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# Sea-water battery for subsea control systems

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# Abstract

This paper describes a power source for the autonomous control system of a subsea well (SWACS) in the Ionian Sea. The unit was deployed in Jan. 1996 at a depth of 180 m. The 650 kWh sea-water battery uses anodes made from commercial magnesium alloys, sea-water as the electrolyte and oxygen dissolved in the sea-water as oxidant. The inert cathodes are made from carbon fibers. The system is composed of six, two-metre high sea-water cells integrated in a steel structure, a d.c./d.c. converter and a valve regulated lead-acid accumulator enclosed in a titanium container together with a monitoring unit which transfers data to the surface via an acoustic link.

Keywords: Magnesium anode reserve batteries; Applications/underwater equipment

# 1. Introduction

This paper describes the application of sea-water batteries (SWB) to subsea wells with autonomous control systems. Development of such wells are a part of the continuing research by Agip S.p.A that began with the SWACS (Subsea Well Autonomous Control System) project. This project commenced in 1982 and culminated in the installation of a SWACS prototype on the Luna 27 gas well, located offshore Crotone, in Dec. 1987. The target of this project was to operate the well via an acoustic link over a distance of 3.5 km from the Luna A platform [1]. The valves controlling the gas flow are hydraulically operated. An electric pump recharges the hydraulic accumulator when necessary.

These eight years of operational experience have highlighted the critical areas within this technology, such as the range of the communication system using hydro-acoustics and the local power supply. The original power supply for the Luna 27 was based on lithium batteries. In addition, due to the prototype nature of the application, a cable from the Luna A platform was provided and the intention was to utilize the lithium battery only to verify its functionality.

As it turned out, the back up cable failed during the first months of operation and the lithium battery was used to exhaustion. This took a period of 18 months with an average consumption of about 15 W. The resulting necessity to substitute the power source illustrated the limitation of a system that would require periodic substitution via an expensive offshore operation. A number of studies have therefore been performed over the years to identify the most suitable power source for autonomous wells. These have included the investigation of photo-electric panels on a buoy situated above the well, various thermoelectric solutions and the construction of a prototype of a gas turbine for multi-well applications.

However, the potentially most suitable system identified for single satellite wells was the use of sea-water batteries (SWB) and led to this system being installed on Luna 27 in Jan. 1996 to provide power for the SWACS.

# 2. The sea-water battery

Primary cells based on metal anodes (e.g. alloys of magnesium or aluminum) which use sea-water as the electrolyte and oxygen dissolved in the sea-water as the oxidant with inert cathodes have been known for some time [2-8]. Such cells need a continuous renewal of the sea-water to supply the cathode with oxygen-rich sea-water and to remove the products of the cell reaction(s). Because of this they must have an open structure, causing leakage currents between serially connected cells to be high. This is why sea-water batteries for low rate discharge are invariably based on a

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single cell or cells connected in parallel. A d.c./d.c. converter changes the low cell voltage (0.9-2 V depending on theparticular cell system) into a regulated voltage (e.g. 28 V). The power limitation of the converter restricts the mean power output of the system, but peak output power can be increased if a secondary battery is connected to the converter output. After discharge of the secondary battery, the difference between the power from the converter and the consumption by the load is used to recharge the secondary battery.

Compared to conventional power sources, such sea-water cells have a very high energy density, as only the anode material (the negative electrode), is consumable. They have a potential for moderate cost, excellent safety and infinite storage ability when dry.

#### 2.1. Cell chemistry

A detailed description of the cell chemistry is given in Ref. [8]. The simplified cell reaction in the magnesium/oxygen cell is

$$2Mg + O_2 + 2H_2O = 2Mg(OH)_2$$
(1)

corresponding to a stoichiometric sea-water consumption of  $31 \text{ dm}^3$  per Ah delivered assuming a typical North Sea oxygen concentration of 0.3 mol m<sup>-3</sup>.

