

# SELECTION OF METALLURGY FOR WATER HANDLING IN OILFIELD OPERATIONS

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## INTRODUCTION

The proper selection of metallic materials often makes the difference between a successful water injection program and an economic failure. Poor selection can often necessitate early abandonment or may limit the quantity of water injected by causing excessive shut-down time. In some floods, even a temporary stoppage of injection can cause oil to be bypassed in the formation and, if nothing worse, decrease the profit from the operation. For these reasons, much care in the selection of metallurgy throughout the water-handling operation is essential.

## DISCUSSION

It has often been stated, tongue-in-cheek of course, that, if only platinum were used in water-handling equipment, no corrosion would occur. While this statement is basically true, there are other things beside the cost which make platinum unsuitable for many parts of a system. Among these are its softness and lack of strength.

Although we have no basic interest in the use of platinum, the point is presented to demonstrate that there is no cure-all for all conditions. For example, 316 SS has generally been used as the ultimate metal in corrosive conditions, yet it is known to fail under certain conditions where less noble alloys do not fail.

It is now accepted by most corrosion specialists that water itself is not a particularly corrosive medium unless it contains certain dissolved substances: oxygen,  $H_2S$ , polysulfides, free sulfur,  $CO_2$ , other acids, and sometimes caustics and certain salts. Some metals which are highly resistant to some of these environments are less resistant to others. In most instances, there is a logical explanation to these varying resistances.

These will be discussed at some length, after which selection of materials for specific environments will be outlined.

Four basic environments should be considered since, with a few exceptions, they will cover the conditions encountered:

1. Nonaerated without  $H_2S$
2. Nonaerated with  $H_2S$
3. Aerated, without  $H_2S$
4. Aerated with  $H_2S$

Nonaerated without  $H_2S$  means, basically, either never having been exposed to oxygen or having oxygen removed to less than 0.05 ppm. Nonaerated with  $H_2S$  means never having been exposed to oxygen and containing more than 1 ppm  $H_2S$ . Aerated without  $H_2S$  means containing more than 0.05 ppm  $O_2$  and less than 1 ppm of  $H_2S$ . Aerated with  $H_2S$  means having at some time been exposed to air and containing more than 1 ppm  $H_2S$ . The limitation on exposure to oxygen in the presence of  $H_2S$  is 10 ppb; however, such a quantity is unmeasurable. Once an  $H_2S$ -bearing water or brine has been exposed to oxygen, some reaction occurs which makes the water react as though oxygen were still present, even though it cannot be measured.

To get some hint of what metals might be suitable in the four environments, let us first look at the position of the various metals in the electromotive series (Table 1). The exact location of the metal or alloy in the series will vary with the electrolyte. The particular series in Table 1 is in sea water at  $25^\circ C$  with a calomel reference electrode.

Note some of the materials shown. The reference used in this discussion is the relationship between each of the metals and steel. Those above steel in the electromotive series will corrode more readily than steel unless protected in some manner.

Looking at the list of potentials, note magnesium at the top of the scale. This metal is much more reactive than any of the other metals shown and has virtually no corrosion resistance.

Zinc is very corrodible, yet it resists corrosion in aerated fresh water. It is used as galvanizing on fresh-water tanks because it forms a tough oxide film. This film does not hold up in an oxygen-free water or any brine.

Aluminum has been used, in drilling particularly, because of its lightness in weight, but has failed when other than a highly aerated fluid is handled or when the film is destroyed by erosion. Aluminum is also strongly attacked by caustics to form aluminates.

Steel does not normally form a protective film but, instead, forms an oxygen starvation cell under any scale; and that cell becomes an anode in an aerated system. Such cells are not strong enough to cause pitting in fresh water but make bare steel unsatisfactory in an aerated brine system.

The 400 series stainless steels also are quite corrodible, but form both a strong oxide and a strong sulfide film. They are seldom recommended for salt water under any condition.

The 300 to 308 stainless steels are in the same category, although both the 300 series and 400 series are better than steel. One of the problems with 410 stainless is the wide difference between active and passive 410 (0.52 to 0.15). Passivated steel is covered with an oxidized film. When both active and passive 410 exist in the same system, the active portion is subject to pitting attack in an electrolyte.

Brasses and copper are not normally used in brine systems although they are very effective in fresh water. Copper should never be used in the presence of hydrogen sulfide, even for instrumentation. In a moist atmosphere containing  $H_2S$ , copper corrodes instantly and forms no protective film.

