SECTION IV

CORROSIOE CONTROL

It has been seen that corrosion arises from a variety of sources and that it can be very destructive. In high resistivity soils corrosion may be very low, but exceptions are known. Pipeline operators are making increasing use of a variety of corrosion mitigation techniques. Previous discussion shows that certain obvious mistakes, such as placing dissimilar metals in contact, must be avoided. Special methods available for corrosion control are discussed in this section. It is probably safe to say that no one method of corrosion mitigation answers all problems.

Out of 373 operating companies 330 said thev have a corrosion control program. The descriptions of these programs were collected and are on file at OPS-DOT. A few companies are in the process of setting up a corrosion control program, while others use consultants. The reasons given for not having a corrosion control program were to the effect that corrosion was not of sufficient magnitude to justify such a program.

The number of operating companies that have sponsored or engaged in corrosion control research are shown in Table 12.

1. Material Selection and Treatment

Although no ferrous metal is untouched by corrosion, the extent of corrosion is significantly influenced by the exact composition of the metal and its thermal and mechanical treatment. Tables 13-18 summarize recent results on various treatments altering resistance to corrosion of various types of

TABLE 12

MAJOR AREAS OF CORROSION RESEARCH ENGAGED IN OR SPONSORED BY THE OPERATING COMPANIES

Research Area	Number of Companies
HVDC	45
Coatings	42
Corrosion resistance of piping and organic coatings in various environments	20
Anode composition & groundbeds	15
Stress corrosion	13
Internal corrosion, inhibitors	12
Cathodic protection	7
Alternating current corrosion	5
Field test methods	5
Over-the-line surveys	5
Stray currents	5
Hydrogen embrittlement	4
Pulse rectification	4
De-icing salt effects	3
Polarization	3
Underground corrosion	3
Bacterial corrosion	2
Cathodic protection criteria	2
Corrosion rate studies	2
Lightning effects	2
Sour gas corrosion	2
Statistical analysis of leak frequency, pitting	2
Telluric earth currents	2
Casings at railroad crossings and roads	1
Copper pipe	1
Fiberglass pipe	1
Insulated fittings	1
Stainless steel tubing for gas distribution	1

metals. As noted previously, susceptibility to stress corrosion cracking, hydrogen embrittlement, sulfide cracking, etc., increases as the yield strength of steel increases.

Many additives improve corrosion resistance by increasing the tendency to form passivating films. Thus, chromium additions (stainless steel) increase resistance to most forms of corrosion, but increase susceptibility to rapid intergranular corrosion arising from certain heating cycles -- especially during welding. Other additives can be used to avoid these problems.

It has been claimed that cast iron pipe has a good record for resistance to underground corrosion by virtue of its large wall thickness and the graphite particles remaining to form a solid graphite-rust coating (788, 789, 142). These residues plug holes in pipe due to pitting and prevent leakage at substantial hydrostatic pressures (788). However, the old gray cast iron was brittle and weak because of the flaky morphology of the graphite. Thus, for example, cast iron gas mains were prone to break in high shrink-swell clays and were replaced by steel pipe (543). Also, catastrophic mechanical failure of graphitized cast iron pipe has been observed. In ductile cast iron, special heat treatments are used to produce nearly spheroidal graphite particles. According to one manufacturer, the result is a ductile metal with twice the initial strength, less strength loss upon pitting, and a slightly lower corrosion rate (142). In seawater, however, gray cast iron corroded twice as fast as mild steel and five times as fast as 18 percent Ni cast Fe.

Equation 11 gives pitting rate as a function of several variables. The parameters K_a and a in Equation 11 were determined empirically from NBS data and are given in Table 19. From this it would appear that cast iron corrodes more rapidly than steel for large exposed areas and slower for small areas.

Cu additions have been found to practically suppress bacterial activity (165). Inclusions of second phase material can often accelerate corrosion by forming local galvanic cells. Sulfide inclusions in stainless steel caused pit initiation (331).

Heat treatment can greatly influence corrosion resistance, as indicated in the tables. Unfortunately, the effect of welding is generally deleterious. The knife-line intergranular corrosion in some stainless steels has been mentioned previously. Hardness is often increased along welds, which increases cracking. Thus, hard electric resistance welds have cracked for hundreds of feet in sulfide environments (338), Post-weld heat treatment has proved beneficial in preventing cracking (337). Oxidation during annealing, heat treating, and welding produced Cr-rich scale and Cr-depleted metal surface on stainless steel (536). Scale and a thin layer of the surface had to be remove? to restore corrosion resistance.

In Table 6 it was shown that leaks have been observed much more often on longitudinal factory and field welds than on spiral factory welds.

Lengthy tests are necessary to determine true differences in underground corrosion. The corrosion rate of cast irons decreases rapidly because of the graphite-rust coating formation.

TABLE 13

METAL TREATMENTS IMPROVING RESISTANCE TO GENERAL CORROSION

Alloy Types	Environment	Factors Improving Resistance	Ref.
--	Underground	Cr, Cu + Ni additions	526
--	Underground	Gray cast iron >> steel and ductile cast iron	282
Steels	Seawater, 16 years	18%Ni cast iron > mild Steel > grey cast iron	330
Steels	Splash and tidal seawater	0.5% Ni, 0.5% Cu, 0.12%P 2X C steel	784
Steels	Marine	2.6 Cr-0.5 Mo 10 X C steel	784
Stainless	3% NaCl	Cr addition >11%	473
18-8 Austenitic	Seawater	-Mo additions -- 18-8 >Cr ferritic and martensitic steels	677
Steels	Atmosphere - Marine	A517 grade F > A242 Type 1 > Cu steel > C steel	784
Low alloy steels	H_2S in H_2O	Cr additions	787
0.007 - 0.15% C	O_2 free, 0.12 N HCl	Avoid cold work	756
0.01 - 0.02% N_2	O_2 free, 0.12 N HCl	Don't cold work & anneal	756
Pure iron	Aerated 0.12N HCl	Avoid impurities, in order of importance P, S, C, As, N, B	280
Fe-Cr-C alloys	0.1N borax	Decrease pearlite/ferrite ratio, prevent cementite	327
Pure iron	1N H_2SO_4	Annealing at 900°C, 1hr. vacuum, and impurities	783
Pure Fe	--	S removal or Mn & Cu addition	319
430 Stainless	--	0.1-0.5% U additions	279
Stainless	--	Smooth surface rather than rough	536

TABLE 14

METAL TREATMENTS IMPROVING RESISTANCE TO PITTING AND CREVICE CORROSION

Alloy Types	Environment	Factors Improving Resistance	Ref.
Cast iron	Underground	15%Ni	525
Cast iron	Underground	Ductile slightly better than grey	788
Fe crystal	Distilled water	(111)*> (100)*> (110)* Purification	492
Steels	Seawater	Ni reductions, mild steel > high strength steel	330
Stainless steels	Cl^-	Ni additions	179
Stainless steels	Marine	316,316-6, 20-Cd, 17 Cr-7Ni -0.7Ti-0.2 Al not corroded: 405, 410, 430, 301, 304, pit	254
18-8 Stainless	0.1N NaCl, 0°C	Re reductions	772
18-8 Stainless	0.1N NaCl, 25°C	Re additions	772
Stainless	- -	Electropassivation (anodizing)	536
Cr-Fe	Cl^-	Cr additions, Ni had no effect	326
Cr-Fe	0.1N NaCl	Increasing Cr	154
15%Cr-Fe	0.1N NaCl	Ni additions	154
Stainless steels	Cl^- in dil H_2SO_4	316 > 321 > 302 > 304	487
Iron + Cr	Cl^- in 1N H_2SO_4	Cr additions	328
Stainless steels	Dil., H_2SO_4	321 > 316 > 304 > 302	487
Various	$CaSO_4$ or $BaSO_4$ paste scale	TK-2>9% Ni > J-55 = N-80	6184
Steels	Atmospheric	0.3% Cu	165

*Miller indices

TABLE 15

METAL TREATMENTS IMPROVING RESISTANCE TO STRESS CORROSION CRACKING

Alloy Type	Environment	Factor Improving Resistance	Ref.
Steels	$Ca(NO_3)_2+ NH_4NO_3^-$, 100°C	Ti addition of 4 X C	175
Steels	--	Decrease N_2, increase C (at constant strength)	301
Steels	--	Use high purity Fe, Cr, Ni	694
4340 Steel	--	Additions of Si > 1.5%, reductions of S & P	530
18-8 Stainless	$MgCl_2$ soln., 154°C	Ferritic >> austenitic	272
Annealed austenite stainless	Boiling 42% $MgCl_2$	C & Ni additions N_2 reductions	321
Cold-worked austenite stainless	Boiling 42% $MgCl_2$	C & Si additions P & Mo reductions	321
--	--	Purity, brittle alloys	691

TABLE 16

METAL TREATMENTS IMPROVING RESISTANCE TO HYDROGEN EFFECTS

Alloy Type	Environment	Factor Improving Resistance	Ref.
18-8 Stainless	Dil. H_2SO_4 + As_2O_3.	austenitic >> ferritic	272
301,17-7	Dil. H_2SO_4 + As_2O_3.	annealed >> cold reduced	272
Steels		Yield strengths <130,000 psi, avoid hard welds	587

TABLE 17

METAL TREATMENTS IMPROVING RESISTANCE TO SULFIDE STRESS CRACKING

Alloy Type	Factors Improving Resistance	Ref.
Low alloy steels	Temper to eliminate martensite	408
Steels	Low yield strength, A285 immune, 365 very susceptible	337

TABLE 18

METAL TREATMENTS IMPROVING RESISTANCE TO INTERGRANULAR CORROSION

Alloy Type	Environment	Factor Improving Resistance	Ref.
Steel	- -	low Ni, C; Ti addition	535
0.1%C, 20%Cr, 3-6% Ni	- -	0.4% TI (sometimes)	289
Austenite 304 stainless	Boiling HNO_3	Small additions of Cb+B	528
304, 316 stainless	- -	Mo addition	654

TABLE 19

VALUES OF MATERIAL PARAMETERS IN EQUATION 11 FROM NBS UNDERGROUND TEST DATA (754)

Parameters	Wrought Iron	Steel	Cast Iron
K_a	1.00	1.06	1.40
a	0.13	3.16	e.22

Steels with 3-5 percent Cr in seawater had lower weight losses for two years, but larger losses after four years.

