Accelerated pipeline degradation

An approach using galvanic corrosion as contribution to offshore pipeline decommissioning

TU Delft

Accelerated pipeline degradation

by

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TU Delft

Executive summary

This graduation thesis *Accelerated pipeline degradation* aims to investigate how accelerated degradation of steel can contribute to offshore pipeline decommissioning. The legislation on sealine decommissioning in the Dutch North Sea is currently unclear. The present methods are limited to in situ decommissioning or full removal options. In situ decommissioning is considered unwanted by major external stakeholders. Full removal options, on the other hand, are accompanied with large environmental, technical and financial impact. Therefore, I commenced with the investigation of alternative options to minimise the impact of decommissioning activities.

After evaluating the current decommissioning methods, I assessed a series of alternative options that can contribute to sealine decommissioning. My assessment has resulted in a further investigation of galvanic corrosion for steel degradation. With this investigation I aimed to evaluate the mechanism of galvanic corrosion to accelerate the corrosion of the steel pipeline. By doing so, the remaining time at the sea bottom would decrease dramatically with respect to in situ decommissioning. The materials that could be applicable for galvanic coupling were considered. Due to its high standard potential and low costs, the use of graphite (carbon) powder is determined to be most suitable.

Subsequently, I performed several small scale tests on low carbon steel. In a laboratory setting the galvanic corrosion of steel was investigated by coupling steel samples to carbon electrodes. Coupling with platinum electrodes is also tested to provide reference scenarios. The results of the tests show an increase of corrosion current with addition of a galvanic couple. An preliminary estimate on the corrosion rate showed that the corrosion rate of steel with coupling to carbon was about ten times higher then for steel alone. However, a proportionality between cathodic surface area and corrosion current was not established. This is due to the kinetics of both oxidation and reduction reactions.

We can conclude that the results show a promising increase in corrosion rate. However, the produced data was insufficient to construct a quantitative relation between surface area ratio and corrosion current. Therefore, I recommend further investigation to establish a universal relation between the effect of surface area ratio and corrosion rate. To this end, it is advised to take into account that enhanced steel dissolution includes *three* main components: the potential difference, the surface area ratio of anode to cathode and the kinetics of both oxidation and reduction.

Besides, the data generated is produced in a lab setting. Whilst designing the test set up I aimed to exclude certain parameters. These parameters are present in the actual situation and influence the corrosion process. Hence, I recommend a field test of the proposed method to investigate the effectiveness in practice.

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Introduction

1.1. Total Exploration & Production Nederland

Total Exploration & Production Nederland (TEPNL) is a Dutch affiliate of the French oil and gas operator Total S.A., also known as the TOTAL Group. The TEPNL affiliate is responsible for the exploration and production activities in the Dutch North Sea. It is one of the main gas operators in the Netherlands, since its establishment in the Netherlands in the seventies.

Currently, TEPNL has interest in 24 offshore production licenses, of which 20 are currently operated. Due to the shape of the TEPNL operated blocks, it is often referred to as the 'Pistolet', see figure 1.1. TEPNL has 12 wellhead platforms, 4 subsea tie-backs and 3 manned treatment centres consisting of 6 platforms that are currently in production. Another 6 remote wellhead platforms and 2 treatment centres consisting in 5 platforms are no longer in production. The production in 2018 is 19 kboe/day and TEPNL has around 175 personnel.

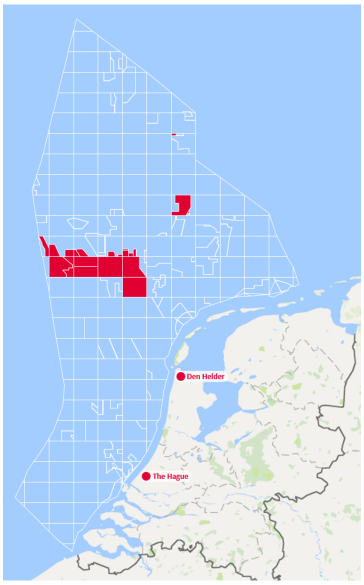


Figure 1.1: The TEPNL operated blocks in the North Sea, the 'Pistolet'

The gas produced is transported by offshore pipelines, called sealines. TEPNL has 39 rigid sealines, resulting in a total of 508 km op pipe. These sealines transport gas and condensate from remote wellhead platforms to treating centres. The sealines are grouped with 3" diethylene glycol (DEG) pipelines. From the treating centres commercial export of gas and condensate is done via the NGT, WGT and NOGAT pipelines. The NGT, WGT and

NOGAT are the main infrastructure for gas export to the coast. TEPNL also holds and interest in some sections of the WGT pipeline.

1.1.1. TEPNL pipelines

The TEPNL sealines can be roughly divided in three groups, based on their steel grade, anti-corrosion coating and anti-corrosion protection mechanism. The anti-corrosion protection mechanisms are either impressed current cathodic protection (ICCP) or sacrificial anodes. The pipeline groups considered can be found in table 1.1 below.

Pipeline group	Material	Anti-corrosion coating	Anti-corrosion protection
1	Carbon steel	Epoxy/Polypropylene	IC
2	Carbon steel	Polypropylene	Anodes
3	Duplex	Polyethylene	N/A

Table 1.1: TEPNL pipelines

Some of the fields have been in production since the seventies. These fields are therefore approaching the end of their production lifetime. The oldest fields and its associated sealines are already in pre-abandonment phase. These are found on the right bottom of the Pistolet and marked blue in figure 1.2.

The decommissioning of the sealines involves a lot of challenges and uncertainties. This thesis will investigate possible alternatives from current decommissioning methods.

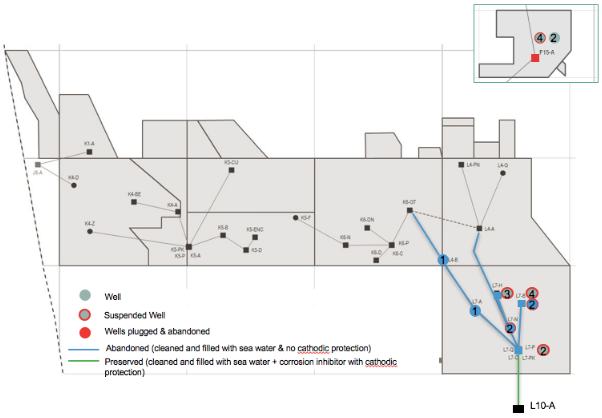


Figure 1.2: The TEPNL operated blocks in the North Sea, the 'Pistolet'

1.2. Pipeline decommissioning: regulations and stakeholders

As facilities in the Dutch North Sea are approaching the end of their production life, the focus shifts from the developing to the decommissioning of facilities. The decommissioning activities of sealines involve applicable regulations and stakeholders.

1.2.1. Regulations

The legislation of pipeline decommissioning is prescribed in the Dutch Mining Act. It is stated in the Mining Decree (MD) that "For pipelines and cables Article 103 MD stipulates that, if a pipeline is no longer used, it is left in situ in a clean and safe manner. The Mining Act attributes a right to the Minister of Economic Affairs to order a complete removal for pipelines and cables. "

Based on article 103 of the Mining Decree and the (currently under revision) act on decommissioning of pipelines, the following is concluded.

- Sealines are allowed to be decommissioned in situ in a clean and safe manner, unless dictated otherwise.
- The pipeline owner is liable for the decommissioned pipeline.
- SodM estimates the pipeline to be in place for at least 100 years
- Pipelines left in situ can form a risk to fishery, shipping, environment or safety.
- To monitor above mentioned risks, the owner is required to do frequent inspections.
- If above risk occurs, the owner is obliged to cover, bury or remove (part of) the pipe.

The above stated regulations are in accordance with the regulations of the Staatstoezicht op de Mijnen (SodM). The SodM is responsible for regulations with respect to mining activities. The regulations of SodM therefore hold as the pipelines are being put out of use to be in so called *pre-abandonment phase*. The sealines are therefore cleaned so that less than 30 ppm of aliphatic hydrocarbon remains. Subsequently, they are filled with sea water and disconnected from the facilities at topside level.
If the sealines are being qualified as abandoned, it is likely that they qualify for the regulations of Rijkswaterstaat as waste. It is expected that Rijkswaterstaat will demand removal of the sealines.

Current decommissioning methods are either a form of in situ decommissioning or full removal. With in situ decommissioning, the sealines are cleaned and left in place. Optionally, minor interventions are done prior to leaving them in situ, such as removing mattresses or applying rock placement. Besides, sections of pipeline that are not buried are to be removed. For full removal decommissioning, several options exist, such as cut-and-lift removal or float-and-tow removal. For all full removal methods large operations are needed and many vessels required.

1.2.2. Stakeholders

In advance of the research, the external stakeholders involved are identified. This will aid to provide an insight of possible opportunities or challenges. Various parties have a judgement about the outcome and can wield a certain influence. They are plotted in the stakeholder diagram in figure 1.3. Each stakeholder is further elaborated below.

Staatstoezicht op de Mijnen

One of the most significant stakeholders for a positive and useful outcome of this research is the Staatstoezicht op de Mijnen (SodM). The SodM is the organisation that is responsible for the legislation on mining natural resources. It is the authority that dictates and enforces the Mining Act. This includes the legislation on decommissioning out-of-use facilities.
The SodM has to approve a proposed solution for alternative pipeline decommissioning and therefore has an enormous influence. Its support is highly dependent on what impact the alternative decommissioning has.

Energie Beheer Nederland

Energie Beheer Nederland B.V. (EBN) is the state's enterprise to invest in hydrocarbons and geothermal energy. It cooperates with the operators in the oil and gas industry to provide energy supply in the Netherlands. It generally holds a 40% share in the oil and gas fields. [12]
As the main partner, EBN will be highly interested in alternative ways for decommissioning. Furthermore, the abandonment expenditure (ABEX) of oil and gas facilities is not taxed. Together with the 40% stake of EBN, this results in approx. 70% of costs for the Dutch state. Together with NOGEPA EBN initiated the NexStep. NexStep is the national platform for the re-use and decommissioning of the oil and gas infrastructure. EBN initiated the 'Netherlands masterplan for Decommissioning and re-use', which aims on a 30 % cost reduction of the decommissioning activities. The activities of EBN within NexStep supports their interest in the decommissioning activities.

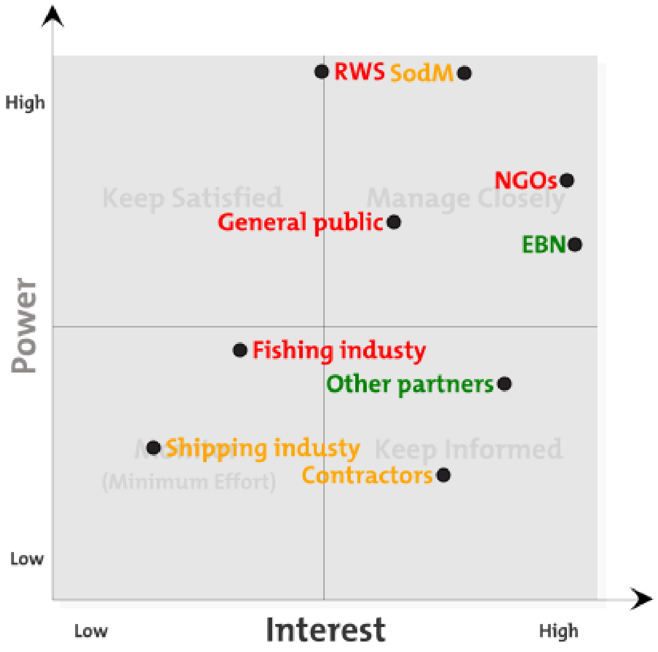


Figure 1.3: External stakeholder diagram

Rijkswaterstaat
Once the offshore infrastructure is abandoned it is considered to to be waste. SodM is no longer the responsible legislator as the sealines are no longer part of mining activities. The responsibility for waste in the North Sea is Rijkswaterstaat (RW). Their judgement is to be respected, hence their power is ultimate. It is expected that they are in favour of removing all the residue from the mining activities. It is likely that RW is less supportive than SodM. However, they are interested in decommissioning methods with as little environmental impact as possible.

NOGEPA
NOGEPA (Nederlandse Olie en Gas Exploratie en Productie Associatie) is the organisation of operators in the Netherlands. It is looking after the interests of the companies who hold a license for the exploration or production of oil and gas. Its main goals are to make the production of hydrocarbons in the Netherlands as safe, efficient and environmental friendly as possible. It also aims to establish a good relationship with the public.
As NOGEPA is one of the NexStep initiators, it has a noteworthy interest and influence on the decommissioning activities in the North Sea.

Other operators
Other operators in the area are also affected by decommissioning challenges. This includes partners of TEPNL who are shareholders in TEPNL exploited fields. As other operators in the North Sea will be subjected to similar challenges,developments in decommissioning methods will be relevant for them. Their interest is represented by the NOGEPA.

Environmental NGOs
Environmental NGOs, such as Greenpeace or Stichting de Noordzee, are likely to have a sceptical view on the matter. This research aims to find a alternative way of decommissioning with a smaller environmental impact than current methods. However, keeping the Shell Brent Spar decommissioning in mind, it remains a delicate subject. The notification of these parties should therefore be well thought-out, to prevent misinterpretations. Furthermore, their power is rather high, as they are capable of influencing public and government.

General public

An important stakeholder to TEPNL is the public. Their opinion is highly valued and their influence in significant. If the public's opinion is influenced into a negative perspective on TEPNL activities, the consequences have a bad impact on the complete TOTAL group. Besides, in an era of increasing interest in sustainability and environmental awareness, decommissioning is a relevant activity. It is therefore advisable to show the public that TEPNL and TOTAL are concerned regarding improving decommissioning methods.

Fishing industry

Another user of the North Sea region is the fishing industry. The Dutch fishing fleet consists of approximately 600 ships. Their activities and locations of activity vary. As the North Sea shelters their primary source of income, fishermen have a large interest on the issues involving this area. The political policy aims to maximise the fishing industry while limiting the negative impact on the marine life [13]. Therefore, the stakes of the fishing industry are taken seriously in the political agenda. Therefore, it is concluded that the influence of the fishing industry for this particular research is noteworthy.

1.3. Problem statement

The legislation on decommissioning pipelines and cables in the North Sea are part of the Dutch Mining Act. Pipelines can be allowed to be left in-situ after decommissioning. The owner of the pipeline will then bear liability for the rest of the pipeline's existence. This liability implies frequent inspection of the pipeline and conducting maintenance work when needed. Moreover, the pipelines may cause risks for other sea users. This risk can cause hazardous situations and can therefore significantly harm the good reputation of the pipeline owner.

However, the Mining Act prescribes that the *Staatstoezicht op de Mijnen* (SodM) can also determine that the pipelines have to be removed after their production life. Within the industry there is limited experience with current methods of pipeline removal in the North Sea. The costs of these operations are rather high and it is difficult to make a precise estimate. Furthermore, pipeline removal involves a large number of vessels and diving operations, resulting in a large environmental impact and safety considerations.

1.3.1. Research questions

It can be concluded that the decommissioning of sealines is accompanied with challenges. These are either the long-term risk of leaving the lines in-situ, or the uncertainties and large costs of the sealine removal operations.

Aiming to investigate an alternative way for pipeline decommissioning, this thesis is constructed to solve the following research question:

How can the accelerated degradation of steel contribute to the decommissioning of offshore pipelines?

This main research question can be answered by researching some sub-questions.

- What are the current methods for pipeline decommissioning?
- How can the degradation of steel be accelerated?
- What is the operational feasibility of the degradation mechanism?

1.3.2. Key risks

The key risks of this research are identified. These risks determine what to keep in mind throughout the process. The key risks are *reputational damage, impact of accelerated degradation* and possible *change in regulations*.

Reputational damage The main risk of the decommissioning activities for the TOTAL group is the risk of damaging the reputation. The risk of social resistance should be taken into account for the current decommissioning methods, as well as for the proposed accelerated degradation methods. The way the general public accepts any decisions is difficult to assess. However, the impact can be mitigated by communicating a clear rationale. It is of importance to keep the demands and wishes of the stakeholders in to constant consideration. The stakeholders are identified in section 1.2.2.

Impact of accelerated degradation A key risk to consider is the impact of the accelerated degradation of steel. The steel degradation implies that the steel dissolves in a shorter period of time into the marine environment. Hence, the concentration of iron in the seawater will increase with respect to not accelerating. Furthermore, the method of accelerating the degradation might also be accompanied with the use of materials or equipment that can have serious impact on marine environment and other aspects.

Change in regulations Another insecurity for the alternative decommissioning methods is the possible change in regulations. As mentioned earlier, the act on decommissioning of pipelines is currently under revision. The SodM, NOGEPA, EBN and Rijkswaterstaat all have varying interest in the decommissioning activities. It is therefore beneficial to investigate different decommissioning methods. However, this comes with the risk that an investigated method is prohibited during the research.

1.4. Research demarcation and assumptions

In this thesis the accelerated degradation of steel is investigated. Therefore, the scope of this research is limited to steel, rigid sealines. The duplex pipelines, cables and umbilicals are not included. Additionally, the anti-corrosion coating of the sealines is not addressed in this research.

For the sealines, the following assumptions and limitations are made:

- All subsea structures have been removed
- Pipelines are flushed and cleaned
- Pipelines will be filled with seawater if left in situ
- Pipelines are trenched or covered
- Pipelines are located approximately 1 meter below the mud line

Furthermore, the research is aiming to accelerate the pipeline degradation to reduce the liability period and the associated risks. The pipelines are therefore considered sufficiently degraded if the remainder of the lines can be left buried in the North Sea, without posing risk to other sea users. The location where the sealines were once positioned should then be able for other use, such as fishery of wind farm construction.
This is assumed to be achieved when:

- The effective thickness is reduced so exposure due to bending does not occur. (in case of uniform degradation)
- The dimensions of the pipeline debris are limited, so they do not pose a risk to other users of the sea. (in case of localised degradation)

1.5. Thesis outline

The current methods of pipeline decommissioning are investigated in chapter 2. A comparative assessment is conducted to illustrate the base case. Besides the assessment, an introduction to elecrtochemical corrosion is provided in chapter 3. With the concepts discussed in this chapter potential methods for accelerated steel degradation are assessed in chapter 4. Based on the outcome of the comparative assessment in chapter 2 and 4, lab tests are conducted regarding the galvanic coupling of steel. The test set-up and test plan for these test is described in chapter 5. The results and recorded values are found in chapter 6. Subsequently, the practical implementation and feasibility is discussed in chapter 7. The conclusions and recommendations are discussed in chapter 8. A schematic overview is given in figure 1.4.

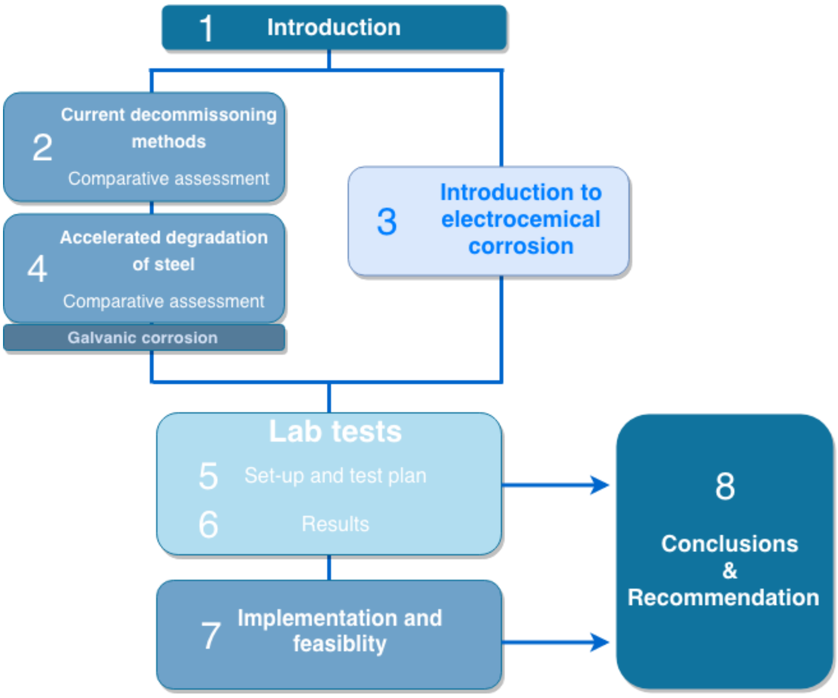


Figure 1.4: Schematic presentation of thesis outline

2

Current decommissioning methods

The TEPNL sealines in the North Sea add up to 508 kilometres of pipeline. All pipelines are buried at depths between 1.0 and 0.8 metre.
After abandonment of the sealines, they are part of the regulations of Rijkswaterstaat. Rijkswaterstaat is in favour of having the remaining pipes removed. Regulations are currently under revision and therefore open to amendments. The possible removal methods are therefore considered. More detail on the regulations is given in section 1.2.1.

2.1. In situ decommissioning

In situ decommissioning implies that the sealines are left at their place after being put out of use. Only the buried sealines can be left in situ. All others, such as risers and subsea equipment will be removed at the same time as the platforms.
At first, the sealines go in to *pre-abandonment phase*. The pipelines are cleaned. The target of TEPNL is to clean the lines so that less than 30 parts per million of hydrocarbons remain in the sealine. Subsequently, the sealines are filled with sea water. They are disconnected from facilities at topside level.
To completely decommission the pipelines in situ, some minor interventions are required prior to abandonment. This involves the removal off all mattresses and rock placement on the exposed sections of the pipelines. Rock placement is also needed at the cut pipeline ends. In case the anti-corrosion protection system is impressed current, it is disconnected.

Ultimately, the pipelines decommissioned in situ are left in such a way that they do not pose a risk to other sea users. As regulations state that the pipeline owner remains liable for the decommissioned sealine, frequent surveys are required. This is done by flyovers. If new exposed or spanned sections occur they are to be mitigated by trenching and/or rock placement.
Due to safety considerations, some mattresses might be left at the sea bottom as well to maintain pipeline stability. It is advised that the decommissioned infrastructure is marked on sea charts and notifications issued to other sea users [9].

2.2. Full removal decommissioning

The considered removal decommissioning methods are cut-and-lift removal and reverse laying methods. These methods require some preliminary operations.
Similar to the in situ decommissioning, the pipelines are cleaned. The sealines are to be removed from their current position. As they are currently buried under approximately 1 metre of soil, they have to be unburied. This is done by jetting the overlaying soil.

2.2.1. Cut-and-lift removal

As the name implies, cut-and-lift decommissioning is performed by first cutting the pipe in pieces and lifting the pipeline sections from the seabed. This method can be used for any diameter and length of sealine.

Once the sealines are exposed after the jetting of the soil, the cutting operations can start. The pipeline can be cut into sections using diver-operated- or remotely operated cutting tools. The pipeline can be cut using a water jet or a diamond wire saw. An impression of a cut-and-lift operation using a diamond wire saw is depicted in figure 2.1.

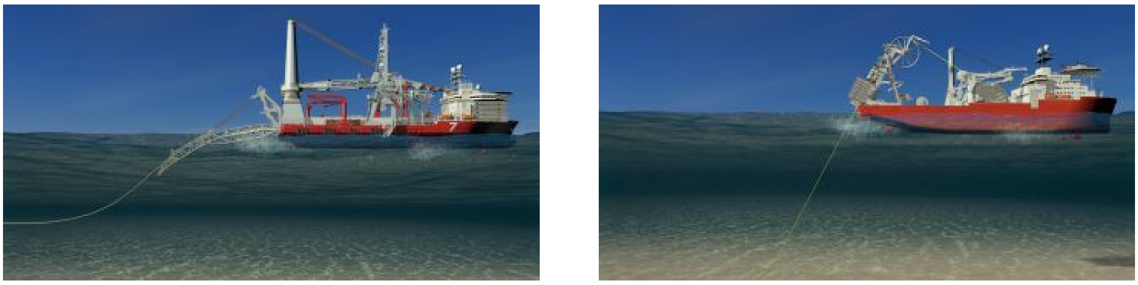
Figure 2.1: An impression of subsea cutting using a diamond wire saw. Image from Seatools BV

The pipeline sections are lifted on to a surface vessel by an on-board crane. The used pipeline sections can either be reused or scrapped, depending on the integrity of the decommissioned pipe.

The variety of operations requires specialised vessels. The fleet needs to be equipped with the underwater cutting equipment which requires a powerful subsea electric drive. Furthermore, the underwater operations require either skilled divers or advanced control systems for ROV support[**?**].

2.2.2. Reverse lay

The reverse versions of pipeline installation methods are also used for sealine decommissioning. This can be reversed S-lay or reel lay.



(a) An S-lay vessel

(b) A reel lay vessel

Figure 2.2: An S-lay (a) and reel lay vessel (b) which both can be used for reversing the installation process

The reverse reel method requires a ship with reeling capabilities. The pipeline is disconnected at topside level and connected to the reeling equipment. The vessel will than slowly reel in the pipeline. The pipeline is winded and wrapped prior being transported to shore.
This method is used in some decommissioning projects in the British North for smaller sections of pipe, for example in the Vampire field. These operations involved flexible pipelines and umbilicals. The reverse reeling of rigid pipelines is also assumed feasible [6]. Reverse reel decommissioning is limited to 16 inch pipelines. Another limiting factor is the reel size.

