
Corrosion Mechanisms and Mitigation Methods for Effluent Clarifiers

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Introduction

Clarifiers are utilized by various chemical process plants, including the pulp and paper industry. Clarifiers are used to minimize the amount and toxicity of suspended solids in the effluent stream. The clarification process incorporates coagulation, flocculation, and sedimentation. The removal of suspended matter by settling without chemical coagulation is rarely encountered today.

There exist many designs for clarifiers; however, the emphasis of this discussion will be based on the type of clarifier depicted in Figure 1. The walls and floor are fabricated from steel reinforced concrete, while the center well, rake, and associated moving parts of the clarifier are constructed from mild steel.

Although clarifiers are the subject of this paper, much of the corrosion theory can be applied to holding and chemical mixing tanks without rake mechanisms.

Corrosion Mechanisms

Prior to a specific discussion on the mechanism of corrosion of mild steel members in a clarifier, a brief overview of the basic corrosion cell is required. Most people are familiar with the fact that if interconnected dissimilar metals are immersed in a common electrolyte, then the metal higher in the galvanic series (more electronegative or active) will become the anode, or corroding element, and the metal lower in this series (more electropositive or noble) will become the cathode, or noncorroding element. Figure 2 shows a simple electrical model of the corrosion cell, assuming the metal resistance is considered insignificant.

The anode and cathode solution potentials are represented by the voltage source V_a and V_c , respectively. The anode to cathode electrical resistance through the electrolyte is depicted as R_e , and the polarization resistance effects are accounted for by R_a and R_c . Therefore, the corrosion current I_c is defined by Equation (1).

$$I_c = (V_a - V_c) / (R_a + R_c + R_e) \quad (1)$$

Actual metal loss at the anode can be determined from the corrosion current (I_c), Faraday's equivalent for the particular metal of interest, and the time the current is allowed to continue. For example, 1 Amp of current discharging for 1 year from a piece of steel will dissolve approximately 10 kilograms of metal. Many factors play a part in the location and magnitude of the anodic and

cathodic sites. In most instances, the polarization resistances of the anodes and cathodes are the predominant factors in determining the corrosion rate.

In a galvanic cell comprised of zinc and copper in sea water (Figure 3), zinc is the anode and copper is the cathode. If these two metals are not in metallic contact with one another, no current flows in the cell and the metals are said to be open circuited. Using a suitable reference electrode, the open circuit potential of the anode and cathode can be determined. When the metallic circuit is closed, a corrosion process commences and a corrosion current flows from the anode through the electrolyte to the cathode. This current flow causes polarization of these two surfaces which results in a reduction of potential difference between them. This process can be shown in an idealized fashion with an Evans diagram (Figure 4) which indicates the open circuit potential of the anode and cathode, and depicts how polarization tends to bring these two potentials closer together as the current flow increases. If a galvanic cell is short circuited, as is usually the case in naturally occurring corrosion situations, then the anode and cathode potentials come very close to each other and are separated by the potential drop through the electrolyte caused by the passage of current (IR drop). Where a single metal is involved, different conditions and properties of the metal surface will establish local anodes and cathodes such that the model in Figure 2 applies to localized corrosion on a single metal surface.

Utilizing this simple model of a corrosion cell and the associated Evans diagram, it is possible to envisage how and why the corrosion of a metallic structure differs in various electrolytes. Further, this cell can be used to demonstrate the method by which corrosion mitigation techniques reduce the corrosion rate.

Corrosion Mechanisms in Effluent

Unfortunately, it is extremely difficult to categorize the corrosion rate of a particular clarifier, as each pulp and paper mill effluent differs in magnitude and composition. However, trends can be established for the three most common types of mills. Tables 1, 2, and 3 list various species that are generally present in the effluent of sulfite, kraft, and thermomechanical pulping mills. A quantitative analysis of the species present in the effluent stream of a Canadian west coast kraft mill is listed in Table 4. Although the chloride level here is greater than 390 ppm, clarifier electrolytes do not necessarily contain a high level of chlorides unless the bleach plant effluent is processed in the clarifier. Generally, bleach plant effluent is only clarified if it contains high suspended solids. Table

