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VPI'S SACRIFICIAL ANODES FOR PROTECTION AGAINST CORROSION

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Summary

The sacrificial anode is one of the most effective methods to protect against corrosion of metal in an electrolyte environment. Aluminium, zinc, and magnesium are the metals mostly employed for sacrificial anode cathodic protection of metals. Each sacrificial alloy anode with different closed-circuit potential and electrochemical capacity can be used in different conditions and environments. This paper presents the sacrificial anodes manufactured by the Vietnam Petroleum Institute (VPI) and their qualities. VPI's sacrificial anode products have been certified by international accreditation organisation (DNV) to conform with DNV RP B401 standard, and the quality management system of VPI has been assessed and found to conform with the requirement of ISO 9001:2015 standard. VPI's products have been installed in petroleum structures and appreciated by customers.

Key words: VPI's sacrificial anode, certificate of anode quality by DNV, certificate of quality management system by Quacert.

1. Introduction

Corrosion of metal is a natural process and its effects in our daily life are both direct, in that corrosion affects the useful service life of our possessions, and indirect, in that producers and suppliers of goods and services incur corrosion costs, which they pass on to consumers. Industrial corrosion is an electrochemical process of great economic importance that has been estimated to consume 4% of the Gross National Product (GNP) of the United States of America (USA), a percentage that is likely to be of the same order globally [1].

The special characteristic of most corrosion processes is that the oxidation and reduction steps occur at separate locations on the metal. This is possible because metals are conductive, so the electrons can flow through the metal from the anodic to the cathodic regions. The presence of water is necessary in order to transport ions to and from the metal, but a thin film of adsorbed moisture can be sufficient.

A corrosion system can be regarded as a short-circuited electrochemical cell in which the anodic process (corrosion process) occurs as Equation (1):

$$Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^- \quad (1)$$

and the cathodic process can be any of Equations (2), (3) or (4), depending on the aqueous environment:

In solution with dissolved oxygen:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (2)$$

In acid solution:

$$H^+ + e^- \rightarrow ½H_{2(g)} \quad (3)$$

In solution with cation of more noble metal:

$$M^{n+} + ne^- \rightarrow M_{(s)} \quad (4)$$

Where M is a metal.

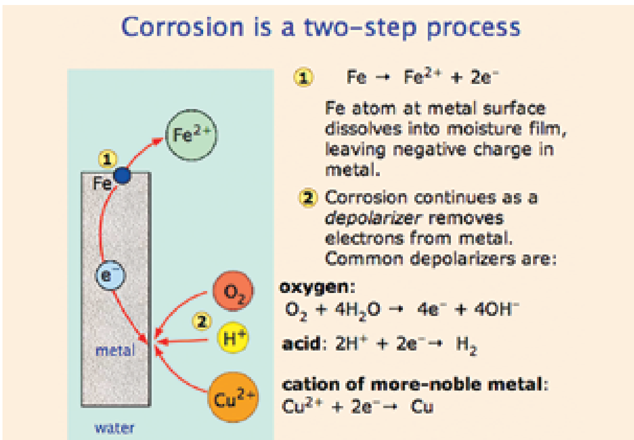

Figure 1. *Electrochemical corrosion of iron.*

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The part of metal at the anodic region will be corroded, and which at the cathodic region will not be corroded. Which parts of the metal serve as anodes and cathodes can depend on many factors, as can be seen from the irregular corrosion patterns that are commonly observed. Atoms in regions that have undergone stress, as might be produced by forming or machining, often tend to have higher free energies, and thus tend to become anodic.

In order to protect buried or submerged metal structures from corrosion, cathodic protection (C.P.) is one of the several techniques that are mainly employed. By maintaining a continual negative electrical charge on a metal, its dissolution as positive ions is inhibited. Since the entire surface is forced into the cathodic condition, the corrosion process cannot occur. The source of electrons can be an external direct current power supply (impressed current cathodic protection), or it can be the corrosion of another, more active metal such as an electric connected piece of zinc or aluminium in the same environment (sacrificial anode cathodic protection or galvanic anode cathodic protection) as shown in Figure 2.

