The Future for Sacrificial Anodes

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Abstract
Sacrificial Anodes have been in use since 1824 but what is the future for this form of Cathodic Protection. The paper reviews where the technology has come from and speculates on its future (in italics).

Introduction
The first reported use of sacrificial anodes was by Sir Humphrey Davy in 1824, who used zinc and iron blocks to prevent corrosion of copper sheets on wooden hulled warships. This application fell into disuse when it was realised that the protection also prevented the minute levels of corrosion on the copper sheets, thus permitting growth of marine fouling which created an unacceptable level of drag slowing the ships. The advent of iron-hulled ships in the late 19th Century lead to renewed interest in cathodic protection but the purity of zinc commercially available at the time meant that the technique was not successful. Revived interest in the protection of steel hulled vessels in the 1930's was based on the use of magnesium but although the anodes had adequate driving potential the consumption rate was excessive. Zinc anodes were again tried but the dense adherent corrosion product meant that they were unsuccessful. The time had come for some serious research into anode materials!

The largest consumption of sacrificial anodes is in the protection of oil and gas related structures in seawater this paper unashamedly concentrates on these.

Anode Alloys
Zinc was the initial choice for marine protection systems but as previously stated purity of commercially available material precluded its use. Several teams of workers studied the effect of alloying elements. In the USA, the navy developed an alloy based on Zinc with 0.5% Aluminium and 0.05% Cadmium. Impurities were kept as low as possible with iron limited to 0.005%. In the UK a similar alloy was developed but in this case additions of silicon were used to sequester the iron and by removing the resultant iron-silicon intermetallic compound the iron levels in the anode alloy could be reduced to the level of 0.0014%. Both alloys found commercial application for production of anodes which provided reliable protection for ships hulls and propellers. The US original alloy is now in world wide use as US mil spec alloy 18001 mainly for the protection of marine vessels. Zinc alloys do not perform well at elevated temperatures. Loss of driving potential and

formation of adherent corrosion products with some reports of high consumption rates means that they are not considered at temperatures much above ambient. Zinc anode alloys have the considerable advantage that their current capacity is unaffected by operating current density and they are therefore well suited to applications where a corrosion coating is present.

With the advent of high volume transport of crude oil in the 1940's the requirement to protect the ballast tanks of the vessels lead to the use of magnesium anodes and these were considered superior to zinc. The higher driving potential meant that they would give rapid polarisation when ballast tanks were filled with seawater and for tanks which alternately held oil and water they would throw off the inevitable coating of oil. Following the Second World War, large amounts of magnesium were available from scrapped aeroplane parts. Several disasters occurred arising from the use of magnesium in confined spaces filled with flammable gasses due to incendive sparking from detached anodes falling onto steel surfaces. The Dow Chemical Company had been a substantial supplier of magnesium anodes for this application and saw the loss of significant business as a challenge. Aluminium was the third metal theoretically capable of providing suitable properties for production of anode alloys but again the adherent corrosion product precluded its use due to lack of driving potential.

Aluminium alloys based on the addition of 5% of zinc and 0.15% tin gave a desirable driving potential but only very low efficiency unless solution heat treated after casting when much better capacity was achieved. Dow Chemical researchers tested over 6000 alloys based on aluminium and came up with two clear winners, Aluminium with 0.5% Zinc and 0.05% Mercury and Aluminium with 5% Zinc 0.02% Indium and 0.2% Silicon. Contemporary and subsequent work around the world has lead to refinements of these basic alloys with considerable efforts to protect compositions by patent and copyright. A number of alloys based on aluminium-zinc-mercury and aluminium-zinc-indium have gained a track record in application for seawater protection in the offshore oil industry for protection of drilling and production structures and submarine pipelines where the density advantages over zinc are important. Aluminium alloy compositions containing magnesium are no longer used due to problems of thermally induced ageing leading to loss of mechanical properties. Of course some zinc alloy anodes are used in offshore oil applications and aluminium alloy anodes are used in some shipping application but for protection of tanks, restrictions are placed on anode sizes to eliminate the possibility of sparking. Aluminium zinc indium alloys have found application at higher temperatures; driving potentials hold up but at the cost of a significant proportion of current capacity. Aluminium anode alloys experience a reduction in current capacity at reduced operating current density this being significant at very low current density such as may be found with well coated pipelines. Concern has also been expressed as to the possibility of anodes becoming passive when operating at low current density but this has not been substantiated in tests on full sized anodes; only on very small samples.

