

Non aqueous phase liquid (NAPL) migration

Description: Small volumes of non-aqueous phase liquids (NAPLs) may be generated from some ILW/LLW waste inventories. Being immiscible, and in some cases less dense than water, NAPLs may be capable of rapid migration as a separate phase. Natural analogues provide an indication of the significance of some of the processes associated with the migration of NAPLs.

Liquid hydrocarbons are normally described by their specific gravity with respect to water, with dense (DNAPL) and light (LNAPL) non-aqueous phase liquids recognised by the groundwater remediation industry. The oil industry uses API gravity, which is inversely proportional to specific gravity ($[141.5/SG \text{ at } 60^\circ\text{F}] - 131.3$). Accordingly oil with an API gravity $>10^\circ$ is a LNAPL and $<10^\circ$ is a DNAPL. For example, many North Sea oils have API gravity $\sim 40^\circ$ which is equal to a specific gravity of 0.83 [Hunt 1979].

NAPL migration depths and rates: Oilfields may be destroyed by a number of processes, principally vertical leakage, lateral spillage and compositional changes. The operation of the former two processes is very common, as shown by the frequent occurrence of oil seeps at the ground surface and on the seabed above oilfields [Macgregor 1996]. Analysis of a database of seeps above giant oilfields suggested that most occurred from reservoirs less than 1 km deep, demonstrating the near-vertical migration of NAPLs over such intervals. There is less evidence for the migration rates but seepage is considered capable of emptying even huge oil reservoirs in 'geologically short periods' [Macgregor 1996]. There is therefore analogue evidence for the rapid and near-vertical migration of LNAPLs.

Gas enhanced transport of NAPLs: Studies of the large undersea gas seeps in the Santa Barbara channel, offshore from California, indicate that oil is transported to the sea bed as globules and as thin films on gas bubbles. NAPL volumes transported as thin films on gas bubbles have been estimated at 94ml per l of gas, with a further 50-70% transported as globules [Hornafius et. al. 1999], indicating that gas-enhanced transport of LNAPLs from a repository may be significant. **Partitioning of heavy metals into NAPLs:** There are only limited data for the heavy metal (defined as an atomic number >20 [Venugopal & Luckey 1975]) content of natural hydrocarbons. These show that solid hydrocarbons and heavy oils have higher concentrations of heavy metals compared with lighter NAPLs. NAPLs derived from marine source rocks have higher heavy metal concentrations than those sourced from terrestrial rocks. Uranium is normally only found at trace levels in NAPLs.

Partitioning of heavy metals between LNAPL and brine shows significant enrichment into the LNAPL phase of those metals that form metal-porphyrin complexes. This is especially so for V, Ni and Cu which are enriched 10^6 , 880 and 12 fold respectively [Manning 1986; Manning & Gize 1993]. Other metals such as Pb and Zn are partitioned into the brine. Transport of particulate uranium minerals in oil has been reported by Leventhal et. al. [1987].

While there is only very limited data it appears that only those heavy metals capable of forming porphyrin-metal complexes are likely to be partitioned into naturally-occurring LNAPLs, but it is unclear how transferable this observation is to processed NAPLs. Uranium does not appear to be highly concentrated in NAPLs, unless as particulates.

Association of uranium ore bodies with NAPLs: There is an association between solid and liquid hydrocarbons and some types of Au, Cu, Hg, U and Th ore bodies [Landais 1993]. This has been attributed to various forms of interactions between hydrothermal solutions or ore bodies with hydrocarbons. The most likely processes involve complexation of the metals by hydrocarbons in solution or the hydrocarbons providing reducing conditions leading to the precipitation of redox-sensitive heavy metals. The latter explanation is favoured by Landais [1993] to account for the association between uranium ore bodies and hydrocarbons because of the generally low concentration of uranium in oils. There would appear therefore to be evidence for the reduction of U(VI) to U(IV) in the presence of LNAPLs.

Relevance: These analogues provide evidence for processes and rates that help inform the consideration of LNAPL migration from repositories. They are of particular relevance to deep repositories with a significant organic component in the inventory.

Position(s) in the matrix tables: No comment here

Limitations: The nature and significance of LNAPL migration may be affected by the presence of barriers to near vertical buoyancy-driven flow which are site specific.

Quantitative information: The analogue data is generally qualitative.

Uncertainties: There are inevitably unstated uncertainties with the numerical data quoted above.

Time-scale: NAPL migration can occur across all timescales.

PA/safety case applications: No previous uses of the analogue studies in PA or safety cases are known.

Communication applications: No examples of the use of these types of analogues are known in communication and dialogue material.

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Added value comments: No comment here

Potential follow-up work: Additional studies into the partitioning of repository-relevant metals into LNAPLs would be very useful.

Keywords: Oil, NAPL, LNAPL

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