Cathodic protection using sacrificial anode method is a very effective and easy way to carry out. This protection method is greatly employed to protect oil pipelines, and marine structures. With this system, electric current is applied by the employment of dissimilar metals with the driving voltage being created by the potential generated between the two metals in the electrolyte. The electrochemical behaviour of sacrificial anode materials is of vital importance for the reliability and efficiency of cathodic protection systems for seawater exposed structures [2]. The anodes are always made from a metal alloy with more active potential than the metal of the structure and are coupled (electrical contacted) to the protected structure. The electrochemical capacity of the sacrificial anode is demonstrated by the current that it provides per unit volume (Ah/kg).

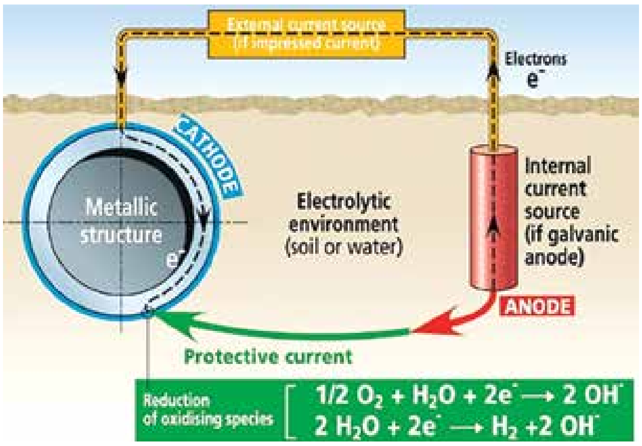


Figure 2. *Principe of cathodic protection.*

Generally, aluminium, zinc, and magnesium are the metals mostly employed for sacrificial cathodic protection of metals. Some recommendations apply to steel structure as Table 1.

These sacrificial anodes have different dimensions and shapes (as blocks, rods, plates or extruded ribbon) depending on the design of the cathodic protection system and each anode material has advantages and disadvantages.

Magnesium sacrificial anode:

Magnesium has the most negative electro-potential of the three anode materials. Therefore, it is more suitable for areas where the electrolyte (soil or water) resistivity is higher, especially onshore pipelines and other buried structures, although it is also used for boats in fresh water and in water heaters. In some cases, the negative potential of magnesium can be a disadvantage. If the potential of the protected metal becomes too negative, hydrogen ions may evolved on the cathode surface (Equation (3)), leading to hydrogen embrittlement or disbonding of the coating [3]. Where this is a possibility, zinc anodes may be used.

Table 1. *Recommendations of anode application*

No	Sacrificial Anodes	Anode specification requirement		Environment application
		Close-circuit potential (V vs Ag/AgCl)	Electrochemical capacity (Ah/kg)	
1	Aluminium Alloy	< -1.100	≥ 2.500	Salt water Bracket water Fresh water with pollution
2	Zinc Alloy	< -1.050	≥ 780	Saltwater Soil
3	Magnesium Alloy	< 1.500	≥ 1.230	Fresh water Soil

Zinc sacrificial anode:

Zinc and aluminium are generally used in salt water, where the resistivity is generally lower. Typical uses are for the hulls of ships and boats, offshore pipelines and production platforms, in salt-water-cooled marine engines, on small boat propellers and rudders, and for the internal surface of storage tanks.

Zinc is considered a reliable material, but is not suitable for use at higher temperatures, as it tends to passivate (becomes less negative); if this happens, current may cease to flow and the anode stops working [4]. Zinc has a relatively low driving voltage, which means in higher-resistivity soils or water it may not be able to provide sufficient current. However, in some circumstances - where there is a risk of hydrogen embrittlement, for example - this lower voltage is advantageous, as overprotection is avoided.

Aluminium sacrificial anode:

Aluminium anodes have several advantages, such as a lighter weight, and much higher capacity than zinc. However, their electrochemical behaviour is not considered as reliable as zinc, and greater care must be taken in how they are used. Aluminium anodes will passivate where chloride concentration is below 1,446 parts per million [5].

One disadvantage of aluminium is that if it strikes a rusty surface, a large thermite spark may be generated, therefore its use is restricted in tanks where there may be explosive atmospheres and there is a risk of the anode falling.

2. Manufacturing process of sacrificial anodes

2.1. Raw material

All raw materials (aluminium, zinc, magnesium, indium, cadmium, and manganese) used in the manufacturing of anodes shall be original metal with high purity. No reclaimed material shall be used.

