oil and gas systems is discussed. The types of pickling inhibitors in different kinds of acid media, inhibitors for the cooling water, alkaline solution, and oil and gas systems are principally talked about in details, respectively.

2. Inhibitors for acid solution

In various corrosive media, acidic gases and liquids are of strong corrosive medium. The rate of metal corrosion in acidic medium is much faster than that in other media, especially in sulfuric acid, hydrochloric acid, nitric acid, phosphoric acid, hydrofluoric acid, citric acid, and sulfamic acid, which are commonly used in pickling and removing iron oxide, descaling and decontaminating of boiler equipment, and so on. In addition, high level of H₂S and CO₂ in oil and gas wells is also the corrosive acidic medium. Since acid has a corrosive effect on metal equipment, especially the corrosion effect of inorganic acid is more serious, and the released hydrogen will diffuse into the interior of the metal, causing hydrogen embrittlement of the equipment to be washed. In addition, as a large amount of acid gas will generate, it will deteriorate working conditions inevitably. Therefore, a suitable corrosion inhibitor should be added during pickling to inhibit the corrosion of the metal in the acidic medium, reduce the amount of acid used, improve the pickling effect, and prolong the service life of the thermal equipment. Table 1 shows the commonly used corrosion inhibitors in corrosive acidic medium.

| Table 1 |
| Inhibitor                        | Acid concentration and temperature | Inhibitor dosage | Inhibition efficiency | Metals          |
|---------------------------------|-----------------------------------|------------------|-----------------------|-----------------|
| Advanced pyridine alkali        | 12% HCl + 5% HF, 40°C             | 0.2%             | <0.1 mm/a             | Carbon steel    |
| 4-Methylpyridine residual       | 10% HCl + 6% HF, 30°C             | 0.2%             | <0.1 mm/a             | Carbon steel    |
| Nitroaniline                    | 2–3 mol/L HNO₃                   | 0.002 mol/L      | High efficiency       | Copper          |
| 1-Phenyl-3-thioformamide        | 20–35% HNO₃                     | 0.0005%          | High efficiency       | Aluminum        |
| Reactant of amine and alkynol   | 5–15% HCl, 93°C                  | 0.01–0.25%       | 99.4%                 | Carbon steel    |
| Methenamine + CuCl₂             | 2–25% HCl                       | 0.6 + 0.02%      | 99%                   | Carbon steel    |
| Methenamine + SbCl₂             | 10–15% HCl                      | 0.8 + 0.001%     | 99%                   | Carbon steel    |
| Furfural                        | 0.2–6 mol/L HCl                  | 5–10/230 mL      | High efficiency       | Copper and alloy|
| Methenamine + KI                | 20% H₂SO₄                       | 0.6% (8:1)       | 99%                   | Carbon steel    |
| Methenamine + thiourea + Cu²⁺   | 10% H₂SO₄                       | 0.14 + 0.097 + 0.003% | 99%                   | Carbon steel    |
| 1,3-Dibutyl-2-thiourea + OP     | 10–20% H₂SO₄, 60–80°C            | 0.5 + 0.25%      | High efficiency       | Carbon steel    |

Table 1. Operating conditions and properties of some common corrosion inhibitors.
2.1 Picking inhibitor in sulfuric acid

For the sulfuric acid solution, organic inhibitors are mainly organic amine, amide imidazoline quaternary ammonium salt, rosin amine, Mooney alkali, thio-urea derivatives and acetylenic compounds, alkaloids, and so on.

In sulfuric acid solution, adding Cl\(^{-}\), Br\(^{-}\), or I\(^{-}\) to acetylenic alcohol and pyridine sulfate inhibitors can significantly improve their corrosion inhibition efficiency. Compounds containing halides, such as alkylbenzylpyridine chloride, cetylpyridinium chloride, urotropine and potassium iodide, and ethylquinoline iodide, are also the novel corrosion inhibitors. In addition, inorganic corrosion inhibitors such as arsenic acid and its salts, antimony trichloride, tin dichloride, and boron trifluoride are also the preferred sulfuric acid pickling inhibitors. Animal protein (KC) and quinoline base (CHM) are sulfuric acid pickling inhibitors as well. Satpati and Ravindran [1] found that 1,2,3-benzotriazole can inhibit the SS304 stainless steel in sulfuric acid solution up to 97%.

2.2 Picking inhibitor in hydrochloric acid

Most of the corrosion inhibitors effective for carbon steel hydrochloric acid pickling are organic heterocyclic compounds containing N, O, S, and P atoms, and most are used as nitrogen-containing compounds. There are three common hydrochloric acid pickling inhibitors:

1. Ammonia compound corrosion inhibitors, including alkyl amines and aromatic amines, saturated and unsaturated nitrogen ring compounds or niscine and quaternary ammonium, amide, polyamine, etc., prepared by ethylene nitride condensed polyamines, such as urotropine.

2. Sulfur-containing compound corrosion inhibitor thiourea and derivatives, in the acid wash, Fe\(^{3+}\) is a strong depolarizer, if accumulated more, it will aggravate the corrosion of the steel and cause pickling. The phenylthiourea and NH\(_4\)HF\(_3\) complex can form a complex with Fe\(^{3+}\) ions, thereby preventing over-pickling. In addition, rare earth thiourea compounds are also the effective corrosion inhibitors.

3. Some phosphorus compounds, such as tributyl phosphate, can inhibit the corrosion of steel and hydrogen permeation to avoid over-pickling. It is also beneficial to the acid regeneration cycle.

Behpour et al. [2] studied 2-([1-methyl-3-[(2-sulfoaminophenyl)imino]butylene]amino)-1-thiophenol and 2-([1,2-diphenyl-2-[(2-phospephenyl)imine]acetal]ammonia)-1-thiophenol for the corrosion inhibition properties of copper in 15% hydrochloric acid. The results show that both of them are mixed corrosion inhibitors. When the mass fraction of two Schiff bases is 500 μg/g, the inhibition efficiency is 95.94 and 96.75%, respectively. Bentiss et al. [3] found that the three 4-hydrogen-1,2,3-triazole derivatives have better corrosion inhibition performance on low carbon steel in hydrochloric acid solution. They are all mixed corrosion inhibitors, in which the corrosion inhibition efficiency of 3,5-bis(4-methylthiophenyl)-4-hydrogen-1,2,4-triazole can be as high as 99.6%.

