

# Plain Galvanized Steel Drainage Pipe Durability Estimation with a Modified California Chart

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**A method for estimation of plain galvanized steel pipe service life based on the use of a modified California Chart has been developed. Certain limitations in the California Chart with respect to pipe waterside corrosion have been addressed. The method, based on results of field studies in the United States and South America, is amenable to use in different climates.**

Interest in methods of estimating drainage pipe durability has been considerable for many years in the United States and is receiving increasing worldwide attention. The use of galvanized steel pipe in the tropical, subtropical, and temperate zones of South America has directed Armco to develop an estimation technique for this material amenable to worldwide conditions. The technique is based on water/soil chemistry, the main factor controlling galvanized steel corrosion.

## GENERAL TECHNICAL BACKGROUND UNDERLYING ESTIMATION TECHNIQUE

Corrosion, an electrochemical process, and abrasion, a mechanical wear process, both contribute to pipe durability problems, but corrosion is the more important problem for any country as a whole. Corrosion problems occur on different types of terrain, but important true abrasion occurs only in or near mountainous/hilly terrain where periodic movement of rock and sand at high velocity occurs during rainfall. Abrasion is a separate topic that will be dealt with in a later Armco report.

### Waterside Corrosion

Advanced waterside corrosion within the lower half or lower quadrant of the pipe circumference has been the main corrosion problem observed in field inspections conducted in South America, the United States, and elsewhere (1–7). Published literature in related fields of technology indicates corrosion of galvanized steel in waters is influenced by several factors, but some are of predominant importance, and evaluating them should permit a reasonably accurate determination of the suitability of galvanized. The most important factor is water chemistry, the essential elements of which are pH, total dissolved solids (usually denoted by conductivity or resistivity), hardness, and alkalinity. Nonchemical factors of

substantial importance include degree of turbulence, temperature, and time of water contact.

**1. Water Chemistry** Hardness and alkalinity salts common to natural waters encourage formation of partially protective scales or films that hinder corrosion of reactive metals like zinc and steel, which otherwise would tend to corrode excessively (8, p. 11; 9, pp. 16, 29, 32, 140; 10, pp. 160, 163; 11, p. 76; 12, pp. 2.15, 2.16, 2.25). These salts, chiefly bicarbonates of calcium and magnesium, are sparingly soluble and tend to produce precipitates (mainly  $\text{CaCO}_3$ ) that deposit onto corroding metal surfaces due to local surface chemical changes induced by corrosion. These salts also tend to modify metal corrosion products to encourage formation of protective insoluble corrosion-product scales. The precipitated salts and modified insoluble corrosion products combine to form the protective scale. Soft pure low-conductivity waters containing very little of any type of dissolved salt, including hardness/alkalinity salts, tend to be fairly corrosive because they possess no scaling tendency and because they lack buffering capacity, which leads to pH lowering. The pH and the total dissolved salt content (or conductivity) are important partly because low pH, due to excessive  $\text{CO}_2$  and organic acid, or high conductivity, due to excessive concentrations of soluble chloride or sulfate, tend to prevent or interfere with scale formation. Acidity and chloride/sulfate salts are also inherently corrosive apart from their effects on scaling. The balance between hardness and alkalinity salts on one hand versus acidity and chloride/sulfate salts on the other is critical in determining whether protective scaling or excessive corrosion will occur (13,14).

A zinc coating tends to increase substantially the effectiveness of water scaling in two different ways. First, despite its high inherent reactivity, zinc tends to form protective scales more readily than steel does, and scaling stifles reactivity and gives long coating life and consequent long barrier protection for the steel substrate (10, pp. 160, 163). Second, before zinc reactivity is stifled by scale formation, it provides galvanic protection that promotes formation of improved protective scale on any bare exposed steel substrate (10, pp. 160, 163). Galvanic protection promotes scale formation on exposed steel through electrochemical influences that encourage mineral precipitation and help ensure good adherence of the deposit.

**2. Degree of Agitation** High water velocity can induce erosion corrosion, a form of accelerated corrosion caused by

scouring of metal surfaces by turbulent water and suspended solids that removes protective scale (12, pp. 2.15, 2.16, 2.25; 15, p. 7220). Water movement is important because it helps promote water aeration that ensures a high content of the dissolved oxygen necessary to support corrosion. High dissolved oxygen is normal in surface waters (12, pp. 2.15, 2.16, 2.25), so scaling tendency becomes the crucial corrosion-controlling factor determining how severe the effect of oxygen will be (16, pp. 149, 161). In waters that are normally stagnant, dissolved oxygen may be depleted by bacterial activity, so oxygen availability can become an important corrosion-controlling factor in such waters.

**3. Temperature** Elevated temperature accelerates corrosion directly and indirectly, and consequent important differences in durability among different climates result. Again, scaling is the critical factor because an effective scale nullifies the detrimental effect of elevated temperature. However, in very corrosive waters where scaling is ineffective, temperature is a factor that should be considered (9, pp. 16, 29, 32, 140).

**4. Time of Water Contact** Obviously, this is a controlling factor in arid climates where pipes are apt to be dry most of the time so that average invert corrosion rates are quite low. It is a very important factor in a pipe high-water zone and in the invert of a pipe that is normally dry where contact is always limited to the time during and shortly after rainfall.

The water chemistry of primary concern for drainage pipe is that of groundwater runoff because this constitutes the predominant stream flow in terms of contact time and is the only flow during extended dry weather. For any pipe in streams with prolonged flow, corrosion in the low-water zone is controlled by the chemistry of groundwater runoff. Groundwater runoff is generally of relatively low corrosivity because it contains primarily scaling salts obtained from intimate prolonged contact with soils containing mainly these salts. Corrosive soft acidic groundwaters or high-chloride/sulfate groundwaters arise from unfavorable soils found in regions of some countries.

The surface runoff that prevails during and shortly after rainfall is usually appreciably corrosive because it (a) contains relatively little of the scaling salts available from the soil due to brief soil contact time and (b) sometimes has enough velocity and turbulence to induce erosion corrosion. However, its corrosivity is usually adequately controlled by the brief pipe contact time. It normally has no effect on a pipe low-water zone in scaling streamwater because protective scales persist through rainfall periods, but under certain conditions it can have an effect in the high-water zone or in the inverts of pipes that are normally dry.

