Bitumens

Description: Bitumen is organic fusable material (extractable by organic solvents) consisting of mixtures of mainly aliphatic and aromatic hydrocarbons of high molecular weight (Figure 1). Bitumen consists mainly of C (about 80 - 88%), H (8 - 11%), O (1 - 12%) S (1 - 7%) and N (up to 1.5%). Bitumens originated in various geological epochs. Technical bitumen is a product of distillation of crude oil widely used in construction industry and also for immobilization of liquid radioactive waste. The large-scale technical production of bitumen by distillation commenced at the beginning of the last century, whereas natural bitumen has been used by humans for more than 5000 years (Helmuth, 1989a). Natural and technical bitumens are not identical, but elemental composition, composition of fractions and physical properties indicate an acceptable level of analogy at least for some natural occurrences.

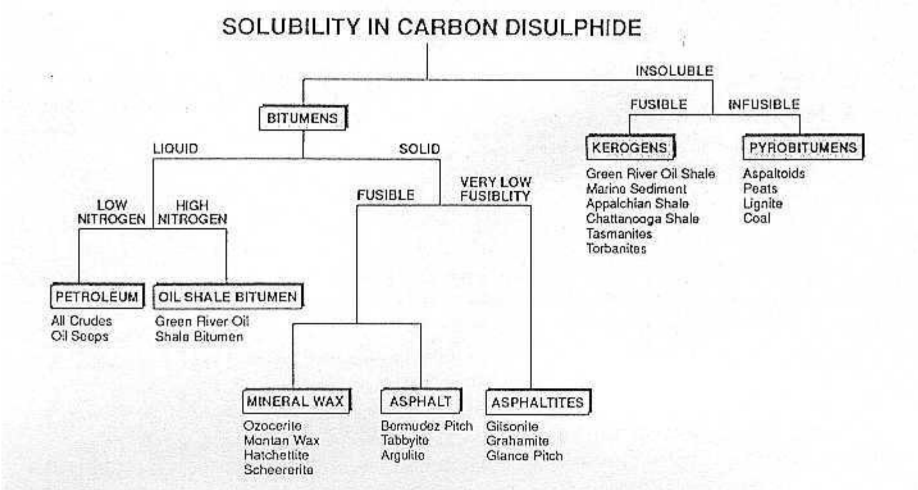

Figure 1 The classification of natural organic material of bituminous and similar character based on their physical state and their reactions with organic solvents (from Helmuth, 1989a).

The following aspects were addressed in respect to the disposal of radwaste: durability and longevity, interactions with environment and leaching and microbial degradation. Natural bitumens have been mainly studied so far, but also some man-made use of bitumenic material was also assessed - ancient use as impermeable coatings and impregnating matter. Special natural analogue studies on bitumens are very rare, but many geological reports probably can be interpreted for such purpose.

Helmuth (1989a) documents various natural and historical occurrences of bitumen - Dead Sea asphalt, asphalt veins from Turkey (USA), asphalt lakes from Trinidad, asphalt impregnations in limestones, sandstones and sands and also occurrences of bitumen in hydrothermal veins. There are many other occurrences of bitumens in the geological environment - references can be found in specialized organic geology literature.

A well-documented study of leaching and durability against the combined attack of environmental factors (evaporation, oxidation, microbes) of bitumen-impregnated limestone profile (Jurassic age) in Holzen (Lower Saxony) was performed by Helmuth (1989b). The complex graben structure in this area consists of a series of Upper Jurassic bitumen-impregnated limestones (Figure 2), which are separated by marlstones and thin claystone layers (Figure 3). The area was earlier a target of mining operations. Observations clearly indicate that bitumen is not indigenous, but the high molecular residue of a former petroleum accumulation. The organic rich strata were exposed to surface conditions approx. 70 Ma ago and for a long time have been subject to weathering and microbial attack. Many samples were collected from various parts of the deposit from various depths (up to 80 m) and were characterized by the same methods as technical bitumens. Although differences in the compositions of subfractions were evident, elemental composition and chromatographic fractions and physical properties allow analogy with technical bitumen used for solidification of radioactive wastes (Heckers et al., 2000). The current form of bitumen can be characterized as highly biodegraded (depletion of n-alkanes and light aromatics), but still in a biodegradable state. The samples from outcrops had direct features of oxidation (contact with air and light), but still preserved their main properties demonstrating relative stability in surface conditions for longer time.

