Materials in sea water aquaristics

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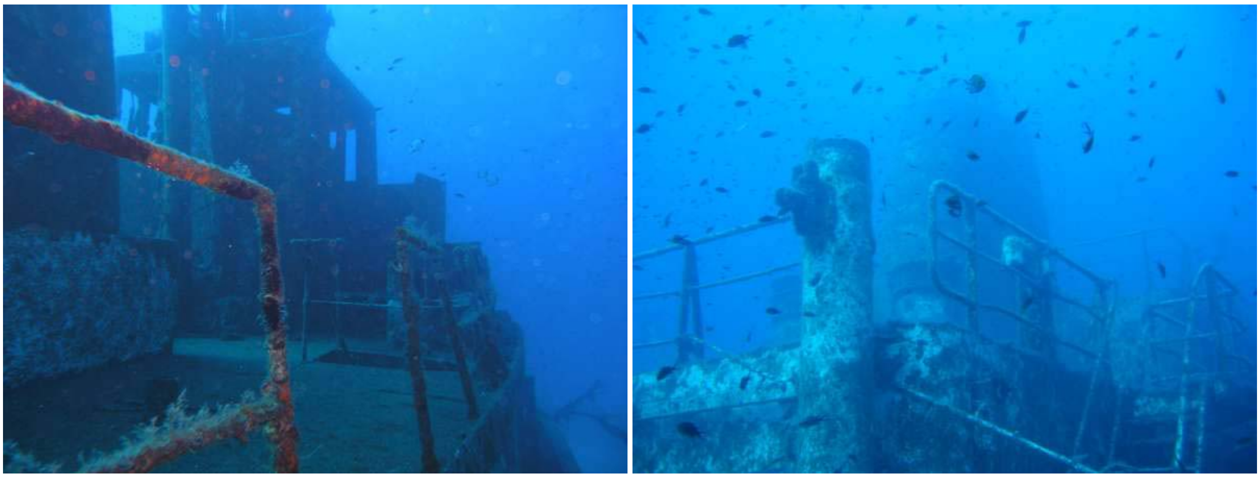


Products of corrosion that have any effects in natural habitats endangers a sea water aquarium. (picture: D. Walber)

Why is sea water aggressive against metals?

In sea water many different salts are dissolved partially in large quantities. On the one hand it means that the electrical conductivity is high (about 100 times more than fresh water) and supports electrolysis processes and on the other hand some of the dissolved substances affect directly the surface of metals.

Electrolysis processes arise if an electrical field exists between two metals that are immersed in an electrolyte. Electrolyte is a substance that is completely or partially disintegrated (ionic form) in e.g. water. If you put table salt (chemical formula NaCl) into water, the salt divides into a sodium ion with positive charge (NA^+) and into a chloride ion with negative charge (Cl^-). Ions – particles with an electrical charge – are moving if they are located in an electrical field: the positive particle (cation) is moving to the negative cathode, the negative particle (anion) is moving to the positive anode: at the anode an oxidation take place, whereas at the cathode a reduction occurs.

Active corrosion protection

If an electrode is immersed in an electrolyte nothing will happen. But if a second different electrode is immersed into the same electrolyte and both electrodes are connected together a galvanic cell is created.

The more ignoble electrode (e.g. zinc or aluminium) sheds electrons to the more noble metal (e.g. iron) – an electric current is flowing. Simultaneously zinc resp. aluminium ions are given to the electrolyte from the anode. In the ship building industry this effect is used with cathodic protection. An more ignoble anode is connected with material that should be protected, e.g. steel hull of ships or pipelines. The anodes must be replaced from time to time to guarantee a permanent protection. – To galvanize steel with zinc has the same effect: the more ignoble zinc is dissolving with the time and protects the steel against corrosion. However to galvanize whole ships is too costly.

It is for this reason that e.g. water pipes should not be built with different metals. The more ignoble metal will be destroyed with the time. But tubes may be protected with anodes, too (cathodic protection).

As a matter of principle metal parts may be protected with anodes or electro galvanizing, too. But in the long term toxic metal ions are brought into the water. If the amounts are very low the metals are important as a trace element, but in larger quantities the metals are toxic.

Corrosion will occur if the same metal is in different electrolytes. In a fissure of a metal the electrolyte (e.g. salt water) has a slight other composition and the ORP (redox) is normally lower than in the outside water. Consequently a very low electric voltage is created and the very low current is flowing. The electrolysis starts and destroys the metal. This way of corrosion is called gap corrosion. To prevent metals against gap corrosion the fissure or small slits may be closed with insulators or the slits must be flushed regularly with the same water that is outside of the slit.