### Soilside Corrosion

Soilside corrosion is a complex and highly variable process, but does not usually control pipe life because typically overall soilside corrosion is much less aggressive than is overall waterside corrosion (1-7, 17-20). Obviously, in soils there are no

problems with abrasion or erosion corrosion, and the near-static state of soil moisture leads to reduced kinetics of overall corrosion due to reduced dissolved oxygen. In less porous soils, oxygen availability for corrosion will be low and will further ensure low overall corrosion rates (although pitting corrosion is likely to increase); in more porous soils where oxygen availability is high, protective corrosion product scales normally help ensure low overall corrosion rates (corrosion product scales are more effective on the soil side). Because of corrosion-mitigating factors like these, there is no overall dependence on  $\text{CaCO}_3$ -type scaling for good performance as there is on the waterside. Soilside corrosion problems that control pipe life do sometimes occur in soils of high acidity or in dry climates in locations where the natural content of chloride/sulfate salts is high and rainfall is inadequate to leach away soluble salts, but some groundwater moisture is present. Thus soil pH and conductivity (or resistivity) measurements provide reasonable indications of the likelihood of soilside corrosion problems.

## DEVELOPMENT OF PLAIN GALVANIZED DURABILITY ESTIMATION TECHNIQUE

### Current U.S. Technique

The estimation technique that has been the most useful in the United States is the California Chart, although in its original form it is generally overly conservative (5, 6, 20-23) and under some circumstances, is overly liberal (25, 26). This technique relates pipe durability to the pH and resistivity of either the waterside or the soilside environment (26). This approach is proper for the soilside environment for which pH and resistivity are generally the most important factors controlling durability of galvanized culvert pipe. However, the technique is not entirely adequate for the more complicated waterside environment which causes most problems.

The main problems with the California Chart are summed up in the statement that the chart does not recognize the effect of water scaling on corrosion behavior. The chart in its original form gives overly conservative results in scaling waters containing some significant hardness and alkalinity, and these waters are predominant in most countries. Conservatism in scaling waters results from the chart presumption that corrosion rates always increase as resistivity decreases at any given pH, a presumption that can be true only if all dissolved salts are present as corrosive salts. Actually decreasing resistivity due to increasing concentrations of protective scaling salts corresponds to decreasing corrosion rates. In most surface waters, protective scaling salts constitute most or much of the total dissolved salt content, and corrosion is much less severe than it would be if all of the dissolved salt content were present as corrosive salts. Thus, ignoring the protective effect of scaling salts results in conservative durability estimates. The resulting degree of conservatism can be significant in any typical region where groundwaters contain some significant hardness and alkalinity. For example, in Florida (5) and Georgia (20), the average service life determined by inspection of pipes that were generally 14 gauge was 70 years or more, whereas average perforation time estimated from the California Chart was 40 years or less. In an area of Iowa

studied by the writer, the excellent condition of several galvanized pipes exposed for 30 years to streams with prolonged flow was indicative of service life in excess of 75 years at 14 gauge, while the chart gave estimated perforation times less than 40 years. The measured water pH and resistivity at one site were 7.02 and 1449 ohm cm for which the chart gives a very conservative perforation time of 32 years. The pipe actually showed no important penetration by corrosion after 30 years. The low water resistivity was due primarily to scaling salts (alkalinity = 258 ppm as  $\text{CaCO}_3$  and hardness = 368 ppm as  $\text{CaCO}_3$ ); attributing a detrimental effect to beneficial dissolved salts caused severe conservatism in the durability estimate.

By not recognizing the detrimental effect of the absence of a significant scaling effect in high-resistivity water, the chart gives liberal durability estimates in soft nonscaling or slightly scaling waters. The results are liberal because the chart suggests that, at a given pH, corrosion rates decrease continuously with increasing resistivity. This estimate conflicts with the fact, known from published literature (27), that at a given pH, soft pure water of high resistivity (and therefore of low alkalinity and hardness) is more corrosive than hard scaling water of much lower resistivity. High resistivity does tend to reduce corrosion rates, but this benefit is unimportant compared with the detrimental effect of the reduced scaling tendency caused by low alkalinity and hardness associated with high resistivity. In the chart, the presumed benefit of high resistivity are much greater than the actual benefit, presumably even offsetting the detrimental effect of reduced pH. By examining the California Chart, the reader can see that along any horizontal constant perforation time line on the chart, the perforation time is supposedly maintained constant as the resistivity increases and the pH decreases. This ongoing condition is quite impossible over the high end of the resistivity range because, in waters of high resistivity, virtually all of the dissolved salt content is present as scaling salts, and increasing resistivity corresponds only to decreasing concentrations of scaling salts and decreasing scaling tendency (high resistivity groundwaters arise in wet climates where any soluble corrosive salts, such as chloride or sulfate, present in early soil development were leached away long ago and only limited amounts of sparingly soluble scaling salts remain). As already noted, even at a fixed pH, decreasing hardness and alkalinity correspond to increasing corrosion rates, and the combined detrimental effect of decreasing pH plus decreasing hardness and alkalinity can only increase corrosion rates faster.

Further evidence can be found in the results of culvert pipe durability studies conducted by state highway departments located wholly or partially in regions with soft high-resistivity groundwater and surface runoff arising from well-leached soils. In such regions, reduced pH is a natural consequence of the low alkalinity contents, so low pH and high resistivity are concurrent. These conditions exist throughout Maine and also in western Washington and in Oregon west of the Cascade Mountains where state highway departments (3, 6, 25) have found average service lives for 14-gauge material of about 35 yr. Of course, this figure should be contrasted with the 70-yr or more average service life found in Florida and Georgia where groundwaters generally have some significant alkalinity and hardness. In Maine and western Washington and Oregon, the one consistent factor that could account for the lesser average durability is the predominance of soft high-resistivity

runoff, so the highway department inspection results appear to be evidence that high resistivity is detrimental and thus does not offset the detrimental effect of reduced pH.

