

Determination and Anaerobic Degradation of Diesel Components in Crystalline Rock and Groundwater

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Introduction and background

In Sweden, as in many other countries, rock vaults in hard rock are used for storage of petroleum, both crude oil and refined products such as gasoline and diesel (Roffey, 1989, Roffey et al., 1989). In Sweden, 45 civil storage facilities recently have been commissioned due to political changes. Before these facilities can be finally phased out, it is necessary to ascertain that petroleum products that may have entered rock fractures during the operational phase will not threaten ground or surface water now or in the future.

This problem initiated a research and technical development program with the aim to find methods to estimate the amounts of petroleum that had entered rock-fractures. One additional question was to find out if there was an ongoing anaerobic microbial degradation of petroleum components in the rock. The results from the investigation should be comprised to a control program for monitoring a possible natural attenuation.

As research-site a repository in Blädinge, Småland was used. The repository consists of 6 rock vaults with a total storage capacity of 73,000m³, where mainly diesel had been stored. Because of the obvious explosion risk associated with opening and cleaning of the vaults, together with high costs, sampling had to be done from ground or from oil-separator and water basins in the economical building in connection with the rock vaults.

Phase one

The first sampling and experimental phase was finished in 1998. The main conclusions from this part were as follows:

Diesel and gasoline can diffuse into the rock matrix from fractures if the porosity is high. This diffusion is a very slow process. Finding diesel-contaminated fractures around the repository was difficult, but fractures completely filled with diesel were found. n-alkane (C₁₀H₂₂ - C₂₅H₅₂) degradation was found in iron-reducing enrichments with rock-fractures from a core-drilled borehole (KB11) as inoculum. n-alkane degradation with concomitant iron-reduction was found in enrichments with groundwater from a hammer-drilled borehole (KM01) with diesel-contamination as inoculum. Active sulphate reduction was ongoing in the same borehole (KM01), which could be confirmed by sulphide production in enrichment cultures and a depletion in oxygen and sulphate concentration and high alkalinity in the groundwater.

Phase two Methods

The second phase of the research program started with growth experiments with enrichment cultures of ferric iron- and sulphate reducing bacteria and deuterised oktadecane and propylbenzene as growth substrates. The enrichments originated from the oil separator and the growth medium used mimicked the ground water. Anaerobic growth bottles in triplicates were inoculated with 1 x 10³ cells ml⁻¹ and incubated in the dark at 21°C, and intermittently shaken. The growth bottles were harvested after 0, 20, 40, 61 and 83 days. As controls were used non-inoculated growth medium with alkane additions. After the harvest, total number of cells with AODC (acridine orange direct count) (Hobbie et al., 1977, Hallbeck & Pedersen, 1990) ferrous and total iron with the Ferrozine-method (Stookey, 1970) and alkane, alkene and carboxylic acid with GC-MS, were measured.

Results and Discussion

Both cultures with oktadecane and propylbenzene increased their cell density from 1 x 10³ to 4 x 10⁶ cells ml⁻¹ during the first 20 days. Concomitantly there was an increase in ferrous iron concentration to 150 mg l⁻¹ in cultures with propylbenzene and 185 mg l⁻¹ in cultures with oktadecane. At 40 days a production of benzoic acid could be detected in cultures grown with propylbenzene. This is in correspondence with results presented by Rabus et al., (1999) where they found alkylbenzoate production in a nitrate reducing enrichment with crude oil as substrate.

Calculation of the carbon requirement for a cell increase from 1 x 10³ ml⁻¹ to 1 x 10⁶ ml⁻¹ correlated with the amount of iron that had to be reduced when grown with propylbenzene and the measured ferrous iron production. The same experiment was performed with a sulphate reducing enrichment.

Searching for degradation products from deuterized alkanes seems to be a promising method to use in the estimation if and to what extent natural attenuation has proceeded around rock vault facilities in granitic rock. Together with groundwater composition it may be parts in a monitoring control program in the future.

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