Unconventional Gas Development

Monitoring of Produced Water

Introduction

The Midland Valley holds the majority of the potential unconventional gas resources in Scotland, primarily due to the abundance of coal seams at depth. Shales also occur in the Midland Valley and elsewhere in Scotland; however, currently the potential shale gas resource is less well defined. Both coal bed methane and shale gas developments present issues associated with management of waste water; the majority of which is derived from water abstracted or returned from the production zone, at depth, which is often termed flowback* and produced water**. Presented here is information on the chemistry of produced water from a coal bed methane exploration site in Scotland. This has been compared to the chemistry of other common water types, with the aim of informing the public, scientific and regulatory community on the issue.

Coal bed methane exploration and development in Scotland is the most advanced in the UK. There are several Petroleum Exploration and Development Licences (PEDLs) in place for a number of potential development areas including parts of Midland Valley, Canonbie and N. Scotland (Figure 1). These PEDL licences, issued by the Department of Energy and Climate Change (DECC), permit the exploration for oil and gas, in principle, within the licensed area. SEPA has regulatory control over many aspects of unconventional gas exploration and development, including licensing of borehole construction, groundwater abstraction, fluid injection and water discharge.

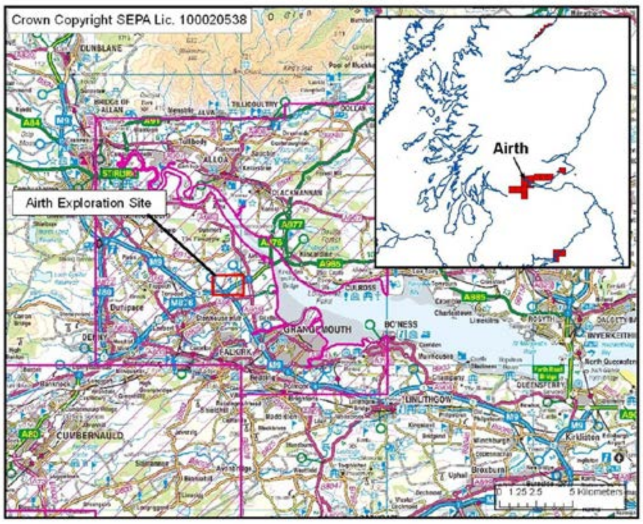

Figure 1- Current PEDL Licences in Scotland and the location of the Airth site

Dart Energy are licensed by DECC, via PEDL 133, to explore the area close to Falkirk and Grangemouth (Figure 1). A number of exploratory boreholes have been drilled close to Airth and permissions for full scale development are currently at the planning stage.

Produced Water

Produced water is water generated during coal bed methane and shale gas exploration and development. Coal bed methane development generally does not require the injection of fluids for fracturing; however, water is produced due to the pumped abstraction of water directly from the coal bed. The action of this water abstraction reduces the natural fluid and gas pressure within the coal bed and encourages gas movement towards the extraction well (Figure 2). This produced water is often saline and contains dissolved constituents indicative of the coal composition, geological formation mineralogy and age of the water.

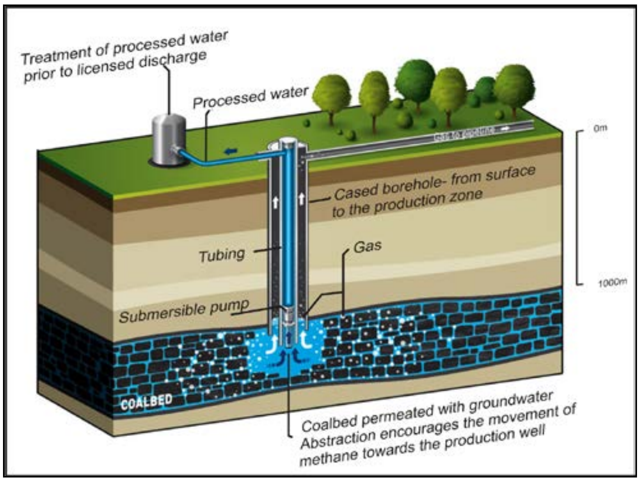

Figure 2- Illustrative diagram of a typical coal bed methane extraction installation. The diagram shows the submersible pump and central tubing where water is extracted from the coal seam in order to reduce the hydrostatic pressure and promote the preferential movement of the previously dissolved and sorbed gases towards the extraction well. The diagram shows a processed water storage tank; this water will require treatment prior to licensed discharge to the environment. (Image adapted from Total.com)