Figure 2 Microphotograph of bitumen-impregnated limestone; scale: width = 7.5 mm (from Helmuth, 1989b)

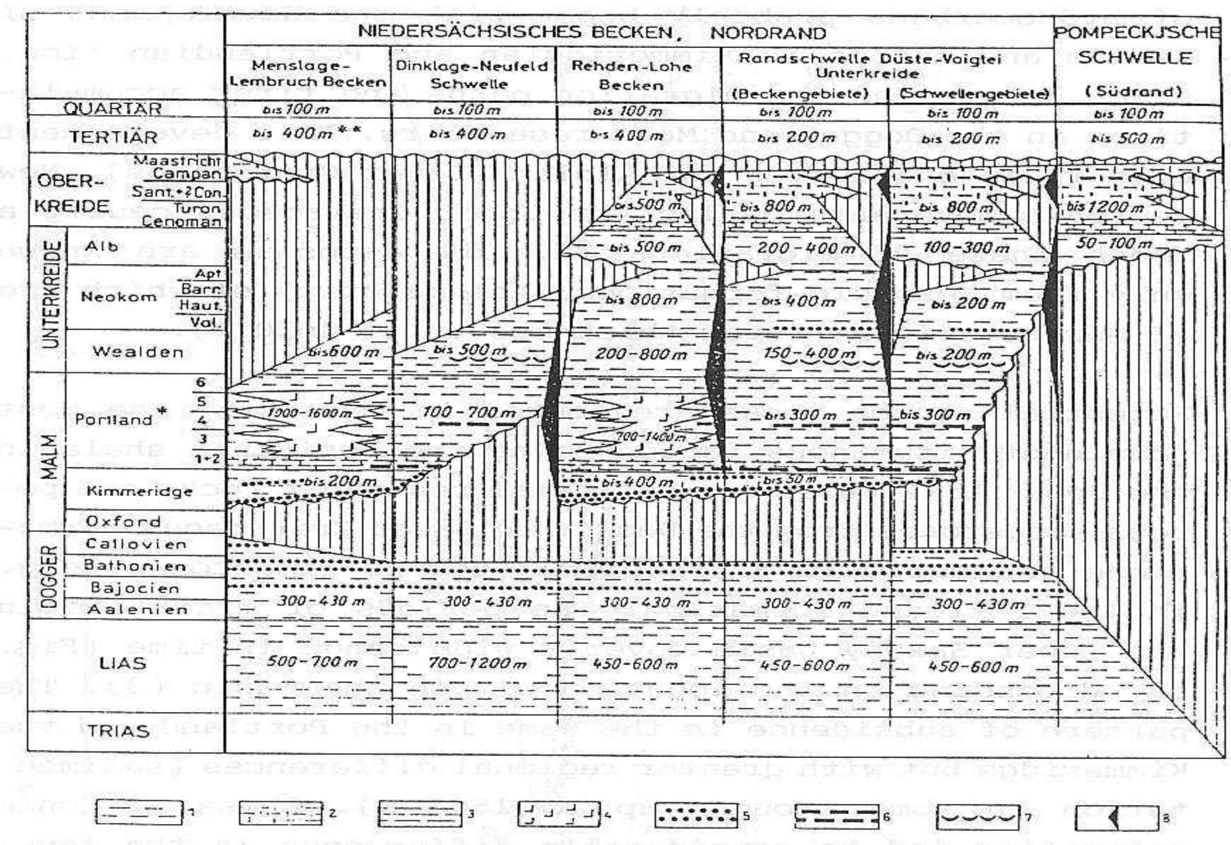

Figure 3 Stratigraphy of Lower Saxony basin and major periods of oil migration (1 - claystone, 2 - marl, 3 - limestone, 4 - rock salt, 5 - permeable sandstone, 6 - permeable limestone, 8 - periods of migration) (from Helmuth, 1989b)