The pipeline is winded on the reel, which has a limiting storing capacity depending on the reel diameter. Hence, the pipeline length that can be decommissioned by reverse reel is limited. For the reverse S-lay method a S-lay vessel is to be converted. As the process is the inverse of the installation operations, the welding station is replaced by a cutting station. This cutting station can make use of a water jet, diamond wire cutter, hydraulic shears or guillotine saw. The reverse S-lay method starts in a similar way as the reverse reel method. The disconnected pipeline end is connected to on the vessel and the pipeline is towed in. After a section on the sealine is on board of the vessel, the pipeline is cut. The cut pipeline sections are temporarily stored aboard the S-lay vessel. Periodically, the pipeline sections are transferred to a supporting vessel. This support vessel takes the decommissioned pipe to shore where the steel can be recycled

2.3. Assessment of current decommissioning methods

Current decommissioning methods can be divided in in situ decommissioning and in full removal decommissioning methods. In previous section the required operations for each method are discussed. A conclusive summary of the methods is given in table 2.1

	In situ	Full removal
Technical impact	Rock placement operations Removal of matresses	Unburial of pipelines Cut-and-lift removal Onshore disposal
Environmental impact	Little vessel duration Small volume of contaminants released	Many vessels involved Large vessel duration Disturbance of seabed
Safety consideration	Little diving/ROV operations Little vessel duration	Many diving/ROV operations Large vessel duration
Risk & Uncertainty	Regulations (SodM, RWS) Public opinion	Limited experience with method Many vessels involved
Remedial Risk Mitigation	Frequent survey operations Remedial operations if required	None
Post Decom Risk	Snagging risk Liabilities	None
Decommissioning cost	Low	High
Post Decom Cost	Survey and remedial operations	None

Table 2.1: Considerations of current decommissioning methods

First, the decommissioning methods will be assessed separately according to six criteria. These criteria are *technical feasibility, environmental impact, safety, societal acceptance, costs* and *sustainability*.

More details on the assessment criteria and the assessment method can be found in Appendix A.

2.3.1. In situ decommissioning

Technical feasibility Due to the minimal amount of intervention for the in situ decommissioning, the technical impact is little. The used techniques have been applied elsewhere in the North Sea [7]. The necessary rock placement for pipelines that become exposed in combination with the cutting of the pipeline ends, lead to a minor risk of operational failure.

Environmental impact A small volume of contaminants are released to the marine environment during the degradation of the pipelines. Without accelerated degradation, the degradation process is expected to take between 100 and 500 years. These small volumes over this period are not likely to result in long-term harm with respect to marine organisms [9].

As the in situ decommissioning requires little intervention, the emissions due to vessel operations are little. Furthermore, the seabed is left untouched.

Safety Since the sealines will be left in place, only a few interventions are required. Therefore, the amount of diving and/or ROV operations will be little. This is also the case for the vessels necessary for this intervention. As there are little operations involved, the chances on hazardous situations are also small. The main safety risks will be during the rock placement operations.

Societal acceptance Although the environmental risks are low, it is unlikely that the public opinion is in favour of in situ decommissioning. The general idea tends to be that one has to clean what one has installed. As can be learned from the Brent Spar incident[1]

Costs The absence of any large operations determine the cost. Little operations are required and therefore the expenses are limited. Main costs are pipeline disconnecting operations and rock placement .
During the remainder of the pipeline survey operations need to be held frequently. This adds up to the expenses for a survey operation every other year plus remedial operation costs if necessary. However, proportional to decommissioning expenditure, these costs are very low. The surveys on the sealines that are required during their service life, consist of multi beam sonar, side scan sonar and burial depth measurement. These scans are conducted every year or every other year, based on the occurring anomalies in prior surveys. The price per kilometre sealine is around €1200. Therefore, the costs for the surveys is in the range between €300k and €600k per year. Assuming a liability period of 100 years, this accumulates to €30 to €60 million. However, if the results show no direct reason to assume a threat in the nearby future, the required frequency of inspection can be reduced. The above mentioned expenses are therefore assumed to be the maximum [7] [9].

Sustainability Leaving the pipelines decommissioned in situ is little sustainable. The steel can not be recycled onshore. However, by leaving the pipelines in situ without further treatment, they are expected to remain for a long period. Studies have investigated the feasibility of reusing gas pipelines for new energy supply [9].

2.3.2. Full removal decommissioning

For the evaluation of the full removal decommissioning, the cut-and-lift method is considered governing. After assessment of several methods in the British North Sea, cut-and-lift removal was judged best suitable of all full removal options[7].

Technical feasibility The cut-and-lift method has been used for the removal of offshore pipelines. These operations involved either removing short sections of a pipeline or the full removal of a short pipeline. To use the cut-and-lift method on such a large decommissioning programme will be a much larger process than the shorter section. The individual operations are proven to be technically feasible, though the large scale on which it will be required will be accompanied by some new challenges. For the large scale the logistics and scheduling are of importance, as the operations require specialised vessels, equipment and personnel. [3].

Environmental impact The cut-and-lift method requires a lot of vessel operations. Due to the larger scale of the project, the full removal of the TEPNL pipelines will use a large fleet for an extensive period. Therefore the emissions are a large factor in the environmental impact. Furthermore, the sealines are stripped of overlaying soil by jetting, causing disturbance to the seabed. The many subsea operations are also a disturbance for the marine life in the area [9].

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[1] The Brent Spar was an oil storage and loading buoy in the Brent oil field. The field was operated by Shell UK and put out of service in 1991. In 1995 the British government and Shell agreed on the decommissioning of the spar buoy by disposing it in the Atlantic Ocean at a depth of 2.5 km. In spite of the technical assessments and consulting of experts stating that the disposal was the safest option, a lot of public resistance developed. Induced by a large media campaign of Greenpeace, Shell service stations in western Europe were widely boycotted and even vandalised. After the severe public and political opposition, Shell did not follow through with the disposal in sea [1].

Safety Due to the many operations safety hazards exist. Due to the many operations the personnel has to carry out, safety risks are widely present. The most significant safety risk is when diving operations are carried out. It is therefore advised to conduct most underwater operations with remote operated equipment, if possible.
Furtermore, the many lifting operations are accompanied by safety risks. The full removal of all TEPNL sealines will be a extensive project with a large impact on safety.

Societal acceptance It is expected that full removal decommissioning will not encounter too much resistance. The general opinion is often that one has to clean up what one has used. The public opinion about the oil and gas industry is quite sceptical. This is also the case when it comes to decommissioning activities. It is therefore expected that the removal of the sealines will be considered as the right thing to do. The high amount of emissions might lead to some criticism.

Costs The large scale of the project, mobilisation of major removal equipment and extensive period of project duration make the cut-and-lift removal expensive. Removing sealines in the North Sea with the cut-and-lift method costs approximately €500k per kilometre [7]. The accumulating decommissioning costs for the TEPNL sealines will therefore be around €250 million.

Sustainability The cut-and-lift method removes all offshore infrastructure. After the operations nothing is available with potential future value. However, as opposed to in situ decommissioning, the steel of the decommissioned sealines is available for recycling.

2.3.3. Assessment score

The current decommissioning methods are evaluated according to the predetermined assessment criteria. The methods are scored based this evaluation. The awarded scores are listed in table 2.2.

The significance of the assessment criteria is determined. Accordingly to how important a criterion is considered, a *maximum score* is assigned. The sum the max scores is 100. The *assessment scores* vary from 1 to 5, where 1 represents a least favourable impact and 5 a most favourable impact of the respective criterion. Subsequently, the *weighted score* of the criteria is determined. This is done by grading the max score proportional to the assessment score. The *total score* is the rounded sum of the weighted scores and can be found in the rightmost column. This is the final score of the assessed method. More elaboration on the assessment method is found in appendix A.

	Technical impact	Environmental impact	Safety	Societal	Cost	Sustainability	
Max. score	13,3	13,3	33,3	20,0	13,3	6,7	**Total score**
In situ							
Assessment score	5	5	5	1	5	1	
Weighted score	13,3	13,3	33,3	4,0	13,3	1,3	**79**
Cut-and-lift							
Assessment score	3	3	3	5	1	1	
Weighted score	8,0	8,0	20,0	20,0	2,7	1,3	**60**

Table 2.2: Comparative assessment of current decommissioning methods

The comparative assessment on the current decommissioning method results in a highest score of **79** for the **in situ decommissioning**. The in situ decommissioning method is therefore the governing base case for the rest of this research.

The positive result for the in situ decommissioning is mainly due to the little intervention the method requires. Due to the small amount of operations required, the in situ method scores well on technical and environmental impact. Furthermore, the safety risk remains low

since personnel is not often exposed to hazardous situations. The minimum interventions also imply minimum expenses.
The fact that most of the infrastructure is left behind, does however have a negative impact on the societal support. The sustainability opportunities are also very limited.

The opposite holds for the cut-and-lift method. For this method the large scale and intensity of the required operations determine the final score. Due to the many vessels and personnel required, the cut-and-lift method scores weakly from technical ,environmental and safety perspective. The high expenses for this method lead to a very poor score on project cost. The societal support, on the other hand, is predicted to be in favour of the removal methods.

3

Introduction to electrochemical corrosion

3.1. Electrochemical corrosion

Corrosion is the destructive result of chemical reaction between a metal or metal alloy and its environment. All aqueous corrosion reactions can be considered to be electrochemical[10]. Electrochemistry describes the reactions of charged particles that cross the interface of two phases of matter. This involves reactions that transfer ions, an electrically charged atom or molecule, or reaction of electrons. These ion- or electron-transfer reactions occur near the surface of the *electrode*. The electrode is the electrical conducting material that is immersed in a conductive medium, the *electrolyte*. Therefore, these reactions are called *electrode reactions*.

The reaction consists of two half-cell reactions, the reduction half-cell reaction and the oxidation half-cell reaction. *Oxidation* is the release of electrons. The metal on which this occurs is called the *anode*. *Reduction* occurs at the *cathode*, which is where electrons are gained. Hence, the corrosion reaction consists of an anodic and cathodic half-cell reaction.

3.1.1. Half-cell reactions

For a metal M the anodic half-cell reaction of the metal is given by equation 3.1. The metal M oxidises as it releases n electrons. The n in the superscript of the ion is also referred to as the oxidation number.

$$\mathrm{M} \longrightarrow \mathrm{M^{n+}} + \mathrm{ne^-} \tag{3.1}$$

The cathodic half-cell reaction depends on the environment in which the metal is placed. The most common reduction reactions are the formation of hydrogen (3.2), reduction of oxygen in an acidic environment (3.3) or in an alkaline or natural environment (3.4) and the reduction of a metal ion (3.5) [15].

$$2\,\mathrm{H^+} + 2\,\mathrm{e^-} \longrightarrow \mathrm{H_2} \tag{3.2}$$

$$\mathrm{O_2} + 4\,\mathrm{H^+} + 4\,\mathrm{e^-} \longrightarrow 2\,\mathrm{H_2O} \tag{3.3}$$

$$\mathrm{O_2} + 2\,\mathrm{H_2O^+} + 4\,\mathrm{e^-} \longrightarrow 4\,\mathrm{OH^-} \tag{3.4}$$

$$\mathrm{M^{n+}} + \mathrm{e^-} \longrightarrow \mathrm{M^{(n-1)+}} \tag{3.5}$$

3.1.2. Overall reaction

The electrons carry an negative electrical charge. The overall reaction is where the electrons released by the anodic reaction and reduced by the cathodic reaction are balanced. That is, the net charge equals zero. The general expression is:

$$\mathrm{Ox} + \mathrm{ne}^- \rightleftharpoons \mathrm{Red} \tag{3.6}$$

The oxidation half-cell reaction results in an electron build up in the electrode, causing a negative charge in the electrode. Consequently, a positive charge is build up near the electrode surface in the electrolyte. For the process to continue, a reaction that restores the electroneutrality is required. Hence, a reduction half-cell reaction that 'captures' electrons is required.

3.2. Electrochemical kinetics

Corrosion is thermodynamically possible in most environemental conditions. Corrosion in aqeous solutions is governed by electrochemical reactions[10]. The kinetics of general corrosion are discussed in this section.

3.2.1. Polarisation

The potential at the surface becomes more negative if electrons are made available. An excess of electrons accumulates at the metal/solution interface waiting for reaction. The reaction is not fast enough to accomodate for all the electrons [10]. This negative potential change that results is called *cathodic polarisation*. A postive potential change due to a deficiency of electrons at the interface is called *anodic polarisation*. The larger the anodic polarisation, the larger the tendency for anodic dissolution. Hence, the anodic polarisation represents a driving force of corrosion.

In an aqeous solution the surface will reach a steady-state potential, E_{corr}. This steady-state potential depends on the rate at which electrons are exchanged. If the surface potential increases to a more positive potential than E_{corr} the anodic reaction rate or corrosion rate will increase [10]. This is depicted schematically in figure 3.1.

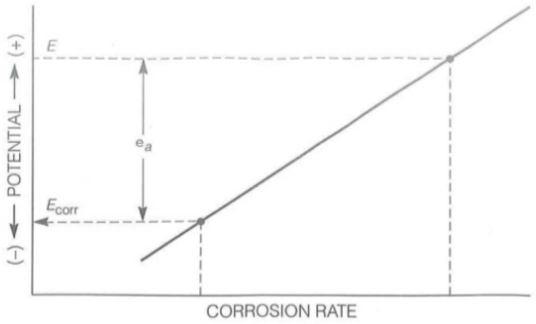


Figure 3.1: Schematic representation of increasing corrosion rate with increasing potential E. Image from *Principles and prevention of corrosion 2nd edition* by D. A. Jones

3.2.2. Polarisation types

Polarisation or overpotential, η, is the potential change from the equilibrium half-cell electrode potential. Cathodic polarisation, η_c, electrons are supplied to the surface. Hence, η_c is negative. For anodic polarisation, η_a, electrons are removed from the electrode and therefore η_a is positive. For $\eta = 0$, i_a and i_c are at equilibrium and both equal to i_0. Here, i_0 is called the *exchange current density*. Polarisation is classified in either *activation* and *concentration*.

Activation polarisation

Activation polarisation is when some step in the half-cell reaction controls the rate of electron flow. The relations between η and rate of reaction represented by current density are given in the equations below. Where (3.7) is for anodic polarisation and (3.8) is for cathodic polarisation.

$$\eta_a = \beta_a \log \frac{i_a}{i_0} \tag{3.7}$$

$$\eta_c = \beta_c \log \frac{i_c}{i_0} \tag{3.8}$$

As η_a is positive, β_a must also be positive. Likewise, because η_c is negative, β_c is also negative. The parameters β_a ad β_c are known as the Tafel constants for the half-cell reactions [10]. The current densities i_a and i_c flow in opposite directions. Equations 3.7 and 3.8 are known as the Tafel relationship. This relationships have universally been observed in experiments for activation polarisation [10].

Concentration polarisation

At high rates, cathodic reduction reactions diminish the adjacent solution of the dissolved species. When this dissolved species are depleted at the surface, the half-cell electrode potential decreases. This decrease is *concentration polarisation*, η_{conc}. It can be writen as a function of current density as:

$$\eta_{conc} = \frac{2,3RT}{nF} \log \left[1 - \frac{i_c}{i_L}\right] \tag{3.9}$$

In this equation i_L is the limiting current density. It is the measure of a maximum reaction rate that cannot be exceeded because of a limited diffusion of dissolved species [10]. The parameter R is the universal gas constant and T is the temperature in kelvin.

Total cathodic polarisation

The total cathodic polarisation is the sum of the activation and concentration polarisation.

$$\eta_{T,c} = \eta_c = \beta_c \log \frac{i_c}{i_0} + \frac{2,3RT}{nF} \log \left[1 - \frac{i_c}{i_L}\right] \tag{3.10}$$

However, as cathodic polarisation is usually not present for anodic polarisation or metal dissolution reactions, above equation reduces to (3.8).

3.2.3. Mixed potential theory

The total rate of oxidation must equal the total rate of reduction. In other words, *the sum of anodic oxidation currents must equal the sum of cathodic reduction currents*[10]. The anodic half-cell reaction of a metal M (3.1) in a solution, has to be balanced by a cathodic half-cell reaction of the solution, for example hydrogen H (3.2) in a acidic solution.

Each species has its own half-cell potential and exchange current density. The two half-cell electrode potentials cannot separately exist on an electrically conductive surface. Hence, each must polarise to a common intermediate potential, E_{corr}. This E_{corr} is called the corrosion potential and is referred to as mixed potential as it is a combination of two half-cell electrode potentials. The half-cell electrode potentials change according to (3.7) and (3.8), respectively, until becoming equal at E_{corr}. For a metal M in a acidic solution, this is schematically depicted in figure 3.2. At E_{corr}, the rate of anodic dissolution, i_a, equals the corrosion current, i.e.:

$$I_c = I_a = I_{corr} \tag{3.11}$$

Corrosion current and corrosion rate

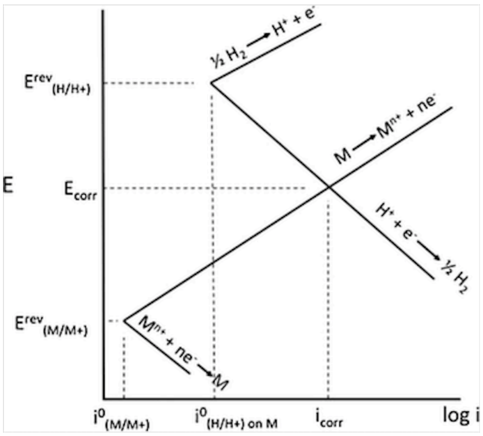


Figure 3.2: Polarisation of anodic and cathodic half-cell reactions for a metal M in an acidic solution, to give the mixed potential E_{corr} and corrosion current density i_{corr}

3.2.4. Faraday's law

Electrochemical reactions consist of electron producing or consuming half-cell reactions. This results in an electron flow, which is measured as a current, I, in ampères. One ampère is equal to one coulomb of charge per second ($6,2 \times 10^18$ electrons per second). Proportionality between current and mass reacted in an electrochemical reaction is given by Faraday's Law:

$$m = \frac{Ita}{nF} \tag{3.12}$$

With	m	Mass reacting in the process	$[g]$
	I	electric current	$[A]$
	F	Faraday's constant	$\approx 96.500\ [Cmol^{-1}]$
	n	number of electrons transferred in the reaction	$[-]$
	a	atomic weight	$[-]$
	t	time	$[s]$

Dividing Faraday's law by time t and the surface area A, the corrosion rate r is obtained:

$$r = \frac{m}{tA} = \frac{Ia}{nFA} \tag{3.13}$$

This determination for corrosion rate is only accurate for uniform corrosion. This approach underestimated the corrosion rate if localised corrosion is occurs.

3.2.5. Corrosion rate based on mass loss

Uniform corrosion rates can be determined by mass loss of the specimens. For accurate results, this is to be done according to predetermined standards. From the mass loss the corrosion rate r in mm/year can be established by:

$$r = K_{ML} \times \frac{\Delta M}{\rho \times A \times t} \tag{3.14}$$

Where	r	corrosion rate	$[mm/year]$
	ΔM	mass loss of the sample over time	$[mg]$
	ρ	density of the sample	$[g/cm^3]$
	A	surface area of the sample	$[cm^2]$
	t	time	$[hours]$
	K_{ML}	factor to account for units	[8, 6]

3.2.6. Corrosion rate from corrosion current

With a determined corrosion current, I_{corr}, equation 3.13 can be modified to:

$$r = I_{corr} \times K \frac{EW}{\rho A} \tag{3.15}$$

In this equation, EW is the the equivalent weight. The equivalent weight is the mass of species that will react with one Faraday of charge. For an atomic species the equivalent weight is the atomic weight divided by the valency, $EW = a/n$. The parameter K is a constant that defines the units for the corrosion rate. For a corrosion rate in mm/year, K equals 3272 $mm/(A.cm.year)$. Again, this determination for corrosion rate is only accurate for uniform corrosion. This approach underestimated the corrosion rate if localised corrosion is occurs.

3.3. Galvanic corrosion

Galvanic corrosion occurs when two dissimilar metals are coupled in presence of an electrolyte. The electrode with the lowest electrode potential acts as an anode. The more noble material act as cathode. The anode is preferentially corroded while the cathode is protected from corrosion.

3.3.1. Galvanic cell

Galvanic corrosion occurs by formation of a galvanic cell, or electrochemical cell. A schematic representation of a galvanic cell is depicted in figure 3.3. The galvanic cell consists of five necessary elements. These are the two electrodes; the *anode* and the *cathode*. The *electrical connection* between these two and the *electrolyte* in which the are immersed. Lastly, there has to be a *potential difference* between the two electrodes.

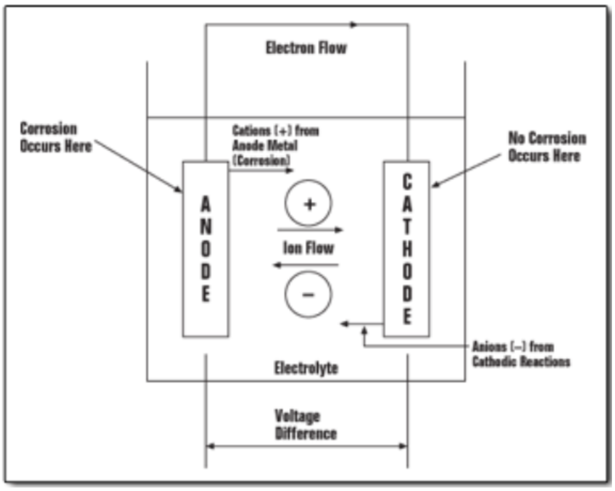


Figure 3.3: An electrochemical cell, image from https://www.nace.org/Corrosion-Basics

Anode The electrode where oxidation occurs, i.e the loss of electrons. The anode has a more negative potential than the cathode and is called less noble. As it has a more negative potential, it is more willing to give up negatively charged electrons. The oxidation half-cell reaction results in metal atoms to give up electrons and becoming a positively charged ions. The positively charged ions are called cations.

Cathode The electrode where reduction occurs, the gain of electrons. The cathode has a more positive potential than the anode and is called more noble. The cathodic reactions result in negatively charged ions, anions. As the cathode is more noble, it is less willing to give up electrons.

Electrical connection An electrical connection between anode and cathode is necessary for electrochemical corrosion to occur. The electrical connection ensures the possibility for electrons to flow from the anode to the cathode.

Electrolyte The electrically conductive medium where the anode and cathode are located. In the electrolyte, a flow from ions balance the flow from electrons . The anions are negatively charged particles result from the cathodic reaction and flow from the cathode to the anode. The cations, the positively charged ions from the anodic reaction, flow towards the cathode

Potential difference The driving force of the corrosion reaction is a potential difference between the anode and cathode. This is the electromotive force of the cell.

3.3.2. Galvanic series

The electrode potential of various materials are found in the galvanic series, depicted in figure 3.4. In this diagram the materials are sorted according to their electrode potential. The potential is found along the horizontal axis and is expressed in volts. The highest potentials are found on the right side of the figure and decrease towards the left side of the figure. According to this axis the materials are depicted from least noble at the top right, down to the most noble at the bottom left.

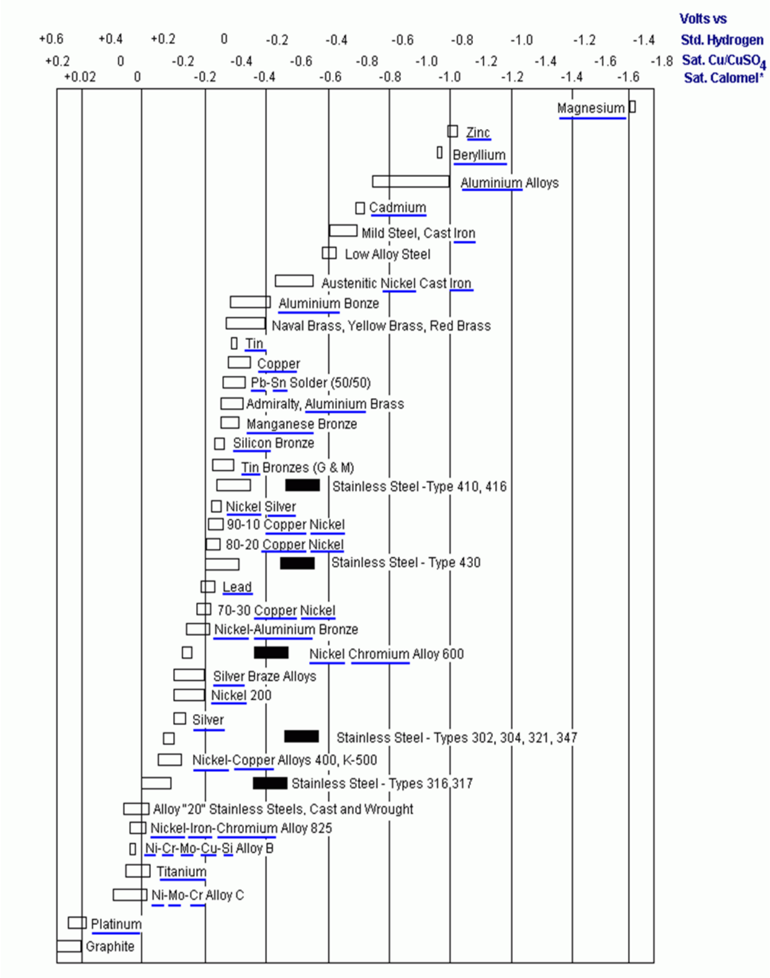


Figure 3.4: The galvanic series for materials in seawater

3.3.3. Anodic index

Usually it is the engineering practice to avoid galvanic corrosion. The so-called *anodic index* is a parameter used in design. The anodic index refers to the compatibility of two different metals in the same environment. The anodic index is a measure of the electrochemical potential of a metal when in contact with gold. These values can be found in table 3.1.