Notes

***Flowback water** is water returned to the surface immediately following hydraulic fracturing. This term generally only refer to shale gas production as hydraulic fracturing is not normally used in coal bed methane production

**** Produced water** is water returned over the life time that a well produces gas, either CBM or shale gas well.

Shale gas development requires the injection of fluid during hydraulic fracturing which is returned to surface containing dissolved minerals from the shale which can result in the waters being highly saline. Water returned from the subsurface immediately following hydraulic fracturing events associated with shale gas development is generally called 'Flowback water', while the water returned over the lifetime that a well produces gas is referred to as produced water.

These produced waters from coal bed methane and flowback and produced waters from shale gas developments, require treatment and appropriate disposal.

SEPA's Involvement

Recent exploratory work at Airth involved the abstraction of water from a borehole for a number of months to confirm the viability of full scale gas development. This water abstraction and the eventual discharge following treatment were controlled by SEPA through licensing under The Water Environment (Controlled Activities) (Scotland) Regulations 2011 (CAR). As part of this licensing SEPA required chemical quality monitoring of the abstracted/produced waters. This activity is now suspended while Dart Energy seeks further permissions to undertake full site development, however, all water that was abstracted during exploration was treated and discharged to the Firth of Forth in compliance with the CAR licence conditions to limit any potential environmental impact.

SEPA undertook analysis on a sample of untreated abstracted water to investigate the chemistry of the produced water which might be expected at this and other future coal bed methane developments in Scotland. Analysis of produced water has been undertaken extensively on produced water from unconventional gas development in America and elsewhere, however, it is well documented that waters differ depending on geology, hydrogeology and production methods. Therefore the analysis presented here is important to help inform the scientific and regulatory understanding of water management for this and other future unconventional gas development in Scotland.

What did we find?

SEPA recovered and analysed a single untreated produced water sample associated with the exploratory unconventional gas development at Airth which confirmed the following:

- SEPA's internal laboratory analysis of abstracted/produced water at Airth confirmed water chemistry with elevated electrical conductivity, consistent with that of water contained in coal beds at depth. Substances detected included chloride, alkalinity (as $CaCO_3$), iron, aluminium, nickel, zinc, lead and a number of organic compounds (benzene, xylene, naphthalene) associated with coals and methane production.
- SEPA's sample was also analysed for radioactive substances by external laboratories. The analysis showed the presence of naturally occurring radioactive materials (commonly called "NORM") at levels similar to that in many rocks throughout the UK, granite being a common example.

When exploration or production of gas at Airth resumes SEPA will undertake further analysis of produced water to confirm and expand upon the analysis presented here as well as ensuring operator compliance and protection of the water environment.

Outlined in Appendix 1 and 2 the produced water chemistry is compared to other common water types. Appendix 3 provides the complete results of the inorganic and organic analysis undertaken by SEPA on untreated produced water and makes comment on the organic compounds identified. Appendix 4 details the NORMs analysis results.

Figure 3- Drill rig used to construct deep boreholes in operation (From Dart Energy information)

Appendix 1- Comparison of Produced water and Seawater

Shown in Figure 4 below is the dominant ion chemistry composition of the untreated Airth produced water in comparison to an average sea water composition.

- The diagram indicates that Airth produced water is less mineralised than the seawater water. It has an electrical conductivity value of 30,500µS/cm in comparison to 50,000µS/cm for average seawater.
- The dominant ion chemistry proportions are similar with chloride and sodium being the dominant ions in both waters.
- The Airth waters are recovered from coal beds at depths where groundwater is commonly saline, although less so than sea water.