2.2. Steel insert

All steel material used for anode cores shall conform to ASTM A283 Grade C Specification [6] or equivalent for structural steel. The carbon equivalent (CE) of insert materials shall be compatible with the structural elements to which it is attached and shall not exceed a value of the steel structure material.

The carbon equivalent of carbon steel can be calculated by Equation (5):

$$CE = C + \frac{Mn}{6} + \frac{Cr + Mo + V}{5} + \frac{Ni + Cu}{15} \quad (5)$$

Type (flat, rod or tube) and dimension of steel core depend on design and different types of sacrificial anodes. In order to improve adherence and electric contact with the anode material, anode steel insert shall be blast-cleaned to Sa 2½ in accordance with ISO 8501 [7] or galvanised according to ISO 1461 [8] for zinc sacrificial anode.

2.3. Anode casting

2.3.1. Casting mould

Based on the shape and dimension of the anode, casting moulds can be designed and fabricated. Moulds shall be visually checked to ensure that they are free of any welding cracks, free of contaminations such as oil, grease and mill scale. Moulds should be coated by mould coating and then be heated before casting.

2.3.2. Casting

Raw main material ingots and additives shall be weighed with a suitable ratio and loaded into the furnace for melting. Depending on the shape and size of the anode, it is possible to choose an opened or closed casting mode.

- Opened cast: This method which is usually selected for large anodes with large shrinkage easily allows compensation and ensures the surface quality of anodes;

- Closed cast: This method is selected for small anodes, allowing for a flat and homogeneous surface.

After alloying and homogenising, when the required pouring temperature is reached, a heated sample shall be poured into the special sample mould. The heated sample shall be taken to the chemical laboratory for spectrometer analysis.

Pouring shall be started only if the chemical analysis is within the specified range. The anode core shall be fitted into the mould prior to pouring the molten metal into the mould. The anodes are stripped from the moulds after natural/air-cooling. On removal from the mould, the anodes shall be measured the dimensions, weighed and then inspected.

2.4. Anode inspection/testing

2.4.1. Chemical analysis

The chemical composition of anode material shall be taken at the beginning and the end of casting for chemical analysis by the emission spectrometry in VPI's factory. Anodes from heats whose chemical composition do not meet required chemical compositions shall be rejected.

2.4.2. Electrochemical quality control

Close-circuit potential and electrochemical capacity of anode material shall be tested in VPI' laboratory for each 15 tons of anode production, according to the DNV RP B401 [9].

In some cases, the electrochemical test can be conducted by Quatest 1 (Vietnam) and/or DNV GL (Singapore) to compare the results.

2.4.3. Other testing

Anode surface quality shall be visually inspected while anode dimensions and weights shall be verified by tape measure and balance with a highly accurate; electric contact between insert core and anode material shall be measured by contact resistance, and anode internal defect shall be tested by destructive test...

All quality control of anode shall meet the requirements of customers or international standards.

