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CORROSION AND SCALING IN SOLAR HEATING SYSTEMS

DECEMBER 1981

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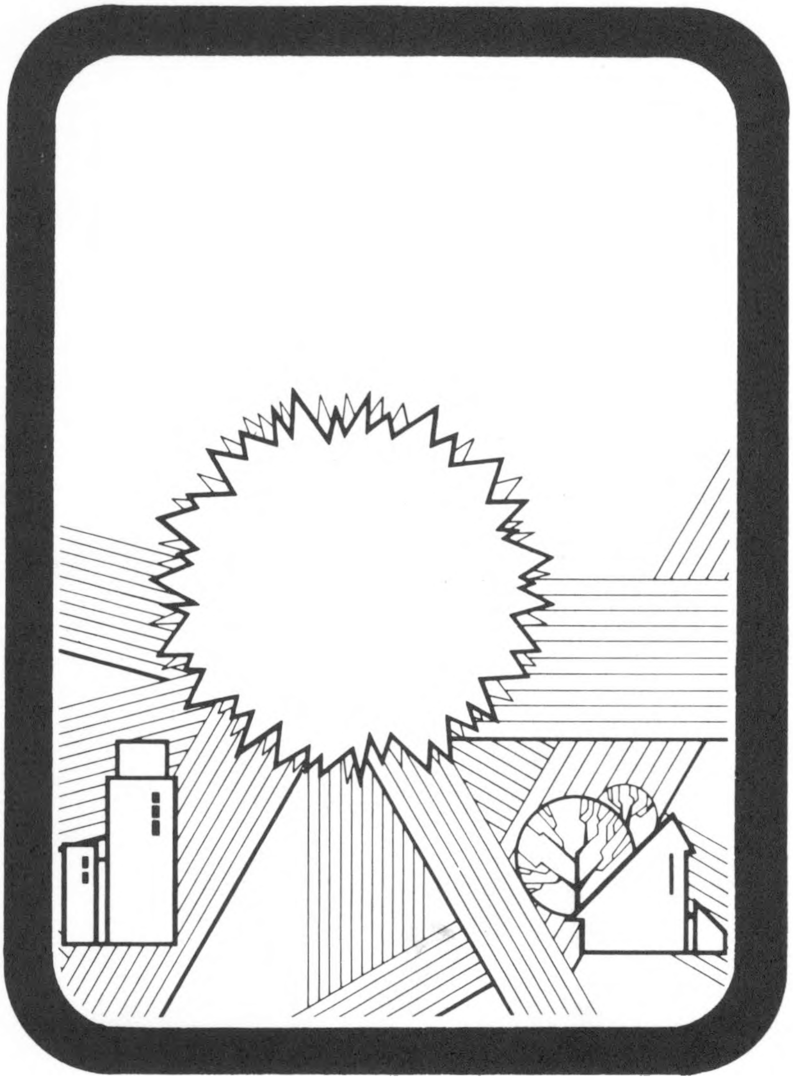

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CORROSION AND SCALING IN SOLAR HEATING SYSTEMS

DECEMBER 1981

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TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

ABSTRACT

Corrosion, as experienced in solar heating systems, is described in simplistic terms to familiarize designers and installers with potential problems and their solutions. The role of a heat transfer fluid in a solar system is briefly discussed, and the choice of an aqueous solution is justified. The complexities of the multiple chemical and physical reactions are discussed in order that uncertainties of corrosion behavior can be anticipated. Some basic theories of corrosion are described, aggressive environments for some common metals are identified, and the role of corrosion inhibitors is delineated. The similarities of thermal and material characteristics of a solar system and an automotive cooling system are discussed. Based on the many years of experience with corrosion in automotive systems, it is recommended that similar antifreezes and corrosion inhibitors should be used in solar systems. The importance of good solar system design and fabrication is stressed and specific characteristics that affect corrosion are identified.

INTRODUCTION

In *active* solar heating systems, a fluid is used to carry, or transfer, heat from the outside of a building to the interior. In selecting a fluid, a variety of physical and chemical properties should be considered. The ideal fluid would have the following physical properties: high heat capacity, high thermal conductivity and low viscosity. From the chemical standpoint, the fluid should be inert, i.e., noncombustible, noncorrosive, and thermally stable. It is also desirable that the fluid be cheap and nontoxic.

No fluid contains all of the above qualities, so the selection of a fluid depends on the specific application. For solar recovery purposes, gases have desirable chemical properties but poor physical properties. Their low density, low heat capacity and low thermal conductivity mean that ducts and heat transfer surfaces must be large and hence difficult to route. The much higher density and heat capacity of liquids allow the usage of much smaller pipes to transport the same quantity of heat. On the other hand, liquids tend to be more chemically reactive than gases. Liquids may be classified as either aqueous solutions or organic compounds. Of all liquids, aqueous solutions represent the optimum, in that they have the highest heat capacity and thermal conductivity, low viscosity, high thermal stability, and are noncombustible. Unfortunately, aqueous solutions tend to react with metal surfaces in a variety of different and complex reactions. This results in leaking, plugging of passages, or scaling. Most organic compounds are hydrocarbons which are unreactive toward metal surfaces, and this often makes them appear to be more desirable heat transfer fluids. However, these liquids have lower heat capacities, lower thermal conductivities, higher viscosities, and are combustible. The silicones are a class of organic compounds that are much less chemically reactive than the hydrocarbons but share most of their unfavorable physical properties. They are also very expensive, usually more than $25.00 per gallon. When the characteristics of fluids are compared, water based solutions are found to be best except for those systems having very severe or unusual operating conditions. Inhibitors are generally added to reduce their corrosive tendency, and various alcohols are added to lower their freezing point.

In a solar heating or cooling system, there are various circuits or loops that employ a heat transfer fluid. Of these, one loop experiences physical conditions of such severity that pure water often cannot be used as a heat transfer medium. Some of the unique characteristics of the collector loop are:

1) There is a wide variation of temperature that can range from subfreezing temperatures to values as high as 300°F.
2) The pressure variation is relatively large due to the expansion and contraction of the fluid. This is likely to cause liquid leaks or the aspiration of air into the system.
3) There is a likelihood of a variety of dissimilar metals in the system including aluminum, steel, and copper.

When flowing aqueous solutions come in contact with metal surfaces, there are a variety of phenomena that can change the physical character of the interface. *Scaling* is the deposition of a solid on the metal surface, usually resulting from some precipitating process. *Corrosion* is the chemical reaction between a metal and its environment. The mechanism of the corrosion process is generally referred to as electrochemical because it involves the flow of electrons. The result of the process can be the formation of an oxide of the base metal or the dissolution of the base metal and its disposition elsewhere in the system. *Erosion* is the term used to describe surface degradation due to physical forces resulting from fluid turbulence. In most systems, all three of these phenomena play a role; complementing another, counteracting another, or independent of the others. Because of these interactions, and the difficulty of separating their effects, the term corrosion is often used as an all-inclusive term to describe the consequence of interaction between metal and environment.

Scaling generally occurs when the solid concentration in a solution reaches a value greater than its saturation concentration. This can be a result of: 1) a loss of water by evaporation, 2) a chemical reaction generating a product in greater quantities than can be dissolved, or 3) localized conditions, such as temperature, that affect solubility. Table I shows the range of inorganic solids found in municipal water systems in the U.S., and Figure 1 shows how mineral content of water varies in different parts of the U.S.