Oxygen is consumed at the cathode under formation of an alkaline layer

$$O_2 + 2H_2O + 4e^- = 4OH^-$$
 (2)

This increase in pH at the cathode surface may lead to the formation of a calcareous deposit [8,9]

$$4Ca^{2+} + 4HCO_3^{-} + 4OH^{-} = 4CaCO_3 + 4H_2O$$
 (3)

This reaction is considered beneficial in connection with cathodic protection of metal structures in sea-water, where it reduces the current and prolongs the life of the sacrificial anodes, but in this case it is essential that only a small part (if any) of the current results in the formation of calcium carbonate. This reaction limits the current that can safely be applied to a sea-water cell. As both the rate of supply of oxygen to the cathode and the rate of removal of the alkaline reaction products from the cathode increases with circulation (sea current), formation of calcareous deposits is also affected by the circulation.

# 2.2. Effects of marine life

Sea-water cells with magnesium anodes and inert cathodes are non-toxic and have no known effects on marine life. Marine life, on the other hand, affects the cell performance both positively and negatively: bacteria colonize on the cathode surface forming slimes which catalyze the reduction of oxygen. This increase in catalytic activity of the cathode results in an increase in the on-load cell voltage from typically 1.2 to 1.6 V. The increase in cell voltage may come after 5 to 45 days, depending on current density, location, light intensity and temperature. It also varies with the season of the year. This catalytic effect has been observed in all sea-water cells with inert cathodes and seems to be permanent.

The negative effect of marine life is that, especially close to the surface, sea-water cells with inert cathodes will be rapidly covered by a dense layer of marine growth. This fouling reduces both the rate of transport of oxygen to the cathode surface as well as the free surface area, thereby decreasing the cell power with time. Turbulence caused by waves, on the other hand, leads to very efficient exchange of the sea-water close to the cathode surface, compared to the exchange rates available in deep waters. Thus for a short time period, surface cells with inert cathodes may perform better in shallow than in deep waters. The usable period depends on the cathode current density, rate of growth and type of fouling. The CFL cell described in Ref. [6] is still operational after 28 months of discharge at a depth of only 23 m.

Cathode deterioration caused by fouling by marine organisms can be avoided by using copper cathodes which are slowly corroding [10–13], but as the cell voltage obtainable with carbon fiber (CF) cathodes is approximately 1.6 V under load compared to 1.0 V for cells with copper cathodes, CF cathodes are preferred. CF also tolerates higher current densities than copper, making CF preferable as long as biofouling is of only little concern.

As one descends from shallow to deep waters, the low light level and the low concentration of plankton organisms reduce the rate of fouling of inert cathodes by marine organisms. It is our experience that CF cells with a life of 6 months or less, can be used at a depth as shallow as 20 m in the summer and close to the surface in the winter.

Under-water videos of the SWACS indicate that biofouling is nearly absent at this depth. Marine life is therefore unlikely to cause problems over the life of the battery in this application. As the anodes are consumed, free surface is continuously generated and no effects on the anode performance from fouling have been observed.

# 2.3. Design basis

Available information on the circulation of sea-water at the LUNA field was sparse and data on circulation versus time were lacking. In the Mediterranean, tidal effects are nearly absent and we have assumed that the mean circulation would be low. Thus a very 'open' structure which allows a nearly unobstructed flow through the battery was selected in addition to a fairly large active cathode area compared to the expected cell load. We assume that as experience builds up, a reduction both in cell size and of the framework for the cells will be possible.

Compared to the North Sea, the higher temperature  $(10-12 \text{ versus } 4-8^{\circ}\text{C})$  and salinity (38.4 versus 34.5 g kg<sup>-1</sup>) of the Mediterranean is beneficial as it increases the sea-water conductivity. This increases the cell voltage under load because the internal ohmic loss in the battery decreases. On the other hand, the increase in temperature and salinity may

also lead to a more rapid growth of calcareous deposits, resulting in a shorter cathode life.

Typical values for the concentration of oxygen in the Ionian Sea is 2–4 ppm. This is 50% of the North Sea value and may give a decrease in the cell voltage under load. The maximum cell power over a short time period is limited by the rate of supply of oxygen to the cathode. Keeping all other factors constant, this rate is proportional to the oxygen concentration.