The degree of error in the chart durability estimate that can result from the combined influence of conservatism and liberalism trends when comparing sites was illustrated to the writer by an example in which groundwater chemistry in streams with continuous flow changed abruptly from scaling to nonscaling over a short distance along a secondary road near Pucallpa, Peru. Near the point of change, the scaling water had a pH of 7.65 and a resistivity of 2,304 ohm cm, and the nonscaling water had a pH of 5.55 and a resistivity of 62,500 ohm cm. The scaling water had 232 ppm alkalinity as  $\text{CaCO}_3$  and 216 ppm hardness as  $\text{CaCO}_3$ ; the nonscaling water, 14 ppm alkalinity as  $\text{CaCO}_3$  and no hardness. On the basis of controlling waterside conditions, use of the California Chart suggests that the time to first perforation for 14-gauge pipe would be 57 years in the scaling water and 52 years in the nonscaling water. The implication is that pH and resistivity are the only important controlling factors and that the detrimental low pH of the nonscaling water is essentially offset by the beneficial high resistivity so that durability is about the same in both waters. In actuality, the service life estimate was more than 75 years in the scaling water and about 20 years in the nonscaling water. Use of the chart results in conservative estimates of service life in the scaling water and liberal estimates in the nonscaling water to such a degree that the total combined error in the estimate differential is on the order of 3.5:1 to 4:1. Some additional examples of the conservatism/liberalism trends of the California Chart are provided in Table 1.

There are some other important reasons why chart estimates are sometimes overly conservative or overly liberal. Severe conservatism occurs in estimates for drier climates where (a) waterside corrosion is generally minimal due to infrequent flow and (b) soilside corrosion generally controls durability. Conservatism arises by using minimum (water-saturated) soil resistivity when pipe corrosion is actually controlled by in situ resistivity which is generally much higher due to limited soil-moisture availability. Liberalism occurs in the estimate for certain wet regions where waters contain large amounts of corrosive molecular free  $\text{CO}_2$  that is not revealed by pH/resistivity measurements.

Another problem in using the California Chart is an uncertainty over whether to use waterside or soilside pH/resistivity parameters. Some authorities have used soilside parameters to estimate durability that is generally controlled by waterside parameters. Although not technically unfounded because groundwater chemistry is related to soil chemistry, this approach does not distinguish between durability controlled by relatively slow soilside corrosion of drier climates from that controlled by the more rapid waterside corrosion of wetter climates. Some authorities have determined both the soilside and waterside parameters and have used the set that gives the most conservative estimate, but this approach does not differentiate between the two environments realistically because at a given set of pH/resistivity values, waterside corrosivity is likely to be quite different from that of the soilside. Soil parameters apply generally in dry climates while water parameters apply in wet or moderately wet climates. When applying waterside parameters, the water alkalinity and hardness must be included with the pH and resistivity.

TABLE 1 EXAMPLES OF OVERLY CONSERVATIVE AND OVERLY LIBERAL CALIFORNIA CHART ESTIMATES

LOCATION	pH	RESIST. (OHM.CM)	ALK. (CaCO <sub>3</sub> )	ESTIMATED DURABILITY AT 14 GAGE		PIPE AGE
				BY CAL. CH	BY INSP.	
<u>OVERLY CONSERVATIVE</u>						
S.D. US	7.34	649	327	34	>100	50
OH.US	8.10	1,754	359	39	>100	50
VENEZUELA	7.80	1,934	234	41	>100	26
MO. US	6.70	2,062	195	29	>60	30
ECUADOR	7.15	6,711	77	52	>75	12
<u>OVERLY LIBERAL</u>						
BRAZIL	4.8	114,940	4.2	54	~10	13
VENEZUELA	5.0	83,330	7	51	~20	13
BRAZIL	5.9	58,825	5	53	~30	18
ECUADOR	6.6	9,090	27	62	~40	10

Since waterside corrosion is the most prominent problem overall, the most crucial aspect of durability estimate is the development of a comprehensive waterside technique that includes the effects of hardness, alkalinity, and CO<sub>2</sub> and thus eliminates the major causes of conservative/liberal trends in the California Chart. Armco has addressed this need, and the result is a modified type of California Chart, based on Armco field data, for depicting waterside corrosion. The pH, conductivity, hardness, and alkalinity are easily determined in the field using simple field meters and simple digital titration equipment; the free CO<sub>2</sub> is calculated from the pH and alkalinity values.

#### Development of a More Comprehensive Waterside Estimation Technique

##### Effects of Alkalinity, Hardness, and CO<sub>2</sub>

Alkalinity, a crucial species determining water scaling tendency, is primarily in the form of bicarbonate salts. Bicarbonate (HCO<sub>3</sub><sup>-</sup>) is readily destroyed by reaction with prevalent organic acids produced by plant decomposition or inorganic sulfuric acid occasionally encountered. These acids remove beneficial HCO<sub>3</sub><sup>-</sup> and substitute corrosive reaction product salts in its place, thus reducing the scaling tendency and increasing water corrosivity. Sometimes the alkalinity is totally consumed, producing free acidity, which results in severely corrosive water. Such water is not dealt with in this report because it is too corrosive to permit use of plain galvanized and other more common pipe materials.

Plant decomposition also produces CO<sub>2</sub> which combines with water to form corrosive carbonic acid, but CO<sub>2</sub> does not destroy HCO<sub>3</sub><sup>-</sup> alkalinity because CO<sub>2</sub> is actually part of the essential chemical reaction by which HCO<sub>3</sub><sup>-</sup> is formed from CaCO<sub>3</sub> in soil and rock. Indeed a little excess unreacted or free CO<sub>2</sub> is necessary to stabilize HCO<sub>3</sub><sup>-</sup> in solution, but any excess free CO<sub>2</sub> above this small amount reduces the scaling tendency and increases water corrosivity. In any natural water with significant alkalinity remaining after reaction with organic

acid, CO<sub>2</sub> is the remaining form of acidity influencing the pH and the scaling tendency. The interaction of free CO<sub>2</sub>, alkalinity, and hardness controls the basic water scaling tendency in any water for which the use of plain galvanized can be recommended.

Hardness (Ca<sup>+2</sup>, Mg<sup>+2</sup>) and alkalinity (HCO<sub>3</sub><sup>-</sup>, HSiO<sub>3</sub><sup>-</sup>) are present in natural waters primarily in the form of calcium bicarbonate or Ca(HCO<sub>3</sub>)<sub>2</sub>, and this salt is a source of insoluble CaCO<sub>3</sub> precipitate for protective scale formation. Any water chemical change that increases pH will first reduce free CO<sub>2</sub> that stabilizes Ca(HCO<sub>3</sub>)<sub>2</sub> in solution and then will reduce reacted or combined CO<sub>2</sub> in HCO<sub>3</sub><sup>-</sup> to encourage CaCO<sub>3</sub> precipitation. This reaction occurs locally on metal surfaces as a consequence of local generation of hydroxide (OH<sup>-</sup>) by corrosion processes, so corrosion itself tends to promote CaCO<sub>3</sub> scale formation in a scaling water. However, increasing free CO<sub>2</sub> acidity lowers the overall pH and renders CaCO<sub>3</sub> precipitation increasingly more difficult and ultimately impossible at some critical concentration. Increasing free CO<sub>2</sub> increasingly hinders scaling and also directly increases zinc/steel corrosion.

