



**SLAG AND ITS RELATION
TO THE
CORROSION CHARACTERISTICS
OF
FERROUS METALS**

This educational bulletin is intended to provide technical information for members of the N.S.A. relating to fundamentals of corrosion, properties of slag, and documentation of service of ferrous metals in an environment of slag.

INTRODUCTION

Determining the causes, and the means for preventing, corrosion requires an understanding of the mechanism of the corrosion reaction on engineering materials.

The selection of materials to fulfill the requirements of long life at low cost requires knowledge of the service conditions to be encountered and their effect on various metals.

It is not proposed to cover all details of this complex subject, but only to simplify the principles so that proper conclusions may be drawn from objective observations.

PRINCIPLES OF CORROSION

Corrosion is defined as the deterioration of a metal by a chemical or electrochemical reaction with its environment.

The fundamental reaction involves the transfer of electrons in which dissolved oxygen or positively charged hydrogen ions in the corroding solution acquire electrons from the metal or alloy going into solution or being corroded. The complete corrosion reaction is divided into an anodic portion (where positively charged metal ions are formed by corrosion) and a cathodic portion (where negatively charged hydroxyl ions are formed from dissolved oxygen) which occur simultaneously at discrete points on the metal surfaces. The anodic reaction (oxidation) represents the acquisition of charges by the corroding metal, while the cathodic reaction (reduction) represents the loss of charges by the hydrogen ions which are discharged. The flow of electricity between the anodic and cathodic areas may be generated by local cells set up either on a single metallic surface or between dissimilar metals.

Because of cracks in the mill scale, the presence of impurities in the steel, and the non-uniform distribution of internal stresses, numerous sites are available on the surface for corrosion to begin. As a flow of current accompanies the corrosion reactions, the sites at which attack begins are called anodes. The unaffected areas surrounding these sites receive the current and are called cathodes. Electrons, from the attacked areas where the iron dissolves in the moist conductive environment, move through the metal to unattacked cathode areas. At these areas hydrogen ions (H^+) and/or hydroxyl ions (OH^-) depending upon conditions, accumulate and accept these electrons. Thus hydrogen gas may form around the cathode area.

This is the essence of the generally accepted electrochemical theory of corrosion. The root cause of corrosion, however, is the instability of some metals in their refined form. Because of the "thermodynamic free energy relationship" most metals tend to revert to their natural oxidized or ore states through the process of corrosion. In the case of iron, the action of water and oxygen forms rust - an oxidized state in which ore is found.

Most of the corrosion of metals such as iron, lead and zinc in underground service at normal temperatures is the result of an electrochemical reaction. For this reaction to occur there must be a potential difference (driving force) between two points that are electrically connected and immersed in an electrolyte (liquid or soil containing ions). A familiar electrochemical system is the so-called dry-cell battery. The carbon electrode acts as a "noble" or corrosion resistant metal (cathode), and the zinc casing as the corrodible anode. The moist paste between the electrodes is the conductive (and corrosive) environment and carries the current.

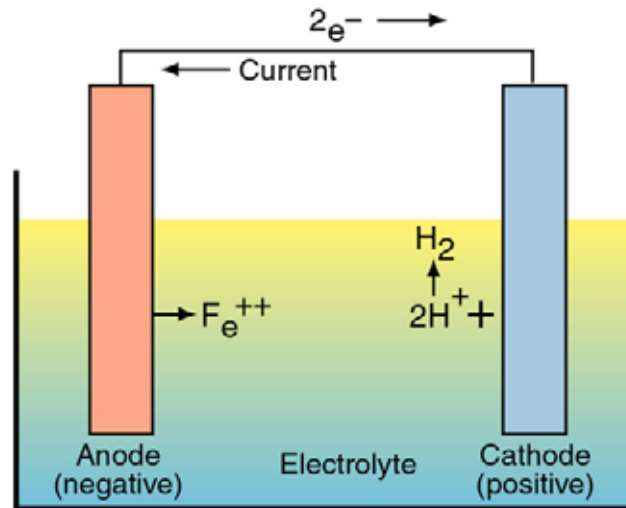


FIGURE 1. Example of Electro-Chemical Reactions

In Figure 1, an Iron (Fe) atom dissolves at an anode site and becomes an Fe⁺⁺ ion. As the Fe⁺⁺ ion enters the electrolyte, the two electrons it left behind travel to a cathode area where they are accepted by two hydrogen ions to form hydrogen (H₂) gas. An electrical or metallic connection is required to facilitate the electron flow.

Thus, the basic requirements for electrochemical corrosion to occur are:

- A. A metal, or sites on a metal, to be oxidized (anode).
- B. A non-corroding material, or sites, to accept electrons (cathode).
- C. Anode/Cathode potential difference (driving force) due to characteristic differences in activity.
- D. A conductive liquid or soil (electrolyte) surrounding the anode and cathode.
- E. A metal conductor to complete an electrical path.

FORMS OF CORROSION

There are primarily eight forms of corrosion, all of which are more or less interrelated. These are briefly described as follows:

1. Uniform or General Attack

Uniform attack is characterized by a chemical or electrochemical reaction which proceeds uniformly over the entire exposed surface. An example is the uniform rusting of an iron surface such as a nail buried in soil or immersed in salt water.

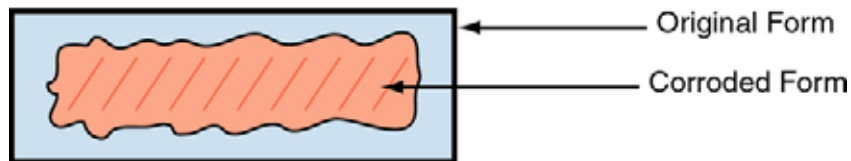


FIGURE 2. Example of Uniform Corrosion

Methods of combating uniform corrosion include:

- A) Selection of materials resistant to the environment aided by protective coatings.
- B) Inhibitors - substance added in small concentrations to the environment which will decrease the corrosion rate.
- C) Cathodic protection - the protection of a metal structure by making it the cathode of a galvanic cell.

2. Galvanic or Two Metal Corrosion

Galvanic corrosion occurs when two dissimilar metals in contact with one another (and having a significant potential difference) are placed in a corrosive environment or a conductive solution which produces an electron flow between them.