2.3 Picking inhibitor in nitric acid

Boiler scale and metal oxides are highly soluble in nitric acid, which sometimes replaces hydrochloric acid. Nitric acid is a very oxidizing acid, and as most of the
corrosion inhibitors are organic, thus they are prone to act as redox reactions. Therefore, there are fewer types of nitric acid pickling inhibitors. Commonly used for nitric acid pickling inhibitors is a mixture of thiourea and Na$_2$S and a mixture of hydrazine (C$_8$H$_7$N) and NH$_4$SCN or Na$_2$S. The corrosion inhibition mechanism of thiourea is that it can decompose nitrous acid, thereby inhibiting the dissolution of metals in nitric acid. The significant inhibition of combining thiourea and Na$_2$S is due to synergistic effect. There are better nitric acid pickling inhibitors as well, such as thiosulfate, aniline chloride, potassium thiocyanate, potassium dichromate, alkaloids, benzoquinone, etc.

2.4 Picking inhibitor in phosphoric acid

The development of phosphoric acid corrosion inhibitors began around the 1930s. Most of the early products were inorganic salts. In the 1940s and 1950s, organic compounds were successively developed as corrosion inhibitors for metals in phosphoric acid solutions. Cu$_3$(PO$_4$)$_2$, molybdate, tungstate, borate, nitrite and nitrate, sodium chromate, dichromate, ammonium hydrogen fluoride, basic salt of arsenic, iodine or bromine, are the inorganic corrosion inhibitors, dodecylamine or 2-aminoicyclohexylamine and potassium iodide, iodoacetic acid, composite corrosion inhibitor compounded with acridine, urotropine and ammonium thiocyanate, oxazole compounds such as triazole and benzotriazole and thiourea, sulfonated imidazoline, polyvinylpyrroldione (PVP), and polyethyleneimine (PEI); are the organic corrosion inhibitors, which are the typical corrosion inhibitors for carbon steel; sodium molybdate, ammonium chloride, sodium silicate, potassium chromate, potassium dichromate, amine compound, aminophenol, pyridine, Tween-85, Tween-20, sodium lauryl sulfate, cetylpyridinium chloride, methylpyridine, and 8-hydroxyquinoline are successfully used for inhibiting the corrosion of aluminum and aluminum alloy; for copper and copper alloy, mercaptobenzothiazole (MBT), benzotriazole, dextrin, tannin, agar, gum arabic, pyroc acid, gelatin, cinnamic acid, and its derivatives are the effective corrosion inhibitors.

2.5 Picking inhibitor in hydrofluoric acid

Hydrofluoric acid is a weak inorganic acid that volatilizes in the air, and its vapor is highly corrosive and toxic. However, it dissolves oxides at a high rate and has the special properties of dissolving silicon scale (silicon oxide). Hydrofluoric acid pickling was first successfully used in a post-operation supercritical pressure boiler in West Germany in 1968. Since then, 40% of the boilers in West Germany have been washed with hydrofluoric acid. Although the use of hydrofluoric acid pickling has the disadvantages of unsafe operation, high price and environmental pollution, considering the characteristics of hydrofluoric acid, its application range is still extensive after the application of new corrosion inhibitors. Alkylthioureas, organic amines, benzotriazole, 2-mercaptobenzimidazole, and 2-mercaptopbenzothiazole are the characteristic corrosion inhibitors for stainless steel and carbon steel.

2.6 Picking inhibitor in citric acid

When citric acid pickling is selected, since the temperature during pickling is high and the circulation speed is fast, the corrosion inhibitor must be applied to such conditions when selecting citric acid pickling. The commonly used corrosion inhibitors are urotropine, thiourea, o-xylene thiourea, ruthenium, industrial xylene thiourea, and so on.
2.7 Picking inhibitor in sulfamic acid

Sulfamic acid is a powdery and moderately acidic mineral acid. In the pickling process, it is stable and good soluble in water. It does not cause salt precipitation and precipitation and does not contain halogen ions. It is suitable for cleaning carbonates and hydroxides. However, it has poor ability to pickle iron oxide, and it decomposes above 60°C. Therefore, it is rarely used for pickling of large boilers and is generally used for pickling of copper pipes. The sulfamic acid pickling inhibitors mainly contain organic amine, dibutylthiourea, dipropynyl sulfide, propargyl alcohol, quaternary ammonium salt, ethyl thiourea, and dodecylamine. The inhibitor of inorganic compound (potassium iodide) also performs excellent performance. Table 2 shows the corrosion inhibition effects of some organic and inorganic compounds in sulfamic acid.

| Compounds               | Inhibitor composition     | Concentration (mg/L) | Corrosion inhibition efficiency (%) |
|-------------------------|---------------------------|----------------------|-------------------------------------|
| Organic amines          | N-butylyl amine           | 146                  | 7.1                                 |
|                         | Twelve amine              | 380                  | 81.7                                |
|                         | Ethylene two amine        | 120                  | 11.2                                |
|                         | Quinoline                 | 258                  | 23.1                                |
|                         | Quaternary ammonium salt | 1130                 | 91.1                                |
|                         | Aliphatic amine fatty acid condensate | 4000              | 84.5                                |
| Thiourea                | Thiourea                  | 150                  | 65.1                                |
|                         | N-cyclohexyl thiourea     | 313                  | 64.9                                |
|                         | 1,3-Diethyl thiourea      | 246                  | 29.5                                |
|                         | 1,3-Dihexyl thiourea      | 487                  | 88.0                                |
| Alkynes                 | Methyl propargyl alcohol  | 112                  | 81.2                                |
|                         | Dipropargyl sulfide       | 168                  | 80.5                                |
|                         | Acetylene propyl disulfide | 220                | 96.3                                |
| Inorganic salts         | Sodium chloride           | 117                  | 17.3                                |
|                         | Potassium bromide         | 180                  | 14.6                                |
|                         | Potassium iodide          | 330                  | 79.7                                |

Table 2. The corrosion inhibition effects of some organic and inorganic compounds in sulfamic acid.

3. Inhibitors for near-neutral solution

The neutral medium includes circulating cooling water, boiler water, heating water, washing water, oil and gas field injection water and neutral salt water, etc., and the application of corrosion inhibitor is mainly in circulating cooling water system. During the operation of the cooling water in the circulating water system, the concentration of harmful ionic dissolved in the water increases with the continuous evaporation of water, which resulting in deterioration of the quality of the cycle water, and fouling and corrosion of the heat exchanger and the cooling tower. In the open circulating cooling water system, biological slime caused by the microbial growth can also accelerate the local corrosion of metal.
The washing water and the neutral salt water systems, which are similar to the circulating water, will not be introduced in this section. The corrosion inhibitors for boiler water and water injection of oil and gas fields will be introduced in Sections 4 and 5, respectively.

### 3.1 Cooling water inhibitor

We can select water treatment agents according to the Ryznar index of cooling water or the possible problem. For example, zinc-phosphonate salts as water treatment agents can be chosen for serious erosion in circulating cooling water system, while polyacrylic acid, hydrolyzed polymaleic anhydride, or phosphonate can be used when a large number of scaling has occurred. As the limited compounds in the figure, it cannot be used as a standard method for choosing the right agents. However, it provides the vital reference for the design of the cooling water treatment system.