Obviously, differentiation of the relative basic scaling tendencies of different waters can be accomplished by quantifying alkalinity, hardness, and free CO<sub>2</sub> concentrations. Alkalinity and hardness will be positive controlling factors, and free CO<sub>2</sub> will be a negative one. An appropriate method to obtain an index of the scaling tendency would be to add the alkalinity and hardness concentrations and to subtract the free CO<sub>2</sub> concentration. This approach is a modification of the classic approach of the Langlier index (and the related Ryznar index) in which the scaling tendency is based on the difference between the sum of the negative logarithms of the alkalinity and hardness concentrations on the one hand and the negative logarithm of the dissociated acid concentration (pH) on the other hand (9, 12, 28, pp. 231, 349). The modified index uses total free CO<sub>2</sub> rather than pH to represent acidity and uses arithmetic concentrations (in ppm) rather than their logarithms. Also total hardness (Ca<sup>+2</sup> + Mg<sup>+2</sup>) is used rather than just Ca<sup>+2</sup> hardness because Mg<sup>+2</sup> also participates in scale formation through pH-dependent precipitation reactions. Alka-



linity (total) is expressed as  $\text{HCO}_3^-$  and hardness as  $\text{Ca}^{+2}$  because these are the primary actual forms in which they exist in waters. For either index, a decreasingly positive value in scaling water corresponds to increasing corrosivity, and corrosivity continues to increase as the index becomes increasingly negative in nonscaling water due to a rising proportion of  $\text{CO}_2$ .

The modified index modifies the Langlier index reliance on the concept of a critical pH of  $\text{CaCO}_3$  saturation above which  $\text{CaCO}_3$  scaling occurs and below which it does not. More recent investigations (27; 29, p. 285) have shown that other factors in addition to the saturation state are involved, and scaling normally occurs in unsaturated waters of pH below the critical value due to scaling stimulation by  $\text{OH}^-$  produced by corrosion reactions on metals. Decreasing pH and decreasing saturation state do reduce the  $\text{CaCO}_3$  scaling tendency, but increasing alkalinity/hardness concentrations permit scaling at lowered saturation states, including substantially unsaturated ones. These observations indicate that the  $\text{CaCO}_3$  scaling tendency on corrodible metals is a continuum with the degree of scaling varying according to the relative amounts of alkalinity and hardness versus the amount of free  $\text{CO}_2$ . The modified index reflects this relative interaction because the scaling tendency, according to the index, increases or decreases continually relative to changes in the three concentrations; and at some low index value, scaling ceases.

Relative changes in the scaling tendency do not correlate completely with metal corrosion behavior as the published literature shows (27), and some further modifications are needed to reflect actual corrosion behavior more closely. The use of arithmetic concentrations rather than logarithmic ones is important because the Langlier index tends to overrate the influence of concentration variations over small ranges. For example, in a 332-ppm  $\text{Ca}(\text{HCO}_3)_2$  solution, a variation in free  $\text{CO}_2$  from 2 ppm to 16 ppm has little influence on corrosivity because the water is supersaturated at both concentrations and readily supplies enough  $\text{CaCO}_3$  to control corrosion throughout this free  $\text{CO}_2$  range. Aggressive free  $\text{CO}_2$  that effectively reduces scaling by inducing an unsaturated state does not appear until the free  $\text{CO}_2$  exceeds 17 ppm, and effective scaling that controls corrosion should persist at free  $\text{CO}_2$  levels well above 17 ppm. However, the change in  $\text{CO}_2$  does affect the pH substantially (8.32 to 7.41) and thus reduces both the degree of supersaturation and the Langlier index substantially (.9 units), suggesting an unrealistic substantial change in corrosivity. The use of arithmetic units in the modified index reflects the change in corrosivity in a more modest and more realistic relative fashion in that the free  $\text{CO}_2$  increase causes a minor drop in the index value from +330 to +316 (332-2 vs. 332-16).

Another important difference in the Armco method is the use of total acidity consisting of dissociated (ionic) and associated (molecular) carbonic acid or free  $\text{CO}_2$  rather than just the dissociated acidity indicated by the pH in the Langlier method. This distinction is important because both forms of carbonic acid hinder scaling but the molecular form is not accounted for in the pH value (30). Molecular carbonic acid is also important because it has a direct adverse effect on metal corrosion rates (14, 31). The total free  $\text{CO}_2$  concentration indicated by the pH and alkalinity determines the severity of corrosion. Strictly speaking it is the excess free  $\text{CO}_2$  beyond that small amount needed to stabilize  $\text{HCO}_3^-$  in solution that

should be determined, but total free  $\text{CO}_2$ , which is more easily calculated, can be used for our purposes.

Total free  $\text{CO}_2$  is related to pH and alkalinity by the equation  $\text{pH} = \log (\text{alkalinity} \times .203 \times 10^7 \div \text{free } \text{CO}_2)$  where alkalinity and free  $\text{CO}_2$  are ppm as  $\text{CaCO}_3$  and  $\text{CO}_2$ . As this equation shows, if the free  $\text{CO}_2$  is fixed, an increase in alkalinity raises the pH. For example, at a fixed free  $\text{CO}_2$  concentration of 50 ppm, an alkalinity of 5 ppm (as  $\text{CaCO}_3$ ) gives a pH of 5.3 and an alkalinity of 50 ppm gives a pH of 6.3. The increase in alkalinity at a fixed  $\text{CO}_2$  and the consequent increase in pH reduces water corrosivity because it increases scaling potential (makes Langlier index more positive).