Galvanic corrosion may be minimized by:

- A) Selecting combinations of metals as close together as possible in the galvanic series. The metals in the table below are arranged according to their tendency to corrode galvanically, with the more anodic or electropositive metals shown at the top of the scale.

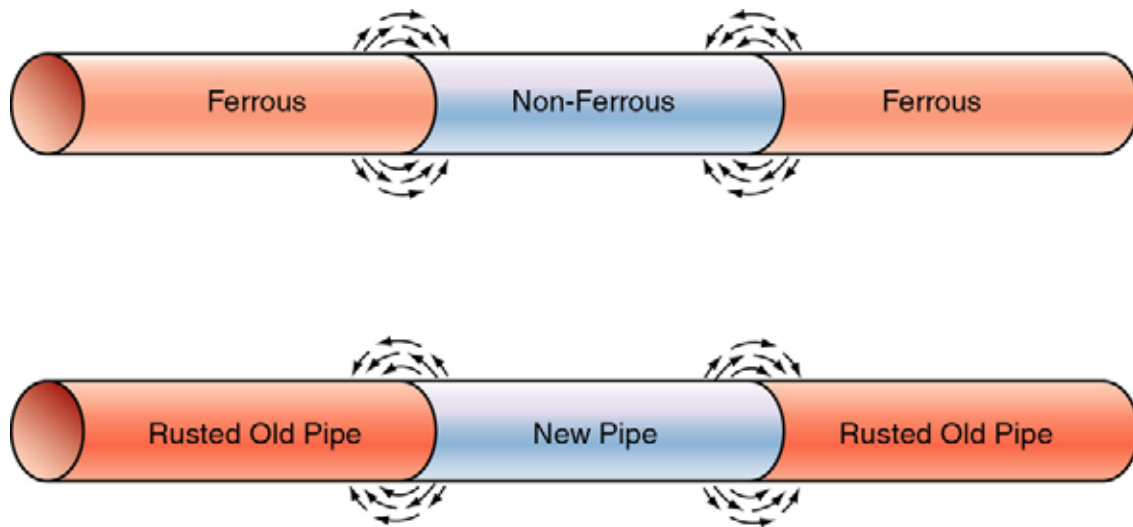


FIGURE 3. Corrosion of Dissimilar Metals

THE GALVANIC SERIES OF METALS

+ANODE
(Increasingly sensitive to corrosion)

Magnesium
Zinc
Aluminum
Iron
Tin
Lead
Brass
Copper
Silver
Graphite
Gold
Platinum

-CATHODE
(Increasingly resistant to corrosion)

Contact of dissimilar metals, when in a conductive environment (electrolyte), will generate a current flow from the metal with the higher potential (the anode) to the metal with the lower potential (the cathode) causing the galvanic corrosion of the metal that is anodic in this battery.

B) If unlike metals must be coupled, avoid the unfavorable area relationship of a small anode and large cathode. An example is the classic failure of steel rivets (anodic) holding together copper plates (cathodic).

- C) Avoid contact of dissimilar metals by insertion of insulators. A common error in this regard concerns bolted joints such as two flanges where the pipe might be steel or lead and the valve bronze or copper.
- D) Apply coatings thoroughly.
- E) Insert a third metal between the galvanic couple which is anodic to both metals.

3. Crevice Corrosion

Crevice corrosion results from intense localized attack, usually associated with small volumes of stagnant solutions in shielded areas while the remaining surface experiences little or no damage. For example, contact between metal and nonmetallic surfaces can result in crevice corrosion. A sheet of 18% chromium and 8% nickel stainless steel can be cut by placing a stretched rubber band around it and then immersing it in seawater.

The following procedures will minimize crevice corrosion:

- A) Use welded butt joints instead of riveted or bolted joints in new equipment.
- B) Eliminate crevices by continuous welding, soldering or caulking.
- C) Avoid sharp corners and design for complete drainage of moisture.
- D) Inspect equipment and remove rust deposits frequently.
- E) Provide uniform environment, if possible, as in the case of back-filling a trench.

4. Pitting Corrosion

Pitting or localized corrosion is the most serious form of attack on metals underground, and also is the most common. It is characterized by anodes of limited area and the formation of deep pits in the metal. Under severely corrosive conditions, the pits may deepen at a rapid rate and produce early and sudden failure by perforation of the metal in pipe lines.

The development of a pit at a break in an otherwise continuous oxide film (such as mill scale on iron) with deposition of corrosion products in the pit is shown in Figure 4. Such corrosion product deposits are usually permeable and, therefore, permit corrosion to continue. In other cases the pits may be open, with deposits of the corrosion products removed to some other location.

Correlation of corrosion theories with actual results in practice has been far from perfect, despite extensive research. It has been shown that the rate of pitting tends to decrease with time in all but the most corrosive environments. The pits rapidly increase

in depth in poorly aerated acid environments, but develop very slowly in well-aerated alkaline environments.