Metal	Potential
Most noble(most cathodic)	+
Gold	0,00
Rhodium	-0,05
Silver	-0,15
Nickel	-0,30
Copper	-0,35
Brass	-0,40
Bronze	-0,45
Chromium resistant steels (18%)	-0,50
Chrome plating (12%)	-0,60
Tin-plate, solder	-0,65
Lead	-0,70
2000 series wrought aluminium	-0,75
Cast iron, steel	-0,85
Wrought aluminium	-0,90
Cast aluminium	-0,95
Zinc galvanised steel	-1,20
Wrought zinc	-1,25
Magnesium	-1,75
Berylium	-1,85
Least noble (most anodic)	-

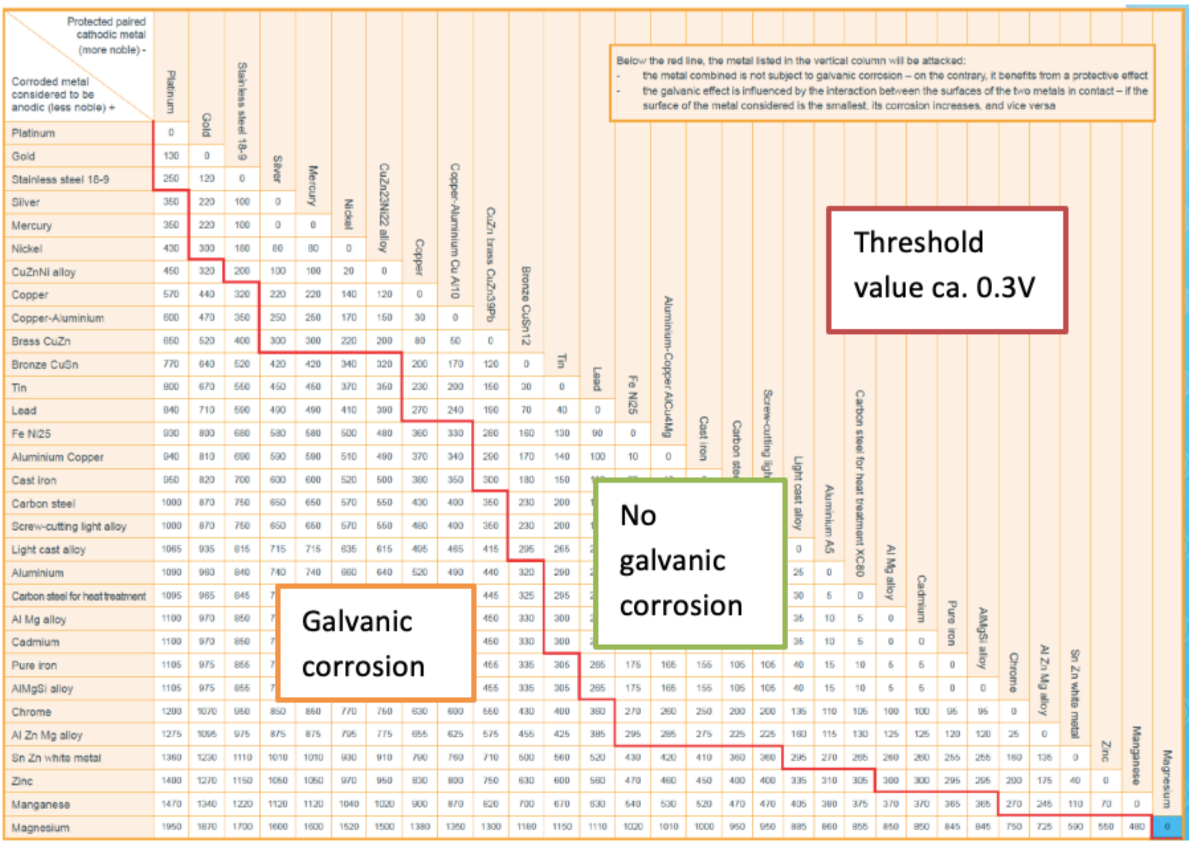
Table 3.1: The anodic index: the electrochemical potential of metals in contact with gold.

The following practical recommendations apply in order to avoid galvanic corrosion:

- For “normal” environment, such as storage in warehouses or non-temperature and no-humidity controlled environments, there should be no more than 0.25 V difference in the anodic index of the electrically coupled metals, intended to use
- For controlled medium, where temperature and humidity are controlled, typically 0.5 V difference can be tolerated
- For harsh environments, such as outdoors, high humidity, sea water (or other salts) environment, there should be no more than 0.15V difference in the anodic index.
- Overall – the accepted threshold value of approximately 0.3V is to be considered for various galvanic couples, as a potential difference between two metals of different electronegativity, depicted in the chart in figure 3.5.

In addition to the above, the practical approach to prevent galvanic corrosion includes:

- Avoid combination of dissimilar metals, well apart in the galvanic series
- Avoid situations where a small anode is coupled to a large cathode
- Insulate the couples metals from the environment
- Reduce the aggressiveness of the environment (e.g. by adding inhibitors)
- Use cathodic protection
- Increase the length of the solution path in low conductivity medium (in high conductivity medium, as sea water, the approach is not efficient)



Below the red line, the metal listed in the vertical column will be attacked:
- the metal combined is not subject to galvanic corrosion – on the contrary, it benefits from a protective effect
- the galvanic effect is influenced by the interaction between the surfaces of the two metals in contact – if the surface of the metal considered is the smallest, its corrosion increases, and vice versa

Protected paired cathodic metal (more noble) - / Corroded metal considered to be anodic (less noble) +	Platinum	Gold	Stainless steel 18-9	Silver	Mercury	Nickel	CuZn23Ni22 alloy	Copper	Copper-Aluminium Cu Al10	CuZn brass CuZn39Pb	Bronze CuSn12	Tin	Lead	Fe Ni25	Aluminium-Copper AlCu4Mg	Cast iron
Platinum	0															
Gold	130	0														
Stainless steel 18-9	250	120	0													
Silver	350	220	100	0												
Mercury	350	220	100	0	0											
Nickel	430	300	180	60	80	0										
CuZnNi alloy	450	320	200	100	100	20	0									
Copper	570	440	320	220	220	140	120	0								
Copper-Aluminium	600	470	350	250	250	170	150	30	0							
Brass CuZn	650	520	400	300	300	220	200	80	50	0						
Bronze CuSn	770	640	520	420	420	340	320	200	170	120	0					
Tin	800	670	550	450	460	370	360	230	200	160	30	0				
Lead	840	710	590	490	490	410	390	270	240	190	70	40	0			
Fe Ni25	930	800	680	580	580	500	480	360	330	280	160	130	90	0		
Aluminium Copper	940	810	690	590	590	510	490	370	340	290	170	140	100	10	0	
Cast iron	950	820	700	600	600	520	500	380	350	300	180	150	[illegible]	[illegible]	[illegible]	[illegible]
Carbon steel	1000	870	750	650	650	570	550	430	400	350	230	200	[illegible]	[illegible]	[illegible]	[illegible]
Screw-cutting light alloy	1000	870	750	650	660	570	560	480	400	360	230	200	[illegible]	[illegible]	[illegible]	[illegible]
Light cast alloy	1065	935	815	715	715	635	615	495	465	415	295	265	[illegible]	[illegible]	[illegible]	[illegible]
Aluminium	1090	960	840	740	740	660	640	520	490	440	320	290	[illegible]	[illegible]	[illegible]	[illegible]
Carbon steel for heat treatment	1095	965	845	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	445	325	295	[illegible]	[illegible]	[illegible]	[illegible]
Al Mg alloy	1100	970	850	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	450	330	300	[illegible]	[illegible]	[illegible]	[illegible]
Cadmium	1100	970	850	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	450	330	300	[illegible]	[illegible]	[illegible]	[illegible]
Pure iron	1105	975	855	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	465	335	305	265	175	165	155
AlMgSi alloy	1105	975	855	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	455	335	305	265	175	165	155
Chrome	1200	1070	950	850	860	770	760	630	600	560	430	400	380	270	260	250
Al Zn Mg alloy	1275	1095	975	875	875	795	775	655	625	575	455	425	385	295	285	275
Sn Zn white metal	1360	1230	1110	1010	1010	930	910	790	760	710	500	560	520	430	420	410
Zinc	1400	1270	1150	1050	1050	970	950	830	800	750	630	600	560	470	460	450
Manganese	1470	1340	1220	1120	1120	1040	1020	900	870	820	700	670	630	540	530	520
Magnesium	1950	1870	1700	1600	1600	1520	1500	1380	1350	1300	1180	1150	1110	1020	1010	1000

Protected paired cathodic metal (more noble) - / Corroded metal considered to be anodic (less noble) +	Carbon ste	Screw-cutting ligh	Light cast alloy	Aluminium A5	Carbon steel for heat treatment XC80	Al Mg alloy	Cadmium	Pure iron	AlMgSi alloy	Chrome	Al Zn Mg alloy	Sn Zn white metal	Zinc	Manganese	Magnesium
Platinum															
Gold															
Stainless steel 18-9															
Silver															
Mercury															
Nickel															
CuZnNi alloy															
Copper															
Copper-Aluminium															
Brass CuZn															
Bronze CuSn															
Tin															
Lead															
Fe Ni25															
Aluminium Copper															
Cast iron															
Carbon steel	[illegible]														
Screw-cutting light alloy	[illegible]	[illegible]													
Light cast alloy	[illegible]	[illegible]	0												
Aluminium	[illegible]	[illegible]	25	0											
Carbon steel for heat treatment	[illegible]	[illegible]	30	5	0										
Al Mg alloy	[illegible]	[illegible]	35	10	5	0									
Cadmium	[illegible]	[illegible]	35	10	5	0	0								
Pure iron	105	105	40	15	10	5	5	0							
AlMgSi alloy	105	105	40	15	10	5	5	0	0						
Chrome	200	200	135	110	105	100	100	95	95	0					
Al Zn Mg alloy	225	225	160	115	130	125	125	120	120	25	0				
Sn Zn white metal	360	360	295	270	265	260	260	255	255	160	135	0			
Zinc	400	400	335	310	305	300	300	295	295	200	175	40	0		
Manganese	470	470	405	380	375	370	370	365	365	270	245	110	70	0	
Magnesium	950	950	885	860	855	850	850	845	845	750	725	590	550	480	0

Figure 3.5: Anodic index depicted as chart. Courtesy La-Clusienne-Clufix

To that end, all above considerations for anodic index, potential differences and way to avoid galvanic corrosion can be used in reversed considerations in view of the objectives of this thesis

4

Accelerated degradation of steel

In this chapter several possibilities of degradation for the steel pipeline are considered. In section 4.1 methods are discussed which use corrosion mechanisms to accelerate the degradation. In section 4.2 ways of physical damaging are also discussed. This is to provide a comprehensive assessment of the possibilities for alternative pipeline decommissioning. This assessment can be found in section 4.4.

4.1. Corrosion degradation

4.1.1. Reversed ICCP

A large part of the TEPNL pipelines are protected against corrosion by impressed current cathodic protection (ICCP). These are mainly the old pipelines, constructed before 1994. Impressed current is a cathodic protection method. The pipeline is connected to the negative pole of a direct current (DC) power source. The positive pole is connected to an auxiliary electrode close to the structure, the anode. By doing this, the pipelines are receiving electrons instead of providing them. Hence, giving the pipelines a cathodic nature instead of an anodic nature. In other words, the corrosion of the pipeline is thermodynamically made impossible. The current is generated by the DC power source. The anodes are usually made from relatively inert material material, such as titanium. This minimises anode consumption.

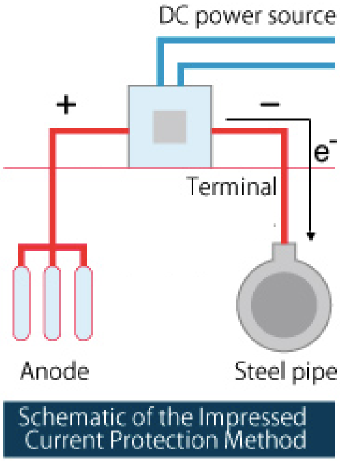


Figure 4.1: A schematic representation of the impressed current cathodic protection method. The current from the power source is impressed on the steel pipe by using inert anode material, such as titanium. (Image adapted from www.JAPEX.co.jp)

This form of protection could be used in reverse to accelerate the corrosion process. The pipe has to be connected to the positive terminal instead of the negative one. Hence, the pipeline will start to act as an anode.

The electrolytic corrosion of a large volume has a very high energy demand. From a financial point of view this solution is therefore troublesome. It could however be considered to install wind turbines to supply in the energy required. Although this is also costly, the wind turbine could be used for future endeavours. Besides, photo-voltaic elements can be used as DC sources as well. This is a common practice in locations where a ground electrical current network is not present.

4.1.2. CO_2-corrosion

Carbon dioxide (CO_2) corrosion is a widely occurring form of corrosion in the oil and gas industry. In aqueous environment the formation of carbonic acid, H_2CO_3, may occur. This can result in severe corrosion. CO_2 corrosion is dependent on several factors, including the concentration of CO_2 and acidic components like H_2S, the water chemistry and the properties of the steel. In an aqueous solution the carbon dioxide reacts with water to produce carbonic acid (H_2CO_3) as follows:

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

The carbonic acid in its turn develops into bicarbonate (HCO_3^-) and subsequently to carbonate (CO_3^{2-}) in the following two steps:

$$H_2CO_3 \longrightarrow H^+ + HCO_3^-$$

and subsequently

$$HCO_3^- \longrightarrow H^+ + CO_3^{2-}$$

The carbonate reacts with the iron in the steel pipeline. This results in the precipitation of ferrous carbonate ($FeCO_3$).

$$Fe^{2+} + CO_3^{2-} \longrightarrow FeCO_3(s)$$

Hence, the overall reaction of CO_2 corrosion can be written as combination of the above equations:

$$\mathbf{Fe + CO_2 + H_2O \longrightarrow FeCO_3(s) + H_2}$$

A visualisation of this process is depicted in figure 4.2.

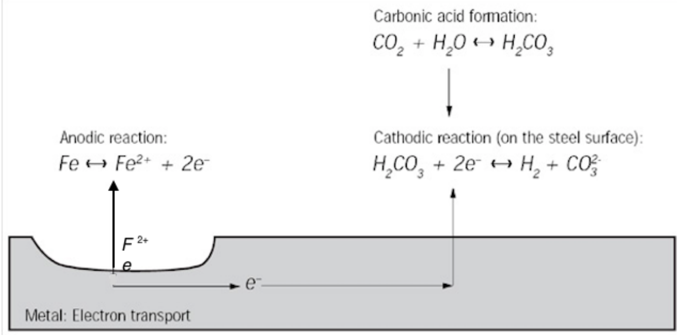


Figure 4.2: The process of carbon dioxide corrosion. Image adjusted from globalccsinstitute.com

The process of CO_2-corrosion is often considered as a huge threat to oil and gas pipelines, as it is one of the major sources of pipeline destruction. How severe the corrosion by carbon dioxide can be, is visible in figure 4.3. Though it is anxiously monitored in the oil and gas

industry throughout, it could be a useful mechanism for this research.
Carbon dioxide is a common known byproduct of the oil and gas industry. Due to its effects on the greenhouse effect it is preferred to keep the production of carbon dioxide to a minimum.

As stated previously, carbon dioxide corrosion occurs in presence of an aqueous solution, such as seawater. A proposed method to accelerate the corrosion of the offshore pipelines therefore is to fill them with a mixture of carbon dioxide gas ad seawater. Optionally, a pump is installed to ensure a flow through the pipeline which results in a higher corrosion rate.

The ferrous carbonate or iron carbonate, $FeCO_3$, that is produced is listed as PLONOR, i.e. to pose little or no risk to the environment according to the definition of the OSPAR convention Convention[1]. It can precipitate as solid surface scales at the inside of the carbon steel pipeline, creating a protective or non-protective layer scale. Discharging the remainder of the iron carbonate which is present in the solution is possible, as the environmental consequences of discharging are little. However, the ferrous carbonate is brightly yellow-coloured. It is therefore not likely to be the most acceptable solution for the social desirability. Some capture system might be necessary to capture excessive production of the ferrous carbonate.

Figure 4.3: A severe case of CO_2-corrosion on a steel pipeline, image from http://himipex.com/

Using carbon dioxide corrosion to accelerate the pipeline deterioration has potential perks but is accompanied by uncertainties. The corrosion mechanism is widely experienced throughout the industry, and often leads to local defects. The local characteristics of CO_2 corrosion make it a doubtful solution for decommissioning purposes.
The method requires many adjustments to existing facilities an continuous pumping of CO_2 is required. These requirements will have financial impact.
Although the corrosion product is PLONOR, it is uncertain what large volumes will cause on the environment and societal impact.
Furthermore, CO_2 corrosion is a slow process and therefore not the most suitable for the purpose of decommissioning. The accumulation of corrosion product will further decrease the velocity of corrosion. In addition to that, if the pipelines are submerged and filled with water, CO_2-corrosion is minimum. In water saturated conditions the effect of gas corrodent is minimal.

4.1.3. H_2S-corrosion

Another corrosion mechanism that is a widely occurring phenomenon in the oil and gas industry is hydrogen sulphide (H_2S) corrosion. This form of corrosion produces a lot of problems in the oil refinery and gas treatment process. One of the most important factors of the corrosion rate for H_2S-corrosion is the formation of scales on the inside surface of the pipeline. Whereas CO_2-corrosion has a quite straight forward way of producing iron carbonate, for H_2S-corrosion this is more complex.

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[1] The Convention for the Protection of the Marine Environment of the North-East Atlantic, or OSPAR convention, is the instrument that regulates the international cooperation and legislation on environmental protection in the North-East Atlantic. The commissions of the 1972 Olso Convention and the 1974 Paris Convention, both on the prevention of pollution of the marine environment, held a meeting in Paris in 1992. The result of this meeting was the OSPAR Convention and the establishment of the OSPAR commission, which administers the convention and develops policy and international agreements on the marine environment [21].

Hydrogen sulphide in combination with water results in iron sulphide. However, instead of resulting in one end product, as it happens with CO_2-corrosion, the final resulting product can vary in several different forms of iron sulphide and other chemical products. It is therefore hard to predict the resulting scales and corrosion rate of hydrogen sulphide corrosion. The mechanism of H_2S-corrosion is poorly known and the kinetics are therefore difficult to quantify [16].

A proposed mechanism for iron dissolution in water byH_2S-corrosion by Sun and Nesic [17] is as follows given below.
At first, the solid hydrogen sulphide is adsorbed in the aqueous solution. Hydrogen dissociates from the molecule.

$$\mathrm{Fe + H_2S \longrightarrow Fe + H_2S_{ads}}$$

$$\mathrm{Fe + H_2S_{ads} \longrightarrow Fe + HS^-_{ads} + H^+_{ads}}$$

For the following steps, more than one mechanism is proposed. The most basic is where the hydrogen further dissociates from the sulfur. Together with iron, the sulfur produces a form of iron sulphide, mackinawite.

$$\mathrm{Fe + HS^-_{ads} + H^+_{ads} \longrightarrow FeS^-_{ad} + 2\,H^+_{ads}}$$

$$\mathrm{Fe + S^-_{ads} + 2\,H^+_{ads} \longrightarrow FeS_{mackinawite} + 2\,H^+_{ads}}$$

Mackinawite is unstable and is often an intermediate product of this reduction process. Therefore, the mackinawite can result in other forms of iron sulphide. For this research, further detail will not have added value and is therefore not included [27].

This corrosion process can be realised by filling the sealines with hydrogen sulphide. The strong acidic properties of the hydrogen sulphide are a risk to the environment. Usage for the intended purpose is therefore to be approached with caution. It also will affect the pumps and other equipment, which needs to be accounted for in the consideration.
The large-scale use of a sort a like product is expected to raise societal uproar.

Hydrogen sulphide is a strongly acidic chemical and is therefore not allowed to be discharged into the marine environment. As the corrosion mechanism will deteriorate the pipeline, it is inevitable for leakage to occur. Capturing the leaking hydrogen sulphide is necessary though hard to achieve. This solution will therefore likely have a large environmental impact.

4.1.4. Microbial corrosion (MIC)

Micro-biologically induced corrosion (MIC) is a complex and challenging phenomena, associated with the metabolism of microorganisms. Corrosion resistance, microstructural properties, overall performance and service life of metallic surfaces in sea water, fresh waters or soil are affected by the inevitable existence of various types of microorganisms. So far there is no single mechanism identified as playing a major role in MIC corrosion and related chemical, bio-electrochemical and purely electrochemical interactions.

One of the particular cases, where a significant corrosiondamage can be at hand is the anaerobic, sulphur-reducing-bacteria(SRB)-induced MIC. Within MIC corrosion in conditions where anaerobic SRB thrive, the common cathodic reaction is the reduction of water (H_2O) to H atoms. By using some of this H in the conversion of sulphate (SO_4^{2-}) to sulphide (S^{2-}) the SRBs cause depolarisation of the cathodic reaction and the corrosion rate is increased. The generated S 2- promotes absorption of H atoms on the steel. Additionally higher corrosion rates are due to the formed iron sulphides (FeS) which behave as very effective cathodic sites. The result is an increased metal surface heterogeneity, enhanced microcell corrosion and, consequently, enhanced corrosion rate overall.

4.1.5. Galvanic corrosion

Galvanic corrosion occurs when a more electronegative metal is electrically connected to a more noble conductive material. More details on the theory of galvanic corrosion is found in section 3.3.

Galvanic corrosion is to occur on the pipeline, if the steel acts as an anode. Hence, it has to be coupled to a far more noble material which acts as cathode. In the galvanic series (section 3.3) the most noble materials are found at the bottom of the list. These include graphite, gold and platinum.
Considering the costs of these materials, graphite (C) is the most logical choice for this possibility. A schematic presentation of an galvanic couple with steel and graphite is depicted in figure 4.4.

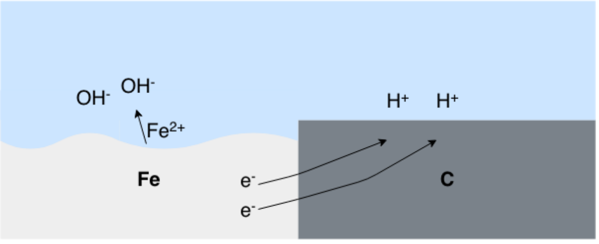


Figure 4.4: Galvanic corrosion of iron (Fe) by coupling with graphite (C)

As the pipelines are buried, it is intended to stimulate the galvanic process from within. This implies that the graphite has to be distributed along the pipeline. It is suggested that the pipeline is filled with graphite gravel or powder. The smaller the particles, the easier the operational implementation. Furthermore, the surface area of the graphite will be larger per volume.

After filling the sealine with graphite and sea water, little further interventions are required. It is however advised to periodically refresh the seawater solution. The minimal operations required have positive effect on the safety and cost.
Furthermore, graphite is listed to be PLONOR [20]. Hence, it is marked to pose little or no risk to the environment. Although graphite as well as iron carbonate are both found in the PLONOR list, the environmental impact should be considered. The large amount of graphite and iron carbonate that can dissolve in the marine environment are noteworthy.
This application of the galvanic corrosion was never investigated before. Therefore, the technical feasibility is uncertain and ought to be further explored.

4.2. Physical damaging

Besides corrosion mechanisms, the steel can also be treated mechanically. In this section we consider some methods to damage or deteriorate the pipelines mechanically. Some methods could also be used in combination with a above mentioned corrosion process, as it might increase the surface area.

4.2.1. Explosives

A possible way of damaging the pipelines is with the help of explosives. However bold it might seem today, a paper from 1996[22] described well abandonment operations with explosives as the 'preferred method'. Explosive methods are cost effective. The debris is mainly small and often covered by the seabed.
Though the paper describes the cost savings and other benefits of the method (mainly for facilities in deeper water), the method also has some severe disadvantages. From a research conducted by NOAA in 2004, there are many lethal effects of underwater explosion on the marine life. Many fish (and other marine life) are killed as the shock wave of the explosion

damage their organs. The radius of lethal consequences can be as large as 350 meters from the facility.

