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Linear Polarisation Resistance (LPR) and Pipeline Corrosion Rates in Soil

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1. Introduction

Estimates of pipeline corrosion rates are an essential element for any adequate risk analysis of major sub-surface utilities (eg Rajani & Kleiner, 2001). Apart from direct detection of surface oxidation, pitting, faults and fractures which can be directly responsible for catastrophic failures, more general observations of wall condition are required to confirm and revise the design estimates for economic longevity based on soil properties and burial history.

Kear et al (2006) have considered a range of factors influencing the corrosion of metals in soil. Water content, temperature, pH and microbial activity are all fundamental factors in the corrosion process. Chemical species influencing corrosion rate include chlorides, sulphates and carbonates. These can arise from both natural and artificial sources. Moreover, non-uniform corrosion processes in soil, such as pitting and crevice corrosion, can rapidly reduce the effectiveness of metallic coatings and ultimately, the service life of buried assets. Consequently electrochemical methods including linear polarisation resistance (LPR) methods have become popular for corrosion analysis.

LPR methods are used extensively by structural engineers to provide an indication of soil corrosivity and electrochemical complexity over metal/soil boundaries. In particular LPR methods can be used to provide an indication of potential pipeline failures in aggressive soils. However pipeline engineers normally require specific estimates of time-to-failure for adequate risk analysis. Consequently raw LPR data (R_p values) must be transformed in order to calculate the actual corrosion rate for pipe materials in-situ.

In principle LPR data be readily transformed by assuming a uniform corrosion mechanism with a continual transfer of electrons based on averaged current densities at the surface of the pipeline (Stern-Geary model). However the situation of uniform corrosion resulting in a homogeneous oxidation rate may be relatively rare. Instead most pipelines exhibit extensive pitting causing accelerated corrosion at the outer surface and consequently a more complex analysis is required.

2. LPR Data

Corrosion may be regarded as an electrochemical response of metals in soils with corrosion rates determined by ion migration in reactive electrolytes. Consequently electrical resistivity has been broadly accepted as a primary indicator of soil corrosivity (eg the DIPRA 10 point scale). In this regard LPR determinations may be regarded as a more sophisticated measure of risk. In particular LPR can be used to determine both soil resistivity and chemical reactivity at the metal/soil interface from a single soil sample. However a final determination of a uniform corrosion rate for any pipe may then be complicated by the nature of the surface materials and the mobility of the corrosion products.

In effect the polarisation resistance (R_p) can be related to the complexity of the electrolyte activity at the pipe surface. In its most basic form this involves a transfer of electrons from iron (Fe) atoms in the pipe wall and a migration of the corrosion products into the sub-soil as a more complex ion species. The soil chemistry and moisture content are critical in this process (these also determine resistivity). However the nature of the metal species at the pipe surface can also be significant. In particular the reactivity of cast (CI), ductile (DI), and mild steel (St) can be moderated by the habit or matrix of the carbon content in each case. For example the extent of graphitisation in CI and the isolation of pit structures in DI can restrict the percolation of ground fluids and the mobility of corrosion products (eg Vasyliov et al 2013).

In view of the complex structures involved, and the variation in the type of pipe materials present, any estimates of corrosion rate based on single values of LPR may be regarded as approximations regardless of the iron species. For example Law et al (2004) demonstrate that LPR methods are well correlated with weight loss methods but provide an overestimate in the order of 1.86 for steel in concrete. Moglia et al (2004) demonstrate similar correlations between LPR and weight loss methods but indicate an offset in data for wrought (WI) and cast (CI) materials. Finally Vasyliov et al (2013) indicate similar reactivities (and LPR values) for different steels in tap water but again indicate an overestimate by a factor of 2.0 compared to weight loss methods.

Although LPR data appear to provide consistent estimates for uniform corrosion rates, Law et al (2004) suggest to the contrary a five-fold increase where there is penetration from pitting. In view of these complications, values of R_p have been used previously by some operators only to rank general risk factors from soil rather than provide a specific corrosion rate. Even these rankings may be compromised for pipelines protected by full coatings of plastic, paint or pitch. Consequently uniform corrosion rates calculated from LPR data may be viewed only as an indication of potential risk following local impact or damage unrelated to final estimates of time to failure.

3. Estimates of Corrosion Rate based on observations of R_p

Electrochemical models for corrosion dynamics have been reviewed by Mansfeld (2009). In general a linear relationship can be assumed for small deviations (ΔE) of an initial metal/soil equilibrium potential (E_{cor}) according to the expression

$$R_p = \Delta E / \Delta i \quad (1)$$

Where ΔE (mV) is an imposed increment to the rest-potential (E_{cor}), Δi (mA/cm²) is the resulting current response, and R_p (ohm-cm²) is the observed polarisation resistance.