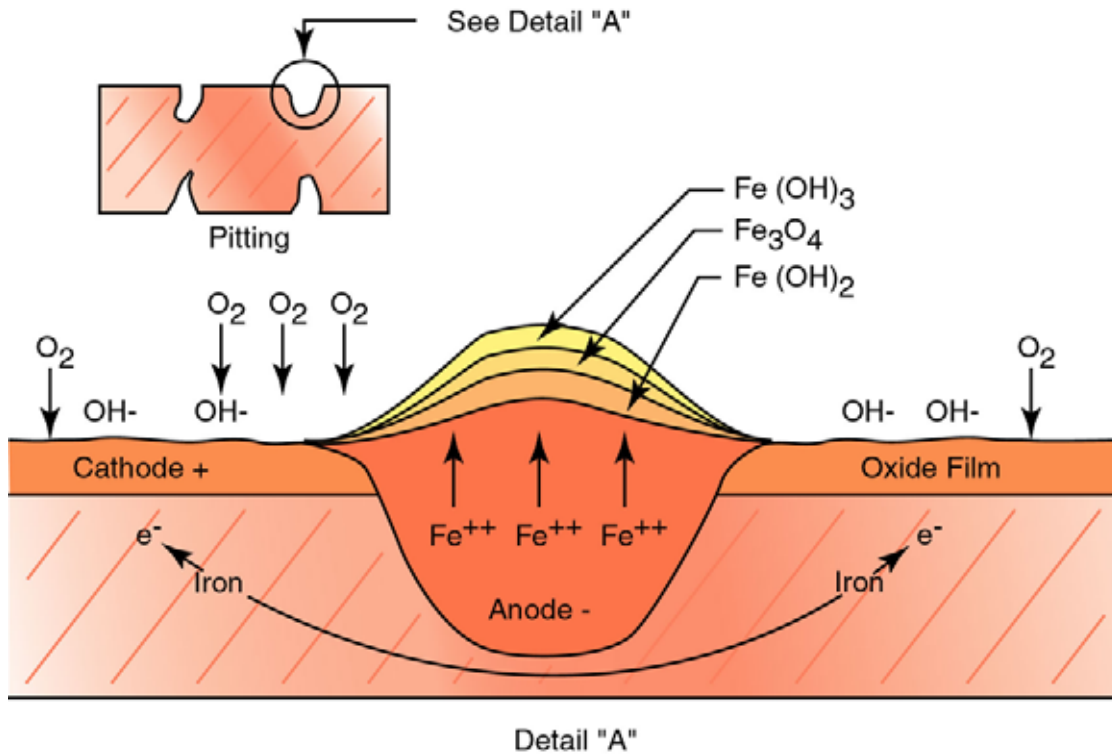


FIGURE 4. development of a Pit in Ferrous Metal

Important methods for decreasing damage from pitting corrosion are:

- A. Damage to underground utilities can be minimized by use of alkaline, well-drained and well-aerated backfill materials.
- B. Use corrosion resistant metals.
- C. Use coatings.
- D. Apply cathodic protection.
- E. Maintain uniformity of exposure conditions throughout the system.
- F. Prevent stagnant conditions such as liquid trapped in a low part of an inactive pipe system.
- G. Provide smooth finished surfaces (polished rather than etched).

5. Erosion - Corrosion

Erosion-corrosion is the acceleration or increase in rate of corrosion of a metal due to relative movement between a moving fluid and the metal. Many erosion-corrosion failures are caused by turbulent conditions produced by interference to smooth flow of fluids in a pipe. This form is not associated with back-fill materials. One form of erosion-corrosion is known as cavitation, which is caused by the formation and collapse of vapor bubbles in a liquid near a metal surface in a pipe as shown in Figure 5.

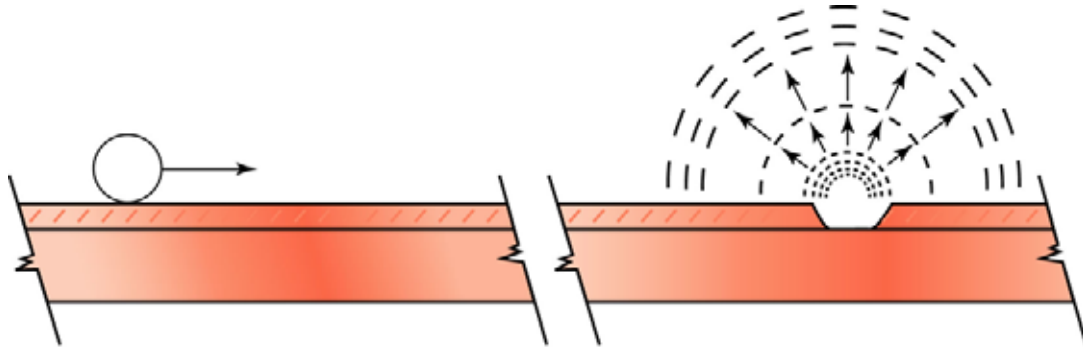


FIGURE 5. Corrosion by Cavitation

To decrease damage from erosion-corrosion:

- A. Select materials with good resistance to erosion-corrosion.
- B. Use proper design - increase diameter of the pipe or decrease liquid velocity, and streamline bends.
- C. Alter the environment by deaeration and addition of inhibitors in the liquid.
- D. Use a coating to produce a resilient barrier.

6. Stress Corrosion

Stress corrosion cracking is caused by the simultaneous application of a tensile stress and a specific corrosive medium. Bent conduits and highly stressed members are especially susceptible to stress corrosion, which may be minimized by:

- A. Lowering the stress by annealing thickening the section or reducing load.
- B. Eliminating the critical environment.
- C. Changing the alloy.
- D. Applying cathodic protection.
- E. Adding inhibitors.

7. Intergranular Corrosion

When a metal has solidified and cooled, the crystal structure or grains meet at boundaries where there is a mismatch in crystal blocks. Because the most stable configuration of the metal is its particular structure or lattice, grain boundaries are high energy areas and more active chemically. Chromium is added to steel to impart corrosion resistance by stimulating the formation of a protective oxide film on the surface. In stainless steel, films of chromium carbide can form in the grain boundaries. This depletes the chromium content from the surrounding areas and intergranular corrosion may result.

Intergranular corrosion is decreased by:

- A. Heat treatment.
- B. Adding stabilizer (carbide former) such as titanium.

8. Selective Leaching

Selective leaching is the selective removal of one element from an alloy by the environment. For example, yellow brass (approximately 30% zinc and 70% copper) turns red or copper color as zinc is extracted (dezincification). Flowing water in brass pipe dissolves the zinc. The most effective means for decreasing the effects of selective leaching is by reducing the aggressiveness of the environment.

ENVIRONMENTAL CONDITIONS INFLUENCING UNDERGROUND CORROSION

1. Dissimilar Soils

Soil characteristics vary from one geographical area to another and from season to season. The same soil can vary in moisture content, pH, aeration and sometimes chemical composition, being acid, alkaline or saline depending upon rainfall. The presence of soluble salts contributes greatly toward the electrical conductivity of the soil.

Potentially corrosive environments are created by differences in oxygen concentration, pH, moisture content, composition, density, organic content, and differential aeration. Many examples of corrosive conditions created by improper design and construction could be cited. These include such common faults as:

- A. Pipe lines laid in soils which have been mixed during construction operations.
- B. Pipe laid in water and covered with soil or granular fill.
- C. Having dense deposits of soil adhering to pipe. The area under clay lumps becomes oxygen starved and acts as an anode.