Magnesium anodes find limited application in seawater but are extensively used in onshore projects for the protection of tanks containing fresh water and buried pipelines where the electrolyte is soil or sand. There is little use of scrap magnesium. Raw material for most alloys is derived from virgin magnesium. Again Dow Chemical was responsible for a lot of the research into alloys. Commercially available alloys are now based on either Magnesium with 6% Aluminium and 3% Zinc or magnesium with very low levels of aluminium and zinc but a deliberate addition of around 1% manganese. The manganese containing alloys have a significantly higher driving potential.

There are unlikely to be any fundamental advances in anode alloys in the foreseeable future.

Zinc aluminium cadmium alloys for shipping applications will remain the preferred choice. Some recent work on zinc alloys containing magnesium in place of cadmium have offered advantages at elevated temperatures but the use of zinc in offshore applications has been limited by opposition by environmental lobbies leading to banning of their use in the North Sea and it is likely that this will extend to other continental shelf operations.

Aluminium zinc mercury anode alloys have likewise attracted environmental opposition both in manufacture and application and are only used in a limited number of locations, which are equally likely to decrease. Aluminium Zinc Indium alloys are virtually universally used in the offshore oil industry.

The issue of anode performance at elevated temperatures still has to be resolved. Testing has shown that anode performance is significantly reduced at elevated temperatures but virtually all that testing has been under isothermal conditions with little testing under heat transfer conditions which is much more likely to be the actual service situation. Testing is addressed later in this paper.

Future oilfield developments can be expected to venture into environments more aggressive than plain seawater. The particular issues surrounding Lake Maracaibo are well documented; less well known are those of the Black Sea where the bed is at great depth and covered with centuries of organic matter discharged into it. The suitability of existing materials and engineering practices will need to be confirmed and if necessary adapted to such applications.

Magnesium alloys do not attract environmental opposition and their use will remain largely unchanged in onshore applications.

Attachment of anodes

Virtually all anodes are produced with an insert of steel which is either grit blasted for aluminium anodes or in the case of zinc anodes coated with zinc by galvanising or electroplating. Zinc coating is also used for inserts for magnesium anodes but may not be used for aluminium anodes due to rapid attack of the steel through the zinc by molten aluminium in the casting process. The steel insert fulfils several purposes. First it provides a means of attachment of the anode either by welding to the structure to be protected or permitting the secure attachment of a cable, which is subsequently attached to the structure to be protected. In some cases the individual anode components may be assembled into an array before attachment to the structure.

The useful life of an anode is a direct function of the design of the insert. In the case of flat anodes a strap insert should be as far from the operating face as possible and the other (back) face should be coated. If the strap is centrally located in the section and the back face coated approximately half the anode material will still be present when the insert is no longer providing support. If the back face is uncoated then the products of anode corrosion may build up under the anode and force it off the structure. With platform anodes mounted off the structure with a centrally located core these problems are less likely to arise and utilisation factors of near to 100% are achievable.

Production of anodes

With the exception of small volumes of very long thin ‘ribbon’ anodes produced by extrusion or similar specialist techniques, anodes are produced by casting the alloy onto the insert in a mould. Some anodes are produced by a semi continuous process but most are gravity die-cast into open or closed permanent moulds made of steel. Care must be taken in the casting process to take account of expansion of moulds & inserts and contraction of anodes. Anode alloys are formulated for their electrochemical properties rather than their structural ones and this has lead to problems of cracking of the anode particularly in aluminium anodes.

It is unlikely that production techniques will change significantly

Application engineering

The shape of an anode will contribute markedly to its performance in a cathodic protection system. For ships hulls, a flat plate with a streamlined profile has found almost universal application, a flat steel strap insert protruding from the body of the anode in two or more places for welding to the hull is the common method of installation although some anodes are provided with cast in recesses for bolted attachment. Protection systems are designed to last between dry dockings subject to a maximum level of coating damage on the hull. Ballast tank anodes are invariably long and thin with a steel rod insert providing a high level of current output to polarise the surfaces to be protected as quickly as possible. Again systems are designed on the basis of a period between dry-docking with a proportion of time ‘in ballast’

Semi submersible drilling rigs used in offshore oil and gas exploration are generally considered as ships hulls and hull type anodes are often used although generally larger than those in shipping applications as streamlining is less of an issue. Ballast tanks are treated as for ships.