Table I. Properties of Finished Water in Public Water Supplies in the 100 Largest Cities in the United States, 1962

Constituent or property	Maximum	Median	Minimum
Chemical analyses, ppm			
Silica (SiO_2)	72	7.1	0.0
Iron (FE)	1.30	0.02	0.00
Manganese (Mn)	2.50	0.00	0.00
Calcium (Ca)	145	28	0.0
Magnesium (Mg)	120	6.25	0.0
Sodium (Na)	198	12	1.1
Potassium (K)	30	1.6	0.0
Bicarbonate (HCO_3)	380	46	0
Carbonate (CO_3)	26	0	0
Sulfate (SO_4)	572	26	0.0
Chloride (Cl)	540	13	0.0
Fluoride (F)	7.0	0.4	0.0
Nitrate (NO_3)	23	0.7	0.0
Dissolved solids	1580	186	22
Hardness as ($CaCO_3$)	738	90	0
Noncarbonate hardness as ($CaCO_3$)	446	34	0
Specific conductance, μ∫ @ 25°C	1660	308	18
pH, pH units	10.5	7.5	5.0
Color, color units	24	2	0
Turbidity	13	0	0
Spectrographic analyses, μg/L			
Silver (Ag)	7.0	0.23	ND
Aluminum (Al)	1500	54	3.3
Boron (B)	590	31	2.5
Barium (Ba)	380	48	1.7
Chromium (Cr)	35	0.43	ND
Copper (Cu)	250	8.3	0.61
Iron (Fe)	1700	43	1.9
Lithium (Li)	170	2.0	ND
Manganese (Mn)	1100	5.0	ND
Molybdenum (Mo)	68	1.4	ND
Nickel (Ni)	34	2.7	ND
Lead (Pb)	62	3.7	ND
Rubidium (Rb)	67	1.05	ND
Strontium (Sr)	1200	110	2.2
Titanium (Ti)	49	1.5	ND
Vanadium (V)	70	4.3	ND

ND: not detected.
Source: C. N. Durfor and Edith Becker, 1962, "Public Water Supplies of the 100 Largest Cities in the United States", U.S. Geological Survey Water-Supply Paper 1812.

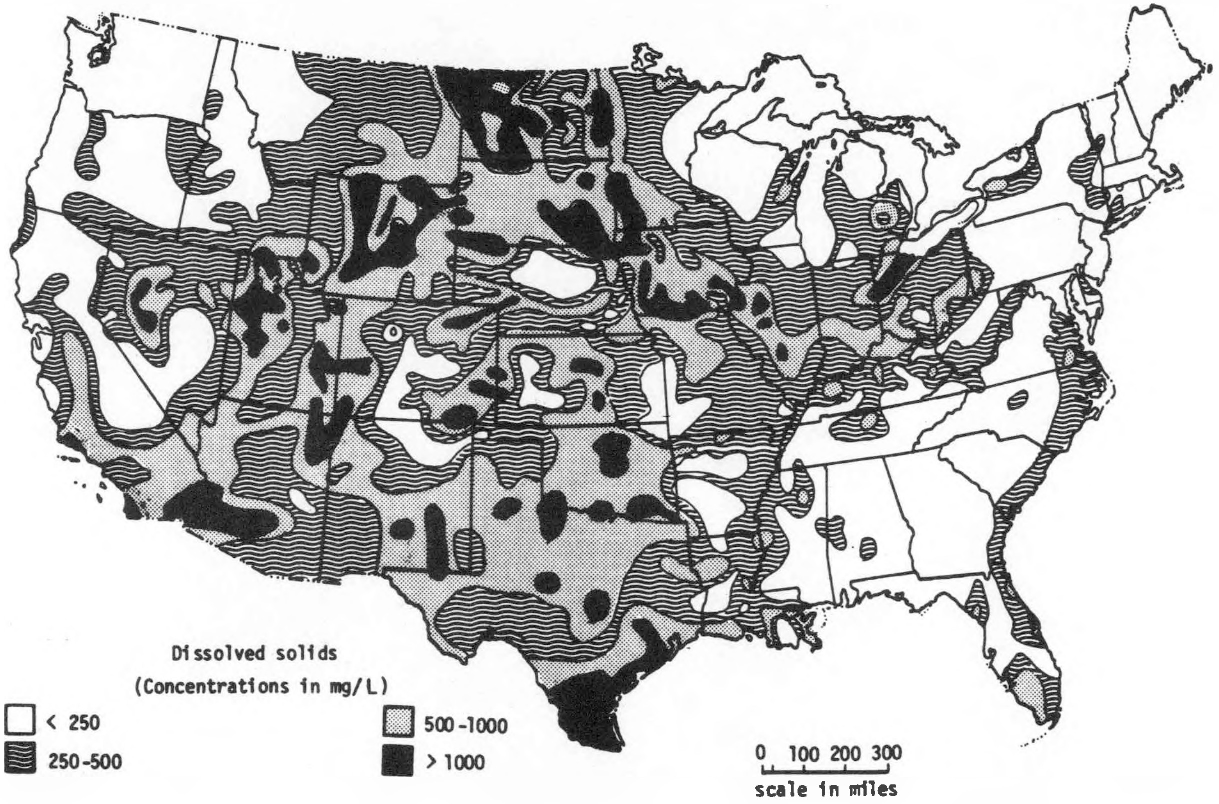

Figure 1. Dissolved Solids in Untreated Groundwater Used for Drinking Supplies, from "Domestic Water Treatment" by Lehr, Gass, et al. Copyright 1980 by McGraw-Hill Inc. Used with permission of McGraw-Hill Book Company.

Although all minerals can cause scaling, calcium and magnesium salts are usually the cause of most scale formation. These two metals form scales of calcium carbonate and magnesium carbonate which account for most of the scaling problems in water systems. The likelihood of scaling by these metals is determined by such parameters as Ca and Mg concentrations, pH, and temperature. Calcium carbonate has temperature solubility characteristics opposite to most other solids, in that its solubility decreases with increased temperature as shown in Table II.

Table II. Effect of Temperature on Solubility of $CaCO_3$

Temperature $T^{o}C$	$CaCO_3$ Solubility ppm at CO_2 press. of 0.0003 atm.
0	95
10	75
20	59
25	53
30	47
50	32

In most instances, scaling is undesirable, depending on the thickness of the scale film. In some cases, the film can become so thick that flow passages become very narrow, and liquid flow rates are significantly reduced. Even when the thickness is not that great, heat transfer is impeded because the scale acts as a thermal insulator. The magnitude of this effect is significant because the thermal conductivity of $CaCO_3$ is only 5% of that of steel. Extremely thin films of $CaCO_3$ scale are considered beneficial in some systems because they inhibit corrosion. This is true where the contact metals are iron, copper, or lead, but not where the metals are aluminum or stainless steel. There are quantitative methods of evaluating scaling effects such as by the Langelier "Saturation Index" but the calculation is complex and the results are questionable.

THEORIES OF CORROSION

Corrosion is a general term used to describe an extremely large number of possible chemical reactions involving metallic surfaces and liquid (or gas) environments. Water is an excellent solvent, and it frequently contains many different chemical compounds which can react with solid surfaces. Since the surface is one of the reactants, the mechanism and rate will depend on the metal constituents and physical characteristics of the surface. As a result, the corrosion processes can be extremely complex, and corrosion rates can be almost impossible to predict with any degree of accuracy.

Corrosion is always explained as an electrochemical process involving a reaction between metallic surfaces and specific mobile ions. Reaction driving forces are identified in terms of electrical potentials of the various cations (i.e., ions attracted to the cathode), referred to some arbitrarily chosen reference, usually hydrogen ions. Although the electrochemical process may appear complex, as described in standard texts, it is relatively simple compared with the other aspect of the problem, namely the physical and chemical interactions between the solid surface and the contacting liquids. The mechanisms and controlling parameters for these processes are so diverse and difficult to identify that their prediction is possible in only the crudest terms.

Whenever a chemical process occurs at an interface, the process requires a series of steps in order to go from the initial reactant to the final products. These steps are sequential and involve: 1) the physical motion of the reactants to the interface, 2) chemical reaction at the interface, and 3) the physical motion of products away from the interface. The net rate of the overall process is controlled by the rates of the individual steps, and if one step is significantly slower than the rest, then it will control the rate of the overall process. Physical motions of molecules can be influenced by such factors as flow velocity, shape of solid, structure of solid surface, temperature, etc. Chemical reaction rates are influenced by the chemical activity of the reactants, concentration of the reactants, and the temperature of the reaction.