Even surface preparation can influence corrosion rates. Rough surfaces were found to corrode faster than smooth surfaces on stainless steel (536). Cold work did not change the corrosion rate of pure iron but did. increase the corrosion rate when some C was present (756). Annealing above 200°C decreased the rate, suggesting that plastic deformation increases corrosion by producing compositional inhomogeneities.

Selection of a particular alloy depends not only on corrosion resistance but on mechanical properties and largely on economic considerations, which include cost of the metal and fabrication, protection necessary, required lifetime, maintenance and repair, damage due to leaks, etc.

2. Inhibitors

An inhibitor is a chemical which significantly reduces corrosion when present in small amounts. Generally, there is a concentration below which the inhibitor accelerates corrosion. On the other hand, it is not economical to use more inhibitor than required. Thus, there is an optimum concentration range -- which must be determined experimentally. This can be accomplished by coupons or hydrogen probes which control automatic injection equipment.

Inhibitors have proven to be a practical means of controlling internal corrosion of pipelines carrying petroleum products. In a 1950 survey of 8215 sour crude wells in the mid-southwest, 44 percent were found to be economically affected by corrosion

(6185). Of those affected, 26 percent were being treated by corrosion inhibitors. In a 1953 survey of 348 sweet crude oil wells in California, it was found that inhibitors caused an 80 percent reduction in iron content of the oil produced (6183). Pulling jobs were reduced 51 percent; rod jobs, 46 percent; tubing jobs, 71 percent; and pump replacements, 36 percent. Inhibitors have been found to be effective not only for controlling pitting but also for reducing sulfide cracking, although some cracking of weld-susceptible steel still occurred (337).

Fifty-seven of the 373 operating companies surveyed in this study used inhibition to control internal corrosion. Fifty-eight used dehydration.

A wide variety of chemicals has been found to inhibit corrosion. In 1955, NACE committee T-3A published a reference list of 68 inhibitors and classes of inhibitors (6186). The composition of many inhibitors is, of course, proprietary and/or secret. Inhibitors may be divided into organic and inorganic. In the 1953 California oil well survey, 65 percent were inorganic and 35 percent organic (6183).

Apparently, several different mechanisms can be involved in inhibition. Strongly oxidizing additives, such as chromate, can cause formation of passivating oxide films. Other additives merely alter the corrosivity of the electrolyte by changing pH or by removing corrosive solutes. The polar organic inhibitors are generally thought to act by forming an adsorbed layer on the metal surface to block reactions there. Radiotracers showed that monolayers were formed and gave protection (693).

Obviously, blockage of any step in the corrosion sequence will be effective and is probably found in the action of some inhibitor. Thus, the function of strong oxidizing agents, such as lead suberate and lead azelate, is to convert Fe2+ to Fe3+ in films (36). Fe^{2+} was thought to he responsible for breakdown of the films. Amines were chemisorbed on Fe and inhibited corrosion only when the surface was not dry (226). The amount of chromate or nitrite required to inhibit corrosion was found to increase as the amount of chloride and sulfate increased (775). A competitive adsorption mechanism between inhibiting ions and aggressive ions was thought to be involved.

The inhibiting action of neutral benzoate was similarly attributed to reduction in breakdown of the film (220). It was hypothesized that hexamethyleneimine 3, 5-dinitrobenzoate inhibits by depolarizing the cathodic reaction, which changes the potential to the positive side and causes passivation (396).

Ammonium ion was found to be an inhibitor independent of pH, H_2S and Cl^- concentrations (706). A certain amount of corrosion occurred before protection was obtained, even if samples were presoaked in the inhibitor. This suggests that inhibition results from interaction of NH_4^+ with film or scale and not with the metal surface itself. Organic and inorganic compounds have been used in conjunction to provide greater inhibition -- a synergistic effect. Of several simple anions, I- was observed to yield the greatest improvement in corrosion mitigation of organic amines.

Only some of the basic experimental and theoretical research done on the inhibition mechanism is mentioned above. Reference 690 gives a lengthy review of these results. One research goal is to enable molecular designing of organic corrosion inhibitors. It would appear that discovery and use of inhibitors is still primarily an empirical art, although eventually rational scientific approaches may be possible. In other words, further quantitative investigation of inhibitor effectiveness and inhibition procedures is needed (Q126).

3. Coatings: General Principles and Surface Preparation

An important method of corrosion mitigation is the deliberate application of a coating to either the interior or the exterior of the pipe.* Interior coating is generally confined to relatively short lengths of metal, as in oil wells, and to large diameter pipes. Only 17 companies surveyed used internal coatings. Coating of the exterior of the pipe on the other hand is very widely employed. In considering pipe coatings one must take care to distinguish between the intact coatings and degraded coatings which are no longer protective. In other words, it is not safe to assume that "once coated -- always coated." All coatings have finite lifetimes, although these may in some cases exceed the useful life of the pipeline. The prevalent circumstances under which coated pipes have developed leaks were summarized in Table 5. The quality of nonconductive coatings can be conveniently judged either by their average conductance or by what is equivalent, the average current density required for cathodic protection.

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*Coatings formed by the corrosion process itself, such as the graphite-rust scale formed on cast irons, are excluded.

Coatings reduce corrosion by many different mechanisms. A given coating may function by more than one mechanism, either simultaneously or sequentially at different stages in its life. Metal coatings may act as sacrificial anodes; as barriers to contact with the electrolyte; as sources of a passive film; by alternation of the surrounding environment; and/or as a source of inhibiting ions. Nonmetal coatings may act as barriers to contact of water and electrolytes with the surface, as insulators to flow of electrical current, and as sources of inhibitors and biocides. The effective life of protective coatings can be considerably extended by quality control of surface preparation, coating selection, and application procedure (82).

Many claims have been made as to the superiority of various coatings. It is true that some coatings have advantages, although which coatings are best depends on a variety of factors including economics, environment, required lifetime, etc. No one coating is best under all conditions, and no coating is absolutely perfect under any given condition (682). Therefore, continued research for the "perfect" coating is worthwhile (Q109, Q436). Improvement in the effectiveness and application (holiday detecting, field joints, bond aging, etc.) of thin film coatings is needed (Q274, Q256, Q323, Q812). Of equal importance to the type of coating is the method cf application. Poor application can negate the protective qualities and could conceivably increase corrosion by providing shielded areas for bacterial action, produce concentration cells, augment density of discharge of interference current, and reduce effectiveness of cathodic protection. In fact instances have been noted in which pitting is more severe with coated than with uncoated metal (131, 682). Table 5 shows that the second most frequent circumstance for leaks in coated pipes was improperly applied coatings. (Damage of the coating was the most frequent circumstance.)

The major types of protective coatings used by the companies surveyed are shown in Table 20. Coal tar enamel was used by 205 companies as first choice. Forty-eight of these companies were oil companies and 144 were gas companies. Asphalt was the first choice of 34 companies. Ten were oil companies and 19 were gas companies.

TABLE 20

MAJOR TYPES OF PROTECTIVE COATINGS USED BY COMPANIES DURIYG THE LAST 5 YEARS BY ORDER OF USE

	Protective Coating	1st	2nd	3rd	4th	5th	6th
(A)	Asphalt	34	37	14	1	3	0
(B)	Coal tar	205	72	30	1	0	0
(C)	Mastic	20	42	50	22	6	1
(D)	Prefabricated film	55	71	53	11	6	0
(E)	Wax	3	11	13	11	1	0
(F)	Other	49	70	24	13	0	0

Table 21 lists the major factors considered by the surveyed companies in selecting coating materials and wrappings.

TABLE 21

FACTORS CONSIDERED IN SELECTING COATING MATERIALS AND WRAPPINGS FOR SPECIFIC APPLICATION

Factor	Number of Companies
Experience	187
Resistance to Deterioration	164
Economics	159
Electrical Properties	154
Soil Stress Resistance	135
Permeability	92
Temperature Stability	76
Ease of Application	54
Compatibility	16
Mechanical Properties	12
Geography and Geology	11
Manufacturer's Specifications	10
Storage	10
Safety of Personnel	1

The materials currently used by the companies to coat field joints and appurtenances are listed in Table 22, Plastic tapes in various forms and modes of application are by far the most widely used.

The first step in proper coating application is surface preparation, as thoroughly reviewed in a NACE report (6171). For good coating adherence a clean surface should be produced by removal of such things as oil, grease, dirt, welding flux,

TABLE 22

MATERIALS CURRENTLY USED TO COAT FIELD JOINTS AND APPURTENANCES

Coating System	Number of Companies
Tapes; plastic, rubber or bitumen adhesives, cold or hot applied	318
Asphalt Mastic	111
Bituminous Materials, hot applied	
Coal tar	88
Asphalt	65
Bituminous Materials, cold applied	5
Miscellaneous Materials	
Cement Mortar	3
Epoxy	18
Glass tape	6
Polyurethane foam	1
Sand	1
Sheet plastic	48

slag, mill scale, rust, etc. For most coatings the surface should be rough, as measured by the surface profile or "anchor" pattern. The rule of thumb has been that anchor depth (bite) should not exceed one-third of the total thickness of the coating system. Instruments have been devised to assess the surface profile (791). Rough corners or bumps, as might result from welding, should be removed.