Taking in to account the length of pipelines, this radius will produce a very large area with lethal consequences. Furthermore, the shock wave can cause lung damage and disorientation to sea mammals in the area.

Considering the above mentioned, the use of explosives for decommissioning purposes in the North Sea is not recommended in an environmental point of view [2].

4.2.2. Brittle fracture

The steel pipeline can be forced to break due to brittle fracture. As it is designed not to do so, it has to be treated priorly.

If the temperature of the steel decreases significantly, the steel becomes more brittle. A possible way to achieve this large drop in temperature, is by treating the pipelines internally with liquefied nitrogen. Nitrogen has a boiling temperature of -195,8 degrees Celcius [14]. As this is below the ductile-to-brittle transition, the amount of energy that can be absorbed during impact decreases significantly[26]. According to the ASTM A514 standard, common steel is not recommended for structural use below -46 degrees Celcius.

As the steel enters the brittle regime, the pipe is easily damaged by applying force or rather impulse. Subsequently it will crack and/or shatter. The impulse loading can be applied the same way as for piling operations.

A rather large amount of liquefied nitrogen is to be used to cool the complete pipe sufficiently. Besides, the pumping installations or other equipment to get the nitrogen in place will also experience extremely low temperatures. This affects the technical feasibility as well as the costs of the operation.

4.2.3. Dredging and scratching

The TEPNL pipelines in the North Sea are buried. The backfill on the pipelines is approximately one metre at most locations. This below the mud line. Hence, the soil surrounding the pipelines is firm sand. The burial of the pipeline has ensured the pipelines to stay in place throughout its operation life. Furthermore, the pipelines have a anti-corrosion coating on the outside surface. This is a thin layer of polyethylene or polypropylene. The coating prevents the steel of having contact with the sea water in the soil, a potential electrolyte. In absence of a electrolyte the corrosion process will not occur.

These measures have protected the pipeline against potential hazards over time. However, these are now limiting factors to the degradation of the steel pipeline. Therefore, a proposed method is to get rid of the backfill and damage the coating.

This can be achieved by dredging away the overlaying soil. Due to the depth of the pipeline and the granularity at that depth, jetting might me needed. Once the soil on top (and on the sides) of the pipeline, the coating can be stripped off. A scratching tool has to be used for this.

As the steel is in contact with the sea water, the sea water can act as an electrolyte. Hence, corrosion mechanisms can occur.

For the dredging operations vessels are required. Once the sealines are exposed, the coating must be removed. A concept for a coating removal tool for this particular purpose is currently in development [24]. However, it is not yet operative. The support of one or more vessels is required for the coating removal tool. The requirement of several vessels has its impact on the financial and environmental impact.

Furthermore, once the operations are complete, the pipeline will lay open an bare at the sea bottom. It is however questionable if this sole change has the desired effect of dissolving the steel rather quickly. Without further treatment it is expected that the degradation of the steel at the sea bottom still takes more than a century.

Therefore, the dredging and scratching method is unlikely to have the targeted technical

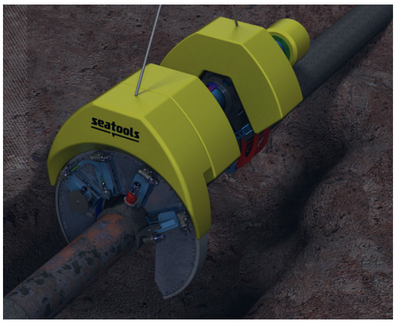


Figure 4.5: The concept of the coating removal tool by Seatools BV. image from seatools.com

feasibility. Together with the rather large financial and environmental impact, this method has little feasibility as an serious alternative for current decommissioning methods.

4.2.4. Crunching or crushing

In the deep sea mining industry the possibilities of excavating precious ores in deep sea regimes is investigated. For this purpose the development of mining ROV's is investigated. The concept is that one ROV is equipped with crunching or crushing hardware at the front. This 'bulk-cutter' looks like an underwater steamroller, but with pins to crush the ore. Once the mineral-rich ore is crushed into smaller debris, an other ROV is deployed to collect the rubble.

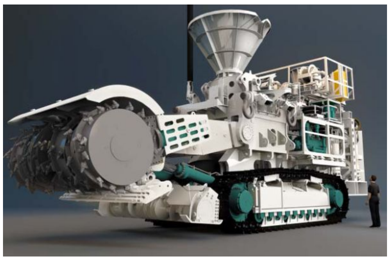


Figure 4.6: An impression of an deep sea bulk-cutter. Image from ethicalmetalsmiths.org

The bulk-cutter, as depicted in figure 4.6, is designed to crush rocky material. Rock has a brittle character and has relative low tensile strength. Steel, on the other hand, is more ductile and has a larger tensile strength. Therefore, the use of a crushing tool is not likely to be sufficient.
More effective could be a sort a like ROV equipped with a crunching tool. Possible concepts for this purpose could make use of two rolls at the front of an ROV rotating in different direction, as is used in industrial metal shredders. An other option is a large hydraulic pincher, which squashes the pipeline. Sort a like hydraulic pinchers are often found on cranes for demolition work.

Although the concept is not yet proven it is deemed feasible from a technical point of view. The crunching of the steel pipeline is expected to have a rather large energy demand. Besides the energy usage the seabed disturbance is a consideration for the environmental impact. The use of ROVs is considered rather safe for subsea operations. However, the the ROVs required are still to be developed and the duration of subsea operations are substantial. These factors contribute to high project cost for this option.

4.2.5. Helix cutting

Most of the methods that use mechanical damaging are aiming to transform the steel pipeline in to smaller bits and pieces of steel. The smaller bits are expected to corrode faster due to a larger surface area and to not pose risk for other sea users.

A considered option is therefore to cut the sealine in sections. Because of the buried state of the sealines, an internal pipe cutter is considered. As cutting the pipeline perpendicular to its axis will merely result in the same situation, but with cuts in the sealine, diagonal cuts are suggested. Two diagonal saws revolving in opposite direction along the pipeline will result in a double helix cut. The pieces of the pipeline will therefore be cut in a chequerboard pattern. This affects the structural integrity of the pipe. During the cutting operations support is required. Hence, a tool ought be developed with sawing and support abilities.

(a) The cutting tool inside a pipeline

(b) An impression of a helix cutting tool

Figure 4.7: The cutting tool with rotating cutter-head for helix cutting, by Enereco [11]

After the completion of the cutting operations, the sealine pieces are still buried under the sea bed. It is likely that the pipe has lost its structural integrity and collapsed under the weight of the seabed.

Although the pieces may not pose threats to users of the sea and are to corrode slowly, it is highly questionable that this is considered a sufficient solution.

4.3. Preliminary discarded options

The methods described in previous section are assessed according to the six predetermined assessment criteria. For some of the methods, initial screening resulted in a severe risk or unwanted consequence regarding on ore more of the criteria. If this is the case, the method is eliminated from further evaluation and not further assessed.

After initial screening six methods are eliminated. These methods are *H_2S-corrosion, explosives, brittle fracture, dredging and scratching, crunching* and *helix cutting*.

For each discarded methods, a brief elaboration on this decision is described below.

H_2S-corrosion Hydrogen sulphide is highly acidic. Due to the corrosion of the sealine leakage is most likely to occur. The H_2S will than leak into the environment, which poses a large risk on the marine life.

This method is therefore disregarded based on its environmental impact.

Explosives Explosives are harmful for the marine life. Within a certain radius is will kill fish and sea mammals. Outside this radius organ damage is still very likely to occur. Considering the substantial length of the sealines, this will endanger a large amount of sea creatures.

Furthermore, the damage imposed on animals is accompanied with a high risk of societal opposition.

This method is therefore disregarded based on environmental impact and societal risk.

Brittle fracture The temperature of steel has to be very low for brittle fracture to occur. This implies that a large amount of energy is required for the preparation of liquefied nitrogen or other cooling method. This has its consequences for the environmental and financial impact of the project.

This method is therefore disregarded based on environmental impact and cost.

Dredging and scratching The operations required for the dredging and scratching method are technically feasible. A concept specifically for a subsea coating removal is currently in development. However, once the pipeline is exposed and the coating is stripped, it is unlikely that the pipeline degradation occurs as much as desired. Besides, the operations required are within the same spectrum as the, already proven technology, cut-and-lift decommissioning. **This method is therefore discarded based on technical feasibility.**

Crunching Crunching of the steel pipeline will require a large amount of energy. The duration of the project will be substantial, which also implies any emissions of the supporting fleet. Additionally, a ROV with the suitable equipment and sufficient power is not yet available. A ROV with the rights specifications has first to be developed.
Therefore, this method is disregarded based on environmental impact and cost.

Helix cutting For helix cutting a new tool is to be developed. The tool requires strong cutting equipment as well as structural support abilities during operation. The operational feasibility to fit such an internal device and the retrieval of the cutting tool are questionable. Besides, the operation results in having cut pipeline sections under the seabed. This is unlikely to be sufficient to be considered a decommissioning method.
Therefore, this method is disregarded based on technical feasibility.

4.4. Assessment score

The methods for accelerated pipeline degradation are evaluated according to the same method as the current decommissioning options in section 2.3.3. The awarded scores are listed in table4.1.

Alike the assessment of the existing decommissioning methods, the weighted score per criterion is the max score proportionally to the assessment score. The total score is rounded and found at the rightmost column.

	Technical impact	Environmental impact	Safety	Societal	Cost	Sustainability	Total score
Max. score	13,3	13,3	33,3	20,0	13,3	6,7	
CO2 corrosion							
Assessment score	3	3	3	3	3	3	
Weighted score	8,0	8,0	20,0	12,0	8,0	4,0	**60**
Galvanic corrosion							
Assessment score	3	5	5	3	5	1	
Weighted score	8	13,3	33,3	12,0	13,3	1,3	**81**
MIC							
Assessment score	3	1	3	1	5	1	
Weighted score	8,0	2,7	20,0	4,0	13,3	1,3	**49**
Reversed IC							
Assessment score	3	3	3	1	1	3	
Weighted score	8,0	8,0	20,0	4,0	2,7	4,0	**47**

Table 4.1: Comparative assessment of accelerated degradation decommissioning methods

In table 4.1 the total weighted scores of the accelerated degradation methods are listed. The most suitable option is to accelerate the steel degradation by **galvanic corrosion** with a total weighted score of **81**.
As concluded in section 2.3.3 on page 13 in situ decommisionning is set as the base case. The assessment score for in situ decommissioning is 79. The galvanic corrosion method is the only score surpassing the score of the base case.

The relative little operations that are required to induce the galvanic corrosion methods is beneficial for its assessment score. Due to the little interventions it has little negative impact on safety and cost. Furthermore, due to the choice for graphite as cathodic product, the project cost and environmental risk are not negatively affected. The technical feasibility needs to be investigated more closely to make an estimate on its effectiveness.

The galvanic corrosion decommissioning mainly differentiates from the other options on cost, safety and environmental considerations.
The effect of inhabiting large amount of microbes the marine life is considered risky. The side effect on marine life or nearby offshore activities is uncertain.
T For the reversed ICCP to be technically feasible the required energy is a determining factor for the project cost.
Carbon dioxide corrosion scores quite average on all criteria. The many adjustments and the continuous pumping required are a negative side note for this option.

5

Lab tests: set-up, measurements & test plan

5.1. Introduction and motivation

In chapter 4 various degradation methods are discussed. These optional methods are ranked using a comparative assessment. The results of comparative assessment are listed in table 4.1 in section 4.4. It is concluded that further investigation of the galvanic corrosion method can be worthwhile.

As discussed in chapter 3 corrosion of a pipeline in seawater occurs due to the formation of electrochemical cells. The driving force in an electrochemical cell is a potential difference between the anode and the cathode. This and other parameters that influence the electrochemical corrosion process and galvanic corrosion are discussed in section 5.1.1 below. An overview of which parameters are included for investigation are listed in table 5.1.
Lab tests are conducted to obtain a quantitative insight in the galvanic corrosion. Measurements of open circuit potential, polarisation resistance and mass loss are performed. The test methods are elaborated in section 5.4. The results of this measurements are found in chapter 6.

5.1.1. Parameters

Galvanic corrosion is dependent on several parameters. In a laboratory setting all these parameters can be investigated to conclude how they influence the corrosion process. However, in the practical situation not every parameter is easily manipulated. Therefore, the parameters are evaluated on how they can contribute to the sealine decommissioning.

The main parameters are discussed below along with the justification to include or exclude them of the lab tests. If a parameter is excluded from the research, the aim is to keep it reasonably constant throughout the tests. These parameters and justification are summarised in table 5.1.

Parameter	In/excluded	Justification
Potential difference	Included	Judge on the driving force for galvanic corrosion
Surface area ratio	Included	Effect on galvanic corrosion rate
Conductivity of electrolyte	Excluded	Maintained constant in view of the cell geometry in lab tests
Material composition of anode	Excluded	Kept as constant as the sealines are composed of carbon steel
Temperature	Excluded	Kept constant as temperature at sea bottom is hard to influence

Table 5.1: Main parameters and their contribution to the tests

Potential difference and anodic index

The potential difference is the driving force of the corrosion cell. With the aim on accelerating the corrosion of the steel pipeline, the larger the difference between the two materials the better. For galvanic corrosion, the potential difference is dependent on the materials coupled to each other. The steel pipeline is the subject to the accelerated degradation, and is therefore fixed as the intended anode. Therefore, the material choice for a cathode is the parameter to be determined.

To create a large potential difference, the steel is to be coupled with a far more noble material than the steel itself. In figure 3.4 on page 20, the galvanic series are discussed. For instance, more noble metals as titanium (Ti), platinum (Pt), gold (Au) and graphite (C) can act as cathodes if coupled to the more electronegative steel.

As already introduced in chapter 3, another point to consider with respect to the objectives of this work is the so-called *anodic index* of metals, but considered in from a inverse point of view. The anodic index for Fe or low carbon steel is $-0,85$ V. This implies that a steel pipeline, electrically coupled to a metal with a noble potential (e.g. Au, Pt, C, Ti) will actively corrode in harsh environment, such as sea water.

Preliminary tests were performed with a noble, yet active material, mixed metal oxide (MMO) Ti. The half-cell potential of MMO Ti in sea water is ca. +110 mV (vs SCE). MMO Ti is normally used as anode for ICCP applications, hence widely available as an engineering material. Results of these tests are briefly presented and discussed in chapter 6, in order to shed light on the results and discussion for the final choices made of the galvanic couples in this work. Carbon for instance was chosen as the most feasible material in view of pipeline decommissioning, although results are also compared to the performance of Pt as a cathode in a galvanic couple with steel.

Surface area ratio

Besides the potential difference, the surface area ratio of the anode to cathode is also of influence for the corrosion rate. A small anode in contact with a (large) cathode would result in an enhanced corrosion rate of the anode. Inversely, a large anode, coupled to a small cathode will result in a marginal increase of the corrosion rate of the anode. At equal (or comparable) surfaces of the anode and the cathode (e.g. at a ratio of 1:1), the corrosion rate of the anode will depend on the external medium and the potential difference between the two metals. In view of galvanic corrosion principles only, a potential difference of < 50 mV results in a marginal increase of corrosion rate. The above principles are considered during the lab tests, maintaining a sequence of proportional increase of the cathodic surface, compared to the anodic one, but also considering the concepts of galvanic corrosion and the anodic index of metals.

Conductivity of the electrolyte

A conductive electrolyte is a necessity for a corrosion cell. A decrease in conductivity of the electrolyte also leads to a decrease in corrosion rate [4]. The aim of this research is to judge on the enhanced rate of corrosion due to galvanic coupling rather than the effects of the electrolyte itself. Therefore the conductivity of the medium is maintained stable: the solution is refreshed daily with a artificial seawater.

Material composition of the anode and the cathode

As aforementioned, the occurrence and rate of galvanic corrosion is dependent on the materials used for both anode and cathode. Steel was of interest in this work as an anode. Steel comes in many different types, e.g. low carbon steel, alloy steel and stainless steel. These types differ in used mixture and within the types several different compositions exist. The sealines addressed in this research are of low carbon steel. The lab tests are therefore conducted with similar steel grade, St37.

Temperature

The corrosion rate is also dependent on the temperature. A 2016 study [8] investigated the galvanic corrosion behaviour of high strength steel in sea water. The corrosion of the steel samples were measured for temperatures varying form 0 ° C to 65 ° C. The research concluded an increase of the galvanic current density with increasing temperature. The current density at 65 ° C was about three times higher than the current density at 0 ° C.

Though this result offers opportunities to increase the corrosion current density, it is not useful for the aim of this research. Temperature will therefore not be an parameter in the conducted lab tests.

The study does however provide an insight to the difference in corrosion potential with respect to temperature. It shows that after being exposed to sea water for 72 hours or more, the differences in corrosion potential in conditions of 5, 15 and 25 ° are minimal [8]. In other words, the temperature does not affect hte corrosion significantly.

Ideally, the lab tests are to be performed at the same temperatures as the sea water in the North Sea. Since the temperatures very over the year, this would have some complications for the lab tests. Therefore, an average sea water temperature of 10 ° C is assumed. Considering the little variation in corrosion[8] and for the sake of simplicity, the test are performed at room temperature of about 20 ° C.

5.2. Test plan

The test plan is designed to investigate the effect of the galvanic coupling of steel. The main parameters that influence the corrosion are considered to be the potential difference, surface area ratio, conductivity of the electrolyte, material composition and the temperature. Based on the practical situations with the corrosion of the sealines, these parameters are evaluated to be either included or excluded in the lab tests, as found in table 5.1. First, preliminary tests are conducted as described in section 5.2.1. Subsequently, relevant test cases are designed, as elaborated in section 5.2.2.

5.2.1. Preliminary tests on galvanic coupling

Initially, some preliminary test were performed. The purpose of these preliminary tests was to evaluate the corrosion activity of steel alone and how this activity changes when a galvanic couple with a more electropositive material is at hand. The preliminary tests served the purpose of fast screening with materials, readily available for lab practice in corrosion research and prior to the tests with the finally chosen cathodes, i.e. Pt and carbon.

A steel electrode was for that purpose electrically connected to mixed metal oxide (MMO) Ti. The ratio between anode (steel) and cathode (MMO Ti) was maintained at 1:1. Additionally, the corrosion activity for the steel electrode, other than galvanic corrosion-induced, was monitored. Diffusion limitations with the formation of corrosion products over time was observed and the results served as a basis for data interpretation of the subsequent test series.

Additionally, surface treatment of the used electrodes was assessed for its importance. For instance, an outcome of these preliminary tests on replicate steel electrodes was that sample preparation (steel surface) needs to be as identical as possible. This aspect was later-on considered in the galvanic couples of Fe|Pt and Fe|C.

5.2.2. Test cases: Fe, Fe|C, Fe|Pt

The tests are conducted to monitor the difference of the corrosion of steel alone and the corrosion of steel in a galvanic couple with a more noble metal. The research aims to investigate the influence of the potential difference between the anode and the cathode and the effect of surface area ratio.

Therefore, first the base case is considered. This is steel only, without any coupling. Subsequently, the steel is coupled to more noble materials, graphite and platinum. This provides a potential difference.

Besides the potential difference it is also within the interest of this study what the influence of the surface area is. Therefore the tests with galvanic couples are also performed with twice the surface of the cathode.

Test case	Discription	Parameter involved
Fe	Steel sample in salted water	Base case
Fe|C	Steel sample connected to carbon in salt water	Potential
Fe|2C	Steel sample connected to carbon with twice the surface area as Fe|C in salt water	Surface area effect
Fe|Pt	Steel sample connected to platinum in salt water	Potential
Fe|2Pt	Steel sample connected to platinum with twice the surface area as Fe|Pt in salt water	Surface area effect

Table 5.2: Description of test cases and involved parameters

The experimental set-up for Fe|C and Fe|Pt are depicted in figures 5.1 and 5.2 respectively.

Figure 5.1: The Fe|C cell

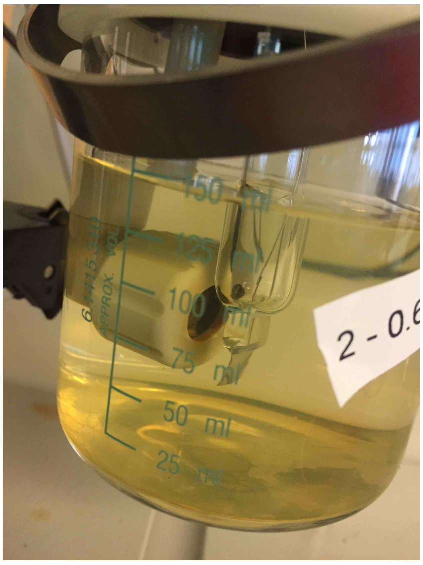


Figure 5.2: The Fe|Pt cell

Fe|Pt and Fe|2Pt are added to have reference results for the galvanic coupling of the steel sample to an additional noble material. However, as platinum is expensive it is not considered a feasible solution for the practical problem.

5.3. Test set-up

Lab tests are conducted to quantify the corrosion rate of the galvanic couple. The used configuration is a standard three-electrode cell configuration. A schematic image of the cell is depicted in figure 5.3.
The components of the cell are discussed in the section 5.3.1. The assembling of the cell is discussed in section 5.3.2.

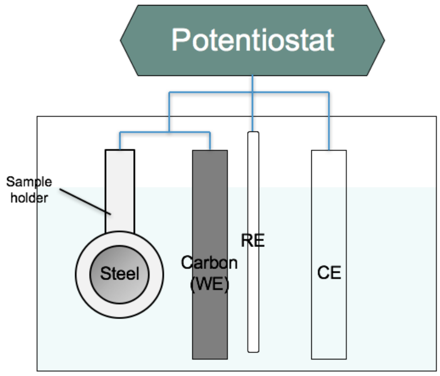


Figure 5.3: Schematic view of the Fe|C cell

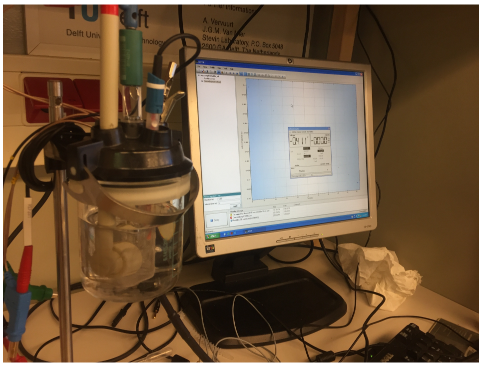


Figure 5.4: A connected cell with the measuring device

5.3.1. Components of the test cell

The cell consists of a working electrode (WE), a reference electrode (RE) and a counter electrode (CE). The electrodes are connected to a the equipement. Furthermore, the cell is filled in with an electrolyte.

Working electrode The working electrode is the electrode for which the electrochemical parameters are recorded. For this research the corrosion of carbon steel alone or as a galvanic couple were investigated. Hence, the WE in this work is either steel alone (test case Fe) or the galvanic couple (test cases *Fe|C, Fe|2C, Fe|Pt* and *Fe|2Pt*).

For Fe, the working electrode consists of a steel sample which is mounted in a sample holder. The sample is connected to the potentiostat by insulated wires within the sample holder. The exposed surface area of the sample is a circular area with a diameter of 1 cm, i.e. an surface area of approximately 78.5 mm^2.

For Fe|C, Fe|2C, Fe|Pt and Fe|2Pt the steel sample is electrically coupled to a more noble material. This is done by connecting a wire to the sample holder at one side and to a carbon or platinum electrode on the other side. The surface area in contact with the electrolyte is therefore the exposed surface area of the steel sample plus the surface area of the more noble electrode.

For these cases, the working electrode therefore consists of both steel and an other material. As discussed in chapter 3, the half-cell potential can not be measured directly. Hence, the measured values are not just from the steel sample, but for the couple. This has to taken into account for the estimation of the corrosion rate, later in this report (section **??**).

Reference electrode The reference electrode is an essential part of the three-electrode cell. This is the electrode versus which the potential of the unknown WE is measured. It is an electrode which has a stable and well-known electrode potential.

For the discussed tests a saturated calomel electrode (SCE) was used. The calomel electrode is a type of a (stable) half-cell in which the electrode is mercury coated with calomel (Hg_2Cl_2) and the electrolyte is a solution of potassium chloride and saturated calomel. In the calomel half-cell the overall reaction is:

$$\mathrm{Hg_2Cl_{2(s)}} + 2\,\mathrm{e^-} \rightleftharpoons 2\,\mathrm{Hg_{(l)}} + 2\,\mathrm{Cl^-} \qquad (5.1)$$

Counter electrode The counter electrode, or auxiliary electrode, is used to polarise the working electrode. The purpose of the counter electrode is to complete the circuit, allowing charge to flow. Polarisation is needed, so that the WE is taken away from its equilibrium condition. Polarisation allows the performance of an electrochemical test in which the corrosion rate is quantified, e.g. a linear polarisation resistance (LPR) method can be used. More detail on the LPR measurements is given in section 5.4.

The CE needs to be produced from a inert material. The surface area of the CE has to be at least twice as large as the working electrode's exposed surface area. Ideally, the shape of the counter electrode mirrors the shape of the working electrode. This is to ensure a proper polarisation of the WE.