To illustrate the effect of the relative rates, one could compare the corrosion of aluminum with that of copper. Chemically, aluminum is extremely reactive, and a fresh metal surface will react instantaneously with oxygen from the surrounding air. The resulting aluminum oxide can withstand considerable physical abuse and act as a barrier to prevent additional oxygen from reacting with the base metal. Its transparency also makes it invisible. Copper, on the other hand, is far less reactive chemically, and exposed metal surfaces will react relatively slowly with oxygen in the surrounding air. The copper oxide also acts as a barrier to continued oxidation (i.e., corrosion) but lacks the physical properties of the aluminum oxide. The copper oxide can be eroded or worn away to expose a fresh metal to the corrosive environment, thus, under a given set of conditions, these two metals might appear to corrode at the same rate, but the mechanisms are vastly different. By changing the conditions, the corrosion rate of one metal might greatly increase and that of the other might decrease.

Even though corrosion is an electrochemical process, it is sometimes easier to explain some of the causes of corrosion in more general terms. For example, three phenomena leading to corrosive conditions are: 1) reactions resulting from dissolved gases, 2) reactions with ionic constituents in the water, and 3) reactions resulting from electrically connected dissimilar metals. These phenomena are only a few of the many that are possible, but they do provide a simple explanation of corrosion observed in solar systems.

In most cases, corrosion is a result of a metal reacting with oxygen to form an oxide. How rapidly this reaction (oxidation) occurs will depend on a variety of factors, but the concentration of oxygen frequently is significant. This is not true for aluminum because its surface is already covered by a dense, impervious oxide layer. But for other metals such as iron and copper, dissolved oxygen does increase the corrosivity of an aqueous environment. Since the solubility of oxygen in water at 75°F is only 0.0045%, this effect can be accelerated by turbulence or other phenomena which cause gaseous entrainment. Carbon dioxide is another gas which can dissolve in water and cause corrosion problems. This gas is a very minor component of air, having a concentration of 0.04%, but it is a principal constituent of exhaust gases from combustion processes. When it dissolves in water, it does not react directly with metallic surfaces but forms carbonic acid which lowers the pH of water solutions. For most metals, and ferrous metals in particular, acidic (i.e., low pH) conditions are very corrosive.

The concentration and composition of electrolytes in water are dependent on the source of the water. In general, well water contains more variety and higher concentrations of minerals than surface water, as indicated in Table III. As shown in Figure 1 and Table III, the concentration of electrolytes also varies according to geographic location. The reactivity of any electrolyte depends on the nature of the metal surface. Some ions that have been found corrosive to such common metals as aluminum, iron or copper are: chloride, sulfate, hydroxide, ammonium, copper, mercury, and sodium.

If two dissimilar metals are immersed in an electrolytic solution and connected electrically, their rates of corrosion are likely to be significantly slower than if they had not been electrically connected. This phenomenon is generally referred to as the *galvanic* effect. A simplified explanation of this follows: All metals when immersed in a conducting solution will develop an electrical potential. If the metal potentials are referred to one specific electrode such as the hydrogen electrode, then each metal can be classified according to its cathodicity relative to hydrogen. See Figure 2.

When two metals are electrically connected, current (i.e., positive charges) will flow from the electrode with the higher potential to the one with the lower potential (but the electronic flow through the conductor will be in the reverse direction). The electrons leaving the anode result from the anodic material entering the solution as positively charged ions (cations), thus the anode corrodes at an accelerated rate. At the same time, the cathode will be donating electrons to molecules or cations in the solution and will be producing hydrogen gas or solid deposit, as shown in Figure 3.

Table III. **HARDNESS OF FINISHED WATER FROM LARGE PUBLIC SUPPLIES IN THE UNITED STATES**

State	Surface supplies			Ground supplies			All supplies		
		Population served			Population served			Population served	
	Hardness as $CaCO_3$ (ppm)	Thousands	Percent of population of State	Hardness as $CaCO_3$ (ppm)	Thousands	Percent of population of State	Hardness as $CaCO_3$ (ppm)	Thousands	Percent of population of State
Alabama	52	878	28.7	68	271	8.8	55	1,149	37.5
Arizona	200	167	22.2	225	271	36.2	216	438	58.4
Arkansas	36	355	18.6	54	187	9.8	42	542	28.4
California	107	7,962	75.2	164	1,945	18.4	118	9,907	93.6
Colorado	107	754	56.9	–	–	–	107	754	56.9
Connecticut	29	1,481	73.7	42	23	1.2	29	1,504	74.9
Delaware	53	128	40.3	81	44	13.7	60	172	54.0
District of Columbia	96	803	100	–	–	–	96	803	100
Florida	104	262	9.4	127	1,218	44.0	123	1,480	53.4
Georgia	24	1,237	35.9	114	294	8.6	41	1,531	44.5
Idaho	92	84	14.3	135	142	24.2	119	226	38.5
Illinois	135	4,901	56.3	348	549	6.3	156	5,450	62.6
Indiana	194	1,310	33.3	334	571	14.5	237	1,881	47.8
Iowa	138	429	16.3	265	592	22.6	212	1,021	38.9
Kansas	163	423	22.2	190	380	20.0	176	803	42.2
Kentucky	101	916	31.1	108	47	1.6	102	963	32.7
Louisiana	72	871	32.4	57	332	12.4	68	1,203	44.8
Maine	20	388	42.4	22	23	2.5	20	411	44.9
Maryland	48	1,677	71.6	27	34	1.4	48	1,711	73.0
Massachusetts	20	3,314	70.7	54	330	7.0	23	3,644	77.7
Michigan	100	3,359	52.7	218	510	8.0	115	3,869	60.7
Minnesota	74	1,012	33.9	261	282	9.5	114	1,294	43.4
Mississippi	73	161	7.4	24	361	16.6	39	522	24.0
Missouri	100	2,099	53.0	184	157	4.0	106	2,256	57.0
Montana	100	205	34.8	226	39	6.6	120	244	41.4
Nebraska	261	264	19.9	232	247	18.7	247	511	38.6
Nevada	79	54	33.5	204	42	26.5	135	96	60.0
New Hampshire	16	194	36.3	56	83	15.6	28	277	51.9
New Jersey	54	2,886	59.7	135	988	20.4	75	3,874	80.1
New Mexico	73	50	7.4	274	222	32.6	237	272	40.0
New York	46	10,660	71.8	112	1,122	7.6	52	11,782	79.4
North Carolina	33	1,194	29.4	66	57	1.4	34	1,251	30.8
North Dakota	111	104	16.8	296	49	7.9	170	153	24.7
Ohio	120	3,952	49.7	284	899	11.3	150	4,851	61.0
Oklahoma	119	774	34.6	163	122	5.5	125	896	40.1
Oregon	14	644	42.3	37	114	7.5	17	758	49.8
Pennsylvania	84	6,387	60.9	128	320	3.0	86	6,707	63.9
Rhode Island	33	672	84.9	26	42	5.2	32	714	90.1
South Carolina	17	615	29.1	25	125	5.9	18	740	35.0
South Dakota	136	67	10.2	394	114	17.5	299	181	27.7
Tennessee	84	790	24.0	50	543	16.5	70	1,333	40.5
Texas	120	1,971	25.6	143	1,890	24.5	132	3,861	50.1
Utah	171	194	28.2	212	179	25.9	191	373	54.1
Vermont	52	103	27.2	59	21	5.6	53	124	32.8
Virginia	60	1,466	44.2	151	93	2.8	65	1,559	47.0
Washington	22	1,029	43.2	118	308	13.0	44	1,337	56.2
West Virginia	71	541	27.0	170	108	5.4	88	649	32.4
Wisconsin	128	1,095	31.9	250	519	15.1	167	1,614	47.0
Wyoming	123	71	24.3	223	64	22.3	171	135	46.6

CATHODIC END

Gold
Silver
Nickel
Copper
Chromium
Tin
Lead
Steel
Aluminum
Zinc
Magnesium

ANODIC END

Figure 2. Simplified Galvanic Series of Metals

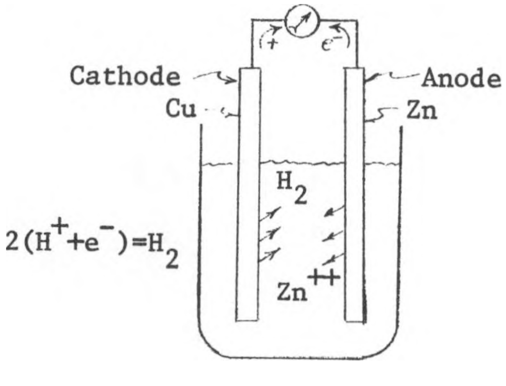

Figure 3. Galvanic Corrosion

Thus, when two metals such as gold or magnesium are connected electrically, the rate of corrosion of the magnesium would tend to be accelerated, while that of the gold would be retarded. The same process will also tend to occur for metals closer to each other in the series such as steel and aluminum, but, since the driving potential will be somewhat lower, the rate of the corrosion is likely to be reduced.