Surface treatments may be roughly divided into chemical and mechanical. Grease and oil must generally be removed before other treatments. This may be accomplished with organic solvents, alkaline solutions, emulsions, or hot watar plus detergents. Scale and rust can be removed by acid pickling and electrolytic pickling. Oil and scale may be removed simultaneously by treatment with solutions of phosphoric acid and organic solvent or alkali phosphate plus detergents. Scale and heavy rust can be popped off by flame conditioning or induction heating. Heating can also be useful for removing hydrogen from the metal interior.

Mechanical methods include wire brushing, impact tool, grinding, blasting with abrasive, and wheel blasting. These operations may be either carried out by hand or by equipment of various degrees of automation. Blasting has been judged by appearance according to the Swedish standards, with a "white" surface the best (731). Normally, it has not been considered economical or necessary to go to a white surface.

Weathering or treatment with phosphoric acid mixtures is required for coatings to adhere to galvanized steel. Acetic and hydrochloric acids have not been recommended.

Application of primer should follow surface cleaning as soon as possible, before oxidation and contamination occur. If it is not possible to prime immediately then several pretreatments are available. Vinyl metal conditioner, or wash primer, consists of a resin-chromate-phosphate mixture providing sealing and inhibiting action. Oils of various types can also be employed.

Red lead paint has been found to be an effective primer in many instances. Cast iron and steel samples with a single coat of red led paint suffered practicaily no corrosion under field conditions for one year in tests conducted in India (639). A

10-year underground test showed that zinc chromate and baked-on red lead primers adhered well and retarded corrosion, but that they provided insufficient protection when used alone (682). In the atmosphere, three coats of red-lead primer showed no signs of rusting after five years in a South African test program (83). Zinc chromate-epoxy resin primers gave similar results and were preferred for marine environments. Lead silico-chromate was also good but kept better in prolonged storage. It was claimed that the passivating action of primers can be determined by measuring the potential of the metal (283).

Organic coatings are commonly used for pipelines. Except for sacrificial anode coatings such as zinc, it is important to minimize the number of holes or "holidays" in the coating. Water and electrolyte can reach the metal surface through holidays and cause rusting. This results in peeling and. blistering of the coating, greatly reducing its effectiveness. Generally, the holiday problem diminishes as the number of coats and the total coating thickness increase. A total of 263 of the companies surveyed used holiday detectors to check the effectiveness of coatings applied to field joints, main line valves, flanges, and taps.

4. Paints

Paints consist of finely divided inorganic pigments and organic binders of various types. They may be applied by brush, roller, spray, dipping, electrostatic spray, etc. Apparently, paints have seldom been used for underground pipelines, although they have almost always been employed for aboveground portions and often on marine pipelines.

The pigments in rust-proof paints are not selected for the sake of appearance but for effectiveness in the control of corrosion. Zn, Al, or Mn dusts have sometimes been used and act as sacrificial anodes (246, 144). Other pigments serve as inhibitors or form protective films by reacting with the surrounding and/or corrosion products to yield new compounds. Red lead, zinc chromate, zinc silicate, zinc oxide, and phosphates have all found favor.

The stability, flexibility, adhesiveness, and permeability of the organic constituents are equally important. In a 14-year study of paints in potable-water tanks, vinyls were found to perform better than phenolics (166). Thermosetting acrylics have been found to adhere better than melamine alkyds. Multilayer coatings have often been favored. Another study concluded that 0.2 mm Zn-rich paint covered with 0.15 mm of bituminous coating was best for water-immersed structural steel (256).

When a coating is subjected to daily temperature fluctuations, it must maintain its flexibility under the thermal stresses generated. Some coating-primer combinations meeting generally accepted specifications have been found to lose much of their original bond under daily temperature fluctuations. The same study found synthetic primed coatings to have clear adhesion superiority over coal tar primed coatings (722).

Best protection against sea air has been reported obtained with pure zinc-dust paint and a synthetic impermeable and mechanically hard binder (246). Marine paints quite often contain biocidal agents and are known as "antifouling." Toxic mercury and copper paints have been found to retard fouling for two to three years. In the use of copper based paints, it is absolutely essential that the undercoating be holiday-free. This is because copper salts can displacement-plate copper metal onto steel and cause rapid galvanic corrosion (254).

5. Metal Coatings

Metal coatings can be applied by various methods including hot dipping, electroplating, flame spraying, and vacuum evaporation, as reviewed, for example, in Reference 546. Heating after coating to permit some diffusion into the iron generally improves adhesion. Metal coatings can be divided into two categories - anodic and cathodic -- according to their position in the galvanic series relative to steel. All metal coatings protect steel by denying access of water, oxygen, and electrolytes to the steel surface. The anodic coatings, in addition, act as a sacrificial anode, dissolving preferentially in place of the steel. The oxidation/corrosion products of the coating may also play an important role in protection.

The oldest of the anodic coatings is zinc, or "galvanizing." Two ounces per square foot of zinc was found to protect steel for 10-15 years in the most corrosive soil tested (603). The corrosion rate of Zn in different atmospheres can vary from 0.01 to 2.9 mpy (679). Heat treatment at 500°C for 10-15 minutes increased the corrosion resistance and plasticity of a Zn coating (201). Protection of Zn by paint is recommended for marine environments (156).

A more recent and promising anodic coating material is aluminum. In a refinery atmosphere a Zn coating was removed completely in three years while ten years was required to remove 94 percent of an equivalent Al coating (546). Aluminum coatings lasted almost five tines as long as Zn in industrial atmospheres (679). A marine atmosphere attacked both slightly (546). Aluminum coatings 0.25 to 0.375 mm thick were recommended for buried conditions (497). In fresh water the attack of Al decreased parabolically with time, indicating buildup of a passivating. aluminum oxide film. Advantages of both Al and Zn were obtained by vapor-depositing Al over galvanized steel (219).

The more noble cathodic coatings often stand up to degradation of themselves better than the anodic coatings. Chromized steel was found to be more resistant to seawater than aluminized and galvanized steel (499). However, any discontinuities in the coating lead to rapid localized attack of the exposed steel due to galvanic action. Thus thick, dense coatings are essential. Chromium platings below 8 microns thickness had poor corrosion resistance while those above 18 microns thick were considerably better (680).

Anodic and cathodic coatings have occasionally been compared. Zinc coatings were found to perform better than Cd in atmospheres rich in SO_2 (222). Effectiveness in reducing stress corrosion cracking of 302 austenitic stainless in boiling 42 percent $MgCl_2$ was in order Ni, Cu, Al, Zn, Pb (477).

6. Organic Coatings

Organic coatings may be classified in many ways: by their method of hardening, by composition, by thickness, by properties, etc. Organics such as coal tar enamel, asphalt, and polyethylene are thermoplastic -- they soften and flow when heated and harden when cooled. These are often applied hot. Others are thermosetting -- they harden irreversibly by chemical reaction when heated. Some harden at room temperature by chemical reaction while others harden by solvent evaporation. In a 1962 survey by the American Society of Civil Engineers about half of 178 firms were not satisfied with the coatings they were using and were seeking better means of controlling corrosion (77).

Application techniques include painting, pouring, spraying, flame spraying, electrostatic spraying, fluidized bed coating, dispersion coating, flock, and solution coating. Machines exist for coating large pipelines fairly automatically. Strengthening agents such as fiberglass, cloth, asbestos, jute, paper, etc., are frequently added to organic coatings -- often by alternate wrapping and coating.

Organic coatings function primarily by excluding water and electrolytes from contact with the pipe. They also resist the flow of electricity and the passage of oxygen and other gases.

A serious problem with organic coatings is attack of the coatings by micro-organisms. Organics are food for many micro-organisms and the necessary oxygen and water for metabolism are present in most pipe trenches. Large populations of bacteria were found adjacent to all pipelines investigated in one study (5025). Asphalts and plastic. tape were found attacked and disbonded (5000). Another study investigated the resistance of several types of coatings to oceanic bacterial attack and found that the rate of attack for all coatings was so low that half-inch thick coating was expected to protect a pipeline for many years (471). Evidence of bacterial attack of polyvinyl chloride lining of sewer pipe has been found (780). Inclusion of biocidal chemicals such as arsenic oxide in coatings to prevent biological deterioration has been suggested but has not been adequately tested. Some organic coatings appear to have some natural resistance. **Also** important in organic coatings is their resistance to water and electrolyte absorption, soil stress, and flow under depression forces (e.g., rocks). Their adhesive strength to the pipe should be about the same as the tensile strength of the coating.

Bituminous coatings have a long history of use in protecting underground structures. These include native asphalts, oils, and resins of both animal and vegetable origin; products derived from these; refined and chemically treated petroleum asphalts and coal tar products; and pitches and residues from treatment and processing of resins and oils.

Coal tar enamel has shown good resistance to water permeation and to flow of electrical current. It adheres and resists abrasion well. However, at temperatures below 40°F it loses its ductility and cracks easily (703). Dock gates at the Panama Canel were coated with hot coal tar pitch up to 3/16 inch thick and found to be in first-class condition after 20 years (501).

Apparently, not all coatings must be tightly adherent. Good results are claimed for loose polyethylene sleeving over cast iron pipe (789, 788, 572, 790). Although not stated, one suspects that care must be taken to exclude moisture, otherwise bacteria could flourish. Polyethylene and polyvinylchloride tapes have been developed for wrapping pipelines (726). Pipe is also coated in the mill, with 750 million feet of plastic coated pipe produced from 1957 to 1966 (556). Joint protection in the field then becomes critical. Melting on of powdered polyethylene under high pressure produced a coating so resistant to abrasion that pipe could be forced through roads, dikes, and soil embankments without damage (566).

Many tests have been devised to judge the quality of an organic coating. For example, adhesion can be tested by resistance to disbonding by cathodic protection currents (557). Measurement of electrical conductance has been suggested as a method for determining the inservice condition of coatings **(48).** Electrical resistance and capacitance measurements have also been proposed for monitoring coating performance (747).