The complex corrosion inhibitors used in the neutral medium include chromate, phosphate, alkaline zinc/organic, molybdate, silicate, and organic programs. Formulations and chemical programs of some examples are discussed in this section.

#### 3.1.1 Chromate programs

The chromate programs are based primarily on the zinc and chromate mixture, with the ratio of \( \text{CrO}_4^{2-} : \text{Zn}^{2+} \) from 6:1 to 8:1, and the chromate reserve varies from 10 to 25 ppm. If low or ultralow chrome program is employed, the ratio of \( \text{CrO}_4^{2-} : \text{Zn}^{2+} \) is typically 1:1, and the chromate reserve is from 3 to 8 ppm, respectively. In order to lower the health and environmental hazard by chromate, polyphosphate, phosphonate, or polyacrylate is often added as well. The level of zinc or other possible inhibitor is correspondingly raised for compensation.

A typical “standard” formulation for a chromate product that may be used as shown in Table 3, for example, in a large coastal petrochemical facility, is described here. This program formulation will tend to be dosed continuously to achieve a 35–50 ppm product reserve in the recirculating cooling water. The pH of the cooling water is typically 6.0–7.0.

#### 3.1.2 Stabilized phosphate programs

In essence, stabilized phosphate programs involve the treatment of controlling ratios of oxygen and phosphate or phosphorus and phosphate and also the other inhibitors combining with a suitable “stabilizing” polymer. Various halogen-stabilized polymers are usually provided. Under prescribed operating conditions, this program can often provide excellent corrosion inhibition.

| Chromate program formulation | w/w % |
|------------------------------|-------|
| Sodium dichromate, dihydrate  | 50    |
| Chromic acid                 | 1     |
| \( \text{H}_3\text{PO}_4 \), commercial acid | 8 |
| \( \text{ZnCl}_2 \)           | 11    |
| HEDP                         | 14    |
| Water                        | 16    |
| Total                        | 100   |

Table 3. A typical "standard" formulation for a chromate product.
In most hard waters, the typical O:P ratio is 2:1, whereas in lower hardness waters it is 3:1. Typically, the total unfiltered O-P$\text{O}_4^{3-}$ reserve is at the concentration of 10–15 ppm. Some “stabilized phosphate” programs contain zinc, which may also be operated at higher pH levels. A formulation for a steelwork or fertilizer plant is shown in Tables 4 and 5, and the pH value of the cooling water is 6.5–7.0, perhaps up to pH 7.5.

This program formulation will tend to be dosed continuously to achieve a total phosphate reserve in the recirculating cooling water based on calcium hardness (as ppm Ca$\text{C}_3$) as shown in Table 6.

### 3.1.3 Alkaline zinc/organic programs

With the growing concerns of the hazard of over phosphate levels in the environment, it has resulted in the development of many programs with lower concentration of PO$_4^{3-}$, thus come out various combinations of zinc and polymers.

| The formulation of phosphate program A | w/w % |
|--------------------------------------|-------|
| KOH, commercial solution | 40 |
| H$_3$PO$_4$, commercial acid | 15 |
| TKPP, commercial solution | 15 |
| TTA, commercial solution | 1 |
| AA/AMPS | 7 |
| Water | 22 |
| Total | 100 |

Table 4. A typical formulation of phosphate program A.

| The formulation of stabilizer program B | w/w % |
|----------------------------------------|-------|
| NaOH, commercial solution | 15 |
| PCA | 10 |
| PAA | 15 |
| AA/AMPS | 15 |
| Water | 45 |
| Total | 100 |

Table 5. A typical formulation of phosphate program B.

| Calcium hardness (ppm) | Product A required (ppm) | Product B required (ppm) | Total PO$_4^{3-}$ in system (ppm) |
|------------------------|--------------------------|--------------------------|----------------------------------|
| 300                    | 100                      | 30                       | 16                               |
| 600                    | 85–90                    | 45                       | 14                               |
| 900                    | 70–75                    | 60                       | 12                               |
| 1200                   | 60–65                    | 75                       | 10                               |

Table 6. The requirement of product A and B for different concentrations of calcium hardness.
In addition, these low $\text{PO}_4^{3-}$ programs have been designed to operate at higher pH levels than that of the stabilized phosphate programs, which reduces the risk of pH upset and iron phosphate deposition. Thus, these treatments have been called alkaline phosphate, alkaline zinc, or zinc/polymer phosphonate programs. The improved deposit control agents and phosphate/zinc stabilizers have promised these programs to operate with high levels of calcium (up to 1200 ppm) and high pH (up to 9.0).

Some key features of these programs are discussed here:

- **Alkaline phosphate programs**: These programs use the reverse ratios of phosphate compared with stabilized phosphate. Typically, the O/P ratio is 1:2, with about 5 ppm $\text{PO}_4^{3-}$ at 100 ppm alkalinity in the cooling water; it is also possibly down to 2 ppm $\text{PO}_4^{3-}$ at 300 ppm alkalinity.

- **Alkaline zinc programs**: These types of programs tend to combine O-PO$_4^{3-}$ and phosphonate, together with a good scale inhibitor (CaCC$_3$)/dispersant and some zinc salt.

- **Zinc/polymer/phosphonate programs**: Here the $\text{PO}_4^{3-}$ is completely removed and substituted with additional organic compounds.

- **Zinc/phosphate/organic programs**: These types of formulations try to incorporate the best treatments and also to operate under more difficult and stressful conditions.

Some examples of formulations were designed to operate with the cooling water products reserving of around 100 ppm as shown in Tables 7 and 8, and the typical pH ranges of these programs are shown in Table 9. These types of formulations were applied in a wide range of general industrial field and comfort cooling systems.

### 3.1.4 Molybdate programs

Most formulators combine molybdate with zinc, orthophosphate, or phosphonate to reduce the cost of sodium molybdate, which maintains the excellent

| Basic formulation materials | Alkaline PO$_4^{3-}$ (%) | Alkaline Zn (%) | Zn/polymer/phosphonate (%) |
|-----------------------------|--------------------------|----------------|---------------------------|
| $\text{H}_3\text{PO}_4$, commercial acid | 5 | 10 | — |
| $\text{H}_2\text{SO}_4$, commercial acid | — | — | 4 |
| TKPP | 6 | — | — |
| $\text{ZnCl}_2$ | — | 5 | 5 |
| HEDP | 5 | 5 | 10 |
| SSMA | 10 | 5 | — |
| TTA, commercial solution | 1 | 1 | 1 |
| PAA | — | — | 5 |
| Water | 73 | 74 | 75 |
| Total | 100 | 100 | 100 |

**Table 7.**
The typical formulation of alkaline zinc/organic program.
corrosion inhibition properties of molybdate. Azole and polymers are also added for this purpose. The relatively high levels of azoles in these formulations are required to make sure that the finished products are strong alkaline. Typically, the reserve of molybdenum in recirculating cooling water for such blended products is on the order of 2–5 ppm. Molybdate has a comparatively low aquatic toxicity, and it is considered as a safe alternative to replace chromate. However, in the United States (partly in response to the possible pressures on the reduction of Mo in wastewater), new formulations have been developed in recent years that perform equally well but with <1.5 ppm Mo.