Although the above processes describe the basic concepts of corrosion, there are numerous other factors that complicate the picture. These are physical factors that are controlled by the operating systems. They include: absolute temperature, temperature gradients, absolute concentrations, concentration gradients, liquid velocity, solid geometry, solid surface characteristics, etc. As an example, absolute temperature has a very strong influence on all chemical processes and hence on corrosion. Temperature also influences solubility of such reactive gases as oxygen. As a result, it is possible that a temperature increase can result in a compound effect. The chemical reaction rate will be increased but the oxygen concentration will be decreased, so the former will tend to increase the reaction, while the latter will tend to decrease it.

Temperature gradients in the liquid can cause circulation currents, which, in turn, will affect concentration of reactants at the solid interface. Temperature gradients in the metal can cause galvanic couples. Liquid velocity can play a variety of direct and indirect roles in the corrosion process. Directly, it can cause cavitation or erosion of the metal or a protective surface on the metal. Indirectly, it can affect distribution of the concentrations of reacting species, thus affecting either the chemical or the physical step in the total process. Solid geometry can cause serious corrosion problems, and, because the result is highly localized, the effect is worse than if the process were spread over a large area. Crevices are classic examples of such a phenomenon. In these regions the distribution of ionic species is such that it generates galvanic cells and causes aggravated corrosion. The same type of phenomenon occurs in pits and, for this reason, corrosion in pits generally cannot be stopped once it has started. Physical stresses and heterogeneous chemical surface properties will also influence the corrosion rate of many metals.

CORROSION OF SOME COMMON METALS

Because of the complexity of corrosion processes, there is always a significant probability of a corrosion problem even in a well designed system. The guidelines used in designing corrosion-free systems are mostly a combination of experience and theory. This is not to imply that the theory is incorrect or inadequate, but rather that there are so many possible factors involved, the selection of the controlling one (or ones) might be impossible. Thus, it is helpful to know, for specific metals, what conditions have been recognized as potentially hazardous from a corrosion standpoint.

Iron is seldom found in the pure state but usually contains other elements added to alter its strength characteristics or its resistance to corrosion. These iron mixtures, i.e., steels, are generally broken down into two categories: carbon steels, and stainless steels. The carbon steels are generally much cheaper and easier to fabricate than the stainless steels, so they are used for most systems unless corrosion conditions are very severe. It should be pointed out that the stainless steels, even though called "stainless" are not resistant to corrosion in all environments.

Carbon steels have a strong tendency to corrode when immersed in water containing significant quantities of dissolved oxygen. Figure 4 shows this effect, and also the effect of temperature on corrosion rates.

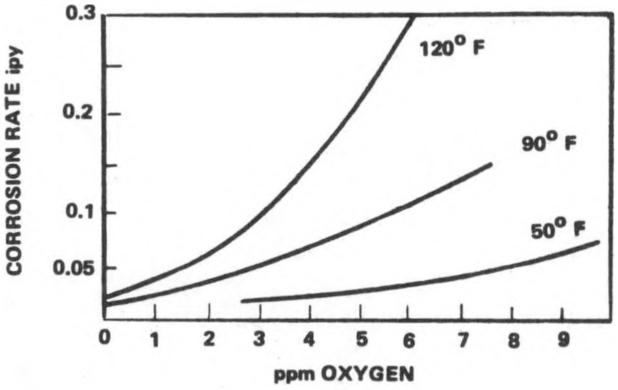

Figure 4. Corrosion Rate for Steel

The basic corrosion effect on carbon steels is the formation of iron oxide on the surface. This oxide provides very little protection against further corrosion of the metal.

pH has a very strong influence on the rate of carbon steel corrosion. This is shown graphically in Figure 5. Acidic conditions, i.e., low pH, cause a rapid dissolution of the metal surface and the evolution of hydrogen gas. Some dissolved gases, notably carbon dioxide and sulphur dioxide, will cause a decrease in pH. Both of these gases are products of combustion. Recent strict laws and environmental controls limit the amount of sulphur dioxide effluent from power plants, however, all power plants generate large quantities of carbon dioxide which can dissolve in water and cause corrosion problems. Low pH can also result in the dissolution of calcium and magnesium oxide scales which form in heating systems using hard water. Thick accumulation of these scales can be highly undesirable because they impede the flow of water and also act as a resistance in the transfer of heat. On the other hand, very thin films of this type can protect metallic surfaces from corrosion.

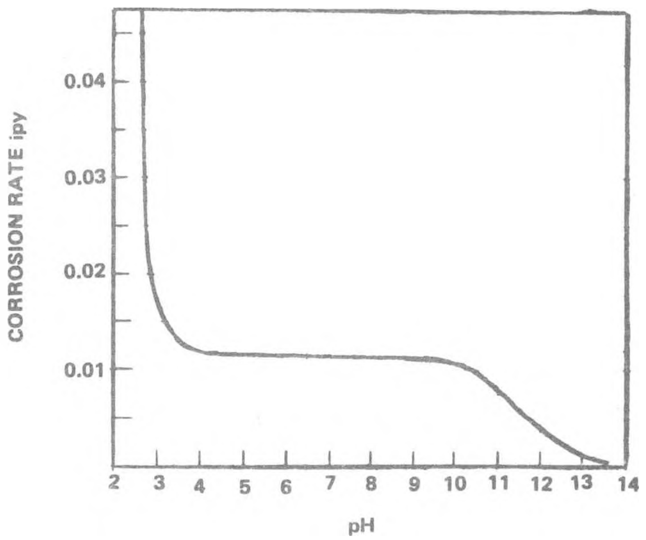

Figure 5. Effect of pH on Corrosion of Iron

Copper, being high (cathodic) in the galvanic series, is very corrosion resistant. This resistance is further enhanced by a surface oxide film which protects the metal from reactants. It is eroded by aerated water flowing at high velocity, i.e., greater than 4 ft/sec. Copper is attacked by oxidizing heavy metal salts such as $FeCl_3$, $Fe_2(SO_4)_3$, etc., and various sulphur compounds. In the presence of ammonium hydroxide, it forms the complex $Cu(NH_3)_4^{++}$ which causes the copper to dissolve. Of particular importance is sodium bicarbonate ($NaHCO_3$) which is found in hard waters that have been passed through a water softener. These devices replace the calcium ions in hard water with sodium ions. The resulting bicarbonate then attacks the surface calcium carbonate film on the copper, exposing it to corrosion. This process is most likely to occur in hot water lines.

Aluminum is low (anodic), on the galvanic scale and would be expected to be highly vulnerable to corrosion. However, because aluminum is so reactive, it immediately forms a surface oxide film as soon as a fresh surface is exposed to the atmosphere. This surface film is transparent, hard, highly adherent, and nonreactive. Therefore, aluminum is often considered to be resistant to corrosion. Unlike most other metals, aluminum is rapidly corroded by high pH (alkaline) solutions. Figure 6 shows this effect at temperatures in the range of 200°F. The pH range is extended somewhat at 70°F, but the use of aluminum at pH's above 9 is not recommended. Traces of heavy metal ions such as copper, lead, tin, nickel, etc., and, to a lesser extent, iron and mercury will cause pitting in aluminum.