Since R_p is finite any initial electrochemical equilibration must conform to the expression

$$I_{cor} = B / R_p \quad (2)$$

Where I_{cor} is the corrosion current, and B is a constant.

Values for B are governed by specific cathode-anode dynamics related to corrosion and ion mobility factors at the metal/soil surface. Normally variations of the Stern-Geary model are adopted to investigate any response (eg Mansfeld 2009; Andrade and Alonso 2004). These are used to derive the expression

$$B = [\beta_a \beta_c] / [2.3 * (\beta_a + \beta_c)] \quad (3)$$

Where B now combines the anodic and cathodic terms (β_a , β_c) reflecting an elaboration of equ (1).

Corrosion rates are readily calculated from observations of I_{cor} (equ 2) along with charge transfer rates determined according to Faraday's law including a term for the metal density of an active species (eg Andrade & Alonso 2004; ASTM G59). In this case (Baboian 2005)

$$CR \text{ (mm/yr)} = K * I_{cor} \text{ (EW}/\rho) = 0.0116 * I_{cor} \quad (4)$$

Where K is a constant = (0.00327 mm g uA⁻¹ cm⁻¹ y⁻¹); EW is equivalent weight (dimensionless = 27.92 for Fe), and ρ is density of working electrode (= 7.86 g/cm³).

It follows from equations (1)- (4) that values of R_p and B are required in order to calculate a corrosion rate for specific soils. However representative values of B are frequently adopted for routine applications. Andrade and Alonso (2004) recommend values of 26 mV consistent with the observations of Vasylijev et al (2013). However Kear et al (2006) also emphasise that any error in B will be less than 20% for a broad range of Tafel gradients (60-120 mV, equ 3). Consequently values of 26 mV for B should provide robust estimates of CR with error dominated by observations of R_p .

Values of R_p can be obtained more precisely using transient galvanostatic pulse methods based on an analysis of a Randle circuit analogue (eg Deo et al, 2014). The resulting data can be used immediately to provide a ranking for the corrosivity of soils. However estimates of corrosion rate consistent with equation (4) are more attractive and provide a better indication for the remaining life of buried pipe lines. Unfortunately most of the preceding discussion assumes uniform corrosion or oxidation on an average surface. Significant modifications to CR estimates may be required where corrosion currents become concentrated by local pitting.

4. New Coupon Observations

New LPR data have now been obtained for steel coupons subject to long-term burial (11-12 mths). Three samples were prepared for burial at depths of 35-40 cm in typical foundation soils (dominantly

clay, m. silts). No additional environmental constraints were imposed and each site was subject to random climatic impacts. However no significant rain was recorded and the soil section appeared free from major percolation during an extended dry period. Each coupon was measured prior to burial and again after retrieval to determine any weight loss. At the same time samples of the soil were extracted for standard determinations of polarisation resistance using the galvanostatic pulse method (Deo et al 2015).

Linear Polarisation Resistance Data									
Project		Coupon corrosion			Rcvd : 25/05/15				
Samples		12.5663 cm ²			Rpt : 05/04/16				
Sample ID- SC	H2O Wt(%)	Soil:Rho (Ohm-m)	Ecorr (-mV)	Cdl (uF/cm ²)	Rp (Ohm-cm ²)		Corrosion Rate (mm/yr)		
					Mean	StdDev	LPR	Pitting	factor
c1	5.8%	832.7	281	5.49	29657	302	0.010	0.223	21.9
c2	5.4%	751.3	304	15.28	23499	108	0.013	0.250	19.4
c3	7.9%	331.4	310	14.40	22242	131	0.014	0.236	17.4
							(1)	(2)	
	(1) Corrosion rates determined by LPR method assuming uniform I _{corr}								
	(2) Pitting rates determined by weight loss coupons								

Table 1 : LPR data for steel coupons in clay soil using galvanostatic pulse method of Deo et al (2015) compared to pitting rates from weight loss data (11 mth burial).

The results for each coupon are summarised in Table 1. High values of Rp are obtained for each sample consistent with the moisture content determined by dessication. These results suggest a uniform corrosion rate of 0.010-0.014 mm/yr based on normal Tafel gradients and Stern Geary transfer models. However an initial inspection of each coupon indicated significant areas of pitting rather than uniform oxidation (Fig 1). The maximum pit depth was determined by noting the total weight loss of each coupon during progressive polishing until a smooth surface was obtained unaffected by pitting (eg Fig 1a-1d). This method indicates a maximum pitting rate in the range 0.22-0.25 mm/yr exceeding the previous calculations for a uniform oxidation rate by a factor of 17-21 (Table 1). These factors appear consistent with a net increase in current density if pitting is assumed to be confined to an area less than 10% of the total coupon surface (Fig 1).