# 2.4. Prototype testing

After some initial calculations based on an assumed mean load of 20 W over 3 years (526 kWh) followed by an exchange of anodes, a battery design based on six cells, each 2 m long, was considered. Assuming a converter efficiency of 70%, the load on the sea-water battery would be 29 W.

Before designing the full scale battery, two prototype cells were produced and deployed in West Norway at a depth of 30 m in Dec. 1994. The shallow depth allowed inspection of the cells by scuba diving. Circulation in the x, y and z direction, conductivity and temperature were continuously monitored with a SIMRAD Optronics UCM ultrasonic current meter over the first 12 months of discharge. The cells were suspended between a weight and a float above the seabed. Each cell was 1 m high with a central anode and a concentric cathode. This is 1/12th of the full scale battery. One cell was based on a catalyzed stainless steel wool (SSW) cathode in an annulus of expanded titanium [3], the other had a CF cathode [14].

The cells were deployed on a small niche in a very steep side of the fjord and the low circulation observed (mean 1– 3 cm s<sup>-1</sup>, peak <7 cm s<sup>-1</sup>) is probably caused by terrain shielding. The circulation was of mainly tidal character. Seawater temperature was between 6 and 8°C and the conductivity typically 43 mS.

Monitoring and loading of the converter voltage was performed via cables to the shore. Data were sampled at least every 20 min and recorded with a Fluke Hydra data logger.

#### 2.5. Components

#### 2.5.1. Anodes

The anodes were made from continuously cast AZ61 magnesium alloy from Norsk Hydro. Anode diameter was 184 mm and their length of 1100 mm included the lifting device. This alloy gives a minimum 1200 Ah kg<sup>-1</sup>, corresponding to a faradaic efficiency of 60%.

One well known problem with magnesium anodes is the formation of an insulating corrosion layer between the current collector and the magnesium metal. In this design, the electrical connection between the anode and the connector should have a life in excess of 3 years. As the cell life should be in excess of 5 years, the anodes must be exchanged at least once during the life of the battery. A proprietary connector which could be opened and closed under water was developed and the connection to magnesium potted in polyurethane.



Fig. 1. Carbon-fiber brush cathode with metal core.

# 2.5.2. Cathodes and cathode framework

The cathode element consisted of a titanium core with CF oriented radially as in a laboratory brush for test-tubes. This design [14] allows rapid material transport at moderate levels of circulation and has been used in the more recent designs of sea-water cells from the Norwegian Defence Research Establishment (FFI). Compared to earlier cathode design [3] based on spinel coated stainless steel wool (SSW), it allows higher current densities per unit of volume, but CF are much more difficult to clean from silt and biofouling. Fig. 1 shows a CF brush cathode.

The CF cathode was composed of fourteen cylindrical CF cathodes, each 90 mm diameter and with a titanium core. These were welded to two, 800 mm diameter, titanium rings within the top and bottom of the cell. The titanium framework, 1 m high, wide and deep, was insulated from the anode and from the d.c. converter tank. This framework was part of the cathode and also ensured a multiple current path to the current collector. Welded connections were used when possible. A copper cable was silver brazed to a titanium block and the connection potted in polyurethane. The titanium block was screw-connected to the titanium frame. The cathodes in the full size battery were identical, each cell using two cathode frames, one on top of the other.

The catalyzed SSW cathode had roughly the same dimensions as the CF cathode.

Fig. 2 shows the prototype CF cell.

#### 2.5.3. D.c./d.c. converter for prototype cell

In order to test the cells realistically, they must be discharged at constant power. With a resistive load, cell current decreases with decreasing cell voltage, in contrast to a constant power load where a decreasing cell voltage (usually



Fig. 3. Cell voltage vs. time after deployment in Dec. 1994. Cell load: 3.6 W.

caused by low oxygen supply) results in an increasing cell current. For this purpose, a d.c./d.c. converter with constant voltage output was connected to a programmable resistor. Load on the converter was a continuous 2 W.