Passive corrosion protection

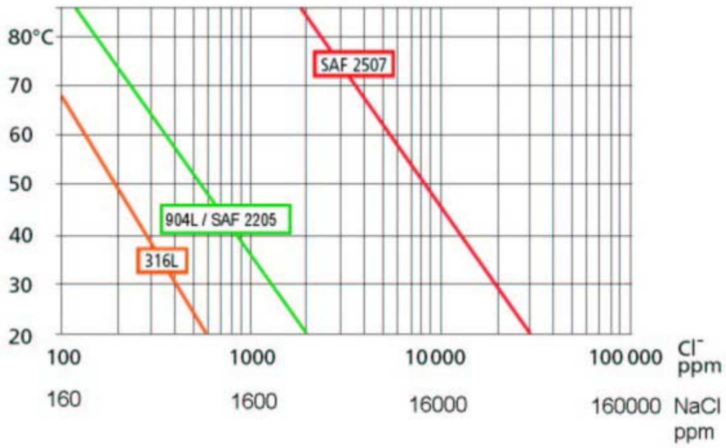
In high-alloyed steels (e.g. chrome alloys with minimum 12% chrome) the chrome part take care that the surface of the metal is occupied with oxygen atoms. This oxygen layer is a barrier against electrolysis and protects the metal against corrosion. These non-corrosive steels (some stainless steels are non-corrosive, but not all!) will not corrode in weak electrolytes (e.g. rain water with a little bit dirt or salts) need not be protected. These steel grades are passivated, that means the surface is covered with a passive layer, e.g. the oxide layer. – On aluminium the passivated layer is fabricated with anodizing.

In strong electrolytes (e.g. sea water) the high amounts of chloride and bromide ions induce pitting corrosion. Some chloride or bromide ions replace the oxygen atoms from the passivated surface. These positions are the starting points progressive corrosion. At low oxygen concentrations and high temperatures the danger of pitting corrosion is higher. If the pitting corrosion has started gap carrions will occur between the hole and the intact metal surface.

The probability of pitting corrosion depends on pH value, temperature and the concentration of some ions, e.g. chloride, bromide.

The graphic below shows the upper chloride concentration depending on the temperature of three different non-corrosive alloyed steels. For orientation: the well know stainless steel "V4A" (AISI 316) is less resistant than the worst steel in the graphic 316 L.

Chloride resistance of three steels depending on temperature (source: Danfoss A/S); 35 ppt



sea water has a chloride concentration of about 18000 ppm Cl.
AISI 316 L = number 1.4404 = DIN: X 2 CrNiMo 17.12.2 (X 2 CrNiMo 18.14.3)
AISI 904 L = SAF 2205 = UNS S31803 = number 1.4462 = DIN: X2CrNiMoN22.5.3 (5) = Duplex steel
SAF 2507 = UNS S32750 = number 1.4410 = X2CrNiMoN25.7.4 = Duplex steel

Organisms sitting on metals induce between them and the metal an electrolyte with a little bit other composition that the outside water. Some organisms are producing additionally acids. This change of the ORP value starts the corrosion (biological corrosion).

Coating of metals with insulators

A very effective protection of metals against sea water is the coating with insulators, e.g. plastics. As a matter of principle every plastic is suitable for coating.

But they should have some special properties. They should not contain softeners – these chemicals (phthalate, phosphate containing substances) will dissolve out of the plastic and may cause damages with the animals.

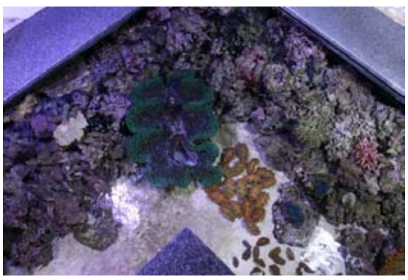
The plastics have to be joined air tight with the metals and should be resistant against ozone (see table below). If the main lights will reach the plastic it has to be UV-resistant to prevent embrittlement.

Epoxy resin or epoxy colours are a very good material to cover steel. If the surface has to be additionally protected against shocks you can admix glass fibres (FRP, GRP) or carbon fibres (CRP) or textures of them. But it is important to know that at high bromide concentrations the bromide is able to diffuse through the epoxy and will corroded the metal beneath.

Materials for aquarium and filter tank

The first aquaria consist of non-transparents in the absence of proper materials. It was only possible to look at the animals from the top. The first fish tanks were common in old Egypt, China and Sumer.