In these lab tests, a tubular platinum mesh was used. For the galvanic couples to allow for a proper polarisation of the (larger in this case) WE, while a Pt sheet electrode (figure 5.2), when tested alone.

Equipment The equipment used for the measurements is a Metrohm Potentiostat 203N.

Electrolyte The electrolyte is the conductive medium in which the electrodes are submerged. To mimic the seawater in which the pipelines are situated, a 3.5 mass-percentage NaCl solution is used.

5.3.2. Preparation of the corrosion cell

The research consists of various test where several parameters are altered for each measurement. For each tests a new carbon steel sample is used. For the results to be reliable, the steel samples have to be identical, with respect to geometry, surface finish etc. Therefore the steel samples are ground and polished in an identical way before immersing in the electrolyte. The grinding is done using four different grinding papers with different grit size. Grinding was performed for equal time, imposing the same pressure and identical alteration of the orientation of the sample over the grinding paper. Furthermore, the samples are cleansed .

Meanwhile the corrosion cell is assembled according to the schematic representation in figure 5.3. The cell consists of a glass vessel with a lid. The cell is filled with the 3.5 %mass-NaCl solution. The glass vessel and the volume of the solution are identical for each prepared cell. The lid contains prefabricated holes to fit the electrodes. The reference electrode is placed in one of these holes.

The clean steel sample is weighted and placed in the sample holder. The sample holder is placed in the cell. The sample holder is clamped to the lid to secure its position. If required, a galvanic couple is made by connecting the sample holder to a carbon or platinum electrode. Once all the other electrodes are in place, the counter electrode is placed. As mentioned previously, a tubular-shaped platinum mesh is used as CE. Therefore, the CE is carefully placed so the other electrodes fit in its diameter. Attention should be paid to the position of each electrode as they should not make direct contact.

When all electrodes are in place, they are connected to the potentiostat. Once they are all connected correctly, the measurements can commence.

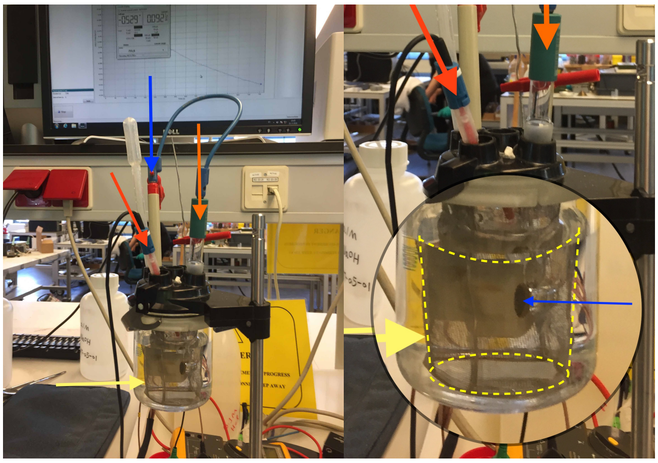
Photos of a assembled Fe|Pt cell are depicted in figure 5.5. In figure 5.5a on the left, the electrodes inserted in the cell are marked with coloured arrows. The working electrode is indicated with a blue arrow and the platinum electrode with an orange arrow. They are connected with the blue wire. The reference electrode is marked in red. In the cell, at the bottom of the photo, the counter electrode is shown with a yellow marker. In figure 5.5b the cell is enlarged. Here the cylindrical shape of the counter electrode can be distinguished. The small blue arrow marks the steel sample of the working electrode.

5.4. Measurements

Several measurements are conducted throughout the test procedure. These include measurements of open circuit potential, linear polarisation resistance and mass loss.

5.4.1. Open circuit potential (OCP)

The open circuit potential (OCP) is the electrode potential of the working electrode with respect to the reference electrode when no external current is applied. It is the difference in potential between WE and RE.



(a) The Fe|Pt cell with working electrode, Pt electrode, reference electrode and counter electrode

(b) The cylindrical CE is fit around the other electrodes. The steel sample of the WE is visible at the blue arrow

Figure 5.5: An assembled Fe|Pt cell with the relevant electrodes.

OCP is a thermodynamic parameter and tells something on the tendency of the working electrode to participate in a corrosion reaction. Metals with a more positive OCP are less willing to give up electrons, thus less likely to corrode.

In figure 5.6 the OCP of a steel sample is depicted. On the vertical axis the potential of the working electrode is shown. The time since the start of the measurement is shown on the horizontal axis. The measurement is chosen to last 20 minutes, i.e. 1200 seconds.

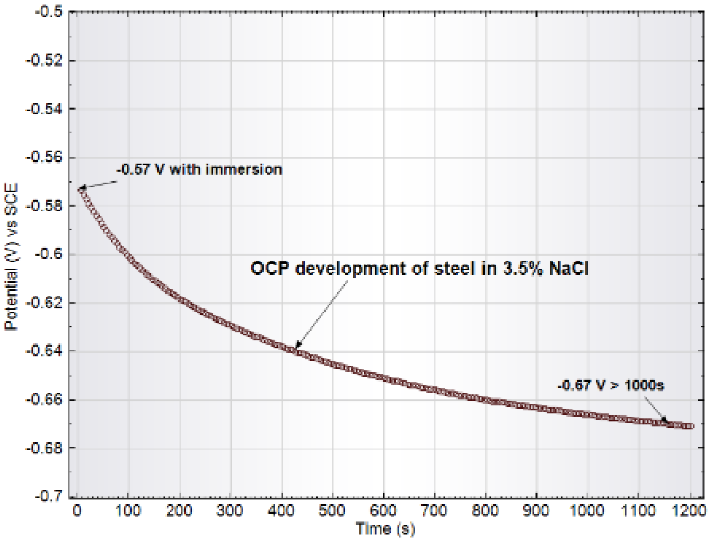


Figure 5.6: The OCP of a steel sample in time

The corrosion process starts as soon as the sample is in contact with an electrolyte. As the corrosion processes occur, the OCP gradually shifts to a steady value, as can be seen in figure 5.6. For the depicted OCP measurement, this change in potential over time is clearly visible. The curve starts at $-0,57$ V and evolves toward more negative values quickly. After some time, the OCP develops more gradually as the equilibrium condition is approached.

As stated previously, the open circuit potential indicates the tendency of the metal to participate in the electrochemical corrosion with the electrolyte. The OCP of the different test cases are compared later in this report. A more cathodic (a more negative) potential will reflect an enhanced corrosion activity.

More important is that the OCP needs to be stable before the LPR measurements can commence. Therefore, the OCP measurements are always conducted prior to the LPR measurements. The LPR measurement is elaborated in the next section.

Open circuit potential (OCP)

- Potential difference between working electrode and reference electrode.
  No external current is applied.
- Thermodynamic parameter that tells something about the tendency to corrode.
  → The more negative the OCP, the more likely the electrode is to corrode
- OCP has to be stable to perform LPR measurement.

5.4.2. Linear polarisation resistance (LPR)

For the LPR measurement the potentiostat applies an external potential. This polarises the working electrode, i.e. the electrode potenital is forced away from its OCP. Due to the induced electrochemical reactions at the electrode surface, a current starts to flow. The potential applied is in the range from -20 to +20 milivolts from the OCP.
With this test the polarisation resistance R_p can be obtained. The expression of the polarisation resistance is:

$$R_p = \left(\frac{\Delta E}{\Delta I}\right)_{\Delta E \to 0} \tag{5.2}$$

Where ΔI is the variation in the electric current resulting from the applied change in cell potential, ΔE. With ΔE in volts and ΔI in ampère. Hence, the polarisation resistance R_p is expressed in ohm (Ω).

The polarisation resistance can be calculated by performing a linear regression on the data as depicted in figure 5.8. The value of R_p can be calculated from the inverse of the slope.

From the polarisation resistance the corrosion current can be determined using the Stern-Geary equation:

$$I_{corr} = \frac{B}{R_p} \tag{5.3}$$

Where B is determined from experimentally derived Tafel constants. If the Tafel slopes are known, B can be determined by:

$$B = \frac{1}{2,303} \frac{b_a b_c}{b_a + b_c} \tag{5.4}$$

The result of a LPR measurement is shown in figure 5.7. The current I is shown along the logarithmic vertical axis. The cell is polarised in linear steps along the horizontal axis. The resulting current due to the polarisation is plotted along the vertical axis at the respective potential. In the middle of the horizontal axis the current decreases to zero. This is at the open circuit potential. As the polarisation is zero at OCP, the current due to the polarisation also equals zero.

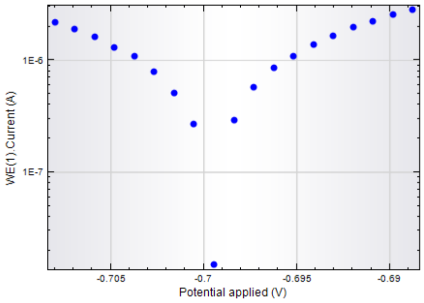


Figure 5.7: LPR measurement of a steel sample.

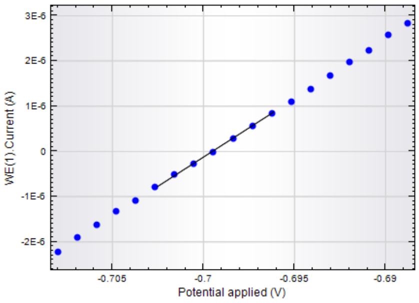


Figure 5.8: Linear regression plot

Linear polarisation resistance (LPR)

- Polarises the sample around OCP.
- Polarisation resistance (R_p) is determined from the slope of the resulting current vs. potential
- Parameter B is experimentally derived from Tafel constants or linear regression.
- Corrosion current (I_{corr}) determined from $\frac{B}{R_p}$

5.4.3. Mass loss measurement

On all samples a mass loss measurement is performed for comparative purposes. The mass loss measurements on these samples are however **not according to scientific standards**. Therefore, the results are not to be used as absolute values, but merely as an indication and a comparison of equally handles specimens after various treatments. Besides, the mass loss is influenced by localised corrosion in parallel to galvanic corrosion.

Before placing the steel sample in the sample holder the steel sample is weighted on a scale. This is done on a analytical balance with a precision of 10^{-4} grams. Subsequently, the sample is placed in the electrochemical cell and treated accordingly to its designated test plan. Once the test plan is completed, the sample holder is taken out of the solution. The sample is flushed with ethanol. The sample is taken out of the sample holder and the ethanol evaporates. The clean and dry sample is again placed on the analytical balance. It mass is subtracted from the precious measurement to obtain the mass loss.

Mass loss measurement

- Samples are weighted prior and after treatment.
- Not according to scientific standards
- For comparative purposes between different treatment of samples

5.5. Test matrix

As discussed in section 5.4 measurements are conducted on open circuit potential and linear polarisation resistance. Subsequently the mass loss is measured.

The OCP and LPR of the different test cases are to be measured. This is done initially (i.e. after immersion and OCP stabilisation), after 24 hours, after 48 hours and 72 hours.

Once the measurements are finished, the mass is measured for the mass loss evaluation. It is to be noted that that this is after the LPR measurement and therefore is affected by the applied polarisation.

A schematic presentation of the time line of the measurement procedure of Fe is given below. The same measurement procedure is used for the other test cases.

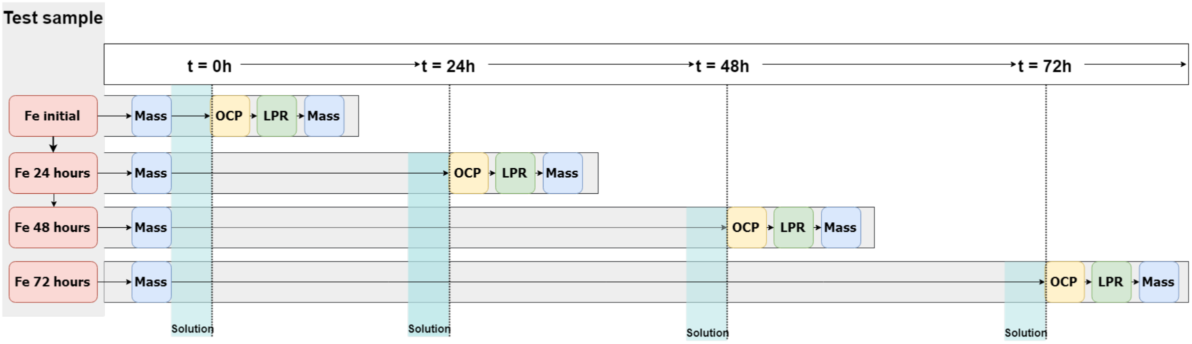


Figure 5.9: A schematic time line of the measurement procedure for the Fe test case.

5.6. Expected behaviour

The lab tests are to provide more quantitative results on galvanic corrosion. They are the first step to assess the option of accelerated sealine degradation discussed in section 4.1.5. The aim of the accelerated degradation by galvanic corrosion is to contribute to pipeline decommissioning purposes. It is therefore beneficial if the corrosion rate increases, such that the remaining period of the sealine is diminished.

Test case Fe is the base case for the lab test and represents the sealine as is. Test cases Fe|C, Fe|2C, Fe|Pt and Fe|2Pt are where a more noble material is coupled to the steel. The lab test are expected to show an accelerated corrosion for the galvanic coupled test cases.

The expected results per measurement are listed in table 5.3 below. The arrows indicate whether an increase (↑) or a decrease (↓) with respect to the base case of the measured value is expected.

	OCP	R_p	$I_c orr$	Corrosion rate
Fe	Base case			
Fe|C	↓	↓	↑	↑
Fe|2C	↓↓	↓↓	↑↑	↑↑
Fe|Pt	↓	↓	↑	↑
Fe|2Pt	↓↓	↓↓	↑↑	↑↑

Table 5.3: Expected values of measured values with respect to the base case.

In table 3.4 on page 20 low carbon steel is listed als mild steel or low alloy steel. From this table, we can determine that the OCP of the base case is expected to be somewhere in the range of $-0,55$ to $-0,7$ volt. Subsequently, by connecting a more noble material the tendency of the steel to give up electrons increases. It is expected to result in relevant OCP changes. A decrease of polarisation resistance is also expected. The corrosion current is inversely proportional to the polarisation resistance, and therefore is expected to increase. An increase in corrosion current results in an larger expected corrosion rate.

6

Lab tests: results

This chapter summarises the outcomes from lab tests on galvanic corrosion, related considerations and discussion per test series. Main conclusions are also included where relevant, for the purpose of clarifying choices made towards the final conclusion and outcome of this report.

6.1. Results of preliminary tests

As introduced in chapter 5, the preliminary tests served the purpose for optimisation of the final experiments. Preliminary tests were performed on steel alone, steel coupled to MMO Ti, and steel coupled in a ratio of 1:1 with Pt and 1:1.5 with C.

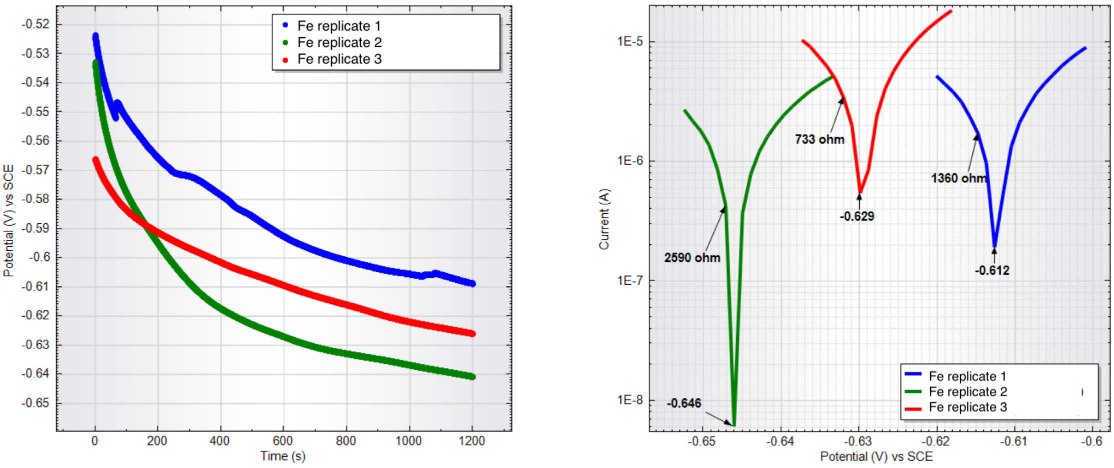
6.1.1. Steel surface preparation effect

Figure 6.1 a and b depict the OCP evolution and the LPR test results for three replicate steel electrodes, where grinding of the samples was executed in the same manner but not for identical timing.

As can be observed, variation of initial potential was relevant, where replicate 3 starts at a more cathodic (negative) potential, compared to replicates 1 and 2. Over time and at the end of the monitoring period ($1200s$) the potential difference between the replicates is 20 to 40 mV. Although surface heterogeneity for otherwise identical steel samples would also account for variation of OCP in time, the results show that sample preparation is important for obtaining reliable and reproducible results.

Figure 6.1b shows these effects on corrosion activity. The replicate 2 presents the most negative corrosion potential of -646 mV, but lowest corrosion current (highest polarisation resistance R_p, respectively, of 2.6 kOhm). The samples 1 and 3 depict variation in R_p values corresponding to their OCPs. A more noble OCP (or E_{corr} during LPR) of $-612mV$ (sample 1) is accompanied by a lower corrosion current and higher R_p of ca. 1.4 kOhm. Sample 3, with a potential of -629 mV presents the highest corrosion activity with an R_p value of 733 Ohm. Consequently, a discrepancy is observed as follows: the most cathodic potential for replicate 2 would normally account for the highest corrosion activity, whereas the most noble potential (replicate 1) would account for the highest corrosion resistance. The relation of OCP and R_p, however, is not straightforward and figure 6.1 proves this (general) dependence and outcome. The OCP is a parameter that gives an indication only of corrosion activity.

In contrast, the kinetics of both oxidation and reduction reactions on the steel surface determine the corrosion activity of the sample in the relevant medium. As seen in figure 6.1b, limitations of the anodic reaction were relevant for replicate 2 (compare the slopes of the anodic portions of the curves, after E_{corr}), resulting in lower corrosion activity for this sample, despite the most cathodic potential. Replicate 3, for which the highest corrosion activity was recorded, was perhaps the most active one from the very beginning of immersion.



(a) The OCP recordings of the preliminary tests

(b) The LPR recordings of the preliminary tests

Figure 6.1: Recordings of preliminary tests of three replicate steel electrodes

This is because the OCP for replicate 3 is the most cathodic one with immersion (figure 6.1a), meaning that this replicate was subjected to a more thorough surface treatment. A clean steel surface would be a more active one, when in contact with the medium.

The conclusions from the above results and preliminary screening are as follows:

- OCP is only an indication for corrosion activity (since it reflects the probability of a corrosion process, also linked to the principles of corrosion thermodynamics)
- Corrosion activity depends on the kinetics of both oxidation and reduction reactions (corrosion kinetics is reflected by the LPR tests in this work). If one of these reactions, or both, are limited, the overall corrosion activity would be reduced. This conclusion reflects, in fact, the well-known fundamental mechanism of electrochemical corrosion. It is, however, here mentioned in order to address the effects of surface finish and the results in Fig.2b);
- Sample surface preparation is important and will affect the reproducibility and reliability of measurements and results. This is especially the case, where a non-significant variation in corrosion activity is expected;

Consequently,if the steel surface finish for different electrodes is not 100% identical, it is logic that a small variation of OCP will not substantiate significant effects and is not conclusive. Maybe more accurate is to state, that only a sustained potential shift and a potential trend are to be discussed and compared, rather than absolute values. This approach was followed later on with respect to the results and discussion for the performance of the galvanic couples of steel with C and Pt in proportionally increased area of the cathode.

6.1.2. Diffusion limitations

When a steel electrode is immersed in NaCl, it is expected that corrosion activity will start and enhance over time. Figure 3 depicts an overlay of LPR curves, taken initially 24h and 72h of treatment of steel in the model medium of 3.5% NaCl. What can be observed is that after an initially more noble, yet active potential of ca. -695 mV (initial Fe in the plot), the potential shifts cathodically towards values in the range of -740 mV after 24h and 72h. The corresponding corrosion activity is higher in the first case and lower (and almost identical) in the latter two cases. Observation of figure 6.2 shows that the initial corrosion current is approximately one order of magnitude higher, compared to the later time intervals. Quantitatively, the linear regression of the curves results in values of 0.2 kOhm for the initial stage versus 1.4 kOhm and 2.2 kOhm for the later stages with the highest R_p for the time interval of 72h.

In other words, despite the cathodic shift in corrosion potential the corrosion activity decreases in the time frame of this experiment. (of course, to be noted is that the magnitude of corrosion currents for all three time intervals present active steel surface, since current density $< 0,1\ \mu A/cm^2$ is the threshold of passivity).

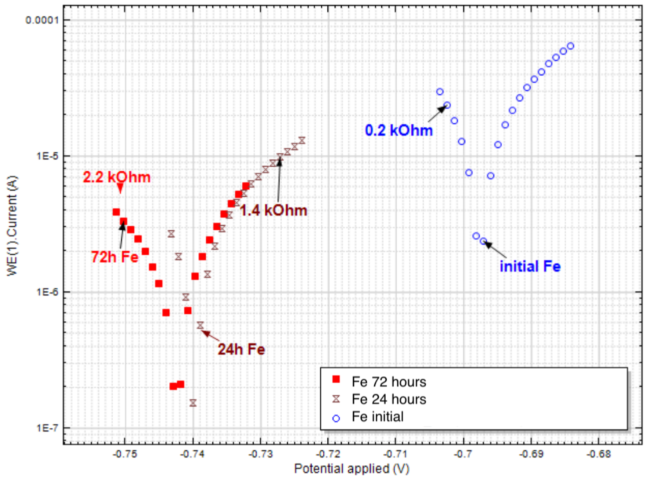


Figure 6.2: LPR test results on steel in 3.5% NaCl after initial immersion (20 min after OCP stabilisation), 24h of treatment and 72h of treatment.

The above observations are in line with, and an illustration of, the previous discussion on limitation of oxidation and/or reduction, resulting in variation of corrosion activity. The limitations here are a consequence of corrosion products formation and accumulation on the steel surface (including, and/or as opposed to localised corrosion propagation and pit growth in this medium).

Initially and after 24h, the LPR results show anodic control, i.e. limited anodic reaction due to corrosion products formation (the slope of the anodic curves is in the range of 24 to 27 mV/dec). This means that the oxidation process is similar at the initial and 24h time intervals. The reduction reaction, though, is enhanced from the initial to the 24h time interval of treatment, as evident from the slope changes for the cathodic branches of the curves - from 10 mV/dec initially to 6 mV/dec after 24h. At the end of the test, i.e. 72h, the steel corrosion process presents a mixed control, with anodic and cathodic reaction rates almost similar (anodic slope of 14 and cathodic slope of 16 mV/dec at 72h).

In other words, with treatment and due to corrosion products accumulation on the surface, the anodic reaction becomes impeded, while the cathodic reaction is enhanced – this results in a drop of overall corrosion activity between the initial and 24h time interval. After 72h, oxidation is enhanced, while the reduction is impeded, resulting in corrosion activity at 72h, similar to the one after 24h.

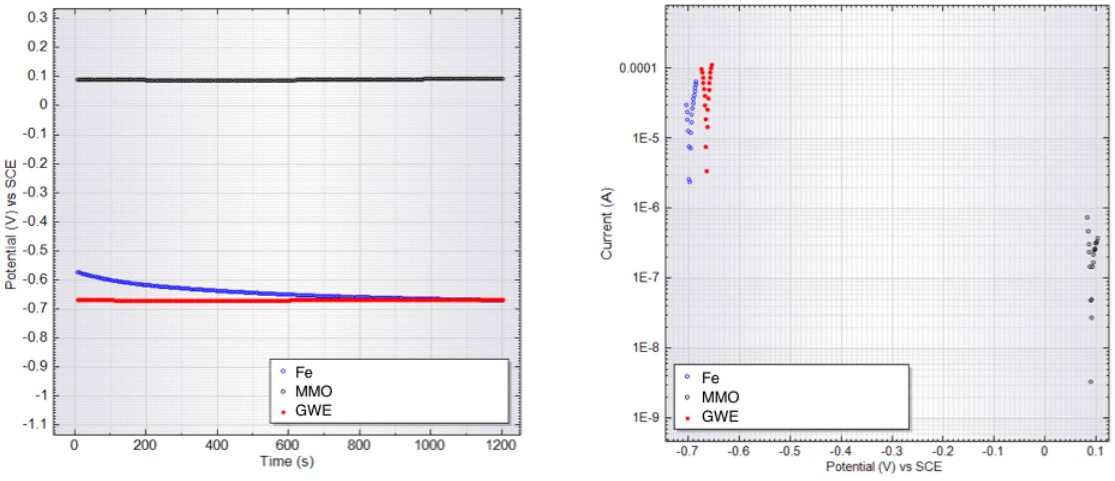
The above results and considerations are important in view of the results and discussion for galvanic couples in the following sense:

- The corrosion activity of a galvanic couple will depend on both oxidation (occurring at the anode) and reduction (occurring predominantly at the cathode);
- Limited oxidation (e.g. due to corrosion products accumulation) will result in reduced corrosion activity overall – this does not mean that the cathode is not active as such. It is rather an indication for re-distribution of the potential difference between the anode and the cathode;

- Similarly, a cathode with higher efficiency for supporting the reduction reaction (of higher catalytic activity) will be more effective in enhancing the corrosion rate, i.e. increase in the rate of reduction will result in increase of corrosion activity at the anode;
- The rate of oxidation and reduction, therefore, are not only dependent on the potential difference or surface ratio as driving forces, but are also largely affected by the reaction kinetics on both the anode and cathode;
- While the mixed potential for a galvanic couple will give an indication of corrosion activity (active or passive state) it cannot be used as a straightforward judgement on increased or decreased galvanic corrosion effect, specifically in a narrow range of potentials. A sustained cathodic shift, supported by increasing corrosion current, would rather justify a continuous corrosion activity due to galvanic coupling.