Two examples of traditional molybdate formulations are shown below. Formulation A is designed for lower hardness makeup waters (i.e., 50–100 ppm or thereabout). Formulation B is designed for higher hardness makeup waters (i.e., 100–200 ppm or thereabout). Both of the formulations are designed to provide excellent corrosion inhibition and deposit control in comfort cooling systems, with a cooling water reserve of about 75–125 ppm. Formulation A will yield ~4.0 ppm Mo, and the operating pH is around 7.5–8.5, while Formulation B will yield ~2.5 ppm Mo with the operation pH of 8.0–9.0 (Table 10).

For those closed circuits, which in reality are semi-open systems, good corrosion control has been obtained by changing from a nitrite-based program to a molybdate program and maintaining the Mo reserve of 8–10 ppm.

### 3.1.5 All organic programs

These programs have become popular and diverse since the presence of improved DCAs, phosphonates, HPA, and other organic inhibitors. They have been widely available since the mid-1980s. They can successfully operate under a

| Basic formulation materials          | Zn/phosphate organic compound (%) |
|-------------------------------------|-----------------------------------|
| $\text{H}_3\text{PO}_4$, commercial acid | 10                               |
| $\text{ZnCl}_2$                      | 5                                 |
| PBTC                                | 5                                 |
| AA/AMPS                             | 5                                 |
| TTA, commercial solution            | 1                                 |
| PAA                                 | 6                                 |
| MA/EAA/VA                           | 6                                 |
| Water                               | 62                                |
| Total                               | 100                               |

Table 8. The typical formulation of Zn/organic program.

| Programs                          | pH range |
|-----------------------------------|----------|
| Alkaline phosphate                | 8.0–9.0  |
| Alkaline zinc                     | 7.0–8.0  |
| Zinc/polymer/phosphonate          | 7.5–8.5  |
| Zinc/phosphate/organic            | 7.5–9.0  |

Table 9. The typical pH ranges of these programs.
variety of operating conditions at high pH level, without the need of acid dosing. It means the operators can increase the cycles of concentration. In addition, this kind of program type is suitable for employing in small industrial and comfort cooling systems, where acid or continual and precise analytical control is not involved.

An example of the all organic program is given below. Typically, this program would be used at the concentration of 75–125 ppm, depending on operating conditions. The pH range is from 7.5 to 9.0, and this formulation is suitable for use with oxidizing biocides, such as bromine (Table 11).

There are numerous permutations of all organic formulations. Formulations containing 6–12% POCA perform good results at the presence of high chlorides. Some formulations also incorporate phosphate-polymer constituent.

### 3.1.6 Soft and lean water and environmental programs

Acceptable cooling water programs usually use either lean water, with very low natural hardness, or ion-exchange softened water as a makeup source. In order to minimize the deposits of calcium carbonate, it must require softened water, of which the total hardness (TH) should be <5–10 ppm, to act as the makeup water

| Basic formulation materials                  | Formulation A (%) | Formulation B (%) |
|---------------------------------------------|-------------------|-------------------|
| NaOH, commercial solution                   | 7                 | 16                |
| MA/EA/VA                                    | 6                 | 6                 |
| ATMP                                        | 4                 | 6                 |
| AA/AMPS                                     | —                 | 6                 |
| TTA, commercial solution                    | 4                 | 4                 |
| PEG                                         | 2                 | 2                 |
| Sodium molybdate solution                   | 25                | 16                |
| Water                                       | 52                | 44                |
| Total                                       | 100               | 100               |

Table 10. Two examples of traditional molybdate formulations.

| Basic formulation materials                  | All organic formulation (%) |
|---------------------------------------------|-----------------------------|
| NaOH, commercial solution                   | 17                          |
| POCA                                        | 6                           |
| HPA                                         | 6                           |
| MEA                                         | 1                           |
| HEDP                                        | 6                           |
| PAA                                         | 6                           |
| TTA, commercial solution                    | 4                           |
| PEG                                         | 54                          |
| Total                                       | 100                         |

Table 11. An example of the all organic program.
according to some authorities. For comfort cooling systems, the presence of calcium carbonate deposits can in turn increase the risk of *Legionella* proliferation.

There is a tendency to operate cooling systems at high cycles of concentration with lean waters, perhaps 10–15 times COC, depending on the particular circumstances (including the limitation of COC for the cooling system). It is not only considering the economic benefits but also reducing the inherent highly corrosive nature in most low-calcium waters. A further benefit is that it may permit the presence of sufficient calcium to serve as a corrosion inhibitor in combination with a silicate, phosphate, or phosphonate formulation component with high COC.

Various programs exist to provide satisfactory corrosion inhibition and good deposit control. The formulations include the inhibitors noted previously. It is important that the selected type of formulation must match the operating conditions because sludge may form in the cooling system with numerous cycles. Also, if bromine is used, certain organic inhibitors may be oxidized, thus compromising the program’s effectiveness with the long retention times. The formulations may also be modified to remove all metals and phosphorus-containing compounds. A typical formulation is shown in Table 12. This is designed to be used at 125–175 ppm reserve in a cooling water system operating at high COC.

### 3.1.7 Closed-loop programs

There is a wide range of metals used in the construction of closed-loop circuits, and the usual differences are the properties of the circulating water (ranging from deionized water to glycol mixtures to brine water). As a consequence, it is not possible to devise a single water treatment formulation that satisfies the requirements of all closed-loop circuits. In addition, some formulators add oxygen scavengers or indicator dyes in their blends additionally. An example of a formulation suitable for a closed-loop circuit, which is primarily for carbon steel construction, is as shown in Table 13. The minimal whole product reserve to be maintained in the closed-loop circuit ranges from 350 to 700 ppm (calculated as nitrite).

### 3.2 Hot-water inhibitor

The function of the oil well heat-tracing system is to prevent the oil temperature at the oil well exit from decreasing rapidly and to ensure that the oil production

| Basic materials                  | Formulation (%) |
|----------------------------------|-----------------|
| NaOH, commercial solution       | 10              |
| TKPP, commercial solution       | 5               |
| Sodium silicate                 | 25              |
| EDTA, commercial solution       | 6               |
| MA/EA/VA                        | 4               |
| PAA                             | 5               |
| TTA, commercial solution        | 3               |
| PEG                             | 2               |
| Water                           | 40              |
| Total                           | 100             |

*Table 12.*

*A typical formulation for soft and lean water.*
fluid flows normally to the gas collection station. Hot-water continuous circulation, many sources of water supply, and high operating temperature will cause severe corrosion and scaling in the heat-tracing system. In the most corrosive areas, some pipelines are even perforated once a week, which brings great hidden dangers to the normal production of oil wells and also causes a large energy waste.