Fixed production platforms have a life expectancy of 30+ years and are generally only provided with coatings in the tidal areas. Anodes for these applications are generally up to 30cm in section and up to 300cm in length of a trapezoidal or circular cross section. Inserts are now invariably a tube with ends bent to facilitate attachment some 30 cm from the surface to be protected. Inserts are made from steels with a composition compatible with welding direct to the structure or via a doubler plate. Early designs of insert incorporating a plate or rolled section failed for a variety of reasons and are not now used other than in exceptional circumstances. A typical production platform may stand in 200 metres or more of water and have 1000 tonnes of anodes providing protection for the life of the structure. Care must be taken in the design to allow for current drain to assorted attachments in the electrolyte, including but not limited to production risers, export pipelines and piling. Failure to make due allowance for such drain may compromise the protection system life or in extreme cases prevent protection being achieved at all.

Probably the most interesting application engineering challenge is anodes for submarine pipelines. These traditionally are segmented or semi cylindrical (half shell) bracelets which are a tight fit to the pipe. During pipe laying, especially in deeper waters, substantial lengths of pipe are suspended over the back of the pipe laying barge resulting in significant force being applied to the bracelet as it runs over the rollers on the ‘stinger’. A taper may be cast into the leading and trailing edges of anodes for smaller diameter pipelines. Larger diameter pipes often have a weight coating of reinforced concrete several centimetres thick over the corrosion coating and bracelets are made to a corresponding thickness in order to minimise any ‘step’ in the surface profile causing impact at the stinger. This militates against standing the anode away from the pipe surface to minimise heat transfer from the product being transported through the pipe steel and thence to the anode. The installation of an insulating barrier between anode and pipe can reduce this heat transfer.

Traditional engineering principles for the cathodic protection of pipelines are therefore a compromise between protection requirements and installation requirements. Future developments are likely to focus on the balance of this compromise in favour of the protection requirements ever recognising that the *political, environmental and economic results of getting it wrong are usually disastrous.*

Magnesium anodes for protection of on-shore structures usually pipelines or buried tanks uses simple castings up to 15cm cross section and 100 cm long with a cable tail attached to the anode insert and insulated with a suitable compound. Anodes are generally provided with a backfill of gypsum bentonite and sodium sulphate to provide a hydrophilic environment contained in a suitable cotton bag for rapid installation.

Current density for protection

It has long been recognised that in almost all cases the cathodic current density to initiate polarisation is substantially greater than that required to maintain it, exceptions being where there is a substantial water velocity past the structure or some other depolarising effect such as frequent storms. Protection system specifications are now recognising this and require an initial polarising current density and (much) lower maintenance current density.

The body of knowledge on growth of cathodic films on structures is growing but is not yet large enough for anything but crude generalisations to be made. Historically structures were provided with a basic sacrificial anode cathodic protection system capable of delivering the maintenance current density for protection and with enough in reserve to repolarise after storms. The initial, higher, current density was then provided by a temporary Impressed Current system, magnesium ribbon or strings of long thin anodes hung over the structure or even additional short life hull type anodes welded to the structure. More recently composite anodes incorporating magnesium components attached to the anode insert or even cast onto the anode during manufacture have been proposed.

It can be envisaged that this area will generate considerable rewards and impact substantially on design philosophy in the future. Any reduction in float out weight can yield significant cost savings and will be relentlessly pursued although the risks alluded to previously in the paper will make such progress slow.

Design of protection systems for coated structures require an estimate of the levels of coating breakdown over the life of the structure to be made the CP system is then designed to cater for this. One North Sea oil operator had a philosophy of coating platforms; a breakdown level of 40% was catered for in the CP system. In the event, levels were much lower than this and an enhanced life was achieved. Few other operators use corrosion coatings on fixed structures.

The selective use of coatings on parts of a fixed structure can lead to reduced anode requirements and greatly assist with the initial polarisation current issue. In the future this combination of coatings and cathodic protection will merit increased attention, as even a low-grade coating with a relatively short life would reduce the initial polarisation current requirement.

Offshore pipelines unlike platforms are almost invariably provided with a very heavy-duty corrosion coating, glass fibre reinforced bitumen up to a centimetre thick being the very minimum; reinforced concrete weight coatings on top are common. Recent advances especially for pipelines without the weight coating include thick (1 cm or more) polymeric coatings intimately bonded to the line. Pipeline coating breakdown levels used in CP design are typically 2.5% over the design life of the line or less. In the case of thick polymer coated lines coating breakdown may only occur at locations where anodes are fitted!