Natural bitumen in hyperalkaline environment has been studied only very rarely - e.g. Maqarin site (Jordan) where there is poor analogy with technical bitumen due to post-depositional combustion. The bitumenous marl contains predominantly non-aromatics, the aromatic amount is small (Geyer et al., 1998).

Retention of radionuclides and radiolytic effects were assessed in the Oklo area, Gabon. Natural fission reactors contain abundant organic matter (generated from syngenetic kerogen) that was partly liquefied at the time of criticality and subsequently was converted to graphitic material

(Mossman et al., 1993, Rigali, 1997) - the similarity of this material with technical bitumen is low. It was documented that graphitic bituminous organic matter greatly helped in immobilization and containment of fission products (Nagy et al., 1991, Nagy et al., 1993, Holliger et al., 1996). Unfortunately, the various generations of bitumen are usually extensively intermixed with each other and the multiphase evolution complicates the situation immensely.

Very good preservation properties of bitumens were documented at many archaeological items (for example from Mesopotamia) when mechanical disruption of the bitumen has not occurred. Unfortunately, uncertainties in the interpretation of findings from archaeological samples are mainly due to lack of knowledge of the original material, the kind of treatment and the conditions of its degradation (Helmuth, 1989a). There is also evidence of preservation of material added into natural bitumens, for example vertebrates, bones or woods in asphalt pits.

Relevance: Bitumen waste matrices is used for immobilization of liquid and semi-liquid of operational radioactive waste from nuclear power plants (Finland, Japan, Czech Republic, etc.). If analogy in properties of bitumen and preferably also in hydrogeochemical conditions can be found, than natural occurrences can support information about durability and behaviour of bitumen waste matrices derived nearly exclusively from laboratory experiments. Heckers et al. (2000) argue that groundwater composition has only a marginal influence on bitumen degradation encouraging this transferability of earlier studies to the near-surface repositories environment.

Position(s) in the matrix tables: (Near-field) Concerning waste form (bitumen) and demonstration of barrier containment (chemical integrity) and nuclide release (dissolution and leaching).

Limitations: Dissimilarities between natural and technical bitumen (the actual composition of bitumen is not easy to study and compare) have to be carefully assessed by physical and organic geochemistry methods. Unfortunately, relevant environmental conditions directly resembling the geochemical conditions of near-surface repositories of low- and intermediate level waste (usually hyperalkaline) are not known. There is only one partially applicable example - Maqarin. On the other hand, Helmuth (1989a) documents that groundwater composition has only marginal influence on bitumen degradation

Quantitative information: Information of quantitative character were produced concerning long-term degradability rate of bitumens in natural conditions.

Uncertainties: Uncertainties stem usually from potential compositional differences of bitumens that are complicated to demonstrate to an acceptable level.

Time-scale: Geological (up to millions of years).

PA/safety case applications: Use of information from natural analogues in performance assessment is not known. Low and intermediate level liquid waste are solidified in bitumen and resulting waste packages are disposed in near-surface repositories - PA calculations are usually limited to shorter time frames in comparison with deep geological repositories and therefore also requirements on reliable data concerning waste forms durability are lower resulting in less need for additional supporting information from bitumen natural analogues.

Communication applications: Information from natural analogues could be used for demonstration of longevity of bitumen materials as waste form (not used so far).

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Added value comments: None

Potential follow-up work: Not known.

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