

Control of Calcium Carbonate Scale Formation by KDF® 55 Process Medium

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Abstract

KDF 55 process medium is a patented high purity copper/zinc alloy that enhances naturally occurring oxidation-reduction reactions in water. Through these reactions, zinc and hydroxyl ions are released into the water. Scale inhibition is the result of these reactions through two separate but related mechanisms. The first is the direct relationship between pH, carbon dioxide concentration and calcite solubility of a solution. As carbon dioxide degasses from a solution, the pH increases and subsequently the solubility of calcite decreases. As KDF 55 process medium increases the pH through the creation of hydroxyl ions subsequently the solubility of calcite must decrease. The second mechanism involves the blocking of scale growth steps (kinks) by zinc ions dislocated from the medium. Along with this blocking, zinc causes the precipitation of aragonite from the water. Aragonite precipitation does not occur as a hard scale but as loose precipitate that is flushed out of the system. Typical applications use a filtration stage prior to the KDF vessels to trap the precipitated solids that are then washed out of the system during backwash.

A simple bench scale test using two 1000-ml samples of rain and treated water was used to examine the processes involved. Changes in pH, calcium, carbon dioxide and zinc concentrations of the raw and treated samples were monitored over a period of 19 hours. Input of the data generated into the computer modeling program WATEQF enabled the calculation of rates of carbonate mineral precipitation. This test showed that waters treated with KDF 55 process medium have increased rates of carbonate precipitation giving evidence for the hypothesized mechanisms.

Introduction

The control of scale formation has been estimated to cost U.S. industry approximately \$12 billion annually. Historically, scale formation has been inhibited by the addition of chemicals to the water. This has proved to be both costly and time consuming as the water chemistry had to be closely monitored and doses adjusted accordingly. One of the drawbacks to this form of treatment is the chemicals have to be stored on the premises and employees hired and trained to conduct water quality tests. Even if the contractor stores the chemical and has the personnel on hand, he has to make regularly scheduled visits to monitor and maintain the system.

Not until recently have new inroads to scale formation inhibition been made. The newest among these is through the use of KDE 55 process medium. This is a stand alone system that in many instances treats only 10%-20% of the cooling system water. Only occasional monitoring of the system is required and no costly chemicals need be stored.

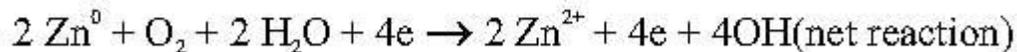
Oxidation-Reduction of KDR 55 Process Medium

Oxidation-reduction of the media is a naturally occurring process. Because the copper and zinc in the alloy are chemically dissimilar and are in direct electrical contact with the water (electrolyte) a galvanic cell is established. Reaction of the more negative metal, zinc, is enhanced along with a partial to complete cathodic protection of the more positive metal, copper.

Reaction between the medium and water occurs through these three basic steps:

1. A neutral zinc ion (Zn^0) from the alloy is oxidized to a positive two valance state; (Zn^{2+}).
2. As a result of the oxidation of Zn^0 to Zn^{2+} , two electrons are released and these flow through the alloy to the cathodic area (Cu)
3. Water in contact with the cathode completes the electric circuit by using the electrons to form hydroxyl ions.

This sequence occurs through the reaction of the alloy with dissolved oxygen and/or other oxidizing agents in the water. The cathodic area of the medium can be much larger as compared to that of the anode. As a result, more water and electrons are made available for reaction. Subsequently, increasing the flow of electrons from the anode increases the release of zinc and hydroxyl ions [Kemmer, 1988]. The set of half cell reactions for this process can be written as:



Experimental

To test the effects that KDE 55 process medium has on scale formation a simple bench scale test was conducted. This test consisted of filling a 9-3/4 inch diameter filter cartridge with one pound of KDE 55 process medium and the remaining void space filled with inert garnet. The filter was attached to a municipal cold water feed line in the laboratory using standard hoses and fittings. An influent (raw) water sample was collected from a sampling port located in advance of the filter. The effluent (treated) sample was collected directly from the discharge end of the filter. In both instances 1000-ml of sample water were collected in acid-washed 1000-ml glass beakers with care being taken not to agitate the water.

Exactly 250-ml of each water sample was removed for analysis and the remaining 750-ml left uncovered and undisturbed for 19 hours. At the end of the 19 hour period the samples were retested. Water quality parameters analyzed were: pH calcium ion concentration, carbon dioxide concentration and zinc ion concentration. Methods used for these analyses were: pH, Standard Method 4500-H. B. (pH meter); calcium ion, HACH Method 8331 (ISE meter); carbon dioxide, HACH Method 8205 (digital titration); zinc ion, Standard Method 3500-Zn F (zincon).