Converter efficiency at 2 W output and an input voltage of 1.6 V was 56%, giving a cell load of 3.6 W. (This converter was *not* optimized for efficiency.) Load curves were taken periodically by varying the load on the converter in sixteen steps from 0 to 4.5 W. With no output load, the converter consumed 0.9 A at 1.7 V from the SWB.

Note that 2 W from the prototype corresponds to 30 W from the full scale system.

#### 2.6. Test results from the prototype cell

Fig. 3 shows the cell voltage versus time for a period after deployment in Dec. 1994. Initially the cell voltage decreased

slightly until bacterial activity catalyzed the reduction of oxygen, causing an increase in cell voltage. The cell voltage versus output current measured in Jan. 1995 compared to the present performance shows that no significant reduction in performance is observed in spite of heavy growth of sea cucumbers (*Ciona intestinalis*) which now totally covers the cathode as shown in Fig. 4. These sea cucumbers impair the flow of water through the cathode and if they die and start to rot, anaerobic areas in the cathode will form. This will probably reduce the cell voltage, especially under conditions of low sea current. As the cell aged, resistance to flow increased and the cell voltage became more 'noisy'. Fig. 5 shows the cell voltage versus time up to 635 days of discharge, at which time the cell has delivered 55 kWh to the d.c./d.c. converter.

Fig. 6 shows typical cell voltage versus converter load. Over the last year, no significant change in the cell voltage

Fig. 4. Carbon-fiber cell in May 1996, showing heavy growth of sea cucumbers around the cathode.

versus converter load (related to the internal resistance of the cell) has been observed.

out of the cell and reinserted in Jan. 1995 and in Dec. 1995. Flawless operation was observed.

1.8

1.2

Cell voltage / V

The prototype, with spinel coated stainless steel wool cathode, was destroyed after 3 months in the sea when the electronics container accidentally contacted the cathode framework and was perforated by galvanic corrosion. At this time, the CF cell had already shown a lower production cost, higher cell voltage and 50% lower internal resistance, thus CF would have been chosen in any case. For some applications SSW may be preferable as SSW is mechanically tougher and easier to clean from silt and other fouling.

A full recharge of the well's hydraulic accumulator from zero pressure requires 16 Ah, whereas normal discharge was expected to be approximately 8 Ah at 17 A. Initial discharge starts at approximately 10 A and increases with increasing oil pressure to 19 A. Nominal cut-off value was 21 V corresponding to 1.75 V per cell. Assuming a life in excess of 5 years and that 60% of the initial capacity will be available at the end of life, a C/1 capacity of 27 Ah should be sufficient.

Two high quality, industrial valve-regulated lead-acid batteries (VRLAB), both based on gelled electrolyte, but with different lead alloys (PbCa and PbSb) and of different plate construction were tested. Batteries with nominal capacities of 105 and 90 Ah were cycled at 10°C with a charge current of 0.7 A to 27.6 V followed by constant voltage charging and discharged into 1.36 ohm for 2 h (35 Ah) over a total of 12 cycles. The duration of each charge was 200 h. Before and after the test, C/10 capacity was measured to a cut-off voltage of 21 V. Lead calcium (PbCa) showed a charge efficiency close to 100% and a very low rate of self-discharge. Both batteries showed a slight increase in capacity over the duration of the test, but PbCa showed a capacity of 5% above nominal and PbSb 5% below the nominal value.

Self-discharge and rate of hydrogen evolution was estimated from the current level at the end of the constant voltage charge period. This current level was  $0.07 \text{ mA Ah}^{-1}$  for PbCa and 0.22 mA  $Ah^{-1}$  for PbSb at the end of the test. Weight

# 2.7. Lead-acid battery



600

Time / h

800

1000

1200

400

# In order to test the anode connector, the anode was pulled

200





loss over 6 months was 0.20% per year for PbCa and 0.25% per year for PbSb. From these data, PbCa was selected for the Luna field application.