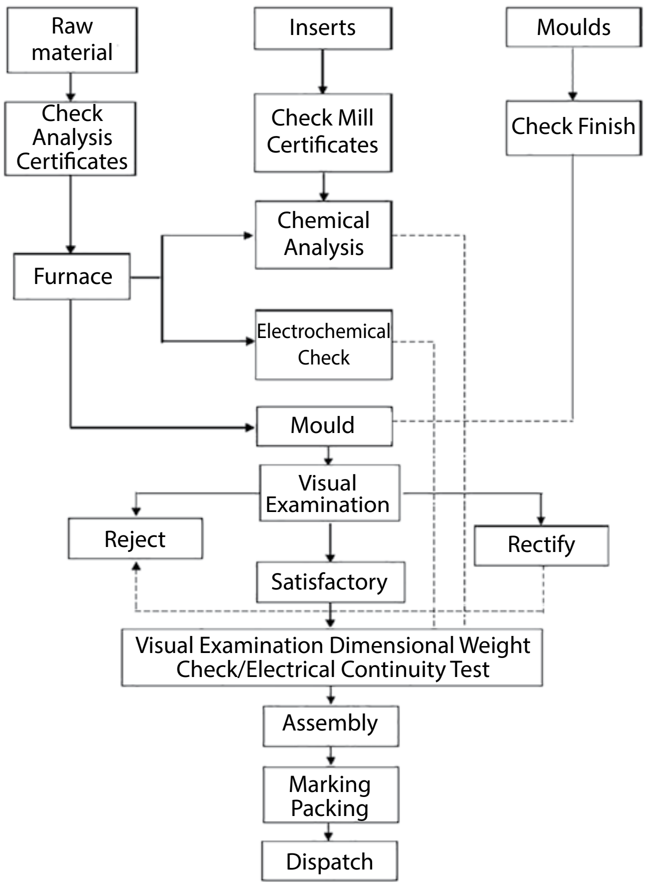


Figure 3. *Procedure of sacrificial anode production.*

Table 2. *Alloy specification of VPI's sacrificial anodes*

No.	Specification		Range	
			According to DNV RP B401	**VPI's anodes**
I	**Aluminium anode**			
1	***Composition***			
	Zn	%	2.50 - 5.75	3.50 - 5.00
	In	%	0.015 - 0.040	0.02 - 0.040
	Cd	%	≤ 0.002	≤ 0.002
	Si	%	≤ 0.12	≤ 0.12
	Fe	%	≤ 0.09	≤ 0.09
	Cu	%	≤ 0.003	≤ 0.003
	Other (each)	%	-	≤ 0.02
	Al	%	Remain	Remain
2	***Electrochemical capacity***	Ah/kg	≥ 2,500	2,500 - 2,700
3	***Open circuit potential*** (at end of the 4th testing period)	V vs Ag/AgCl	≤ -1.05	≤ -1.05
II	**Zinc anode**			
1	***Composition***			
	Al	%	0.10 - 0.50	0.2 - 0.4
	Cd	%	≤ 0.07	0.025 - 0.07
	Fe	%	≤ 0.005	≤ 0.005
	Cu	%	≤ 0.005	≤ 0.005
	Pb	%	≤ 0.006	≤ 0.006
	Total other	%	-	≤ 0.1
	Zn	%	Remain	Remain
2	***Electrochemical capacity***	Ah/kg	≥ 780	780 - 850
3	***Open circuit potential*** (at end of the 4th testing period)	V vs Ag/AgCl	≤ -1.00	≤ -1.00