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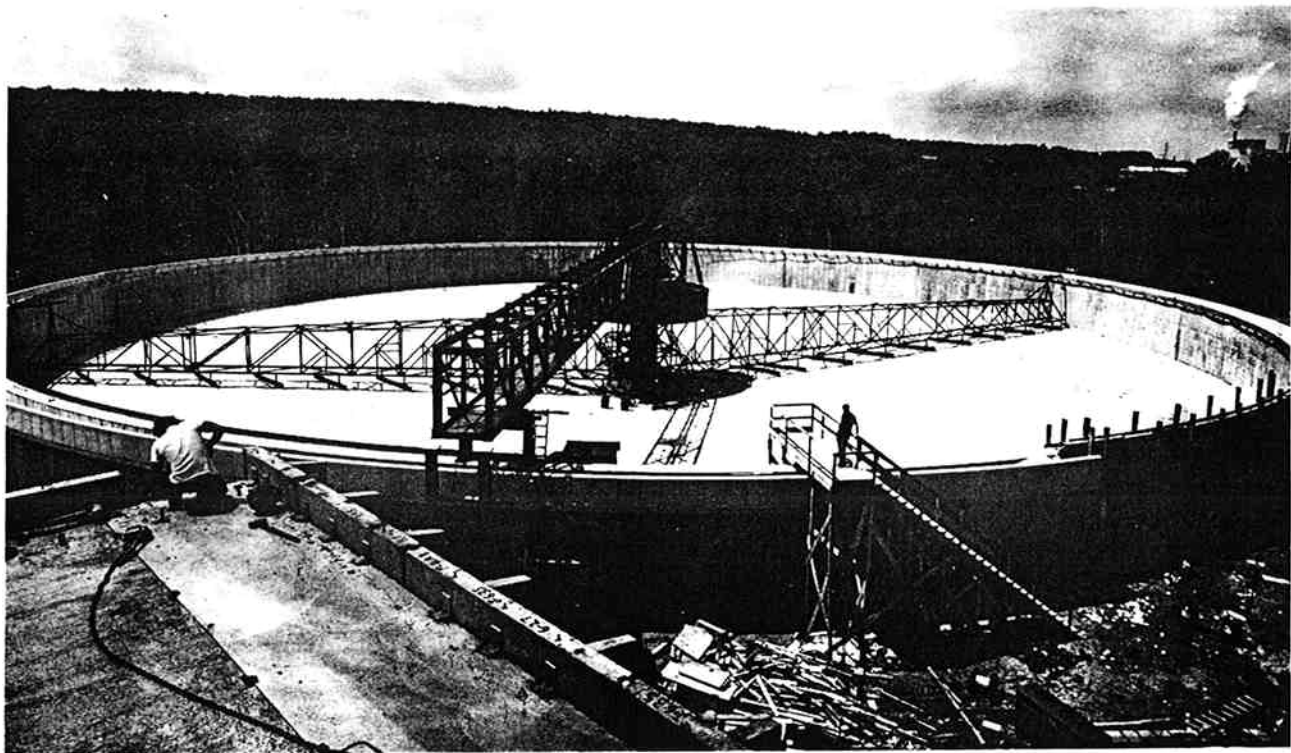


FIGURE 1 — Typical effluent clarifier.

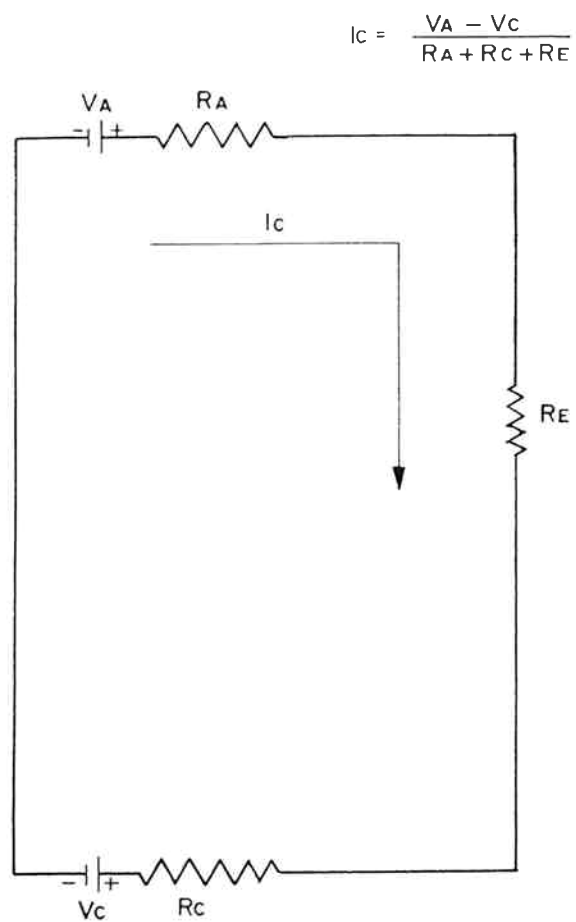


FIGURE 2 — Simple electrical model of a corrosion cell, assuming no metal 'IR' drop.