6.1.3. Galvanic coupling

As aforementioned, preliminary tests on galvanic coupling of steel and a readily available electropositive (noble) material were conducted in order to fine tune the subsequent experiments. Figure 6.3 presents the results for steel, MMO Ti and the galvanic couple steel with MMO Ti in a surface area ratio of 1:1. The LPR results in figure 6.3b were recorded after 20 min OCP stabilisation for all cases (figure 6.3a).



(a) OCP measurements

(b) LPR measurements

Figure 6.3: OCP (a) and LPR (b) results for steel, MMO Ti and the galvanic couple steel/MMO Ti in NaCl solution

As seen from the plots, the potential difference between steel and MMO Ti is significant, ca. 700 mV. The MMO Ti presents a stable noble potential of ca. 100 mV, while steel stabilises around -680 mV after 20 min (figure 6.3a). What can be also observed is that the driving force for an enhanced steel dissolution is well established upon galvanic coupling of the two materials. The mixed potential for the galvanic couple (denoted as GWE in figure 6.3a) establishes after 20 min around the same value as that for steel alone. What is also observed is that the mixed potential for the couple is, in fact, ca. -680 mV immediately after establishing the electrical contact.

This means that both anodic and cathodic reactions are not limited at this stage and the steel corrosion rate should be enhanced, if compared to the corrosion rate of steel alone. This is as observed in figure 6.3b, where the corrosion current for the couple is approximately half an order of magnitude higher that the corrosion current of steel alone. In contrast and for comparative purposes, the corrosion current for MMO Ti alone is significantly lower (as expected) - approx. 2.5 orders of magnitude lower than the Fe|MMO Ti couple. What needs to be emphasised is the fast reduction reaction on the surface of MMO Ti – the cathodic branch of the LPR curve is almost a vertical line prior to the current drop in the proximity of the corrosion potential . This same observation, but for the anodic reaction, holds for the steel alone, i.e. a rapid anodic reaction is well observed. Hence, as previously commented, galvanic coupling of both materials will result in enhanced corrosion rate for the steel (being an anode) since in this case none of the oxidation (on steel) and reduction (on MMO Ti) reactions are limited.

The reaction kinetics on both the anode and the cathode with further immersion in the medium will determine the "efficiency" of the galvanic coupling in view of enhanced (or not) steel dissolution. The evolution of the mixed potential for the couple was monitored in the course of treatment for 24h, 48h and 72 and is depicted in figure 6.4. What can be observed is as follows:

- After the stable 1200 s interval (figure 6.3a), an ennoblement of approx. 40 mV was observed and within a 24h period the mixed potential reaches values of ca. -643 mV.
- The subsequent 48h treatment brings the potential to stabilisation around -645 mV.
- After 72h the mixed potential tends to become even more cathodic with a trend towards values more negative than -650 mV.

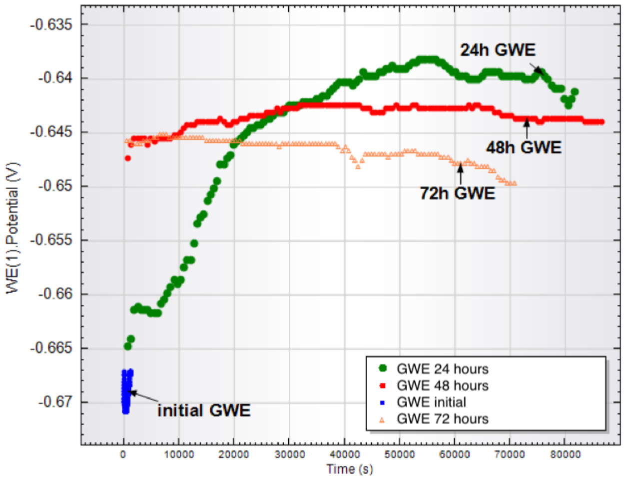


Figure 6.4: Corrosion potential for the galvanic couple Fe|MMO Ti from initial to 72h

The above observation implies that after initially more active state for the couple (specifically, enhanced dissolution of the anode), corrosion products formation and re-distribution obviously start playing a role, but are not significant. In other words, MMO Ti, supporting the reduction reaction, brings the reaction mechanisms towards an effective anode dissolution, despite the observed potential fluctuations and slight ennoblement. The point to emphasise is that a sustained cathodic potential was observed with treatment, which would indicate an enhanced corrosion activity at the anode.

6.1.4. Preliminary results on Fe|C and Fe|Pt

The already designed approach was investigated for the galvanic coupling of steel with more noble materials than MMO Ti. Graphite and platinum were used. For the graphite a glass carbon electrode was used, while the Pt was a sheet electrode. Both electrodes are used in conventional electrochemical cells as counter electrodes, hence purity and surface morphology vary, if compared to pure C or Pt. The OCP of C, Pt and steel are depicted in figure 6.5. A very thoroughly surface preparation and cleaning was performed on the steel electrode. This resulted in an OCP with immersion of ca. -300 mV, reaching to ca. -500 mV after 1200s. The OCP of Pt was about 120 mV more noble than that of C (ca. 420 mV for Pt vs ca. 300 mV for C). The potentials of both C and Pt were stable soon after immersion in the solution.

Considering these potential values, it would be expected that the driving force in a galvanic couple of steel with Pt will be larger than that for steel and C. Therefore, the trial was executed with variation in surface areas of the cathode. For the Fe|Pt test, the anode and cathode surface areas were the same, ie.e a ratio of 1:1. The Fe|C test was conducted with a cathode-over-anode ratio of 1,5:1. It might be expected that a larger cathode surface area for Fe|C would result in corrosion rate similar to a smaller cathode surface when Pt was used (due to the more noble potential for Pt, compared to C). This, however, was not as observed and is another illustration of the importance of the reduction kinetics.

Starting with the mixed potentials for the couples in figure 6.5, a more cathodic potential was observed for the Fe|Pt couple, establishing even more negative values than the steel alone. This means that the corrosion rate of the anode (steel) was enhanced significantly, compared to the corrosion rate of steel alone. It also means that the reduction reaction on Pt was also not limiting the corrosion activity of the couple.

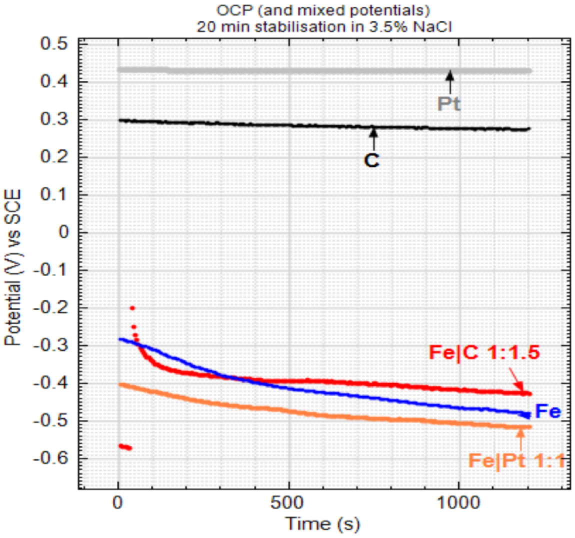


Figure 6.5: Potential evolution of steel (Fe), C, Pt and the galvanic couples of steel/C (Fe/C) and steel/Pt (Fe/Pt) after initial immersion in 3.5% NaCl (t=0 s) and until 20 min (t=1200s)

6.2. Enhanced steel corrosion by galvanic coupling

In this section, the results of a systematic investigation on galvanic coupling of steel with a more noble material is presented, mainly with regard to surface area ratio effects. Pt and C, as preliminary tested, were the choices for a cathode. The influence of prolonged treatment is discussed too.

Table 6.1 summarises the designation of the test cases, total surface of the working electrode (i.e. steel alone or galvanic couples) and the anode (steel) to cathode (Pt or C) surface area ratio.

To be noted is an important difference between the surface area ratios, where C or Pt were used as cathodes: for the case of a carbon cathode, the surface area ratio was always 3 times larger than the cases were platinum was used. This is because: 1) the available carbon and platinum electrodes were pre-fabricated such with a defined surface area, that was not possible to alter; 2) platinum is known to have a higher catalytic activity for the reduction reaction, the preliminary result in Fig. 6 showing this dependence. Therefore, potentially enhanced steel (anode) dissolution in the case of lower cathode area (if compared to carbon) was investigated here as well.

Figure 6.6 depicts the recorded OCP values (or E_{corr} for the galvanic couples, respectively) over time. As can be observed, all potentials shift in cathodic direction with treatment, reflecting enhanced activity, steel dissolution respectively. The most noble potential at the beginning of the test is for the Fe|C galvanic couple, while the most cathodic one – for the

Test case	total surface [cm^2]	C/A ratio
Fe	0.79	
C	3.55	
Pt	1.12	
Fe|C	4.33	4.52
Fe|2C	7.88	9.04
Fe|Pt	1.91	1.43
Fe|2Pt	3.03	2.85

Table 6.1: Total WE surface area and surface area and surface area ratio of the several test cases

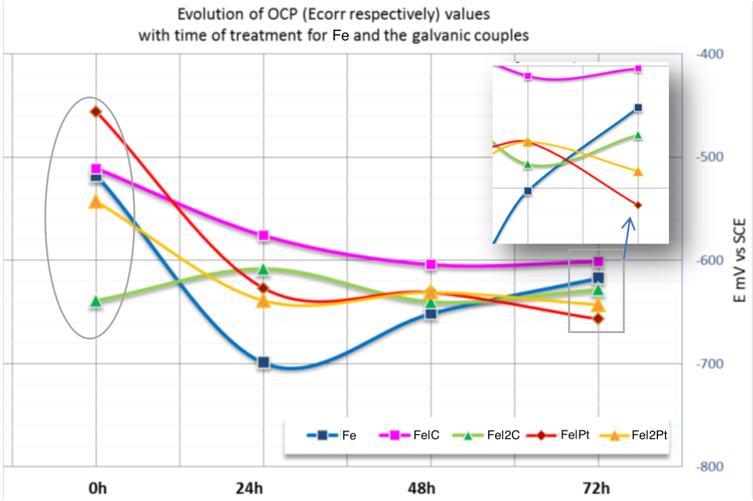


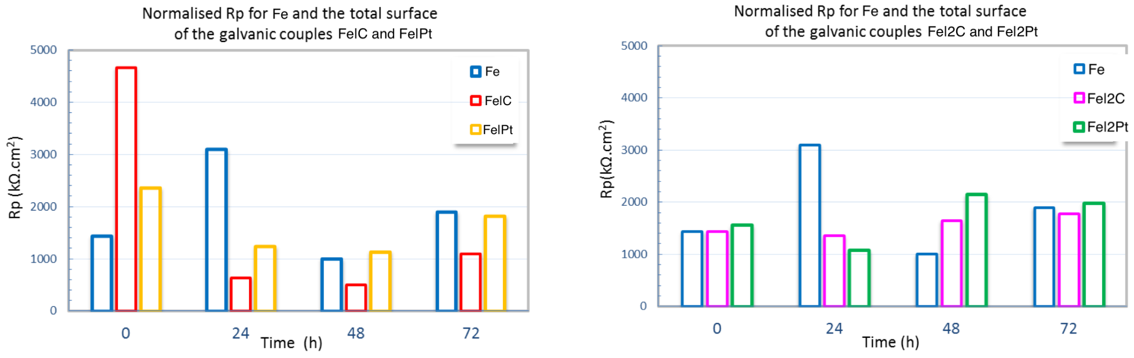
Figure 6.6: OCP (E_{corr} respectively) evolution for steel (Fe) and the galvanic couples Fe|C, Fe|2C, Fe|Pt and Fe|2Pt with time of immersion in 3.5% NaCl.

Fe | 2Pt galvanic couple. These are followed by a decrease in the case of Fe | C and a stable, yet cathodic values, for the case of Fe | 2Pt. The result indicates that Pt is more effectively leading to enhanced anode dissolution, despite the smaller surface area, if compared to carbon. In addition to that, if potentials only are considered (figure 6.6), 2x increased surface area of carbon as cathode – case Fe | 2C, does not really show a significantly more positive effect on steel dissolution. The values for Fe | 2C are the most noble throughout the test.

Similarly, a reduced surface area of a platinum anode (case Fe | Pt) does not significantly alter the process of steel dissolution i.e. both Fe | Pt and Fe | 2Pt effectively lead to anode dissolution, with the exception of more noble values for Fe | Pt in the first time intervals. In other words, although an increase in the area of the cathode is (fundamentally) expected to increase the dissolution rate of the anode, this relationship is not straightforward and largely depends on the kinetics of the reduction reaction.

The driving force for enhanced steel dissolution includes three main components: the potential difference (anode vs cathode), the surface area ratio of anode to cathode and the kinetics of both oxidation (on the steels surface) and reduction reactions, specifically when the cathode surface area changes. These aspects are discussed in what follows, based on the recorded reaction kinetics and derived parameters

Figure 6.7 presents the normalised polarisation resistance (R_p) values for all cases. Figure 6.8 presents the recorded R_p values and OCP values. With respect to the R_p results, it should be noted that R_p reflects the corrosion resistance of a system under investigation i.e. R_p is a result of both oxidation and reduction on a working electrode. Therefore, if R_p is to be normalised, the full surface area of a working electrode (steel alone or galvanic couples) is to be considered. Moreover, the R_p is inversely proportional to corrosion current (see the theory



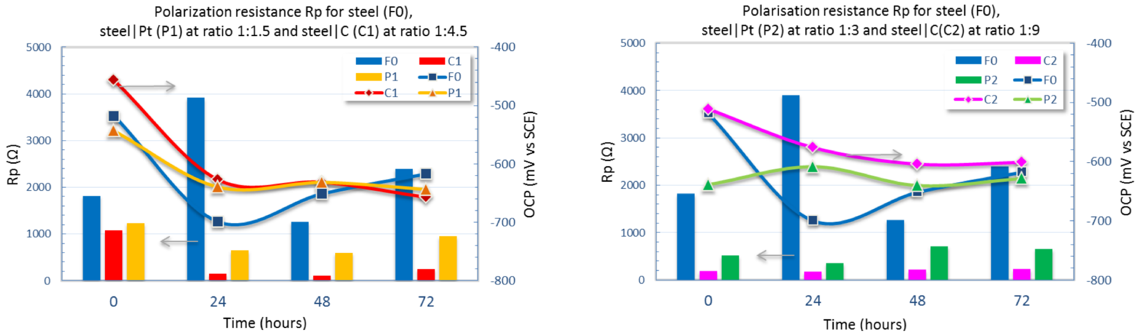
(a) Fe vs. Fe|C and Fe|Pt

(b) Fe vs. Fe|2C and Fe|2Pt

Figure 6.7: Normalised polarisation resistance values for steel (Fe) and the galvanic couples

on Stern-Geary equation on page 40). In other words, the lower the R_p value, the higher the corrosion current and the corrosion activity. However, it should be also noted that the corrosion activity in a system as the galvanic couples Fe|C, Fe|2C, Fe|Pt and Fe|2Pt is in fact proportional to the galvanic corrosion current i.e. C and Pt are inert and reduction is the predominant reaction on their surfaces, while oxidation will be predominant on the (coupled) steel surface. To that end, figure 6.8 presents the recorded R_p for all cases without normalisation. The inverse values in figure 6.8 reflect the galvanic current, or the activity of steel, when coupled to C or Pt.

As seen in figure 6.7, the R_p values for steel alone (case Fe) fluctuate over time and in some cases are comparable to the values for the couples. The lowest normalised R_p values are observed for the C1 case, which was steel-to-carbon ratio of 1 to 4.5. Increase in the surface area of carbon (case Fe|2C), did not result in reduction of R_p, on the contrary – higher values were observed. For platinum as a cathode (ca. 3 times lower surface compared to carbon in both Fe|Pt and Fe|2Pt cases, see table 6.1), altered Pt surface did not result in substantial decrease in Rp values i.e. a stable rate of steel dissolution was relevant for both Fe|Pt and Fe|2Pt cases. The results in figure 6.7 are in line with the OCP records (figure 6.6) and reflect the discussion above on driving forces for the galvanic corrosion of steel when coupled to C and Pt.



(a) Fe vs. Fe|C and Fe|Pt

(b) Fe vs. Fe|2C and Fe|2Pt

Figure 6.8: Polarisation resistance (R_p) vs OCP values for steel (Fe) and the galvanic couples as recorded.

Figure 6.8 presents information linked to the galvanic corrosion current. As mentioned above, the recorded R_p in figure 6.8 can be directly linked to the activity of steel during treatment. A reduction in R_p values is proportional to an increase in the galvanic current. Consequently, the main observations are as follows: 1) steel alone presents fluctuations (as aforementioned), reflecting dissolution of the steel electrode and limitations with corrosion products formation; 2) increasing the surface area of the cathode in case of carbon (cases

Fe|C and Fe|2C) does not result in enhanced corrosion rate for the anode. For instance, although initially Fe|C is at the most noble potential and higher R_p (figure 6.8a), enhanced galvanic current is observed later on, ending up in the range of activity as recorded for the C2 case, where the cathode are is the largest of all cases (figure 6.8b); 3) for the Fe|Pt and Fe|2Pt cases – again, increased cathode surface area does not change much the corrosion activity. More important here is the fact that a sustained and stable reduction in R_p was observed in both P1 and P2 cases, where potential difference seems to be determining the driving force for galvanic corrosion at a smaller anode to cathode ration (Fe|Pt), while both potential difference and surface area effects determine the galvanic corrosion process in Fe|Pt; 4) in all cases of the galvanic couples, reaction kinetics determine the process of steel dissolution, leading to an enhanced galvanic current for the anode.

The synergy of the components of the driving force for galvanic corrosion of steel (as above described) are discussed in what follows.

Figures 6.9 to 6.12 present the linear polarisation resistance curves for Fe, Fe|C, Fe|2C, Fe|Pt and Fe|2Pt at the first and last time intervals. Table 6.2 summarises kinetic parameters for the oxidation and reduction reactions (the slope of the anodic and cathodic curves in this case). Table 6.3 lists the recorded R_p values and the calculated corrosion current (I_{corr}) values (analytical calculation was performed using the Stern-Geary equation, page 40, where the value of 18 mV/dec was used for the constant B, which is based on experimentally derived Tafel constants for steel in 2.5% NaCl). Since R_p is the recorded (rather than normalised) value (as already discussed above) the corrosion current is to be seen as galvanic current, rather than a mixed corrosion current for the working electrodes Fe|C, Fe|2C, Fe|Pt and Fe|2Pt.

	Fe	Fe72	Fe|C	Fe|C72	Fe|2C	Fe|2C72	Fe|Pt	Fe|Pt72	Fe|2Pt	Fe|2Pt72
anodic	22	19	26	17	19	16	14	21	21	13
cathodic	10	13	14	15	13	15	15	14	13	23

Table 6.2: Slopes (mV/dec) of the anodic and cathodic half-cell reactions ($\frac{\Delta E}{\Delta I}$) in mV (E) over 1 decade of current (I) (the slopes basically indicate a faster reaction (lower number) vs an impeded reaction (higher number)

	Fe		Fe|C		Fe|2C		Fe|Pt		Fe|2Pt	
time	Rp Ohm	Icorr µA	Rp ohm	Icorr µA	Rp ohm	Icorr µA	Rp ohm	Icorr µA	Rp ohm	Icorr µA
0	1807	10	1075	17	172	105	1226	15	512	35
72	2400	8	251	72	226	78	952	19	630	29

Table 6.3: Recorded R_p and I_{corr} for t=0 and t=72

Fe Anodic dissolution is well observable and increases over time; the corrosion rate overall decreases (table 6.3, figure 6.9) due to limited reduction reaction (table 6.2), compared to the initial rates. Fluctuations (ups and downs) throughout are observed ad these are expected for steel performance in NaCl for the time duration of this test.

Fe|C Initially impeded galvanic corrosion due to the most significantly limited, among all cases, oxidation reaction (table 6.2, figure 6.9); this results in the most noble $E_c orr$ (figure 6.9) for the initial time interval (0h). The reduction reaction was also limited, compared to Fe alone (table 6.3). The result is similar corrosion activity of the Fe|C couple to Fe alone at the initial stage (table 6.2, figure 6.9). Consequently – the driving force for galvanic corrosion in the Fe|C couple was not immediately increased due to potential differences, but was dependent on the reaction kinetics on Fe and on C. After 72h - enhanced galvanic corrosion is relevant, table 6.2 and figure 6.9 (anodic reaction on Fe predominantly) and almost mixed control (Ox and Red at comparable rates, table 6.2, figure 6.9) – the driving force here is the potential difference between C and Fe mainly, rather than limitations of Ox or Red reactions.

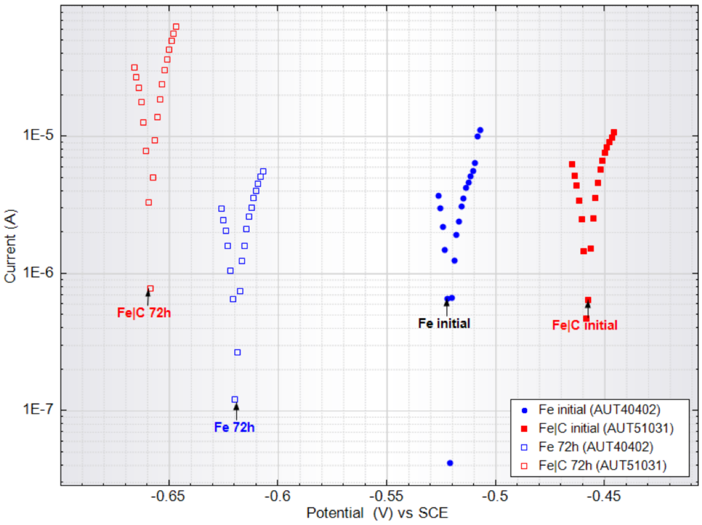


Figure 6.9: Overlay of LPR curves for Fe and Fe|C at initial (0h) and 72h time intervals

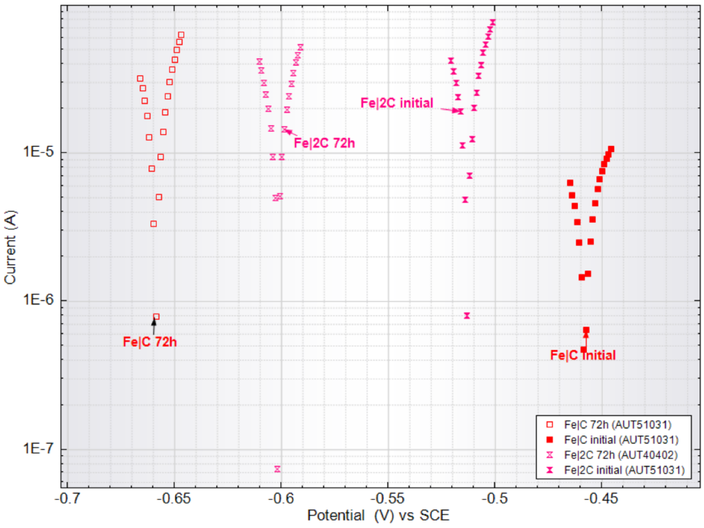


Figure 6.10: Overlay of LPR curves for the Fe|C and Fe|2C galvanic couples at initial (0h) and 72h

Fe|2C initially pronounced (faster) oxidation (compared to both Fe alone and Fe|C, table 6.2, figures 6.10 and 6.10) Here, the surface area effect is well seen, resulting in the highest corrosion activity among all tested cases (table 6.3, figure 6.9 and 6.10). After 72h – a slight increase in oxidation, is observed, but impeded reduction, which in fact is at levels as in the Fe|C couple (table 6.2 and 6.3). This means that 2x surface area of the cathode does not necessarily result in enhanced galvanic corrosion for the tested time intervals. In fact, the corrosion activity at the initial and the 72h stages for Fe|2C is similar (figure 6.10), ending up with a decrease in corrosion activity and reduced corrosion current up to the levels of the Fe|C couple (table 6.2, table 6.3 and figure 6.10).