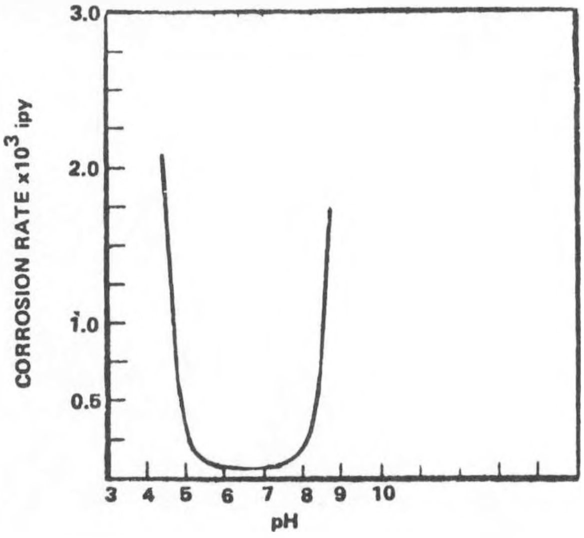

Figure 6. Effect of pH on the Corrosion Rate of Aluminum

CORROSION INHIBITION

The most obvious solution to the corrosion problem is to cover the metal surface with some protective coating. Paint, though usually thought of as an aesthetic medium, is primarily a rust inhibiting coating. It is reasonably effective on external surfaces of equipment where it can be easily applied, and repaired when scratches or nicks occur. On internal surfaces, this type of coating will retard initial corrosion, but can often accelerate the process wherever holes or breaks occur. At these points, reactants are often retained by capillary action or boundary layer flow disturbances, and this causes the reaction to proceed faster than if no coating were present.

For internal surfaces of containers that are filled with water, it is important to have a coating that is easily applied and also easily repaired or reinstalled if damaged. One of the oldest and simplest such coatings is calcium carbonate. It is a naturally occurring mineral in almost all well waters and it, along with magnesium salts, has the added virtue of a buffering effect which maintains the pH at a level above 7. Care must be exercised with calcium carbonate because it does not coat the surface uniformly, but, because of its reduced solubility at elevated temperatures, it tends to form a heavier coating on high temperature surfaces. This scale can then cause plugging or reduced heat transfer rate.

Another chemical which produces a coating is sodium silicate. This is most effective in hot water and tends to form colloidal particles which deposit as a gel on metal surfaces. Sodium mercaptobenzothiazole (NaMBT) forms a protective coating which is particularly effective on copper. It also prevents copper from plating out on metals lower in galvanic series such as iron and aluminum.

There are a wide variety of inhibitors used for both specific and general conditions. These are usually designed for systems consisting of iron, aluminum, and copper because these metals are the most frequently used in aqueous heat transfer systems. The fact that these metals are often used in combination makes the problem much more complex. As an example, iron and copper react with acidic solutions while aluminum is attacked by strong alkaline solutions. In order to maintain pH in some median range such as 7-9, buffers are usually employed, such as borax, trisodium phosphate, sodium hexametaphosphate, etc. These compounds often play additional roles which are complex and difficult to define.

Some inhibitors form inert, passive, chemical compounds on the metal surface. The most common inhibitors in this category are the chromates and dichromates. They form an anodic film of iron-chromium compounds on iron surfaces. Since these compounds do not react readily with oxygen, corrosion of the iron is inhibited. In solutions containing glycol antifreezes, chromates and dichromates cannot be used because their strong oxidizing characteristics would result in decomposition of the glycol. They are also suspected of having carcinogenic characteristics and should not be used where they might contaminate potable water. Nitrites produce a similar anodic film on iron and to a lesser extent on aluminum and copper at pHs of 9-10. Nitrates are mild inhibitors for iron and aluminum but are generally used to retard corrosion of solder.

The large number of chemical reactions and their complexity prevents the tailoring of a rust inhibitor which will prevent all water from rusting all metallic containers. As a result, rust inhibitor formulations are usually generated by a combination of science and trial-and-error experiments. Characteristic of the composition of an inhibitor developed by General Motors for use with ethylene glycol antifreeze solutions in automobile systems containing aluminum is the following:

1.0 gm/liter	Sodium Nitrate
2.0 gm/liter	Trisodium Phosphate
2.5 gm/liter	Sodium Mercaptobenzothiazole
3.0 gm/liter	Sodium Borate
1.0 gm/liter	Sodium Silicate
1.0 gm/liter	Sodium Hydroxide

CORROSION IN SOLAR SYSTEMS

It is impossible to quantitatively design a mixture of corrosion inhibitors that can be added to any type of water and be used in all systems consisting of dissimilar metals. Solar systems do represent a variety of complex corrosion problems, both in terms of types of metallic components and water quality. The components of these systems range from plastics to metals such as aluminum, copper, cast iron, and a variety of steel alloys. The systems are being installed in all parts of the country where the mineral content of the water varies over wide limits (see Figure 1). Water composition is also affected by the source in any given locality. For example, well water normally contains higher concentrations of minerals than surface water. The problem is further complicated by the fact that many solar heating systems are used in areas where the temperatures might fall below freezing. This means that antifreeze must be added to the water, thus adding a new parameter to the problem and also limiting the choice of inhibitors.

Corrosion has been a serious problem in solar systems. This is evidenced by the fact that it has been publicized in the popular press and has been documented in the National Solar Data Network (NSDN). Because of corrosion problems, the manufacture of iron and aluminum collectors has been almost terminated. Probably the main cause of corrosion in solar systems has been the lack of experience in the installation of such systems. The similarities of these systems to standard heating systems have resulted in their design and installation by plumbing contractors who have a limited experience with corrosion processes. These contractors install solar systems in the same manner as they install hydronic heating systems. The hydronic systems generally contain only copper and cast iron components, contain local potable water, and operate at elevated pressures which exclude fresh air. By contrast, solar systems might have: collectors constructed of aluminum, copper, or carbon steel; storage tanks made of carbon steel; pump housings made of cast iron; and tubing made of copper. These systems usually contain ethylene glycol or prophylene glycol antifreeze, are sometimes vented to the atmosphere, and consequently, admit a continuous supply of oxygen.

In the solution of most corrosion problems, it is customary to rely on experience gained from similar systems. Because automobile cooling systems utilize inhibited ethylene glycol solutions, and the components are generally cast iron, copper, and aluminum, it is logical to use automotive antifreezes in solar collector loops. However, some investigators have expressed a feeling that the conditions in solar systems are more severe than in automotive systems and, consequently, automotive antifreezes might not be effective. This logic is open to some question, particularly for the following reasons:

- *Constant admission of air.* Although automotive cooling systems appear to be sealed, they are generally not well maintained. There is considerable interaction between the liquid and air. Elevated temperatures, vibrations, etc., cause leaky hoses and radiator caps. When the system heats up, the system expands causing an increase in pressure. Air and sometimes liquid are expelled, and then drawn back when the engine cools. This constant replenishment of oxygen in the system constitutes a potential corrosion problem for iron surfaces and also provides the oxygen necessary for the oxidation of organic antifreezes such as ethylene glycol.

- *Varied water composition.* Mineral content in water is dependent on location. Since the driver has no way of knowing the concentration, he uses whatever is convenient. Thus, unpredictable quantities and qualities of minerals are introduced.

- *Water boil-off.* Since automotive systems are designed to operate above atmospheric pressures, any leaks in the system will result in evaporation of water. When additional water is added, there will be an increase in mineral concentrations. This will cause scaling or possibly increase corrosion.

- *Localized hot spots.* Engine malfunctions or severe operating conditions will result in either localized or general overheating. The boiling point of a 50% ethylene glycol solution at 15 psig is

260°F. Although an automobile engine does not operate under boiling conditions, there will be considerable temperature variations particularly if the engine has been abused or flow passages have become clogged after extended use. Almost all engines are made of cast iron which has a relatively low thermal conductivity. This results in uneven temperature distributions and, in many instances, the severity is such that the cylinder head will crack or warp. Temperatures in excess of 300°F in some parts of automotive cooling systems should not be too surprising.

- *Exhaust gas leakages.* Exhaust gases often leak past the cylinder head gasket and into the coolant. Since these gases have a high concentration of carbon dioxide, they will cause the pH of the coolant to be reduced.

Corrosion is a process that occurrs over a period of time and therefore an acceptable rate is largely dependent on overall cost. Noble metals have a negligible corrosion rate but they are expensive and it is more cost effective to use a less noble metal which has a higher corrosion rate, and replace the component when it deteriorates. The manufacturers of closed collector systems have, in almost all instances, used copper. It is relatively cheap and has good corrosion characteristics.