In the absence of hydrogen sulfide, zincless bronze (Type 63 Bronze) is satisfactory for parts not exposed to velocity of fluid. The first alloy from the top which is truly corrosion resistant in brine is aluminum bronze. Aluminum bronze mentioned in this report will mean ASTM B 150, Alloy 614, (wrought) or B 148, Alloy 954 (cast). It has the advantage of having no passive state. Aluminum bronze has failed in some environments containing both oxygen and hydrogen sulfide. It appears that pitting occurs under this condition,

but the mechanism is still in question.

Nickel aluminum bronze has been found almost completely resistant for most parts in all waters and brines. Nickel aluminum bronze as referred to in this paper means ASTM B 150, Alloy 630 (wrought), or B 148, Alloy 955 (cast). Cracking failures have occurred in some castings, and forged nickel aluminum bronze is recommended for severe service.

Worthite is highly resistant to all brines and has not shown pitting attack in spite of the spread between the active and passive states.

Type 316 SS is resistant in all brines with or without hydrogen sulfide, except that pitting will occur in shielded areas in aerated systems, because 316 SS has different potentials in the absence of oxygen and in its presence. It has limited physical strength and poor resistance to cracking unless properly annealed.

Carpenter 20 is highly resistant to all brine environments and is only limited by its mechanical properties.

There are Inconels of many different properties, all highly resistant to corrosion, but some are susceptible to cracking.

Titanium is one of the most resistant metals and is coming into more and more use. It is a common metal and will become less expensive as its use increases. It tends to creep with time when its yield strength is approached.

Hastelloys are very hard materials and are used where hard surfaces are required, but not under stress.

Monel is very resistant to general attack. Series 400 Monel will crack in the presence of hydrogen sulfide; however, Series 500 is more resistant to cracking.

A number of hard metals have been developed for sealing surfaces, etc. Some of these are tungsten carbide, the colmonoys, and stellites.

Nickel and chromium are used for plating other metals. They should never be used over base metals or alloys, however, because any holidays in nickel will expose pinpoint anodes in the base metal and cause sharp pitting attack. Chromium i

A. Water supply wells: Domestic water pumps using nonalloy materials usually are satisfactory for fresh water.

Brines which have a pH above 6 and contain no hydrogen sulfide usually can be handled with ni-resist pumps. Cables become a problem, however, if submersible pumps are used. A galvanized sheath usually has a short life. Monel sheaths will resist the environment; but, unless isolated from tubing and casing, will cause the pipe to be attacked. The sheath may be covered with a nonmetallic material if hydrogen sulfide is present. Ni-resist has been highly subject to failure, particularly from corrosion, but is the standard material for such pumps. If purchasers insist, other materials such as 316 SS, aluminum bronze, nickel aluminum bronze, or titanium can be made available. However, many failures to date have been due to poor seals between motor and pump or where the cable is attached; and even though many weaknesses are corrected, better materials will not solve the problem. Shaft should be of 316 SS, bearings of graphite, motor case of coated steel. Alloys are not generally the answer to tubing corrosion.

B. Supply wellhead equipment: exposed area should be coated steel; behind tubing, use steel plus inhibitors.

C. Water supply lines and tanks are best coated. Aluminum is not satisfactory except for fresh water; neither is galvanizing.

D. Low-pressure valves usually are designed to expose only nonmetals to the system.

E. Booster pumps in sweet, fresh water may be ni-resist; but in brine, zincless bronze is the lowest grade material recommended; and Carpenter 20, Worthite, or 316 SS are necessary for sour water.

#### F. Piston Pumps:

Fluid end	Ti, Monel 400, Monel 500. Alloy 20 and Inconel 625 are theoretically good for this service, but experience is limited. NiAl Bronze, Al bronze, and 316 SS are the most common materials for this service.
Plunger	Ceramic, steel/colmony (steel overlayed with colmony)

Valves	Nonmetallic, Ti NiAl bronze, 316 SS, 17-4 PH, 15-7 Mo PH
Valve seats	Monel 400, NiAl bronze, 316 SS
Valve spring	Ti, Inconel 600
Stuffing box	Al bronze, 316 SS

#### G. Meters:

Body	Ni Al bronze, low carbon 316 SS
Rotors	Nickel
Rotor shaft	Tungsten carbide
Bearings	Tungsten carbide
Vanes, discs, or propellers -	NiAl bronze, Nickel

#### H. Valves:

Body	316, NiAl bronze, coated steel
Stem	K-500 Monel, 17-4 PH
Gate	316 SS coated with tungsten carbide, Stellite, or Colomonoy, Monel 400 coated with Ni, or 316 coated with Ni.
Seats	Inconel (all grades), Monel 400 (no H <sub>2</sub> S), 316 SS, Stellite, nonmetallic
Carrier nut	316 SS, Inconel, Monel 400, 410 SS, NiAl bronze