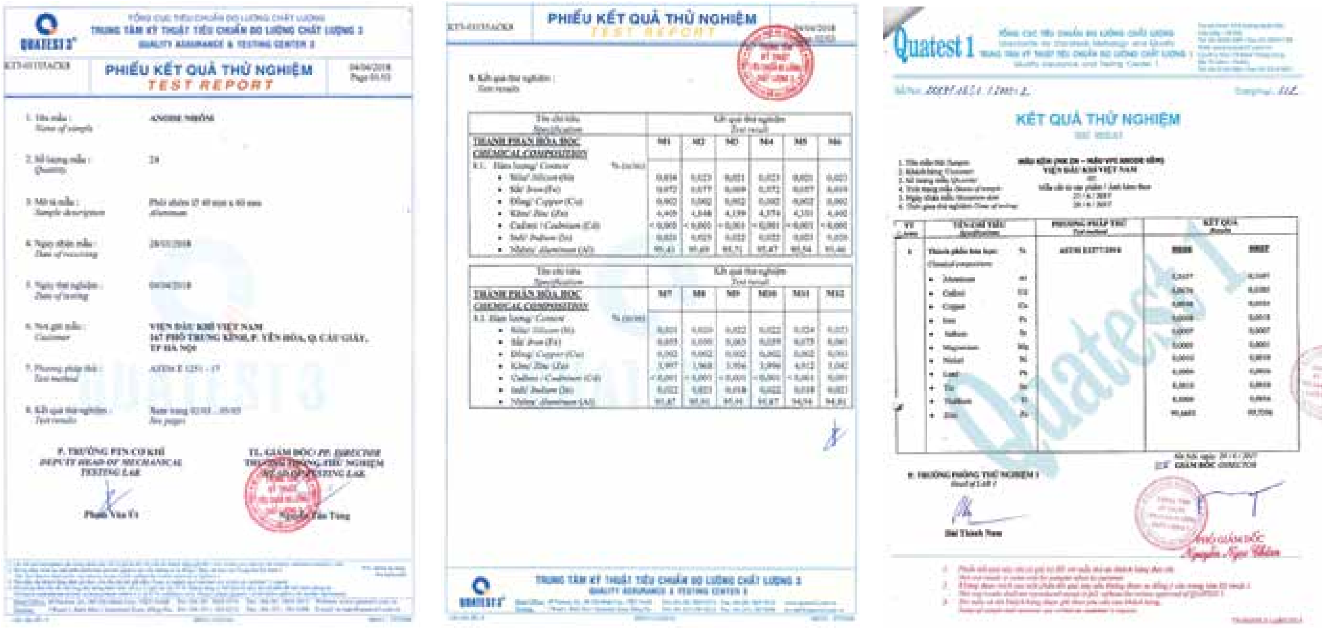
Before *After*

Zinc Anode material

Before *After*

Aluminium anode material

Figure 4. *Images of sample surface before and after the electrochemical test.*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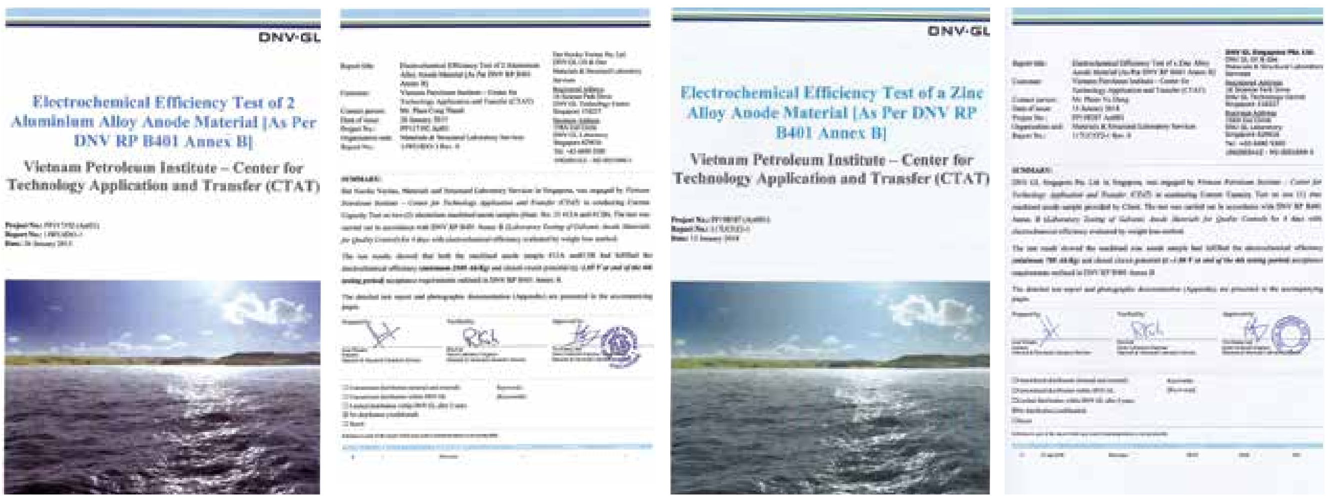
TEST REPORT

PHIẾU KẾT QUẢ THỬ NGHIỆM
TEST REPORT

Quatest 1

KẾT QUẢ THỬ NGHIỆM

Figure 5. *Composition of sacrificial anode certified by QUATEST.*


DNV·GL

Electrochemical Efficiency Test of 2 Aluminium Alloy Anode Material [As Per DNV RP B401 Annex B]

Vietnam Petroleum Institute – Center for Technology Application and Transfer (CTAT)

DNV·GL

Electrochemical Efficiency Test of a Zinc Alloy Anode Material [As Per DNV RP B401 Annex B]

Vietnam Petroleum Institute – Center for Technology Application and Transfer (CTAT)

Figure 6. *Electrochemical Test of sacrificial anode certified by DNV-GL.*

Figure 7. *ISO certificate for VPI.*

Figure 8. *Some images of VPI's sacrificial anode.*

3. VPI's sacrificial anode production

3.1. Quality of VPI's sacrificial anodes

The procedure for production of VPI's sacrificial anode is described in Figure 3.

The VPI's anode alloy has been chosen with great care to ensure an even corrosion pattern and reliable electrochemical capacity with a long working lifetime. The alloys used for standard sacrificial anodes have specifications as shown in Table 2. Upon request, VPI can cast anodes with different alloy specifications.

Images of sample surface before and after evaluating the electrochemical quality of anode material are shown in Figure 4.