Experience in the NSDN has indicated that most corrosion problems have resulted from poor construction or operating conditions. A typical example is shown in Figure 7. This is a photograph of the interior of a steel hot water storage tank. The three holes are each connected to copper pipes carrying water into or out of the tank. Each of these copper pipes is connected directly to the steel tank without electrical insulation. The top pipe is above the water level, and therefore shows no effect. The lower two pipes, however, are partially filled with a deposit resulting from galvanic effect. The tank is in the shape of a vertical cylinder standing on end, and around the entire periphery are heavy deposits of corrosion products in vertical streaks. It appears that the corrosion process started at certain active sites near the water level line where the oxygen concentration was

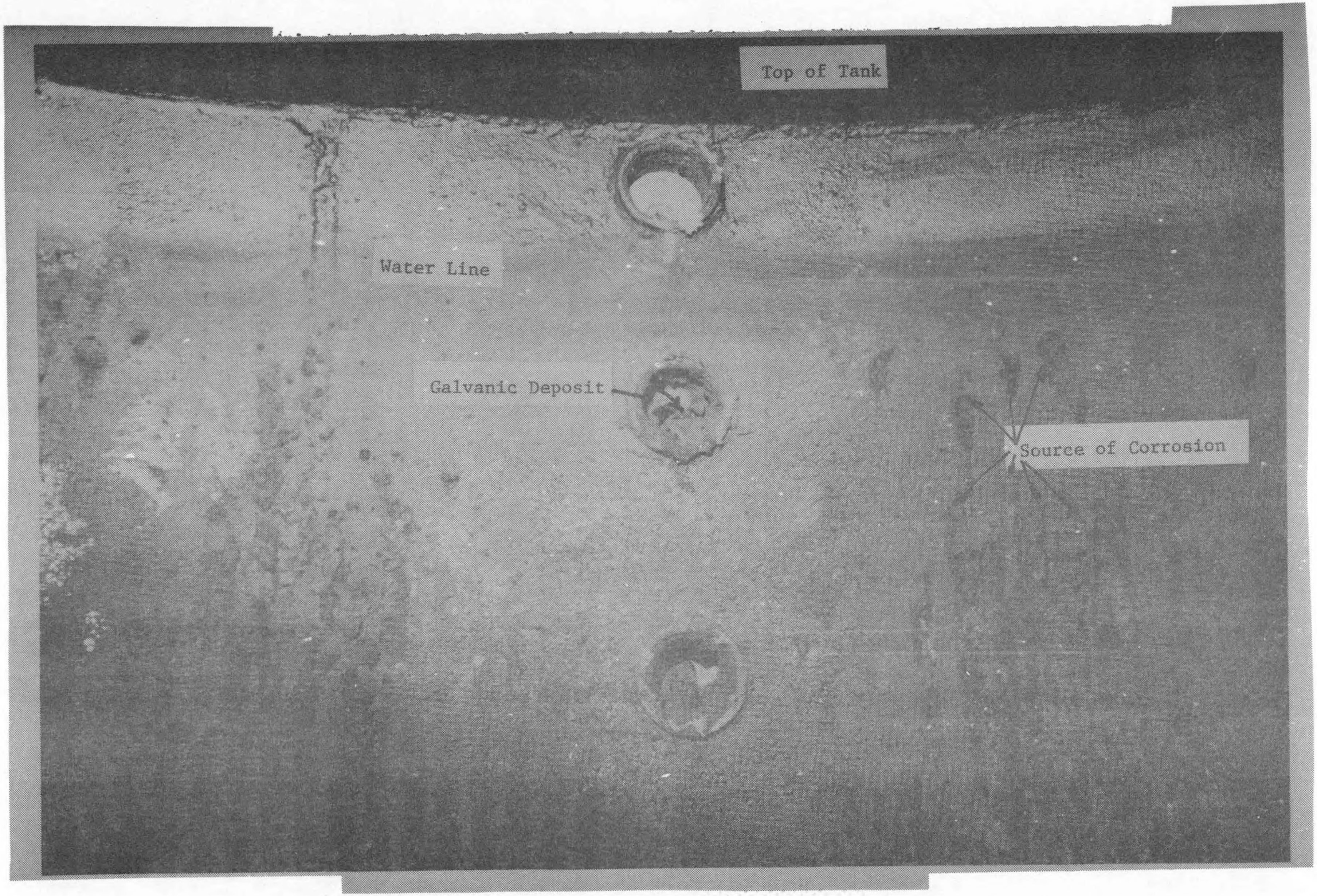

Figure 7. Steel Hot Water Tank Interior

highest. The red iron oxide products then fell by gravity through the water and were deposited at lower levels on the walls of the tank. This system was in operation for approximately three years before catastrophic leads developed. It is a classic example of the combination of effects of galvanic action resulting from the connection of dissimilar metals, and aggravated corrosion due to the presence of oxygen. The former could have been prevented by electrical insulation between the copper and the steel; the latter could have been prevented by exclusion of air or use of proper inhibitors.

Reasonable care in the design, construction, and operation of a solar heating system should result in long, trouble-free performance. Unfortunately, there is a considerable amount of conflicting corrosion information that has permeated the literature. As an example, many authors state that glycols decompose thermally and form acids that corrode metal surfaces. At the same time, several investigators have reported no measurable breakdown of glycols at temperatures below the liquid boiling point. Apparently, the conflict is caused by a difference in experimental conditions. Some of the studies have been conducted in an air atmosphere while others were conducted in an inert (i.e., oxygen-free) atmosphere. While the thermal decomposition of glycols seems unlikely at such low temperatures, the slow oxidation process is plausible. If the aging process only results in the generation of acids which, in turn, lower the solution pH, then the solution can be rendered noncorrosive by the addition of a suitable base such as sodium hydroxide or a buffer such as borax. On the other hand, when a rust inhibitor is designed to protect aluminum in a system, then one of the components usually is sodium silicate. This compound retards corrosion by coating metallic surfaces with a gelatinous film. After a couple of years, the sodium silicate agglomerates and plugs small passages. This condition can only be prevented by replacing the coolant.

Design

From a corrosion point of view, the system design should minimize the number of different metals in the system and control the passage of air into the system. It is recognized that it would be very expensive or impractical to design all systems so that only one metal would be used, but it should be recognized that passive conditions for one metal are sometimes active for others. Copper, iron and aluminum alloys are the metals most frequently used and their behavior is best understood. Unusual metals or alloys could produce unusual and expensive results. In all installations, electrical insulators should be used at all points where dissimilar metals are connected. Examples of typical fittings are shown in Figure 8. Rubber hose or tubing can also be used, but is not recommended because of its tendency to produce crevice corrosion and leaks. In those systems or portions of systems where rust inhibitors cannot be used, some strongly anodic material should be installed in the system to perform as a sacrificial element (sometimes referred to as a getter). Magnesium is the metal often used for this purpose, and it may be in the form of a cylindrical rod inserted in a tank or as lumps of metal placed in a canister in the pipe line, Figure 9.

As indicated earlier, the presence of air in a system increases the likelihood of corrosion, particularly if part of the system is constructed of iron. Frequently, air is deliberately trapped in an expansion tank to allow for liquid expansion during the heat absorption cycle. Although more expensive, it is preferrable to use an expansion tank containing a flexible diaphragm separating the air from the liquid. If the tank contains no diaphragm and the system is completely sealed, then the oxygen component of the air will gradually react with the metallic surfaces to form metallic oxides. The gas remaining in the expansion tank will then be nitrogen, which is inert, and at this point, the corrosion will stop. In a drainback solar system, sealing the system will require more gas and result in an increase in system complexity. If the collectors are iron, it would probably be advantageous to use pure nitrogen rather than air and seal the system as shown in Figure 10.