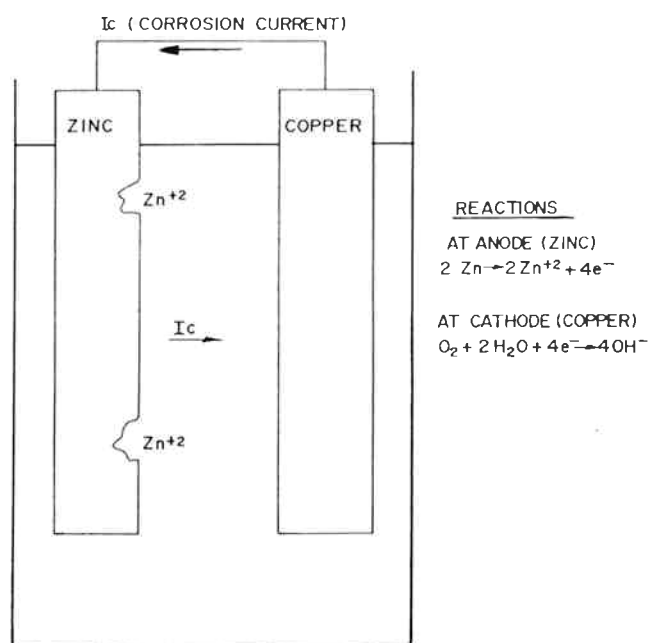


FIGURE 3 — Simple electrochemical corrosion cell.

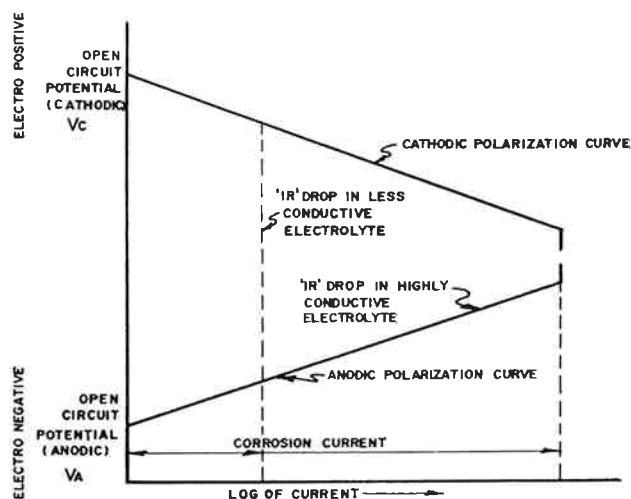


FIGURE 4 — Evans diagram, assuming no metal 'IR' drop.

TABLE 1 — Typical Species Present in Sulfite Effluent and Normal pH

1	Bleach Plant Filtrate
2	Calcium Salts
3	Magnesium Salts
4	Ammonium Salts
pH	1-4

TABLE 2 — Typical Species Present in Kraft Effluent and Normal pH

1	Various Organics
2	Chlorides
3	Chlorinated Phenolics
4	Reduced Sulfides
5	Thiosulfates and Sulfates
6	Mercaptans
pH	2-10

5 shows some typical corrosion rates of mild steel in some of the possible chemical species present. At this point, it is imperative to realize that the published corrosion data takes into account no interreaction between these chemical contaminants. As a result, it is not possible to simply take the corrosion rate of mild steel in each of the various contaminants and calculate a weighted average to predict the overall corrosion rate. Previous work¹ indicated that the corrosion rate of mild steel in a common sewer line was independent of the proportions of different sewer effluents. Their investigation further concluded that: "Undoubtedly, the acid sewer, alkaline sewer, and combined outfall sewer contained some poorly dissociated acidic and basic species (either inorganic from the bleach plant chemicals based on chlorine compounds or organic from wood residuals), but they did not appear to be present in quantities sufficient to exert a major influence on the corrosion rate behavior."