Hot-water boilers and heating systems generally use alkaline chemicals for water treatment to prevent corrosion and fouling of boilers and heating systems. However, due to the increasing use of heating equipment made of copper and aluminum in heating systems, corrosion is very serious under alkaline water conditions. In particular, radiators made of aluminum are often perforated by alkali corrosion in less than one heating period. Therefore, if there is heating equipment made of copper or aluminum in the hot-water boiler and heating system, it is necessary to add additional copper and aluminum corrosion inhibitor, which greatly increases the cost of water treatment.

4. Inhibitors for alkaline solution

4.1 Boiler water inhibitors

Supplemental water for boilers should be chemically treated in advance, for lowering the possibility of corrosion and scaling to increase the heat transfer effect. Steam is often needed for power generation, thus deposition of SiO$_2$ on the turbine blades is inevitable if enough silicon component is contained in supplemental water. It is necessary to control the scaling by getting rid of the Ca$^{2+}$ and Mg$^{2+}$ with different kinds of methods, such as by ion-exchange resin and apposite precipitants. In order to control the corrosion process, the essential treatments include degassing, adding alkali and using corrosion inhibitor.

4.1.1 Extrude dissolved O$_2$ and CO$_2$

If residual dissolved O$_2$ in the supplemental water obeys stoichiometric ratio with the metal ions in the boiler system under the conditions of high pressure, it will cause serious pitting of the metal tubes. Degassing of the supplemental water and then adding of appropriate scavenger, such as Na$_2$SO$_3$ and N$_2$H$_4$, is the effective method for deoxygenation. The acceptable concentration of O$_2$ should be kept lower than 0.005 ppm. Degassing may cause the reduction of CO$_2$ content, especially if the supplemental water is pre-acidified to release H$_2$CO$_3$ from the dissolved

| Basic materials                  | Closed-loop formulation (%) |
|----------------------------------|-------------------------------|
| NaOH, commercial solution       | 15                            |
| Borax                           | 6                             |
| Sodium silicate                 | 8                             |
| Sodium nitrite                  | 30                            |
| PAA                             | 3                             |
| TTA, commercial solution        | 2                             |
| Water                           | 36                            |
| Total                           | 100                           |

Table 13. A typical formulation for closed-loop program.
carbonates. \( \text{H}_2\text{CO}_3 \) is aggressive to steel without dissolved \( \text{O}_2 \), but adding of alkali into the boiler water will mitigate the corrosion raised by \( \text{CO}_2 \).

Iron return pipe systems undergo critical corrosion; thus, if the concentration of \( \text{CO}_2 \) in the boiler water is high enough, the iron carbonate will be formed, and it changes to ferrous hydroxide and \( \text{CO}_2 \) further, which is the obvious corrosive medium. The Cu-Al cooling system also endures corrosion when both of the dissolved \( \text{O}_2 \) and \( \text{CO}_2 \) are together, but the Cu base alloys are not easily attacked when there is a lack of \( \text{O}_2 \). As \( \text{CO}_2 \) is not depleted at all during the corrosion stage, it will gather inevitably in the boiler during the process of adding supplemental water, and the concentration of \( \text{CO}_2 \) may decrease if with occasional venting.

4.1.2 Adding alkali

Addition of alkali into boiler waters is a routine operation for many boilers under high pressure in the United States and abroad. Supplemental water for a boiler with high pressure is restricted to the minimal pH of 8.5 to reduce the corrosion of iron at room temperature, and the acceptable pH value should be at the range of 9.2–9.5. For Cu alloys, the optimal pH value is from 8.5 to 9.2. As both iron and Cu alloys are usually used in boiler systems, the balanced pH value range is suggested to be between 8.8 and 9.2. Adding buffer ions, such as phosphate, will restrict the rise of pH value. Such ions also have advantage of preventing high concentrations of hydroxide in the boiler waters, which can give rise to stress corrosion cracking of any section of the boiler under high external stress. It reported that when pH value of the boiler water is 9.5–10.0, phosphate with the concentration of 5–10 ppm was more efficient than either sodium hydroxide or ammonia in slowing down the corrosion rate of boiler tubes under high-pressure conditions.

4.1.3 Adding inhibitors

It is feasible to select suitable inhibitors for inhibiting two kinds of typical corrosion in boiler systems, mainly stress corrosion cracking and return pipe systems corrosion, and the former can be restricted by supplement of phosphate. Corrosion raised by dissolved \( \text{CO}_2 \) in steam condensate can be limited by supplying volatile amines for the boiler water. Two kinds of characteristic volatile amines are chosen for neutralizing amines and film formation. The former group species contain benzylamine, cyclohexylamine, or morpholine. When one provided into the boiler water with adequate amount, it can neutralize \( \text{CO}_2 \) and alkalinize the steam condensate, thus dropping the corrosive rate of the condensate. The latter group species include volatile hexadecylamine, octadecylamine, or dioctadecylamine, which is the typical film-forming inhibitor, which prevents corrosion from constructing the stable protective film on the surface of the condenser. The film-forming amine is regarded as more apposite to the circumscription of the inhibitor, while others are only used mainly for neutralizing actually.

4.2 \( \text{O}_2 \) scavenger

\( \text{O}_2 \) scavengers are reagents which are often used to get rid of the dissolved \( \text{O}_2 \) from water through reduction reactions, thus prohibiting the corrosion ascribed to the \( \text{O}_2 \) in water. For this purpose, the desirable characters of \( \text{O}_2 \) scavengers should be (1) excellent reducing ability against \( \text{O}_2 \), (2) no violently actions of the thermal decomposition products and the final reaction products with \( \text{O}_2 \) countering the equipment.
The species and reagent names of $O_2$ scavengers are displayed in Table 14 [4]. The optimal reagent is hydrazine, but it is limited by its highly toxic properties. Thus, the replacement for hydrazine was inevitable.

4.3 Corrosion inhibitors for condensate line

As mentioned before, volatile amines for neutralizing and amines for film formation are also two kinds of classic corrosion inhibitors for prohibiting the corrosion of condensate lines. Volatile amines prevent the erosion by adjusting the pH values of the condensates, while water barrier at the surface of metal can be formed attributed to the amines for film formation, which block the touching between metals and the aggressive substances, for example, $O_2$ and $CO_2$.