Charging of valve-regulated lead-acid batteries inevitably involves the generation of hydrogen as does the corrosion of lead in the negative electrodes. In addition to the safety aspect of hydrogen/oxygen explosions, a pressure build-up in the battery container will take place. To minimize the risk of hydrogen explosions, a heat-sinked, platinum catalyzed aircathode was used for the catalytic combustion of hydrogen. As this unit only works in the presence of oxygen, a small perforated container filled with 1 kg silver-doped  $MnO_2$ [15,16], was also put into the battery container. These hydrogen removal systems were verified experimentally. In case of a massive failure such as a cell short in the VRLA, the amount of hydrogen generated under charge would be very high and a safety vent in the battery container was considered the only practical solution.

#### 3. The full-scale sea-water battery

#### 3.1. The battery

From the prototype test results it was decided to use a battery of six cells, each cell twice as high as the prototype. The cells were mounted in and insulated from a framework made from carbon steel, protected against corrosion by painting and by sacrificial anodes. The titanium container housing the converter and the lead-acid battery is installed at the centre of the frame. Outline dimensions of the complete battery unit are  $5.2 \text{ m} \times 3.2 \text{ m} \times 4.2 \text{ m} (L \times W \times H)$ . In order to make it possible for an ROV or a crane to replace the anodes, the frame is fitted with six guide funnels on the top. The weight of each anode in air is 118 kg and in water 51 kg. Available energy from this system is in the order of 650 kWh between each exchange of anodes. The design life of the system is 15 years.

# 3.2. D.c./d.c. converter

The converter operates at an input voltage of 1.1-1.6 V from the sea-water battery and delivers a nominally constant voltage output of 27.6 V(d.c). with a current limit of 1.2-1.4 A for the constant voltage charging of a 24 V, 42 Ah lead-acid buffer accumulator. There is electronic separation between input and output.

In order to protect the sea-water battery cells from destruction during low sea-current conditions with risk of precipitation of calcium carbonate, the load is switched off automatically whenever the cell voltage falls below a set low value and switched on again when the sea-water battery cell voltage exceeds a high value [17]. Maximum available output power from the converter is approximately 40 W at 1.5 V input voltage, decreasing to approximately 30 W with a 1.2 input voltage from the sea-water battery. The efficiency of the d.c./d.c. converter is 70–75% depending on the load.

# 3.3. Monitoring system

A failure of the SWB will result in the accumulator voltage dropping below 21 V and a complete shut-down of the well. In addition to this somewhat rough monitoring, it was intended to monitor the battery system in more detail. Simrad developed a monitoring unit using an acoustic link for transfer of data [18]. This enables monitoring of the system using a small surface vessel located directly above the well. Retrieved data are stored on diskettes for later processing off-line. Parameters to be monitored are sea-water battery voltage, accumulator voltage, charge (Ah) delivered from the d.c./d.c. converter and charge delivered to the SWACS. In order to reduce data transfer to a minimum, and still be able to monitor voltage variations, the subsea monitoring unit continuously calculates average, minimum and maximum values of battery and accumulator voltages. These data are stored in a buffer in the subsea unit. Whenever data are successfully retrieved to the surface, the averaging of voltage data and minimum



Fig. 7. Installation of anodes on board DSV Anfitrite.

and maximum voltage calculations restarts. This enables us to monitor variations in voltages within the time period between two interrogations without retrieving all the sampled data from the subsea unit.

#### 3.4. Installation

In Jan. 1996, the battery system was successfully installed and connected to the Luna 27 well control system at 180 m depth, using divers for guidance and connection of the interconnecting cable to the well. Fig. 7 shows the battery on board DSV Anfitrite during the installation of the anodes.

# 3.5. Measurements after deployment

The system was deployed at 2:50 p.m. on 19 Jan. 1996. The data were retrieved acoustically from the sea-water battery (SWB). Data retrieved were time since power up, Ah produced by the converter, Ah delivered by the system (leadacid battery (LAB) and d.c./d.c. converter), minimum, average and maximum SWB voltage, minimum, average and maximum LAB voltage. The data were retrieved at intervals of 5.5 or 10.5 min. Fig. 8 shows the average SWB voltage and Fig. 9 the average LAB voltage during the first 40 h.