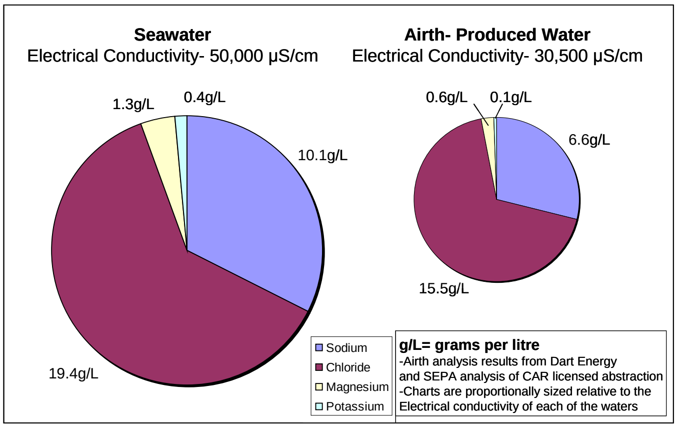

Figure 4- Proportional pie charts showing the dominant ion chemistry of Seawater and Airth- Produced Water. The pie charts are proportionally sized according to the EC-electrical conductivity of the waters which is indicative of the total mineralisation of the waters; the pie chart segments show selected ion composition of the waters in grams per litre g/L. While this diagram indicates that the dominant ion chemistry of the produced water is similar to that of sea water the produced water also contains concentrations of trace elements and metals (outlined in Appendix 2).

Appendix 2- Comparison of Produced Water to Scottish Mine Waters

Mine waters occur commonly in many river catchments within the Midland Valley, due to the legacy of abandoned coal and oil shale mining. Some major mine water discharges are treated by the Coal Authority and occasionally by Local Councils using passive treatment schemes to minimise the discharge of contaminants to the environment; some other smaller less contaminated discharges are not treated but are diluted within river systems with minimal environmental impact. Produced water generated during unconventional gas development will always require extensive treatment using more intensive active treatment methods to ensure compliance with SEPA imposed CAR licence conditions. However, while the regulatory controls on produced waters and mine waters differ it is useful to compare the two as they are derived from the same or similar rock types in the subsurface and it can be seen that while produced waters represent a new potential source of contaminants their chemistry is similar to many Scottish mine waters; which have been successfully treated for several decades in Scotland. Furthermore, all the waters produced at Airth to date have been treated and discharged in compliance with licence conditions and any future produced waters from Airth or any other CBM development in Scotland will require treatment and discharge under licence.

Table 1, below, outlines the chemistry of Scottish mine waters in comparison to the Airth produced water sample and indicates that the Airth produced water is generally more mineralised than the mine waters (probably due to the source depth of the water, Appendix 1), however, metals such as iron, manganese, aluminium, zinc, nickel and cadmium show similar concentrations at Airth to those found in mine waters. Chromium, copper and lead concentrations although higher than those found in the mine waters are generally low (at 1 in a billion magnitude concentrations).

Determinand	Units	Airth Produced Water	Scottish Mine Waters†	
			Min	Max
Electrical Conductivity	µS/cm	30500	350	19350
Suspended solids (0.5^{o}C)	mg/L	60.2		
pH	pH units	6.89	3.6	6.9
Chloride	mg/L	12300	9	5880
Alkalinity (as CaCO3)	mg/L	416	0	854
Sulphate (as SO4)	mg/L	0.235	37	1346
Metals (Total)				
Cadmium	µg/L	0.068	<0.05	0.601
Chromium	µg/L	6.43	<0.05	0.24
Copper	µg/L	18.9	0.43	0.78
Lead	µg/L	5.4	<0.05	0.09
Nickel	µg/L	42.6	1.8	94.9
Zinc	µg/L	19.8	0.01	28.9
Aluminium	µg/L	<8.0	0.02	11.2
Iron	mg/L	68.5	0.3	137
Manganese	mg/L	0.789	0.3	11.5

Table 1- Results of key chemical parameters and metals analysis on untreated Airth Produced water undertaken by SEPA in comparison to Scottish mine water chemistry.

(†Scottish Mine Water data from Younger 2001- Mine water pollution in Scotland: nature, extent and preventative strategies, STOTEN 265 (excluding mine waste results) and Ó Dochartaigh et al. 2011, Baseline Scotland: groundwater chemistry of the Carboniferous sedimentary aquifers of the Midland Valley, British Geological Survey Open Report, OR/11/021.)

Appendix 3- SEPA chemistry analysis results on untreated produced waters including organic compounds

Appendix 1 and 2 outline the chemistry of untreated produced water in comparison to other common water types to provide a contextual understanding of the type of water produced at the Airth coal bed methane exploration site. Outlined in table 2 is the complete range of (non-radiological) analysis undertaken by SEPA on the produced water sample recovered from the Airth site. The analysis indicates:

- The majority of the organic compounds analysed, in the produced waters were not identified and as such are reported as below the limit of detection (<LOD)
- The organic compounds which were identified such as naphthalene, benzene, pyrene and xylene while derived from the natural organic content of the coal could be of concern if released to the groundwater or surface water environment <u>without</u> prior treatment.

