Understanding shale gas plays through the application of inorganic geochemistry

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The rapid increase in interest in exploring shale units for shale oil and gas has highlighted the need to develop a thorough understanding of shale units. Not only does possessing a detailed understanding of shale stratigraphy enable accurate volume calculations to be undertaken, but knowing the mineralogical composition of shale can provide information on rock mechanics to enable greater well completion success. In addition, a comprehensive understanding of anoxia proxies can be used to identify sweet spots in the play. All of this information can be potentially provided through the use of inorganic geochemical techniques.

This paper will discuss the application of a range of analytical techniques to shale gas plays, from rapid and non-destructive analysis by hand held X-Ray fluorescence to highly precise and accurate data produced by inductively coupled plasma mass spectrometers. In addition we will show how inorganic geochemical analysis can be integrated with other techniques such as XRD and TOC analysis to enable extra information to be gained from the analysis, for example enabling rock brittleness, a key parameter for fracking, to be established. Importantly we do not rely on samples to be provided from rare drill core, but we also analyse side wall core or drill chippings.

We will utilise case studies from to UK onshore Bowland shale sections and key US shale to demonstrate the wide variety of ways that the inorganic geochemical data produced can be utilised to aid in the understanding of shale gas plays.

Immobilisation of PTEs by water treatment residual: A potential amendment for contaminated land

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"Water Treatment Residual" (WTR) from the drinking water treatment process is a waste product largely composed of amorphous Al or Fe (oxy)hydroxides and organic matter and is commonly disposed of by landfill. Seasonal and geographical variations in WTRs were studied over 12-months at 10 water treatment works (WTWs) in England. Total solids ranged from 15 to 30%, of which organic matter formed 35 to 70%, Fe 25 to 37% and Al 10 to 21%. pH ranged from 4 to 7. Variation between works appears more pronounced than seasonal variation within them.

Immobilization of oxyanions such as P and As from aqueous solutions to Fe- and Al-WTR has been demonstrated [1] but research into immobilization of other Potentially Toxic Elements (PTEs) is limited. Batch experiments using aqueous solutions of Cu(II), Cd(II), Pb(II) and Zn(II) investigated the adsorption behaviour of an Fe rich WTR as a function of time, solid:solution ratio, pH and initial contaminant concentration and demonstrated effective removal of metal ions from solution. The sorption capacity of the WTR demonstrates some pH dependence, but significant sorption is observed in the low pH regime: 24% Cd, 28% Cu, and 45% Zn is sorbed at pH 3.2, 3.5 and 3.5 respectively, whilst Pb immobilisation remains > 98% from pH 3 to 9, using an initial mass load of 8.0 mg/g. The WTR's ability to function as a metal sorbent over a broad pH range may be due to the intimate intermixture of iron (oxy)hydroxides and organic matter [2]. The fractionation of sorbed PTEs within the WTR is being determined using a new sequential extraction technique: "Chemometric Identification of Substrates and Element Distribution" [3].

These results support the hypothesis that WTRs may have potential as an amendment for remediation of contaminated land.

[1] Makris *et al* (2006), *Chemosphere* 64(5), 730-741. [2] Moon and Peacock (2012), *Geochimica et Cosmochimica Acta* 92, 203-219. [3] Cave *et al* (2004), *Geochemistry: Exploration, Environment, Analysis* 4(1), 71-86.

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