

Permanent Buried Reference Electrodes: Technical Note on Significant Inaccuracies and Medium Term Trials

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Introduction

In 2012, as part of an extensive upgrading of a cathodic protection system for an approximately 90km buried oil pipeline in the UK, some 50 No. permanent Cu/CuSO₄ sat permanent reference electrodes were installed by limited dig, primarily jetting, techniques along the pipeline. The pipeline is subject to stray dc current interaction from a mainline electrified railway system. The pipeline also has some threats of ac corrosion from high voltage overhead transmission systems which parallel and cross the pipeline.

Coupons (1cm²) were installed adjacent to each of these permanent reference electrodes for both instant OFF dc potential measurements and ac measurements. Both electrodes and coupons were installed adjacent to and at pipe invert level.

In order to provide more rigour and flexibility in the testing regime, uPVC pipes were also installed at each location to enable portable electrodes or coupons to be introduced to pipe invert level between the fixed electrodes and coupons. Thus, approximately 1.5m to one side of the pipeline, were installed in a line with approximately 500mm between each item, a reference electrode, an open ended uPVC pipe and a coupon.

The permanent Cu/CuSO₄ reference electrodes were from a reputable manufacturer and stated as having been developed for direct burial with a micro porous tubular body and a solid matrix electrolyte preventing leaching of sulphates from the electrode; they had a claimed life of 25 years and stability of +/-5mV.

Within only a few months after installation, these electrodes were producing unexpected pipe/soil/electrode potential data. A full survey was undertaken to compare their electrode potentials with those of clean, calibrated, portable Cu/CuSO₄ sat reference electrodes introduced down the uPVC tube (within 500mm of the permanent electrodes at the same distance from the pipe and at the same depth as the permanent electrode). Many electrodes were presenting potentials >30mV from their theoretical potential and some >100mV. Within months the greatest error was >200mV. At the last full assessment in week 11 of 2013 the following errors were determined by measurement between the permanent electrodes and a clean calibrated Cu/CuSO₄ portable electrode placed proximately (within 500mm at the same depth) to the permanent electrode:

Table 1: Errors of Permanent Electrodes installed in 2012 Measurements in Week 11 of 2013 All electrodes of common type Cu/CuSO₄ “solid electrolyte”

Location	Electrode Error mV	Location	Electrode Error mV
TP1	-29	TP50	-49
TP2	-67	TP53	-60
TP4	-63	TP56A	+29
TP6	-1	TP61	-61
TP7	-14	TP62	-52
TP9	-187	TP64	-53
TP10	-47	TP67	-39
TP12	-199	TP68	-41
TP12A	-153	TP70	-39
TP15	-6	TP72	-55
TP17	-66	TP73	+129
TP18	-224	TP74	-102
TP20	-84	TP76	-110
TP22	-78	TP78	-113
TP26	-67	TP 81A	-46
TP28	-53	TP83	-57
TP30	-66	TP85B	-62
TP31	-20	TP89	-38
TP33	-66	TP92	-39
TP34	-195	TP94	-59
TP36	MISSED	TP97	-164
TP38	-51	TP101	-187
TP40	-126	TP102	-171
TP41	-51	TP104	-69
TP43	-22	TP106	-76
TP45	-111	TP109	-97
TP45A	-13	TP111	-202
TP48	-191	TP113	-47
		TP115	-17

It is clear that these permanent electrodes can not be classed as "reference electrodes". It would be reasonable to expect competent reference electrodes to be accurate to +/- 5mV before installation and say +/- 10mV after installation.

The ground conditions along the pipeline were not prone to known contaminants, such as chlorides, that are known to contaminate Cu/CuSO₄ reference electrodes. Most electrodes were located below the water table in clay or silty clay; some were in drier chalk and marl soils. There was a suspicion that at some locations the sub surface water flows might be sufficient to encourage accelerated electrolyte loss from within the porous tube electrodes; it has not been possible within the present program of activity to retrieve any electrodes and examine them in detail. It is hoped that this will be done in the next few months. The priorities were to progress with the extensive improvement works for the CP systems and to pragmatically select accurate and reliable electrodes for the balance of the works.

The Trials

A program was instigated to procure what, by reputation, were anticipated to be high quality reference electrodes from reputable manufacturers from the UK and USA, to assess their build quality and to install them at a single location on the same pipeline in a test site that replicated the previous installations.

Reference electrodes were procured from:

In the UK:

Anglia Cathodic Protection Services Ltd (ACAPS)
Cathodic Protection Company Ltd
Corrpro Companies Europe Ltd
Silvion Ltd

In North America (USA & Canada):

Corrpro Inc.
Electrochemical Devices Inc.
GMC Electrical Inc.
M C Miller Co. Inc.

In total 12 No. permanent reference electrodes of different manufacturers' and types were tested. This included "old fashioned" ceramic porous pot electrodes with a high volume of Cu/CuSO₄ electrolyte and quite large copper electrode area, to claimed "high technology" Cu/CuSO₄ electrodes with ion exchange membranes, some claiming suitability for use in high chloride soils, and the full range of simple to complex in between. One Ag/AgCl/0.5M KCl electrode claimed to be designed for soil usage was also trialed. We did not include in the testing regime well known manufacturers with whom we had previous experience of poor performance.