4.3.1 Inhibitors used in condensate lines of boilers under low pressure

Under low pressure, the main aggressive substances in the pipelines of boilers are $O_2$ and $CO_2$. The existence of slight $CO_2$ in the condensation product will decrease the pH, which will accelerate metal corrosion. Thus, volatile amines for neutralizing and amines for film formation are provided as the suitable corrosion inhibitors. The use of volatile amines for neutralizing displays the wonderful inhibition effect, but the efficiency is discounted at the presence of $O_2$. Amines for film formation can adsorb on the surface of the metal and then construct the hydrophobic protective film even on low concentration. However, once the corrosion products are covered on the surface of the metal, it will take long time to form the protective film. Therefore, the synergistic effect of using both of these two amines should be considered.

4.3.1.1 Neutralizing amines

Cyclohexyl amine ($C_6H_{13}N$), monoisopropanol amine [$NH_2CH_2CH(CH_3)OH$], morpholine ($C_4H_9NO$), and ammonium hydroxide ($NH_3·H_2O$) are usually used for neutralization reaction in boiler systems. They are also dosage by dose for condensate lines. The amine is complemented to the supplemental water and then mixed with the water vapor produced from the boiler. When the water vapor cools down in the condensate line, the amine will dissolve in condensation product and neutralize $CO_2$ ($H_2CO_3$). Therefore, the pH value of the solution in the condensate line will be raised, and the crisis of metal corrosion will be eased. Table 15 displays the needed

| Species                  | Reagent names                      |
|-------------------------|------------------------------------|
| $N_2H_4$-based $O_2$ scavengers | $N_2H_4H_2O$  
                             | $N_2H_4H_2SO_4$  
                             | Hydrazine phosphate             |
| $SO_3^{2-}$-based $O_2$ scavengers | $NaSO_3$  
                               | $NaHSO_3$  
                               | $Na_2S_2O_3$                   |
| Other $O_2$ scavengers  | Saccharides  
                             | Tannins  
                             | Hydrazide  
                             | L-ascorbic acid  
                             | Hydroquinone  
                             | Alkanol amines |

Table 14. Some species of $O_2$ scavengers.
concentrations of amines for the neutralization reaction when the concentration of \( \text{CO}_2 \) is 1 mg/L. \( \text{NH}_3\cdot\text{H}_2\text{O} \) is efficient for the neutralization reaction for \( \text{CO}_2 \) revealed in Table 15; however, it is not appropriate for the copper condensate lines in boilers because it may accelerate copper corrosion.

### 4.3.1.2 Amines for film formation

Alkylamines (R-NH\(_2\)), where R is alkyl group which contains 10–20 carbon in the alkyl chain, are considered as the film-forming corrosion inhibitors. Octadecylamine (ODA) has 18 carbon atoms in the alkyl chain and is the typical amine for film formation. As ODA cannot dissolve in water, emulsifiers are usually needed for dispersion. The -NH\(_2\) in ODA can adsorb on the surface of the metal and then construct single or several layer molecular adsorption coating, which is hydrophobic and can block the aggressive medium.

The influencing factors, such as the concentration of ODA, M-alkalinity of supplemental water, temperature of condensation product, and so on, will affect the corrosion inhibition effect of ODA. For instance, under the concentration of 25 mg/L ODA in the supplemental water and in order to control the corrosion rate of iron lower than 10 mg/dm\(^2\)-day, it will extend 1 day when the M-alkalinity of CaCO\(_3\)/L raise from 50 mg (2 days) to 100 mg (3 days). Therefore, the beginning corrosion inhibition effect of ODA is affected as the increase of the M-alkalinity in the supplemental water. However, it will show slight influence after the ODA film is formed. In addition, it has also reported that ODA displays the superior corrosion inhibition effect lower than 45°C. ODA performs the wonderful inhibition effect when the dissolved O\(_2\) is as low as 0.2 mg O/L; however, the inhibition effect is obviously hazarded when the concentration of dissolved O\(_2\) is as high as 3 mg O/L. Therefore, minimizing transfer of dissolved O\(_2\) from boiler to the condenser by degassing and/or O\(_2\) scavengers is extremely important to enhance the corrosion inhibition effect of ODA.

### 4.3.1.3 Combined use of neutralizing amines and amines for film formation

A high amount of neutralizing amine is needed to prohibit the corrosion behavior of condensing pipes effectively if the M-alkalinity of supplemental water is high; amines for film formation demand a relatively long period to fabricate the hydrophobic deposited film for preventing the corrosion of the metal. Therefore, the combining of these two kinds of amines must improve the corrosion inhibition enormously.

**Table 15.** The species and amounts of amines for neutralizing \( \text{CO}_2 \).

| Neutralizing reagent | Needed concentrations of amines for the neutralization reaction for 1 mg/L \( \text{CO}_2 \) (mg/L) |
|----------------------|--------------------------------------------------|
| \( \text{NH}_3\cdot\text{H}_2\text{O} \) | 0.4 |
| \( \text{C}_6\text{H}_{13}\text{N} \) | 2.3 |
| \( \text{NH}_2\text{CH}_2\text{CH(\text{CH}_3)}\text{OH} \) | 1.8 |
| \( \text{C}_4\text{H}_9\text{NO} \) | 2.0 |

**Table 16** displays the corrosion inhibition synergistic effect by combining use of two kinds of the amines. With the treatment of neutralizing amine, the corrosion rate of iron drops accompanying the raise of the pH value; with the treatment
Formulation of Corrosion Inhibitors
DOI: http://dx.doi.org/10.5772/intechopen.88533

of amines for film formation, the corrosion rate cut down when the pH value is reduced further. The collaborative processing outstandingly enhances the corrosion inhibition effect. Even with dissolved O$_2$ in the condensing pipes, the combined treatment behaves the prior corrosion inhibition effect compared to the treatment of only with single filming amine.

4.3.2 Inhibitors used in condensate lines of boilers under moderate or high pressure

As softened water at low temperature is usually provided for boilers under moderate or high pressure, it is not easy to cause the corrosion problems in condensate lines before entering the deaerator. However, the piping and the auxiliary apparatus after the deaerator will erode sometimes as the ill control of water quality or operation of deaerator, which is due to the rise of temperature. Therefore, the pre-control of supplemental water pipeline is as important as that of the condensate line. Neutralizing amines are then selected as the corrosion inhibitors for the supplemental water and stream condensing pipe because they are fit for pH value control and stable at high temperature under moderate or high pressure.

5. Inhibition for oil and gas systems

5.1 Drilling fluid inhibitor

As the high concentration of Cl$^-$ in the oil field sewage, and also the role of CO$_2$, H$_2$S, dissolved oxygen, oil stain and miscellaneous, it results the serious pitting problems. At present, organic amine, organic polyol phosphate complex, imidazole, and their derivatives and long carbon chain amide carboxylate are well used in this field.

5.2 Fracturing acid inhibitor

If the gas field is dominated by carbonate fracture-porosity gas reservoirs, acid fracturing is an important stimulation method to increase the production for such gas reservoirs. Therefore, the corresponding research and application of acid chemical additives, pre-fracturing fluid chemical additives, and fracturing acid inhibitors have become important tasks in the gas field development.