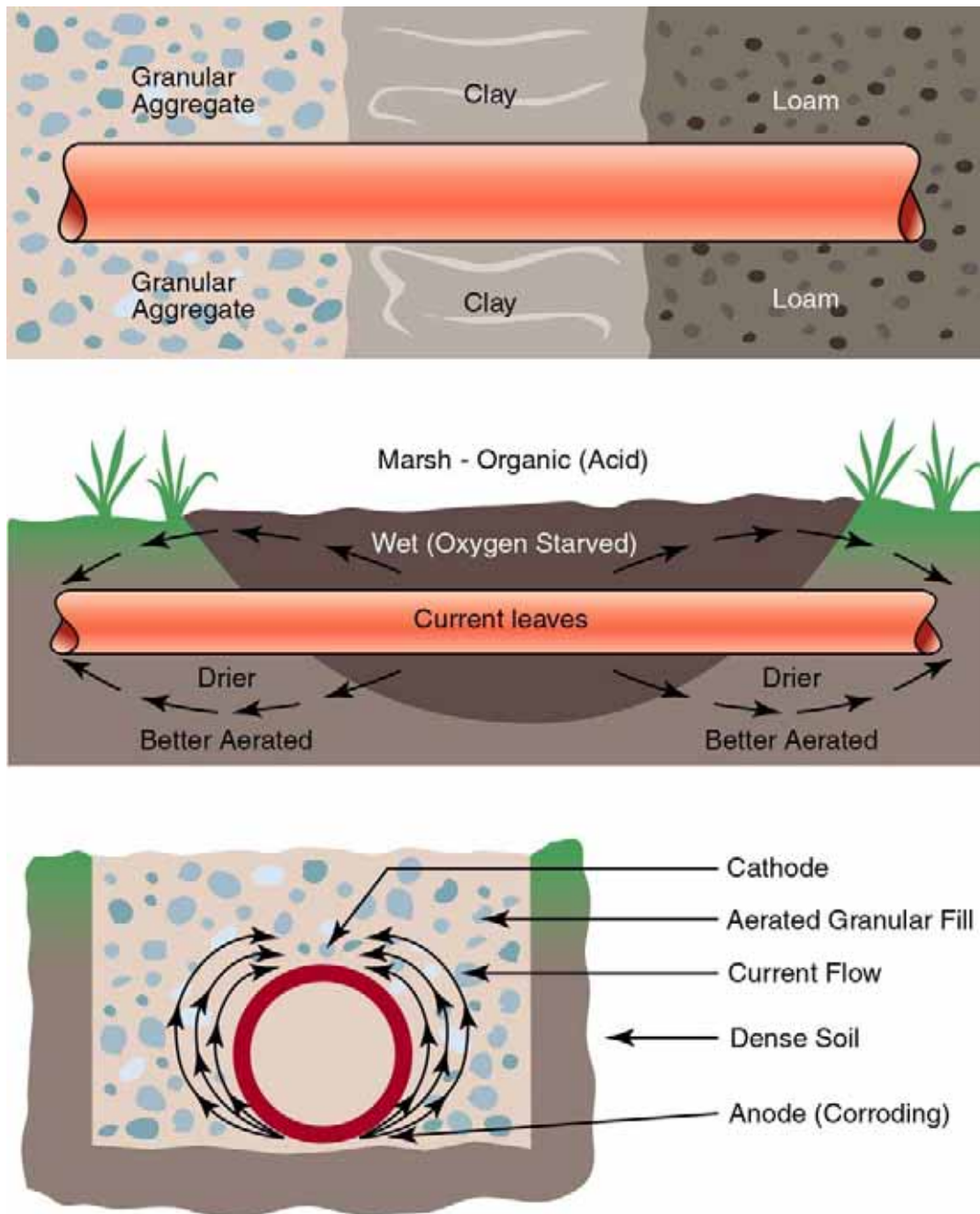


FIGURE 6. Examples of Potentially Corrosive Environments

Proper use of corrosion resistant backfill materials will minimize difficulties mentioned above. These materials should have the following general characteristics:

- A. Low moisture content (well drained).

- B. High pH (alkaline).
- C. Free from decaying organic matter.
- D. Well aerated.
- E. Relatively cool temperature.
- F. Uniformity of environment (metal should be completely surrounded by uniform backfill material).

2. External Voltage (Stray Current)

Leakage emanating from external power sources such as improperly grounded or poorly insulated welding machines, motors on well pumps, or electrical generating equipment located in mines, utility rectifiers or manufacturing plants can jump onto an isolated nearby utility line. Corrosion normally occurs at the point where the invading current leaves the line.

3. Bacterial or Anaerobic Corrosion

Certain anaerobic bacteria are capable of transforming sulfate containing soils into sulfides. This occurs in the presence of organic soils deficient in oxygen. For the bacteria to function, it is necessary to (1) have essentially an oxygen-free environment, (2) presence of assimilable organic nutrients and minerals, and (3) presence of sulfate in the soil. Anaerobic corrosion does not occur in well drained and aerated soils. Iron bacteria use ferrous iron for sustenance and leave the alloy vulnerable to attack through the action of the bacterial tubercles. These iron bacteria are commonly found in water mains and similar equipment.

METHODS OF CORROSION CONTROL

Methods of controlling corrosion are summarized as follows:

1. Environmental Modification

- A. Investigate the composition, concentration, homogeneity and nature of the electrolyte.
- B. Adjust pH of soil components.
- C. Use of inhibitors.
- D. Cathodic and anodic protection - this basically is artificially reversing an existing electrical potential by giving a positive (+) charge to the soil surrounding the structure. This causes the structure being protected to act as a cathode.
- E. Maintain the environment as uniform as possible.

2. Selection of Metals

- A. Use of special structural metals - composition, homogeneity, and crystal structure.
- B. Coatings - metallic, nonmetallic or organic.

3. Design and Fabrication

- A. Avoid bi-metallic couples.
- B. Avoid localized stresses.
- C. Avoid concentration cells.
- D. Minimize surface/volume ratio.
- E. Keep surface smooth, streamlined (no sharp corners).