7. Ceramic and Concrete Coatings

Fused coatings are nonporous, nonconducting, and nonreactive. They are, unfortunately, brittle. Glass-lined steel has been used in very corrosive chemical environments (163). Vitreous enamel coated thermal pipelines have been very successful in the Soviet Union (195). These coatings were reported to be practically wear-free and the most long lasting and reliable protection for thermal networks.

Concrete has been shown to be potentially useful for corrosion control. Wet Portland cement has a pH of about 12.4, normally causing passivation of steel (165, 792). Initiation of corrosion requires free oxygen at the steel surfaces and a ratio of chloride to hydroxyl ion activity of at least 0.6 (172). Chloride ions in the mixing water are effective in destroying passivation, only 1 percent being required. Adding inhibitors such as nitrite, chromate, and phosphate to the mixing water was found to be beneficial (312). Salt can diffuse in through concrete but is hindered by high quality, low permeability, low water-cement ratio concrete (281). With good concrete, difficulty is encountered only if the NaCl concentration exceeds about 4 percent.

Stress corrosion can occur in prestressed concrete (165). Stray current flow in concrete coated steel can lower the pH where current leaves the steel and eventually cause corrosion. Galvanized steel lasts better than black steel. When corrosion of steel in concrete does occur, the corrosion products can expand with enough force to crack the concrete. Usually, however, corrosion occurs only where the concrete is first cracked.

Calcium carbonate coatings may be precipitated by application of cathodic protection when the backfill has been treated with calcium bicarbonate. This process reduced the cathodic protection current by 80 percent in a 6-month trial (131).

8. Anodic and Cathodic Protection

The dissolution rate of iron depends on potential, as illustrated by Figure 1. With no external current supply attached, the metal potential becomes the corrosion potential at which anodic and cathodic reaction rates are equal. One can see from Figure 1, however, that the anodic reaction rate can be decreased either by lowering the potential or by increasing the potential into the passive region. The method of shifting the potential in the more noble direction by an external power source is called anodic protection. It is particularly useful for very corrosive environments. The current drawn is very nearly equal to the corrosion current. Unfortunately, the potential must be controlled so that it lies in the passive region. Potential excursions outside the passive region can cause drastic increases in corrosion. Thus, expensive instrumentation is required, which probably explains why the method has not been used for control of pipeline corrosion.

Lowering the potential also reduces the corrosion rate. This is called cathodic protection and is widely applied for control of underground corrosion. It has also been used for protection against internal corrosion (202). Cathodic protection is so widely applied, in fact, that it is well to caution at the outset that correct utilization is not trivial nor without problems. Although 213 of the companies surveyed designed their own cathodic protection installations, 95 companies employed consultants.

It is difficult to achieve adequate cathodic protection in high resistivity soils. Cathodic protection is ineffective in the splash zone of seawater (which is usually the most rapidly corroded area) (128). When the period of planned usage is small, it may be uneconomical to protect pipe even in corrosive soils (158). Cathodic protection is not very effective in holes, crevices, and internal corners (69). Unwanted contaminants can be introduced into the soil at the anode (e.g., Pb). Adequate cathodic protection under congested city streets is very difficult to achieve without causing interference.

Cathodic protection can actually increase corrosion rates under certain conditions. When it is applied to an old and leaky pipeline, several months must be allowed for a noticeable reduction in the failure rate. Cathodic protection of old pipelines may, in fact, increase the leak rate during the first year because liberated hydrogen can loosen adherent rust scale which had previously covered small holes (490). Cathodic protection can also increase the pH to the point where rust dissolves. Several instances have been reported where application of cathodic protection apparently had deleterious effects under special circumstances (257, 264, 334).

The current density required for cathodic protection varies widely under different conditions; representative examples are summarized below. More current was required to stop crevice corrosion of 304 stainless in flowing seawater than was required for quiescent seawater (584). When sulfate reducing bacteria were present, 50 percent more current was required in indirect sunlight than in the dark (538). In aerated solutions the minimum current was found to be equal to the corrosion current, while it was twice the corrosion current in deaerated solutions (729). In 3 percent NaCl the current required to protect steel was reduced by a short preliminary period of exposure without protection (531). In high resistivity soil, three times the corrosion current (intersection in Figure 1) was required for protection (532). Current required to stop stress corrosion cracking of stainless increased rapidly with the depth of the crack (579).

One study (729) found that cathodic protection in seawater caused protective layers of $CaCO_3$ and $Mg(OH)_2$ to form roughly in proportion to the current density. At lower current densities (< 150 mA/sq ft), the formations were predominantly $CaCO_3$; at higher current densities, $Mg(OH)_2$ was more prevalent. The $CaCO_3$ layers were found to be less porous and to provide more protection.

Many factors must be taken into account in design of a cathodic protection system. A soil conductivity survey is advised before laying the pipe so that cathodic protection can be centered in areas of higher conductivity (763). This would ensure maximum efficiency and minimum damage to coatings, if used. There are basically two methods of applying cathodic protection (482). One is to use sacrificial anodes and the other is to use externally applied impressed current.

Sacrificial anodes typically consist of Mg, Zn, or Al. These may be connected by insulated wire to the pipe, in the form of bracelets attached at pipe joints (728), or as coatings. Alloy additions can markedly affect the performance of sacrificial anodes. Aluminum containing 0.01-0.02 percent Indium and 0.5-5 percent Zn was found to be particularly effective, yielding a potential of about 1.1 V and a current efficiency greater than 80 percent at current densities about 1 mA/cm^2

(21, 95). Small amounts of Fe and Si improved performance, while 0.01 percent Cu markedly degraded it. Aluminum containing 0.45 percent Zn and 0.045 percent Hg was found to be promising from an economic standpoint for marine applications (529). Zn alloys are also useful in seawater. The zinc should contain less than 0.0014 percent Fe (105). Addition of 0.5 percent Al to Zn was found to reduce the deleterious effect of Fe (150). Zn with 0.3 percent Al plus 0.05 percent Cd, or 0.3 percent Al plus 0.5 percent Cd and 0.1 percent Si exhibited superior performance (388). Depleted uranium has also been successfully used as a sacrificial anode (85). One difficulty in the use of many sacrificial anodes over a length of pipe is that they will expire over a wide range of time, making optimal replacement difficult.

Table 23 indicates the choice of materials for anodes among the companies surveyed, and Table 24 summarizes the anode performance experience reported in this survey.

TABLE 23

NUMBER OF COMPANIES FAVORING DIFFERENT GALVANIC ANODES

	1st Choice	2nd Choice	3rd Choice
Aluminum	9	9	10
Magnesium	308	8	3
Zinc	14	79	2
Other	1	4	0

TABLE 24

PERFORMANCE OF GALVANIC ANODES

	Earth Exposure		
	Best	2nd Best	3rd Best
Aluminum	10*	8	45
Magnesium	282	5	2
Zinc	6	106	8
Other	1	0	0
	Marine Exposure		
	Best	2nd Best	3rd Best
Aluminum	7	18	7
Magnesium	28	16	15
Zinc	32	13	0
Other	4	2	1

*Number of companies reporting best performance.

The second, and most popular, means of applying cathodic protection is by impressed current, externally applied. Direct current is required and may be supplied by a variety of means, including step-down and rectification of commercial AC power, solar cells plus batteries, thermoelectric cells using fuel from the pipeline, fuel cells, and nuclear generators (278, 335). Generators with moving parts, e.g., windmills, generally require too much maintenance to be efficient.

In the simplest case, currents are periodically set manually to provide the required potential. Increasing use will be made of automatic controllers, especially if HVDC presents the problems that are feared (335, 357, 296, 120, 76, 576). Automatic control is also desirable in marine installations where current requirements change with time because of variations in velocity, aeration, etc. (384). Recent innovations include silicon controlled rectifiers, constant-current rectifiers, permanent pipe potential indicating meters, and telemetering potentials down the pipe itself (335).

Table 25 lists the types of rectifiers used by the companies surveyed. The numbers and types of generators reported in use by these companies are summarized in Table 26.

TABLE 25

TYPES OF RECTIFIERS USED

	Number of User Companies
(A) Selenium	289
(B) Silicon	148
(C) Copper Oxide	19
(D) Other	9

TABLE 26

NUMBER OF GENERATORS IN USE PER COMPANY

	Number of Generators				
	1-5	6-10	11-25	26-50	Over 50
(A) Fuel powered	20	4	0	2	0
(B) Pulse	5	0	2	0	0
(C) Solar	1	0	0	0	0
(D) Thermoelectric	21	10	7	1	1
(E) Other	6	0	1	1	0

If pipe is to be cathodically protected, an anode must be placed in the ground to complete the electrolytic circuit. The anode must be of sufficient size to operate at reasonable current densities and to last a long period of time. Silicon iron (146), Ti plated with a very thin film of platinum (357), Pb alloys for seawater (388), Pb with embedded Pt pins (391, 491), Pb–Ag alloys (75), graphite and carbon (542), Si-Cr iron (541), and steel (540) have all been employed as anodes. In arid or semiarid soils, electro-osmosis can significantly increase the soil resistivity around an anode ground bed by reducing the moisture content (405). To avoid this effect, current densities should be kept low.

In soil, anodes are generally surrounded with coke or graphite "breeze" which transmits the current to the soil. The function of the coke breeze is both to extend the life of the anode (since it reacts minimally with electrolysis products), and to lower the current density. The anode must also be located so as to provide good current distribution on the pipe to satisfy the potential criterion everywhere. One development devised to achieve this is the deep ground bed anode. The deep ground bed is located beneath the pipeline and so requires no additional right of way (540). Geological formations, however, can conceivably cause an unfavorable potential distribution. Since gases are usually generated at the anode, a standpipe to the surface is required for their escape. Steel standpipes have been noted to be attacked by the cathodic protection current (542). For this reason, perforated plastic pipe is often used. The performance of impressed current anodes reported by the companies surveyed is outlined in Table 27.