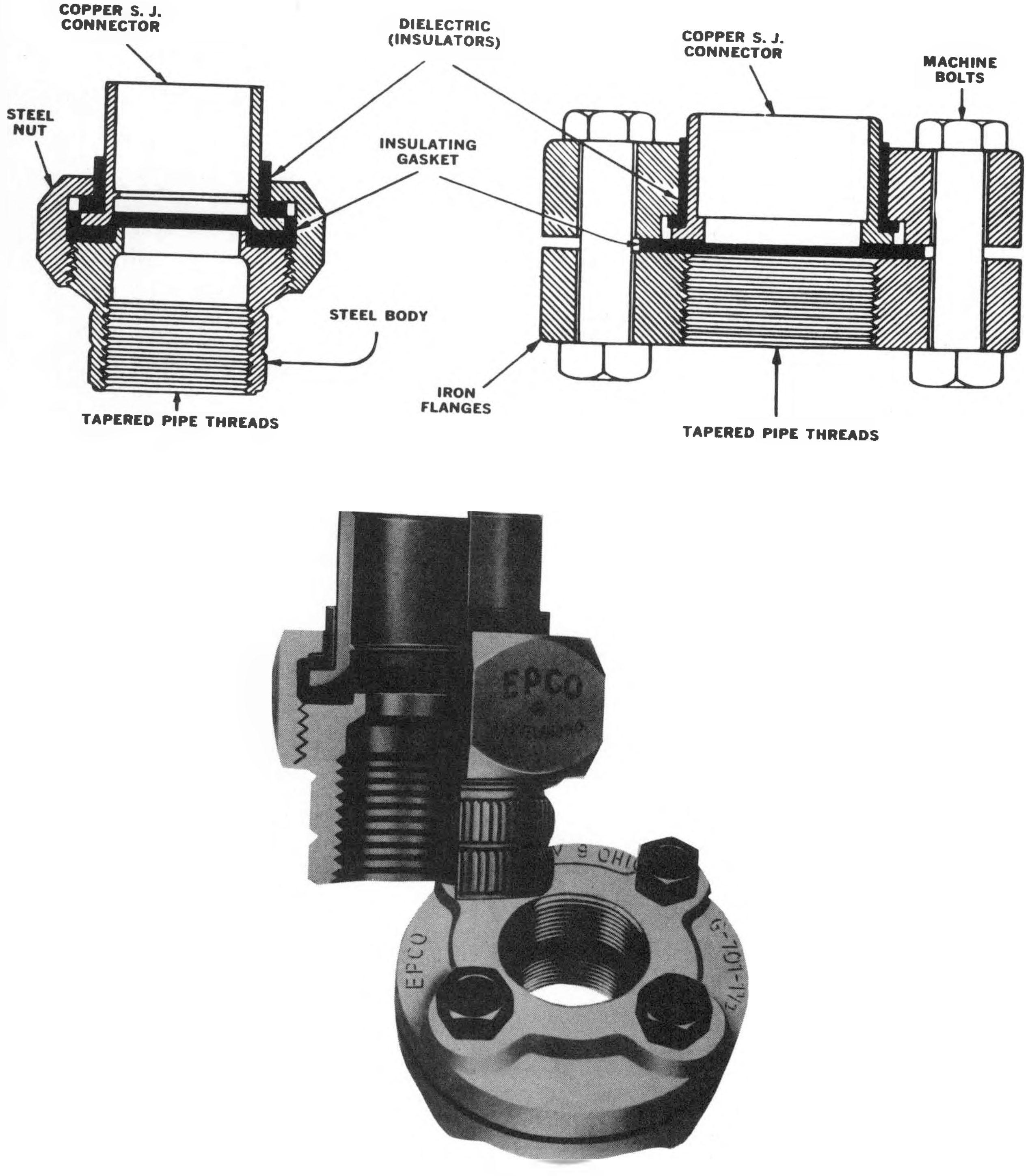

Figure 8. Electrically Insulated Pipe Fittings
Courtesy of EPCO Sales Inc.