#### I. Throttling valves:

Body and bonnet	316 SS, coated steel
Stem	316 SS, Monel K-500, 410 SS
Seat	Stellite
Disc	Stellite, 316 SS
Carrier nut	316 SS, Inconel, Monel 400, 410 SS, NiAl bronze

#### J. Filters:

1. D. E. Shell	(Diatomaceous Earth) 316 SS, Monel 400, NiAl bronze, wrought all bronze, coated steel
Shaft	316 SS, Monel 400, NiAl bronze, wrought all bronze
Leaves	316 SS, 400 Monel, non-metallic
2. Well-Head Shell	NiAl bronze, wrought all bronze, 316 SS, Monel 400, coated steel

Tube	Same	NO-NO's
3. Others		
Shell	Coated steel	A. Do not design a system assuming only present supply. Conditions almost always get worse.
Internals	Nonmetallic or coated steel	B. It is O.K. to put an alloy nipple or valve in a steel system, but not vice versa.
K. Oxygen stripping:		C. Do not put a bare 316 SS shaft in a plastic-coated steel filter.
Shell	Steel, coated steel	D. Keep air out of H <sub>2</sub> S systems.
Trays	304 SS, 316 SS (both annealed and insulated from shell)	E. Keep sufficient head on pump suction. Overdesign lines to suction. Pumps are usually designed with too small inlet.
Caps or valves	304 SS or 316 SS, 316 SS-coated (all annealed)	F. Be a hero! Don't cut corners. Use the materials which will be most economical in the long run.
Packing	Nonmetallic	
L. H <sub>2</sub> S removal:		
Shell	Coated steel or annealed 316 SS	
Trays	Annealed 316 SS, insulated from shell	
Valves	Annealed 316 SS, Monel 400	
Caps	Nonmetallic, coated annealed 316 SS, or Monel 400	
M. Bourdon Tubes:	Al bronze, 316 SS, Hastelloy "C", Ti	

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TABLE 1 - ARRANGEMENT OF METALS AND ALLOYS IN A GALVANIC SERIES BASED ON POTENTIAL MEASUREMENTS IN SEA WATER

Velocity of Flow - 13 feet per second -- Sea Water Temperature 25° C (77° F)		Volts
Magnesium (H-1)	-----	1.48
Zinc	-----	1.03
Aluminum (Alclad 3S)	-----	0.94
Aluminum 3S-H	-----	0.79
Aluminum 61S-T	-----	0.76
Aluminum 52S-H	-----	0.74
Cast Iron	-----	0.61
Carbon Steel	-----	0.61
Stainless Steel, Type 430 (17% Cr)	-----	0.57
Ni-Resist Cast Iron (20% Ni)	-----	0.54
Stainless Steel, Type 304 (18% Cr-8% Ni)	-----	0.53
Stainless Steel, Type 410 (13% Cr)	-----	0.52
Ni-Resist Cast Iron (30% Ni)	-----	0.49
Ni-Resist Cast Iron (20% + Cr)	-----	0.46
Naval Rolled Brass	-----	0.40
Yellow Brass	-----	0.36
Muntz Metal	-----	0.36
Copper	-----	0.36
Red Brass	-----	0.33
Aluminum Brass	-----	0.32
Aluminum Bronze	-----	0.31
Comp. G. Bronze (88-10-2)	-----	0.29
Admiralty Brass	-----	0.28
90:10 Cupro Nickel (0.8% Fe)	-----	0.28
70:30 Cupro Nickel (0.06% Fe)	-----	0.27
70:30 Cupro Nickel (0.47% Fe)	-----	0.25
Stainless Steel, Type 430 (17% Cr)	-----	0.22
Worthite (24% Ni, 20% Cr, 3% Mo, 1.75% Cu)	-----	0.21
Nickel	-----	0.20
Stainless Steel, Type 316 (18% Cr, 12% Ni, 3% Mo)	-----	0.18
Carpenter 20	-----	0.17
Inconel (79.5% Ni, 13% Cr, 6.5% Fe)	-----	0.17
Stainless Steel, Type 410 (13% Cr)	-----	0.15
Titanium (Commercial)	-----	0.15
Silver	-----	0.13
Titanium (High Purity from Iodide)	-----	0.10
Stainless Steel, Type 304 (18% Cr, 8% Ni)	-----	0.08
Hastelloy "C"	-----	0.08
Monel	-----	0.08
Stainless Steel, Type 316 (18% Cr, 12% Ni, 3% Mo)	-----	0.05
Worthite (24% Ni, 20% Cr, 3% Mo, 1.75% Cu)	-----	0.042

Those metals mentioned twice have different potentials for the active and the passive state. Basis this table - calomel reference electrode; to convert to basis CuS 4, add 0.075.