A phenomenon of wide concern in cathodic protection is interference (e.g., 267). Since cathodic protection generates an electric field in the soil, current tends to flow in any conductor placed in the soil. Where this (positive) current leaves the pipe, corrosion is rapid. In London an anode 460 feet deep was used in an unsuccessful attempt to avoid interference (146).

The best method to avoid interference has proved to be holding all buried metal structures and pipes at or near the same potential. Avoidance of interference from existing pipelines in crowded areas can be very difficult. Owners of different pipelines and structures in the same area must coordinate cathodic protection efforts. Coordination is carried out by informal local cathodic protection groups which maintain maps showing underground metal, hold meetings to discuss problems, advise local governmental units, etc. Sacrificial (e.g., Mg) anodes are believed to produce minimum interference with bare lines (592).

Table 28 lists the major sources of information that the surveyed companies used. to determine the presence of interference currents. (An alphabetical listing of Electrolysis or Corrosion Interference Committees compiled during the survey is included as Table 49, Appendix 111.) Criteria utilized by the companies surveyed to determine whether interference has been mitigated are summarized in Table 29.

TABLE 27

IMPRESSED CURRENT ANODES ACCORDING TO PERFORMANCE

		Earth Exposure				
Anode Material	Best	2nd	3rd	4th	5th	E*
Graphite in coke breeze	152	70	19	3	2	4
Graphite	0	15	5	10	2	1
Lead	0	0	0	0	0	3
Lead-silver alloy	1	0	0	0	0	3
High silicon cast iron in coke breeze	104	85	3	4	0	1
High silicon cast iron	13	19	29	21	0	3
Scrap iron in coke breeze	1	6	23	5	3	0
Scrap iron	11	11	46	15	4	3
Platinized titanium	0	0	0	0	0	3
Platinized tantalum	2	0	0	0	0	2
Other	6	2	6	0	0	0

	Marine Exposure			
Anode Material	Best	2nd	3rd	E*
Graphite in coke breeze	2	0	0	1
Graphite	7	3	3	1
Lead	0	0	0	0
Lead-silver alloy	8	0	3	3
High silicon cast iron in coke breeze	3	2	0	0
High silicon cast iron	36	4	1	0
Scrap iron in coke breeze	0	5	0	0
Scrap iron	2	6	1	0
Platinized titanium	2	1	0	0
Platinized tantalum	1	0	0	0
Other	1	0	2	0

*Experimental

TABLE 28

MAJOR SOURCES OF INFORMATION ABOUT THE PRESENCE OF INTERFERENCE CURRENTS

	1st	2nd	3rd	4th
	Number of Companies			
(A) Electrolysis or Corrosion Interference Committees	85	53	64	0
(B) Direct Communication from Other Companies	85	174	35	0
(C) Current and Voltage Measurements	143	61	88	0
(D) Other	1	2	7	9

Table 29

CRITERIA USED TO DETERMINE WHEN INTERFERENCE HAS BEEN MITIGATED

Criteria	Number of User Companies
No Change in Pipe Potential with Rectifier On and Off	74
Line Current Measurements or When all Current Flow on Pipe is Toward the Drain Bond	34
Restoration of Original Pipe Potential to Those Values Which Existed Prior to Interference	84
Earth Current Technique	10
Pipe-to-soil Potential is -0.85 Volts or more	10
Adjustment of the Slope of the Beta Curve at Location of Maximum Exposure	None
Other	25

It was once common practice, and often required by state or municipal code, to place a metal casing around a pipeline where it passed under a roadway. Unfortunately, this procedure can reduce or negate the beneficial effects of cathodic protection (561). In addition, corrosion of the inner surface of the casing can be accelerated by the currents passing through it (563). Accelerated corrosion of the casing can be prevented by electrically connecting the pipe and the casing, but this completely negates the cathodic protection of the pipe. One suggestion is to grout the annulus (594) or to dry and fill it with grease (561) if the pipe and the casing are shorted. Another approach is to swage down the ends of the casing, weld them to the pipe at each end, and fill the annulus with saturated lime solution (563). Similar effects can be obtained with wire mesh reinforced mortar coating. Connection of mesh to pipe is recommended. Similarly, pipe clamps should be bonded to the pipe and the pipe surface coated with insulating material (594). When possible nonconductive reinforcing materials are recommended to avoid screening effects. The companies surveyed had a total of 22,669 casings shorted to the carrier pipe. Three hundred and two leaks were reported inside pipeline casings.

Some pipelines contain nonconductive joints. When cathodic protection is applied to such a pipeline, it is essential to use bond strap electrical couplings across these joints. It has been estimated that with up to 150 joints per mile one should expect one missed joint every 50 miles (575). This missed joint may be located by applying cathodic protection and making a pipe to soil potential survey. One must also consider electrical discontinuities in old underground. structures when seeking to avoid interference from cathodic protection of a new pipeline (267). In such cases a simple bond from the pipeline to the structure will not solve the interference problem.

Various techniques have been developed for designing cathodic protection systems. Analog models consisting of wires immersed in an electrolyte have been suggested for solution of complex interference problems (494). Mathematical analysis has been used for design of impressed current protection of internal pipe surfaces (569). Computers have also been employed for calculations of current and potential distributions under different conditions. Generally, the mathematical models ignore polarization, which may have a controlling influence.

9. Cathodic Protection of Coated Pipelines

Nonconductive coatings and cathodic protection are quite often used together for protection of pipelines from corrosion. Coatings and cathodic protection complement each other nicely. Coatings are usually not perfect -- some holidays remain, at which corrosion can occur. Cathodic protection serves to protect the pipe at the holidays, and may be considerably cheaper than efforts to produce a perfect coating. On the other hand, the coating drastically reduces the current required to protect the pipe -- so much so, in fact, that the required current is often taken as a measure of the quality and integrity of the coating. Coatings and cathodic protection may economically be a good investment since well preserved pipe is worth more after its useful life in a particular application. The pipe may then be recoated and reused.

Figure 6 is a graph of the leak history on an aqueduct, which shows the effectiveness of coating combined with cathodic protection. The aqueduct was a 65-inch diameter, 90-mile, welded steel pipe coated with a bituminous mastic. Cathodic protection was interrupted twice as two additional aqueducts were installed in the same 100-foot right-of-way (Q114).

The performance of pipe with and without protection reported by the companies surveyed is shown in Table 30. As may be seen, the number of leaks per mile was much less with any type of protection than with bare unprotected pipe. The leaks per mile for cathodically protected and coated steel pipe were widely distributed over the age groups, whereas bare pipe with and without cathodic protection or coated pipe without cathodic protection had significant leak rates for pipe installed over 10 years.

Cathodic protection can damage coating materials under certain conditions. Water can be driven by electro-osmosis through small holidays to form blisters under the coating. Cathodic protection generates hydrogen when the potential exceeds the hydrogen overvoltage of steel and can cause disbonding of coatings to different degrees. In fact, cathodic polarization is one test for bonding of coatings. Disbonding increases as the potential becomes more negative, as temperature increases, and as external pressure decreases, and is greater in seawater than in 3 percent NaCl. The temperature effect varies widely from coating to coating, however (684). If the coating is disbonded, corrosion can occur under the coating even with cathodic protection (570).

It was found that cathodic protection may fail to stop micro-

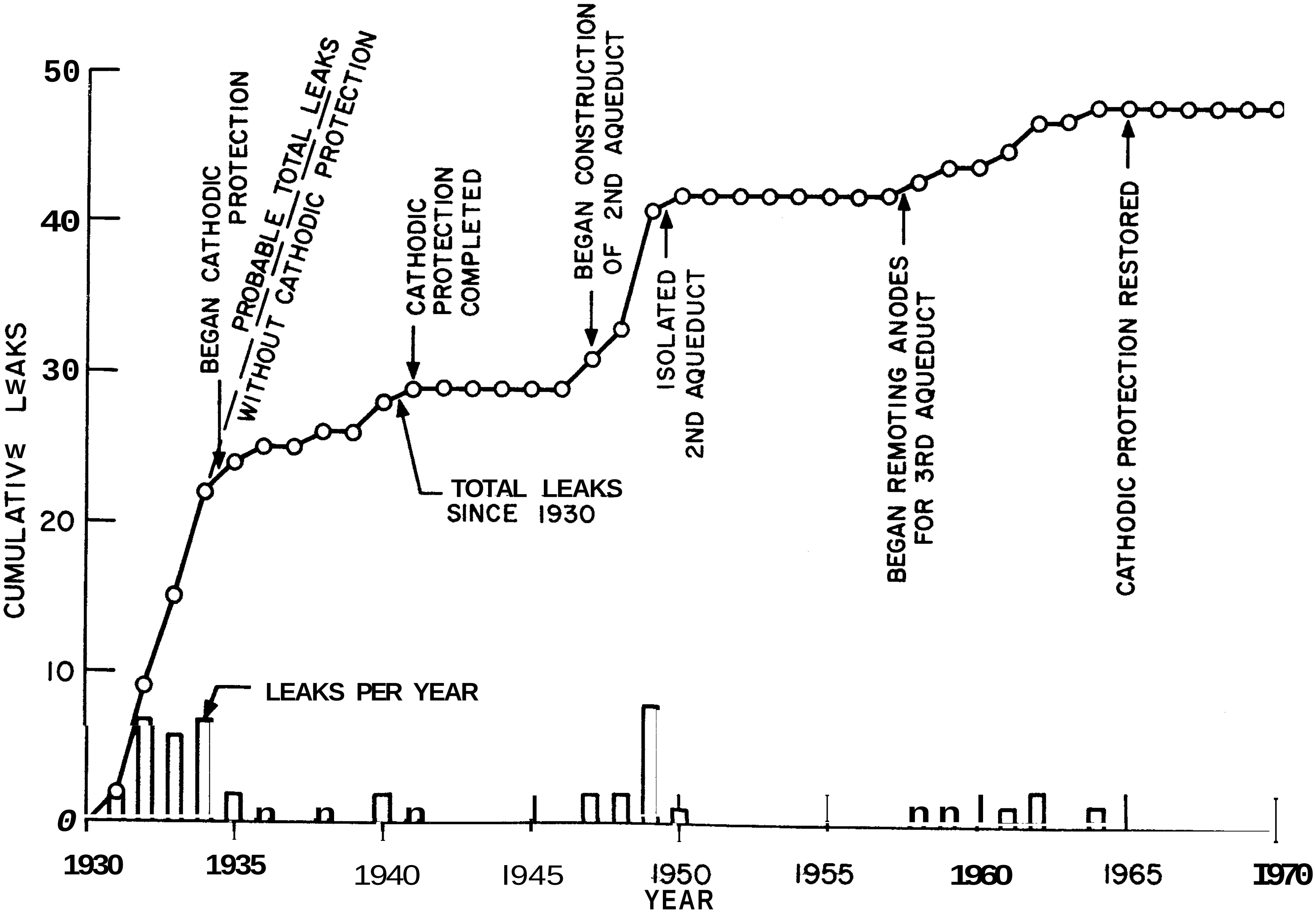

Figure 6. Effectiveness of Cathodic Protection.