Determinand	Units	Airth Produced Water
Electrical Conductivity	µS/cm	30500
Suspended solids (0.5°C)	mg/L	60.2
pH	pH units	6.89
Chloride	mg/L	12300
Alkalinity (as CaCO3)	mg/L	416
Sulphate (as SO4)	mg/L	0.235
Biological Oxygen Demand	mg/L	<9.4
Metals		
Cadmium	µg/L	0.068
Chromium	µg/L	6.43
Copper	µg/L	18.9
Lead	µg/L	5.4
Nickel	µg/L	42.6
Zinc	µg/L	19.8
Aluminium	µg/L	<8.0
Iron	mg/L	68.5
Manganese	mg/L	0.789
Mercury	mg/L	<0.00950
Organics		
Naphthalene	ng/L	1510
Acenaphthylene	ng/L	<LOD
Acenaphthene	ng/L	<LOD
Fluorene	ng/L	20.8
Phenanthrene	ng/L	1290
Anthracene	ng/L	6.4
Fluoranthene	ng/L	<LOD
Pyrene	ng/L	15.6
Benzo-a-anthracene	ng/L	<LOD
Chrysene	ng/L	<LOD
Benzo-b-fluoranthene	ng/L	<LOD
Benzo-k-fluoranthene	ng/L	<LOD
Benzo-a-pyrene	ng/L	<LOD
Dibenzo-a,h-anthracene	ng/L	<LOD
Benzo-(ghi)-perylene	ng/L	<LOD
Indeno (1,2,3-cd) pyrene	ng/L	<LOD
Benzo(B+K)Fluoranthene	ng/L	<LOD
Benzo-(ghi)-perylene + Indeno(123-cd)pyrene	ng/L	<LOD
Dichloromethane	µg/L	<LOD
Methyl tert-butyl ether	µg/L	<LOD
Chloroform	µg/L	<LOD
1,1,1 Trichloroethane	µg/L	<LOD
1,2 Dichloroethane	µg/L	<LOD
Benzene	µg/L	32.2
Carbon tetrachloride	µg/L	<LOD
Trichloroethene	µg/L	<LOD
Toluene	µg/L	19.1
Tetrachloroethene	µg/L	<LOD
Ethyl benzene	µg/L	2.3
o-Xylene	µg/L	9.5
para+meta-Xylene	µg/L	27.7
Xylene	µg/L	37.2
1,3 Dichlorobenzene	µg/L	<LOD
1,4 Dichorobenzene	µg/L	<LOD
1,2 Dichlorobenzene	µg/L	<LOD
Nonylphenyl ethoxylates (1-30 ethoxylate units)	µg/L	<LOD
Octylphenyl ethoxylates (1-30 ethoxylate units)	µg/L	<LOD
Total Nonionic Detergent	µg/L	<LOD
1,2,4 Trichlorobenzene	ng/L	<LOD
1,3,5 Trichlorobenzene	ng/L	<LOD
1,2,3 Trichlorobenzene	ng/L	<LOD
Trichlorobenzene -	ng/L	<LOD
Hexachlorobutadiene	ng/L	<LOD
Hexachlorobenzene	ng/L	<LOD
Pentachlorobenzene	ng/L	<LOD
4-Chlor-2-Nitrotolue	ng/L	<LOD

Table 2- Analysis results on untreated Produced water at the Airth CBM Exploration site.

Appendix 4- Analysis of naturally occurring radioactive materials (NORM)

NORM analysis shows that radium-226 (2.29 Bq/kg) is one of the radioactive materials present at the highest concentrations in the sample taken of untreated produced water. In comparison the average value for natural radioactivity in soil in Western Europe is approximately 40 Bq/kg for radium-226. The results of this preliminary analysis have to be viewed with caution; they are only indicative of the radioactivity present. Further analysis of the produced water will be needed and a radiological impact assessment will also be required to assess the measured NORM concentrations against public dose constraints as set out in radioactive substances legislation.

Determinand	Result	Units	Uncertainty (±%)
Bismuth-214	2.248	Bq/kg	15.2
Lead-214	2.29	Bq/kg	12.3
Lead-210	<0.664	Bq/kg	
Actinium-228	2.99	Bq/kg	19.5
Radium-226	2.29	Bq/kg	12.3
Radium-228	2.99	Bq/kg	19.5

Table 3- NORM analysis results on untreated produce water at Airth