Fig 1. Progressive polishing of coupon samples (following 11 mth burial) from (a) as exhumed, (b) oxide removal, (c) moderate pitting, (d) remanent deep pits close to total removal. Pit depths calculated from weight loss through polishing.

Rajeev et al (2013) have investigated the average corrosion rates for failed water pipes in Australia. They suggest that pipe failures occur when pit depths exceed 75% of the original wall thickness. Furthermore average corrosion rates from 0.2-0.3 mm/yr are observed in their data for pipes aged 40-60 years broadly in agreement with the coupon pitting rates observed in the current work conducted over a much shorter period (~1 year).

Assuming a linear relationship the current study suggests an expression of the form

$$PR \text{ (mm/yr)} = F * B / [Rp \quad] \quad (5)$$

where the pitting or acceleration factor F is in the range 5-20 accommodating the observations of Kasahara and Kajiyama (1983).

5. Pitting Rates and Polarisation Resistance

Crevice and pitting corrosion are forms of localised corrosion, which means that the corrosion occurs in a limited area on the pipe. The corrosion rate is often high and is generally higher than that for uniform corrosion, due to a large cathode/anode ratio. A severe attack is therefore usually observed, and the pit or crevice may cut through the pipe wall thickness to form a hole. For a defect-free perfect surface, pitting corrosion is caused by variations in the soil environment (geo-chemistry) that may contain aggressive chemical species (such as chloride) as well as fluctuations in moisture level.

Chloride is particularly damaging to the passive oxide film generated by general corrosion and consequently pitting may result from oxide breaks.

Pit growth rates may be controlled by the same factors that control any electrochemical reaction: charge-transfer processes (including R_p), galvanic resistance, and mass-transport considerations (eg Frankel, 1998). Pit stability is determined by the maintenance of conditions at the pit surface severe enough to prevent re-passivation. The role of many of the environmental and material parameters that are critical to the pitting process, such as surface potential, alloy composition, electrolyte concentration, and temperature, can be explained in terms of the dipole double-layer at the metal-soil interface, and consequently measurements of polarisation resistance (R_p).

Zapp (1996) has reviewed the dynamics of pit growth in steel. He provides a statistical analysis of the expected penetration rates based on a power law consistent with the observations of Romanoff (1957); these conform to the expression

$$PD = k t^n \quad (6)$$

where PD(mm) is pit depth, t (yrs) is time, while $k (=8.3)$ and $n (=0.46)$ are considered constants. Frankel (1998) provides a review of similar expressions with $n=0.5$. However, the most suitable values for k and n remain contentious (Rajani & Klein 2001); consequently Zapp proceeds to a maximum depth model reflecting the complex kinetics of pit growth. Similarly Petersen and Melchers (2002) suggest a compound model incorporating multiple corrosion scales. Consequently more complex expressions may be required to extrapolate the present results (summarised by eq 5) to include forensic observations over longer times.

In one example of forensic analysis Dafter (2014) has reported a correlation of pitting rates (PR) with values of R_p for different pipes with variations in age and construction methods. Good correlations were obtained for specific pipes but no general relationship could be determined. Typical values conform to expressions of the type (from Ferguson and Nicholas)

$$\ln PR \text{ (mm/yr)} = 0.564 - 0.0159 R_p \quad (7)$$

where the specific coefficients may vary with pipe construction methods.

Expressions of this type can be generalised to provide the form

$$PR \text{ (mm/yr)} = F * B / [R_p]^g \quad (8)$$

where g varies with material and soil properties (note $g=1.5$ in Kasahara & Kajiyama 1983).

6. Conclusions

LPR methods provide an attractive option for pipeline engineers involved in risk analysis. Instantaneous values of the soil corrosion rate can be determined using small samples of bedding material with no impact on pipeline integrity. Different regions can be ranked immediately for risk analysis based on values of polarisation resistance and nominal corrosion rates for newly installed pipes. However any final lifetime estimates may be incorrect where pitting corrosion is significant.

The present data indicates that pitting can cause an acceleration of penetration leading to failure at a rate 5-20 times faster than predicted by uniform oxidation. Further extended analyses or additional forensic data are required to verify the form and the specific values of each parameter in equations (5) and (8) but the current data indicate a greater risk than previously expected from standard derivations using polarisation resistance alone.

A tendency to pitting corrosion requires a distribution of anode-cathode activity levels at the macro or micro-scale. The micro-scale distribution may be dominated by metallurgical variations whereas geochemical complexity will dominate macro-cell activity (characterised by different levels of ion activation and electron transfer over lateral spans). As a consequence abrupt lateral variations in polarisation resistance (R_p) may be considered a significant indicator of pitting risk reflecting geochemical complexity. In these circumstances broader sampling may be required for a comprehensive LPR analysis rather than relying on single samples yielding uniform corrosion rates.

7. References

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