TABLE 30

NUMBER OF CORROSION LEAKS PER LINEAR MILE OCCURRING IN 1969 FOR STEEL PIPE

Age Groups	Number of Companies								
	Bare Steel Pipe, Not Cathodically Protected								
Over 30 years	0	3	1	13	12	46	22	1	1
21-30 years	1	4	1	12	14	37	9	2	2
11-20 years	0	4	0	19	10	19	10	2	0
6-10 years	1	4	2	2	7	7	2	0	0
0-5 years	2	3	1	3	1	5	1	0	0
	Bare Steel Pipe, Cathodically Protected								
Over 30 years	0	4	2	13	10	9	4	0	0
21-30 years	0	4	1	11	3	6	4	1	1
11-20 years	1	2	1	4	5	4	1	0	1
6-10 years	0	1	2	0	1	2	1	0	0
0-5 years	0	0	0	0	0	0	0	0	0
	Coated Steel Pipe, Not Cathodically Protected								
Over 30 years	0	3	1	6	3	18	9	0	0
21-30 years	1	6	1	7	14	14	2	0	0
11-20 years	1	8	3	10	11	15	5	0	0
6-10 years	1	6	1	11	8	5	4	0	0
0-5 years	0	2	2	3	7	4	3	0	0
	Coated Steel Pipe, Cathodically Protected								
Over 30 years	4	5	3	11	2	6	0	0	0
21-30 years	6	8	3	4	2	5	0	0	0
11-20 years	7	15	7	5	5	3	2	0	0
6-10 years	8	5	3	7	4	2	2	0	0
0-5 years	4	2	3	1	1	0	0	0	0

biological corrosion in moisture pockets under disbonded coatings (5024).

Loss of adhesion and blistering of vinyl coatings on cathodically protected ships has been attributed to development of localized alkalinity at holidays **(364).** Na^+ and K^+ diffused through the film under the applied potential. Little blistering and peeling of vinyl paint has been found to occur if less noble potentials were employed, which lowered the current density to about 3 mA/m^2. Zinc anodes are reportedly gaining favor over Mg for the hulls of ships, partly because they make it possible to avoid overprotection harmful to paint (99).

It has been reported that the normal cathodic protection potential of -0.85 V to $CuSO_4$ electrode causes red-lead paint to blister, does not affect coal tar enamel, and affects other coatings to intermediate extents.* Another study (259) found paints based on linseed/tungsten oil phenolic varnish, aluminum bituminized oil and metallic pigmented epoxy good to -0.85 V; aluminum vinyl primer with cuprous oxide paint good to -1.0 V; and coal tar epoxies to -1.25 V.

Table 31 shows the maximum pipe potential or instantaneous open circuit potential at the rectifier location that best describes the surveyed companies' practice of limiting potential.

10. Standard Cells and Potentials in Cathodic Protection

A major problem in cathodic protection is the establishment of criteria whereby under any given set of circumstances it may be manifested by test that the pipe is protected against corro-

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*January 1970 Meeting of Los Angeles Section of NACE.

TABLE 31

MAXIMUM PIPE POTENTIAL OR INSTANTANEOUS OPEN CIRCUIT POTENTIAL AT THE RECTIFIER LOCATION

Pipe-to-Soil Potential (Volts)	Number of Companies
up to 1.5	83
1.6 to 2.5	164
2.6 to 3.5	59
3.6 to 5.0	16
Other	23
Instantaneous Open Circuit Potential (Volts)	**Number of Companies**
up to 1.00	45
1.01 to 1.05	36
1.06 to 1.20	**44**
Other	7

sion and that this protection is not attained at the expense of other components of the underground pipe, e.g., the coating. Such criteria, including those directed more particularly toward design than to adequacy, depend in *most* instances upon measurement of the electric potential of the pipe, pile, ship, tank or other structure, with respect to some reference potential. Several possible reference potentials are described briefly in following paragraphs.

In electrochemistry the universal reference is the standard hydrogen electrode (SHE), the potential of which is arbitrarily taken as zero. The physical and chemical characteristics of this half cell are represented as follows:

$$\mathrm{Pt} \mid H_2(\mathrm{gas},\ 1\ \mathrm{atm}) \mid H^+(a = 1);\ E° = 0$$

Pt indicates the chemically inert platinum electrode, about which equilibrium is established between hydrogen gas at 1 atmosphere pressure and the proton at unit activity.

This equilibrium was earlier presented as one reaction basic to corrosion and was shown at the cathode in the schematic representation of the underground corrosion process, Figure 4. It is also of paramount importance in cathodic protection since the protected structure is, in essence, a hydrogen electrode.

According to the Nernst equation of chemical thermodynamics (e.g., Equation 5) the potential E of any metal M of unit activity in equilibrium with M^{n+} ions at activity $a_M n+$ may be written in the form

$$E = E° + (0.05916/n) \log a_M n+ \qquad \text{(Eq. 12)}$$

for room temperature, where the standard potential E° for the metal is experimentally determined for unit activity of metal ion with reference to the SHE and n represents the number of faradays of electricity entering into the reaction. For the hydrogen/hydrogen ion half-cell reaction at unit hydrogen pressure, E° equals zero by convention and Equation 12, in millivolts, reduces to

$$E = 0 + 59.16 \log (H^+) = -59.16\ \mathrm{pH} \qquad \text{(Eq. 13)}$$

assuming the hydrogen ion activity equals its concentration (H^+) and, by definition, $-\log (H^+) = \mathrm{pH}$.

The reaction for oxygen at unit pressure in equilibrium with hydroxide ion (Equation 3) is also monofaradaic (n = 1), and

Equation 5 is applicable with E° = +1.229 volts with respect to the SHE at zero pH.

The hydrogen and oxygen cell potentials are given in Table 32 for several values of pH.

TABLE 32

HYDROGEN AND OXYGEN ELECTRODE POTENTIALS

pH	E (Hydrogen Electrode)	E (Oxygen Electrode)	pOH
0	0	+1229 mv	14
7	-414 mv	+815	7
9.33	-551.9	-	-
12.45	-736.5	-	-
14	-828	+401	0

The SHE is far too cumbersome for use in the field. The saturated copper sulfate electrode on the other hand is sturdy, reliable, and almost universally used and understood by corrosion engineers. This simple electrode and its potential at room temperature are as follows:

$$\text{Cu (solid)} \mid CuSO_4 \text{ (saturated solution)} \mid E^\circ = \mathbf{0.441}$$

$$\mathbf{E} = 441 - 29.58 \log a_{cu^{++}} \quad \text{mV} \qquad \text{(Eq. 14)}$$

When the activity of the cupric ion $a_{cu^{++}}$ is that of a solution of copper sulfate in equilibrium with the hydrated salt, $CuSO_4 \cdot 5H_2O$, the potential to the SHE is +298.1 mV. The electrode is never used at any other cupric ion concentration, so that **it** is sufficient and unambiguous to refer to this reference electrode simply as "the copper sulfate electrode." **It** is relatively insensitive to contamination.

The saturated calomel electrode, SCE, is an even more reliable reference electrode and consists of Hg | Hg_2Cl_2 (saturated solution). It is used extensively in the laboratory but is less convenient in the field than the copper sulfate electrode. Nevertheless, it is used in the field by some corrosion engineers to check the potential of the copper sulfate electrode.

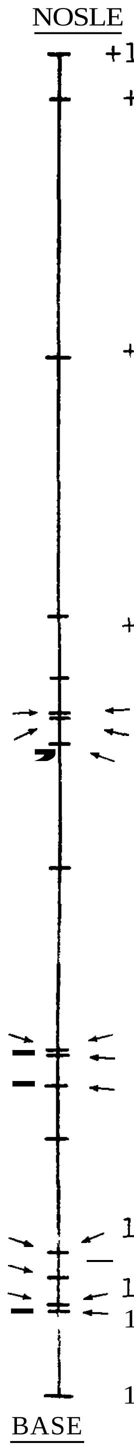
The silver chloride electrode is entirely different in performance, in that the electrode is responsive to the chloride ion concentration of the solution into which it is dipped. The electrode is formed by "plating" silver chloride onto a silver rod or button. It is particularly useful in marine environments, and its potential on the hydrogen scale in average seawater is computed to be 195.5 mV. The electrode is also responsive to hydroxide ion concentration, and to avoid contamination from OH- a rejuvenating circuit is sometimes used in seawater which intermittently applies a positive potential to the electrode to nudge it into its equilibrium value. The silver chloride electrode is destroyed by the sulfide ion. Its use below the mud line in marine installations may, therefore, be inadvisable.