TABLE 3 — Typical Species Present in Thermomechanical Effluent and Normal pH

1	Cellulose Breakdown Products
2	Formic Acid
3	Acetic Acid
4	Furfural
5	Resin Acids
6	Fatty Acids
pH	4-5

TABLE 4 — Analysis of Effluent From A Kraft Mill

Element	Acid Sewer	Alkaline Sewer	Combined Outfall
Iron, ppm	0.70	2.1	1.08 ⁽¹⁾
Sodium, ppm	219.	613.	416. ⁽¹⁾
Calcium, ppm	109.	121.	115. ⁽¹⁾
Zinc, ppm	<0.1	<0.1	<0.1 ⁽¹⁾
Total Chloride, ppm	700.	390.	545. ⁽¹⁾
Sulfate as Na ₂ SO ₄ , ppm	<50.	580.	294. ⁽¹⁾
Total Sulfur, ppm	<10.	130.	68.
Total Organic Carbon, ppm	146.	307.	226. ⁽¹⁾
pH on Site	2.6	11.	4.1
pH in Laboratory	2.4	11.45	5.4
Dissolved Oxygen	—	—	6.16
Residual Active Chlorine	—	—	0

⁽¹⁾Based on equal volumes of acid and alkaline sewers. ppm = parts per million by weight.

TABLE 5 — Typical Corrosion Rate of Mild Steel in Various Chemical Species

Species	Concentration (Wt %)	Corrosion Rate (mm/yr at 25 C)
Acetic Acid	0-100	>1.27
Ammonium Bisulfite	0-40	>1.27
Ammonium Sulfite	0-60	>1.27
Ammonium Thiosulfate	10	>1.27
Calcium Bisulfite	10	>1.27
Magnesium Sulfite	0-20	>1.27

The pH of a solution has a significant effect on the corrosion of mild steel. Generally, higher or lower pH decreases the resistivity of the solution, and therefore allows a higher corrosion current to flow. However, the predominant effect of pH on the dissolution of mild steel involves the solubility of the corrosion product. If the corrosion product is soluble, then the effective anode resistance (R_a) is decreased, resulting in higher corrosion rates. Figure 5 depicts the effect of pH on the corrosion rate of mild steel in a typical kraft mill effluent.¹ As can be seen, low pH values produce high corrosion rates, while the high pH electrolytes generally result in a low corrosion rate.

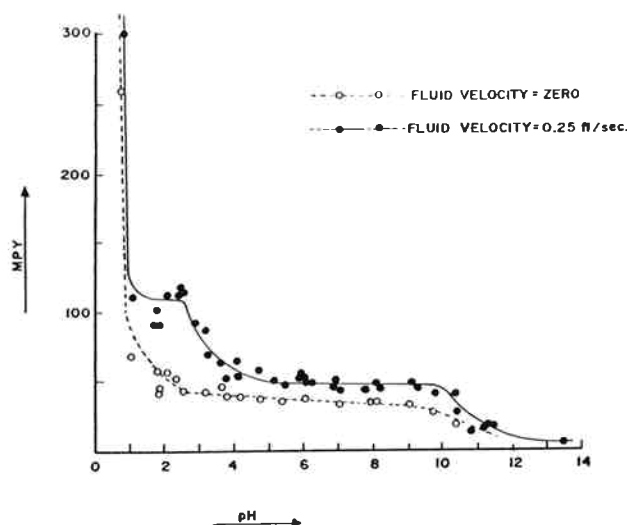


FIGURE 5 — Mild steel. Instantaneous corrosion rates in outfall sewers (23 C)—laboratory tests.

In addition, other factors increase the attack of metallic clarifier components. Aggressive cells can be set up between the area at the bottom of the rake in the sediment and the region in the bulk effluent. In general, the area in the sediment corrodes at a higher rate than above this level, as the differential aeration and/or concentration effect tends to increase the open circuit potential difference between the anodic and cathodic zones. Generally, the effluent entering the clarifier contains a different concentration of dissolved oxygen than the bulk effluent, further increasing the corrosion rate of the concentration cell. Depending on the consistency of the sediment, it is possible to generate local cells at locations where pulp adheres to the steel member.

Another significant contributor to the corrosion of the mild steel clarifier parts is the establishment of a couple between the rake mechanism and the reinforcing steel in the concrete wall and floor. There are many locations at which the reinforcing steel can be in electrical contact with the mild steel structure. With a common electrolyte, steel in alkaline concrete is usually cathodic to immersed steel not in concrete. Although the cathodic current density is low on the reinforcing rod, the large surface area of reinforcing can result in a relatively high corrosion rate of the steel rake and center support.