Solubility product constants for the carbonate minerals from the two samples were computed using the geochemical computer modeling program WATEQF developed by the United States Geological Survey. This program only required the input of pH, temperature, calcium ion concentration, zinc ion concentration, temperature and alkalinity. Temperature used were: 15 degrees Celsius for t=0 and 21 degrees Celsius for t=19 hours. The alkalinity used in both instances was 390 mg/l as CaCO₃.

Results /Discussion

Data from the test is included in Tables 1.1 and 1.2 on below. Initially the treated water showed only a slight increase in the pH with a corresponding drop in the carbon dioxide content. The computed solubility product for calcium and zinc carbonate minerals does show some decrease as is expected from the relationship of pH, carbon dioxide content and carbonate solubility.

After 19 hours of being exposed to the atmosphere both samples showed decreases in calcium ion concentration, carbon dioxide ion concentration, and an increase in pH. However, these decreases were more pronounced in the treated sample. Also the treated water sample showed evidence of a fine film of carbonate mineral on the surface that was absent on the raw sample.

The zinc concentration in the effluent water has also decreased indicating that zinc is being either absorbed into the calcium carbonate structure or precipitating itself. It is not known whether this would be through coprecipitation with calcium carbonate or through a separate precipitation reaction. The calculated reaction rate for the precipitation of the carbonate minerals has increased. Comparing this to the decrease in zinc ion concentration gives an indication that the addition of the zinc ions is the primary controlling factor.

Mechanisms for the Control of Scale Formation

In order for calcium carbonate to precipitate out of solution a driving force for the reaction must be present [Nicholson, et.al, 1982]. This driving force can be direct, such as the addition of calcium or carbonate, or

indirect such as an increase in pH or a decrease in carbon dioxide [Nicholson, et.al, 1982].

Metal ions present in the water can also act as a driving force. Previous studies of the influence of impurities on the growth rate of calcite have shown that zinc, even in low concentrations can inhibit calcium carbonate crystal formation [Meyer, 1984]. Foreign ions, such as zinc, influence reaction rates in two different ways. The first being in the solution where they can form complexes with the reaction ions altering both activity coefficients and the rate at which transformation reactions occur [Reeder, 1990].

Secondly, the foreign ion can be adsorbed onto the surface of the reacting solid. If this foreign ion is a cation, such as zinc, it can cause an increase in the surface carbonate concentration [Reeder, 1990]. Adsorption of these foreign ions is preferred at the higher energy sites that are also favored for dissolution and crystal growth [Reeder, 1990]. An 80% inhibition of the growth rate of calcium carbonate at zinc concentrations of 2×10^{-5} mol/l (0.01 mg/l) has been reported [Meyer, 1984].

This same reference also reported that the inhibition of calcite growth can cause the formation of aragonite by sample precipitation at 1×10^{-5} mol/l (0.650 mg/l) zinc [Meyer, 1984]. It is believed that this is how the existing carbonate scale in a system is removed. X-Ray diffraction studies of "muds" found at the bottom of cooling system cold wells showed that they were composed of aragonite. These muds were not present in the systems until after treatment by KDF 55 process medium.

Conclusion

KDF 55 process medium alters the chemistry of water directly inhibiting calcium carbonate scale formation. Inhibition is through two related mechanisms:

1. Dissolution of zinc ions from the medium blocks calcite carbonate growth steps and induces aragonite precipitation. This in effect means that calcium carbonate scale formation in the system stops and any existing scale is removed.
2. An increase in the pH of the water, caused by the production of hydroxyl ions, lowers the carbon dioxide content of the water and consequently the solubility of calcium carbonate. Scale will want to form but the zinc ions will inhibit its formation as a hard scale. Instead, a "soft scale," aragonite, forms that does not adhere to surfaces. The aragonite scale can be removed from the system by simple filtration through a bag or sand type filter.

| | Raw | Effluent |
|-------------------------|--------|----------|
| pH | 7.50 | 7.55 |
| Ca ²⁺ (mg/l) | 83.8 | 85.8 |
| CO ₂ (mg/l) | 93.8 | 84.8 |
| Zn ⁺² (mg/l) | 0.10 | 2.55 |
| K CaCO ₂ | 0.6437 | 0.6748 |
| K ZnCO ₃ | -1.254 | 0.1667 |

| | Raw | Effluent |
|-------------------------------|-------|----------|
| pH | 7.90 | 7.94 |
| Ca ²⁺ (mg/l) | 69.9 | 69.3 |
| CO ₂ (mg/l) | 63.0 | 59.0 |
| Zn ⁺² (mg/l) | 0.10 | 0.243 |
| Rate [dC/dt] CaCO (mg/l/hour) | 0.732 | 0.868 |
| Rate [dC/dt] ZnCO (mg/l/hour) | 0.00 | 0.006 |

References

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Results are from a controlled laboratory test. Actual results may vary slightly from those reported due to differences in water chemistry.