Keeping the pH constant while increasing the alkalinity is accomplished by increasing the free  $\text{CO}_2$ , which changes water corrosivity to a degree that depends on the value chosen for the fixed pH. The effect on water corrosivity depends on the relative amounts of free  $\text{CO}_2$  and alkalinity, which in turn depend on whether the fixed pH value is above or below 6.3. This can be seen by rearranging the equation for the pH/alkalinity/ $\text{CO}_2$  relationship to read  $\log \text{CO}_2 = \log \text{alk.} + 6.307 - \text{pH}$ . Obviously, the free  $\text{CO}_2$  concentration (as  $\text{CO}_2$ ) is equal to the alkalinity concentration (as  $\text{CaCO}_3$ ) at pH 6.3, becomes less than the alkalinity at any higher pH value, and becomes greater than the alkalinity at any lower pH value. For example, at pH 6.5 the free  $\text{CO}_2$  is 3.2 ppm at 5 ppm alkalinity and 32 ppm at 50 ppm alkalinity. Thus, at this pH, the alkalinity exceeds the free  $\text{CO}_2$ , and the increase in  $\text{CO}_2$  as alkalinity is increased is from 3.2 to 32 (28.8 ppm). On the other hand, at pH 6.0, the free  $\text{CO}_2$  is 10 ppm at 5 ppm alkalinity and 100 ppm at 50 ppm alkalinity. At this pH, the free  $\text{CO}_2$  exceeds the alkalinity, and the increase in free  $\text{CO}_2$  as alkalinity is increased is from 10 to 100 ppm (90 ppm). At some relatively low fixed pH value, increasing alkalinity will begin to correspond to increasing water corrosivity to steel because the corrosive effect of free  $\text{CO}_2$  will become predominant. The  $\text{CO}_2$  predominates because only a relatively small portion of the increasing  $\text{CO}_2$  available when alkalinity is increased at a fixed pH is needed to stabilize the increasing alkalinity in solution, leaving an increasing proportion of aggressive free  $\text{CO}_2$  available for scaling suppression and corrosion acceleration. Another reason corrosivity will increase is that increasing alkalinity increases water conductivity, thus increasing corrosivity when the free  $\text{CO}_2$  is too great to permit any protective scaling.

These relationships between pH/alkalinity/ $\text{CO}_2$  and water corrosivity have been documented in the published literature (14; 31; 32, p. 88), and they must be reflected in the modified scaling index if the index is to be realistic. As the Langlier and Ryznar indices would do, the modified index must reflect changing corrosivity when the pH is changed due to changing alkalinity: $\text{CO}_2$  ratios. Obviously, the index should show reduced water corrosivity when the free  $\text{CO}_2$  is kept constant and the alkalinity is increased. For example, if free  $\text{CO}_2$  is fixed at 50 ppm, increasing the alkalinity from 5 to 50 ppm (as  $\text{CaCO}_3$ ) would increase the pH substantially and induce a substantial reduction in corrosivity.  $\text{CaCO}_3$  at 5 ppm yields 6 ppm  $\text{HCO}_3^-$  and 2 ppm  $\text{Ca}^{+2}$  for an index value of -42 ( $6 + 2 - 50$ ), which is indicative of severe corrosivity as would be expected in water of low scaling tendency and high free  $\text{CO}_2$  (pH = 5.31).  $\text{CaCO}_3$  at 50 ppm yields 61 ppm  $\text{HCO}_3^-$  and 20 ppm  $\text{Ca}^{+2}$  for an index value of +31 ( $61 + 20 - 50$ ), which is indicative of considerably less corrosivity as would be expected

(pH = 6.31). On the other hand, if alkalinity were fixed at 50 ppm, reducing the  $\text{CO}_2$  from 50 ppm to 5 ppm would decrease corrosivity substantially, and this reduction would be reflected by a substantial index increase from +31 ( $61 + 20 - 50$ ) to +76 ( $61 + 20 - 5$ ).

The index is also a convenient indicator of the increased corrosivity resulting when alkalinity is increased at a relatively low fixed pH. For example, Armco laboratory tests showed that the short-term corrosion rate of mild steel in a calcium bicarbonate solution of 90 ppm (as  $\text{CaCO}_3$ ) at pH 5.8 was nearly three times as great as the corrosion rate in a 14-ppm calcium bicarbonate solution (as  $\text{CaCO}_3$ ) at the same pH. At pH 5.8, the 90-ppm solution had 289 ppm free  $\text{CO}_2$  by calculation, and the 14-ppm solution had 44 ppm free  $\text{CO}_2$ . The index gives a value of -143 for the 90-ppm solution ( $110 + 36 - 289$ ) and a value of -21 for the 14-ppm solution ( $17 + 6 - 44$ ), reflecting the actual greater corrosivity of the 90-ppm solution. The Langlier and Ryznar indices do not reflect this relationship because they suggest the 14-ppm solution is more corrosive (Langlier index would be about -2.3 for the 90-ppm solution and about -3.9 for the 14-ppm solution). This is the type of problem that arises from the use of pH rather than total free  $\text{CO}_2$  to represent the acidity factor. Corrosive molecular  $\text{CO}_2$  is very high in the 90-ppm solution, but is not accounted for in the pH value. Thus, the Langlier index underrates the corrosivity of this solution. Of course, the Langlier index does not apply to waters of pH below 6.5 because Professor Langlier was concerned mainly with water distribution systems. A modified index is necessary to account for molecular  $\text{CO}_2$  and to handle the range of natural waters found in culvert environments where  $\text{CO}_2$  concentrations can be very high at times.

The index appears to be most realistic with no weighting for any of its three components (alkalinity, hardness, or  $\text{CO}_2$ ). The data fit the completed durability estimation graph best when no weighting is assigned.

### *Effects of Alkalinity, Hardness, and $\text{CO}_2$ in Combination with Conductivity*

It is now necessary to consider the interrelationship of the scaling tendency with conductivity to adequately depict water corrosivity. In scaling water there is a critical balance between the scaling tendency and corrosive salts, such as chlorides and sulfates, because such salts tend to interfere with scale formation at some critical concentration. Also, in acidic non-scaling water, the corrosive effect of acidity is compounded by increasing conductivity, so the combined effect of a negative scaling tendency and higher conductivity is quite severe. These relationships can be depicted on a graph with the basic scaling tendency (alkalinity + hardness -  $\text{CO}_2$ ) on the vertical axis and the conductivity on the horizontal axis as has been done in Figure 1. In Figure 1, line AB depicts the relationship between the scaling tendency and the conductivity at a given fixed service life. There is also a line XY along which all of the conductivity is due to hardness/alkalinity salts, and water corrosivity is minimal. Conductivity values that fall below or to the right of XY are the result of corrosive salts and ionic carbonic acid contributing to conductivity. Also, in Figure 1, there must be a critical sloped line like AB separating satisfactory performance from unsatisfactory, and AB represents the limiting water chemistry range at which some arbitrary fixed pipe service life can be attained. The reason for the slope becomes obvious by considering any pair of horizontal lines such as CD and EF. On line CD, the scaling tendency or the sum of hardness plus alkalinity minus  $\text{CO}_2$  is fixed, and increasing conductivity is due to other salts, which are corrosive salts like chloride and sulfate. Eventually at some critical higher conductivity value, the corrosive salt concentration is high enough and scaling is sufficiently negated that the corrosion rate increases to the level represented by the service life of line AB. On line EF, the acidity is higher and the inherent scaling tendency is lower initially and less