Increased velocity of the effluent usually increases the corrosion rate of the structure. Generally, areas in which the electrolyte is moving at a higher velocity are subject to higher rates of corrosion. Also, the velocity of the solution tends to reduce whatever polarization would normally take place. As a result (Figure 2), this mechanism reduces the effective resistance (R_a) and increases the corrosion at the higher velocity locations. Figure 5 indicates almost a factor of two increase in the corrosion rate of mild steel in kraft effluent by a solution velocity increase from 0 to 0.25 feet/second. Further extrapolation of corrosion studies¹ indicated that the corrosion rate of mild steel in kraft mill effluent could be related to velocity as in Equation (2), where R = corrosion rate in mpy and V = velocity in feet/second, for the pH range 4.6 to 9.4.

$$R = 7.5 + 7.14(V)^{1/3} \quad (2)$$

Although the rotational speed of the rake is low, the actual velocity at the tip of the rake farthest from the center well can be significant in large diameter clarifiers. The differential velocity between the tip and center well can establish a corrosion cell along the length of the rake. Slight turbulence of the electrolyte, resulting from the motion of the rake mechanism, establishes a velocity and concentration cell between the forward and trailing edges of the rake. The general manifestation of this is a knife edge attack along the forward edge of the rake mechanism.

Clearly, the corrosion rate of the steel components in clarifiers is dependent upon many variables. The important issue for mill personnel is not the corrosion mechanism, but the optimization of methods to mitigate the corrosion problem.

Corrosion Mitigation Techniques

Referring to Figure 2, corrosion prevention systems should minimize or stop the corrosion current (I_c). Each type of protection changes or eliminates some component of the corrosion cell. Often two or more techniques are utilized simultaneously to mitigate a corrosion problem.

Protective Coatings

Protective coatings attempt to isolate the structure from the surrounding environment. The corrosion current I_c can now be defined as in Equation (3), where R_p is the effective coating resistance.

$$I_c = (V_a - V_c) / (R_a + R_c + R_e + R_p) \quad (3)$$

If the value of R_p is large, as in the case of good quality coatings, the corrosion current decreases to a small value. The coating must have a low permeability to moisture, be resistant to abrasion, and be chemically resistant to the environment.

Any small voids in the coating are anodic to the remainder of the surface and result in accelerated corrosion of the structure in immersion service. Frequently, coating schemes are supplemented with cathodic protection. In general, coating a structure is the only economical method of preventing atmospheric (nonimmersed) corrosion. Zinc rich coatings and galvanizing provide some degree of cathodic protection, even in atmospheric exposure.

The coating on the steel members of a clarifier is subject to aggressive conditions. Mechanical abrasion and velocity effects of the effluent can cause defects to form in the coating system. Without additional corrosion protection, it is possible that the coating can be undercut by the resulting corrosion product. However, the selection of a protective coating system for steel components in pulp and paper effluent clarifiers is not unduly complex. There are several coating systems which provide comparable performance. The selection of a particular coating system is primarily based on the amount of the coating that is to be shop and/or field applied.

Since most clarifiers have a concrete floor and wall, protective coatings are usually limited to the rake and center well areas. Both immersed and nonimmersed steel is usually coated. Surface preparation in each case should involve sandblasting to at least a commercial grade sandblast, such as SSPC-SP6. Selecting a system that is suitable for the owner's long term requirements is important.

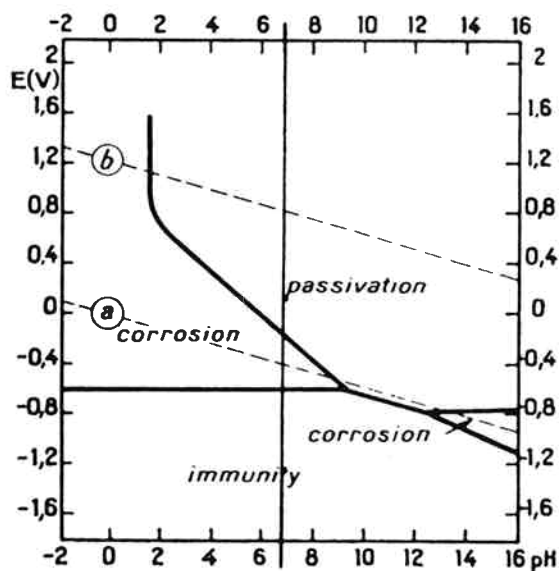


FIGURE 6 — Pourbaix diagram for iron with reference to a hydrogen electrode.