The future may well include much superior corrosion coatings than some of those used at present. Cathodic protection designs could therefore be of far fewer unit anode installations, attenuation of protection along the length of the line will be a serious consideration and anodes may be installed only at the ends of relatively short lines or fewer anode structures added after the line has been laid in the case of longer lines

Quality control and quality assurance

The importance of effective QC & QA cannot be overstressed, a great deal of effort and expenditure has gone into developing effective anode materials and the engineering and appurtenances associated with them in the production of reliable anodes. All anode producers use instrumented analytical techniques such as infrared spectrophotometry spark emission spectroscopy atomic absorption spectroscopy and plasma emission spectroscopy to control alloy chemistry. When undertaken by properly trained technicians with access to traceable standards these methods provide rapid and reliable compositional data.

The use of steels carrying appropriate certification and welding to coded practices can give suitable assurance in respect of inserts.

Aluminium sacrificial anodes based on Al- Zn-Sn compositions cannot be certified by chemical analysis alone, as post casting heat treatment is required to develop full performance. In order to provide assurance that the heat treatment has been effective additional tests are needed. These can be either microscopy on suitably prepared sections or based on electrochemical properties. In these tests a sample of the alloy is heat treated alongside the actual anode. The sample can then be sectioned, polished and etched and viewed under a microscope to ensure that the structure reflects the solution

heat treatment. Alternatively the sample can be cleaned and subjected to an impressed current in a suitable electrolyte. In this latter test hydrogen generated at the anode is a measure of the effectiveness of the heat treatment If the heart treatment has been successful the current capacity will be high and hydrogen generation low. If the heat treatment has been unsuccessful the anode current capacity will be low and relatively large amounts of hydrogen will be generated. Collection of the hydrogen in a graduated burette will give a simple go-no go indication and permit release of the anode for use or sanction further heat treatment.
Similar electrochemical testing has been extensively used as a comparator in the development and refinement of anode alloys.

The extension of electrochemical testing as a quality control procedure has become mandatory on alloys other than those requiring heat treatment and a whole industry has grown up around such testing both by producing foundries and independent test houses. The testing procedures now used involve small samples of anode alloy often prepared in such a manner as to remove the entire ‘as cast’ surface. Great store is placed on the absolute values of current capacity per unit weight obtained.

In more than 25 years of practice in the use and manufacture of aluminium alloy sacrificial anodes the author of this paper has never heard of a report of the failure of an anode to operate as expected whose chemical composition was within specified tolerance. Thousands of electrochemical tests have been undertaken at great expense for no benefit whatsoever.

It is to be hoped that the future will see realism and this waste of effort and resource consigned to history.

System design

The calculation of the weight of anode alloy required to protect a structure is given by a simple calculation

$$\mathbf{W = \frac{A \times C \times L}{Z}}$$

Where
W = Weight in Kg
A = Area to be protected in M^2
C = Polarisation Maintenance Current Density in Amperes / M^2
L = System life in Hours
Z = Anode current capacity in Ampere Hours per Kg

The individual components of this equation with the exception of design life are known but only approximately.

- It is a brave designer that claims to know the true surface area of the structure. Dimensional tolerances of rolled sections of the sizes from which offshore structures are made are known quite accurately but it is surprising what bits get left out of the calculation let alone any correction for surface irregularity (one authority quoted the difference to be a factor of x2).
- Maintenance current density is variously quoted at figures between 0.140 A/M^2 and 0.040 A/M^2 for the same location, a factor of almost 4 times.
- Anode current capacities for Al-Zn-In alloys are variously quoted between 2550 Ahrs/Kg & 2750 Ahrs/Kg In general the lower figure is on the basis of long term field tests and the higher figure is on the basis of those short term lab tests mentioned previously.

Future design of Sacrificial Anode systems should focus on true surface areas and the current density required to polarise them rather than squeezing the last drop of performance out of the anode alloy, and then justifying it with spurious testing.

Acknowledgements and references

The opinions expressed in this paper are my own and are necessarily not those of any employer present or past. The paper is based on more than 30 years in the Cathodic Protection Industry.
To provide a list of references is outside the scope of the paper but I am more than happy to give reasonable further information on any specific aspect at no cost but without liability E-mail crundwell@aol.com.

Finally

“ If I have seen further than most it is because I have stood on the shoulders of giants”

This paper is dedicated to Chuck Schreiber and John Morgan two giants