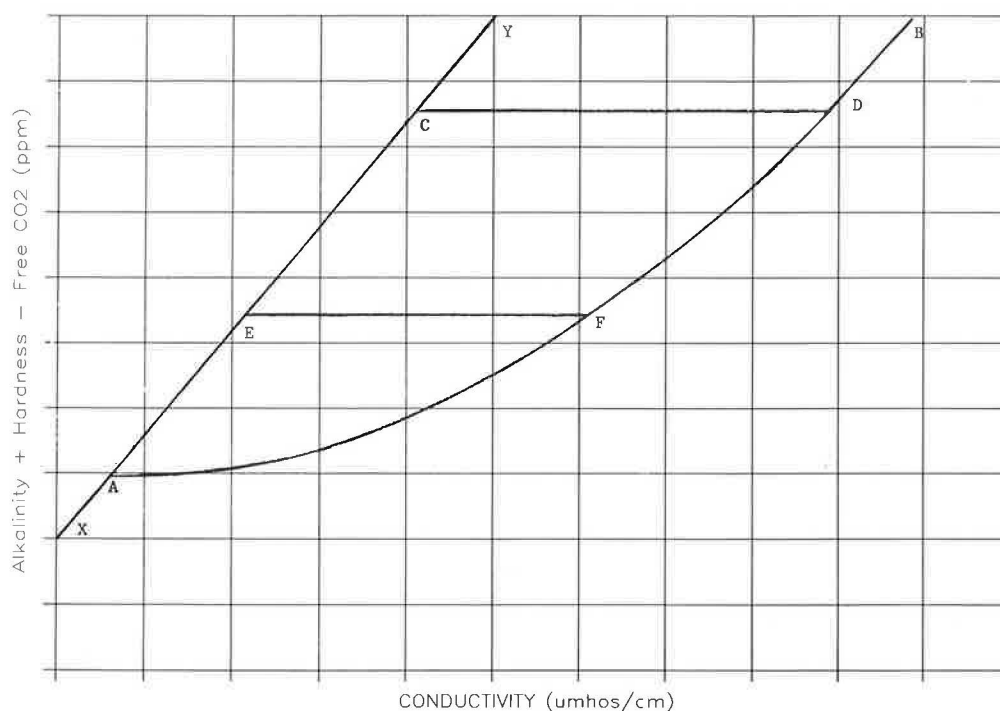


FIGURE 1 Chemistry limits for a given service life.

chloride and sulfate can be tolerated, so with increasing conductivity the critical point is reached at a lower conductivity.

It is to be expected that line AB will show changing slope over a wide range of conductivity because AB represents the ratio of scaling tendency to conductivity which, if the effect of free  $\text{CO}_2$  is ignored, is comparable to the ratio of scaling salts to total dissolved salts (scaling + corrosive salts). If this ratio were constant, AB would be a straight line, and as conductivity is decreased the fixed service life would be maintained simply by decreasing scaling salts and corrosive salts in balanced linear proportion. However, even if this balance is sustained, the corrosion rate will still increase as conductivity is decreased due to the weakening scaling tendency inherent with decreasing scaling salts, which increases corrosion rates even in the absence of corrosive salts. This means that as conductivity decreases, fixed unit reductions in the scaling salt concentration must be accompanied by increasingly larger reductions in the corrosive salt concentration to maintain the fixed service life. Thus as conductivity decreases, the ratio of scaling salts to total dissolved salts must increase and the slope of AB must decrease. In soft waters of low scaling salt content, the scaling tendency becomes low enough and the potential corrosivity becomes great enough that proportionately large decreases in corrosive salt content are needed to sustain the fixed service life, and the slope of AB can approach zero. Of course the fixed service life can be sustained by decreasing free  $\text{CO}_2$  as well as by decreasing corrosive salts; and in very pure waters of very low conductivity where the influence of further decreases in all dissolved salts is minimal, free  $\text{CO}_2$  becomes the primary factor controlling service life.

#### *A Modified California Chart*

The similarity of Figure 1 to the California Chart is readily seen by first realizing that the scaling tendency expression  $\text{alkalinity} + \text{hardness} - \text{free } \text{CO}_2$  includes the effect of pH because specifying the alkalinity and free  $\text{CO}_2$  necessarily specifies the pH. The pH can be substituted for  $\text{CO}_2$  in the above expression to give the following expression in which alkalinity is as  $\text{HCO}_3^-$  and hardness is as  $\text{Ca}^{+2}$ :

$$\text{Alkalinity} + \text{Hardness} - \frac{\text{Alkalinity}}{\text{antilog}(\text{pH} - 6.22)} \quad (1)$$

In this expression, the effect of any given pH value on water corrosivity will vary with variations in alkalinity and hardness (or  $\text{CO}_2$ ). In effect, the scaling tendency expression can be viewed as the effect of pH on corrosivity after correction for alkalinity and hardness scaling effects. In addition to the effect of scaling tendency, also specified on Figure 1 is the proportion of corrosive salts at a given conductivity because once alkalinity/hardness concentrations are specified, the balance of salts contributing to that conductivity value are corrosive salts. A modified California Chart emerges once AB lines for various fixed service lives are entered and service life is depicted as a function of conductivity (inverse of resistivity) and a pH-related factor. As pH increases, service life increases to the extent that the scaling tendency increases and to the extent permitted by corrosive chloride/sulfate salts included in the conductivity value.