For long term maintenance free life, one of the possible options is a two coat system of coal tar epoxy applied approximately 8 to 10 mils per coat. One coat can be applied in the fabrication shop, while the second coat can be applied in the field after the rake has been installed. It is also possible that both coats can be applied in the fabricator shop. The majority of owners have specified coal tar epoxy due to reasonable cost and quality. This system will perform well in conjunction with further corrosion protection systems, such as cathodic protection. Unfortunately, coal tar epoxy has poor drying properties, and there is a history of failures due to equipment being shipped prior to the coating achieving a reasonable cure.

The decision as to which product and applicator is selected is extremely important. As mentioned in previous papers,² inspection of the installation by the owner and/or the coating manufacturer representative is imperative to ensure quality coating applications.

Cathodic Protection

Cathodic protection combats corrosion by impressing an externally produced electrical current on the structure, ensuring the entire metal becomes a cathode. The electrical current changes the potential of the cathodes to a value at least as negative as the open circuit solution potential of the anodes. As can be seen from Equation (1), if V_a is equal to V_c , then the corrosion current becomes zero. In addition to minimizing the potential difference of the anodes and cathodes, the protective current also increases the value of R_c , the effective polarization resistance of the cathode.

There is another definition of cathodic protection. Whether the metal will corrode or not in a specific environment has to do with the thermodynamic stability of the metal and the kinetics of the various processes that take place at the anodic and cathodic sites. Pourbaix has produced diagrams which show domains of immunity, corrosion, and passivity in a plot of solution potential vs pH. Since the equations used in the production of this diagram are thermodynamic, interpretation of the diagram in-

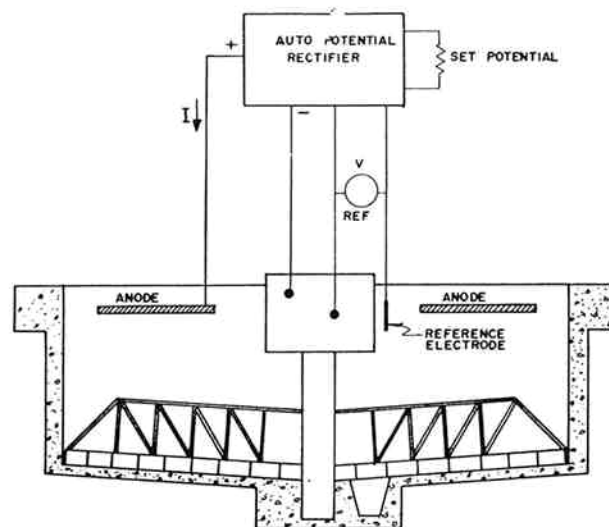


FIGURE 7 — Diagram of the essential parts of a cathodic protection system.

dicates potential/pH conditions where corrosion, immunity, and passivity domains can occur theoretically under equilibrium conditions. One could state (Figure 6) that a piece of iron in a solution of pH 7 would not corrode at a potential of -800 millivolts. Conversely, Figure 6 predicts that iron will corrode between the potentials of -600 and -200 mV, but gives no information whatsoever on the possible rate of corrosion.

If iron can be held at the potential that would keep it within the immunity domain, then corrosion is thermodynamically impossible. Unfortunately, it is difficult to produce Pourbaix diagrams for all metal/electrolyte combinations.

In the practical application of cathodic protection, the criterion for protection must be established, and the current required to achieve this potential calculated. At this juncture, an economic analysis of the preliminary design should aid in the decision of whether or not to rely upon galvanic anodes (magnesium or zinc) as a source of protective current, or to design around a powered rectifier and an inert anode system.

Galvanic anodes represent prepaid power, and are much more expensive than the equivalent power purchased from the electrical power company. Their advantage lies in their simplicity and low maintenance. They are used on well coated structures with small current requirements. Powered systems represent greater initial capital outlay, since even for small systems the minimum equipment required includes a rectifier and semiinert anodes. For the majority of clarifiers, the most cost effective approach is the utilization of an impressed current type system due to the large current density required to ensure complete protection. Figure 7 shows a conceptual diagram of a cathodic protection system.