4. Make Anodic Area Larger Than Cathodic Areas

CHEMICAL AND PHYSICAL PROPERTIES OF SLAG

1. Blast Furnace Slag

A. Definition

The American Society for Testing and Materials defines blast-furnace slag as the non-metallic product consisting essentially of silicates and aluminosilicates of lime and other bases which is developed in a molten condition simultaneously with iron in a blast furnace. (ASTM Designation C125).

Further definitions under ASTM Designation C125 are as follows:

Air Cooled Blast-Furnace Slag - The material resulting from solidification of molten blast-furnace slag under atmospheric conditions. Subsequent cooling may be accelerated by application of water to the solidified surface.

"Granulated Blast-Furnace Slag" - The glassy granular material formed when molten blast-furnace slag is rapidly chilled as by immersion in water.

"Expanded Blast-Furnace Slag" - The lightweight cellular material obtained by controlled processing of molten blast-furnace slag with water or with other agents such as steam or compressed air or both.

B. Production

The incidental production of slag as a by-product in the smelting of iron from iron ore dates to antiquity. Modern production practices have developed high efficiencies in the process; however, the basic principles are the same today as in the past.

Iron ore along with coke and fluxstone is progressively charged into the top of the blast furnace. Pre-heated air is blown through several ports near the bottom of the tall furnace column. Air burns the coke and at a temperature of about 3000° F, hot gases reduce the iron ore to molten metallic iron. At the same time other mineral products contained in the iron ore and coke are chemically combined with fluxstone to form a molten slag. Both the iron and slag accumulate in a layered pool at the bottom of the furnace and are periodically drawn as molten liquids from the furnace and each flow its separate way for further processing. The iron so produced is the crude product for further refinement to steel. The slag is called blast-furnace slag which is processed to finished products.

C. Chemistry and Mineralogy

In the operation of a blast-furnace the composition of the slag must be closely controlled so that the amount of silica plus alumina balances (quantity wise) with the total of lime and magnesia to produce a composition of slag which will readily melt and flow from the furnace at the temperature of molten iron.

These limitations on the chemistry of blast-furnace slags to permit efficient furnace operation provide quite a narrow band in the chemical composition of all blast furnace slag. There may be a limited variation between the constituents silica plus alumina and lime plus magnesia, however, the ratio of the composition fluctuates only a small amount.

The four major constituents of blast-furnace slag - silica, alumina, lime and magnesia - constitute about 95% of the total composition. Hundreds of chemical analyses of blast furnace slag from many sources are shown to fall within the following range of composition:

Silica	SiO ₂	32 - 40%
Alumina	Al ₂ O ₃	9 - 17
Lime	CaO	34 - 44
Magnesia	MgO	5 - 1.8
Sulfur	S	1 - 3
Iron Oxide	FeO	0.3 - 1.5
Manganese Oxide	MnO	0.2 - 1.5

When molten blast-furnace slag is rapidly chilled and is being quenched in water as granulated slag, the solid phase is predominately a granular and cellular glass. When such molten slag is more slowly cooled, crystallization takes place while the slag is

cooling. The predominate crystal phase in air-cooled blast furnace slag is called melilite, a name applied to any series of solid solutions extending from akermanite ($2\text{CaO}\cdot\text{MgO}\cdot 2\text{SiO}$) to gehlenite ($2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$). Other minerals found to be present in blast furnace are pseudowollastonite, monocalciumsilicate, olivine, pyroxene, merwinite, calcium sulfide, ferrous sulfide and manganous sulfide. The same or similar minerals are frequently found in igneous rocks.

D. Sulfur in Slag

Although blast-furnace slag has been used as a select granular fill and back-fill material for many years with an excellent service record, the presence of a small amount of sulfur compounds has occasionally raised fears that corrosion of metals might result.

Around the turn of the century the use of coal ashes as fill material had been found to cause corrosion of embedded metals. It was suggested at this time that sulfur compounds in this material formed an acidic environment. The idea developed that the presence of sulfur was harmful and should be avoided. Much of the prejudice against the use of slag derives from early experiences with sulfur bearing coal residues. The reported effects of the sulfur compounds in coal ashes has contributed to doubts regarding the effects of slag despite the fact that slag is completely different in chemical composition

The concern that slag may have an affect on metals is based on the presence of sulfur in slag. The unjustified assumption is that, in the presence of moisture and oxygen, corrosive solutions are formed. It is interesting to note that no such conclusion has been reached after a study of the chemical analysis of hydraulic cements which may contain as much sulfur as slag. Blast-furnace slag is used in the manufacture of Portland cement (ASTM C-150) Portland blast-furnace slag cement (ASTM C-595 Type IS) and slag cement (ASTM C-595 Type 5). In many cases slag may be the major constituent in the cement.

The predominant occurrence of sulfide in slag is in the form of calcium sulfide with smaller amounts of iron and manganese sulfides. In air cooled slag these sulfides appear in crystal form. In the glassy phase of slag the sulfides occur in the colloidal state and strongly affect the color of glass, producing yellows and brown. The sulfide compounds found in slag are slightly soluble in water but in solution are always associated with a highly alkaline environment. This is precisely the opposite situation from the acidic condition associated with sulfur bearing coal residues such as cinders.

In the case of coal cinders, the sulfur compounds are in a potentially acid forming environment. Coal ashes or coal cinders are composed essentially of compounds of silica (SiO^2), alumina (Al_2O_3) and iron oxide (FeO) which form acid environmental conditions in the presence of moisture. The strong alkaline forming compounds of calcium and magnesium so predominant in blast-furnace slag are present in cinders in

such small quantities that they are ineffective in creating an alkaline environment. Therefore, the sulfur compounds in coal ashes are active in an acid environment and consequently would promote a corrosive medium.

Hydrogen sulfide which is sometimes evolved from moist slag can be detected in extremely small amounts, having an average odor sensitivity of 5 parts in 1,000,000,000 parts of air. The odor of hydrogen sulfide from slag has occasionally created concern for some who have associated this odor unfactually with corrosive potential.