The modified chart reflects the detrimental effect of non-scaling low-conductivity soft water by line XY and lines just below and parallel to XY. Decreasing conductivity caused by decreasing alkalinity/hardness concentrations at a fixed concentration of corrosive salts and  $\text{CO}_2$  follows such lines, and these lines intersect decreasing service life levels as conductivity decreases. Decreasing alkalinity at a fixed free  $\text{CO}_2$  content is necessarily accompanied by decreasing pH, so the combined effect of lower pH and high resistivity common to soft water is illustrated.

#### *Adding the Effect of Temperature*

In its final form, the modified chart must incorporate the effect of mean annual temperature to be accurate enough for use in different climates. Reduced temperature tends to reduce the corrosivity of aggressive water chemistry. Thus, the graph could be expected to reflect the fact that galvanized pipe can be used successfully over a wider range of water chemistry limits in cooler climates. Denoting the effect of temperature in the graph is accomplished by constructing different AB chemistry limit lines for different climates or different temperature levels. The difference between the positions of these lines should be greater when a shorter service life is specified because a shorter service life is attainable in waters of lower scaling tendency where the effect of temperature is greater.

#### *Graphing of Available Data*

Finding the actual position and slope of line AB for any specified service life requires plotting of sufficient field data in which pipe condition as a function of age is related to water conductivity, alkalinity, hardness, free  $\text{CO}_2$ , and temperature. All of the more accurate available data from wet sites (130 sites with continuous or very prolonged flow) inspected in South America and the United States have been plotted in Figure 2.

Figure 2 is the low-conductivity end of the graph illustrating the temperature climate AB line. Two pipes shown (E) had erosion corrosion in the high water zone that made performance much worse than the graph estimate. These are from a small area where erosion corrosion is extreme and are included here to show the degree of erosion-corrosion interference possible. One seemingly abnormally good pipe is at a site with a low mean temperature. Diamond-shaped and X-shaped data points represent sites in temperate climates; square-shaped and cross-shaped data points represent those in tropical climates. All cross-shaped and X-shaped data points represent pipes that in the author's estimation have average corrosion rates low enough to resist important perforation for at least 35 years at 14 gauge. All square and diamond-shaped data points represent pipes that have higher corrosion rates. The average corrosion rate of each pipe over its exposure time in service was determined crudely on the basis of an estimation of remaining pipe invert thickness by using a pick blade to test metal yielding. Estimates were conservative so that errors would be in the direction of conservatism. In Figure 2, line AB represents, for either a temperate or a tropical climate, a reasonable approximation of the position and slope when the line denotes minimum water chemistry conditions at which

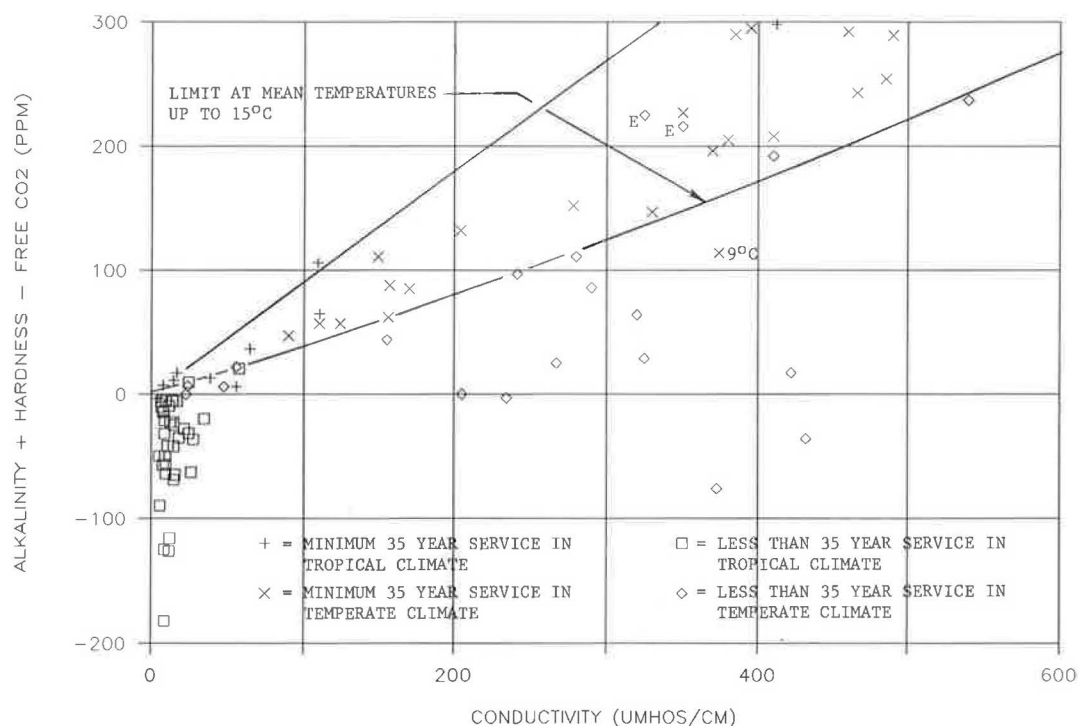


FIGURE 2 Chemistry limits for 35 years of service at 2.00 mm (14 gauge).