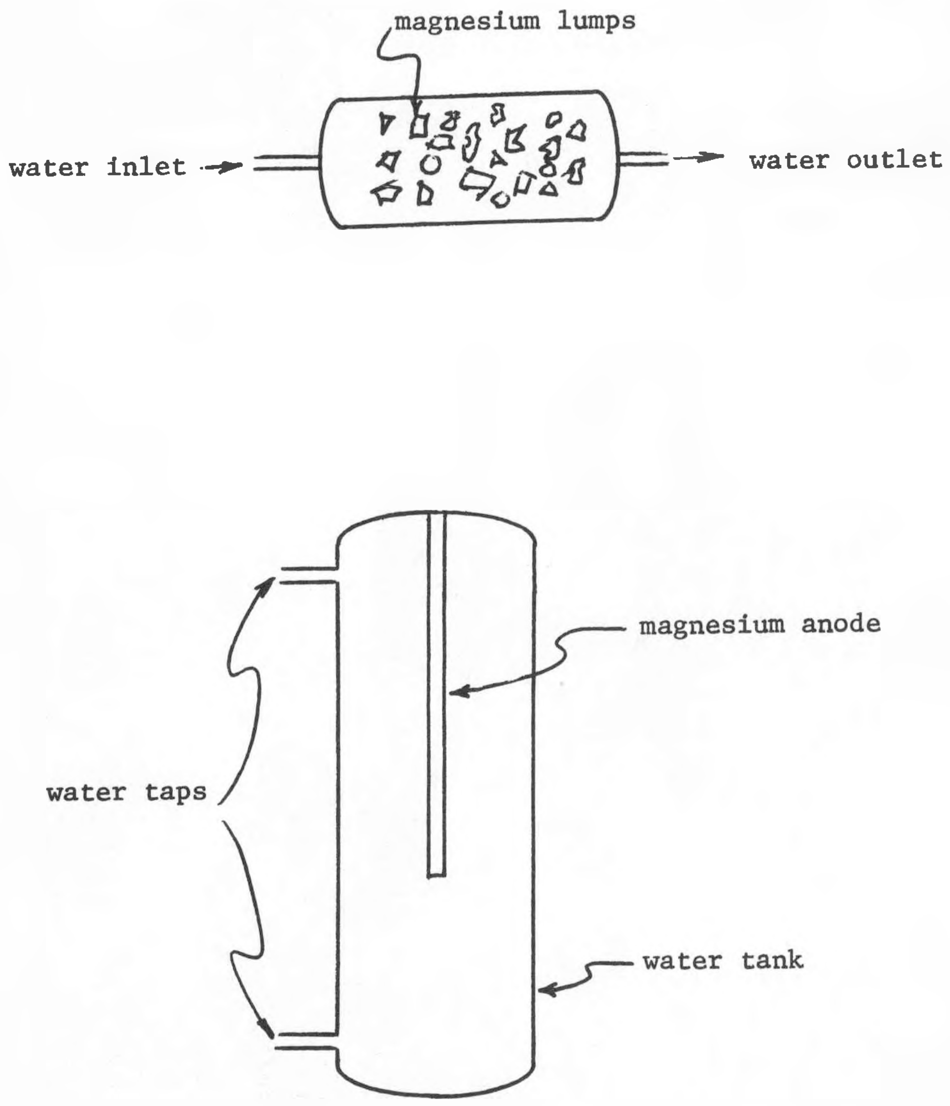

Figure 9. Examples of Sacrificial Anodes

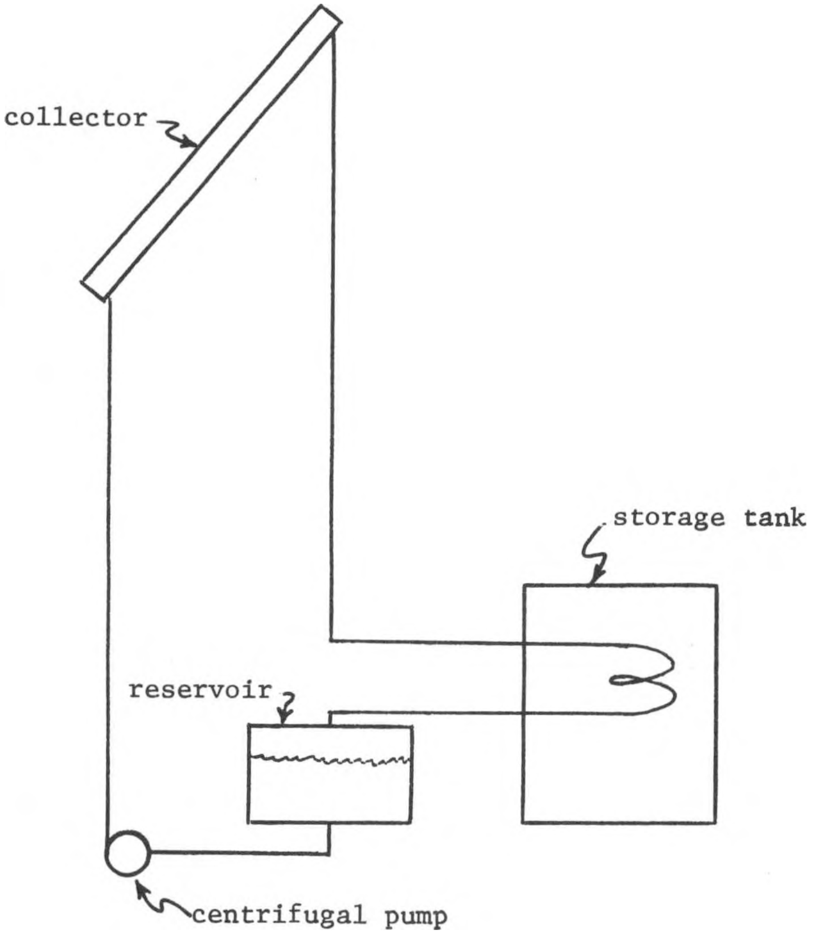

Figure 10. Closed Drainback System

Construction

Because of the severe consequences of aggressive corrosion conditions in a solar system, mechanics should be well educated concerning construction details. After construction is completed, there should be a thorough inspection to insure that no equipment substitutions were made for construction convenience, which might cause an aggravated corrosion condition. Mechanics have a tendency to substitute construction materials which are more readily available or easier to use than those specified. As an example, a galvanized fitting might be substituted for a brass fitting or a noninsulating fitting substituted for an insulated fitting.

It is customary to join copper pipes and fittings with solder. For water plumbing systems, this is a soft solder, usually a 50% lead-tin alloy, which melts in the range of $374^{\circ}F$ - $421^{\circ}F$ and uses a flux having $ZnCl_2$ as the active ingredient. The main virtues of this combination are its low cost and ease of application. Zinc chloride fluxes are very corrosive, even when they are advertised as noncorrosive, but, in these water systems, durability and corrosion are usually not critical because operating conditions are not severe and residual zinc chloride is eventually flushed away by the water. Where greater strength or higher melting temperatures are required, a hard solder, a silver-copper alloy, is used with a borax flux. This is generally used for the fabrication of collector panels where temperatures might become abnormally high during stagnation and where fabrication is done in a factory with specialized tools. Because of more adverse fabricating conditions and larger pipe sizes, this type of solder is not suitable for solar system assembly.

A practical compromise to the common solders is a soft solder having a composition of 95% tin and 5% silver. This solder has excellent physical properties including high creep strength, high tensile strength, excellent wetting of copper and excellent capillary properties. Its melting point is $430^{\circ}F$ which is quite suitable for solar loop applications. The cost of this solder will depend on the market value of silver, but it will likely be in the range of five times the cost of conventional soft solder. Although this may seem expensive, the total cost would be a relatively small percentage of the total cost of any installation. Conventional (i.e., $ZnCl_2$) fluxes are suitable for this solder, but an alkaline flux similar to Kester 2151 should be used to minimize corrosion.

A properly designed and constructed solar system should give the best performance with an aqueous heat transfer fluid. Because of the potential corrosion problems with aqueous solutions, it should be either carefully prepared or monitored. The recommended approach is to start with deionized water, which is equivalent to distilled water but more easily produced. It is available through local water treatment companies. Softened water is not recommended because the softening process merely replaces calcium and magnesium ions with sodium ions. The resulting sodium bicarbonate solution is corrosive to copper. If antifreeze is not required, the use of untreated water would probably cause no serious problem in many areas of the country, especially if the system is well sealed. In either case, it would be a wise precaution to add a suitable commercial rust inhibitor, available at automotive and plumbing supply stores.

In most instances, antifreeze is required. Rather than custom formulating corrosion inhibitors that will be compatible with antifreeze, it is better to use an antifreeze mixture marketed by a major manufacturer - and follow the instructions supplied by that manufacturer. The antifreeze market is varied and somewhat confusing. Through many years of experiment and application, ethylene glycol has been found to be the optimum compound for use in automobiles. On the other hand, in applications in the food industry where toxicity is a factor, propylene glycol has been used. Even though ethylene glycol is not extremely toxic, many areas of the country require the use of propylene glycol wherever the antifreeze passes through a heat exchanger heating a potable water supply.

Antifreeze is marketed by a variety of organizations. There are a small number of major chemical companies that manufacture the glycols, add inhibitors and sell the product under a specific trade name. These same companies also sell the glycols to other companies who add inhibitors, water, etc., and market the product under their trade name. These manufacturing companies will also add inhibitors to glycols according to a customer's specifications, after which this customer (frequently a major retail chain) markets the product under his own name. Since none of the marketing organizations list the corrosion inhibitors on the label (they generally consider this to be proprietary information), the consumer has no way of judging the quality, except by the reputation of the supplier. Because the inhibitor packages in these various antifreezes might vary significantly, it should not be surprising that their performances would also vary. Thus, some suppliers recommend that antifreeze should be changed at regular intervals, others recommend the addition of special inhibitors at specified intervals of time, and others imply indefinite life with no need for additions or changes.

Operation

If good design and construction procedures are utilized, operational problems should be at a minimum. If the system contains antifreeze, chemical analysis twice during the first year would be a wise precautionary measure. The significant measurements, pH and reserve alkalinity, would probably cost approximately $20.00 in most analytical laboratories. It the pH falls below 7, the fluid should be drained, and the system should be flushed with water and refilled with fresh antifreeze solution. Changes in reserve alkalinity are more significant than absolute values. Values in the range of 9 or greater are desirable, but lower values that remain constant over significant periods of time are acceptable. Decreasing reserve alkalinity indicates that the pH will ultimately fall below 7. This should be prevented by draining the system before the reserve alkalinity reaches zero.

Many automotive antifreezes contain silicates to protect aluminum components of the system. Because these compounds tend to form a gelatinous substance after a period of time, the manufacturers recommend that they should be drained at specific intervals. Chemical analysis cannot accurately identify this phenomenon, so it is wise to follow the manufacturer's instructions. Seven to 20 years are given as estimates of the life of antifreezes which contain no silicates.

Liquid leaks or admission of air should be held to a minimum. If leaks do develop, then makeup solution should be of the same quality and composition as the original mixture. As indicated earlier, air is a source of oxygen which forms rust on iron surfaces. Air entrapped in the expansion tank will have its oxygen content depleted by corrosion processes during the operation of the system. This will leave only inert nitrogen. Each time the system is drained, new air will be admitted with the resulting corrosion process. Therefore, unnecessary draindowns should be avoided.

CONCLUSIONS

Corrosion is affected by many physical and chemical parameters. Because of this, many investigators fail to observe or report critical parameters and this leads to much conflicting information in the literature. While this document is not intended to provide specific design parameters, a number of "good practice" principles can be listed.

DO:

1. Use deionized water whenever possible.
2. Maintain the pH slightly on the alkaline side, (i.e., between 7.5 and 9).
3. Exclude oxygen and carbon dioxide from the system whenever possible.
4. Use electrically insulated unions (or flanges) whenever connecting dissimilar metals.
5. Use a rust inhibitor containing a surface coating agent, such as sodium silicate, in systems containing aluminum.
6. Use an inhibited glycol base antifreeze where necessary and follow the manufacturer's instructions.

DON'T:

1. Allow pH to fall much below 7, particularly if there is any iron in the system.
2. Allow pH to rise above 9 if the system contains aluminum.
3. Use water from a water softener, particularly if the system contains copper.
4. Allow concentrations of heavy metal ions such as mercury, copper, lead, tin, etc., to persist in aluminum systems.
5. Allow sodium silicate rust inhibitors to stay in a system for more than two years.
6. Use rust inhibitors with sodium silicate in systems that do not contain aluminum.

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