Beside the test results in VPI laboratory, the quality of sacrificial aluminium alloy anodes manufactured by VPI has also been certified to meet the international quality standard by QUATEST and DNV as shown in Figures 5 and 6. In addition, VPI's anodes have also been tested in the laboratory and in the field at Vietsovpetro Joint Venture with very good results, confirming its quality in protecting marine structures.

With high electrochemical capacities, VPI's sacrificial anodes can give efficient protection with a long working life and good economic efficiency. Sacrificial anode products of VPI have satisfied the ISO 15589-2:2012 standard [10] and been certified by Quacert as shown in Figure 7.

The quality management system of VPI for manufacture of sacrificial anodes and the provision of related technical services for cathodic protection have been certificated to conform with the requirements of the ISO 9001:2015 standard [11] (Figure 7).

3.2. VPI's sacrificial anode production

VPI's sacrificial anode products with a weight from few kilograms to hundreds of kilograms per anode have been supplied to Vietsovpetro, Dung Quat Refinery (BSR), PVCoating, PTSC, and Vung Ang Thermal Power Plant, etc., and installed at many projects of the oil and gas industry and other customers, who highly appreciated these products. Some typical sacrificial anode products are shown in Figure 8.

4. Conclusion

VPI's sacrificial anode has been successfully manufactured with good quality, uniformity, and stable procedure. Its quality (alloy composition, electrochemical and other properties) meets the strictest requirements for sacrificial anode products. This is the first anode product in Vietnam with its quality being certified according to standards DNV RP B401 and ISO 15589-2:2012; and the quality management system complies with the ISO 9001:2015 standard. VPI's sacrificial anode products have been commercialised and installed on pipelines, equipment, and structures in the oil and gas industry and are trusted and appreciated by customers.

Reference

[1] L.H.Bennett, J.Kruger, R.L. Parker, E. Passaglia, C. Reimann, A.W. Ruff, and H. Yakowitz. *Economic effects of metallic corrosion in the United States. A report to congress by the National Bureau of Standards.* Forgotten Books, 1978.

[2] Juan Genesca and J.Juarez-Islas, "Development and testing of galvanic anodes for cathodic protection", *Contributions to Science*, Vol. 1, pp. 331 - 343, 2000.

[3] A.W.Peabody, *Peabody's control of pipeline corrosion, 2nd edition.* NACE International, 2001.

[4] Walter von Baeckmann, Wilhelm Schwenck, and Werner Prinz, *Handbook of cathodic corrosion protection, 3rd edition.* Gulf Professional Publishing, 1997.

[5] Oladis Troconis de Rincón, Miguel Sánchez, Orlando Salas, Matilde F. de Romero, Carlos Palacios, Juan Carlos Basile, Jorge Suárez, Gustavo Romero, and Rafael Zamora, "Comparative behavior of sacrificial anodes based on Mg, Zn, and Al alloys in brackish water", *NACE International, CORROSION 2010, San Antonio, Texas, 14 - 18 March, 2010.*

[6] ASTM, "ASTM A283/A283M-2018: Standard specification for low and intermediate tensile strength carbon steel plates". [Online]. Available: https://www.astm.org/Standards/A283.

[7] ISO, "ISO 8501-1:2007: Preparation of steel substrates before application of paints and related products - Visual assessment of surface cleanliness - Part 1: Rust grades and preparation grades of uncoated steel substrates and of steel substrates after overall removal of previous coatings", 5/2007. [Online]. Available: https://www.iso.org/standard/43426.html.

[8] ISO, "ISO 1461:2009: Hot dip galvanized coatings on fabricated iron and steel articles - Specifications and test methods", 5/2009. [Online]. Available: https://www.iso.org/standard/43431.html.

[9] DNV-GL, "DNV RP B401: Cathodic protection design". [Online]. Available: https://www.dnvgl.com/oilgas/download/dnvgl-rp-b401-cathodic-protection-design.html.

[10] ISO, "ISO 15589-2:2012: Petroleum, petrochemical and natural gas industries - Cathodic protection of pipeline transportation systems - Part 2: Offshore pipelines", 12/2012. [Online]. Available: https://www.iso.org/standard/51992.html.

[11] ISO, "ISO 9001:2015. Quality management system - Requirements", 9/2015. [Online]. Available: https://www.iso.org/standard/62085.html.