The potential of the silver chloride electrode can be fixed by maintaining the chloride ion concentration constant. In one commercial! unit the electrode is surrounded by a silver chloride-saturated 4N KCl solution. The potential is then +243.7 mV. This silver chloride electrode has been successfully used to measure the chloride ions in soil and the infiltration of the ions in soil into concrete. A conventional pH meter is used with the acidified sample and results reported as pCl^- ($-\log(Cl^-)$). Similar electrodes, which are sensitive to sulfate ion cencentration, have been devised. These electrodes, however, have not yet been used to measure the important sulfate ion concentrations in the soil.

Referring to the potentials given in Table 32, it is now evident that the pH 9.33 corresponds to the potential -850 mV with respect to the copper sulfate electrode (which is often used as a criterion in cathodic protection). The potential -736.5 + (-298.1) = -1034.6 mV with respect to the copper sulfate electrode is the potential of the hydrogen electrode at the pH of saturated calcium hydroxide solution. This potential, often encountered in practice, lends support to the contention that a cathodically protected pipeline is, in essence, a hydrogen electrode.

The several potentials described above are shown on a nomogram in Figure 7. These are useful for an understanding of (a) the sign of electrode potentials, (b) the relationship between the several reference electrodes, (c) the powerful role that oxygen must surely play in the underground corrosion process, and (d) the potentials of certain salts of iron which are important in cathodic protection. The corrosion engineer would do well to commit a few potentials to memory for orientation with respect to nobility and sign.

The sign of the potential is to some extent arbitrary, and depends on one's viewpoint. The sign convention used here is that which appears on the instrument. terminals; i.e., the



Millivolts to SHE	Millivolts to $CuSO_4$	Half Cell
	NOSLE	
+1300.0	+1000.0	
+1229.0	+930.9	Oxygen, pH 0(1)
+815.0	+516.8	Oxygen, pH 7(1)
+401.0	+102.9	Oxygen, pH 14(1)
+298.1	0.0	Copper sulfate (saturated)
+243.7	54.4	Silver chloride (4N KCl)
+243.1	57.1	Calomel SCE
+196.6	101.5	Silver chloride (seawater)
0.0	298.1	Hydrogen (2), pH 0, SHE
414.0	712.1	Hydrogen, pH 7(2)
414.5	712.6	Ferrous chloride (saturated)
468.0	766.1	Ferrous sulfate (saturated)
551.9	850.0	One protection criterion
736.5	1034.6	Hydrogen, pH 12.45(2)
777.8	1075.9	Ferrous sulfide, pH 7(3)
822.2	1120.3	Ferrous sulfide, pH 8.5(3)
828.0	1126.1	Hydrogen, pH 14
970.1	1268.2	Ferrous sulfide, pH 14(3)
	BASE	

(1) At oxygen pressure of 1 atmosphere
(2) At hydrogen pressure of 1 atmosphere
(3) At hydrogen bisulfide ion (HS) activity = 1

Figure 7. Nomogram of Some Oxidation Potentials at 25°C

potential between the SHE and the copper sulfate electrode is -298.1 millivolts with the positive instrument terminal connected to the copper sulfate electrode. The reverse sign convention has also appeared in the literature.

The SCE is negative with respect to the copper sulfate electrode, but positive with respect to the SHE. To avoid confusion it is helpful to consider the metals silver, copper and mercury as more noble, and hydrogen and iron as more basic as shown in Figure 7. To obtain the sign of a reaction between any two of the half cells, the more noble potential is subtracted from the more basic. Thus, on the hydrogen scale

$$H_2 = 2H^+ + 2e^- , \quad E = 0.0 \qquad \text{(Eq. 15)}$$

$$\underline{Cu = Cu^{++} + 2e^- , \quad E = 298.1}$$

subtracting, $H_2 + Cu^{++} = Cu + 2H^+ , \quad E = -298.1$

Thus, the negative sign above indicates that in measuring the potential of the SHE to the copper sulfate electrode the electron flow will be from the baser half cell, through the instrument, to the more noble half cell. A half cell will give up electrons to a reaction toward the more noble end of the scale.

A glance at the alignment chart will show that the pipe potential will also always be, according to the convention adopted, negative to the copper sulfate electrode. Therefore, to avoid repeated use of the negative sign, in practice the absolute values nay be reported and the positive sign used when and only when the measured potential is positive with respect to the reference. The nomogram and the following text is in accord with this suggestion.

Most of the electrodes in common use are clustered within a narrow range of 100 mV. Their relationship has been discussed on previous pages and further amplified in the paragraph immediately above.

On certain rare occasions aluminum, a base metal, may be observed corroding with release of hydrogen gas which bubbles through voluminous white creamy hydroxide. A flame ignites the gas showing it to be hydrogen. Similar corrosion has not been reported for iron. If the underground corrosion of iron is substantially that portrayed in Figure 4 and the anolyte in the pit is saturated with ferrous chloride, then, in the absence of oxygen, evolution of hydrogen and corrosion cannot continue if the pH is greater than 7 or 8, as is evident in the nomogram. The argument is more apparent if we consider a pit in the metal beneath a crack in a concrete coating, the pH of which is that of a saturated lime solution, i.e., pH = 12.45. Taking the potentials from the nomogram and following the rule

$$\begin{array}{lll}
\text{Base: } H_2 = 2H^{+}(Ca(OH)_2) + 2e- & E = -736.5\text{mV} & \text{(Eq. 16)} \\
\text{Noble: } Fe = Fe^{++}(FeCl_2 \cdot 4H_2O) + 2e^{-} & E = -414.5 & \\
\hline
H_2 + Fe^{++} = Fe + 2H^{+} & E = -322.0 &
\end{array}$$

Thus, the reaction tends to proceed from left to right so that corrosion of iron cannot occur. Instead, iron will tend to plate out under a potential of about one-third of a volt. Using any one of the oxygen potentials with the same iron potential would show that corrosion would certainly proceed.

Since, in fact, corrosion does occur under the conditions stated, either (a) there is some mechanism for the liberation of hydrogen on an iron surface not understood, or (b) the energy for the oxidation of iron is derived from the reduction of oxygen. There is abundant experimental evidence for the second alternative.

Unfortunately, many of the computed potentials listed in the nomogram are difficult to confirm in the field. The causes of these difficulties result from irreversibility of the "oxygen electrode" and the still mysterious metal oxide films and other effects. Nevertheless, many of these potentials have been observed, including the reference cells, the iron-ferrous chloride equilibrium potential, and in general all of the hydrogen potentials when hydrogen is evolved during cathodic protection. The potentials correlate with the pH at the metal surface.

11. Measurements on Pipelines Under Cathodic Protection

Properties of a pipeline under cathodic protection open to measurement by the corrosion engineer include (a) the electric potential of the pipe, (b) the transaxial and radial current flow between pipe and soil, (c) the current flow in the pipe itself, and (d) the very practical measure of the reduction in rate of leaks with time. These are discussed further below.

a. Pipe Potential

The pipe potential lends itself to a variety of measurements, many of which are related to specific properties of the system. In its most general. application to buried pipelines, the reference electrode is positioned on the ground surface in the vertical plane through the pipe's horizontal axis. This is the point on the earth's surface closest to the pipeline.

The potential E_h is defined as the natural or base potential in the absence of cathodic protection. It is stable and invariant with respect to the reference electrode although the potential will move slowly in the more noble direction with time. The interaction of the pipe with the reference electrode supplies the energy to operate the measuring instrument. For example, the reaction

$$Fe + Cu^{++} = Fe^{++} + Cu \qquad \text{(Eq. 17)}$$

indicates that a quantity of iron corrodes to give up a stream of electrodes which pass through the instrument and plate out cupric ions on the copper electrode of the reference cell. This trivial example can be extended to the natural potential which may be a resultant of potentials of two interconnected couples reacting naturally underground.

If the pipeline is coated and under cathodic protection, several new factors become involved. These include IR drops through (1) the coating: (2) the coating-soil interface, attributable in the absence of total submergence to imperfect contact between pipe and soil: and (3) the soil between the coated pipe surface and the location of the reference electrode. An additional potential drop is due to the polarization necessary to drive the formation of new chemical species at the pipe surface. Thus, summarizing, the potential measured at height h over the pipe is

$$E_h = E_P + \Delta E_c + \Delta E_s \qquad \text{(Eq. 18)}$$

where E_P is the new or polarized potential, ΔE_c is the potential. difference between the pipe surface and the coating exterior

(IR drop) combined, and ΔE_s is the IR drop through the soil.

Fortunately, the three potentials on the right of Equation 18 can be determined with sufficient accuracy for practical purposes. The potential increment AE_s may be measured in two ways which have in general been found to agree well. One is by direct measurement with an auxiliary probe electrode at the pipe surface. This increment is obtained by interruption of the energizing circuit which eliminates the residual IR drop attributable to natural soil currents or polarization. The second method is to measure the IR drop with two electrodes placed along the earth's surface in the plane perpendicular to the vertical plane through the pipe's axis at a point x. The span x-h is fixed by the geometry existing such that the potential between X and h measures the increment ΔE_s. The potential, ΔE_c, may similarly be estimated by measuring the difference between the probe electrode and the pipe with and without the circuit energized.

If the cathodic protection circuit is opened, there results the potential E_p which is reasonably independent of the electrode location and quite reproducible. It may under some circumstance be remarkably stable. However, with the circuit open, the potential may move slowly in the noble direction; i.e., the pipe will depolarize.