All electrodes were installed at a single site, in the same manner to that which had been employed in the original enhancement programme, using a water jetting technique to produce a hole of the required dimensions to inset the electrode. The optimum hole size for installation at all the sites intended was only 80mm diameter

but at the test site there was a good local water supply and larger holes were produced for the larger diameter electrode assemblies. Electrodes were backfilled initially in a gypsum/bentonite backfill intended to keep them securely moist and in good contact with the soils; this approach had been taken during the initial deployment in 2012. It is known that some claim that such backfilling can cause small errors in junction potential; it was our assessment that any such errors are small compared with risks of electrodes drying out or having poor contact with the soil. The holes were then "hand tamped" full with compacted soil removed from the hole.

Later this test site was supplemented to allow field gradient measurements to be made proximate to the electrodes, to ensure that the apparent changes in electrode potential that were being measured were not influenced by the sometimes fluctuating field gradients. This was confirmed; the field gradient across a 1m distance, in the same direction as the 500mm spacing between the permanent and portable electrodes, was typically less than 5mV and the peak value measured was 10.4mV.

12 No. electrodes were tested, and continue to be tested, with data currently at 28 weeks after installation showing, of the 12 No. electrodes tested from the 8 No. manufacturers, one was in error by >130mV. The least accurate electrode was not from the originally selected manufacturer whose electrodes showed errors of approximately -200mv to +130mV as in Table 1 above. The electrode of the same type as deployed along the pipeline in 2012 was in error by >60mV at the test site.

The 2 No. simple "old fashioned" porous pot electrodes were amongst the best performing electrodes with one showing a maximum error of +25mV and the other +21mV. Both of these would have presented dimensional problems for the optimum method of installation.

Only 5 No. of the 12 No. electrodes were accurate to +/- 20mV of their theoretical potential (which was assessed to include a maximum of 10mV soil potential gradient "error").

The Ag/AgCl/0.5M KCl electrode which was included in the testing (converted to Cu/CuSO₄ by a debateable 40mV conversion factor) was accurate throughout the trials to within 14mV (which was assessed to include a maximum of 10mV soil potential gradient "error").

In parallel to the field testing, all of the electrodes which could not be viewed during construction were sectioned in order to visually assess the construction quality. The intention of this visual assessment was to attempt to make subjective assessments of the cable to electrode connection and its insulation from the electrolyte, of the assembly quality and to determine from visual appearance of the electrolyte how it had been either gelled (with a gelling agent such as gelatine) or made "solid" typically with "Plaster of Paris" or gypsum.

The simple porous pots were both assessed as reasonably well constructed and both performed relatively well.

The claimed high technology units from two manufacturers were assessed as reasonably well constructed; of these one performed particularly poorly and two performed reasonably well. One performed extremely well, better than its more expensive, claimed superior, sibling from the same manufacturer.

Three units of claimed high technology were assessed as particularly poorly constructed but all performed reasonably well; this may indicate that the subjective quality assessments from the sectioning of the cells were not as rigorous or appropriate as they were thought to be when the assessment was undertaken.

The full data sets, anonymised, are presented in Figure 1.

Conclusions

The accuracy, or lack of accuracy, of permanent reference electrodes from a reputable manufacturer was only detected by the field provisions of unusually rigorous (at least in UK practice) testing provisions which allowed “calibration” of these with portable calibrated electrodes, at the same depth, within 500mm of the permanent electrodes. The errors were very significant and continue after some 12 months of deployment.

Many of “high quality” “premium producer” electrodes performed poorly in the subsequent field tests intended to select accurate and stable electrodes for future works. The errors were very significant in electrodes from several manufacturers.

We selected to use the only Ag/AgCl/0.5M KCl electrode in the trial for the ongoing installations on the basis of the good performance, small diameter which suits the preferred “limited dig” water jetting installation procedure and would also be suitable for the small proportion of test sites where chlorides are high.

We do plan to recover some of the “failed” electrodes and to attempt to determine the cause of the inaccuracy. We will report this publicly if this is possible.

Acknowledgement

Thanks are expressed to my Client for permission to publish this work, with the intention of bringing to the attention of others in the pipeline cathodic protection community what we consider are important errors arising from the use of poorly selected reference electrodes. I thank them also for them being prepared to undertake trials, at their cost, in order to quickly determine what electrodes would be best for future works. I thank my colleagues who have assisted and provided technical support and guidance throughout all aspects of this complex project and undertaken much of the data collection for this small element of the overall work to improve the cathodic protection performance of these assets.

Figure 1: Permanent Reference Electrode Potential vs Calibrated Portable Electrode (500mm spacing at same depth) at same site.
Weeks are not linear: “Week 16” is actually after 28 weeks of trial. The Ag/AgCl/0.5M KCl electrode is corrected to Cu/CuSO₄ equivalent by 40mV. It is series 10