However today a fish pond is attractive, too. But normally a pond is build outside in the garden or in parks. You will find inside pool very rarely.



A sea water pond in the salesroom of AquaPerfekt, Bergheim, Germany: in particular fluorescent colours of e.g. *Tridacna* spec. are very powerful. Picture: AquaCare.

Now aquaria are made of transparent materials. Very small tanks consists of injection moulded acrylic glass (Perspex) or with silicone glued glass plates. Medium sized tanks are made of acrylic glass plates glued with acryl adhesives. These version is very common in earthquake areas. A cheaper and more common way is to use glass plates glued with silicone. Very large tanks have a stable skeletal structure of reinforced concrete with opening for acrylic windows. Instead of concrete you can use other materials, if the dimensions are not too large. Structures made of wood, plastics or fiber-cement make sure that the water pressure is controlled.

Both plate materials – glass or acrylic glass – have their advantages and disadvantages. Glass is more brittle than acrylic glass, so it cracks more easier. In process of time the brittleness increases. After 2 to 3 years it is a great risk to drill holes into glass.

If an aquarium is exposed to strong vibrations (e.g. earth quakes) glass will crack very soon. Because of the better brittleness or acrylic glass the cracks will occur later.

But the surface of acrylic glass is softer and it happens very easily that deep scratches rise during cleaning the plates. The scratches affects the transparency massively.

The larger the tank the thicker the plates must be calculated. Acrylic glass has in comparison to glass a lower refractive index of 1.49 to 1.52

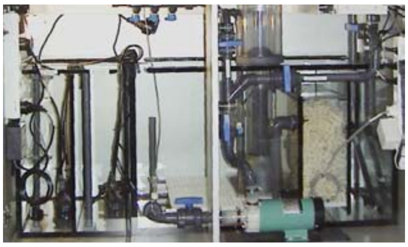
(http://de.wikipedia.org/wiki/Brechzahl, www.mbm-techglas.de/pdf/ floatglas.pdf, Dec. 2007). Additional the acrylic plates are thinner than glass plates to get the same stability. Both factors – a lower refractive index and thinner plates – decrements the optical distortion, if you look at a very low angle into an aquarium.

The transparency of acrylic glass is very good. A 10 mm float glass has a translucence of 86%. If the glass is thicker you can see a green discoloration that affects the colours of the animals. In fresh water tanks this effect is minor because the main colour is green (plants). But in sea water the colours of the animals are not optimal. Special white glass is not so green and the light transmission of a 10 mm thick glass is with 91% higher (www.mbm-techglas.de/pdf/ floatglas.pdf, Dec. 2007). But the brilliancy of acrylic glass is unsurpassed: even through several decimetres thick acrylic glass you cannot see any own colour.

If you want to build an aquarium with extraordinary forms you have to take acrylic glass: you can curve and glue this material arbitrary.

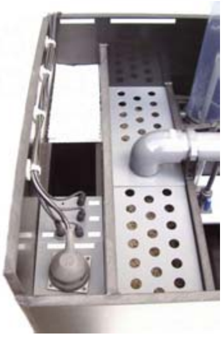
With glass you can realize only slightly curved plates. Only some very specializes companies are able to create more forms with glass.

Small filter tanks are normally manufactured of normal float glass. This version is cheap and the transparency allows to have an overview of the state of the filter systems very easily. If sediments accumulate you will see it. If a part of the technique fails you are able to react very fast.



Filter tank, refill tank and mixing tank made of glass for a sea water aquarium. Picture: AquaCare.

It is better to manufacture large filter tanks with plastics. PVC or PE are proved. These plastics are rigid and have a long time stability without leaking. If something falls into a plastic tank normally any crack will occur.



Large filter tank type *Basic* 750 with connected skimmer ACF6000V. Pictures: AquaCare

Water pipes

In the field of sea water aquaria there are a lot of different filters, to create the currents is costly and a lot of pipes has to be connected. The very common PVC hoses are not the best choice in sea water. The PVC contains softeners to ensure the flexibility of hoses. By and by these softeners will dissolve out of the PVC and load the water. Some of the softeners are made of phthalates that are under suspicious to be carcinogenic. Some others contains phosphates. If the softeners are dissolved out the hose is not any longer flexible. Very easily the hose will jump off the hose nipple if it is not secured with a hose clip. Large diameters will snap off and lower the water flow.