In other words, the driving forces in the Fe|C galvanic couple are both potential difference and surface area effect, however these are not necessarily proportional. The potential difference has a significant effect at the initial time interval, when the surface area of the cathode is increased (Fe|2C couple, figure 6.10), but the effect vanishes at later stages. After 72h the corrosion current for Fe|2C decreases (table 6.3, figure 6.10). Inversely, the 1:1 ratio (Fe|C couple) determines a larger impact in the run of the test and at later stages. This is because the mixed corrosion potential shows the most significant cathodic shift (figure 6.10), on one hand, and the corrosion current increases over time (table 6.3).

Similar observations hold for the surface area effect in the Fe|Pt and Fe|2Pt couples.

Fe|Pt The potential difference plays a similar role in all Fe|Pt cases and is irrespective of the surface area of the cathode – in all cases a negative potential shift was observed, figure 6.11 (this is in contrast to the Fe|C couple, figure 6.10). The effect is more significant for the smaller anode to cathode ration (case Fe|Pt), rather than for a double cathode surface (case Fe|2Pt). The potential difference, as a component of the driving force, at smaller ratio is more significant also in time (initial towards 72h, figure 6.11), resulting in increasing, rather than stabilised or decreasing galvanic currents (table 6.3, figure 6.11);

Larger surface area of the cathode: the effect is pronounced at the initial stages only (table 6.2) i.e. increased galvanic currents and negative potential shift (figure 6.11) for the Fe|2Pt couple, compared to Fe alone and the Fe|Pt. The galvanic current, however, increases (table 6.3) because of a relatively faster reduction reaction, rather than enhanced oxidation at the anode (table 6.2). For the Fe|2Pt couple after 72h, oxidation increases but reduction is significantly impeded (the most impeded reduction reaction of all tested cases, table 6.2) – this results in an overall stable corrosion activity of the Fe|2Pt couple between the initial time interval and the final 72h stage i.e. there was a marginal effect on enhanced galvanic corrosion (figure 6.11), with actually decreased corrosion current from initial to 72h (table 6.3). The corrosion current, however, is not reduced as significantly as in the Fe|2C couple, but rather remains stable and at higher levels than Fe alone .

Obviously, and from the results on all galvanic couples, compared to Fe alone, the corrosion activity only increases in time for the smaller anode-to-cathode ratio in Fe|C and Fe|Pt. In contrast, an initial significant increase, but later on reduced corrosion activity is relevant for the larger ratios (both Fe|2C and Fe|2Pt), with the (current reduction) effect more pronounced for the Fe|2C couple.

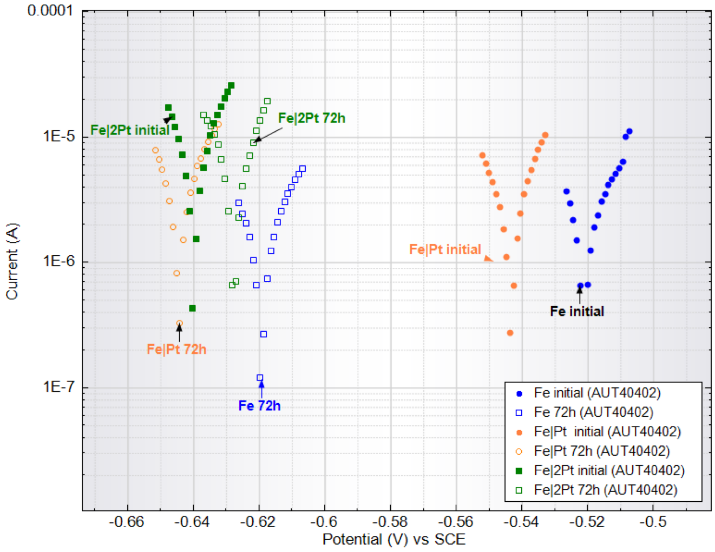


Figure 6.11: Overlay of the LPR curves for Fe and galvanic couples Fe|Pt and Fe|2Pt at 0h and 72h

What can be concluded from the results in this chapter is that both potential difference and cathode area have effects on the galvanic corrosion process. However, for materials as glass carbon and Pt, the corrosion activity is largely affected by the kinetics of the reduction reaction, especially when electro catalysts (as Pt) are concerned. This can be well seen from the comparison of results for the Fe|2C and Fe|2Pt couples, figure 6.12, where despite the fact that the cathode surface area for the Fe|2C case is three times larger than that for the Fe|2Pt case, the currents in the Fe|2C case are not significantly higher. Moreover, the corrosion potential in the Fe|2Pt cases are more cathodic at all times. In other words, the Fe|2Pt case maintains a more efficient galvanic corrosion for the coupled steel.

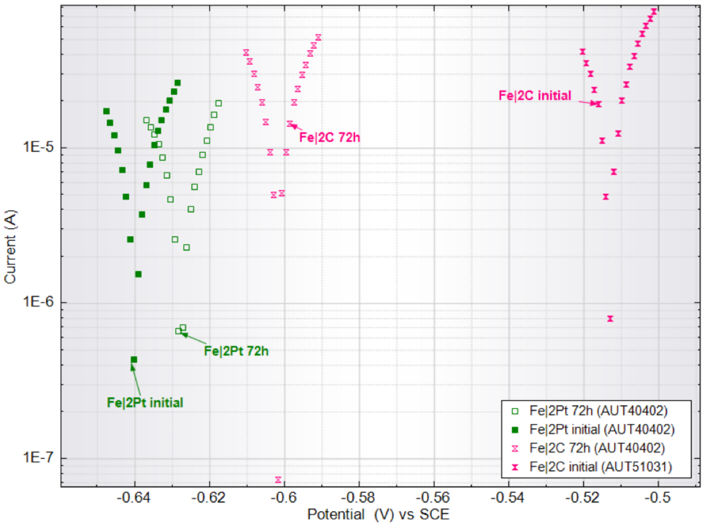


Figure 6.12: An overlay of the LPR curves for Fe|2C and Fe|2Pt at initial (0h) and final (72h) time intervals

This is what was here observed: twice the surface area of the cathode in both Fe|C and Fe|Pt cases results first in enhanced oxidation of the anode, however, a lower corrosion rate was observed in time and this is due to limited reduction reaction on the cathode in the cases of smaller anode-over-cathode ratio (NOTE: at a smaller ratio a sustained increase of the corrosion rate of the anode was observed). In other words, while for Pt as a cathode, an enhanced surface does not really increase the activity of the couple in the long term (figure 6.11, table 6.3), for C – a significant initial increase of activity results from enhanced cathode surface (figure 6.10, table 6.3). The effect for C, however, diminishes over time, while for Pt the effect is on a smaller scale, but stable and sustained over time (figure 6.12, table 6.3).

6.3. Mass loss measurements

For each test case the samples are weighted prior to treatment in the corrosion cell. After the treatment the samples are again weighted on a analytical balance. Samples have been treated in the corrosion cell for 24, 48 and 72 hours.
In table 6.4 the average mass loss and corresponding corrosion rate are listed. The corrosion rate is depicted in figure 6.13.

Test case	Average mass loss [mg/day]
Fe	0,15
Fe|C	1,79
Fe|2C	5,53
Fe|Pt	0,81
Fe|2Pt	1,41

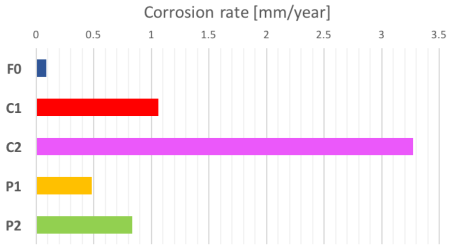


Table 6.4: Average mass loss and corrosion rate per test case

Figure 6.13: Corrosion rate based on mass loss

The table demonstrates a larger mass loss with galvanic coupling. In other words, the increase of surface area of the noble material leads to to enhanced galvanic corrosion and weight loss for the steel sample. To be noted is that the mass loss measurements are indicative rather than following standards for gravimetric loss. The measurements were performed to visualise the effect of galvanic corrosion, which was clearly observed on the surface of the steel samples, figure 6.14 and 6.14.

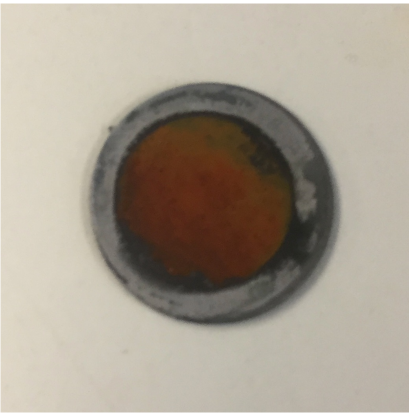


Figure 6.14: A steel sample with a layer of corrosion product on its surface

Figure 6.15: Several samples after treatment after removal of the corrosion product

6.4. Incidental polarisation

Another reason for the observation of the steel surface after the tests and mass loss measurements, was to differentiate successive test from those, where due to short circuit in the cell, a large incidental polarisation leads to almost complete destruction of the steel sample. As can bee seen in figure 6.17 and 6.16.

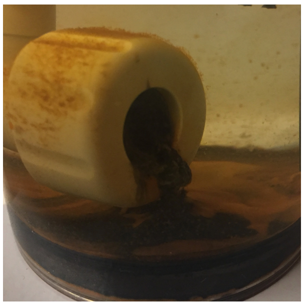


Figure 6.16: The severe corrosion due to polarisation

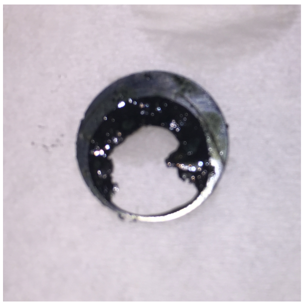


Figure 6.17: The polarised sample after cleaning

Although this event does not contribute to the research on galvanic corrosion, the incident is an interesting result. No further inquiries are made to the magnitude of the applied current. However, the damage to the steel sample was quite severe (figure 6.17). Therefore, it can be beneficial to consider the investigation of the decommissioning method by means of electrolytic corrosion, as discussed in section 4.1.1 on page 23.

6.5. Corrosion rate determination

For uniform corrosion, corrosion rate is determined following the theory in chapter 3. Corrosion rate for the test cases was determined based using equation 3.15 in chapter 3 and the corrosion current values listed in table 6.3).

	Fe	Fe|C	Fe|2C	Fe|Pt	Fe|Pt
Time	Corr. rate	Corr. rate	Corr. rate	Corr. rate	Corr. rate
hours	$[mm/year]$	$[mm/year]$	$[mm/year]$	$[mm/year]$	$[mm/year]$
0	0,1	0,04	1,5	0,2	0,5
72	0,1	0,8	0,9	0,2	0,3

Table 6.5: Estimated corrosion rate at t=0 and t=72 hours

However, it should be noted that these values are only for comparative purposes of the tested cases, and should not be taken as absolute values. Moreover, corrosion rate calculations are only meaningful for uniform corrosion. In this report, the test cases were subjected to a combination of galvanic and localised corrosion.

7

Implementation and feasibility

7.1. Main steps for implementation

Practical implementation of the galvanic corrosion decommissioning method is discussed in this section. Although further investigation on the feasibilty of the process is required, the requirements for implementation are discussed schematically. A schematic time line for implementation is depicted in figure 7.1. The steps are further elaborated below.

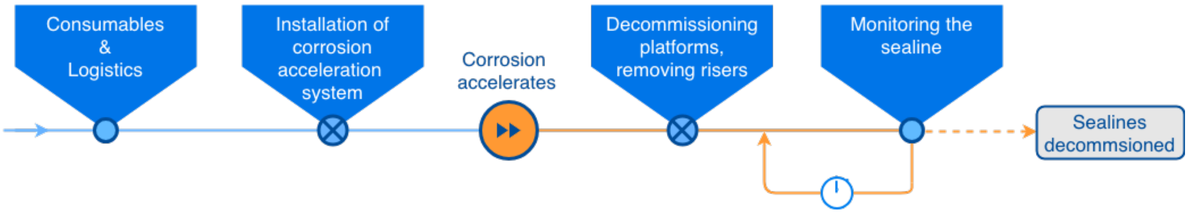


Figure 7.1: Schematic time line for implementation of graphite powder. Once the graphite is transported to site (1) the injection of the graphite can commence (2). The graphite particles settle and the galvanic process starts. Afterwards the platforms and risers are decommissioned (3) resulting in open end of the sealine. Sonar surveys are conducted every 4 years (4) to monitor the sealine. Eventually, the sealine is sufficiently degraded to be considered decommissioned (5).

1 Consumables & logistics

Before the actual implementation can commence the product needs to be available and at the right location. The graphite grit available for industrial use is found in four mesh sizes, ranging from XL flakes (+50 mesh) to small flakes (-100 mesh). The XL flakes listed as +50 mesh means that its particles are larger than 297 micrometer. The small flakes with -100 mesh has particles that are smaller than 149 micrometer. Considering the feasibility for injecting the powder (discussed later) and a aim for a large surface diameter, it is assumed that the smallest particles are preferable. The average price of small graphite flakes is €850 per tonne[18].

Once the graphite is acquired it needs to be transported to the site. Considering the large amount of graphite powder required, the product needs to be shipped. Whether the storage of the product can be done on an existing platform, depends on the size of the facility, the progression of the decommissioning of topside equipment and the weight of the graphite to be injected.

2 Installation of corrosion acceleration system

With the graphite powder on site, the injecting in the sealine can commence. The injecting is most likely done from a vessel. This can be seen similar as pigging operations, where the pig is loaded into the launcher from a vessel and subsequently pumped through the pipeline. To that end, it is convenient to inject the graphite before the risers are decommissioned.

The injecting of the graphite is best done immediately after the cleaning of the pipe. The graphite can then be injected from the same vessel used for the pigging. The intelligent pigging operations that TEPNL currently performs for pipeline inspection use a vessel where the launcher is located at the vessel. These operations cost approximately €200k to €300k per pipeline. The injecting operation cost are expected to be alike.

The injection is done by pumping the graphite into the pipeline. Therefore, the solid particles will be suspended in seawater. Hence, smaller particles of graphite are more favourable. Lower concentration mixtures allow suspended particle transport. If the concentration of the graphite requires to be higher, a slug flow can occur. For the latter, caution is advised to prevent clogging of the pipeline.

The graphite solution is pumped in the sealine to replace the present seawater. The concentration of the solution exiting the sealine on the other end is measured. Once the concentration of graphite equals the conccentration up front, one can assume a homogeneous solution in the sealine. Subsequently, the graphite particles settle in the sealine. The graphite and steel pipe make contact at the pipe surface. The galvanic acceleration of the pipeline corrosion can begin.

3 Decommissioning the facilities

The sealine is filled with the graphite and the galvanic corrosion process is expected to initiate. The platform including the risers can now be decommissioned. As mentioned above, the risers are used to inject the graphite. Therefore they are not decommissioned earlier. The risers are disconnected from the sealines at the sea bottom. These disconnections are left open. With the open ends it is aspired to have some flow within the sealine. The conductivity is expected to be maintained if the seawater in the sealine is refreshed gradually. The corrosion product is then gently discharged in the sea and diluted. It is to be investigated if this refreshment is feasible. Other options, such as puncturing of the pipe can be considered

4 Monitoring the sealine

The sealines are to be monitored. This is in line with the regulations for operational and in situ decommissioned pipelines. The legal requirements are that the sealine is to be surveyed every 4 years. This is given the condition that no anomalies are found in previous surveys.

The monitoring currently conducted on sealines is a sonar survey. This only gives information on whether or not the steel of the pipeline is still in place. Changes in wall thickness or other parameters of corrosion can not be measured with this survey. It can however detect where the steel of the sealine has dissapeared.

A pipeline potential survey is able to provide more information on the electrical resistivity of the sealine. This survey is however expensive[23].

5 Sealine decommissioned

Eventually it is aimed to consider the sealine decommissioned. The Dutch law is not clear on what this definition entails. Therefore, in this research the sealines assumed to be decommissioned when the remainder of sealine does not pose risk to other sea users.

Ideally, the former location of the pipeline should be able to be reused. In order to achieve this the debris of steel ought to be small enough to avoid snagging risk for fishermen. Besides, the remains should not interfere with future use of the seabed, e.g. construction of offshore wind farms. However, prior to any reuse a survey ought to be conducted. The remaining parts of steel are to be located.

The coating of the sealine will not be degraded by the proposed corrosion mechanism. It is to be assessed how the coating behaves once the steel is dissolved. The environmental impact is to be investigated. Nonetheless, the coating residue will not cause safety issues for other sea users.

7.2. Feasibility and operational challenges

The implementation of the proposed decommissioning method is suggested according to the four main steps discussed in previous section. The goal is to successfully reach the fifth step: sealines that are sufficiently degraded to be considered decommissioned. Whilst evaluating the practical implementation some challenges can be foreseen. Some operational items that require additional attention are discussed below. The challenges are also listed in table 7.1.

7.2.1. Injecting the material

The TEPNL sealines are coated and buried beneath the mud line in the North Sea. One aim of this investigation is to leave the seabed undisturbed during decommissioning activities. Hence, for the graphite to be in contact with the steel pipeline, the graphite ought to be inside of the sealine. Therefore, it needs to be injected.

The graphite particles are suspended in seawater and subsequently injected in the sealine using a pump. The pumping of solid particles can be accompanied by challenges. Due to the solid particles slug flow can occur. Furthermore they can cause wear in the equipment. Obviously, lower density mixtures are easier to pump. However, the aim is to have a large surface area of graphite within the steel. Therefore, a trade-off between operational feasibility and effectiveness might arise.

Besides, the planning of other decommissioning operations is to be taken into account. As suggested in figure 7.1, the injecting ought to be done prior to the decommissioning of the platforms. At that moment, the riser is still accessible for the injection. If the riser is already decommissioned, diving operations are required. This will make the total project more complex. more expensive and less safe.

7.2.2. Refreshment of the solution

Once the graphite particles are in place the steel and graphite form an galvanic couple. The seawater with which the particles are injected functions as the electrolyte. The corrosion of the steel sealine will accelerate.

The lab test conducted on small scale showed this process. The galvanic coupling to carbon lead to an increase in corrosion rate. Consequently, this also lead to an increase of corrosion product. The solution in the glass cell turned cloudy and orange-brown.

The lab tests were aimed to investigate other parameters than the conductivity of the medium and therefore the NaCl-solution was refreshed. Before piloting the proposed method, it is therefore necessary to investigate the role of the medium. The accumulation of corrosion product affects the conductivity of the medium. Hence, the corrosion process is affected. It is to be assessed if the method is feasible without refreshment of the medium. Otherwise, measures should be considered to achieve some sort of freshening of the medium, such as puncturing the sealine. It is undesirable to have a need for active refreshing of the medium. After the graphite is injected in the sealine, it is aimed to have little as intervention as possible.

7.2.3. Condensate in the pipelines

As this research states, the addition of graphite accelerates the corrosion of steel. The results of the lab tests show an increase in corrosion current as the carbon electrode was connected to the steel sample. In the lab tests, the connection between steel and the more noble material is secured with insulated wires. The wires are manufactured to minimise their influence on the process. The situation for the galvanic corrosion tested in the lab is aimed to exclude external factors influencing the corrosion.

The situation within the existing pipeline, however, is subjected to various influences. For instance, the galvanic connection is made at the surface area of the sealine. The sealine has been in use for decades as a gas transport pipeline. During this service life, the sealine has been subjected to condensate production. The condensate is deposited along the pipeline wall. Although the sealines are cleaned for the pre-abandonment phase, residual condensate will remain. The condensate layer can complicate the contact between the steel and the graphite. Hence, the condensate can have an preventing role in the galvanic corrosion process. Considering a additional cleaning might be beneficial. Flushing the sealine with an alkaline solvent for example might reduce the condensate residue.

7.2.4. Anti-corrosion coating

Throughout their lifetime the TEPNL sealines are protected against corrosion. One of the protection measures is the use of anti-corrosion coating on the exterior of the pipeline. The materials of the coating vary. The TEPNL pipelines consists of coatings of epoxy, polyethylene and polypropylene.

The coating are applied to isolate the steel from its environment, i.e. prevent the contact with an electrolyte. Hence, the coating does not contribute to the corrosion process. It is therefore likely that the coating will remain present if no action is taken. The behaviour of the coating is to be investigated. The environmental consequences of the coating have to be evaluated. As the coating are synthetic material it is undesirable to be discharged in the marine environment.

Although the coating residue is to be investigated from an environmental point of view, the remainder do not impose safety hazards. If the steel is degraded as prospected, the coating does not lead to risk for other sea users. No snagging risk for fishermen exist. Besides, the area could be reusable for the construction of offshore wind farms. The elimination of risk of decommissioned sealines is one of the main goals of this research.

7.2.5. Sacrificial anodes

Besides the anti-corrosion coating the sealines are protected with anti-corrosion mechanisms. These mechanisms are either impressed current cathodic protection (ICCP) or protection with sacrificial anodes.

The older sealines that are protected with ICCP are disconnected from the power source for decommissioning. Hence, this protection mechanism will not longer be effective during the process of galvanic corrosion.

The protection against corrosion with sacrificial anodes is the opposite of the proposed acceleration. The steel pipeline is connected to a *less* noble metal. For the TEPNL sealines the anodes are made of a mix of zinc and aluminium. The anodes will corrode before the steel sealine does. The effect of this corrosion protection needs to be taken in to account during further investigation of the feasibility.

The anodes of the TEPNL sealines are currently in a well preserved condition. For this research aim, a well preserved condition is a complication. The location of the anodes are known. It could be worth assessing the demounting of the anodes. This implies diving or ROV operations, from which the latter has the preference if feasible.

7.2.6. Environmental impact

Galvanic corrosion is proposed to accelerate the degradation of the steel sealines. By doing so a large volume of graphite is injected in the sealines. Although carbon is listed as PLONOR according to the definition of the OSPAR convention, the effect on the environment can not be neglected. The large volume of graphite used can be of influence on the ambient environment.

Additionally, the degradation of the steel is accelerated. The corrosion product is produced over a shorter period of time. Although the corrosion product of steel in PLONOR too, the concentration in the vicinity of the sealine will be higher than usual. The consequences for the marine life and environment are to be considered.

7.2.7. Stakeholder management

Besides the technical challenges that arise, the stakeholders also need to be informed.

First of all, the internal stakeholders are to be involved. Most importantly, this is the TO-

TAL group. They bear the final responsibility. The main interests of TEPNL and the TOTAL group are obviously similar. Hence, resistance is not expected.

The external stakeholders are identified in section 1.2.2 on page 3. The general public, NGO's and governmental institutions are most important to inform. Their goals are different than TEPNL's and therefore they are to be carefully managed.

The governmental institutions are involved with and responsible for the legislation of decommissioning. It is therefore essential to acquaint them of new developments regarding sealine decommissioning. This facilitates them to express their views on the proposed method. It allows for the decommissioning method to fit within the legal framework that is constructed.

The aim to provide a more environmental friendly solution for sealine decommissioning is to be elaborated clearly and extensively. Misinterpretations can lead to resistance. It is important to consider their concerns and include them in the process.

7.2.8. Scaling of the results

Lastly, the tests results are to be scaled. The tests conducted in this research are done in a laboratory. The samples are small pieces of steel. The equipment and the lab set up are fabricated for the purpose to measure corrosion. In the actual situation of the sealine more parameters are involved on the process. It is to be investigated if the galvanic corrosion is feasible in a more realistic test set up. Therefore, a field test is proposed. Some considerations for this field test are found in the next section.

7.3. Considerations for field test

Several parameters have to be evaluated in a field test. The field test provides realistic results. The challenges discussed in previous section are taken into account to investigate. Likewise, some implications regarding the testing procedure are discussed in section 7.3.2.

7.3.1. Operational challenges

A field test is proposed to investigate the effectiveness of the method in actual circumstances. The challenges identified above need to be taken in to account for the test design. A list with challenges is found in table 7.1. These challenges affect the set-up of the field test. These implication are found beside each challenge. They are further elaborated below.

Challenges	Consideration
Injecting the material	Pumping the graphite at the start of the test in a similar way as the real situation.
Refreshing the electrolyte	Checking feasibility without active refreshment
Condensate	Out-of-service sealine to be used
Anti-corrosion coating	Monitoring the coating and further reseach on coating materials
Sacrificial anodes	Attaching an anode in test set up
Evironmental impact	Measuring test environment. Monitoring the water quality.
Scale of tests	Large size of test. Pipeline of significant size

Table 7.1: Identified challenges and proposed testing method

Injecting the material The injection of the graphite in the test pipeline is done in a similar way as it would be from a platform. Hence, the graphite particles are suspended in seawater and distributed in the pipe using a pump. For lower density mixtures a centrifugal pump can be used. The solid particles can cause wear in the pump, especially at high flow velocities. For high density mixtures slug flow occurs. This is best managed with a rotary or axial piston pump. These are more expensive, though are efficient and have high pressure ratings. **The type of pump to be used should be determined by an evaluation on mixture density and required flow velocity.**

Refreshing of the electrolyte The need of refreshment should be investigated. The conductivity of the seawater affects the corrosion. When the electrolyte turns cloudy its conductivity declines. Hence, periodically freshening of the seawater in the sealine would be beneficial.