Initially, the LAB was rapidly charged fully, resulting in a low load on the SWB, power being only required for the relays that disconnect the output to the SWACS. After approximately 6 h, the relays were closed (de-powered) connecting the SWACS to the SWB, and a further increase in the SWB voltage was observed. From 21 h after deployment, full load, which included two periods of motor power for the hydraulic system, was applied. Running of the hydraulic pump can be seen as a rapid increase in energy consumption and in a reduction in LAB voltage down to 23 V. Between the two pumping events, high activity on the hydro-acoustic communication between Luna Alfa and SWACS took place.

From the slope of energy production and consumption versus time, an average power from the d.c./d.c. converter can be estimated to be 28 W. The consumption by the



Fig. 8. Average sea-water battery voltage vs. time after deployment.



Fig. 9. Average lead-acid battery voltage vs. time after deployment.

SWACS is also 28 W in periods of low acoustic activity and significantly higher (36 W) in the period between the two pumping events.

After 39 h, the SWACS was disconnected from the SWB and connected to cable power, resulting in a rapid increase in LAB voltage as the full SWB power is now used for LAB recharge. Monitoring was interrupted when the vessel left the Luna field 40 h after deployment.

After recharge of the LAB, the SWB was running idle with the exception of a short period after roughly 960 h. A formal approval to switch from cable to SWB power was given by the government and from 2140 h after deployment, the SWACS has been powered by the SWB.

The number of measurements are low, and we have had problems with 'noisy' acoustic communication between the SWB and the surface vessel.

Average load in the disconnected state is estimated to be 1.4 W (50 mA). From 2140 to 3120 h, the SWB has been loaded to an average of 8 W, considerably less than expected. This low load is in agreement with the high mean SWB voltage over the period (1.05 V min., 1.72 V mean and 1.84 V max.) The corresponding LAB voltages were 24.68 V min., 27.24 mean and 27.40 max. The LAB value of 24.68 V is probably related to acoustic communication as valve operations resulting in a recharge of the hydraulic accumulator led to lower LAB voltage (Fig. 9). The low minimum sea-water battery voltage observed for this period is probably caused by voltage delay. This is a normal reaction for magnesium-based batteries when a rapid switch from a low to a high load is made (i.e. pumping or acoustic communication). It is caused by the breakdown of a passive film which forms on magnesium under low current conditions. The duration of the 'voltage delay' is short and it has no practical consequences in batteries with buffer accumulators. The corresponding values for average and maximum cell voltage in this period are 1.72 and 1.84 V, indicating perfectly normal operation under low (8 W) and no load. The no-load condition is caused by the electronics which switched off the converter for a short period after the low reading.

The last recorded measuring period was from 3120 to 3130 h: the LAB voltage versus time shows that, after a discharge at 3124.5 h, the charge balance was positive for a short period (increasing V and mA), but negative over the 2 h period as a whole. From the Ah balance, a production of 36.4 W can be estimated. The cell voltage was 1.46 V. The Ah balance from 3120 to 3124 h was slightly positive, but slightly negative from 3124 to 3126 h.

Based on the measured data, a mean power consumption in the 'no activity' mode is 8 W. (C. Chimisso in 1992 estimated 13 W.) Under monitoring of the well, power consumption increased to 35 W which is close to the maximum power of the d.c./d.c. converter.

Cell voltage at maximum power was 1.46 V after 3000 h compared to 1.22 V when deployed and 1.36 V after 990 h. This increase in voltage with time agrees well with the data from the prototype in Bergen. It also shows conclusively that the same environmental factors which cause an increase in the cell voltage with time in Norwegian waters also operate in the Mediterranean. 1.46 V under maximum load is slightly lower than the corresponding value observed in Norway. This difference probably reflects the decreased oxygen content in the Ionian Sea.

### 4. Conclusions

Sea-water batteries are attractive power sources for longterm discharge applications as they have very high energy density, low cost, excellent safety characteristics and an infinite storage capability. The experience from Norwegian waters is that the system is reliable and predictable. This seems to be the case also when applied in the Mediterranean, but more time is needed for verification. The present battery design is conservative, and it is expected that the overall battery weight and dimensions can be reduced when more experience is gained.

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