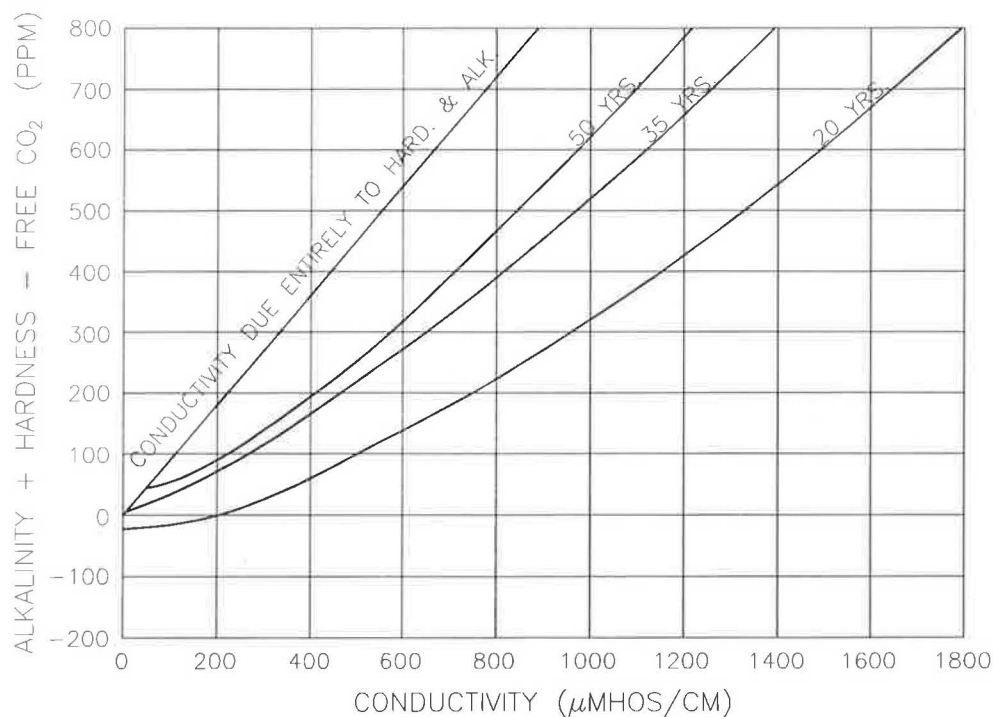


FIGURE 3 Modified estimation graph—durability in temperate climates.

a general level of 35 years of satisfactory service at 2 mm (14 gauge) can be expected. Durability increases with increasing distance above line AB. Of course, durability increases with increasing pipe wall thickness above 2.0 mm, and judging by the California Chart gauge adjustment factors, 3.5 mm material (~10 gauge) should provide up to as much as 1.75 times as long service life as 2.0 mm material does.

After AB lines for 20-year and 50-year service life levels have been determined, Figure 2 can be made to resemble the California Chart more closely. It is necessary to place AB lines for different service lives on one graph and to construct such a graph for both temperate and tropical climates. The resulting graph for temperate climates is shown in Figure 3. The reader will recognize that the California Chart axes for



the service life and the pH-related factor have been transposed in the modified graph.

### Use of the Estimation Graph

The effects of groundwater chemistry trends on durability trends in different geographic regions are illustrated in the graph. For example, in regions having soft groundwater below 50  $\mu\text{mho/cm}$  conductivity (above 20,000  $\text{ohm cm}$  resistivity) and having minimum free  $\text{CO}_2$ , the 14 gauge service life attainable ranges from 50 to about 35 years. In regions with harder groundwater above 50  $\mu\text{mho/cm}$  conductivity (below 20,000  $\text{ohm cm}$  resistivity), the service life attainable ranges from 50 years to much higher life for all conditions not involving excessive free  $\text{CO}_2$  or excessive  $\text{Cl}^-/\text{SO}_4^{2-}$ .

An illustration of how the graph could have been used to identify troublesome areas and thus prevent unsuspected severe corrosion problems can be seen in the results of field performance studies in project areas in the Amazon Basin of Brazil where extremes in poor behavior have been observed. For example, on one such project a typical pipe site had water chemistry values of 100,000  $\text{ohm cm}$  resistivity and 5.0 pH for which, in the California Chart, relatively good life is indicated for plain galvanized pipe at 1.62 mm thickness due to the very high resistivity. Very good life is also indicated, according to the chart, at greater pipe wall thicknesses. The projected times to first perforation according to the chart are 41 years at 1.62 mm, 54 years at 2.00 mm, 74 years at 2.77 mm, and 94 years at 3.50 mm. In actuality, 3.50 mm material at this site had a service life of less than 20 years due to low hardness and alkalinity and high free  $\text{CO}_2$ . The alkalinity was 1.9 ppm as  $\text{CaCO}_3$ , the hardness was 1.5 ppm as  $\text{CaCO}_3$ , and the calculated free  $\text{CO}_2$  was 68 ppm. In this water, corrosion was so rapid that 3.5-mm-thick material could not provide useful service life. In the modified Armco graph for tropical climates, this water chemistry falls far below the limiting line for 20-year service life at 2.00 mm thickness where corrosion is severe enough that the effect of increased wall thickness is not useful. Thus a correct understanding of the effects of water chemistry on durability would have led to avoidance of plain galvanized pipe on this project and would have emphasized the need for a coating more protective than zinc.

### Limitations of the Estimation Graph

#### *Influence of Seasonal Water Chemistry Variations*

The graph is based on one-time water testing, but seasonal variations in chemistry (mainly acidity) can have a limited effect on graph accuracy. For highest accuracy, it would be necessary to determine mean or average dry-weather parameters by testing at different seasons, but this would not be practical. The best compromise is to conduct one-time testing in dry summer weather when groundwater acidification is greatest so that areas are characterized according to worst-case or near-worst-case conditions. Each region will have relatively stable basic water chemistry characteristics due to stable general features of climate, soil, and terrain. Favorable regions or areas with hard or modestly hard water will be

evident as will unfavorable ones where soft acidic water, or high  $\text{CO}_2$ /conductivity water, or high salinity water is present.

#### *Influence of Water Flow Characteristics*

The modified chart applies best to pipe handling streams with persistent groundwater flow. Under certain conditions non-persistent surface runoff can induce erosion corrosion or other accelerated corrosion in a pipe high-water zone that causes pipe life to deviate considerably from the graph estimate (three such pipes are inserted in data of Figure 2). Durability of pipes or pipe zones contacted only by nonpersistent surface runoff can be adequately characterized by climate/terrain features alone as discussed elsewhere in this Record. The graph will yield overly conservative results for stagnant waters that usually contain more free  $\text{CO}_2$  and yet are less corrosive than flowing water due to low dissolved oxygen, and stagnant waters should not be used to characterize regional durability trends.

### Galvanized Durability Estimation in Soil Environments

In dry regions, most pipes are dry most of the time and soilside corrosion controls pipe durability, so use of the California Chart on the basis of soil resistivity and pH should give useful though conservative estimates of galvanized durability (except at occasional sites with groundwater flow). The chart could also be used in any climate on projects involving only soil exposure, such as highway underpasses or tunnel liners. It could also be used in any climate for pipes having long-term invert pavement protection. First perforation time upon which the chart is based does not mark the limit of pipe service life, and the American Iron and Steel Institute has proposed a modification of the chart that may reflect actual service life in soils more realistically (33, p. 222). The modification is based on National Bureau of Standards soil test results that indicate that overall metal weight loss at the time of first perforation is only about 13 percent in soils. The modification predicates a service life based on about twice this much metal loss and so would tend to compensate for conservatism arising in dry climate soils of low moisture content.

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