To connect the different filter systems substantial the best solution for hobbyists is a hard PVC tubing (PVC-u). Tubes and fittings are bounded together with a special PVC glue. There are two kinds of adhesives: with organic solvents or with water as solvent – both are suitable. Please, follow the instructions for working with the glues.

After 24 hours the connection is fully hardened. After flushing with clear water any remains will danger the life in the sea water tank. But the connection is only to loose with a saw. So the planning of the whole tubing should be done very precise: include possibilities for cleaning, enlargements with unions and additions connectors. A good aquarium manufacturer and aquaristic shop dealer is able to create the tube system.

orderly laid tubes ensure a maximum amount of safety and lettering of the tubes ensures the usability by hobbyists. Picture: AquaCare.

Equipment that need very low water flows (e.g. lime reactors, nitrate filters, phosphate eliminating stages) may be connected with hoses.

Suitable materials are PE (reverse osmosis tubes) and silicone. But please protect the connections with

Property	Acrylic glass / Perspex	Float glass (normal)	White glass
transparency / brilliancy	+	−	+/−
costs	−	+	+/−
brittleness / durability	+	+/−	
options in fabrication	+	−	
resistance against scratches	− −	+	
resistance against fractures	+	−	
durability of the joints	+	−	
weight	+	−	

Overview of advantages and disadvantages of acrylic and float glass for aquaria hose clips or cable fixer. As an alternative you can use push-fit fittings. These connection are safe against accidental jumping off.

Gas pipes

Some units must be connected with air supply. PVC hoses with softener are suitable if the hoses has any contact with water. But if this material is in contact with water the softeners will dissolve out. Only with air contact this leaching is very slow.

A better solution is silicone. This materials is resistant against sea water and contains any softener.

For CO_2 supplies you need pressure resistant hoses / tubes. PE material is a good choice. You can use hoses for reverse osmosis units, normally they are made of PE. PE is not very flexible and to realise narrow curves you need proper fittings. If you want to use a more flexible tube it is important that it is only build in after valves or solenoids. Otherwise the high pressure (0.5…3 bar) will destroy the hoses. Silicone is not gas tight – the CO_2 will diffuse through the material.

Attachments inside of the aquarium

Sometimes you have to fix things inside the aquarium. There are silicones that will harden under water. Also two component glues are on the market ("coral sticks"). Cable fixer made of PA, screws made of plastic, PVC tubes and plastic strips are other materials to fix items.

With "Coral stick" you can fix young corals under water. Picture: AquaCare.

General resistance of materials

	PS	PMMA	PC	PA	SAN	ABS	PVC-U	POM	PE	PP	PTFE	PVDF
Weak acids	o	-	o	o	o	o	+	-	+	+	+	+
Strong acids	o	-	-	-	-	-	+	-	+	+	+	+
Alkaline	+	+	-	o	+	o	+	+	+	+	+	+
Alcohol	+	-	+	o	+	+	+	+	+	+	+	+
Fuel	-	+	o (+)	+	o (+)	+	+	+	o (+)	o	+	+
Calcium chloride	+	+	+	-	+		o	+	+	+	+	+
Calcium hydroxide	+	+	-	+	+		+	+	+	+	+	+
Chlorine fluid	-	-	-	-	-		-	-	-	+	+	+
Acetic acid 50%	o	-	+	-	+		+	o	+	+	+	+
Ethanol 100%	-	-	+	+	o	o	+	+	+	+	+	+
Ozone	o	+	+	-	+	+	+	-	+ HDPE o LDPE	+	+	+
Hydrochloric acid 35%	o	o	-	-	o	o	o	-	+	+	+	+
hydrogen peroxide	+	-	+	+	+		+	+	+	+	+	+
Sea water		+		+		+	+	+	+	+	+	+

All specifications at room temperature; partly contradictory resistances are found / This information is supplied without liability.
+ resistant, o partially resistant, - not resistant

Chemical resistance of some sealing materials

	PTFE	Si	NB NBR	EP EPDM	EP FPM "Viton"
Weak acids	+	o	+	+	+
Strong acids	+	-	o	+	+
Alkaline	+	+	o	+	+
Alcohol	+	+			
Fuel	+	-	+	-	+
Calcium chloride	+	o			
Calcium hydroxide	+	+	o	+	-
Chlorine fluid	+	-			
Acetic acid 50%	+	+	-	o	-
Ethanol 100%	+	+			
Ozone	+	+	o	+	+
Hydrochloric acid 35%	+	o			
hydrogen peroxide	+	+			
Sea water	+	+	+	+	+

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+ resistant, o partially resistant, - not resistant