Rewriting the equation

$$E_h \text{ (pipe potential)} = E_P \text{ (polarization potential)} + \Delta E_{ch} \text{ (total IR drop)} \qquad \text{(Eq. 19)}$$

The easily measured polarization potential is of great importance in connection with Figure 4 and the nomogram, Figure 7. The total IR drop through the soil is used to estimate the current density with the aid of the soil resistivity at the point of test. The IR drop through the coating, together with current density, yields the coating conductance. Thus, if for example, too much current has been applied to the pipe at the point of drainage, then it may be expected that the coating is disintegrated and the conductance serves as a measure to compare the coating conductance with the current density elsewhere along the pipeline.

b. Current Flow Between Pipe and Soil

The density of current entering the pipe from the soil in the transaxial plane can be measured in three ways: (1) by measurement of transaxial gradient as explained above, (2) by determination of voltage and current attenuation along a pipe, and (3) by use of the McCollum earth current meter. Methods 1 and 2 are limited to bare or poorly coated pipelines. Method 1 is inapplicable to multiple parallel pipelines. Attenuation theory leads to average values over large lengths of pipe. An excavation is required for the earth current meter which can then be used to explore the radial current densities as at the hours on the face of the clock. The method is applicable in streets congested with pipelines where other methods may be impracticable.

c. Current Flow in Pipe

The current flowing in the pipeline is easily measured.

It is attentuated in excellent conformity with theory under a variety of boundary conditions including pipelines which terminate at wells with near zero resistance or at isolating flanges with near infinite resistance and any intermediate terminal boundary condition.

d. Cumulative Leaks

A plot of cumulative leaks attributable to corrosion versus time may be used for corrosion control. A plot of leaks on an area chart can be used to indicate where cathodic protection has been effective in distribution systems.

12. Protection Criteria Reported by Companies Surveyed

Cathodic protection criteria utilized by the companies surveyed are summarized in Tables 33 and 34.

TABLE 33

VOLTAGE VALUES AT WHICH THE COMPANIES CONSIDER PROTECTION HAS BEEN ACHIEVED

Criterion Used for Bare Pipe	Protected Voltage or Delta E Shift (Volts)							
	0.85	0.30	0.10	0.1–0.3	0.31–0.5	0.51–0.84	0.86–1.0	Over 1 Volt
Pipe Potential	104*	3	3	1	4	29	4	0
Voltage Shift	1	114	20	35	4	0	4	0
Polarization Voltage Shift	6	7	43	16	0	0	0	0
Criterion Used for Coated Pipe	**Protected Voltage or Delta E Shift (Volts)**							
	0.85	0.30	0.10	0.1–0.3	0.31–0.5	0.51–0.84	0.86–1.0	Over 1 Volt
Pipe Potential	268	5	4	0	1	6	28	3
Voltage Shift	5	106	3	15	13	1	0	0
Polarization Voltase Shift	0	12	42	12	2	2	1	0

*Number of companies

TABLE 34

OTHER CATHODIC PROTECTION CRITERIA USED BY THE COMPANIES

Criteria	Number of Companies
Current Loss and Gain on the Structure	34
Current Tracing in the Electrolyte Perpendicular to the Pipeline	13
Polarization Potential	6
Small Interval or Continuous Pipe Potential Surveys	11
Other	18

The cathodic protection criteria listed under "Other" in Table 34 included pH measurement, decrease in leak rate, corrosion coupons, corrosometer probes, analysis of calcareous deposit in pits, rusty iron reference electrodes, correlation with soil resistivity, etc. Most of the companies surveyed used several criteria to determine if the piping is protected. Table 35 shows where the companies normally placed their reference electrode when determining if the criteria of cathodic protection has been achieved.

TABLE 35

NORMAL PLACEMENT OF REFERENCE ELECTRODE

Electrode Position	Number of Companies Bare	 Coated
On Surface Over Pipe	202	292
Remote from Pipe	50	52
Immediately Adjacent to Pipe	34	57
Other	6	14

13. Discussion of Cathodic Protection Criteria

a. Fixed Pipe Potential

The pipe potential (circuit energized) is the simplest measure used to gage the effectiveness of cathodic protection. The generally used value is 0.850 volt to the copper sulfate electrode. It is, according to the convention stated earlier, negative with respect to the reference. The criterion is a minimum in that the pipe potential everywhere is numerically equal to or greater than the selected value (commonly 0.85 V). Its widespread use attests to its popularity and success in the field. Further advantages include the low cost of collecting and storing periodic readings. The magnitude of such effort may be envisioned on a 350-mile long, well coated pipeline with test stations at mile intervals. The criterion is independent of sequentially adjacent cathodic protection units on the same pipeline.

A disadvantage is that a fixed pipe potential criterion contains acknowledged but unknown IR drops through soil and coating, as discussed previously. These might well permit insufficient current for protection. A serious break in an otherwise perfect coating remote from the point of test could well reflect an apparent satisfactory potential, a large component of which is, in fact, an IR drop in the soil. To avoid IR drops in the soil, some observers use an electrode at the pipe surface. The electrode can be placed there upon excavation. Probe type electrodes can be forced to the pipe surface. Permanent direct burial electrodes can be laid on the pipe upon construction as a component of the test station.

Another shortcoming in a fixed pipe potential criterion is that there is no provision for taking account of unusual conditions. For example, potential readings can vary with the temperature of the reference electrode. Also, reaction potentials may vary with the temperature of protected structures such as hot oil lines, hot fuel oil tank bottoms, etc. Accordingly, unusual conditions which may be present should be taken into account in utilizing a fixed pipe potential protection criterion.

b. Polarization Potential

The requirements to arrest corrosion in the typical case as depicted in Figure 4 may be examined before describing other simple potential criteria. One possibility would be to reverse the current flow from the pit. It would be helpful toward this end to eliminate oxygen as a contributor to the cell's overall potential. This could be done by supplying sufficient electrons to the pipe surface to tax the incoming oxygen's ability to react with the surface layer of monatomic hydrogen -- in short, to render the pipe surface negative. On new pipe a potential just sufficient to repel the chloride or sulfate ions would prevent the development of a corrosion cell.

A criterion advanced by Brown and Mears states that cathodic protection of a metal will be achieved at any instant if the cathode in a corrosion cell is brought to the potential of the most anodic potential existing on the metal at that instant. This condition, plus the experimental fact that the iron in the corroding pit as earlier discussed is in equilibrium with its saturated salt, leads to a promising theoretically based criterion. To achieve cathodic protection, then, it would be necessary, according to the nomogram, only to bring the cathode to a potential of 712.6 or 766.1 mV depending upon the chemistry of the electrolyte i.e., if the predominant salt is, respectively, ferrous chloride or ferrous sulfate. If the cathode is brought to either of these values, it should assure that at least the depolarizing effect of oxygen has been overcome.

The objective potential is the polarization potential of the cathode. It should be measured by eliminating all the IR drops in the catholyte as previously discussed. It could be most simply and closely approximated by reading the pipe potential immediately upon interruption of the applied current.

c. Depolarization Increment

Conditions in the field are extraordinarily varied. Accordingly, special measures or techniques have appeared as criteria for cathodic protection. Among these is a depolarization increment of potential of at least 100 millivolts measured from the instantaneous open circuit potential (the polarization potential) to the potential at some unspecified later time. A disadvantage of the criterion is that there is no apparent technical basis for it other than experience. Further, under some circumstances, including high current densities, the depolarization essentially vanishes.

d. The E-log I Curve

The critical potential representing the criterion for protection is read at the intersection of the extrapolated linear portions of the curves obtained for a series of associated values of E and I when plotted on semilogarithmic coordinates (Figures 2 and 3 and Equation 6). However, a linear connection between the variables, considering the faults of measurement, could be interpreted on the logarithmic plot as distinct linear curves having the sought intersection upon extrapolation. A change in reaction at the metal surface may cause a proportionate change in E as the current is increased. For example, when iron becomes saturated with monotomic hydrogen and molecular hydrogen begins to form, a proportionate change in E results as the current is further increased. Other such changes could come about when sufficient hydrogen is formed to react with available oxygen or when the anode of a corrosion cell becomes a cathode. The method, thus, has considerable merit both as a design and a protection criterion.

Disadvantages include locating anodic points on the system to be tested. The most desirable point to test would be the most anodic point if it could be found. To base protection on measurements at a cathodic point would lead to failure or a forced evaluation of a purely logarithmic curve. Further for reasons of instrumentation, only a single point in a system can be tested at a time because once tested the system is so polarized that a repeated test would not duplicate the original test. Thus an E-log I test on a cathodically protected pipeline would not be conclusive because there would be no change in chemical reaction at the metal surface already cathodically polarized. However, on a long pipeline the method can be modified advantageously in such a way that the point at which further increase in current would not be profitable (no increased polarization) can be determined by plotting the driving voltage (current density) against the polarization. Applied in this manner the method becomes a design criterion and can be exceedingly useful.

e. Radial Earth Current

If in an excavation it is determined by test that a pipe is receiving current through the soil along every radius, then it is assured that the pipe is protected at that particular location. Like the E-log I method, however, the determination is limited to the point of test. It has a great advantage in that it can be used under conditions of crowded pipelines. Further determinations are precise for each radius and any marked variations in current strength about the circumference will be evident and can possibly be correlated with neighboring structures. It is, therefore, especially useful in cathodic interference problems. A disadvantage is the high cost of excavation.

f. Pipe Potential Probability Curve

A statistical method has been developed to establish a criterion of protection, unique for the system under test. The method has been applied to copper piping under ground, but its usefulness with steel is impaired because of the redox potential existing in the corrosion product mantle between pipe and soil. The methcd has not been published and will, therefore, not be further elaborated here.

g. Summary

It has probably become apparent that there is no one. criterion for cathodic protection that will be applicable under all conditions. On the other hand, the criteria mentioned above, plus several other standards and methods not mentioned, can be quite satisfactory when applied within the constraints governing their use. Often a combination of criteria is necessary to properly evalute the effectiveness of cathodic protection of a particular structure or system.