The majority of conventional impressed current anodes, such as graphite and high silicon cast iron, are impractical for cathodic protection of clarifiers due to their size and weight. Mechanical support of these materials is difficult.

The excellent properties of platinum have made it an important material for laboratory and industrial electro-

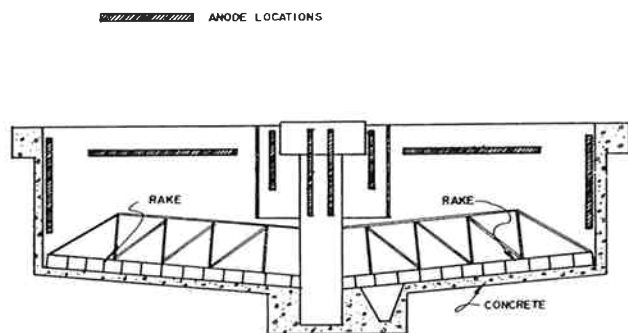


FIGURE 8 — Typical impressed current anode locations for cathodic protection.

chemical anodes. However, the high cost of solid platinum anodes prevented their general usage except when no other material was suitable. Modern metal cladding techniques have allowed a thin layer of platinum to be metallurgically bonded to a dissimilar, less expensive metal. To minimize the cost of platinum clad anodes, a substrate material was required that would resist anodic dissolution as a result of current discharge. Niobium was chosen because of its ability to develop a protective oxide film which would withstand over 120 volts without anodic breakdown.

Platinum clad niobium anodes are extremely lightweight, and have a low consumption rate while discharging the current density required to protect clarifier internal mechanisms. Anode location is important to ensure even current distribution to the structure. Figure 8 depicts a typical location of anodes for the protection of a clarifier.

The DC power source used to power the anode materials should be an automatically potential controlled unit. This rectifier senses the solution potential of the structure and automatically adjusts the current output to ensure the submerged metal surfaces are continually protected, regardless of changes in the electrolyte, such as pH and conductivity.

The most practical approach in cathodically protecting a clarifier is to install the system during clarifier construction. However, because of the small amount of necessary hardware, this system can easily be installed on existing clarifiers, sometimes without having to dewater the unit. Actual costs of such systems depend on various factors such as the amount of submersed metal and the current density required. The most cost effective solution for the mitigation of corrosion on the submersed structures of new clarifiers is the utilization of a good quality coating supplemented with cathodic protection. Where an existing clarifier is not coated or poorly coated, the most cost effective solution is the implementation of cathodic protection, thus saving recoating and down time costs.

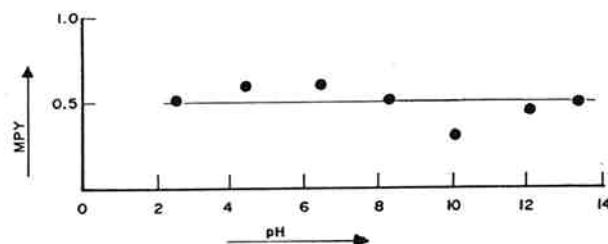


FIGURE 9 — Stainless steel Type 316. Instantaneous corrosion rates in simulated combined outfall sewers (23 C)—laboratory tests. Fluid velocity = 0.25 feet/second.

Metallurgical Alloying

Additions of certain elements to iron can increase the corrosion resistance dramatically. Additions of chromium (more than 11.5%) to steel produces a stainless steel. The chromium additions produce corrosion products on the surface of the metal which effectively isolate the structure from the environment. Figure 9 indicates that Type 316 stainless steel has a low corrosion rate in kraft mill effluent from pH 2.5 to 14 at fluid velocities of 0.25 foot/second.¹ However, when stainless steel alloys do corrode, the usual mechanism of destruction is crevice corrosion or pitting due to local protective film breakdown. They are particularly vulnerable to pitting attack in solutions containing chlorides. If stainless steels are utilized in the construction of a clarifier, it is imperative to minimize the amount and size of incipient crevices. The author is unaware of any pulp and paper mills utilizing stainless steel effluent clarifiers.

Summary

Corrosion of carbon steel components in an effluent clarifier can be a serious problem. The actual corrosion rates are a complex function of mill effluent characteristics and clarifier design. Coatings, cathodic protection and metallurgical alloying are possible mitigation techniques that can be utilized to prevent corrosion failure of clarifier equipment. Application of a coal tar epoxy coating supplemented by cathodic protection will assure complete corrosion protection.

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