The acid solution strongly corrodes the steel, and the corrosion inhibitor is the key to ensure the smooth operation of the acidification operation. According to the long-term acidification construction experience, the degree of corrosion

| Treatment                  | pH value | Amount of the amines for film formation | Corrosion rate of iron (mg/dm$^2$·day) |
|----------------------------|----------|----------------------------------------|----------------------------------------|
| None                       | 5.3      | 0                                      | 124.5                                  |
| Neutralizing amines        | 6.6      | 0                                      | 78.4                                   |
|                            | 7.0      | 0                                      | 54.8                                   |
| Amines for film formation  | 5.3      | 20                                     | 32.1                                   |
| Combining of both          | 6.6      | 20                                     | 11.2                                   |
|                            | 7.0      | 20                                     | 11.8                                   |

Table 16. The corrosion inhibition synergistic effect by combining use of two kinds of the amines.
inhibition of acid has a recognized standard according to indoor evaluation. It is generally required that the amount of corrosion of steel in an acidizing operation does not exceed 98 g/m²; in deep well operations, it is acceptable to not exceed 245 g/m²; pitting corrosion shall not occur. Since the 1970s, fracturing acid inhibitors have gradually developed into a variety of varieties. The main types of compounds are amines and their derivatives, pyrenes, acetylenic alcohols, etc., and some nonionic surfactants and alcohol solvents are added for the fabrication of a multicomponent formulation. In order to improve the temperature resistance, iodide or telluride is also used as a synergist, and the well temperature can be as high as 204°C to achieve the degree of corrosion inhibition required for acidification construction.

5.3 Oil and gas well inhibitor

Oil well acidification is performed through injecting hydrochloric acid, soil acid (hydrofluoric acid and hydrochloric acid mixture), or other acid solution into stratum, by means of acidic fracturing equipment. After the dissolution of the rock by the acid solution, the enlargement of the penetration channel of the rock in the reservoir, and the treatment of the blocks in the seepage channel or the cause by artificial cracks, the gas passages will be unblocked to achieve the purpose of increasing oil and gas production. For the acidification of carbonate oil and gas layers, these are the following chemical reactions.

Lime petroleum gas rock formation reacts with hydrochloric acid:

\[
\text{CaCO}_3 + 2\text{HCl} \rightarrow \text{CaCl}_2 + \text{H}_2\text{O} + \text{CO}_2 \uparrow
\]  

Dolomite oil and gas layer reacts with hydrochloric acid:

\[
\text{MgCa(\text{CO}_3)_2} + 4\text{HCl} \rightarrow \text{CaCl}_2 + \text{MgCl}_2 + 2\text{H}_2\text{O} + 2\text{CO}_2 \uparrow
\]  

The reaction of sandstone oil and gas layer with soil acid solution:

\[
\text{CaAl}_2\text{Si}_2\text{O}_8 + 16\text{HF} \rightarrow \text{CaF}_2 + 2\text{AlF}_3 + 2\text{SiF}_4 + 8\text{H}_2\text{O}
\]  

Hydrofluoric acid reacts with carbonate:

\[
\text{CaCO}_3 + 2\text{HF} \rightarrow \text{CaF}_2 + 8\text{H}_2\text{O} + \text{CO}_2 \uparrow
\]

From Eqs. (3) and (4), CaF₂ is formed in the reaction of hydrofluoric acid with sandstone. When the concentration of the acid solution is lowered, it precipitates and blocks the pores. While the acid solution contains HCl, it can suppress or reduce the sinking of CaF₂ precipitate. This is why hydrofluoric acid and hydrochloric acid are mixed in the soil acid solution. The commonly used soil acid solution is 7% HCl + 3% HF or 12% HCl + 6% HF, depending on the clay composition of the sandstone reservoir containing silicate, quartz or carbonate.

From Eqs. (1) and (2), the higher the concentration of hydrochloric acid, the stronger the ability to dissolved rocks and the less volume of acid required to dissolve a certain volume of carbonate and the residual acid solution, thus the easier it is to be discharged from the formation and the favorable oil and gas output; in addition, high concentration of hydrochloric acid has a longer chemical activity time. Therefore, the concentrated hydrochloric acid solution is chemically activated before it is consumed, and its distance between the
rock formations is relatively far, and the effect of acidification of the oil wells for improving the production is better. It is popular of acidizing oil wells with high concentration of hydrochloric acid and increasing oil and gas production. However, the corrosion problem caused by the acidic solution at high temperature must be solved.

From the 1960s to the 1970s, the oil wells were shallow, generally between 1000 and 2000 m, and the downhole temperature was not high. The acidizing corrosion inhibitors in oil well mainly contained formaldehyde, urotropine, arsénious acid (arsenic) and other compounds. Later, after the compound test, two or more corrosion inhibitors were compounded, such as urotropine + potassium iodide, urotropine + OP, butynediol + potassium iodide, butynediol + OP, butynediol + potassium iodide + OP, etc. The HCl concentration should be not more than 15% (10% in general) and the well temperature does not exceed 80°C. Due to the low acid concentration and temperature, the composite corrosion inhibitor can make the corrosion rate of carbon steel within the allowable conditions of construction. During this period, the acidification operation is not much, and the acid corrosion inhibitor research has just started.

After 1970s, the ultra-deep wells were above 6000 m, and the downhole temperature was as high as 180–200°C. It has been discovered that the acidification of oil wells with high concentration of hydrochloric acid can significantly increase the effect of oil and gas production. However, in such high-temperature ultra-deep wells, when the acidification is carried out with concentrated hydrochloric acid solution, the acidification inhibitor must be required to protect the mild steel in such concentrated hydrochloric acid at 200°C. Therefore, it played a driving role for the research and development of oil acidification inhibitors.

Currently, a variety of alkyl pyridine and quinoline-based benzyl quaternary ammonium salt substances can well disperse in hydrochloric acid and soil acid solution. They can become clear and transparent brown liquid and show very good corrosion inhibition for carbon steel in hydrochloric acid or soil acid solution. They have certain corrosion inhibition effect on ferric ions and are highly corrosive to H₂S. They are the concentrated hydrochloric acid acidification corrosion inhibitors with high-temperature resistance of 180–200°C. The ketone amine aldehyde condensate compounded with alkynol compound has good dissolving and dispersing property in hydrochloric acid. It has good corrosion inhibition effect on carbon steel in a hydrochloric acid solution at 105–180°C. The alkynyl oxymethylamine modified derivative also has good corrosion inhibition effect on carbon steel in hydrochloric acid or soil acid. The combination of a ketone aldehyde amine condensate, an alkynyl alcohol and a cationic surfactant and a solvent to prepare a solution, is suitable for 15–28% HCl solution at 130°C, which has been applied in oil fields. Growcock and Lopp [5] developed a well-acidified corrosion inhibitor “PPO” (3-phenyl-2-propynyl alcohol), which is used in high-temperature downholes with 1–9 mol/L hydrochloric acid. The corrosion inhibition effect is as high as 99%. Table 17 lists the types of corrosion inhibitors commonly used in oil fields.