However, for decommissioning purposes it is most interesting if no further operational actions are needed after implementation. As the graphite is injected in the sealine the platforms and risers are disconnected and removed. Operations are then more complicated and more expensive. Moreover, an aim of this decommissioning method is to reduce the risk of decommissioning. Periodically recurring diving operations are a safety risk for personnel.

To assess if the galvanic corrosion can have a substantial contribution to decommissioning of sealines, the process should be feasible without intervention. **The corrosion process should be assessed without refreshing the seawater in the pipeline. Puncturing the sealine to achieve a more open setting can be considered**.

Condensate in the pipeline The condensate that deposited along the sealine walls can be an obstruction for the galvanic corrosion process. Even though the pipes are cleaned, some residue persists. This can influence the effectiveness of the galvanic corrosion, as it disrupts the electrical connection between the graphite and the steel. To investigate this influence, a decommissioned sealine is to be used. The sealine is to be treated as entering the pre-abandonment phase and then to be retrieved. **The effect of the condensate on the internal walls of the sealine can then be investigated**.

Anti-corrosion coating The anti corrosion coating should be examined during the field test. Besides the field test the environmental consequences of the coating should be assessed. It is possible that the coating peels off of the sealine when the steel degrades. **The effect of small particles of polymers in the marine environment is therefore to be investigated**.

Sacrificial anodes The TEPNL sealines are either protected with impressed current cathodic protection (ICCP) or sacrificial anodes. The IC can be easily disconnected during the decommissioning process. The sacrificial anodes protect the sealine against corrosion, using the same corrosion mechanism as is intended to accelerate the process. Obviously, this has an impact on the feasibility and process duration.

- Therefore, a decision is to be made regarding the field test:
  The field test can be conducted **without** additional anodes, resulting in a feasibility study for the sealines protected with IC. If successful, the test can be repeated with sacrificial anodes.
- The field test can be conducted **with** additional anode(s). If the results are desirable, galvanic corrosion is a feasible solution for both types of TEPNL sealines. However, if the anodes prevent a sufficient degree of acceleration, the method could still be feasible for the IC protected pipelines.

Moreover, it is to be considered if the anodes are to be decommissioned. The feasibility of this operations should be assessed.

Environmental impact An important parameter to monitor is the environmental impact. The effect of the graphite in the seawater has to be evaluated. Besides, a large concentration of corrosion product will be suspended in the medium. The effect on the marine life is to be assessed. Therefore, **the water quality is to be monitored during the field test**.

Scale of the test As stated previously are the discussed tests in this research on lab scale. The steel samples which are tested are not similar to the steel pipeline in shape nor in dimension. A field test gives results that are scalable. Therefore, a steel sealine of significant length is used, i.e. a length at which the area of measurements is not affected by changes at the pipeline ends. Furthermore, **it is advised to conduct measurements at several locations in the pipe, so possible influences of the pipeline ends can be identified**.

7.3.2. Testing method

Besides the operational challenges, the test must fulfil some other criteria. These are related to how the test is performed. During the test a reference sealine ought to be monitored simultaneously. This reference sealine ought to be a similar piece of the piloted sealine, but without the addition of the graphite powder.

Criteria	Consideration
Monitoring of test	Monitoring test without stopping or interupting the process.
Time-scale of test	Aging test to provide relevant results within an reasonable time

Table 7.2: Considerations for testing method of the field test

Monitoring the test without stopping the process During the field test the progress is monitored. This should be done in such a way that is does not interfere with the results. In the conducted lab tests, the complete test needed to be stopped once the LPR measurement was conducted. For the field test this has to be avoided. Hence, non-destructive testing methods are required. Besides, an evaluation on mass loss of the pipe is valuable. This will affect the choice of location of the test.

Time-scale of test The time scale of the method is several years. The testing has to provide an insight in the remaining time of the sealine. It has to do so in a smaller period of time. Therefore, accelerated ageing tests are required. For example, this can be done by a heat ageing test.

7.4. Rough estimate on required graphite

A preliminary estimate is made for the implementation of graphite powder in the sealines. For this estimate a -100 mesh natural flake graphite is used. This graphite powder has density of $1,8$ grams per cubic centimetre [5]. Furthermore, it assumed that the specific surface area (SSA) is $0,6$ metre squared per gram [25]. No universal relation between surface area ratio and corrosion current has been demonstrated. Therefore, **the estimate is strictly hypothetical**. Besides, the assumption is made that that the surface area ratios and respective corrosion currents used in the lab tests can be considered representative. Subsequently, the corresponding corrosion rates discussed in section **??** are assumed reasonable. A cathode over anode surface area ratio of 10 is considered. This is a larger cathode surface area than Fe|2C but is assumed to have a similar corrosion rate, as the powder will have less efficiency. After consulting table 6.5 on page 55, a corrosion rate of $0,8$ millimetre per year is assumed for this scenario. The used values are listed in table 7.3.

Assumed values		
Mesh size	-100	mesh
Density	1800	kg/m^3
Specific surface area	0,6	m^2/g
Surface area ratio	10	
Corrosion rate	0,8	$mm/year$

Table 7.3: The parameters used and their assumed values

The TEPNL sealines that are currently out of use are considered for the estimation. These sealines are cleaned and filled with seawater. The cathodic protection is not longer active. These sealines can be categorised in three representative sealines, a 12", 10" and $3,5$" pipe. The dimensions of these pipelines are listed in table 7.4.

Subsequently the sealines are evaluated per linear kilometre. First the surface area of the steel, A_{steel}, is calculated from the nominal diameter[1]. Multiplying A_{steel} by the cathode

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[1] Initially the internal surface area would be approximated by using the nominal diameter minus the wall thickness. Subsequently,

Sealine	Diameter	Wall thickness	Length
	D	t	L
	$[m]$	$[mm]$	$[km]$
12”	0,305	21,41	22,8
10”	0,254	24,61	22,8
3,5”	0,089	9,52	10,1

Table 7.4: Dimensions of the considered 12”, 10” and 3,5” sealine

over anode surface area ratio, $R_{C/A}$, results in the required surface area of the graphite, $A_{graphite}$. The required volume of graphite powder, $V_{graphite}$, follows from dividing $A_{graphite}$ by the specific surface area of the powder, SSA. By multiplying the volume of graphite with the density of the graphite the required mass per kilometre is determined. The required volume and mass can therefore be written as equation 7.1 and 7.2, respectively. The results of the above described calculations are found in table 7.5.

$$M_{graphite} = \frac{A_{steel} \bullet R_{C/A}}{SSA} L = \frac{\pi D \bullet R_{C/A}}{SSA} L \tag{7.1}$$

$$V_{graphite} = \frac{M_{graphite}}{\rho_{graphite}} = \frac{\pi D \bullet R_{C/A}}{SSA \times \rho_{graphite}} \tag{7.2}$$

With			
	$M_{graphite}$	Mass of graphite	$[kg]$
	$V_{graphite}$	Volume of graphite	$[m^3]$
	$A_{graphite}$	Surface area of graphite	$[m^2]$
	L	length	$[km]$
	$\rho_{graphite}$	Density of graphite	$[kg/m^3]$
	D	Diameter of steel sealine	$[m]$
	$R_{C/A}$	Cathode over anode ratio	$[-]$
	SSA	Specific surface are of graphite powder	$[m^2/g]$

Sealine	Steel surface area	Graphite surface area	Mass graphite	Graphite volume
	A_{steel}	$A_{graphite}$	$M_{graphite}$	$V_{graphite}$
	$[m2/km]$	$[m2/km]$	$[kg/km]$	$[m3/km]$
12”	958	9576	16,0	0,0089
10”	798	7980	13,3	0,0074
3,5”	279	2793	4,7	0,0026

Table 7.5: Required graphite for a 12”, 10” and 3,5” sealine

It can be concluded that the amount of graphite needed to achieve the determined surface area ratio is rather little. This is due to the large specific surface area of the graphite powder. Due to the small particle size of graphite the specific surface area is large. Based on the determined values, a thin layer of graphite powder in the sealines would suffice. Furthermore, the smaller the particle size, the higher the porosity [19]. Hence, it is assumed that the graphite is in sufficient contact with the electrolyte. This is to be validated prior the field test.

The volumes of graphite found in table 7.5 are determined by using the same surface area ratio as used in the lab test. We assume that the corrosion rate of steel is therefore similar to the corrosion rate determined in the lab tests. Based on that corrosion rate the remaining time of the sealine is estimated. For this estimation the corrosion rate is considered constant over time.

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the steel would corrode and the internal diameter would increase over time. For the sake of simplicity and considering the accuracy of the estimation the use of a constant diameter over time suffices

Sealine	Wall thickness	Estimated remaining period
	$[mm]$	$[years]$
12”	21,41	27
10”	24,61	31
3,5”	9,52	12

Table 7.6: Estimated remaining time of sealine assuming a constant corrosion rate due to the initially injected graphite

For all three sealines, the estimated remaining period is based on the same surface area ratio. Hence, the amount of injected graphite differs the assumed corrosion rate is the same. Therefore, the remaining time is proportional to the wall thickness of the pipe. To further decrease the remainder period the surface area ratio can be increased. Based on the desired remaining time of the sealines, the amount of graphite used in the field test has to be determined.

7.5. Discussion and conclusive remarks

This research is conducted to investigate alternatives for current pipeline decommissioning methods. The scope of the investigation was set to focus on accelerated degradation of steel. The structure of the report is therefore constructed to first evaluate the present decommissioning methods. Subsequently, potential alternative methods are evaluated. The method using a galvanic couple to accelerate the steel degradation was selected for further investigation. Small scale lab tests were conducted.

7.5.1. Alternative decommissioning methods

Current pipeline decommssioning methods can be categorised in in situ decommissioning or full removal decommissioning. This research aims to find alternative methods that can contribute to a decrease of environmental and financial impact for decommissioning activities. Therefore, several alternative options are considered and assessed. Thereupon, I decided to investigate the feasibility of galvanic corrosion to contribute to sealine degradation.

However, limiting the research to one of the observed methods does not mean the other methods ought to be discarded. Alternative methods, other than galvanic acceleration, are worth investigating. Especially, further research of reversed IC can be useful, considering the damage of the steel sample after accidental polarisation during the lab tests.

7.5.2. Feasibility for decommission purposes

The lab results show that further investigation into the concept of pipeline decommissioning by galvanic corrosion is interesting. The tests were designed to investigate the influence of two parameters, which both form the driving force of the galvanic corrosion. The first on is the potential difference between the metals forming the galvanic couple. The second parameter is the cathode-to-anode surface area ratio effect

Both potential difference and surface area have effect on the galvanic corrosion process. However, this is not necessarily proportional. For an efficient galvanic corrosion of steel the cathode should support a fast reduction reaction.

Consequently, for an effective practical application, the reaction kinetics need to be considered in addition to potential differences (anode to cathode) and surface area effect (area of the cathode basically). This is specifically the case, where the reduction reaction on the cathode can be impeded because of enlarged surface area and slower reaction kinetics – overall resulting in limited reduction. In turn – this will reduce the oxidation or the galvanic corrosion of the coupled steel.

Although the lab tests show the potential application of graphite, addition research to determine optimum surface area ratio needs to be executed. By doing so, the remainder time of the steel sealine can be determined more accurately.

8

Conclusions and recommendations

8.1. Conclusions

The aim of this research was to investigate alternatives for the current pipeline decommissioning methods. The scope of this research was to explore the contribution of accelerated degradation of steel. This accelerated degradation is considered to limit the time which the sealines remain in situ. Based on a comparative assessment the feasibility of **galvanic corrosion** is further assessed. Based on the galvanic series and cost of the material, the cathode material is chosen to be **graphite** (carbon).

Lab test are conducted where the effect of coupling carbon to steel was investigated. The acceleration of corrosion is investigated. Furthermore, it was aimed to quantify the effect of surface area ratio on the corrosion current.

Throughout the tests the measurements were conducted at several time intervals. The measurements were done initially, and after 24, 48 and 72 hours. Linear polarisation resistance (LPR) measurements were conducted to measure the polarisation resistance R_p. Subsequently, the corrosion current I_{corr} is derived. The results of the LPR test show a rather large fluctuation for the several time intervals. The reasons behind are related to the kinetics of both oxidation and reduction reactions. Diffusion limitation (corrosion product accumulation) and the catalytic activity for the reduction reaction of the cathode.

Irrespective of related limitations the corrosion current is determined analytically based on the LPR results. It reflects the expected increase in galvanic corrosion for the steel anode. More specifically the following conclusions can be drawn:

- The corrosion activity of a galvanic couple depends on both oxidation and reduction reactions.
- Limited oxidation (example, due to corrosion product accumulation) will results in reduced corrosion activity overall.
- A higher efficiency of the cathode towards supporting the reduction reaction will enhance the galvanic corrosion rate.
- The mixed potential of the galvanic couple is an indication of the corrosion activity. However, a sustained cathodic shift only would justify continuous corrosion activity.

To that end carbon can be effectively employed as cathode for applications of sealine decommissioning. It should be taken into account that the driving force for **enhanced steel dissolution includes three main components: the potential difference (anode vs cathode), the surface area ratio of anode to cathode, and the kinetics of both oxidation and reduction**. This would reflect potentially different outcomes when the cathode surface area changes.

8.2. Recommendations

The results of this research are based on small scale tests. Therefore, **a field test is recommended** as discussed in chapter 7. The field test provides results for a more realistic situation. Hence, challenges of the practical situation are to be addressed. The field test is to be designed to monitor the challenges mentioned in section 7.2. For some of the foreseen challenges additional research is recommended.

The proposed method to accelerate the degradation is by applying a galvanic couple. The sealine starts to act as an anode. The sealine will therefore corrode faster. However, part of the sealines are protected with sacrificial anodes. The protection mechanism works the same as the proposed acceleration mechanism. It is expected that elongation of the degradation process is significant when the anodes are still connected. Therefore, **assessing the feasibility of decommissioning the anodes is recommended**.

Besides an assessment on the decommissioning on the anti-corrosion protection, **an investigation on the anti-corrosion coating is also recommended**. The proposed method of galvanic corrosion is meant to degrade the steel of the pipeline. The coating on the sealines is expected to remain if the steel is dissolved. It is not preferable to get involved in retrieval operations for the anti-corrosion coating. Hence, the residue of polymer is left in situ. Before agreeing on leaving this in situ, the consequences are to be assessed. The environmental impact and potential effect on the marine life are important to investigate.

The internal stakeholders ought to be briefed on the field test. The alternative decommissioning method affects TOTAL group. In a beneficial way, if the results of the field test are positive. However, also in a unfavourable way, as some resistance or scepticism is likely to arise. Hence, the Total S.A. is to be involved. The field test an commence as their approval is granted.

If the proposed method is taken into a further stage of development after the field test, **the external stakeholders are to be involved** too. It is advised to first involve EBN and SodM. The concept can be discussed with the mutual aim to develop a more environmental friendly and cost efficient decommissioning method. This involvement is possible to address within the NexStep platform. Subsequently, Rijkswaterstaat can be involved on the matter. Simultaneously, the main environmental NGO’s can also be invited to share their perspective. For the involvement of RW and the NGO’s it is important to stress the ambition to develop a method which does not involve disturbing the seabed, nor does it involve leaving the complete sealines in place.

Lastly, the investigated method in this research is the accelerated corrosion due to galvanic coupling of the steel sealines. The choice to evaluate the feasibility of galvanic coupling is resulting from an comparative assessment. This comparative assessment ranked several options, elaborated in chapter 4. In the results of this assessment, the method using reversed IC, or electrolytic corrosion, scores lower than the galvanic coupling. The results resulting from the accidental polarisation of the steel sample, described in section 6.4, give reason to **reconsider the method of reversed IC decommissioning**. The corrosion rate due to the polarisation was significant. Hence, additional investigation into the feasibility is recommended. However, it should be borne in mind that a continuous supply of power is needed. This leads to operational challenges as the facilities are planned to be decommissioned. Besides, the effect on CAPEX and OPEX is to be taken into account whilst considering this option.

Acronyms

ABEX abandonment expenditure. 3, 68

CAPEX Capital Expenditure. 68
CE counter electrode. 37, 68

DC direct current. 23, 68
DEG diethylene glycol. 1, 68

EBN Energie Beheer Nederland B.V.. 3, 68
EMF electromotive force. 68

ICCP impressed current cathodic protection. 2, 23, 60, 62, 68

LPR linear polarisation resistance. 68

MD Mining Decree. 2, 68
MIC Microbial corrosion. v, 26, 68
MMO mixed metal oxide. 34, 35, 68

NGO Non Governmental Organisation. 4, 68
NGT Noordgastransport. 1, 68
NOGAT Northern Offshore Gas Transport. 2, 68
NOGEPA Nederlandse Olie en Gas Exploratie en Productie Associatie. 4, 68

OCP open circuit potential. 38, 68
OPEX Operational expenses. 68

PDP potentiodynamic polarisation. 68
PLONOR pose little or no risk to the environment. 25, 27, 60, 68
ppm parts per million. 3, 68

RE reference electrode. 37, 68
ROV Remote operated vehicle. 10, 60, 68
RW Rijkswaterstaat. 4, 68

SCE saturated calomel electrode. 37, 68
SI International System of Units. 68
SodM Staatstoezicht op de Mijnen. 3, 68

sonar sound navigation and ranging. 58, 68

TEPNL Total Exploration & Production Nederland. 1, 68

WE working electrode. 37, 68

WGT Westgastransport. 1, 68

A

Assessment methodology

The investigated methods of decommissioning are compared to one another. The comparative assessment is based on six criteria. These criteria are described in more detail in section A.1. The criteria are weighted in a multi criteria analysis(MCA) and result in a weighted percentage per criterion (A.2).

The weighting of the criteria allows a more objective comparison of the several methods assessed. The assessment criteria are *technical impact, environmental impact, safety, societal risk, cost* and *sustainability.*
Since the research revolves around new and progressive methods for decommissioning, the assessments are highly qualitative.

A.1. Description of assessment criteria

The assessment is conducted with the criteria *technical impact, environmental impact, safety, societal risk, cost* and *sustainability*. A brief elaboration on the factors considered for each criteria is listed below.

Technical impact

The technical impact is assessed qualitatively and is based on the technical feasibility and the risk on project failure. During the assessment estimations are made on the number of operations, the complexity of these operations and the infield experience with the required operations.

Environmental impact

Environmental impact is assessed by identifying potential environmental hazards accompanying the method. The impact on the seabed and the threats for the marine life are taken into account.
Furthermore qualitative estimations on energy usage and emissions. The amount of vessels required and durations are evaluated. The energy usage depends on the required operations and their duration.

Safety

Safety is a core value and therefore taken into account in the assessment. To limit the potential loss of life, the number of operations, the complexity of these operations and the infield experience with the required operations are estimated. For each operations the potential safety hazards are considered.

Societal risk

For each method considered the risk on societal opposition is taken into account. The impact on the public opinion is hard to assess. It is therefore predicted if the proposed method will be accompanied by any public resistance.
Besides the public opinion, NGO's also have t be taken into account.

Costs

An always recurring factor is project cost. During the assessment the expected expenses are estimated. This is done by looking at the CAPEX of the project and the required OPEX.

Sustainability

During this assessment, sustainability is considered to be having positive value for the future endeavours. It is predicted if the proposed method brings opportunities to reuse the materials of facilities for other purposes.

A.2. Multi criteria analysis

On the selected criteria a multi criteria analysis (MCA) is conducted. In the MCA the criteria are assessed with respect to one another. The MCA is found in table A.1 below.

The criteria in the left column of the table are assessed with respect to the criteria in the top row. If the criterion is considered of higher value than the one in top row, the score is 1. If not, the score is 0[1]. Eventually, a weighted percentage of each criteria is obtained in the last column.

	Technical impact	Environmental impact	Safety	Societal	Cost	Sustainability	Weighted value
Technical impact		1	0	0	0	1	**13,3**
Environmental impact	0		0	1	1	0	**13,3**
Safety	1	1		1	1	1	**33,3**
Societal	1	0	0		1	1	**20,0**
Cost	1	0	0	0		1	**13,3**
Sustainability	0	1	0	0	0		**6,7**

Table A.1: Multi criteria analysis

A.3. Comparative assessment

Once the criteria have been appointed a weighted value, they can be used for assessing the projected methods. The assessed methods will each obtain a score for the assessment criteria. If the assessed method has a desirable outcome it is assigned a score of 5. If the outcome of the assessment is judged acceptable, its score is 3. In case that the method is assessed with a negative impact, it is assigned a 1. The weighted score is relative to the weighted value of the criteria and its associated score. The methods and their scoring is found in table A.2.

Finally, the current decommissioning methods as well as the proposed new methods are assessed according these scores. Their final scores can then be compared to one another. The method with the highest score is judged to be the most desirable.

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[1] A MCA with scores varying from 0 to 5 was also conducted. In this MCA the score represented more nuance in importance between criteria. However, both analyses resulted in similar weighting percentages. Therefore, for the sake of clarity, the MCA with binary score is used.

Criterium	Assessment	Score	Weighted value
Technical impact	Low	5	13,3
	Medium	3	8,0
	High	1	2,7
Environmental impact	Low	5	13,3
	Medium	3	8,0
	High	1	2,7
Safety	Slight safety hazards	5	33,3
	Minor safety hazards	3	20,0
	Moderate safety hazards	1	6,7
Societal	Low resistance	5	20,0
	Medium resistance	3	12,0
	High resistance	1	4,0
Cost	Low	5	13,3
	Medium	3	8,0
	High	1	2,7
Sustainability	Large future value	5	6,7
	Possible future value	3	4,0
	No future value	1	1,3

Table A.2: Scoring options for assessment criteria

B

Lab tests: results

Table B.1: Lab test results

~	~	~	~
Fe	OCP measurement	LPR measurement	Mass loss measurement
Time	OCP [V]	Rp [Ohm]	Mass loss [\%]
0	-0,518	1622,900	~
24	-0,699	3915,300	0,044
48	-0,651	1264,100	0,015
72	-0,617	2399,700	0,044
Average	-0,621	2300,500	~
~	~	~	~
Fe|C	~	~	~
Time	OCP [V]	Rp [Ohm]	Mass loss [\%]
0	-0,456	1075,200	~
24	-0,627	147,150	0,118
48	-0,631	117,120	0,922
72	-0,657	255,320	0,678
Average	-0,593	398,698	~
~	~	~	~
Fe|2C	~	~	~
Time	OCP [V]	Rp [Ohm]	Mass loss [\%]
0	-0,511	181,980	~
24	-0,576	171,490	1,229
48	-0,604	208,640	1,458
72	-0,601	225,670	1,696
Average	-0,594	201,933	~
~	~	~	~
Fe|Pt	~	~	~
Time	OCP [V]	Rp [Ohm]	Mass loss [\%]
0	-0,543	1233,200	~
24	-0,639	646,500	0,103
48	-0,631	596,200	0,438
72	-0,643	951,460	0,104
Average	-0,614	856,840	~
~	~	~	~
Fe|2Pt	~	~	~
Time	OCP [V]	Rp [Ohm]	Mass loss [\%]
0	-0,639	511,850	~
24	-0,608	352,850	0,142
48	-0,640	707,240	0,476
72	-0,628	653,550	0,798
Average	-0,629	556,373	~
~	~	~	~

Table B.2: Lab test results

C

Lab results: Mass loss measurements

F0					
Duration	Mass before [g]	Mass after [g]	Mass loss [g]	Mass loss [\%]	Corrosion rate [mm/y]
24	0,6799	0,6796	0,0003	0,04	0,178
48	0,6728	0,6727	0,0001	0,01	0,030
72	0,6843	0,6840	0,0003	0,04	0,059
				Average	0,089
C1					
Duration	Mass before [g]	Mass after [g]	Mass loss [g]	Mass loss [\%]	Corrosion rate [mm/y]
24	0,6767	0,6759	0,0008	0,12	0,474
48	0,6613	0,6552	0,0061	0,92	1,806
72	0,6781	0,6735	0,0046	0,68	0,908
				Average	1,062
C2					
Duration	Mass before [g]	Mass after [g]	Mass loss [g]	Mass loss [\%]	Corrosion rate [mm/y]
24	0,6756	0,6673	0,0083	1,23	4,914
48	0,6653	0,6556	0,0097	1,46	2,871
72	0,6074	0,5971	0,0103	1,70	2,033
				Average	3,273
P1					
Duration	Mass before [g]	Mass after [g]	Mass loss [g]	Mass loss [\%]	Corrosion rate [mm/y]
24	0,6797	0,6790	0,0007	0,10	0,414
48	0,6842	0,6812	0,0030	0,44	0,888
72	0,6710	0,6703	0,0007	0,10	0,138
				Average	0,480
P2					
Duration	Mass before [g]	Mass after [g]	Mass loss [g]	Mass loss [\%]	Corrosion rate [mm/y]
24	0,6355	0,6346	0,0009	0,14	0,533
48	0,6725	0,6693	0,0032	0,48	0,947
72	0,6520	0,6468	0,0052	0,80	1,026
				Average	0,835

Table C.1: Test result from mass loss measurements

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