When discussing slag with a metallurgist, reference is sometimes made to an "acid" slag which to the layman might lead to the erroneous assumption of a potentially corrosive material. The meaning of the terms "neutral", "basic" and "acidic" as applied by the metallurgist are the same as those assigned by the chemist.

Silica (SiO_2) and Alumina (Al_2O_3) are considered as acid constituents in natural or synthetic mineral composition by the metallurgist and mineralogist. In the presence of moisture they produce a weak acid solution. Lime (CaO) and magnesia (MgO) are considered to be basic constituents. In the presence of moisture they produce a strongly alkaline reaction.

The metallurgist, when applying the terms basic or acidic to slag, refers to an arbitrary ratio of basic oxides (lime and magnesia) to the acidic constituents (silica and alumina). A so-called "acid slag" is one where the silica plus alumina exceeds the composition content of lime plus magnesia, but it does not contain free acids. Slag is always alkaline in its reaction with water. The pH of this reaction is normally in the range of 9 to 11. As a matter of fact, slag is frequently used to eliminate acid conditions in industrial operations as well as being used to neutralize acid soil conditions in agriculture.

2. Steel Making Slag

A. Definition

Although steel-making slags are not formally defined in the literature of ASTM, they are non-metallic by-products consisting essentially of compounds of silica, alumina, lime, magnesia, iron oxides and manganese oxides, developed during the refining of crude iron products to steel.

B. Production

In the United States practically all steel is produced in either basic oxygen, open hearth, or electric arc furnaces. In all of the processes, fluxing materials are added which results in the desired composition of molten steel and a slag by-product. The slags from all of the refining processes are called steel slags.

C. Chemistry

The major impurities of the crude iron and scrap used in steel making furnaces include elements such as carbon, silicon, manganese, titanium, phosphorus and sulfur. The refinement of the impure iron to steel requires certain chemical reactions designed primarily to remove or reduce them to such levels as may be beneficial to steel and products desired.

The lining of the furnaces are made from materials such as burned magnesite (MgO), dolomite (CaO.MgO) and cements made from magnesia (MgO). These linings plus the fluxes which are added form a slag which is basic in character.

The chemical composition of steel slag varies over quite a large range as compared to blast-furnace slag. The required composition of the steel in this metallurgical process controls to a great extent the composition of the slag. Typical of this variance, the following is taken at random of steel slags from ten sources:

Silica	SiO ₂	11.1 - 23.2%
Alumina	Al ₂ O ₃	5.0 - 12.6
Manganese Oxide	MnO	0.9 - 9.1
Iron Oxide	Fe ₂ O ₃	19.8 - 35.3
Lime	CaO	14.8 - 44.5
Magnesia	MgO	6.7 - 20.1
Sulfur	S	0.1 - 0.2

Steel making slag would produce an alkaline condition in the presence of moisture and have the capability to neutralize acid through its content of lime and magnesia.

DOCUMENTATION OF SLAG USAGE

The real test of a product's performance is the field use over a significant period of time to demonstrate the properties of the material in service.

Slag aggregate has been marketed extensively in the United States since the early 1900's. Applications have ranged from Portland cement concrete, bituminous concrete, ballast, and prestressed concrete, to fills of all kinds. As a fill item it has been utilized for structures containing steel piling, piers, bridge members, utility pipes (water, gas and electric), metal culvert and numerous others.

To date, in excess of 1,000,000,000 tons of slag has been marketed over a period of fifty years. There have been no confirmed cases reported where slag has been the prime cause of corrosion of ferrous metals.

If slag aggregate caused any corrosive reaction, the engineering literature would now contain many references to the problems encountered. No such reports exist. Severe corrosion and, in some cases, failure, may be caused by violation of any of the basic principles of corrosion control, regardless of the materials used.

1. Tests Performed by The National Slag Association

A. Five Year Field Corrosion Study of Steel Pipe to Determine Effects of Backfill Materials - NSA 165-1, Highway Research Record No. 140, 1965 - Highway Research Board - By E. W. Bauman and D. W. Lewis.

This paper reported results of a corrosion study involving exposure of galvanized and black pipe specimens for five years in various backfill materials. These materials included blast furnace and steel furnace slags, limestone, gravel, natural sand, coal cinders and the native soil which was similar to that at the National Bureau of Standards corrosion Test Site No. 55. It was considered typical of well-drained, high resistivity soils found in the eastern part of the United States ("Underground Corrosion" by Melvin Romanoff, National Bureau of Standards Circular 579, 1957).

Specimens were removed at the end of five years, cleaned and the corrosion evaluated with the assistance of Mr. Romanoff, Corrosion Section, Metallurgy Division, National Bureau of Standards, using procedures described in NBS Circular 579. The black pipe specimens were evaluated by depth measurements of corrosion pits using a dial micrometer depth gage, while galvanized specimens were rated on the basis of the area of bare steel exposed by loss of the zinc coating.

The black pipe (bare carbon steel) was severely pitted in the coal cinder backfill. Extent of pitting that occurred in the slag, limestone, gravel, natural sand and native soil backfills was similar and variations between them were within the range of variability shown by the NBS studies for duplicate specimens in the same material. Comparisons of the results with tests over a 5-year exposure period reported in NBS Circular 579 indicated that, except for the coal cinders, somewhat less corrosion was found with all of the backfill materials used than would be expected with an average natural soil.

As might be expected, the galvanized specimens showed less evidence of corrosion than did the unprotected steel. Pitting or loss of the zinc protective coating was very minor or non-existent on all specimens except that from the coal cinder backfill. In the case of the coal cinders, all of the zinc had been removed by corrosion exposing the base steel over the entire pipe, and extensive pitting had begun.

The results, therefore, show that no significant difference existed between any of the backfill materials tested, except for the coal cinders, which were highly corrosive. NBS studies show a leveling off of corrosion with time for materials other than poorly aerated soils and cinders which maintain a high corrosion rate over long periods of time. Little

additional corrosion would be expected from longer exposure times with the slags and natural aggregates used in this study. All of them are indicated to be somewhat better than an average natural soil.

B. Alkalinity and Acidity Tests of Slag and Water Solutions - Research Laboratory - National Slag Association - by H. T. Williams, P.E., June 1960.