### 5.4 Oil field-produced water treatment inhibitor

Metal equipment in oil field water injection systems, such as various heat exchangers, pumps, valves, oil casings, and storage tanks, are corroded by sewage, causing corrosion and perforation of equipment. It will cause serious impact on production and even force the oil well to stop production. In the construction of oil well acidification, the development of ultra-deep wells and extremely deep wells puts higher requirements on corrosion inhibition performance.
It is possible that the effective corrosion inhibitor for industrial circulating cooling water may not be suitable for the treatment of oil field sewage, which containing large concentration of Cl\(^-\). The typical oil fields in China, such as Shengli, Zhongyuan, Jianghan, Dagang, and Huabei Oilfield, are with the NaCl up to around 200,000 mg/L in the sewage, which also include CO\(_2\), H\(_2\)S, dissolved oxygen, oil stain and miscellaneous, etc. CT2-7 corrosion inhibitor (the main component is organic amine) is mixed with HEDP and 1227, which is the promising reagent for oil field.

### 6. Results and discussion

Corrosion inhibitors are classified into inorganic corrosion inhibitors and organic corrosion inhibitors according to their composition. Inorganic corrosion inhibitors passivate the metal on the surface of the anode by its inorganic anion or prevent ions from the anode portion of the metal surface from entering the solution, thereby inhibiting corrosion. The organic corrosion inhibitor mainly forms a precipitation film by the reaction between a reactive group on the organic molecule and a metal ion generated during the etching process and suppresses the electrochemical processes of the anode and the cathode. They have good adsorption to

| Main chemical composition | Acid-base concentration (%) | Temperature range (°C) |
|---------------------------|----------------------------|-----------------------|
| Pyridine slag quaternary ammonium salt | 15–20 HCl | 70–90 |
| Coal tar pyridine residue extract | 15–20 HCl | 80–120 |
| Coal tar pyridine residue extract adding dyeing agent | 15–28 HCl | 90–180 |
| Pyridine hydrochloride residue and surfactant | 15–20 HCl | 80–120 |
| Ketoamine aldehyde condensate | 15–28 HCl | 90–150 |
| Imidazoline | 15 HCl | 90 |
| Imidazoline plus formaldehyde | 15–28 HCl | 80–150 |
| Pyridine hydrochloride slag + alkyl sulfonate | 15–28 HCl | 90 |
| MBT, thiourea, OP, and other pyridine residues | 7 HCl + 3 HF | 30–70 |
| Benzyl quaternary ammonium salt | 15–28 HCl | 90–190 |
| Pyridine derivatives, formaldehyde, etc. | 15–28 HCl | 90–120 |
| Cyclohexanone aniline | 15–28 HCl | 90–180 |
| Ketoamine condensate | 15–28 HCl | 90–150 |
| Cyclohexanone aniline, etc. | 15–28 HCl | 90–160 |
| Pyridine quaternary ammonium salt, etc. | 12 HCl + 6 HF | 120 |
| Quinoline quaternary ammonium salt, etc. | 12 HCl + 6 HF | 150 |
| Alkylpyridine quaternary ammonium salt and other components | 15–28 HCl | 196 |
| Ketoamine aldehyde condensate, alkynol, etc. | 15–28 HCl | 90–130 |
| Imidazoline derivative | 15 HCl | 90–100 |
| Imidazoline | 15 HCl | 90 |
| Pyridine quaternary ammonium salt, etc. | 15–28 HCl | 90–120 |

*Table 17. Acidification inhibitors commonly used in oil fields and their application conditions.*
the metal surface in the corrosive medium. Many corrosion inhibitors containing heteroatoms rely on functional groups to adsorb on the metal surface. The nitrogen atoms in the corrosion inhibitor become cations after quaternization and are easily adsorbed by the negatively charged metal surface to form a monomolecular protective film. The charge distribution and interfacial properties of the metal surface tend to stabilize the energy state of the metal surface. The process can increase the activation energy of the corrosion reaction, slow down the corrosion rate, and greatly inhibit the discharge of hydrogen ion, inhibit the cathode reaction, and effectively improve the corrosion inhibition efficiency of the corrosion inhibitor.

7. Summary conclusion

Corrosion inhibitors play an important role in metal protection engineering and the national economic construction. Judging from the current anticorrosion of equipment and other industrial fields, the use of corrosion inhibitors is an effective and economical anticorrosion method. The research on the theory, testing technology, and calculation method of inhibitor has made certain progress, which has promoted the development and application of new corrosion inhibitors.

In the future, the mechanism of the corrosion inhibitor and the relationship between the molecular structure of the corrosion inhibitor and the corrosion inhibition effect should be further developed. More complete and specific environmental performance assessment methods need to be proposed; neural networks, density functional theory, and other computer science, quantum chemistry, and other research methods should be better applied to the development and evaluation of new corrosion inhibitors, and the new high-efficiency corrosion inhibitors should be designed and synthesized. In addition, promote green chemistry and research on the corrosion inhibitors with low-cost and non-polluting chromium-free, zinc-free, low-phosphorus, and even phosphorus-free which is the promising development direction of water treatment corrosion inhibitor. The corrosion inhibitors can be made from natural raw materials, thereby expanding the application range. Furthermore, researchers should pay more attention to the development of multifunctional corrosion inhibitors used in different working conditions. It should focus on the development of copolymer corrosion inhibitors and other multi-purpose corrosion inhibitors that have the properties of scale inhibition, biocidal, and biodegradability.
References

[1] Satpati AK, Ravindran PV. Electrochemical study of the inhibition of corrosion of stainless steel by 1,2,3-benzotriazole in acidic media. Materials Chemistry and Physics. 2008;109:352-359

[2] Behpour M, Ghoreishi SM, Salavati-Niasari M, Ebrahimi B. Evaluating two new synthesized S-N Schiff bases on the corrosion of copper in 15% hydrochloric acid. Materials Chemistry and Physics. 2008;107:153-157

[3] Bentiss F, Bouanis A, Mernari B, Traisnel M, Vezin H, Lagrenee M. Understanding the adsorption of 4H-1,2,4-triazole derivatives on mild steel surface in molar hydrochloric acid. Applied Surface Science. 2007;253:3696-3704

[4] Tetsuo H. Kurita Handbook of Water Treatment. Second English ed. Japan: Kurita Water Industries Ltd; 1999

[5] Growcock FB, Lopp VR. The inhibition of steel corrosion in hydrochloric-acid with 3-phenyl-2-propyn-1-ol. Corrosion Science. 1988;28:397-410