The primary purpose of this investigation was to determine what happens to solutions leached from slag or water in contact with slag relative to their alkalinity or acidity when permitted to stand for long periods of time. Air-cooled, granulated and expanded slag specimens were placed in distilled water and aged up to a period of 30 weeks.

In the discussion it was brought out that "As long as slag remains in the presence of water, the water solutions are alkaline."

2. Tests Performed by Other Agencies

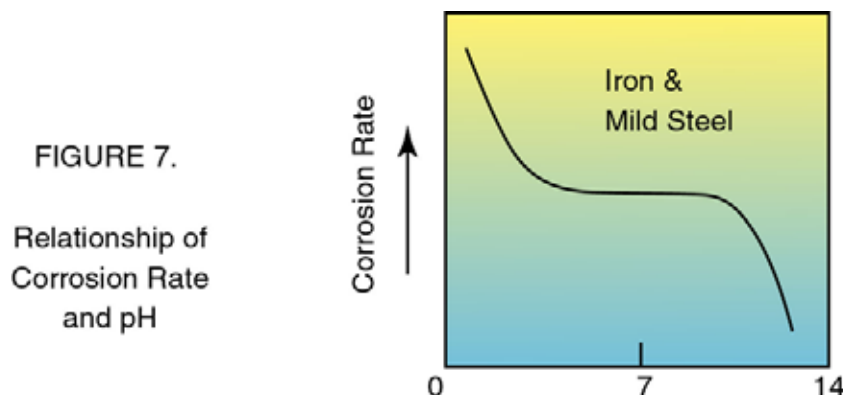
A. Testing Laboratory - Smith Emery Co., Los Angeles, California. In 1970 a section of culvert in contact with blast-furnace slag aggregate for 19 years was examined to determine the rate of corrosion.

The report verifies the excellence of air-cooled blast furnace slag as a back fill against steel culverts. Over a period of 19 years the total loss of metal was only 5.67% (0.008 inches/0.141 inches) in the sample section tested. Taking a straight line average the percentage loss per year of use is only 0.30%. Assuming that the culvert would still satisfactorily function at an average loss of metal of 40%, it would last 134 years on a straight line basis. Using corrosion engineering principles which indicate that the rate of loss of metal becomes less with time, a projected life of infinity is possible.

Another test was performed by the same laboratory where samples of blast furnace slag from eight different sources were placed in distilled water and allowed to stand for 60 hours. At the end of this period, the liquid was extracted and tested for pH value. The results were a low value of pH 9.4, a high value of pH 11.7, and an average of pH 10.6.

The alkalinity of slag fills, and the corrosion resistance of such fills, may be demonstrated by interpreting the pH values as previously stated. Blast furnace slag fills against steel and cast iron structural elements of all types demonstrate the corrosive resistant nature of slag in the past and will continue to do so in the future as ground water adjacent to steel and cast iron structural elements backfilled with air-cooled blast furnace slag increases in its alkalinity thus assisting in the preservation of steel and cast irons.

In the September 22, 1958 issue of Chemical Engineering, Dr. Robert V. Jelinek's article on "How pH Affects Corrosion" points out that pH is an important variable, with acid solutions being more corrosive than neutral or alkaline ones. He stated that corrosion rates decrease with increasing pH, and that a relationship similar to that shown in Figure 7 is usually observed. The high pH values of slag solutions should, therefore, inhibit the corrosion rate.



3. Statements of Recognized Authorities

A. S. K. Coburn, Corrosion Engineer, U. S. Steel

A conference and symposium on the subject of pipe corrosion arranged by Mr. L. V. Struble, Chief Plumbing Inspector of Mahoning County, was held in Youngstown, Ohio in December 1963. Included in attendance at the meeting were representatives from steel corporations, the Cast Iron Soil Pipe Institute, the Copper Development Association, Municipal Planning Commissioners, architects, inspectors of installations, as well as union representatives of the Plumbers and Steamfitters Union, plumbing contractors and the mineral aggregate industries, all of whom contributed learned information and experience.

Among the subjects discussed, was the possibility of corrosion of ferrous metal pipe in the presence of blast furnace slag. While none of the conference participants offered any adverse experiences with slag, it was recognized that "slag" and "cinders" are often used synonymously and that slag is, therefore, suspected of being a cause of corrosion. Mr. S. K. Coburn, corrosion engineer for the United States Steel Corporation who is a recognized authority in his field, discussed the principles of corrosion and the facts of slag use at some length, which in abstract is summarized as follows:

In the chemical composition of blast furnace slag there is about 1-1/2% sulfur (occurring principally as calcium sulfide), which of itself is not a major cause of corrosion. The corrosion phenomenon is a matter of electrolytic cells. The difference in concentration of

salts and moisture from one point to another along a steel pipe is the key to corrosion and pitting.

Slag, in the presence of water, forms an alkaline solution and alkaline solutions are not very aggressive at pH's of 9 or 10. If the pH of the solution goes up to 11, steel can become quite passive to corrosion. Corrosion is limited because the compounds of calcium and magnesium in the slag are alkaline. They over-power any acid tendencies of the sulfide. You may possibly detect the smell of hydrogen sulfide when moisture is present. Its characteristic odor may be strong enough with only a few molecules present, that you may think that a dangerously acid condition is present. Actually, it is so weak that it is non-effective.

When slag is present, it is not part of the question! Those who may believe that it is corrosive have been fighting the wrong culprit. To write a code around a failure, one must, by no means, ignore the failure but you must understand how it happened and call in people who are knowledgeable.

- B. Bureau of Mines - Bulletin 479 - Iron Blast Furnace Slag - Production, Processing, Properties and Uses - by G. W. Josephson, F. Sillers, Jr. and D. G. Runner (1949).

Page 58 & 59 - Relation of Chemical Composition to Use - "Experience has shown that sulfides in slag do not corrode metals, and significant quantities of sulphur in elemental or acid form are never present in commercial slag. Slag is alkaline and alkalinity generally prevents corrosion. "

Page 208 - Railroad Ballast - "Contrary to early apprehension, experience has shown the slag ballast has no corrosive effect on rails, track fastenings, steel ties and interlocking signal systems." Millions of tons of slag have been marketed each year for many decades to various railroads networks throughout the country with many years of excellent performance.

Page 98 - Figure 60 shows a photograph of an excavation in Youngstown, Ohio uncovering steel pipes embedded in granulated slag from 1911 to 1948. The caption indicates "Steel pipes shown in foreground were well preserved."

- C. J. C. Hudson - D. Sc., F.I.M. - Journal of Iron & Steel Institute, August, 1963.

"It seems reasonable to conclude that it is unlikely that blast furnace slag back fill will have a serious corrosion effect. Any effect due to the presence of sulfide in the slag will probably be found to be of the same order as the difference observed between various types of natural soil. Indeed, if and when the matter is put to test by field trials of steel

buried in a range of soils and of slags, the slags may well be found to lie towards the less corrosive end of the array of sites."

This statement confirms the findings and conclusions of Melvin Romanoff of the National Bureau of Standards as previously reported.

4. Specification Agencies

Specifying agencies such as A.S.T.M., A.A.S.H.O., U.S. Corps of Engineers and 15 States in which slag aggregate is produced do not place any restrictions on applications for the use of slag aggregate relative to corrosion.

5. Field Projects - Performance

A. City of Warren, Ohio

In a letter provided by Joseph C. Hapgood, Superintendent, City of Warren Water Department, Mr. Hapgood relates that a 6" cast iron water line installed at South. St., S.W. in 1916, a 20" cast iron water line installed in 1923 at Summit Street, S.W. and many others were uncovered at various times up to the time of the letter (October 27, 1952), "...in no case was there ever any evidence of pitting or deterioration where slag was used as a back fill."

B. Camden, New Jersey - Garden State Parkway

Galvanized corrugated and perforated metal drainage pipe was embedded in blast furnace slag aggregate in 1946 and evidenced as performing satisfactorily when examined for performance in 1960.

C. Tonawanda, New York

Buffalo Gravel Corp., a ready mixed concrete producer at River Rd., Tonawanda, New York. In November 1970 a water line connection to a 61' steel line embedded in blast furnace slag aggregate screenings since 1929 was made and found to be in good condition and still serviceable.

D. Niles, Ohio - City Water Department

In a letter provided by Mr. Bert Holloway refers to a 24" cast iron water pipe that was embedded in granulated slag in 1922 for a length of 4,525 feet, uncovered in 1952 and "...the 24" line was found to be in perfect condition.

E. Ohio Department of Highways

Mr. Thomas M. McVey, Inspector for the Ohio Department of Highways upon examination of metal pipe (gas, water, electrical and telephone) buried in granulated slag since 1911 and uncovered in 1948 provided a letter stating that "...We noted during the excavation the excellent preservation of all metal pipes, in contact with granulated slag which included the steel as well as the cast iron lines. No cases were observed where there was external corrosion of the pipes."

SUMMARY

For every case of metal corrosion there is scientific reason for its occurrence. In some cases, it is more economical to accept it as inevitable rather than to make vast investments for its control. In most cases, however, to be knowledgeable of why and how corrosion does occur will permit a defense to be built into a system to control, delay, or retard the forces which promote corrosion.

It is a natural human tendency to jump to a conclusion with a little bit of knowledge rather than to admit to one's self that he is not qualified to analyze all of the complexities which surround a problem.

The preceding text has endeavored to cite some of the fundamentals surrounding the science of corrosion. It is appreciated that no such discourse could be all encompassing on the subject as there are a multitude of volumes written, and many more will be submitted to print by scientists as knowledge progresses.

It may be of interest to review and summarize some of the fundamentals and experiences as related to the use of slag as an environment surrounding ferrous metals.

It is generally accepted that corrosion of ferrous metals occurs by the creation of electrolytic cells and a flow of current at these cell points. The modification factors lie basically in 1) the environment surrounding the metal and 2) the structural and metallurgical properties of the metal. Each of these two modification factors has numerous controlling and various condition features which determine the rate or severity of corrosion.

The hydrogen ion concentration or pH value of the surrounding environment of the ferrous metal has a profound effect upon the rate of corrosion. A low pH (acid) value will accelerate the rate of corrosion and higher pH (alkaline) values will slow the rate of corrosion (see Figure 7).

Slag in the presence of moisture produces an environment of high pH values conducive to retardation of the rate of corrosion. It should not be assumed that a high pH value at

one point in the environment of a continuous piece of ferrous metal can alone control the rate of corrosion.

A change in environment along the continuous piece of metal or a differential in environment at one or more points can create an electrolytic current differential and cause accelerated corrosion. In more simple terms, a continuous section of steel pipe which is laid in soil, say of relatively low pH, then through a layer of relatively high pH material such as slag or limestone and then to the air or through water approximately neutral (pH 7) could suffer accelerated corrosion. However, if the pipe was continuously in the high pH medium, the corrosion rate would be substantially lowered.

Thus it is strongly recommended that the medium around iron or steel pipe be as continuous and uniform as possible and of relatively high alkalinity (have a pH value as high as may be economically available). Be cautious that induced or connected direct currents do not pass through the pipe line as the points at which the current leaves (dissimilar metals in the pipe circuit) the pipe to the ground, will suffer corrosion. There have been millions of tons of slag used in bulk form for many construction purposes such as for fills, as well as foundations and bases for domestic, commercial, municipal and industrial construction wherein iron and steel have been incorporated into the slag construction as utility lines for water, gas and conduits for electricity.

There have been so many of these types of construction without any report of adverse corrosion that the slag industry has never found it necessary to record and tabulate a substantial documentation of its successful use.

The preparation of this publication was undertaken to better acquaint potential users of slag with certain fundamentals pertaining to the corrosion of iron and steel under contact environment and to allay certain unfounded suspicions that may exist. To the professional corrosion engineer this short treatise may seem an over-simplification of an extremely complex field. We have not attempted to cover all conditions of environment, all metals and all circumstances of use, only those most common to bulk uses of slag in intimate contact with iron or steel.

REFERENCES

1. Homberg, E. G., "Corrosion Fundamentals and Properties" Highway Research Board - 1958 Proceedings.
2. Romanoff, M., U. S. Department of Commerce, National Bureau of Standards, Circular 579.
3. Fontana, M. G., and Greene, N. D., "Corrosion Engineering" 1967 McGraw-Hill.